

A Review: Six Common Syngas Generation Pathways and Comparison in Terms of Carbon Emissions

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Abstract: To shift to sustainable development, syngas generation has been regarded as a promising industry. Syngas is a valuable intermediate for greenhouse gas re-utilization and various value-added products production. For syngas production, there are various pathways and mechanisms using different phases of feedstocks under distinct temperature and pressure conditions. This paper based on the data from existing literature gives insight into the mechanism of six common syngas generation pathway: dry reforming, steam reforming, partial oxidation, autothermal reforming, bireforming, and gasification, while the feedstock is methane or underground coal. Simultaneously, the mechanism suggests a possible origin of carbon emissions from heating. A overview of environmental impact of carbon dioxide emissions from several channels is presented to facilitate a horizontal comparison among each technique. The comparison indicates a hierarchy of various mechanisms from a sustainability standpoint, demonstrating that autothermal reforming exhibits the highest performance in minimizing environmental impact. The limitations and prospects of sustainability research in syngas generation are articulated, including methods to enhance sustainability evaluation.

Keywords: Syngas, Sustainability, Carbon Emission, Syngas Generation

1. Introduction

Many products are made from alkane, acetic acid, and its derivatives. To produce these feedstocks, a more sustainable way is to use syngas, a combination of carbon monoxide and hydrogen gas [1]. In the perspective of fuel, syngas also plays an important role as an intermediate feedstock in the synthesis of liquid fuel [2]. The assessments involve its downstream products, which the quantified data is adjusted to. Syngas is a great raw material that utilizes low-valued emissions and produces value-added products. During the production of syngas, there are different pathways. Each method has a different mechanism. They need different feedstock, such as steam, biomass, methane, or carbon dioxide, and various temperature and pressure conditions. Carbon emissions play an important role in the accessibility of sustainability. Since carbon dioxide and methane are part of greenhouse gases, and biomass or organic waste is a source of carbon emissions, the production of syngas is regarded as a potential way to utilize these materials to reduce carbon emissions and gives a way to generate value-added products like acetic acid or long-chained alkane by Fischer-Tropsch synthesis [3]. Furthermore, it's important to ensure the production of syngas should be sustainable enough to achieve the goal of sustainability.

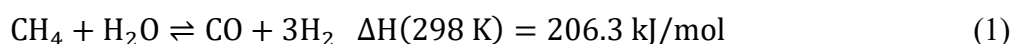
Currently, researchers put effort in inventing more methods of syngas generation and utilization pathways, designing catalysts with higher efficiency and low risks of deactivation, or examining the sustainability of each method in terms of carbon emission, ecotoxicity, etc. [4-5] This work synthesizes existing research material, elucidating the mechanics of various approaches and examining the balance between fuel use and greenhouse gas emissions across multiple pathways. This study compares various methodologies regarding carbon emissions to illustrate their sustainability, while also highlighting the limitations of existing technology and the trajectory of future development. Investigating more sustainable syngas production processes could enhance both production sustainability and societal welfare through reduced emissions and an improved living environment.

2. Overviews of different Syngas generation pathways

In the syngas generation methods, they can be divided into two categories. One is gas-phase reforming, and the other is solid-phase gasification. Reforming, which uses methane as feedstock, includes steam reforming of methane (SRM), partial oxidation of methane (POM), autothermal reforming of methane (ARM), bireforming of methane (BRM), dry reforming of methane (DRM), and so on. In practice, the methane can also be replaced by liquefied propane gas, stationary use, liquid hydrocarbon fuel, methanol, and so on. This paper will assess the methods associated with methane, considering the potential benefits for sustainable development. Gasification is used when the feedstocks are solid materials such as biomass or coal. Syngas could be generated from any hydrocarbon raw materials via gasification.

2.1. Steam reforming of methane (SRM)

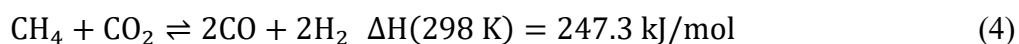
Steam reforming of methane is one of the syngas generations by converting methane with water to syngas. The main reaction gives a ratio of carbon monoxide and hydrogen gas as 1 to 3, shown in Eq. (1). Take advantage of this high hydrogen carbon monoxide ratio; SRM technology is the most common method in the production of hydrogen gas from natural gas, which takes up 50% of the hydrogen production in the whole world [6]. Meanwhile, side reactions like the water-gas shift reaction Eq. (2), coke formation Eq. (3). These will interfere with the production of formation, especially for the coke formation, which will deactivate the catalyst.



According to Eq. (1), the use of methane indicates it can be a beneficial way to utilize the greenhouse gas. However, this reaction is endothermic, indicating the need for a sustained heat supply. In other words, a large amount of fuel is required to generate heat [1, 3].

2.2. Dry reforming of methane (DRM)

Dry reforming of methane uses methane and carbon dioxide with the help of a catalyst to produce syngas at a ratio of 1 to 1 (Eq. (4)). There are three competing side reactions: methane decomposition (Eq. (5)), the Boudouard reaction (Eq. (6)), and the reverse water-gas shift (Eq. (7)). Both methane decomposition and the Boudouard reaction show the high possibility for coke formation, leading to deactivation of the catalyst.





The primary reaction demonstrates its significantly endothermic characteristics [7]. This indicates a significant requirement for heat and fuel to guarantee the successful execution of this reaction [8]. DRM employs two types of greenhouse gases—carbon dioxide and methane—to produce value-added syngas, demonstrating potential for carbon emission reduction and reuse.

The issue of DRM development lies in the dangers associated with coke production. The selected catalysts significantly influence the rate of their deactivation. Researchers are currently focusing on building catalysts with a reduced likelihood of associated dangers, finding that nickel and nickel-based catalysts have commendable stability and catalytic performance.

2.3. Partial oxidation of methane (POM)

Partial oxidation method can be separated to two different measure—thermal partial oxidation (TPOX) and catalytic partial oxidation (CPOX). The overall reaction equation is Eq. (8).



For thermal partial oxidation, the reaction demands a high temperature for operation, up to 1200°C [9]. This demanded reaction condition demonstrates a great amount of carbon emission. As for catalytic partial oxidation, with the help of catalysts, the reaction temperature is around 700-1000°C, which is much less than that required in TPOX [7]. CPOX shows better sustainability than TPOX in terms of carbon emission. Besides, because of the exothermic nature of reaction, POX doesn't need an extra energy supply but drives itself [9].

In general, the challenge of partial oxidation of methane utilization is the high energy consumption and costs of production, which take up to 50-55% of the final cost of the product [9]. Although utilizing CPOX reduces energy consumption, CPOX has the risks of coke forming and catalyst deactivation [10].

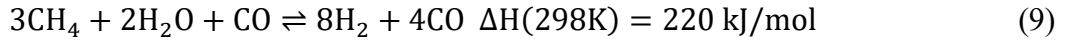
2.4. Autothermal reforming of methane (ARM)

Autothermal reforming of methane is a combination of steam reforming and partial oxidation as element steps. The partial oxidation is exothermic, while the steam reforming is endothermic. As a result, partial oxidation can release energy to drive the steam reforming reaction. They can form a self-sustaining process and contribute to a great reduction of fuel consumption for the whole system. With less consumption of fossil fuel, ARM has a good performance in the carbon emission perspective. Plus, the fundamental steps, partial oxidation and steam reforming, both take methane as the feedstock. Higher consumption of this greenhouse gas helps ARM be considered as a great promising method to reduce the carbon emission content in the production. To have a higher rate of reaction for higher efficiency in practical production, the concentration of oxygen should be increased. Nonetheless, it will decrease relative production of syngas. Alternatively, controlling the supply of heat to boost the reaction rate is crucial.

2.5. Bireforming of methane (BRM)

Bireforming of methane, similar to the ARM, combines dry reforming of methane and steam reforming of methane as two fundamental steps to acquire syngas with various ratios of carbon

monoxide and hydrogen gas. The main reaction is Eq. (9). Side reactions are the water gas shift (Eq. (10)) and reverse water gas shift reaction (Eq. (11)), which occur with the BRM at the same time.



A large variety of sources of carbon emissions could be converted into syngas through BRM. Since the reforming of methane requires a high temperature of about 800-1000°C, it also needs a large amount of fuel to supply heat, suggesting the carbon emission [5]. Apart from that, one of the major problems as a commercialization hindrance of BRM is coke deposition on the catalyst surface because of the decomposition of methane at high temperature. BRM has the advantages of great economic performance at high-pressure conditions. Nevertheless, its use will increase the rate of coke formation [11]. These disadvantages limit the potential of BRM in syngas production for practical applications.

2.6. Gasification

Gasification is one of the syngas production methods, which uses low pressure (1-20 bar) but a very high temperature (over 700°C) to convert various feedstock into combustible gas with the help of oxidant, also known as gasification agent, under a condition of substoichiometry [1, 12]. Gasification is a very complex process and produces not only syngas but also a solid called char, a liquid called tar, and other light gas as well. As Fig. 1 revealed, gasification could be divided into several steps. They are drying, pyrolysis, reduction, and tar decomposition.

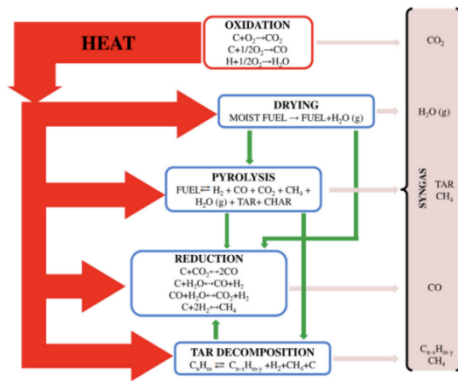


Figure 1: Main stages of gasification process [13]

Gasification can utilize various biomass and organic waste, showing a great ability for sustainability development [12]. Nevertheless, heating, as an important part of this set of reactions, will cost over half of the original raw materials to ensure enough temperature to drive the reaction to go on. Furthermore, since gasification will leave a large amount of char that is required to be burned, it will bring a large cost of energy [14]. Besides, a great emission source of gasification is coming from the treatment of waste char or harmful waste gas, which is usually processed by burning [15].

3. Horizontal comparison among different methods in terms of carbon emissions

Although every syngas production can bring the society a more sustainable way to produce value-added products or new fuel, carbon emission happens during the production. Table 1 shows a summary of carbon emission from different syngas production methods. It organizes data from

different literature. To assess the environmental impact, different papers use a variety of methods and standard. Reports utilize equivalent carbon emissions to quantify the environmental impact of the unit. Various literatures employ distinct calculation boundaries, including direct emissions or the entire life cycle. This paper collects data under uniform settings, categorizing diverse pathways into the same group, so facilitating horizontal comparison of pathways within that group. In each individual literature, the unit is further refined by considering downstream products, such as purified hydrogen or methanol derived from syngas. For the same method, the difference in data from different papers doesn't indicate the distinction in environmental performance. The data for the same pathway that are examined in different papers allow comparison between different groups. Under the same unit, 0.426 kg of equiv CO₂ N-1 m-3 of H₂ is larger than 0.245 kg of equiv CO₂ N-1 m-3 of H₂ and 10 kg / kg H₂ shows a greater emission than 9.8 kg / kg H₂ [16-17]. Steam reforming of methane often results in higher CO₂ emissions compared to the autothermal reforming method. Table 1 indicates that dry reforming exhibits reduced emissions compared to both steam reforming and bi-reforming of methane. Partial oxidation exhibits superior performance compared to dry reforming of methane regarding carbon dioxide emissions. Gasification exhibits significant variability based on the analyzed sample. Various studies indicate that coal samples from diverse locations exhibit varying elemental proportions, which will affect the carbon emissions measured and computed during gasification. Autothermal reformation of methane demonstrates reduced carbon emissions compared to these technologies. It proves to be really promising.

Table 1: Summary of carbon emission of different methods

Pathways	Environment impact	Reference
Steam reforming of methane	0.426 kg of equiv CO ₂ N-1 m-3 of H ₂	[16]
Autothermal reforming of methane	0.245 kg of equiv CO ₂ N-1 m-3 of H ₂	
Gasification of coal	0.100 kg of equiv CO ₂ N-1 m-3 of H ₂	
Dry reforming of methane	0.19 kg CO ₂ per kg syngas	[18]
Partial oxidation of methane	0.58 kg CO ₂ per kg syngas	
Dry reforming of methane	1.3 kg CO ₂ per kg syngas	
Autothermal reforming of methane	0.38 kg CO ₂ per kg syngas	[19]
Dry reforming of methane	5.23 tonne _{CO₂} /tonne _{MeOH}	
Bireforming of methane	1.907 tonne _{CO₂} /tonne _{MeOH}	
Steam reforming of methane	1.909 tonne _{CO₂} /tonne _{MeOH}	[20]
Steam reforming of methane	10 kg / kg H ₂	
Autothermal reforming	9.8 kg / kg H ₂	
Steam reforming of methane	11.518-11.237 kg-CO ₂ -eq/kg-H ₂	[15]
Underground coal gasification	18.258 kg-CO ₂ -eq/kg-H ₂	

4. Conclusion

Syngas is a promising product for sustainable development in various synthesis and fields. Meanwhile, it shows not only the potential to utilize the waste gas into valuable intermediates. However, the main methods of syngas generation still have a problem of carbon emissions along with the syngas production. Based on the analysis of various methods, autothermal reforming has demonstrated a good performance in reducing carbon emissions. This method is promising. Nevertheless, apart from the carbon dioxide emission evaluated in this paper, other environmental impacts, such as the other emissions of waste gas, sulfur oxides, and nitrogen oxides, or the ecotoxicity of waste effluent, also need to be considered to ensure the comprehensive assessment of

the methods in order to find the most eco-friendly generation to improve the sustainable syngas generation. As the consumption of fuel increases, economic analysis is considered prior to the sustainability assessment. It's because the externality of carbon emissions is too difficult to quantify and evaluate the real impact caused by it. Furthermore, real industries don't take the responsibility of pollution. These factors discourage a detailed examination of the carbon footprint. To improve the syngas generation, the analysis should quantify and consider the balance between the positive impact of waste utilized and the negative impact resulting from the production itself to find the most sustainable generation.

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