CCEMC GRAND CHALLENGE
ROUND 1 FINAL REPORT

CO_2 Conversion to Methanol through Bi-reforming

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1 Executive Summary

Several technology options to convert CO_2 into higher value fuels and chemicals are currently available, including well known pathways for methanol and dimethyl ether (DME) production. However, these pathways are commercially feasible under very few circumstances and the search for improved methods is ongoing. In addition to potentially improving the economic viability of Carbon Capture and Sequestration (CCS) projects, converting CO_2 into commercially valuable products will also improve the economic viability of renewable and non-renewable carbon-based energy production by creating additional revenue streams, significantly decreasing net Greenhouse Gas (GHG) emissions.

Here, we propose the capture and conversion of CO_2 from large point sources such as fossil fuel power plants into synthesis gas (syngas) through a combination of steam and dry reforming, referred to as bi-reforming. The novelty of the process proposed here is an innovative pyrochlores based catalyst with superior thermal stability and activity compared to existing options for the dry reforming reaction. Pyrochlores are crystalline oxides of the general composition A2B2O7, where A is a trivalent rare earth and B is a tetravalent transition atom. These materials have the essential properties required for this process: 1. Proven thermal stability, 2. Oxygen ion conductivity, and 3. Catalytic activity. The syngas is then converted into methanol, a valuable chemical that serves as a feedstock for a wide range of end products and fuels.

Experimental and modeling work was conducted as part of the project to evaluate the catalyst performance and to optimize the overall process configuration. The laboratory scale experimental results show that the catalyst is potentially commercially viable and has shown promising stability under desired bi-reforming conditions. This catalyst enables the production of methanol using CO_2 as a feedstock, resulting in significant reduction of the product methanol's Carbon Intensity.

A Life Cycle Analysis (LCA) of the proposed pathway along with a baseline pathway based on existing methanol production technology has been conducted. The LCA is conducted using a combination of the 'GHGenius' LCA model, Aspen Plus process simulations and existing literature and industry data. The results show that the proposed pathway can decrease the net GHG emissions from an industrial process in Alberta by one million tonnes per year through a single commercial scale plant sized at 15,000 TPD of methanol production capacity.

The key outcomes of Round 1 project are:

(a) Within the conditions tested at LSU (including temperature, gas compositions, pressure, and time-on-stream), the Ni-pyrochlore catalyst has demonstrated stable performance.

(b) The catalyst properties include stable crystallinity, tolerance to oxidiation/reduction, and close approach to equilibrium at practical temperatures.

(c) The technology has the potential to reduce the Carbon Intensity of an industrial scale methanol production plant by a million tonnes per year in Alberta

The results suggest that further research and development of the catalyst would be required to deploy the overall process. More detailed modeling and Life Cycle Analysis are also required to move forward towards commercialization.

2 Project Description

- Introduction and background

Several technology options to convert CO_2 into higher value fuels and chemicals are currently available, including well known pathways for methanol and dimethyl ether (DME) production. However, these pathways are commercially feasible under very few circumstances and the search for improved methods is ongoing [1-5] . In addition to potentially improving the economic viability of Carbon Capture and Sequestration (CCS) projects, converting CO_2 into commercially valuable products will also improve the economic viability of renewable and non-renewable carbon-based energy production by creating additional revenue streams, significantly decreasing net Greenhouse Gas (GHG) emissions.

Here, we propose the capture and conversion of CO_2 from large point sources such as fossil fuel power plants into synthesis gas (syngas) through a combination of steam and dry reforming, referred to as bi-reforming. The novelty of the process proposed here is an innovative catalyst with superior thermal stability and activity compared to existing options for the dry reforming reaction. The syngas is then converted into methanol, a valuable chemical that serves as a feedstock for a wide range of endproduct and fuels.

Syngas, a mixture of H_2 and CO, is a feedstock for the production of final products such as methanol, Fischer-Tropsch diesel, and various chemicals. Currently methanol is primarily produced through steam reforming of natural gas, as shown in Equation 1. This technology is mature and industrially practiced. An alternative to steam reforming is the 'dry reforming' reaction shown in Equation 2.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^\circ_{1047} = 226.2\ \text{kJ/mol} \qquad (1)$$
$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^\circ_{1023} = 261\ \text{kJ/mol} \qquad (2)$$

The syngas can be converted into methanol using existing commercial processes (Equation 3).

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^\circ_{523} = -49.2\ \text{kJ/mol} \qquad (3)$$

The dry reforming reaction consumes CO_2 to produce syngas but requires a higher energy input compared to conventional steam reforming. The H_2/CO ratio required for methanol production can be produced by reforming a mixture of methane, CO_2 and steam:

$$3CH_4 + CO_2 + 2H_2O \rightarrow 4CH_3OH \qquad \Delta H^\circ_{773} = 177\ \text{kJ/mol} \qquad (4)$$

The energy required for methanol synthesis through this pathway is estimated to be 1.73 MJ/kg of CH_3OH and the process consumes 0.25 kg of CO_2 per kg of CH_3OH produced [6].

The proposed project will utilize commercially mature technologies for all the steps in this pathway except for the dry reforming reaction. The proposed catalyst option for the dry reforming step is discussed below.

Pyrochlores based Dry Reforming:
Dry reforming to produce syngas [(reaction (1) above] has been well-studied [7]. The reaction produces a syngas with a H_2/CO ratio of 1:1 and requires temperatures of about 900° C to achieve

complete conversion to H_2 and CO. A great number of catalysts have been studied for this reaction, including those based on Ni [4, 8, 9], hydrotalcites [10], hexaaluminates [2, 11], perovskites [12] and supported cobalt [13] or rhodium [14], among others.

Collectively, these studies show the importance of minimizing both carbon deposition, which inevitably accompanies this reaction, and thermal deactivation due to sintering or loss of the crystalline structure of the catalyst. Recent research has shown that a class of materials known as pyrochlores can be modified to produce catalysts that are active and stable at the severe conditions required for CO_2 reforming [11, 15, 16]. Pyrochlores are crystalline oxides of the general composition A2B2O7, where A is a trivalent rare earth and B is a tetravalent transition atom. These materials have the three essential properties required for this process:

(a) Proven thermal stability. Although their use as catalysts is new, pyrochlores have been used as thermal barrier coatings for gas turbines at temperatures exceeding those required for CO_2 reforming [17].
(b) Oxygen ion conductivity. Defects in the pyrochlore structure can be intentionally introduced to improve the conductivity of oxygen ions at these high temperatures, greatly decreasing carbon deposition.
(c) Catalytic activity. Work at Louisiana State University (LSU) and the US Dept. of Energy (DOE) has shown that various catalytically active metals can be isomorphically substituted into the pyrochlore structure to produce a thermally stable material capable of catalyzing CO_2 reforming reactions at temperatures above 900º C [11, 15, 16].

- Technology description

The proposed technology is designed to produce methanol from CO_2 in three main steps (Fig. 1):

(1) capture of CO_2 from large point sources such as fossil fuel power plants,
(2) generation of steam which is reacted with this CO_2 and natural gas to produce synthesis gas (“syngas”; primarily CO + H_2), a process known as “bi-reforming”, and
(3) conversion of this syngas to methanol, a marketable commodity chemical.

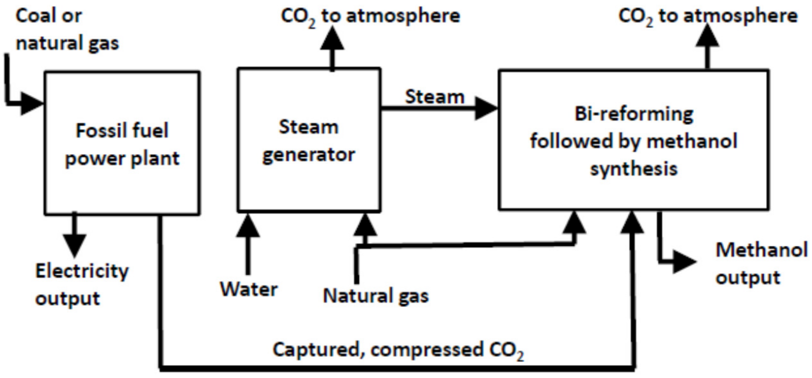


Fig. 1. Schematic of proposed methanol synthesis process

Process description. The first step of the process is to separate and concentrate CO_2 from the flue gas of a large point source such as a fossil fuel power plant. In the second step, steam is generated from natural gas in a conventional boiler. The third step consists of two separate catalytic reactors, shown in one block in Fig. 1. In the first, methane reacts catalytically with CO_2 and steam to produce synthesis gas (H_2 + CO) at the proper 2/1 H_2/CO ratio required for methanol synthesis. In the next reactor, this syngas reacts to form methanol, using a different catalyst. *It is the $CH_4/CO_2/H_2O \rightarrow$ syngas step that is the subject of research here.* The other steps are based on proven technology (although CO_2 separation from flue gas has yet to be widely demonstrated at large scale, the scaleup of the technology is generally considered to be straightforward).

The net reduction in CO_2 emissions is primarily due to the capture of carbon that would otherwise be released as $CO_2$from an existing point source in the methanol molecule. Methanol is a highly marketable commodity, with significant growth forecast in the coming years as it penetrates markets for use as a conventional fuel, chemical intermendiate, and as a feed to clearn energy systems such as fuel cells.

Advantages. There are several advantages to this process. First, it takes advantage of current developments in the capture of CO_2 in concentrated form from large-scale power plants. These include improvements in conventional amine-based absorption processes [31] and “chemical looping”, a more advanced process in which combustion and CO_2 removal are carried out in separate reactors [20, 35]. Second, it is based on well-proven technologies for steam production and syngas-to-methanol catalysis, suggesting little technical risk for these steps. Third, the process produces a commodity chemical that is readily marketable—methanol is used in a wide range of industrial processes as an intermediate, and as a fuel.

Novelty. The novelty of the process proposed here is an innovative catalyst for the reforming of natural gas with CO_2 *and* steam. Temperatures of ~900°C are required to reach complete conversion to syngas. These temperatures, coupled with the presence of steam, are extremely demanding, and *few materials can withstand these conditions*. We can take advantage of ongoing research at LSU in which pyrochlores, a class of thermally stable catalysts, have shown stability in CO_2 reforming of methane at these temperatures [10, 11, 13, 26]. However, they have *not* been tested in the “bi-reforming” of CO_2 and steam to produce syngas. This project will be the first demonstration of the pyrochlore catalysts for the bi-reforming reaction.

The target criteria and deliverables for the Tasks above can be described as follows.

Target criteria and deliverables

Task	Target	Deliverables
Task 1: Aspen Plus simulation development	Material/energy balances based on literature values for all steps except syngas generation; output includes quantification of CO_2 emission reduction and energy efficiency	Process simulation accounting for all mass flows and energy in/out; quantifiable balances for various process options based on uncertainty of syngas generation step—catalyst activity/selectivity/stability
Task 2: Bi-reforming experimental work	Space-time yields of at least 3,000 scc/g cat-min with less than 5% decrease in conversion over 200 hrs	Experimentally verified space-time yields for syngas as a function of catalyst

	at 900°C. Active metal loading of less than 2 wt%; no change in bulk properties such as crystallinity (by XRD)	composition, temperature, space velocity, and reactant gas composition ($CH_4/CO_2/H_2O$)
Task 3: Process evaluation	CO_2 reduction of one million tonnes/yr compared to conventional process technology for methanol production	Process simulation based on experimentally verified syngas generation catalysis
Task 4: Preliminary design development	Methanol annualized cost less than current spot market cost (~30 cents/lb) based on ROI of 15%	Detailed process simulation and costs analysis with documented cost basis

- Project goals

Overall objective: to develop an optimized catalyst for the conversion of CO_2 into syngas using the bi-reforming reaction.

This objective was achieved through the completion of the below tasks.

Project Tasks:

Task 1: Aspen Plus simulation development

Task 2: Bi-reforming experimental work

Task 3: Process evaluation

Task 4: Preliminary design development

- Work scope overview

The project scope can be described in four Tasks:

Task 1: Aspen Plus simulation development: develop detailed material and energy balances for all steps in the overall process using Aspen Plus software, which has the necessary database required for this simulation. This will include power and steam generation, CO_2 separation, catalytic conversion of $CH_4/CO_2/H_2O$ to syngas, and syngas to methanol (Fig. 3). The model will be developed based on thermodynamics, and existing literature. These simulations will include sensitivity analysis with both energy efficiency and CO_2 sequestration as objective functions. Input variables such as mass flow rates for the power generation step and energy in/out will be based on literature values. We will consider both conventional CO_2 separation process such as amine scrubbing and more advanced methods such as chemical looping (Section 1., p.2). The model will be used to optimize the 'experimental matrix' for Task 2.

Task 2: Bi-reforming experimental work: synthesize, characterize, and test pyrochlore catalysts for the reforming of $CH_4/CO_2/H_2O$ to syngas. These tests will specifically include experiments to measure selectivity to syngas, and overall $CH_4/CO_2/H_2O$ conversion as a function of reactant gas composition, space velocity, pressure, temperature, and time. Initial ranges of variables to be tested are as follows:

Parameter	$CH_4/CO_2/H_2O$ ratio	Temp, °C	Press., atm	SV, scc/min-g cat
Experimental range	(1-3)/(1-2)/(1-2)	600-1000	1, 15, 30	10^3-10^4

These variable ranges are designed to provide quantitative input into the process simulation and economic analysis—allowing the effect of trade-offs in the bi-reforming step to be quantified.

These experiments will involve pyrochlore catalysts with various A- and B-site dopants, with initial candidates including Ca and Sr for the A-site, and Rh, Co, Ni for the B-site, all at substitution levels less than 5 wt% (which is the upper limit on the level of substitution that can be used while retaining the pyrochlore structure). The goal will be to identify the optimum catalyst, as measured by activity and selectivity to syngas.

The experimental setup consists of a reactor typically containing ~100mg of catalyst in a temperature controlled oven. The flow rate, gas composition, pressure, and temperature can be varied using experimental control software. The product composition is monitored continuously with a quadrupole mass spec with spot checks using a GC/MS.

The initial screening tests will be followed by longer term tests (several hundred hours) on the most active/selective catalysts to determine the rate and mechanism of deactivation, with the goal of minimizing it—*and* testing ways to regenerate the spent catalyst (e.g., by temperature programmed oxidation, TPO, of the spent catalyst). Understanding the deactivation mechanism (carbon deposition, sintering, etc) will allow us to design catalysts that will meet the demanding conditions of commercial practice and minimize catalyst costs.

The experimental work will be split between LSU and UCR. LSU will conduct the catalyst synthesis and characterization and also the 'core' baseline experiments that will evaluate catalyst performance under the anticipated optimal conditions. UCR will then conduct detailed 'parametric evaluation' by conducting long test runs to study deactivation, effect of a wider range of parameters and other tests suggested by experimental/simulation data. Similar experimental setups will be used and this will allow the team to evaluate a wider range of options over the project period.

The results of this Task will provide input into the material/energy balances for the syngas generation step - space/time yields as a function of reaction conditions, for example. This information will be used in the preliminary economic analysis (Task 3).

Task 3: Process evaluation: develop material/energy balances based on experimentally verified reaction conditions for the syngas generation step. Information needed for the simulation of other steps in the overall process is the subject of Task 1 and is not repeated here. Because the results in Task 2 may affect the conclusions from Task 1, integrating the syngas generation conditions/output into the overall process simulation is essential. The Aspen Plus model will incorporate the experimental data to produce 'semi-empirical' modules that better predict process performance. This task will be conducted simultaneously along with Task 2. This Task will provide the necessary input into the economic analysis of Task 4.

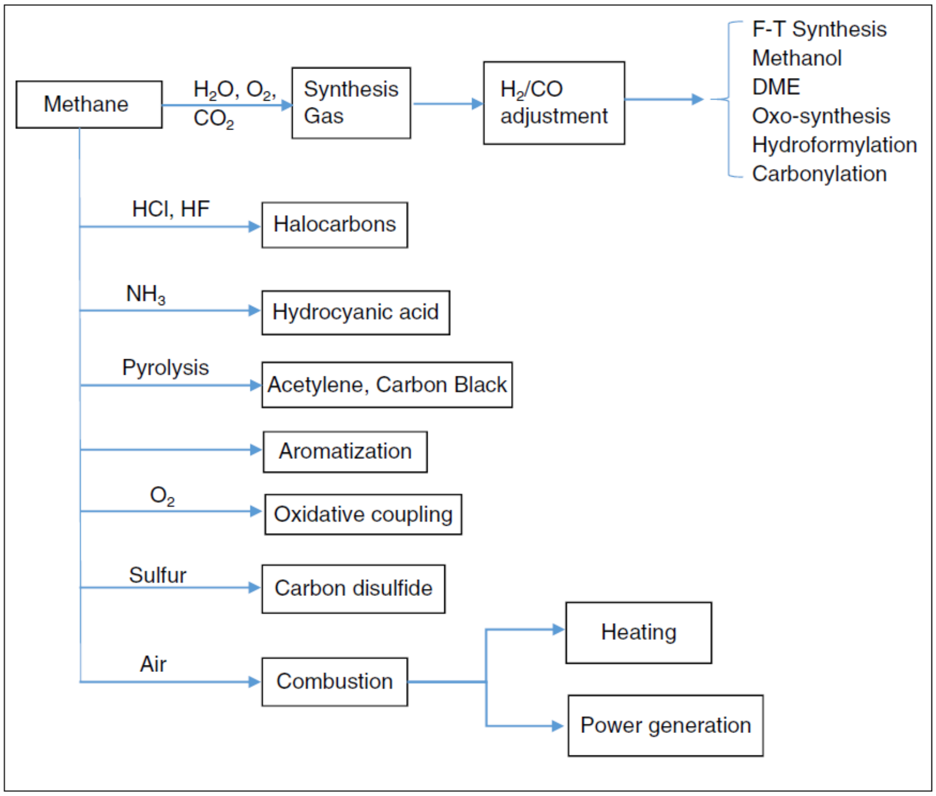
Task 4: Preliminary design development: develop specific process design parameters and configurations on results from Task 3. After identifying optimal conditions as measured by overall energy efficiency and CO_2 sequestration, preliminary capital/operating costs will be developed. Careful sensitivity analyses will be carried out to determine those variables that impact process costs (expressed as "annualized" costs that reflect return on investment and other factors) most significantly. For example, we may find that the cost of CO_2 separation has a greater effect on operating costs than annualized catalyst cost for the syngas generation step, suggesting that a more costly, but more selective, bi-reforming catalyst has an insignificant effect on annualized costs. We may also find that catalyst lifetime is more significant than selectivity, so that minimizing deactivation is a key objective of Task 2.

3 Outcomes and Learnings

- Literature review

CH_4 conversion

First, consider the processes in which methane can be converted to higher value products. Generally, the conversion of CH_4 to higher value products can be divided into indirect and direct routes (shown in Fig below).



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:

$$CH_4 + (H_2O, CO_2, O_2) \rightarrow xCO + yH_2$$

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:

$$(1) \qquad CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H_{298K} = +206\ kJ/mol,\ \ \Delta G_{298K} = +142\ kJ/mol$$

Like all methane reforming process, this reaction is highly endothermic and temperatures typically above 800-900^{0}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:

$$(2) \qquad CH_4 + \tfrac{1}{2}O_2 \rightleftharpoons CH_3OH, \qquad \Delta H_{298K} = -126\ kJ/mol,\ \Delta G_{298K} = -112\ kJ/mol$$

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 $CO_2 + H_2O$.

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

$$(3) \qquad 6CH_4 \rightleftharpoons C_6H_6 + 9H_2 \qquad \Delta H_{298K} = +531\ kJ/mol,\ \Delta G_{298K} = +433\ kJ/mol$$

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].

CO_2 conversion

Large scale techniques to capture CO_2 from combustion and other processes have provided the incentive to develop methods to convert CO_2 into higher value products. Presently, only a small fraction of CO_2 potentially available for synthesis of higher value products is used for conversion. Indirect routes: Commercial processes in which methane is reformed with CO_2 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-CO_2 reforming, and bi-reforming:

Dry reforming: (4) $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$
$\Delta H_{298K} = +247\ kJ/mol,\ \Delta G_{298K} = +170\ kJ/mol$

Oxy-CO_2 reforming: (5) $3CH_4 + CO_2 + O_2 \rightleftharpoons 4CO + 6H_2$
$\Delta H_{298K} = +58\ kJ/mol, \Delta G_{298K} = -1\ kJ/mol$

Bi-reforming: (6) $3CH_4 + CO_2 + 2H_2O \rightleftharpoons 4CO + 8H_2$
$\Delta H_{298K} = +220\ kJ/mol,\ \Delta G_{298K} = +151\ kJ/mol$

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 H_2/CO syngas produced by dry reforming is not directly useful for chemical synthesis, which typically requires 2/1 H_2/CO syngas for most oxygenates, Fischer-Tropsch and other processes.

Oxy- CO_2 reforming has the appeal of autothermal operation, but safety concerns associated with the presence of oxygen has limited its use.

Compared to other CO_2-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 it derivatives.

Direct routes: These processes include the synthesis of urea and its derivatives, salicylic acid, and carbonates. In another process, CO_2 hydrogenation produces chemicals and fuels such as methanol, dimethyl ether (DME), and hydrocarbons. In recent years, the hydrogenation of CO_2 is being intensively studied because of its fundamental and practical applications in catalysis and surface science. For example, the direct conversion of CO_2 via hydrogenation is a straightforward way to produce methanol [8].

$$(7) \qquad CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O, \quad \Delta H_{298K} = -50\ kJ/mol,\ \ \Delta G_{298K} = +3.5\ kJ/mol$$

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 CO_2 via this route using improved catalysts.

Review of bi-reforming

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 CH_4 and CO_2, 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 CO_2/H_2O ratio) and (ii) matching the 2/1 H_2/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-CO_2 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 CO_2. Reforming using dry or bi-reforming eliminates the need to separate CO_2 and methane, an expensive step.

The next sections will briefly compare bi-reforming with the two alternatives for conversion of CO_2 and CH_4, and discuss the carbon deposition, and the bi-reforming itself.

1. Processes for reforming of CH_4 and CO_2

There are three processes to reform CO_2 and CH_4 into syngas, all of which require temperatures above ~800 °C to reach thermodynamically complete conversions:

1.1 CH_4 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].

$$(4) \quad CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H_{298K} = +247\ kJ/mol,\ \ \Delta G_{298K} = +170\ kJ/mol$$

However, the low H_2/CO ratio (1/1) from dry reforming requires the addition of H_2 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].

1.2 Oxy-CO_2 Reforming:

The oxy-CO_2 reforming of methane has been investigated [10, 11] and found to have improved energy efficiency of the process as compared to dry reforming:

$$(5) \quad 3CH_4 + CO_2 + O_2 \rightleftharpoons 4CO + 6H_2 \qquad \Delta H_{298K} = +58\,kJ/mol,\ \Delta G_{298K} = -1\,kJ/mol$$

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 H_2/CO ratio of oxy-reforming (1.5/1) has greatly limited its industrial use.

1.3 Bi-Reforming:

The reforming of methane with a combination of CO_2 and steam is known as bi-reforming:

$$(6)\ 3CH_4 + CO_2 + 2H_2O \rightleftharpoons 4CO + 8H_2\ \Delta H_{298K} = +220\,kJ/mol,\ \Delta G_{298K} = +151\,kJ/mol$$

Like dry reforming, syngas from bi-reforming can convert CO_2 into higher value products. Also, like dry reforming, bi-reforming can be used to produce syngas from natural gas containing significant amounts of CO_2 and can also be used to react CO_2 separated from flue gases from fossil fuel combustion [7]. Unlike dry reforming, bi-reforming results in a H_2/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 H_2/CO ratio can be adjusted by changing the $H_2O/(H_2O + CO_2)$ ratio to meet the downstream requirement [12, 13].

2. 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.

2.1 Background:

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

$$(8) \quad CH_4 \rightleftharpoons C_{(s)} + 2H_2 \qquad Methane\ decomposition$$

$$(9) \quad 2CO \rightleftharpoons CO_2 + C_{(s)} \qquad CO\ disproportionation/Boudouard\ Reaction$$

$$(10) \quad CO + H_2 \rightleftharpoons C_{(s)} + H_2O \qquad CO\ Reduction$$

All these reactions are reversible, and may remove the $C_{(s)}$ through gasification[1] [footnote (1)]. At temperatures above ~700 °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}. 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].

2.2 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 ~850^{0}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 ~800^{0}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^{0}C. This is the net result of the CH_4 decomposition, Bouduard reaction, and CO reduction (reactions 8, 9, and 10 respectively), resulting in more steam than the initial amount (2 kmol).

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[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.

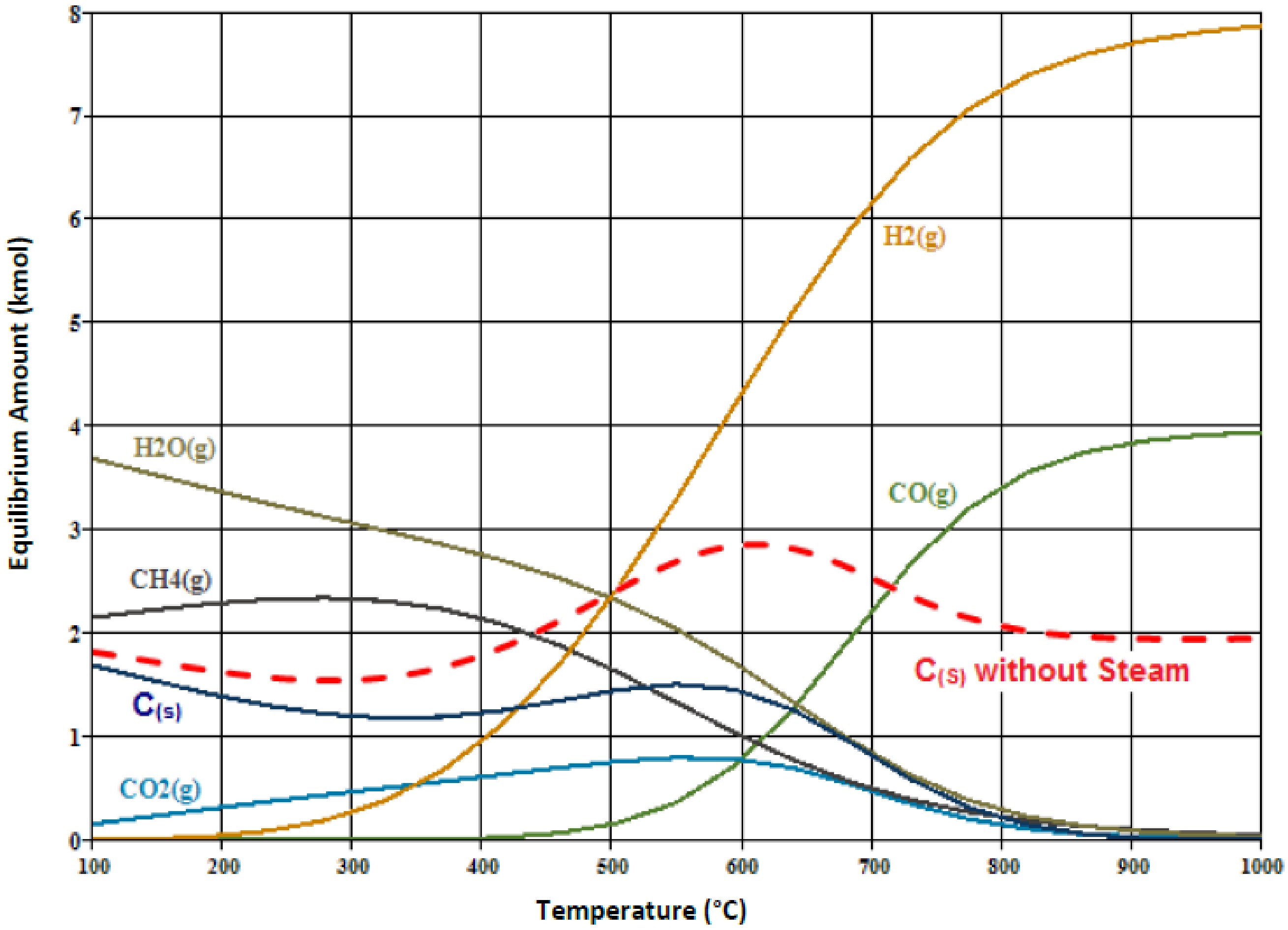


Figure 3. Equilibrium composition for bi-reforming reaction at different temperatures and atmospheric pressure calculated by HSC Chemistry. The initial amounts of reactants in kmol are CH_4=3, CO_2=1, H_2O=2. Allowed products are CO, H_2, and $C_{(s)}$. The dotted curve shows $C_{(s)}$ formation under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

3. 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.

3.1 Advantage of bi-reforming over other reactions utilizing both CH_4 and CO_2:

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, CO_2 and CH_4 to syngas. In order to reduce the carbon formation on the catalyst surface, adding water and/or O_2 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 H_2 and CO (based on methane conversion), because the net formation of CO_2 or H_2O becomes zero while the H_2/CO ratio can be controlled [18, 19]. From an energy balance perspective, replacing part of the steam in the inlet with CO_2 reforming consumes the same overall amount of energy while utilizing carbon dioxide [17].

Bi-reforming with a specific ratio of $CH_4/H_2O/CO_2$ can in practice be easily adjusted to the desired stoichiometric ratio of 3/2/1 by adding steam or CO_2, because typically the sources of natural gas, biogas and coal bed methane are CH_4-rich. This produces the desired 2/1 H_2/CO syngas. Even other components in natural gas such as ethane and propane can also be bi-reformed in accordance to the overall conversion:

$$(11) \qquad 3C_nH_{2n+2} + (3n-1)H_2O + CO_2 \rightarrow (3n+1)CO + (6n+2)H_2$$

3.2 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 CO_2, 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. CeO_2 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 $CH_4/H_2O/CO_2$ and observed stable activity for 320 h with a H_2/CO product ratio of 2/1. The selectivities for CO and H_2 were 100% and 98% respectively and conversions of both CH_4 and CO_2 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 H_2/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 H_2/CO ratio increases slightly from 1.99 to 2.02. Moreover, doubling the steam and CO_2 amount at 7 atm enhanced the CH_4 conversion from 71% to 85%.

One of the industrially significant results by Olah et al. [7] was that they were able to adjust the H_2/CO ratio in the product gases by changing the CO_2/H_2O 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 H_2/CO ratio for the oxy-CO_2 methane reforming process. For bi-reforming reactions carried out by the same group [19, 24], the product H_2/CO ratio was varied from 1.5 to 2.5 by manipulating the relative concentrations of stream and CO_2 in the feed.

3.3 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 $^{13}CO_2$ transient experiment showed that carbon formed from CO_2 or CO decomposition was less active than adsorbed CH_x species formed from CH_4 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 CO_2 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 CH_4. Therefore, the intermediate is consumed to form CO and decreases the amount of CO_2 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 CH_4:

$$CH_4 + 2M \rightarrow CH_3{-}M + H{-}M$$
$$CH_3{-}M + 2M \rightarrow CH{-}M + 2H{-}M$$
$$CH{-}M + M \rightarrow C{-}M + H{-}M$$

Decomposition of H_2O and CO_2:

$$H_2O + 3M \rightarrow O{-}M + 2H{-}M$$
$$CO_2 + 2M \rightarrow O{-}M + CO{-}M$$

Reaction of adsorbed species:

$$CH_x{-}M + O{-}M + (x-1)M \rightarrow CO{-}M + x\,H{-}M$$

Production of CO and H_2:

$$CO{-}M \rightarrow CO + M$$
$$2H{-}M \rightarrow H_2 + 2M$$

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].

4. Outlook

The bi-reforming reaction to produce syngas from CH_4 and CO_2 offers significant advantages over dry reforming and oxy-CO_2 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.

- Technology development, installation and commissioning

The path toward commercialization is straightforward. The process proposed here is based on proven technology with the exception of the bi-reforming step. This minimizes technical and economic risk in evaluating the process for commercialization. For the bi-reforming step, the final product of the research we propose is a catalyst formulation that can be washcoated on an industrially practical support using *proven* technology, Material and energy balances described here clearly show the reduction in net CO_2 emissions, coupled with the production of a widely marketable commodity chemical (as shown below in section 7) for which Canada is a large net importer.

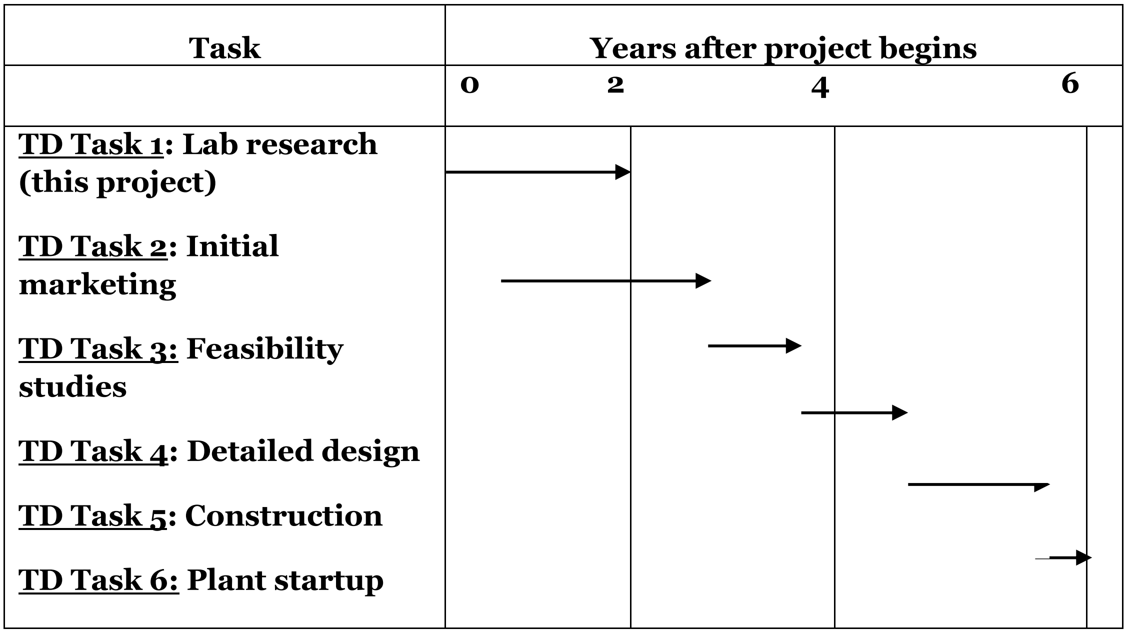
Once the research proposed above is complete, a process based on the steps shown in Fig. 1 must be marketed to chemical and engineering firms where a detailed technical/economic evaluation will be carried out. This will include both generic and site-specific cost factors with the objective of determining the return on investment once the plant is complete. Of particular significance is that this process is based on natural gas. Virtually all projections of natural gas costs show a long-term significant cost advantage for this resource, providing some assurance to potential investors that current estimates of process economics will involve minimum risk.

Technip Inc. (www.technip.com), one of the world's largest Engineering, Procurement, and Construction (EPC) companies and a leading commercial provider of reforming technologies for hydrogen production, has expressed possible interest in the proposed technology based on the information in this proposal. *A letter from Technip is attached at the end of Appendix A.*

Commercial organizations typically require that the technology they wish to evaluate be patented. That is the case here. This allows the companies access to the technology on terms they feel are best for their company—e.g., non-exclusive license, purchase of the technology, exclusive license.

Any projection of a timeline for commercialization of the lab-scale research proposed here is speculative. However, based on the marketing efforts already underway by Pyrochem, we suggest that a 5-7 year horizon for marketing, design, construction, and production of a green-field plant is reasonable. *This compares favorably to the 10+ year horizon that is typical of processes with less proven technology*. Even this relatively short timeline could be considerably shortened if the process proposed here is added to existing infrastructure (e.g., a natural gas-fired power plant), in which case implementation within 2-3 years after completion of the work proposed here is possible. An approximate timeline for deployment of the technology based on a 6-yr horizon is shown below.

Technology development timeline



Milestone:		
	Δ1	Complete lab research proposed here
	Δ2	Identify prospective companies
	Δ3	Secure commitment of potential companies to carry out feasibility studies
	Δ4	Complete feasibility studies, decision to proceed to design.
	Δ5	Begin construction
	Δ6	Startup

- Experimental procedures/methodology

Catalyst Preparation. The 1% LNZ pyrochlore catalyst was prepared by using a modified Pechini method. The preparation method produces highly uniform pyrochlore crystallites and is explained in detail in the literature [1-6]. The precursors used for La, Ni, and Zr were Lanthanum nitrate [$La(NO_3)_3.6H_2O$] (GFS Chemicals), Nickel nitrate [$Ni(NO_3)_2.6H_2O$], and Zirconium nitrate [$ZrO(NO_3)_2.nH_2O$] (Alfa Aesar) respectively. The nitrate salts were separately dissolved in de-ionized water and then mixed with a citric acid (CA) solution in a molar ratio of CA:metal=1.2:1. The solution was continuously stirred and heated to 75 ˚C to ensure complete metal complexation. At 75 ˚C, a 1:1 molar ratio of ethylene glycol (EG) to CA was added to the solution. The solution was kept stirred on the hot plate until most of the water had evaporated and a transparent, viscous gel was obtained. After this the stirring was stopped and the gel was left on the hot plate to promote the polyesterification reaction between EG and CA to form an organic polymeric network. The nitrate precursors started to decompose at this condition, which was evident from the large plumes of NOx and bubbling in the gel. The resulting mixture foam was placed in an oven at 110 ˚C to dry overnight. The mixture was then calcined at 1000 ˚C for 8 h to oxidize the organic precursors to form the pyrochlore catalyst. The bulk density of the catalyst was measured to be 0.77 g/cc.

Temperature Programmed Reduction (TPR). Temperature programmed reduction (TPR) profiles of the calcined catalyst were recorded using an Altamira AMI 200 unit equipped with a thermal conductivity detector (TCD). 50 mg of catalyst sample was first oxidized in a fixed-bed micro-reactor system under flowing 5% O_2/He at 950 ˚C. It was then cooled to 25 ˚C under helium flow. TPR was performed using a 10% H_2/Ar mixture at a flow rate of 50 cm^3/min while the temperature was linearly ramped from 25 ˚C to 950 ˚C at 10 ˚C/min. The catalyst was then cooled to 25 ˚C under helium flow and then again oxidized under 5% O_2/He at 950 ˚C. The catalyst was again cooled to back 25 ˚C under helium flow. A second TPR was carried out under the same conditions as those of the first TPR mentioned above. The hydrogen consumptions under different peaks were calculated by deconvoluting the TPR profile and calculating the areas under the individual peaks, which directly correspond to hydrogen consumption. The thermal conductivity detector was calibrated with a standard silver oxide sample, where area under the peak was correlated to the H_2 consumption.

X-Ray Characterizations. X-ray absorption (XAS) spectra were measured at the electron storage ring of the Center for Advanced Microstructures and Devices (CAMD), Louisiana State University, USA. This synchrotron light source operates the storage ring at 1.3 GeV with a ring current between 50 and 150 mA. The measurements were made at the High Energy X-Ray Absorption Spectroscopy Beamline located on an 11-pole, 7.5 Tesla multi-pole wiggler. The edge was calibrated to 8333 eV with a nickel foil. XAS spectra were collected for the Ni K-edge in fluorescence mode from -200 eV to 14 k relative to the Ni K-edge energy. The steps were 5 eV from -200 eV to -30 eV, 0.3 eV from -30 eV to 30 eV around the edge, and 0.05 k up to 14 k. Fluorescence spectra were obtained with an 80 mm^2 Ketek silicon drift detector by averaging at least four to five scans. XAS spectra were also collected for reagent grade NiO (Alfa Aesar) and nickel foil in transmission. Spectra were analyzed with Athena [7] in Demeter and WinXAS [8]. In extended X-ray absorption fine structure (EXAFS) analysis the amplitude reduction factor (S_0^2) was obtained from standards and kept fixed for the catalyst spectra.

X-ray diffraction (XRD) experiments were carried out using Empyrean x-ray diffractometer (PANalytical) using Cu K_α radiation ($\lambda = 1.5406$Å). The scan angle was varied from 0˚ to 90˚ with a step size of 0.017˚. Data analysis was done using the software X'Pert HighScorePlus (v3.0).

Catalyst activity test. Catalytic activity tests were carried out in a ¼" size flow reactor made of quartz, which can withstand up to 1200 ˚C under 1 atm. The pretreatment of the catalyst involved oxidation under 10% O_2/He flow at a temperature of 800 ˚C before cooling down to room temperature under pure helium. The catalyst was then reduced under 10% H_2/He flow at 800 ˚C. After the reduction, the catalyst was cooled to the reaction temperature under helium flow.

The schematic of the reactor and gas analysis system is presented in Figure 1. The reactor system consists of various mass flow controllers for metered flow of gases. The water was fed to the reactor using a HPLC pump. The water flows through a vaporizer where steam is formed, which is later mixed with other gases before flowing through the catalyst bed. The dotted lines in Figure 1 represent heat-traced lines, which were typically kept at 200 ˚C to avoid any condensation of steam. The reactor is equipped with a thermocouple that is inserted directly into the catalyst bed to measure the actual temperature of the catalyst. Both ends of the catalyst bed were plugged with quartz wool to avoid entrainment of any catalyst particles with the gas stream. Outlet gases were analyzed using an inline gas chromatograph (GC) equipped with a flame ionization detector (FID). The GC uses a Restek™ RT-Q Bond column (25 m), where helium is used as a carrier gas. Part of the gases coming out of the GC column was split and fed to a mass spectrometer (MS) at the same time as FID to check the reproducibility of the analysis. Both, FID and MS detectors were calibrated with standard gas mixtures using a minimum of 3-point calibration, corresponding to 3 different concentrations. A calibration curve was made for each component and used for the reaction data analysis. Mass spectrometer was calibrated with various concentrations of water, since it cannot be detected in the FID. The GC/FID system (Shimadzu GC-2014) is also equipped with two thermal conductivity detectors (TCD), used to analyze CO, CO_2 and H_2.

The bi-reforming reaction was carried out at temperatures starting from 700 ˚C till 950 ˚C, in the increment of 50 ˚C. The catalyst was kept for 24 h at each temperature to reach the steady state. At the end of the reaction, the temperature was brought back to 750 ˚C in order to have a comparison with the previous results and see the deactivation of the catalyst after high temperature runs. A temperature programmed oxidation (TPO) was carried out on the spent catalyst after the reaction. For TPO, the catalyst was heated from room temperature to 950 ˚C under 10%O_2/He mixture and CO_2 signal was recorded in a mass spectrometer. A blank experiment was carried out at bi-reforming conditions to see the activity of the reactor without the catalyst. For blank experiment, quartz wool was used in the quartz tube and temperature was increased from 700 ˚C till 950 ˚C in the increment of 50 ˚C. The gas and water flow rates were kept the same as those of the experimental conditions and samples were taken at each temperature. The results presented in this work are after subtraction of the blank experiment results at the corresponding conditions. The carbon balance is within 95% confidence limits.

The gases used for the reactions were 10%CO_2/He, and 10%CH_4/He. The experiments were carried out at 1 atm pressure and space velocity of 98,700 scc.h^{-1}g.cat^{-1}. The following molar ratios of various gases were used for the bi-reforming reaction on a helium free basis. All in mol%: CO_2 = 16, CH_4 = 51, H_2O = 33. The molar ratios were kept close to the stoichiometric ratios for the bi-reforming reaction (reaction 3).

Following relations were used for calculating various parameters.

$$CH_4\ Conversion\ (\%) = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \times 100$$

$$CO_2\ Conversion\ (\%) = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} \times 100$$

$$CO\ Selectivity\ (\%) = \frac{moles\ of\ CO\ produced}{Total\ moles\ of\ carbon\ produced} \times 100$$

$$CO\ Yield\ (\%) = \frac{Actual\ amount\ of\ CO\ formed}{Theoretical\ amount\ of\ CO\ expected} \times 100$$

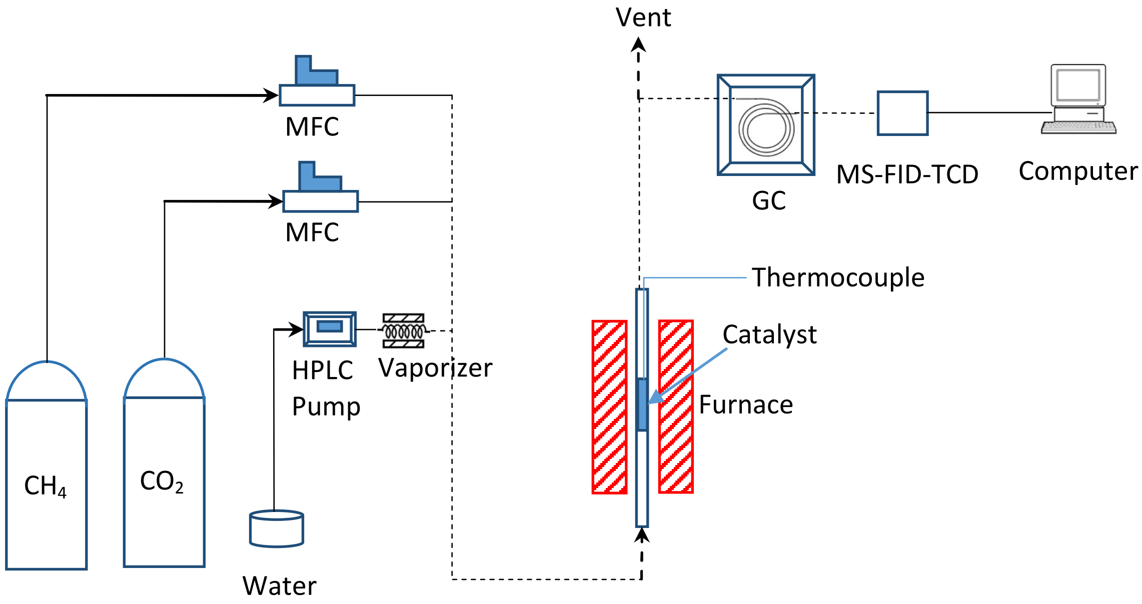


Figure 1. Schematic diagram of experimental setup for bi-reforming reaction. The dotted lines are heat traced to avoid condensation of steam.

For CO selectivity calculations, total moles of carbon produced was calculated by counting all the carbons in the product, except those in the CH_4 and CO_2. For yield calculations, the theoretical amount of product was calculated from the stoichiometry of the bi-reforming reaction.

- <u>Modelling details</u>

- A model for simulation/calculation of the process parameter is developed by using Aspen plus process simulator. The basic model assumptions are described below:

- CO_2 is separated from coal based power plant. The flue gas composition is: O2 – 4.4%, N2 – 76.65 %, CO2 – 12.75%, H2O – 6.2%[1]. The temperature of the flue gas is 57 °C [2]. The energy required for CO_2 separation is not more than 4.32 GJ/tonne [3]. After CO_2 separation the temperature goes down to 25 °C. The CO_2 enters to the system at an atmospheric pressure.
- CH_4 from the natural gas pipeline enters to the bi-reforming system at 2 atm pressure and 25 °C.
- Water enters to the system at room temperature.
- Heat supply for the bi-reforming system, steam generation are supplied by CH_4 burning inside a combustor and heat recovered from the system.
- CH_4 is burned 40% excess air to ensure complete combustion of the fuel.

- Air supplied to the combustor at 25 °C and 1 atm
- Gaseous flow pressure is increased with an isentropic multistage compressor to the desired pressure. The mechanical efficiency of the compressor is 70% and pump is 65% [4,5].
- Mixed bi-reforming feed heated up from bi-reforming product inside a heat exchanger before entering to the bi-reformer. The reformate gas leave the heat exchanger at 350 °C.
- Bi-reformer is operated at 25 atm pressure and 900 °C [6,7]. The CH_4/CO_2/steam ratio is maintained at 3/1/2.
- Produced syngas goes through a separator before entering to the methanol synthesis system. The separator separates 100% CH_4, 25% CO, 25% CO_2 and 23.5% H_2.
- Separated syngas pass through multistage compressor and cooler before entering to the methanol synthesis reactor.
- Syngas to the methanol synthesis reactor is the mixture of the syngas produced from the bi-reformer and recycled unreacted syngas from the methanol synthesis reactor
- Product from methanol synthesis reactor is a mixture of unreacted syngas, steam, methanol which is feed to a distillation column. The distillation column separates the CH_3OH mixed with water from the unreacted syngas containing CO, CO_2 and H_2.
- Methanol synthesis reactor; 265 °C, 45 bar, 5% of CO and CO_2 converted to CH_3OH [8–13].
- Heat supplied to the steam generator is from the combustor and the heat recovery from the process.
- Heat generated from the methanol synthesis reactor is utilized the distillation column or separator.
- The model use Peng-Robinson equation of state for thermodynamic calculations.
- A simulation model for CH_4 bi-reforming process coupled with methanol synthesis reactor was developed by using Aspen Plus chemical process simulator. The model was based on a bi-reformer, a methanol synthesis reactor, a combustor for heat generation for steam generation and a heat recovery system for bi-reforming reactor heat supply. Fig. 1 shows the simulation model for the coupled overall process.

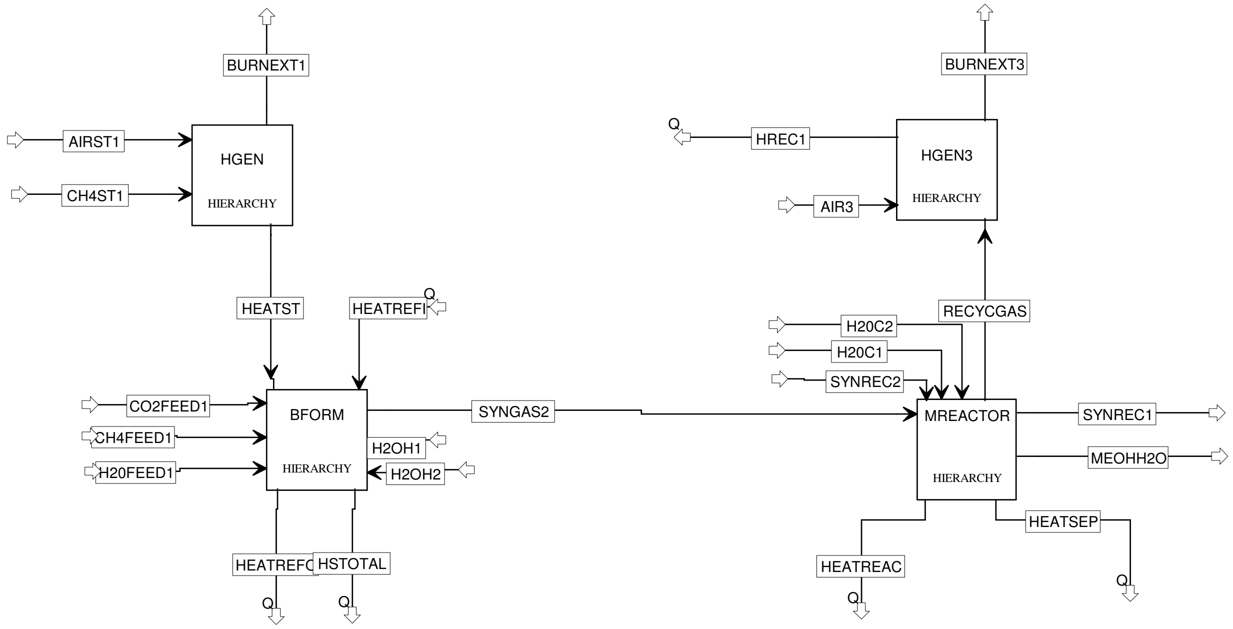


Fig. 1: Simulation model for the combined process.

Initially CH_4, CO_2, and water are heated up and mixed before entering to the bi-reforming reactor (BFORM HIERARCHY). After passing through the reformer the feed gas converts to syngas which enters to the methanol synthesis reactor system (MREACTOR HIERARCHY). A part of syngas is separated and supplied to the heat recovery unit (HGEN3 HIERARCHY). The separator helps in syngas conditioning for achieving the desired syngas ratio needed for the methanol synthesis reactor. Feed gas is pressurized in all the stages required and the compressed gas is cooled by cooling water where necessary. The heat recovered by cooling water is utilized for steam generation. The steam generation required additional heat produced by a furnace system (HGEN HIERARCHY). All the reactors used for the model are stoichiometric reactors that converts the pre-specified fraction of the reactant.

The detail of the bi-reforming section is given in Fig. 2. The bi-reformer needs 3 feed: CH_4, CO_2 and steam. Both CH_4 and CO_2 comes through 2 stage compressor and the temperature and pressure of the individual gases are about 400 °C and 25 atm. The water comes through a pump and initially heated up by the heat recovered from the syngas pressurization section of the methanol synthesis unit. The heated water then goes to a boiler and which generates steam by utilizing the heat from a CH_4 burned furnace. The steam exits the reactor at 250 °C and 25 atm. Then the CH_4, CO_2 and steam get mixed together and reach at a temperature of about 360 °C. The mixed feed then heated up inside a heat exchanger and where the heating gas is produced syngas from the bi-reformer. The syngas leaves the heat exchanger at 350 °C. The heated feed reacts inside the bi-reformer and the heat required for the bi-reforming reactions to occur is supplied from another furnace that utilizes the unreacted CH_4, separated CO and H_2 from the produce syngas mixture. In case the produced heat is not enough for the bi-reformer, additional CH_4 and air is added to the bi-reformer.

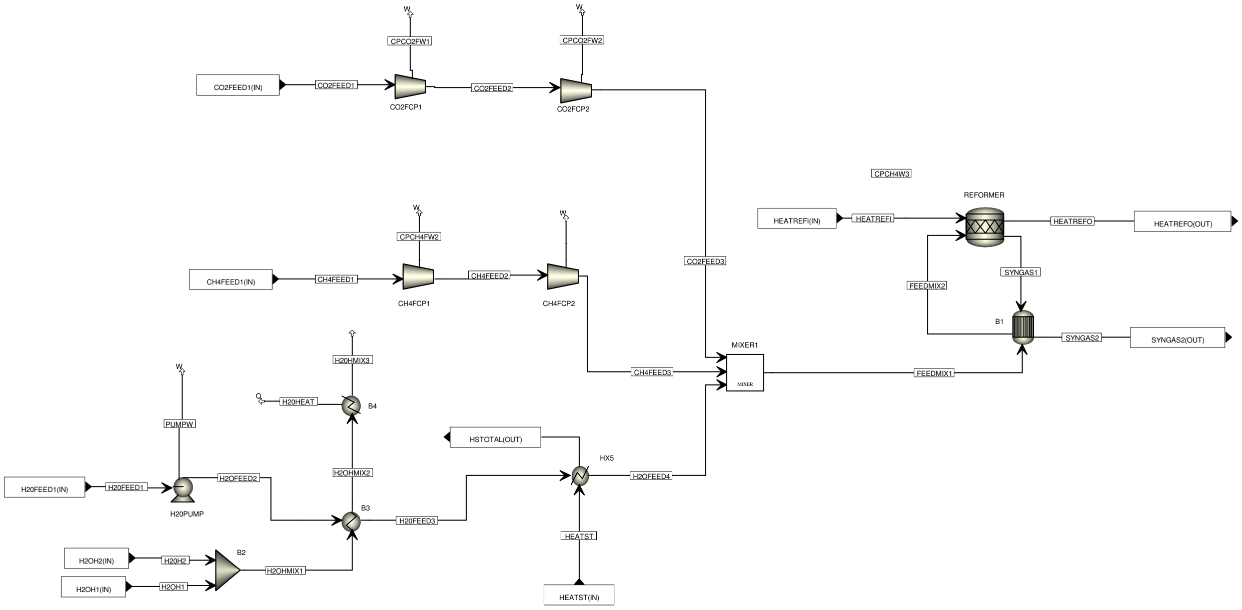


Fig. 2: The bi-reforming reactor system for the combined process.

The syngas conditioning and methanol synthesis reactor system is shown in Fig. 3. The generated syngas leaves the heat exchanger at 350 °C and 25 atm. The syngas contains other components that are need to remove before sending them to the methanol synthesis reactor. Moreover, the syngas is required to pressurize to about 45 atm before feeding. The separator separates all the CH_4 present in the syngas, 25% CO, 25% CO_2 and 23.5% H_2 from the syngas mixture. No water is separated from the gas mixture. The flue gas from the separator goes to the furnace system since they contains some combustible gas. The heat generated from the furnace is utilized in the bi-reforming reactor. The syngas from separator passes through 2 stage compressor and cooling system and reaches at the pressure of 25 atm and 265 °C. The heat recovered from the cooling system is utilized in preheating of water before boiler.

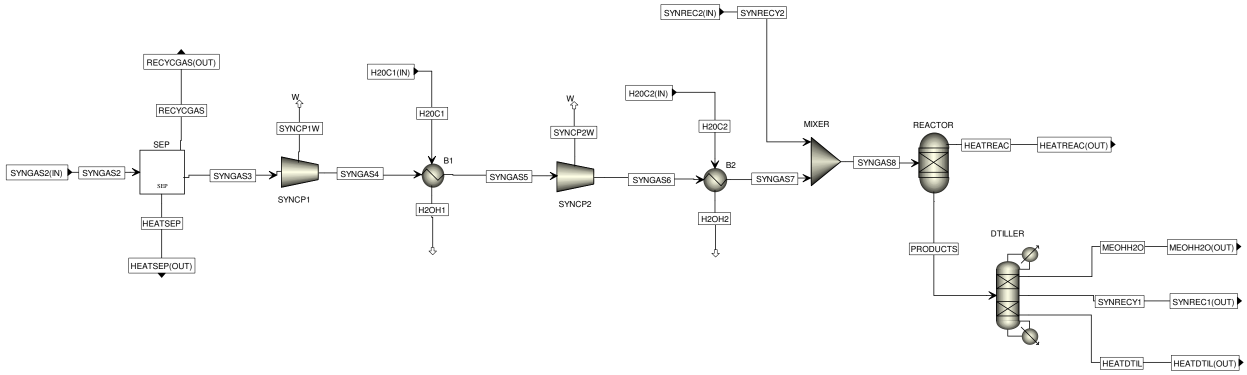


Fig. 3: The methanol synthesis reactor system for the combined process.

The conditioned syngas get mixed with the recycled stream and feed to the methanol synthesis reactor which converts only 5% of the feed to CH_3OH supplied to the reactor. The product from the reactor is feed to a distillation column which separates the CH_3OH and water from the unreacted syngas mixture. The separated unreacted mixed gas is recycled back to the reactor. CH_3OH synthesis reaction is exothermic. The heat generated from the reactor is recovered and supplied to the distillation column.

The heat recovery gas from the separator of the methanol synthesis reactor system is utilized in a heat recovery/generation unit which is shown in Fig. 4. The recovered gas is mixed with 40% excess air and supplied to a furnace. The furnace is a stoichiometric reactor that burn all the combustible components.

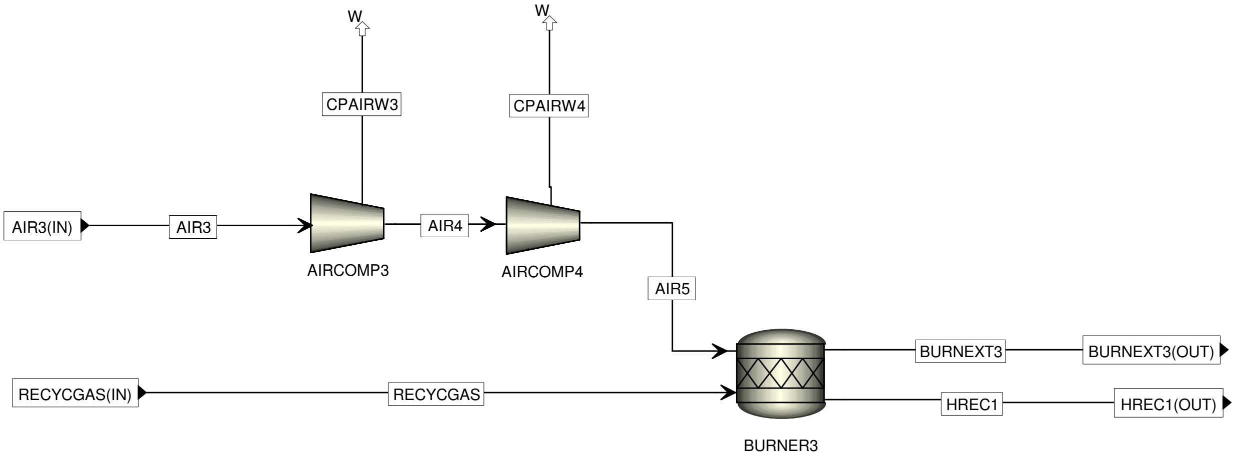


Fig. 4: Heat recovery from the syngas produced from the bi-reformer.

The steam generator/boiler requires heat supply which is done by additional CH4 burning. The heat generation unit detail is shown in Fig. 5. Both CH_4 and air is compressed and feed to a combustor where all the CH4 is burned to supply the heat necessary for the stem generation.

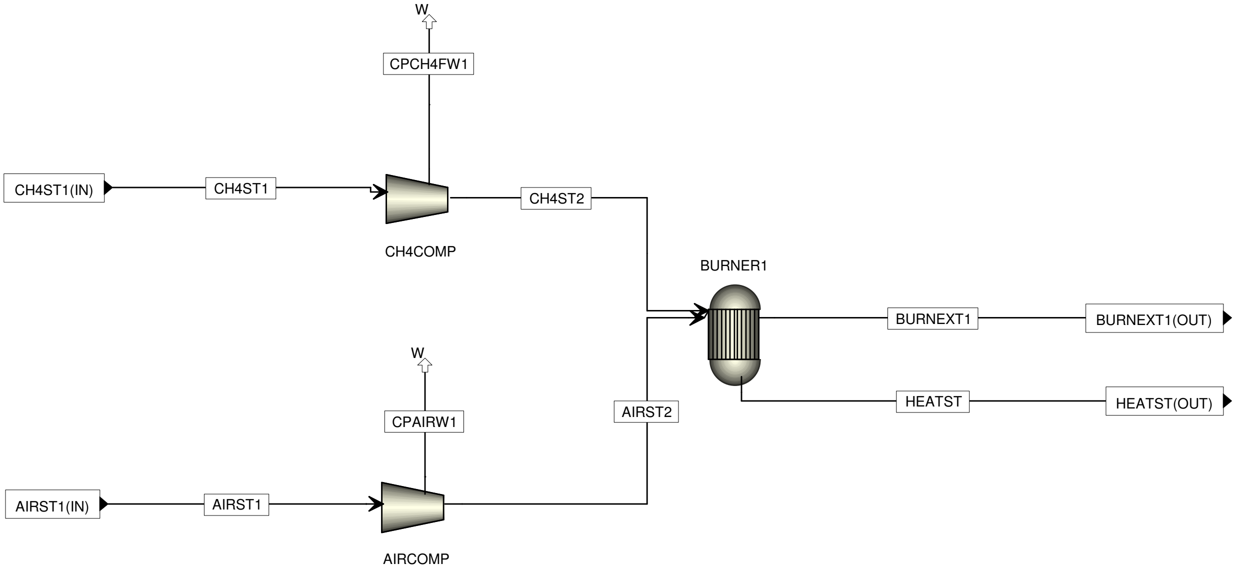


Fig. 5: Heat generation for steam generation.

- Results of experiments, model simulations

Temperature Programmed Reduction. The TPR results are shown in Figure 2. The two spectra represent two consecutive identical TPRs with an intermediate oxidation step. The reason is to determine the reproducibility of the reduction process and to investigate whether the catalyst retains its structure in the second TPR after the high temperature treatment in the first TPR. Figure 2 shows that these two successive TPR profiles are fully reproducible, which indicates that the reduction of NiO and oxidation of metallic Ni are completely reversible. At least as measured by TPRs, there is no detectable change in the structure of the catalyst, nor any sintering of the metal as a result of exposure to hydrogen up to 950 ˚C.

Figure 2 also shows a series of reduction steps from nickel oxide to metallic nickel. These four steps correspond to four peaks in the TPR. The peak at 305 ˚C can be attributed to the reduction of bulk NiO [9, 10]. The two peaks at 352 ˚C and 411 ˚C can be assigned due to the sequential reduction of Ni^{3+} to Ni^{2+} and Ni^{2+} to Ni^0, respectively [11]. Finally, most of the nickel in the catalyst is reduced under the peak at 550 ˚C, which can be attributed to the reduction of highly dispersed NiO species, which appear to be interacting strongly with the pyrochlore structure [12]. This could be the result of initial stage of crystal formation between the Ni and the La, which is known to form mixed oxides at the temperatures used for the calcination of these catalysts (e.g. La_2NiO_4). Another alternative explanation has been suggested by Rodulfo et al. [10], who assigned the high temperature peak at 565 ˚C due to the reduction of a new phase formed by solid-state reaction of NiO with the La_2O_3 support. In our case, however, this does not seem like a possibility because the EXAFS results (discussed in the next section) clearly show the presence of NiO species.

The amount of H_2 consumed by reducible nickel species per gram of catalyst is shown in Table 1. Although there are several distinct transitions of the nickel, the greatest proportion is due to relatively dispersed clusters, which interact closely with the support.

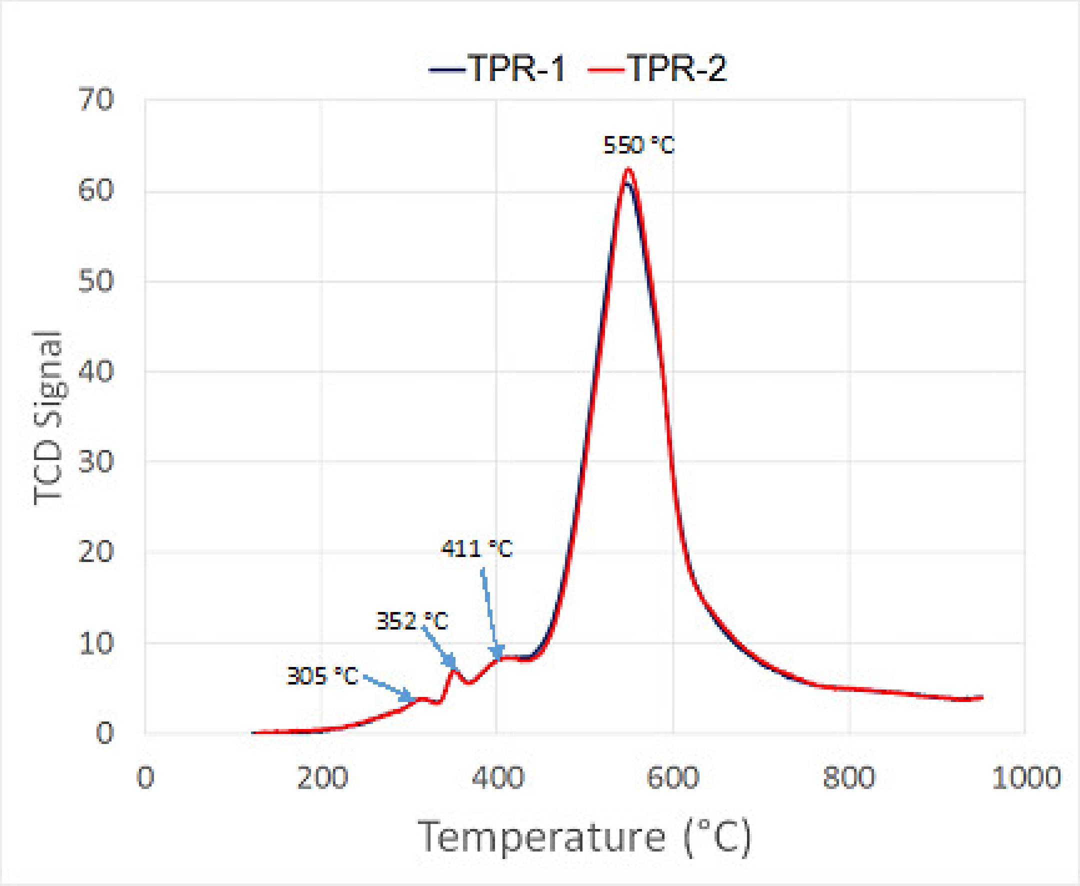


Figure 2. Temperature programmed reduction (TPR) results for 1%LNZ catalyst. The two curves represent two consecutive TPRs with an oxidation step in-between.

It can also be seen from Table 1 that the ratio of peak 3 to peak 2 is approximately 2, which corresponds to the stoichiometry for the reduction of $Ni^{3+} \rightarrow Ni^{2+}$ (under peak 2) and $Ni^{2+} \rightarrow Ni^0$ (under peak 3). This supports these peak assignments.

Table 1. Hydrogen uptake calculation by deconvoluting the TPR peaks in Figure 2.

Peak	Temperature (°C)	H_2 uptake (mg H_2/g-cat)

1	305	0.0124
2	352	0.0110
3	411	0.0225
4	550	0.2948

X-ray Absorption Spectroscopy (XAS). X-ray absorption near edge structure (XANES) Ni K-edge spectra of the catalyst in various states along with those of the standards are shown in Figure 3. After the TPR/TPO cycle, the catalyst is left in an oxidized state with TPO being the last treatment. There is a strong similarity between the NiO standard, the fresh catalyst, and the catalyst after the TPR/TPO cycle. The peaks, for example, the white line A and higher energy peak B in Figure 3a are at identical energies, suggesting that the nickel in the catalyst is in the form of NiO. This also suggests that no new phase of nickel is formed by the solid state reaction with the support. However, the peak intensities are weaker, indicating a lower degree of crystallinity. The catalyst after TPR/TPO cycle does not change with respect to the fresh catalyst, suggesting that the catalyst is not affected by the cycles of heat treatments under these cyclic reducing and oxidizing conditions.

In contrast, the spent catalyst after the bi-reforming reaction is very similar to metallic Ni with reduced amplitudes, indicating poor crystallinity. The white line for the spent catalyst (peak C) is slightly different. Linear combination fitting (by Athena [7]) shows a small amount of NiO (13%), while the rest of the Ni is still in the metallic form after bi-reforming reaction.

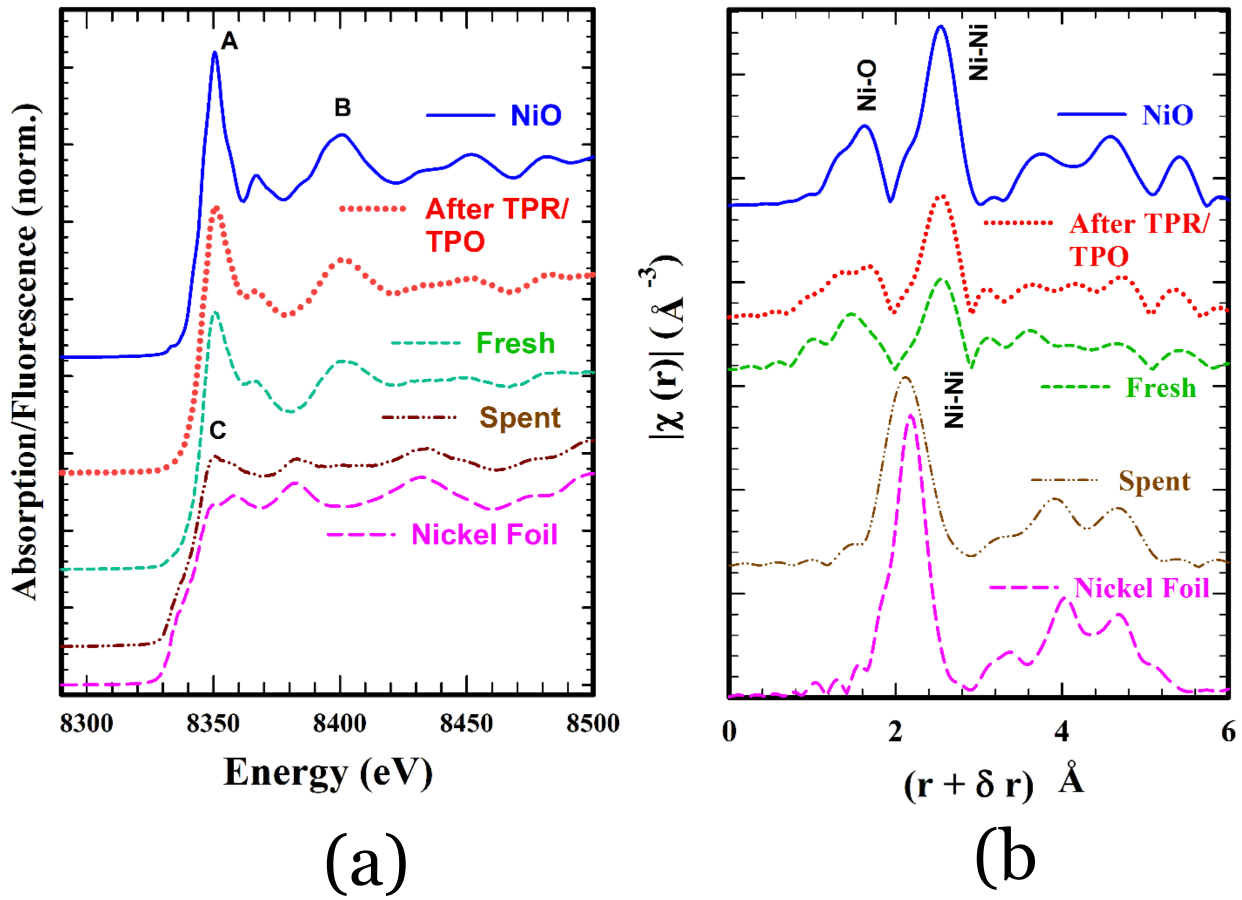


Figure 3. (a) XANES spectra and (b) Fourier transform magnitude of EXAFS for 1%LNZ catalyst in comparison with standards NiO and Ni.

Results from EXAFS analysis using WinXAS [8] are shown in Table 2 and the Fourier transform magnitude are shown in Figure 3b. Only the first shell (Ni-Ni) was fitted for the spent catalyst while first two shells were fitted for the NiO catalyst. Qualitatively the higher shells of all the catalysts show reduced amplitude, indicative of degree of crystallinity (Figure 3b). The goodness of fit criterion (χ^2) is higher for the catalyst compared to those of the standards due to higher noise in the spectra. Ni-O first shell for the fresh catalyst and the one after the TPR/TPO cycle shows a slightly higher coordination and a high Debye-Waller factor. The higher values are within error, however. The first shell appears slightly contracted in the fresh catalyst, but is quite similar to that of the crystalline NiO after the TPR/TPO cycle. In these catalysts, the second shell (Ni-Ni) distance is identical to that of crystalline NiO, but the coordination is reduced. The Ni-Ni shell for the spent catalyst is similar to that of the metallic nickel with a slightly reduced coordination, suggesting a higher dispersion.

Table 2. EXAFS analysis results summary

	Ni-O	Ni-Ni		

	N*	R (Å)	σ^2 ($x10^{-3}$)	E_0 (eV)	N*	R (Å)	σ^2 ($x10^{-3}$)	E_0 (eV)	S_0^2	Reduced χ^2
NiO Standard	5.63	2.08	5.0±0.001	-1.49±0.11	12.10	2.93	6.0±0.03	-5.36±0.04	0.89	6.67
After TPR/TPO	6.63	2.07	1.3±0.001	0.69±0.11	8.55	2.92	6.0±0.05	-8.33±0.05	0.89	10.85
Fresh Catalyst	6.93	2.00	1.4±0.08	-5.34±0.05	7.48	2.93	8.0±0.03	-9.05±0.02	0.89	10.84
Spent Catalyst					10.32	2.48	6.0±0.10	-3.30±0.01	0.84	12.63
Nickel Foil					11.91	2.47	5.0±0.02	5.82±0.03	0.84	5.18

N – coordination number; R – bond distance (± 0.02 Å); σ^2 – Debye-Waller factor; * within ±20%

From the EXAFS results it is clear that reduction and oxidation are reversible and has no effect on the bond distances of Ni-O or Ni-Ni species. This is consistent with the TPR results discussed above.

X-ray diffraction (XRD). The XRD results for the fresh 1%LNZ and the spent catalysts are shown in Figure 4. The spent catalyst was obtained after the bi-reforming reaction, during which the catalyst underwent temperatures from 700 ˚C to 950 ˚C for a cumulative period of 170 hrs.

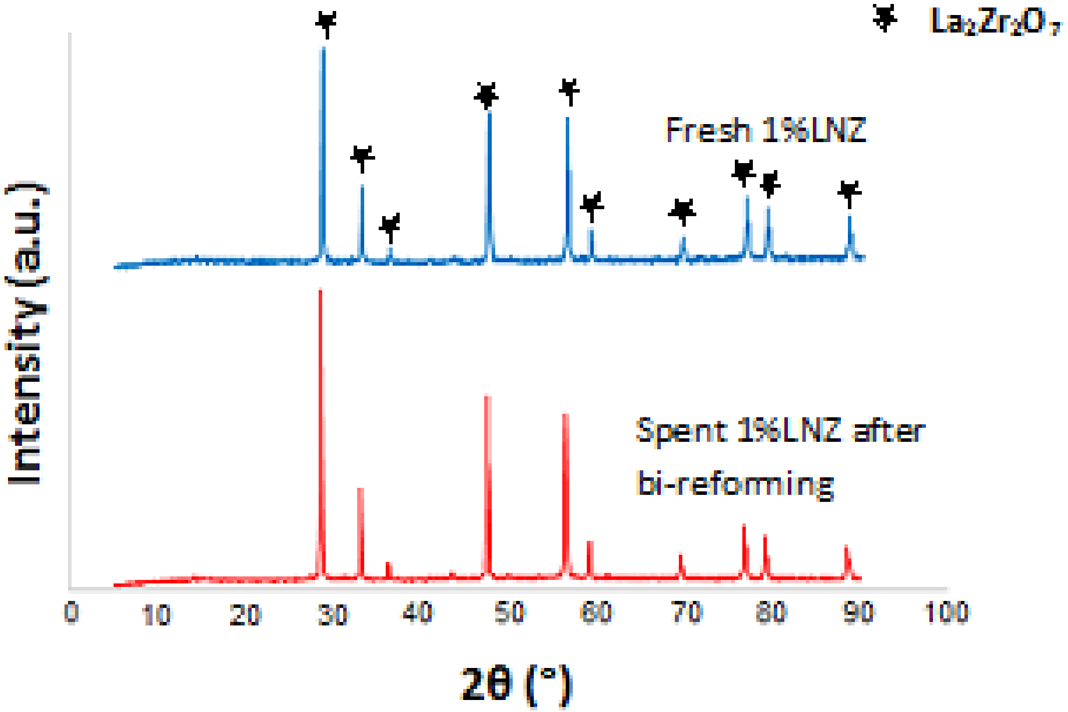


Figure 4. XRD patterns for fresh and spent 1%LNZ catalyst. The spent catalyst was obtained after bi-reforming reaction at different conditions.

Figure 4 shows that there is no change in the peak ratios or positions for the fresh and spent catalysts, which indicates that the crystalline structure of the catalyst does not change under bi-reforming conditions. All the peaks seen in Figure 4 correspond to that of the $La_2Zr_2O_7$. No peaks corresponding to NiO or metallic Ni phases are observed, due to low metal loading and high dispersion of Ni in the catalyst. These results also support the argument that the pyrochlore structure is unaffected as a result of reforming at high temperatures. Ashcroft et al. [13] also used pyrochlore catalysts containing rare earth metals to study dry reforming, but their structure was not stable and they observed a breakdown of the pyrochlore structure during the dry reforming at 660 ˚C. In our case, on the other hand, the XRD pattern for spent catalyst was not affected by the bi-reforming tests, indicating a high degree of thermal resistance of the catalyst.

Catalyst activity. Results for the activity of 1%LNZ catalyst for bi-reforming reaction are discussed in the following sections.

Blank runs for bi-reforming: Blank runs were carried out under bi-reforming conditions at different temperatures (700 ˚C – 950 ˚C). The CO_2 and CH_4 conversions were calculated corresponding to each temperature. Methane conversion in the absence of catalyst was below 0.75% at 950 ˚C and was less than detectable limit below 750 ˚C.

Time-on-stream studies: The results for 1%LNZ catalyst tested under bi-reforming conditions are presented in Figure 5. Here, CO_2 and CH_4 conversions are plotted as a function of time-on-stream at 750 ˚C.

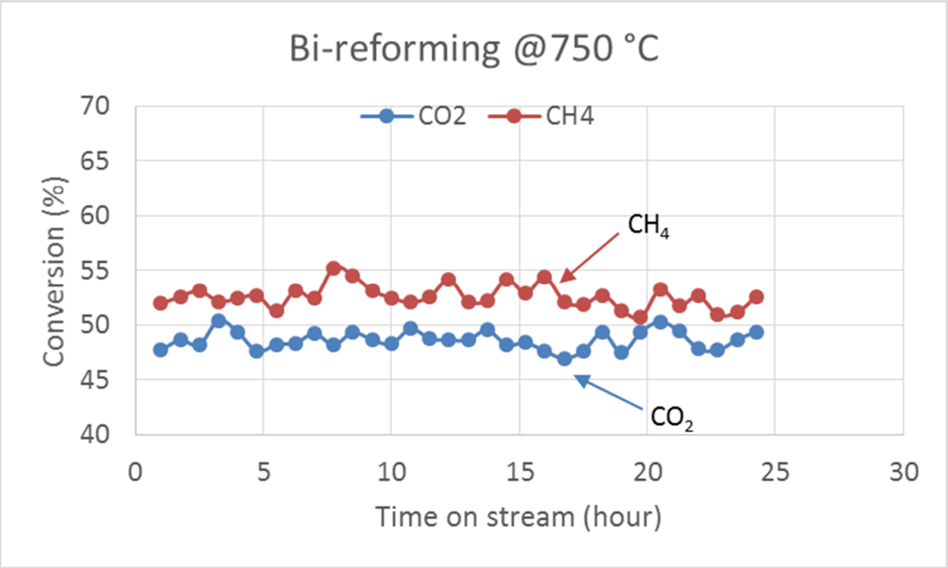


Figure 5. Time on stream tests under bi-reforming conditions at 750 ˚C and 1 atm pressure for 1%LNZ catalyst

The catalyst does not deactivate for at least 24 h time on stream at 750 ˚C under bi-reforming conditions. The same catalyst has been studied for dry-reforming of methane [6] and deactivated rapidly at 750 ˚C. It has been reported [14-18] that the presence of oxidizing agents, such as O_2 or H_2O, can help remove surface carbon deposited during the reaction. The mechanism of carbon removal is generally thought to be due to the oxidation of the carbon precursor species (partially dehydrogenated CH_x species and/or $C_{(s)}$) in the presence of H_2O [14]. The following example illustrates these types of reactions.

$$C_{(s)} + H_2O \rightleftharpoons CO + H_2$$

$$\Delta H_{750C} = +132\ kJ/mol,\ \ \Delta G_{750C} = -60\ kJ/mol$$

Catalyst activity for bi-reforming: The activity of 1%LNZ catalyst as a function of temperature under bi-reforming conditions is shown in Figure 6. Both CH_4 and CO_2 conversions increase rapidly when temperature is increased from 800 ˚C to 850 ˚C. Figure 6 also compares the equilibrium conversions for CH_4 and CO_2 with that of the experimental conversions. Both CH_4 and CO_2 conversions approach near equilibrium at temperatures ≥850 ˚C.

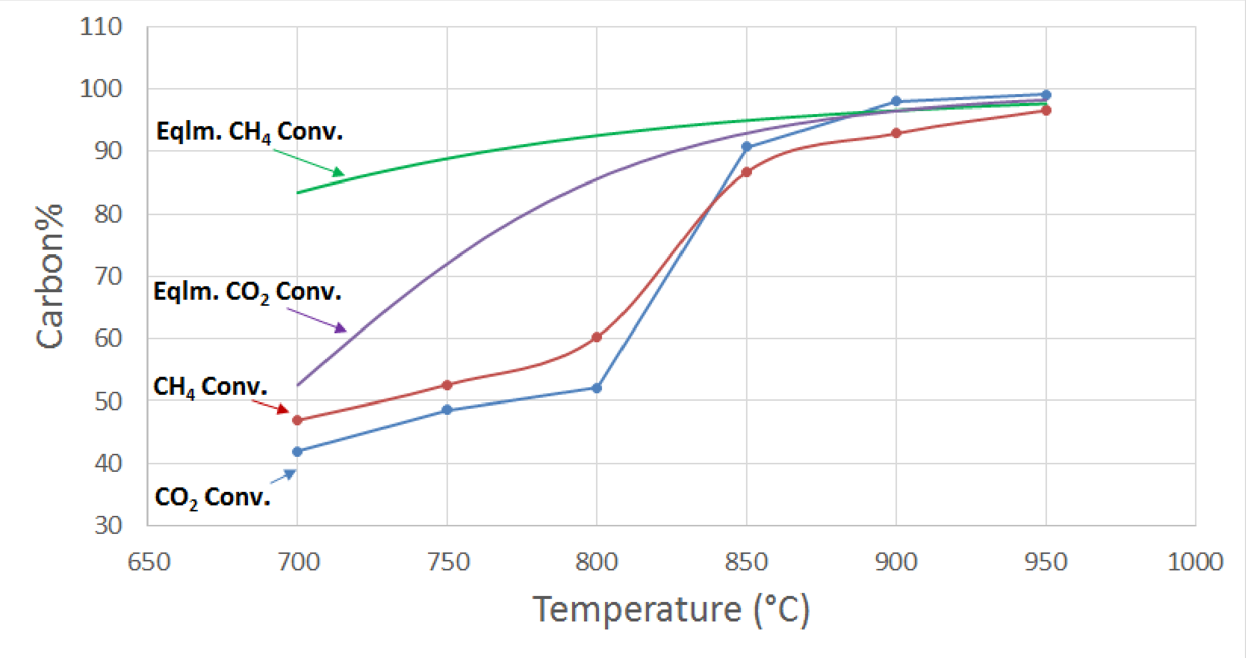


Figure 6. Activity of 1%LNZ catalyst for bi-reforming reaction at different temperatures. Catalyst was held at each temperature for 24 h. The equilibrium conversions are calculated using HSC Chemistry software.

Table 3 summarizes the results obtained for the bi-reforming reaction at different temperatures. The CO selectivity was greater than 95% at all the conditions, while the CO yield increased with temperature. The H_2/CO ratio was found to be close to 2/1 at all temperatures. This agrees with the literature on bi-reforming [17, 19].

Table 3. Summary of results for bi-reforming reaction at different temperatures*

Temperature (˚C)	CH_4 Conversion (%)	CO_2 Conversion (%)	CO Selectivity (%)	CO Yield (%)	H_2/CO ratio
700	46.9	41.9	95.8	43.5	2.2
750	52.6	48.6	97.3	50.2	2.1
800	60.3	52.1	99.7	58.1	2.3
850	86.7	90.8	99.8	87.6	1.9
900	92.9	98.0	99.8	94.0	1.8
950	96.6	99.1	99.5	96.8	1.9

*All values are reported as within 95% confidence limits.

There are very few reports in the literature on the bi-reforming reaction, and none directly comparable to those presented here. Olah et al. [19, 20] performed the bi-reforming reaction over 15%NiO/MgO catalyst at 7 atm pressure and 830 ˚C and showed constant activity of the catalyst for about 320 h. The activities reported in the present work, although cannot be directly compared due to different conditions, are comparable to that reported by Olah et al. Chaudhary et al. [17] carried out bi-reforming tests on NiO-CaO (Ni/Ca =3) catalyst at 850 ˚C at GHSV = 32,250 $cm^3g^{-1}h^{-1}$ and reported no deactivation of the catalyst after 10 h time-on-stream. Their H_2/CO ratio was similar to what we report here at the comparable feed ratio of H_2O/CO_2. The H_2/CO ratio has been found to be a strong function of the feed composition, particularly the ratio of H_2O/CO_2 [17]. Another report [21] shows that 5% Co-Pt/Al_2O_3 catalyst is active and stable for bi-reforming at much lower temperatures than those studied here. Koo et al. [22] used Ni-Ce/$MgAl_2O_4$ (Ce/Ni=0.25) catalyst for bi-reforming and their CH_4 and CO_2 conversions at 700 °C were significantly higher than those reported here, probably because of a highly active catalyst and different feed ratios. Their catalyst was also found to be resistant to carbon deposition. They attributed this due to the high Ni dispersion and high oxygen storage capacity resulting from the intimate contact between Ni and CeO_2 on the surface of the catalyst [23].

Carbon deposition for bi-reforming: The carbon deposition was studied using temperature programmed oxidation (TPO) for the spent catalysts from bi-reforming reaction. The results for CO_2 signal (mass 44) are plotted in Figure 7.

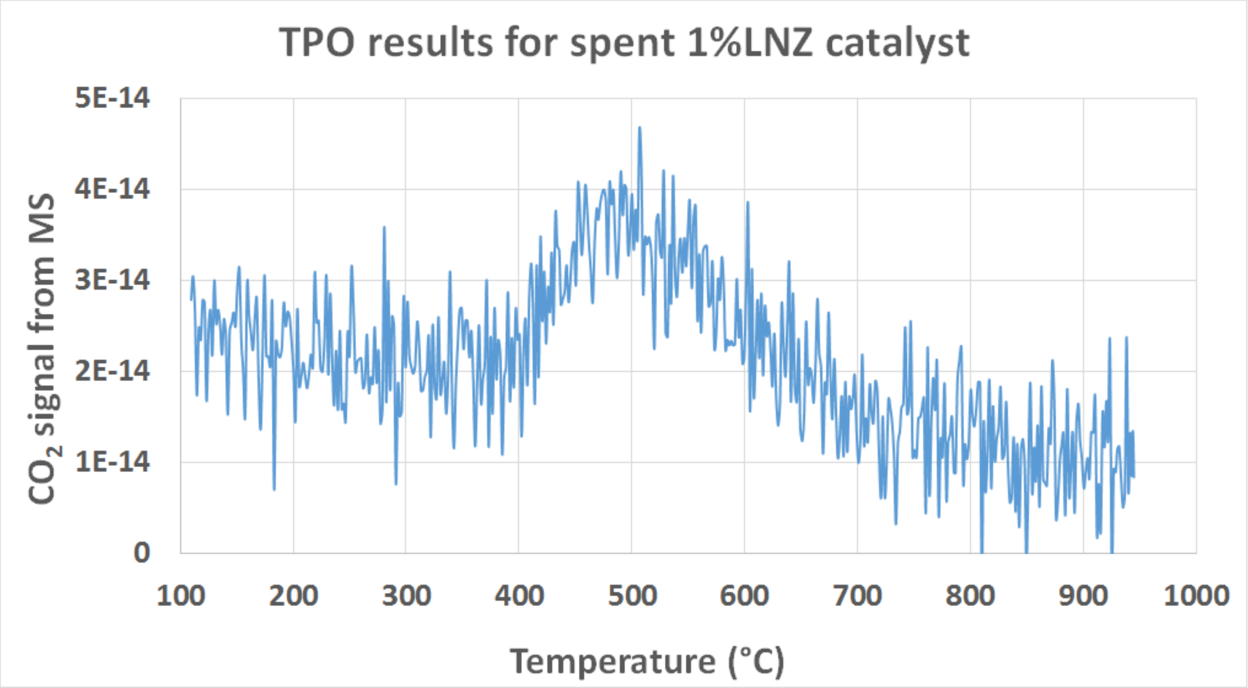


Figure 7. Temperature programmed oxidation results for spent catalysts after bi-reforming reaction.

Figure 7 shows a very small peak at around 500 ˚C that can be assigned due to atomic carbon, C_α, which can be relatively easily oxidized [21, 24, 25]. The amount of carbon is too small to quantify within error limits, but is apparent, as noted in the greatly expanded y-axis of Figure 7. The presence of a negligible amount of carbon indicates that the catalyst is resistant to carbon deposition under bi-reforming reaction conditions. This can explain the lack of measurable deactivation during bi-reforming, as seen in Figures 5 and 6. As previously shown, the catalyst retains its activity under bi-reforming conditions. This is consistent with both, the lack of any significant carbon deposition, and the fact that nickel remains in the active, metallic state with no sign of oxidation, as shown in Figure 3, at least at the conditions studied here.

Comparison of carbon deposition: The carbon deposition was studied using temperature program oxidation (TPO) for the spent catalysts from all three reactions.

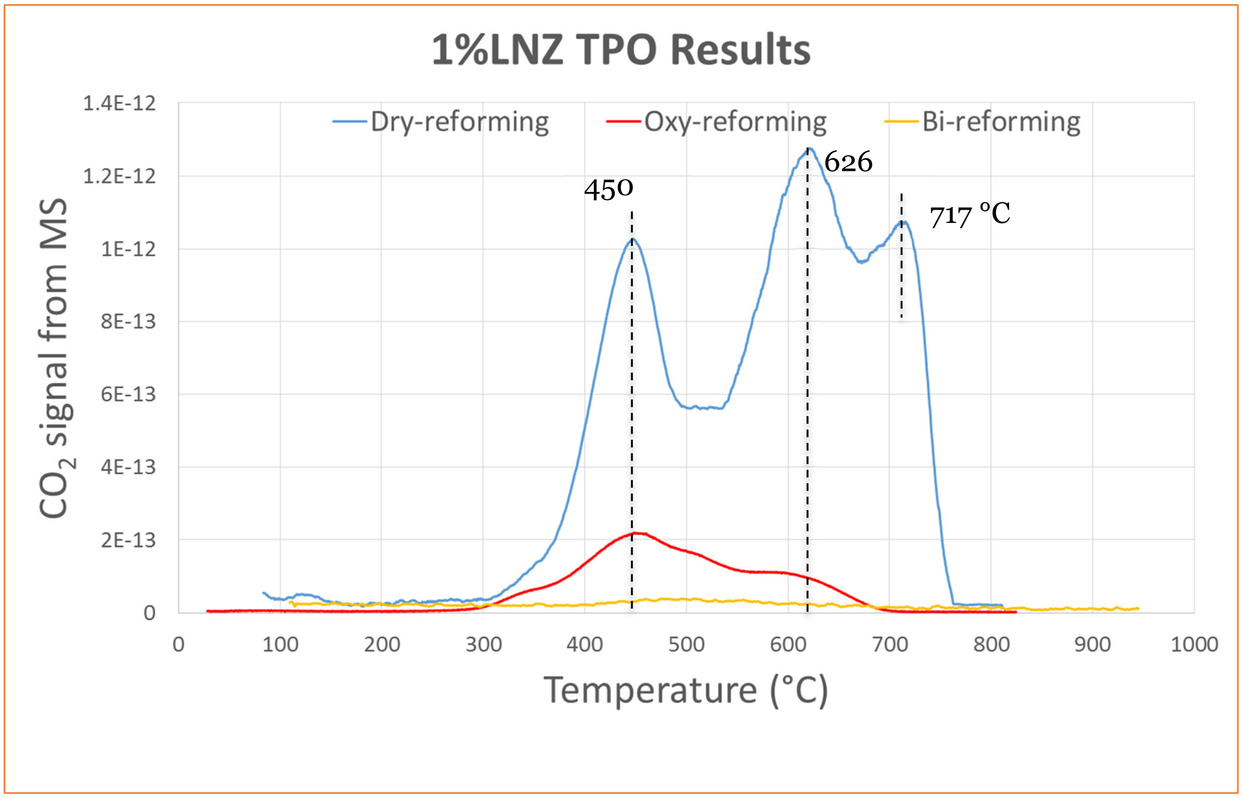


Figure 5. Temperature program oxidation results for spent catalysts from different reactions.

Figure 5 shows three distinct peaks for the spent catalyst from dry-reforming. The peak at 450 ˚C can be assigned due to atomic carbon, C_α, which can be relatively easily gasified [21, 24, 25]. Peak at 626 ˚C could be due to the polymeric carbon, C_β, which can form as a result of rearrangement of the C_α carbons and are relatively less reactive. Finally, the peak at 717 ˚C can be assigned due to the formation of carbon filaments or graphitic form of carbon, also known as 'whiskers' [25-27]. These whiskers are mechanically very strong and can permanently deactivate the catalyst.

For the spent catalyst from oxy-reforming, only peaks corresponding to C_α and C_β are observed and no graphitic carbons are present. The less reactivity, and less amount, of carbon in oxy-reforming compared to dry-reforming is clearly the reason that there is far less deactivation in oxy-reforming than in dry-reforming (Figs. 4a, 4b). For example, this is also evident from the fact that the C_β peak is much smaller in area compared to that of the C_α peak for the oxy-reforming reaction. This is not the case with the dry-reforming reaction, where C-C chain growth is pronounced for the carbon deposition, leading to the formation of refractory graphitic carbon. For the spent catalyst after the bi-reforming reaction, however, no significant amount of carbon is observed in the TPO, indicating that steam in the reactants appears to react more rapidly with the surface carbon than under oxy-reforming conditions.

The activity of the catalyst with time on stream for these reactions (Figure 4) can be directly correlated to the amount of carbon deposited on the active sites of the catalyst. A rapid decrease in the catalytic activity under dry-reforming conditions is due to excessive carbon deposition under more highly reducing conditions of dry-reforming compared to the other reforming conditions.

The far less rapid decrease in activity with time on stream for the oxy-reforming reaction (Figure 4b) is directly related to far less amount (and far less reactive) of carbon deposited on the catalyst, as seen in Figure 5.

Finally, the lack of any significant deactivation under bi-reforming conditions is due to the lack of any significant carbon deposition. The carbon depositions for the spent catalysts from all three reactions are consistent and directly attributable with their deactivation. These results are also consistent with the thermodynamics of carbon deposition as shown in Figure 3.

Modeling Results Summary

The bi-reforming reactor is simulated using a built in stoichiometric reactor module in Aspen Plus. The bi-reformer is heated using gas-fired furnaces similar to steam reformer furnaces currently prevalent in the hydrogen production industry. A key to the energy balance in this process is that the efficiency of these furnaces approaches 90%. The fuel input to the reformer furnace is calculated to be twice the energy required based on the heat of reaction of the bi-reformer. The excess heat generated by the furnace is recovered and used for operating the auxiliary systems in the plant. These assumptions are based on standard practices of existing commercial syngas and hydrogen production facilities. The CO_2 produced from the furnaces is released to the atmosphere. The syngas from the reformer is then sent to a methanol synthesis reactor to generate the final product.

A block flow diagram with relevant stream flow rates of the proposed system is shown in Fig. 1. The relevant energy flows are shown in italicized, underlined text and dashed arrows are used to indicate energy flows into or out of a process stage. The process conditions such as pressure & temperatures are based on thermodynamic analysis of the systems.

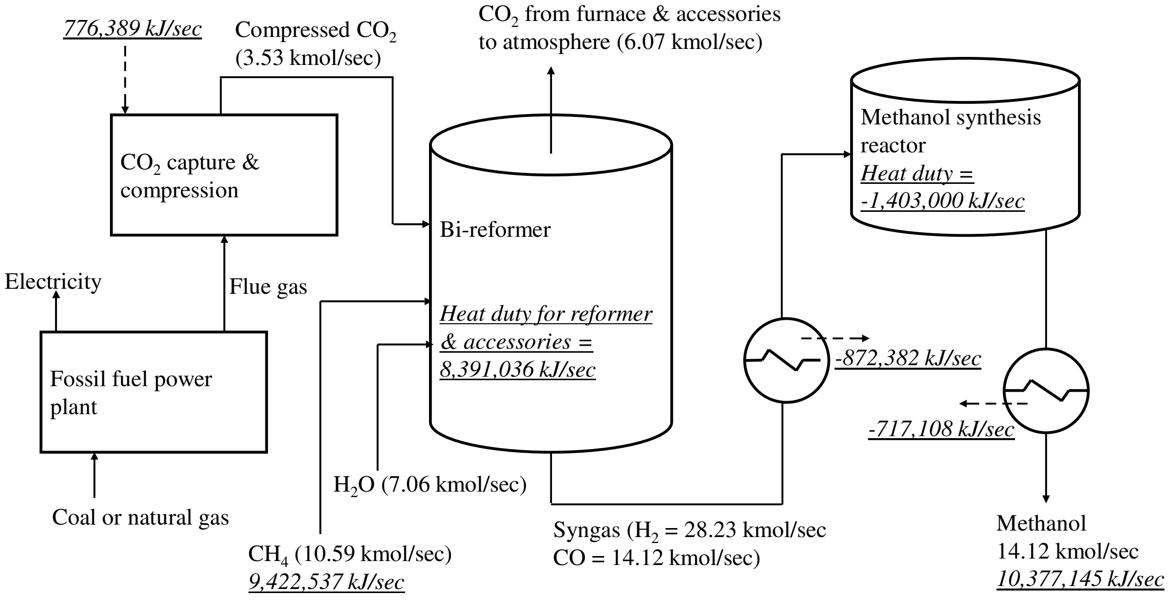


Fig. 1. Block flow diagram of the proposed bi-reforming process

In the proposed process (Fig. 3), CO_2 is captured from a large point source such as a fossil fuel power plant and used as feedstock for the bi-reforming reactor, in which CO_2 reacts with CH_4 and steam to produce syngas using the pyrochlore catalysts. The energy required for the capture, conditioning and compression of the CO_2 is estimated to be 4-7 GJ per metric tonne of CO_2. Based on different scenarios (involving process technologies/blocks with differing efficiencies), the range of thermal efficiency has been estimate to be:

Process net thermal efficiency range (energy output/energy input) = 55-72%
The thermal efficiency under common operating conditions is 65%.

- Project outcomes

A key outcome of this project is that a potentially commercially viable catalyst that has shown promising stability at bi-reforming conditions. A practical catalyst for the overall CO2-reducing process is a key requirement of the process that has simulated at UC-R.

This catalyst enables the production of methanol using CO_2 as a feedstock, resulting in significant reduction of the product methanol's Carbon Intensity.

- Analysis of results

Analysis of the results suggests that further research and development of the catalyst would be required to deploy the overall process. More detailed modeling and Life Cycle Analysis are also required to move forward towards commercialization.

- Discussion

As indicated above, the bi-reforming step is a critical one. The bi-reforming process consumes CO2 and contributes significantly to the overall, net reduction of CO2 emissions.

With the commitment from Methanex to our Round 2 proposal, the Methanex-UC-R-LSU team is well positioned to implement the CO2 reduction steps that will be integral to the methanol plant in Alberta.

- Important lessons learned

Lessons learned include the following:

(a) To date, Ni-based bi-reforming catalysts can be shown to be active and stable at the demanding conditions required industrially.

(b) Fundamentally, we have carefully characterized the fresh and spent Ni-pyrochlore catalyst to understand its tolerance of bi-reforming conditions.

4 Greenhouse Gas and Non-GHG Impacts

A Life Cycle Analysis (LCA) of the proposed pathway along with a baseline pathway based on existing methanol production technology has been conducted. The LCA is conducted using a combination of the 'GHGenius' LCA model, Aspen Plus process simulations and existing literature and industry data. The GHGenius LCA model was chosen for its extensive database of Canadian information for all the pathways and the option to perform the calculations for specific provinces such as Alberta. The two pathways considered and the GHG emission results are given below.

1. Baseline Case Pathway: This case considers the synthesis of methanol using conventional steam reforming technology as currently practiced in Alberta, Canada

The total GHG emissions from the Baseline Case pathway are estimated to be 24,791 grams of CO_2e GHGs per GJ of methanol produced on an LHV basis (498 kilograms of CO_2e GHGs/ tonne of methanol produced).

2. Bi-reforming Pathway: This option considers the synthesis of methanol through the proposed new bi-reforming technology option as it would be implemented in commercial scales in Alberta, Canada.

The total GHG emissions from the bi-reforming are estimated to be 10,098 grams of CO_2e GHGs per GJ of methanol produced on an LHV basis (330 kilograms of CO_2e GHGs/metric tonne of methanol produced).

The GHG emission reductions achieved through the proposed bi-reforming pathway can be calculated directly from the results for the two pathways. The results are given below.

- Plant design basis: 15,000 metric tonnes per day (TPD) of methanol produced
- Location: Alberta, Canada

The proposed pathway can decrease the net GHG emissions from an industrial process in Alberta by one million tonnes per year through a single commercial scale plant sized at 15,000 TPD of methanol production capacity.

5 Overall Conclusions

(d) Within the conditions tested at LSU (including temperature, gas compositions, pressure, and time-on-stream), the Ni-pyrochlore catalyst has demonstrated stable performance.
(e) The catalyst properties include stable crystallinity, tolerance to oxidiation/reduction, and close approach to equilibrium at practical temperatures.
(f) The technology has the potential to reduce the Carbon Intensity of an industrial scale methanol production plant by a million tonnes per year in Alberta

6 Scientific Achievements

List of Published Papers:

1. Kumar, Nitin; Roy, Amitava; Wang, Zi; L'Abbate, Enrico Mario; Haynes, Daniel; Shekhawat, Dushyant; Spivey, J.J., Bi-reforming of methane on Ni-based pyrochlore catalyst, Applied Catalysis A: General, 517 (2016), 211-216

2. Kumar, Nitin; Shojaee, Maryam; Spivey, J.J., Catalytic bi-reforming of methane: From greenhouse gases to syngas, Current Opinion in Chemical Engineering, 2015, 9, 8-15

List of Conference Presentations:

1. Kumar, Nitin; Roy, Amitava; L'Abbate, Mario; Haynes, Daniel; Shekhawat, Dushyant; Spivey, J.J., Catalytic bi-reforming of methane using Ni-based pyrochlores, 6th International Symposium on energy Challenges and Mechanics (ECM6), Scotland, UK, 14-18 Aug 2016

2. Kumar, Nitin; L'Abbate, Mario; Haynes, Daniel; Shekhawat, Dushyant; Spivey, J.J., CO_2 reforming of methane over Ni-based 6%LSNZ pyrochlore catalyst, 22nd International Congress of chemical and Process Engineering, CHISA, Prague, Czech republic, 28-31 Aug 2016; Serial No.: 679

3. Kumar, Nitin; Kanitkar, Swarom; Spivey, J.J., Dry reforming of methane on Ni-based pyrochlore catalysts: Understanding carbon deposition mechanism, 11th Natural Gas Conversion Symposium (NGCS11), Tromso, Norway, June 5-9, 2016; Abstract No.: 1038

4. Kumar, Nitin; Kanitkar, Swarom; Spivey, J.J., Study of dry reforming of methane using isotopic $^{13}CO_2$ switching, 251st ACS National Meeting, San Diego, CA, Mar. 13-17, 2016; Division of Industrial and Engineering Chemistry; Abstract No.: 2389403

5. Spivey, J.J.; Kumar, Nitin, Dry reforming over doped Ni-based pyrochlores, 251st ACS National Meeting, San Diego, CA, Mar. 13-17, 2016; ENFL: Division of Energy and Fuels; Paper No.: 289

6. Kumar, Nitin; Haynes, Daniel; Shekhawat, Dushyant; Berry, Dave; Pakhare, Devendra; Spivey, J.J., Dry reforming of methane over Ni-based pyrochlore catalysts using transient pulsing, 2015 AIChE Annual Meeting, Salt Lake City, UT, Nov. 8-13, 2015; Paper ID: 436800

7. Kumar, Nitin; Spivey, J.J.; CO_2 reforming of methane over Ni-based pyrochlore catalyst in the presence of oxygen, 250th ACS National Meeting, Boston, MA, Aug. 16-20, 2015; Division of Catalysis Science and technology

8. Spivey, J.J.; Kumar, Nitin; ;Pakhare, D.; Shekhawat, D.; Berry, D.A.; Haynes, D.; Smith, M., Reforming of methane using substituted pyrochlores; XXIV International Materials Research Congress – 6A, Advanced catalytic materials, Cancun, Mexico; August 16-20, 2015

9. Kumar, Nitin; Shojaee, Maryam, Haynes, Daniel; Shekhawat, Dushyant; Berry, David; Spivey, J.J.; CO_2 conversion via bi-reforming over Ni-based pyrochlore catalyst; 24th North American Catalysis Society Meeting, Pittsburgh, PA, June 14-19, 2015; Abstract# 10155

List of Students from KTH who worked for CCEMC project at LSU:

1. Maryam Shojaee (KTH-Stockholm)
2. Mario Enrico L'Abbate (KTH-Stockholm)

7 Next Steps

Next steps for the technology

As part of our Round 1 project, UC-R and LSU have met with Methanex, the largest methanol producer in Alberta, and one of the largest in the world, in response to EECMC's need to significantly reduce CO2 emissions. We will submit a Round 2 proposal designed to develop a process to that will reduce 1 million tons/yr of CO2. UC-R and LSU will work with Methanex to optimize the process with the object of reducing CO2 emission.

Long-term plan for commercialization

Based on progress in Round 1, Round 2 will carry out the detailed process design/analysis and economic analysis necessary before the project is implemented. In Round 2, Methanex will serve as the prime contractor, which will ensure that both the economic and scientific goals of the project are met. We are confident that the ultimate goal can be met--full commercialization of an optimum economic and environmental process, located in Alberta. This will be one that demonstrates how the synergism required by the academic and commercial sectors can be successful.

Commercialization-related actions to be undertaken within two years

Within completion of Round 2, Methanex, UC-R, and LSU plan to complete process design, with sufficient detailed economic analysis to implement construction. We believe that the demonstrated experience of Methanex, in particular, will greatly ensure project success.

Potential partnerships

In addition to the Methanex--UC-R--LSU team, we anticipate that a proven supplier for the bi-reforming catalyst will be needed. Fortunately, LSU has worked with DoE/NETL and Pyrochem, Inc. in developing the pyrochlore catalyst specifically synthesized for bi-reforming. Pyrochem has licensed the technology from DoE, and has shown success in scaling the synthesis process from a batch to a continuous process, a key step in scaling up the manufacture of the catalyst. We plan to work with Pyrochem and DoE in Round 2 to ensure that commercial quantities of the catalyst are available when needed.

The logical next steps include the following:

(a) The Aspen and Life Cycle Analysis modeling have been conducted using existing literature data. However, more detailed versions of the models must be developed, especially with input from a commercial methanol producer. This is critical since literature data can often be approximate or outdated. The partnership with Methanex during Round 2 will enable UCR to accomplish this.

(b) Despite positive results to date, we realize that tests of at least hundreds of hours on stream is necessary to have confidence in the catalyst. Work at this point have has provided insight into the fundamental steps on the catalyst surface, which will logically improve the performance of the catalyst.

(c) To develop and deploy a commercially successful methanol process that meets the CCEMC CO2 reduction targets, the pyrochlore catalyst that has been tested at LSU must be produced at industrial quantities. The technology needed to produce large amounts is not a simple. We will work directly with our commercially partner (Methanex) and their catalyst suppliers to scaleup the process used in the lab to synthesis the catalyst.

8 Communications plan

Communication of information developed in Round 2 will rely on periodic project meetings, typically quarterly. The proximity of two Methanex sites, one to CCEMC leadership in Alberta, and a second one less than 10 miles from LSU in Louisiana will greatly facilitate communication. We anticipate travel to/from UC-R the project meetings as well. We will take advantage of travel to national conferences for PIs to minimize travel costs.

Project findings include scientific results, process design, simulation, and economic findings. These will be shared using conventional electronic tools, which we have find to be useful but are no substitute to person-to-person meetings. Communication with third parties will ensure that no proprietary information is disclosed.

Technology details, advantages, and other relevant information will also be communicated to the public, policy makers and other stake holders through conferences, communications through media outlets, technology demonstration and publications.

9 References

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