Synthesis of LPG from Biomass-derived Syngas

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Abstract:

LPG (a mixture of propane, butane and pentane) is widely used in Japan, present of which is a by-product of natural gas. NEDO (New Energy and Industrial Technology Organization) started a bio-LPG project in 2010, which consisted of entrained-flow biomass gasification and direct LPG synthesis process with hybrid catalyst. Through the first two-year study, it became clear that bio-LPG is suitable for present LPG-supply chain in Japan and for local production for local consumption. Its greenhouse gas emission based on the life cycle assessment is estimated to be quite low, however, its total energy conversion rate from biomass to LPG is only 0.38. Catalytic gas reforming for improving the total energy conversion rate and acquiring engineering data of LPG synthesis are main subjects of the latter of two-year period.

1. Introduction:

As Japan is an island country, municipal gas is available in limited areas of large populations. Rest of Japan, area of more than 90%, LPG (a mixture of propane, butane and pentane) is supplied to. "Energy Kihon Keikaku (Basic Energy Plan in Japan)" classified LPG as a distributed source of energy.

Fossil-LPG is a by-product of natural gas. The LPG of about 15-16Mt is consumed in every year, energy of which is about 750-800PJ and is corresponding to about 6% energy of petroleum and natural gas imported from abroad (Table 1).

	2008	2009	2010	2011
LPG	16 245kt	15 081kt	14 644kt	15 008kt
municipal gas	35 727Mm3	32 954Mm3	35 206Mm3	35 109Mm3
petroleum oil	207 670ML	193 396ML	197 209ML	1973 056ML
gasoline	57 247ML	57 447ML	58 368ML	56 864ML
diesel oil	34 246ML	32 247ML	33 057ML	32 658ML
electric power	913 138GWh	846 725GWh	901 522GWh	859 663Wh

Table 1. Energy applications in Japan.

The second-generation bio-fuel, gaseous and liquid bio-fuels from non-edible biomass, is expected as one of promising measures for reducing GHG (greenhouse gas) emission and nominated in the "Biomass Nippon Sougou Senryaku (Biomass Nippon Strategy and Technology)" and in the "Jisedai Jidosha Nenryo Initiative (Next Generation of Vehicles and Fuel Initiative)."

In 2009, the "Energy Kyokyu Koudoka Hou (Act of Sophisticated Methods of Energy Supply Structures)" was established for energy suppliers to promote the use of non-fossil energy resources and the efficient use of fossil energy resources. LPG suppliers and municipal gas companies are mandated to introduce bio-gas. Bio-DME (bio-dimethyl ether) is one of candidates substituting fossil LPG, however, many kinds of LPG instruments need improvements to use DME because DME dissolves seals in some cases. To establish thermo-chemical processes to bio-syngas, such as bio-LPG and bio-SNG (synthesized natural gas from biomass), is strongly and urgently required.

NEDO (New Energy and Industrial Technology Development Organization) started a bio-LPG project in 2010 as a part of "Project to Develop Next-generation Technology for Strategic Utilization of Biomass Energy." Japan Gas Synthesis Co. Ltd, the University of Kitakyushu and AIST (National Institute of Advanced Industrial Science and Technology) contracted with NEDO. In this report, results of the first two-year study and subjects of the latter two-year period are briefly explained.

2. Process overview and advantages of bio-LPG

The bio-LPG process consists of entrained-flow biomass gasification and direct LPG synthesis processes, properties of which are respectively studied by using a laboratory-scale biomass gasifier (Fig.1) [1] and laboratory-scale catalytic synthesis reactors. Based on these results, performances of a 100t/day-scale commercial system are estimated, scale of which is determined as considering MHI reports [2, 3].

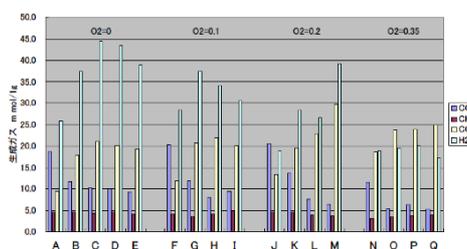| O2/C \ H2O/C	0.5	2.5	5	10
0	A	B	C	D
0.1	F	G	H	I
0.2	J	K	L	M
0.35	N	O	P	Q

Fig.2: Gas composition-dependence on gasification agents when gasifying Japanese cedar wood at 900°C using Lab-scale gasifier.

Fig.1: Lab-scale entrained biomass gasifier.

For catalytic synthesis, a mixture of H_2O and O_2 is used as a gasification agent, instead of H_2O and air, in order to reduce both gas capacity and compressing energy. Around biomass injector in the gasifier, feedstock biomass is partially oxidized to produce heat and to keep 900°C for proceeding gasification reactions. Rest of the gasifier, biomass is reacted mainly with H_2O. The obtained gas contains no O_2 because O_2 is highly active. About half or more content of the gas is unreacted H_2O because H_2O is less active. H_2, CO, CO_2 and CH_4 are 4 main components of the produced gas as previously reported [4]. H_2, CO and CO_2 contents are highly controllable by adjusting gasification conditions, such as feed rates of H_2O, O_2 and biomass, while CH_4 content is almost constant of about 8-10% (Fig.2). Molecular ratios of H_2O/C and O_2/C are important parameters, where C expresses carbon molecule in the

feedstock biomass. When increasing H_2O/C, H_2 content increases. When increasing O_2/C, both H_2 and CO contents decrease, and H_2 decreases more because H_2 is more active than CO. O_2 feed rate should be controlled to satisfy heat balance in a practical gasifier, while heat balance is not satisfied in the laboratory-scale one with an electric furnace. Mitsubishi Heavy Industries, Chubu Electric Power Company, Incorporated, and our group in AIST developed a 2t/day-scale test plant to study gasification properties of woody biomass (Fig.3) [2]. Considering these results, we developed simulators to estimate performances of a 100t/day-scale commercial plant. Cold gas efficiency, total energy conversion rate from biomass to produced gas, of the 100t/day-scale plant is estimated to be 75% or higher [2]. Yields of tar and char are about 1% and 5%, respectively, but reducible to about 0.1% and 1% when operating with tar absorbing and char recycling systems [3]. Because of low yields of the by-products, its running cost is low.

Direct LPG synthesis catalyst is a hybrid of methanol and zeolite catalysts [5]. Because of the hybrid, reversible and irreversible chemical reactions simultaneously progress (an insert of Fig.4): $CO + 2H_2 \leftrightarrow CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \rightarrow C_nH_{2n} \rightarrow C_nH_{2n+2}$, $H_2 \rightarrow 2H^+$ and $CO_2 + H_2 \leftrightarrow CO + H_2O$. The LPG is synthesized from H_2, CO and CO_2, while many kinds of BTL, such as FT oil, are from H_2 and CO. Properties of the LPG synthesis are dependent on molecular ratios of H_2, C and CO_2. For example, CO conversion rate is roughly dependent on $H_2/(CO+CO_2)$ and water shift reaction is on $CO_2/(CO+CO_2)$. When their optimal values are satisfied: $H_2/(CO+CO_2) \geq 2.5$ and $0.1 \leq CO_2/(CO+CO_2) \leq 0.4$, CO conversion rate of one-pass process is 80% or higher even under relatively moderate conditions of 260°C and 2.0MPa. Because of one-path process and moderate conditions, the LPG synthesis reactor is simple structure and low cost. Off-gas is a general name of out-gas from the LPG synthesis reactor, a mixture of H_2, CO, CO_2, CH_4, C_2H_6.
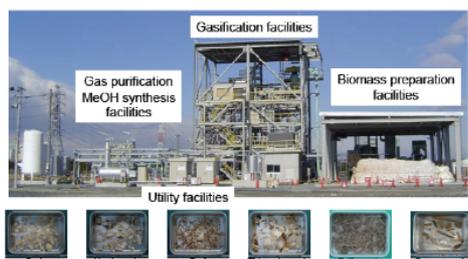

Fig.3 : Overview of 2-t/day-scale test plant (MHI) and tested woody biomass feedstocks.
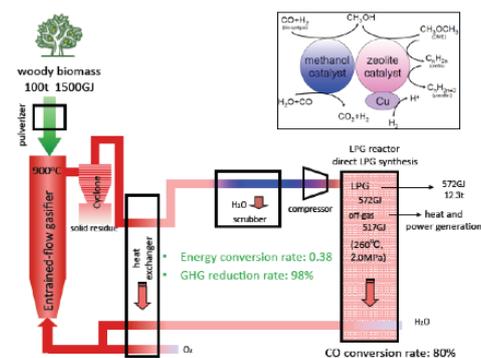
Fig.4: Schematic of bio-LPG Process and estimated performances of 100t/day-scale plant.

According to estimation, performances of an integrated system of biomass gasification and LPG synthesis are dependent on the gas compositions and heat recovery. As explained above, about half or more content of the obtained gas is the unreacted H_2O. Sensible heat of the obtained gas is usable for heating the gasification agent, however, latent heat released from the H_2O at 100°C is hardly recovered. Only heat of the LPG synthesis reaction and combusting the off-gas are usable for evaporating H_2O. Feed rate of the gasification agent, especially H_2O feed rate, has a practical limit. As explained above, gas contents are highly controllable by adjusting H_2O and O_2 feed rates, however, their controllable ranges have

practical limits: practical values are $H_2/(CO+CO_2) \leq 1.5$ and $CO_2/(CO+CO_2) \geq 0.5$. According to the estimation considering these conditions, about LPG of 12.3tons (572GJ) are synthesized from biomass of 100tons (1500GJ) (Fig.4). It means the total energy conversion rate from biomass to LPG is about 0.38, in spite of the high cold gas efficiency ($\geq 75\%$) and the high CO conversion rate ($\approx 80\%$). Rest of the energy is to the off-gas and heat loss. No GHG is emitted because the auxiliary electric power, such as biomass pulverization and gas compression, is generated from the off-gas. According to life cycle assessment (LCA), fossil fuel is used only when collecting the feedstock biomass and delivering the synthesized bio-LPG. GHG reduction rate is about 98%: total GHG emitted during life cycle of 100t-bio-LPG, including collection and delivery, is almost equal to that from 2t-gasoline.

3. Subjects of the latter two-year study

As explained in the previous section, the produced gas contains about 8-10%-CH_4. When catalytically reforming 1mol-CH_4 with H_2O ($CH_4 + H_2O \rightarrow CO + 3H_2$), 3mol-$H_2$ and 1mol-CO are produced. Both $H_2/(CO+CO_2)$ and $CO_2/(CO+CO_2)$ approach to their optimal values of the LPG synthesis: $H_2/(CO+CO_2)$ increases and $CO_2/(CO+CO_2)$ decreases. Catalytic water gas shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$) is also effective to increase $H_2/(CO+CO_2)$. Catalytic gas reforming is our first subject.

CCS (Carbone dioxide Capture and Storage) is simple and effective process to increase $H_2/(CO+CO_2)$ and decrease $CO_2/(CO+CO_2)$. Biomass energy application is thought to be carbon neutral because of carbon fixation during growing. When operated with the CCS, bio-LPG will be very effective to reduce GHG emission because net CO_2 in the atmosphere will be reduced: negative GHG emission.

Catalysts for CH_4 reforming and water gas shift reaction are easily deactivated by minor components in the obtained gas, such as S and Cl, originated from the feedstock biomass. Ultra gas purification is our second subject.

Long-term stability and reactivating procedure of the hybrid LPG catalyst have been studied. Industrial process of the catalytic synthesis is studying. The LPG synthesis is exothermic reaction. Design principles and engineering data of a multi-tubular type LPG synthesis reactor of plant-scale, such as effective heat removal and recovery, are studying by using a single tube reactor.

We continue studying on improvement of the hybrid catalyst, such as CO conversion rate, life span and reactivation process. When total energy conversion rate will be improved, calorie of the off-gas will decrease and electric power from it will hardly satisfy the auxiliary power. It is necessary to recover the latent heat of the unreacted H_2O, which is wasted now, and to use heat of the LPG synthesis reaction more effectively.

4. Conclusion

In 2010, NEDO started the bio-LPG project, consisting of entrained-flow biomass gasification and direct LPG synthesis process. Through the first two-year study, it became clear that GHG reduction rate of the bio-LPG is high but total energy conversion rate is only 0.38. Improving total energy conversion rate to 0.49 and studying engineering data of a commercial plant are subjects of the latter two-year period.

It also became clear that bio-LPG is suitable for present LPG supply chain in Japan for local production and local consumption because it is directly mixable to fossil-LPG with no limitations. Figure 5 shows a present LPG-supply chain in Japan and a concept of bio-LPG

mixture. Japan has 47 prefectures. According to rough estimation, it is possible to collect woody biomass of about 100tons every day in each prefecture. There are 50 LPG second bases of about 100kt-scale. If one base will have a bio-LPG plant, about bio-LPG of about 5.8kt will be produced every year, which will correspond to about 750 million Japanese yen or more than 9 million US dollar because whole sale price of present LGP is about 130 000 Japanese yen or about 1 600 US dollar per 1t-LPG. If all LPG bases will have their own plants, bio-LPG of about 288kt will be produced every year, about 2% of total LPG consumption in Japan.
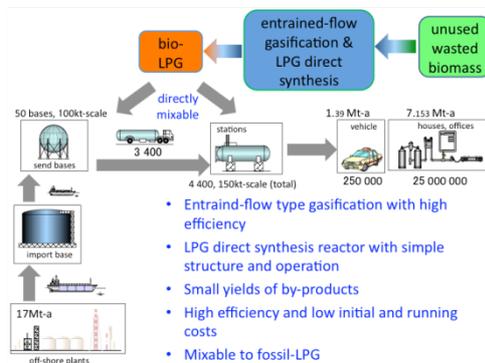

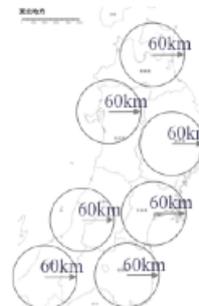Fig.5: LPG-supply chain in Japan and concept of bio-LPG.

Fig.6: North-East of Japan.

5. Acknowledgements

6. References

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