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Removing CH_4 from the Waste Gas of Biogas Upgrading#

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ABSTRACT

A methane (CH_4) slip is normally un-avoided during biogas upgrading, and water scrubbing is the most widely adopted upgrading technology. As CH_4 is also a key greenhouse gas, such a slip can damage the carbon neutrality of bioenergy and result in a positive emission. In order to eliminate the negative influence, a post treatment to handle the released CH_4 is essential. Regenerative thermal oxidation (RTO) is a commercially available air pollution control technology, and it can be used for the post treatment. This paper aims to analyze the technical and environmental performance of RTO for removing CH_4 from the waste gas of biogas upgrading by water scrubbing. A three-dimensional numerical model was developed for the thermal flow-reversal reactor (TFRR). CH_4 content in waste gas is investigated as the key factor, and the energy consumption, the amount of CH_4 elimination and associated CO_2 equivalent avoidance are estimated as key performance. It was found that the higher CH_4 content benefits maintaining the operation of RTO. With the increase of CH_4 content, the energy consumption of CH_4 removal decreases. For example, it decreases from 8.05kWh/kg to 1.22kWh/kg when CH_4% rises from 0.28% to 0.42%. The case study on a real biogas plant that produces 3909ton biogas per year shows that removing CH_4 corresponds to a CO_2 equivalent avoidance of 231.38ton/year.

Keywords: biogas upgrading, methane slip, regenerative thermal oxidation, energy consumption, CH_4 removal

NONMENCLATURE

Abbreviations	
RTO	Regenerative Thermal Oxidation
TFRR	Thermal Flow-Reversal Reactor
GWP	Global Warming Potential
CFD	Computational Fluid Dynamics
UDF	User Defined Functions
Symbols	
D	Length of the inner square channel
δ	Thickness of solid wall
L	Channel length
A_r	The preexponential factor
β_r	The temperature exponent
E_r	Activation energy for the reaction
Q_{reac}	The heat of reaction (energy from the combustion of products)
Q_{supp}	Supplemental thermal energy added to the oxidizer combustion chamber
Q_{loss}	The thermal losses from the system
Q_{gas}	The energy required to maintain adequate chamber temperatures
T_{sp}	Oxidizer chamber setpoint temperature
T_{pg}	Process gas temperature
C_{pm}	The mean heat capacity over the temperature range
M_{pg}	The mass flow rate of the process gas
η_{th}	The thermal efficiency

1. INTRODUCTION

Biogas production is growing and there is an increasing demand for upgraded biogas (biomethane), which can be used as vehicle fuel or injected to the natural gas grid. Water scrubbing is the most widely applied technology of biogas upgrading [1]. However, the methane (CH_4) loss cannot be avoided since some CH_4 are also dissolved into the washing water. Since CH_4 has a global warming potential (GWP) of 27-30 times CO_2 equivalents over a 100-year time horizon [2], even a small amount of emission of CH_4 can damage the carbon neutrality of bioenergy and have negative consequences on climate change. In order to eliminate the negative influence, the post treatment to remove the emitted CH_4 is needed.

Regenerative thermal oxidation (RTO) is a commercially available air pollution control technology. It can oxidize CH_4 into CO_2 and H_2O at high temperature via combustion of CH_4 lean mixtures. For example, it has been applied to reduce the CH_4 emission in a biogas upgrading plant in Denmark using membrane [3]. it was found that the RTO can remove 99.5% of the emitted

CH_4. To further study RTO and optimize its design and operation, numerical simulations are employed. For example, Lan et al. [4] performed the numerical investigation on RTO of lean coal mine CH_4 in a thermal flow-reversal reactor by the finite volume method. It was found that the maximum temperature of the reactor rises significantly with the increases of CH_4 concentration and inlet velocity.

For water scrubbing, the waste gas from biogas upgrading normally consists of 0.2-0.7% of CH_4 [3]. Currently, limited attention has been paid to using RTO to remove CH_4 released from biogas upgrading. Its performance remains unclear. In addition, although RTO can remove CH_4 effectively, there will be N_2O formation, which has an even higher GWP than CH_4. Few studies have investigated the additional influence of N_2O. To bridge the knowledge gap, this paper aims to estimate the performance of RTO on CH_4 removal by simulations. The results will provide insights to biogas upgrading plants regarding the implementation of RTO for CH_4 removal.

2. METHOD

2.1 Physical model

The thermal flow-reversal reactor (TFRR) is the most representative technology of RTO, which uses the ceramic media to transfer the heat released by CH_4 reaction to the feed gas [5]. When the waste gas goes through the honeycomb monolith bed, it is heated until the temperature reaches the ignition of CH_4 for thermal oxidation. The high temperature zone of reaction tends to move towards the end of the bed, which will make the reactor fail to be operational as time goes by. Therefore, the flow of waste gas is periodically reversed to maintain the operation of TFRR.

Honeycomb bed is the key component of TFRR. It contains millions of parallel channels, and the flow and thermal performance of each channel is similar. Therefore, only a single channel is modelled, with the geometry shown in Figure 1. D, δ and L stand for the side length of the inner square channel, the thickness of solid wall, and the channel length, respectively.

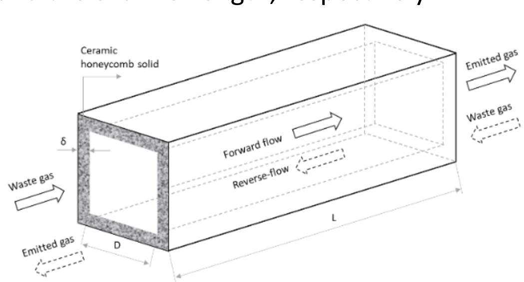

Fig.1 Geometry model of regenerative thermal oxidizer

2.2 Numerical method

A computational fluid dynamics (CFD) model is built for the simulation of TFRR, which is implemented in Ansys Fluent. For simplicity, the following assumptions are introduced in the modelling: (1) radiative heat transfer is neglected. (2) The outside walls of the channel are assumed adiabatic. (3) The gas phase is assumed to be incompressible ideal gas.

One-step methane-air reaction mechanism is employed for the species transport model, as shown in Eqn.1, with the kinetic parameters shown in Eqn.2. The reaction rate depends on both chemical kinetic and eddy-dissipation by considering the turbulence-chemistry interaction.

$$\mathrm{CH_4} + 2\mathrm{O_2} \rightarrow \mathrm{CO_2} + 2\mathrm{H_2O} \tag{1}$$

$$A_r = 2.119e + 11;\ \ \beta_r = 0, E_r = 2.027e + 05 \tag{2}$$

where A_r is the preexponential factor, β_r is the temperature exponent, and E_r is the activation energy for the reaction (J/mol).

The velocity-inlet boundary condition is applied for the inlet and pressure-outlet is applied for the outlet. In order to enable the periodical flow reversal, User Defined Functions (UDF) are used to exchange the boundary condition of inlet and outlet. Coupled thermal boundary condition is used for the interface between the waste gas and solid. The outer wall of the channel is assumed to be adiabatic.

The thermophysical properties of gas mixtures are calculated by mixing-law, with the properties of species obtained by polynomial functions of the local temperature. For the solid of ceramic honeycomb, the specific heat and thermal conductivity of solid are calculated by polynomial function of the local temperature [6].

The PISO scheme is applied to solve pressure-velocity coupling of transient by setting the time step size and number of time steps. PRESTO! scheme is used for pressure and second order upwind is used for solving momentum, species and energy. Before the calculation, UDF is used to initialize the temperature distribution of honeycomb bed, which is the result of the preheat process of honeycomb bed. The preheat process is not simulated in the paper.

2.3 Key performance

2.3.1 Technical performance

The energy balance is calculated as Eqn.3.

$$Q_{reac} + Q_{supp} = Q_{gas} + Q_{loss} \tag{3}$$

where Q_{reac} is the heat of reaction (energy from the combustion of products), Q_{supp} is the supplemental thermal energy added to the oxidizer combustion chamber, Q_{loss} is the thermal losses from the system, and Q_{gas} is the energy required to maintain adequate chamber temperatures, which can be further calculated as Eqn.4.

$$Q_{gas} = M_{pg} \times C_{pm} \times (T_{sp} - T_{pg}) \times (1 - \eta_{th}) \quad (4)$$

where T_{sp} is oxidizer chamber setpoint temperature, T_{pg} is the process gas temperature, C_{pm} is the mean heat capacity over the temperature range and M_{pg} is the mass flow rate of the process gas. η_{th} is the thermal efficiency.

2.3.2 Environmental performance

NO$_x$ formation is also estimated since N_2O has an even higher GWP than CH_4, which is 310 times of CO_2 equivalents. Thermal NO$_x$ and prompted NO$_x$ formation are both considered, with the N_2O intermediate model activated. In order to better study the environmental influence, CO_2 equivalent avoidance is calculated, which considers not only CH_4 elimination, but also extra CO_2 production and N_2O emission. By considering different GWPs of N_2O and CH_4, CO_2 equivalent avoidance is defined and calculated by Eqn.5.

$$CO_2\ equivalents\ avoidance = GWP_{CH4} \times CH_4\ elimination - GWP_{N2O} \times N_2O\ emission - Extra\ CO_2\ production \quad (5)$$

3. RESULTS

3.1 Model validation

In order to validate the model, the experimental results from [7], are used, which operating conditions are listed in Table 1. The waste gas is from coal mine ventilation air. The simulated results are compared with the experimental values, as shown in Fig. 2. In general, the simulated solid temperature profiles are in agreement with the experiments. The maximum deviation on temperature appears in the middle of high temperature zone. It is mainly due to the heat loss in the experiment. Even though the outside wall is insulated, the adiabatic reaction cannot be guaranteed as the temperature is high. Such a heat loss results in lower temperatures.

Tab. 1 The input for model validation [7]

Parameter	Input data	
Geometry size	D	2.5mm
	δ	0.5mm
	L	2m
Waste gas	Velocity	0.93m/s
	CH_4	0.7vol.%
	CO_2	0.3 vol.%
	N_2	78 vol.%
	O_2	21 vol.%
Cycle time	t_c	60s

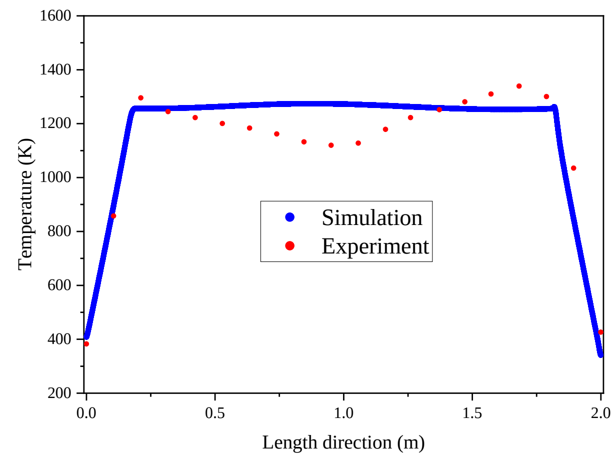

Fig.2 Comparation of temperature profiles of solid bed between simulation and experiment

3.2 Performance of CH_4 removal

To study the performance of RTO for removing CH_4 from waste gas, the same cycle time of 60s, and same initial values of temperature distribution of honeycomb bed are used in the simulation. For water scrubbing, the composition of waste gas depends on the operating conditions. The CH_4 slip is mainly due to the dissolved CH_4 in the water. Table 2 shows the waste gas from commercial upgrading plants by water scrubbing. The content of CH_4 in the waste gas is different since the gas composition from the anaerobic digester also varies, which will influence the performance of RTO.

Tab. 2 Waste gas from commercial upgrading plants [3]

Biogas plant		Waste gas (%)			
		CH_4	CO_2	N_2	O_2
Water scrubbing	1	0.42	15.1	66.32	18.16
	2	0.41	13.1	68.33	18.16
	3	0.65	22.29	60.88	16.18
	4	0.28	14.72	67.07	17.93

Based on the performance of the single channel reactor, a multi-channel reactor can be designed and used to treat the waste gas from biogas plants. A real plan in Sweden is employed as a case study, which produces biogas 3909ton per year. The biogas upgrading process produces waste gas at a rate of 327kg/h. The results are shown in Table 3. It can be seen that the higher CH_4 concentration results in higher released heat from reaction. When the CH_4 content is 0.65%, there is no need for supplemental energy. More supplemental energy is needed for the treatment of lower CH_4 concentration waste gas, which are 6.92MWh/year and 30.45MWh/year when the CH_4 contents are 0.42% and 0.28%, respectively. The corresponding consumption of natural gas are 743m^3/year and 3273m^3/year, respectively when natural gas is used as the supplemental fuel. It was found that the supplemental energy per unit CH_4 removal increases with the decrease of CH_4 content. When the CH_4 contents are 0.42%, 0.41% and 0.28%, the energy consumptions are 1.22kWh/kg, 1.41kWh/kg and 8.05kWh/kg, respectively.

Tab. 3 Simulated results of RTO for different cases

Biogas upgrading plant	Water scrubbing			
CH_4%	0.42	0.41	0.65	0.28
Technical performance				
Released heat from reaction (kW)	9.839	9.704	14.733	6.571
Supplemental energy (MWh/year)	6.92	7.89	0	30.45
Natural gas consumption (m^3/year)	743	848	0	3273
Supplemental energy per unit CH_4 removal (kWh/kg)	1.22	1.41	0	8.05
Environmental performance				
N_2O emission (ppm)	0.0023	0.0024	0.0019	0.0023
NO_2 emission (ppm)	0.4153	0.4221	0.3419	0.4189
NO emission (ppm)	360.248	365.875	319.918	362.801
CH_4 elimination (ton/year)	5.67	5.59	8.49	3.79
Extra CO_2 production (ton/year)	15.55	15.33	23.29	10.38
N_2O emission (ton/year)	8.63E-06	8.99E-06	7.11E-07	8.76E-06
CO_2 equivalent avoidance (ton/year)	154.53	152.41	231.38	103.19

NO_x can be formed in RTO, including NO, N_2O and NO_2. Although the content of NO_2 and N_2O are low, NO removal technology should be employed since high content of NO can be transferred to NO_2, which will cause secondary pollution. Although the negative effect of both N_2O formation and extra CO_2 production are considered, RTO also results in positive CO_2 equivalent avoidance. The CO_2 equivalent avoidance is found to increase when the CH_4 concentration increases, which are 231.38ton/year and 103.19 ton/year when the CH_4 contents are 0.65% and 0.28%.

4. DISCUSSION AND CONCLUSIONS

4.1 Discussion

Since methane-air reaction is simplified to one-step mechanism, it cannot reflect the actual complicated reaction, such as intermediate products and free radicals. It is expected that the performance of the models can be improved by employing two-step methane-air reaction mechanism or even more complicated reaction package (such as chemkin-gri30) [4].

4.2 Conclusions

A three-dimensional numerical model is used to investigate the technical and environment performance to remove CH_4 from waste gas of the biogas upgrading plant by using RTO. Based on the results, the following conclusions were drawn:

- The operation of RTO can be self-maintained in the case of 0.65% CH_4 content.
- Supplemental energy is needed to maintain CH_4 removal, in the other three cases with 0.42%, 0.41%, and 0.28% CH_4 content.
- Demand of supplemental energy decreases with the increase of CH_4 content. It will decrease from 8.05kWh/kg to 1.22kWh/kg when CH_4% rises from 0.28% to 0.42%.
- CO_2 equivalent avoidance increases with the increase of CH_4 content. For a case study with 3909ton/year of biogas production, CO_2 equivalent avoidance is 231.38ton/year.

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