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CHARACTERISTIC OF HYDROGEN PRODUCTION FROM COAL TAR WITH HIGH TEMPERATURE AND HIGH PRESSURE WATER

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ABSTRACT

A steam gasification method of "HyPr-RING" is a new hydrogen production process from organic matters such as coal, biomass and waste with high temperature and high pressure water and calcium-based CO_2 sorbent. In this study, the gasification characteristic of tar was investigated using a small batch reactor heated in a fluidized sand bath. As a result, CH_4 and H_2 were mainly produced from tar as well as coal. The amounts were decreased but the ratio of CH_4 to H_2 in product gas was increased with decreasing temperature. The predominant production was in the initial stage including heating period. The behavior for the tar is similar to that for coal, suggesting that the CH_4 and H_2 production from coal in the initial stage should be caused by tar in coal and especially, H_2 production in the second stage should be by char in coal. These results indicate that tar discharged above the bed is reduced as much as possible, when the coal gasification as the HyPr-RING is carried out in a fluidized bed reactor, and that CH_4 production from tar remained in the bed is reduced and H_2 production by catalytic reaction or polymerization of tar is promoted in the bed.

KEYWORDS

Hydrogen production, Coal tar, CO_2 sorbents, Gasification, High pressure steam

INTRODUCTION

The utilization of hydrogen energy is one of most available method to reduce the environmental impact and the hydrogen production of coal is one of the clean coal technologies. The HyPr-RING (Hydrogen Production by Reaction Integrated Novel Gasification) is a new gasification method to produce hydrogen from hydrocarbon resources such as fossil fuel, biomass and waste with the high temperature and high pressure steam and simultaneously to reduce CO_2 by calcium-based sorbent[1)].

Figure 1 shows the concept of HyPr-RING method. Almost all of organic materials such as coal can be reacted with steam and sorbent to produce mainly H_2 and $CaCO_3$. $CaCO_3$ can be regenerated to CaO by calcinations and CO_2 in high concentration can be collected. It starts being developed with a continuous bench-scale unit with a fluidized bed reactor.

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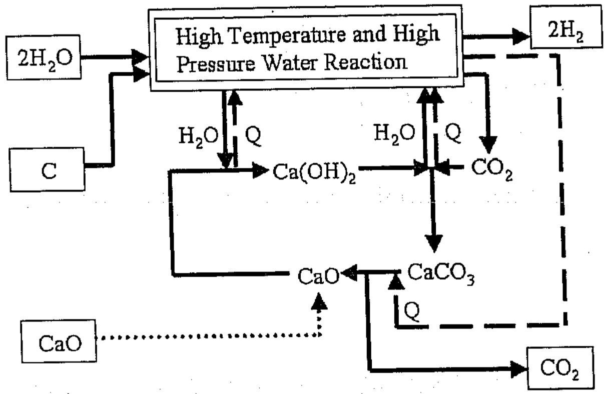


Fig.1 Concept of HyPr-RING method.

Objective of this study is to clear the behavior of tar produce in the initial stage of coal gasification, which would be devolatilized with pyrolysis reactions during heating period of coal particles even in the fluidized bed. The tar would produce CH_4 as a by-product together with H_2 as a target product. In this study we are focusing on the CH_4 production from the tar in the initial stage reaction.

EXPERIMENTAL

In the present study, tar of Taiheiyo-coal (Japanese subbituminous coal) was used as a tar sample and it was gasified with steam under the condition of temperatures of 873 to 973 K and pressure of 19.8 MPa (subcritical condition) using a tubing-bomb micro-reactor (TB reactor).

Tar sample

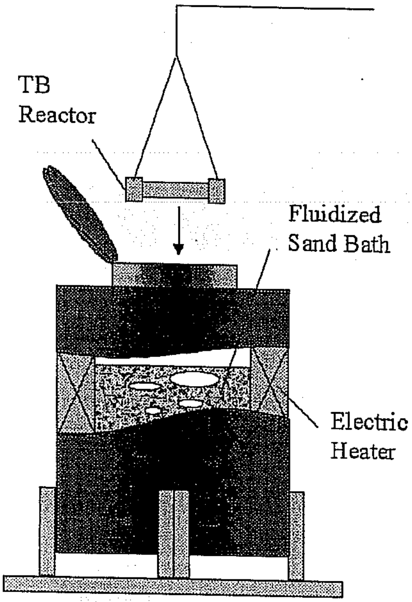
Tar was made by thermal cracking of Taiheiyo-coal at 873 K for 2 hour in N_2 flow. The chemical property is shown in **Table 1**. As a CO_2 sorbent, reagent grade $Ca(OH)_2$ of Nacalai tesque, Kyoto, Japan was used.

Table 1 Chemical property of Taiheiyo-coal tar.

Proximate analysis (dry) [wt%]				Ultimate analysis (daf) [wt%]			
VM	FC	Ash	Moist.	C	H	N	O, S (dif.)
98.10	1.46	0.46	0.00	75.50	9.74	0.59	14.17

Experimental Conditions and Apparatus

Experimental conditions and apparatus are shown in **Fig. 2**. A TB reactor was a seamless tube of 100 mm long, O.D. 12.7 mm, an internal volume of 7.2 cm^3, which was made of stainless steel (SUS-316). The reactor was sealed at both ends with SUS-316 caps. It was externally heated to the desired temperatures with a fluidized sand-bath heater, whose inner diameter was 400 mm, bed height was 450 mm, and bed material was silica sand.



Tube Reactor

- Seamless Tube Made of SUS-316
  - Length = 100 mm
  - Outer Diameter = 13 mm
  - Inner Diameter = 9 mm
- Sealed at Both Ends with SUS-316 Caps.
- Inside Volume = 7.2 cm^3

Fluidized bed sand bath

Inner Diameter = 400 mm
Bed Heater = 450 mm
Bed Material: Silica Sand

Fig. 2 Experimental conditions and apparatus

Experimental Procedure

A mixture of tar, distilled water and $Ca(OH)_2$ was put into the TB reactor with nitrogen. The TB reactor was soaked in the fluidized sand bath, rapidly heated and hold at 873 to 973 K. The mixing ratio of the tar, sorbent and water is shown in **Table 2.**

Table 2 Mixing ratio of the tar, sorbent and water.

	Pressure	Tar	$Ca(OH)_2$	Water	H_2O/C	Ca/C
873 K	19.8 MPa	0.062 g	0.407 g	0.407 cm^3	5.9	1.4
923 K		0.057 g	0.376 g	0.376 cm^3		
973 K		0.060 g	0.350 g	0.350 cm^3	5.2	1.3

As confirmed in our previous research[2], the TB reactor with a less heat capacity can be more rapidly heated up to a desired temperature than a conventional autoclave. The average heating rate was about 330 K/min and it took about 2 minutes under the present heating conditions. The measurement temperature and pressure in the reactor corresponded to calculation results estimated by the sand bath temperature and the amount of water in the reactor.

After gasification, the reactor was quickly pulled up from the sand bath, and it was rapidly cooled down to room temperature with water to quench the reaction. Produced gases were collected by the water substitution method[2] and the volume of the gas was measured with a graduated cylinder. The compositions of collected gas, H_2, O_2, N_2, CH_4, CO, CO_2, C_2H_4 and C_2H_6 were analyzed by TCD-micro gas chromatographs (Aera, model M200; (1) with MS-5A and PPQ columns and Ar carrier gas, (2) with a PPU column and He carrier gas).

RESULTS AND DISCUSSION

Changes of Gas yields from Tar with Reaction Time

First of all, coal conversions to gases are shown in **Fig. 3**. It was about 40% at 2 min and 60% at 30 min. Yields of gas produced from the coal and the steam are shown in **Fig. 4** together with product gas yields from char and tar as reactants. From these figures, it can be seen that in the condition of the HyPr-RING methods by using the TB reactor, which enabled rapid heating, the composition of product gas from coal is strongly dependent on the initial stage of gasification or pyrolysis reaction until 5 minutes.

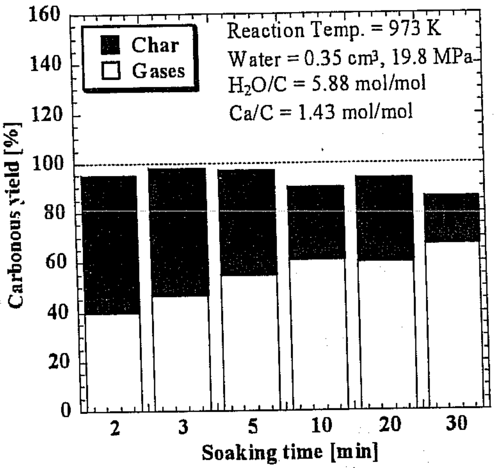


Fig. 3 Coal conversions to gas at 973K.

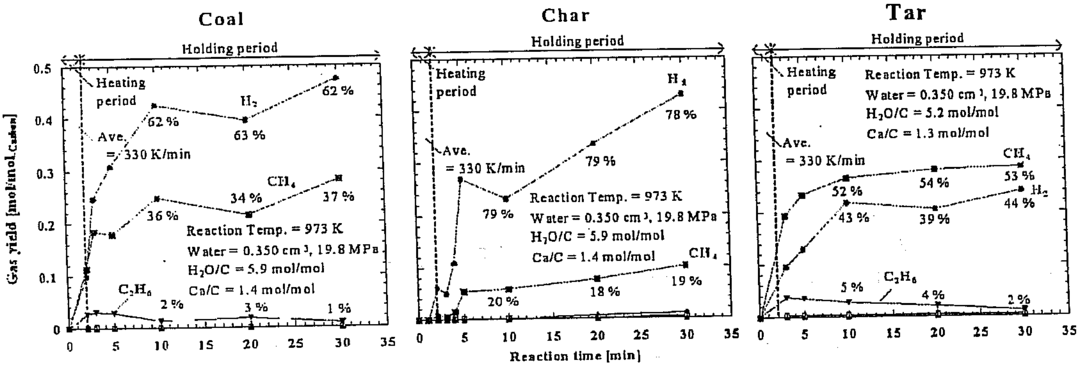


Fig. 4 Changes of yield of CH_4 and H_2 produced from coal, char and tar with reaction time at 973 K

Carbon source of hydrogen production with the reaction of coal and stem is divided roughly into char and tar. The char is mainly converted into H_2 and the tar into CH_4 and H_2. Objective of the HyPr-RING is to produce H_2, which means that CH_4 is a by-product. Because CH_4 production took place in the initial stage when tar was used as a reactant, CH_4 production in the initial stage when coal was used should be due to the tar in coal.

The dependence of CH_4 production on the gasification temperature is shown in **Fig. 5**. The amount of CH_4 was decreased with decreasing temperature but the ratio of the yields of CH_4 to H_2 was increased, as 53/44 at 973 K and 60/22 at 873K.

Additionally, at 873 and 973 K, C_2H_6 was also produced and CO_2 was little. In the heating period and the initial stage within 5 minutes, the yields of H_2, CH_4 and C_2H_6 produced from the tar were rapidly increased. The rapid production should be caused by the thermal cracking and gasification of tar. After 5 minutes, the yields of H_2, CH_4 and C_2H_6 were not significantly increased with reaction time. If the remained tar was partially polymerized to the reactive char, it would produce much more H_2 with the reaction of the char and steam. Furthermore, a little of increase of CH_4 might be due to production of the reactive char and

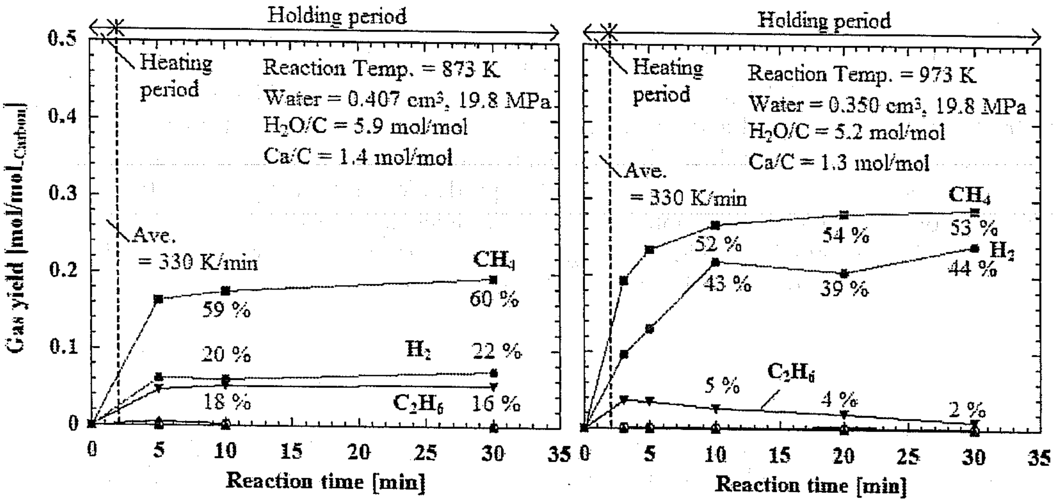


Fig. 5 Comparison of gas yields of CH_4 and H_2 produced from tar at 873 and 973 K.

the following reaction[3]:

$$2C+H_2O+Ca(OH)_2 \rightarrow CH_4+CaCO_3 \qquad \Delta H_{973} = -31.2 \text{ kJ/mol} \qquad (1)$$

Consequently, even if tar changes into char, it seems not so reactive or not so much amount in the present edxperimental conditions. On the other hand, C_2H_6 was slowly decreased after 3 min at 973 K. It suggests that a part of hydrocarbon might participate in the H_2 and CH_4 production after 5 minutes.

Changes of H_2 and CH_4 Produced from with Reaction Temperature

As previously described on the dependence of temperature on yields of the produced gases, the ratio of the yields of CH_4 and H_2 was increased. The yields from tar at 30 min are plotted as a function of reaction temperature in **Fig. 6**.

Both yields of H_2 and CH_4 were linearly increased with reaction temperature. In addition, the production rate of H_2 is higher than that of CH_4. This might suggest a possibility that increase of H_2 production in the second stage is due to the char produced from tar and steam as following reaction:

$$C+2H_2O+CaO \rightarrow CaCO_3+2H_2 \qquad \Delta H_{973} = -69.2 \text{ kJ/mol} \qquad (2)$$

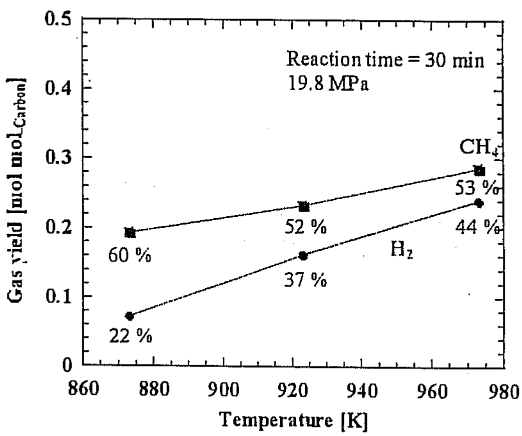


Fig. 6 Changes of gas yields of H_2 and CH_4 from tar for 30 min with reaction temperature.

Application to Fluidized Bed Reactor

As previously described, the HyPr-RING project will be developed with a continuous bench-scale fluidized bed reactor. Coal particles fed into the fluidized be reactor produce tar during the heating period and the initial stage of gasification with steam, which is discharged into the freeboard above the bed and causes tar trouble or carbon loss. The tar production should be reduced as much as possible. In addition, if CH_4 produced from tar is needless, tar in the bed should be reduced and selective H_2 production by catalytic reaction or polymerization of tar should be promoted in the bed. Since tar is easily produce at low temperature, heating by passing rapidly through the low temperature period and coking reaction by deposition of tar on the bed material at high temperature should be available.

CONCLUSIONS

To understand of the reaction mechanism and the role of tar to produce rich hydrogen by the HyPr-RING method, we studied on tar gasification by using micro reactor under the high pressure and temperature steam and obtained the following conclusions;

(1) H_2 and CH_4 are mainly produced from tar, and increased with reaction time. The yield of H_2 is lower than that of CH_4.
(2) The yields of H_2 and CH_4 are increased with reaction temperature, which are rapidly produced in the initial stage. The increasing rate in the second stage after 5 minutes is increased with reaction temperature.
(3) Behavior of CH_4 production in the initial stage of coal gasification is similar to that of ta r gasification.

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