

# Integrating life cycle assessment for design and optimization of methanol production from combining methane dry reforming and partial oxidation



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## ABSTRACT

CO<sub>2</sub> capture and utilization (CCU) is a potential solution for combating global warming potential. Utilization of CO<sub>2</sub> as a renewable raw material for producing methanol has been intensively investigated. Nevertheless, the benefits of CO<sub>2</sub> utilization cannot be guaranteed unless the entire production process is rigorously evaluated and optimized. This study attempts to minimize CO<sub>2</sub> emissions of the methanol production process via the synthesis of intermediate syngas using the dry methane reforming (DR) method in combination with the partial oxidation (PO) of methane. We noted that the contributions from DR and PO to the overall reaction process depended on the input raw material ratios. Marked differences in desired operating conditions were noted when maximizing syngas and methanol yields, thereby making process optimization difficult. Herein, to find the optimal operating conditions for minimizing overall CO<sub>2</sub> emissions, effective process design and simulation, and the cradle-to-gate life cycle assessment (LCA) were integrated. Process CO<sub>2</sub> emissions, including those from all sources of indirect and direct CO<sub>2</sub> emissions from raw materials, utility production processes, and “end-of-pipe” waste treatment option were evaluated based on noted variations in the identified key variables. Suitable operating conditions for reducing the total process CO<sub>2</sub> emissions were proposed. Although the current study results in low level of CO<sub>2</sub> utilization, it attains a low CO<sub>2</sub> emissions process for producing methanol via syngas (i.e., 0.81 kg CO<sub>2</sub>/kg methanol). The results obtained herein highlight the significance of implementing LCA method using suitable evaluation boundary to design environmentally friendly CO<sub>2</sub> utilization processes.

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## 1. Introduction

The environmental and economic impact of global warming due to the steady increase of greenhouse gas (GHG) emissions has become a priority issue for governments worldwide. As of 2014, 76% of all GHGs are CO<sub>2</sub> emissions, most of which result from human activities and industrial processes (IPCC, 2014). Thus, reducing CO<sub>2</sub> is the linchpin strategy in a global effort to combat climate change and promote sustainable development. Carbon capture and storage and carbon capture and utilization (CCU) are possible pathways towards CO<sub>2</sub> mitigation. Many researchers believe that CCU is a more feasible strategy, as CO<sub>2</sub> can be used as a renewable

raw material for producing valuable chemical products. Extensive investigations into finding suitable catalysts and processes for converting CO<sub>2</sub> to different types of chemicals have been conducted (Artz et al., 2018; Rafiee et al., 2018). Here, the direct conversion of CO<sub>2</sub> to methanol via hydrogenation is an effective strategy for mitigating large amounts of CO<sub>2</sub>. Nevertheless, this strategy's successful application hinges on an ample supply of carbon-free H<sub>2</sub> raw material that is currently not available for large-scale industrial production processes (Pérez-Fortes et al., 2016). Methane is an economical, readily available feedstock that can be used for the dry reforming (DR) reaction of methane, thereby providing a potential pathway towards CO<sub>2</sub> utilization. Equation (1) highlights the use of methane to produce syngas mixture, an essential intermediate product used for producing ammonia, hydrogen, methanol and synthetic fuels.



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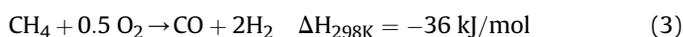
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Despite these advantages, the use of DR for CO<sub>2</sub> fixation suffers from two main drawbacks. First, the high endothermicity associated with the required high-temperature conditions results in unacceptably high energy consumption. Second, the product ratio of the H<sub>2</sub>/CO is quite low (~1), thereby limiting the use of syngas as a raw material for gas-to-liquid processes. The efficient use of syngas for manufacturing high-demand chemicals or Fischer–Tropsch liquid fuels is only possible when the syngas' molar compositions satisfy the requirement of stoichiometric number M, calculated using Equation (2) (Song and Guo, 2006). For example, high yield methanol production from syngas is only possible when M is close to 2 (Shahhosseini et al., 2018).

$$M = \frac{H_2 - CO_2}{CO + CO_2} \quad (2)$$

These limiting problems can be overcome by combining DR with the partial oxidation (PO) of methane. The use of a combined DR/PO protocol increases the M value while reducing the energy requirement of this process by making use of the high exothermicity of the PO reaction:



Previous studies (e.g., Ruckenstein and Hu, 1998; Meshkani et al., 2014; Jalali et al., 2019) proposed operating conditions and catalysts to combine DR/PO reactions, attempting to decrease thermal heat demand and increase methane conversion and H<sub>2</sub>/CO ratio. The results were expected to contribute to reduce energy consumption for operating the reactor, thereby reducing production cost and CO<sub>2</sub> emissions of syngas synthesis process. Afzal et al. (2018) and Noureldin et al. (2015) proposed several methods to optimize the operating temperatures and ratios of input raw materials (CH<sub>4</sub>/CO<sub>2</sub>/O<sub>2</sub>) for producing syngas of various H<sub>2</sub>/CO ratios. However, since these studies were mainly focused on syngas synthesis, the optimal results obtained were not evaluated in cases where the system boundary was extended to produce a specific downstream target product. Roh et al. (2016) stated that the reported results of previous studies should be carefully analyzed with consideration for the width of the process boundary. Since syngas is an important intermediate for producing various products, optimizing its synthesis for subsequent downstream processes is essential for reducing the production chain's overall CO<sub>2</sub> emissions. In other words, the temperature and pressure conditions of syngas synthesis and the raw material input ratios that directly determine the CO<sub>2</sub> utilization and energy-saving contributions of the respective DR and PO processes in the combined method should be analyzed in relation to the operating conditions required for downstream manufacturing. Conversely, the life-cycle CO<sub>2</sub> emissions of the input raw materials used in the upstream process and the "end-of-pipe" waste treatment of unused products should be included in a thorough evaluation of the process CO<sub>2</sub> emissions to provide sufficient information for designing environmentally friendly, optimized protocols for CO<sub>2</sub> utilization.

In the current study, the entire process of syngas synthesis via a combined DR/PO method and the downstream conversion of syngas was designed and entirely optimized for the minimization of the overall CO<sub>2</sub> emissions. Herein, methanol was the final target product as it is a popular chemical feedstock, fuel source, and hydrogen carrier (Riaz et al., 2013). It is a high-demand compound and one of the most extensively used syngas derivatives. Recently, design and optimization of methanol production processes using syngas obtained from different reforming technologies and various feedstocks have been intensively investigated (e.g., Yao et al., 2018; dos Santos et al., 2018; Gao et al., 2020). Nevertheless, a comprehensive and simultaneous optimization of both syngas and

methanol syntheses has not been implemented for minimizing the overall process CO<sub>2</sub> emissions. Design and optimization of the entire methanol production process required assessments of a large number of operating parameters. Moreover, product yields of syngas, which served as an intermediate for the subsequent production of methanol, was maximized at low pressures and high temperatures, whereas methanol synthesis benefitted most from high pressures and low temperatures. In the current study, considering the above-mentioned unsolved issues, the optimization of the overall operating conditions was done with consideration for both synthetic reactions for minimizing total process CO<sub>2</sub> emissions. Herein, process design and optimization were performed in integration with cradle-to-gate life cycle assessment (LCA). Process simulator was employed to design the target process. Process simulations revealed the key variables that significantly impacted raw material and energy consumption and CO<sub>2</sub> utilization. A thorough evaluation of the associated CO<sub>2</sub> emissions was conducted via LCA based on the evaluation boundary constructed for all methanol production stages, including CO<sub>2</sub> capture, the synthesis of both syngas and methanol, and "end-of-pipe" waste treatment. By integrating the LCA into the process design and simulation, suitable operating conditions were established for producing methanol using low-emission protocols.

## 2. Material and methods

### 2.1. Evaluation boundary and method

The aim of this study was to design an environmentally friendly process for methanol synthesis using the syngas product of the combined DR/PO of methane. Life cycle assessment (LCA) has been proved to be an important tool used for evaluating the environmental impacts of new production processes or products (Visentin et al., 2020). Generally, the environmental impacts of a chemical process can be assessed using various indicator parameters such as climate change, ozone depletion, and terrestrial acidification (Kralisch et al., 2015). Due to the pressing environmental problems associated with global warming, we selected GHG emissions (CO<sub>2</sub> emissions equivalent) as the main indicator for optimizing the target chemical production process.

Herein, the total amount of CO<sub>2</sub> emitted from the production process was evaluated using the cradle-to-gate LCA method to account for all sources of both direct and indirect CO<sub>2</sub> emissions. A functional unit of 1 kg of the target product was selected for the assessment. Direct CO<sub>2</sub> emissions refer to all emissions that are directly released into the environment, including CO<sub>2</sub> remained after the synthesis and CO<sub>2</sub> produced from the incineration system. Indirect CO<sub>2</sub> emissions account for all sources of CO<sub>2</sub> arising from the production of raw materials and utilities supplied to the process. The total amount of CO<sub>2</sub> emitted from the respective syntheses is the sum of direct and indirect CO<sub>2</sub> emission amounts less the amount of CO<sub>2</sub> used as input raw material, and is described by the following equation:

$$CO_2 = \sum_m^M c_{R,m} * f_{R,m} + \sum_n^N c_{U,n} * f_{U,n} + \sum_o^O f_o - \sum_i^I f_i \quad (4)$$

where  $c_{R,m}$  and  $c_{U,n}$  are CO<sub>2</sub> emission factors of input raw material type  $m$  and utility type  $n$ , respectively.  $f_{R,m}$  and  $f_{U,n}$  are the flowrates of raw material type  $m$  and utility type  $n$  supplied to the process to produce 1 kg of the target product, respectively. The  $f_i$  and  $f_o$  represent the flowrates of CO<sub>2</sub> input to and output from the synthesis process, respectively.  $c_{R,m}$  and  $c_{U,n}$  can be obtained from any available LCA databases (e.g., Ecoinvent, SimaPro, etc.), and may

vary depending on the methods used for producing the required raw materials and utilities. The  $f_{R,m}$ ,  $f_{U,n}$ ,  $f_o$  and  $f_i$  were calculated using the mass and heat balance data obtained from design and simulation of the target synthesis process. In the current study, we used factors obtained from a Japanese LCA database, namely, IDEA (2019) which reflected the widely accepted operating conditions and production technologies currently being employed in Japan. In cases where the relevant data sources were not available due to gaps in the published reports, the respective factors were calculated via the application of process design and simulation. Table 1 shows the CO<sub>2</sub> emission factors of the various raw materials and utilities used in this study.

Fig. 1 shows the boundary of cradle-to-gate life cycle assessment applied in this study. Here, all required stages for methanol synthesis were included, starting with the input of CO<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub> as the main raw materials. The stages for the synthesis of syngas and methanol were simultaneously considered. Heat waste which was released from the cooling reaction product mixtures and the incinerating gaseous waste was used to generate steam that was then fed back to the system. This was done to reduce the energy consumption of the entire process. CO<sub>2</sub> that was directly released could be captured and used as a raw material.

It was assumed that the CO<sub>2</sub> raw material was captured from in-process emission sources (e.g., gaseous waste stream) or nearby industrial plants (e.g., power plant containing approximately 10% mol fraction of CO<sub>2</sub>). Monoethanolamine (MEA)-based absorption, the most common method for capturing CO<sub>2</sub> (Hasan et al., 2012; Giordano et al., 2018; Zarogiannis et al., 2020), was applied. Herein, a simplified CO<sub>2</sub> capturing process using MEA was designed and simulated, thereby providing the necessary data for evaluating CO<sub>2</sub> emissions due to the energy consumption associated with the capturing process and serving as the basis for estimating the emission factor of the CO<sub>2</sub> raw material. More details are provided in Fig. S1.

The O<sub>2</sub> raw material was produced using conventional air separation technology, namely, cryogenic distillation, which is best suited for large-scale production (Tachibana, 2010; Wankat et al., 2010; Caspari et al., 2019). The CO<sub>2</sub> emission factor of the O<sub>2</sub> raw material was calculated using available information related to the O<sub>2</sub> separation plant's energy consumption. Since the CO<sub>2</sub> emission factor of the CH<sub>4</sub> raw material can vary depending on the source, e.g., via shale gas extraction or refinery cracking processes, it was assumed that the CH<sub>4</sub> used in this study was obtained from unconventional natural gas production processes that generated approximately 0.58 kg of CO<sub>2</sub> per kg of CH<sub>4</sub> (Skone et al., 2014). The CO<sub>2</sub> emissions arising from fossil fuel consumption incurred while transporting the raw material were not considered in this study.

**Table 1**  
CO<sub>2</sub> emission factors of main utilities and raw materials.

Raw material/Utility	Unit	GHG emissions (kg CO <sub>2</sub> /unit)
Raw Material		
CO <sub>2</sub>	kg	0.3 <sup>a)</sup>
O <sub>2</sub>	kg	0.28 <sup>b)</sup>
CH <sub>4</sub>	kg	0.58 (Skone et al., 2014)
Utility		
steam	kg	0.2 (IDEA, 2019)
fuel oil	kg	3.46 <sup>c)</sup>
electricity	kWh	0.53 (IDEA, 2019)
cooling water (recycled)	kg	0

<sup>a</sup> Estimated using process design and simulation, more detail shown in supporting information.

<sup>b</sup> Estimated using information obtained from ref. (Tachibana, 2010).

<sup>c</sup> Estimated using data obtained from IDEA (2019).

## 2.2. Process design

Fig. 2 shows the process flowsheet of methanol production using syngas produced by subjecting methane to the combined DR/PO method. Generally, 99.5 wt% pure methanol is produced on a scale of 1 million tons/year using this method. The associated process was designed using the PRO/II™ process simulator in which the Peng–Robinson equation of state (PR EOS) was employed to determine the main thermophysical properties driving this simulation. Here, data related to mass and energy balances were extracted for process assessment and optimization. In this study, the simulated process was separated into two main stages, namely, syngas synthesis and methanol synthesis.

### 2.2.1. Syngas synthesis

There is a reversible water–gas shift reaction (defined by Equation (5)) that typically accompanies the general synthesis of syngas via Equations (1) and (3) (Chein et al., 2015; Oyama et al., 2012; Lim et al., 2012):



Since DR reaction defined by Equation (1) is highly endothermic, a high energy input must be invested to operate the reactor, while the extreme exothermicity of the reaction governed by Equation (3) generates “hot spots” on the catalyst (Ruckenstein et al., 1998; Meshkani et al., 2014; Jalali et al., 2019). The combined effects of these reactions can help solve the inherent problem of each reaction, but arising concerns of reaction conversion rate and selectivity which motivate extensive efforts to find various catalysts and synthesis conditions. Nevertheless, there is limited information about an applicable reaction kinetic model for process design and simulation. Herein, the syngas synthesis stage was designed using the simplified Gibbs reactor model included in the PRO/II™ process simulator. This simple reactor model has previously been used for the design and optimization of methane reforming processes in numerous studies (e.g., Dave and Foulds, 1995; Medrano-García et al., 2017; Julián-Durán et al., 2014; Ehlinger et al., 2014; Zhang et al., 2015; Zhu et al., 2018). It calculates the reaction conversion rate and product selectivity by minimizing the participating reactions' Gibbs free energy with respect to synthesis conditions such as reaction temperature and pressure.

As shown in Fig. 2, the syngas synthesis starts with the input of the gaseous CH<sub>4</sub>, CO<sub>2</sub> and O<sub>2</sub> raw materials at normal temperature, pressure and suitable molar ratios. First, CH<sub>4</sub> and CO<sub>2</sub> are mixed in mixer a1, and the unexpected combustion of methane was avoided by separately compressing this mixture using compressor b1 while increasing the pressure of O<sub>2</sub> flow in compressor b2. Multiple stages of compression were applied, depending on the pressure required for the synthesis of syngas. Flows 2 and 8 which consisted of the raw materials were passed through heat exchangers c1 and c2, respectively; this was done to increase their internal temperatures via the thermal heat transferred from the product mixture in stream 5. The temperature of these flows was further elevated to the required reaction temperature by passing them through heaters d1 and d2. The resulting streams 4 and 10, which were at the appropriate temperature and pressure, were led into reactor e1 where syngas mixture is produced following the reactions defined by Equations (1), (3) and (5) with the support of a suitable catalyst. Product stream 5 was released at high temperatures and consisted of the unconverted CH<sub>4</sub>, CO<sub>2</sub>, CO, and H<sub>2</sub> raw materials, as well as a large amount of H<sub>2</sub>O. After transferring heat to the input raw materials streams, stream 5 was further cooled using cooler f1, thereby facilitating the separation of water in flash g1. After the water was removed, the syngas product mixture, which consisted mainly of

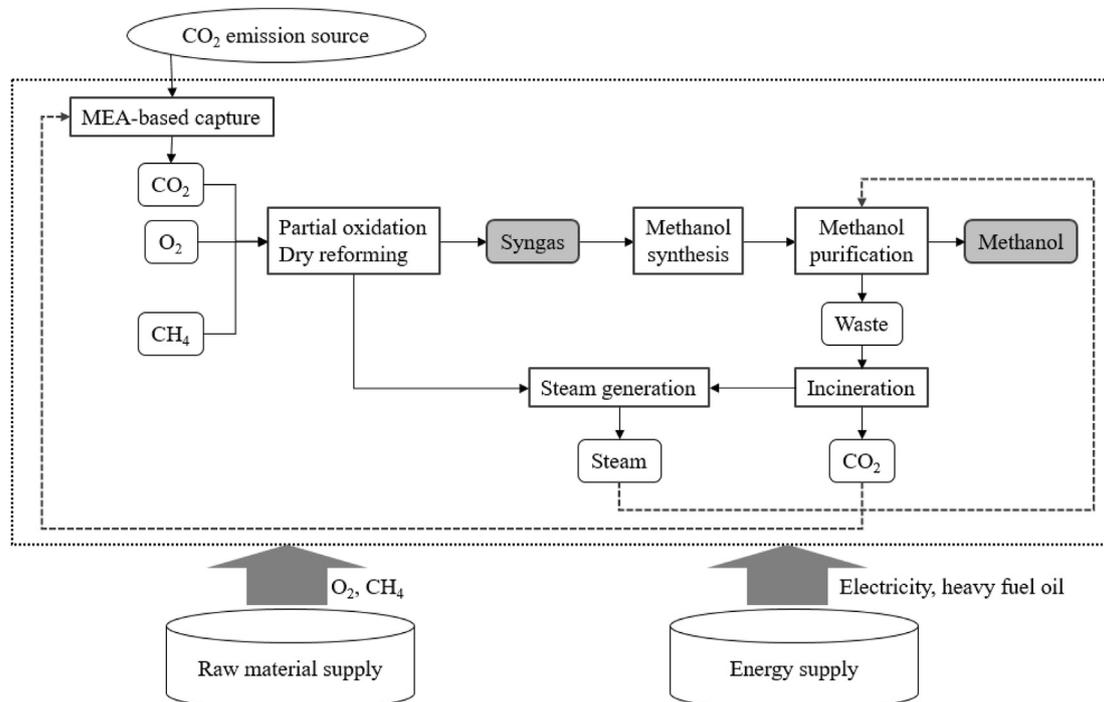


Fig. 1. Boundary of evaluation.

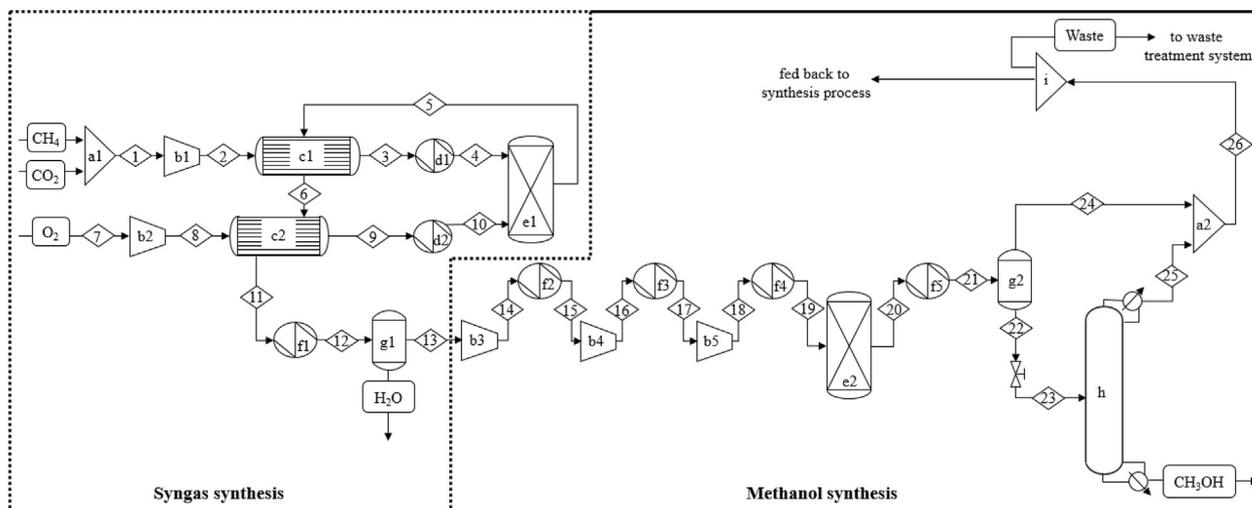
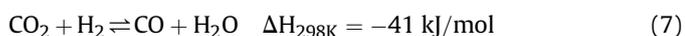
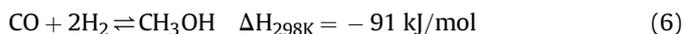


Fig. 2. Methanol synthesis process.

CO, CO<sub>2</sub>, and H<sub>2</sub>, was then led to the downstream process for methanol synthesis.

### 2.2.2. Methanol synthesis

From the syngas mixture, methanol was synthesized following the equilibrium reactions defined by Equations (6)–(8):



Different kinetic models have been proposed for designing

methanol synthesis reactor (Bussche and Froment, 1996; Graaf et al., 1998; Seidel et al., 2018). Based on the dataset obtained from 234 experiments, Slotboom et al. (2020) rigorously assessed the prediction capability of these proposed models. The steady-state kinetic model developed by Bussche and Froment (also known as the BF model) (1996) was shown to be one of the few models relevant for designing PFR and CSTR reactors using industrial catalysts; here, reactions were conducted in temperature and pressure ranges of 180°C–280 °C and 15–51 bar, respectively. Abrol and Hilton (2012) successfully used this kinetic model to design and control the methanol production process using variable synthesis gas feeds. In the current study, the methanol synthesis reactor was designed using the BF model, and primarily based on the reactions defined by Equations (7) and (8) above. The

equilibrium reactor model included in the PRO/II™ process simulator was employed, and the reaction constants shown in Table 2 were used to design and simulate reaction conditions during methanol synthesis.

As shown in Fig. 2, the stream 13 output from the syngas synthesis section was passed through multi-stages of compression (b3, b4 and b5) with intermediate cooling using coolers f2 and f3). The temperature of stream 18 was adjusted to match the reaction temperature after it was passed through cooler f4. Stream 19 is led to reactor e2 which was packed with the commercial catalyst Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>. Methanol was synthesized in this reactor as defined by Equations (6)–(8). Stream 20, which consisted primarily of the methanol product, the water byproduct, and the remaining syngas, was cooled in cooler f5. In g2 gas separator, stream 24, which contained CO, CO<sub>2</sub>, and H<sub>2</sub>, was separated and then mixed with the gaseous stream 25. In splitter i, a small fraction of this mixture (namely, waste stream) was split and incinerated in a waste treatment system for steam production. The remaining mixture was fed back into the system and mixed with the new raw material flows for the new synthesis. Stream 23, which consisted primarily of methanol with small amounts of CO<sub>2</sub> and H<sub>2</sub>O, was then fed into distillation column h, where the remaining CO<sub>2</sub> rose to the top to give stream 25, while methanol at high concentration was collected from the bottom fraction. Heuristic knowledge was used to select suitable specifications (i.e., the number of stages, feed stage, reflux ratio, and pressure) for the column design to ensure the production of methanol at the desired purity while still achieving low costs for the column construction and energy consumption.

The reboiler attached to the distillation column h was operated using steam generated from the waste treatment system and other sources of heat waste (i.e., heat removed from the cooling of the syngas mixture). As such, extra energy was not required for this methanol purification column. Depending on the intended end use of the methanol product, i.e., as a commodity chemical or transportation fuel, further distillation can be conducted to remove excess water, thereby producing the methanol at the desired purity. When the intended use of methanol was as a chemical intermediate, the desired purity was 99.5 wt%; thus, no additional distillation step was needed.

### 2.3. Key parameter identification for process optimization

As Fig. 2 shows, the two main stages of the process, i.e., syngas and methanol syntheses, consisted of a number of processing units, each of which was specified by operating parameters such as temperature and pressure. The analysis and optimization of the entire process were quite challenging due to the existence of many parameters within the same system. As shown in Equation (4), the total process CO<sub>2</sub> emissions were inherently correlated with the consumption of raw materials and utilities. Thus, the task burden was reduced by identifying the main parameters that directly impacted the amounts of raw materials and utilities that were utilized. Process simulations revealed that the impact of these key parameters varied within a validity range. An evaluation of the sensitivity of the total process CO<sub>2</sub> emissions to the changes in any or all of these parameters was conducted to determine the

**Table 2**  
Kinetic equilibrium constants used for designing methanol synthesis reactor (Bussche and Froment, 1996).

Reaction ID	$K_{eq} = 10^{(A/T+B)}$	A	B
(7)	$K_{eq, 7}$	-2073	2.029
(8)	$K_{eq, 8}$	3066	-10.592

optimum of each parameter.

#### 2.3.1. Syngas synthesis operating conditions

The syngas and methanol synthesis stages each required vastly different operating conditions to maximize production yield. The operating conditions of the former stage determined the output conditions, yield, and composition of the syngas mixture. When the former stage, i.e., syngas synthesis, was conducted at low pressures, the energy consumption needed to compress the raw material input flows could be minimized. However, the conditions associated with the corresponding output of the syngas mixture must be altered to make it appropriate for downstream methanol synthesis. This adjustment was conducted by compressing the syngas product mixture to the elevated pressure of the methanol synthesis, thereby requiring large energy consumption.

The yield and composition of the syngas mixture (i.e., CO, CO<sub>2</sub>, and H<sub>2</sub>) influenced the M value, and, ultimately, the amount of methanol synthesized downstream. Low methanol productivity resulted in high raw material demands. Increasing the CH<sub>4</sub> and O<sub>2</sub> demands led to higher indirect CO<sub>2</sub> emissions caused by the associated production processes, while increasing the CO<sub>2</sub> raw material demand contributed to reduction of the overall CO<sub>2</sub> emissions. Moreover, higher raw material flow rates also triggered higher amount of energy supplied to the preheating and compressing process units (i.e., heater and compressor) when elevated temperature and pressure were required for the syngas synthesis.

#### 2.3.2. Raw material input ratios

As shown in the reactions defined by Equations (1), (3) and (5), the input molar ratios of the raw materials (i.e., CH<sub>4</sub>/CO<sub>2</sub>/O<sub>2</sub>) determined the contribution of these reactions to the syngas product yield and composition, as well as the energy requirement of the syngas synthesis stage; this occurred in addition to the demands associated with optimum operating temperatures and pressures during the synthesis of syngas. When CO<sub>2</sub> was used at high molar ratios, the endothermic reaction (Equation (1)) became dominant, thereby promoting further utilization of CO<sub>2</sub>. This, in turn, produced more CO than H<sub>2</sub>, resulting in an M value smaller than 2. In addition, more energy was supplied for maintaining the syngas synthesis reactor at elevated temperatures. In contrast, when O<sub>2</sub> was used at ratios higher than the requirement, the syngas synthesis stage was dominated by the exothermic reaction (Equation (3)), which, in turn, reduced the energy consumption needed to operate the reactor. Nevertheless, a high utilization of the O<sub>2</sub> raw material resulted in higher indirect CO<sub>2</sub> emissions during the air separation process for O<sub>2</sub> production.

#### 2.3.3. Methanol synthesis operating conditions

A stoichiometric number M close to 2 was required to gain high methanol yield (Riaz et al., 2013). When M < 2, there were a deficiency of H<sub>2</sub> and an excess of carbon oxide mixture. A fraction of the latter was remained and incinerated after the methanol synthesis, thereby causing high direct CO<sub>2</sub> emissions. In contrast, when M > 2, there was an excess of H<sub>2</sub> and a scarcity of carbon dioxide mixture. Both cases directly impacted methanol product yield. Herein, M was calculated by using the molar compositions of the substances included in the syngas mixture, and its value was directly influenced by the operating conditions of the syngas synthesis stage and the input molar ratios of the raw materials. In addition to the M value, the methanol yield also depended on the pressure and temperature used for its synthesis. The high product yield meant that there was a low requirement of raw materials, which resulted in low energy consumption for the pretreating of the input raw materials and vice versa.

The inherent characteristics and the stoichiometric coefficients

of the gaseous reactants and products of the syngas and methanol synthesis reactions showed marked differences in the preferred reaction conditions of these stages. Intermediate syngas product yield was maximized at low pressures and high temperatures, whereas methanol synthesis benefitted most from high pressures and low temperatures. Thus, the operating conditions of both syngas and methanol syntheses were simultaneously considered for selecting the most suitable ones that could lower CO<sub>2</sub> emissions of the overall process. Since methanol could be produced using a wide range of operating temperature and pressure parameters (Riaz et al., 2013), the most suitable parameters were chosen to encourage high methanol yield without inversely affecting the synthesis of syngas.

Separation of the crude methanol mixture output during the methanol synthesis stage to produce the target methanol product at the desired purity was conducted using a distillation column that exhibited several degrees of freedom, including the number of stages, feed stage, reflux ratio, and operating pressure. These parameters could be individually adjusted, and the most suitable ones were selected based on the desired methanol product composition. Optimization of the distillation column was done using heuristic knowledge. In the current study, these were not considered as key variables for optimizing the target synthesis process.

Table 3 summarizes the key parameters of this process. Based on the available information, the upper and lower limits of the respective variation ranges were specified and used for sensitivity analysis to determine the most suitable operating conditions for a low-emission process design.

### 3. Process optimization results and discussion

#### 3.1. Optimization of key parameters

The key parameters and their variation ranges were used for process simulation to obtain the relevant mass and energy balance data for evaluating the total CO<sub>2</sub> emissions under each operating condition by using Equation (4). The fluctuations observed in these main parameters caused various changes in the M value and the carbon oxide mixture and final product yields. As a result, various changes in the raw material and energy consumptions and thus total GHG emissions were noted. This, in turn, allowed us to select the operating conditions that generated the smallest amount of CO<sub>2</sub>. The selected operating conditions were summarized in Table 4. More details about the impact of the key parameters on the carbon oxide mixture (using CO as the representative) yield, M value, and methanol yield can be found in Figs. S2–S4.

##### 3.1.1. Syngas synthesis operating conditions

Herein, the operating conditions (i.e., temperature and pressure) of the syngas synthesis were varied to examine their impact on the total process GHG emissions, while the preferred operating conditions of the methanol synthesis were selected and maintained.

**Table 3**  
Main variables considered in process optimization.

Main variables	Variable ID	Unit	Variation ranges
Syngas synthesis section			
Reaction temperature	T <sub>1</sub>	°C	627–1400
Reaction pressure	P <sub>1</sub>	bar	1–25
Input molar ratio CO <sub>2</sub> /CH <sub>4</sub>	X	–	0.1–1
Input molar ratio O <sub>2</sub> /CH <sub>4</sub>	Y	–	0.1–1
Methanol synthesis section			
Reaction temperature	T <sub>2</sub>	°C	180–280
Reaction pressure	P <sub>2</sub>	bar	15–50

The observed trend in this case was similar for all raw material input ratios, as demonstrated by the selected representative ratios (i.e., CO<sub>2</sub>/CH<sub>4</sub> = 0.1 and O<sub>2</sub>/CH<sub>4</sub> = 0.5). The combination of the reactions defined by Equations (1), (3) and (5) clearly indicated that the syngas synthesis stage benefitted from high reaction temperatures and low pressures. Fig. 3 shows the impact of these parameters on the energy consumption of the syngas synthesis stage (i.e., heating duty) and the overall process CO<sub>2</sub> emissions.

As Fig. 3a shows, an increase in the temperature parameter of the syngas synthesis reduced the overall GHG emissions. Herein, although higher thermal heat supply was required when elevated temperatures were employed, the amount of energy required to operate the reactor was almost negligible in the syngas synthesis due to the high exothermicity of the PO reaction (Equation (3)). High temperature stimulated the DR reaction (Equation (1)). In addition to an observed increase in the CO yield and M value, the methanol productivity steadily increased (see Fig. S2a). As a result, the amounts of raw materials and utilities supplied to the process could be significantly reduced, which, in turn, decreased the overall CO<sub>2</sub> emissions at high temperatures. When the reaction temperature exceeded 927 °C, only minor gains in the total GHG emissions were obtained, despite the need for more expensive material to construct the reactor. Thus, 927 °C was selected as the most suitable temperature for syngas synthesis.

As shown in Fig. 3b, an increase of pressure employed for syngas synthesis caused an increase of energy consumption required to compress the raw material mixture. The lowest total process GHG emissions was achieved at 3 bar. When the pressure parameter exceeded 3 bar, the output syngas mixture exhibited higher pressure, which, in turn, helped to reduce the pressure differences between the syngas and methanol synthesis stages, the latter of which required much higher pressure to produce high methanol yield. As a result, less energy consumption is required to compress the syngas mixture to appropriate pressure for methanol synthesis, thereby reducing the amount of CO<sub>2</sub> generated in the methanol synthesis stage. However, increasing the pressure during the syngas synthesis stage noticeably decreased the CO yield and M value, resulting in a considerable decline in the methanol product yield (Fig. S2b). Thus, producing a unit of methanol required more raw materials, leading to high energy demand for the raw material compression, thereby increasing the amount of CO<sub>2</sub> generated in the syngas synthesis stage. If, however, this CO<sub>2</sub> emission increase was dominated by the CO<sub>2</sub> emission decrease benefitted from the reduction of two stages' pressure differences, the overall process CO<sub>2</sub> emissions could be decreased. This was exemplified at a pressure of 3 bar, which only slightly reduced the downstream methanol yield. Given these findings, we determined that a pressure parameter of 3 bar was suitable for the syngas synthesis stage.

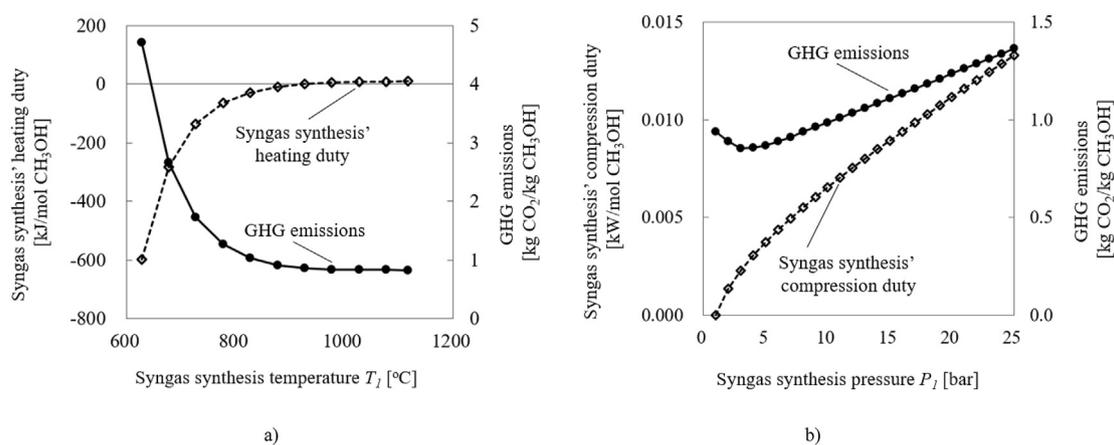
##### 3.1.2. Raw material input ratios

Fig. 4 shows the impacts of altering the molar input ratios of CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/CH<sub>4</sub> on the syngas synthesis stage's thermal energy consumption (i.e., heating duty) and the overall process' GHG emissions. To examine these impacts, the operating conditions mentioned above for syngas and methanol syntheses were employed.

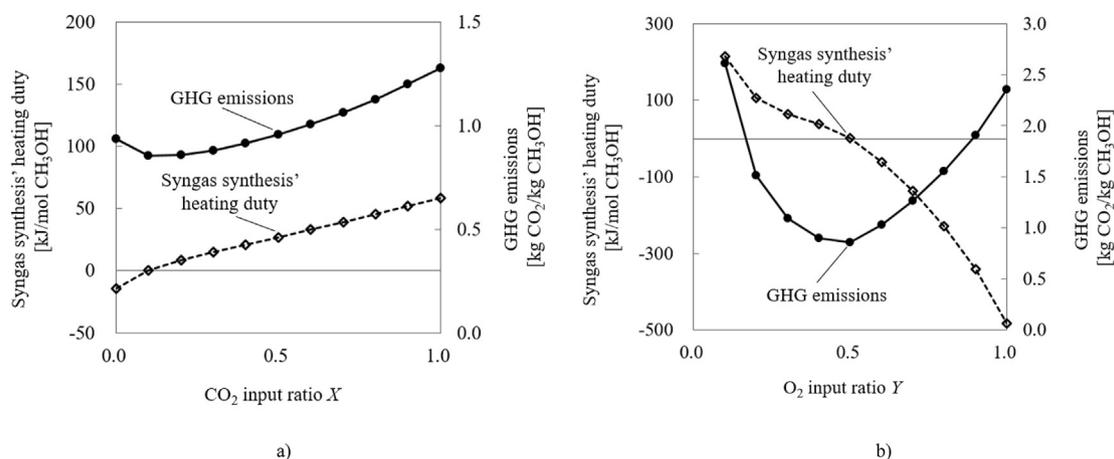
Fig. 4a shows the impact of altering CO<sub>2</sub>/CH<sub>4</sub> ratio while maintaining O<sub>2</sub>/CH<sub>4</sub> at stoichiometric ratio (i.e., O<sub>2</sub>/CH<sub>4</sub> = 0.5, as defined by Equation (3)). More energy was required to heat the syngas synthesis reactor when the CO<sub>2</sub> input was higher. The lowest GHG emission was observed when the CO<sub>2</sub>/CH<sub>4</sub> ratio was 0.1. Herein, increasing the CO<sub>2</sub> input molar ratio promoted more efficient CO<sub>2</sub> utilization by increasing the DR reaction's contribution to the overall process. Since this reaction was extremely endothermic, the

**Table 4**  
Optimal operation conditions compared with previous studies.

	This study	Previous studies	
		Dataset 1 (Afzal et al., 2018)	Dataset 2 (Noureldin et al., 2015)
Process boundary	Syngas + methanol syntheses	Syngas synthesis	Syngas synthesis
Optimization target	Minimize kg CO <sub>2</sub> per kg methanol	Minimize kg CO <sub>2</sub> per kg syngas	Maximize kg CO <sub>2</sub> fixed per kg methane
DR/PO reactor type	Combined reactor	Parallel reactor	Combined reactor
Proposed conditions			
T <sub>1</sub> [°C]	927	1400 for PO 1100 for DR	747
P <sub>1</sub> [bar]	3	20	1
X [-]	0.1	0.74	1.32
Y [-]	0.5	0.53	0.68
T <sub>2</sub> [°C]	200	N/A	N/A
P <sub>2</sub> [bar]	50	N/A	N/A



**Fig. 3.** Impact of syngas synthesis conditions.



**Fig. 4.** Impact of raw material input molar ratio.

energy required to heat the syngas synthesis reactor to the desired elevated temperatures increased dramatically. This energy was provided by burning heavy fuel oil, which was associated with a rather high CO<sub>2</sub> emission factor (Table 1), thereby resulting in high CO<sub>2</sub> emissions. The total molar flow rate of CO increased proportionally to the rise in the CO<sub>2</sub> input molar ratio (Fig. S3a). Since CO was the main syngas component contributing to the production of methanol, this trend reduced the demands of raw materials to produce a unit amount of methanol; this, in turn, reduced the indirect CO<sub>2</sub> emissions caused by the CH<sub>4</sub> production process.

However, this benefit was notable only if the  $M$  value was close to 2 for high-yield methanol production. Increases in the contribution of the reactions defined by Equations (1) and (5) steadily decreased the  $M$  value, which was indicative of a paucity of H<sub>2</sub>. Thus, the methanol yield decreased when the CO<sub>2</sub>/CH<sub>4</sub> input increased, leading to higher demands of raw materials and significantly higher energy consumption for raw material preheating and compression; this ultimately resulted in higher CO<sub>2</sub> emissions from indirect sources. Moreover, the lack of H<sub>2</sub> for methanol production meant that the carbon oxides included in syngas could not be fully utilized

for methanol synthesis. Thus, a considerable amount of the unconverted mixture (i.e., 10%) was finally incinerated, resulting in more direct CO<sub>2</sub> emissions. The increase in the CO<sub>2</sub>/CH<sub>4</sub> ratio was particularly disadvantageous when the sum of the amounts of both the indirect and direct CO<sub>2</sub> emissions was higher than the amount of CO<sub>2</sub> utilized as the process' raw material. When the CO<sub>2</sub>/CH<sub>4</sub> molar ratio was approximately 0.1, the M value was slightly lowered than 2 and sufficient amount of CO was produced. This resulted in the highest methanol product yield and the lowest CO<sub>2</sub> emissions. Thus, it can be concluded that the suitable CO<sub>2</sub>/CH<sub>4</sub> input ratio was 0.1 for syngas synthesis.

Fig. 4b shows the impact of the O<sub>2</sub>/CH<sub>4</sub> molar input ratio on the syngas synthesis; here, the above selected CO<sub>2</sub>/CH<sub>4</sub> ratio of 0.1, as well as the temperature and pressure operating conditions, were fixed in the syngas and methanol syntheses, whereas the O<sub>2</sub>/CH<sub>4</sub> molar input ratio was varied. Increasing O<sub>2</sub>/CH<sub>4</sub> input ratio decreased the heating duty of the syngas reactor operating at high temperatures. Additionally, the GHG emissions appeared to be dependent on the O<sub>2</sub>/CH<sub>4</sub> molar input ratio. At a low O<sub>2</sub>/CH<sub>4</sub> ratio (i.e., ≤0.5), the syngas synthesis was dominated by the DR reaction in which excessive heat was needed to operate the reactor. Thus, the increased thermal energy demand, which was fulfilled by burning heavy fuel oil, resulted in higher CO<sub>2</sub> emissions. Moreover, CO yield was rather low, resulting in low yield of methanol (Fig. S3b). As a result, higher amounts of raw materials and energy were supplied to produce a unit amount of methanol, thereby, resulting in higher total process CO<sub>2</sub> emissions. When the O<sub>2</sub> input was higher than the stoichiometric ratio dictated by Equation (3) (i.e., O<sub>2</sub>/CH<sub>4</sub> ratio > 0.5), the syngas reactor was overwhelmed by the reaction's exothermic nature, resulting in the generation of hotspots on the catalysts and temperature control issues due to the unscheduled release of large amounts of energy (Jalali et al., 2019; Meshkani et al., 2014; Ruckenstein and Hu, 1998). Excessive O<sub>2</sub> input led to the mostly complete consumption of input CH<sub>4</sub>, as dictated by Equation (3). Noticeable decreases in the M value and CO and methanol yields were observed (Fig. S3b). This was properly contributed by the reversible water–gas shift reaction (defined by Equation (5)) which formed large amount of CO<sub>2</sub>. Herein, high demands of raw materials (i.e., CH<sub>4</sub> and O<sub>2</sub>) together with direct emission of considerably high amount of unused CO<sub>2</sub> led to high CO<sub>2</sub> emissions. From these results, we concluded that an O<sub>2</sub>/CH<sub>4</sub> input molar ratio of 0.5 was suitable for syngas synthesis as it resulted in the highest methanol yield and negligible heating duty in the reactor.

### 3.1.3. Methanol operating conditions

Using the temperature and pressure ranges (i.e., 180 °C–280 °C and 15–50 bar) for the applied reaction kinetic model, we focused on determining suitable conditions for operating the methanol synthesis. Here, the operating conditions of syngas synthesis, molar ratios of input raw materials, and the input syngas' composition were fixed. Due to the fixation of these parameters, M value and CO yield were constant during the investigation of methanol synthesis' operating conditions (Fig. S4a).

As Fig. 5a shows, methanol synthesis under elevated temperatures resulted in increased GHG emissions due to the diminishing of the methanol yield (Fig. S4a). This result was expected, given that the reactions for methanol synthesis were quite exothermic (Equations (6)–(8)). Thus, low-temperature synthesis was preferable in this case. Evaluation of the total process CO<sub>2</sub> emissions clearly showed that the lowest CO<sub>2</sub> emissions were noted at a reaction temperature of 180 °C. However, the commercial catalyst used for methanol synthesis was only active at temperatures above 200 °C (Bozzano and Manenti, 2016). Thus, we determined that the most suitable temperature for the methanol synthesis was 200 °C,

as this allowed us to strike a balance between catalyst activation and low CO<sub>2</sub> emissions without significantly sacrificing product yield.

In Fig. 5b, the increase in the pressure used for the methanol synthesis resulted in a slight increase in the methanol synthesis' compression duty but noticeable decrease in the total GHG emissions. The stoichiometric ratios of the reactants and products involved in Equations (6)–(8) indicated that high-pressure conditions promoted better product yield. Indeed, increasing the reaction pressure boosted the methanol yield (Fig. S4b) and lowered the amounts of raw material input and unconverted carbon dioxides output, thereby retarding the overall CO<sub>2</sub> generation from the process. Herein, high-pressure methanol synthesis required more energy consumption to compress the syngas mixture prior to the methanol synthesis reactor. Nevertheless, the amount of energy consumed depended on the difference of pressures between the syngas and methanol synthesis stages. Large difference resulted in high energy consumption, and vice versa. Thus, high-pressure methanol synthesis was only beneficial if this energy consumption resulted in relatively low amount of CO<sub>2</sub> emissions. At the optimal syngas synthesis pressure of 3 bar, methanol synthesis pressure of 50 bar was noted to attain the lowest CO<sub>2</sub> emissions. Thus, 50 bar was selected as a suitable pressure parameter for methanol synthesis.

### 3.2. Comparison with previous studies

The results in the current study were compared with the results obtained from previous reports. Noureldin et al. (2015) and Afzal et al. (2018) investigated suitable operating conditions for combining DR with PO to produce syngas of different H<sub>2</sub>/CO ratios. The former study aimed to gain high CO<sub>2</sub> fixation rate and to provide sufficient thermal heat for DR reaction, whereas the latter aimed to maximize syngas productivity by considering production cost and CO<sub>2</sub> emissions. Both of these studies solely focused on optimizing the operating conditions of syngas synthesis without consideration of the downstream process' requirements (i.e., operating conditions and product yield of methanol synthesis). Thus, they proposed markedly different operating conditions for syngas synthesis (i.e., raw material input ratios, temperature and pressure), as shown in Table 4. In the current study, as stated earlier, the optimized operating conditions for syngas and methanol syntheses were determined relative to each other, with the highest outcome priority on minimizing the total process CO<sub>2</sub> emissions. Thus, the crux of our research was balancing these multiple objectives. Given existing discrepancies between this study and the previous ones, a basis for comparison was established by applying the same optimal operating conditions for methanol synthesis, whereas different operating conditions for syngas synthesis via combination of DR and PO were employed. A comprehensive evaluation of the total CO<sub>2</sub> emissions was conducted using the same cradle-to-gate evaluation boundary shown in Fig. 1. The same baseline emission factors for the raw materials and utilities shown in Table 1 were employed.

Fig. 6 shows the comparison result of total process GHG emissions produced at the conditions employed by this study and the previous studies (Afzal et al., 2018; Noureldin et al., 2015). The comparison clearly showed that the operating conditions reported in the published studies stimulated more CO<sub>2</sub> utilization (shown as the negative bar in Fig. 6). However, as stated above, the high input molar ratio of CO<sub>2</sub> encouraged higher syngas production in total, but low M value. As a result, when the syngas mixture was used for the methanol synthesis, high amount of carbon oxides was remained and treated in the waste treatment system, thereby generating higher direct CO<sub>2</sub> emissions.

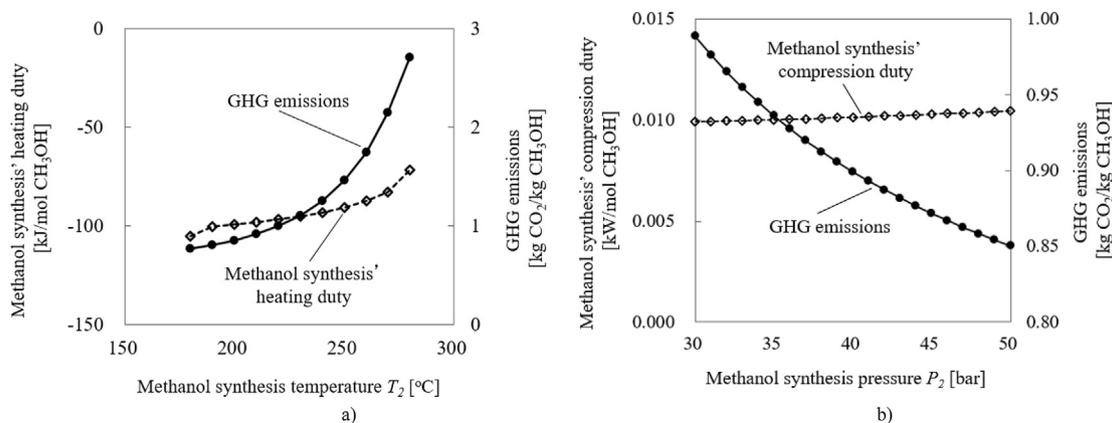


Fig. 5. Impact of methanol synthesis conditions.

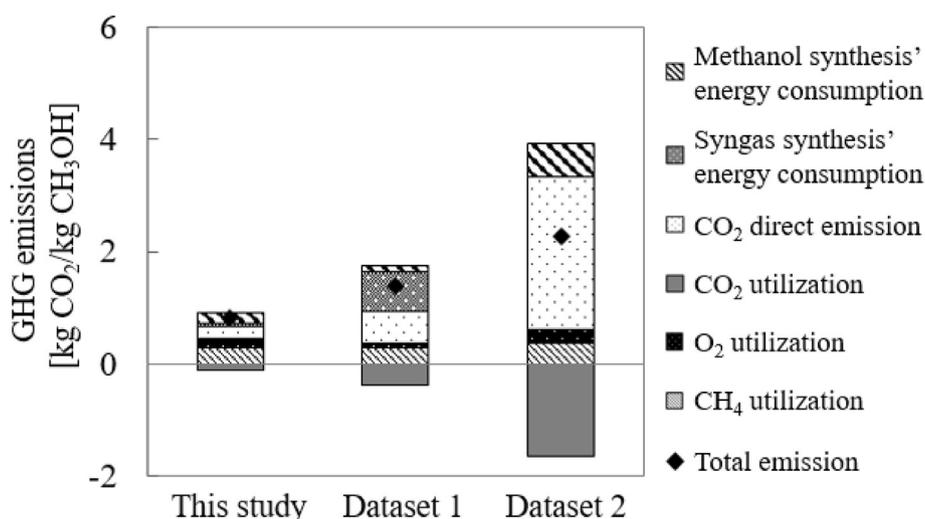


Fig. 6. GHG emissions comparison result.

The high-pressure syngas synthesis (i.e., 20 bar) employed by Afzal et al. (2018) reduced the energy consumption required to compress the syngas mixture in the methanol synthesis stage. This, in turn, increased the raw material compression burden; as such, the pressure of the reaction had to be elevated in the syngas synthesis stage. In Fig. 6, the associated energy consumptions used for syngas mixture compression and raw material compression were allocated to the methanol and syngas synthesis stages, respectively. In the study by Afzal et al. (2018), although small amount of CO<sub>2</sub> was generated in the methanol synthesis stage, noticeably high amount of CO<sub>2</sub> was produced in the syngas synthesis stage. In total, quite high overall process CO<sub>2</sub> emissions were resulted. In the study by Noureldin et al. (2015), as low-pressure was employed for syngas synthesis (i.e., 1 bar), the adverse effect was observed. Although operating at this pressure maximized the syngas product yield, the marked difference between the operating pressures of the syngas and methanol synthesis stages led to markedly high energy demand for compressing the syngas mixture in the methanol synthesis stage.

In our study, the cradle-to-gate LCA approach was employed to simultaneously determine the optimal operating conditions for both the syngas and methanol synthesis stages. Herein, the main focus was to reduce the CO<sub>2</sub> emissions of the overall process rather than to simply maximize the output of either the syngas- or

methanol-synthesis stages. As a result, the total CO<sub>2</sub> emissions (i.e., 0.81 kg CO<sub>2</sub>/kg methanol) obtained in our study were much lower than those observed in the previous studies (Afzal et al., 2018; Noureldin et al., 2015) with the sole focus of maximizing syngas production or CO<sub>2</sub> fixation in the syngas synthesis. This narrowed focus on minimizing the total carbon footprint of the syngas synthesis stage resulted in generally higher total process CO<sub>2</sub> emissions. Thus, when the syngas mixture is produced and used as an intermediate feedstock for producing other valuable products, it is prudent to consider both its production and conversion processes thoroughly. The proposals of this study have implications for generating more effective and comprehensive process design and assessment strategies to help decision makers rigorously and accurately evaluate the economic and environmental efficiency of future chemical production processes for sustainable development.

#### 4. Conclusion

In this study, a comprehensive evaluation of the total process CO<sub>2</sub> emissions was conducted by employing the cradle-to-gate life-cycle assessment method. Here, the aim was to determine suitable conditions for producing methanol using the syngas mixture obtained from the combined DR/PO reactions of methane. Both the syngas and methanol synthesis stages were simultaneously

considered when optimizing the raw material input molar ratios in addition to the operating temperatures and pressures. Under the conditions proposed in the current study, the total process CO<sub>2</sub> emissions obtained was as low as 0.81 kg CO<sub>2</sub>/kg methanol. Since this study focused on determining the suitable operating conditions for reducing CO<sub>2</sub> emissions of the total production process, the CO<sub>2</sub> emitted due to transportation of the raw material was neglected. In reality, the carbon footprint of the transportation step will vary depending on the location and transportation conditions.

Although the operating conditions proposed by our group stimulate lower levels of CO<sub>2</sub> utilization, we were able to achieve much lower total CO<sub>2</sub> emissions relative to the results observed in the previously reported studies when the produced syngas mixture was used for producing valuable products such as methanol. This marked difference in results clearly highlighted the need to extend the evaluation boundary to appropriately incorporate the optimization of the syngas synthesis and its conversion to the final target product processes concurrently. The cradle-to-gate life-cycle assessment is more data-intensive; however, the information garnered therein allows for a more comprehensive evaluation of the factors influencing CO<sub>2</sub> emissions throughout this process.

In light of the growing threat posed by global warming and climate change, it is believed that the methods proposed in this study can offer useful insight for the development of novel techniques and technology geared towards reducing CO<sub>2</sub> emissions. The information garnered in the current study will help design more effective, environmentally friendly production processes by developing more rigorous process evaluation procedures and more inclusive outcome boundary.

#### CRediT authorship contribution statement

**Thuy T.H. Nguyen:** Conceptualization, Methodology, Investigation, Writing - original draft. **Takehiro Yamaki:** Resources. **Satoshi Taniguchi:** Resources. **Akira Endo:** Conceptualization, Supervision, Funding acquisition. **Sho Kataoka:** Conceptualization, Writing - review & editing, Supervision, Project administration.

#### Declaration of competing interest

We declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2021.125970>.

\*In the study by Afzal et al. (2018), PO and DR were used in parallel, with adding of some water in each reactor (i.e., H<sub>2</sub>O/CH<sub>4</sub> = 0.17 in DR and H<sub>2</sub>O/CH<sub>4</sub> = 0.1 in PO). To evaluate CO<sub>2</sub> emissions of this study, the process structure of the syngas synthesis stage shown in Fig. 2 was modified by adding water input flows, separating DR and PO into two parallel reactors and reallocating the corresponding heat exchangers.

(a) Mixer; (b) compressor; (c) heat exchanger; (d) heater; (e) reactor (e1 and e2 are used for syngas and methanol synthesis, respectively); (f) cooler; (g) gas-liquid flash; (h) distillation column;

(i) splitter.

a) Impact of temperature  $T_1$  ( $P_1 = 3$  bar,  $T_2 = 200$  °C,  $P_2 = 50$  bar,  $X = 0.1$ ,  $Y = 0.5$ ); b) Impact of pressure  $P_1$  ( $T_1 = 927$  °C,  $T_2 = 200$  °C,  $P_2 = 50$  bar,  $X = 0.1$ ,  $Y = 0.5$ )

a) Impact CO<sub>2</sub> input ratio  $X$  ( $T_1 = 927$  °C,  $P_1 = 3$  bar,  $T_2 = 200$  °C,  $P_2 = 50$  bar,  $Y = 0.5$ ); b) Impact O<sub>2</sub> input ratio  $Y$  ( $T_1 = 927$  °C,  $P_1 = 3$  bar,  $T_2 = 200$  °C,  $P_2 = 50$  bar,  $X = 0.1$ );

a) Impact of temperature  $T_2$  ( $T_1 = 927$  °C,  $P_1 = 3$  bar,  $P_2 = 50$  bar,  $X = 0.1$ ,  $Y = 0.5$ ); b) Impact of pressure  $P_2$  ( $T_1 = 927$  °C,  $P_1 = 3$  bar,  $T_2 = 200$  °C,  $X = 0.1$ ,  $Y = 0.5$ )

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