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The Direct Conversion of Methane to Methanol by Controlled Oxidation

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I. Introduction

In recent years, sustained efforts have been made in many parts of the world to find a substitute for gasoline as a transportation fuel. Gasoline–alcohol blends (gasohols) have been introduced in many countries including the United States, and neat alcohols are also being used in Brazil. Propane, liquified at 10 atm, is also being used as transportation fuels. Among all the gasoline substitution candidates, methanol has certain advantages as a liquid fuel and can be manufactured from a variety of raw materials such as natural gas, coal, municipal solid waste, animal refuse, and biomass. At present almost all of the methanol produced comes from natural gas via a two-stage process (reforming to synthesis gas and catalytic conversion of syngas).

The existing commercial process for the production of methanol from natural gas (essentially methane) involves the intermediate formation of synthesis gas.

$$CH_4(g) + H_2O(g) \xrightarrow[\text{heat}]{[\text{Ni}]} CO(g) + 2H_2(g) \qquad (1)$$

$$\Delta H^\circ = 49.3 \text{ kcal}$$

The "synthesis gas" is then converted into methanol by a catalytic process after appropriate balancing for CO and H_2 (the excess H_2 is used to generate the steam required in reaction 1).

$$CO(g) + 2H_2(g) \xrightarrow[\text{50–100 atm}]{\text{cat.}} CH_3OH(g)$$

$$\Delta H^\circ = -21.7 \text{ kcal}$$

A recent description of the overall process using either natural gas or coal as a starting material has been presented by Piquette.[1] This process suffers from the requirement of complicated engineering steps and also from the relative inefficiency of carrying out extensive oxidation of methane to carbon monoxide and then reduction of carbon monoxide to methanol. In addition, the "synthesis gas" must be clean, free from sulfur, chloride, and other catalyst poisons. The overall efficiency of a 2000 tonne/day plant is expected to be about 70% for fuel grade methanol provided that the excess steam produced can be utilized on site or sold.

Clearly a direct conversion of methane to methanol, where the oxidation process is intercepted at the stage of initial oxidation, not only yields a liquid product in one step but is also preferred because it will be energetically more efficient.

$$CH_4(g) + {}^1/_2O_2(g) \rightarrow CH_3OH(l)$$

$$\Delta H^\circ = -30.7 \text{ kcal}$$

The recent demand for methanol as a fuel and a starting material for many industrial processes has indicated[2] that new technology must be developed for the commercial production of methanol.

With substantial reserves of natural gas worldwide, a single step conversion process of methane to methanol can have far reaching economic implications.

This paper reviews the research which has been concerned with the conversion of methane to methanol and also carefully examines the process conditions which are most conducive to the direct oxdiation process.

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II. Early Work

The oxidation of hydrocarbons in general, and methane in particular, has been studied for over a century. The kinetics and mechanism for the oxidation reaction have been elucidated for the complete combustion of methane to carbon dioxide and water. The intermediate products, hydrogen, carbon monoxide, formaldehyde, and formic acid, were identified by 1903. Despite many efforts, no evidence of methanol as an intermediate product was found until the reaction was carried out at high pressure.[3-12]

Because of the focus of this review is the production of methanol by oxidation of methane, we have chosen to express the "yield" of methanol as a function of the methane *consumed*. Although the term "selectivity" is often used in the same way as we use "yield", it is our feeling that, in keeping with classical physical chemistry, "selectivity" should be expressed as a normalized ratio. Thus, a reaction which gave CH_3OH, HCHO, CO_2, and CO in "yields" of 85, 10, 3, and 2% (based on methane consumed) would have a "selectivity" for $CH_3OH:HCHO:CO_2:CO = 8.5:1.0:0.3:0.2$. If one multiplies conversion percent times "yield" percent, one obtains the yield of product per pass in reactor.

A. Static System

In 1932 Newitt and Haffner[8] reported the formation of methanol in the high-pressure oxidation of methane. These authors also reported that formaldehyde and formic acid were produced as condensable products. They were not able to detect the presence of peroxides. Under Newitt and Haffner's conditions, the maximum yield of methanol was about 22% of the methane consumed. The maximum methanol to formaldehyde ratio was 40. The reaction was carried out in a static system at temperatures from 360 to 393 °C and pressures of 50–150 atm. The reaction time varied from 1 to 100 min in the presence of either excess methane or inert gases such as nitrogen, carbon dioxide, and water. Some typical results reported by Newitt and Haffner are given in Table I. The conversion (the percentage of CH_4 consumed) at optimum yield was 1.6% at 106 atm, and all the oxygen was consumed.

B. Flow System

The high-pressure partial oxidation of methane to methanol was studied independently by Pichler and Reder[9] under both static and flow conditions. In the static experiments the pressure was varied up to a maximum of 160 atm, and in the flow system pressures up to 100 atm were used. Under static conditions of 160 atm and 350 °C, the yield of methanol was a maximum (14.8% of the methane consumed) when the oxygen content was at 10%. Under flow conditions at 100 atm and 500 °C with a reaction time of 10 s in a 4-mm porcelain-lined capillary reactor, the yield of methanol increased from 2.4% at 10% oxygen to 60% at 0.6% oxygen. A study of the explosive oxidation of methane at 160 atm and 10% oxygen showed that the yield of methanol dropped from 9% to less than 1% when the initial temperature was increased from 100 to 250 °C.

Newitt and Szego[10] studied the slow, high-pressure oxidation of methane and related compounds in a flow system. Their results, summarized in Table II, indicate that as much as 50% of the methane consumed is converted to methanol by using low reaction times and low concentrations of oxygen. No formic acid was detected, and the ratio of CO/CO_2 was approximately 1. The authors concluded that methanol was the initial product from the oxidation reaction. The conversion of methane to methanol at high pressures was optimal at 450 °C.

TABLE I. The Effect of Temperature upon the Survival of Methyl Alcohol and Formaldehyde in the Products of Methane Oxidation at High Pressures[8]

Initial Mixture CH_4/O_2 = 8.1/1

initial temp, °C	rise in temp, °C	duratn of inductn/reactn, min		ratio CO/CO_2 in gaseous products	yield as % of CH_4 reacted		ratio $CH_3OH/HCHO$
					CH_3OH	HCHO	
				Initial Pressure = 48.2 atm			
360	7	14	12	0.28	3.2	0.5	6.4
367	7	7	8	0.04	5.2	0.5	10.4
370	9	5	4	0.15	11.2	0.7	16.0
373	12	1.5	4	0.21	13.7	0.7	19.6
				Initial Pressure = 106.4 atm			
336	4	53	35	0.05	10.1	0.30	33.6
339	10	14	33	0.01	14.1	0.36	39.2
341	14	2.5	9.5	1.5	22.3	0.75	29.4
343	10		12	1.0	20.0	0.93	21.5
				Initial Pressure = 150 atm			
335	13	14	33	1.04	11.9	0.3	39.6
341	17	5	11	0.06	19.0	0.6	31.6
343	32		[a]	2.1	21.1	0.4	52.7

[a] Instantaneous.

TABLE II. Yield of Methanol and Formaldehyde from the Oxidation of Methane in a Flow System at 50 atm[10]

initial mixture	initial temp of reaction tube, °C	rise of temp, °C	duration of heating, s	yield as % of CH_4 reacted		ratio $CH_3OH/HCHO$
				CH_3OH	HCHO	
CH_4 (90)	430	5	5	51	4.1	12
O_2 (3)	430	5	7	49	3.2	15
N_2 (7)	410	15	10	43	3.2	13
	400	28	20	12	2.16	5.6
CH_4 (90)	410	35	5	29.0	1.4	21
O_2 (5)	410	46	7	18.0	0.9	20
N_2 (5)	400	75	10	3.0	1.0	3.0

In 1934 Wiezevich and Frolich[11] reported on their study of the direct oxidation of saturated hydrocarbons at high pressures in a flow system. These authors showed that the optimum pressure for production of methanol was 135 atm. They also showed that the flow rate did not have a significant effect on the yield of methanol. At 135 atm the temperature for the onset of the oxidation reaction with methane was about 500 °C. When the reaction was carried out with natural gas at 390 °C, 135 atm, and 5.4% oxygen content, as much as 30% of the condensed liquid was methanol. However, the total liquid product represented only a 3.7% yield in terms of reacted methane. Most of their experiments were done with natural gas containing about 2% ethane. When the ethane content in the inlet gas was increased to 12%, the yield of methanol in the liquid product increased from 14% to about 32%. Since the increased yield of methanol could not be accounted for by the increased amount of ethane present, it was concluded that the methanol was formed by the oxidation of methane sensitized by the ethane present. Contrary to the conclusion of Pichler and Reder,[9] these authors found that catalysts such as iron, nickel, and aluminum tended to increase the yield of methanol.

Further work on the low-pressure (1 atm) oxidation of methane and intermediate products has been reported by Norrish and Foord,[13] Bone and Gardner[14] and Newitt and Gardner.[15] These authors were primarily concerned with solving the dispute regarding the hydroxylation mechanism and the role of peroxides.

In 1937, Newitt reviewed much of the early work on high-pressure oxidations of methane and other hydrocarbons.[16] It was also in this year that Boomer and his students at the University of Alberta published three articles on the oxidation of methane at high pressures.[17-19] Using natural gas containing 90% methane, 3.5% ethane, and 5% nitrogen, they showed that copper was an effective catalyst in the formation of methanol in a high-pressure flow-through system. Some typical results from Boomer's work are recorded in Table III.

Boomer's work presents a number of interesting points. First, the yield of methanol increased as the concentration of oxygen decreased. Second, the effect of flow rate was more pronounced at low oxygen concentrations than it was at high oxygen concentrations and only a slight increase in methanol yield was observed when the flow rate was decreased. Third, these authors reported the detection of hydrogen which previously had only been observed in the explosion reaction. And fourth, the copper catalyst was easily poisoned by traces of sulfur resulting in about 50% reduction of its normal catalytic value.

When methane containing 5.7% nitrogen was used as a reactant,[19] much higher temperatures were required than those found necessary for natural gas. These results confirmed what had been found by Pichler and Reder[9] and by Wiezevich and Frolich.[11] The lower temperatures required for reactions with natural gas were attributed to the presence of ethane and propane which underwent oxidation at lower temperatures than methane. Intermediates in the oxidation of ethane and propane presumably catalyze the overall oxidation of methane. At a pressure of 180 atm, temperature of 475 °C, 3.2% oxygen, and 16.78% nitrogen, the yield of

TABLE III. Experiments at a Pressure of 185 atm, Showing the Effect of Temperature, Rate of Flow, and Oxygen Concentrations on Yields (Boomer et al.)[18]

expt no.	86	67	58	77	80	81	79	85	91
temp, °C	325	350	350	350	350	350	350	400	425
off-gas flow, L/min	0.95	0.86	0.80	0.78	1.0	1.04	1.30	0.94	1.00
in-gas anal.									
O_2	4.1	8.45	12.0	3.76	3.68	3.66	3.73	3.71	3.68
CH_4	72.2	54.0	38.8	76.4	75.3	75.4	75.3	73.8	77.1
C_2H_6	2.76	1.79	1.21	1.88	2.42	2.63	2.66	2.03	2.0
N_2	20.94	35.76	47.99	17.96	18.6	18.31	18.31	19.88	17.2
off-gas anal.									
CO_2	0.58	1.76	3.31	0.61	1.07	0.95	2.45	0.53	0.42
O_2	0.0	0.74	0.65	0.32	0.21	0.21	0.5	0.0	0.0
H_2	0.63	0.82	1.17	0.47	0.42	0.53	0.5	0.53	
CO	0.63	2.57	2.11	1.21	1.08	1.24	1.21	0.53	
CH_4	74.9	55.8	40.1	77.8	78.5	77.6	75.0	75.1	
C_2H_6	1.81	0.31	0.1	1.1	0.81	1.5	1.48	2.68	
N_2	21.45	38.0	52.6	18.49	17.9	17.97	18.86	20.63	
vol. in-gas/vol. out-gas	1.03	1.08	1.14	1.04	1.04	1.04	1.03	1.05	1.00
condensate, g/100 L in-gas at NTP									
CH_3OH	2.20	2.06	1.37	1.73	1.60	1.72	1.83	1.97	2.06
CH_2O	0.194	0.159	0.114	0.198	0.166	0.151	0.185	0.198	0.094
$HCOOH$	0.063	0.063	0.016	0.031	0.037	0.040	0.033	0.02	0.01
H_2O	2.90	6.32	3.64	2.46	2.76	2.35	2.11	2.66	3.15
alcohol in condensate, %	41.0	23.9	13.5	39.0	35.1	40.3	44.0	40.6	38.8
total carbon oxidized, %	3.73	9.73	14.2	3.92	4.16	4.31	6.17	3.24	
yields, as % of total carbon burned to									
CH_3OH	53.3	25.9	16.5	38.8	33.8	34.6	25.8	54.3	
CH_2O	5.02	2.12	1.46	4.75	3.72	3.25	2.77	5.75	
$HCOOH$	1.06	0.51	0.14	0.48	0.54	0.57	0.32	0.37	
total	59.38	28.54	18.1	44.03	38.06	38.32	28.9	60.42	
total Inlet Oxygen accounted for, %	87.0	95.0	86.3	99.0	111.0	105.0	146.0	87.0	

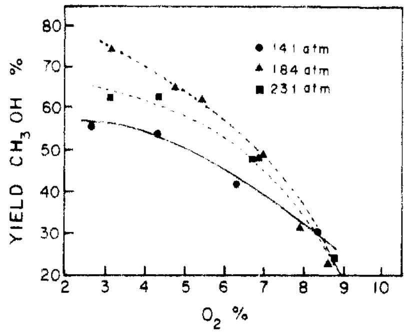

Figure 1. Methanol yield as a function of pressure and oxygen concentration in a flow system at 475 °C.[19]

methanol was 74% with a flow rate of 0.84 L/min. Under these conditions the amount of methane consumed during the reaction was only 1.9%. A material balance for oxygen showed that 75% of the oxygen was accounted for in the products.

These results were similar to those observed by previous workers.[9,11] Figure 1 correlates the yield of methanol with the oxygen concentration at various pressures.

Boomer's results indicated that other catalysts, namely, steel, silver, and glass, could also be used. All three catalysts were found to be as effective as copper. However, since the reactor used was copper-plated, it was hard to distinguish between the exposed catalyst and the remaining part of the apparatus. Boomer and Naldrett[20] reported some interesting effects with regard to the form of the catalyst. Copper in the form of gauze was less effective than blocks of copper. The difference was attributed to the greater free space in the reaction zone. Comparison of nickel, zinc, and silver gauzes showed that nickel was the most effective and zinc gauze the least effective in catalyzing the conversion of methane to methanol. Interestingly, nickel gauze was more effective than copper gauze. Experiments with Monel metal (a nickel–copper alloy) showed it to be highly effective as a catalyst. Boomer concluded from his work that to attain commercial feasibility for the process a recycling system should be used so that high yields could be achieved under conditions of low conversion rates.

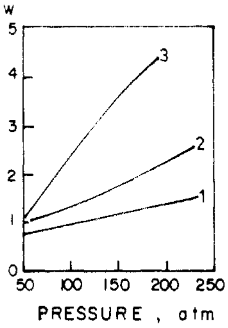

Figure 2. Methane to methanol conversion at 400 °C and 50 L/h.[21] Methanol yield, *w* (g/100 L of gas), as a function of pressure. O_2 concentration: 1 = 2.6%; 2 = 4.4%; 3 = 5.5%.

C. Russian Work

Russian workers started to study methanol formation in 1946 when Furman[21] reported on the high-pressure oxidation of methane in a flow system. The results are summarized in Figures 2 and 3. Fruman's results appear to contradict previous work[9,19] which showed higher methanol yields at lower O_2 concentrations. Fruman and Tsiklis[22] also studied the oxidation of methane under adiabatic compression. The reaction was reported to commence at 1200 K. Though formaldehyde was detected, no methanol was found. These authors also studied the oxidation reaction at 365–400 °C and at 10–300 atm with air and oxygen.

More recently, Nalbandyan and co-workers[23] reexamined the oxidation of methane under adiabatic com-

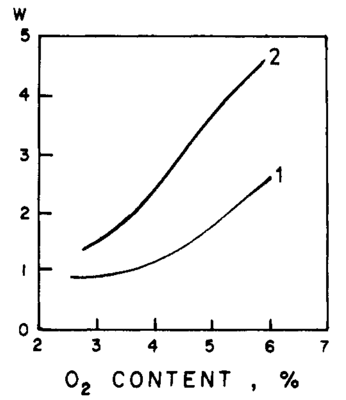

Figure 3. Methane to methanol conversion at 400 °C and 50 L/h.[21] Methanol yield, *w* (g/100 L of gas), as a function of oxygen pressure. Pressure: 1 = 100 atm; 2 = 200 atm.

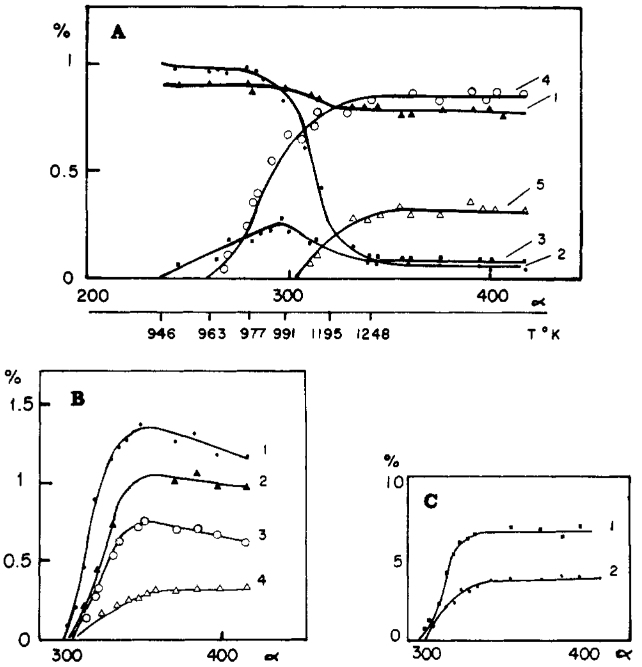

Figure 4. Yield of products as a function of compression ratio α in the adiabatic oxidation of methane.[23] A: 1 = $CH_4 \times 10^{-2}$; 2 = $O_2 \times 10^{-1}$; 3 = CH_2O; 4 = CH_3OH; 5 = $C_2H_5OH \times 10$. B: 1 = C_2H_6; 2 = C_2H_4; 3 = C_2H_2; 4 = $C_3H_6 \times 10$. C: 1 = CO; 2 = H_2.

pression. Their results are showing Figure 4. Other products analyzed for were H_2, C_2H_6, C_2H_4, C_2H_2, and C_3H_6. These products are shown as a function of compression ratio in Figures 5 and 6. The authors concluded that the methanol and formaldehyde were formed by the following reactions:

$$CH_3O\cdot + CH_4 \rightarrow CH_3OH + CH_3\cdot$$

$$CH_3\cdot + O_2 \rightarrow CH_3OO\cdot$$

$$CH_3OO\cdot + CH_4 \rightarrow CH_3OOH + CH_3\cdot$$

$$CH_3OOH \rightarrow CH_3O\cdot + \cdot OH$$

$$CH_3OO\cdot \rightarrow CH_2O + \cdot OH$$

The thermodynamics of the oxidation of alkanes to alcohols[24] showed that lower temperatures favored alcohol formation.

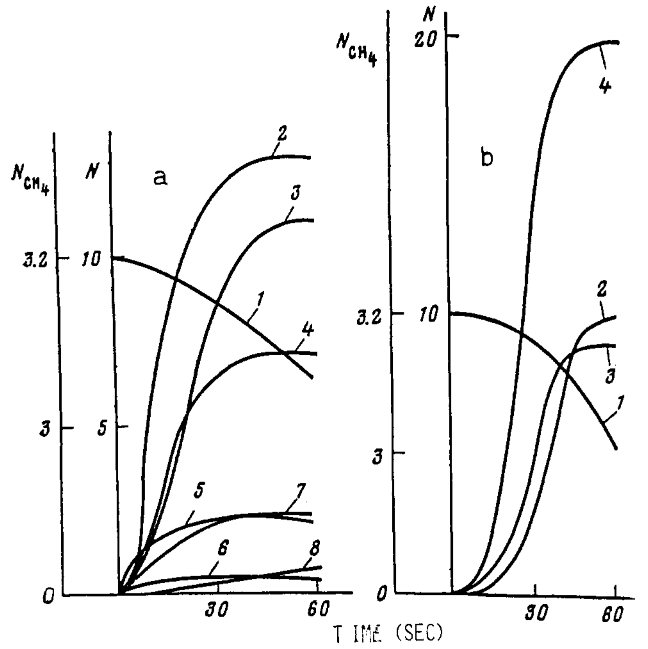

Figure 5. Calculated (a) and experimental (b) kinetic curves of the consumption of 1 = CH_4 and accumulation of 2 = $HO_2\cdot$, 3 = H_2O_2, 4 = CH_2O, 5 = CH_3OOH, 6 = $CH_3O_2\cdot$, 7 = $CH_3\cdot$, and 8 = CH_3OH for C (particles/cm^3):[53] (1) $N \times 10^{18}$; (2) $N \times 10^{12}$; (3), (4), and (8) $N \times 10^{15}$; (5) $N \times 10^{14}$; (6) and (7) $N \times 2 \times 10^{12}$ (the calculation was carried out without variations of the rate constants, and the experiment was carried out at 738 K in a reactor treated with boric acid).

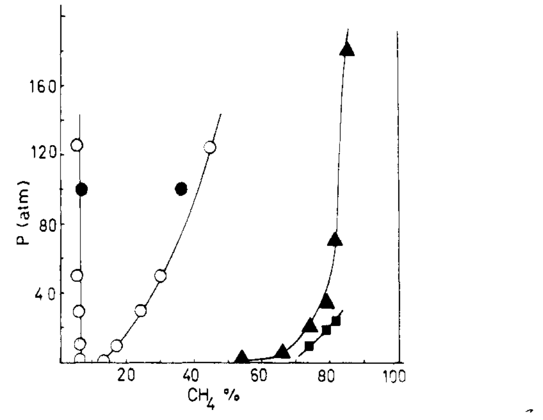

Figure 6. Explosion limits for CH_4 with air (circles) and O_2 (triangles) at 20 °C and for CH_4 with O_2 at 300 °C (squares). Open symbols are from ref 65 and filled symbols are from ref 66.

D. Surface Effects

The effect of HF treatment of the glass walls of reactors in static, low-pressure system[25] was to lower the rates of oxidation and to bring the methanol yields down to values closer to those of formaldehyde. The plot of $R_{CH_3OH}/R_{CH_2O}[CH_4]$ against $1/T$ gave an activation energy difference of about 20 kcal/mol for the two proposed reactions:

$$CH_3O\cdot + CH_4 \xrightarrow{k_A} CH_3OH + CH_3\cdot$$

$$CH_3O\cdot \xrightarrow{k_F} CH_2O + H\cdot$$

$$E_F - E_A = 20 \text{ kcal}$$

Though much has been written about the effect of surfaces in the oxidation reactors on the conversion of methane or methanol,[13,26-30] very little has been reported concerning the effects of specific catalysts on the yield of methanol. The work of Boomer quoted earlier seems to be the single major contribution in the field.[19,20]

III. Recent Work

A. General Discussion

The spontaneous ignition of methane–air mixtures at high pressure was studied by Melvin in 1965.[31,32] The activation energy for both the ignition delay and the rate of the slow reaction preceding the explosion ranged from 39 to 45 kcal/mol. The products detected during the ignition delay included H_2, CO_2, methanol, and formaldehyde together with minute amounts of ethane and ethylene. Carbon monoxide did not appear during the ignition delay time. The reaction was studied at pressures from 58 to 110 atm and at an initial temperature of about 350 °C. The activation energy for the reaction in the initial stage of the explosion was 20–25 kcal/mol. Explosion products included relatively large amounts of hydrogen and ethane indicating that the reaction mixture was dominated by hydrogen atoms. The hydrogen atoms were possibly formed by the following reaction:

$$\cdot OH + CO \rightarrow CO_2 + H\cdot$$

However, since hydrogen appears before carbon monoxide, it is more probably that the following reaction is the initial source of the hydrogen atoms:

$$\cdot OH + H_2 \rightarrow H_2O + H\cdot$$

The partial oxidation of methane at pressure up to 13 000 atm (200 000 psi) was studied in a static system by Lott whose Ph.D. Thesis[33] constitutes an excellent review of the subject to 1965. At 3500 atm (50 000 psi) and at the initial temperature of 262 °C the yield of methanol was 40% for a residence time of about 10 min. The methane reacted was 6.3% whereas 95.2% of the oxygen was consumed for the initial ratio of $CH_4/O_2 = 10$. Other products analyzed for were formic acid, formaldehyde, and methyl formate, as well as CO and CO_2. Cool flame phenomenon was observed at 3300 atm (48 000 psi) and 262 °C. A portion of Lott's thesis has been published.[34]

At this time Knox reviewed the low-temperature oxidation of hydrocarbons in the gas phase.[35,36] Hoare and co-workers also reported on the relative rates of reaction of OH radical with methane and various intermediates. However, the formation of methanol was not reported.[37]

The low-temperature, low-pressure oxidation of hydrocarbons has been summarized by Antonik and Lucquin[38] who, by means of four interrelated mechanisms, attempted to account for explosion, cool flame, and slow oxidation reactions. The same authors studied[39] the oxidation of methane at 440 °C and 700 torr. They showed that methanol, formaldehyde, and hydrogen peroxide all pass through maxima at between 5 and 10 min reaction time. In the presence of 0.2% hydrogen bromide the maxima shifts down to 2 min of reaction time with the absolute amount depending on the methane/oxygen ratio.

The following reactions were proposed to explain the observed results:

$$CH_4 + O_2 \rightarrow \cdot CH_3 + HO_2\cdot$$
$$\cdot CH_3 + O_2 \rightarrow CH_3O_2\cdot$$
$$CH_3O_2\cdot \rightarrow CH_2O\cdot + \cdot OH$$
$$\cdot OH + CH_4 \rightarrow \cdot CH_3 + H_2O$$
$$CH_3O_2\cdot + CH_2O \rightarrow CH_3OOH + HCO\cdot$$
$$HCO\cdot \rightarrow H\cdot + CO$$
$$CH_3OOH \rightarrow CH_3O\cdot + \cdot OH$$
$$CH_3O\cdot + CH_4 \rightarrow CH_3OH + \cdot CH_3$$

In the presence of HBr additional reactions may also occur as follows:

$$HBr + O_2 \rightarrow HO_2\cdot + \cdot Br$$
$$\cdot Br + CH_4 \rightarrow HBr + \cdot CH_3$$
$$CH_3OO\cdot + HBr \rightarrow CH_3OOH + Br$$

On the basis of the ratio of products at maximum yield, the authors concluded that the methanol is formed from the $CH_3O\cdot$ which originates from the $CH_3OO\cdot$ and that the presence of an abstractable hydrogen in formaldehyde or HBr favors the reaction. This overall mechanism is inconsistent with high-pressure results where formaldehyde is not present.

The partial oxidation of methane in a flow system at atmospheric pressure and over a temperature range of 450–700 °C was studied under a variety of conditions. Though formaldehyde and hydrogen peroxide were detected the production of methanol was not reported.[40,41]

The oxidation of methane in the presence of low concentrations of chlorine, representing from 0.2 to 0.8% of the reaction mixture, showed a decrease in the induction period of the reaction at 440 °C and 700 torr for stoichiometric oxygen–methane mixtures. In general, the yields of methanol and hydrogen peroxide were larger in the absence of chlorine whereas formaldehyde was unaffected by chlorine at high methane concentrations and increased in the presence of chlorine at lower methane concentrations. The formation of performic acid was considered a key step in the oxidation process.[42]

The difference between the effect of HBr and Cl_2 (or HCl) is attributed to the stronger bond energy for HCl than HBr. Therefore HCl cannot act as a H donor.

The oxidation of methane in a static system at 700 torr and in stoichiometric methane–oxygen mixtures has been studied.[43] The yield of methanol as a function of reaction temperature and time was examined over the temperature range of 400 to 472 °C. The methanol yield as a function of reaction time passed through a maximum which increased and broadened as the temperature decreased. The effect of pressure on the methanol yield was studied at 445 °C using the same stoichiometric methane–oxygen mixture. As the pressure dropped from 700 to 200 torr, the maximum in the yield of methanol dropped and shifted to longer reaction time. The results were interpreted in terms of reactions which have previously been proposed and which included the performic acid radical which is formed by the reaction

$$HCO\cdot + O_2 \rightarrow HCO_3$$

and which reacts according to

$$HCO_3 + H_2CO \rightarrow HCO_3H + HCO$$

$$HCO_3H \rightarrow HCO_2\cdot + \cdot OH$$

$$HCO_2\cdot \rightarrow H\cdot + CO_2$$

$$HCO_3\cdot \rightarrow \cdot CO_3H \rightarrow CO + HO_2\cdot$$

Though some of these reactions have been previously proposed for other systems, their role in methane oxidation must be questioned.

The French workers have extended their studies[44] to include a recirculating system for the oxidation of methane as well as a study of the effect of N_2 and NO on the reactions. Increasing NO (0.05–0.5%) in a static system at 620 °C showed a slight increase in the maximum rate of formation of formaldehyde (0.9–1.25%) but the yield based on CH_4 consumed decreased (22.5–15%). The effect of NO on methanol formation was not reported. Nitrogen (12–63%) increased the yields of CH_2O (7–10.5%) as well as its maximum rate of formation (0.55–0.80%). Nitrogen had little effect on the yield of methanol.

A study of the high-pressure, static oxidation of methane was reported for the pressure range of 1700–3400 atm using a mixture of 92% methane and 8% oxygen.[45] Products analyzed for were carbon monoxide, carbon dioxide, formaldehyde, water, methanol, ethanol, and formic acid. Hydrogen and hydrogen peroxide were not detected. In some cases small quantities of acetone were found in the liquid product. The temperature range covered in this study was from 270 to 480 °C with residence times of approximately 30 min. At 290 °C and 1700 atm all products increased with an increase in residence time from 15 to 60 min. The yield of water and carbon dioxide seemed to be affected most.

B. Mechanisms

A study[46] of the formation of methanol during the gas-phase oxidation of methane at 456 °C in a static system under atmospheric conditions was reported for the methane–oxygen ratios of 9/1, 4/1, and 2/1. Maximum methanol yields of about 20% were obtained for reaction times of 200 and 300 s in the cases of the 4/1 and 9/1 ratios. The 2/1 mixture gave a maximum methanol yield of approximately 12% at a reaction time of 200 s.

The additional reactions proposed to account for the results are as follows:

$$2CH_3O_2\cdot \rightarrow 2CH_3O\cdot + O_2$$

$$2CH_3O\cdot \rightarrow CH_3OH + CH_2O$$

$$CH_3O\cdot + O_2 \rightarrow CH_2O + HO_2\cdot$$

$$CH_3O\cdot + CH_4 \rightarrow CH_3OH + CH_3\cdot$$

$$CH_3O\cdot + CH_2O \rightarrow CH_3OH + CHO\cdot$$

$$CH_3O\cdot + M \rightarrow CH_2O + H\cdot + M\cdot$$

In a series of six papers, Karmilova, Enikalopyan, and Nalbandyan[47-52] have examined the kinetics and mechanism of methane oxidation. Stoichiometric ratios of CH_4 to O_2 were used at subatmospheric pressures over the temperature range of 423–513 °C. Products reported were CO, CO_2, H_2, H_2O_2, H_2O, CH_2O, and CH_3OH. The induction period had an activation energy of 36 kcal/mol—about 7 kcal/mol less than that of the consumption of CH_4. Maximum yields of hydrogen peroxide were similar to those of CH_2O—the ratio of H_2O_2/CH_2O being 1.6 at 400 °C and 0.4 at 500 °C. The H_2O_2 was believed to form from the CH_2O which had an activation energy of formation of 7.8 kcal/mol.

By including the following additional reaction scheme the authors[49] showed an excellent agreement between the calculated and experimental kinetic parameters.

$$CH_4 + O_2 \rightarrow CH_3\cdot + HO_2\cdot$$

$$CH_3\cdot + O_2 \rightarrow CH_2O + \cdot OH$$

$$CH_4 + \cdot OH \rightarrow CH_3\cdot + H_2O$$

$$CH_2O + \cdot OH \rightarrow HCO\cdot + H_2O$$

$$CH_2O + O_2 \rightarrow HCO\cdot + HO_2\cdot$$

$$HCO\cdot + O_2 \rightarrow CO + HO_2\cdot$$

$$CH_4 + HO_2\cdot \rightarrow CH_3\cdot + H_2O_2$$

$$HO_2\cdot + CH_2O \rightarrow H_2O_2 + HCO\cdot$$

The effect of H_2O_2 (0.1–0.4%) and H_2O on the reaction kinetics was studied at 423–491 °C. The H_2O_2 decreased the induction period as the formation of OH· starts the chain reaction via

$$CH_4 + \cdot OH \rightarrow CH_3\cdot + H_2O$$

Water (up to 6%) had no effect on the induction period at the higher temperatures (472–513 °C). However, at lower temperatures a slight effect was noted. The reaction

$$CO + \cdot OH \rightarrow CO_2 + H\cdot$$

was proposed[51,52] as an important step accounting for CO_2 formation.

Nalbandyan and co-workers[53] have recently used computer modeling to calculate the product profile for the thermal oxidation of methane. The reactions used and their corresponding rate constants are given in Table IV.

A comparison between the calculated and experimental results for 465 °C where reaction 13′ from Table IV is omitted is shown in Figure 5.

The calculated maximum rate of 50 s agrees with the experimental results but the calculated yields for H_2CO, CH_3OOH, and CH_3OH were much lower than observed. Variation of the values of k_4, k_{12}, k_{14}, k_{17}, k_{23} and k_0 had an appreciable affect on the kinetics. Modified values of (k') the rate constants were $k_4' = 3k_4$, $k_{14}' = 5k_{14}$, $k_{17}' = 5k_{17}$, $k_{23}' = 2k_{23}$, $k_0' = 1/100k_0$, and $k_{12}' = {}^1/_3k_{12}$.

Increasing k_{14} further by a factor of 3 brought the calculated value for CH_3OH to within a factor of 1.8 of the experimental yield. The omission of reaction 7 or increasing its value 10 times did not alter the calculated yields. Similar results were obtained when reactions 13, 16, 20, and 24 were omitted. Including reaction 13′ or increasing its value to 10^{-11} did not improve the results. On the other hand, reactions 10, 11, 12, and 25 were shown to be essential to the overall reaction scheme. It would be most appropriate to examine this model in terms of increasing pressure to determine the fate of the methanol.

Though several other choices can be made for some of the rates, it must be noted that the computer modeling is instructive and it is hoped that some high-

TABLE IV. Reactions and Rate Constants for Methane Oxidation[a]

(0) $CH_4 + O_2 \rightarrow \cdot CH_3 + HO_2\cdot$	$k_0 = 10^{-10} \exp(-55000/RT)$
(1) $\cdot CH_3 + O_2 \rightarrow CH_3O_2\cdot$	$k_1 = 4 \times 10^{-13}$
(1′) $CH_3O_2\cdot + M \rightarrow \cdot CH_3 + O_2 + M$	$Mk_i = 10^{14} \exp(-26000/RT)$
(2) $CH_3O\cdot + O_2 \rightarrow CH_2O + HO_2\cdot$	$k_2 = 5 \times 10^{-14}$
(2′) $CH_3O\cdot \rightarrow CH_2O + H\cdot$	$k_{2'} = 10^{13} \exp(-30000/RT)$
(3) $CH_4 + \cdot OH \rightarrow \cdot CH_3 + H_2O$	$k_3 = 10^{-10} \exp(-8500/RT)$
(4) $CH_4 + HO_2\cdot \rightarrow \cdot CH_3 + H_2O_2$	$k_4 = 10^{-10} \exp(-23000/RT)$
(5) $CH_2O + \cdot OH \rightarrow \cdot CHO + H_2O$	$k_5 = 1.6 \times 10^{-10.1} \exp(-2500/RT)$
(6) $CH_2O\cdot + HO_2\cdot \rightarrow \cdot CHO + H_2O_2$	$k_6 = 1.9 \times 10^{-11} \exp(-13000/RT)$
(7) $CH_2O + O_2 \rightarrow \cdot CHO + HO_2\cdot$	$k_7 = 7.5 \times 10^{-11} \exp(-41000/RT)$
(8) $CHO\cdot + O_2 \rightarrow CO + HO_2$	$k_8 = 10^{-13}$
(9) $H_2O_2 + M \rightarrow 2OHc + M$	$k_9 = 2.83 \times 10^{-7} \exp(-46300/RT)$
(10) $CH_3O_2\cdot + CH_4 \rightarrow CH_3OOH + \cdot CH_3$	$k_{10} = 10^{-10} \exp(-19700/RT)$
(11) $CH_3O_2\cdot + CH_2O \rightarrow CH_3OOH + \cdot CHO$	$k_{11} = 10^{-13}$
(12) $CH_3OOH \rightarrow CH_3O\cdot + \cdot OH$	$k_{12} = 10^{12.65} \exp(-40500/RT)$
(13) $CH_3O_2\cdot + HO_2\cdot \rightarrow CH_3OOH + O_2$	$k_{13} = 1.6 \times 10^{-11.5}$
(13′) $CH_3O_2\cdot + CH_3O_2\cdot \rightarrow 2CH_3O\cdot + O_2$	$k_{13'} = 1.75 \times 10^{-13}$
(14) $CH_3O\cdot + CH_4 \rightarrow CH_3OH + \cdot CH_3$	$k_{14} = 10^{-12.2} \exp(-11000/RT)$
(15) $CH_3O\cdot + CH_2O \rightarrow CH_3OH + \cdot CHO$	$k_{15} = 1.6 \times 10^{-14.4} \exp(-3000/RT)$
(16) $CO + \cdot OH \rightarrow CO_2 + \cdot H$	$k_{16} = 1.6 \times 10^{-12.5} \exp(-810/RT)$
(17) $CO + HO_2\cdot \rightarrow CO_2 + \cdot OH$	$k_{17} = 2.2 \times 10^{-10} \exp(-23000/RT)$
(18) $H\cdot + CH_2O \rightarrow H_2 + \cdot CHO$	$k_{18} = 1.6 \times 10^{-10.08} \exp(-4330/RT)$
(19) $H\cdot + CH_4 \rightarrow H_2 + \cdot CH_3$	$k_{19} = 5 \times 10^{-9} \exp(-11900/RT)$
(20) $H\cdot + O_2 + M \rightarrow HO_2\cdot + M$	$k_{20} = 10^{-32}$
(21) $HO_2\cdot \xrightarrow{\text{wall}} {}^1/_2H_2O + {}^3/_4O_2$	$k_{21} = 1$
(22) $HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$	$k_{22} = 4 \times 10^{-12}$
(23) $H_2O_2 \xrightarrow{\text{wall}} H_2O + {}^1/_2O_2$	$k_{23} = 0.1$
(24) $OH\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot$	$k_{24} = 1.7 \times 10^{-11} \exp(-1820/RT)$
(25) $CH_3OOH \xrightarrow{\text{wall}} CH_2O + H_2O$	$k_{25} = 0.1$
(26) $CH_3OO\cdot \xrightarrow{\text{wall}} CO + H_2O + {}^1/_2H_2$	$k_{26} = 0.84$
(27) $H\cdot + CH_3OH \rightarrow H_2 + \cdot CH_2OH$	$k_{27} = 1.6 \times 10^{-11.88} \exp(-8500/RT)$
(28) $HO_2\cdot + CH_3OH \rightarrow H_2O_2 + \cdot CH_2OH$	$k_{28} = 10^{-12} \exp(-11500/RT)$
(29) $\cdot CH_2OH + O_2 \rightarrow CH_2O + HO_2\cdot$	$k_{29} = 1.6 \times 10^{-11} \exp(3900/RT)$
(30) $\cdot CH_3 \xrightarrow{\text{wall}} {}^1/_2C_2H_6$	$k_{30} = 100$
(31) $\cdot CH_3 + \cdot CH_3 \rightarrow C_2H_6$	$k_{31} = 3 \times 10^{-11}$

[a] Rate constant units are in s^{-1}, cm^3/molecule s, and cm^6/molecule^2 s for first-, second-, and third-order reactions, respectively. R units are cal/mol.

pressure calculations will be made soon to add to the selection of relevant reactions.

Lunsford and co-workers have developed a new process for the oxidation of methane to give methanol and formaldehyde using N_2O as an oxidant. The MoO_3/SiO_2 catalyst for the process was prepared by the equilibrium adsorption method from an aqueous solutions of $(NH_4)_6Mo_7O_{24}$ at a pH of 11. While the initial results[54] were very promising, the recent work[55] by Lunsford's group has not been able to duplicate those results. In general, with conversions of several percentages the total selectivity toward HCHO and CH_3OH varied between 0.78 and 1.0 with the HCHO to CH_3OH ratio being about 4.

Commercial interest in the conversion of methanol to formaldehyde is well established. The patent literature seems to have anticipated the scientific literature. Two Canadian patents[56,57] were filed in 1928, and, though claiming all types of catalysts, no detailed experimental conditions were given. A later patent[58] continued to stress catalysts such as copper gauze with zinc chromate. In this patent high yields of formaldehyde along with methanol were claimed. Two recent patents[59,60] have been issued for the controlled oxidation of methane to methanol–formaldehyde mixtures. Brockhaus[59] obtained high yields (H_2CO = 47.5% and CH_3OH = 71.1%) with up to 45% conversion of methane by a medium-pressure (8–60 atm) flame with a residence time of 1.08×10^{-3} to 1.76×10^{-3} s. The H_2CO and CH_3OH produced were dissolved in water. When oxygen was used instead of air, the 60–80% CH_4 in the waste gas was recycled. The second patent[60] describes a thermal oxidation at 300–600 °C at 5 atm with velocities of 1–15 m/s for CH_4 and 75–250 m/s for O_2. Combined yields of 91% for H_2CO and CH_4OH were obtained.

Recently Koenig[61] of Wesseling, West Germany, revealed in a patent application (DOS s.101.024, 1982) that methane could be converted to methanol with 92% selectivity in the liquid phase (aqueous solution of $Fe_2(SO_4)_3$, pH 1.0) using Pd–Ag alloy (0.6 wt %) on graphite. Optimal reaction conditions are T = 20–30 °C and P = 30–60 bar. The reoxidation of Fe^{II} to Fe^{III} is conducted in a separate reactor with air at 130–170 °C and 6–10 bar of pressure.

In an attempt to optimize the yield of methanol, Morton, Hunter, and Gesser have studied the high-pressure oxidation of CH_4 in a flow system as a function of pressure, temperature, reaction time, and CH_4/O_2 ratio.[62] The optimum yield of methanol (81%) was obtained at 50 atm at 450 °C with a flow rate of 36 mL (NTP)/min and CH_4/O_2 ratio of 20. The conversion under these conditions was estimated to be about 8%. At 125 atm using added nitrogen as an internal standard it was possible to obtain a good (about 95–98%) material balance for carbon but the material balance for oxygen showed an excess of oxygen in the products.

The above results were obtained by premixing the O_2 and CH_4. When separate gas flows were used and blended just before entering the reactor, inconsistent results were obtained due to the difficulty of obtaining uniform mixing at high pressures. This problem could account for the divergence in results obtained by previous workers.

TABLE V. Summary of Methane to Methanol Conversion

ref	operating temp, range, °C	operating press range, atm	residence time, min	oxygen concn, %	methanol yield, %	remarks[a]
Newitt and Haffner[8]	360–393	50–150	1–100	11	22	S
Richler and Reder[9]	350	160		10	14.8	S
	500	100	0.17	10–0.6	2.4–60	F
	100–250	160		10	9–1	explosive oxidation flow
Newitt and Szego[10]	400–430	50	0.08–0.5	3–5	51.0 max	F
Wiezevich and Frolich[11]	390–500	135		3–8.1	3.7–6.2	F
Boomer et al.[17–19]	320–425	140–230	0.01–0.025	3.66–12.0	16–54 74 max	F
Lott[33,34]	262	100–3500	4–140	9	15–26 36.5 max	S
Luckett and Mile[46]	456	1	3–5	10–30	12–20	S
Hunter, Gesser, and Morton[62]	450	50–125	10–205	5–20	30–81	F

[a] S = static. F = flow.

IV. Conclusions

A. Effect of Temperature, Pressure, Oxygen Concentration, and Residence Time

On the basis of the available data from some of the references cited in this review, the effect of reaction conditions on methanol yield is summarized in Table V. The wide range of operating conditions employed by various researchers provide only a general trend from this comparison. Within the range of the variables reported in Table V, the conversion of methane to methanol is favored by high pressure, high temperature, and low oxygen concentration. The residence time, which primarily depended on the experimental system used, does not seem to have a significant affect on methanol yield.

B. Effect of Catalysts and Presence of Higher Hydrocarbons

Metal surfaces, such as nickel, copper, silver, steel, and certain alloys, seem to have a catalytic effect on the oxidation reaction of methane to methanol. A systematic study to ascertain the effect of various catalysts on methanol yield would be of considerable value.

The presence of higher hydrocarbons, especially ethane, in small quantities seems to have a favorable influence on the oxidation of methane to methanol. However, the exact mechanism by which ethane improves the methanol yield has not been investigated. The finding will be of special interest for oxidation processes in which natural gas instead of methane is used as a feedstock for methanol production.

C. Need for Future Work

Most of the work on the oxidation of methane performed in the past was aimed at elucidating the reaction mechanism during oxidation. It was of special interest at that time since free radicals had just been introduced as reactant intermediates in oxidation and decomposition reaction. Obviously no effort was made to optimize the production of methanol.

In the new context of alternative transportation fuels[63,64] the direct oxidation reaction of methane should be reexamined as a process to commercially produce methanol. Future work in this area should therefore address all aspects for optimizing methanol production. This would include the determination of optimum operating conditions (pressure, temperature, residence time, CH_4/O_2 ratios), effect of the presence of other hydrocarbons (ethane, propane etc), and the catalytic effect of various substances. Research should also be directed toward improving product selectivity. The presence of an easily abstractable hydrogen greatly increases the yield of methanol from the methoxy radical. The energetics of the various intermediate reactions would help locate optimum conditions for methanol conversion. In addition, computer modeling can be used to study the sensitivity of the mechanism to determine the reactions which are most significant for methanol formation. Finally, one problem which must be resolved before higher conversions can be attained by increasing the O_2 level is the onset of explosions. The explosion limits vary with pressure, temperature and nitrogen concentration. Figure 6 shows some of the available[65,66] data. There seems to be no results available for natural gas with air or oxygen at high pressures and elevated temperatures. Such a study is essential if any further progress is to be made on this subject.

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Registry No. CH_4, 74-82-8; CH_3OH, 67-56-1.

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