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Co-generation of energy and synthesis gas by partial oxidation of methane

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Abstract

Catalytic partial oxidation (CPO) of methane was carried out over a Rh/γ-Al_2O_3 foam monolith catalyst at pressures up to 1.5 MPa and normal gas flow rates of up to 35 L/min. It was shown that the reaction took place autothermally once the reaction had lit off. Maintenance of short catalyst contact time and reactor cooling was necessary to prevent coke formation at elevated pressures.

The concept of obtaining both syngas and energy from the partial oxidation of methane was tested using two geometries. In the first, the hot exit gases from partial oxidation catalysts were used to drive a turbine. In the second, a partial oxidation catalyst was deposited on turbine blade materials, converting ca. 55% of feed methane to syngas. The novelty in generating energy by this method lies in the combination of CPO, the catalyst configuration and the ability to capture energy via the turbine without further processing of valuable syngas product. Based on the conditions of pressure, conversion and gas composition used in this study, it has been calculated that up to 60 MW of power could be generated from 2500 tonnes per day (TPD) methane feed when the combination of CPO for syngas generation and a turbine are used.

Keywords: Methane; Combustion; Partial oxidation; High pressure; Turbine; Syngas; Energy; Co-generation; Coke

1. Introduction

Synthesis gas produced from natural gas or coal is an important intermediate in the production of a range of fuels and chemicals [1,2]. On an industrial scale, steam reforming (Eq. (1)) is preferred [3–5] but the reaction is endothermic and is usually carried out in combination with fuel combustion (Eq. (2)) to provide the necessary heat for the reaction as in autothermal reforming [4,5]. Dry, or carbon dioxide (CO_2) reforming (Eq. (3)) may be favoured when gas reserves contain significant amounts of CO_2 [6,7].

$$CH_4 + H_2O = CO + 3H_2, \quad \Delta H^\circ = 207\,\text{kJ mol}^{-1} \qquad (1)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \quad \Delta H^\circ = -802\,\text{kJ mol}^{-1} \qquad (2)$$

$$CO_2 + CH_4 = 2CO + 2H_2, \quad \Delta H^\circ = 247\,\text{kJ mol}^{-1} \qquad (3)$$

The necessity to provide oxygen for autothermal reforming adds significantly to the cost of the industrial application [3,4].

Thermal or catalytic partial oxidation offer alternative routes to syngas (Eq. (4)) [8,9].

$$CH_4 + (1/2)O_2 \rightarrow CO + 2H_2, \quad \Delta H^\circ = -36\,\text{kJ mol}^{-1} \qquad (4)$$

The catalytic partial oxidation (CPO) reaction has been studied extensively, mostly at atmospheric pressure [9–11]. It has been reported that catalytic partial oxidation (CPO) of methane can achieve methane conversions of up to 91% and syngas selectivities of over 96% provided millisecond contact times are employed to favour net partial oxidation over total oxidation [10,12,13]. There has been some conjecture as to whether CPO of methane occurs directly, as in Eq. (4), or indirectly via a sequential combination of combustion (Eq. (2)) followed by reforming reactions (Eqs. (1) and (3)). Early investigations postulated the reaction was direct partial oxidation (Eq. (4)) [12,14] but more recent work suggests the combination of combustion and reforming reactions gives the syngas product [15–17]. One study by Weng et al. suggests the catalyst and support material used determines the reaction mechanism for CPO [18]. Weng et al. suggest that Rh supported on γ-alumina has a greater oxygen affinity than Rh supported on silica and the resultant CPO mechanisms are different. The

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alumina support gives rise to the sequential combustion/reforming mechanism and the silica support to direct partial oxidation.

Regardless of the reaction mechanism, the conditions employed for CPO (volumetric expansion on reaction, exothermicity and high volumetric flow rates) are similar to those used in catalytic combustion [19,20], but, unlike catalytic combustion, only limited studies of the effect of pressure on the CPO reaction have thus far been reported [17,21]. Consideration of the CPO reaction led to the concept that partial oxidation product gases produced at high pressure could be sufficient to drive a turbine and to generate electricity. This paper reports the results of experiments designed to test this concept.

The use of a turbine driven by the products of autothermal reforming has been disclosed in the patent literature [22,23], but no previous work reporting the use of CPO of natural gas to obtain energy and syngas without further processing of the syngas has been reported until now [24].

The present study has investigated CPO operated at pressures up to 1.5 MPa and has shown that, with proper reactor design, high conversions and selectivities to syngas are possible. The concept of driving a turbine using the high pressure, high temperature gas from the reaction has been demonstrated. Preliminary studies have shown the feasibility of using catalyst supported on the blades of a turbine.

2. Experimental

All CPO experiments except those testing the viability of the catalyst on turbine blade material were conducted using a 5%Rh on monolithic foam γ-alumina catalyst inside an 18 mm i.d. quartz reactor tube. The quartz tube was sheathed in a stainless steel tube. The foam monolith was made of zirconia toughened α-alumina (Vesuvius, USA). The monolith had dimensions 18 mm diameter, length up to 10 mm and nominal pore size of 80 pores per linear inch. The catalyst was prepared by impregnation of aqueous rhodium nitrate onto the monolith followed by calcination in air at 600 °C.

The catalyst was heated to light-off temperature using an electric furnace. Light-off occurred at catalyst temperatures between 300 and 400 °C. Gas mixtures containing methane and oxygen in the ratio 1.8:1 with 20% N_2 were introduced using electronic mass flow controllers (Brooks 5850E). The nitrogen acted as an internal standard for measurement of gas concentrations as well as maintaining the reactant gas mixture outside the flammable range. Gas flow rates of 5–35 L/min were employed, with the contact time over the catalyst bed being maintained by increasing the flow rate as the system pressure increased. Gas analysis was carried out using quadrupole mass spectrometry and gas chromatography. Non-volatiles were analysed by GC–MS.

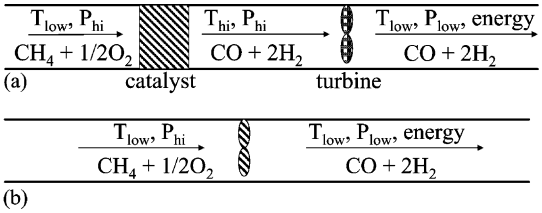

Fig. 1. (a) Schematic showing CPO of methane followed by a turbine and (b) schematic showing CPO of methane on turbine blade.

The concept of co-generation of syngas and energy was tested using catalyst and turbine configurations described in Fig. 1. The turbine used in the system depicted in Fig. 1(a) was modified from a Daihatsu Charade turbo charger. A digital video camera was used to capture any movement of the turbine. The purpose of videoing the turbine was purely qualitative and served only as evidence of the system's functionality. That is, no effort was made to relate the frequency of rotation of the turbine blade to energy derived. In the second system (Fig. 1(b)), disks of turbine blade material, both ceramic (high density α-alumina) and metallic (MCM 41 and IN 738) (dimensions 2 mm length and 4 mm diameter), were coated with Rh impregnated γ-alumina. It was reasoned that testing thermal and mechanical stability of the catalyst on materials commonly used in turbine blade applications would confirm or otherwise the viability of the catalyst on the blades of the turbine system. This mixture could be coated directly on the ceramic material, but the metallic materials were coated with nickel aluminide thermal barrier coating prior to coating with the Rh/γ-alumina catalyst. The method of application of thermal barrier protection is used in industry and produces layers of good uniformity, thus not affecting the balance of the turbine. A description of the methodology used to apply the thermal barrier coating has been described elsewhere [25]. The γ-alumina washcoat was prepared from 100 μm particles (Aldrich) by ring milling followed by stir milling with 2 mm ceramic beads for 10 min. This produced γ-alumina with an average particle size of 2.5 μm. After the ceramic and metallic turbine blades were dip coated with acidified γ-alumina slurry, rhodium was impregnated in the form of $Rh(NO_3)_3$. The impregnated material was then calcined in flowing air for 2 h at 600 °C. This gave a catalyst with a nominal Rh concentration of 5% (w/w).

The effects of pressure, catalyst mass, cooling and contact time on conversion and selectivity were investigated as described below. The stabilities of the catalyst itself and of the catalyst material on the metallic and ceramic disks were evaluated by both repeated use over time and by scanning electron microscopy (SEM).

Table 1
Conditions for calculation of power output for co-generation systems

Compressor isentropic efficiency: 0.85
Turbine isentropic efficiency: 0.85
Atmospheric pressure: 0.10 Mpa
Atmospheric temperature: 298 K
Specific heat of oxygen: 0.922 kJ/(kg K)
Specific heat of methane: 2.254 kJ/(kg K)
Specific heat of reactants: 1.588 kJ/(kg K)
Specific heat of products: 2.687 kJ/(kg K)
Ratio of specific heats of oxygen: 1.4
Ratio of specific heats of products: 1.4
Stagnation pressure ratio over reactor: 0.8
Heat release of reaction (kJ/kg): 1156.25 kJ/kg

Theoretical calculations of power output for co-generation systems based on the CPO reaction were made. The conditions used for these calculations appear in Table 1. Net power output is a function of the heat of reaction, the pressure and temperature change across the turbine and the efficiencies of the turbine, compressor (used to compress oxygen) and the CPO reaction. CPO reaction efficiency is a measure of conversion and selectivity. It is assumed that the calculated power outputs are applicable to both co-generation systems. The calculations are based on industrial scale facilities to best illustrate the usefulness of the co-generation concept.

Methane and oxygen conversions and selectivities to hydrogen and carbon monoxide were calculated as follows:

$$CH_4 \text{ conversion}(\%) = \left[1 - \left(\frac{CH_{4out}}{CH_{4in}}\right)\right] \times 100 \quad (5)$$

$$O_2 \text{ conversion}(\%) = \left[1 - \left(\frac{O_{2out}}{O_{2in}}\right)\right] \times 100 \quad (6)$$

$$\text{CO selectivity}(\%) = \left[\frac{CO_{out}}{2 \times (C_2H_2 + C_2H_4 + C_2H_6 + \cdots) + CO + CO_2}\right] \times 100 \quad (7)$$

$$H_2 \text{ selectivity}(\%) = \left[\frac{2H_{2out}}{2(H_2 + C_2H_2 + H_2CO + H_2O + \cdots) + 4C_2H_4}\right] \times 100 \quad (8)$$

3. Results

3.1. High pressure catalytic partial oxidation of methane

The effect of pressure on methane conversion and syngas selectivity for the uncooled system is shown in Fig. 2(a). Temperature at the rear of the catalyst bed increased with pressure by about 20 °C/100 kPa. Temperatures measured at the front of the catalyst also increased with pressure, but the rise was not as great. The increase in pressure did not result in a decrease in methane conversion or a loss of syngas selectivity as might have been expected due to effects of equilibrium. CPO of methane involves a 2:1 volume increase in moving from reactants to products (Eq. (4)). Normally, this would suggest a decrease in yield with an increase in pressure. This was not observed.

As pressures increased, significant quantities of coke and high molecular weight aromatic compounds were observed. However, the formation of these products did not alone account for the increase seen in methane conversion over the pressure range (67% at 200 kPa; 80% at 1250 kPa; Fig. 2(a)). The calculated mass balances suggested that less than 1% of the methane converted produced products other than CO or CO_2.

In an attempt to minimize formation of undesirable products the exit-gas stream was cooled immediately after the catalyst bed using a nitrogen cooled probe. Post-catalyst-bed temperatures decreased by up to 240 °C and coke formation and formation of other high molecular weight hydrocarbons was also reduced. Methane and oxygen conversion were reduced (Fig. 2(b)) and hydrogen selectivity was higher for the nitrogen-cooled reactor. This suggests that some of the methane conversion, particularly that seen at the higher pressures, is due to reactions producing products other than syngas.

GC–MS analysis of the liquid products of the high pressure CPO reaction revealed a collection of poly aromatic hydrocarbons (PAHs), the most plentiful of which were naphthalene, fluorene, biphenylene, anthracene and phenanthrene.

3.2. Co-generation of energy and syngas

Two catalyst and turbine arrangements were tested for use in the CPO of methane. These are depicted in Fig. 1. The first – catalyst followed by turbine – was tested at atmospheric pressure using a gas flow rate of 30 L/min. The presence of the turbine had no negative effect on the CPO of methane. Prior to reaction light-off there was no evidence of turbine rotation, however on light-off the turbine began to turn.

The second catalyst/turbine configuration was tested by using sections (disks) of turbine blade material as catalyst supports. These disks, both metallic and ceramic, were coated with Rh/alumina and tested in the same way as the foam monolith catalysts. Although the surface area and orientation

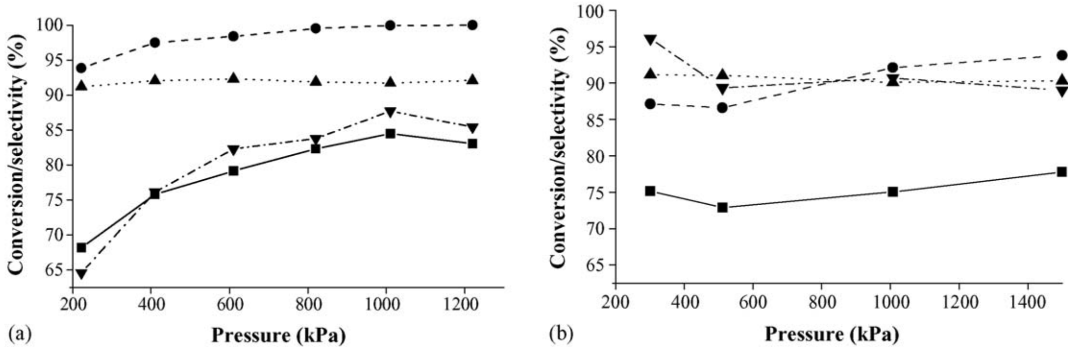

Fig. 2. Effect of pressure on methane conversion and syngas selectivity: (a) reactor not cooled; (b) reactor cooled. (■) CH_4 conversion; (●) O_2 conversion; (▲) CO selectivity; (▼) H_2 selectivity. CH_4:O_2 = 1.8; flow rate: 5–35 L/min (pressure dependant).

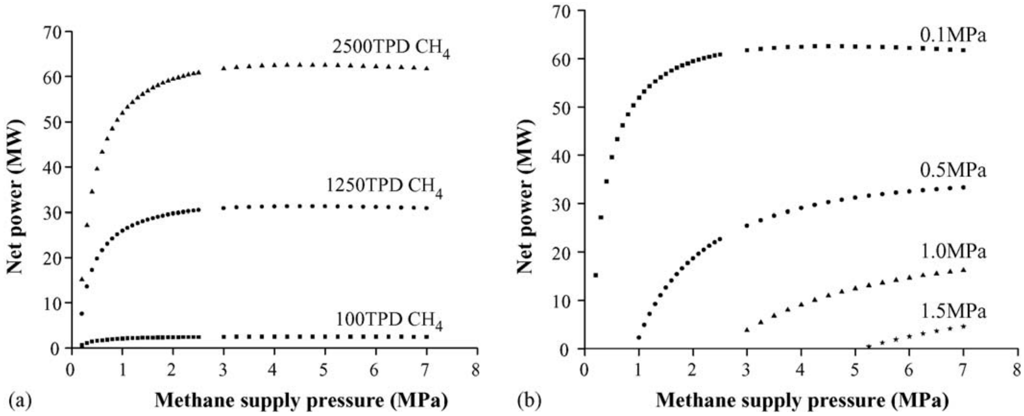

Fig. 3. Expected net power output for combined syngas and energy production: (a) effect of methane throughput; (b) effect of turbine exit pressure (based on 2500 TPD feed).

of these catalyst beads was far from ideal (gas bypass, lower catalytic surface area) the CPO reaction was autothermal once light-off had occurred. Conversions (CH_4-54%; O_2-86%) and selectivities (CO-89%; H_2-65%) were somewhat lower than for the monolithic catalysts due to the non-optimised nature of the system. The catalysts also required a higher temperature to achieve light-off. The coated turbine blade materials suffered no loss of performance after 50 h of testing but build-up of solid material on the beads may cause deactivation over time.

Expected power output from a co-generation system using CPO was calculated. The conditions are shown in Table 1. The effect of methane throughput on net power output over a range of feed pressures was then calculated (Fig. 3a) as was the effect of turbine exit pressure on net power output based on a methane feed rate of 2500TPD methane (Fig. 3(b)). The calculations take into consideration the necessary compression of oxygen but assume compression of methane or natural gas is not required since this can be delivered at pressure from the well or reservoir.

4. Discussion

4.1. High pressure catalytic partial oxidation of methane

Although CPO reactions are important at high pressures, comparison of results from cooled and uncooled experiments (Fig. 2) show that the systems are far from simple. Both methane and oxygen conversion decreased on cooling the exit gases, suggesting that some oxidation took place after the catalyst in the uncooled reactor. The CO selectivity remained the same in both cases and was independent of pressure. H_2 selectivity was only independent of pressure when the system was cooled (Fig. 2(b)). It appears that methane pyrolyses to a small extent in the uncooled system to produce carbon and hydrogen, some of which is oxidized after the catalyst bed, as well as the PAHs detected by GC–MS in the liquid phase analysis. The exit temperatures from the uncooled system (ca. 1200 K at the highest pressures tested) are such that some pyrolysis can be expected [26], remembering that the gas phase analysis does not take into account any deposition of coke.

Some support for the suggestion of pyrolysis in the uncooled system comes from the identification of small amounts of high molecular weight hydrocarbons in the products. Previous investigations have shown that increasing pressure led to increasing contributions from gas phase reactions [7,27], producing such compounds as naphthalene and fluorene.

It should be noted that oxidation reactions after the bed are more significant than pyrolysis reactions. The increased exit temperatures detected at elevated pressures are not the result of pyrolysis reactions, given that pyrolysis reactions are endothermic and oxidation reactions are exothermic. Also, the fact that hydrogen selectivity is lower for all pressures in the uncooled system suggests that some hydrogen is oxidized to water in the gas phase. This is supported by Burke [28] who tested a range of catalysts under conditions of methane partial oxidation and found that no hydrogen was formed while oxygen existed in the gas stream for all catalysts except those based on rhodium.

The improvement in methane conversion with pressure may result from improved heat transfer from the surface of the catalyst (where the reaction takes place) to both the catalyst support and the gas stream itself. This, of course, assumes that the temperature increase is the result of the exothermic reactions (CPO or oxidation) taking place on the surface of the catalyst, with the heat transfer improvement being a function of gas density and flow rate.

It was interesting to note that selectivity to CO did not change over the range of pressures for either the uncooled or cooled systems (Fig. 2a and b). Selectivity to CO would have been expected to decrease as methane conversion increased if the increase was due entirely to gas phase oxidation of methane occurring downstream of the catalyst or the formation of higher molecular weight products. The increase in H_2 selectivity with pressure in the uncooled system may be partly due to the decrease in oxygen species, making the formation of hydroxide ions and water less likely with the decrease in free oxygen concentration. The higher hydrogen selectivity of the cooled reactor suggests that even at higher pressures in the uncooled system there is still some oxidation of hydrogen either on the surface of the catalyst or in the gas phase.

It is suspected that for the cooled reactor experiments, a portion of the reactant gases bypassed the catalyst bed since there was evidence of a small amount of coking on the outside of the quartz reactor tube used in these experiments.

4.2. Co-generation of energy and syngas

Both the catalyst followed by a turbine (Fig. 1a) and the catalyst on turbine blade materials (Fig. 1(b)) have been shown to be effective in producing syngas. The turbine blade material system showed lower conversions and hydrogen selectivity but this is almost certainly due to the lack of optimisation and to the susceptibility of the coated materials as used in these experiments to gas bypass. Neither are the heat transfer characteristics of the coated beads likely to be as well optimized as those for the blown foam monolith catalyst. As a result, any contribution from endothermic reforming reactions (Eq. (1) and (3)) would be limited.

The lower conversions seen over the catalysts supported on the turbine blade materials give rise to a higher concentration of oxygen, either on the catalyst or in the gas phase. This would have the tendency to oxidise some of the produced hydrogen to water, causing a lowering of the hydrogen selectivity, as observed.

The calculated net power outputs for the co-generation of syngas and energy (Fig. 3) show the benefits of capturing the energy of the product gas stream. The net power from the co-generation process is dependent on the methane throughput, the pressure/temperature drop across the turbine, the efficiency of the plant equipment (turbine, compressor) and the efficiency of the partial oxidation reaction. For a plant operating at a methane feed rate of 2500TPD at delivery pressures in excess of 3 MPa and a turbine exit pressure of 0.1 MPa (atmospheric pressure) more than 60 MW of power can be produced. The resulting cost benefits will allow more economically favourable processing of natural gas, with the energy generated being used reduce plant operating costs or fed into power grids.

5. Conclusions

CPO of methane at pressures up to 1.5 MPa has been demonstrated. As pressure increased gas phase reactions became more prevalent and cooling of the reactor was necessary.

The possibility of using a turbine to co-generate energy and syngas was investigated. Both of the catalyst/turbine configurations tested showed that co-generation of energy and syngas could be achieved, with no major loss in conversion efficiency. The potential for reduction in operating cost through use of co-generation technologies seems possible based on the results presented in this study and optimization and scale up studies will be the next steps towards commercialisation.

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