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Hydrogen-rich synthesis gas production from waste wood via gasification and reforming technology for fuel cell application

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Abstract The purpose of this study was to establish a fuel process for an advanced power generation system in which hydrogen-rich synthesis gas, as the fuel for the molten carbonate fuel cell (MCFC), can be extracted from biomass via gasification and reforming technologies. Experiments on waste wood gasification were performed using a bench-scale gasification system. The main factors influencing hydrogen generation in the noncatalytic process and in the catalytic process were investigated, and temperature was identified as the most important factor. At 950°C, without employing a catalyst, hydrogen-rich synthesis gas containing about 54 vol% hydrogen was extracted from feedstock with appropriately designed operation parameters for the steam/carbon ratio and the equivalence ratio. However, by employing a commercial steam reforming catalyst in the reforming process, similar results were obtained at 750°C.

Key words Hydrogen · Gasification/reforming · Waste wood · Catalytic · MCFC

Introduction

Hydrogen is anticipated to become an alternative energy source for a future “hydrogen society” in which fuel cell automobiles and power generation systems will play an important role in the social infrastructure.¹ To turn this dream into a reality, it is necessary to develop a variety of hydrogen-producing processes, not only by the cracking and reforming of natural gas and the electrolysis of water, but also by extracting hydrogen from biomass as well as wastes.^{2,3} The purpose of this study was to establish a fuel-processing system in which hydrogen-rich synthesis gas can be efficiently extracted from biomass via gasification and

reforming technologies, with the product gas well within the tolerance level of fuels for molten carbonate fuel cells (MCFCs).

Thus far, gasification is considered a competitive means for efficient reuse of biomass, and the gas products are normally used as the fuel of internal combustion engines or gas turbines for power generation. Therefore, in conventional gasification systems, emphasis is usually placed on high C-conversion as well as on cold gas efficiency.^{4–6} In general, to promote the decomposition of feedstock and tar cracking, increasing the operating temperature is considered a promising method. Consequently, one of the characteristics of conventional gasification systems is the necessity to supplement the system with a large amount of air or oxygen, which is expected to burn out char and tar to supply the required thermal energy for decomposition and reforming reactions. However, since hydrogen has a higher flame propagation speed than the other principal combustible components, it is usually oxidized before char and tar, causing a severe decrease in the hydrogen component, and typical synthesis gases are deficient in hydrogen.

In the application of biomass gasification as a fuel process for MCFCs, special emphasis must be placed on the components of the gas product. Specifically, the main gas components should be hydrogen and carbon monoxide, whereas the presence of hydrocarbons and oxygen should be strictly limited. Furthermore, the removal of a significant amount of tar, soot, and acidic gases as well as other impurities from the gas product is also required to successfully meet the tolerance level of MCFCs.⁷

The addition of steam has been reported to significantly promote the formation of hydrogen in the biomass gasification process, in which the water-gas and reforming reactions of hydrocarbons are promoted by the presence of steam.^{8–12} On the other hand, even though the presence of oxygen in the gasification process has a slightly negative effect on hydrogen formation, the addition of oxygen is also considered a necessary element in establishing a commercial system involving the supply of combustion-based thermal energy to maintain a self-sufficient energy system.^{13,14} To resolve the apparent discrepancy regarding

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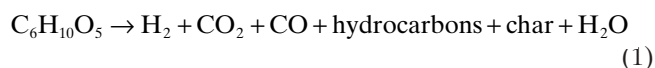
the effect of oxygen addition on hydrogen generation, optimization of the operating conditions such as operating temperature, steam/carbon (S/C) ratio, and equivalence ratio (ER), becomes extremely important. In this study, to obtain detailed information about hydrogen conversion from waste woods during the gasification and reforming processes, experiments were performed using a bench-scale two-step fluidized bed experimental facility under various operating conditions. A follow-up survey was conducted to investigate the mechanism of hydrogen formation, the gasification characteristics of waste wood, and the key operating factors.

One of the disadvantages of conventional gasification systems is low cold gas efficiency because of the high-temperature operation. To reduce the operating temperature, it is necessary to decrease the activation energy of complex decomposition and reforming reactions by using a catalyst. Extensive studies have been published regarding experimental investigations of the catalytic gasification process of hydrogen production at low temperatures, and a number of catalysts have been confirmed to exhibit a high activation in the production of hydrogen, namely dolomite, ZnCl_2 , and K_2CO_3 .^{15–20} The most interesting of these include promising reports regarding a Rh catalyst in the gasification process, in which the synthesis gas contained about 40 vol% hydrogen at only 550°C.^{21,22} With this technology, it is expected that the gasification and reforming processes will be performed using only one gasifier, resulting in a more compact system. The catalyst was assumed to cause weakness in the intermolecular interaction of polymeric chains and, at the same time, not only catalyze interlinked dehydration, but also prevent the formation of stable chemical structures. However, most of the catalysts displayed moderate deactivation as a result of the buildup of surface carbon and “sintering” effects. Consequently, the benefits of these catalysts were significantly reduced.^{23,24} Considering the longevity requirements and the cost of catalysts, commercially available Ni catalysts are considered more economical than other more expensive metal catalysts, such as Rh and Pt. Thus, interest has also focused on commercial Ni catalysts.²⁵ In this study, one type of commercial Ni catalyst (FCR-4) was employed in an attempt to reduce the operating temperature and to evaluate the performance of the catalyst on hydrogen formation.

The gasification process consists of many concurrent and consecutive reactions, making it virtually impossible to identify all of the elementary chemical reactions in hydrogen conversion. In this study, identification of the main hydrogen-forming events corresponding to variations in operating factors was attempted.

Generally, the chemical formula of wood can be described as $\text{C}_6\text{H}_{10}\text{O}_5$, and the main decomposition reactions taking place in the gasification section are expressed as Eqs. 1 through 6; the reforming reactions are expressed as Eqs. 7 through 10:

Devolatilization reaction of wood:



Devolatilization reaction of hydrocarbons (gas and tar yields)



Steam gasification reactions:



Complete and incomplete combustion reactions:



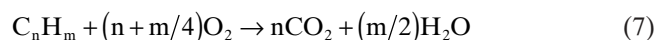
Combustion of char:



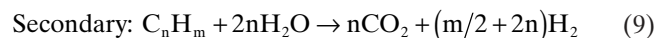
Water-gas reaction of char:



Oxidation of hydrocarbons:



Primary and secondary reforming reactions:



Water-gas shift reaction:



Experimental method

Raw materials

Most of the houses in Japan used to be built of wood, and the old ones that are torn down produce about 5 million tons of architectural salvage per year. The reuse and recycling of these waste woods have become a severe problem. Thermal disposal, especially via gasification, is considered an appropriate recycling means. Consequently, in this study, architectural salvage was used as feedstock in the gasification experiments, in which it was crushed and sieved to a particle size of 1–2 mm. The results of ultimate and proximate analysis of architectural salvage as well as analysis of the main metals contained in the ash are summarized in Table 1. In the catalytic gasification experiments, the commercial steam reforming catalyst FCR-4 (Süd-Chemie Catalysts, Tokyo, Japan. Metal content: Ni 12 wt%, supported by Al_2O_3) was employed in the form of spheres 3–5 mm in diameter.

Experimental facility and analysis system

A bench-scale gasification unit was built to conduct the experiments; a schematic of the system is shown in Fig. 1. This system essentially consisted of two reactors in series: a primary reactor (gasifier) was followed by a secondary reactor (reformer); both were made of quartz glass tube.

The primary reactor was designed as a fluidized bed, with an outside diameter (OD) of 55 mm, an inside diameter (ID) 50 mm, and a height (H) of 1390 mm. The capacity was around 0.15–0.34 kg/h. The secondary reactor was designed as a tubular model, with OD 55 mm, ID 50 mm, and H 1620 mm. Two distributors were incorporated, one at the bottom of the primary reactor to support the feedstock and the other at the top of the secondary reactor to support the catalyst. The gas line between the two reactors was heated to above 250°C using a ribbon heater, preventing the condensation of steam and tar. Both reactors were preheated

using ovens at a maximum temperature of 1100°C. The maximum gas space velocities in the gasifier and reformer were 1.6 and 1.8 m/s (900°C), with residence times of up to 0.6 and 0.7 s, respectively. However, in the catalytic gasification experiments, the catalysts were loaded in the reformer vessel near the entrance partition of the gas products. The depth of the actual catalyst bed in the reformer was about 70 mm (0.15 kg).

When the experiments were carried out, the feedstock was loaded into a feed hopper. After the reactors were preheated to the desired temperature, the feedstock was continuously screw fed from the hopper to a transport pipe and then carried to the bottom of the primary reactor by the carrier gas (N_2), falling down onto the distributor. The feed rate was controlled by regulating the screw speed. Distilled water was sucked up from a tank using a micro pump and was quantitatively pumped into a steam generator. The gaseous mixture of steam and oxidizing agents were injected into the primary reactor from the bottom. As these gases passed through the distributor, the feedstock was blown upwards, producing a fluidized state. Feedstock particles struck the internal wall of the reactor, resulting in the particles being heated both by heat transfer and by absorbing radiant heat. Volatile matter escaping from the feedstock accompanied decomposition reactions. The solid products (char) were carried upwards via the pyrolysis gas stream, leaving the reactor from the top and entering the cyclone cylinder where the char was removed from the raw gas. Tar remained in the high-temperature gas stream and was carried into the secondary reactor where tar was reformed into light gas components such as H_2 , CO , CO_2 , and CH_4 .

Table 1. Properties of architectural salvage

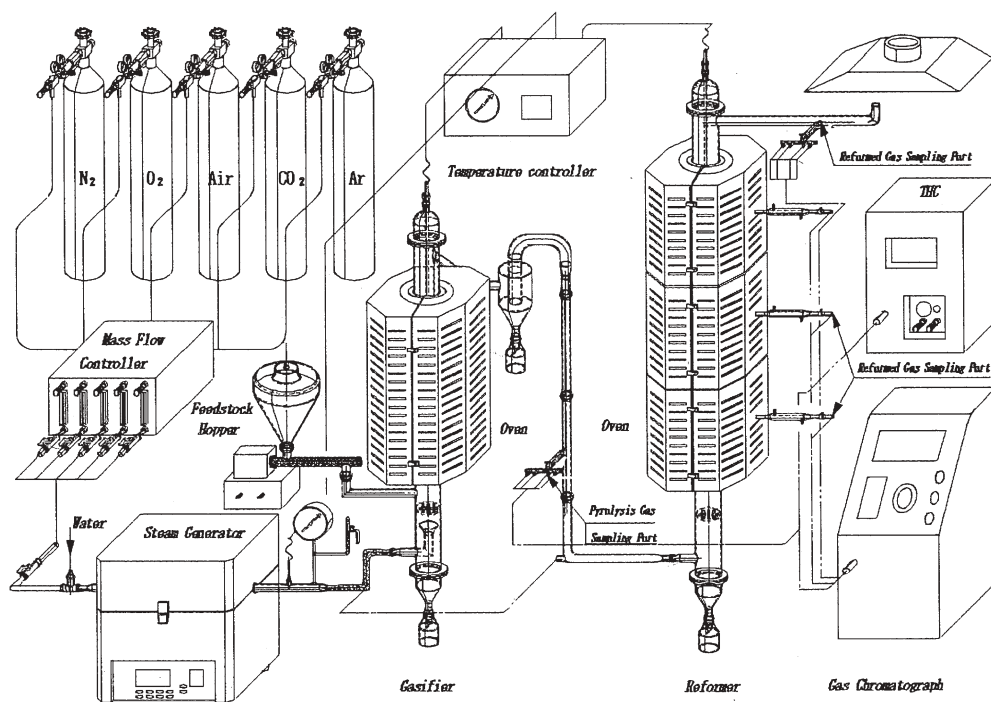
Proximate analysis		Ultimate analysis	
Volatile (wt% dry)	80.0	H (wt% dry)	5.9
Fixed carbon (wt% dry)	18.0	C (wt% dry)	51.4
Ash (wt% dry)	2.0	O (wt% dry)	40.7
Moisture (wt% dry)	9.0	N (wt% dry)	<0.1
HHV (MJ/kg dry)	20.5	Cl (wt% dry)	<0.01
LHV (MJ/kg dry)	17.2	S (wt% dry)	<0.02
Ash analysis			
Al (wt% dry)	3.1	Cd (mg/kg dry)	<5
Ca (wt% dry)	4.9	Pb (mg/kg dry)	58
Fe (wt% dry)	6.3	As (mg/kg dry)	21
Si (wt% dry)	12.6	Cr (mg/kg dry)	16
Na (wt% dry)	2.5	Cu (mg/kg dry)	200
K (wt% dry)	7.7	Hg (mg/kg dry)	<0.05
Se (mg/kg dry)	<5	Zn (mg/kg dry)	360

HHV, higher heating value; LHV, lower heating value

Fig. 1. Schematic of the bench-scale experimental facility.

THC, Anatec Yanaco, Kyoto,

Japan



Temperature measurement

Since both the primary and secondary reactors were preheated by ovens, it was assumed that temperature gradients were present in the interior of the reactors. To monitor the temperature in the reaction zones of the gasifier and reformer, three thermocouples were set in the reaction zones of both reactors to monitor the temperature at the center, the internal wall, and the midpoint of these two positions. Moreover, to control the temperature of the steam and the sample gas stream, three thermocouples were also set at different locations in the series of gas lines.

Tar measurement

Two gas-sample probes were set downstream of the cyclone cylinder and reformer outlet. The sample gases were injected into six tar impinger bottles that were located in an ice-water cooling bath. The gas sampling lines were wrapped with a ribbon heater, keeping the temperature above 250°C to prevent condensation of the steam and tar. As the sampling gas passed through the impinger bottles, the tar and steam were condensed and deposited in the bottles. After this, tar-free gas samples passed through a series of measurement devices to determine the composition of the gases. After the experiments, the gas lines were cleaned with acetone to recover deposited tar. Furthermore, to prevent reactions from taking place among the components of the sample gases, the sampling lines were designed to be as short as possible.

Gas products analysis

The composition of tar-free sample gases after leaving the series of tar impinger bottles was determined regularly at 3-min intervals by a microgas chromatograph (Agilent 3000, Yokogawa Analytical Systems Inc, Tokyo, Japan) equipped with two columns: PLOT U, 3m × 0.32mm diameter / MS 5A PLOT, 10m × 0.32mm, for H₂, O₂, N₂, CH₄, and CO using helium as a carrier gas. Moreover, a Shimadzu (Kyoto, Japan) GC 7000 series was used to determine CO₂, a GC 8000 was used for O₂, and a Yanaco (Kyoto, Japan) THC 7000 was used for C_nH_m (2 ≤ n ≤ 4).

The quantitative determination of dry gas products was calculated by a volumetric gas meter and converted to normal conditions. The values of the dry gas yield and composition reported in the following sections were obtained after being corrected for the nitrogen flux added to the biomass feeding system.

Experimental results and discussion

Effect of temperature on hydrogen formation

It is well known that raising the operating temperature can improve gas yield conversion and promote a low tar level

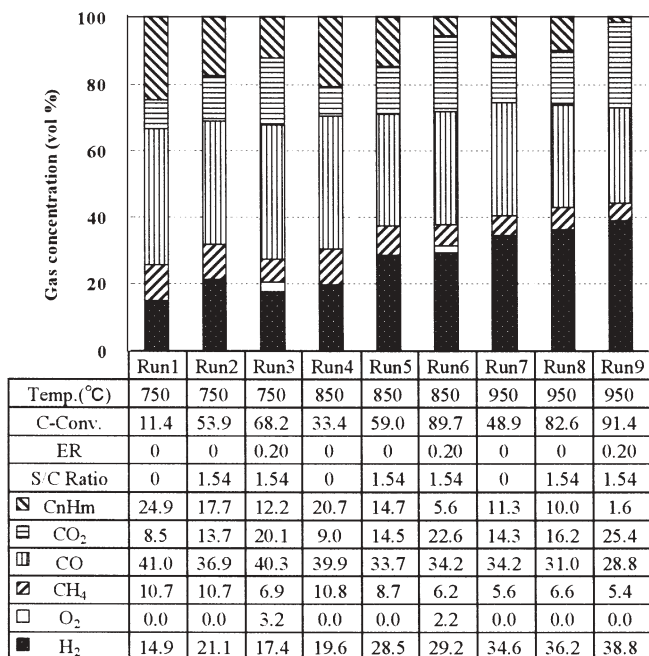


Fig. 2. Effect of gasification temperature on reformed gas yields (feed rate = 5.6 g/min, d = 1.5 mm, reforming temperature = 900°C). C-Conv, carbon conversion; ER, equivalence ratio; S/C ratio, steam/carbon ratio; CnHm, hydrocarbon

in the gasification process.^{26,27} To verify hydrogen formation rates corresponding to different operating temperatures, experiments were conducted at the following three temperatures: 750°, 850°, and 950°C. The results are summarized in Fig. 2.

These experimental results indicate that hydrogen conversion was promoted with the increase of temperature over the test series (from 750° to 950°C). The maximum hydrogen content of about 39 vol% was generated at 950°C with the addition of steam and oxygen (S/C = 1.54, ER = 0.20). Moreover, methane and other hydrocarbons almost completely disappeared, with only 1.6 vol% hydrocarbons remaining in the reformed gases. However, in pyrolysis experiments at 750°C, the hydrogen concentration was a minimum at 14 vol% and a much greater amount of hydrocarbons (25 vol%) remained in the reformed gases. Comparing the results of experiments in which the reactor temperature was increased from 750° to 950°C in 100°C increments with all other conditions (S/C ratio and ER) remaining constant, all runs showed further evidence of a tendency toward improved hydrogen and carbon dioxide formation at higher temperatures and a remarkable reduction in carbon monoxide and methane as well as hydrocarbons. Clearly, increasing the temperature had a positive effect on hydrogen formation. However, comparing the composition of gas generated under three different operating conditions (pyrolysis, steam gasification, and gasification), it is also clear that the addition of steam and oxygen enhanced the temperature effect for improving hydrogen conversion. Furthermore, because similar hydrogen levels were found in synthesis gas generated from the above three

processes at temperatures up to 950°C, it also revealed that temperature plays a dominant role in hydrogen formation, whereas the addition of steam and oxygen mainly improved the thermal degradation of hydrocarbons and led to a slight increase in carbon dioxide.

In the gasification process, the dominant reactions of hydrogen formation vary according to the operating parameters. In the pyrolysis process, because of the absence of oxygen and steam, devolatilization reactions (Eqs. 1 and 2) are assumed to be the dominant reactions, and hydrogen is assumed to be converted mainly by the devolatilization of feedstock and hydrocarbons. High-temperature operation makes it possible to supply the necessary thermal energy to the above two endothermic reactions, and is advantageous in the formation of light gases such as H₂, CO₂, and CO; in particular, the promotion of Eq. 2 would lead to a high hydrogen concentration in the gas product. This assumption was backed up through a comparison of pyrolysis experimental results at 750°, 850°, and 950°C.

Effect of steam addition on hydrogen formation

During the steam gasification experiments, steam first contacted feedstock and chars because it was injected from the bottom of the primary reactor, resulting in the steam gasification reaction of feedstock (Eq. 3) and the water-gas reaction of char (Eq. 6), simultaneous with devolatilization in the primary reactor. Moreover, residual steam would be consumed in the reforming reactions of tar in the secondary reactor. As a consequence of steam gasification and reforming reactions (Eqs. 8–10), hydrocarbons would be decomposed, and hydrogen, as the product of these reactions, would appear to increase significantly in reformed gas compared to that generated from the pyrolysis process, as shown in the results illustrated in Fig. 2. These results indicate that steam addition has the same effect as increasing temperature on hydrogen formation as well as enhancing the decomposition of hydrocarbons. To verify the effect of steam addition on hydrogen conversion, the quantity of steam was varied from S/C = 0 to 4.44 while holding temperature and ER constant.

Although published reports have stated that steam gasification is advantageous in hydrogen formation,^{9,11,12} the results in this study indicated this is not completely accurate. As shown in Fig. 3, by varying the quantity of added steam in the wood gasification process, steam can have both a positive and a negative effect on hydrogen conversion. The hydrogen content increased from 18.7 to 27 vol% on increasing S/C from 0 to 1.67. However, when S/C exceeded 1.67, the hydrogen content apparently decreased on the addition of more steam. Moreover, the maximum S/C ratio of 4.44 resulting in the lowest recorded hydrogen content of only 14 vol%. As a consequence of this experiment, S/C = 1.67 appeared to be the optimal value for this feed rate (3.9 g/min of feedstock) and oxygen level (ER = 0.57). These experiments also indicated that gas yields are easily affected by the presence of oxygen. The lower hydrogen content with oxygen still present in the gas was assumed to be the result

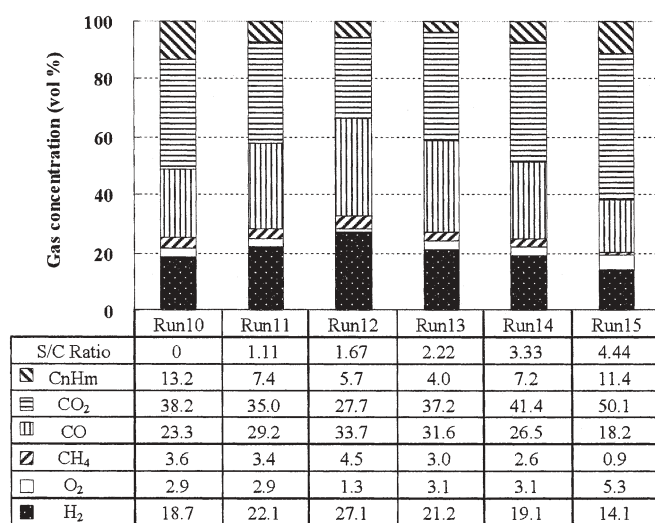


Fig. 3. Reformed gas yields as a function of S/C ratio (gasification and reforming temperature = 900°C, feed rate = 3.9 g/min, ER = 0.57)

of too much oxygen being supplied (ER = 0.57) to be completely consumed in the gasification and the reforming processes.

Hence, the above experimental results indicate that the effect of adding steam on promoting hydrogen formation is based on the partial counterbalancing of oxidized and pronounced oxidative characteristics. Furthermore, excess steam addition led to increased CO₂ and hydrocarbon formation and decreased hydrogen.

These facts are not successfully explained by considering Eqs. 1–10 alone. In spite of this, either steam gasification reactions or reforming reactions lead to an increase in hydrogen and a decrease in hydrocarbons corresponding to the quantity of steam added. But in the experimental results, only CH₄ appeared to have tendencies similar to hydrogen, whereas the other hydrocarbons exhibited opposite tendencies.

This phenomenon was previously assumed to stem from the temperature decrease corresponding to steam injection because of the large thermal capacity of steam. But in the experiments, only a 30°C temperature variation was found in the fluidized bed layer over the range of steam flows, and it is difficult to explain these results in terms of this temperature variation. When we assumed that feedstocks were cooled by the great amount of added steam, leading to a sharp decrease in solid temperature, the results of the oxidation reactions were obstructed. The temperatures indicated by the thermocouples were assumed to mainly represent the temperature of the gas products but not of the feedstock; in other words, the temperature of the feedstock was not correctly represented. Consequently, to resolve the discrepancy in the positive and negative effect corresponding to the amount of steam addition on hydrogen formation, it was proposed that a counterbalance approach should be taken by controlling the quantity of steam addition to attain the optimal value.

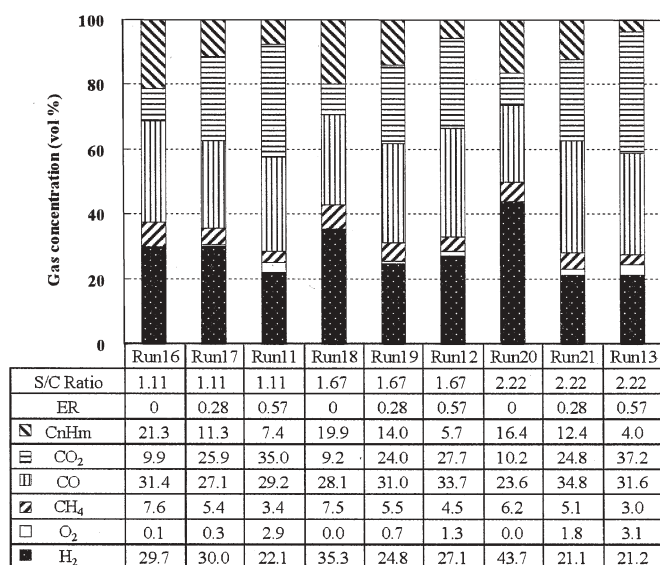


Fig. 4. Reformed gas yields as a function of ER (gasification and reforming temperature = 900°C, feed rate = 3.9 g/min)

Effect of oxygen addition on hydrogen formation

To investigate the effect of the amount of oxygen addition on hydrogen conversion, especially in the case where steam was present, steam gasification experiments were conducted and the quantity of oxygen was varied. The results are shown in Fig. 4. Usually, oxygen addition leads to oxidation reactions as well as combustion reactions (Eqs. 4, 5, and 7). These oxidation reactions caused a sharp decrease in H₂, CO, and CH₄ as well as in hydrocarbons, whereas CO₂ levels increased. The results shown in Fig. 4 indicate a significant reduction in hydrogen formation as more oxygen was added, except in the case of S/C = 1.11, when a similar hydrogen content was generated for both steam gasification and oxygen addition at an ER of 0.28. With increased steam addition (S/C = 1.67 and 2.22) addition of oxygen exhibited a stronger negative effect on hydrogen formation. In particular, in the case of ER = 0.28 and S/C = 2.22, the hydrogen concentration was only 21 vol%, compared with a value of 43 vol% for S/C = 2.22 and no added oxygen.

Against the negative effect on hydrogen levels generated, oxygen exhibited a positive effect on the decomposition of hydrocarbons. The hydrocarbons were successfully cracked in proportion to the amount of oxygen added, especially when accompanied by the appropriate amount of added steam. Consequently, the addition of oxygen is considered to improve the combustion reactions, leading to a decrease of hydrogen and hydrocarbons and a slight increase in CO₂.

However, with an S/C ratio of 1.11, the hydrogen concentration did not vary greatly and the results show a decrease in hydrocarbons as more oxygen was added. Thus, the appropriate addition of oxygen is considered necessary to promote the shift reaction and the reforming reactions by supplying thermal energy through the combustion of hydrocarbons.

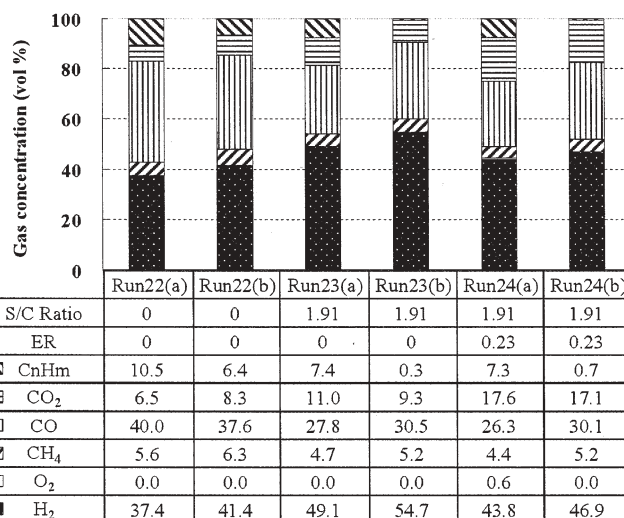


Fig. 5. Comparison of pyrolysis gas yields and reformed gas yields (pyrolysis temperature = 950°C, reforming temperature = 900°C, feed rate = 2.4 g/min; d = 1.5 mm). a, pyrolysis gas; b, reformed gas

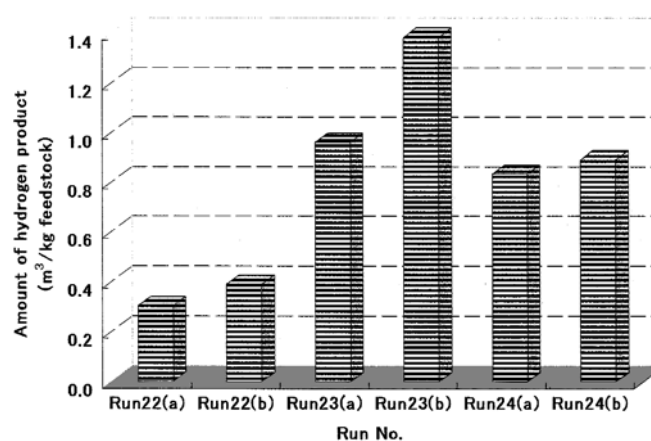


Fig. 6. Effect of operating conditions on hydrogen production (the operating conditions are the same as for Fig. 5)

Effect of reforming performance on hydrogen formation

The reforming performance was evaluated by comparing the gas yields generated from pyrolysis and reforming processes for the same experimental conditions. From Figs. 5 and 6, it is clear that the amount of hydrogen generated and the hydrogen content were substantially increased with reforming for all three sets of conditions.

The increase in hydrogen levels during the reforming process is considered to be the result of the cracking of hydrocarbons and tars. During run 23, with steam injection, hydrocarbons were almost completely reformed into hydrogen and the maximum value of the hydrogen content, 54 vol%, was achieved after reforming. In contrast, only 41 vol% hydrogen was generated from the pyrolysis test. In the case of steam gasification, the reduction of CO₂ after

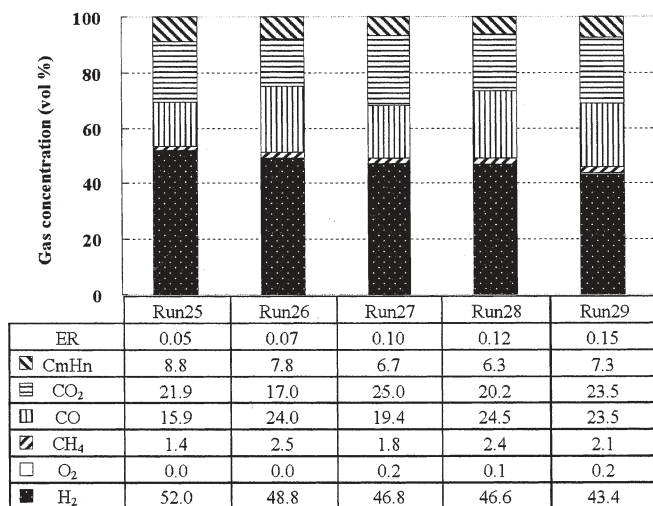


Fig. 7. Effect of ER on reformed gas yields utilizing a catalyst in the reforming process (temperature = 750°C, feed rate = 1.78 g/min, d = 2 mm, S/C ratio = 1.83)

reforming was assumed to be the result of dilution by the large amount of H₂ and CO generated simultaneously. Because of the high-temperature operation, the concentration of hydrocarbons were distinctly lower as a result of both steam gasification and oxygen addition. Clearly, reforming had a significant effect on conversion of hydrocarbons into hydrogen.

The reforming performance was also verified by the overall quantity of hydrogen formation. Figure 6 shows the quantity of hydrogen generated before and after reforming. The results indicate that the quantity of hydrogen generated from the reforming process was much higher than that from the pyrolysis process alone. With a steam addition of S/C = 1.91, about 1.3 m³ hydrogen was generated per kilogram of feedstock after reforming, which proves that the reforming process is indispensable for hydrogen production. From these results, it is clear that reforming improves not only the concentration but also the quantity of hydrogen generated.

Evaluation of catalyst performance

As described above, hydrogen-rich synthesis gas could be generated at high temperatures, especially with appropriate steam and oxygen addition. Low-temperature gasification is an interesting alternative from the energy point of view, but this process usually causes a high tar yield. However, with the use of a catalyst, it was expected that tar could be eliminated. In this study, to confirm the performance of commercial Ni reforming catalyst on the promotion of hydrogen conversion at lower temperatures, catalytic experiments were carried out at 750°C; the experimental results are shown in Fig. 7. The results show that hydrogen was effectively extracted from feedstock through the utilization of the commercial Ni catalyst in the reformer at lower operating temperatures in the presence of steam. Compared

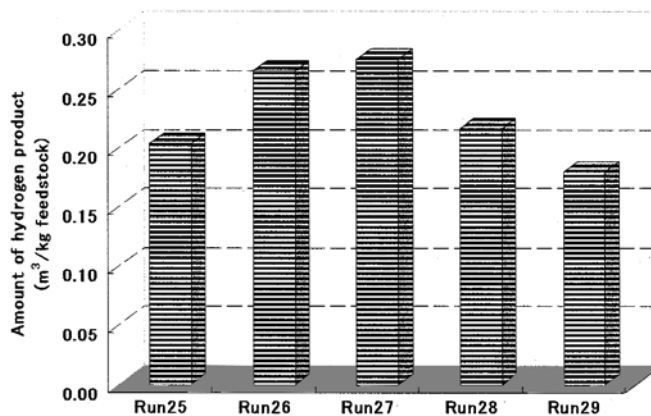


Fig. 8. Influence of operating conditions on hydrogen production (the operating conditions are the same as for Fig. 7)

with the results obtained from noncatalytic gasification experiments, the maximum hydrogen concentration present in the synthesis gas was 52 vol%, which is similar to the results generated from the experiments of noncatalytic steam gasification at 950°C. This indicates that even though the temperature was rather lower, at 750°C, with catalyst utilization, hydrogen-rich synthesis gas could also be effectively generated. These experimental results proved that the activation of commercial FCR-4 Ni catalyst was somewhat higher in the secondary reactor and was stable, with no further deactivation found after 20 h. Moreover, coke formation was not observed on the catalyst surface.

The performance of the catalyst was also evaluated in terms of the overall quantities of hydrogen produced. The quantities of hydrogen from the catalytic gasification experiments are shown in Fig. 8; however, even though hydrogen concentration is similar to that from non-catalytic gasification at 950°C, the overall quantity of hydrogen generated is much less. The reason is considered to be that the amount of pyrolysis gas generated was less as a result of incomplete devolatilization at the lower temperature. Taking account of the hydrogen concentration and the amount of hydrogen produced, the maximum hydrogen conversion was achieved with added oxygen at ER = 0.07 in the FCR-4 catalytic gasification process.

Another advantage of using catalysts in the reforming process is considered to be the promotion of tar cracking. In the absence of catalyst in reforming at 750°C, the average tar level in the reformed gases (from run 1 to 3) was 27.3 g/m³_N. However, at the same temperature, this value was successfully reduced to 8.3 g/m³_N on using FCR-4 catalyst in the reforming process (runs 25–29).

Conclusions

From the above experimental results, we concluded that hydrogen can be efficiently extracted from biomass via high-temperature steam gasification and reforming tech-

nologies with considerable oxygen addition. Temperature was verified as the most important factor influencing hydrogen formation. Although the appropriate amount of steam and oxygen addition promotes hydrogen conversion, excessive addition had a negative effect. Therefore, the optimal design of operating parameters for efficient hydrogen production is essential. At 950°C, with appropriately selected operating conditions, hydrogen-rich synthesis gas containing about 54 vol% hydrogen was generated. However, it was also demonstrated that the use of a catalyst could promote hydrogen generation, and by using a commercial steam reforming Ni catalyst in the reforming process, similar hydrogen concentrations as above could be generated at only 750°C. Therefore, the application of a catalyst is considered as a potential means to effectively produce hydrogen via low-temperature gasification and reforming.

References

- Kawamoto K, Kuramochi H, Wu W (2004) Current status and future prospects of hydrogen production from biomass and wastes by using a pyrolysis–gasification and reforming process (in Japanese). *Waste Manag Res* 15(6):443–455
- Fierro V, Klouz V, Akdim O, Mirodatos C (2002) Oxidative reforming of biomass-derived ethanol for hydrogen production in fuel cell applications. *Catal Today* 75:141–144
- Bjorklund A, Melaina M, Keoleian G (2001) Hydrogen as a transportation fuel produced from thermal gasification of municipal solid waste: an examination of two integrated technologies. *Int J Hydrogen Energy* 26:1209–1221
- Belgiorno V, De Feo G, Bella Rocca C, Napoli RMA (2003) Energy from gasification of solid wastes. *Waste Manag* 23:1–15
- Morris M, Waldheim L (1998) Energy recovery from solid waste fuels using advanced gasification technology. *Waste Manag* 18:557–564
- Lange HJD, Barbucci P (1998) The thermie energy farm project. *Biomass Bioenergy* 15:219–224
- Dayton DC (2001) Fuel cell integration – a study of the impacts of gas quality and impurities: Milestone Completion Report. National Renewable Energy Laboratory Press, Colorado, USA
- Caglar A, Demirbas A (2002) Hydrogen-rich gas mixture from olive husk via pyrolysis. *Energy Convers Manag* 43:109–117
- Encinar JM, Gonzalez JF, Gonzalez J (2002) Steam gasification of *Cynara cardunculus* L.: influence of variables. *Fuel Process Technol* 75:27–43
- Demirbas A (2002) Pyrolysis and steam gasification processes of black liquor. *Energy Convers Manag* 43:877–884
- Turn S, Kinoshita C, Zhang Z, Ishimura D, Zhou J (1998) An experimental investigation of hydrogen production from biomass gasification. *Int J Hydrogen Energy* 23:641–648
- Franco C, Pinto F, Gulyurtlu I, Cabrita I (2003) The study of reactions influencing the biomass steam gasification process. *Fuel* 82:835–842
- Drift AVD, Doorn JV, Vermeulen JW (2001) Ten residual biomass fuels for circulating fluidized-bed gasification. *Biomass Bioenergy* 20:45–56
- Mathieu P, Dubuisson R (2002) Performance analysis of a biomass gasifier. *Energy Convers Manag* 43:1291–1299
- Rapagna S, Jand N, Foscolo PU (1998) Catalytic gasification of biomass to produce hydrogen-rich gas. *Int J Hydrogen Energy* 23:551–557
- Rapagna S, Jand N, Kiennemann A, Foscolo PU (2000) Steam gasification of biomass in a fluidised-bed of olivine particles. *Biomass Bioenergy* 19:187–197
- Baker EG, Mudge LK, Brown MD (1987) Steam gasification of biomass with nickel secondary catalysts. *Ind Eng Chem Res* 26:1335–1339
- Demirbas A (2001) Yields of hydrogen-rich gaseous products via pyrolysis from selected biomass samples. *Fuel* 80:1885–1891
- Rapagna S, Provendier H, Petit C, Kiennemann A, Foscolo PU (2002) Development of catalysts suitable for hydrogen or syn-gas production from biomass gasification. *Biomass Bioenergy* 22:377–388
- Schmieder H, Abeln J, Boukis N (2000) Hydrothermal gasification of biomass and organic wastes. *J Supercrit Fluids* 17:145–153
- Asadullah M, Ito S, Kunimori K, Yamada M, Tomishige K (2002) Biomass gasification to hydrogen and syngas at low temperature: novel catalytic system using fluidized-bed reactor. *J Catal* 208:255–259
- Asadullah M, Tomishige K, Fujimoto K (2001) A novel catalytic process for cellulose gasification to synthesis gas. *Catal Commun* 2:63–68
- Fatsikostas AN, Kondarides DI, Verykios XE (2002) Production of hydrogen for fuel cells by reformation of biomass-derived ethanol. *Catal Today* 75:145–155
- Carcia L, French R, Czernik S, Chornet E (2000) Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. *Appl Catal A: General* 201:225–239
- Courson C, Udron L, Swierczynski D, Petit C, Kiennemann A (2002) Hydrogen production from biomass gasification on nickel catalysts: tests for dry reforming of methane. *Catal Today* 76:75–86
- Kim HY (2003) A low-cost production of hydrogen from carbonaceous wastes. *Int J Hydrogen Energy* 28:1179–1186
- Franco C, Pinto F, Gulyurtlu I, Cabrita I (2003) The study of reactions influencing the biomass steam gasification process. *Fuel* 82:835–842