Initiatives for Social Implementation of Green LP Gas

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ABSTRACT Green LP gas, easy to store and transport, a synthesis technology developed by the company is in progress aiming for a social implementation by 2030. This technology is characterized by a high Liquefied Petroleum Gas (LPG) selectivity and a long life compared with other companies' technologies. Applying this technology, Green LP gas was provided to Tochigi-Kokutai (Tochigi National Sports Festival) in 2022, and a plant is under construction in Hokkaido Shikaoi Town Environmental Conservation Center, aiming to validate our technology as one of the first in the world. This paper introduces the social implementation plan for 2030, the latest progress in the development of Green LP gas, and the status of its achievement towards the social demonstration.

1. INTRODUCTION

The Company has been in research and development in the Green LP gas technology as a part of its "environment-friendly businesses" to contribute to the achievement of a carbon neutrality and a circular economy portrayed in the "Furukawa Electric Group, Vision 2030" (Vision 2030)[1]. For the contribution to achieving the carbon neutrality through this technology, the collaborative approach is necessary which involves not only the Company but also various stakeholders, the LPG industry, and local governments.

In 2022, this project was selected as one of the projects for the New Energy and Industrial Technology Development Organization (NEDO) Green Innovation Fund "Development of Technology for Producing Fuel Using CO_2, etc." "Development of technology for synthesizing green LP gas without fossil fuels", since then we have been accelerating the development in collaboration with the gas companies and the local government with the target to complete the demonstration of the technology to produce 1,000 tons of Green LP gas per year in 2030. A demonstration plant is currently under construction to prove our technology.

This paper introduces the social implementation plan for 2030, the latest progress in the development of Green LP gas, and the status of achievement towards the social demonstration.

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2. SOCIAL IMPLEMENTATION PLAN TO BE ACHIEVED WITH THIS TECHNOLOGY

Since the founding of the company in 1884, we have focused our businesses on the transmission, the connection and the storage of energy, information and heat, with four core technologies - metals, polymers, photonics and high-frequency, and we provided a wide range of technologies, products and services in the field of infrastructure, including telecommunications and energy, as well as in the automotive products and electronics.

In Japan, the introduction of Renewable Energy is expanding for the achievement of the carbon neutrality declaration by 2050. However, due to the increasing proportion of asynchronous power sources such as solar and wind power in the power grids, a lack of adjustment capacity to respond to output fluctuation is becoming apparent[2]. The Seventh Strategic Energy Plan (draft version) also places a focus on electrification and a shift to non-fossil fuel energy, while also calling for the promotion of initiatives such as encouraging demand response (DR) and rationalizing energy use. Though efforts to the next-generation power grids and utilize free power capacity are underway, the introduction of new infrastructures in all regions is difficult due to the population decrease due to aging. Therefore, we have focused on a combustible LPG consisting of propane (C_3H_8) and butane (C_4H_{10}), as one of the various options for achieving a decarbonized society. LPG has the advantage of being portable and easy to store as it is not supplied through a pipeline system but a decentralized supply system in cylinders. If LPG is not decarbonized, domestic CO_2 emissions will reach 24 million tons/year[3], however currently no practical technology has been established. Green LP gas has started to be sold overseas, but it is a by-product of green diesel then a process to produce Green LP gas as the main product does not exist yet. So, if the yield of the main product increases, the amount of the by-product produced will be decreased.

Therefore, we are developing and demonstrating a process that can produce Green LP gas as the main product by synthesizing carbon monoxide and hydrogen. We considered that by focusing on biogas*1 as an available carbon source in the transition period until hydrogen becomes available at a low cost, and by using all of the methane and carbon dioxide derived from biogas as feedstocks, not only greenhouse gases can be reduced through recycling greenhouse gas but also Local Production for Local Consumption would be available.

*1 Biogas is a mixture of methane (CH_4) and carbon dioxide (approximately 60% CH_4 and 40% CO_2) obtained by methane fermentation of organic waste (livestock manure, paper waste, food waste, etc.). Since CH_4 contained in biogas can be used as fuel for electricity generation, it is regarded as one of the RE. In addition, as CO_2 in biogas is a non-flammable gas, so it is not utilized and released into the atmosphere.

3. LATEST DEVELOPMENT PROGRESS OF GREEN LP GAS CATALYST TECHNOLOGY

As mentioned above, we are focusing on biogas obtained from the methane fermentation process of organic waste such as livestock manure as a feedstock for Green LP gas, and developing a two-stage process in which synthetic gas is produced through a reforming reaction such as a Dry Reforming (DRM) reaction (DRM reaction: $CO_2 + CH_4 \rightarrow 2CO + 2H_2$), and from there to proceed with LPG synthesis reaction (Figure 1). In the two-stage process, we have solved the technical issue of the existing catalysts by a catalyst development.

In the DRM reaction required for using biogas, the technical issue of the catalyst deterioration had to be resolved. As previously reported[4)], we have confirmed that Ramune Catalyst*2 has an excellent tolerance of sintering and prevention of coke formation through encapsulating metal particles in a porous material, and based on these facts both excellent catalytic activity and long life are achieved. Based on further improvement of reaction conditions, over 100 days of stable activity was maintained as shown in Figure 2, and the equilibrium conversion rate (theoretical limit) became possible to be maintained. This paper introduces that LPG synthesis reaction as the second-stage reaction, resulted in being able to synthesize propane at a high selectivity.

*2 This new catalyst structure (the structure in which the catalysts are fixed inside the porous material) is named Ramune Catalyst as it resembles a bottle of Ramune in which a glass ball is fixed.

In the second-stage reaction, the main product of propane (C_3H_8) is synthesized using hydrogen and CO which are the synthetic gasses from the DRM reaction. This LPG synthesis reaction uses the catalyst developed by the Company. Although it shows good LPG yield in the initial characteristics, there was an issue that catalyst deterioration tends to happen within a short period. The catalyst before the reaction was observed with a Scanning Electron Microscope (SEM) (SU8020, Hitachi High-Tech Corporation), and a schematic diagram is shown in Figure 3. LPG synthesis catalyst utilizes the technology of the Ramune Catalyst and a combination of multiple catalysts is used. From the fact that the particle size of one type of catalyst had increased after the reaction (Figure 3, (b)), it was considered that a decrease in activity was caused by the reduction in surface area due to catalyst growth (sintering).

The sintering generally makes progress due to the high reaction temperature. However, even in the experiment where the reaction temperature was lowered to a level where this rarely occurs, LPG yield decreased within approximately one week (Figure 4 A). This led us to assume that the problem may be caused by other factors than temperature, and experimental verification was carried out. As a result, it was found that the efficiency of the LPG synthesis reaction could be improved by optimizing the mixture ratio. As shown in Figure 4 B, LPG yield*3 of approximately 30% or more was maintained even after 140 days, and as shown in Figure 5, a propane selectivity*4 of 75% or more was achieved.

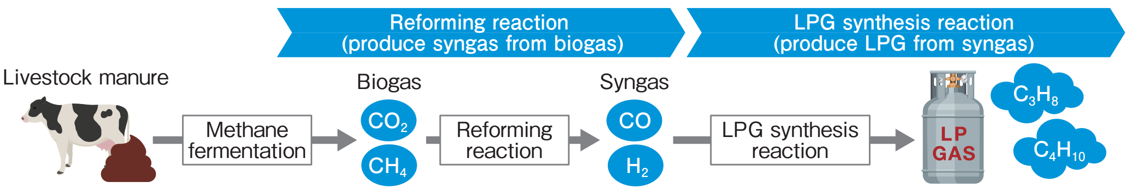

Figure 1 Process for producing Green LP gas from livestock manure (outline).

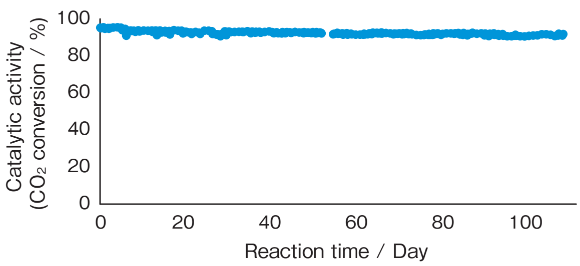

Figure 2 Dry reforming performance of a Ramune Catalyst.

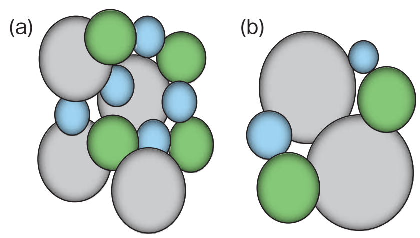

Figure 3 SEM observation pictures of LPG synthesis catalysts. (a) before the reaction, (b) after the reaction

*3 LPG yield: The total amount ratio of propane (C_3H_8) and butane (C_4H_{10}) contained in the produced gas (C-mol%).
*4 Propane selectivity: The proportion of propane in the total produced amount of propane and butane (vol%).

Table 1 shows a comparison of our technology with that of others.

Compared with other companies' technologies, our technology is characterized by an over 50% of LPG yield as shown in Figure 4, and a high propane selectivity (80% or more at initial characteristics), both are obtained through utilizing biogas.

By further devising the catalytic reaction conditions and temperature, and synthetic gas from those shown in Figure 4, we successfully improved the propane yield. In particular, the gas in the process possibly be utilized for the reaction at higher efficiency by adjusting the ratio of synthesis gas during the reaction. Details are omitted in this paper as the patent application is still in process. The prospection of an extremely highly efficient LPG synthesis has become apparent when this development is implemented in the demonstration plant planned to be constructed. We will diligently continue to refine our technology by utilizing the knowledge of catalysts being gained through the development of the Ramune Catalyst.

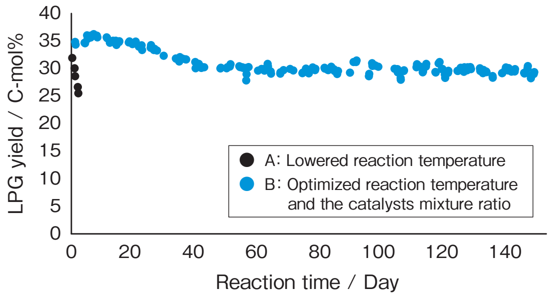

Figure 4 LPG yield (C-mol%) vs. lifespan.

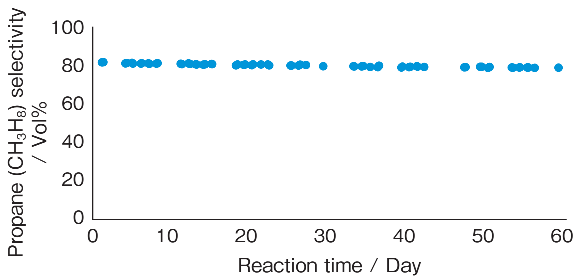

Figure 5 Propane selectivity vs. lifespan.

Table 1 Comparison with other companies' technologies.

Company		Feedstock	Producing process	Strength
Furukawa Electric	Biomass	Livestock manure → Methane fermentation → Biogas (CO_2, CH_4)	Reforming reaction → Syngas (CO, H_2) → LPG synthesis reaction → LP GAS (C_3H_8, C_4H_{10})	High LPG yield (50%) High propane selectivity (80%) —> World's leading
GTI Energy	Biomass	Methane fermentation → CO_2, CH_4	Reactor → CO, H_2 → Reactor → LP GAS	High LPG yield (39%) Butane rich
A	Biomass	Straw, etc. → Cellulose → Decomposition	$C_6H_{12}O_6$ → Reactor → Reactor → LP GAS	No H_2 required
B	CO_2 & H_2	Air → CO; H_2	Reactor → LP GAS	Suitable for mass production due to large amount of CO_2/H_2 reserves
C	CO_2 & H_2	Air → CO; H_2	Reactor → CO, H_2 → Reactor → LP GAS	
SHV Energy	Biomass	Municipal waste → Gasification	CO, H_2 → Reactor → DME (Similar physical properties to LPG) → Blend with Fossil fuel LPG	Technology is mature

4. PROGRESS TOWARDS SOCIAL IMPLEMENTATION

Here, in addition to the catalyst development, this paper introduces our initiatives to demonstrate a series of Green LP gas production processes, which have been carried out with the goal of completing the demonstration of technology to produce 1,000 tons of Green LP gas per year in 2030.

4.1 Provision of Green LP Gas at Tochigi-Kokutai

In 2022, Green LP gas was provided as an "environmentally friendly and fuel for Local Production for Local Consumption" for the torch at the Ichigo Ichie (once-in-a-lifetime encounter) Tochigi-Kokutai. The torch is based on the Olympic flame, and was used as part of the fuel for the torch at the opening ceremony, as shown in Figure 6.

Figure 6 Ichigo Ichie, Tochigi-Kokutai torch.

We aimed to produce Green LP gas using the process shown in Figure 1. However, until providing Green LP gas in this matter, only laboratory-scale catalytic testing was carried out. And, two reactions, the DRM reaction and LPG synthesis reaction, were evaluated separately. Therefore, to investigate the production of LPG for use in the torch, the laboratory-scale apparatus was scaled up, and an attempt was made to recover LPG by conducting the DRM reaction and LPG synthesis reaction continuously.

The investigation started in actually, several issues arose associated with the scale-up, which were resolved as follows. This paper introduces two of these issues: one is components other than the base components of biogas (CH_4, CO_2), the other is coking and temperature variation in the dry reforming reaction.

(1) Biogas components

Through the components analysis from the collected biogas, seasonal variation in the components, and mixing of moisture and oxygen in the biogas were revealed. Since both oxygen and water are highly provable to provide adverse effects on the catalyst, an oxygen and water removal device was installed in the front stage of the DRM reaction reactor.

(2) Variation of coking by temperature in the DRM

As an initial investigation, an up-scaled reaction reactor from the laboratory experimental system was designed, and a trial run was conducted after filling it with the molded Ramune Catalyst. As a result, it was confirmed that a large amount of coke was deposited inside the reactor, causing the inside of the reactor to become clogged. Coking is a phenomenon in which deposits on a catalyst, and it is believed that carbon lumps are formed by hydrocarbons polymerized on the catalyst. As a result of the investigation, the coke formation induced by the trace components contained in the reaction tube was suspected. Then, by changing the material inside the reactor, the formation of coking inside the reactor could be suppressed. Next, by measuring the temperature in the center portion of the catalysts packed bed, insufficient heating was found in the center portion relative to the target temperature for the DRM reaction. This tendency was more noticeable towards the top of the catalysts packed bed, and the monitored temperature at the top was lower than the target temperature. The reason for this is believed to be a drop in temperature in the center portion caused by an endothermic reaction proceeded in the upper part of the catalysts packed bed where the reaction proceeds most rapidly, as the DRM reaction described above is a rapid endothermic reaction as shown in equation (1).

$$CH_4 + CO_2 \rightarrow CO + 2H_2$$
$$\Delta H = +247 \text{ kJ/mol (endothermic)} \qquad (1)$$

When the reaction temperature falls below the target temperature, a catalyst deterioration or a blockage of the reactor may occur due to coking or oxidation. So an equipment capable of uniform heating in the center portion is required. Therefore, by changing the reactor shape, its inner diameter, and a temperature control method to enable uniform heating, the temperature drop inside the reactor was reduced. And, the coking formation and the temperature drop in the DRM reaction were successfully suppressed.

Through the above investigations, it was confirmed that the actual production of LP gas using biogas as a feedstock is possible by continuously carrying out the two-step process devised by us. By carrying out the reaction, which has been studied in the laboratory, under the scaled-up condition using actual biogas, the issues related to influences of oxygen and moisture mixed in biogas and to the reactor for the DRM reaction that arose due to the scaling-up, could be addressed and resolved ahead of the demonstration plant.

Furthermore, as this Green LP gas uses actual biogas produced from livestock manure collected at Tochigi Prefectural Livestock & Dairy Experimental Center, it has been demonstrated that it is possible to achieve Local Production for Local Consumption of energy within Tochigi Prefecture.

4.2 Groundbreaking Ceremony for Green LP Gas Demonstration Plant

As part of initiatives by the NEDO Green Innovation FUND project, Green LP gas synthesis process demonstration plant is under construction in Hokkaido Shikaoi Town, a groundbreaking ceremony was held in August 2024. Mayer Tomoki Kii and other related parties attended the ceremony and prayers for the safety of the construction work were offered (Figure 7).

A comprehensive partnership agreement was signed in 2022 with Hokkaido Shikaoi Town, and towards the establishment of the demonstration plant, studies have been carried out. This is the construction of the plant aiming to demonstrate our technology as one of the first in the world. And the plan is to start producing 100 to 200 tons of Green LP gas per year starting 2026 using biogas produced from livestock manure at the Shikaoi Town Environmental Conservation Center.

Figure 7 Picture of the groundbreaking ceremony.

5. CONCLUSION

Green LP gas that we are developing refers to “Propane and butane synthesized using carbon fixed from the atmosphere by plants such as plants and carbon-neutral hydrogen or carbon-neutral energy, or produced as a by-product in the production of other carbon-neutral energy[5]”. As mentioned above, when using biogas as a feedstock, since carbon derived from livestock manure, fixed from the atmosphere by plants, is used as the feedstock, then it can be handled as 100% carbon-neutral propane/butane. And this makes it possible to reduce all of the CO_2 generated when propane is burned.

Discussion at Green LP Gas Promotion Public-Private Partnership Council[6] has set a target to make 2 million tons of LP gas, which is 16% of the expected demand, carbon neutral by 2035 as a transition period to achieve carbon neutrality by 2050. As part of the measures, the import and domestic production of Green LP gas, for which the Company is beginning to make initiatives on at the demonstration plant mentioned above, is included as the numerical targets. The production of Green LP gas using our technology is highly promising.

In September 2022, the Company set up an organization that promotes the practical use of Green LP gas in an integrated manner with marketing, sales, research and development, and MONOZUKURI. Thus, the Company aims to produce and provide Green LP gas in cooperation with Facility Assets Department and Global Marketing Sales Division. In addition, for the Company, handling LP gas is a new challenge, especially regarding the distribution of Green LP gas, it is necessary to ensure Green LP gas does not have any issues compared to existing LP gas on safety and can be handled in the same way, and establish standards and systems to certify Green LP gas domestically. The Company is therefore proceeding with the development in partnership with domestic gas companies such as Astomos Energy Corporation and Iwatani Corporation, and moved into action to build a supply chain. An effective domestic production and distribution system will be built utilizing the existing gas distribution network.

Furthermore, when aiming all the domestically distributed LP gas to make carbon neutral, it is necessary to keep our eyes on overseas production, in consideration of the amount of biomass feedstock available in Japan. In 2022, the Company signed the Memorandum of Understanding (MOU) with Futuria Fuels in SHV Energy Group as a producing and supply partner for the development of Green LP gas overseas. Our collaboration will be accelerated to establish a system for producing and supplying several million tons per year of Green LP gas per year from various synthetic gas feedstock including biogas, by combining our technology with the commercialization know-how of Astomos Energy and SHV Energy Group and utilizing their international LP gas supply network.

The Company will continue to contribute to the greening of LP gas demanded in Japan by synthesizing 1,000 tons of Green LP gas per year by 2035 at a large-scale demonstration plant. In addition, through the social implementation of Green LP gas, the Company will not only contribute to a decarbonized society but also promote“Succession of local resources and local culture for the future” of energy.

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