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Production of synthesis gas from methane using compression ignition reformer

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Abstract−A new form for a partial oxidation compression ignition reformer, which is different from existing methods of reformation, is suggested to which the concept of super-adiabatic combustion is applied. In addition, experiments are conducted on variables such as the oxygen/methane ratio, the total flow rate, the intake preheating temperature, and the oxygen enrichment ratio, all of which affect the production of hydrogen, in order to understand the optimal features of the movement of the reformer. Results showed that the concentration of hydrogen and carbon monoxide was 20.84% and 13.36%, respectively, under the optimal standard conditions of an oxygen/methane ratio of 0.26, a total flow rate of 106.5 L/min, and an intake preheating temperature of 355 °C. Under the same conditions, the concentration of hydrogen decreased to 20.31% when the oxygen enrichment ratio was 55.6%, while that of carbon monoxide increased to 20.85% when the oxygen enrichment ratio was 50.33%.

Key words: Synthesis Gas, Hydrogen Production, Reforming, Biogas, Compression Ignition Engine

INTRODUCTION

Interest in low-pollution alternative energies has been gradually increasing as environmental problems such as global warming caused by the use of fossil fuels have been escalating. One of the technologies considered to be realistic at present is the production of synthesis gas using methane, which is the principal ingredient of natural gas and biogas. Methane, in particular, constitutes some 50-70% of the biogas that is generated from landfills and from anaerobic digesters of wastewater treatment plants. If methane could be utilized as an energy source for the production of synthesis gas, synthesis gas using methane will be an eco-friendly technology that will enable not only the treatment of methane gas, which has a 20 times greater global warming potential (GWP) than carbon dioxide, but also the production of pollution-free energy.

So far, two methods have largely been applied to the production of synthesis gas based on methane: steam reforming and partial oxidation. Currently, the steam reforming method [1-3] is used most widely because of its advantages such as a high throughput of gas processing and a high ratio of synthesis gas production. However, the method also has some shortcomings: it requires exterior energy sources such as a high temperature and high pressure and it needs to be massive in size. On the other hand, partial oxidation reforming [4-7] uses the incomplete combustion of fuels, and the whole reaction is therefore operated through exothermic reaction. However, the method also has a technical difficulty since it requires a low oxygen/fuel ratio to maintain the high yield of synthesis gas and concentration.

While the partial oxidation reforming method shows a high efficiency compared with other existing methods and has benefits in terms of energy costs because it uses its own generation of heat, other difficulties are associated with the method due to its narrow combustibility range in the case of biogas, which has low a caloric value. To compensate for these weak areas, super-adiabatic combustion reforming [8] was suggested for further research. Still, in this case, the regenerator should also be used for the method. It is also considered inappropriate for mass production.

In this study, therefore, a new form for a compression ignition reforming reactor was devised with the utilization of a super-adiabatic compression reforming method in order to resolve the above-mentioned problems associated with the existing methods. It was proved through experiments that the proposed reformer is an efficient reactor, which does not use a catalyst, enables partial oxidation, and guarantees a high yield of synthesis gas and a high throughput. Furthermore, the optimal conditions for the operation of the proposed reformer are also proposed in this study through an experiment on the variables that affect the production of synthesis gas.

EXPERIMENTAL

1. Experimental Apparatus

Fig. 1 shows the experimental apparatus used in this study. It is made up of the gas supply line, the compression ignition reformer and the measurement and analysis system.

The gas supply line is comprised of the methane supply line, oxygen supply line and air supply line. Methane is supplied through the compressed natural gas (CNG) cylinder which is filled at a high pressure of 22 MPa (224.3 kg_f/cm^2), and the methane is then injected through the mixer via a regulator, a flowmeter (Dwyer, USA) and a surge tank (7.5 *l*) for mixture with air. The oxygen supply line is comprised of an oxygen cylinder, a regulator and a flowmeter. The air supply line is made up of an orifice flowmeter (KFE, Korea), a surge tank (19 *l*), a diaphragm with a 10 mm orifice diameter, a safety valve, and a 6 kW electric heater. A mixer from an LPG motor vehicle was used for the mixture of methane.

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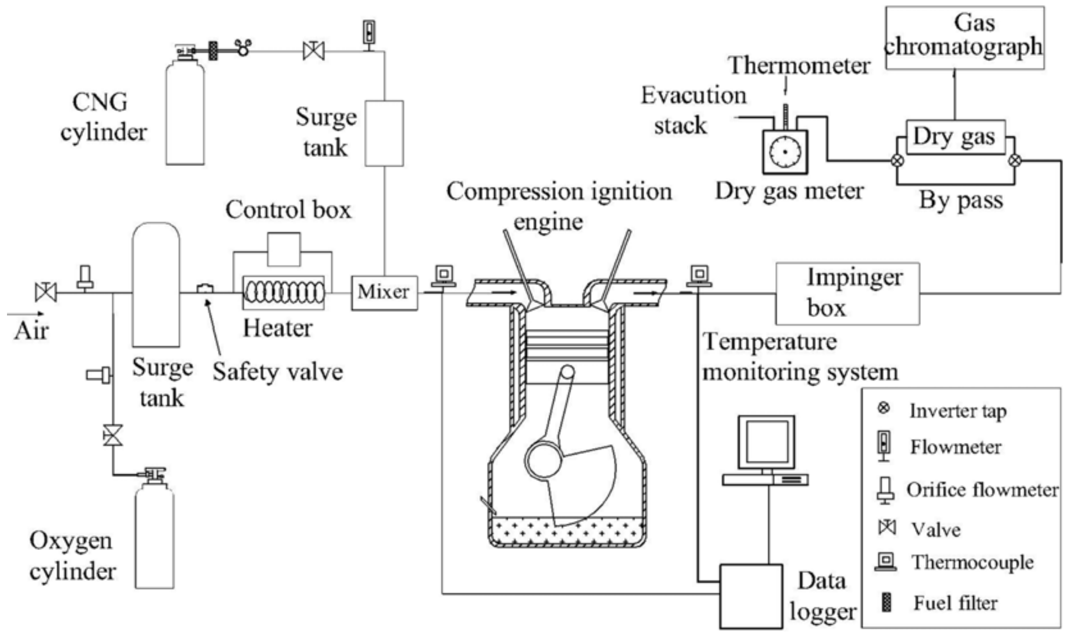


Fig. 1. Experimental apparatus of compression ignition reformer.

Table 1. Technical data of compression ignition reforming reactor

Item		Specification
Model		Daedong, ND130DIE
Type		Horizontal water-cooled 4 cycle diesel engine
Fuel injection		Direct injection
Cylinder number		1
Bore (mm) & Stroke (mm)		95×95
Compression ratio		18 : 1
Displacement (cc)		673
Power (PS/rpm)	Max	13/2400
	Rated	10/2200

A commercial diesel engine was used for the compression ignition reformer and its technical data is shown in Table 1.

The measuring system is comprised of the measurement of temperature and the measurement of the engine's rotational frequency. To measure temperature, a thermocouple (K-type, OD: 6 mm) was installed onto the intake manifold and exhaust manifold and a data logger (FLUKE, USA) was used for temperature monitoring. A magnetic-type temperature control device was also made and used to control the temperature of the heater. For the measurement of the rotational frequency, a tachometer (HIOKI, Japan) was installed onto the engine poly. For the exhaust gas analysis system, a sampling probe was inserted into the exhaust line at a point 390 mm away from the exhaust valve. Exhaust gas was inhaled through a vacuum pump (Gast Manufacturing Inc., USA) and then passed through the impinger so that soot and moisture could be eliminated. The waste gas was then analyzed by a gas chromatograph (SHIMADZU, Japan).

2. Experimental Method

To secure the recurrence of the experiment, the refiner was first test-run for 15 minutes with gasoline, and only after the temperature inside the engine became stabilized, the refining fuels of methane and air were injected. To minimize the connection between factors that affect the yield of fuel-rich syngas, the optimal condition was determined as a standard condition through repeated experiments. Experiments were then carried out in accordance with each of the variables, including an oxygen/methane ratio, a total flow rate, an intake preheating temperature and an oxygen-enrichment ratio. Experiments were carried out in two ways: the basic experiment and the oxygen-enrichment experiment. In the basic experiments, two variables were fixed in order to show the influence the other variable had on the production of synthesis gas.

In the oxygen-enrichment experiments, the rate of oxygen enrichment was first set at 21% and then the amount of oxygen was gradually added up. Oxygen was poured into the flowmeter, with the pressure of the exit of the pure oxygen cylinder decompressed to 0.1 MPa (1 kg_f/cm^2). In the initial stage, the standard condition of oxygen/methane ratio was set at 0.26. However, the ratio later changed in accordance with the addition of oxygen. As aforementioned, methane has a high self-ignition temperature, and therefore has a high compression ratio. The preheating of the intake temperature is therefore required in order to operate the engine via methane [9]. The addition of oxygen promotes a faster reaction with methane and results in an increased thermal efficiency and an improved output of the engine [10].

Experiments were carried out using an increasing amount of oxygen from the lowest temperature condition of the engine, which was first operated under the standard condition. The oxygen enrichment ratio was calculated from the following Eq. (1) [11].

$$\mathrm{OEC}(\%) = \frac{0.21\mathrm{A} + \mathrm{O}_{2add}}{\mathrm{Q}_{total}} \times 100 \tag{1}$$

In this equation, OEC is the oxygen enrichment concentration, A is the amount of air inflow, O_{2add} is the amount of added oxygen,

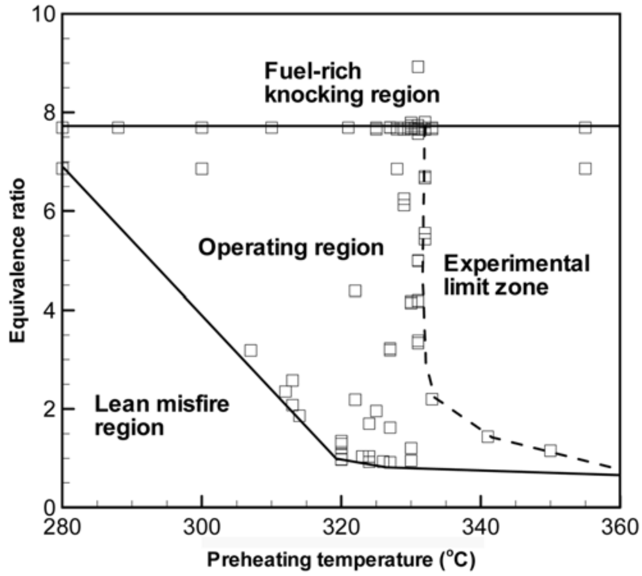


Fig. 2. Combustibility range of compression ignition reformer.

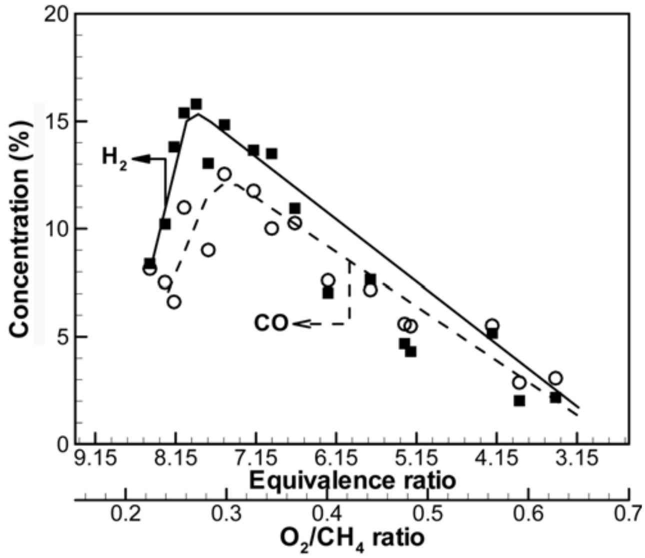


Fig. 3. Concentrations of oxygen/methane ratio.

Table 2. Experimental conditions by variables and standard condition

Conditions	O_2/CH_4 ratio	Total gas flow rate (L/min)	Intake temperature (°C)	Oxygen enrichment (%)
Experiment range	0.22-0.63	59.0-171.4	280-355	21.0-60.53
Reference	0.26	106.5	330	55.6

and Q_{total} is the sum of the air inflow and the added oxygen.

To analyze the concentration of the reformed gas collected by the sampling probe, a gas chromatograph was used. A TCD detector was used for the analysis, while molecular sieve 5A (80/100 mesh) was used for hydrogen, molecular sieve 13X (80/100 mesh) for carbon monoxide and HayeSep R (100/120 mesh) for carbon dioxide and C_mH_n.

RESULTS AND DISCUSSION

1. Limit of Combustibility

Since this study is aimed at the production of synthesis gas through partial oxidation in the fuel-rich state, the characteristics of the engine and the range of combustibility were first examined, which are shown in Fig. 2.

The experimental limit zone refers to the area where the experiments could not be carried out due to problems such as the capacity of the heater and the durability of the engine.

The fuel-rich knocking region is the area where knocking, an incomplete combustion, took place, and there were difficulties with the operation of the engine due to an excessive inflow of fuel compared to that of air inflow. Knocking in this region is caused by increased pressure due to the sudden combustion, which is the result of delayed ignition caused by the lack of oxygen due to the fuel-rich state.

The lean misfire region, on the other hand, is the area where normal operation of the engine was difficult due to weak generation power. It is the area where the fuel is relatively rare compared to the combustibility-operating region. A misfire resulted, as the total caloric value of the mixed gas decreased below the level of ignition temperature. In the area where the temperature was high, the range of combustibility of the lean mixer was somewhat expanded in tandem with the increased heat content.

2. Results of the Parametric Studies

2-1. Effect of Oxygen/Methane Ratio

Fig. 3 shows the concentration of the hydrogen and carbon monoxide when the oxygen/methane ratio was changed from 0.22 to 0.63 with the total flow of the mixed gas set at 106.5 L/min and the intake preheating temperature set at 330 °C.

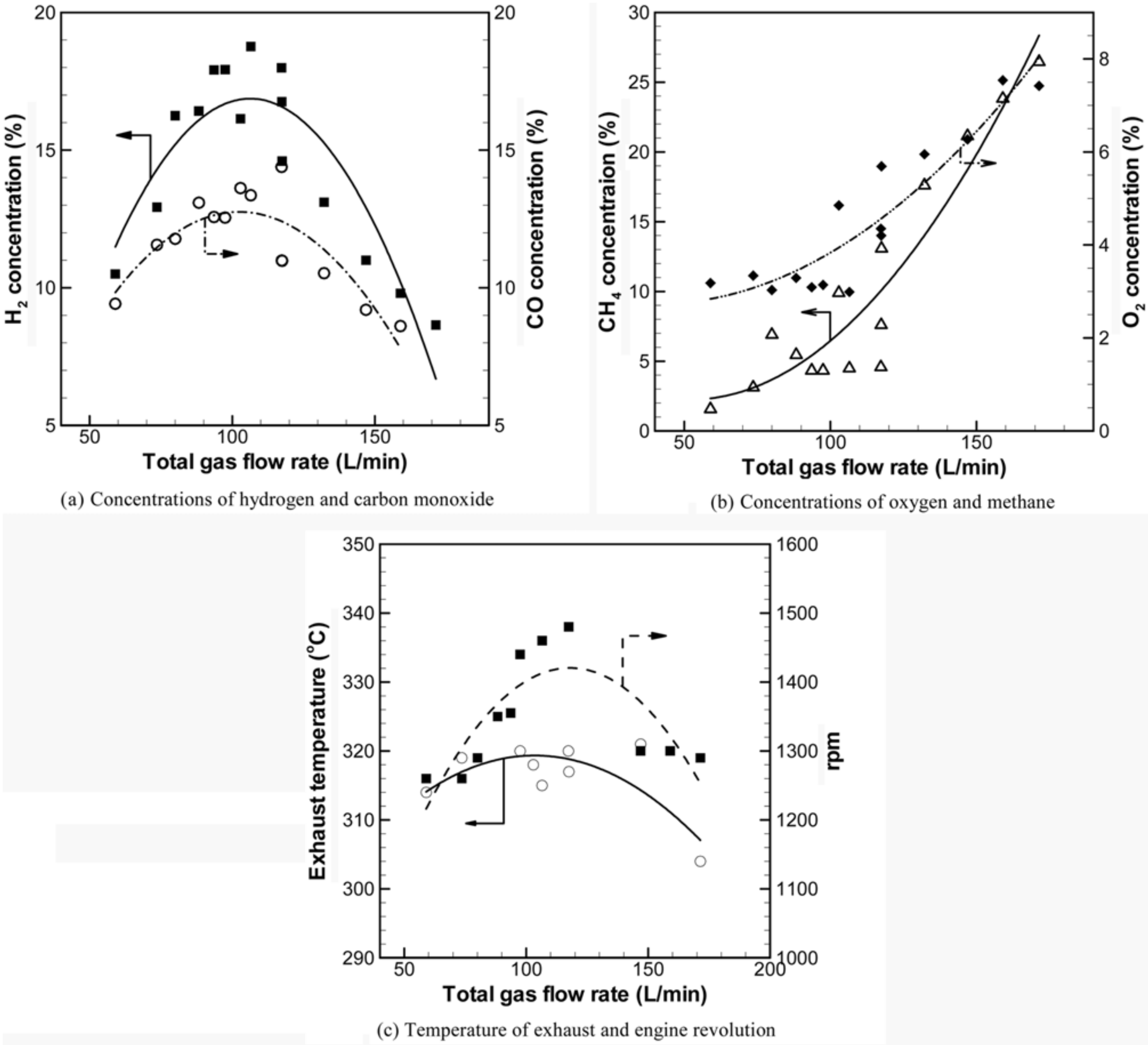
As the oxygen/methane ratio increased, the concentration of hydrogen also increased. When the oxygen/methane ratio increased to 0.26, it reached a peak of 15.39% and then began to decrease again. A similar pattern was found for the carbon monoxide.

As shown above, the concentration of hydrogen and carbon monoxide increases as the oxygen/methane ratio increases. This is because the combustibility is enhanced due to the sufficient supply of oxygen, which enables the promotion of partial oxidation due to the decreased equivalent ratio. On the contrary, the concentration decreased after it reached the maximum point, despite the continual increase in the oxygen/methane ratio. This is because of the excessive supply of air which causes the loss of waste heat, thereby leading to the reduced partial oxidation reaction and dilution of air.

An increase in the oxygen/methane ratio implies the decrease of fuel in a state where air is fixed. When the oxygen/methane ratio was below 0.22, a normal operation became difficult due to the pre-ignition and knocking, or to an abnormal combustion caused by the fuel-rich state. In the area where the ratio increased to above 0.63, the lack of fuel and the exhaust loss caused a misfire.

2-2. Effect of Total Flow Rate

Fig. 4 shows the results of the measurement of the concentration of reformed gas, the temperature of the exhaust, and the engine frequency, when the total flow was changed to between 59 L/min and 171 L/min, with the oxygen/methane ratio fixed at 0.26 and the intake



(a) Concentrations of hydrogen and carbon monoxide

(b) Concentrations of oxygen and methane

(c) Temperature of exhaust and engine revolution

Fig. 4. Results of total flow rate.

preheating temperature was set at 330 °C.

Fig. 4(a) indicates the concentration of hydrogen and carbon monoxide within the reformed gas.

When the total gas flow stood at 106.5 L/min and 117.3 L/min, the concentration of hydrogen and carbon monoxide reached maximums of 18.76% and 14.39%, respectively. As the total flow increased, the amount of hydrogen and carbon monoxide from the total synthesis gas also increased, due to the increase of the amount of oxygen in tandem with the amount of injected methane. However, while there are a number of differences in the flow of hydrogen and carbon monoxide, the maximum state of concentration began to decrease after it reached its peak. This is because the increased amount of mixed gas causes a quenching effect inside the cylinder during the intake process, forming a generally low combustion temperature and decreasing the concentration of synthesis gas.

Fig. 4(b) shows the result of the analysis of the concentration of methane and oxygen included in the reformed gas. As the total amount of gas increased, that of methane and oxygen also increased. This is because the increased flow lowers the combustibility inside the cylinder, as well as the reactivity of methane and oxygen within the engine. In this situation, the gas does not react well and is expelled from the engine. In particular, if the total flow is increased in a large quantity, the conversion into synthesis gas is not carried out successfully and the methane is expelled in its original condition, as previously illustrated in Fig. 4(a).

Fig. 4(c) shows the relationship between the temperature of exhaust gas and the number of rotations of the engine in accordance with the change in the total gas flow. As the total flow increased, the temperature and the frequency increased to the maximum value and then began to decrease. This could be explained in a similar way to the graph in Fig. 4(a), where the amount of synthesis gas production is shown. As aforementioned, the temperature inside the combustion chamber increases in tandem with the increased flow, raising the engine frequency. However, the temperature and

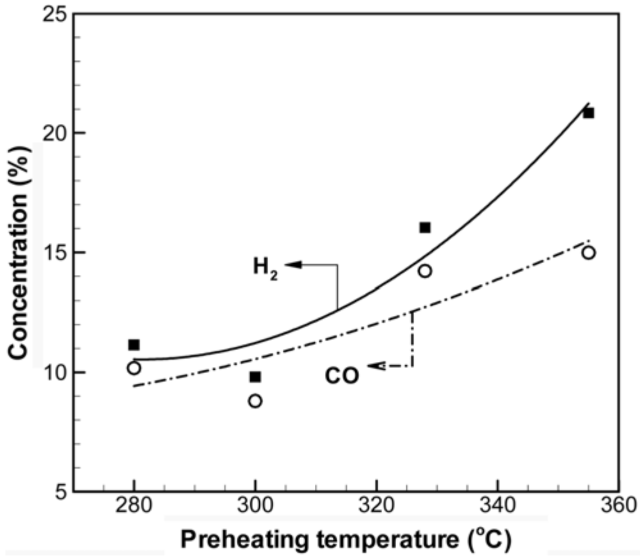
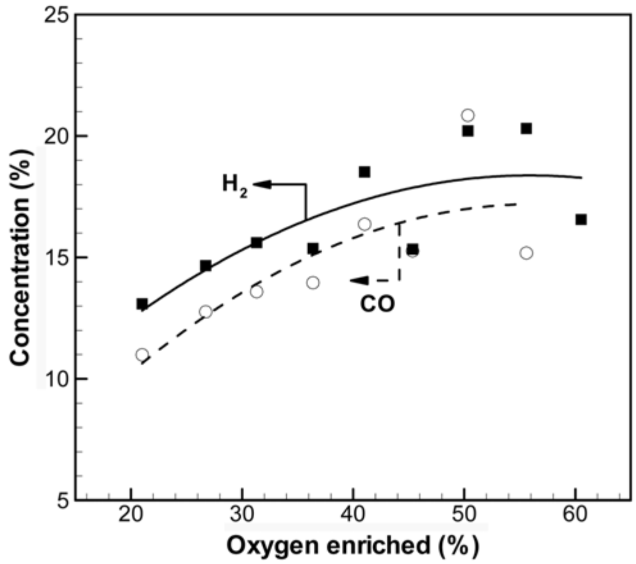
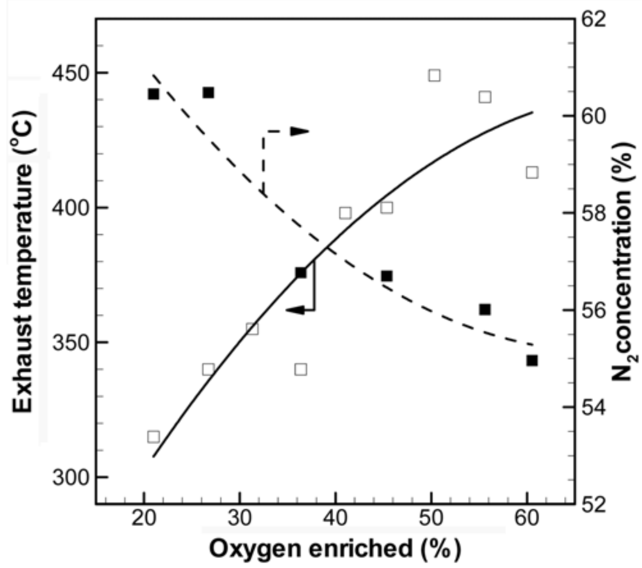


Fig. 5. Influence of intake preheating temperature.



(a) Concentration of hydrogen and carbon monoxide



(b) Temperature and concentration of nitrogen

Fig. 6. Influence of oxygen enrichment.

the engine frequency decreased after reaching their peaks, because the supply of a large amount of mixed gas caused a quenching effect inside the cylinder. In this experiment, the reaction of methane was most active and the engine frequency was the highest in the area where the hydrogen yield was high. As seen in the experimental results, the temperature of exhaust gas and the engine frequency have a very close relationship. This implies that the combustion state of an engine could be verified by simply checking the number of rotations of the engine.

2-3. Effect of Intake Preheating Temperature

Fig. 5 shows the concentration of hydrogen and carbon monoxide when the intake temperature is increased to 355 °C, with the oxygen/methane ratio fixed at 0.26 and the total mixed gas flow is set at 106.5 L/min.

This compression ignition reformer was operated normally with the preheating of the mixed gas maintained at above 280 °C and the self-ignition temperature. As the preheating temperature increased, the concentration of hydrogen and carbon monoxide also increased continuously. At the maximum temperature of 355 °C, the concentration of hydrogen and carbon monoxide reached the maximums of 20.84% and 14.99%, respectively. By increasing the intake preheating temperature, the concentration of the mixed gas also increased. This is because the total calorie increases due to the increase in entropy and because the inside of the reactor is brought to a state of high pressure, a sufficient condition for partial oxidation.

2-4. Effect of Oxygen-enrichment

Fig. 6 shows the results of the experiment in order to verify the yield of synthesis gas in accordance with the addition of oxygen in the reformer. Under the standard condition, the oxygen/methane ratio was fixed at 0.26, the total gas flow at 106.5 L/min and the intake temperature at 330 °C. The oxygen enrichment was raised from 21% to 60.53%.

Exhaust gas fluctuation became relatively serious in accordance with the oxygen enrichment. As seen in Fig. 6, there was some fluctuation in the concentration of synthesis gas. However, the concentration of hydrogen and oxygen increased to the maximums of 20.31% and 20.85%, respectively, in tandem with the general increase in the oxygen enrichment ratio. This is because the discharge loss decreases in accordance with the decreased amount of nitrogen, which raises the temperature and improves combustibility. The temperature and the concentration of nitrogen can be verified in Fig. 6(b).

CONCLUSIONS

A commercial diesel combustion engine was partially altered to set up a compression ignition reforming system in order to carry out experiments on the production of synthesis gas. Through repeated experiments, the standard condition, under which the amount of hydrogen within the total synthesis gas reached the maximum, was determined. According to the experimental results, the concentration of hydrogen and carbon monoxide became 20.84% and 13.36%, respectively, when the oxygen/methane ratio was set at 0.26, the total gas flow was 106.5 L/min and the intake preheating temperature was 355 °C. Also, under the same conditions, the concentration of hydrogen and carbon monoxide decreased to 20.31% and increased to 20.85%, respectively, when the oxygen enrichment ratio was about 53%.

Furthermore, the feature of the reformer's movement was also examined through experiments carried out on the variables that affect the yield of hydrogen. As the oxygen/methane ratio and the total gas flow increased, the concentration of the synthesis gas also increased to the maximum value and then began to decrease. Therefore, it would be important to determine the optimal condition for the abovementioned variables in order to obtain the maximum yield. Also, the synthesis gas yield increased in proportion to the increase in the intake preheating temperature and the oxygen enrichment ratio. This means that if only the economic efficiency was secured, a higher temperature and enrichment ratio would be favorable to the yield.

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