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EFFECT OF H_2S IN RAW BIOGAS ON THE PERFORMANCE OF BIOGAS UPGRADING WITH HIGH PRESSURE WATER SCRUBBING

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ABSTRACT

Using renewable energy sources is an important pathway to meet the global energy demand, and the upgraded biogas has been prioritized. High pressure water scrubbing (HPWS) has been widely used for biogas upgrading, while the effect of H_2S has not been studied well. The work aimed to study how H_2S affects HPWS and to investigate whether and when an independent pre-desulfurization process is required for H_2S removal. In this work, the H_2S content in the raw biogas and the requirement on the upgraded biogas were surveyed, and the performance of HPWS was evaluated with different amounts of H_2S in the raw biogas. The simulation shows that when H_2S in the raw biogas is more than 1000 ppm, HPWS without any adjustment cannot meet the requirement of H_2S removal; the removal of CO_2 and H_2S can be achieved by enhancing the desorption, leading to a slight increase of specific total annual cost, while the option of using hot air combined with a heat exchanger is worse than that of adding more air when the H_2S in the raw biogas is more than 1600 ppm.

Keywords: Biogas upgrading, high pressure water scrubbing, H_2S, Aspen Plus

NONMENCLATURE

Abbreviations	
ACC	Annual capital cost
HPWS	High pressure water scrubbing
O&MC	Operation and maintenance cost
TAC	Total annual cost
Symbols	
i	Economic life of the equipment
n	Interest rate

1. INTRODUCTION

The use of renewable energy sources is an important pathway to meet the global energy demand, and biogas is the largest renewable contributor providing nearly 13% of the total global energy demand [1]. Meanwhile, a great amount of low-grade biomass (manure, crop straw, municipal solid wastes) are produced, and the discharge of these low-grade biomass will directly cause environmental pollution, making it essential to treat low-grade biomass in an efficient way. Anaerobic digestion is one of important options to treat such wastes, and the produced biogas can be used as bio-energy, making biogas production via anaerobic digestion of low-grade biomass being a most important option to achieve biofuel production and sustainable waste management simultaneously.

Depending on the raw material and digestion process, the composition of the produced raw biogas is various. Typically, the raw biogas mainly contains methane (CH_4, 40-70 vol%), carbon dioxide (CO_2, 15-60 vol%), water (H_2O, 5-10 vol%), as well as hydrogen sulfide (H_2S), volatile organic compounds, and other trace component [2]. To use biogas as vehicle fuels or natural-gas grid injection, the raw biogas needs to be upgraded, and the upgraded biogas is called biomethane.

Several technologies have been developed and commercially used for biogas upgrading, such as high pressure water scrubbing (HPWS), membrane separation, chemical absorption, pressure swing adsorption, organic physical scrubbing, and cryogenic separation [3, 4]. Among the developed technologies, HPWS is widely used. HPWS is a reliable technology with low capital and operational costs, and it is also simple and easy to maintain. In particular, for the raw biogases with low H_2S content, no pre-treatment of H_2S is needed for HPWS [5].

Since biogas process plays an important role in waste-treatment and bio-fuel production, a considerable expansion is on-going and will be even more, driven by regulations and incentives as well as a large public interest. The expansion calls for a broad range of wastes, leading to a varying H_2S content that can be up to 3%. HPWS has a certain capacity to remove CO_2 and H_2S simultaneously, but it is unclear how the H_2S content will affect the performance of HPWS, how to adjust the HPWS process to fulfill the increase of H_2S, and whether and when an individual H_2S removal unit is needed. To answer these questions, process simulation is a best option for studying, while to the best of our knowledge, such work has not been conducted. Meanwhile, the performance of HPWS strongly relates to the H_2S content with all possible substrates and the requirements on the biomethane, calling for data survey and summary.

The aim of the work was to study how H_2S affects HPWS and to investigate whether and when an independent process is required for H_2S removal. To achieve this, in this work, the H_2S content in the raw biogas and the requirement on the upgraded biogas were surveyed, the commercialized software Aspen Plus was used as a tool to simulate the process of biogas upgrading with HPWS with different amounts of H_2S in the raw biogas. To improve the treatment capability of H_2S, two new strategies of hot air and hot air with heat exchanger were proposed, studied and compared.

2. METHODOLOGIES

2.1 Process description

A typical process of biogas upgrading with HPWS can be illustrated in Fig 1. It mainly consists of three parts: (1) CO_2 absorption, the biogas is injected into the bottom of the scrubber (Absorber) at the pressure of 8 bar after a process of pressurizing with a multistage-compressor (Mcompr). Meanwhile, water is fed from the top of the column. The gas leaving from the top of the scrubber is around 97% CH_4 that can be dried and used in other applications; (2) flash, the CO_2-enriched water leaving the scrubber (Absorber) is transferred to the flash column (Flash), where the pressure is 3 bar for the purpose of minimizing methane loss. The gas released from the flash column contains CO_2, CH_4, H_2S, N_2, O_2, and water mixed with the raw biogas and recirculated to the multistage-compressor; and (3) solvent regeneration, after the flash column, the water is sent to desorption column (Desorber). It is regenerated by decreasing the pressure to the atmosphere with an aeration of air using a blower that brings N_2 and O_2 into this system at the temperature of 20 °C.

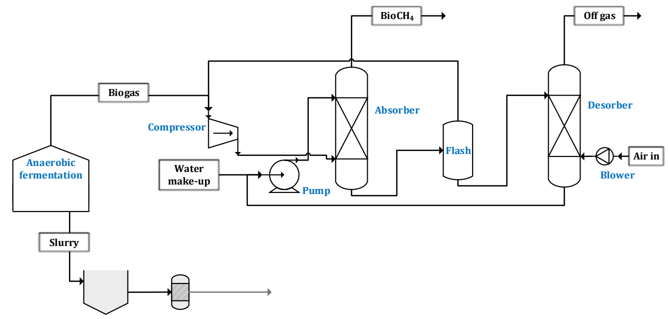

Fig 1 Process scheme of a typical HPWS

To further improve process performance, two new strategies were proposed: to increase the amount of air (scenario 1); to increase the temperature of air and reduce the temperature of circulating water by adding a heat exchanger between the blower and pump (scenario 2) as shown in Fig 2. The overall structure and composition are basically the same as the previous process. The difference was that hot air ranged from 20 to 80 °C was used to enhance desorption. Considering that high temperature of air may lead to hot recirculated water which is not favorable to absorption, a cooling system was added, and the solvent temperature was reduced to 20 °C after the heat exchanger (in scenario 2).

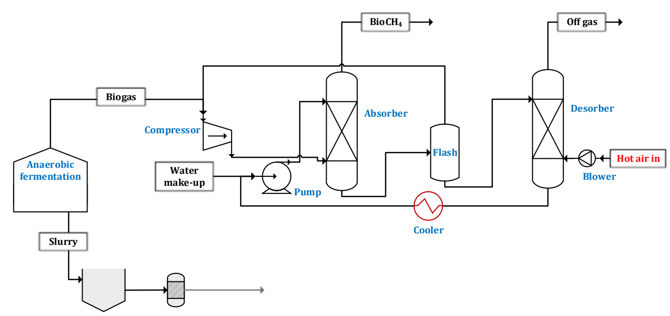

Fig 2 HPWS integrated with hot air and cooling system

2.2 Process simulation

In simulation, the absorber and desorber were modeled with the Radfrac model without condenser and reboiler. The models with the parameters for describing properties, phase equilibrium and kinetics were taken from Aspen Plus, and the reliability has been verified in our previous work[6-8]. The process operating parameters were set to be those summarized in Table 1, while the H_2S content was set to be in a range of 0 to 5000 ppm, and the remaining component was CO_2.

Table 1. The operational parameters for the biogas upgrading process

Parameters	Value
Raw biogas/$Nm^3 \cdot h^{-1}$	1250
CH_4 content in biogas/%	60
Absorption pressure/bar	8
Desorption pressure/bar	1
Flash tank pressure/bar	3
Raw biogas temperature/°C	55
Compressed biogas temperature/°C	20
Liquid temperature/ °C	20
Temperature of air/ °C	20
Packing materials plastic pull ring(mm)	38

2.3 Cost estimation

The cost was estimated based on the method describe in our previous work [4], and only a brief summary was provided in this section. The total annual cost (TAC) is a summation of the annual capital cost (ACC) and the operation and maintenance cost (O&MC). The annual capital cost (ACC) was converted from the total capital cost (TCC) according to Eq. (1)

$$\mathrm{ACC} = \mathrm{TCC} \cdot \frac{i(1+i)^n}{(1+i)^n - 1} \qquad (1)$$

where n and i were assumed to be 15 and 0.09, which correspond to the economic life of the equipment and the interest rate, respectively.

The total capital cost (TCC) was calculated based on the percentage of equipment cost as summarized in our previous work [9]. The operation and maintenance cost (O&MC) consists of maintenance cost, operating supplies cost, research and development cost, utility costs (i.e. electricity, steam and cooling water), and absorbent replacement cost, and each term was estimated based on the method of Scholz et al. [10] and Huang et al. [11].

In the cost estimation, an annual operation of 8600 h was used when calculating the operating cost. The price of water was assumed to be 0.5 \$/t, and the electricity price was set to be 0.10 \$/kWh [9], corresponding to the results of the actual plant.

3. RESULT AND DISCUSSION

3.1 Survey of H_2S content and biomethane standards

Currently, the materials that can be used for biogas process mainly include sewage from waste-water treatment, waste from farmers (manure) and agriculture, etc. The materials that can produce H_2S are listed in Table 2. In general, the H_2S of the sewage in slaughterhouse is higher than others which can achieve 30000 ppm. The minimum H_2S content is 100 ppm for the municipal sewage. But for most of the fermentation materials, the H_2S contents are below 5000 ppm. This is why we chosen the H_2S content being in a range of 0 to 5000 ppm for study in this work.

Table 2. H_2S in different biogas produced by different fermentation materials

Raw material	H_2S in biogas (ppm)
Cow dung	1500-2500
Pig manure	2500-3500
Chicken manure	>3500
Sewage in slaughterhouse	2000-30000
Municipal sewage	100-500
Biodegradable waste	500-5000
Silage corn	500-1000

The standards of sulplur in biomethane vary with country as listed in the Table 3. In addition, France has two levels of requirements for the upgraded biogas with different restrictions applied for the injection of low and high quality gases [12, 13]. As we can see from Table 3, the methane content requires a great increase from 40-70 to 80 -99 vol%, the carbon dioxide content needs to be less than 2 - 6%, and the total sulplur content should be no more than 100 mg/Nm^3. It is worth noting that a standard of 15 mg/Nm^3 (about 9.8 ppm) was set in China as listed separately [13]. Thus, the H_2S content of less than 9.8 ppm in the production was set in this work.

Table 3. Standard of sulplur in biomethane in different countries.

Country	Sulplur (mg/Nm^3)
China	≤ 100
France	< 100[a]
	< 75[b]
Germany	< 30
Sweden	< 23
Switzerland	< 30
Austria	≤ 5
The Netherlands	< 45

[a]Maximum permitted [b]Average content

3.2 Effect of H_2S on HPWS

Currently, the materials used for biogas process mainly include the sewage from waste-water treatment, and the operational parameters for the current biogas upgrading process are listed in Table 1. Based on this information, the effect of H_2S contends in the raw biogas on the current process was simulated with Aspen plus.

The simulation result shows that when H_2S in the raw biogas is more than 1000 ppm, the current process without any modification cannot meet the requirement of H_2S removal any more.

The performance of the current process may be further enhanced by adjusting the operation of desorption. To verify this, firstly, the amount of air for desorption was increased to fulfill the requirement of biomethane with H_2S less than 9.8 ppm (Scenario 1). The simulation results are summarized in Fig 3. It shows that the simultaneously removal of CO_2 and H_2S can be achieved without a pre-desulfurization when the H_2S content is up to 5000 ppm. The specific TAC will increase with a biggest value of 9.4%.

To check the possibility for further improvement, Scenario 2 was studied, where the air temperature was set to be 20 to 80 °C. The process performance was compared with that in scenario 1 as illustrated in Fig. 3. When the H_2S content is low, the performance of scenario 2 is better but it changes to be worse when the H_2S content is more than 1600 ppm. When the H_2S in raw biogas is 5000 ppm, the specific TAC of scenario 2 is 2.8% higher than that of scenario 1.

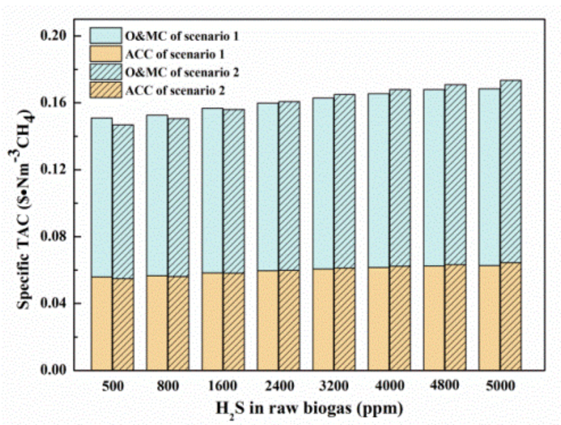

Fig 3. Specific TAC with different H2S content.

4. CONCLUSION

In this work, the survey shows that the H_2S content can be up to 30000 ppm but most probably less than 5000 ppm; the H_2S standards strongly depends on countries, and 9.8 ppm is a most rigorous level. The studies of the H_2S effect on the performance of HPWS conducted by process simulation reveals that, by adjusting the amount of air, it is possible to remove both CO_2 and H_2S simultaneously without a pre-desulfurization process when H_2S in raw biogas is up to 5000 ppm, and, in general, the HWPS integrated with hot air and cooling system cannot work better compared to the HWPS with high amount of air.

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