Cellulosic ethanol production system – Energy creation from non-food sources

Kawasaki constructed a demonstration plant of bioethanol production in Akita Prefecture in FY2009 and demonstrated its operation until FY2012 under a subsidized project of the Ministry of Agriculture, Forestry and Fisheries. With a view to commercialization, we developed our technologies based on demonstration to produce the bioethanol more economically and make our process compact by increasing the concentration of raw material in hot-water saccharification.

Preface

Resource depletion and global warming caused by CO_2 emissions have been pointed out as the likely scenario of our continued use of fossil fuels, and reducing our reliance on them has become a matter of global concern. On the other hand, in the world of plants, a carbon-neutral system in which carbon circulates without either increasing or decreasing is established. By using plant resources which have such properties as an alternative energy source, we will be able to reduce CO_2 emissions. Ethanol is one such fossil-fuel alternative that has been attracting much attention. In particular, hopes are running high for the practical application of bioethanol that is manufactured from non-food sources.

1 Objective

One of the ways in which non-food biomass resources can be converted into a liquid fuel that is easy to handle is to manufacture ethanol from the cellulose contained in plants. Various methods have been developed to saccharify cellulose—the key element in this approach—including a method that uses sulfuric acid and one that uses enzymes.

With an aim to establish a low-cost manufacturing process for cellulose-derived ethanol to make it sufficiently price competitive, Kawasaki has been developing a saccharification technology that uses hot water instead of sulfuric acid, and a high-efficiency fermentation technology for the resulting saccharification liquid. This approach aims to increase saccharification yield and minimize fermentation inhibition (due to excess decomposition products) by setting the reaction time precisely and preventing the excessive decomposition of sugar. While this approach yields lower saccharification rates than methods using sulfuric acid and enzymes, it will keep down the total cost of manufacturing ethanol, including running costs.

In a joint study conducted with the New Energy and Industrial Technology Development Organization (NEDO) of Japan from FY2006 to FY2008, Kawasaki developed the technology to manufacture ethanol from bagasse, the fibrous matter that remains after crushing sugar cane. Then in the second half of FY2008, Kawasaki constructed a demonstration plant for the production of ethanol from rice straw, and demonstrated its operation until FY2012 under a subsidized project of the Ministry of Agriculture, Forestry and Fisheries (MAFF), in cooperation with Akita Agriculture Public Corporation and the government of Akita Prefecture.

2 Overview of the demonstration of ethanol production technology

In this demonstration project, Kawasaki was responsible for the demonstration of biofuel (ethanol) production and a driving test using the manufactured fuel. The manufacturing facility of biofuel covered the entire process from the reception of the raw material (rice straw) to the production of dehydrated ethanol. Kawasaki was

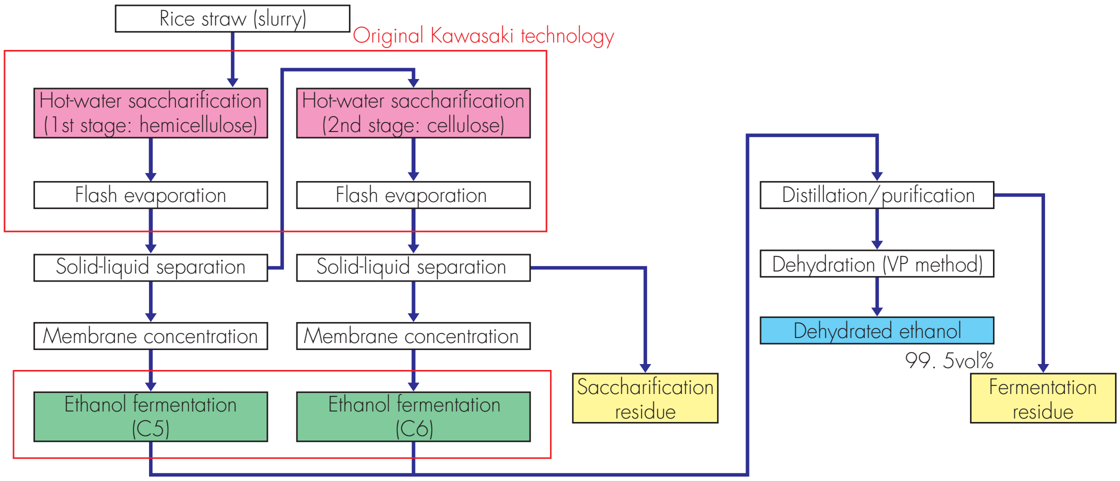

Fig. 1 System flow overview

responsible for the design, construction, and operation of the plant, as well as the demonstration of ethanol production technology and identification of issues to be addressed in commercializing the technology.

(1) Demonstration facility

In FY2009, Kawasaki constructed the facility shown in the photograph above in an industrial park in Katagami City, Akita Prefecture for the demonstration of biofuel production.

The ethanol production flow in this facility is shown in Fig. 1. After receiving rolls of rice straw, they are crushed and slurried, then they undergo saccharification, concentration, fermentation, distillation, and dehydration processes before turning into ethanol.

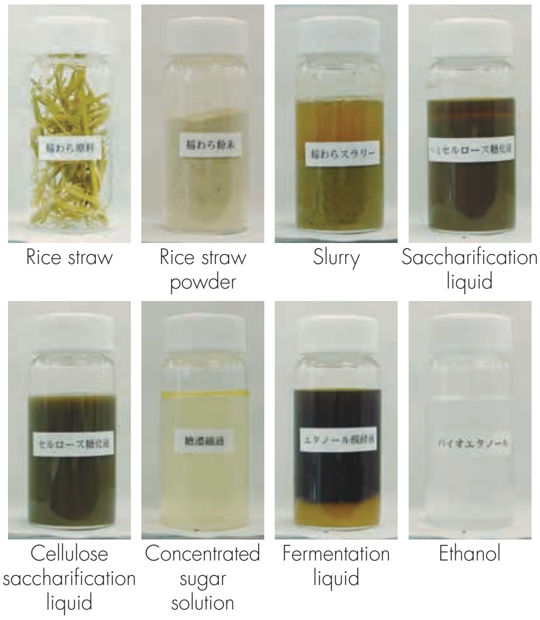
Rice straw
Rice straw powder
Slurry
Saccharification liquid
Cellulose saccharification liquid
Concentrated sugar solution
Fermentation liquid
Ethanol

Fig. 2 Products of each process

A notable characteristic of this facility is that hemicellulose and cellulose—main ingredients of rice straw—are saccharified separately by changing the hot-water condition during the saccharification process. The two types of saccharification liquid obtained are fermented using yeast that has not been genetically modified. Then the fermentation liquids are mixed together and distilled. When the resulting product is dehydrated through vapor permeation (VP) using a zeolite membrane, dehydrated ethanol with a concentration of 99.5 vol% is obtained. Products obtained in each process are shown in Fig. 2.

(2) Hot-water saccharification technology

The hot-water saccharification technology adopted in this facility uses the property of water molecules under high temperature, high pressure conditions to enter into the binding sites of organic macromolecules and break them into smaller molecules in a process called hydrolysis.

As shown in Fig. 3, this system breaks hemicellulose into xylose and xylooligosaccharide in the first stage hot-

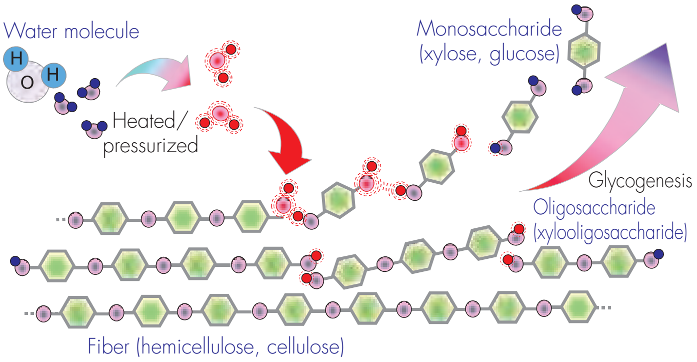

Fig. 3 Concept of saccharification process

water saccharification (150-200 °C, 0.5-1.2 MPa), and cellulose into glucose in the second stage hot-water saccharification (220-260 °C, 2-5 MPa). The saccharification reactor of the demonstration facility employed a shell and tube system in which slurried rice straw is passed through the tubes and heated to a given temperature by applying steam from outside the tubes, then rapidly cooled via flash evaporation.

(3) Fermentation process

In the joint study with NEDO conducted prior to the demonstration operation, a special yeast developed with Kobe University was used for the fermentation process. This microorganism was given the ability to simultaneously convert two types of sugar—xylose and glucose—that are obtained by saccharifying bagasse into ethanol through genetic modification.

Since this genetically-modified yeast could not be used for the demonstration, Kawasaki made improvements to a non-genetically modified yeast for the fermentation of hemicellulose saccharification liquid, which cannot be fermented using the yeast normally used to produce alcohol.

For the base yeast, we used Pichia segobiensis (JCM No. 10740), which has the ability to take up xylose as a nutrient, and improved it using a unique mutant selection method to enhance the ethanol fermentation capability.

As a result, we obtained the mutant strain K5-611⊿ shown in Fig. 4. Fig. 5 shows that the ethanol yield of the mutant strain K5-611⊿ is more than 20 percentage points higher than the yeast (wild strain) before mutant selection was performed.

(4) Results of biofuel production demonstration

The saccharification rate, fermentation efficiency, and manufacturing efficiency obtained in the final year are shown in Table 1. C5 and C6 in the table refer to saccharification liquids obtained from hemicellulose and cellulose, respectively. While the saccharification rate of cellulose was slightly lower than the target value, overall more than 150 liters of ethanol was produced from 1 ton of dry rice straw, demonstrating the effectiveness of Kawasaki's technology.

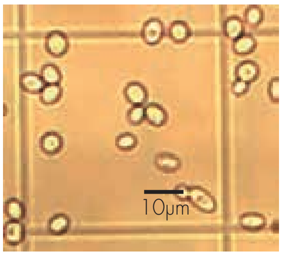

Fig. 4 Mutant strain K5-611⊿

Table 1 Saccharification rate and fermentation efficiency (raw material: rice straw)

Item	Target values	FY2012 results
Hemicellulose saccharification rate (%)	70	70
Cellulose saccharification rate (%)	50	46
C5 fermentation efficiency (%)	70	88
C6 fermentation efficiency (%)	80	91
Manufacturing efficiency* (L/t-dry)	150	153

* Loss from distillation and dehydration not included in manufacturing efficiency

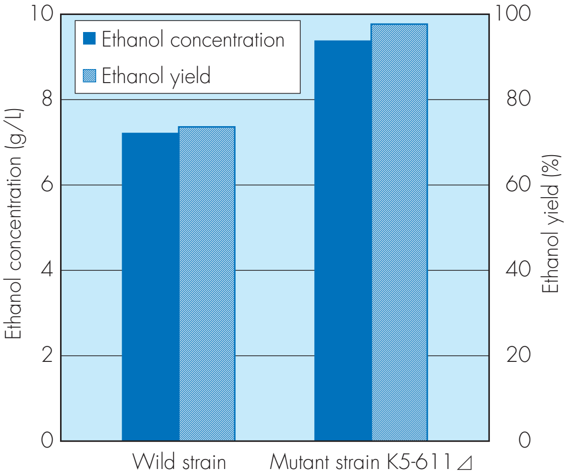

Fig. 5 Fermentation test results

Table 2 Ethanol quality analysis results

Item	Results	JIS standard
Appearance	Colorless	Colorless, transparent
Ethanol content (vol%)	99.8	≧ 99.5
Methanol content (g/L)	1.0	≦ 4.0
Water content (Wt%)	0.35	≦ 0.70
Organic impurities (g/L)	5.6	≦ 10
Electrical conductivity (μS/m)	10	≦ 500
Residue on evaporation (mg/100mL)	0.2	≦ 5.0
Copper content (mg/kg)	< 0.10	≦ 0.10
Acidity (wt%)	0.0031	≦ 0.0070
pHe (reference)	5.2	(*)
Sulfur content (mg/kg)	< 1	≦ 10

* To be agreed between relevant parties

The quality analysis results of the manufactured ethanol are shown in Table 2. The quality of ethanol to be used as automobile fuel is stipulated by the JIS standard. Our manufactured ethanol met this standard.

3 Technological improvements toward commercialization

In the demonstration project performed in Akita Prefecture, we also sought to identify issues that needed to be addressed to realize operation on a larger scale. The biggest issue was reducing facility and running costs, which we aimed to achieve by increasing the concentration of processed materials to enable making the facility smaller. While the concentration of slurry in the hot-water saccharification process was 5% in the demonstration, we were able to raise this to 30% in the component test facility by adopting a high-concentration continuous two-axis paddle system in the saccharification reactor (Table 3). This reduced the facility size and the amount of heat required for heating to one-sixth. As a next step, we are studying a technology to produce enzyme on-site as a way to reduce enzyme costs. In the enzyme method for improving the saccharification rate of cellulose, the high price of enzyme is a major factor that is driving up the cost.

(1) High-concentration processing in hot-water saccharification

When the concentration of processed material is increased, the frequency of contact between the material and hot water decreases, slowing the hydrolysis reaction. As a measure to address this issue, we adopted a two-axis paddle type saccharification reactor (Fig. 6) that is capable of agitation in the vertical direction to enable the material and hot water to come into contact in a uniform manner, and also form a plug flow (in which the material is pushed in one direction to prevent the mixture of material in the back and front) to keep the reaction time constant. This reactor also comes with a self-cleaning function. The saccharification reactor used in the component test facility is shown in Fig. 7.

Table 3 Transition of saccharification reactor

Item	NEDO joint study	Akita-MAFF demonstration facility	Akita component test facility
Development period	2006–2008	2008–2012	2011–2015
System	Medium-concentration batch	Low-concentration continuous	High-concentration continuous
Equipment type	Vertical vessel	Shell & tube	Two-axis paddle
Concentration	5–10%	2–5%	25–30%

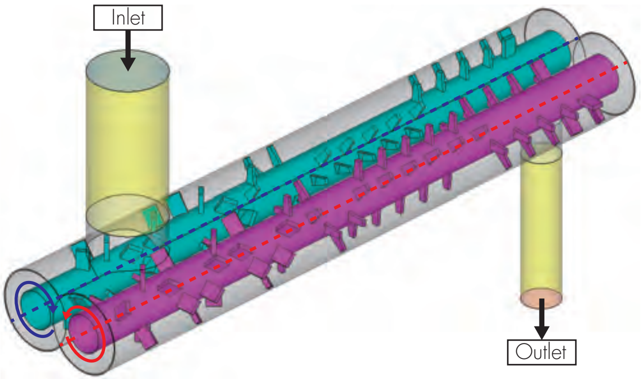

Fig. 6 Schematic diagram of a high-concentration continuous two-axis paddle-type saccharification

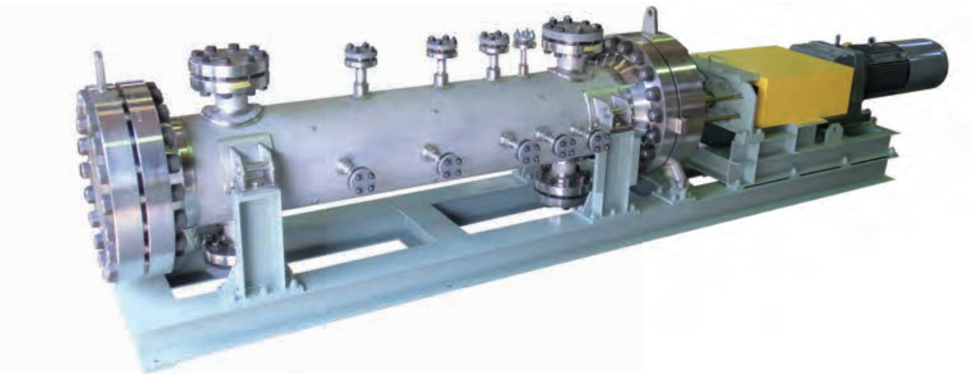

Fig. 7 Saccharification reactor used for the demonstration test in Akita

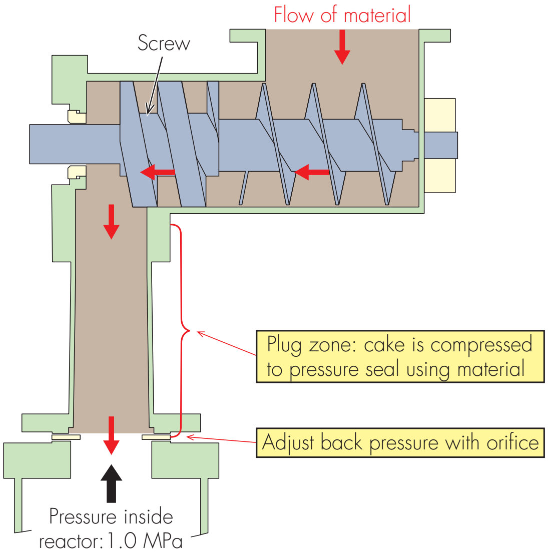

Fig. 8 First-stage plug screw pump for hemicellulose

For feeding material into the high-pressure saccharification reactor, we adopted the plug screw pump shown in Fig. 8. As the material to be fed has high solid-liquid separability, we could not use equipment such as the mohnopump and kneader that used to be employed for feeding high-concentration material. Therefore, we made improvements on a two-axis screw pump (a non-contact positive displacement pump normally used for food applications) and succeeded in pumping the material while it got separated into solid and liquid. Since the solid and liquid are separated while being pumped, the liquid enters the reactor first, followed by the solid. The lower water content causes the material at the inlet of the reactor to be further compressed, serving as a plug that prevents the reflux of high-pressure steam from inside the reactor and enabling continuous feeding.

Table 4 Saccharification and fermentation efficiency (raw material: bagasse)

Item	Target values	C5 hot-water saccharification + C6 hot-water saccharification	C5 hot-water saccharification + C6 enzyme saccharification
Ethanol yield (L/ton-dry)	206	151	242
Saccharification efficiency (%)			
Overall	65	60	72
Hemicellulose	80	80	80
Cellulose	55	50	70
Fermentation efficiency (%)			
Overall	78	60	80
Xylose (C5)	75	60	80
Glucose (C6)	80	60	80

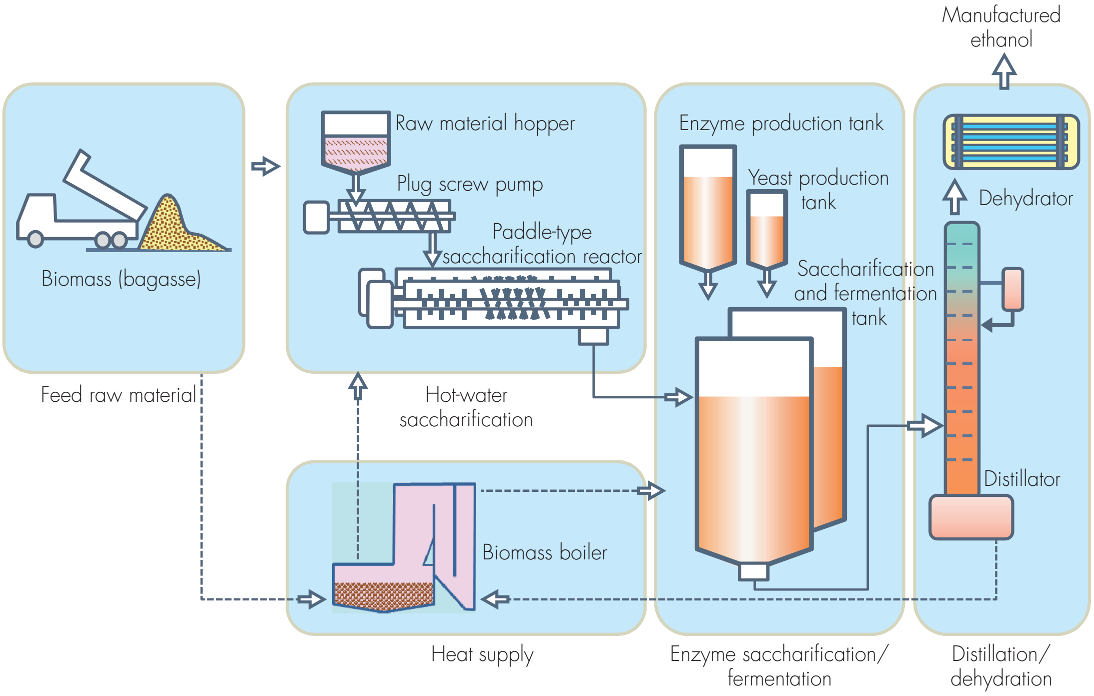

Fig. 9 Outline of cellulosic ethanol production commercial process

(2) High-concentration processing in enzyme saccharification

As for the saccharification of cellulose, there is high demand for enzyme saccharification from users seeking to maximize the ethanol yield per unit of material as shown in Table 4. In response, we are working to improve the enzyme saccharification process that responds to the high-concentration saccharification of hemicellulose mentioned above.

To address the issue of cost with the enzyme method, we have adopted a simultaneous saccharification and fertilization method that can improve the efficiency of enzyme saccharification, and also installed an enzyme production equipment in the ethanol production plant. This will enable the on-site production of enzyme to be directly supplied to the saccharification process without having to purify the solution containing the enzyme, and thus achieve a reduction of enzyme costs (Fig. 9).

Concluding remarks

In the test using the demonstration facility constructed in Akita Prefecture, we consummated the technology for high-concentration saccharification. At present, we are validating the systems for the on-site production of enzyme and simultaneous saccharification and fermentation. We are moving full speed ahead to complete the validation as soon as possible for an early launch of the equipment.

Part of the results of this study has been obtained in the course of the Ministry of Agriculture, Forestry and Fisheries soft cellulose utilization project.


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