Technology for Producing Green LPG With Ramune Catalyst

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ABSTRACT A cooperative study with Hokkaido University is in progress to reduce greenhouse gas emissions, which is a global social issue. A technology to convert biogas into Liquefied Petroleum Gas (LPG) has been successfully developed by applying the developed metal catalyst fixing technology. LPG produced, by using this technology, from carbon dioxide and methane obtained from livestock manure is easy to store and transport, and can be used as energy in ordinary households and in industrial sites such as dairy farming, as well as in the event of a disaster. We believe that this technology not only contributes to a decarbonized society but also to the formation of a circular and ecological economy by promoting local consumption of local production on energy assisting the new social infrastructure of the region.

1. INTRODUCTION

Furukawa Electric Group has formulated "Furukawa Electric Group Vision 2030 (the Vision 2030): In order to build a sustainable world and make people's life safe, peaceful and rewarding, Furukawa Electric Group will create solutions for the new generation of global infrastructure combining information, energy and mobility." and promoting initiatives for the Vision 2030.

We have identified the "creation of social issue-solving businesses" as a part of materiality for exploiting revenue opportunities toward achieving Vision 2030.

While there are many social issues before us, one of the biggest challenges for our Group is the realization of a decarbonized society, namely, the initiatives aimed at carbon neutrality[1)].

From the initiatives of Furukawa Electric (FEC) regarding the carbon neutrality, an activity of the Sustainable Technology laboratory is introduced in this paper. Our mission is to create new business seeds through the "search for budding technologies" which anticipate advanced technology in order to build a new social infrastructure that converts social issues into value. The research and development on "Green LPG synthesis technology using greenhouse gases as raw materials" is proceeding as one of the "seeds for new businesses". With this theme, we have been working closely with social issues from its setting to its research and development. The latest progress of the research and development will be introduced.

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2. THEME SETTING BASED ON OUTSIDE-IN APPROACH

The fundamental idea of the Group in the carbon neutrality is "1 Eliminate or reduce direct CO_2 emissions", "2 Eliminate or reduce CO_2 emissions by customers and society", and "3 Capture or transform the CO_2 that is emitted". We have been selected as a CDP Climate Change A-listed company for the second consecutive year, based on the evaluation of our goal-setting and actions in efforts to address climat change, and transparancy. For further growth of the initiative, also for achievement of the Vision 2030, we are considering developing products and services that make effective use of CO_2.

We focused on the carbon recycling technology. On developing the carbon recycling technology, the important thing is "What shall be created from CO_2". By hearing opinions directly from various people, we extracted two keywords, "dairy farming / livestock industry", and "natural disasters".

"Dairy farming / Livestock industry"

At COP26 held in 2021, the attention was focused on methane gas which accounts for approximately 30% of the greenhouse gas effect. More than half of the world's methane generation sources come from fossil fuels, waste, and agriculture / dairy farming, of which the largest amount of methane is said to be in the agriculture / dairy farming[2)]. Methane gas generated from agriculture / dairy farming and wastes is the greenhouse gas if it is released into the atmosphere, but it can be effectively used as energy when it is retrieved actively in sufficient amount. For example, a biogas power generation using methane fermentation of livestock manure is one of the utilization methods, and it is playing an active role as a regional energy supply source. On the other hand, we could confirm the followings: surplus electricity has generated at some of regions where livestock manure can be collected. In addition, another problem is, even though wishing to supply to other regions, the electricity cannot be transmitted due to lack of power system capacity, especially lack of transmission capacity. Therefore, we considered to provide a method that can utilize biogas as alternative energy by avoiding limitation described above.

“Natural disaster”

When considering about energy, we focused on “rapidly increasing natural disaster”. Recently, heavy rainfalls once every 100 years occur almost every year causing a great damage in each case. In such of us, LPG, which has been rooted in our lives for a long time, is evaluated for its high resilience again. As shown in Figure 1, after the Great East Japan Earthquake, recovery of LPG was faster than other energy as it is easy storability / transportability and availability in distributed independence[3]. Therefore, we considered that when LPG could be generated from livestock manure, at the same time of the reduction of greenhouse gases, energy can be supplied to the region simultaneously with the disaster countermeasure implementation, and the self-reliance of the region would be established.

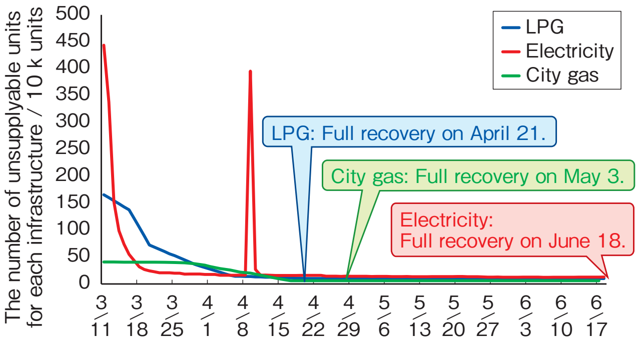


Figure 1 **Changes in the number of unsupplyable units for each infrastructure in the three disaster prefectures (including estimates)[3].**

3. – DEVELOPMENT OF GREEN LPG SYNTHESIS TECHNOLOGY – CONVERTING CO_2 (GREENHOUSE GAS) TO A USEFUL COMMODITY

We proceeded with the development in a two-step process. First, syngas was produced from biogas* (dry reforming reaction). From there, LPG was synthesized from syngas (LPG synthesis reaction). The details are shown in Figure 2. In order to achieve this process, an issue for the catalyst technology was required to be solved.

* Biogas is a mixed gas consists of methane (CH_4) and carbon dioxide (CO_2) obtained by methane fermentation of organic waste (livestock manure, paper waste, food residue, etc.) (CH_4 approx. 60%, CO_2 approx. 40%). Since electricity can be generated by using CH_4 in the components as fuel, it is positioned as one of the renewable energy. And, CO_2 in biogas is not utilized, as it is a nonflammable gas, and released into the atmosphere.

3.1 Issues Regarding the Catalyst

The issues differ depending on the type of reaction, the issues regarding catalysts can be divided into (1) the catalytic activity and (2) the catalyst life. In general catalysts, in order to improve the activity, a method to ensure an effective surface area is taken by supporting metal particles having catalytic activity on supports in highly dispersed state. However, in a catalyst having such a structure, sintering of metal particles tend to occur on the supports during the reaction. In addition, in reactions that use hydrocarbons as a raw material, coking is caused at the same time as sintering. Coking is a phenomenon of deposit of carbon on the catalyst, and it is thought that a mass of carbon is formed by polymerizing hydrocarbons on the catalyst.

When such sintering and coking occur, the effective area as a catalyst decreases, then the catalytic activity decreases. As a result, problems such as the need to replace and regenerate the catalyst in a short period of time occur (Figure 3).

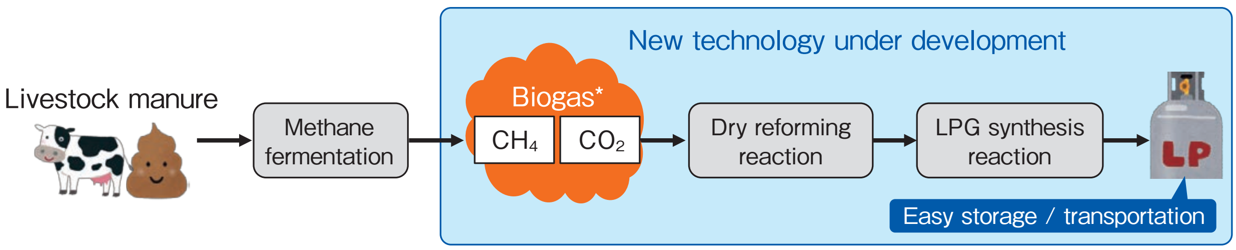


Figure 2 **Green LPG production process from manure (outline).**

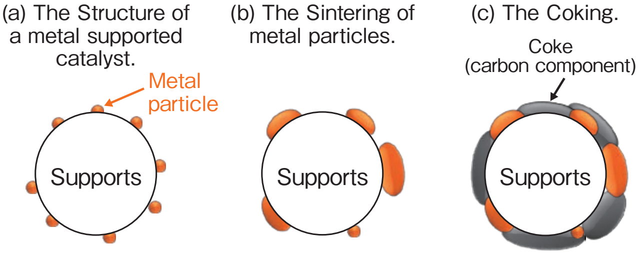


Figure 3 Image of supported catalyst structure, metal particle sintering and coking.

3.2 New Structural Catalyst, Features and Evaluation Results of Ramune Catalyst

To solve sintering and coking of the catalyst, we proceeded with the creation of ideas, through the collaboration with Professor (Specially-appointed) Takao Masuda of Faculty of Engineering, Hokkaido University (currently Emeritus Professor, Hokkaido University), who has been active in the field of catalytic reaction engineering over a period of time. As a result, we developed an idea to suppress sintering and coking by encapsulating metal nano particles in a porous material (Figure 4). The collaborated idea has the following two features. The first feature of the collaborated idea is the encapsulation of metal nano particles in a porous material with small pores. The second feature is to prevent sintering and coking by fixing metal nano particles in the porous material.

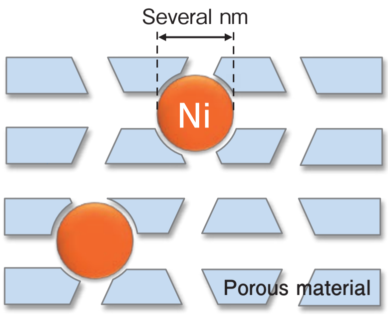


Figure 4 Structure of our novel catalyst (Ramune catalyst).

3.2.1 Ramune catalyst structure analysis

We made a prototype of the developed catalyst and its structure was analyzed. The cross section of the prototype catalyst was cut out, and the cross-sectional elemental analysis was performed with a Scanning Electron Microscope (SEM) (SU8020 from Hitachi High-Tech Corporation) and with an Energy Dispersive X-ray spectroscopy) (EDX) (X-Max by HORIBA, Ltd.) also the cross-section was observed with a Transmission Electron Microscope (TEM) TITAN G2 from FEI Company Japan Ltd.).

As a result of the cross-sectional elemental analysis, the Nickel element (Ni) was detected inside the catalyst. Furthermore, by using the photographed cross-sectional TEM image, 100 or more Ni particles were arbitrarily selected, and the most frequent particle diameter was calculated by measuring each particle diameter. As a result, we confirmed that mode diameter of nickel particle contained in the prototype catalyst was approximately 4 nm.(Table 1) However, in principle, TEM can obtain only local information in the prototype catalyst. Then, in order to obtain the average information of the Ni particle contained in the entire prototype catalyst, an observation with a Small-Angle X-ray Scattering (SAXS) was performed. For the SAXS measurement, SPring-8 beam line BL19B2 was used. From the obtained SAXS data, with assumption that the electron density of the particles was uniform, the particle diameter was calculated using Guinier approximation. The result is shown in Table 1.

Table 1 Observation result on the Nickel particle size of the Ramune Catalyst.

Measuring method	Cross-sectional TEM	SAXS
Ni particles size	4 nm	2-3 nm

From the cross-sectional elemental analysis, the cross-sectional TEM and the SAXS analysis, we confirmed that the prototype catalyst had a structure in which several nm of Ni particles were encapsulated inside the porous material as shown in Figure 4 which is our design. 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.

3.2.2 Catalyst performance of Ramune Catalyst

On producing LPG from the biogas, the dry reforming is necessary. Dry reforming ($CO_2 + CH_4 \rightarrow 2CO + 2H_2$) is one of the focused reactions in the field of carbon recycling, for its opportunity to utilize greenhouse gases. Ni has been reported to be active as a catalyst, but this reaction has the problem of deactivation of the catalyst due to coking on Ni particles.

We evaluated Ramune catalyst for dry reforming performance. The result is shown in Figure 5, and the evaluation result for the catalyst after the reaction is shown in Table 2. As shown in Figure 5 and Table 2, the conventional Ni-based catalyst was deactivated in a few hours and a large amount of coke was detected in the catalyst after the reaction. On the other hand, Ramune Catalyst maintained stable activity for 100 days or more, and the amount of coke formation was below the lower limit of the analysis. From these results, we confirmed that Ramune catalyst has an excellent tolerance of sintering and prevention of coke formation, and these characteristics achieve good catalytic activity and stability required as practical catalysts.

In this paper, only the results of the first-stage dry reforming reaction are introduced, but we have confirmed that our catalyst under development also exhibited good performances for the LPG synthesis catalsyt.

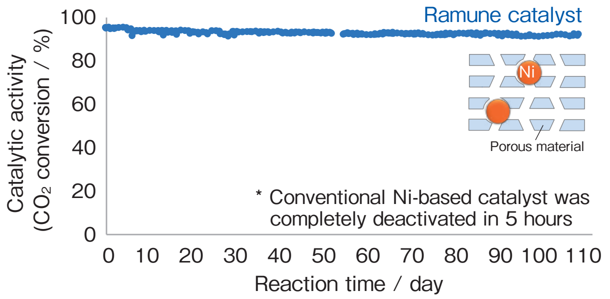
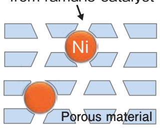
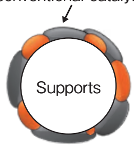


Figure 5 Performance of the dry reforming on the Ramune Catalyst in the test result.

Table 2 Results of the analysis on the catalytic activity and amount of coke of Ramune Catalyst.

		Ramune Catalyst	Conventional Ni-based catalyst
Analysis result	Reaction time	107 days	5 hours
	Catalyst activity	(Initial activity) Over 90% (After 100 days) Over 90%	(Initial activity) Over 90% (After 5 hours) Over 0%
	Coke amount after the reaction*	<0.3wt%	30wt%
Catalyst structure after dry reforming (Image diagram)		·Ni particle maintained nano-size ·Coke wasn't detected from ramune catalyst 	Large amount coke was formatted on conventional catalyst 

* Carbon sulfur analysis result.

4. CO_2 REDUCTION AMOUNT

We decided to calculate the LPG amount produced based on the laboratory evaluation results with the catalyst under development in the Company. LPG amount obtained from one cattle and CO_2 reduction amount were calculated. The result is shown in Figure 6.

LPG currently used is from fossil fuels, but if Green LPG derived from livestock manure can be replaced with the conventional LPG, CO_2 can be reduced by the amount of the replacement. Based on the above consideration, CO_2 reduction amount is calculated by the formula shown below.

The Green LPG amount obtained from the manure of one cattle is 86 kg/year. Here, since LPG emits three times as much CO_2 when burned, the amount of CO_2 reduction of the Green LPG is approximately 260 kg/year from a cattle. Furthermore, the CO_2 reduction amount in Japan and in the world are calculated by multiplying the number of cattle in Japan and the number of cattle in the world.

CO_2 reduction amount = LPG consumption derived from livestock manure × CO_2 emission factor of petroleum derived LPG (3 kg-CO_2/kg)

5. IMPACT OF THIS TECHNOLOGY ON SOCIETY AND SOCIAL IMPLEMENTATION SCHEDULE

This technology uses CO_2 and CH_4 as raw materials, and the greenhouse gas reduction can be expected. In addition, since the Green LPG can be easily stored and transported like existing LPG, then it can contribute to use as an energy in the event of disasters and to solve a problem of lack of capacity in power grids.

In Japan, the LPG supply is heavily depending on imports. Against this fact, our technology enables us to generate LPG domestically, then “local consumption of local production regarding the Green LPG” will be enabled. Thus we believe that this technology will contributes to job creation and regional revitalization. We are aiming for “local production, a wealth for local future generations*” regarding the Green LPG by inheriting this industry to the next generation (Figure 7) (Table 3).

* “Local production, a wealth for local future generations” is to pass on (or inherit, succeed) natural resources, facilities, traditions, culture, etc. existing in a community to the next generation[4].

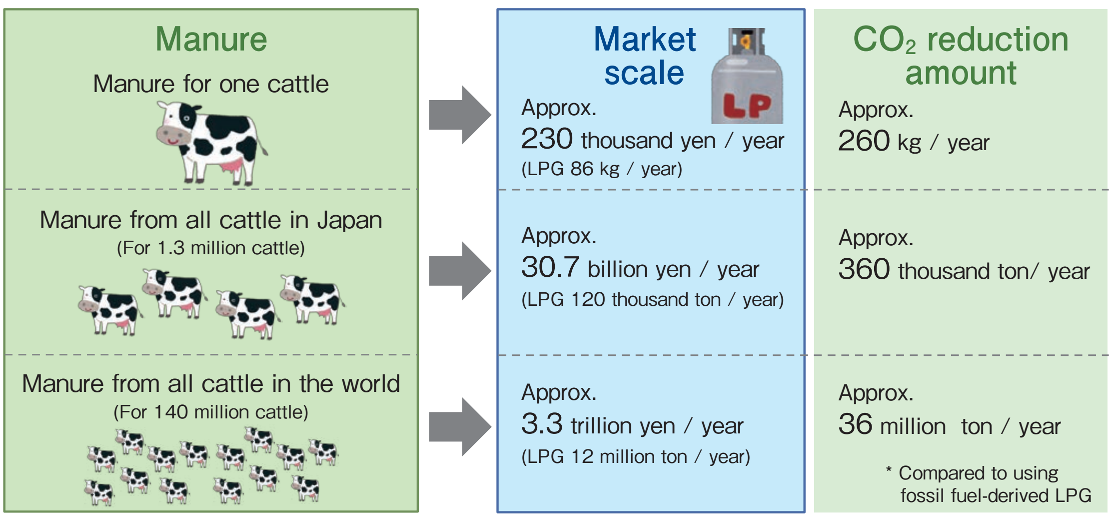
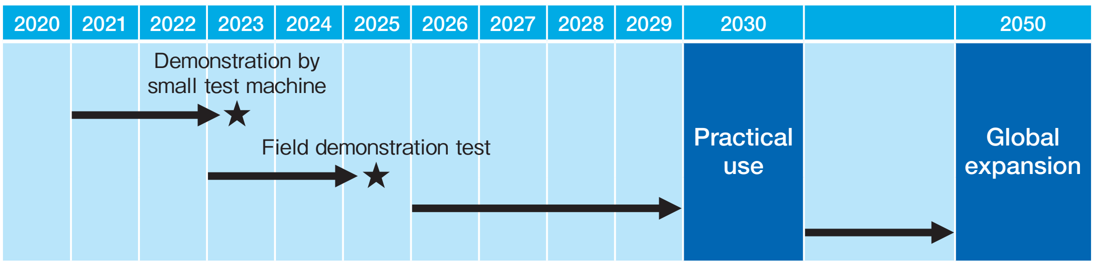


Figure 6 Market scale and amount of CO_2 emission reduction.

Figure 7 New community created by our Green LPG.

Table 3 Social implementation schedule.



6. CONCLUSION

The CO_2 generation amount is directly related to the primary energy production amount. The net amount of CO_2 generation can be reduced by producing a primary energy using renewable bio-derived resources as an alternative resource to fossil resources. Also, instead of transferring primary energies over a wide area as secondary energy such as electricity, if the primary energy can be stored in a simple and stable manner for a long period, it will be a Business Continuity Plan (BCP) against disasters. From this point of view, producing LPG, which is easily accepted by the general public, from the biogas and supplying it is considered to be an extremely advanced and rare technology which is closely serving the general public. We are convinced that this technology is a Japanese-launched type that can be applied to most region of the world where natural gas supply facilities are not well equipped, and its practical realization is much-needed.

Therefore, the Company will continue to promote the development of this technology to produce LPG from the biogas, toward its practical application.

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