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Biomethanol Production and CO_2 Emission Reduction from Forage Grasses, Trees, and Crop Residues

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Abstract

With a wide array of potentially renewable energy resources, the concept and proposed benefits evolving from the use of biofuels are inspiring. Recently, a new approach for gasification of biomass by partial oxidation and subsequent biomethanol production has been developed and is being evaluated at the "Norin Green No. 1 (renamed as Norin Biomass No. 1)" test plant in Nagasaki, Japan. To determine a useful protocol for producing biomethanol, various kinds of biomass resources, such as sawdust and bark of Japanese cedar, chipped Japanese larch, bamboo, salix, cut waste wood from demolition sites, sorghum, and bran, straw, and husks of rice were evaluated for their biofuel-use characteristics. From this analysis, lignocellulosic resources (wood materials) and rice bran were estimated to produce a high methanol yield (55% by weight), whereas rice straw and husks were estimated to produce lower methanol yield of 36% and 39%, respectively. On the basis of the data obtained from the test plant, the net heat yield by the methanol production of a full-scale commercial plant was estimated to be ca. 40%. Each of these products is a clean material, readily obtained and highly useful for biomethanol production. Developing nations interested in constructing a national energy policy should focus upon the establishment of a biofuel-based economy. Recycling of agricultural and forest industry by-products has been previously shown to reduce the demand for fossil fuels and provides a more ecologically friendly energy resource. Our research suggests that additional sources of biomethanol production could be developed through the utilization of cellulosic and lignocellulosic raw materials.

Discipline: Biofuel
Additional key words: biomass, gasification, lignocellulosic material, Norin Green No. 1 test plant, rice

Introduction

More than ten billion tons of fossil fuels (oil equivalent) are annually consumed in the world[5] and these fuels cause acid rain, photochemical smog, and the increase of atmospheric carbon dioxide (CO_2). Researchers warn that the rise in the earth's temperature resulting from increasing atmospheric concentrations of CO_2 is likely to be at least 1ºC and perhaps as much as 4ºC if the CO_2 concentration doubles from pre-industrial levels during the 21st century[1]. A second global problem is the likely depletion of fossil fuels in several decades even though new oil resources are being discovered. To address both of these issues, we need to find alternative fuel resources.

Stabilizing the earth's climate depends on reducing carbon emissions by shifting from fossil fuels to the direct or indirect use of solar energy. Among the latter, utilization of biofuel is most beneficial because, 1) the solar energy that produces biomass is the final sustainable

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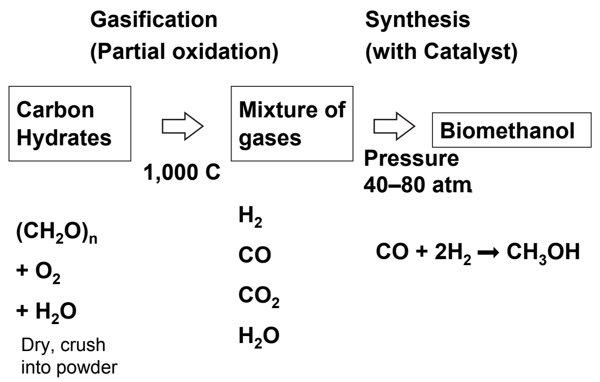

Fig. 1. Principle of methanol synthesis by gasification method (the C1 chemical transformation technology)

energy resource; 2) it reduces atmospheric CO_2 through photosynthesis and carbon sequestration; 3) even though combustion produces CO_2, it does not increase total global CO_2; 4) liquid fuels, especially bioethanol and biomethanol, provide petroleum fuel alternatives for various engines and machines; 5) it can be managed to eliminate output of soot and SO; and 6) in terms of storage, it ranks next to petroleum, and is far easier to store than batteries, natural gas and hydrogen.

Utilization of biomass to date has been very limited and has primarily included burning wood and the production of bioethanol from sugarcane or maize. The necessary raw materials for bioethanol production by fermentation are obtained from crop plants with high sugar or high starch content. Since these crops are primary sources of human nutrition, we cannot use them indiscriminately for biofuel production when the demand for food keeps increasing as global population increases. Recently, a new method of gasification by partial oxidation and production of biomethanol from carbohydrate (Fig. 1) has been developed[6]. This process enables any source of biomass to be used as a raw material for biomethanol production. We report on data obtained from test plants using this new technology for biofuel production from gasification of diverse biomass resources, such as wood materials, forages, and residues of agricultural products.

Materials and methods

Nine types of materials were tested: 1) sawdust of Japanese cedar (*Cryptomeria japonica*); 2) bark of Japanese cedar; 3) chipped Japanese larch (*Larix leptolepis*); 4) bamboo (*Phyllostachys pubescens*); 5) salix (*Salix sachalinensis* and *S. pet-susu*); 6) cut waste wood: sawn wood and demolition waste (raw material for particle board); 7) the plant of sorghum (*Sorghum bicolor*: Sudan-type sorghum hybrid "Chugoku Kou 34"; the plants were harvested at the ripened stage with sickles, cut to a length of 30 cm and dried in a dryer for 7 days at 70ºC); 8) rice bran (*Oryza sativa*: cv. Koshihikari); and 9) straw (cv. Yumehitachi), and husks (cv. Koshihikari) of rice.

Characteristics important for gasification were evaluated for the above materials: 1) Content of water and ash were measured after drying at 107 ± 10ºC for 1 hour and subsequently burning it at 825 ± 10ºC for 1 hour, respectively. 2) Percent carbon (C), hydrogen (H), oxygen (O), nitrogen (N), total sulfur (T-S), and total chloride (T-Cl): C and H weights were estimated by CO_2 and H_2O weight after burning the materials at 1,000 ± 10ºC by adding oxygen; weight of O was calculated by the equation, O = 100 – (C + H + T-S + T-Cl); weight of N was estimated by the amount of ammonia produced by oxidation with sulfur acid to generate ammonium sulfate and following distillation; total sulfur was estimated by SO_2 after burning at 1,350ºC with oxygen; and total chloride was estimated by the water soluble remains after burning with reagent and absorption. 3) Higher heating value was measured by the rise in temperature in water from all the heat generated by burning. Lower heating value was estimated by the calculation, higher heating value – 600 (9h + w)/100 [h: hydrogen content (%); w: water content (%)]. 4) Chemical composition (molecular) of the biomass was determined. 5) Size distribution of the various biomass types was measured (diameter, density of materials [g/ml]. 6) gas yield and generated heat gas were estimated by the process calculation on the basis of chemical composition and heating value. Heat yield or cold gas efficiency was calculated by (total heating value of synthesized gases)/(total heating value of supplied biomass). 7) The weight and calories generated as methanol, given a production boiler capacity of 100 t dry biomass/day, were estimated by the process calculation. The practical methanol yield of crushed waste wood (ca. 1 mm in diameter) produced by ball-mill was also measured by operating "Norin Green No. 1" test plant with a boiler capacity of 240 kg dry biomass/day.

Results and discussion

Water and ash content for the different materials evaluated are shown in Fig. 2. The materials were preserved in different ways, and ranged from 3.4% (wood waste) to 13.1% (bark) moisture. Water content of sorghum was low (4.6%) because this material was dried in a mechanical drier. The other materials were not mechanically dried and the water content averaged ca. 10%. Although individual elements are not reported, the ash content of wood materials, such as sawdust, bark, chip, and bamboo was very low, 0.3% for sawdust, 1.8% for bark, and 2.2% for wood waste. Although the ash content of rice straw and husks was very high (22.6% and 14.6%), probably due to the high Si content of rice plants, the ash content of rice bran was much lower (8.1%). The ash content of sorghum plant was 5.8%.

The percent by weight of some elements in the raw materials is shown in Fig. 3. Carbon content was high in wood materials and averaged 48.3% for wood waste and 51.8% for bark. Rice bran carbon content averaged 48.3% and sorghum carbon content was ca. 45%. Rice straw and rice husks were lower at 36.9 and 40.0%, respectively. Hydrogen content ranged from 4.7 to 7.0% for rice straw and rice bran, respectively. Although rice bran had the highest hydrogen content, the others were only marginally different and the range of wood materials was narrow (from 5.6 to 5.9% for bark and salix, respectively). Oxygen content ranged between 32.5% and 43.9% for rice straw and salix, respectively with wood materials and sorghum in the higher range. Nitrogen content was between 0.12% (sawdust) and 2.44% (rice bran), with wood materials showing low values except for wood waste (1.92%). Nitrogen content of sorghum plant was 0.45%. The content of sulfur was very low in all of the

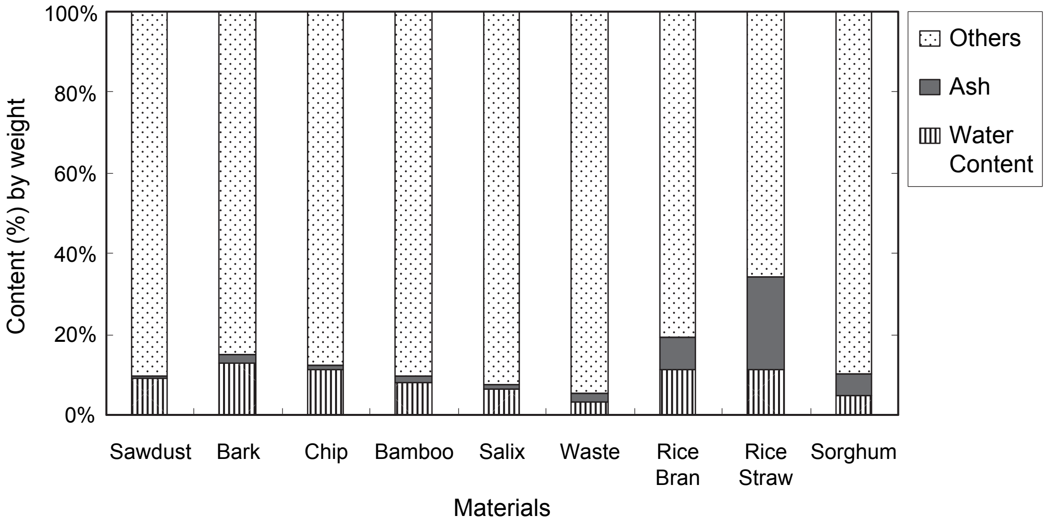

Fig. 2. Content of water and ash in materials
Sawdust: Japanese cedar sawdust, Bark: Japanese cedar bark, Chip: Japanese larch woodchip, Bamboo, Salix, Waste: sawn wood and demolition waste (raw material for particle board), Sorghum: sorghum foliage.

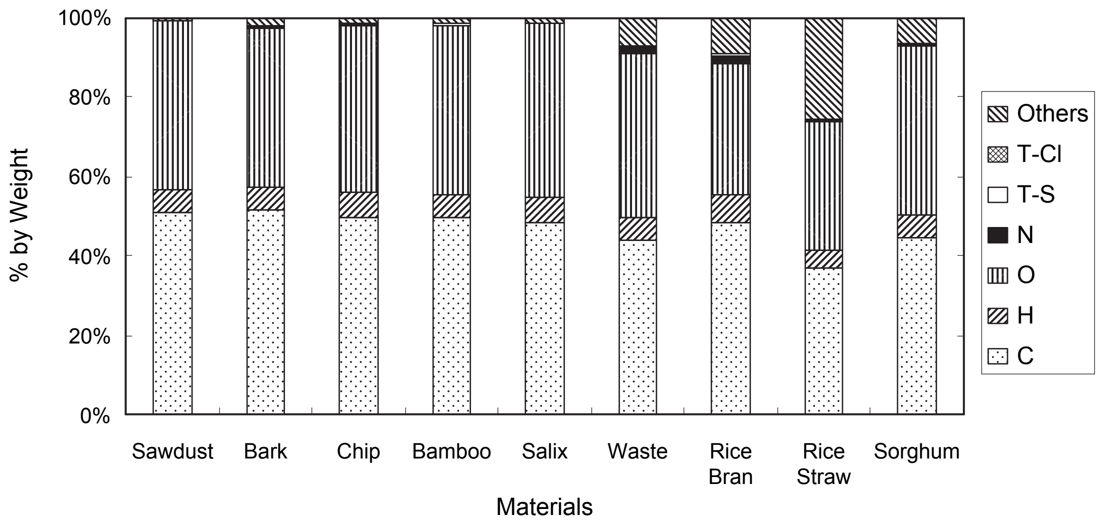

Fig. 3. Content of some elements in materials without water (% by weight)
C: carbon, H: hydrogen, O: oxygen, N: nitrogen, T-S: total sulfur, T-Cl: total chloride.

materials and ranged between 0.02% (sawdust) and 0.22% (rice husks). Chlorine content ranged from 0.01% (sawdust) to 0.41% (rice husk). This data demonstrates that these materials are much cleaner than coal and other fossil fuels. Based on previous experience and data, we expect chemical properties of harvested tropical grasses to be similar to those of sorghum.

Higher and lower heating values of materials are shown in Fig. 4. Among the materials tested, heating values of wood materials were high and ranged between 4,570 kcal/kg (sawdust: higher heating value) and 4,320 kcal/kg (bark). Rice bran was also high (4,520 kcal/kg), although rice straw and husks were at the low end, 3,080 kcal/kg and 3,390 kcal/kg, respectively. Heating value of sorghum plant was intermediate among the materials evaluated and was 3,940 kcal/kg.

Molecular ratios of C, H and O in various materials are shown in Table 1. Most of the materials had similar ratios for $C_nH_2O_m$ (n between 1.28 and 1.54, and m between 0.87 and 0.93) except for rice bran which contains considerable quantities of lipid resulting in n = 1.15 and m = 0.59. The ratio is important since it will affect the condition of gasification when oxygen and vapor are added as gasifying agents.

Estimated volume percent for each gas in the gas mixtures produced from various materials using the gasification by partial oxidation process are shown in Fig. 5. In the mixture of produced gases, contents of hydrogen (H_2) and carbon monoxide (CO) are the most important compounds for methanol production. Although the variation of values is small, H_2 percentage and CO percentage are high in wood materials, ranging from 46.8% for bark, 47.9% for wood waste, 47.3% for salix, and 47.7% for sawdust, respectively. The H_2 percentage of rice straw and husks was the same (44.7%) and CO percentage was 17.1% and 17.3%, respectively. Sorghum H_2 and CO values were intermediate among the materials tested.

The estimated methanol yield by weight and by heating value for each material tested, calculated from the contents of the gas mixtures produced by gasification, is shown in Fig. 6. The values are correlated to carbon con-

Table 1. Molecular ratios of C, H, and O ($C_nH_2O_m$)

Material	C	H	O
Sawdust	1.44	2	0.90
Bark	1.54	2	0.90
Chips	1.39	2	0.88
Bamboo	1.42	2	0.93
Salix	1.38	2	0.93
Waste	1.42	2	0.90
Rice Bran	1.15	2	0.59
Rice straw	1.31	2	0.87
Sorghum foliage	1.28	2	0.93

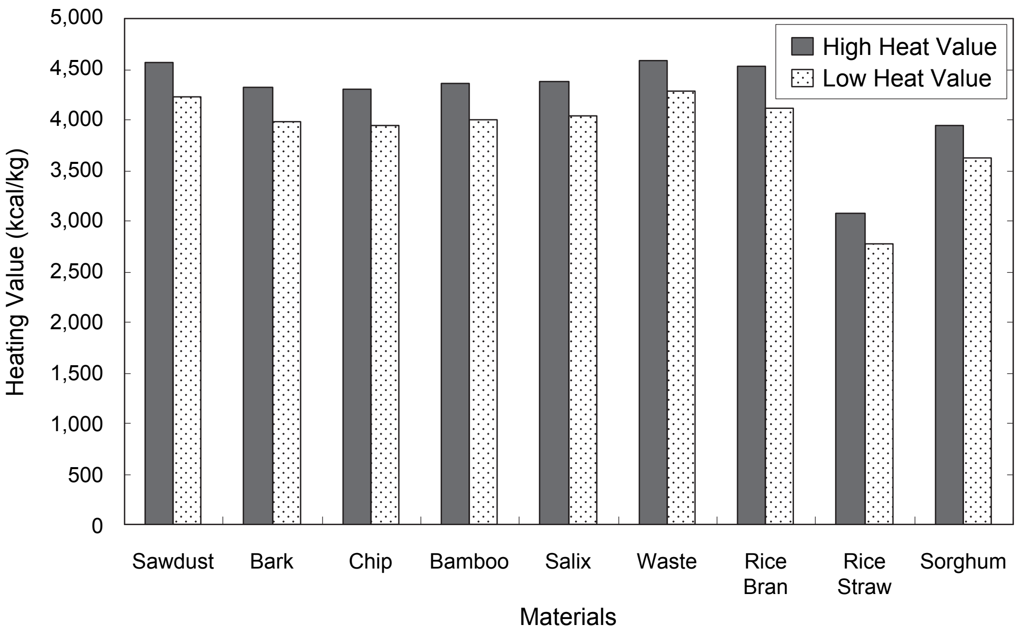

Fig. 4. Higher and lower heating value of materials
Lower heating value = Higher heating value – [(9 × H + water) × 6].

tent and heat emission. Wood materials showed high methanol yield by weight and ranged from ca. 53.0% (salix) to ca. 56.0% (sawdust). Rice bran also demonstrated a high methanol yield potential (ca. 55%) but rice straw and rice husks had considerably lower potentials, ca. 36% and 39%, respectively. Although estimated methanol yield by weight differed among sawdust, rice bran, rice straw, and sorghum, the estimated heat yield of 54–59% by heating value was rather constant in the different materials. Nakagawa et al.[4] showed that methanol yield potential of sorghum grain heads (ca. 48% by dry matter weight), which contain much starch, and sorghum foliage (ca. 44%), which contains much fiber and lignin, were intermediate with little difference between them. These results indicate that significant levels of methanol can be produced without utilizing our high starch and sugar food

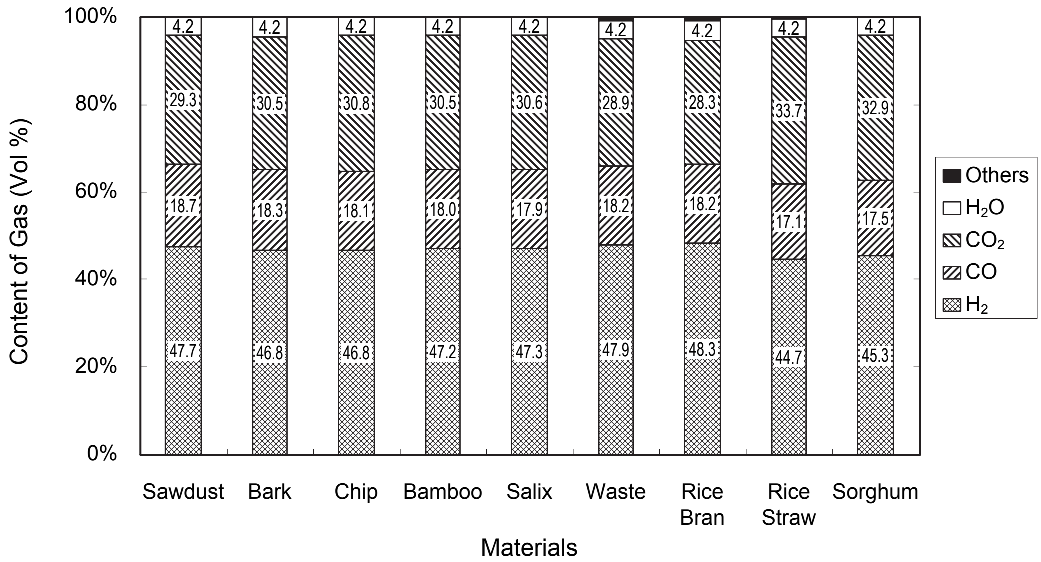

Fig. 5. Mixture of gases by gasification of partial oxidation produced by various materials

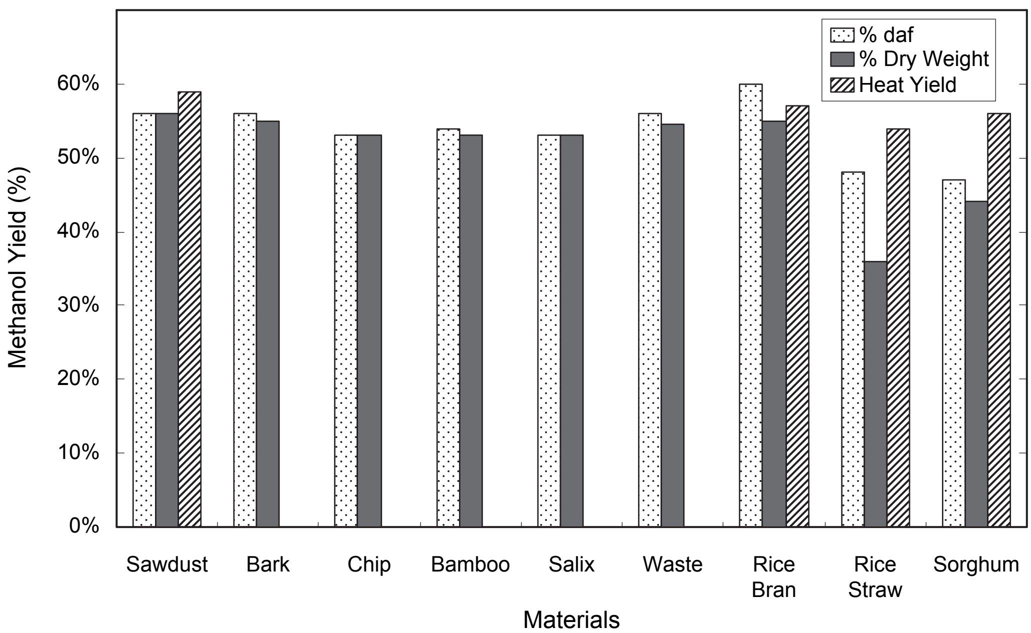

Fig. 6. Methanol yield (weight %) and heat yield of various biomass materials

daf: Percentage of methanol weight to dry biomass weight without dry ash.

sources for biofuel production. Instead, we can utilize the residues of agriculture and forest industries, which were previously cast off or just burnt. Plant breeders do not need to select materials on the basis of material component in biomass but can focus their efforts on biomass quantity. Heat yield of the various materials tested, regardless of their heating values, was high and demonstrate the efficiency of this technology.

For perfect gasification of any biomass materials, it is necessary to convert the materials into powder, ca. 0.1–0.9 mm in diameter (micro-crushing). The physical characteristics of the raw materials and the handling procedures needed to prepare these raw materials for biomethanol production are shown in Table 2. As rice bran is very fine, there was no need for any prior preparation. Although the diameter of sawdust is ca. 0.8 mm, we can utilize it directly for the gasification. Though the rice straw was long, it required only micro-crushing. Sorghum was harvested at the ripened stage with sickles, cut to a length of 5 cm and dried in a dryer. This procedure made this material very hard to process and both rough-crushing (1.0–3.0 mm) and micro-crushing were needed to prepare sorghum for gasification. Usually, a mechanical harvester is used to cut sorghum plants into lengths of less than 10 cm. This latter harvest method will require much less subsequent preparation than was needed in this study.

We developed the test plant, named "Norin Green No. 1 (renamed as "Norin Biomass No. 1", Fig. 7)" to obtain data for methanol yield. The gasification and biomethanol synthesis system is shown in Fig. 8. The test plant comprises of a supplier of crushed biomass, a boiler for gasification, and an apparatus for gas purification and for methanol synthesis by the use of a catalyst. Table 3 shows the capacity of the test plant (the test plant gasifier can process 240 kg/day of dry biomass) when we use crushed waste wood as a raw material and the estimated capacity of a commercial scale plant (a gasifier capable of processing 50–100 t/day of dry biomass). The cold gas efficiency, that is a percentage of [total heating value of synthesized gases by gasification] divided by [total heating value of supplied biomass] of the test plant was from 65 to 70%, and methanol yield was from 9 to 13%. A commercial scale plant would be large enough to maintain critical temperature (900 to 1,000ºC) utilizing the raw materials without the need for additional supplemental heat. Although our data shows that the heat yield of the methanol production is 54–59% (Fig. 6), the net yield of a commercial scale plant after reducing the energy needed for crushing of the biomass (1.0–5.0% of the quantity of heat) and operation of the plant (5–10%), and heat loss from the surface of the boiler (ca. 5%), however, is estimated by simulation using the test plant data to be ca. 40%. A larger pilot plant utilizing the same gasification technology and capable of processing 2 t/day has been developed in Japan and similar trials are currently underway. Methanol yield of this larger pilot plant has been ca. 20% by weight so far (personal communication), which supports our simulation data.

Table 2. Size and handling characteristics of various materials

Biomass	Size (mm)		Density (g/ml)	Handling Characteristics
	Diameter	Length		
Bran	0.31	–	0.31	No micro-crushing needed
Straw	3.0–4.0	400	–	Micro-crushing needed
Husk	2.05	–	0.11	Micro-crushing needed
Sawdust	0.78	–	0.07	No micro-crushing needed
Sorghum	7.9	50	0.07	Rough- and micro-crushing needed

Table 3. Objective ability of methanol production from crushed waste wood: test plant and practical plant

Item	Test Plant	Practical Plant
Boiler Size (Dry biomass to be processed)	240 kg/day	100 t/day
Yield (Heating value %)	65–70%	75–80%
Methanol Yield	9–13%	38–50%

Yield (Heating value %) = Gas mixture produced / Raw material.
Yield (Weight %) = Methanol produced / Dry weight of raw material.

Fig. 7. "Norin Green No. 1", a pilot plant of biomethanol production (MAFF and Mitsubishi Heavy Industries)
Gasifier: 1) Capacity: 240 kg-biomass/day, 2) Type: entrained flow gasification, 3) Gasifying agent: oxygen and steam, 4) Pressure and temperature: normal pressure at 750–1,100ºC.
Methanol synthesis devise: 1) Capacity: equivalent to 20 kg-biomass/day, 2) Type: catalyst type, 3) Pressure and temperature: 30 kg/cm^{2}g at 180–250ºC.

Conclusion

As a result of population growth, the impact of climate change on food production, and other factors, we may be facing not merely an energy crisis but an age of food crisis as well. Therefore, it is extremely important to stress that biofuel production from biomass should not compete with food production.

This study demonstrates that the practical oxidation reaction during gasification of readily available biomass materials could be optimized for methanol production, yielding ca. 40 to 60% of dry weight. This opens the way to utilization of a wide range of harvested plant material low in sugar and starch, including byproducts of other processing operations such as sawdust, bran, straw and husks of rice. Sawdust, rice bran and rice husks are particularly attractive biofuel resources since factories already produce large quantities.

The potentially positive economic impact of biomethanol production on Japanese farming and social systems from planting grasses and trees in unutilized land is immense[2,3]. Reduced CO_2 emissions, recycling of abandoned upland and paddy field and woodland in mountainous areas, and recycling of wastes of agricultural products

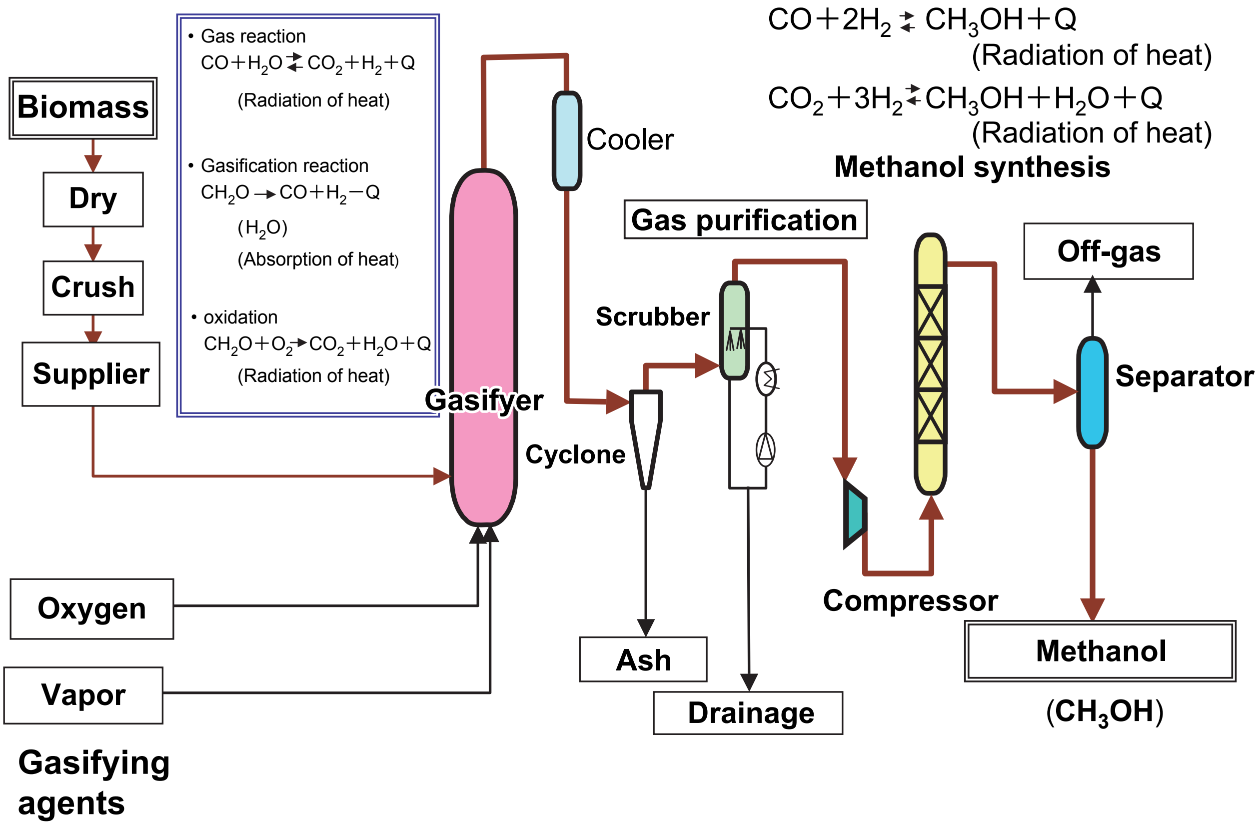

Fig. 8. Biomethanol synthesis system

would all be possible by promoting biofuel production systems based on this new method of gasification. This technology is particularly attractive since biomethanol can be produced from a wide range of biomass raw materials.

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