Oxidative Pyrolysis of Methane to Higher Hydrocarbons: Effects of Water in Feed

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Direct conversion of methane into higher hydrocarbons (ethane, ethylene, and to small extent C_{3-4} hydrocarbons) by its partial oxidation with oxygen in the absence of catalyst has been investigated. It was carried out in a quartz flow reactor at atmospheric pressure under nonflame conditions at different temperatures (1,123–1,273 K), CH_4/O_2 ratios (1.7–9.0), space velocities (500–5,000 h^{-1}), and water concentrations (0.0–80 mol %) in the feed. No coke deposition was observed in the reactor, but there was a formation of small amounts of tarry matter in the reaction at $\geq 1,223$ K, particularly for the lower CH_4/O_2 ratios (≤ 3.5). The product distribution in the process was strongly influenced by the dilution of feed with N_2 or water. Addition of water in the feed was highly beneficial to obtaining higher yield and/or to selectivity for the higher hydrocarbons and suppressing almost completely the formation of tarry matter.

Introduction

Direct conversion of methane to higher hydrocarbons, especially to ethylene, is of great practical importance. Methane is available in large quantities from natural gas deposits, petroleum processing off-gases, and biogas. World reserves of natural gas are constantly being upgraded, and more natural gas has been discovered than oil. Because of the predicted oil shortage in the future, methane is considered an important raw material for the production of higher hydrocarbons and petrochemicals. However, since methane is most inert among the hydrocarbons, its direct conversion to higher hydrocarbons is very difficult.

Thermal cracking of methane (which is a highly endothermic process) occurs at very high temperatures (>1,473 K) and yields a large amount of coke, resulting in very low yields for ethylene and acetylene (Back and Back, 1983). In the Benson process (Benson, 1980), methane is converted to acetylene, ethylene, ethane, and higher hydrocarbons by igniting Cl_2–CH_4 mixture above 1,273 K. In this process, methane is converted at lower temperatures, but the formation of coke or carbonaceous matter is still a problem. Recently, Senkan (1987a,b) has described a chlorine-catalyzed oxidative pyrolysis (CCOP) process for producing acetylene and ethylene from methane. This process involves chlorination of methane in the presence of oxygen under nonflame conditions, and there is little or no formation of carbonaceous deposits. However, both the Benson process and CCOP process require chlorine in stoichiometric quantities and involve formation of HCl, which is highly corrosive as a coproduct. This renders these processes unattractive for practical applications.

Recently, Asami et al. (1987) have observed oxidative coupling of methane in the absence of catalyst to ethane and ethylene under pressure (up to 1.6 MPa) in the temperature range of 923–1,073 K, but no reaction was observed without catalyst under atmospheric pressure. More recently, Yates and Zlotin (1988), Lane and Wolf (1988), Choudhary et al. (1988), and Onsagar et al. (1989) have observed the formation of ethane and ethylene to an appreciable extent in homogeneous noncatalytic oxidation of methane under atmospheric pressure at 873–1,123 K. It is therefore very interesting to know the results on the noncatalytic oxidative methane pyrolysis (OMP) process when operated at high methane conversions from a commercial application point of view and also to know the influence of various process variables and the addition of water in the feed on the methane conversion and product selectivities in the process.

This article reports on the beneficial effects of an addition of water in the feed (consisting of a mixture of pure methane and O_2) on the yield and/or selectivity for higher hydrocarbons (C_{2-4} hydrocarbons), on oxidative pyrolysis of methane carried out under atmospheric pressure at 1,123–1,273 K covering a

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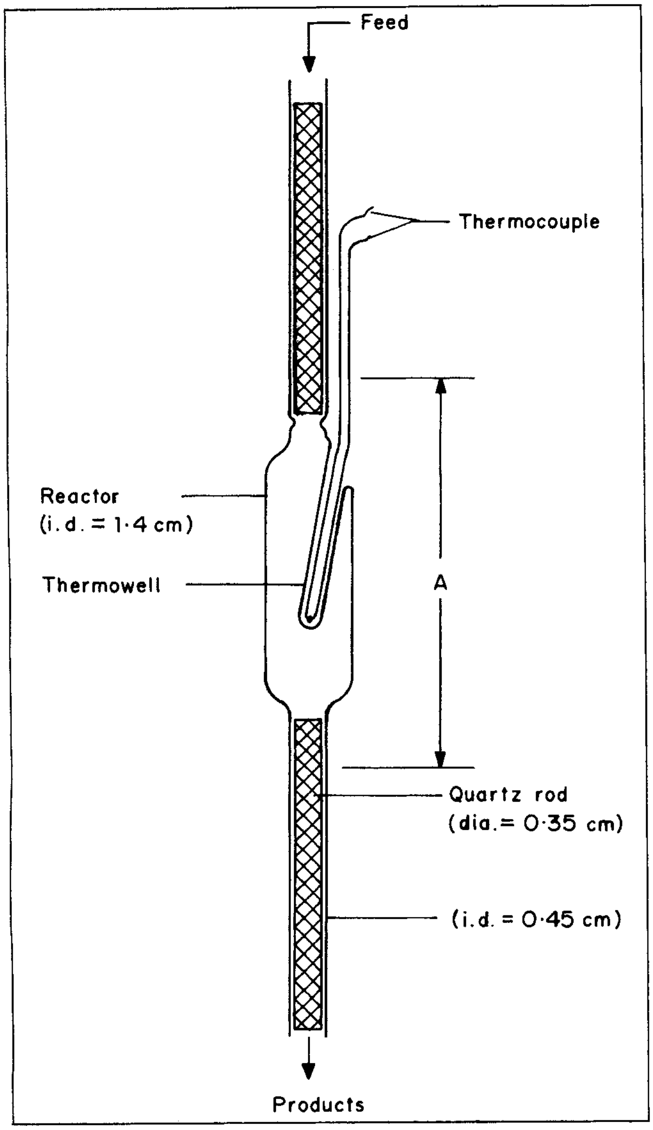

Figure 1. Quartz flow reactor used for oxidative pyrolysis of methane.

A = constant temperature zone

wide range of process variables (CH_4/O_2 ratio in the feed, space velocity, and water concentration in the feed).

Experimental Studies

Oxidative methane pyrolysis (OMP) was carried out at atmospheric pressure (0.95 atm) in an empty quartz tubular reactor (1.4 cm ID, 7.4 cm^3 capacity) located in the constant temperature zone of a tubular furnace. The reactor is shown schematically in Figure 1. The dead volume in the reactor inlet and outlet tubes (0.45 cm ID, 0.61 cm OD) was minimized by inserting quartz rods (0.35 cm dia.). The reaction temperature was measured using Chromel-Alumel thermocouple located in the center of the reactor. To add water in the feed (which is a mixture of pure methane and oxygen), a syringe pump was used. The reactor effluent gases (methane, ethane, ethylene, CO, CO_2, O_2, and $C_{3\text{-}4}$ hydrocarbons) after removing water by condensation were analyzed by an on-line gas chromatograph using porapak-Q and spherocarb columns. Formation of formaldehyde and C_{5+} hydrocarbons in the reaction under the process conditions used in the present investigation was negligibly small.

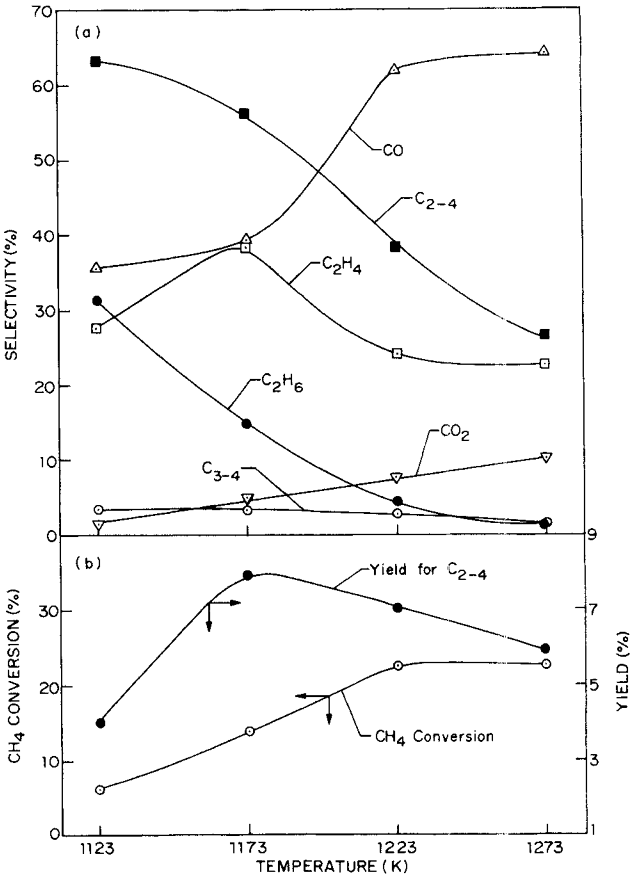

Figure 2. Influence of temperature on methane conversion and product selectivity in OMP process in the absence of water in the feed.

Feed = 78% CH_4 and 22% O_2; GHSV = 1,500 h^{-1}

The OMP reaction was carried out as follows. The reactor temperature was attained while passing pure nitrogen (50 $cm^3 \cdot min^{-1}$) through the reactor. When the temperature was attained, the N_2 flow was replaced by methane flow along with water vapors, if added, in the feed. The O_2 concentration in the feed is increased gradually in a period of about 15 minutes to a desired value. The products were analyzed after a steady state was reached. There was a near isothermal conditions during the experiments. The reactor temperature could be controlled within 3-4 K, and there were no fluctuations in the reactor temperature during the experiments. The carbon balance between the feed and product gases was above 94%. The conversion/selectivity data were calculated from the analysis of all the carbon-containing products and unconverted methane in the product stream.

Methane (99.995%) and oxygen (99.5%) used were acquired from L'Air Liquide (France) and Indian Oxygen Ltd. (Bombay), respectively. The gases were used directly from the cylinders, and their flow rates were controlled by using rotameters and fine needle valves. A thorough mixing of methane and oxygen in the feed was ensured by passing their mixture through a long stainless steel tube (0.5 cm ID, 10 m long) before introducing the gas mixture in the reactor.

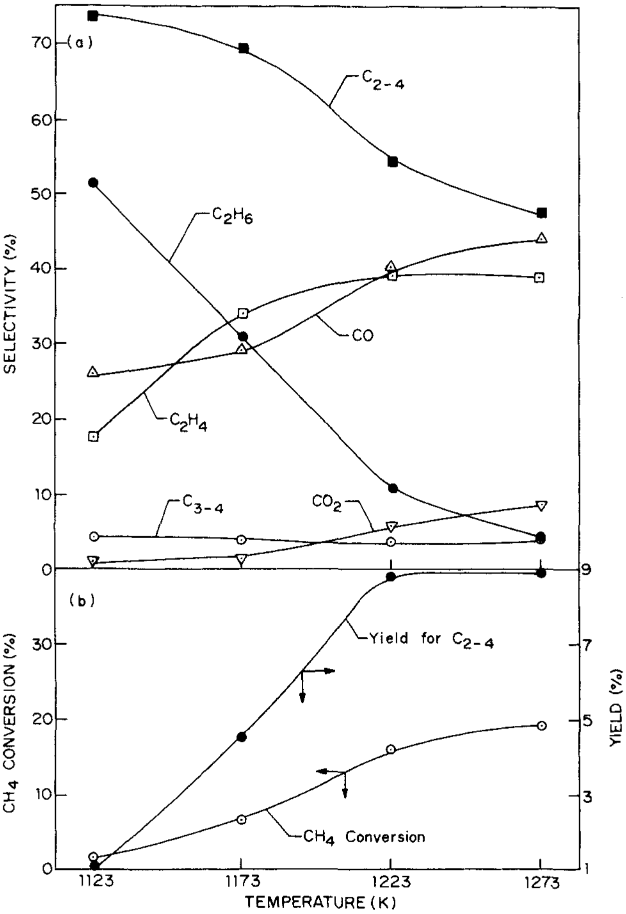

Figure 3. Influence of temperature on methane conversion and product selectivity in OMP process in the presence of water (50 mol %) in the feed.

Feed = 39.0% CH_4, 11.0% O_2, and 50% H_2O; GHSV = 1,500 h^{-1}

Results and Discussion

The methane conversion and product selectivities in the oxidative methane pyrolysis process were done at different temperatures (1,123-1,273 K), CH_4/O_2 ratios (1.7-9.0), gas hourly space velocities (GHSV) (500-5,000 h^{-1}), and concentrations of water in feed (0.0-80.0 mol %). In addition, the results obtained in the absence and presence of water in the feed are compared.

Figures 2 to 7 show the influence of temperature, CH_4/O_2 ratio in feed and gas hourly space velocity (measured at STP) on the methane conversion, yield of higher hydrocarbons (C_{2-4} yield), and product selectivity in the OMP process in the absence and presence of water (50.0 mol %) in the feed. Figure 8 shows an effect of the concentration of water in the feed on the conversion and selectivity in the OMP process. The effects of various process variables on the ethylene/ethane and CO/CO_2 ratios in the products are shown in Figure 9.

Influence of temperature

Figure 2 shows that when the reaction temperature is increased from 1,123 to 1,273 K in the absence of water in the feed, the conversion of methane in the OMP process is increased up to 1,223 K and then remained almost constant; the yield for C_{2-4} hydrocarbons and selectivity for ethylene are passed through a maximum around 1,173 K and then decreased; and the selectivities for ethane and C_{3-4} hydrocarbons are decreased continuously, whereas the selectivities for CO and CO_2 are increased.

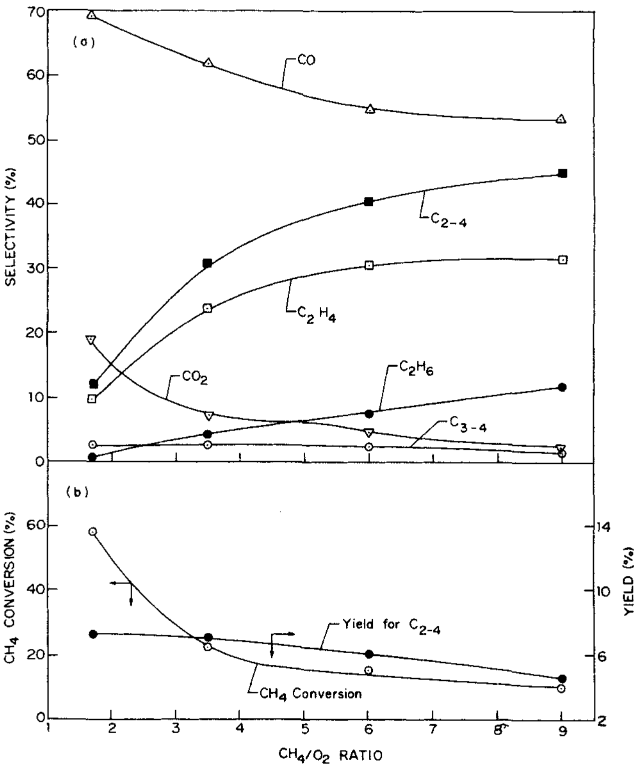

Figure 4. Influence of CH_4/O_2 ratio in feed on methane conversion and product selectivity in OMP process in the absence of water in the feed.

Feed = mixture of CH_4 and O_2; GHSV = 1,500 h^{-1}; temperature = 1,223 K

Because of the addition of water (50 mol %) in the feed (Figure 3), for the same GHSV and CH_4/O_2 ratio the dependence of the yield for C_{2-4} hydrocarbons and selectivity for ethylene on the temperature are changed; they are increased with the temperature up to 1,223 K and then remained almost constant. The trends for the selectivities for the other products are not affected. The methane conversion, however, is decreased, and the selectivities for ethylene (except at $\leq 1,173$ K), ethane and C_{3-4} hydrocarbons and the yield for C_{2-4} hydrocarbons at $\geq 1,223$ K are increased appreciably due to the addition of water in the feed.

The ethylene/ethane and CO/CO_2 ratios in the products are increased and decreased, respectively, with the temperature increase (Figure 9).

At any temperature (1,123-1,273 K), there was no deposition of coke (or carbonaceous matter) in the reactor. However, deposition of small amounts of blackish tarry matter on inner walls of the reactor outlet and water condenser was observed at higher temperatures ($\geq 1,223$ K) in the absence of water in the feed. The conversions of methane to tarry material at 1,223 and 1,273 K were 0.6% and 1.1%, respectively. But when water was added in the feed, the formation of tarry matter even at 1,273 K was not detected.

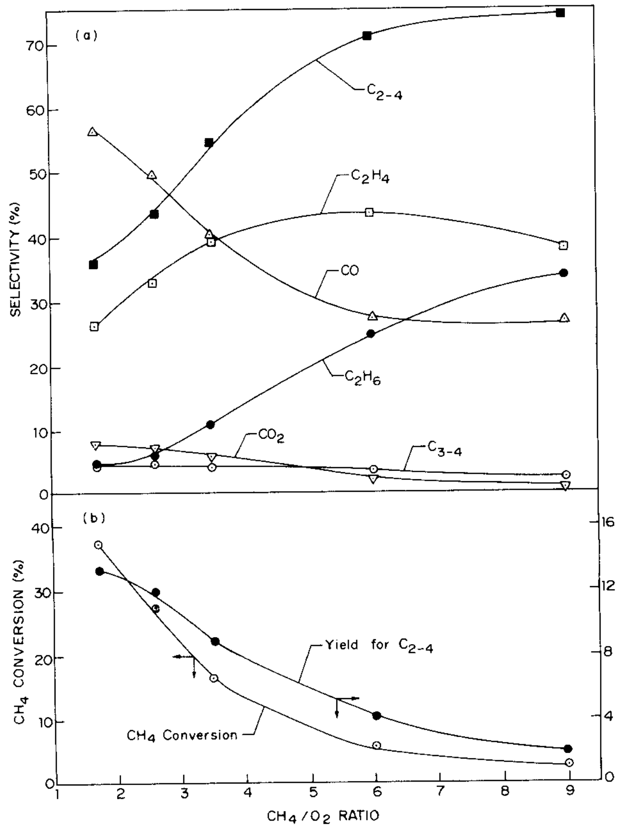

Figure 5. Influence of CH_4/O_2 ratio in feed on methane conversion and product selectivity in OMP process in the presence of water (50 mol %) in the feed.

Feed = mixture of CH_4, O_2 and H_2O; GHSV = 1,500 h^{-1}; temperature = 1,223 K

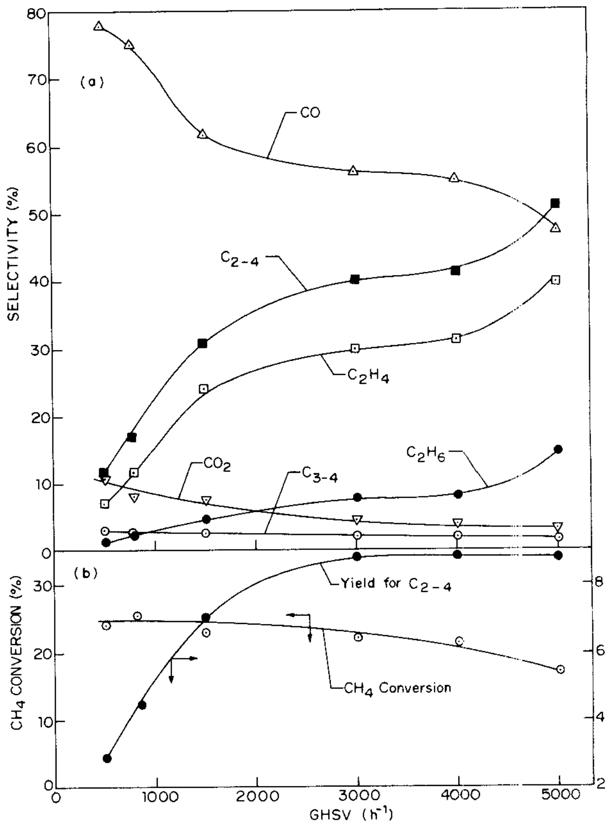

Figure 6. Influence of GHSV on methane conversion and product selectivity in OMP process in the absence of water in the feed

Feed = 78% CH_4 and 22% O_2; temperature = 1,223 K

Influence of CH_4/O_2 ratio

Figure 4 shows that, in the absence of water in the feed, the conversion of methane and yield for $C_{2\text{-}4}$ hydrocarbons in the OMP process are decreased, whereas the selectivities for ethylene and ethane are increased and those for CO, CO_2 and $C_{3\text{-}4}$ hydrocarbons are decreased with the increase in the CH_4/O_2 ratio in the feed.

Due to the addition of water (50 mol %) in the feed, for all the CH_4/O_2 ratios, the selectivities for ethylene, ethane and $C_{3\text{-}4}$ hydrocarbons are increased markedly, whereas those for CO and CO_2 are decreased (Figure 5). The presence of water in the feed caused a decrease in the conversion of methane but caused an increase in the yield for $C_{2\text{-}4}$ hydrocarbons at the CH_4/O_2 ratio of 3.5.

The ethylene/ethane and CO/CO_2 ratios in the products are decreased and increased, respectively, with the increase in the CH_4/O_2 ratio in the feed (Figure 9).

For all the CH_4/O_2 ratios (1.7–9.0), no deposition of coke was observed in the reactor at 1,223 K. However, in the absence of water in the feed, for the lower CH_4/O_2 ratios (≤ 3.5) small amount of tarry material was found to be deposited on the inner walls of the reactor outlet and the water condenser. The conversions of methane to tarry material at the CH_4/O_2 ratio of 1.7 and 3.5 were 1.9% and 0.6%, respectively. On the other hand, because of the addition of water in the feed, the formation of tarry matter even at the CH_4/O_2 ratio of 1.7 was not observed.

Influence of GHSV

Figure 6 shows that, in the absence of water in the feed, when the gas hourly space velocity of feed is increased from 500 to 5,000 h^{-1} (in the absence of water in the feed) the methane conversion is decreased to a small extent but there is a large increase in both the selectivity and yield for $C_{2\text{-}4}$ hydrocarbons. The selectivities for ethylene and ethane are increased and those for CO and CO_2 are decreased significantly. However, the selectivity for $C_{3\text{-}4}$ hydrocarbons is decreased slightly.

For the case when the water was added in the feed (Figure 7), with the increase in the GHSV the methane conversion is decreased to a larger extent, the yield for $C_{2\text{-}4}$ hydrocarbons and selectivity for ethylene are passed through a maximum at GHSV of about 1,500 h^{-1}, and the selectivity for ethane is increased to a larger extent. It is interesting to note that because of the addition of water in the feed, the yield for $C_{2\text{-}4}$ hydrocarbons at the lower space velocities (500–1,500 h^{-1}) is increased appreciably. However, at the higher space velocities ($> 1,500$ h^{-1}), the yield is decreased due to a large decrease in the methane conversion.

The ethylene/ethane ratio in the products is decreased, and the CO/CO_2 ratio is increased with the increase in the GHSV

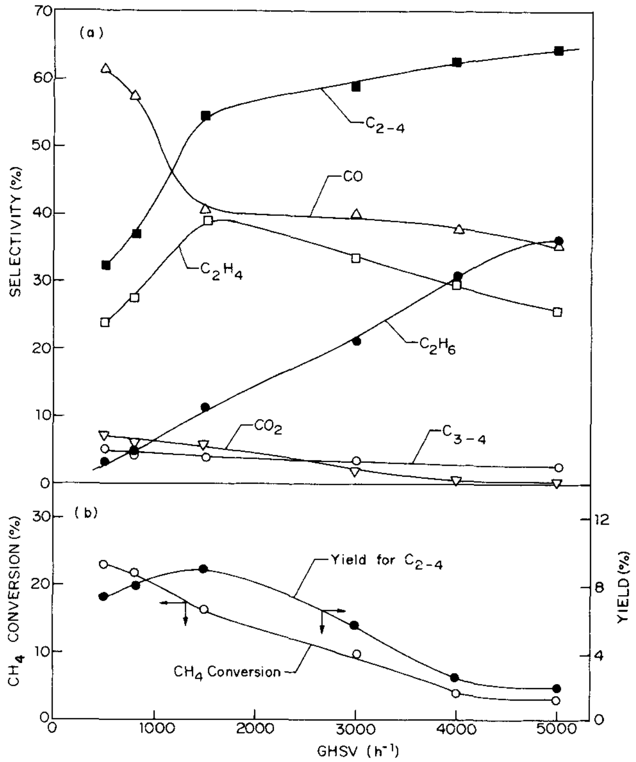

Figure 7. Influence of GHSV on methane conversion and product selectivity in OMP process in the presence of water (50 mol %) in the feed.

Feed = 39% CH_4, 11% O_2, and 50% H_2O; temperature = 1,223 K

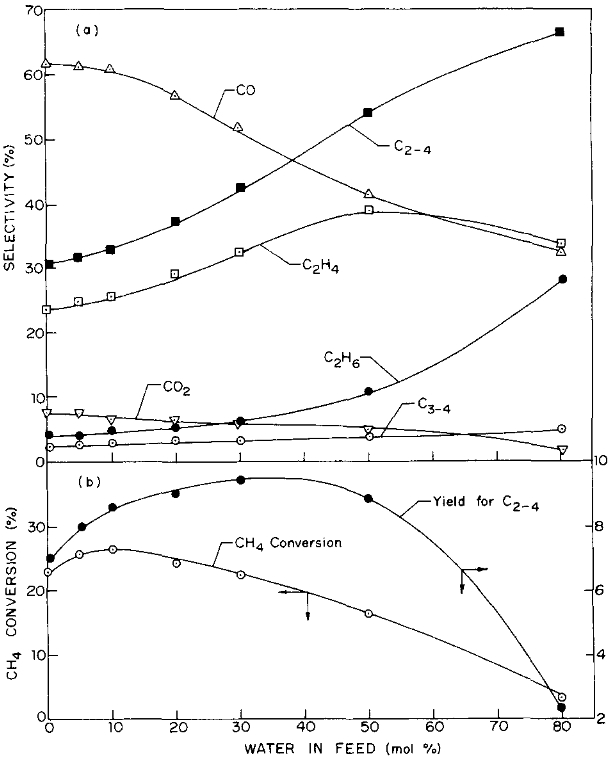

Figure 8. Influence of concentration of water in the feed on methane conversion and product selectivity in OMP process at 1,223 K.

Feed = mixture of CH_4, O_2 and H_2O; CH_4/O_2 = 3.5; GHSV = 1,500 h^{-1}

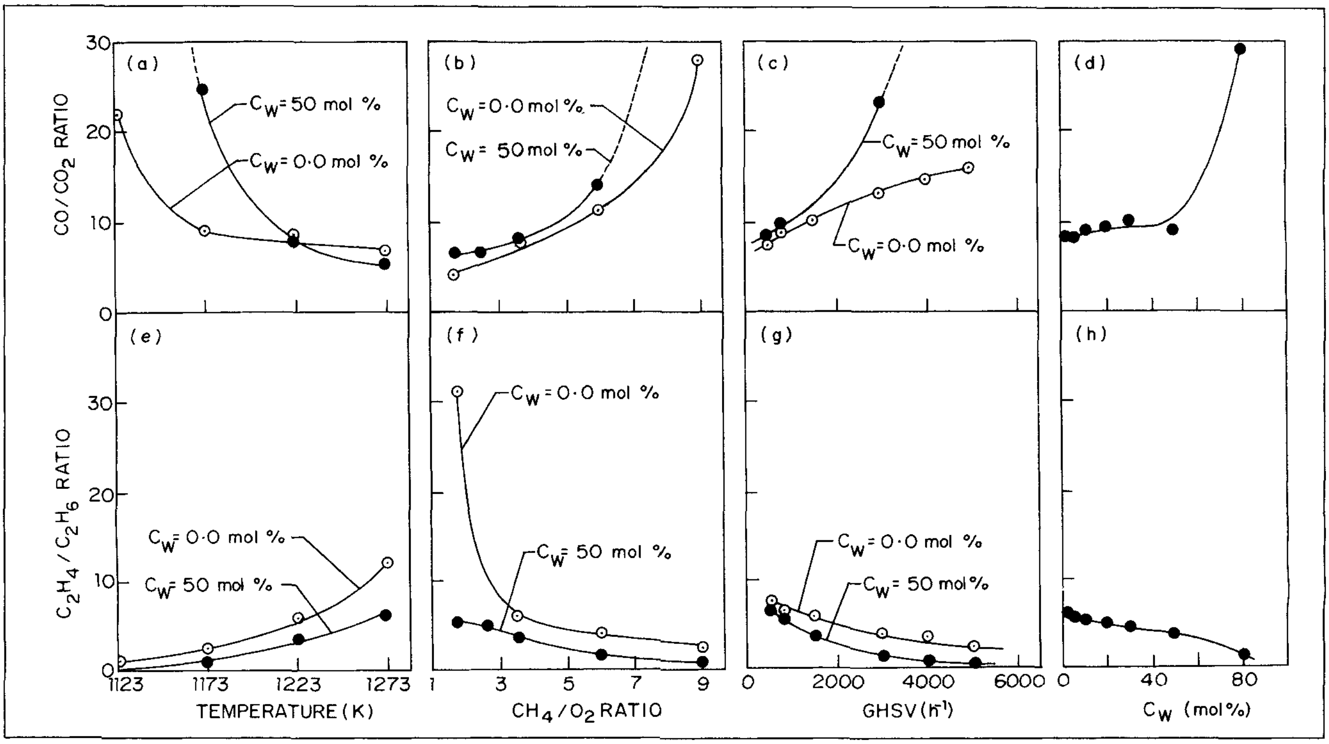

Figure 9. Influence of process variables on ethylene/ethane and CO/CO_2 ratios in the products.

C_w = concentration of water in the feed

Process Conditions: (a,e) CH_4/O_2 = 3.5, GHSV = 1,500 h^{-1}; (b,f) GHSV = 1,500 h^{-1}, temp. = 1,223 K; (c,g) CH_4/O_2 = 3.5, temp. = 1,223 K; (d,h) GHSV = 1,500 h^{-1}, CH_4/O_2 = 3.5, temp. = 1,223 K

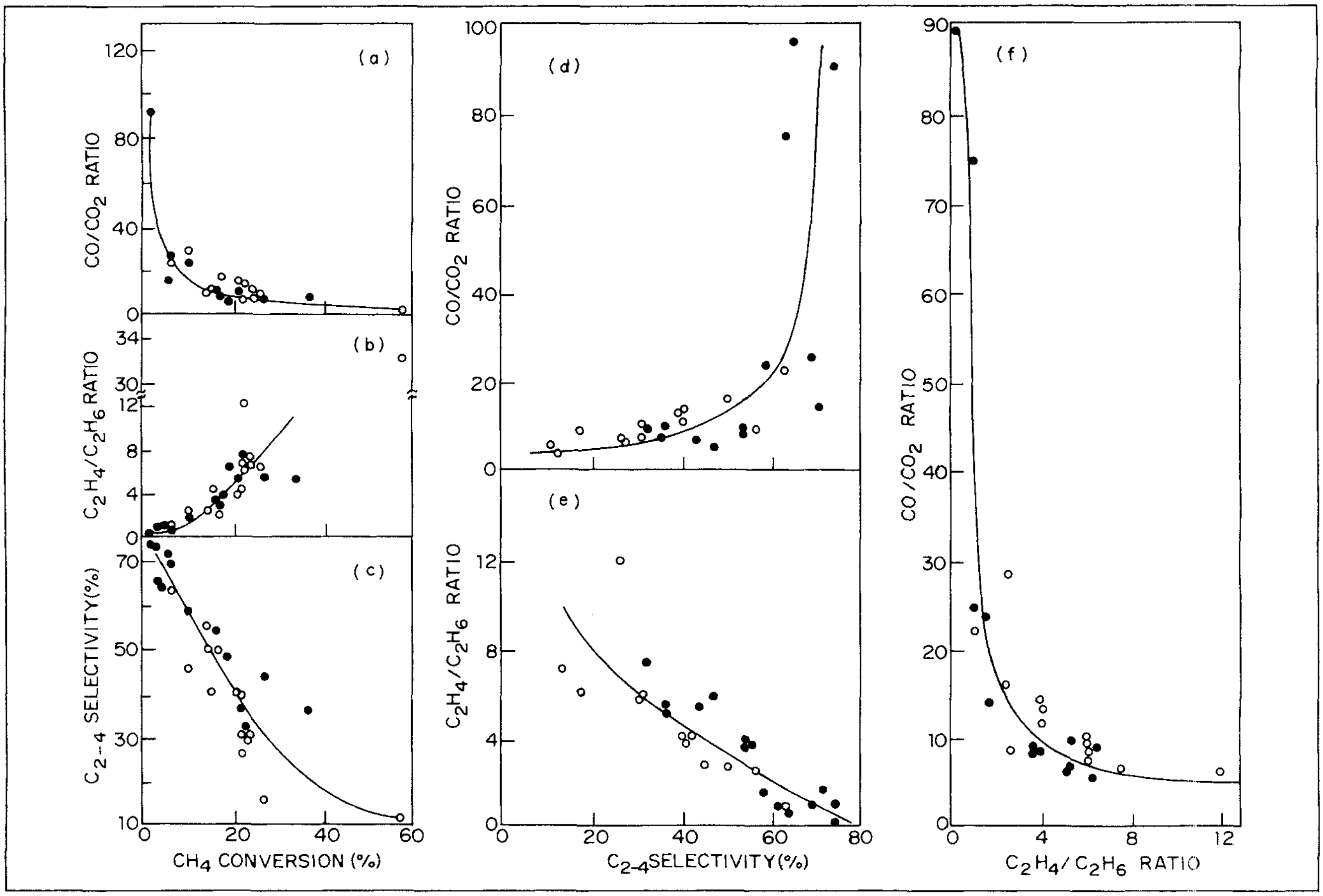

Figure 10. Relationships between CH_4 conversion, C_{2-4} selectivity, C_2H_4/C_2H_6 ratio, and CO/CO_2 ratio in the OMP process.

○, without water in the feed; ●, with 50 mol % water in the feed

(Figure 9). However, due to the presence of water in the feed, there is a large decrease in the ethylene/ethane ratio and a large increase in the CO/CO_2 ratio, particularly at the higher space velocities (or at the lower contact times).

Influence of concentration of water in feed

The results in Figure 8 show that when the concentration of water in the feed was increased from 0.0 to 80 mol %, the methane conversion and C_{2-4} yield are passed through a maximum at the water concentrations of around 10.0 and 35.0 mol %, respectively, and the selectivity for C_{2-4} hydrocarbons is increased markedly, and the formation of CO and CO_2 is decreased to a large extent. However, the selectivity for ethylene showed a maximum around the water concentration of about 50.0 mol %. Figures 9d and 9h show that the ethylene/ethane ratio in the products is decreased to a large extent, and the CO/CO_2 ratio is increased with the increase in the concentration of water in the feed, particularly at the higher water concentrations.

Product distributions in OMP process

The products formed in the OMP process at 1,123-1,273 K are ethylene, ethane, propylene, propane, butylenes, butanes, CO, CO_2, H_2O, H_2, and traces of C_{5+} hydrocarbons and formaldehyde. The above results show that the methane conversion and product selectivity and consequently the product distribution are influenced by the process variables (temperature, CH_4/O_2 ratio or O_2 concentration relative to CH_4 concentration in the feed, GHSV or contact time and concentration of water in the feed) as follows.

- The mathane conversion is increased with the increase in temperature, contact time and O_2 concentrations (or O_2/CH_4 ratio), whereas it is passed through a maximum with the increase in the water concentration in the feed.
- The selectivity for higher hydrocarbons (C_{2-4} hydrocarbons) is increased with the decrease in temperature, O_2 concentration and contact time, but it is increased with the increase in the water concentration in the feed.
- The formation of ethylene as compared to ethane is much higher. The ethylene/ethane ratio is increased with the increase in temperature, O_2 concentration and contact time, but it is decreased with the increase in the water concentration in the feed.
- As compared to CO_2, CO is formed to a very large extent. The CO/CO_2 ratio in the products is decreased with the increase in temperature, O_2 concentration and contact time, but it is increased with the increase in the water concentration in the feed.

It is very interesting to note that the selectivity for C_{2-4}

Table 1. Influence of Addition of Water or N_2 in Feed on Formation of Higher Hydrocarbons in the OMP Process ($GHSV = 1,500\ h^{-1}$)

Temp. (K)	Feed Composition (mol %)				CH_4/O_2 Ratio	Total CH_4 Conv. (%)	Selectivity for (%)			Total Selectivity for C_{2-4} (%)	Yield for C_{2-4} Hydrocarbons (%)	CO/CO_2 Ratio	C_2H_4/C_2H_6 Ratio
	CH_4	O_2	H_2O	N_2			C_2H_4	C_2H_6	C_{3-4}				
1,173	78.0	22.0	—	—	3.5	20.5	31.4	9.4	3.4	44.3	9.1	11.2	3.3
1,173	39.0	11.0	50	—	3.5	11.5	33.4	29.7	4.1	69.2	8.0	11.7	1.1
1,173	39.0	11.0	—	50	3.5	12.3	29.6	16.4	3.3	49.3	6.1	25.7	1.8
1,223	78.0	22.0	—	—	3.5	27.1	24.7	3.0	2.5	30.1	8.1	10.2	8.2
1,223	39.0	11.0	50	—	3.5	16.2	39.2	10.9	4.0	54.1	8.8	8.2	3.6
1,223	39.0	11.0	—	50	3.5	21.4	27.9	5.7	3.0	36.6	7.8	13.7	4.9
1,223	86.0	14.0	—	—	6.1	15.8	32.4	7.1	5.3	44.8	7.1	17.2	4.6
1,223	43.0	7.0	50	—	6.1	8.9	36.8	15.4	5.8	58.1	5.2	19.7	2.4
1,223	43.0	7.0	—	50	6.1	9.2	30.8	14.3	4.7	49.8	4.6	45.0	2.1

hydrocarbons and the ethylene/ethane and CO/CO_2 ratios in products are interrelated and are also related to the methane conversion as follows.

- The C_{2-4} selectivity is decreased with the increase in the methane conversion.
- The C_2H_4/C_2H_6 ratio is increased with the increase in the methane conversion, but it is decreased with the increase in the C_{2-4} selectivity and the CO/CO_2 ratio.
- The CO/CO_2 ratio is decreased with the increase in the methane conversion and the C_2H_4/C_2H_6 ratio, but it is increased with the increase in the C_{2-4} selectivity.
- The CO/CO_2 ratio is decreased with the increase in the C_2H_4/C_2H_6 ratio. For showing the above relationships, the data obtained with and without water in the feed (Figures 2-7) are plotted in Figure 10. The scatter of the data is due to a complex influence of the process variables.

Beneficial effects of water in feed

The selectivity and yield for higher hydrocarbons (C_{2-4} hydrocarbons) in the absence of water in the feed (Figures 2, 4 and 6) were compared with those in the presence of water (50 mol %) in the feed (Figures 3, 5 and 7). Figure 8 shows the influence of water concentrations in the feed on the results. These figures reveal that an addition of water in the feed is highly beneficial to achieving higher yields and/or selectivities for the higher hydrocarbons in the OMP process. Yet, another important advantage of the presence of water in the feed is that the formation of tarry material observed at higher temperatures ($\geq 1,223$ K) and lower CH_4/O_2 ratios (≤ 3.5) is eliminated almost totally. Further, the OMP process, which involves highly exothermic reactions, could be carried out in a very safe manner due to the dilution of methane and oxygen in the feed by the added water and also because of the increased heat capacity of the reaction mixture. Also, since the water from the product gases can be removed easily by condensation, the dilution of feed with water does not lead to dilution of the desired products (ethylene, ethane, and higher hydrocarbons).

Results showing the influence of the presence of water or inert gas (N_2) in the feed on the formation of higher hydrocarbons are presented in Table 1. The product distribution in the OMP process is affected strongly by the dilution of feed with nitrogen or water. It is very interesting to note that the increase in the selectivities for ethylene, ethane and C_{3-4} hydrocarbons, or in the total selectivity for higher hydrocarbons (C_{2-4} hydrocarbons) due to the addition of water (50 mol %) in the feed is relatively much higher than that observed for the addition of N_2 (50 mol %) in the feed. Also, the increase in the CO/CO_2 ratio in the products due to the addition of N_2 in the feed is very much higher than that observed when the feed was diluted with water. A comparison of the data obtained by diluting the feed to the same extent with N_2 and water shows that both the selectivity and yield for C_{2-4} hydrocarbons is higher when the feed is diluted with water. Further, a comparison between two cases with similar conversion (e.g., data of run nos. 1 and 2, 2 and 3, and 5 and 7) clearly shows that the beneficial effect of water is not just due to a dilution of the feed.

The above facts reveal that the role played by N_2 and water as feed diluent in the OMP process is quite different and/or water does not act just as a feed diluent. The increase in the yield and/or selectivity for C_{2-4} hydrocarbons due to the addition of water in the feed indicates that the CO and CO_2 forming reactions are inhibited greatly due to the presence of water. Why and how this happens are not known. Further studies are necessary for clearly understanding the role of water in the OMP process for the observed beneficial effects.

Conclusions

Oxidative pyrolysis of methane to higher hydrocarbons is a very complex process involving a large number of reactions. The methane conversion and product selectivities in the process are controlled by a combined effect of the process parameters (temperature, contact time, O_2 concentration or CH_4/O_2 ratio, and the presence of water or inert gas in the feed). The product distribution is influenced strongly by the feed dilution with water or N_2. There is no coke deposition in the reactor.

The addition of water in the feed is highly beneficial for obtaining higher yield and/or selectivity for higher hydrocarbons and also for eliminating the formation of tarry material under the severe operating conditions (at higher temperatures and lower CH_4/O_2 ratios). Also, in the presence of water, the process occurs in a highly controllable manner.

The selectivity for higher hydrocarbons and the ethylene/ethane and CO/CO_2 ratios in the products of the OMP process are interrelated and are related to the methane conversion. With an increase in the conversion, the selectivity for higher hydrocarbons and the CO/CO_2 ratio are decreased, whereas the ethylene/ethane ratio is increased. At higher selectivity, the ethylene/ethane ratio is lower, but the CO/CO_2 ratio is higher.

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