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Catalytic partial "oxidation of methane to syngas" at elevated pressures

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In this work we demonstrate catalytic partial oxidation of methane into syngas at pressures up to 0.8 MPa, power densities up to 15 MW/L and selectivity greater than 85%. The product composition profiles indicate high initial selectivity to CO and low initial selectivity to H_2, suggesting direct partial Oxidation of methane primarily into CO and water, while most hydrogen is produced in the consecutive steam reforming of methane.

KEY WORDS: catalytic Partial Oxidation; natural Gas; syngas; microlith.

1. Introduction

Converting natural gas into a mixture of H_2 and CO, known as synthesis gas or syngas, is an important intermediate step in many existing and emerging energy conversion technologies (figure 1). In recent years Gas-to-Liquids (GTL) process is becoming a mature technology attracting multi-billion dollar investments. For example, in October of 2003 Shell and Qatar Petroleum signed an agreement for construction of the largest to-date GTL plant with a production capacity of 140,000 barrels per day, in which Shell will invest some 5 billion [1]. Construction of several smaller GTL plants having 70,000–75,000 barrel per day production capacity has also been announced [2]. Preparation of synthesis gas is the most capital-intensive part of this size GTL plant, accounting for 50–75% of the capital cost [3]. In addition, reforming natural gas or liquid hydrocarbons into syngas is the initial step in all fuel reforming systems being developed to power the 'hydrogen economy' of the future [4]. In hydrogen Production systems syngas generation is generally followed by a water gas shift (WGS) and a CO clean up reactors or a hydrogen separation device to yield fuel cell quality hydrogen [5,6]. In combustion systems operating on natural gas, such as power turbines and utility burners, preliminary conversion of methane into syngas can help in stabilizing lower temperature flames, reducing NO_x emissions [7].

Currently most syngas is produced by steam reforming (SR). In this endothermic reaction, generally represented by equation (1), methane is contacted with steam over a heated catalyst at high pressures and temperatures to produce a high hydrogen content syngas. Although, SR is a mature technology, it requires large heat exchange reactors, demanding large initial investment [8]. Furthermore, stringent heat balance requirements in the SR process make scaling these reactors to smaller sizes extremely difficult.

Catalytic partial oxidation (CPOX) of methane is a relatively inexpensive alternative to syngas generation. In the CPOX process, generally represented by equation (2), methane is reacted with oxygen over a catalyst bed to yield syngas with H_2 to CO ratio near 2. Examples of recent publications in this area are those of D.A. Hickman and L.D. Schmidt who demonstrated that near complete conversion of methane to mostly hydrogen and carbon monoxide could be achieved at reaction times as short as 1 ms, promising dramatic reduction in a reactor size and complexity, as compared to existing syngas production technologies [9,10].

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H = +206\,\text{kJ/mole} \tag{1}$$

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \quad \Delta H = -38\,\text{kJ/mole} \tag{2}$$

To avoid the energy losses associated with compression of hot, high hydrogen content, gases the CPOX reactor should be operated at pressures in the range of 0.5 to 4 Mpa compatible with downstream processes (figure 1). Surprisingly, despite much interest over the last decade and extensive development of this technology by the

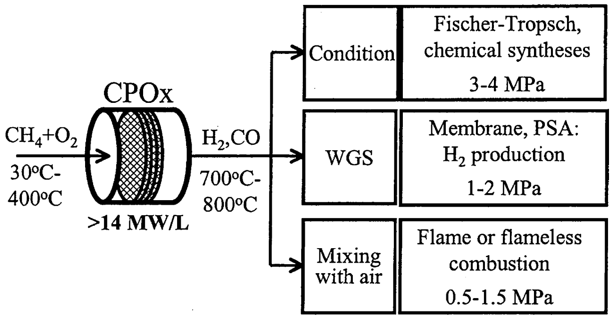

Figure 1. Routes for natural gas utilization opened or facilitated by conversion of natural gas into syngas in a high power density CPOX rector.

major petrochemical companies, such as Shell, ExxonMobil, ConocoPhillips, only very limited work on high-pressure CPOX of methane has been reported in scientific literature [11,12,13]. Furthermore, in these works testing at very small scale [11], augmentation with steam and CO_2 [12] or exotic catalyst structures, such as honeycombs made of fused Rh foils [13], were used, making the results only indirectly applicable to practical applications of the CPOX process.

In this work, we demonstrate robust, steady-state, operation of a methane CPOX reactor at pressures up to 0.8 MPa with near equilibrium conversion of methane to above 90% and process selectivity about 90%. A series of discrete, metallic screen substrates (trademarked by Precision Combustion, Inc. as Microlith®) [14] coated with a high surface area ceramic washcoat and impregnated with Rh were used to construct a catalytic reactor. A characteristic feature of these substrates is the short length of each element, which prevents development of a boundary layer over the catalytic surface greatly enhancing heat and mass transfer coefficients for the system [15,16]. These properties of the Microlith based catalytic systems make them perfectly suited for short contact time oxidation reactions. In recent years such catalytic systems have been applied to catalytic combustion [17], automotive exhaust aftertreatment [18] and fuel reforming [19]. Microlith based catalysts are relatively inexpensive, manufactured *via* an automated continuous production process and allow a high degree of flexibility in reactor design, making them readily adaptable for applications on an industrial scale.

2. Experimental

The reactor used in this work was built by stacking Microlith screens with catalyst loading of ~5.5 wt%. Gas sample probes made of 1/16" OD high temperature alloy tubing and 0.02" K-type thermocouples were inserted between the screens at several locations along the length of the reactor. Gas samples extracted by the sample probes were passed through a chiller to remove water vapor and analyzed by an on-line gas chromatograph. Concentrations of H_2, N_2, O_2, CH_4, CO, CO_2, C_2H_4 and C_2H_6 species were measured. Nitrogen was assumed to be internal in the reaction and was used as an internal standard. Water concentration in the sample was calculated using hydrogen balance. Overall mass balance of all species was within 10%.

The total length of the reactor was ~6 cm (including the length of the partitions, required to install the instrumentation). The length of the catalyst itself was 2 cm, and this length is used below in the reactor profile Plots (figure 3) and in the estimates of the reactor volume and power density. The gas flow diameter was 20 mm, such that the volume of the catalyst bed was 6.3 cm^3 amounting to the total amount of precious metal loading of ~0.25 g.

Prior to the start up the catalyst was pre-heated to 250 °C by passing the flow of hot air through the reactor. Ignition of the reaction occurred as soon as the methane/air mixture was introduced and the reactor achieved steady state operation in less than 15 s (figure 2).

3. Results and discussion

In all experiments reported here the flow rates of methane and air were increased proportionally to the operating Pressure, to maintain constant linear flow velocity and residence time. In the experiment at $P = 0.8$ Mpa, methane was fed into the reactor at a rate of 160 standard liters per minute (SLPM) (~0.11 mole. CH_4 per second), which is equivalent to 88 kW_t of thermal power input. Normalized to the reactor volume this equals ~14 MW_t/L power density in the tested CPOX reactor.

At this power density a 1 L CPOX reactor applied to the GTL process can produce enough syngas to make ~100 barrels Per day of synthetic fuel (assuming 50% overall conversion efficiency of CH_4 into $(CH_2)_n$ and 0.8 g/cm^3 density of the produced Synthetic oil). Alternatively, for a fuel cell power system having ~35% overall efficiency this amount of syngas may be converted into hydrogen to fuel ~5 MW_e PEM fuel cell. For an estimated ~50 kW_e fuel cell powered mid-sized car this is equivalent to the amount of hydrogen consumed by a fleet of 100 cars. In gas turbine applications a 1 L CPOX reactor can produce enough hydrogen (without additional WGS reactor) to provide 10% augmentation to natural gas fuel for a 100 MW gas turbine (assuming 35% turbine efficiency) for flame stability and reduced NO_x emissions.

Gas composition and temperature profiles measured along the length of the catalyst bed (figure 3)

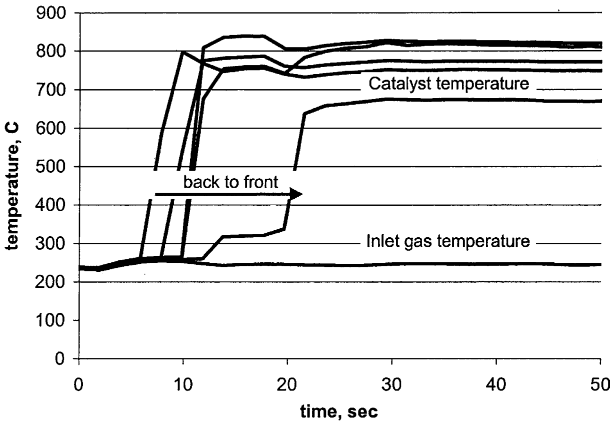

Figure 2. Light off of the Microlith based COPX of methane reactor. $P = 0.6$ Mpa.

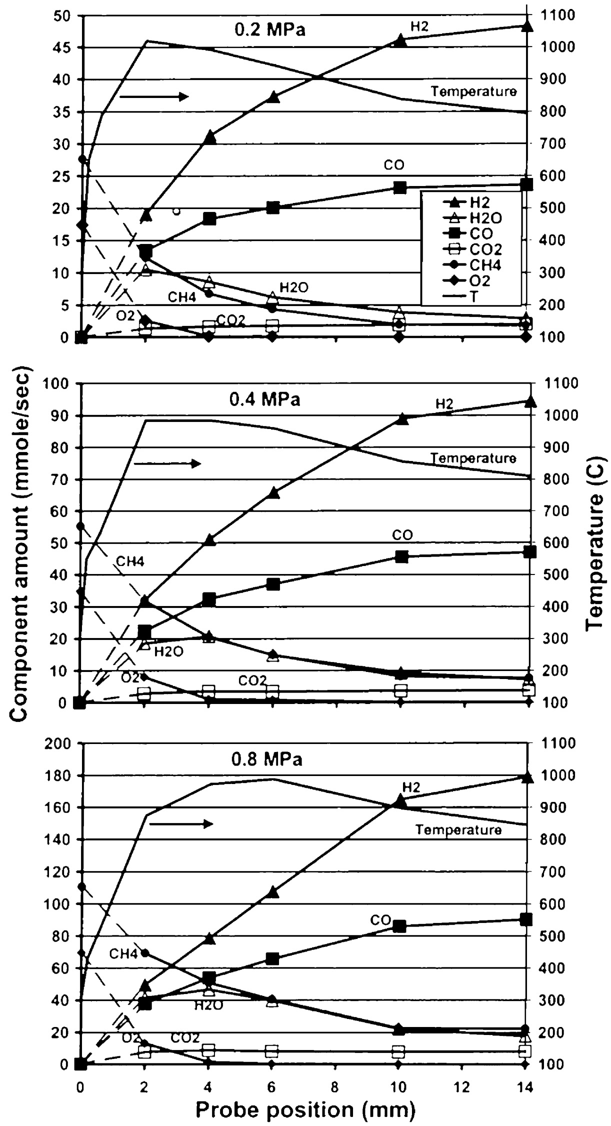

Figure 3. Species concentration and temperature profiles along the length of the catalyst bed at 0.2, 0.4 and 0.8 Mpa and O:C = 1.2. Concentration of N_2 in the sample was used to convert species concentrations into the flow rate units (mmole/sec) based on the known rate of air supply to the reactor inlet and assuming that nitrogen remains inert under the reaction conditions. Values at $x = 0$ position are made of the inlet methane and air flow as measured by the mass flow meters.

demonstrate that in spite of very short contact time, the CPOX process does not occur in a single reaction, but consists of sequential oxidation and reforming steps. While oxygen to methane ratio in the feed stream is O_2:CH_4 = 0.6, oxygen is consume at a rate up to 1.34 times higher than methane at the front of the reactor. This stoichiometry suggests that simultaneous complete and partial oxidation reactions occur at the onset of the CPOX process. (For the partial oxidation reaction (2) the O_2:CH_4 consumption ratio equals 0.5, while for complete oxidation, equation (3), it equals 2).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H = -802\,\text{kJ/mole} \quad (3)$$

Under all tested operating pressures essentially all of the oxygen was consumed by ~4 mm into the catalyst bed (corresponding residence time ~0.5 msec), at which point, methane conversion was between 55 and 75%. It was also found that at constant inlet flow velocity the reaction rate linearly increases with pressure between 0.2 and 0.8 MPa. For multi-step processes, such as partial oxidation, first order dependence of the kinetic rate on pressure is unlikely. Scaling of the reaction rate with pressure, therefore, suggests that the CPOX process rate is limited by the transport of oxygen–the limiting reactant–across the boundary layer to the surface of the catalyst.

Surprisingly, much more water than CO_2 was formed at the front of the reactor. A large peak in the H_2O profile is consistent with the indirect pathway for the CPOX process, in which complete oxidation of methane on the front of the reactor is followed by reforming reactions [20]. On the other hand, low and near constant concentration of CO_2 along the reactor, is consistent with direct partial oxidation pathway in which partial oxidation products directly form on the front of the reactor [10,21,22]. Linear extrapolation of product selectivity vs. conversion plots to zero methane conversion (figure 4) suggests initial partial oxidation reaction as represented by equation (4). Therefore, CO is directly produced with high selectivity on the oxidation step at the onset of the CPOX process. However, selectivity for direct production of H_2 is low, such that high H_2 selectivity of the CPOX process is mainly due to the secondary steam reforming reaction.

$$CH_4 + 1.34O_2 \rightarrow 0.82CO + 0.18CO_2 + 0.5H_2 + 1.5H_2O$$
$$\Delta H = -449\,\text{kJ/mole} \quad (4)$$

A detailed model for the CPOX process based on literature data for the kinetic parameters of multiple surface elementary reactions, proposed by L.D. Schmidt *et al.* [23,24,25] did not predict the difference in the initial selectivity for CO and H_2 observed in our experiments. This discrepancy can be attributed to the two assumptions made in the Schmidt model: (1) of reversible adsorption of O_2 onto the surface of the catalyst and (2) of high activation energy for the surface reaction between the adsorbed O* and H* species on the Rh catalyst, effectively eliminating the surface hydrogen oxidation pathway.

At low coverages of all surface species characteristic of a high temperatures CPOX process and with the oxygen adsorption rate being limited by the rate of mass transfer, adsorption of both methane and oxygen on the surface of the catalyst is most likely irreversible. Therefore, all molecules dissociated onto the surface are consumed in the oxidation reaction, Equation (4) indicates that the ratio between partial and complete oxidation products is determined by the relative rates of methane and oxygen dissociation onto the surface. The

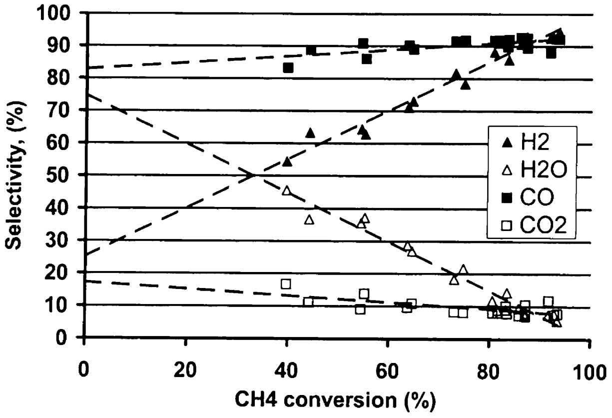

Figure 4. Selectivity to complete and partial oxidation products as a function of methane conversion. Calculated based on the species concentrations shown in Figure 3 for all tested conditions. $S(H_2) = H_2/(H_2+H_2O), S(H_2O) = H_2O/(H_2+H_2O), S(CO) = CO/(CO+CO_2), S(CO_2) = CO_2/(CO+CO_2)$.

mass transfer limited rate of oxygen adsorption has only weak dependence on temperature, while the rate of methane adsorption increases exponentially with temperature. Therefore, selectivity towards partial oxidation products on the oxidation step of the CPOX process increases exponentially with the increase in the catalyst temperature. This was also observed in our previous work on methane oxidation under fuel rich conditions over the catalysts with externally controlled surface temperature [26].

For the intermediate surface species–CO* and H*–two competing pathways exist-to desorb as molecular CO and H_2 forming partial oxidation products; or to be further oxidized to CO_2 and H_2O. The difference in the rate of CO* and H* oxidation observed in the experiment can be explained by the difference in the desorption mechanism for these species. At low surface coverages first order CO* desorption is much faster than the second order H* desorption. This leads to higher steady state surface coverage of H* species, making them more susceptible for reaction with O* to produce OH* and water.

Before oxygen is consumed from the gas phase on the front of the reactor homogeneous oxidation reactions may take place. In these non-selective free radical reactions methane, hydrogen and carbon monoxide can be oxidized to CO_2 and H_2O decreasing selectivity of the CPOX process and increasing the peak temperature. Good fit by a single line of all data points collected in the experiments with a 4-fold difference in the operating pressure (figure 4) demonstrates that in the tested pressure interval the gas phase reactions were insignificant. Excellent transport properties of the Microlith substrate ensure high rate of the mass transfer limited surface reactions and free radical quenching, such that high selectivity to partial oxidation products can be achieved even at high operating pressure. In fact, it was found that peak temperature decreased slightly when the process pressure was increased from 0.2 to 0.4 and to 0.8 MPa (figure 5).

Under all tested conditions methane conversion increased linearly with increasing O:C ratio (figure 5). The decrease in the peak temperature with pressure allowed compensation for decreasing methane conversion by operating the reactor at higher O:C ratio, such that conversion above 90% could be reached even at $P = 0.8$ MPa. This also suggests the likelihood of successful operation of the CPOX process at even

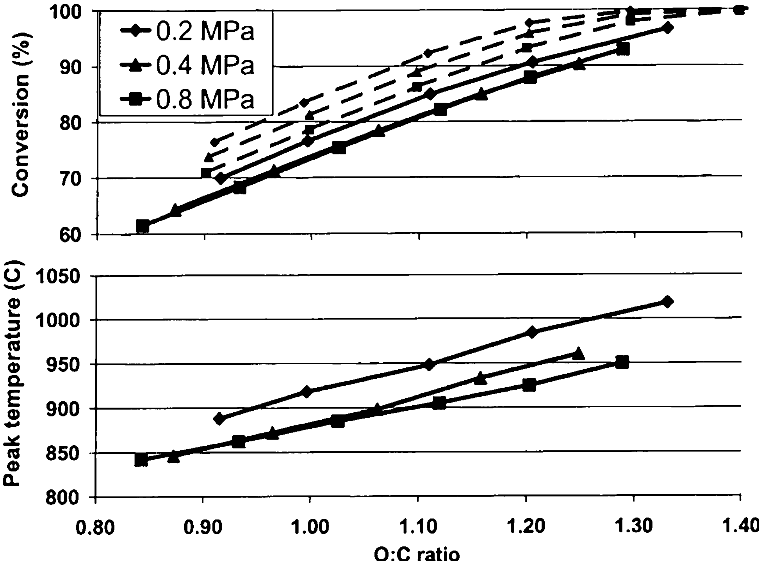

Figure 5. Dependence of methane conversion and peak TC reading on the amount of air added to the reactor. Methane flow – 40 SLPM at 0.2 MPa, 80 SLPM at 0.4 Mpa and 160 SLPM at 0.8 MPa – constant throughout each test. Air flow is increased stepwise to increase O:C ratio. Dotted lines show the thermodynamic prediction for methane conversion in adiabatic process under these inlet conditions.

higher pressures. (Note that in our experiments the pressure was limited to 0.8 MPa by the design of the test rig, but not by the observed performance of the catalyst). Although figure 5 shows that methane conversion did not reach the equilibrium value over the length of the reactor, we believe that minimizing heat losses would allow bringing the conversion closer to the equilibrium values. After oxygen consumption at the front of the reactor, methane conversion proceeds through a slower SR reaction. Therefore, increasing the length of the catalyst bed and adding steam to the reactor inlet may also help bring the final conversion closer to the equilibrium point.

In addition to smaller size, control over a CPOX reactor is simpler than over a SR reactor. In the SR process assuring balance between heat generation on the combustion side and heat consumption on the reforming side along the entire length of the reactor requires intensive control over the flow rates and flow distribution. In the CPOX process, performance is essentially determined by the methane to oxygen ratio in the inlet mixture, such that only this parameter should be controlled. Furthermore, at the extremely high power density for the CPOX process (in excess of 14 MW/L) small, simple and inexpensive bench scale reactors can be directly used to produce syngas for industrial scale applications. This will promote utilization of natural gas in a broad range of efficient and environmentally friendly energy generation processes.

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