BIOMETHANOL PRODUCTION FROM VARIOUS FORMS OF BIOMASS: UTILIZATION OF 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 determined to produce the highest methanol yield (55% by weight), whereas rice straw and husks were determined to produce lower methanol yields 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 represents a clean material, readily obtained and highly useful for biomethanol production. The data suggests that about 22.7 million tons of biomethanol will be annually produced from crop residues and forest industries in Japan if we would apply this technology to biomass feedstocks. The data also suggests that 29.3 million tons of biomethanol will be produced only from byproducts of palm oil industry in Malaysia, and 21.2, 1.4 and 0.53 million tons of biomethanol will be produced from the palm oil industry in Indonesia, Thailand, and China, respectively. 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 provide 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.

Key words: Biomethanol, biomass, renewable energy, Japan
INTRODUCTION

Social, Economical and Technological Circumstances for the Development of the Technologies

More than 10 billion tons of fossil fuels (oil equivalent) are annually consumed in the world and these fuels are known causes of acid rain, photochemical smog, and the increase in 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. A second global problem is the likely depletion of fossil fuels in several decades even though new oil resources are continually being discovered. To address these issues, alternative fuel resources need to be identified.

Stabilizing the earth’s climate depends on reducing carbon emissions by shifting from fossil fuels to direct or indirect use of solar energy. Among the alternatives, use of biofuel is most beneficial because the solar energy that produces biomass is the final sustainable energy resource. Besides, it reduces atmospheric CO$_2$ through photosynthesis and carbon sequestration. Even though combustion produces CO$_2$, it does not increase total global CO$_2$. Liquid fuels, especially bioethanol and biomethanol, provide petroleum fuel alternatives for various engines and machines. Biofuel can be managed to eliminate output of soot and SO. In terms of storage, it ranks next to petroleum, and is far easier to store than batteries, natural gas, and hydrogen.

The Ministry of Agriculture, Forestry and Fisheries (MAFF) in Japan has carried out large biomass projects, “Green Energy Project (1978-87),” “Biomass Conversion Project (1981-89),” “Ecosystem Project (2000-2005),” “Bio-Renascence Project (1991-2000),” and “Biorecycling of waste from agriculture, forestry and fisheries” Project (2001-2006). These projects focused on basic research regarding biomass production of various plants, including improvement of photosynthetic pathway, cultivation and harvest system of biomass crops, and utilization of natural and unused energy resources after the experience of the two oil crisis in 1972 and in 1978. However, in those years, the results gleaned from these projects were not immediately applicable to Japanese industries. Technologies for efficient use of biomass were lacking. What existed were technologies on bioethanol production by fermentation from crops with high sugar and starch content and use of trees as burning fuels for heating and generation of electricity.

The Japanese Government promoted researches on liquid fuel production from biomass after the U.N. Earth Summit for the prevention of global warming held in Kyoto Japan in 1997 agreed to the recommendations of the Kyoto Protocol, which aims to reduce the greenhouse gases emission to at least 5% below 1990 level. Research efforts on biofuel have been promoted as the targeted goal of the reduction of greenhouse gas emission for the period 2008-2012 was drawing near. A new project “Development of technologies of biomass utilization for activation of rural areas” was initiated in 2007 (http://www.s.affrc.go.jp/docs/project/2007/outline/2007_project_4_1.pdf). The project includes “Improvement of resource crops and development of low-cost cultivation technology towards domestic biofuel production” subproject. The subproject includes improvement of sugar beet, potato, sorghum, sweet potato, and sugarcane. Another new project “Improvement of biomass-forage crops by establishing rice genome resources, gene isolation, and functional analysis” has started in 2008. The project is based on the results of the Rice Genome Project and the genome information obtained in rice will be applied into the analysis of gramineae crops such as sorghum and wheat by comparative mapping as well as molecular breeding of rice.

The necessary raw materials for bioethanol production by fermentation, however, are obtained from crop plants with high sugar or high starch content. Since these crops are primary sources of human nutrition, their use in biofuel production is controversial at a time when the demand for such crop increases with the rising global population rates. Recently, a new method of gasification by partial oxidation and production of biomethanol from carbohydrate (Fig. 1) has been developed. This process enables any source of biomass to be used as a raw material for biomethanol production. This
paper presents the 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.

**Availability of Resources**

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 70°C; 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; 2) Percent carbon (C), hydrogen (H), oxygen (O), nitrogen (N), total sulfur (T-S), and total chloride (T-Cl); 3) Higher heating value (HV) was measured by the rise in temperature in water from all the heat generated by burning. Lower HV was estimated by the calculation, lower HV = 600 (9h + w)/100 [h: hydrogen content (%), w: water content (%)]; 4) Chemical composition (molecular) of the biomass; 5) Size distribution of the various biomass types (diameter, density of materials [g/mL]); 6) Gas yield and generated heat gas were estimated by the process calculation based on chemical composition and heating value. Heat yield or cold gas efficiency was calculated by (total HV of synthesized gases)/(total HV of supplied biomass) and; 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 a ball-mill was also measured by operating “Norin Green No. 1” test plant with a boiler capacity of 240 kg dry biomass/day.

Fig. 2 shows the water and ash content for the different materials evaluated. The materials were preserved in different ways ranging 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 drier. The other materials were not mechanically dried in the process 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 silicon (Si) content of rice plants, the ash content of rice bran was much lower (8.1%). The ash content of sorghum was 5.8%.

Fig. 3 shows the percent by weight of some elements in the raw materials. Carbon content was high in wood materials and averaged 48.3% for wood waste and 51.8% for bark. Rice bran carbon content averaged
Fig. 2. Content of water and ash in materials.\textsuperscript{8}  

Fig. 3. Content of some elements in materials without water (% by weight).\textsuperscript{8}  

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 exhibited 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 was 0.45\%. The content of sulfur (S) was very low in all the materials and ranged between 0.02\% (sawdust) and 0.22\% (rice husks). Chlorine (Cl) content ranged
Lower heating value = Higher heating value - [(9 × H + water) x 6]

Table 1. Molecular ratios of C, H, and O

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>H</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sawdust</td>
<td>1.44</td>
<td>2</td>
<td>0.90</td>
</tr>
<tr>
<td>Bark</td>
<td>1.54</td>
<td>2</td>
<td>0.90</td>
</tr>
<tr>
<td>Chips</td>
<td>1.39</td>
<td>2</td>
<td>0.88</td>
</tr>
<tr>
<td>Bamboo</td>
<td>1.42</td>
<td>2</td>
<td>0.93</td>
</tr>
<tr>
<td>Salix</td>
<td>1.38</td>
<td>2</td>
<td>0.93</td>
</tr>
<tr>
<td>Waste</td>
<td>1.42</td>
<td>2</td>
<td>0.90</td>
</tr>
<tr>
<td>Rice Bran</td>
<td>1.15</td>
<td>2</td>
<td>0.59</td>
</tr>
<tr>
<td>Rice straw</td>
<td>1.31</td>
<td>2</td>
<td>0.87</td>
</tr>
<tr>
<td>Sorghum foliage</td>
<td>1.28</td>
<td>2</td>
<td>0.93</td>
</tr>
</tbody>
</table>

from 0.01% (sawdust) to 0.41% (rice husk). This data demonstrates that these materials are cleaner than coal and other fossil fuels. Based on previous experience and data, chemical properties of harvested tropical grasses are expected to be similar to those of sorghum.

Fig. 4 shows the higher and lower HVs of materials. Among the materials tested, HVs of wood materials were high and ranged between 4,570 kcal/kg (sawdust: higher HV) 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. The HV of sorghum was intermediate among the materials evaluated and was 3,940 kcal/kg.

Table 1 shows the molecular ratios of C, H and O in various materials. Most of the materials had similar ratios for C\(_n\)H\(_2\)O\(_m\) (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.
Fig. 6 shows the estimated methanol yield by weight and by HV for each material tested, calculated from the contents of the gas mixtures produced by gasification. The values are correlated to carbon content and heat emission. Wood materials exhibited 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. 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 differences observed between the plant parts. These results indicate that significant levels of methanol can be produced without utilizing high starch and sugar food sources for biofuel production. Instead, the utilization of agricultural and forestry residues which are typically cast off or burned could be an important component of an energy development plan. Plant breeders do not need to select materials based on material component in biomass but can focus their efforts on biomass quantity. Heat yield of the various materials tested, regardless of their HVs, was high demonstrating the efficiency of this technology.

For perfect gasification, biomass materials must be converted into powder, ca. 0.1-0.9 mm in diameter (micro-crushing). Table 2 shows the physical characteristics of the raw materials and the handling procedures needed to prepare these raw materials for biomethanol production. Rice bran is very fine; there is no need for any prior preparation. Sawdust can be used directly for gasification although its diameter is ca. 0.8 mm. Long rice straws require only micro-crushing. Sorghum is harvested at the ripened stage using sickles, cut to 30 cm long and dried in a dryer. This procedure makes processing of sorghum difficult and both rough-crushing (1.0-3.0 mm) and micro-crushing are required to prepare sorghum for gasification. Usually, a mechanical harvester is used to cut sorghum plants into lengths less than 10 cm. This harvest method requires lesser subsequent preparation.

A test plant, named “Norin Green No. 1 (renamed as “Norin Biomass No. 1”, Fig. 7)” to obtain data for methanol yield was developed. Fig. 8 shows the gasification and biomethanol synthesis system. The test plant comprises a supplier of crushed biomass, a boiler for gasification, and an apparatus for gas purification and methanol synthesis using a copper/zinc-based catalyst. Table 3 illustrates the capacity of the test plant (the test plant gasifier can process 240 kg/day of dry biomass) when crushed waste wood is utilized as the raw material, and the estimated processing capacity of a commercial scale plant (a gasifier can process 50-100 t/day of dry biomass). The cold gas efficiency, that is a percentage of [total HV of synthesized gases by gasification] divided by [total HV of supplied biomass] of the test plant varied from 65 to 70%, and methanol yield varied from 9 to 13%. A commercial scale plant would need to be large enough to maintain critical temperature (900 to 1,000°C) 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 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 2t/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, which supports our simulation data.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Size (mm)</th>
<th>Density (g/mL)</th>
<th>Handling characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bran</td>
<td>0.31</td>
<td>0.31</td>
<td>No micro-crushing needed</td>
</tr>
<tr>
<td>Straw</td>
<td>3.0-4.0</td>
<td>-</td>
<td>Micro-crushing needed</td>
</tr>
<tr>
<td>Husk</td>
<td>2.05</td>
<td>0.11</td>
<td>Micro-crushing needed</td>
</tr>
<tr>
<td>Sawdust</td>
<td>0.78</td>
<td>0.07</td>
<td>No micro-crushing needed</td>
</tr>
<tr>
<td>Sorghum</td>
<td>7.9</td>
<td>0.07</td>
<td>Rough- and micro-crushing needed</td>
</tr>
</tbody>
</table>
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 – 1,100°C. Methanol synthesis devise: 1) Capacity: equivalent to 20 kg-biomass/day, 2) Type: catalyst type, 3) Pressure and temperature: 30 kg/cm² at 180 – 250°C.

Fig. 8. Estimated dry matter weight of byproducts and residues from agriculture and forest industry per year in Japan (Total: 45.3 M tons).
ADVANTAGE AND DISADVANTAGES OF THE TECHNOLOGIES

The above data indicate that the most important advantage of this technology is that it can utilize any form of biomass feedstock for high yield of methanol production.

The disadvantage of the system is with the size of the processing facility. The larger the plant, the higher is its efficiency. The biomethanol yield from a 100 t/day-gasifying boiler would be more than twice that of the 2 t/day-boiler 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 wood factories). Moreover, required permits and licenses to operate such a large-scale boiler in Japan, would entail additional costs.

Prof. Sakai, of the Nagasaki Institute of Applied Science, one of the authors of this report, has developed another type of small plant, named “Norin Biomass No. 3,” whose energy efficiency is lower than the 100 t/day plant. If the plant can be portable, it can be transported to another location when the biomass feed stocks are used up. This type of operating system may be more feasible and practical in the future.

Methanol is listed as a 4th level of poison in Japan, and many regulations prohibit the utilization of biomethanol. As the industrial use of methanol is expanding such as direct methanol fuel cell for battery (i.e. DMFC). Note: Methanol is toxic and flammable. However, the International Civil Aviation Organization’s (ICAO) Dangerous Goods Panel (DGP) voted in November 2005 to allow passengers to carry and use micro fuel cells and methanol fuel cartridges when aboard airplanes to power laptop computers and other consumer electronic devices. On September 24, 2007, the US Department of Transportation issued a proposed rule-making to allow airline passengers to carry fuel cell cartridges on board. The Department of Transportation issued a final ruling on April 30, 2008, permitting passengers and crew to carry an approved fuel cell with an installed methanol cartridge and up to two additional spare cartridges. It is worth noting that 200 mL maximum methanol cartridge volume allowed in the final ruling is double the 100 mL limit on liquids allowed by the Transportation and Security Administration in carry-on bags (http://en.wikipedia.org/wiki/Direct_methanol_fuel_cell), biodiesel production process etc. The regulation could be changed in the future.

TECHNOLOGY TRANSFER AND COMMERCIALIZATION

The country may face both energy and food crises due to high population growth, the impact of climate change on food production, and other factors. Under this situation, 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, providing yields in the range of 40 to 60% of total feedstock dry weight. This creates an opportunity toward the utilization of a wide range of harvested plant material low in sugar and starch, including byproducts of other processing operations such as sawdust,
The palm oil industry is very important in Malaysia and the amount of byproducts and residues produced from the industry is increasing annually. The area for oil palm cultivation in Malaysia was 3.37 M ha in 2003 although it was as high as 1.29 M ha 20 years ago. The total amount of biomass produced by the palm oil industry in Malaysia, including trunk (7.6 M tons), fond (cut leaves (1.4 M tons), and fruit (35.0 M tons), empty fruit bunch (5.2 M tons), and fiber (5.5 M tons) and shell (3.7 M tons) of fruit is estimated at 58.4 M tons per year. This translates into the production of ca. 29.3 M tons of biomethanol from byproducts of palm oil industry in Malaysia, and the potential production of 21.2, 1.4 and 0.53 M tons of biomethanol produced from the palm oil industries in Indonesia, Thailand, and China, respectively (Fig. 9).

Second only to food production policies, energy policies are among the most important subjects confronting Asian and African nations. The consumption of electricity and petroleum is increasing dramatically and developing countries located in tropical and subtropical regions should attempt to pursue the development of a biofuel-based energy resource.

The technology is particularly attractive since biomethanol can be

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**Fig. 9.** Estimated biomethanol weight produced from byproducts and residues from palm oil industry in Malaysia, Indonesia, Thailand, China and others per year in Asia (Total: 52.24 Million tons/year).
produced from a wide range of biomass raw materials. Hopefully soon, a totally new type of agriculture will include the cultivation of raw materials for biofuel production. The development of a sustainable biofuel production technology or adherence to traditional fossil fuel technologies will certainly have consequences for the environment, earth, and humanity.

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