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Tri-Methane Reforming Process for Conversion of Biogas and CO_2 into Chemicals and Fuels

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Abstract

The world is focused on reducing anthropogenic carbon dioxide (CO_2) emissions due to this being the most abundant greenhouse gas (GHG) arising from human activities. Tri methane reforming (TMR) is a low-carbon intensity CO_2 utilization technology that produces synthesis gas, also called syngas (a mixture of CO and H_2). In this paper, Climate Cure Corporation provides examples of how its tri-reforming process can be used to produce methanol from captured CO_2.

Established gas-to-liquids (GTL) technologies exist to produce methanol from syngas. However, these processes can be very expensive due to the high cost of syngas production. TMR is an innovative technology for the efficient and economical conversion of CO_2 and methane to syngas. TMR has the flexibility to process various feedstocks. Biogas is an especially conducive feedstock for the TMR process since it is a mixture of CO_2 and methane.

Syngas generation processes include steam methane reforming (SMR), dry methane reforming (DMR), partial oxidation (POX), and auto-thermal reforming (ATR), with each having advantages and disadvantages. The TMR technology is a combination of three reforming reactions in one reactor with the goal of combining the benefits of the individual reactions while offsetting their drawbacks. The SMR process is a widely used, proven technology. However, it is highly endothermic and does not consume CO_2. The DMR process consumes CO_2. However, it is also endothermic, susceptible to coke formation, and produces syngas with a low $CO:H_2$ ratio. The POX process is exothermic but also does not consume CO_2.

SMR:	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	$\Delta H^{\circ}_{rxn} = 206$ KJ/mol	(1)
POM:	$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2$	$\Delta H^{\circ}_{rxn} = -38$ KJ/mol	(2)
DMR:	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	$\Delta H^{\circ}_{rxn} = 247$ KJ/mol	(3)

As is shown above, the molar ratio of carbon monoxide (CO) to hydrogen (H_2) can vary significantly based on the reforming reaction. The TMR process is flexible enough to allow a portion of the TMR syngas to be processed through the Water-Gas Shift (WGS) reaction to alter the $CO:H_2$ ratio. The CO_2 produced from the WGS reactor can be recycled back to the TMR reactor feedstock. Make-up methane addition is required to maintain the target CO_2 to methane ratio.

CO Hydrogenation:	$CO + 2H_2 \leftrightarrow CH_3OH$	$\Delta H^{\circ}_{rxn} = -91$ KJ/mol	(4)
WGS:	$CO + H_2O \leftrightarrow CO_2 + H_2$	$\Delta H^{\circ}_{rxn} = -41$ KJ/mol	(5)

Although the TMR process is more efficient than other methane reforming technologies, it is still endothermic. Therefore, it is beneficial to have thermal and stoichiometric integration with downstream syngas processing reactions to take advantage of stoichiometric and energy balance benefits. The process simulation model developed by Climate Cure can be used to evaluate the applicability of TMR for various feedstocks and products.

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1. Overview of Methane Reforming

Significant efforts are being made to capture and sequester CO_2 emissions. In parallel, CO_2 utilization rather than sequestration is the focus of ongoing technological development activities. Often economic viability is a challenge due to high energy input requirements and limited market size for these products. It is essential that utilization technologies have two key features to play a critical role in creating a circular carbon economy. First, the carbon from the CO_2 must displace carbon that would otherwise have been sourced from petroleum. Second, the product must have an existing commercial market, preferably with a size that will be a meaningful outlet for the captured CO_2.

Established GTL technologies exist to produce methanol from syngas and dimethyl ether (DME) from methanol. However, the GTL technologies are very expensive due to the high cost of syngas production. TMR is an innovative technology for the efficient and economical conversion of carbon dioxide and methane to syngas. The carbon dioxide feedstock can be sourced from biogas, direct air capture, or post combustion capture. Using biogas as a feedstock is especially conducive to the TMR process since biogas is a mixture of carbon dioxide and methane, two significant GHGs.

The method of syngas characterization is the stoichiometric number (SN) which is an indication of the hydrogen to carbon ratio:

$$SN = (molesH_2 - molesCO_2) / (molesCO + molesCO_2) \quad (6)$$

SMR is a process where steam is co-fed together with natural gas to a reformer furnace. The main reactions are: 1) conversion of methane and steam to carbon monoxide and hydrogen (Equation 7), and 2) conversion of carbon monoxide and steam to carbon dioxide and hydrogen (Equation 8).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (7)$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (8)$$

In DMR, also known as CO_2 reforming of methane, the main benefit is that CO_2 can be utilized as a feedstock. The main reactions for DMR are: 1) conversion of methane and carbon dioxide to carbon monoxide and water (Equation 9), and 2) conversion of carbon monoxide and water to carbon dioxide and hydrogen (WGS reaction, Equation 10).

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad (9)$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (10)$$

Partial oxidation of methane (POX) is a combustion process with a limited amount of oxygen. This results in incomplete combustion and produces carbon monoxide and hydrogen. The main reactions are: 1) oxidation of methane to carbon monoxide and hydrogen (Equation 11), 2) oxidation of carbon monoxide to carbon dioxide (Equation 12), and 3) oxidation of hydrogen to water (Equation 13).

$$CH_4 + \frac{1}{2} O_2 \leftrightarrow CO + 2H_2 \quad (11)$$
$$CO + \frac{1}{2} O_2 \leftrightarrow CO_2 \quad (12)$$
$$H_2 + \frac{1}{2} O_2 \leftrightarrow H_2O \quad (13)$$

The benefits of each of these processes listed below:

- SMR – technically mature, widely used
- DMR – utilizes carbon dioxide feedstock
- POX - exothermic (no direct heat required)

The drawbacks of each process:

- SMR - highly endothermic, does not utilize carbon dioxide feedstock
- DMR - highly endothermic, coke formation, low SN
- POX - requires pure oxygen, does not utilize carbon dioxide feedstock

2. Tri- Methane Reforming Technology Description

The overall net TMR reaction is dependent upon the feedstock composition. In cases where the CO:H_2 ratio is greater than desired, apportion of the syngas can be processed through a WGS reactor to increase the hydrogen content. The carbon dioxide generated by the WGS reaction will be separated and recycled back to the TMR feedstock. This approach will require the addition of make-up methane into the feedstock to maintain the appropriate carbon dioxide to methane ratio entering the TMR reactor. This flowsheet is shown in Figure 1.

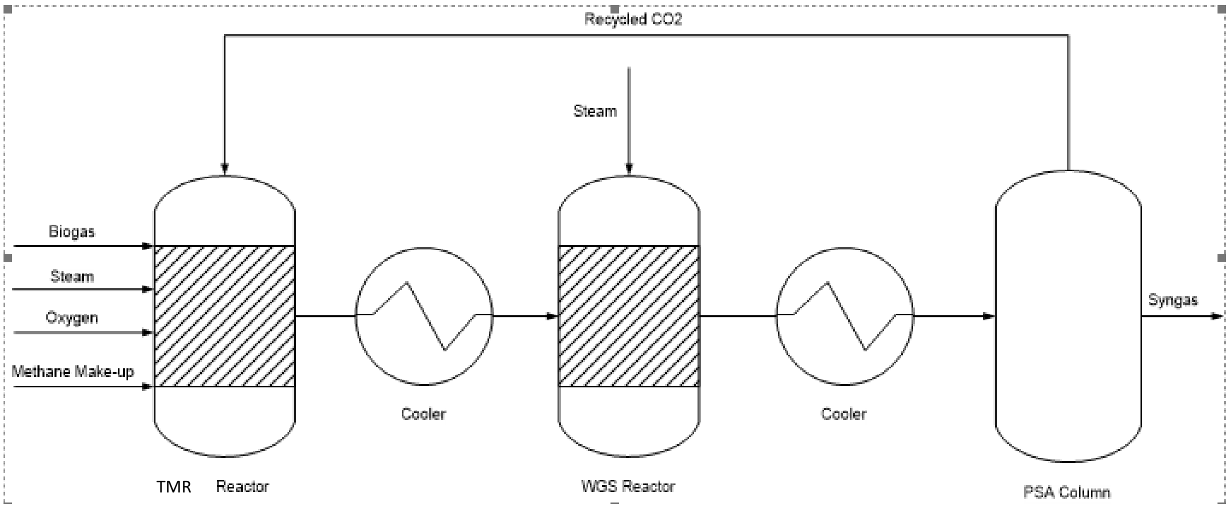

Figure 1. Example Tri-Reforming Flowsheet

Traditional reforming processes are endothermic reactions at high temperatures with a high CO_2 intensity. The novelty and innovative aspect of this project involves the utilization of the TMR process which will utilize a portion of the exothermic energy release resulting from combustion of the natural gas within the reactor to provide the energy required for the endothermic part of the process. The energy demand for the reforming process can be further reduced through the thermal integration of the downstream syngas processes. For example, both the carbon monoxide hydrogenation and carbon dioxide hydrogenation processes for producing methanol are exothermic. Another potential product is DME, which also has an established commercial market. The net overall reaction for production of DME is also exothermic. This holistic approach allows for effective CO_2 utilization.

The TMR process is adaptable to various feedstocks although the examples provided are for biogas feedstock. The first process flowsheet consists of a TMR reactor, a WGS reactor, and a pressure-swing adsorption (PSA) system for separation of carbon dioxide. The feedstock to the TMR reactor is biogas with a methane to carbon dioxide molar ratio of 60:40. Additional inputs to the reactor are oxygen for the POX reaction and steam for the SMR reaction. The intended use of the syngas product is to produce methanol. This requires that the molar ratio of CO:H_2 in the syngas is 1:2. To achieve this ratio, a portion of the TMR reactor outlet gas must be processed through the WGS reactor. This product is then processed through the PSA system and the separated carbon dioxide is recycled to the TMR inlet. Make-up methane is injected with the feedstock to maintain the desired inlet carbon dioxide to methane ratio.

This case was modeled using process simulation software. The results show that approximately 16% of the TMR reactor outlet gas should be processed through the WGS reactor to achieve the target CO:H_2 molar ratio. The mass balance is shown in Table 1 and the corresponding block flow diagram is shown in Figure 2.

	Units	BIOGAS	O2	STEAM (TRM)	STEAM (WGS)	Recycled CO2	Makeup CH4	Syngas Produced
Temperature	C	25.0	25.0	200.0	350.0	200.0	25.0	729.1
Pressure	bar	1	1	1	1	1	1	1
Mass Flow	ton/day	1.000	0.179	1.009	0.203	0.695	0.543	2.935
Mole fraction								
CH4		0.600	0.000	0.000	0.000	0.005	1.000	0.002
CO2		0.400	0.000	0.000	0.000	0.642	0.000	0.052
H2		0.000	0.000	0.000	0.000	0.084	0.000	0.616
CO		0.000	0.000	0.000	0.000	0.018	0.000	0.230
H2O		0.000	0.000	1.000	1.000	0.251	0.000	0.100
O2		0.000	1.000	0.000	0.000	0.000	0.000	0.000
Splitting Ratio	16.5%							

Table 1. Mass Balance Table for Biogas Feedstock with WGS Reactor and CO_2 Recycling

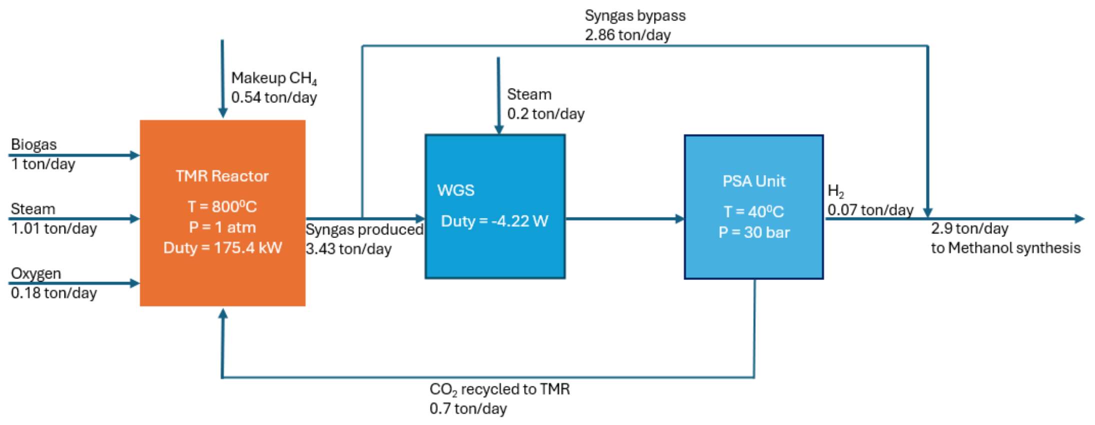

Figure 2. Block Flow Diagram for Biogas Feedstock with WGS Reactor and CO_2 Recycling

3. Summary

The reduction of carbon dioxide emissions is one of the key challenges facing the world due to it being the most abundant greenhouse gas arising from human activities. CO_2 utilization, which is the focus of ongoing technological development activities, faces issues around economic viability due to energy input requirements and limited market size for these products. Tri-methane reforming is an innovative technology for the efficient and economical conversion of carbon dioxide and methane to syngas. Established GTL technologies can then be used to produce methanol from the syngas. This product must have an existing commercial market, and the utilized CO_2 will displace carbon that would otherwise have been sourced from petroleum. The CO_2 feedstock can be sourced from biogas, direct air capture, or post combustion capture. Using biogas as a feedstock is especially conducive to the TMR process since biogas is a mixture of carbon dioxide and methane, two significant greenhouse gases.

TMR technology is a combination of three reforming reactions in one reactor with the goal of combining the benefits of the individual reactions while offsetting their drawbacks. The SMR process is a widely used, proven technology. However, it is highly endothermic and does not consume CO_2. The DMR process consumes CO_2. However, it is also endothermic, susceptible to coke formation, and produces syngas with a low $CO:H_2$ ratio. The POX process is exothermic but also does not consume CO_2.

The molar ratio of carbon monoxide to hydrogen can vary significantly based on the reforming reaction. The TMR process is flexible enough to allow a portion of the TMR syngas to be processed through the WGS reaction to alter the $CO:H_2$ ratio. The CO_2 produced from the WGS reactor can be recycled with the TMR reactor feedstock. Make-up methane addition is required to maintain the target CO_2 to methane ratio in the feedstock.

Although the TMR process is more efficient than other reforming processes, it is still endothermic. Therefore, it is beneficial to have thermal and stoichiometric integration with downstream syngas processing reactions to take advantage of stoichiometric and energy balance benefits. For example, both the carbon monoxide hydrogenation and carbon dioxide hydrogenation processes for producing methanol are exothermic. Another potential product is DME which also has an established commercial market. The net overall reaction for production of DME is also exothermic. This holistic approach allows for effective CO_2 utilization.

It is anticipated that additional applications for TMR technology will be identified as it becomes more well established. The process simulation model developed by Climate Cure can be used to evaluate the applicability of TMR for various feedstocks and products.

Nomenclature

DME	Dimethyl Ether
DMR	Dry Methane Reforming
GHG	Greenhouse Gas
POX	Partial Oxidation of Methane
PSA	Pressure Swing Adsorption
SN	Stoichiometric Number of Syngas
SMR	Steam Methane Reforming
TMR	Tri Methane Reforming
WGS	Water Gas Shift

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