

Steam Gasification of Coal with Salt Mixture of Potassium and Nickel in a Fluidized Bed Reactor

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Abstract—Australian coal loaded with a mixed catalyst of $K_2SO_4+Ni(NO_3)_2$ has been gasified with steam in a fluidized bed reactor of 0.1 m inside diameter at atmospheric pressure. The effects of gas velocity ($2-5 U_g/U_{mf}$), reaction temperature (750-900 °C), air/coal ratio (1.6-3.2), and steam/coal ratio (0.63-1.26) on gas compositions, gas yield and gas calorific value of the product gas and carbon conversion have been determined. The product gas quality and carbon conversion can be greatly improved by applying the catalyst; they can also be enhanced by increasing gas velocity and temperature. Up to 31% of the catalytic increment in gas calorific value could be obtained at higher temperatures. In the experimental runs with variation of steam/coal ratio, the catalytic increments were 16-38% in gas calorific value, 14-57% in carbon conversion, 5-46% in gas yield, and 7-44% in cold gas efficiency. With increasing fluidization gas velocity and reaction temperature, the unburned carbon fraction of cyclone fine for catalytic gasification decreased 4-18% and 13-16%, respectively, compared to that for non-catalytic gasification.

Key words: Coal Gasification, Catalyst, Fluidized Bed, Calorific Value

INTRODUCTION

Conversion of coal to gaseous fuel has been considered as a major contribution to the energy picture in the future. Currently, a great deal of effort is being expended to improve the performance of existing coal conversion processes [Kim et al., 2001; Saffer and Ferrell, 1988; Watkinson et al., 1983; Gutierrez and Watkinson, 1982] and to develop a new type of gasifier for processing larger volumes of coal [Riley and Judd, 1987; Kikuchi et al., 1985]. Many studies have been conducted on catalytic coal gasification [Choi et al., 1993; Song and Kim, 1993; Sue-A-Quan et al., 1991; Dhirendra et al., 1986; Tomita et al., 1985], because a reduction in gasification temperature would result in several advantages, and the catalyzed process appears to be especially attractive in the direct production of methane or hydrogen from coal. In the Exxon catalytic coal gasification process [Nahas, 1983], coal is impregnated with K_2CO_3 catalyst and is gasified with steam around 973 K. However, the product gas contains a considerable amount of hydrogen and carbon monoxide as by-products, which are separated from the methane and recycled into a gasifier. A previous kinetic study of catalytic coal gasification with a thermobalance [Lee and Kim, 1995] revealed that the catalytic activity of $K_2SO_4+Ni(NO_3)_2$ is the highest among the mixed salts tested under steam atmosphere. However, the thermogravimetric method gives little information as to the product, like

tar or gas, and the residue; and the obtained reaction rate is larger than that in a fluidized bed reactor. A literature survey revealed that research work on catalytic coal gasification in fluidized bed reactors is relatively sparse.

The objective of the present study is to perform steam gasification of coal in a fluidized bed gasifier with $K_2SO_4+Ni(NO_3)_2$ that was developed in the previous study. The effects of fluidization gas velocity, reaction temperature, air/coal ratio, and steam/coal ratio on the product gas compositions, gas yield and gas calorific values, and carbon conversion have been determined.

EXPERIMENTAL

Fig. 1 shows a schematic diagram of a fluidized bed reactor (0.1 m - i.d. × 1.6 m height). This gasifier is made of stainless steel columns and consists of the following parts: feeding part of air and steam, gas plenum, main column, freeboard, coal feeder, cyclone, product gas cleaning, gas sampling and analysis.

Distilled water was fed into the steam generator (1 kW) through a 'Masterflex' pump. Steam generated was mixed with compressed air and introduced into the gas plenum. The inside of gas plenum was filled with inert material to improve the mixing of air and steam, and an electric heater (2 kW) installed on the plenum wall preheated the feed gas mixture. A bubble cap gas distributor having seven caps was situated between the main column and gas plenum for the feed gas to be evenly distributed through the bed. Main reactor column was 0.1 m - i.d. × 0.85 m high and was expanded into a larger column (0.2 m - i.d. × 0.6 m high) to reduce the entrainment of bed particles. An electric heater of 6 kW was installed at the reactor wall to heat the bed to the ignition temperature of coal (around

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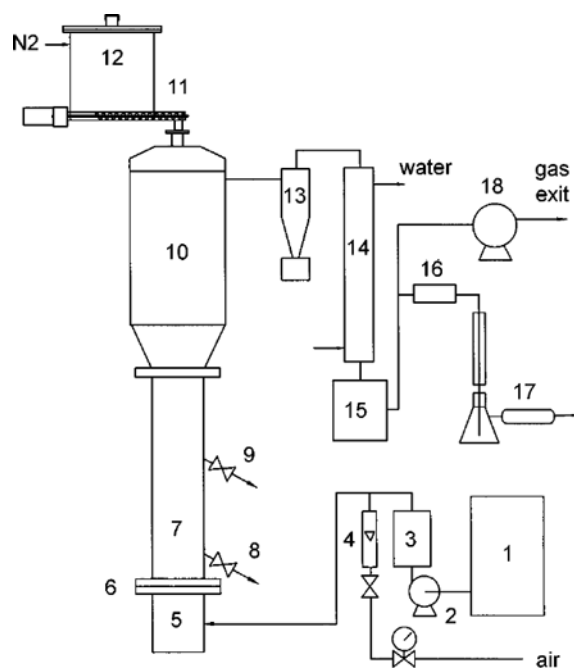


Fig. 1. Schematic diagram of a fluidized bed gasifier.

- | | |
|--------------------|-------------------------|
| 1. Water reservoir | 10. Freeboard |
| 2. Masterflex pump | 11. Screw feeder |
| 3. Steam generator | 12. Coal hopper |
| 4. Air flow meter | 13. Cyclone |
| 5. Gas plenum | 14. Condenser |
| 6. Gas distributor | 15. Collector |
| 7. Main bed | 16. Dust collector |
| 8. Bed drain | 17. Gas sampling bottle |
| 9. Overflow | 18. I.D. fan |

500 °C). The reactor was insulated by 'Kao-wool'. One sight glass was mounted at 0.5 m above the gas distributor and an ash drain port at the bottom, and an overflow drain port at 0.45 m above the distributor. To measure pressure drop along the bed height eight pressure taps were mounted flush on the reactor wall at 0.1 m height intervals above the distributor. Also, six K-type thermocouples were mounted along the bed height. The coal was fed into the top of the reactor through a screw feeder, where the feed rate of coal was controlled by a variable DC motor. The product gas was cooled down passing through cyclone, condenser and a dust collector. A small amount of product gas was sampled at the outlet of dust collector and its composition was determined by gas chromatograph (HP 5890 II) with a thermal conductivity detector with 'Molecular sieve 5A' and 'Porapak Q' columns.

The Australian sub-bituminous coal used in this study was 0.25-1 mm in diameter and its properties are shown in Table 1. In order to evaluate the catalytic activity of the salt mixture in the present fluidized bed reactor, a relatively large amount of coal was impregnated with an aqueous solution of $K_2SO_4 + Ni(NO_3)_2$ in a large stirred vessel. The content of vessel was mixed and heated by the hot plate without boiling for 15 hr. The resulting coal was dried in the oven for 24 hr. As the optimum loading of catalyst is known to be 10-20 wt% [Nahas, 1983], the amount of salts impregnated on coal was kept at 10 wt% and the mole ratio of two salts was kept at unity, an equimolar.

Table 1. Analyses of Australian sub-bituminous coal

	wt%		wt%
Ultimate analysis (daf base)		Ash analysis	
C	72.6	SiO ₂	60.2
H	5.4	Al ₂ O ₃	26.8
N	2.6	Fe ₂ O ₃	7.1
S	0.4	CaO	0.4
O	19.0	MgO	0.2
		TiO ₂	1.4
Proximate analysis (dry base)		K ₂ O	1.7
Volatile	29.1	MnO	0.1
Fixed carbon	56.0		
Ash	14.9		
Heating value (kcal/kg)	6141		

At the beginning of the experimental run, the electric heater was turned on to heat the bed of sand particles ($d_p = 0.27$ mm) with feeding only air. When the bed temperature reached 450-500 °C, the salt impregnated coal was fed into the reactor and then the bed temperature rose rapidly due to coal combustion. When the temperature reached to a desired level, steam was introduced into the air stream. It usually takes about 40 min for the reactor to reach its steady state. At the steady condition, gas samples were taken and the amount of collected particles in the cyclone was measured. The reactor operating variables could be changed by adjusting air/coal and steam/coal feed ratios.

RESULTS AND DISCUSSION

A number of chemical reactions occur in a coal gasifier, of which the main reaction is steam gasification of char as follows:



In addition, partial combustion of char and hydrogasification of char, and the water-gas shift reaction usually occur. One typical result for the effect of fluidization gas velocity on product gas composition at a temperature of 850 °C is shown in Fig. 2. The change of product gas composition for catalytic gasification is similar to that for non-catalytic gasification. Compared to the gas concentration for non-catalytic gasification, H₂, CO, and CO₂ in the product gas for catalytic gasification increase 12-22%, 31-56%, and 0.5-1%, respectively. On the other hand, the content of CH₄ decreases a little with increasing fluidization gas velocity. When the gas velocity is increased, the solids mixing within the reactor is enhanced and the contact frequency between coal and reactants becomes higher. These phenomena at high gas velocity may provide the overall reaction rate of coal gasification in a fluidized bed high. It can be seen in the plot that the activity of $K_2SO_4 + Ni(NO_3)_2$ slightly changes with gas velocity.

The effect of fluidization gas velocity on carbon conversion and product gas yield (N₂-free) is shown in Fig. 3. Carbon conversion was calculated from the contents of CO, CH₄, and CO₂ in the product gas, gas yield and coal feed rate. When the gas velocity is increased, carbon conversion and gas yield linearly increase. These results can be attributed to the enhancement of overall reaction rate

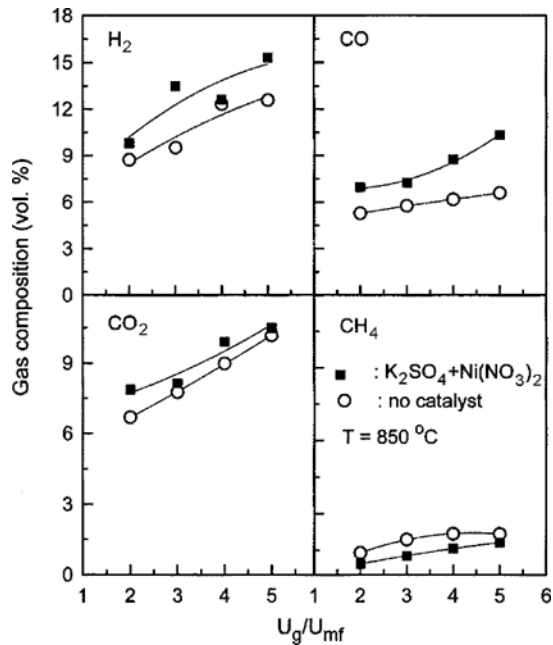


Fig. 2. Effect of fluidization gas velocity on product gas compositions at 850 °C, air/coal of 1.6, and steam/coal of 0.63.

of char gasification by more extensive solid mixing in a fluidized bed reactor. In addition, the catalyst promotes the rate of steam-char reaction (1) and thus it also gives a higher carbon conversion and more gas yield. The enhancement of carbon conversion by the mixed catalyst became high (up to 32%) at higher gas velocities, and that of gas yield was 24-33% within the gas velocities employed at 850 °C.

The effect of gas velocity on gas calorific value and cold gas efficiency at 850 °C, air/coal of 1.6, and steam/coal of 0.63 is shown

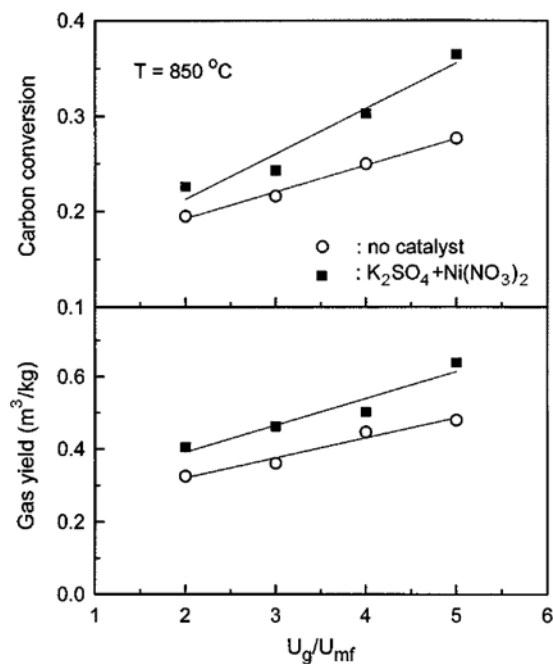


Fig. 3. Effect of fluidization gas velocity on carbon conversion and gas yield at 850 °C, air/coal of 1.6, and steam/coal of 0.63.

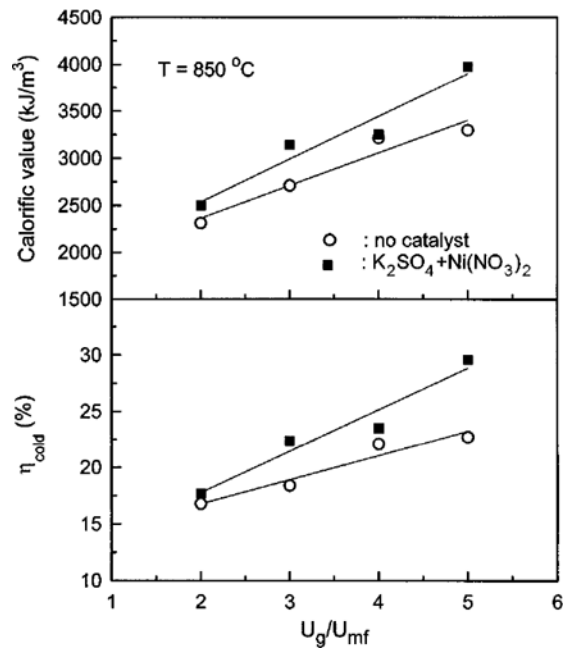


Fig. 4. Effect of fluidization gas velocity on gas calorific value and cold gas efficiency at 850 °C, air/coal of 1.6, and steam/coal of 0.63.

in Fig. 4. The product of the gas calorific value and gas yield divided by the heating value of coal fed represents the cold gas efficiency. It can be seen that the mixed catalyst increases gas calorific value and cold gas efficiency by 7-21% and 5-24%, respectively, at gas velocity of 2.5 U_{mf}.

The effect of reaction temperature on product gas compositions at gas velocity of 3 U_{mf}, air/coal ratio of 1.6, and steam/coal of 0.63 is represented in Fig. 5. The use of catalyst in coal gasification enhances

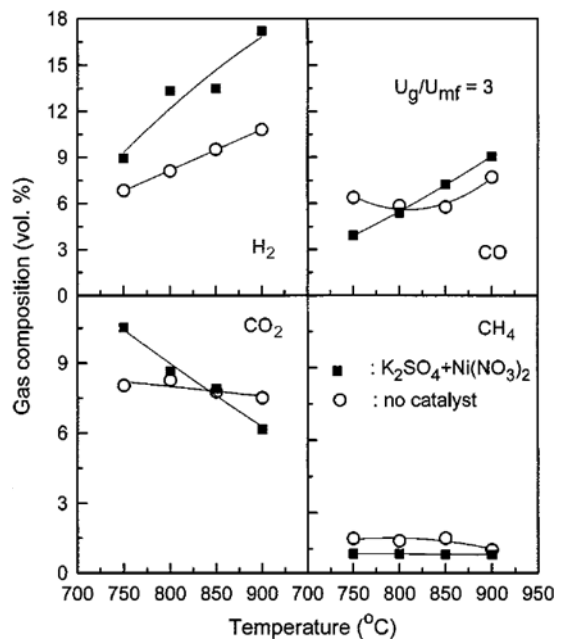


Fig. 5. Effect of reaction temperature on product gas compositions at 3 U_{mf}, air/coal of 1.6, and steam/coal of 0.63.

the reaction rate and as a result, the corresponding reaction temperature of this endothermic reaction can be reduced. Both H_2 and CO , the main product gases, increase not only with temperature but also with employing the mixed catalyst. Also, the increments of H_2 and CO by the catalyst are larger at relatively high temperature range as like the result in the previous kinetic study with thermobalance [Lee and Kim, 1995]. The content of CO_2 linearly decreases with temperature. Such a change in the product gas composition can be attributed to the fact that the rate of steam-char gasification reaction (1) and the activity of the mixed catalyst increase with temperature, whereas the water-gas shift reaction, an exothermic reaction, is suppressed with an increase of temperature. On the other hand, CH_4 is nearly constant with temperature and CH_4 for catalytic gasification is found to be lower than that for non-catalytic gasification. This may be due to the decomposition of CH_4 by the catalyst. It has been reported that hydrogen content in the product gas has been enhanced by decomposition of CH_4 , light hydrocarbon and tar [Tomita et al., 1985]. Dhirendra et al. [1986] investigated the effect of various single catalysts and combination of K_2CO_3 and $Ni(NO_3)_2$ on gasification of high ash Indian coal with reaction temperature of 500-800 °C in a fluidized bed gasifier. They showed that the product gases like H_2 , CO , CO_2 , and CH_4 from the gasification with 10% K_2CO_3 +1% $Ni(NO_3)_2$ were higher than those with the other catalyst.

The effect of reaction temperature on carbon conversion and gas yield (N_2 -free) is shown in Fig. 6. When reaction temperature is increased, carbon conversion and gas yield linearly increase. The enhancement of carbon conversion by use of the mixed catalyst is relatively small (5-8%) and that of gas yield is found to be 8-34% at the temperatures employed in this study. Watkinson et al. [1987] have reported 10-20% enhancement of carbon conversion in their spouted bed coal gasifier at 1,000 °C with addition of K_2CO_3 catalyst. The carbon conversion in the present catalytic gasification system is found

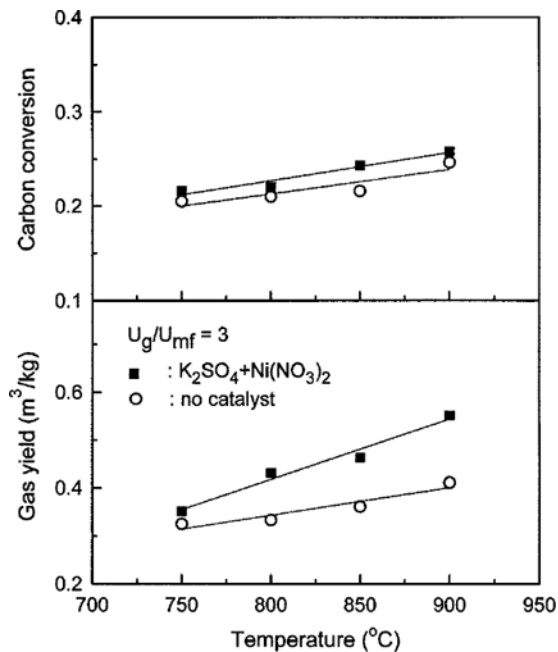


Fig. 6. Effect of reaction temperature on carbon conversion and gas yield at $3 U_{mf}$, air/coal of 1.6, and steam/coal of 0.63.

to be quite low compared to that obtained in the thermobalance [Lee and Kim, 1995]. This may be partly due to the entrainment of fine coal/char particles in the fluidized bed. Another possible reason is the difference in steam/coal ratio in feed between the two systems: The steam/coal ratio used in the present fluidized bed gasifier was 0.63, whereas an excess steam has been used in the thermobalance. Also, the gaseous diffusion process that affects the overall reaction rate must be quite different between the two systems.

The effect of air to coal ratio in the feed on the product gas compositions at 850 °C is shown in Fig. 7. The increase in the content

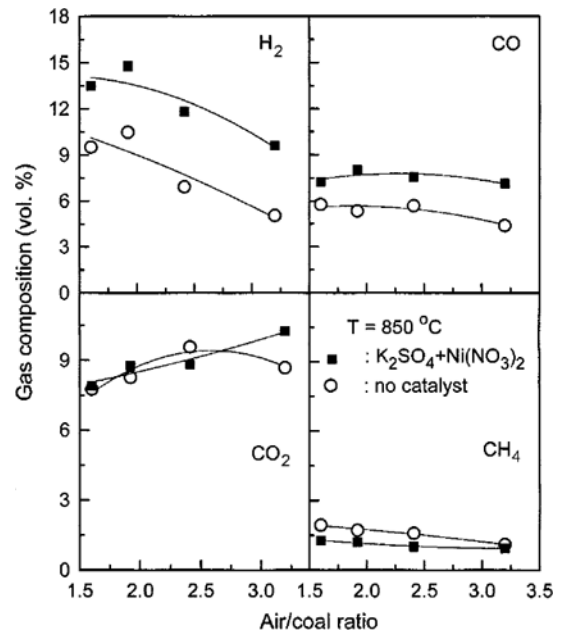


Fig. 7. Effect of air/coal ratio on product gas compositions at 850 °C, $3 U_{mf}$, and steam/coal of 0.63.

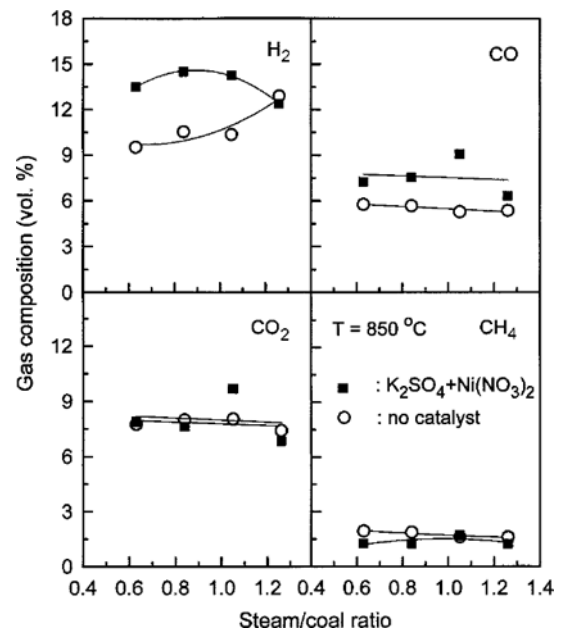


Fig. 8. Effect of steam/coal ratio on product gas compositions at 850 °C, $3 U_{mf}$, and air/coal of 1.6.

of H₂ by the catalyst is 42-91% and that of CO is 26-63%. The content of CO₂ increases with air/coal ratio due to the combustion of char. The content of CH₄ for catalytic gasification slightly decreases with air/coal ratio. When oxygen content is rich, K₂SO₄+Ni(NO₃)₂ can be deactivated to the oxide form, which provides little catalytic activity for C-H₂O reaction.

The effect of steam/coal ratio on the product gas compositions at 850 °C is shown in Fig. 8. The changes of H₂ and CO in the plot are not pronounced and the changes of CO₂ and CH₄ are hardly observed with the variation of steam content in feed. The effect of steam concentration on the reaction rate for catalytic coal gasification seems to be smaller than that for non-catalytic gasification.

The unburned carbon fraction in the cyclone fines (UCF) and overall efficiency calculated from cyclone capture are summarized for the coal gasification with and without the catalyst in Table 2. The overall efficiency is calculated from the ratio of carbon in particles captured at cyclone to carbon in coal feed. It can be seen from Table 2 that UCF decreases and overall efficiency slightly increases by employing the mixed catalyst or by increasing temperature. The effects of air/coal and steam/coal on UCF and overall efficiency are also included in Table 2. When air/coal ratio in feed is increased at constant steam/coal ratio, UCF decreases by 15%, and the overall efficiency increases by 15% for catalytic gasification due to the increase of reactivity for coal-oxygen reaction. The trends of UCF and overall efficiency with the variation of steam/coal ratio are almost same as above. However, the effect of air is more pronounced than that of steam in the feed because the rate of char combustion is much faster than the rate of char -H₂O reaction.

CONCLUSIONS

The catalyst K₂SO₄+Ni(NO₃)₂ was found to enhance the rate of

Table 2. Unburned carbon fraction and overall efficiency at various operating conditions

Temp. (°C)	U _g / U _{mf}	Air/ Coal	Steam/ Coal	UCF		η _{ov} **		H ₂ /CO	
				none	cat*	none	cat*	none	cat*
750	3	1.6	0.63	0.80	0.70	82.2	86.8	1.07	2.28
800	3	1.6	0.63	0.81	0.63	83.3	88.5	1.39	2.47
850	3	1.6	0.63	0.76	0.62	85.0	91.1	1.65	1.86
900	3	1.6	0.63	0.78	0.65	89.0	86.6	1.40	1.89
850	2	1.6	0.63	0.80	0.68	89.8	94.1	1.56	1.41
850	3	1.6	0.63	0.76	0.62	85.0	91.1	1.65	1.86
850	4	1.6	0.63	0.77	0.66	81.6	87.1	2.00	1.37
850	5	1.6	0.63	0.68	0.63	84.1	83.8	1.91	1.49
850	3	1.6	0.63	0.76	0.62	85.0	91.1	1.65	1.86
850	3	1.9	0.63	0.80	0.66	85.9	88.3	2.04	1.85
850	3	2.4	0.63	0.77	0.66	85.2	88.1	1.54	1.56
850	3	3.2	0.63	0.74	0.66	83.1	85.9	1.15	1.35
850	3	1.6	0.84	0.80	0.66	83.2	87.7	1.86	1.93
850	3	1.6	1.05	0.69	0.66	86.3	88.6	1.96	1.56
850	3	1.6	1.26	0.79	0.65	85.0	90.4	2.41	1.95

* : values for the catalytic gasification.

** : overall efficiency of carbon.

coal gasification and product gas quality in the present fluidized bed system. The enhancement of carbon conversion by K₂SO₄+Ni(NO₃)₂ was especially larger (up to 32%) at higher gas velocities, and that of product gas yield was 24-33% within the gas velocities employed at 850 °C. The main product gases, H₂ and CO, increased not only with temperature but also with employing the mixed catalyst. Also, the increment by the catalyst was larger at relatively higher temperature. The catalytic increment of up to 31% could be obtained in gas calorific value at higher temperature range. In the experimental runs with variation of steam/coal ratio, the catalytic increments were 16-38% in gas calorific value, 14-57% in carbon conversion, 5-46% in gas yield, and 7-44% in cold gas efficiency. With increasing gas velocity and reaction temperature, the unburned carbon fraction decreased 4-18% and 13-16%, respectively, and the overall efficiency increased 5-6%.

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