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Simulation of Decarbonization of Natural Gas to Methanol Conversion Process Using Microwave-Assisted Dry Reforming with Integrated Chemical Looping for Hydrogen Production

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ABSTRACT

In this research, a chemical looping scheme is combined with dry reforming of natural gas in a novel microwave reactor to produce industrial quantity of methanol. Simulation results show that the chemical looping scheme can produce all the hydrogen required by the methanol reactor as well as a significant portion of the carbon dioxide required for the syngas reactor. A heat exchanger network is developed to substantially reduce the hot and cold utility usage. A technoeconomic analysis indicates a significant positive net present value along with a substantial reduction in carbon dioxide emissions as well as a reduction in energy consumption.

Keywords: Microwave-assisted dry reforming, Chemical looping, Carbon-neutral methanol synthesis, CO_2 utilization, Decarbonization technologies

INTRODUCTION

Methanol is valued for its versatility as a feedstock and energy carrier. As a key component in producing formaldehyde, acetic acid, and methyl tert-butyl ether (MTBE), it supports a wide array of industries, including plastics, textiles, and automotive. Methanol also plays a growing role in renewable energy solutions, such as biodiesel production and as a hydrogen carrier for fuel cells. Global demand for methanol estimated to be $41.91 billion by 2026 [1], driven by expanding applications in petrochemicals and clean energy technologies. As global efforts toward sustainability intensify, methanol's importance as a low-carbon fuel alternative is set to rise. While methanol can be produced from different feedstocks, the most common feedstock is natural gas, primarily because it is available in abundant quantities at a cost-effective price [2]. In this process natural gas (primarily methane) is reformed into synthesis gas (syngas), a mixture of carbon monoxide, carbon dioxide, and hydrogen via steam methane reforming (SMR), where natural gas reacts with steam at high temperatures (700–1,000°C) and in the presence of a nickel-based catalyst. Alternatively, autothermal reforming (ATR) or partial oxidation can be used, especially in large-scale plants. The resulting syngas is then passed through a methanol synthesis reactor under high pressure (50–100 bar) and moderate temperatures (200–300°C), where it reacts over a copper-based catalyst to form methanol. The crude methanol is subsequently distilled to remove water and other impurities, yielding high-purity methanol. This process accounts for the majority of global methanol production, leveraging natural gas as a cost-effective and abundant feedstock. However, this process is highly energy intensive and contributes to greenhouse gases (carbon dioxide) to the atmosphere. As a result, there is significant interest to explore alternative pathways for methanol production that are more energy-efficient and environmentally sustainable.

One promising method is the microwave-assisted conversion of natural gas to methanol via dry reforming. This method uses electromagnetic waves to activate the natural gas molecules and create reactive species that can react with oxygen or carbon dioxide to form methanol. The advantages of this method include operation at lower temperatures and pressures, reduced number of

process steps, enhanced selectivity, and yield of methanol, and the utilization of carbon dioxide as a raw material [3]. However, dry reforming requires a source of hydrogen and it important to consider the energy cost and environmental impact of hydrogen production when considering dry reforming of methane as an alternative route for producing methanol.

In this paper, we explore the use of a chemical looping scheme that produces two separate streams of hydrogen and carbon dioxide that are then utilized in the production of methanol via dry reforming. The overall objective of this research is to develop a simulation model of a novel decarbonized microwave-assisted dry reforming process integrated with chemical looping for methanol production. Specifically, three key objectives are pursued: (1) investigate the impact of replacing the conventional syngas reactor with a microwave reactor for dry reforming of methane, (2) explore the feasibility of utilizing chemical looping for utilizing methane to produce the required hydrogen for methanol production, and (3) conduct a techno-economic analysis to evaluate the viability of the integrated process.

REACTION CHEMISTRY AND REACTOR DESIGN CONSIDERATIONS

The current industrial approach to produce methanol involves steam reforming of methane to produce syn gas followed by catalytical conversion of syn gas to methanol [4]:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$

Some of the carbon monoxide reacts further with steam to form carbon dioxide via the water-as shift reaction:

$$CO + H_2O \rightarrow C0_2 + H_2 \quad (2)$$

An alternative method to produce syn gas is via methane dry reforming (MDR), Which uses carbon dioxide as a reactant, making advantageous for reducing greenhouse gas emissions [5]. The MDR reaction can be represented by the following equation:

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad (3)$$

The MDR reaction is thermodynamically favorable at high temperatures (800-1000 °C) and low pressures, but it requires a suitable catalyst to overcome the kinetic limitations and avoid the formation of carbon deposits. Once syn gas is produced, it is possible to utilize this intermediate to produce methanol [4]:

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (4)$$

The hydrogen to carbon monoxide ratio needs to be adjusted to a 2:1 ratio. Typically, the dry reforming process does not produce sufficient hydrogen, and so additional hydrogen needs to be added to the feed stream of the methanol reactor. This provides the motivation to utilize a chemical looping reactor system that converts methane and steam into separate streams of hydrogen and carbon dioxide. The hydrogen is sent to the methanol reactor feed, and the excess carbon dioxide is recycled back to the syngas reactor for dry reforming.

PROCESS MODELING

Methodological Framework

This research is divided into the following sections: (1) steady-state model development, (2) heat exchanger network (HEN) design, and (3) techno-economic analysis. In the first step, a comprehensive process model is developed for the integrated microwave-assisted dry reforming (MDR) and chemical looping processes, followed by methanol synthesis and product purification. The purpose of incorporating chemical looping is to generate additional hydrogen, compensating for the lower stoichiometric ratio (H_2 - CO_2) / (CO + CO_2) produced in conventional dry reforming. The goal is to achieve the target ratio of 2, which is optimal for methanol synthesis. Chemical looping provides a steady hydrogen source through an indirect oxidation process, using metal oxides to facilitate controlled oxygen transfer and ensure the required stoichiometric balance. Key process information, reaction kinetics, and operating conditions are taken from recent studies on chemical looping and microwave-assisted MDR5, with feed specifications aligned with the commercial Natgasoline process [4]. The steady-state simulation, developed in Aspen Plus v11, includes syngas production, methanol synthesis, and product purification. Next, a detailed HEN is designed using Aspen Energy Analyzer (AEA) v11.0 software. The HEN design targets energy optimization by creating a network that maximizes heat recovery and minimizes utility consumption. This configuration balances utility costs with capital. The resulting HEN grid meets targeted utility requirements, capital constraints, and optimal surface area, enabling efficient heat integration both in the microwave-assisted and chemical looping processes. Finally, a techno-economic analysis (TEA) is conducted using Aspen Process Economic Analyzer (APEA) v11 to account for capital and operating costs based on the Aspen Plus simulation specifications. Key economic indicator such as net present value (NPV) is calculated to evaluate the profitability of this novel methanol production process.

Figure 1 shows a schematic of the novel microwave-assisted dry reforming process. While the process development closely follows the flowsheet that is utilized commercially at Natgasoline LLC, two major changes are made to the process. First, the steam is replaced by carbon dioxide in the feed to the syn gas reactor and

secondly, an additional hydrogen stream, which is produced by chemical looping, is added to the inlet of the methanol reactor to have the correct carbon monoxide to hydrogen ratio. The carbon dioxide produced via chemical looping is recycled to the syngas reactor feed. In addition, there is a change in the process equipment where the conventional multi-tubular syn gas reactor is replaced by a microwave reactor. The separation train of distillation columns are essentially the same type as those found in the Natgasoline process; however, since the flow rates of some of the gaseous components are different, these distillation columns are sized appropriately. The final product stream is 14,201 lbmol/h of 99.9% pure methanol, which is the same as that produced via the conventional Natgasoline process.

ASPEN PLUS Modeling

The methanol production process is modeled in two integrated subplants: Subplant 1, which handles hydrogen generation through chemical looping, and Subplant 2, where syngas is synthesized using a microwave reactor, supplemented by the H_2 stream from Subplant 1. The thermodynamic package RK-SOAVE is used for the syngas part while NRTL is used for the methanol production part and PENG-ROBINSON is used for the chemical looping. In Subplant 1, the chemical looping process is configured as a three-reactor, countercurrent setup to enable hydrogen production and CO_2 capture, based on the conditions outlined in the work of Riley et al [5]. The looping system uses $CaFe_2O_4$ as an oxygen carrier, which alternates between oxidized and reduced forms to facilitate methane and steam conversion in a controlled series of reduction and oxidation cycles. Process feed conditions and specifications for this setup are summarized in Table 1. Conditions such as temperature, pressure, and gas flow rates, are adapted from Riley et al. [5], but are further adjusted to meet the specific H_2 demand of our methanol synthesis setup.

The chemical looping system operates as follows: Natural gas is introduced into the fuel reactor (FR) to react with the oxidized $CaFe_2O_4$, producing CO_2 and H_2O while reducing the oxygen carrier. This stage is conducted at elevated temperatures, allowing efficient conversion of methane into products that can be further processed. In the air reactor (AR), the reduced $CaFe_2O_4$ is re-oxidized by reacting with air, regenerating the oxygen carrier. In the steam reactor (SR) the re-oxidized $CaFe_2O_4$ interacts with steam, producing H_2 and H_2O. The operating conditions for each reactor in the chemical looping process are shown in Table 2. The H_2 generated in this stage is directed to Subplant 2 to supplement the syngas stream, achieving the necessary H_2 ratio for methanol synthesis. In Subplant 2 the methanol production process utilized in this research is modeled similarly to the commercial setup at Natgasoline LLC, with adjustments to the syngas production, feed conditions, and reactor configurations [6]. The syngas feed for methanol synthesis is through a microwave-assisted dry reforming reactor, where methane (CH_4) and recycled carbon dioxide (CO_2) are converted into a syngas stream. This process is conducted at 800°C and 1 bar and is modeled as a stoichiometric reactor. The H_2 ratio in the syngas is optimized by supplementing it with hydrogen generated from the chemical looping process in Subplant 1. The operating specifications for the microwave-assisted syngas production are provided in Table 2. The conditioned syngas is then compressed to approximately 76 bar and distributed across two parallel methanol synthesis reactors, each operating at 254°C and 76 bar. Here, CO and CO_2 undergo hydrogenation in the presence of a Cu/Zn-based catalyst to produce methanol and water. The product gas from reactors is then preheated by exchanging heat with the reactor feed stream before undergoing a final conversion step in an additional reactor operated

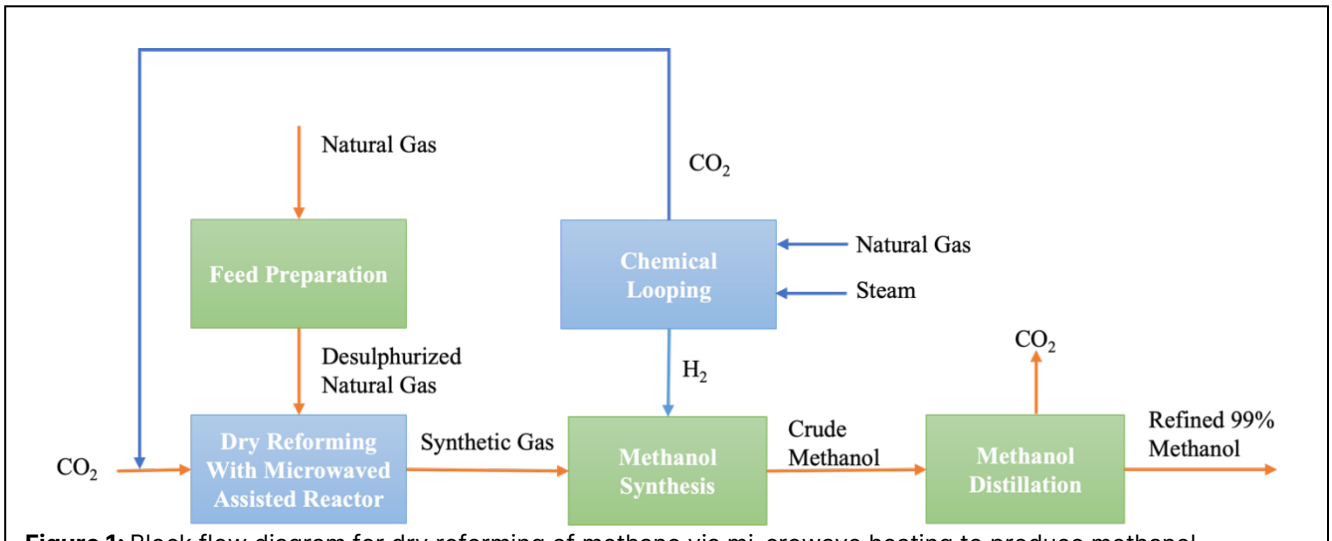

Figure 1: Block flow diagram for dry reforming of methane via mi-crowave heating to produce methanol.

Table 1: Feed Specifications for Syngas and Chemical Looping Processes

	Natural Gas			Water	CO_2	CAFE	Air
Stream	NG	NG-CL	NG-HEAT	STM-SR	CO2	CAFE	AIRFEED
Temperature (°C)	30	25	25	230	30	970	25
Pressure (bar)	1	2	1	2	1	2	1
Flow Rate [kmol/h]	2648	3320	100	8597	1168	71297	133446

Table 2: Reactor Operating Conditions in Chemical Looping and Methanol Synthesis

Reactor	Subplant	Function	Temperature (°C)	Pressure (bar)
Fuel Reactor (TOP-FR)	1	Reduce Oxygen Carrier	960	2
Fuel Reactor (BTM-FR)	1		870	2
Air reactor (AR)	1	Oxygen Carrier Regeneration	928	2
Steam Reactor (SR)	1	H2 Production	875	2
R-1	2	Hydrodesulphurization	375	1
Microwaved Reactor (R-MW)	2	Syngas Production	800	1
R-2	2	Methanol Production	254	76
R-3	2		254	76
R-4	2		220	71

at 220°C and 71 bar. This additional reactor stage helps maximize methanol yield by enhancing the conversion of residual CO and CO_2. The reactor outlet gas, containing methanol, water, and unreacted gases (H_2, CO, CO_2, CH_4, and inert gases like N_2), is directed to a separator, where crude methanol is separated at 40°C and 67 bar. A portion of the unreacted gases is recycled back to the reactors to improve process efficiency, while a portion is purged.

The purification of crude methanol is achieved through a series of steps involving a flash tank and three distillation columns. First, crude methanol is depressurized in the flash, allowing off-gas, which mainly consists of CO_2, H_2, and CH_4, to be vented. The liquid phase is directed to the first column for initial purification. This column separates residual CO_2 and trace gases, which are flared, while the methanol-rich bottom stream is pumped into the second column for further separation. Here, methanol of approximately 99.99% purity is collected as the distillate, while the remaining mixture of methanol and water proceeds to the third column, where the final methanol product with a purity of 99.99 mol% is produced. The data from the steady-state simulation in Aspen Plus was imported to Aspen Energy Analyzer (AEA) v11 to design and optimize the Heat Exchanger Network (HEN) for maximum energy recovery. The HEN was designed separately for each subplant, with a larger HEN configuration applied to the microwave-assisted dry reforming process in Subplant 2 and a smaller HEN configured for the chemical looping process in Subplant 1.

RESULTS

The steady-state simulation results for the integrated chemical looping and microwave-assisted reforming process demonstrate effective syngas production, hydrogen supplementation, and methanol synthesis, achieving high efficiency and purity. In Subplant 1, the chemical looping process is configured to produce a hydrogen stream of 22,299 lbmol/h, meeting the precise hydrogen requirement for the syngas production in Subplant 2. The chemical looping configuration also produces 7,163 lbmol/h of carbon dioxide. However, the syngas production reactor in Subplant 2 requires 9,746 lbmol/h of carbon dioxide. This additional amount of carbon dioxide (2,583 lbmol/h) has to be purchased separately or obtained from a separate decarbonization campaign in another part of the chemical plant. In Subplant 2, the microwave-assisted dry reforming reactor achieved a methane conversion rate of 97%. The resulting syngas composition is 40.3% H_2, 41.5% CO, 17% CO_2, and 0.57% CH_4, with an H_2 ratio of 0.971. This ratio is then optimized by supplementing the syngas with the hydrogen stream from Subplant 1 to achieve the ideal stoichiometric conditions for methanol synthesis. Moreover, the microwave-assisted dry reforming process reduced natural gas feed requirements by 12% and steam feed

consumption by 6%, demonstrating the process's enhanced resource efficiency compared to conventional methods. The methanol produced reaches 14,201 lbmol/h with a high purity of 99.9%, aligning with commercial methanol production rate and quality. The process overall achieves a net CO_2 utilization rate of -1,117 lbmol/h, indicating that it consumes CO_2 rather than emitting it. Compared to a baseline emission rate of 575 lbmol/h in conventional steam reforming processes, this setup achieves a CO_2 emission reduction of 294.3%. This reduction highlights the environmental benefits of integrating CO_2 into the process, furthering the goal of sustainable and decarbonized methanol production. The HEN design employed a mixed-integer linear programming (MILP) approach to achieve optimal heat recovery, thus, the utility requirements showed substantial reductions: Hot utility demand dropped from 2923 MMBTU/hr to 478 MMBTU/hr, representing an 83.6% reduction. Cold utility demand decreased from 3968 MMBTU/hr to 1482 MMBTU/hr, achieving a 62.7% reduction. The integration of HEN not only reduces operational costs but also aligns with decarbonization goals by lowering the environmental impact through reduced energy consumption.

Capital costs for standard equipment items were estimated by mapping the equipment items from the Aspen Plus plant-wide model to Aspen Process Economic Analyzer (APEA) V11. Costs for the microwave-assisted reactor (MW-reactor) was estimated separately as quoted equipment in APEA, broken down into the magnetron (including other electrical ancillaries) and pressure vessel. The magnetron cost, including electrical ancillaries, accounts for components such as the cavity, generator, controls, transformers, switches, installation, and setup, obtained from a vendor based on the power (kW) rating. The pressure vessel cost was estimated using correlations from Turton et al [7]., considering the material of construction and operating pressure. Additional costs, such as assembly, commissioning, and markup, were accounted for with escalations, given the novel state of MW-assisted reactor technology. Utilities such as electricity, cooling water, steam, and flow rates of raw materials were obtained from the Aspen Plus process model. The economic analysis of the proposed methanol production process shows that the integrated process achieves a TCI of $515.68 million, annual operating costs of $486.13 million and a combined NPV of $1439 million. The integrated design leverages the strengths of both subplants, offering significant economic potential through high methanol production and CO_2 utilization.

An additional amount of carbon dioxide (2,583 lbmol/h) is required to operate the syngas reactor, and this carbon dioxide cost can affect the NPV. The economic analysis presented in Table 3 assumes a cost of carbon dioxide as $38.59/ton. To assess the impact of key cost variables on the operating expenses (OPEX), a sensitivity analysis was conducted on electricity price (ranging from 0.01 to 0.12 cents/kWh) and methane price (ranging from 0.1 to 2 $/MMBtu).

Table 3: Economic Summary for Integrated Process.

Parameter	Integrated Process
Total capital cost ($MM)	515.68
Total Operating Cost ($MM/year)	486.13
Raw Material Cost ($MM/year)	162.25
Utility Cost ($MM/year)	279.14
Methanol Production (lb/year)	3.99×10^9
NPV ($MM)	1,439

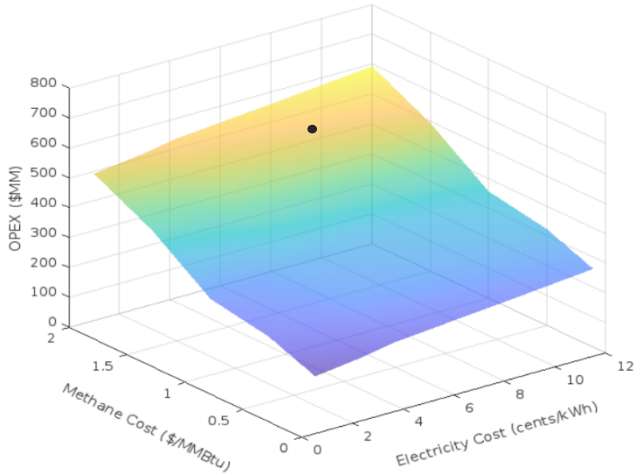

Figure 2. Sensitivity Analysis of OPEX to Electricity and Methane Costs

Figure 2 shows that OPEX increases with both electricity and methane costs, with a stronger sensitivity observed toward methane pricing. The lowest OPEX value, $160.84 MM, occurs at the lowest electricity and methane cost combination, whereas the highest OPEX, $592.20 MM, corresponds to the most expensive conditions. The black marker in the plot highlights the current cost scenario (electricity = 8.72 cents/kWh, methane = $1.8/MMBtu), which results in an OPEX of $486.13 MM. The findings emphasize that while both variables impact operational costs, controlling methane costs presents the most effective strategy for cost optimization in the proposed process.

CONCLUSION

Current industrial practice for methanol is very energy intensive and produces a large amount of carbon dioxide. The use of a novel microwave-assisted conversion of natural gas to methanol via dry reforming has the potential to reduce energy costs and reduce carbon dioxide

emissions. However, this method requires the use of hydrogen. It is shown via simulation studies in this research that the hydrogen required for methanol production can be generated via chemical looping. Furthermore, chemical looping also produces a pure stream of carbon dioxide that can be utilized in the dry reforming step. Technoeconomic analysis indicates that this integrated plant has the potential to be profitable.

While the use of microwave reactors is promising and moves the chemical industry in the direction of electrification of process energy, further research is needed to make commercial-scale microwave reactors at a price comparable to traditional jacketed reactors that operate using hydrocarbon combustion. The scale-up of microwave reactors using multiple units of pilot-scale equipment and the effect of reactor cost on the manufacturing cost of methanol is being evaluated [8]. Another factor under consideration is the stability of the catalyst under microwave conditions, which is an area of active research [9]. While chemical looping is shown to be feasible for producing the necessary hydrogen for dry reforming, this method requires the transport of solids, which require special pneumatic handling techniques for smooth long-term operation. These issues, along with a quantitative comparison with current industry methods will be addressed in a future publication.

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