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Biogas partial oxidation in a heat recirculation reactor for syngas production and CO_2 utilization

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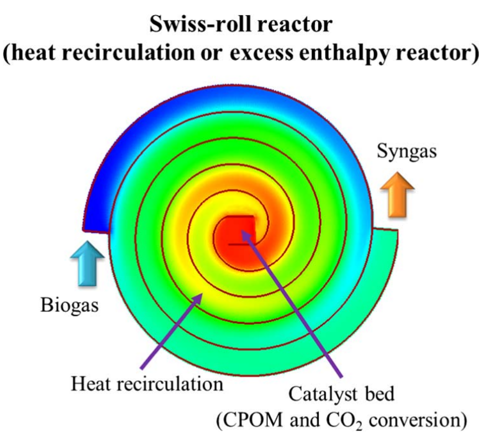
HIGHLIGHTS

- Catalytic partial oxidation of methane (CPOM) in a spiral Swiss-roll reactor is studied.
- Landfill, sewage and farm biogases are taken into consideration.
- The reactor with heat recovery can substantially enhance the CH_4 conversion.
- The maximum CO_2 conversion and syngas yield are 31.12% and 2.80 mol/(mol CH_4), respectively.
- The reactor can efficiently achieve syngas production and CO_2 utilization from biogas.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon dioxide and methane are two most important gases causing global warming; they are also the most crucial constituents in biogas. To efficiently convert the two greenhouse gases from biogas into synthesis gas (or syngas), the catalytic partial oxidation of methane (CPOM) triggered by a rhodium-based (Rh-based) catalyst in a spiral Swiss-roll reactor is studied. Three different biogases, including landfill, sewage, and farm biogases, are taken into consideration and the O_2-to-CH_4 (O_2/CH_4) molar ratio is between 0.6 and 0.7. It suggests that the reactor with heat recovery can substantially enhance the CH_4 conversion when compared with that without heat recirculation, and almost all CH_4 in the three biogases is converted. On account of certain amount of CO_2 contained in the biogases, the role played by dry reforming on CPOM is beyond those played by methane combustion and steam reforming. Within the investigated range of O_2/CH_4 ratio, the maximum CO_2 conversion is 31.12%. The higher the CH_4 concentration and the lower the CO_2 one in a biogas, the better the H_2 and CO selectivity. The highest syngas yield is 2.80 mol/(mol CH_4), accounting for around 93% of theoretical result. Overall, the CH_4 conversion, H_2 yield, and H_2/CO ratio in the product gas are higher than other studies, revealing that the excess enthalpy reactor is a promising device to simultaneously achieve syngas production and CO_2 utilization from biogas in industry.

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Nomenclature

a	starting point
b	distance of curve (cm)
F_i	mole fraction
ΔH^0	change of total enthalpy on standard state ($kJ\,mol^{-1}$)
R_i	reaction rate of species i ($kmol\,m^{-3}\,s^{-1}$)
V	volume (m^3)

Greek letter

θ	radian
π	pi

Subscript

CH_4	methane
CO	carbon monoxide
CO_2	carbon dioxide
DR	dry reforming
H_2O	water
in	inlet
MC	methane combustion
Out	outlet
SR	steam reforming

1. Introduction

Nowadays global warming is an issue that is of considerable concern, ascribing to the significant increase in the emissions of anthropogenic greenhouse gases (GHGs) such as carbon dioxide, methane, nitrous oxide, and fluorinated gases. Currently CO_2 accounts for the biggest share of anthropogenic GHG emissions, mainly generated from fossil fuel combustion [1]. The CH_4 concentration in the atmosphere is much lower than CO_2; nevertheless, its global warming potential (GWP) is around 25 folds (based on 100 years) of that of CO_2 [2]. For this reason, CH_4 also plays a crucial role in deteriorating the atmospheric greenhouse effect. In the atmosphere, part of the anthropogenic CO_2 and CH_4 emissions are due to the formation and release of biogas.

Biogas is the gas evolved from a process termed anaerobic digestion [3]. Anaerobic digestion is a biological process in which organic compounds are degraded into simple substances by microorganisms living in an environment lack of oxygen [3–6]. Accordingly, anaerobic digestion is a useful route for the transformation of waste materials into energy sources through the treatments of various organic wastes in some sites or facilities such as landfills, sewage digesters, and farm biogas plants. Wastes from these facilities are hazardous if they are not managed suitably and treated correctly. The prime and minor components of biogases from the aforementioned facilities are summarized in Table 1 [7–17].

Biogas has been considered as a renewable energy source [18] which is mostly composed of CH_4 and CO_2; other trace gases such as ammonia, hydrogen sulfide, hydrogen, carbon monoxide, oxygen, and nitrogen may also be included [19–21]. Biogas can be burned directly for heat and power generation after it is treated [8]. To refine biogas into gaseous fuel or hydrogen-rich gas, up to now a variety of thermochemical processes such as steam reforming (SR) [22–24], dry (or CO_2) reforming (DR) [25,26], partial oxidation (POX) [27], autothermal reforming (ATR) [28,29], and tri-reforming (TR) [30,31] have been practiced, as shown in Table 2.

In SR, on account of the addition of steam in the feedstock, the chemical reaction has a higher H_2 yield when compared with other reactions [24]. The development of DR is receiving growing attention in recent years in that CO_2 is used as a feedstock for CH_4 reforming, thereby simultaneously reaching the goals of syngas production and CO_2 utilization [32]. Seeing that CO_2 is reduced to CO in DR, it leads to a higher CO yield [33]. Both the SR and DR pertain to endothermic reactions so that additional heat is required to drive syngas production. In POX, CH_4 reacts with insufficient oxygen, normally under the aid of catalysts [34]. Unlike SR and DR, POX of CH_4 inherently belongs to an exothermic reaction. ATR combines both the SR and POX, and CH_4 reforming proceeds under the control of oxygen supply for giving a mildly exothermic reaction [35]. As for TR, it integrates SR, DR, and POX of CH_4 in a reactor [30,31].

Among the aforementioned routes, catalytic partial oxidation of methane (CPOM) is an advanced option inasmuch as it has a number of advantages over the other reactions. CPOM pertains to a slightly exothermic reaction in nature and is expressed as

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2, \quad \Delta H^0 = -36\ kJ\ mol^{-1} \tag{1}$$

This chemical reaction, with the aid of catalysts, can thus proceed fast and be triggered autothermally with high syngas selectivity [36]. The produced syngas is featured by the H_2/CO ratio of approximately 2

Table 1
A list of composition of biogas from different sources.

Source	CH_4 (vol%)	CO_2 (vol%)	N_2 (vol%)	O_2 (vol%)	H_2 (vol%)	H_2S (ppm)	NH_3 (ppm)	Benzene ($mg\,m^{-3}$)	Toluene ($mg\,m^{-3}$)	Siloxane ($mg\,g^{-1}$)	Reference
WWTP	55.1–57.8	28.5–32.5	7.5–12	1.8–2.9	–	104–1852	–	–	–	–	[7]
POME biogas	60–70	30–40	< 1	–	–	10–2000	–	–	–	–	[8]
Sewage plant	55–65	35–45	< 1	–	–	10–40	–	–	–	–	[8]
Landfill biogas	45–55	30–40	5–15	–	–	50–300	–	–	–	–	[8]
Landfill biogas	30–65	25–47	< 1–17	< 1–3	0–3	30–500	0–5	–	–	< 0.3–36	[9]
Landfill biogas	47–57	37–41	< 1–17	< 1	–	36–115	–	0.6–2.3	1.7–5.1	–	[10]
Sewage digester	61–65	36–38	< 2	< 1	–	–	–	0.1–0.3	2.8–11.8	–	[10]
Farm biogas plant	55–58	37–38	< 1–2	< 1	–	32–169	–	0.7–1.3	0.2–0.7	–	[10]
Landfill biogas	59.4–67.9	29.9–38.6	–	–	–	15.1–427.5	–	21.7–35.6	83.3–171.6	–	[11]
Landfill biogas	37–62	24–29	–	< 1	–	–	–	< 0.1–7	10–287	–	[12]
Landfill biogas	55.6	37.14	–	0.99	–	–	–	3.0	55.7	–	[13]
Landfill biogas	44	40.1	13.2	2.6	–	250	–	–	65.9	–	[14]
Sewage digester	57.8	38.6	3.7	0	–	62.9	–	–	–	–	[15]
Sewage digester	62.6	37.4	–	–	–	–	–	–	–	–	[16]
Sewage digester	58	33.9	8.1	0	–	24.1	–	–	–	–	[17]
	30–70	24–50	1–17	0–2.9	0–3	10–2000	0–5	0.1–35.6	0.2–287	0.3–36	

WWTP: waste water treatment plant; POME: palm oil mill effluent