Methane Mitigation by Thermal Oxidation in a Reverse Flow Reactor

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Abstract: - Methane is a potent atmospheric greenhouse gas (GHG) and second only to carbon dioxide as a contributor to global warming. To reduce the methane emissions, a thermal reverse flow reactor packed with the ceramic honeycomb monoliths was developed. The methane thermal oxidation characteristics were studied experimentally. Different methane concentrations (0.2-1%) on a volume basis were used for experiments of the methane oxidation in the reverse flow reactor. The results show that the lean methane oxidation that are not normally auto-thermal can be run and sustained in the reverse flow reactor; the methane conversion efficiency achieved is over 95%; the lowest methane concentration limit at which methane will oxidize reliably is approximately 0.3%; the highest temperature in the reactor is lower than the detrimental temperature of the ceramic monolith, the stability and reliability of the reactor can be ensured. Also, it was found that the influence of the switch time on the performance of a reverse flow reactor is significant. The principles to optimize the switch time and methods to determine the optimal switch time are discussed.

Key-Words: -Methane; Thermal oxidation; Reverse flow reactor; Ceramic monolith; Greenhouse gas

1 Introduction

Global warming is a major issue in the world today. So far, many countries have signed the Kyoto Protocol and committed to minimizing GHG emissions. The combined effort will be required to reach the goals set out by the Kyoto Protocol. Methane is classified as a GHG, and large volumes of methane in the atmosphere are believed to be a main contributor to climate warming today. Contribution of methane emissions to the greenhouse effect represents 17% of all greenhouse gases emissions. Methane has a global warming potential 21 times that of carbon dioxide [1]. Reducing methane emissions will have a strong impact on greenhouse gases emissions. The importance of finding efficient methods of reducing methane emissions is apparent.

These methane emissions come from a variety of sources [2]. They come from fugitive emissions in the oil and gas sector, the solid fuels and coal mining sector, and the agricultural activities, etc. Methane liberated from fugitive emissions can vary in quality depending on where and how it is liberated. Some of them is of very high concentration (over 90% methane), often used to pipeline natural gas. Some is of medium quality (approximately 30–90% methane), often used to gas engine main fuel. However, most of them is of lower concentration (typically under 1% methane), often vented to the atmosphere, as lean methane disposal is difficult.

The typical lean methane is at ambient temperature. To oxidize methane at a higher rate and greater efficiency, the reaction must proceed at much higher temperatures [3]. However, in order for an ambient methane to react at higher temperature, that feed stream must be preheated before the reaction takes place. This is difficult to do efficiently. There are several methods that can be used to preheat the inlet ambient feed to a higher temperature. A simple method is to use an external heater to heat the feed stream. The method requires the additional consume of power. Another method is to run the hot outlet gas through a heat exchanger to preheat the feed. There is an added pressure drop associated with a heat exchanger. The method used in this paper is reverse flow operation. In a flow reversal reactor the feed is periodically switched between the two ends of the reactor using control valves, while switching the direction of flow can preheat the feed with the energy of oxidation. The concept of reverse flow was first discussed 50 years ago [4]. The concept has been used in many applications

[5]. The lean methane catalytic oxidation in a reverse flow reactor has also been studied [3,5,6,7]. However, the adaptation of reverse flow to the thermal oxidation of lean methane mixtures is new. The thermal oxidation has the advantage of considerably lower cost and is preferred where catalyst poisoning could be a problem. The objective is to develop a thermal reverse flow reactor and investigate the lean methane thermal oxidation characteristics in the reverse flow reactor.

2 Experimental reactor system

2.1 Reactor structure

Tests of methane thermal oxidation were carried out in a reverse flow reactor. The pilot scale reactor is 300 mm wide, 300 mm high, and 2800 mm long. The entire configuration of the test apparatus is shown in Fig.1.

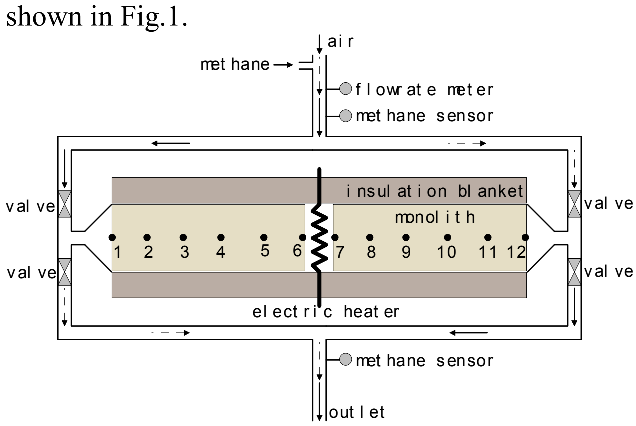

Fig.1 Configuration of the test apparatus

A reverse flow reactor does not have a fixed inlet or outlet. The inlet or outlet is periodically switched between two sides of a reactor using switching valves. Thermal energy generated in an exothermic methane oxidation reaction and exit gasses can be captured with the solid heat storage medium. Then, with switching the flow direction, the captured thermal energy within the heat storage medium can be used to preheat the feed. This allows a reactor core to remain at high reaction temperatures, even if the inlet feed is at lower temperatures. With reverse flow, the lean methane oxidation reactions that are not normally auto-thermal may be run and sustained at lower inlet temperatures and higher conversions.

It is clear that the thermal mass (product of density and heat capacity) of the solid heat storage medium is very important to the reverse flow reactor, the higher thermal mass will give the higher stability. In the experiments presented in this paper, the ceramic honeycomb monoliths were used as heat storage medium. Honeycomb monoliths consist of a structure of parallel channels with porous walls, which hold outstanding characteristics of high thermal mass, high mechanical strength, high geometrical area, and low pressure drop at high mass flows [6, 7]. The monolith properties are showed in Table 1.

Table 1 Properties of the ceramic monolith

Property	Value
Width of square hole (mm)	2.25
Thickness of wall (mm)	0.7
Density (kg/m^3)	2400
Specific surface area (m^2/m^3)	1005
Porosity (Void/%)	57
Thermal conductivity (W/(m·K))	8
Heat capacity (J/(kg·K))	1200
Bearing temperature (ºC)	1350

To prevent heat losing from the reactor to the surroundings, the reactor was surrounding with a layer of insulation ceramic fiber blanket 350 mm thick. The ceramic fiber blanket properties are showed in Table 2.

Table 2 Properties of the ceramic fiber blanket

Property	Value
Density (kg/m^3)	100
Heat capacity (J/(kg·K))	1340
Thermal conductivity (W/(m·K))	0.144

2.2 Forward and reverse flow

For a determined length of time, the reactor run in forward flow, indicated by the solid arrows. With time progressing, more energy accumulated at the outlet section of the reactor. After a determined length of time, the flow direction was reversed, indicated by the dotted arrows, and the thermal energy stored in monoliths was used to preheat the feed. This time is typically before the reactor begins to lose thermal energy to the outlet stream. Again, after a determined length of time, the direction was switched. Thus, there are two different flow directions in a reverse flow reactor.

2.3 Starting up operation

At the start, a reverse-flow reactor needs some initial thermal energy to bring the reactor core and the packed monolith to higher temperature, then, without the external thermal energy, a adiabatic reactor should be able to thermally sustain itself once running. In the experiments, starting up of the reactor was accomplished through an electric heater on the central position of the reactor. This heater was used to bring the monoliths on the central position of the reactor from ambient temperature to a temperature sufficient to achieve methane oxidation. Once the central position of the reactor was preheated to a certain temperature, lean methane mixture was supplied to the reactor, and the heater was turned off.

2.4 Gas feed sources

Air was supplied to the reactor using an air compressor. The inlet air was at ambient temperature. The methane gas was supplied from the gas cylinder. The methane gas was 99% methane on a volume basis, the remainder gas was inert. The flow rate of inlet methane air mixture was measured using a flow rate meter. The methane concentration in the feed was adjusted using the valve manually operated and measured using a methane concentration sensor. In the experiments, the methane concentration was below 1% over time.

2.5 Data acquisition and control system

The data acquisition and control system run a software package developed independently on PLC and PC computer. The system recorded all sensor values at a specified interval. That interval was generally 1 second. Data were saved as data files for analysis.

The four switching valves controlled the flow direction. The valves were powered by electricity, and controlled by the computer control system. The valves were switched on the operator's direct command or the given switch time via the computer control system.

The methane concentration in the feed and outlet stream was measured using the methane concentration sensor. Two methane concentration sensors were installed in the reactor pipeline system. One was near inlet valve (before the inlet valve), and another was near outlet valve (after the outlet valve). A small gas stream was continuously pumped out of the pipeline, and through the sensor sample chamber. As the response time of the sensor is less 0.1 seconds, continuous online methane concentration data acquisition was completed for these experiments. The sensors were used to verify the feed concentration and overall methane conversion.

Thermal profiles from the reactor were obtained using twelve thermocouples (denoted from 1 to 12 in Fig.1). All thermocouples were placed along the centerline of the reactors, ten were used to obtain profiles in the monolith sections, and two on both sides report temperatures in inlet and outlet. Thermocouples were inserted from the side, through the insulation and reactor wall. The locations of the thermocouples may be seen in Fig.1.

3 Results and discussion

3.1 Ignition temperature

An electric heater was used to bring the monoliths on the central position of the reactor from ambient temperature to a temperature sufficient to achieve methane oxidation. Once the central position of the reactor was preheated to a certain temperature, the heater was turned off and then lean methane mixture was supplied to the reactor. If the methane concentration from the outlet stream is adequately low, this temperature can be considered the ignition temperature of methane oxidation. Otherwise, tests were repeated at a higher temperature till the methane concentration from the outlet stream was adequately low and the flaring temperature of methane oxidation was found. Finally, the results showed that the ignition temperature was approximately 980ºC [8, 9].

3.2 Typical temperature profiles

The axial temperature profiles recorded for the typical experiments are shown in Figures below. The experiments run for several hours with an inlet concentration of 0.8 % methane. The inlet velocity at inlet temperature (25°C) was 0.4m/s. Each cycle was 300 seconds long, the switch time was 150 seconds accordingly. The profiles recorded at the end of flow from left to right are shown in Fig.2. Over the cycles, the overall temperature in the reactor increases, the reactor tends to accumulate thermal energy. The results show that the reactor is auto-thermal and self-sustaining under these conditions.

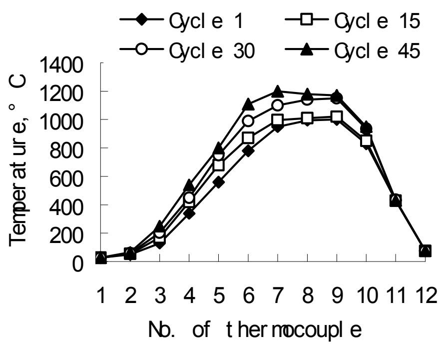

Fig.2 Axial temperature profiles at the end of the

forward flow

Fig.3 shows a comparison of the temperature profiles between the two sides. The profiles were obtained for a full cycle, that is, at the end of the forward flow and reverse flow. There is a little of difference in the profiles. At the end of the forward flow the temperature in the right side is slightly higher than the temperature in the left side at the end of the reverse flow. The reason is that there are some differences in material, structure, flow resistance and so on between the two sides.

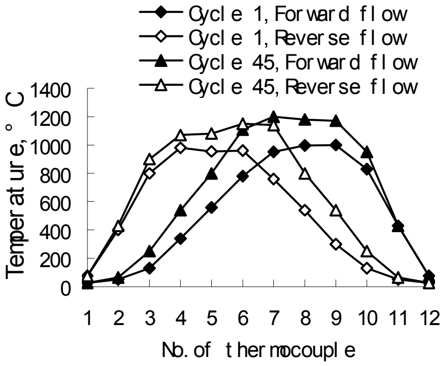

Fig.3 Axial temperature profiles at the two sides

The effect of decreased feed concentration of methane is showed in Fig.4. The conditions were the same as those of experiment described above, except that the inlet concentration of methane was decreased to 0.4 %. It can be seen that the experiment with lower methane concentration leads to lower reactor temperatures and slower temperature rise.

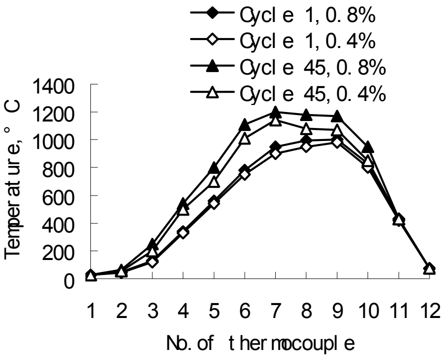

Fig.4 Effect of different feed concentrations on temperature profiles

Based on a number of experiments carried out, it was found that the lower auto-thermal limit of methane concentration is approximately 0.3% methane. Certainly, this value may vary with different inlet conditions. The highest temperature in the reactor is approximately 1250°C under the condition of 0.8 % methane concentration. This value is lower than the detrimental temperature of the ceramic honeycomb monolith (1350°C). The results under the condition of 1 % methane concentration show that the operation with higher methane concentration will lead to higher reactor temperature and faster temperature rise, and the temperature in the reactor will get too high in shorter time, the ceramic honeycomb monolith may be damaged. So heat removal is very necessary in the operation of a reverse flow reactor [10]. Heat removal can be accomplished by heat exchangers or through hot gas withdraws in the reactor centre. Heat removal can keep the reactor within an acceptable temperature range and ensure the stability and reliability of the reactor. The energy extracted from the reactor can be used as a utility heat source.

3.3 Methane conversion efficiency

The effect of the methane oxidation can be assessed with the methane conversion efficiency. The methane conversion efficiency η is calculated according to the following equation.

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times \%$$

Where C_{in} is the methane concentration in the feed, C_{out} is the methane concentration in the outlet stream.

Based on experiments carried out under the conditions described above, the methane conversion efficiency reaches 95 percent. The removal efficiency of methane emission is higher.

3.4 Switch time

It was found that the switch time influenced the overall conversion, the peak temperature and average temperature in the reactor. To obtain the best performance of a reverse flow reactor, the switch time must be optimized. But there are a number of difficulties in determining the optimal switch time [11]. Although the optimal switch time is not presented in this paper, the relationship between reactor performance and switch time was found. To retain more energy within the reactor and sustain itself under the lower methane concentration conditions, the shorter switch times should be used. To distribute thermal energy throughout the reactor and avoid the higher peak temperature under the higher methane concentration conditions, the longer switch times should be used.

Obviously, much more work would be required for optimizing the structure and operation of the reactor system.

4 Conclusion

The thermal reverse flow reactor packed with the ceramic honeycomb monoliths is an effective technology for reducing methane emission. Over 95% decrease in methane emission is achieved. The reactor can sustain oxidation reliably with gas having methane concentration down to approximately 0.3 %.

The highest temperature in the reactor is approximately 1250°C under the condition of 0.8 % methane concentration. Thermal failures by cracking and melting the ceramic monolith can be avoided. The operation with higher methane concentration will lead to higher temperature in the reactor. So to ensure the stability and reliability of the reactor, heat removal is very necessary in the operation of a reverse flow reactor.

The switch time is of important influence on the performance of a reverse flow reactor. The principles to optimize the switch time are to use the shorter cycle times under the lower methane concentration conditions and use the longer cycle times under the higher methane concentration conditions. Optimization of the structure and operation of the reactor is in progress.

Acknowledgments

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