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# Role of Catalyst and Its Fluidization in the Catalytic Gasification of Biomass to Syngas at Low Temperature

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The catalytic gasification of cellulose at much lower temperature than the usual methods such as noncatalytic and dolomite-catalyzed gasification became possible by the combination of the high-performance catalyst and fluidized-bed reactor. In the catalyst development, it is found that the Rh/CeO<sub>2</sub>/SiO<sub>2</sub> with 35% CeO<sub>2</sub> content showed the best performance with respect to the carbon conversion and product distribution. Enough fluidization is very important for the removal of char deposition on the catalyst surface. In addition, the introduction of air from the bottom of the reactor is also very important because of the direct contact between the catalyst and oxygen molecule. The catalyst for this process has the high activity of combustion and reforming and the smooth redox properties. The fluidized-bed reactor plays important roles in the mixing of the catalyst and pyrolyzed products of cellulose and catalyst circulation between reduced and oxidized states. Almost no tar and char were yielded under the conditions of feeding rate = 12 g/h, equivalence ratio = 0.12, steam feeding rate = 1.80 g/h, and weight of catalyst/feeding rate of biomass = 0.25 h at 873 K, and this makes the process useful.

## Introduction

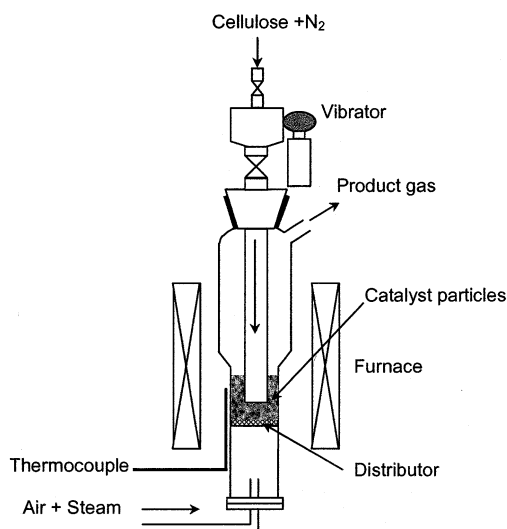
Syngas production from biomass gasification has emerged nowadays as one of the most promising methods to utilize renewable energy resources.<sup>1–3</sup> This is because the syngas can be used as a power generation fuel and can be converted to superclean liquid fuels such as Fischer–Tropsch oil,<sup>4</sup> methanol,<sup>5</sup> and dimethyl ether,<sup>6–8</sup> which all can be used in internal combustion engines. Hydrogen can also be produced from biomass gasification.<sup>9,10</sup> However, as a fuel resource, biomass has stood in the shadow of petroleum for most of its history because the existing state of the art of biomass conversion to liquid or gaseous fuels is not both technically and economically viable. For example, although the commercial scale of biomass gasification is yet to be established, the low-scale pilot plants or the laboratory-scale processes are feasible only at temperatures of 1023–1193 K.<sup>11–16</sup> Although the processes are operated at this temperature range, the product gas from all of the gasification reactors contains tars (a complex mixture of heavy hydrocarbons and oxygenates) and chars (solid carbonaceous materials), which, if not be removed, would damage the engine or turbine for power generation or deactivate the catalyst of methanol, Fischer–Tropsch, and dimethyl ether synthesis reactions.<sup>17–19</sup> The formation of tar and char is a function of temperature.<sup>20</sup> It is known that increasing the temperature decreases the tar content in the product gas; however, it is always unsuitable because of the high energy consumption, causing high production costs of the syngas. To decrease the production costs as well as energy consumption, the process should be operated at lower temperature. However, the operation of the existing biomass gasification process at lower than 973 K provides more tar and char, causing severe problems in the syngas utilization systems. Thus, the syngas from biomass gasification has to be cleaned to a high level of

purity with regard to tars and particulate in order to be compressed and catalytically converted. While physical cleaning systems are feasible, they are not very effective and also produce an effluent treatment and disposal problem, which can aggravate rather than solve the problems.

The catalytic cracking of tar and char either in the primary reactor or in the secondary reactor has been considered as the most promising route for producing clean product gas. The optimized gasifier (design and operation variables) followed by a catalytic reactor has nowadays been widely used.<sup>21,22</sup> Dolomites<sup>23–25</sup> and steam-reforming nickel-based catalysts<sup>26–31</sup> are the most common catalysts for tar cracking in the secondary reactor at 1073–1173 K for dolomite and 973–1073 K for nickel-based catalysts. On the basis of the reports, about 90–99% tar (depending on the temperatures of 973–1073 K and catalyst types) has been converted to gas on the nickel-based catalysts in the secondary reactor. However, the in-bed use of dolomite or nickel catalysts is less effective with respect to tar reduction because of the deactivation of the catalysts.<sup>32,33</sup>

Of course, the results of the secondary bed reactor are promising; however, from the technical and economical points of view, the process must be more developed, such as the one-step process being much better than the two-step one. In addition, the char or coke produced in a great extent in the primary reactor has a chance to take part in the catalytic cracking on the primary bed catalyst. Thus, it seems that the use of the catalyst in the primary reactor would simplify the overall process and both the tar and char would be catalytically converted to gas. A small number of reports demonstrated such a process using the nickel-based catalysts under the conditions of  $W/mb$  (weight of catalyst/feeding rate of biomass) = 0.833 h and throughput = 37 kg/h·m<sup>2</sup> at 1023 K.<sup>34,35</sup> This process gave 90% carbon conversion with 10% solid. However, in this system the nickel-based catalysts were deactivated by carbon deposition on the catalyst surface within a matter of a few minutes.

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**Figure 1.** Diagram of the continuous-feeding fluidized-bed reactor.

On the other hand, it has been reported that the catalyst was deactivated within 25 min when  $W/mb$  was lower than 0.6 h and throughput = 17–50 kg of biomass/ $h \cdot m^2$  at 973 K.<sup>36–38</sup> The coke-like materials were deposited on the catalyst surface and deactivated the catalyst suddenly.

Although the primary bed catalytic gasification of biomass is the most promising, a very limited number and types of catalysts have been investigated with the less successful information. To find an efficient catalyst, we have previously investigated various types of supports and supported noble metal catalysts. Fortunately, we have found  $CeO_2$  to be a quite good in-bed material for the batch-feeding fluidized-bed reactor that shows a much better performance in cellulose gasification, especially for hydrogen production, than the so-called basic oxide such as  $MgO$  or  $CaO$ . The loading of Rh metal on  $CeO_2$  efficiently converted the total carbon in the cellulose at low temperature (823 K).<sup>39,40</sup> However, the catalyst activity gradually decreased during the reaction because of sintering of  $CeO_2$  under the reaction conditions. Thus, we have further developed the catalyst by loading  $CeO_2$  on the high surface area  $SiO_2$  (380  $m^2/g$ ) followed by Rh loading. The Rh/ $CeO_2$ / $SiO_2$  catalyst showed an excellent performance in cellulose gasification at very low temperature. In this paper, we describe the effect of various operating variables of the cellulose gasification reaction.

## Experimental Section

**Experimental Procedure.** The continuous-feeding fluidized-bed reactor was used for cellulose (Merck) gasification. The operational system has been previously described;<sup>39</sup> however, the reactor dimension and the feeding system have been modified. The gasification reactor is a quartz tube of 66 cm height and 15 mm i.d. and included a fluidized-bed section. The sketch diagram of the gasification reactor is shown in Figure 1. The feeder consisted of a glass vessel with a valve at the bottom, which makes the feed almost adjustable. The feeder was constantly vibrated with a vibrator for cellulose transportation through the valve. Cellulose particles were transported to the catalyst bed by the flow of  $N_2$  gas through an inner tube of 7 mm i.d. Two streams were introduced from the bottom of the reactor;

one is air, and the other one is steam. The steam was supplied by using a microfeeder through a capillary tube inserted from the bottom to the middle of the reactor. The water vaporized inside the stainless steel capillary tube and mixed with air inside the reactor.

The outside temperature of the reactor and the temperatures at different points inside the catalyst bed were measured by thermocouples. The process was operated at atmospheric pressure. The concentrations of  $CO$ ,  $CO_2$ , and  $CH_4$  were determined by a flame ionization detector gas chromatograph (FID-GC) equipped with a methanator by using a stainless steel column packed with Gaskuropack 54, and the concentration of hydrogen was determined by a thermal conductivity detector GC (TCD-GC) using a stainless steel column packed with molecular sieve 13X. The flow rate of the effluent gas was measured by a soap membrane meter. The gas yield was calculated as  $m^3/kg$  of cellulose from the GC analysis of the effluent gas. Carbon conversion to gas (C conversion) was calculated from the equation (yield of  $CO + CO_2 + CH_4 + C_2$  hydrocarbon)/(total C feeding of cellulose)  $\times 100$ . In the catalytic reaction, the formation of  $C_2$  hydrocarbons was almost negligible under some conditions. The C conversion and the gas yield are averaged over 25 min. The yield of char was determined by the amount of gas (mainly  $CO_2$ ) formed after stopping the feed of cellulose under air flow at the reaction temperature. The amount of tar was calculated by subtracting the amounts of C conversion (%) and char yield (%) from 100.

**Catalyst.** To prepare  $CeO_2/M$  type supports,  $Ce(NH_4)_2(NO_3)_6$  was loaded on M [ $M = SiO_2$  (Aerosil 380; 380  $m^2/g$ ),  $Al_2O_3$  (Aerosil aluminum oxide C; 100  $m^2/g$ ), and  $ZrO_2$  (Daiichi-Kigenso Co. Ltd., 100  $m^2/g$ )] by an incipient wetness method using an aqueous solution of  $Ce(NH_4)_2(NO_3)_6$ , and then the solid was dried at 393 K for 12 h followed by calcination at 773 K for 3 h under an air atmosphere. The loading amount of  $CeO_2$  is denoted in parentheses. Rh was loaded on the support by the impregnation of the support with an acetone solution of  $Rh(C_5H_7O_2)_3$ . After drying for 12 h, the catalyst was pressed, crushed, and sieved to 75–150, 150–250, and 250–850  $\mu m$  particle size. In each run, 3 g of catalyst was used and was pretreated by hydrogen flow of 40  $cm^3/min$  at 773 K for 30 min. The composition of the commercial catalyst (TOYO CCI, G-91) for steam reforming was 14 wt % Ni, 65–70 wt %  $Al_2O_3$ , 10–14 wt %  $CaO$ , and 1.4–1.8 wt %  $K_2O$ . The composition of the dolomite was 20.7–21.0 wt %  $MgO$ , 30.0–31.2 wt %  $CaO$ , 0.7 wt %  $SiO_2$ , 0.1 wt %  $Fe_2O_3$ , and 0.5 wt %  $Al_2O_3$ . Before reaction the dolomite was calcined at 773 K for 3 h followed by hydrogen treatment at 773 K for 0.5 h. The particle size of G-91 and dolomite was 150–250  $\mu m$ .

The fresh (after  $H_2$  treatment) and used catalysts were characterized by a Brunauer–Emmett–Teller (BET) analysis and transmission electron microscopy (TEM). The TEM observation of the fresh and used catalysts was carried out by means of a JEM-2010F microscope (JEOL) operated at 200 kV. Samples were dispersed in tetrachloromethane by a supersonic wave and put on Cu grids for TEM observation under an air atmosphere.

## Results and Discussion

**Catalyst Development and Comparison with the Usual Methods.** We have prepared various types of Rh/

**Table 1. Performance of Various Catalysts in the Gasification of Cellulose**

	Rh/CeO <sub>2</sub> /SiO <sub>2</sub>					Rh/CeO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>	Rh/CeO <sub>2</sub> / ZrO <sub>2</sub>	Rh/ CeO <sub>2</sub>	Rh/ SiO <sub>2</sub>	G-91	dolomite	none	none <sup>a</sup>
CeO <sub>2</sub> content (wt %)	10	20	35	50	80	20	10	98.8					
operating conditions													
catalyst wt, W (g)	3	3	3	3	3	3	3	3	3	3	3		
cellulose feeding rate, mb (g/h)	5.40	5.40	5.40	5.40	5.40	5.40	5.40	5.40	5.40	5.40	5.40	5.40	5.40
W/mb (g of catalyst h/g of cellulose)	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56
throughput (kg of cellulose/h·m <sup>2</sup> )	28	28	28	28	28	28	28	28	28	28	28	28	28
moisture in cellulose (wt %)	5	5	5	5	5	5	5	5	5	5	5	5	5
oxygen (g/h)	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	
nitrogen (g/h)	6.19	6.19	6.19	6.19	6.19	6.19	6.19	6.19	6.19	6.19	6.19	6.19	6.87
ER	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	
temperature (K)	823	823	823	823	823	823	823	823	823	823	823	823	823
reaction time (min)	25	25	25	25	25	25	25	25	25	25	25	25	25
gas composition (vol %, N <sub>2</sub> - and H <sub>2</sub> O-free)													
H <sub>2</sub>	38.66	32.44	30.34	30.83	30.16	23.87	29.05	44.48	36.53	38.31	8.33	8.51	18.25
CO	37.02	30.67	29.49	29.47	29.78	43.63	24.49	31.19	33.89	19.88	30.78	26.88	67.13
CO <sub>2</sub>	19.05	23.96	24.77	22.81	25.55	30.49	28.61	23.03	23.28	31.41	55.54	62.94	11.48
CH <sub>4</sub>	4.91	12.91	15.41	16.89	14.56	2.01	17.51	1.30	5.11	9.89	3.35	1.11	2.85
C <sub>2</sub> H <sub>6</sub>	0.39	0.19	tr	tr	tr	0.10	0.35	tr	1.20	0.52	2.00	0.57	0.38
gas yield (m <sup>3</sup> /kg of cellulose)	1.21	1.15	1.16	1.11	1.02	1.04	0.91	1.34	0.96	1.10	0.37	0.25	0.09
tar yield (g/kg of cellulose) <sup>b</sup>	25.43	4.23	8.46	25.39	50.78	25.43	59.27	29.61	71.92	12.66	105.77	283.36	321.68
tar concentration (g/m <sup>3</sup> ) <sup>b</sup>	11.76	1.98	3.80	11.50	23.12	12.82	27.55	11.59	36.70	6.21	77.37	227.38	292
char yield (g/kg of cellulose) <sup>b</sup>	33.86	21.16	16.93	21.16	21.16	38.12	50.79	29.61	50.79	76.19	143.90	29.62	63.48
carbon conversion to gas (%)	86	90	94	89	83	85	74	86	71	79	39	26	9.00
BET surface area of catalysts (m <sup>2</sup> /g)													
fresh	285	250	208	183	82	66	87	59	312	33	1		
used	277	247	206	176	77	61	86	13	310	31	1		

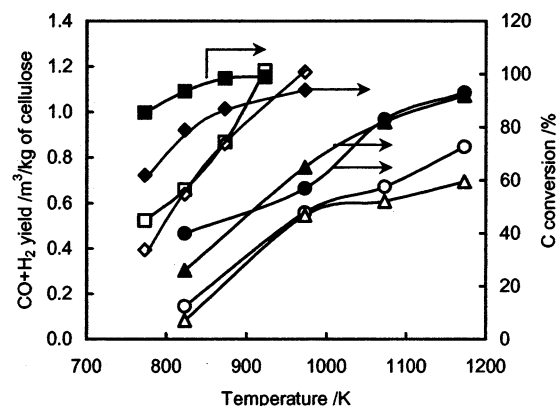
<sup>a</sup> Cellulose pyrolysis. <sup>b</sup> Based on carbon.

CeO<sub>2</sub>/M (M = SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>) catalysts with different CeO<sub>2</sub> loadings and tested them in the cellulose gasification reaction in a continuous-feeding and fluidized-bed reactor. The performances of catalysts with respect to the carbon conversion (C conversion), gas, tar, and char yields, product gas composition, and tar concentration are listed in Table 1. The results of noncatalyzed and dolomite-catalyzed reactions are also listed in Table 1. In an ideal gasification of cellulosic biomass, the total carbon and hydrogen in the cellulose should be converted to CO and H<sub>2</sub>; however, in practice some tar, char, H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, and higher hydrocarbons are usually formed. The level of the tar and char formation is a function of the type of oxidant (air, oxygen, steam, or pyrolytic), temperature, and geometry of the reactor. In our gasification system, the cellulose was first subjected to the pyrolysis reaction in the feeding tube, where only 9% carbon (Table 1) in the cellulose converted to gas, mainly to CO (67%) because nitrogen is used as the carrier gas of cellulose. The rest of the carbon in cellulose was yielded in the tar and char as 321 (76 wt % C) and 63 g/kg (15 wt % C) of cellulose. This pyrolytic product composition of cellulose at 823 K is almost the same as that reported.<sup>41</sup> The pyrolytic products then were blown to the gasification zone by the flow of nitrogen through the inner tube. As in Table 1, in the noncatalytic gasification, the total C conversion to gas is only 26%, where the H<sub>2</sub> concentration was very low (8.51 vol %) at 823 K. The presence of a well-known bed material, dolomite, for biomass gasification remarkably increased the C conversion (39%) and also the CO concentration at 823 K; however, the H<sub>2</sub> concentration slightly increased. On the other hand, 79% C conversion with 1.1 m<sup>3</sup>/kg of cellulose gas yield was achieved at 823 K by in-bed use of a commercial G-91 catalyst in

our system (Table 1). The formation of H<sub>2</sub> (38 vol %) promoted drastically by G-91 may be due to the reforming activity of this catalyst. The Rh/CeO<sub>2</sub> catalyst gave 86% C conversion and 1.34 m<sup>3</sup>/kg of cellulose gas yield with higher concentrations of H<sub>2</sub> (44 vol %) and CO (31 vol %). However, the substantial decrease of the surface area of this catalyst because of CeO<sub>2</sub> sintering during the reaction decreased the activity. The Rh/SiO<sub>2</sub> gave 71% C conversion with much lower gas yield (0.96 m<sup>3</sup>/kg of cellulose) under the same conditions. The tar (72 g/kg of cellulose) and char (37 g/kg of cellulose) yields on this catalyst were very high. Interestingly enough, high C conversion (94%) on Rh/CeO<sub>2</sub>/SiO<sub>2</sub> (35) at 823 K was achieved, compared with the noncatalytic and other catalytic reactions. On this catalyst, the tar (8.46 g/kg, 3.8 g/m<sup>3</sup>) and char (17 g/kg of cellulose) yields are very low compared with other catalysts tested. The performance of the Rh/CeO<sub>2</sub>/SiO<sub>2</sub> catalyst was much dependent on the amount of the CeO<sub>2</sub> content in the catalyst with respect to all terms considered in Table 1. The 35% CeO<sub>2</sub> content in the catalyst exhibited the highest performance at such a low temperature (823 K, Table 1). In addition, the surface area of the catalyst was maintained during the reaction. CeO<sub>2</sub> on the other support showed the lower performance.

Figure 2 shows the dependence of the CO + H<sub>2</sub> yield and C conversion on Rh/CeO<sub>2</sub>/SiO<sub>2</sub> (35%), dolomite, G-91, and noncatalyst with respect to temperature. The figure clearly shows that the 100% C conversion with a much higher yield of CO + H<sub>2</sub> was achieved on Rh/CeO<sub>2</sub>/SiO<sub>2</sub> (35%) catalyst at 873 K; however, this value is much lower on dolomite and in noncatalytic reactions even at a much higher temperature (1173 K). Compared with conventional systems where the nickel and dolomite catalysts have been extensively researched as





**Figure 2.** Effect of the temperature on the C conversion and CO + H<sub>2</sub> yield in the gasification of cellulose. Catalyst weight = 3 g; cellulose feeding rate = 5.4 g/h; ER = 0.14. ■, ●, ▲, and ◆: C conversion. □, ○, △, and ◇: CO + H<sub>2</sub> yield. ■ and □: Rh/CeO<sub>2</sub>/SiO<sub>2</sub>. ◆ and ◇: G-91. ● and ○: dolomite. ▲ and △: noncatalyst.

catalysts for tar cracking in both the primary and secondary reactors within 973–1073 K for the nickel catalyst and 1073–1173 K for the dolomite catalyst, our system is much better because it gives a high C conversion and low tar and char yields.<sup>21</sup> Baker et al., at Pacific Northwest Laboratory (PNL), has reported that in the primary bed some of the nickel-based catalysts can result in the maximum of 90% carbon conversion to gas with 10% solid product at 1023 K when  $W/mb = 0.833$  h and throughput = 37 kg/h·m<sup>2</sup> were used.<sup>34,35</sup> However, in this system the nickel-based catalysts were deactivated by carbon deposition on the catalyst surface within a matter of some minutes. On the other hand, Garcia et al. has reported that the catalyst was deactivated within 25 min when  $W/mb$  was lower than 0.6 h and throughput = 17–50 kg of biomass/h·m<sup>2</sup> at 973 K. The C conversion and tar yield were 80.7% and 54 g/kg of biomass on the nickel catalyst even at 1073 K with equivalence ratio (ER) = 0.27.<sup>42</sup> However, in our system the C conversion is 94% on Rh/CeO<sub>2</sub>/SiO<sub>2</sub> (35%) at as low as 823 K under the conditions of  $W/mb = 0.56$  h, throughput = 28 kg/h·m<sup>2</sup>, and ER = 0.14. The tar yield and concentration were 8.5 g/kg of cellulose and 3.8 g/m<sup>3</sup>, respectively. The tar conversion is a function of ER,  $W/mb$ , temperature, and finally the catalyst activity. In our system almost all of the conditions are very mild but difficult for tar and char cracking by conventional catalysts described above; however, only the much higher catalytic activity resulted in higher C conversion with low yields of tar and char. The in-bed use of a well-known dolomite catalyst resulted in 8 g/m<sup>3</sup> of tar content and 27 g/kg of dry biomass of char yield when the conditions applied were 1073 K, ER = 0.20, and  $W/mb = 0.58$ –0.85 h.<sup>43</sup> It showed a better performance to reduce the tar from the product gas than the noncatalytic system as we found; however, its deactivation in the in-bed system decreased the possibility of practical use.<sup>32,33,43–46</sup> The use of dolomite in the secondary reactor within the same temperature range seemed to be more successful than in-bed additions, with up to 95% reduction in tar being reported by Corella et al., although the dolomite appeared to deactivate.<sup>46,47</sup> The nickel-based steam-reforming catalyst in the secondary bed reduced the tar content with about 99% at above 1073 K; however, the problems of substantial catalyst deactivation were caused by the char deposition.<sup>26</sup>

**Table 2.** Minimum Fluidization Velocity of the Catalyst of Various Particle Sizes<sup>a</sup>

particle size (μm)	minimum fluidization velocity (cm/s)
75–150	0.57
150–250	1.43
250–840	4.49

<sup>a</sup> The pressure difference was measured at 823 K using a N<sub>2</sub> flow.

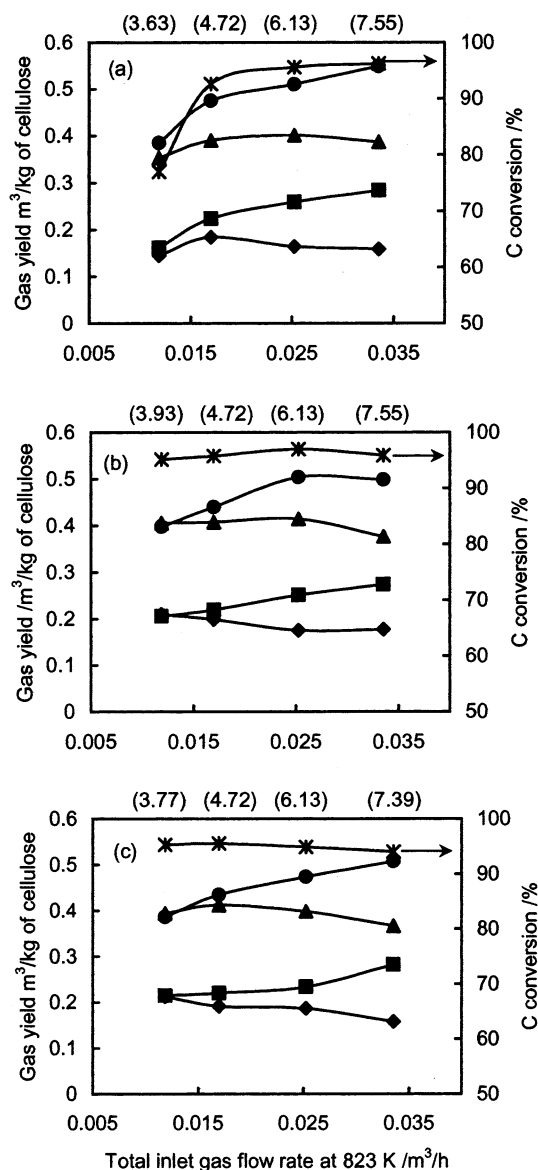
**Table 3.** Effect of Fluidization Velocity on Char and Tar Yields on Various Particle Sizes of Catalyst at 823 K<sup>a</sup>

particle size (μm)	inlet gas velocity (cm/s)	outlet gas velocity (cm/s)	tar yield (g/kg of cellulose)	tar concn (g/m <sup>3</sup> )
75–150	1.87	3.77	11.42	5.85
	2.67	4.72	9.73	4.04
	3.97	6.13	8.46	2.62
	5.27	7.39	11.43	2.67
150–250	1.87	3.93	13.12	6.8
	2.67	4.72	12.69	5.7
	3.97	6.13	1.69	0.52
	5.27	7.55	6.34	1.29
250–840	1.87	3.62	63.48	36.03
	2.67	4.72	22.86	10
	3.97	6.13	13.54	4.25
	5.27	7.55	10.98	2.73

<sup>a</sup> Conditions: catalyst, 3 g; ER, 0.12; steam, 0.60 g/h.

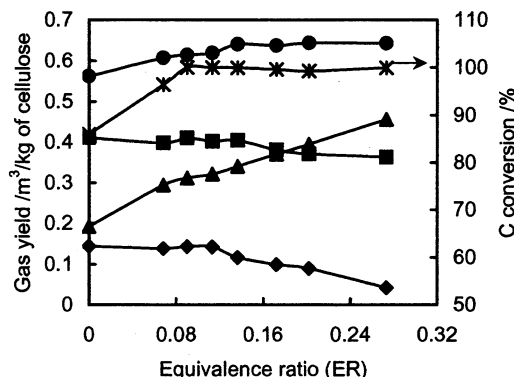
**Effect of Fluidization in the Catalytic Gasification of Cellulose.** The catalytic gasification reaction in a fluidized-bed reactor is affected by the catalyst fluidization rate. The fluidization velocity of the catalyst is much more dependent on the catalyst particle size under a specific fluidization condition. Table 2 shows the minimum fluidization velocity for different sizes of catalyst particles. In this experiment, the nitrogen gas was used for catalyst fluidization. The minimum velocities were 0.57, 1.43, and 4.49 cm/s for 75–150, 150–250, and 250–840 μm particle sizes, respectively.

Figure 3 shows the C conversion and product distribution in yield at various inlet total gas flow rates at 823 K with respect to the different particle sizes of the catalyst. To investigate the effect of fluidization from the minimum to maximum with respect to the particle sizes, the experiments were carried out by using a lower feeding rate (3.78 g/h) of cellulose and pure oxygen at considerably low temperature (823 K). This is because the gasification products can also fluidize the catalyst. The catalyst fluidization velocity is usually decreased with an increase in the particle size under the same conditions. In Figure 3a, the total outlet gas velocity was 3.63 cm/s at the inlet gas flow rate of 0.012 m<sup>3</sup>/h at 823 K. The outlet gas velocity is below the minimum fluidization velocity (4.49 cm/s) over the catalyst with 250–840 μm. The C conversion was much lower when insufficient fluidization of catalyst particles of 250–840 μm occurred (Figure 3a). The tar and char yields within 25 min of reaction under variable fluidization velocities of different particle sizes are shown in Table 3. On the catalyst of particle sizes 250–840 μm, the tar and char yields were much larger than those of other particle sizes. This indicates that insufficient fluidization causes the much larger tar and char yields and the smaller C conversion. The particle size of 150–250 μm showed the constant C conversion within the range of the fluidization velocity (Figure 3b). However, in the case of 75–150 μm particle size (Figure 3c), the C conversion gradually decreased with an increase of the fluidization velocity. This is because the catalyst particles are



**Figure 3.** Effect of the catalyst particle size on the C conversion and various gas yields. Particle sizes = (a) 250–480, (b) 150–250, and (c) 75–150  $\mu\text{m}$ . Catalyst weight = 3 g; cellulose feeding rate = 3.78 g/h; ER = 0.14;  $\text{H}_2\text{O}$  = 0.60 g/h; temperature = 823 K. \*: C conversion. ●:  $\text{H}_2$ . ■: CO. ▲:  $\text{CO}_2$ . ◆:  $\text{CH}_4$ . The values in parentheses above each graph are the product gas flow rates at 823 K.

floating with the higher gas flow, and then the density of the catalyst bed becomes lower. In this case, the pyrolyzed product of cellulose does not contact properly with the catalyst particles. Furthermore, the CO and  $\text{H}_2$  yields slightly increased and  $\text{CO}_2$  and  $\text{CH}_4$  yields decreased with an increase in the gas flow rate in all cases. This suggests that  $\text{CO}_2$  and  $\text{CH}_4$  are secondary products in this reaction. For example, methane is formed by the CO hydrogenation. In addition, the product distribution is almost similar to each other over three kinds of catalysts in the case that the fluidization is enough. This indicates that the diffusion rate of pyrolyzed products is much higher than the reaction rate under typical reaction conditions ( $\text{N}_2$ , 0.003  $\text{m}^3/\text{h}$ ; air, 0.003  $\text{m}^3/\text{h}$ ; cellulose 5.4 g/h; 823 K). The flow rate of gasification products over Rh/CeO<sub>2</sub>/SiO<sub>2</sub> (35%) with 150–250  $\mu\text{m}$  particle size corresponded to 0.034  $\text{m}^3/\text{h}$  (5.3 cm/s). This was higher than the minimum fluidiza-

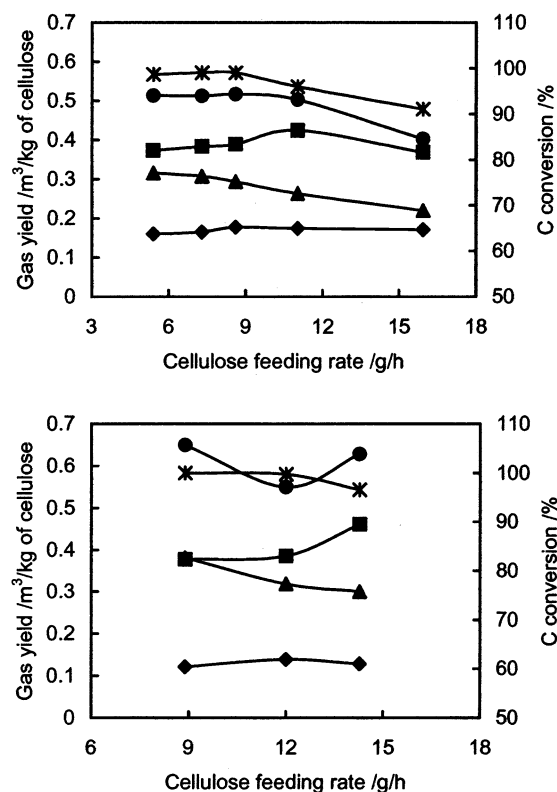


**Figure 4.** Effect of ER on the C conversion and various gas yields. Catalyst weight = 3 g; cellulose feeding rate = 5.4 g/h; ER = 0.14;  $\text{H}_2\text{O}$  = 0.90 g/h; temperature = 873 K. \*: C conversion. ●:  $\text{H}_2$ . ■: CO. ▲:  $\text{CO}_2$ . ◆:  $\text{CH}_4$ .

tion velocity (1.43 cm/s at 823 K). This indicates that the fluidization is enough under the usual reaction conditions.

**Effect of the ER.** Figure 4 represents the dependence of the various gas yields and C conversion with the different ERs. In the absence of oxygen, when an insufficient amount of steam (0.88 g/h) was introduced, the C conversion was as low as 86% with substantial yields of tar and char. The yields of CO and  $\text{CH}_4$  were higher; however, the yields of  $\text{H}_2$  and  $\text{CO}_2$  were lower. The C conversion jumped to the 100% level when at least ER = 0.09 was used, and there was no change in C conversion until ER = 0.27 was used. The char combustion in the presence of oxygen is much faster than the reforming in the presence of steam, and thus the total C conversion increased with an increase in ER. Complete C conversion was achieved where no tar and char were yielded at ER = 0.09, and this value is much lower than the usual gasification conditions (ER = 0.2–0.35). This means that the catalyst Rh/CeO<sub>2</sub>/SiO<sub>2</sub> (35%) used here is much more active than the usual gasification catalysts. The  $\text{CO}_2$  yield constantly increased with an increase in ER. This is because the combustion reaction of tar, char, and  $\text{CH}_4$  as well as the overoxidation of CO increased with an increase in the amount of oxygen supply and, thus, CO and  $\text{CH}_4$  formation rates decreased. Simultaneously, the water gas shift reaction and methane partial oxidation also proceeded, and thus the formation of  $\text{H}_2$  remained almost constant. The total gas yield increased with an increase in ER, and the maximum value (1.51  $\text{m}^3/\text{kg}$  of cellulose) was achieved at ER = 0.14.

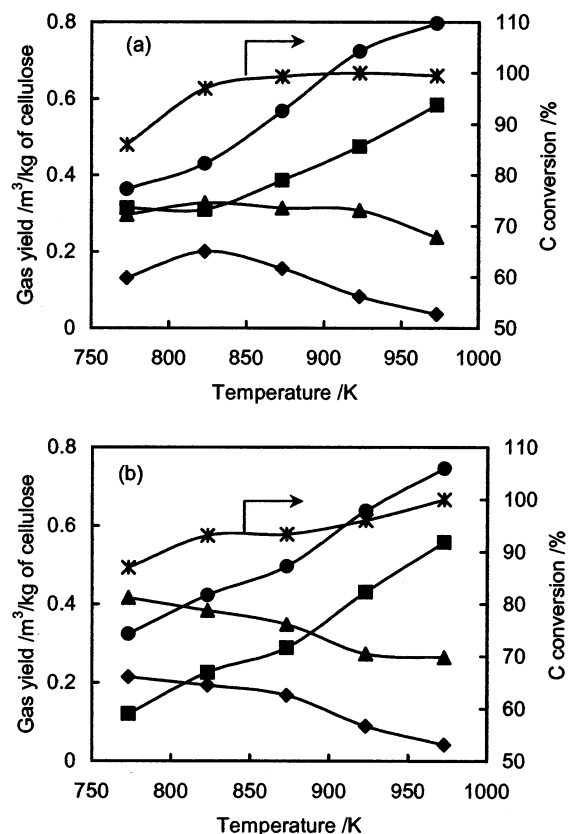
**Effect of the Cellulose Feeding Rate.** The C conversion, gas yield, and the tar and char yields directly depend on the feeding rate under specific reaction conditions, especially under a constant flow rate of the gasifying agents such as the air and steam used here. The results of the feeding rate are shown in Figure 5. The C conversion remained at the 100% level until the feeding rate of 8 g/h, where ER = 0.09, and then decreased with an increase in the feeding rate (Figure 5a). At the higher cellulose feeding rates, when the air and steam feeding rates doubled, the C conversion further achieved a 100% level until the feeding rate of 11.2 g/h (ER = 0.12) and a 97% level until the feeding rate of 14.7 g/h (ER = 0.09) of cellulose (Figure 5b). The CO yield slightly increased until the feeding rate of 11.8 g/h. This is because the increase of the feeding rate at a constant supply of air results in the decrease of ER. The lowering of ER facilitates the reforming reaction



**Figure 5.** Effect of the cellulose feeding rate on the C conversion and various gas yields. Catalyst weight = 3 g; cellulose feeding rate = 5.4 g/h. (a) Air = 3.56 g/h; H<sub>2</sub>O = 0.90 g/h; temperature = 873 K. (b) Air = 7.12 g/h; H<sub>2</sub>O = 1.80 g/h; temperature = 873 K. \*: C conversion. ●: H<sub>2</sub>. ■: CO. ▲: CO<sub>2</sub>. ◆: CH<sub>4</sub>.

to yield CO and H<sub>2</sub> instead of the combustion reaction to yield CO<sub>2</sub>. Consequently, the CO<sub>2</sub> yield decreased in this experiment, as shown in Figure 5. However, at a higher level of feeding, ER becomes insufficient and the C conversion and gas yield decreased remarkably.

**Air from the Top of the Reactor Together with Cellulose.** All of the above experiments were carried out using the air and steam from the bottom, and cellulose was introduced from the top and was transported to the catalyst bed by nitrogen through the inner tube, where the oxygen was completely absent and thus the cellulose was pyrolyzed inside the inner tube. The pyrolyzed products then contacted with the catalyst, and the combustion and reforming reactions proceeded. Figure 6 shows a comparison between the results of the present experiments, where the air was introduced from the top with the cellulose and nitrogen was introduced from the bottom for fluidization of the catalyst (Figure 6b), and those of the previous experiments, where the air and nitrogen were introduced from the bottom of the reactor (Figure 6a). In the case of Figure 6b, oxygen is present in the inner tube, and thus some of the non-catalyzed combustion and partial oxidation of cellulose and pyrolyzed products such as tar, char, methane, and higher hydrocarbons proceeded. We thought that the total oxygen supplied was consumed by these reactions. Consequently, in the catalyst bed only reforming reactions of pyrolyzed products proceeded. However, the char/coke formed from the cellulose and/or tar, which was mainly removed from the catalyst bed by the combustion reaction in the presence of oxygen, did not convert to the gas within this low-temperature range (773–923 K). The net char/coke formation on the catalyst surface during the 25 min reaction time was

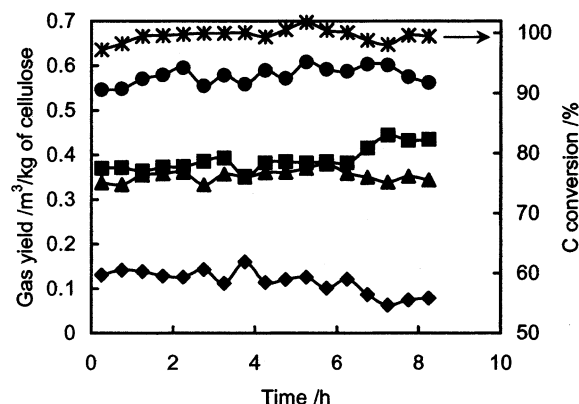


**Figure 6.** Effect of the cellulose feeding with different carrier gases on the C conversion and various gas yields. (a) ER = 0.14; air flow from the bottom. (b) ER = 0.14; air flow with cellulose from the top. H<sub>2</sub>O = 0.90 g/h; temperature = 873 K. \*: C conversion. ●: H<sub>2</sub>. ■: CO. ▲: CO<sub>2</sub>. ◆: CH<sub>4</sub>.

38–13 g/kg of cellulose for the reaction conditions of Figure 6b and 19–0.8 g/kg of cellulose for the reaction conditions of Figure 6a within the temperature range of 773–923 K. Thus, the C conversion was lower until 923 K (Figure 6b) than that of the process, where the air was introduced from the bottom (Figures 6a). However, at high temperature (973 K), where the catalytic steam-reforming reaction is very fast, the total carbon converted to gas (Figure 6b). Because the C conversion is lower until 923 K, the total gas yield is reasonably lower; however, the yield of CO<sub>2</sub> is higher because of the noncatalytic combustion of cellulose and pyrolyzed products in the inner tube. Furthermore, although the yield of reforming products (CO and H<sub>2</sub>) increased with an increase in the temperature, the overall gas yield is comparatively lower. The methane yield is favorable at the lower temperature and decreased with an increase in the temperature.

**Catalyst Life Test.** Figure 7 shows the catalyst life test results at 873 K for 8 h using 150–250  $\mu$ m catalyst particles. The cellulose feeding rate was maintained at 5.36 g/h. The C conversion and the various product gas yields were almost constant within the experimental error range over the reaction duration. This suggests that the catalyst did not lose the activity for cellulose gasification under the conditions applied. The BET surface area was determined, and TEM images were taken for the used catalyst. The BET surface area remained almost constant. Furthermore, the TEM images showed that the catalyst structure remained intact. These suggested that the catalyst will be able to be alive in the prolonged reaction time. However, we have





**Figure 7.** Catalyst life test. Catalyst weight = 3 g; cellulose feeding rate = 5.4 g/h; ER = 0.14; H<sub>2</sub>O = 0.9 g/h; temperature = 873 K. \*: C conversion. ●: H<sub>2</sub>. ■: CO. ▲: CO<sub>2</sub>. ◆: CH<sub>4</sub>.

observed some attrition of the catalyst particles, which is known to be a common problem of the fluidized-bed process.

**Function of Fluidization.** In the catalytic gasification of cellulose using a fluidized-bed reactor, the catalyst and the reactor are thought to be multifunctional. The gasification reactor may be divided into three sections such as (1) pyrolysis zone (feeding line), where the oxygen and external steam are completely absent, (2) combustion zone (bottom part of the catalyst bed), where oxygen is present and the catalyst particles exist in the oxidized form, and (3) reforming zone (upper part of the catalyst bed), where oxygen is absent and the catalyst particles exist in the reduced form. In the feeding line of the reactor, the cellulose thermally decomposed to the tar, char, steam, and a small fraction of the product gas. The pyrolyzed products such as the volatile tar and solid char first contact the catalyst particles in the combustion zone, where part of the tar and char may take part in the combustion reaction to form CO<sub>2</sub> and H<sub>2</sub>O. Because the catalyst particles are in the fluidized conditions, the oxidized catalyst with adsorbed tar and/or char quickly moved up and turned out to be reduced at the upper part, where the tar and char take part in the reforming reaction in the presence of steam on the catalyst surface to form CO and H<sub>2</sub>. In the fluidized-bed catalyst, if oxygen is used, the characteristic reduction and oxidation cycle of the catalyst exists. Thus, an ideal catalyst must convert the tar and char to a useful gas in the presence of steam and/or oxygen completely by the reforming and combustion reactions. The reforming reaction of comparably active hydrocarbons in the presence of steam proceeds to produce CO and H<sub>2</sub> over the reduced catalyst; however, the combustion reaction of any carbonaceous materials characteristically proceeds to produce CO<sub>2</sub> and H<sub>2</sub>O over the oxidized catalyst. In addition, the combustion reaction is faster than the reforming reaction. Furthermore, the biomass-derived tar is more active than char. Consequently, the tar usually takes part in the reforming reaction on the reduced surface at the upper part; however, the char is more refractory in nature and takes part in the combustion reaction on the oxidized catalyst at the bottom part. In biomass gasification, both reactions are very important for complete conversion of carbon in the feed. On the dolomite and G-91, the C conversion was much lower even at high temperature because of lower of the reforming and combustion activity of tar and char on them. However, interestingly enough, the Rh/CeO<sub>2</sub>/SiO<sub>2</sub> (35%) catalyst promoted both

of the reactions remarkably, resulting in the complete C conversion to gas even at low temperature. Furthermore, in the case that the catalyst fluidization was not enough, a larger amount of char was formed. This is because the deposition rate of char on the catalyst surface is much higher than the removal rate by the reforming and combustion reactions. Because the oxygen supply was limited (ER = 0.07–0.27), the total char formed was not completely burned during the reaction. Methane combustion activity has been tested using the gas of 2% CH<sub>4</sub> in air, and it was found that Rh/CeO<sub>2</sub>/SiO<sub>2</sub> (35%) had a much higher activity than Rh/CeO<sub>2</sub>, Rh/SiO<sub>2</sub>, and G-91. In addition, it has been reported that the fluidized-bed reactor is very effective in removing the low reactive carbonaceous species in the methane reforming with CO<sub>2</sub> and O<sub>2</sub>.<sup>48–50</sup> The high performance of the Rh/CeO<sub>2</sub>/SiO<sub>2</sub> (35%) catalyst is thought to be due to the smooth redox properties in the combination of Rh and CeO<sub>2</sub>. In terms of the stability, Rh/CeO<sub>2</sub>/SiO<sub>2</sub> (35%) also exhibited a high performance. Sintering of CeO<sub>2</sub> is prohibited by SiO<sub>2</sub>, and thus Rh metal particles remained highly dispersed on CeO<sub>2</sub>/SiO<sub>2</sub>. According to the TEM observation, the particle size of Rh was estimated to be 4 ± 1 nm. In addition, the fluidized-bed reactor can promote the heat transfer from the exothermic zone to the endothermic zone and make the reactor temperature homogeneous. In our system, the lower part of the reactor is an exothermic zone, and the upper part of the reactor is an endothermic zone.

## Conclusions

(1) The Rh/CeO<sub>2</sub>/SiO<sub>2</sub> (35%) catalyst showed an excellent performance with respect to the C conversion and gas yield at low temperature compared with the non-catalytic and dolomite-catalyzed reactions at high temperature.

(2) The fluidization rate greatly affected the C conversion. The insufficient fluidization caused lower C conversion and a larger amount of char.

(3) The catalyst particle size of 150–250 μm was found to be the best for suitable fluidization in our reaction system.

(4) The introduction of O<sub>2</sub> enhanced C conversion effectively even by the small amount of O<sub>2</sub>.

(5) Complete C conversion was achieved when the maximum feeding rate was 12 g/h under the conditions of ER = 0.12, steam feeding rate = 1.80 g/h, and W/mb = 0.25 h at 873 K. Almost no tar and char were formed either in the gas product or on the catalyst surface. The conditions applied here are very mild but difficult for tar and char cracking in a conventional gasification method.

(6) The air flow from the top through feeding tube decreased the C conversion. This suggests that the catalyst can contact with oxygen for the gasification when air is introduced from the bottom.

(7) The catalyst performance remained constant without deactivation until the reaction was performed (8 h). The BET surface area remained almost constant after a long reaction time. The structural change of the catalyst was not observed by TEM and BET surface area measurements. A small attrition of the catalyst particles, which is common to all fluidized-bed systems, was observed.

(8) For the catalytic gasification of biomass at low temperature, the combination of the excellent catalyst with the fluidized-bed reactor is very important. The



function of the catalyst is reforming of tar to syngas and the combustion of inactive char. The function of the fluidized-bed reactor is to make contact of the catalyst and biomass-derived tar and char. In addition, catalyst circulation in an oxidizing and reducing atmosphere can reproduce the fresh surface in the reactor during the reaction. Under some mild conditions in this investigation, no tar and char/coke were yielded, and this makes the process useful.

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## Literature Cited

- (1) Bridgwater, A. V. The Technical and Economic Feasibility of Biomass Gasification for Power Generation. *Fuel* **1995**, 74, 631.
- (2) Ramachandra, T. V.; Joshi, N. V.; Subramanian, D. K. Present and Prospective Role of Bioenergy in Regional Energy System. *Renewable Sustainable Energy Rev.* **2000**, 4, 375.
- (3) Maniatis, K.; Millich, E. Energy from Biomass and Waste: the Contribution of Utility Scale Biomass Gasification Plants. *Biomass Bioenergy* **1998**, 15, 95.
- (4) Schulz, H. Short History and Present Trends of Fischer-Tropsch Synthesis. *Appl. Catal. A* **1999**, 186, 3.
- (5) Yaning, C.; Yuqin, N.; Zhenghua, C. Synthesis of Methanol and Isobutanol from Syngas over ZrO<sub>2</sub>-Based Catalysts. *Fuel Process. Technol.* **1997**, 50, 163.
- (6) Ng, K. L.; Chadwick, D.; Toseland, B. A. Kinetics and Modelling of Dimethyl Ether Synthesis from Synthesis Gas. *Chem. Eng. Sci.* **1999**, 54, 3587.
- (7) Huang, Y.; Ge, Q.; Li, S.; Qiu, F. Bifunctional Catalysts for Conversion of Synthesis Gas to Dimethyl Ether. *Appl. Catal. A* **1998**, 167, 23.
- (8) Shikada, T.; Ohno, Y.; Ono, M.; Mizuguchi, M.; Tomura, K.; Fujimoto, K. *Stud. Surf. Sci. Catal.* **1998**, 119, 515.
- (9) Garcia, L.; Frence, R.; Czernik, S.; Chornet, E. Catalytic Steam Reforming of Bio-Oils for the Production of Hydrogen: Effects of Catalysts Composition. *Appl. Catal. A* **2000**, 201, 225.
- (10) Minowa, T.; Inoue, S. Hydrogen Production from Biomass by Catalytic Gasification in Hot Compressed Water. *Renewable Energy* **1999**, 16, 1114.
- (11) Narviez, I.; Orfo, A.; Aznar, M. P.; Corella, J. Biomass Gasification with Air in an Atmospheric Bubbling Fluidized Bed. Effect of Six Operational Variables on the Quality of the Produced Raw Gas. *Ind. Eng. Chem. Res.* **1996**, 35, 2110.
- (12) Vriesman, P.; Heginuz, E.; Sjöström, K. Biomass Gasification in a Laboratory-Scale AFBG: Influence of the Location of the Feeding Point on the Fuel-N Conversion. *Fuel* **2000**, 79, 1371.
- (13) Blasi, C. D.; Signorelli, G.; Portoricco, G. Countercurrent Fixed-Bed Gasification of Biomass at Laboratory Scale. *Ind. Eng. Chem. Res.* **1999**, 38, 2571.
- (14) Gil, J.; Aznar, M. P.; Caballero, M. A.; Frances, E.; Corella, J. Biomass Gasification in Fluidized Bed at Pilot Scale with Steam-Oxygen Mixtures. Product Distribution for Very Different Operating Conditions. *Energy Fuels* **1997**, 11, 1109.
- (15) Beenackers, A. A. C. M. Biomass Gasification in Moving Beds. A Review of European Technologies. *Renewable Energy* **1999**, 16, 1180.
- (16) Muccio, F.; Moersch, O.; Spliethoff, H.; Hein, K. R. G. Generation and Conversion of Carbonaceous Fine Particles during Bubbling Fluidized Bed Gasification of a Biomass Fuel. *Fuel* **1999**, 78, 1473.
- (17) Maniatis, K.; Beenackers, A. A. C. M. Tar Protocols. IEA Bioenergy Gasification Task. *Biomass Bioenergy* **2000**, 18, 1.
- (18) Abatzoglou, N.; Barker, N.; Hasler, P.; Knoef, H. The Development of a Draft Protocol for the Sampling and Analysis of Particulate and Organic Contaminants in the Gas from Small Biomass Gasifiers. *Biomass Bioenergy* **2000**, 18, 5.
- (19) Knoef, H. A. M.; Koele, H. J. Survey of Tar Measurement Protocols. *Biomass Bioenergy* **2000**, 18, 55.
- (20) Brage, C.; Yu, Q.; Chen, G.; Sjöström, K. Tar Evaluation Profiles Obtained from Gasification of Biomass and Coal. *Biomass Bioenergy* **2000**, 18, 87.
- (21) Bridgwater, A. V. Catalysis in Thermal Biomass Conversion. *Appl. Catal. A* **1994**, 116, 5.
- (22) Sutton, D.; Kelleher, B.; Ross, J. R. H. Review of Literature on Catalysts for Biomass Gasification. *Fuel Process. Technol.* **2001**, 73, 155.
- (23) Pérez, P.; Aznar, M. P.; Caballero, M. A.; Gil, J.; Martin, J. A.; Corella, J. Hot Gas Cleaning and Upgrading with a Calcined Dolomite Located Downstream a Biomass Fluidized Bed Gasifier Operating with Steam-Oxygen Mixtures. *Energy Fuels* **1997**, 11, 1194.
- (24) Corella, J. Criteria for Selection of Dolomites and Catalysts for Tar Elimination from Biomass Gasification Gas; Kinetic Constants. *Fuel Abstr.* **1997**, 38, 163.
- (25) Delgado, J.; Aznar, M. P.; Corella, J. Biomass Gasification with Steam in Fluidized Bed: Effectiveness of CaO, MgO, and CaO-MgO for Hot Raw Gas Cleaning. *Ind. Eng. Chem. Res.* **1997**, 36, 1535.
- (26) Caballero, M. A.; Corella, J.; Aznar, M. P.; Gil, J. Biomass Gasification with Air in Fluidized Bed. Hot Gas Cleanup with Selected Commercial and Full-Size Nickel-Based Catalysts. *Ind. Eng. Chem. Res.* **2000**, 39, 1143.
- (27) Corella, J.; Orio, A.; Toledo, J. M. Biomass Gasification with Air in a Fluidized Bed: Exhaustive Tar Elimination with Commercial Steam Reforming Catalysts. *Energy Fuels* **1999**, 13, 702.
- (28) Corella, J.; Orio, A.; Aznar, P. Biomass Gasification with Air in Fluidized Bed: Reforming of the Gas Composition with Commercial Steam Reforming Catalysts. *Ind. Eng. Chem. Res.* **1998**, 37, 4617.
- (29) Aznar, M. P.; Caballero, M. A.; Gil, J.; Martin, J. A.; Corella, J. Commercial Steam Reforming Catalysts to Improve Biomass Gasification with Steam-Oxygen Mixtures. 2. Catalytic Tar Removal. *Ind. Eng. Chem. Res.* **1998**, 37, 2668.
- (30) Caballero, M. A.; Aznar, M. P.; Gil, J.; Martin, J. A.; Frances, E.; Corella, J. Commercial Steam Reforming Catalysts to Improve Biomass Gasification with Steam-Oxygen Mixtures. 1. Hot Gas Upgrading by the Catalytic Reactor. *Ind. Eng. Chem. Res.* **1997**, 36, 5227.
- (31) Narviez, I.; Corella, J.; Orio, A. Fresh Tar (from a Biomass Gasifier) Elimination over a Commercial Steam-Reforming Catalyst. Kinetics and Effect of Different Variables of Operation. *Ind. Eng. Chem. Res.* **1997**, 36, 317.
- (32) Aznar, M. P.; Delgado, J.; Corella, J.; Lahoz, J. In *Pyrolysis and Gasification*; Ferraro, G.-L., Maniatis, K., Buekens, A., Bridgwater, A. V., Eds.; Elsevier Applied Science: London, 1989; p 629.
- (33) Aznar, M. P.; Delgado, J.; Corella, J.; Lahoz, J.; Aragües, J. L. In *Biomass for Energy, Industry and Environment*; Grassi, G., Collina, A., Zibetta, H., Eds.; 6th EC conference; Elsevier: Amsterdam, The Netherlands, 1992; p 707.
- (34) Baker, E. G.; Mudge, L. K.; Brown, M. D. Steam Gasification of Biomass with Nickel Secondary Catalysts. *Ind. Eng. Chem. Res.* **1987**, 26, 1335.
- (35) Baker, E.; Mudge, L.; Wilcox, W. A. Catalysis of gas-phase reactions in steam gasification of biomass. In *Fundamentals of Thermochemical Biomass Conversion*; Overend, R. P., et al., Eds.; Elsevier Applied Science: London, 1985; p 863.
- (36) Garcia, L.; Salvador, M. L.; Arauzo, J.; Bilbao, R. Catalytic Steam Gasification of Pine Sawdust. Effect of Catalyst Weight/Biomass Flow Rate and Steam/Biomass Ratios on Gas Production and Composition. *Energy Fuels* **1999**, 13, 851.
- (37) Garcia, L.; Salvador, M. L.; Arauzo, J.; Bilbao, R. CO<sub>2</sub> as a Gasifying Agent for Gas Production from Pine Sawdust at Low Temperatures using a Ni/Al Coprecipitated Catalyst. *Fuel Process. Technol.* **2001**, 69, 157.
- (38) Arauzo, J.; Radlein, D.; Piskorz, J.; Scott, D. S. Catalytic Pyrogasification of Biomass. Evaluation of Modified Nickel Catalysts. *Ind. Eng. Chem. Res.* **1997**, 36, 67.
- (39) Asadullah, M.; Tomishige, K.; Fujimoto, K. A Novel Catalytic Process for Cellulose Gasification to Synthesis Gas. *Catal. Commun.* **2001**, 2, 63.
- (40) Asadullah, M.; Tomishige, K.; Fujimoto, K. Catalytic Performance of Rh/CeO<sub>2</sub> in Gasification of Cellulose to Synthesis Gas at Low Temperature. *Ind. Eng. Chem. Res.* **2001**, 25, 5894.

- (41) Güllü, D.; Demirbas, A. Biomass to Methanol via Pyrolysis Process. *Energy Convers. Manage.* **2001**, *42*, 1349.
- (42) Kinoshita, C. M.; Wang, Y.; Zhou, J. Effect of Reformer Conditions on Catalytic Reforming of Biomass-Gasification Tars. *Ind. Eng. Chem. Res.* **1995**, *34*, 2949.
- (43) Gil, J.; Caballero, M. A.; Martin, J. A.; Aznar, M.-P.; Corella, J. Biomass Gasification with Air in a Fluidized Bed: Effect of the In-Bed Use of Dolomite under Different Operation Conditions. *Ind. Eng. Chem. Res.* **1999**, *38*, 4226.
- (44) Ekstrom, C.; Lindman, N.; Pettersson, R. In *Fundamentals of Thempchemical Biomass Conversion*; Overend, R. P., Milne, T. A., Mudge, L. K., Eds.; Elsevier Applied Science: London, 1985; p 601.
- (45) Vassilatos, V.; Brage, C.; Taralas, G.; Sjöström, K. In *Biomass for Energy, Industry, and Environment*; Grassi, G., Collina, A., Zibetta, H., Eds.; 6th EC conference; Elsevier: Amsterdam, The Netherlands, 1992; p 762.
- (46) Corella, J.; Herguido, J.; Gonzalez-Saiz, J.; Alday, F. J.; Rodriguez-Trujillo, J. L. In *Research in Thermochemical Biomass Conversion*; Bridgwater, A. V., Kuester, J. L., Eds.; Elsevier Applied Science: London, 1988; p 754.
- (47) Corella, J.; Aznar, M. P.; Delgado, J.; Aldea, E.; Martinez, P. In *Biomass for Energy, Industry, and Environment*; Grassi, G., Collina, A., Zibetta, H., Eds.; 6th EC conference; Elsevier: Amsterdam, The Netherlands, 1992; p 714.
- (48) Tomishige, K.; Matsuo, Y.; Sekine, Y.; Fujimoto, K. Effective Methane Reforming with CO<sub>2</sub> and O<sub>2</sub> under Pressure Using NiO–MgO and Fluidized Bed Reactor. *Catal. Commun.* **2001**, *2*, 11.
- (49) Tomishige, K.; Matsuo, Y.; Yoshinaga, Y.; Sekine, Y.; Asadullah, M.; Fujimoto, K. Comparative Study between Fluidized Bed and Fixed Bed Reactors in Methane Reforming Combined with Methane Combustion for the Internal Heat Supply under Pressurized Condition. *Appl. Catal. A* **2002**, *223*, 225.
- (50) Matsuo, Y.; Yoshinaga, Y.; Sekine, Y.; Tomishige, K.; Fujimoto, K. Autothermal CO<sub>2</sub> Reforming of Methane over NiO–MgO Solid Solution Catalysts under Pressurized Condition: Effect of Fluidized Bed Reactor and Its Promoting Mechanism. *Catal. Today* **2000**, *63*, 439.

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