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 such as grasses, wood, and other non-edible plant material. This is in contrast with first-generation ethanol, which uses food crops as its feedstock and therefore negatively impacts food security and competes with food and feed supplies. So 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 describes the achievements in the pilot test and discusses the future prospects of our process.

1 Introduction

"Bioethanol" is a collective term for ethanol made from biomass as feedstock, and the facts that biomass feedstock is renewable and it absorbs CO2 from the atmosphere as it grows are absolute advantages to achieve environmental sustainability. Therefore, bioethanol has been raising its global interests as a carbon-neutral energy source that does not increase the amount of CO2 in the atmosphere when used as a fuel. In order to mitigate climate change caused by use of fossil fuels, as well as to enhance promotion of the agricultural industry and energy self-sufficiency in agricultural countries, the practical outcomes has been a wider use of fuel blends mandated around the world, e.g. gasoline with 10% ethanol (E10) and with 20% ethanol (E20), and gasoline with 3% ethanol (E3) permitted in Japan. Bioethanol is already a major global industry, with the amount used globally exceeding 100 million kL in 2018. In the U.S. alone, annual production is approx. 60 million kL, meaning that it is produced on a scale that exceeds Japan's annual total gasoline consumption of approx. 51 million kL.

However, current bioethanol is mostly produced with first generation bioethanol production technologies using sugar or starch from edible biomass as feedstock such as corn or sugarcane, which has raised concerns that it is driving up food prices. Hence, it is hoped that the early adoption of the cellulosic ethanol (second-generation ethanol) production technologies that produce bioethanol from non-edible woody and herbaceous biomass in the form of agricultural wastes or energy crops.

Nippon Steel Engineering has previously completed the development of technologies for first-generation bioethanol production and has successfully established a process that uses food waste[1)] and squeezed citrus fruit residue obtained from beverage plants[2)]. In this current year, the company has also successfully developed its own second-generation technology for the production of cellulosic bioethanol (see Table 1).

This paper describes the results of pilot plant testing of the production of cellulosic bioethanol from herbaceous biomass in the Philippines and the prospects for the future.

2 Features of Cellulosic Bioethanol Production

Figure 1 shows a flowchart of the production process for cellulosic bioethanol.

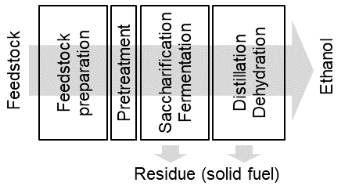

Fig.1 Process flow for biomass-to-ethanol conversion

Table 1 Development history of bioethanol production technologies

	Feedstock		Scale of Pilot/Commercial plants	~	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019
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				

The cellulosic bioethanol production process involves five steps: [1]feedstock preparation, aimed to mainly crush and wash the biomass feedstock, [2] pretreatment, which uses chemical and steam to render the cellulosic biomass for saccharification, [3] saccharification, in which enzymes convert the pretreated biomass into fermentable sugars, [4] fermentation, in which yeast converts the sugars into ethanol, and [5] distillation and dehydration. In addition, the residues generated from saccharification, fermentation, and distillation can be used as a solid fuel for a boiler-turbine-generator set to produce steam and electricity.

[1]Feedstock preparation: As sugarcane bagasse is already ground into small fibrous particles of a few centimeters in length when it leaves the sugar mill (see Fig. 2), it does not require further crushing for use as an ethanol feedstock. Non-food energy crops (see Fig. 3) or agricultural wastes, on the other hand, is delivered with leaves and stalks still intact and therefore needs to be crushed finely at the ethanol plant. The biomass may also collect contaminants such as dust or stones while being stored outside or during collection at the farm. In this step, accordingly, crushing and washing machinery removes such contaminants.

Fig.2 Sugarcane bagasse (Photo)

Fig.3 Energy crop (photo)

[2] Pretreatment: Because the process developed by Nippon Steel Engineering uses herbaceous biomass such as sugarcane bagasse as feedstock, the pretreatment employed a method of steaming with dilute sulfuric acid, which is suitable for herbaceous biomass. As intensity of the pretreatment increases, degradation of biomass is enhanced and the efficiency of the subsequent saccharification increases. The challenge here, however, is that it also incurs excessive degradation and volatilization of the biomass material, hence leads to loss of biomass feedstock amount. Accordingly, Nippon Steel Engineering has identified the feedstock-specific optimal conditions that increase the percentage of material retained and ensure the saccharification rate.

[3] Saccharification: This step converts the cellulose and hemicellulose in the pretreated biomass into sugars (glucose and xylose, respectively) using enzymes (cellulase) as additives. As the enzymes account for a large part of the cost of cellulosic ethanol production, how to maintain the sugar and ethanol yield while reducing the quantity of enzyme additions represents a major challenge. Nippon Steel Engineering has succeeded in reducing enzyme use by optimizing the pretreatment conditions.

[4] Fermentation: This step uses ethanol fermentation yeast to convert the sugars produced in the previous step to ethanol. As the sugars produced from cellulosic biomass include xylose, which cannot be fermented by normal yeasts, Nippon Steel Engineering obtained an improved high-performance yeast from an external yeast developer for use in this process.

[5] Distillation and dehydration: As the concentration of ethanol in the fermentation liquor produced by fermentation is too low for use as fuel, the liquor is concentrated and dehydrated to raise its concentration to the 99.5% or higher standard for fuel-use ethanol.

3 Pilot Plant Trials of Bioethanol Production Technology

In order to complete the development of the company's own technology for cellulosic bioethanol production, we started design and construction of a pilot plant from 2015, and commenced trials in October 2016. Table 2 lists the plant specifications and Figure 4 shows a photograph. Target steps of the pilot plant process includes feedstock preparation (feedstock crushing and washing), pretreatment, saccharification and fermentation, and solid-liquid separation; distillation was eliminated from this pilot trial as an already proven technology.

Table 2 Overview of pilot plant

Feedstock	Herbaceous biomass (sugarcane bagasse, etc.)
Plant capacity	1t-dry/day (dry weight) (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	45m × 35m (approx.)
Location	Philippines

Fig.4 Pilot plant (photo)

Ethanol yields were checked by the measurement of ethanol concentration in the fermented liquor; the fermented liquor was processed as waste after the measurement.

The objectives of the pilot plant trials were to:

[1] Achieve an ethanol yield of 250L/t-dry or better

[2] Achieve 15-day continuous operation of the pretreatment equipment

[3] Collect engineering data for the commercial plant

More than 140 test runs were conducted over a period of 30 months (including two breaks) (see Fig. 5)

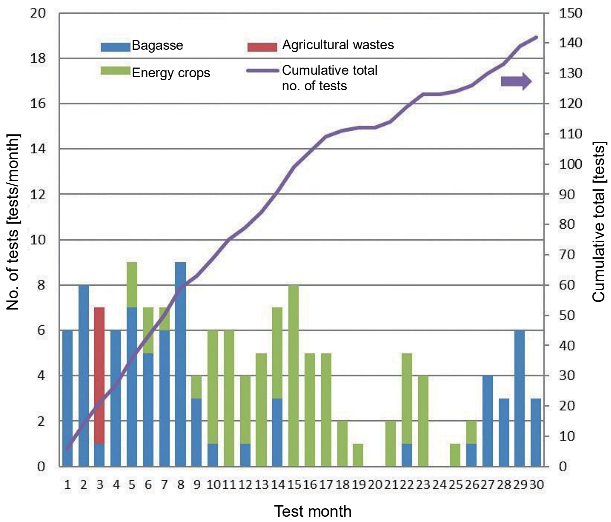

Fig.5 Month-by-month test run frequency

4 Results of Pilot Plant Trials

4.1 Achieving target ethanol yield

4-1-1. Identification of optimal pretreatment conditions for bagasse

Dilute sulfuric acid method for pretreatment, which Nippon Steel Engineering employs, involves the pretreatment intensity (on which biomass degradation effect depends) typically controlled by: [1] the pH of the added sulfuric acid, [2] steaming temperature, and [3] steaming time[3]. To identify the optimal pretreatment conditions, we tested saccharification in lab-scale using various types of biomass samples pretreated in different intensity of pretreatment. Figure 6 shows example results in which the steaming temperature was varied while keeping the pH and steaming time constant. The horizontal axis represents pretreatment temperature and the vertical axis is the sugar yield at each temperature, normalized such that 100% represents the sugar yield at the optimal temperature.

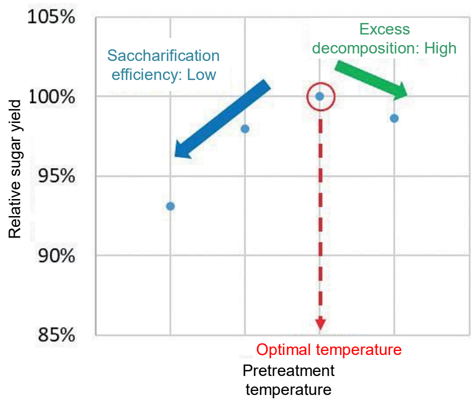

Fig.6 Relationship between pretreatment temperature and sugar yield

When the pretreatment intensity is low (with either a low steaming temperature, a high pH, or a short steaming time) it incurs low efficiency in subsequent saccharification, resulting in the lower amount of sugar yield than that when the intensity is optimal. Likewise, when the pretreatment intensity is high (with either a high steaming temperature, a low pH, or a long steaming time), inevitable excessive degradation of the feedstock incurs reduction of the quantity of cellulose and hemicellulose(substances to be converted into sugars) available for saccharification, also resulting in lower amount of sugar yield than that when the intensity is optimal. Through this investigation process of the optimal pretreatment conditions, we successfully achieved the ethanol yield of 304L/t-dry, even higher than the target yield, while still keeping the enzymes dose at the lowest.

4-1-2. Measures for improving yield of ethanol from energy crops

Although the above method for identifying the ideal pretreatment conditions for bagasse was also applied to energy crops, changes to the pretreatment intensity alone did not succeed in achieving the target ethanol yield of 250L/t-dry. Therefore, in addition to the above method, the following two measures were adopted to improve ethanol yield: [1] increase the amount of sugar from the pretreated biomass, and [2] recover free sugar.

For the first of these, the physical characteristics of the feedstock were examined with the aim of increasing the amount of sugar. As the fibers in sugarcane bagasse shown in Figure 2 can be seen to be loosened, having passed four or five times through presses during sugar milling, this is not the case for energy crops that have undergone crushing (see Fig. 7). Because of this, problems can be foreseen in the case of energy crops with the uniformity of the sulfuric acid in pretreatment and therefore a preceding step in which the biomass is soaked in sulfuric acid was added. Figure 8 shows how the sugar yield changes depending on whether or not soaking is used. As can be seen in the graph, the addition of soaking increased sugar yield by 22%.

Fig.7 Energy crop after crushing (photo)

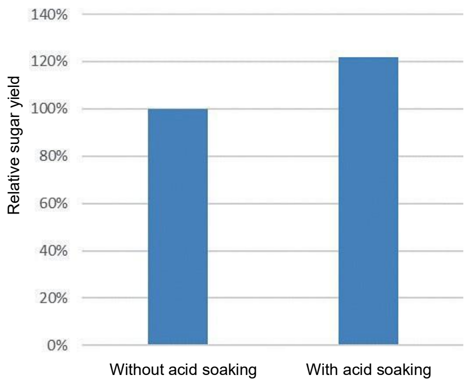

Fig.8 Difference in sugar yield when soaking used

The second improvement measure was the recovery of free sugar. "Free sugar" is the general term for the sugars present in sugarcane or fruit juice. These sugars can be fermented into ethanol without having to first go through a saccharification process. While it is known that a certain amount of free sugar is present in herbaceous biomass[4], analysis of the composition of the energy crops used in Nippon Steel Engineering's pilot plant trials found that these too contained free sugar. As this free sugar decomposes in the pretreatment process, it is important to recover it prior to pretreatment. Adding a step for the recovery of free sugar to the crushing and washing steps of feedstock preparation succeeded in increasing ethanol production by 38L/t-dry.

This work, which encompassed a study of operating conditions that included these two measures, succeeded in achieving an ethanol yield of 282L/t-dry, surpassing the target of 250L/t-dry.

4.2 Achieving 15 days of continuous operation of pretreatment equipment

Nippon Steel Engineering's process for ethanol production uses batch processing for saccharification and fermentation, with the number of plant operating days being determined by how many days it can continuously operate the previous steps, including pretreatment. Then we confirmed that 15 days of a continuous operation of pretreatment can secure the target total operating days for a commercial-scale plant, allowing for the planned shutdowns for regular periodic maintenance of the equipment such as boilers. Hence, we set a target of 15 days for the number of continuous operating days for the pilot plant trials. Furthermore, testing defined continuous operation as: [1] no halts in operation due to problems with the pretreatment equipment, and [2] no change in the quality of the pretreated biomass during continuous operation.

With regard to the first criterion of operational halts caused by pretreatment, the greatest initial concern was of a buildup of biomass inside the equipment. Figure 9 shows a diagram of the pretreatment equipment.

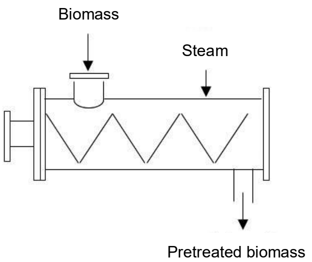

Fig.9 Pretreatment equipment

As the pretreatment equipment works by passing biomass through an atmosphere of saturated steam at a constant rate, the concern was that a buildup of biomass might result in a shutdown due to overloading of the conveyor motors. In practice, however, operation was not truly continuous due to factors such as power outages, halts for the replacement of consumables, or downstream problems, with the result that no shutdowns occurred due to pretreatment equipment such as overloaded motors and the 15 days of continuous operation was achieved.

The second criterion of no change in the quality of the pretreated biomass during continuous operation was assessed by plotting the change in sugar yield over time, with serial laboratory-scale saccharification tests being conducted on the pretreated biomass. Figure 10 shows the results, with a value of 100% representing the sugar yield at the start of continuous operation.

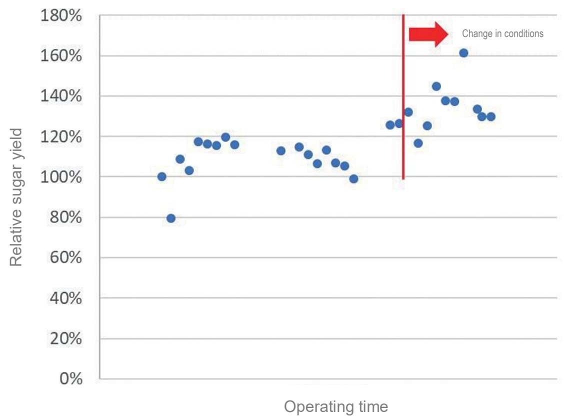

Fig.10 Changes in sugar yield over time

While these test results show variations in sugar yield due to changes in operating conditions in the latter stages of operation, there is no overall decline in yield, indicating that any changes in the quality of the pretreated biomass during continuous operation are minimal.

5 Future Plans

The completion of this pilot plant trial marked the completion of Nippon Steel Engineering's project to develop the technologies for cellulosic bioethanol production. Along with an intention to proceed to commercialization based on the trial results, there are also plans to continue in parallel: [1] investigation on expanding the scope of application of the technologies, and [2] further development to contribute to improving the economics of cellulosic bioethanol. The following are some examples of this work.

5.1 Modifying existing bioethanol plants to accept different feedstock

As noted above, most first-generation bioethanol is made from sugarcane or corn, meaning that the cost of feedstock is highly sensitive to market prices. Cellulosic biomass, on the other hand, is usually obtained from sources that would otherwise go unused or that have limited alternative uses, and as a result feedstock prices tend to be comparatively low and stable. Accordingly, it is anticipated that an increasing number of ethanol producers will retrofit certain second-generation technologies to their existing first-generation bioethanol plants to expand their range of feedstocks. As this approach allows for the shared use of existing plants, it requires less initial investment than a newly built cellulosic bioethanol plant. While first-generation bioethanol plants fall into two categories depending on whether they make ethanol from sugar or starch, the second-generation technology described here is comparatively easy to add in both cases.

5.2 Utilization of ethanol residue

The composition of the herbaceous biomass used here is (approximately) 35% cellulose, 25% hemicellulose, 25% lignin, and 15% other material. The process for cellulosic ethanol production shown in Figure 1 converts the cellulose and hemicellulose in the feedstock first to sugar then to ethanol, and recovers the lignin and other material as the ethanol residue shown in Figure 11. This means that the ethanol residue contains a high proportion of lignin, providing cost advantages in recovering lignin as by-product, compared to recovering from original biomass. Another advantage of our process is that, because there is very little denaturalization of the lignin during this process, the original characteristics of the lignin structures from the feedstock. Lignin has a high value as a fuel due to its high calorific value and high ash melting point. Furthermore, because lignin has resistance to flame and heat as well as good hardness properties, lignin has potential uses as a feedstock for bioplastics or other biochemical products. Nippon Steel Engineering is developing a technique for extracting lignin from ethanol production residue (see Fig. 12) and seeking applications where it can be used. The idea is that the economics of cellulosic bioethanol can be improved further by taking the lignin that under current plans is to be used as a fuel in the ethanol process and transforming it into a chemical feedstock or other product with high added value.

Fig.11 Residue from ethanol production process (photo)

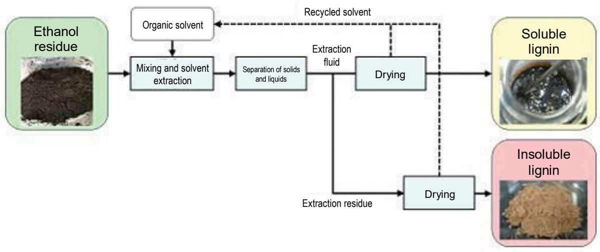

Fig.12 Lignin extraction process

6 Conclusion

This paper has described the results of pilot plant trials and future plans for the development of technology for the production of cellulosic bioethanol from inedible biomass. The production technologies of Nippon Steel Engineering have achieved yields in excess of 280L of ethanol per dry-weight ton of both sugarcane bagasse and energy crop feedstocks in a pilot-scale plant. It was also concluded that the target operating time for a commercial plant could be achieved through the continuous operation of the pretreatment process.

In the future, Nippon Steel Engineering intends to proceed with commercialization with the aim of helping overcome a diverse variety of challenges through the wider adoption of technologies for cellulosic bioethanol production, including preventing global warming, maintaining food price stability, and facilitating agricultural development and energy self-sufficiency in farming nations.

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