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The carbon dioxide reforming of methane in a thermal diffusion column reactor (TDCR) and a pyrolysis reactor (PR)

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Abstract

The CO_2 reforming of CH_4 in a thermal diffusion column reactor (TDCR) was conducted from 800°C to 1175°C on a tungsten wire in a vertical and inclined (45°) mode. Comparison was made with a horizontal pyrolysis quartz reactor with coiled wire. The wall temperature of the pyrolysis reactor was controlled by a tubular furnace. The longer coiled wire in this reactor gave higher conversion than the TDCR for comparable wire temperatures and flow rates. The conversion of CH_4 and the yields of H_2, CO and H_2O were compared with calculated values and indicate that the hot wire reactors are non-equilibrium systems due to the different diffusion characteristics of the reactants and products. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Most natural gas fields in Indonesia have carbon dioxide content in the range 10–72%. The carbon dioxide usually creates some problems, i.e. corrosion in gas pipelines, high cost CO_2 separation processes, and earth's greenhouse problem if it is released into atmosphere. These problems result in restricted exploration of these natural gas fields. One approach to utilization of the natural gas from these fields is to use the CO_2 present to carry out reforming of the methane. The CO_2 reforming of methane proceeds according to the reaction

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2, \quad \Delta H^0 = 247\,\mathrm{kJ/mol} \tag{1}$$

and thus has the possibility of solving the above problems. The reaction is of much interest: the reaction consumes methane and carbon dioxide as carbon sources (both are greenhouse gases); second, CO_2 as a carbon source could save half of the total carbon needed in reactions (compared to steam reforming and partial oxidation). In other words, it could save half of the methane required to form CO; and third, the synthesis gas produced has a theoretical CO/H_2 ratio of 1 which is suitable as a feedstock of some chemical industry or liquid fuels [1]. In certain potential applications (e.g. energy storage and transmission) this process has a number of advantages over steam reforming and is likely to become an increasingly important industrial reaction in the future [2]. Another advantage of this reforming is the increase in the added value of natural gas with high content of CO_2 since it is converted into synthesis gas which is a petrochemical raw material.

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The catalyzed CO_2 reforming reaction has been summarized by Ross et al. [3]. A patent has been issued [4] and a recent report [5] has shown that of the three isolated carbonaceous species two have been associated with the deactivation of the supported Ni catalysts. A study of CH_4 reforming with a mixture of H_2O and CO_2 has also been reported [6]. A preliminary report [7] on the use of the TDCR has shown that conversion of up to 97% could be achieved with wire temperatures of about 1150°C. No carbon deposition was observed.

The reforming of methane with carbon dioxide has as yet had no commercial application and much has still to be developed. The major problem accompanying the reforming reaction is carbon deposition since it can deactivate the catalyst. On the basis of thermodynamics, coke is predicted to form by decomposition of methane

$$CH_4 \rightarrow C + 2H_2, \quad \Delta H^0 = 75\,\mathrm{kJ/mol} \qquad (2)$$

as well as by the reaction

$$2CO \rightarrow C + CO_2, \quad \Delta H^0 = -173\,\mathrm{kJ} \qquad (3)$$

Water formation is expected by the reverse water gas shift reaction.

$$CO_2 + H_2 \rightarrow CO + H_2O, \quad \Delta H^0 = 40\,\mathrm{kJ/mol} \qquad (4)$$

Supported noble metals such as Pt, Ir, Rh and Pd are used [3,8] if carbon deposition is to be avoided. An advantage of the hot wire reactor is that expensive noble metal catalysts are not needed and any carbon deposition does not affect the course of the reaction.

The aim of the present work was to establish the characteristics of the CO_2 reforming of methane by a hot wire in a TDCR.

2. Experimental

The experiments used two types of reactors that consist of pyrolysis reactor (PR) and a thermal diffusion column reactor (TDCR). A hot wire was used to generate the heat required for reaction. The PR was a horizontal quartz tube with dimensions of 40 cm length and 2.1 cm i.d. The reactor used tungsten or chromel wire of 0.025 cm diameter and 30 cm length. The wire was in a spiral form (coil diameter=1 cm) in order to create a uniform heat and temperature distribution inside the reactor tube. The wire was heated by an AC power supply and controlled by a variable autotransformer. Voltage and current to the wire were measured by a voltmeter and ammeter, respectively. The reactor was inserted into a split furnace in order to either heat the walls or to prevent heat lost from the reactor. The temperature was almost uniform along the wire as measured with an optical pyrometer which had been calibrated with a digital thermocouple thermometer.

The TDCR was a water cooled Pyrex reactor similar to that used previously [7]. The dimensions were 90 cm length and 2.2 cm i.d. The straight wire was installed at the center of the reactor tube. The TDCR was either in a vertical or inclined (45°) mode. The tungsten wire was 60.5 cm long and 0.025 cm in diameter.

The gas flow was 10, 20, 40 and 70 ml/min and the wire temperature was varied in the range 830–1020°C for the TDCR. The premixed reactant gas (CH_4+CO_2) had a small amount of N_2 (~2%) to serve as an internal standard. The yields for CO and H_2 are, as previously reported [7], expressed in terms of the stoichiometry of reaction (1) and for 100% conversion of CH_4, the optimum yields for CO and H_2 are each 50%. Yields for CO which are greater than 50% are due to the occurrence of reaction (4). The material balance for carbon was based on the ratio of reactants and products to the N_2 content [7] and ranged from 90% to 110%. The apparatus and the analysis procedures have been previously described [7].

3. Results and discussion

The comparison between the PR and TDCR for methane conversion as a function of temperature is shown in Fig. 1 for a ratio $CH_4/CO_2=1$, and flow rate of 20 ml/min. The equilibrium composition of the reaction was calculated at various temperatures using reactions (1)–(4) and compared with the experimental results. The methane conversion for the PR is close to equilibrium at temperatures from 830°C to 980°C. On the other hand, in the downward flow the conversion in the TDCR only reached equilibrium at the highest temperature (1175°C). The reaction in the inclined upward flow in the TDCR was not as complete for this flow rate. The greater conversion for the PR than for the TDCR is probably due to the spiral form of the

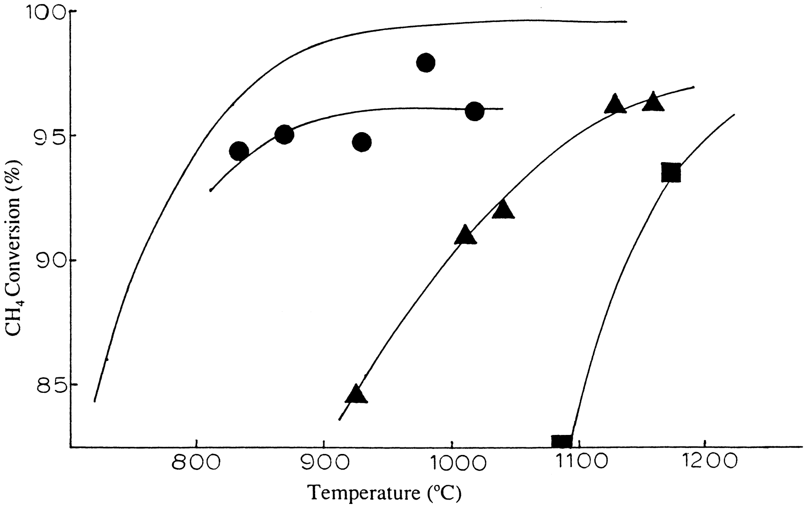

Fig. 1. Methane conversion as a function of temperature: (———) Equilibrium; (– ● –) pyrolysis reactor; (– ▲ –) vertical TDC reactor downward flow; (– ■ –) inclined TDC reactor upward flow. Flow rate=20 mL/min.

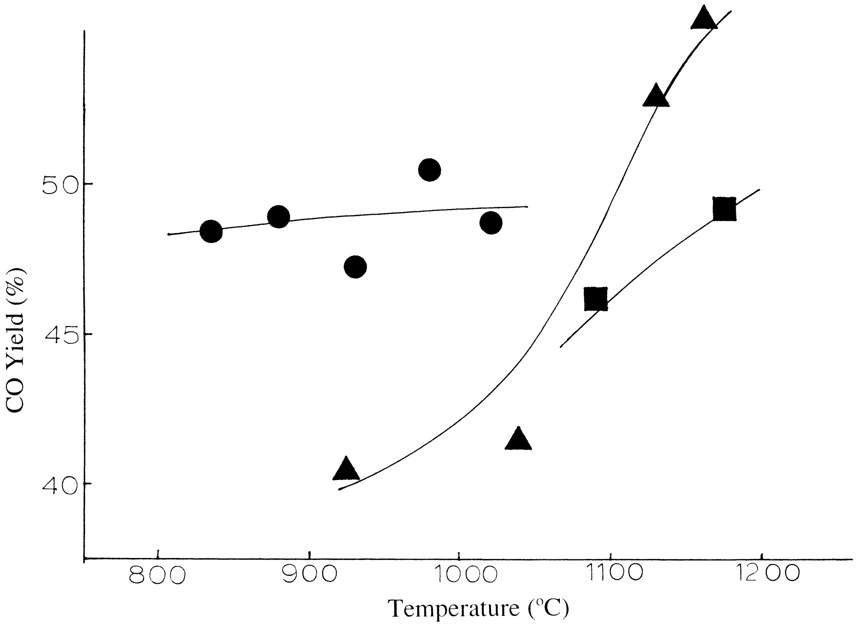

Fig. 2. CO yield as a function of temperature: (– ● –) Pyrolysis reactor; (– ▲ –) vertical TDC reactor downward flow; (– ■ –) inclined TDC reactor upward flow. Flow rate=20 mL/min.

wire which occupied more of the reactor volume. This implies that a multi-wire reactor with proper spacing can possibly lead to improved conversion.

When the furnace temperature for the PR was raised to the wire temperature the conversion dropped significantly though it was still larger than for the furnace alone. This illustrates the importance of the temperature gradient to separate the lighter hydrogen from the other gases.

Figs. 2 and 3 show the CO and H_2 yield for the PR and TDCR. The CO and H_2 yield of the PR increase sharply as the temperature increases but the increase

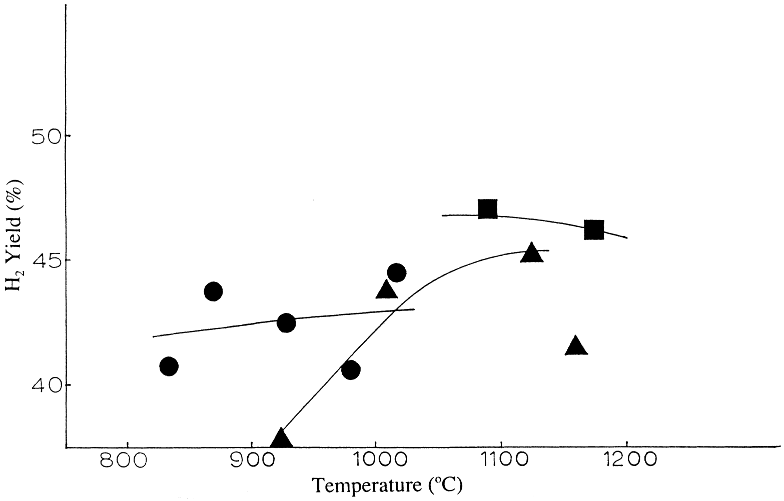

Fig. 3. H_2 yield as a function of temperature: (– ● –) Pyrolysis reactor; (– ▲ –) vertical TDC reactor downward flow; (– ■ –) inclined TDC reactor upward flow. Flow rate=20 mL/min.

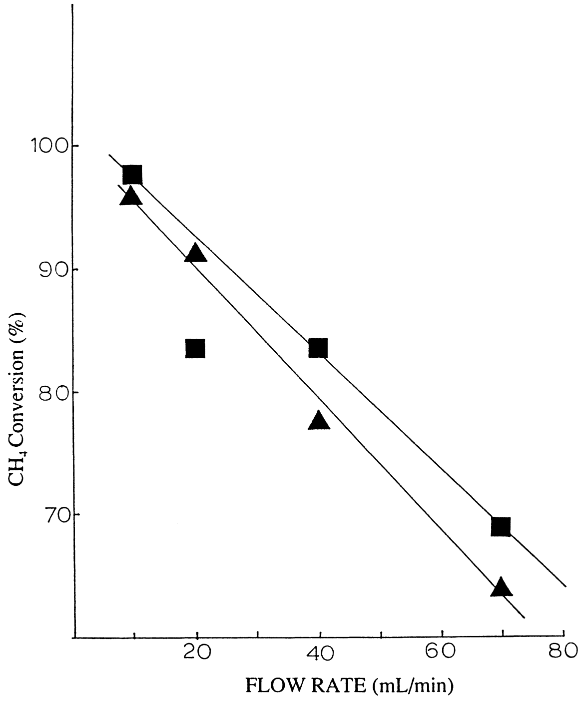

Fig. 4. Effect flow rate on CH_4 conversion for the TDC reactor: (– ▲ –) vertical reactor downward flow; (– ■ –) inclined reactor upward flow. Temperature=1100°C.

for the TDCR was significantly less. The big differences in CO and H_2 yield between PR and TDCR parallel the differences noted for the conversion trends.

The CO/H_2 ratio for both the PR and TDCR are usually greater than 1. This is probably due to reaction (4). Water was observed and, when calculated from the mass imbalance, was shown to pass through a maximum as predicted thermodynamically. However, the experimental maximum appeared at higher temperatures than calculated. A comparison of the CH_4 conversion by the inclined TDCR in upward flow with the vertical TDCR in downward flow is shown in Fig. 4 as a function of flow rate at 1100°C. The general trend shows that the inclined TDCR is slightly superior to the vertical reactors. It has been calculated [9] that the inclined flat plate columns should show a substantial increase in isotopic separation efficiency over the vertical column. Its inferior performance at lower temperatures has yet to be explained.

4. Conclusions

A coiled or multi-wire inclined TDCR column could be an effective method of converting a CH_4/CO_2 mixture to syngas. The formation of volatile tungsten oxide due to the reaction of $W+CO_2$ requires that wires other than tungsten need to be evaluated. Chromel wire used in two sets of experiments at 980°C and 1020°C in the PR showed similar conversion characteristics without the accompanying wire reaction. Other high temperature conductors such as Mo, Ta, Nb and Hf should be tested.

Acknowledgements

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