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SIMULTANEOUS REMOVAL PROCESS OF HYDROGEN SULFIDE AND SILOXANES AND FIELD APPLICATION OF IRON HYDROXIDE DESULFURIZATION AGENT FOR GREEN HYDROGEN PRODUCTION FROM BIOGAS

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ABSTRACT
Biogas, one of renewable energies, is a key element necessary for a carbon-neutral policy and to build a hydrogen economy. In order to utilize biogas, impurities of biogas such as moisture, hydrogen sulfide (H_2S), siloxanes, and VOCs should be removed. In particular, since H_2S causes corrosiveness of equipment by sulfur oxides, and is very harmful to the human body if leaked, it is a major target material to be removed. The minimum concentration of H_2S obtainable from the wet method is several ppm. It is known, however that the iron hydroxide-based adsorbent in the dry method can obtain ultimately low concentration of H_2S down to 0.1 ppm or less. The DeHyS was manufactured through a series of processes such as mixing iron cloride solution or iron sulfate solution, NaOH solution, and inorganic binder. During the adsorption process, H_2S was removed in the form of iron sulfide through a chemical reaction, and siloxanes are known to be removed through physical adsorption. It was also applied to various biogas plant sites such as landfill gas, sewage sludge, livestock manure, and food waste. At this time, the H_2S removal efficiency was known to be 99.9% or more, while simultaneous removal of 90% or more of the total siloxanes was possible. Moreover, the biogas produced at the Chungju Food Bioenergy Center was pretreated using the DeHyS and supplied to the nearby Chungju Bio Green Hydrogen Charging Station to produce hydrogen through steam methane reforming (SMR), producing 500 kg of hydrogen from 8,000 m^3 of biogas per day.

1. INTRODUCTION

According to the Intergovernmental Panel on Climate Change [IPCC] special report (IPCC, 2018), the average global temperature in 2017 has risen by about 1°C compared to the pre-industrial period (1850-1900) due to human activities based on fossil fuels, and global warming is increasing at the current rate. If it continues, it is predicted that the global temperature rise will exceed 1.5°C between 2030 and 2052, and exceed 3°C by 2100. In order to limit the increase in global temperature to less than 1.5°C by 2100, it is recommended that the reduction of CO_2 of at least 45% compared to 2010 by 2030 as well as the achievement of zero net CO_2 emission by 2050 be necessary.

In December 2015, the Paris Agreement, a common norm of the international community, was adopted at the 21st COP21 of the UN Framework Convention on Climate Change [UNFCCC] to reduce greenhouse gas emissions (UNFCCC 2015). Republic of Korea declared carbon neutrality in October 2020 to participate in the efforts of the international community. Republic of Korea in December 2020, also promoted low-carbon in all areas of the economic structure and a low-carbon industrial ecosystem, and the ‘2050 Carbon Neutral Promotion Strategy’ was announced, focusing on strengthening neutral infrastructure, etc (Ministry of Environment in the Republic of Korea, 2020). In addition, 10 core technology areas for carbon-neutral technological innovation were selected through consultation with experts and related ministries. It is therefore expected that the energy market will grow rapidly as changes in the energy ecosystem.

In particular, hydrogen can be used for large-capacity energy storage, long-distance transport and a mobility and distributed power source as needed. However, at present, about 99% of domestic hydrogen production is gray hydro-

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gen produced through steam methane reforming(SMR) from natural gas. On the other hand, eco-friendly hydrogen produced by the electrolysis of water called as green hydrogen and waste resources are hardly commercialized (The Government of the Republic of Korea, 2019). Therefore, in order to realize carbon neutrality, it is important to increase the proportion of blue hydrogen that captures carbon dioxide from fossil fuel such as natural gas and green hydrogen produced from steam reforming of methane from renewable energy resource such as biogas.

Biogas is produced by anaerobic microorganisms from organic waste such as food waste, livestock manure, and sewage sludge, which is usually composed of CH_4 50-65%, CO_2 30-40%, H_2S less than 1%, and others. Methane in biogas is then converted to hydrogen through steam reforming reaction. It is known as a carbon-neutral renewable energy source that must be actively used because it is essential through human life.

As of 2021, there were a total of 110 domestic biogas facilities with an annual biogas production of 360 million Nm3 (0.05 GW). Although only 6.9% of the current market potential is being converted into energy, it is known that the existing feed and composting facilities can be converted to biogas plants of new construction/extension and can be expanded up to 14.4 times higher than the current biogas production (Ministry of Environment of the Republic of Korea, 2022).

In order to utilize biogas, impurities of biogas such as moisture, hydrogen sulfide, siloxanes, and VOCs should be removed. Since hydrogen sulfide causes corrosiveness of equipment by sulfur oxides, and is very harmful to the human body if leaked, it is a major target material to be removed. H_2S removal in biogas can be achieved either by wet or dry method. In the wet method, chemical cleaning and iron chelate cleaning are used, while in the dry method, various adsorbent systems such as iron oxide-based adsorbents, magnesium-based adsorbents, activated carbon, and iron hydroxide-based adsorbents can be used . The minimum concentration of hydrogen sulfide obtainable from the wet method is several ppm. It is known, however that the iron hydroxide-based adsorbent in the dry method can obtain ultimately low concentration of H_2S down to 0.1 ppm or less (Magnone, E., Kim, S. D., & Park, J. H., 2018).

In particular, since the proton exchange membrane fuel cell (PEMFC) operates at a relatively low temperature compared to other fuel cells, impurities such as CO and H_2S are easily adsorbed to the catalyst, which may cause poisoning and thus deactivation of catalyst. The US Department of Energy recommends that hydrogen used as fuel be included in the amount of CO and H_2S well below 50 ppm and 1 ppm, respectively to reduce performance degradation caused by fuel cell poisoning (Solutions, 2000). More recently, international organization for standardization(ISO) set the CO concentration limit for the conventional Pt anode as 0.2 ppm (Li et al., 2021; St-Pierre, 2010). Consequently, hydrogen production from biogas requires more stringent pretreatment. In Republic of Korea, the acceptable limit of H_2S from biogas in various application fields is classified, based on the concentration of H_2S and sulfur(S) as follows (Figure 1). Gas engine power generation requires less than 150 ppm as the most tolerant application field for hydrogen sulfide concentration, followed by city gas with less than 30 ppm on sulfur content, compressed transport gas less than 10 ppm on sulfur basis, and gas conditions for hydrogen production is known to be 0.01 ppm or less based on hydrogen sulfide.

Through this case study, we would like to investigate the gas conditions for hydrogen production from biogas, and introduce the principle and field application results of H_2S and siloxanes removal of iron hydroxide-based desulfurization agents. In addition, we will discuss the expansion of the scope of biogas utilization while introducing representative domestic sites that produce hydrogen from biogas and use it as a fuel for hydrogen vehicles.

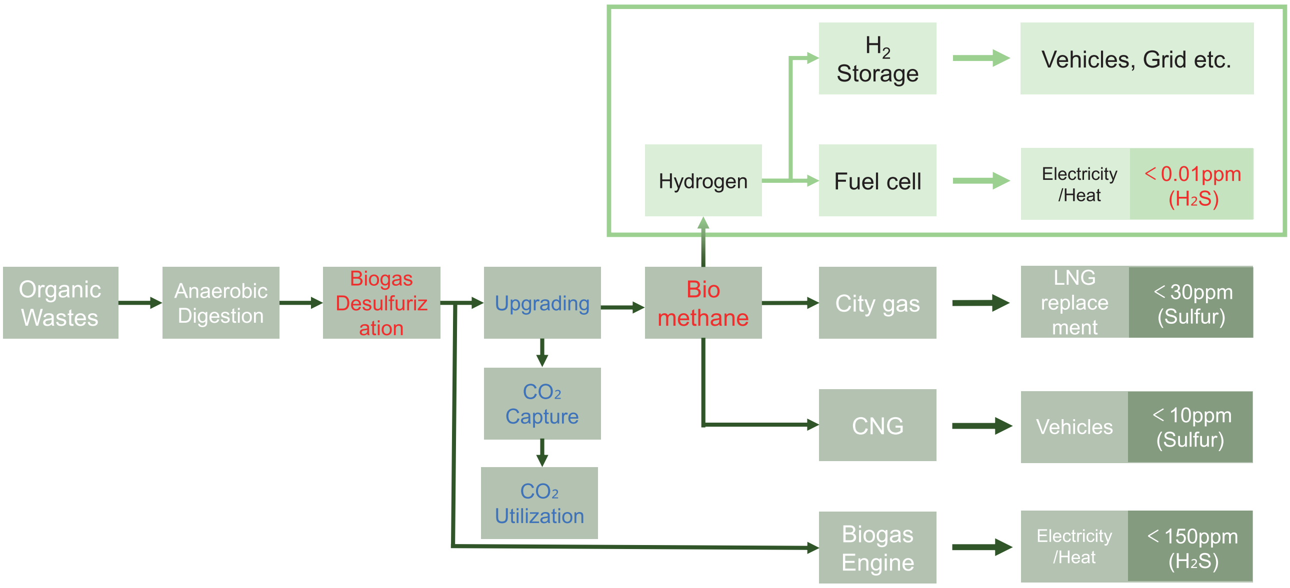

FIGURE 1: The acceptable limit of H_2S and sulfur from biogas in various application fields.

2. EXPERIMENTAL

2.1 Materials

The adsorbent used for the removal of H_2S and siloxane was porous and amorphous iron hydroxide-based commercial product, DeHyS (E&Chem Solution CO.). The DeHyS was identified using the X-ray diffraction analysis (XRD, Model D/Max 2200, Rigaku) with CuKα radiation source. 40 kV and 30 mA were adopted at 5° min^{-1} and 0.08° angular resolution based on 2θ scan. DeHyS was manufactured by several steps; that is, appropriate ammounts of NaOH solution and inorganic binder (Magnone et al., 2018) were vigorously mixed under agitation to which iron chloride or iron sulfate solution was added, followed by additional 1 hr of agitation. Upon completion of agitation, the iron hydroxide-based precipitate was filtered using vacuum pump, followed by sufficient washing using distilled water. The precipitate so obtained was dried at 150°C until water content was reduced to less than 30% and cylindrical shape of pellet with diameter of 3 to 10 mm was then fabricated. The physical properties of DeHyS are summarized in Table 1 (Ryu et al. 2017).

2.2 Adsorption process

2.2.1 Removal of hydrogen sulfide

Different volume of adsorbent was loaded into the adsorption tower to which feed gas containing different concentrations of H_2S and space velocities with field site as shown in Table 2 and Figure 2 was fed at ambient temperature. The packing density of adsorbent (DeHyS) in adsorption tower is 0.5~0.7 g/mL. The effluent gas passing through the adsorption tower was collected at the outlet of the tower and the residual concentration of H_2S was identified by GC using pulsed flame photometric detector (GC/PFPD, Varia 450).

2.2.2 Removal of siloxane

Siloxane was simultaneously removed with H_2S as described in previous section. In order to identify the removal efficiency of siloxane, its concentrations at the inflow and outflow of the desulfurization tower at Yeoyang Farm, Tancheon Water Treatment Center, and the Sudokwon Landfill Site were measured as follows. Total 12 L of sample was collected in a methanol absorption solution (10mL) at a flow rate of 100 mL/min for total 120 minutes, and the concentration of siloxane was then identified by GC/MS (Shimadzu, GC-2010/QP-2010).

3. RESULTS AND DISCUSSION

3.1 Results of field application for purifying biogas

The XRD pattern of DeHyS is shown in Figure 3. As can be seen in this figure, it does not show any sharp peak indicating that DeHyS is amorphous phase.

TABLE 1: Specification of Iron hydroxide-based desulfurization agent (DeHyS).

Content	Range	Standard Method
Dimensions (diameter)	3~10 mm	KS B ISO13385-1
Fe $(OH)_3$ content	> 50 % (as Fe_2O_3)	KS L ISO 26845
Loss on drying	< 20 %	KS M 0009
Specific surface area	> 250 m^2/g	KS A 0094
Pore volume	0.25 cm^3/g	
Average pore size	36 Å	
Adsorption capacity	0.25 g/g	
Packing density	0.5~0.7 g/mL	

The DeHyS was applied to the desulfurization tower of the dry process, and the dry process comprises three steps: dehumidification process, desulfurization process, and dust removal process. It was applied to various fields such as food-derived biogas facilities, sewage sludge digester facilities, livestock manure biogas facilities, and landfill gas facilities at landfills in the Sudokwon (Table 2). The H_2S concentration in biogas feed stream was varied from about 77.60 ppm to 4,450ppm depending on the site, but the that in deplete biogas stream passing through adsorption tower was measured to be 0.01ppm or less (based on KTL official test report). It showed that the required H_2S concentration in the field was highly satisfied, resulting in the H_2S removal efficiency up to 99.9% or more as shown in Table 2.

In Yeoyang Farm, it seems that almost no siloxanes were detected in case of biogas derived from livestock

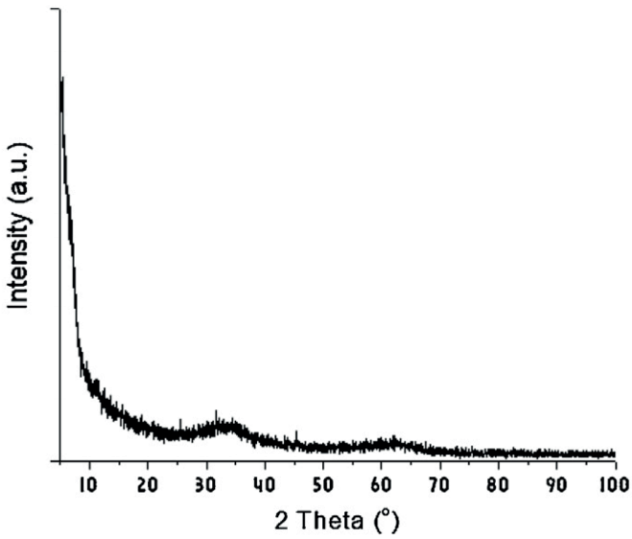

FIGURE 3: XRD pattern of DeHyS.

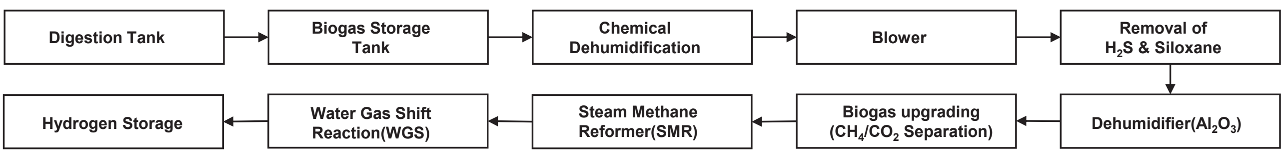

FIGURE 2: Schematic diagram of overall process for H_2 production through the removal of H_2S and siloxane using DeHyS.

TABLE 2: H_2S removal efficiency of DeHyS in various fields.

Application site	Volume (m^3/d)	H_2S requirement (ppm)	H_2S removal Efficiency (%)	Adsorbent loaded (m^3)	Space velocity (hr^{-1})	Applications
Tancheon Water Regeneration Center	40,000	10	99.99 (In: 902.50ppm, Out: 0.00ppm)	24	70	Gas engine power generation, Burner fuel
2nd stage sludge fuel conversion facility in Sudokwon Landfill Site	86,400	10	99.98 (In: 88.80ppm, Out: 0.00ppm)	25	144	Burner fuel
3rd stage sludge fuel conversion facility in the Sudokwon landfill site	187,200	10	99.98 (In: 77.60ppm, Out: 0.00ppm)	40	195	Burner fuel
Chilsung Energy Agricultural Corporation Cheongyang Plant	12,000	10	99.99 (In: 389ppm, Out: 0.00ppm)	5	100	Gas engine power generation
Yeoyang Farm	3,600	30	99.96 (In: 4,450ppm, Out: 1.4ppm)	3	50	Gas engine power generation
Hongcheon Eco-friendly Energy Town	3,600	5	99.99 (In: 805ppm, Out: 0.00ppm)	8	19	City gas production
Chungju Food Bio Energy Center	8,000	5	99.99 (In: 950ppm, Out: 0.01ppm)	5	67	Hydrogen production
IksanSewage Treatment Plant Food Biogasification Facility	13,000	20	99.99 (In: 800ppm, Out: 0.01ppm)	5	108	Transfer of drying facilities
Changwon Food biogas facility	12,700	30	99.99 (In: 500ppm, Out: 0.01ppm)	20	26.5	Gas engine power generation

manure. On the other hand, at the Tancheon Water Treatment Center, an inflow concentration of 129.98 ppb based on total siloxanes was detected for the biogas derived from sewage sludge, and the removal efficiency was 99.45% with an outflow concentration of 0.71 ppb. In addition, the inflow concentration of 32.94 ppb based on total siloxanes was detected for the biogas derived from landfill gas in the Sudokwon landfill site, and the removal efficiency was 91.77% with an outflow concentration of 2.71 ppb (Table 3).

Based on the removal efficiency of H_2S and siloxane obtained from the adsorption process using DeHyS as an adsorbent, it is concluded that during the adsorption process at ambient temperature, H_2S should have been removed in the form of iron sulfide through a chemical reaction, while siloxanes are trapped in the pores through physical adsorption as shown in Figure 4 due to the well-defined pore characteristics of meso- and macro-pores (Magnone, E., Kim, S. D., Kim, G. S., Lee, K. H., & Park, J. H., 2020).

3.2 Results of field application for producing hydrogen

A representative site for producing hydrogen from domestic biogas is the Chungju Bio Green Hydrogen Charging Station located at 649-8 Bongbang-dong, Chungju-si, Chungcheongbuk-do. Approximately 8,000 m^3 of biogas per day in the anaerobic digester of the Chungju Bioenergy Center is produced from 80 tons/day of food waste generated in the Chungju area. In order to produce hydrogen from biogas, it is important to purify biogas before the reforming process. The DeHyS desulfurization agent and dry process system were applied to this facility.

At the beginning of the project, biogas was purified to upgrade to biomethane that can be supplied as fuel for city gas pipelines and vehicles. In May 2019, a hydrogen production process using biogas was introduced as the first model for the hydrogen economy by the Chungju Bio Hydrogen Charging Station Project (Figure 5).

The facility started commercial operation in March 2022, and currently produces about 500 kg of green hydrogen per day by biomethane reforming, and distributes it to nearby areas or sells it on site. This facility is equipped with fuel reforming system, hydrogen compression system, and hydrogen charging system that can accommodate all of the 700 bar hydrogen vehicle charging and 450 bar / 200 bar tube trailer charging (Figure 6).

The Chungju Bio Green Hydrogen Charging Station, which enables entire processes including waste treatment and hydrogen production through a series of processes, has demonstrated an innovative model that combines the role of both an on-site hydrogen refueling station and a mother station. Currently, It produces hydrogen directly from biogas, which is cheaper than natural gas. The cost of raw materials and distribution can be reduced, and hydrogen is being supplied at 7,700 won (about 5.7 US $),which is 9.1% lower than the national average unit price of hydrogen charging stations (as of August 30, 22) of 8,377 won (about 6.2 US $) per kg. Moreover, DeHyS as desulfuriza-

TABLE 3: Siloxane removal efficiency of DeHyS in various fields.

Item	Yeoyang			Tancheon			Sudokwon		
	In (ppb)	Out (ppb)	Remo-val. (%)	In (ppb)	Out (ppb)	Remo-val. (%)	In (ppb)	Out (ppb)	Remo-val. (%)
L2	ND	ND	-	ND	ND	-	2.87	2.46	14.28
L3	ND	ND	-	0.08	ND	-	ND	0.06	-
L4	ND	ND	-	0.40	ND	-	0.10	ND	-
L5	ND	ND	-	0.10	ND	-	ND	ND	-
D4	0.05	0.02	60	3.78	0.06	98.41	20.37	0.06	99.70
D5	0.07	0.02	71.42	123.92	0.56	99.54	9.47	0.05	99.47
D6	0.03	0.02	33.33	1.65	0.08	95.15	0.13	0.08	38.46
Total siloxanes	0.15	0.06	60	129.98	0.71	99.45	32.94	2.71	91.77

ND: Not detected(< 0.01 ppb)

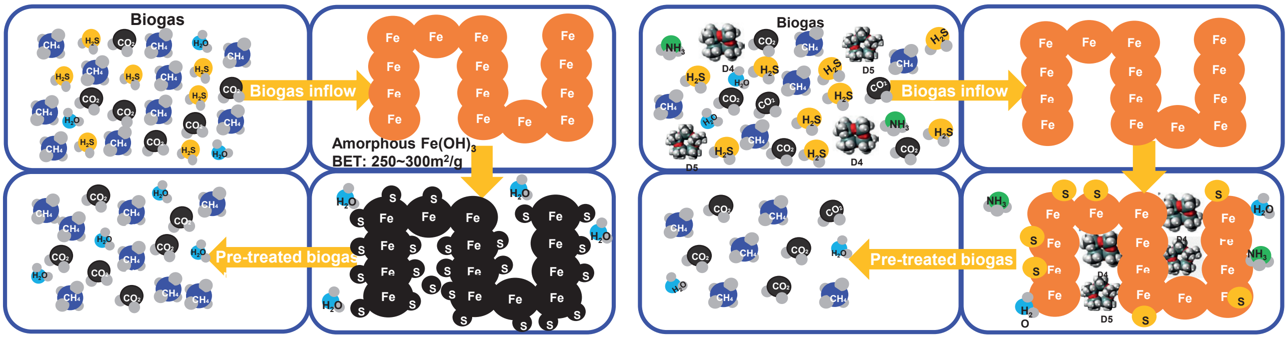

FIGURE 4: Schematic diagram of H_2S and siloxane removal from biogas by meso/macro-porous adsorbent, DeHyS.

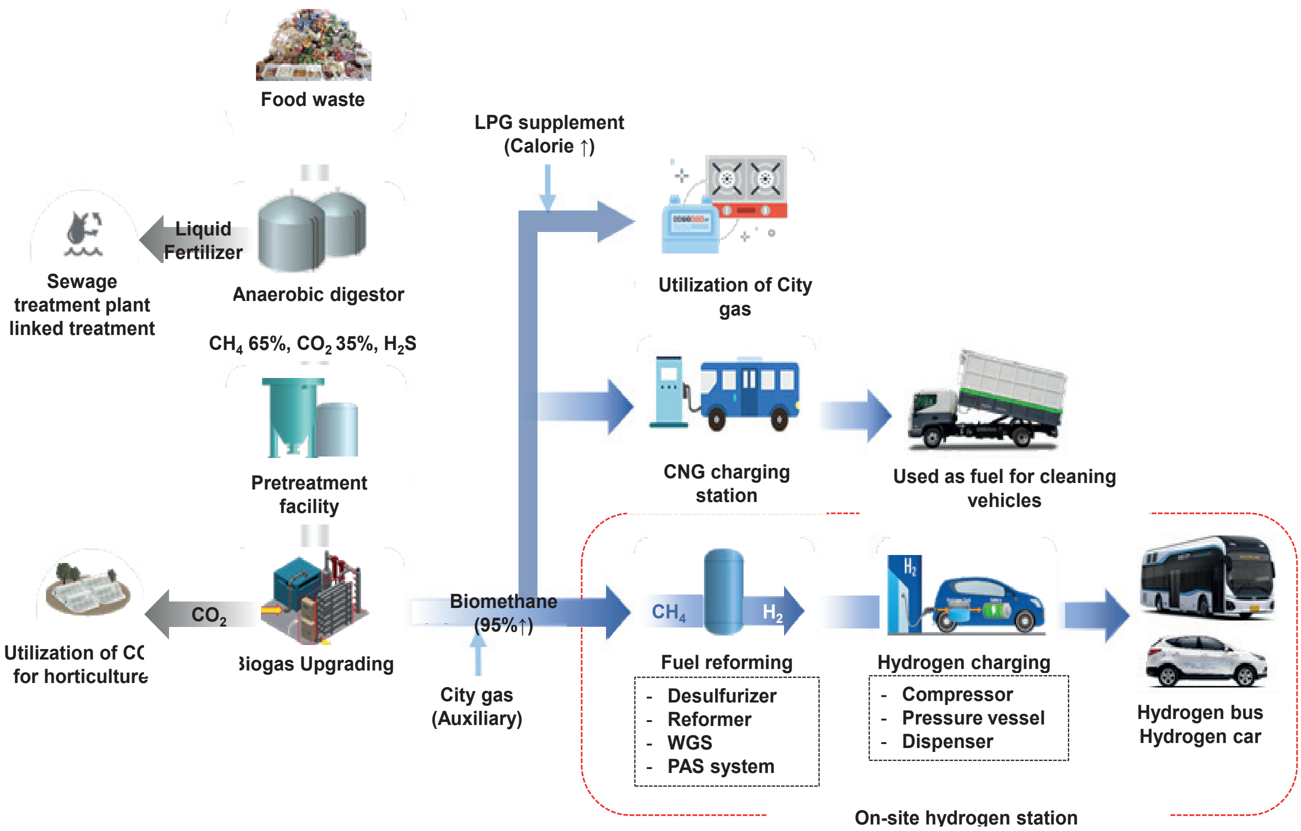

FIGURE 5: Schematic diagram of hydrogen production from biogas in Chungju.

FIGURE 6: The panorama of Chungju Bio Green Hydrogen Charging Station.

tion agent with extremely high removal efficiency for H_2S and siloxanes is also highly propective in economic point of view due to its competitive price (e.g. 3.74 US $/L).

4. CONCLUSIONS

Biogas, one of renewable energy, is a key element necessary for a carbon-neutral policy and to build a hydrogen economy. In order to utilize biogas, impurity such as H_2S must be removed firstly. The application of biogas varies depending on the concentration of H_2S.

In the Republic of Korea, the acceptable limit of H_2S in biogas is classified, based on the concentrations of H_2S and sulfur. In particular, it is known that the H_2S standard is 0.01 ppm or less to prevent catalyst poisoning of the hydrogen reformer during the production of hydrogen from biogas.

The DeHyS is a desulfurization agent capable of reducing H_2S from biogas to a concentration of 0.01 ppm or less, and it can also remove siloxanes simultaneously. Unlike conventional adsorbents using organic binder that require high temperature treatment to eliminate organic matter, the manufacturing process for DeHyS is very simple and highly economic due to simple drying process at mild condition. Furthermore, the H_2S removal efficiency was known to be 99.9% or more, and it was known that simultaneous removal of 90% or more of the total siloxanes was possible. Therefore, it has shown to be higly effective for the stability of downstream equipment. It has already been applied to many sites for anaerobic digestion of various raw materials such as food waste, livestock manure, and sewage sludge.

In particular, it showed that the Chungju Bioenergy Center can produce 500 kg of green hydrogen per day through pretreatment and hydrogen reforming process of biogas produced from anaerobic digestion by merging about 60 tons of food waste and livestock manure per day. Currently, it is being supplied at a price more than 9.1% cheaper than hydrogen produced from natural gas.

As the expansion of the construction of hydrogen infrastructure in the future would increase the demand for green hydrogen produced from biogas, DeHyS with removal efficiency for H_2S and siloxanes would be highly prospective in the economic point of view due to its competitive price.

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REFERENCES

IPCC. Special Report on Global Warming of 1.5°C. 2018. Retrieved from https://www.c40knowledgehub.org/s/article/IPCC-Special-Report-on-Global-Warming-of-1-5-C?language=en_US&gclid=EAIaIQobChMIr7uxh9L1-QIV2MFMAh1oTQJAEAAYAiAAEgKyhfD_BwE#RelatedKnowledge

Magnone, E., Kim, S. D., & Park, J. H. (2018). A systematic study of the iron hydroxide-based adsorbent for removal of hydrogen sulphide from biogas. Microporous and Mesoporous Materials, 270, 155–160. https://doi.org/10.1016/j.micromeso.2018.05.018

Magnone, E., Kim, S. D., Kim, G. S., Lee, K. H., & Park, J. H. (2020). Desiloxanation process of biogas using an amorphous iron hydroxide-based adsorbent: A comparison between laboratory and field-scale experiments. Chemical Engineering Research and Design, 163, 149–156. https://doi.org/10.1016/j.cherd.2020.08.026

Ministry of Environment of the Republic of Korea. Roadmap to expand bio-water energy using environmental facilities. 2022. Retrieved from https://eiec.kdi.re.kr/policy/ callDownload. do? num=227143 &filenum=2&dtime=20220621204205
Ryu, S. H., Seo, Y., Park, J., Kim, S. D., & Park, S. S. (2017). Adsorption Characteristics of Hydrogen Sulfide on Iron Hydroxide-based Adsorbent. Journal of Korea Society of Waste Management, 34(5), 468–473. https://doi.org/10.9786/kswm.2017.34.5.468
Solutions, E. A. E. (2000, October 31). Fuel Cell Handbook, Fifth Edition. OSTI.GOV Title Logo. https://www.osti.gov/biblio/769283
Li, Y., Wang, X., Mei, B., Wang, Y., Luo, Z., Luo, E., Yang, X., Shi, Z., Liang, L., Jin, Z. (2021) Carbon monoxide powered fuel cell towards H2-onboard purification. Sci. Bull. 66 , 1305–1311.
St-Pierre, J. (2010). PEMFC contaminant tolerance limit—CO in H_2. Electrochim. Acta, 55 , 4208–4211.
The Government of the Republic of Korea. Hydrogen Economy Roadmap. 2019. Retrieved from https://policy.nl.go.kr/search/searchDetail.do?rec_key=SH2_PLC20190231080&kwd=
The Government of the Republic of Korea. Carbon Neutral Promotion Strategy. 2020. Retreved form http://www.motie.go.kr/motie/ne/presse/press2/bbs/bbsView.do?bbs_seq_n=163606&bbs_cd_n=81&currentPage=1&search_key_n=&cate_n=&dept_v=&search_val_v=
UNFCCC. The Paris Agreement. 2015. Retrieved from https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement