**THE THERMAL DECOMPOSITION OF METHANE
IN A TUBULAR REACTOR**

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THE THERMAL DECOMPOSITION OF METHANE
IN A TUBULAR REACTOR

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Abstract

The reaction rate of methane decomposition using a tubular reactor having a 1 inch inside diameter with an 8 foot long heated zone was investigated in the temperature range of 700 to 900 C with pressures ranging from 28.2 to 56.1 atm. Representing the rate by a conventional model, $-dC_{CH_4}/dt = k_1 C_{CH_4} - k_2 C_{H_2}^2$, the rate constant k_1 for methane decomposition was determined. The activation energy, 31.3 kcal/mol, calculated by an Arrhenius Plot was lower than for previously published results for methane decomposition. This result indicates that submicron particles found in the reactor adhere to the inside of the reactor and these submicron high surface area carbon particles tend to catalyze the methane decomposition. The rate constant has been found to be approximately constant at 900 C with pressure range cited above. The rate of methane decomposition increases with methane partial pressure in first-order. The rate of the methane decomposition is favored by higher temperatures and pressures while the thermochemical equilibrium of methane decomposition is favored by lower pressures.

1. Introduction

The Hydrocarb Process⁽¹⁾ consists of the two main reactions; (1)hydrogasification of the carboneous feedstock to produce a methane-rich gas and (2)the thermal decomposition of methane to produce carbon black and a hydrogen-rich gas. The section on methane decomposition is especially important in order to maintain high efficiency in the process. A key element in the process is that the hydrogen-rich gas produced in the methane decomposition reactor is recycled to the hydrogasification reactor as the reactant gas. Furthermore, the product carbon black is produced in the methane decomposition section.

This work was performed in order to investigate the phenomena of methane decomposition and to obtain data on the kinetic rate of the reaction for the purpose of designing the methane decomposition reactor.

2. Chemical Equilibrium

Since the methane decomposition is endothermic, the methane concentration decreases with increasing temperature. Due to the increase of volume during methane decomposition, the decomposition of methane is favored by decreasing pressure.

Figure 1 shows the equilibrium data of the methane at temperature from 600 to 1200 C and at pressures of 25, 30, 40, and 50 atm. These data are calculated from the following Gibbs Free Energy and equilibrium constant.

$$R \quad T \quad \ln K_x = -dG \quad (2)$$

$$K_x = X_{H_2}^2 / X_{CH_4} \quad (3)$$

where X is the mol fraction of each gaseous component, and

$$K_p = (pp_{H_2})^2 / pp_{CH_4} \quad (4)$$

where pp is the partial pressure of each component

3. Experimental

Figure 2 shows the schematic flow sheet of the experimental equipment which mainly consists of a tubular reactor, a carbon trap, a gas-chromatograph and gas meter. Methane enters the system through a remotely controlled regulator located next to the methane cylinders which keeps the pressure approximately constant at selected pressure of 28.2, 41.8 or 56.1 atm in the system. Methane then flows through a preheater and enters into the reactor which consists of a 1 inch inside diameter by 1/4 inch wall Inconel 617 tube. The total length of the reactor tube is 11 feet of which the first 8 feet is externally heated and selectively maintained at constant experimental temperatures of 700, 800 and 900 C by clamshell electric heaters. Methane is decomposed into carbon and hydrogen in the heated reactor and the effluent gas flows through the carbon trap connected at the bottom of the reactor, where the carbon generated by the reaction is separated. Gas is sampled before and after the reactor through sampling lines to an on-line gas-chromatograph. The concentrations of CH₄, CO, and CO₂ in the gas are measured using the thermal conductivity detector. The flow rate of exit gas is controlled in the range between 10 and 150 liters/min. by a flow valve located after the reactor. The exit gas

flows through the gas meter where the flow rate is measured and the gas is finally vented to the atmosphere.

4. Experimental Result and Discussion

Table 1 shows the results of the data for the experimental runs to measure the conversion of methane into hydrogen and carbon at 700, 800, and 900 C and at 56.1, 41.8 and 28.2 atm. Figure 3 shows the relationship between the methane concentrations in exit gas and residence time in the reactor under these conditions. The residence time of the methane gas in the reactor is given by the inlet gas velocity. The concentration of the methane decreases with increasing temperature and residence time. At both 700 and 800 C and at 56.1 atm the concentration of methane decreases less with residence time than that at 900 C and 56.1 atm. Under the latter conditions, the concentration of methane decreases dramatically with residence time and appears to be approaching equilibrium conditions. The concentration of methane at a residence time of 103 seconds was 48.1 vol%, and in this case the equilibrium concentration of the methane is 39.6 vol%.

The equilibrium data at the lower temperatures of 700 and 800 C and at 56.1 atm are 54.3 and 69.3 vol% respectively and higher than that at 900 C. Taking these conditions into account and considering the curves of methane decomposition in Figure 3, the rate of methane decomposition in the lower temperature range seems to be much smaller than that at the higher temperature of 900 C.

Generally the equation for the rate of decomposition of methane

is derived as follows;

where k_1 is the rate constant of methane decomposition, and k_2 is the rate constant of methane formation. The rate equation for this reversible reaction can be written as follows;

$$\begin{aligned} -r_{\text{CH}_4} &= -dC_{\text{CH}_4} / dt = k_1 C_{\text{CH}_4} - k_2 C_{\text{H}_2}^2 \\ &= k_1 C_{\text{CH}_4} \left(1 - 1 / K_e \times C_{\text{H}_2}^2 / C_{\text{CH}_4} \right) \end{aligned} \quad (6)$$

where C_{CH_4} , C_{H_2} are the molar concentrations of CH_4 and H_2 respectively

The above differential equation for methane decomposition in the tubular reactor is solved for the condition of $C_{\text{H}_2\text{O}} = 0$ (initial concentration of hydrogen is 0), for inlet methane concentration $C_{\text{CH}_4\text{O}}$, exit methane concentration C_{CH_4} , and equilibrium concentration of methane $C_{\text{CH}_4\text{E}}$. Figure 4 shows a model of the tubular reactor and the derivation of the following rate equation.

$$k_1 \times t = \frac{C_{\text{CH}_4\text{O}} - C_{\text{CH}_4\text{E}}}{C_{\text{CH}_4\text{O}} + C_{\text{CH}_4\text{E}}} \ln \frac{C_{\text{CH}_4\text{O}}^2 - C_{\text{CH}_4} \times C_{\text{CH}_4\text{E}}}{C_{\text{CH}_4\text{O}} \times (C_{\text{CH}_4} - C_{\text{CH}_4\text{E}})} \quad (7)$$

where t is the residence time

Table 2 shows the calculated data of inlet, outlet and equilibrium concentrations of methane, inlet flow rate, and $k_1 \times t$ values. Figure 5 shows the relationship between $k_1 \times t$ value versus residence time at 700, 800, and 900 C and at 56.1 atm. Each slope in the Figure 5 indicates a rate constant k_1 of the methane decomposition at each temperature. Table 3 represents the k_1 value at these conditions.

Table 3 Rate constants at 56.1 atm

Temperature		k1 value	
700	C	5.758E-4	1/sec
800	C	1.753E-3	1/sec
900	C	9.306E-3	1/sec

In Figure 6, the rate constants, k_1 , for methane decomposition are plotted versus reciprocal temperature. From this Arrhenius plot an activation energy for methane decomposition and the rate constant k_1 are calculated as follows;

$$E = 31.3 \quad \text{kcal/mol}$$

$$k_1 = 5.4 \times 10^3 \exp(-E/RT) \quad 1/\text{sec} \quad (8)$$

The activation energy appears to indicate a diffusion controlled process which usually has values up to about 30 kcal/mol as opposed to a chemical reaction controlled process which has much higher activation energies ranging above 50 kcal/mol. From the limited methane decomposition data in the literatures (2,3,4,5, and 6), the homogeneous activation energy for methane decomposition is determined to be 65 kcal/mol. The data gathered in these experiments appears to be influenced by a heterogeneous effect of surfaces. During our experiments some of the carbon formed from methane decomposition adhered to the walls of the Inconel high alloy steel of the tubular reactor. In fact, at the end of several extended runs, it was found that the carbon plugged the tube to the extent that it restricted the gas flow. Thus, the fine submicron carbon particles could tend to catalyze the thermal decomposition of the methane. References 7 and 8 clearly indicate that different

materials increase the rate of the methane decomposition in the order of iron oxide, alumina, graphite, and quartz. In the tubular reactor the small submicron particle size of the carbon presents a very large surface area on which methane can decompose and thus a lower activation energy for decomposition results.

The influence of the total pressure in this system on the rate constant of the methane decomposition was investigated because the Hydrocarb Process is being operated under pressure and it is important to determine the influence of the total pressure on the reaction rate. Figure 7 shows the relationship between the $k_1 \times t$ value and residence time at 28.2, 41.8, and 56.1 atm at 900 C. The slopes in Figure 7 represent the rate constants k_1 at their respective conditions. These values are calculated and listed in Table 4.

Table 4 Rate constants at 900 degree centigrade

Pressure	k1 value	
28.2 atm	1.066E-2	1/sec
41.8 atm	1.380E-2	1/sec
56.1 atm	9.306E-3	1/sec

average rate constant 1.126E-2 1/sec

Although there is not enough data to establish a relationship with pressure, the rate constant appears to be approximately constant with pressure. The variation in the rate constant with pressure is probably within the deviation in the experimental measurements for this type of equipment. Some other studies to obtain the rate data of carbon formation from methane on silicate substrate indicate that the rate increased in first-order with pressure up to 15

atm⁽²⁾. The rate equation(6) modelled in this paper indicates that since the methane molar concentration is first-order in pressure, the result that the rate constant is constant and independent of pressure is in accord with other published results; and the rate of the methane decomposition indeed increases with partial methane pressure approximately in first-order. The thermochemical equilibrium for methane decomposition is favored by lower pressures, but as our results indicate, the rate is favored by higher pressure.

5. Conclusion

The influence of the temperature and total pressure on the rate of the methane decomposition has been determined by using a tubular reactor assembly. The following results and conclusions were obtained.

(1) A model for methane decomposition was developed, which resulted in the following rate equation;

$$\begin{aligned} -r_{CH_4} &= -dC_{CH_4} / dt = k_1 C_{CH_4} - k_2 C_{H_2}^2 \\ &= k_1 C_{CH_4} \left(1 - 1 / K_e \times C_{H_2}^2 / C_{CH_4} \right) \end{aligned}$$

k₁ value was calculated as follows;

$$k_1 \times t = \frac{C_{CH_4O} - C_{CH_4E}}{C_{CH_4O} + C_{CH_4E}} \ln \frac{C_{CH_4O}^2 - C_{CH_4} \times C_{CH_4E}}{C_{CH_4O} \times (C_{CH_4} - C_{CH_4E})}$$

An Arrhenius Plot of the k₁ values resulted in the following rate constant equation.

$$k_1 = 5.4 \times 10^3 \exp (-31.3 \text{ kcal/RT }) \quad 1/\text{sec}$$

The activation energy appears to indicate a diffusion controlled process most likely influenced by the high surface area of the submicron carbon particles deposited in the reaction zone.

(2) Although a definitive influence of the total pressure on the rate constant of the methane decomposition could not be clearly determined, at 900 C, within experimental error, the rate constant appears to be constant and independent of pressure in the range of 28.1 to 56.1 atm. Taking into account the rate equation modelled in this paper, the rate of decomposition is influenced by the methane partial pressure to

the first-order. Taking into account these results together with literature data, the conclusion is reached that although the thermochemical equilibrium decomposition of methane is favored by lower pressure, the rate of methane decomposition is favored by higher pressure.

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Table 1 Experimental Data of Methane Decomposition

Run Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Temperature centigrade	900	900	900	900	800	800	800	700	700	700	900	900	900	900	900	900
Pressure atm	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	28.2	28.2	28.2	41.8	41.8	41.8
Methane concentration in inlet gas vol%	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Exit gas flow rate at standard condition liters / min. (25°C, 1 atm)	54.34	30.24	21.89	15.85	50.57	20.6	14.89	56.63	26.96	15.06	65.58	36.53	17.25	149.0	86.99	27.24
Residence time sec. based on inlet gas flow rate	21.8	42.3	60.5	103.0	23.7	58.9	83.6	22.8	48.3	86.8	8.94	16.8	37.0	5.54	10.3	35.7
Methane concentration in exit gas vol%	78.6	65.4	59.7	48.1	92.6	89.8	85.7	97.4	95.7	95.7	81.2	72.7	66.4	90.8	75.5	61.8
Methane conversion %	10.7	17.3	20.2	26.0	3.7	5.1	7.2	1.3	4.3	2.5	9.4	13.7	16.8	4.6	12.3	19.1

Table 2 Calculated Data of Methane Decomposition

Run Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Temperature centigrade	900	900	900	900	800	800	800	700	700	700	900	900	900	900	900	900
Pressure atm	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	28.2	28.2	28.2	41.8	41.8	41.8
Methane concentration in inlet gas vol%	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Inlet gas flow rate liters / min. at environmental condition	3.40	1.75	1.23	0.72	3.12	1.26	0.89	3.25	1.53	0.85	8.29	4.40	2.00	13.4	7.19	2.07
Residence time sec. based on inlet gas flow rate ¹⁾	21.8	42.3	60.5	103.0	23.7	58.9	83.6	22.8	48.3	86.8	8.94	16.8	37.0	5.54	10.3	35.7
Inlet methane conc. mol/liter $C_{CH_4}^{inlet}$	0.583	0.583	0.583	0.58	0.637	0.637	0.637	0.703	0.703	0.703	0.293	0.293	0.293	0.434	0.434	0.434
Exit methane conc. mol/liter $C_{CH_4}^{exit}$	0.458	0.381	0.348	0.280	0.590	0.572	0.546	0.684	0.672	0.668	0.238	0.213	0.195	0.394	0.328	0.268
Equilibrium conc. mol/liter $C_{CH_4}^{eq}$	0.231	0.231	0.231	0.231	0.346	0.346	0.346	0.487	0.487	0.487	0.083	0.083	0.083	0.150	0.150	0.150
$k_1 \times T^2$ (-)	0.246	0.457	0.578	0.976	0.073	0.109	0.158	0.026	0.044	0.052	0.210	0.325	0.423	0.097	0.288	0.516

¹⁾ Reactor Volume 1.236 liters
²⁾ $k_1 \times T^2 = \frac{C_{CH_4}^{inlet} - C_{CH_4}^{exit}}{C_{CH_4}^{inlet} + C_{CH_4}^{exit}} \ln \frac{C_{CH_4}^{inlet} - C_{CH_4}^{exit}}{C_{CH_4}^{inlet} \times C_{CH_4}^{exit}}$

Figure 1 Schematic Flowsheet of Tubular Reactor
For Methane Decomposition

Figure 2 Equilibrium Data of Methane

Figure 3 Methane concentrations vs. residence time

Tubular Reactor Model

Mass Balance of A component

$$F_a = F_a + dF_a + (-r_A) \times dV$$

$$-dF_a = (-r_A) \times dV$$

$$F_a = F_{a0} \times (1 - X_A)$$

$$dV/F_{a0} = dX_A/(-r_A)$$

$$F_{a0} = Q_0 \times C_{a0}$$

$$dV/Q_0 = C_{a0} \times dX_A/(-r_A)$$

$$dV/Q_0 = dt$$

$$C_a = C_{a0} \times (1 - X_A)$$

$$-dC_a/dt = -r_A$$

F_a : molar velocity (mol/sec)
 Q : volume velocity (liters/sec)
 C_a : concentration of A component (mol/liter)
 X_A : degree of conversion of A component (-)
 Subscript o : initial condition

Reaction Rate Model

$$-r_{\text{CH}_4} = -dC_{\text{CH}_4}/dt = k_1 \times C_{\text{CH}_4} - k_2 \times C_{\text{H}_2}^2$$

initial condition

$$\text{at } t = 0 \quad C_{\text{H}_2} = 0$$

$$\text{at equilibrium} \quad -dC_{\text{CH}_4}/dt = 0$$

solution of differential equation

$$k_1 \times t = \frac{C_{\text{CH}_40} - C_{\text{CH}_4\text{E}}}{C_{\text{CH}_40} + C_{\text{CH}_4\text{E}}} \ln \frac{C_{\text{CH}_40}^2 - C_{\text{CH}_4} \times C_{\text{CH}_4\text{E}}}{C_{\text{CH}_40} \times (C_{\text{CH}_4} - C_{\text{CH}_4\text{E}})}$$

k_1 : methane consumption rate constant (1/sec)
 k_2 : methane production rate constant (liter/sec/mol)
 t : residence time (sec)
 C_{CH_40} : methane initial concentration (mol/liter)
 C_{CH_4} : methane concentration of outlet (mol/liter)
 $C_{\text{CH}_4\text{E}}$: methane equilibrium concentration (mol/liter)

Figure 4 Tubular Reactor Model and Derivation of Rate Equation

Figure 5 $\frac{C_{CH4O} - C_{CH4E}}{C_{CH4O} + C_{CH4E}} \ln \frac{C_{CH4O}^2 - C_{CH4} \times C_{CH4E}}{C_{CH4O} (C_{CH4} - C_{CH4E})}$
 vs. residence time at various temperatures
 (at 56.1 atm)

Figure 6 Rate constant of Methane Decomposition vs. reciprocal temperature (at 56.1 atm)

Figure 7 $\frac{C_{CH4O} - C_{CH4E}}{\ln \frac{C_{CH4O}^2 - C_{CH4} \times C_{CH4E}}{C_{CH4O} (C_{CH4} - C_{CH4E})}}$ vs. residence time at various pressures (at 900 °C)

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