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Biomethanol Production from Forage Grasses, Trees, and Crop Residues

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1. Introduction

About 12 billion tons of fossil fuels (oil equivalent) are consumed in the world in 2007 (OECD 2010) and these fuels influence the production of 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 1°C and perhaps as much as 4°C if the CO_2 concentration doubles from pre-industrial levels during the 21st century (Brown *et al.* 2000). A second global problem is the likely depletion of fossil fuels in several decades even though new oil resources are being discovered. To address these issues, we need to identify 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 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_x; and 6) in terms of storage, it ranks second 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 in Brazil or maize in the USA. 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

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demand for food keeps increasing as global population increases. Although fermentation of lignocellulosic materials, such as wood of poplar (*Populus* spp.) (Wyman *et al.* 2009), switchgrass (*Panicum virgatum*) (Keshwani and Cheng 2009) and Miscanthus (*Miscanthus* spp.) (Sørensen *et al.* 2008), straw of rice (*Oryza sativa*) (Binod 2010), old trunks of oil palm (*Elaeis guineensis*) (Kosugi *et al.* 2010) are being attempted by improving pre-treatment of the materials, yeast and enzymes, establishment of the technology with low cost and high ethanol yield will be required. Recently, a new method of gasification by partial oxidation and production of biomethanol from carbohydrate resources has been developed (Sakai 2001). This process enables any source of biomass to be used as a raw material for biomethanol production. We report on the estimated gas mixture and methanol yield using this new technology for biofuel production from gasification of diverse biomass resources, such as wood, forages, and crop residues etc. Data obtained from test plant operation is also provided.

2. Gasification technology and the test plants

The idea and technology of gasification systems that generate soot and tar is not new. Our methods of gasification technology through partial oxidation and implementation of a new high calorie gasification technology, has been developed focusing on the perfect gasification at 900-1,000°C without the production of soot and tar. The result of these technologies is the production of a superior mixture of biogases for producing liquid biofuels through thermo-chemical reaction with Zn/Cu-based catalyst or electricity through generator. The first test plant, named "Norin Green No. 1 (the "Norin" means Ministry of Agriculture, Forestry and Fisheries in Japanese; later renamed as "Norin Biomass No. 1")" was completed on April 18, 2002 and second plant with a new high calorie gasification technology, named "Norin Biomass No. 3" was completed in March in 2004.

2.1 Gasification technology of partial oxidation

Figure 1 shows the concept of our new method of gasification by partial oxidation. This production of biomethanol from carbohydrate (Sakai 2001) has been given the term "C1
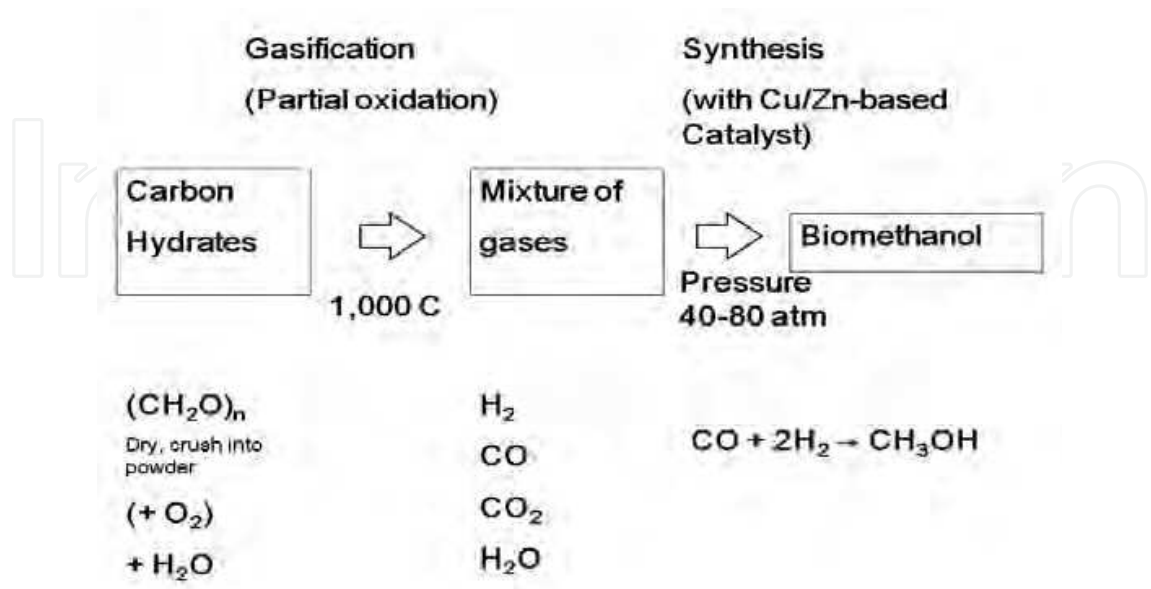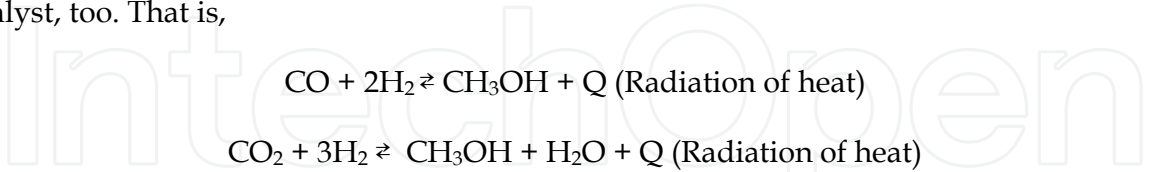

Fig. 1. Principle of methanol synthesis by gasification method (the C1 chemical transformation technology)

chemical transformation technology". In this process, the biomass feedstock must be dried and crushed into powder (ca. 1mm in diameter). When the crushed materials are gasified at 900-1000°C with gasifying agent (steam and oxygen), all carbohydrates are transformed to hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and vapor (H_2O). The mixture of gases is readily utilized for generating electricity. The mixture of gases is transformed by thermo-chemical reaction to biomethanol under pressure (40-80 atm) with Cu/Zn-based catalyst, too. That is,

$$CO + 2H_2 \rightleftarrows CH_3OH + Q \text{ (Radiation of heat)}$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O + Q \text{ (Radiation of heat)}$$

All the ash contained in the materials is collected in the process (Fig. 2). This process enables any source of biomass to be used as a raw material for biomethanol production.
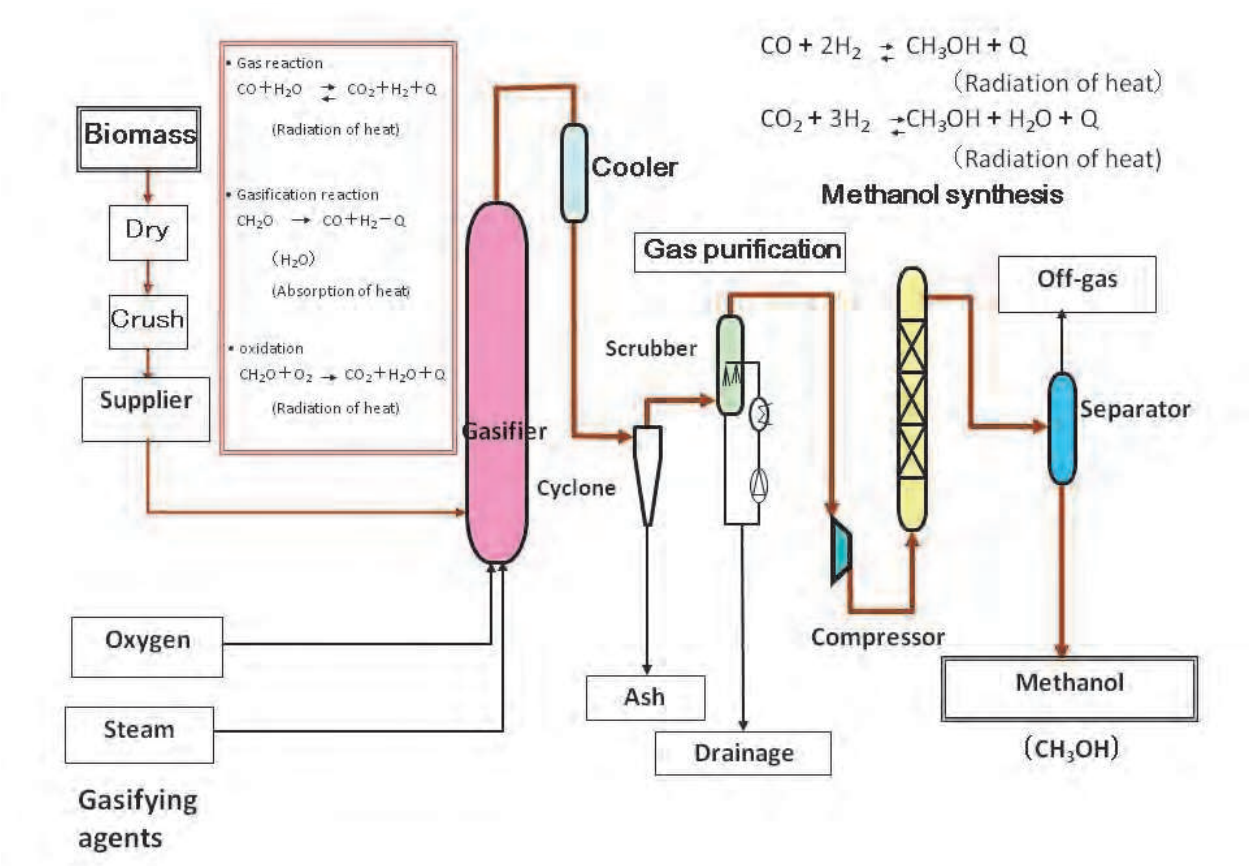

Fig. 2. Gasification and biomethanol synthesis system (Nakagawa *et al*. 2007)

2.1.1 Materials and methods
Twenty materials were tested: 1) sawdust (wood of Japanese cedar (*Cryptomeria japonica*), without bark, was isolated by passing through a 2 mm mesh sieve); 2) rice bran (*Oryza sativa*: cv. Koshihikari); 3) rice straw (cv. Yumehitachi: only the inflorescences are harvested in September and the plants were left in the field until cutting in December); 4) rice husks (cv. Koshihikari: rice was threshed in October and kept in plastic bags following typical

post-harvest practices); 5) sorghum heads (*Sorghum bicolor*: var. Chugoku Kou 34 (medium maturing hybrid line between a male sterile grain sorghum line and sudangrass; with mature seeds at ripened stage); 6) leaf and stem of sorghum (*ibid.*; at ripened stage, cut to a length of 30 cm and dried in a dryer for 7 days at 70°C); 7) total plant of sorghum (*ibid.*); 8) sorghum (cv. Kazetachi; extremely late maturing dwarf type; before flowering); 9) sorghum (cv. Ultra sorgo; late maturing tall type; heading stage); 10) sorghum (cv. Green A; medium maturing hybrid between sudangrass and grain sorghum; heading stage); 11) sorghum (cv. Big Sugar: late maturing tall sweet sorghum: milk-ripe stage); 12) guineagrass (*Panicum maximum* cv. Natsukaze ; heading stage); 13) rye (*Secale cereale* cv. Haru-ichiban; heading stage); 14) Japanese lawngrass (*Zoysia japonica* cv. Asamoe; before flowering); 15) *Erianthus* sp. Line NS-1; heading stage; 16) bark of Japanese cedar; 17) chipped Japanese larch (*Larix leptolepis*); 18) bamboo (*Phyllostachys pubescens*); 19) salix (*Salix sachalinensis* and *S. pet-susu*); 20) cut waste wood: sawn wood and demolition waste (raw material for particle board).

Characteristics important for gasification were evaluated for the above materials: 1) Water content and ash were measured following drying at 107 ± 10°C for 1 hour; then followed by combustion at 825 ± 10°C for 1 hour; 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 combustion at 1,000 ± 10°C by adding oxygen. The estimate of O was calculated by the equation, O = 100 – (C + H + T-S + T-Cl); estimates of N were determined by the amount of ammonia produced by oxidation with sulfuric acid to generate ammonium sulfate. Following distillation, total sulfur was estimated by SO_2 following combustion at 1,350°C with oxygen. Total chloride was estimated by the water soluble remains following combustion with reagent and absorption of the gas; 3) The higher heating values were measured by the rise in temperature in water from all the heat generated through combustion. The lower heating value was estimated by the calculation (the higher heating value – (9×h+w)×5.9) [h: hydrogen content (%); w: water content (%)]; 4) Chemical composition (molecular) of the biomass was calculated based on molecular weight of the elements; 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 the 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 gasifier capacity of 100 tons dry biomass/day, were estimated by the process calculation. These data were obtained in different years.

2.1.2 Results and discussion

Water and ash content for some materials evaluated are shown in Fig. 3. The materials were prepared in various ways. Water contents ranged from 3.4% (wood waste) to 13.1% (bark). 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 are shown in Fig. 4 and Table 1. Carbon content was high in wood materials and averaged 48.3% for wood waste and 51.8% for bark. Rice bran carbon content was 48.3% and sorghum carbon content was ca.

45%. Carbon content of rice straw and husks were lower at 36.9 and 40.0%, respectively. Four sorghum cultivars with different plant types exhibited a narrow range of carbon content (45.5 - 46.1%). Carbon content of the sorghum heads (with seeds), is higher than leaf and stem of sorghum (with lignin) by 2.3%. Rye, Japanese lawngrass and Erianthus exhibited slightly higher carbon content and guineagrass was at the lower end of the range.
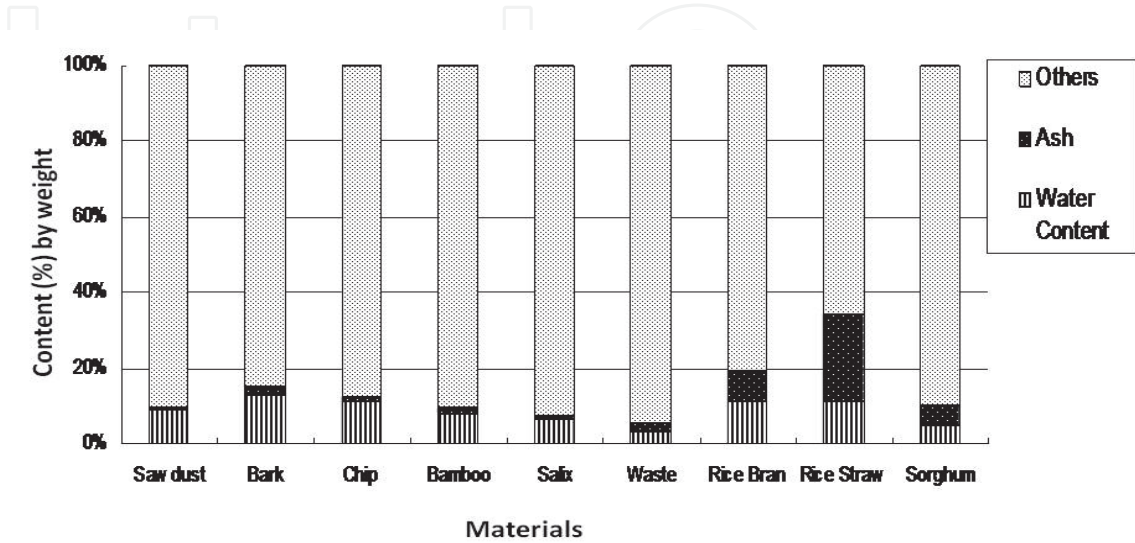
The numbers of materials are same as those in Materials and Methods. Saw dust (1); Bark (16); Chip (17); Bamboo (18); Salix (19); Waste (20); Rice Bran (2); Rice straw (3); sorghum (7).

Fig. 3. Content of water and ash in materials (Nakagawa *et al.* 2007).
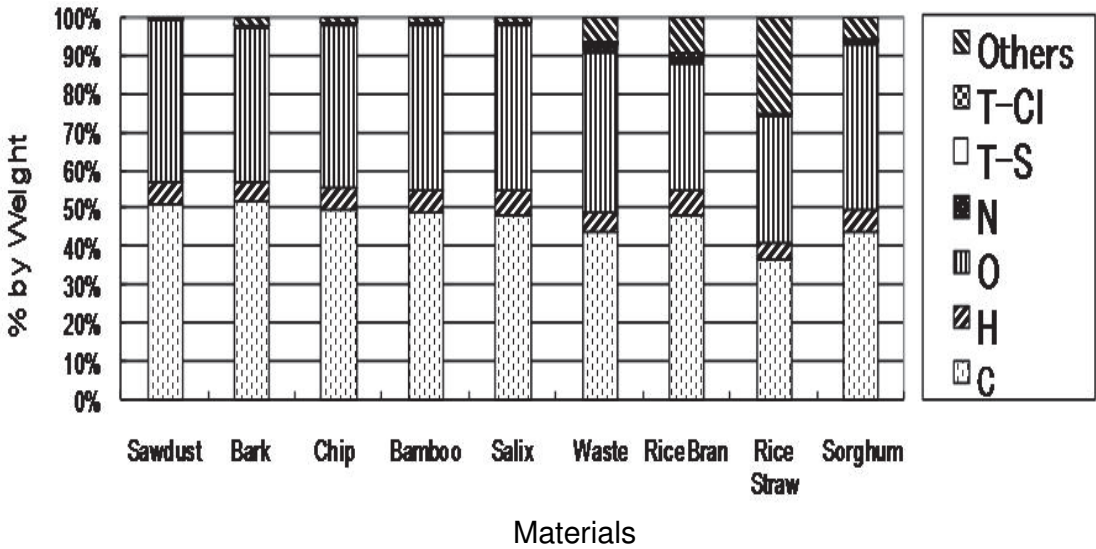
The numbers of materials are same as those in Materials and Methods. C: carbon; H: hydrogen; O: oxygen; N: nitrogen; T-S: total sulfur; T-Cl: total chloride; Saw dust (1); Bark (16); Chip (17); Bamboo (18); Salix (19); Waste (20); Rice Bran (2); Rice straw (3); sorghum (7)

Fig. 4. Content of some elements in materials without water (% by weight) (Nakagawa *et al.* 2007).

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 exhibiting low values except for wood waste (1.92%). Nitrogen contents of sorghum cultivars ranged from 0.80 to 1.30 % and sorghum heads exhibited 1.68%. The sulfur content was very low in all of the materials and ranged between 0.02% (sawdust) and 0.30% (Japanese lawngrass). Chlorine content ranged from 0.01% (sawdust) to 1.31% (rye). These data demonstrates that these materials are much cleaner than coal and other fossil fuels and, we expect chemical properties of harvested tropical grasses to be similar to the grasses used in this report.

| Biomass Materials	C	H	O	N	T-Cl	T-S	Ash
Sawdust (1)	51.1	5.9	42.5	0.12	0.01	0.02	0.3
Rice bran (2)	48.3	7.0	33.0	2.44	0.05	0.21	8.1
Rice straw (3)	36.9	4.7	32.5	0.30	0.08	0.06	22.6
Rice husk (4)	40.0	5.2	37.3	0.76	0.41	0.22	14.6
Sorghum Head(5)	46.7	6.1	40.7	1.68	0.08	0.14	4.3
Leaf and Stem of Sorghum (6)	44.4	5.8	42.9	0.45	0.23	0.15	5.8
Sorghum 'Kazetachi' (8)	45.7	5.8	39.5	1.30	0.78	0.08	6.2
Sorghum 'Ultra sorgo' (9)	45.5	5.7	41.6	0.80	0.79	0.03	5.4
Sorghum 'Green A' (10)	46.1	5.7	40.6	1.20	0.57	0.04	5.5
Sorghum 'Big sugar' (11)	45.9	5.7	41.2	1.00	0.50	0.05	5.4
Guineagrass (12)	42.8	5.4	37.9	1.50	0.89	0.11	10.4
Rye 'Haruichiban' (13)	45.7	5.8	39.2	1.40	1.21	0.07	6.2
Japanese lawngrass 'Asamoe' (14)	46.4	6.1	37.9	2.15	0.43	0.30	6.4
Erianthus sp. Line 'NS-1' (15)	47.1	6.1	42.3	0.80	0	0.22	3.5

C: carbon, H: hydrogen, O: oxygen, N: nitrogen, T-Cl: total chloride, T-S: Total sulfur

Table 1. Content of some elements in dry matter (% by weight). (The numbers of materials are same as those in Materials and Methods)

The higher and lower heating values of materials are shown in Fig. 5 and Table 2. Among the materials tested, the higher heating values of wood materials were high and ranged between 4,570 kcal/kg (sawdust: 19.13 MJ/kg) and 4,320 kcal/kg (bark: 18.08 MJ/kg). Rice bran was also high (4,520 kcal/kg: 18.92 MJ/kg), although rice straw and husks were at the low end, 3,080 kcal/kg (12.89 MJ/kg) and 3,390 kcal/kg (14.19 MJ/kg), respectively. The higher heating value of total sorghum plant of Chugoku Kou 34 was intermediate among the materials evaluated and 3,940 kcal/kg. Sorghum cultivars exhibited mostly similar higher heating value of 17.4 MJ/kg.

Molecular ratios of C, H and O in various materials are shown in Table 3. 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 an n =

1.15 and m = 0.59. This ratio is important since it will affect the condition of gasification when oxygen and steam are added as gasifying agents.
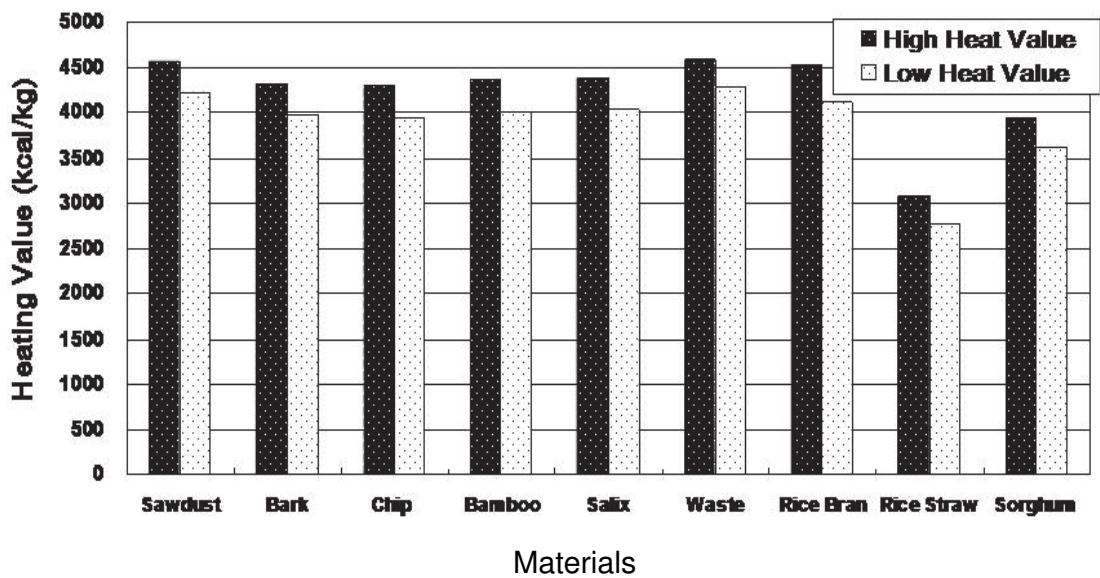
Materials

The numbers of materials are same as those in Materials and Methods. Sawdust (1) ; Bark (16); Chip (17); Bamboo (18); Salix (19); Waste (20); Rice Bran (2); Rice straw (3); sorghum (7)

Fig. 5. Higher and lower heating value of materials (Nakagawa *et al.* 2007).

Biomass Materials	HHV (MJ/kg)	LHV (MJ/kg)
Sawdust (1)	19.13	17.66
Bark of Japanese Cedar (16)	18.08	16.65
Waste Wood (20)	19.08	17.91
Rice Bran (2)	18.92	17.25
Rice Straw (3)	12.89	11.64
Rice Husk (4)	14.19	12.89
Sorghum Head(5)	17.41	15.99
Leaf and Stem of Sorghum (6)	16.49	15.15
Sorghum 'Kazetachi' (8)	17.04	15.56
Sorghum 'Ultra sorgo' (9)	17.50	16.12
Sorghum 'Green A' (10)	17.41	16.03
Sorghum 'Big sugar' (11)	17.45	16.11
Guineagrass (12)	15.82	14.48
Rye 'Haruichiban' (13)	17.58	15.57
Japanese Lawngrass cv. 'Asamoe' (14)	18.59	17.17
Erianthus sp. Line 'NS-1' (15)	18.56	17.16

Table 2. Higher and lower heating value of Materials. (The numbers of materials are same as those in Materials and Methods)

Material	C (n)	H	O (m)
Sawdust (1)	1.44	2	0.90
Bark (16)	1.54	2	0.90
Chips (17)	1.39	2	0.88
Bamboo (18)	1.42	2	0.93
Salix (19)	1.38	2	0.93
Waste (20)	1.42	2	0.90
Rice Bran (2)	1.15	2	0.59
Rice Straw (3)	1.31	2	0.87
Sorghum (7)	1.28	2	0.93

Table 3. Molecular ratios of C, H, O ($C_nH_2O_m$) in the materials (The numbers of materials are same as those in Materials and Methods)

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. 6 and Table 4. 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 across 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, for H_2, and 18.3% for bark, 18.2% for wood waste, 17.9% for salix, and 18.7% for sawdust, respectively, for CO. The H_2 percentage of rice straw and husks was the same (44.7%) and CO percentage was 17.1% and 17.3%, respectively. H_2 and CO values of sorghum were intermediate among these materials tested, and those of sorghum varieties have narrow range such as 46.3-47.0% for H_2 and 17.7-17.8% for CO. Japanese lawngrass and Erianthus exhibited a slightly elevated CO percentage than sorghum and approximated that of the wood materials.
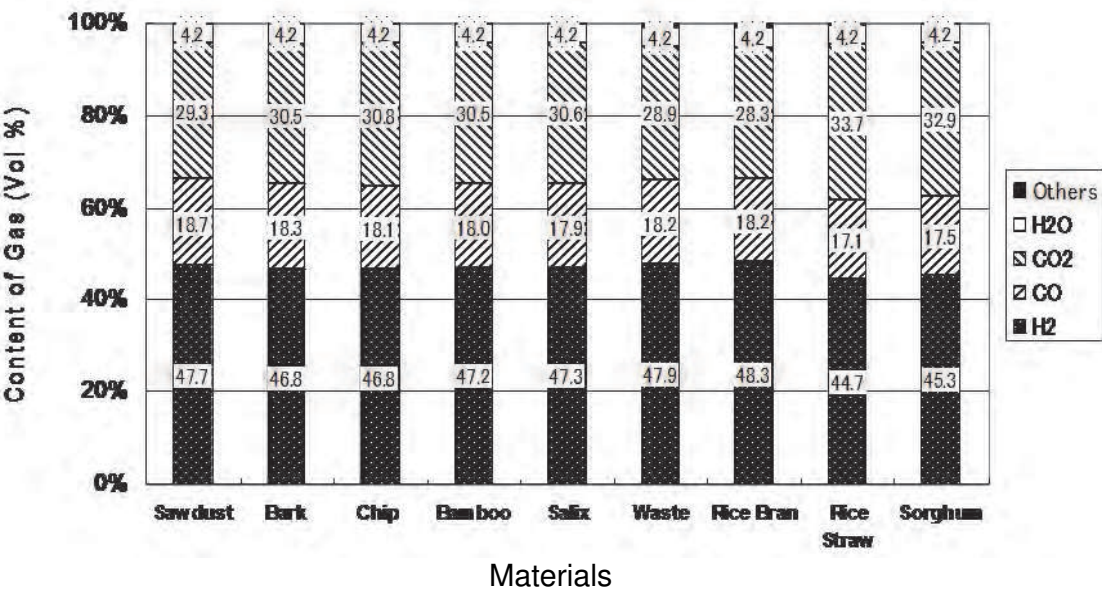
The numbers of materials are same as those in Materials and Methods Sawdust (1) ; Bark (16); Chip (17); Bamboo (18); Salix (19); Waste (20); Rice Bran (2); Rice straw (3); sorghum (7)

Fig. 6. Volume % of H_2, CO, CO_2, H_2O and other gasses produced from some materials (before the entrance to methanol synthetic system) (Nakagawa *et al*. 2007) .

Biomass Materials	H_2 (vol%)	CO (vol%)	CO_2 (vol%)	H_2O (vol%)	HHV (MJ/kg -wet)
Sawdust (1)	47.7	18.7	29.3	4.2	9.54
Rice Bran (2)	48.3	18.2	28.3	4.2	9.67
Rice Straw (3)	44.7	17.1	33.7	4.2	8.25
Rice Husk (4)	44.7	17.3	33.4	4.2	8.29
Sorghum Head (5)	46.1	17.7	31.3	4.2	8.83
Leaf and Stem of Sorghum (6)	45.3	17.5	32.9	4.2	8.50
Sorghum 'Kazetachi' (8)	46.3	17.7	31.1	4.2	8.92
Sorghum 'Ultra sorgo' (9)	47.0	17.7	30.7	4.2	9.13
Sorghum 'Green A' (10)	46.7	17.8	30.8	4.2	9.00
Sorghum 'Big sugar' (11)	46.6	17.7	31.1	4.2	8.96
Guineagrass (12)	46.2	17.7	31.1	4.2	8.92
Rye 'Haruichiban' (13)	46.9	17.8	30.5	4.2	9.13
Japanese Lawngrass 'Asamoe' (14)	47.6	18.0	29.3	4.2	9.00
Erianthus sp. Line 'NS-1' (15)	46.6	18.6	30.3	4.2	8.96

HHV: higher heating value.

Table 4. Composition and higher heating value of product gas derived from biomass gasification for methanol synthesis. (The numbers of materials are same as those in Materials and Methods)

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, are shown in Fig. 7 and Table 5. The values are correlated to carbon content and heat emission. Wood materials exhibited high methanol yield by weight and ranged from 53.0% (salix) to 55.8% (sawdust) based on dry biomass weight. This means that 530 kg and 558 kg of methanol will be produced through the gasification of 1 ton of dry salix and sawdust, respectively. Rice bran also exhibited a high methanol yield potential (ca. 55%) but rice straw and rice husks had considerably lower potentials, 35.8% and 39.4%, respectively. Sorghum varieties with different plant types exhibited similar potentials (ca. 47 - 49%). Interestingly, methanol yield potential of sorghum heads (with starch of the grain) exhibited 48.6% and higher than that of leaf and stem of sorghum (with higher amount of lignin) at the ripening stage (44.1%) but the difference is only 4.5%. This means that there is little difference in methanol yield between starch and lignin. This suggests that there may be little need to utilize food starch resources and competitive methanol yields can be generated through the utilization of crude lignocellulosic materials. This indicates that significant levels of methanol can be produced from previously cast-off residues and byproducts of agriculture and forest industries. Japanese lawngrass and Erianthus exhibited higher methanol yield potentials than sorghum cultivars. Although estimated methanol yield by weight differed among materials, the estimated heat yield of 54 – 59% by heating value was rather constant in the different materials. Heat yield of the various materials tested, regardless of their heating values, was high and demonstrate the efficiency of this technology.
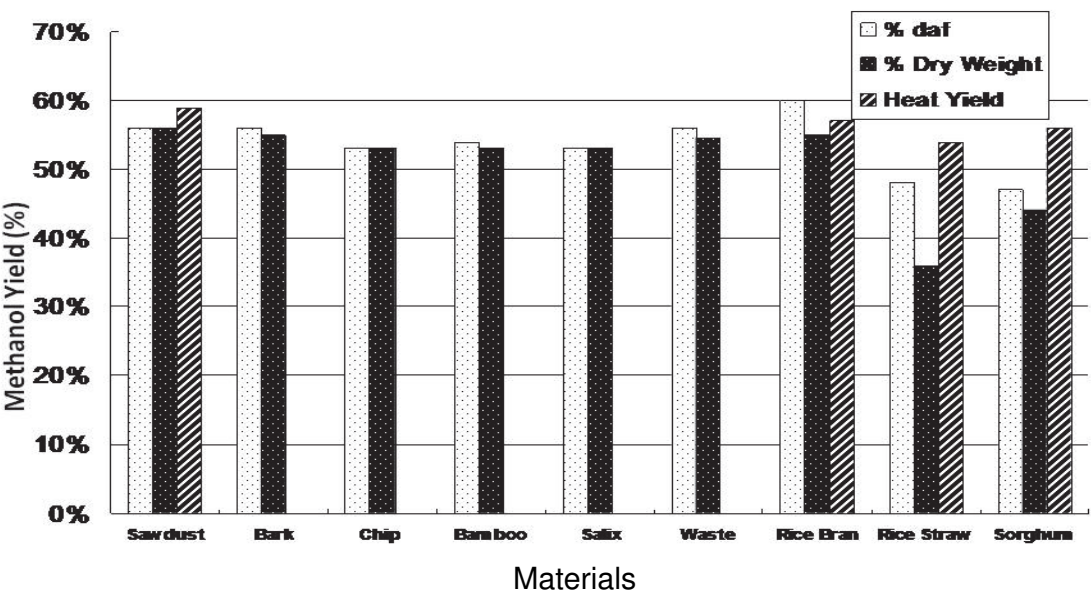
The numbers of materials are same as those in Materials and Methods.Sawdust (1) ; Bark (16); Chip (17); Bamboo (18); Salix (19); Waste (20); Rice Bran (2); Rice straw (3); sorghum (7) daf: percentage of methanol weight to dry biomass weight without ash

Fig. 7. Estimated methanol yield (weight %) and heat yield of various biomass materials (Nakagawa *et al.* 2007).

Biomass Materials	methanol yield	
	daf	dry
Sawdust (1)	56.0	55.8
Rice Bran (2)	60.0	54.5
Rice Straw (3)	48.0	35.8
Rice Husk (4)	47.0	39.4
Sorghum Head (5)	51.0	48.6
Leaf and Stem of Sorghum (6)	47.0	44.1
Sorghum 'Kazetachi' (8)	51.1	47.7
Sorghum 'Ultra sorgo' (9)	51.3	48.4
Sorghum 'Green A' (10)	52.0	49.0
Sorghum 'Big sugar' (11)	51.0	48.1
Guineagrass (12)	51.0	45.2
Rye 'Haruichiban' (13)	55.9	52.2
Japanese Lawngrass 'Asamoe' (14)	55.1	51.4
Erianthus sp. Line 'NS-1' (15)	53.4	51.5

daf: based on dry ash free biomass weight, dry: based on total dry biomass weight with ash

Table 5. Estimated methanol yield (% by weight) (The numbers of materials are same as those in Materials and Methods).

For perfect gasification of any biomass material, it is necessary to convert the materials into ca. 0.1-0.9 mm in diameter powder through 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 6. 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 the powder smaller than ca. 1 mm directly for the gasification. Though the rice straw dried in the field was long in length, it required only micro-crushing without extra-drying in a dryer. Sorghum was harvested at the ripened stage with sickles, cut to a length of 30 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.

Material	Size (mm)		Density	Handling
	Diameter	Length	(g/ml)	Characteristics
Sawdust (1)	0.78	-	0.07	No micro-crushing needed
Rice Bran (2)	0.31	-	0.31	No micro-crushing needed
Rice Straw (3)	3.0-4.0	400	-	Micro-crushing needed
Rice Husk (4)	2.05	-	0.11	Micro-crushing needed
Sorghum head (5)	15.0	250	-	Rough- and micro-crushing needed
Leaf and Stem of Sorghum (6)	20 (width) 0.5 (thickness)	300	-	Rough- and micro-crushing needed
Sorghum (7)	7.9	50	0.07	Rough- and micro-crushing needed

Table 6. Size and handling characteristics of various materials (The numbers of materials are same as those in Materials and Methods) (Nakagawa *et al.*, 2000) .

2.1.3 "Norin Green No. 1" test plant

The test plant, named "Norin Green No. 1" (Fig. 8), was utilized to obtain data for heat yield and methanol yield through the gasification and biomethanol synthesis system shown in Fig. 2. The test plant comprises a supplier of crushed biomass, a gasifier for gasification, and an apparatus for gas purification and methanol synthesis by the use of a Cu/Zn-based catalyst. The practical methanol yield of crushed waste wood (ca. 1 mm in diameter) produced by pin-type-mill was also measured by operating both "Norin Green No. 1" test plant at Nagasaki Research and Development Center, Mitsubishi Heavy Industries ltd. with a gasifier capacity of 240 kg dry biomass/day and another test plant at Kawagoe Power Station of Chubu Electric Power Co., Inc. with a gasifier capacity of 2 t dry biomass/day (Matsumoto *et al.* 2008).

Table 7 indicates the heat yield and methanol yield of the two test plants (the test plant gasifier can process 240 kg/day (Norin Green No. 1 test plant) or 2t/day (a test plant constructed by Chubu Electric Power Co., Inc) of dry biomass) by operating these plants, when crushed waste wood is utilized as a raw material, and the estimated capacity of a commercial scale plant (a gasifier capable of processing 100 t/day of dry biomass). The commercial scale plant would be large enough (larger than 100 t/day) to maintain critical temperature (900 to 1,000°C) within the gasifier by adding the raw materials into the gasifier without the addition of supplemental heat. Our data indicate that the estimated heat yield of

methanol production by commercial scale plants is 54 - 59 % (Fig. 7). However, the real heat 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; biomass feedstock with 2-3 mm in diameter is available), operation of the plant (5 - 10 %), and heat loss from the surface of the gasifier (1-2 %), estimated by simulation using the test plant data will be ca. 40 %.

The cold gas efficiency, that represents a percentage of the total heating value of synthesized gases by gasification divided by the total heating value of supplied biomass of the test plant, varies from 65 to 70% and methanol yield varied from 9 to 13% in the "Norin Green No. 1" test plant. Heat yield and methanol yield of another test plant capable of processing 2 t/day constructed by Chubu Electric Power Co., Inc. with the support of New Energy and Industrial Technology Development Organization (NEDO) Project, has, however, achieved ca. 20% of methanol yield by weight by its operation (Ishii *et al*. 2005; Matsumoto *et al*. 2008; Ogi *et al*. 2008).

Item	Test Plant		Practical Plant
(Gasifier Size: Dry biomass to be processed)	(240kg/day)	(2t/day)	(100t/day)
Heat Yield (Heating Value %)	60-70%	65%	70-75%
Methanol Yield (by weight)	9-13%	20%	40-50%

Table 7. Ability of test plants and estimated practical plant.

2.1.4 Conclusion

The above data indicate that the most important advantage of this technology is that it can utilize any form of biomass feedstock for H_2 and CO generation. The mixture of gases can be utilized as direct burning both for heat and for electricity generation. High yields of methanol will be efficiently produced from the mixture of gases by using a Cu/Zn-based catalyst. The disadvantage of the system is with the size of the processing facility. The larger the plant, the higher the efficiency. The biomethanol yield from a 100 t/day gasifier would be more than twice that of the 2 t/day gasifier from the same raw materials. Although it is feasible to construct a biomethanol plant of this size, it may be very difficult to collect and provide the required 100 dry matter tons of biomass each day for the operation; with the possible exception of large sugarcane mills and palm oil industry in Southeast Asian countries. In addition, required permits and a license of boiler operation to operate such a large-scale gasifier in Japan, would add additional costs.

Prof. Sakai, of the Nagasaki Institute of Applied Science, one of the authors of this report, has developed another type of plant in the university, named "Norin Biomass No. 3" test plant (Fig. 9) by using another gasification technology, called as "high-calorie gasification reaction", that is introduced in the following sentence.

2.2 "Norin Biomass No. 3" test plant

The "Norin Biomass No. 3" Test Plant (Fig. 9, 10), which represents a "Suspension/external heating type" with a boiler (1-2 Dry t/day) was newly developed for improving the disadvantages associated with the "Norin Green No. 1" test plant through the introduction of a new type of gasification called "high-calorie gasification reaction".

Gasifier: entrained-type; processing 240 dry kg/day of biomass
Method: gasification through partial oxidation
Gasifying Agent: O_2, H_2O
Pressure/temp.: Standard pressure/750-1100°C

Methanol Synthesis: processing equivalent to 50 dry kg/day of biomass
Method: Cu/Zn-based catalyst
Pressure/temp.: 3-12 MPa/180-250°C

Fig. 8. "Norin Green No. 1", a test plant of gasification and biomethanol production, located in Nagasaki Research & Development Center, Mitsubishi Heavy Industries ltd, Nagasaki, Japan.

Fig. 9. "Norin Biomass No. 3" test plant located in Sakai Kougyo, ltd., Isahaya City, Nagasaki, Japan.

2.2.1 Essential of the high-calorie gasification reaction

In the high-calorie gasification method, finely crushed biomass of 1-3 mm in diameter is subjected to the gasification reaction together with steam in an atmosphere of 800-1000°C within the reaction tube. At this time, the reaction tube is heated using high-temperature combustion gas that is separately combusted using additional biomass. The introduced biomass raw materials leave only ash, and all organic content is gasified, resulting in a clean, high-calorie gas (ca. 12MJ/Nm³) composed of H_2, CO, CH_4, etc. The basic principle of the technology is illustrated in Fig. 10.
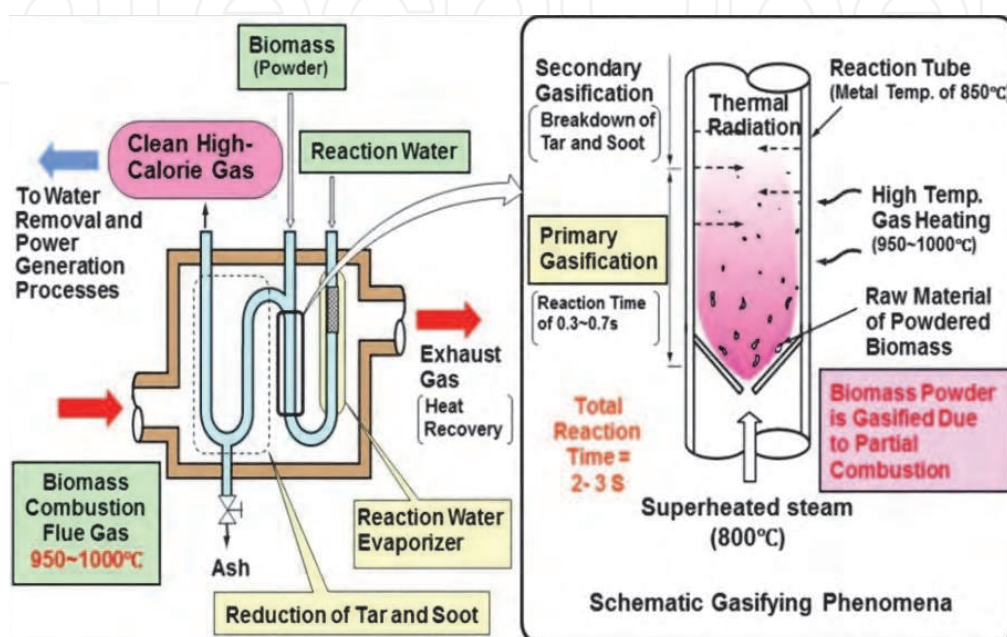
Fig. 10. Suspension/external heating type high-calorie gasification.

The gas composition varies with gasification reaction conditions such as reaction temperature, residence time (reaction time), and the [steam]/[biomass carbon] mode ratio, but an example is represented by the following reaction formula.

(Endothermic reaction)
$C_{1.3}H_2O_{0.9}$ + 0.4 H_2O → $0.8H_2$ + 0.7CO + $0.3CH_4$ + $0.3CO_2$ + 165.9kJ/mol
(Biomass)   (Steam)   (Resulting gas fuel)   (Absorbed heat)
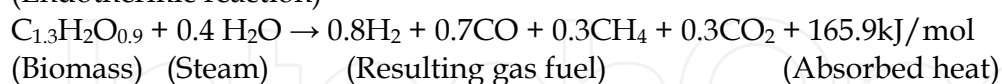
In this process, the total biomass material reacts with steam and is converted to an [H_2, CO, CH_4, CO_2] gas mixture. The application of external heat is required due to the fact that the gasification reaction is endothermic. However, the potential heat stored in the gas mixture generated in the reaction is greater than that contained in the raw biomass material, such that the cold gas efficiency surpasses 100%. In the formula shown above, a figure of ca. 115% is obtained by solving for cold gas efficiency (Ec). On the other hand, the externally supplied heat used in the reaction, is not considered in the calculation of Ec, and the total gasification efficiency is ca. 85% when this external heat is taken into account.

While the previous biomass gasification technology of "Norin Green No. 1" test plant mentioned above uses the partial oxidation technology, this high-calorie gasification technology enables the production of a high-calorie gas fuel that was not possible with the conventional method due to the formation of an exhaust gas. The principle is illustrated in Fig. 11.
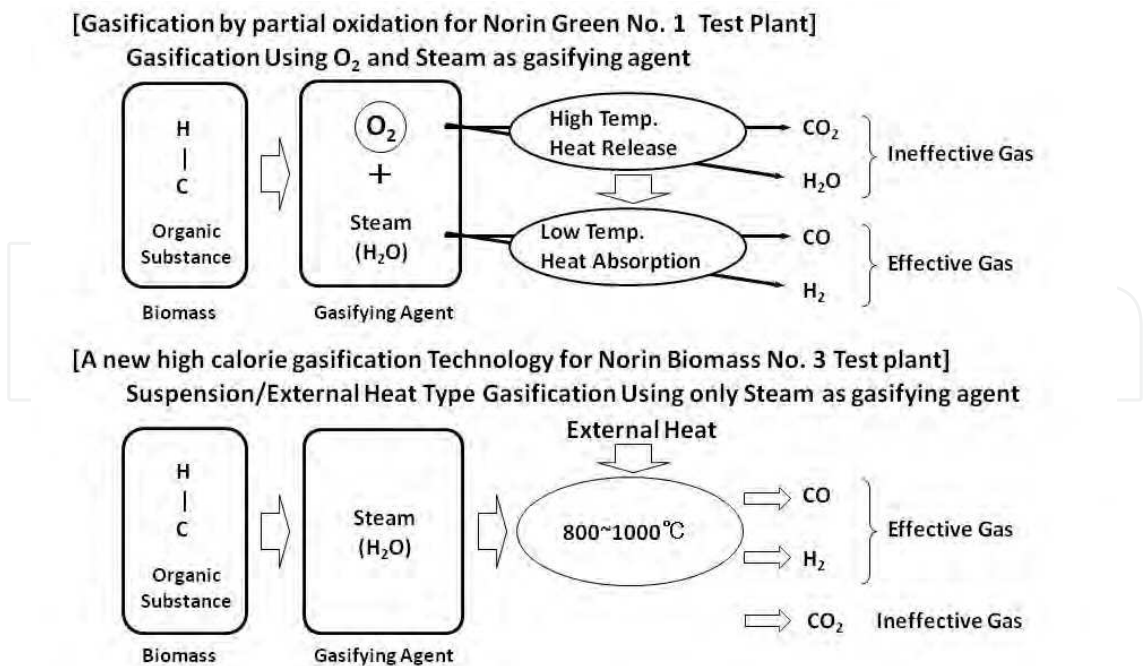
Fig. 11. Principle of a new high calorie gasification technology compared with gasification by partial oxidation technology.
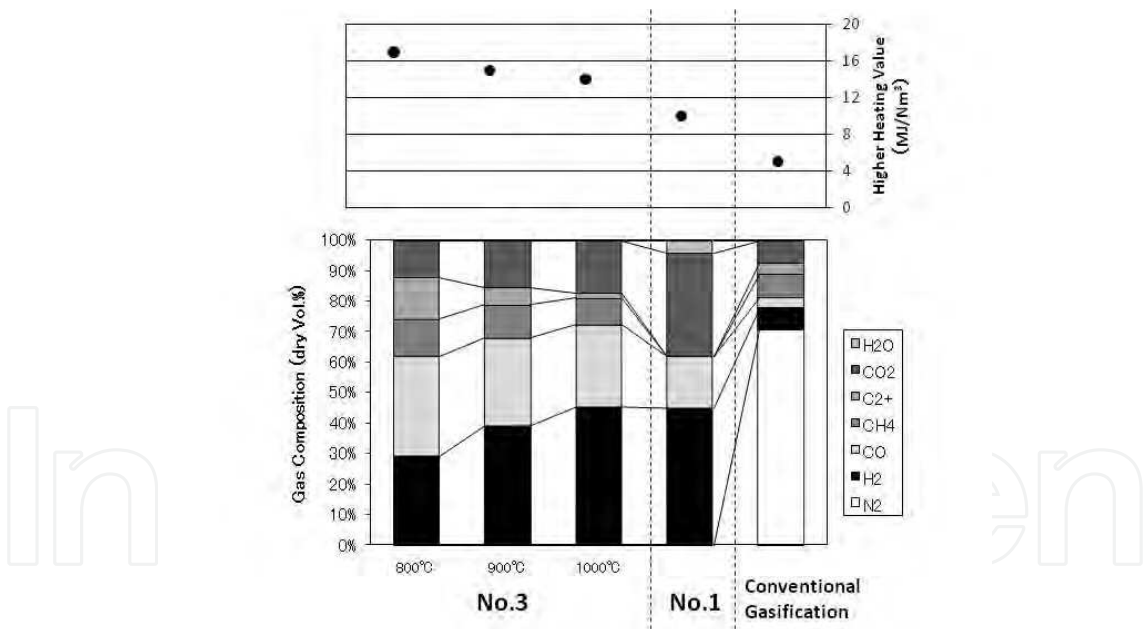

Fig. 12. Composition (bar chart) and higher heating value (line chart) of high calorie gasification gas (No. 3), partial oxidation (No. 1) and conventional gas generated by partial oxidation with air as gasifying agent.
No.1: "Norin Green No. 1": gasification by partial oxidation using O_2 and H_2O as gasifying agents.
No. 3: "Norin Biomass No. 3": high calorie gasification using only H_2O as a gasifying agent at 800, 900, and 1000°C
Conventional gasification: gasification using air as a gasifying agent.

2.2.2 Basic high-calorie gasification reaction

According to the results obtained by the operation, it has been confirmed that the output gas mixture possesses the properties indicated in Fig. 12. As shown in the figure, high-calorie gas featuring 15-18MJ/Nm^3, that could not be achieved by gasification by "Norin Green No. 1" test plant through partial oxidation (ca. 10 MJ/Nm^3; using O_2 and H_2O as gasifying agents) or conventional gasification using air as a gasifying agent (ca. 5 MJ/Nm^3), can be produced when the reaction temperature is 800-900°C, H_2O/C mole ratio is lower than 5.0, and the reaction time is ca. 2 seconds. In addition, this gas mixture contains over 20% hydrogen (H_2). This value is higher than the threshold value of 10% for applicability in terms of ignition and combustion rate for gas engines and micro gas turbines, which indicate that the gas mixture is a high-quality gas fuel. Besides, given that the compositional ratio of H_2 to CO is higher, the threshold combustion temperature is 90°C higher than that of methane. Figure 13 explains a comparison of theoretical combustion temperatures of this gas mixture and various fuels, such as methane, gasoline, propane, methanol and ethanol.
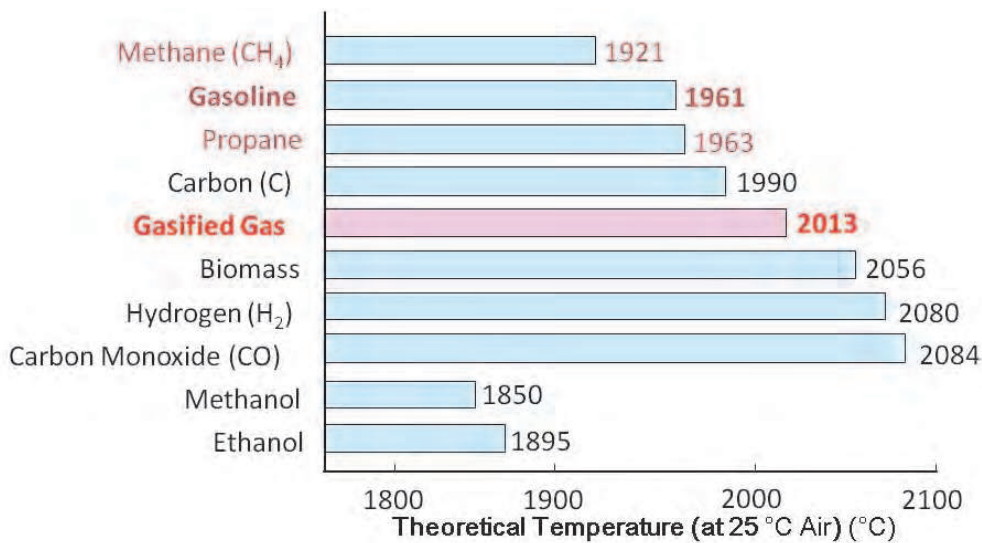

Fig. 13. Comparison of theoretical combustion temperature for gasified gas generated by Norin Biomass No. 3 Test Plant and various fuels.

Biomass means any form of lignocellulosic materials.

3. Conclusion

As the gas mixture generated with "Norin Green No. 1" test plant and high-calorie gas produced with "Norin Biomass No. 3" test plant using the high calorie gasification technology is temporarily stored in a cold gas state, it can be used in a manner similar to natural or city gas, with widespread applications.

Obviously, since "Norin Biomass No. 3" plant, which efficiently converts biomass into high calorie gas mixture with a small system, can be easily used as a fuel for gas engines and micro gas turbines, it can also be used for small-scale power generation and co-generation. Accordingly, high-efficiency and small-scale power generation can be achieved.

The potential applications of the gas mixture generated by gasification through high-calorie gas production are as follows;

1.   Co-generation in buildings, hospitals, industrial parks, factories, etc.

2. Commercial power (targeted efficiency of 25-35%, with at least 1 million kWh/year)
3. Peak cut (reduction of contracted power) and emergency use for large-scale factories
4. Gas fuel for industrial parks (e.g. ceramics and porcelain)
5. Supplementary fuel for incinerator (dioxin countermeasure for industrial waste processing)
6. Fuel for boilers of greenhouse agriculture
7. Fuel for food processing industries by the use of residues produced in the process.
8. Synthesis of biomethanol for BDF production, for batteries of direct methanol fuel cell (DMFT), and a liquid fuel mixed with gasoline for flexible fuel vehicles (FFV).

Three "Norin biomass No. 3" plants processing 4-6 dry t/day of biomass feedstock are under construction by private companies and local government with the 50% financial support from the Government.

This study demonstrates that the gasification of readily available biomass materials both by partial oxidation technology and by high calorie gasification technology could be optimized for generation of gas mixtures primarily composed of H_2, CO and producing methanol yields ranging theoretically from ca. 40 to 60% by dry weight. A test plant utilizing gasification through partial oxidation with 2t/day gasifier can achieve a methanol yield of ca. 20% from the biomass raw material (by weight). This creates an opportunity to utilize a wide range of high yielding with low sugar and starch content such as Erianthus and Miscanthus. Non-palatable lignocellulosic byproducts such as sawdust and crop residues such as straw and husks of rice from various industries would also have suitable application. Sawdust, rice bran, refuse of sugarcane mills (bagasse etc.) and rice husks are particularly attractive and provide a ready-to-use biofuel resource. It is anticipated that the cultivation and utilization of biomass crops will be attractive as carbon neutral biomass feedstocks for biofuel production in the future.

The potentially positive economic impact of biomethanol production on Japanese farming and social systems from planting grasses and trees in unutilized land is immense (Nakagawa 2001; Harada 2001). Reduced CO_2 emissions, recycling of abandoned upland and paddy field and woodland in mountainous areas, and recycling of wastes of agricultural products would all be possible by promoting biofuel production system based on the gasification technologies. This technology is particularly attractive since biomethanol can be produced from a wide range of biomass raw materials.

4. Acknowledgements

5. References

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