Technical Report

Development of Cellulosic Ethanol Production Technology —Results of Pilot Test for High Yield Bioethanol Process—

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Abstract

Cellulosic ethanol, also called second-generation ethanol, is bioethanol produced from cellulosic biomass, e.g., grasses, wood, and other plant materials that are non-edible biomass. In contrast to first-generation ethanol, which uses food crops as feedstock and negatively impacts food security, cellulosic ethanol does not compete with food and feed supplies. Therefore, it is hoped that cellulosic ethanol production and use will spread rapidly and widely. We developed our own high yield cellulosic ethanol production technology following a successful pilot test. We worked on engineering and construction of the pilot plant starting in 2015, and completed the pilot test in 2019. This paper presents the achievements obtained in the pilot test, and discusses the future prospects of our developed process.

1. Introduction

Carbon recycling technologies are attracting global attention because the reduction of carbon dioxide emissions is strongly demanded for the realization of a carbon-free society. Bioethanol is the general term to denote the ethanol produced from biomass as material, and the material biomass is renewable, and it grows by absorbing carbon dioxide in the air. Therefore, bioethanol does not substantially increase carbon dioxide in the air even when used for combustion, and can be used as a liquid fuel like gasoline without increasing carbon dioxide and/or as a material for plastic bags and/or PET resins. Therefore, its production technology is expected to be a core technology of the carbon recycling technologies.[1] Furthermore, bioethanol emits high-concentration carbon dioxide from the fermentation process that converts sugar to ethanol. Thus, if it is captured, and used or stored, the process will be of a negative emission technology that reduces carbon dioxide in the air, and is attracting global attention therefor.

In fact, globally, the use of 10% ethanol-mixed gasoline (E10) and 20% ethanol-mixed gasoline (E20) is expanding for various purposes such as the prevention of global warming with the nonuse of fossil fuel, and strengthening of energy self-supply and the agricultural industry in agricultural countries. In Japan as well, ethanol is presently used as a gasoline base material. In terms of the production amount, for example, the bioethanol production in the United States alone is about 60 million kL/year, which exceeds the Japanese gasoline consumption of about 51 million kL/year. The bioethanol industry has grown into one of the largest industries in the world with its consumed amount exceeding 100 million kL/year globally as of 2020.

On the other hand, most of the bioethanol currently produced is based on the first-generation technology of producing ethanol from sugar and/or starch, and most of it is produced from edible biomass such as corn and/or sugarcane. Some argue that the technology has triggered the soar in food prices. Therefore, the production technology of cellulosic bioethanol from the agricultural residues and/or non-edible biomass such as woody biomass like energy crop and herbaceous biomass materials (second generation bioethanol) is expected to become more widely employed in the early stage.

Until now, Nippon Steel Engineering Co., Ltd. (hereinafter referred to as Nippon Steel Engineering) has tackled the development of the first generation ethanol production technology using the biomass of residues as its material, and has completed the development of bioethanol production technology from food waste[2] and/or citrus residues produced in beverage plants. In 2019, the development of cellulose-based bioethanol production technology,[3] which is a second-generation technology, was completed (**Table 1**).

This paper describes the results of the plant test conducted in the Philippines and the future prospects with respect to the cellulosic bioethanol production technology using herbaceous biomass as its material.

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Table 1 Development history of bioethanol production technologies

	Feedstock		Scale of Pilot/Commercial plants	2005	~	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
1st generation	Food Waste		400 L/day	Development Pilot test												
1st generation	Citrus residue		5 000 L/day		Development Trial operation		Commercial operation									
2nd generation	Woody biomass		250 L/day		Research & Development		Pilot test									
2nd generation	Herbaceous biomass		300 L/day					Research & Development			Pilot test					

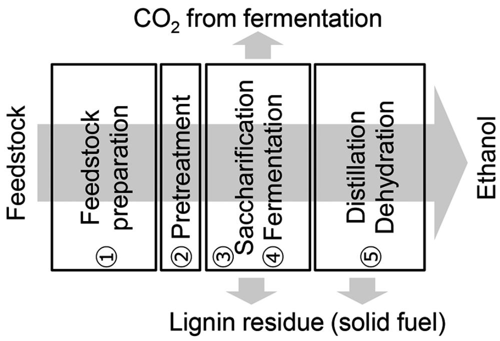

Fig. 1 Process flow of biomass-to-ethanol conversion

Fig. 2 Sugarcane bagasse

Fig. 3 Energy crop

2. Characteristics of Cellulosic Bioethanol Production Technology

Figure 1 shows the flow of the cellulosic bioethanol production process.

The cellulosic bioethanol production process consists of five processes:

(1) Feedstock preparation process that crushes and washes the biomass
(2) Pretreatment process that processes cellulosic biomass with chemicals or steam to be readily saccharified
(3) Saccharification process in which the pretreated biomass is saccharified by an enzyme
(4) Fermentation process in which the sugar is converted to ethanol by yeast
(5) Distillation and dehydration process

Furthermore, the residues produced in the saccharification fermentation process and the distillation and dehydration process can be used as solid fuel, and steam and/or electricity can be produced by using a boiler, a turbine, and a power generator.

(1) Feedstock preparation process: when sugarcane bagasse is discharged from a sugar plant, it is already in the form of fine fibers with a length of several cm (**Fig. 2**), and crushing is unnecessary for use as a material of ethanol. On the other hand, the energy crop (**Fig. 3**) and/or farmland agricultural residues are transported to the plant with leaves and stems unremoved. Therefore, they need to be crushed finely in the ethanol production equipment. In addition, the biomass may be contaminated with impurities such as sand and/or stones due to outdoor storage and/or collection at farmland. Therefore, in this process, impurities of the biomass are removed by crushing and washing.

(2) Pretreatment process: in Nippon Steel Engineering's process, the herbaceous biomass such as sugarcane bagasse is used as the material. Therefore, in the pretreatment process, the steaming treatment using dilute sulfuric acid, which is suitable for the herbaceous biomass, is used. If this treatment is applied strongly, although the saccharification in the subsequent process is promoted more readily, the biomass itself is decomposed, vaporized, and reduced in quanti-

ty. To solve this problem, Nippon Steel Engineering has established a processing condition specific to the material wherein the yield of the material is high, and the satisfactory saccharification yield is secured.

(3) Saccharification process: in this process, an enzyme (cellulase) is added to the pretreated biomass, and the cellulose and/or the hemicellulose contained in the biomass is converted to sugars (glucose, xylose). The enzyme cost accounts for the majority of the cellulosic ethanol production cost, and how to secure the sugar yield and the ethanol yield while reducing the amount of the enzyme to be added was a major issue, and Nippon Steel Engineering has succeeded in reducing the enzyme by optimizing the pretreatment condition.

(4) Fermentation process: this process converts the sugar produced in the preceding process to ethanol with fermenting yeast. Xylose is contained in the sugar derived from the cellulosic biomass. Xylose cannot be fermented with general type yeast. However, Nippon Steel Engineering employs an improved-type yeast of high performance that has been introduced from an external yeast development organization that can ferment xylose and glucose simultaneously.

(5) Distillation and Dehydration process: the ethanol concentration of the fermented ethanol broth produced in the fermentation process is low. Since the ethanol broth cannot be used as fuel as it is, in this process, the broth is condensed and dehydrated to above the 99.5% concentration to meet the standard of fuel use ethanol.

3. Outline of Bioethanol Production Technology Pilot Test

With the target of completing the development of cellulosic bioethanol production technology, we started designing and the construction of a pilot plant in 2015, and then started the pilot test in October 2016. **Table 2** shows the specifications of the pilot plant, and **Fig. 4** shows the photograph of the pilot plant. The pilot plant process consists of the processes of feedstock preparation (material crushing, washing), pretreatment, saccharification and fermentation, and solid-liquid separation. Since the distillation can be managed by an existing technology, it was excluded from the scope of the pilot plant. The ethanol yield was confirmed with the ethanol concentration of the fermentation broth, and then the fermentation broth was dumped as waste.

In the pilot plant test, the following three goals were targeted:

(1) Ethanol yield of 250 L/t-dry or more
(2) Continuous operation of the pretreatment equipment for 15 days
(3) Acquisition of the actual data of the engineering parameters

More than one hundred and forty plant tests were conducted across thirty months (two equipment stoppage periods included) (**Fig. 5**).

4. Result of Pilot Test

4.1 Toward the achievement of the ethanol yield target

4.1.1 Search for pretreatment condition for bagasse

In the dilute sulfuric acid method that Nippon Steel Engineering has adopted as the pretreatment method, the pretreatment intensity (the intensity of the capability of decomposing material) is generally controlled by the following three factors: (1) pH of the sulfuric acid to be added, (2) steaming treatment temperature, and (3) steaming treatment time.[4] In the pilot test, various types of material with a variety of treatment intensities were prepared, and the optimal pretreatment condition was pursued in the laboratory-scale saccharification test. As an example, **Fig. 6** shows the result when the pretreatment temperature is changed while pH and the steaming time are kept constant. In this graph, the pretreatment temperature is on the horizontal axis, and on the vertical axis, there is the relative sugar yield at each temperature, taking the sugar yield at the optimum temperature as 100%.

When the pretreatment intensity is weak (like the cases of low steaming temperature, high pH, short steaming time), the efficiency in the subsequent saccharification process deteriorates, so the amount of sugar obtained by saccharification is lower than that of the one obtained with the optimum intensity. On the other hand, when the pretreatment intensity is high (high steaming temperature, low pH, and long steaming time as well), the excessive decomposi-

Table 2 Overview of pilot plant

Feedstock	Herbaceous biomass (sugarcane bagasse, etc.)
Plant capacity	1 t-dry/day (equivalent to ethanol production of 250 to 300 L/day)
Process	Feedstock preparation (crushing / washing) Pretreatment (steaming) Saccharification and fermentation Solid-liquid separation
Site area	45 m × 35 m (approx.)
Location	Philippines

Fig. 4 Pilot plant

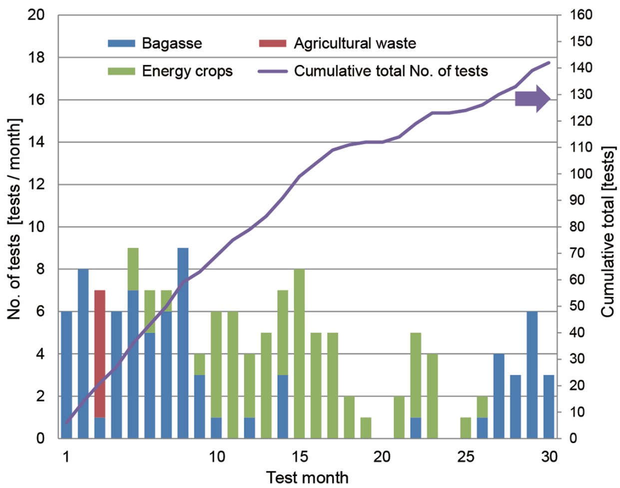

Fig. 5 Monthly number of pilot tests

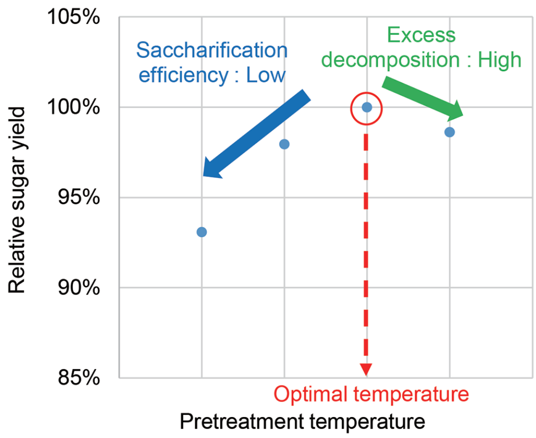

Fig. 6 Relation between pretreatment temperature and sugar yield

Fig. 7 Energy crop after crushing

tion of the material in the pretreatment process can result in the deterioration of the amount of the components (cellulose, hemicellulose), and as a result thereof, the amount of sugar obtained by saccharification is less than that obtained at the optimum intensity. By searching for this pretreatment condition, we achieved an ethanol yield of 304 L/t-dry, which exceeded the target yield even with a small amount of enzyme.

4.1.2 Measures to improve ethanol yield from energy crop

We also searched for the optimal pretreatment condition for the energy crop as in the case of the bagasse in the preceding section. However, the target ethanol yield of 250 L/t-dry could not be achieved by simply changing the pretreatment intensity. Therefore, with the aim of improving the ethanol yield, we employed two measures: (1) improvement of the sugar yield from the pretreated material, and (2) recovery of free sugar.

In (1) aiming for improvement of the sugar yield, we first focused our attention on the physical characteristics of the materials. Since the sugarcane bagasse shown in Fig. 2 passed through the squeezer four to five times in the sugar-making process, fibers have been loosened while the energy crop fibers after crushing are not loosened (**Fig. 7**). Based on this, we presumed that there is a problem with the uniformity of the sulfuric acid in the pretreatment process in the case of energy crop, and we decided to provide a process of soaking in sulfuric acid in advance. **Figure 8** shows a comparison of the sugar yields between with and without the soaking process. As shown in the graph, a 22% improvement in sugar yield was achieved by adding the soaking process.

As for the second improvement measure, we also tackled (2) free sugar recovery. Free sugar is a general term for the sugar contained in the squeezed sugarcane liquid and/or fruit juice, and can be used as the material for ethanol fermentation without going through the saccharification process. Free sugar is also contained in a certain amount in the herbaceous biomass,[5)] and as a result of a component analysis, it was found that it is also contained in the energy crop used by Nippon Steel Engineering in the pilot test. Since the free sugar is excessively decomposed in the pretreatment process, it is important to recover it before the pretreatment process. In the pilot test, as a result of adding a free sugar recovery process to the feedstock preparation process for crushing and washing, it became possible to increase the production of ethanol by 38 L/t-dry. By examining the operating condition including (1) and (2), the ethanol yield from the energy crop became 282 L/t-dry, achieving the target of above 250 L/t-dry.

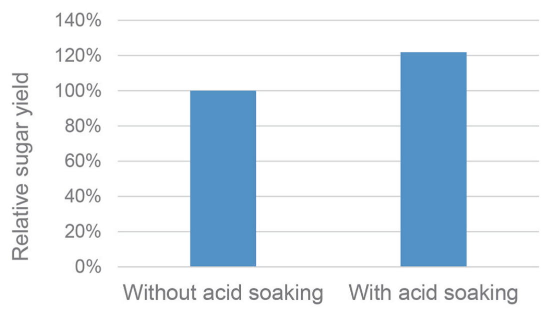

Fig. 8 Difference of sugar yield with or without soaking process

4.2 To achieve 15-day continuous operation of pretreatment equipment

Since, in Nippon Steel Engineering's ethanol production process, the saccharification and fermentation process is of the batch type, the number of days of continuous operation in the pretreatment process determines the number of working days of the entire plant. Furthermore, it became clear that: when the planned plant shutdown like the boiler maintenance is taken into consideration, the 15-day continuous operation of the pretreatment equipment will secure the working days required by a commercial plant. From this, the continuous operation of 15 days was targeted in the pilot test. In addition, the achievement of the continuous operation was evaluated based on: (1) no operation stoppage due to equipment factors in the pretreatment process, and (2) no change in the properties of the pretreated material during continuous operation.

With respect to (1) operation stoppage due to the equipment stoppage of the pretreatment process, the accumulations of the biomass in the pretreatment equipment were of most concern. **Figure 9** shows the schematic drawing of the pretreatment equipment.

The pretreatment equipment transfers the biomass at a constant speed in the steam-saturated atmosphere. Therefore, once a biomass accumulation takes place, the stoppage of the transfer motor due to an overload becomes a concern. However, in the actual continuous operation, although the equipment was compelled to stop and could not be fully continuous due to power shutdown, exchange of consumables, and problems in the subsequent process, the operational stoppage due to equipment problems like the overload of the motor did not occur, and though not fully continuous, an operation of 15 days in total was achieved.

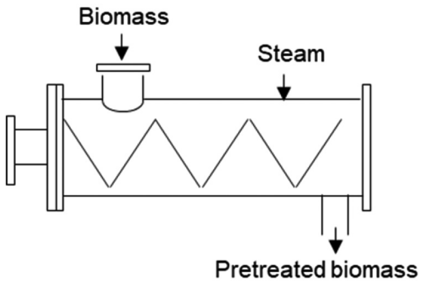

Fig. 9 Pretreatment equipment

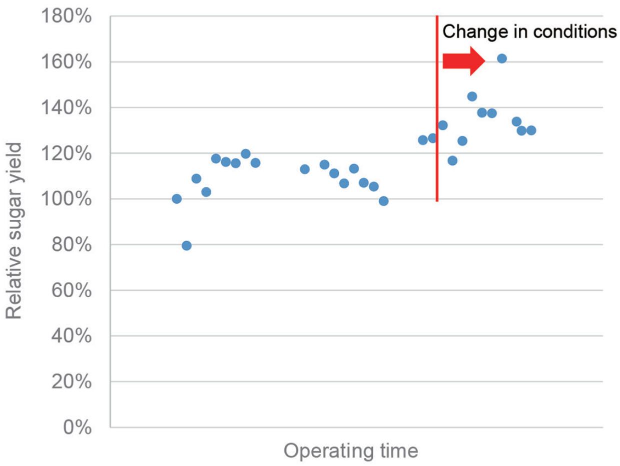

Fig. 10 Time course of sugar yield

With respect to the change of the material properties during the continuous operation as referred to in (2), the hourly timewise change of the pretreated material properties was checked by the laboratory saccharification test, and the time course change of the sugar yield vs. pretreated material was confirmed. **Figure 10** shows the time course change of the sugar yield when the sugar yield in the early stage is 100%.

From this test result, although a change in the sugar yield is observed in the later period of operation due to a change in operation conditions, no time-dependent deterioration of the sugar yield was observed, and there was little change in the pretreated material properties during the continuous operation.

5. Future Prospect

With the completion of this pilot test, the development of Nippon Steel Engineering's cellulosic ethanol production technology was completed. Hereafter, we will promote the commercialization of the technology based on the results obtained in this pilot test, and in parallel with it, we will conduct (1) the study on the expansion of the sphere to which our technology is applicable, and (2) the continuation of the development of the technologies that contribute to the improvement of the economic efficiency of the cellulosic ethanol. An example of such future efforts is shown below.

5.1 Expansion of material type in existing bioethanol plant

As described above, much of the first-generation bioethanol uses sugarcane and corn as the material. Therefore, the material cost is susceptible to the market price. On the other hand however, in many cases, the cellulosic biomass used to remain unused or has limited usages, and the material cost is relatively stabilized. Accordingly, we consider that more ethanol manufacturers will expand the type of materials by adding in part the second-generation bioethanol plant technology to their existing first-generation bioethanol plants. Since, in this way, the utilization and/or sharing of the existing equipment are possible, the initial investment can be lowered as compared with the case of newly constructing a cellulosic bioethanol plant. There are two types of first-generation ethanol plant, one uses the sugar type material, and the other uses the starch type material. Our second-generation ethanol plant technology can be annexed to either of them relatively easily.

5.2 Effective utilization of residue of ethanol

The herbaceous biomass material that Nippon Steel Engineering mainly uses consists of approximately 35% cellulose, 25% hemicellulose, 25% lignin, and 15% others. By going through Nippon Steel Engineering's cellulosic ethanol production process, the cellulose and the hemicellulose in the material are converted to ethanol through saccharification, and the other components such as lignin and others are recovered as the ethanol residue (**Fig. 11**). Accordingly, the ethanol residue contains a large amount of lignin, and the process is advantageous in terms of cost by exploiting the lignin. Furthermore, in Nippon Steel Engineering's process, since the change in the properties of lignin in the ethanol production process is nil, the characteristic of the structure of the lignin contained in the material can be utilized as it is. Lignin has a high calorific value with high ash-melting temperature, and therefore has a high value as fuel. In addition, lignin contains an aromatic structure, is excellent in fire/heat resistance, has high hardness, and is a material applicable to resin and/or chemicals. Nippon Steel Engineering is currently developing the technology for extracting lignin from the ethanol residue (**Fig. 12**), and conducting a search for the usage of lignin. In the present project, we consider that higher cellulosic bioethanol economic efficiency is obtained by converting the lignin that is used simply for the fuel in the ethanol process to a high-value-added re-

Fig. 11 Residue from ethanol production process

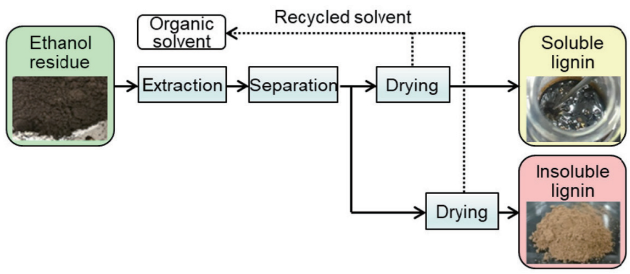

Fig. 12 Technology for extracting lignin

source like the material of chemical products.

5.3 Capture and utilization of CO_2 from fermentation

In the fermentation process that converts sugar to ethanol in the bioethanol production process, carbon dioxide with high concentration (above 95%) of a volume equivalent to that of ethanol is emitted. Therefore, if the carbon dioxide is captured, utilized, converted, or stored, the more the ethanol is produced, the more the carbon dioxide in the air is reduced, and such technology becomes a negative emission technology. Although such technology has a similar concept to that of the Bio Energy with Carbon Capture and Utilization (BECCU) that captures, condenses, and utilizes the carbon dioxide contained in the exhaust gas emitted from a biomass power plant, in the utilization of the carbon dioxide from fermentation, the carbon dioxide condensing process is omitted or alleviated, and our process will become very efficient (**Fig. 13**).

The effect of capturing the carbon dioxide from fermentation is very large from the viewpoint of reducing the global warming gas emissions as indicated by **Fig. 14** that shows the emission of CO_2 per specific calorific value of fuels. Firstly, since gasoline is a fossil fuel, when gasoline is consumed, 84.1 g-CO_2/MJ of carbon dioxide is emitted from the auto exhaust gas, and from oil-well drilling and transportation. On the other hand, in the case that Brazilian sugarcane ethanol is used in Japan, the carbon dioxide emitted when used is taken as carbon neutral, and counted as zero. Therefore, 33.6 g-CO_2/MJ of carbon dioxide produced in sugarcane cultivation, ethanol production, and international transportation is emitted. This corresponds to 40% of the carbon dioxide amount emitted from the use of gasoline, and the reduction of global warming gas from gasoline is calculated as 60%. Furthermore, with respect to the cellulosic ethanol produced in Japan, since by-products are used as the material and international transportation is not required, the carbon dioxide emission amount becomes 6.4 g-CO_2/MJ.[6] In the BECCU process proposed this time, the carbon dioxide from ethanol fermentation is captured and utilized, the carbon dioxide emission amount is further reduced, and if the emission amount is subtracted, the emission amount becomes −30 g-CO_2/MJ. Actually, although the carbon dioxide emitted when capturing and using has to be taken into consideration, CO_2 from fermentation is of high concentration as described earlier, and the load required for the condensation is low and the amount of condensation is limited.

Thus, in ethanol production, the BECCU process that captures and uses CO_2 from fermentation is able to reduce the carbon dioxide gas that already exists in the air, and therefore has high potentiality as a negative emission technology, and it will be an important study subject hereafter.

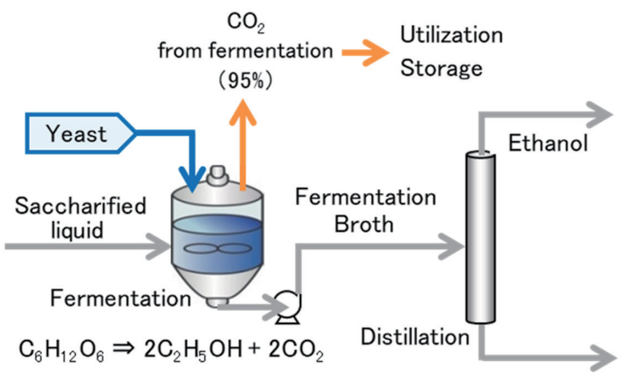

Fig. 13 CO_2 utilization from ethanol fermentation

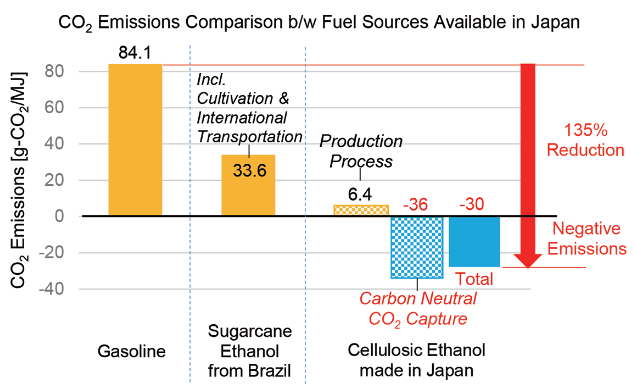

Fig. 14 Negative CO_2 emissions effect of cellulosic ethanol production with BECCU

6. Conclusion

This article described the results of the pilot test and the future prospects with respect to the development of cellulosic ethanol production technology using nonedible biomass.

By using the production technology owned by Nippon Steel Engineering, a high yield of more than 280 L/t-dry was achieved with material either of sugarcane bagasse or energy crop. In addition, through the continuous operation of the pretreatment equipment, we have obtained the possibility of achieving the target commercial plant working days.

Hereafter, by spreading the cellulosic ethanol production technology, we are determined to promote its commercialization so that we can contribute to the solution of various issues such as the prevention of global warming, stabilization of the food price, agricultural industry development, and energy independence in the agricultural countries.

Acknowledgements

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