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Hydrogen production by the partial oxidation and steam reforming of tar from hot coke oven gas

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Abstract

Hot coke oven gas (COG) with a temperature of about 1050 K was produced from a test unit for coke production, the capacity of which was 80 kg of coal. The COG was introduced into an experimental unit with a tar converter where oxygen and steam were injected. Over 98% of the total carbon in the hot COG was partially oxidized, reformed with steam and converted to hydrogen and CO. About 1 Nm^3/h of hydrogen was continuously produced for 5 h in this experiment. The experimental results suggest that three to five times the amount of hydrogen and CO that were present in the original COG could be recovered by this technology, utilizing the heat of the hot COG for the reaction. The feasibility study showed that hydrogen can be produced by this technology at a lower cost and higher efficiency than by the separation of cold COG.

Keywords: Coke oven gas; Hydrogen production; Tar reforming

1. Introduction

Efficient, high performance and low cost technologies for producing hydrogen are urgently needed to encourage hydrogen utilization in the future. Hydrogen can be produced by several processes, including the steam reforming of methane and naphtha. Coke oven gas, referred to as COG, contains 50% hydrogen and is a high-potential source of hydrogen in countries where coke ovens are utilized. In some iron works, hydrogen is separated from cold clean COG after aqueous ammonia quenching by means of pressure swing adsorption, PSA. However, it would be highly desirable to recover more hydrogen from COG at a lower cost in the future.

Hot COG, with a temperature of about 1050 K, which is produced from coke ovens, contains tar and methane as well as hydrogen and CO. The liquid hydrocarbon, so called tar, accounts for about 30 wt% of the hot COG. About half of the tar is equivalent to a gas oil fraction. This paper introduces a new technology for producing hydrogen, by means of partial oxidation and the steam reforming of tar in the hot COG, without the use of a catalyst. The heat from the hot gas is utilized to drive the reaction and the heat of the converted gas can be recovered in this process.

The thermal decomposition of tar vapor contained in COG without a catalyst, converting it to gas and liquid products with laboratory-scale apparatuses, has been described by several researchers [1–4]. In the temperature range of 1050–1150 K, methane is the major product. At temperatures over 1170 K, hydrocarbon gases are converted to hydrogen and CO in the presence of steam. Carbon is produced mainly by the decomposition of paraffin even at temperatures less than 1170 K and from hydrocarbon gas, such as methane at temperatures over 1170 K. Resident time is an important factor in achieving higher yields of gas. Kobata et al. [5] reported on the effect of the gas composition of COG on the pyrolysis of the tar.

Meanwhile, several types of catalysts, including synthetic zeolite and mordenite have been examined, in attempts to convert tar to gases. Similar conversion rates were measured at lower temperatures, to compare the pyrolysis reaction without a catalyst [6,7]. However, carbon deposits cause plugging of the catalyst bed, resulting in a decrease in efficiency. The steam reforming of tar with a catalyst tended to reduce carbon formation and produce CO and hydrogen at high temperatures [8,9]. Liuyun et al. [10] reported that the addition of steam dramatically suppressed carbon deposition and enhanced the yield of hydrogen, when a Ni catalyst was used.

Carbon formation is a critical issue, even small amounts, in applications of fixed bed catalytic reactors for large-scale

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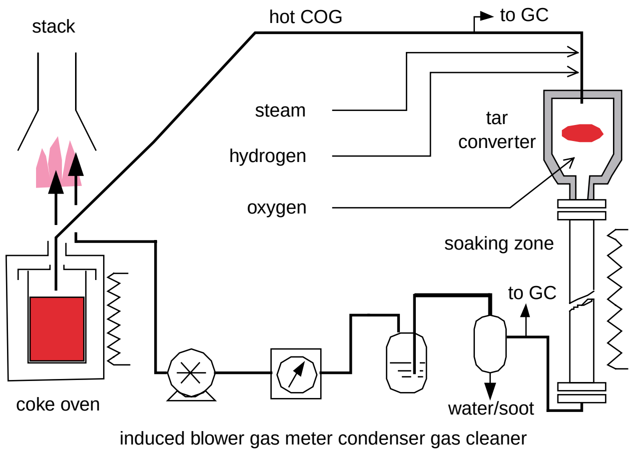

Fig. 1. Schematic of the experimental unit used in the study.

plants, which require long-term operation. To avoid such problems, oxygen and steam were introduced into the hot COG, the tar of which was partially oxidized via a steam reforming reaction to produce hydrogen and CO without the use of a catalyst in this research. The effect of the mixing of gases as well as reaction conditions were examined to obtain design information for a large-scale unit, using several types of converters. A fresh gas, which contained tar vapor, was used immediately after its production, because the reactivity of fresh tar is likely to be different from that of liquid tar obtained by the condensation of tar vapor.

2. Experimental

The experimental unit was installed at the Kimitsu Laboratory of Shinnikka Environmental Engineering Co., Ltd, Chiba, Japan to obtain yield data for the tar converter. Fig. 1 shows a schematic diagram of the unit, which consists of a small-scale coke oven, the tar converter, an induced blower, and piping and instruments. The coke oven was operated in a batch fashion with 80 kg of coal. The unit was originally designed to examine the properties of coke made from metallurgical coal. A part of the exhausted gas flowed into the head of the tar converter (i.d.; 170 mm) followed by the soaking zone (i.d.; 102 mm, length; 2500 mm), which was heated with electric heaters. As shown in Fig. 1, the gas was introduced into the head through the feed nozzle with oxygen and steam and the outlet gas from the tar converter was cooled.

Four types of the heads, Types 1, 2, 3, and 4, as shown in Fig. 2 were used to examine the effect of configurations and flow characteristics. Type 1 was equipped with a horizontal nozzle, while Types 2, 3, and 4 had vertical nozzles. The edge of the nozzle was directed to the center of the tar converter in the case of Type 1. The configuration of the vertical nozzles was determined based on the plan of a large-scale plant. In the case of Type 3, oxygen was tangentially injected through three nozzles, toward the center of the head at an angle. The three oxygen nozzles used in the Type 3 head were modified in Type 4. Oxygen was injected precisely toward the center of the head in such a manner as to directly obstruct the flow of COG in the case of Type 4. A junction of these flows was located 50 mm below the edge of the feed nozzle for Type 4A and 100 mm for Type 4B to investigate the effect of this configuration.

The composition and amount of hot COG produced from the small-scale coke oven varied with the time on stream. As shown in Fig. 3, the tar concentration in COG produced from the small-scale coke oven decreased from 50 to 20–30 mg/l 4 h after the initiation of heating. The hydrogen concentration gradually increased, while the methane concentration decreased, as shown in Fig. 4. After heating the tar converter with LPG, gas was introduced into the tar converter for four and a half hours from 5 h after the start of heating the test oven to minimize changes in the composition of the hot COG. 80 kg of blended coal typically used in commercial coke ovens, as shown in Table 1, was used in one batch operation. A typical example of the gas used is shown in Table 2. The tar content of the gas was less than that in the gas from commercial coke ovens due to the characteristics of the unit and the timing of the samples.

Experimental conditions for over twenty operations are shown in Table 3. Since, the flow rate of the outlet gas was controlled at about 1.4 Nm^3/h, the flow rate of the induced COG ranged from 0.5 to 0.9 Nm^3/h, which constituted about half of the produced hot COG, to avoid inducing air. Two types of operations were conducted. One involved a partial oxidation mode and the other a steam reforming mode. In the case of the partial oxidation mode, the injected hydrogen and part of the injected oxygen were combusted to supply heat and the remainder of the oxygen was used for the partial oxidation.

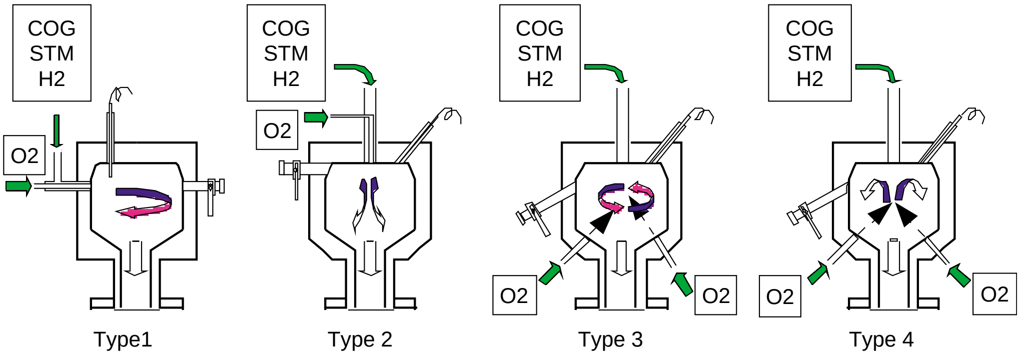

Fig. 2. Schematic drawings of the heads of the tar converter.