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3 RESEARCH AND DEVELOPMENT STUDY

RELATED TO THE SYNTHESIS OF

FORMALDEHYDE FROM CO<sub>2</sub> and H<sub>2</sub> 4

GARD Project 1416

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SYNTHESIS OF FORMALDEHYDE

1. Introduction

This report summarizes the activities of the General American Research Division during August through October, 1966 on Contract NAS2-3889, Synthesis of Formaldehyde. The activities during this period were concerned with (1) general survey of the published abstracts of literature pertaining to the synthesis of formaldehyde (2) a review of methods for the synthesis of formaldehyde and their suitability for space applications (3) detailed literature survey on the oxidation of methane to formaldehyde.

2. General Survey of the Abstracts of Literature Pertaining to the Synthesis of Formaldehyde

A literature search on the synthesis of formaldehyde was initiated with a general survey of published abstracts and reviews. The general subject headings used in all phases of the literature search were:

1. Formaldehyde: formation, production, manufacture, catalysts and catalytic processes, polymerization, separation, analysis, kinetics and mechanism;
2. Methane: oxidation, formaldehyde from, catalysis - catalytic processes, uses, products, reactions of, methanol from, formic acid from;
3. Methanol: formation, preparation, manufacture, synthesis, formaldehyde from, reactions of, electrolysis;
4. Oxides of carbon: reduction, hydrogenation, catalysis - catalytic processes, formation of formaldehyde, methanol, formic acid.

The following publications were examined and abstracts of pertinent papers were obtained from them:

- (a) Chemical Abstracts
- (b) U.S. Patent Index and the Official Gazette of the U. S. Patent Office
- (c) Technical Announcement Bulletin (TAB), and Technical Abstract Bulletin (TAB), published by the Defense Documentation Center (DDC)
- (d) Scientific and Technical Aerospace Reports (STAR), and Technical Publication Announcements (TPA), published by the National Aeronautics and Space Administration (NASA)
- (e) International Aerospace Abstracts (IAA), published by the American Institute of Aeronautics and Astronautics (AIAA)
- (f) Nuclear Science Abstracts (NSA), published by the Atomic Energy Commission (AEC)
- (g) U.S. Government Research Reports (U.S.G.R.R.), published by the Commerce Department, Office of Technical Services (OTS), and U.S. Government Research and Development Reports (U.S.G.R.D.R.) and Government Wide Index of Research and Development Reports (G.W.I. R.D.R.), published by the Clearinghouse of Federal Scientific and Technical Information (C.F.S.T.I.)
- (h) Monthly Catalog of U.S. Government Publications, published by the Superintendent of Documents, U. S. Government Printing Office (U.S. G.P.O.)
- (i) Chemical Reviews
- (j) Warden, E.C., "Chemical Patents Index", Chemical Catalog Co., New York, N.Y., 1927

- (k) Kirk, R.E. and Othmer, D.F., "Encyclopedia of Chemical Technology",  
Vol. 6, The Interscience Encyclopedia, Inc., New York, N.Y., 1951
- (l) Ulmanns Encyklopädie der technischen Chemie, 2nd Ed., Urban and  
Schwarzenberg, Berlin, 1929
- (m) Ulmanns Encyklopädie der technischen Chemie, 3rd Ed., Urban and  
Schwarzenberg, München - Berlin, 1956
- (n) Beilsteins Handbook der organischen Chemie, 4th Ed., Friedrich  
Richter, Drittes Ergänzungswerk, Springer Verlag, Berlin, 1960
- (o) Walker, J. F., "Formaldehyde", 3rd Ed., Reinhold Publishing  
Corp., New York, N.Y., 1964
- (p) Miscellaneous publications, periodicals, books, etc.

The abstracts and reviews obtained from the above sources were carefully reviewed and the information categorized according to the reactions for systematic evaluation; final selection was made of those publications which were to be obtained in complete form.

### 3. Review of Methods for the Synthesis of Formaldehyde

Literature reveals essentially three possible routes for the synthesis of formaldehyde from  $\text{CO}_2$  and  $\text{H}_2$ , namely, direct formation of formaldehyde, formation of methanol with subsequent conversion to formaldehyde, and production of methane which can be then oxidized to formaldehyde. Commercially, most of the formaldehyde is produced by the oxidation of methanol; some of the formaldehyde, particularly in the European countries, is obtained from the oxidation of methane and other hydrocarbons. However, successful commercial methods are not necessarily the most suitable for space applications.

Therefore, it is important to consider the advantages and the disadvantages of each method in the light of space conditions and limitations.

(a) Direct synthesis of formaldehyde from  $\text{CO}_2$  (or  $\text{CO}$ ) and  $\text{H}_2$ . Because of its direct, one step reaction, this method is very attractive. The formation of formaldehyde from carbon oxides and hydrogen is thermodynamically unfavorable and requires high pressures to proceed at all. Fischer<sup>(1)</sup> calculated that pressures of  $10^3$  to  $10^4$  atmospheres would be required to obtain practically acceptable formaldehyde yields ranging from 1.6 to 13 mol % of the carbon oxide. Although there are claims, particularly in the older literature, of catalysts and processes leading to direct production of formaldehyde from carbon oxides, there has never been any industrially developed process. In fact, Neuman and Biljcevic<sup>(2)</sup> reinvestigating all these claims could not find any of practical value. It seems that because of the very high pressures needed, even if suitable catalysts could be found, this reaction would be difficult to apply to space conditions.

(b) The methanol route is a two step operation where the carbon oxides are first converted to methanol which is then oxidized to formaldehyde. The conversion of methanol to formaldehyde is a rather easy process and is being used extensively for commercial production of formaldehyde. It involves passing a methanol vapor and air mixture over solid catalysts at essentially atmospheric pressure and absorbing the formaldehyde formed in water. The

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(1) F. Fischer, *Oel und Kohle* 39, 521 (1943)

(2) B. Neuman and Biljcevic, *Z. angew. Chemie* 40, 1469 (1927)

usual catalysts are silver, copper, or iron-molybdenum oxide. The reaction is run at temperatures of 450 - 600°C with yields of formaldehyde ranging from 83 to 92% of the methanol reacted. The process, if run under suitable conditions, produces practically no side reactions, the only products being formaldehyde, water, and unreacted methanol.

The investigation of the methanol route will be centered mainly on the formation of methanol from the carbon dioxide and hydrogen. The free energy of reaction is influenced both by temperature and by the pressure and high conversions can be obtained at elevated pressures. Several solid catalysts are being used for commercial production of methanol; however, most of them operate at high pressures, usually around 280 atmospheres. For instance, a ZnO catalyst containing 0.25%  $\text{Fe}_2\text{O}_3$  produces methanol at 300 - 325°C and 200 - 210 atm; a Cu- $\text{Al}_2\text{O}_3$  catalyst gives best results at 285 - 400 atm. pressures. Literature also indicates processes and catalyst claims which permit the conversion of  $\text{CO}_2$  to methanol at pressures only slightly above atmospheric.

(c) The carbon dioxide - methane - formaldehyde route is also a two-step process. The catalytic reduction of  $\text{CO}_2$  by  $\text{H}_2$  to form  $\text{CH}_4$ , however, is very well known and produces up to 99% conversion of  $\text{CO}_2$  to methane at moderate temperatures (357°F) and at atmospheric pressures using a ruthenium powder catalyst.<sup>(3)</sup> The oxidation of methane to formaldehyde has been the subject of numerous investigations using solid and gaseous catalysts, and non-catalytic devices. While the yields of formaldehyde are not as high as those obtained from the oxidation of methanol, the methane route has the advantage that the entire process can be carried out at atmospheric pressure.

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(3) G.A. Remus, R.W. Ferris, and J.D. Zeff, GATC Final Report, Contract AF 33(615)-1210, December 31, 1964.

Based on the general literature survey, it appears that the methane route may be the most suitable for space applications, primarily because the reactions proceed at atmospheric pressure thus avoiding high pressure equipment and operations which would cause additional weight and energy penalties. Therefore, the carbon dioxide - methane - formaldehyde process was selected to be investigated first and a detailed literature review has been made from the actual publications instead of the abstracts used in the general survey.

(d) The process of formaldehyde formation by first converting  $\text{CO}_2$  and  $\text{H}_2$  into formic acid and then obtaining formaldehyde either by reduction or decomposition of formic acid has not been investigated extensively. Catalysts, however, have been proposed both for the formation of formic acid and for its conversion to formaldehyde. At this time, it is unclear whether this process would be more advantageous than other methods.

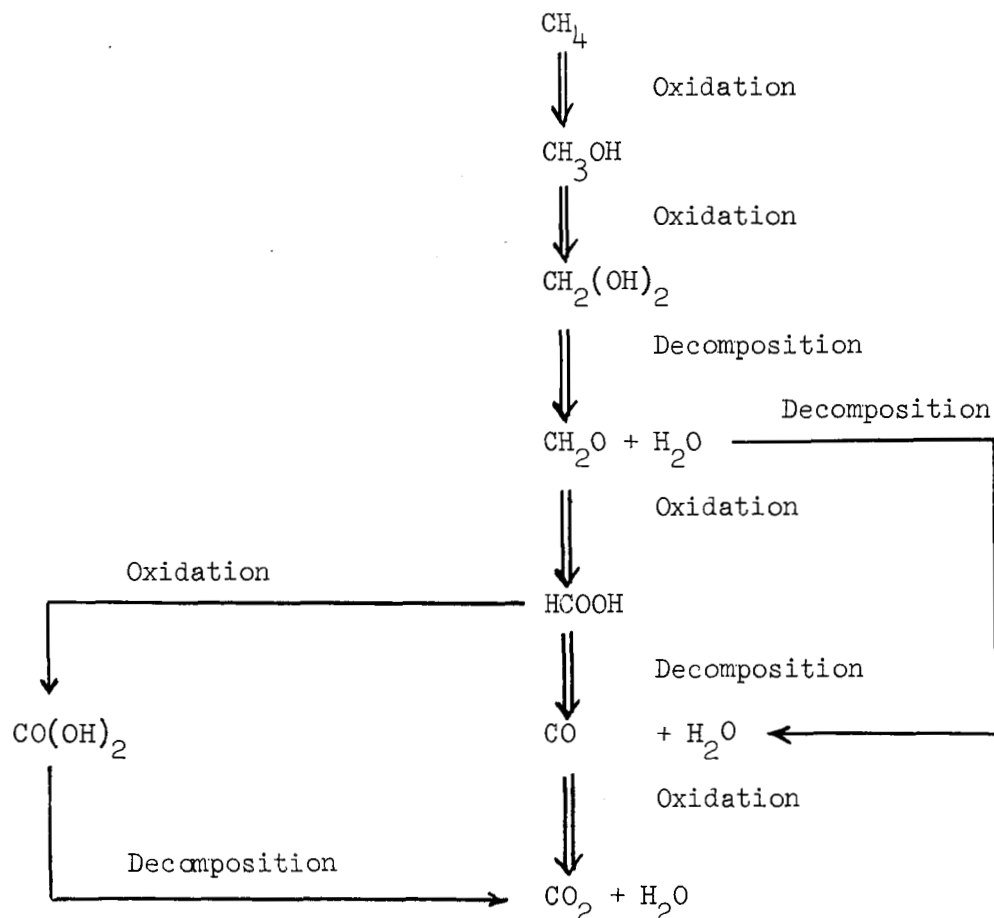
#### 4. Oxidation of Methane to Formaldehyde

##### (a) General

Based on the information obtained from various abstracts, copies of complete articles and publications pertaining to the oxidation of methane to formaldehyde were obtained for detailed study and review. Efforts were made to secure a collection, as complete as possible, of publications on the subject. Over 90% of all the U.S. and foreign articles and patents, mostly in their original languages, were obtained and evaluated. The remainder consist of either obscure publications generally not available in the U.S., articles which seemed to have little pertinence, or repeat patents issued in various countries but covering the same subject. It is interesting that most of the articles on

the oxidation of methane to formaldehyde have been published outside of the U.S., the early ones being mostly British or German, with the Russian publications accounting for more than one half of the published material after World War II.

The oxidation of methane is a complex reaction leading to a mixture of products whose composition depends on the reaction conditions. This variety of products is readily explained by the hydroxylation theory of Bone.<sup>(4)</sup> The course of the methane oxidation according to Bone's theory, as constructed by Wheeler and Blair<sup>(5)</sup> proceeds as follows:



(4) W. A. Bone and Drugman, J. Chem. Soc. 89, 676 (1906)

(5) Wheeler and Blair, J. Soc. Chem. Ind. 42, 81-92T (1923)



Double lines indicate the usual course of the oxidation; however,  $\text{CH}_2(\text{OH})_2$  and  $\text{CO}(\text{OH})_2$  have not been isolated. The difficulty in a complete acceptance of the hydroxylation theory was the failure of early investigators, conducting oxidation experiments mainly without the use of catalysts, to isolate any methanol. Later work<sup>(6)</sup> showed that, indeed, there was some methanol formed.

The experimental data on the formation of alcohol and formaldehyde and the kinetics of their oxidation accumulated in the literature raised the question whether Bone's theory represents a true picture of the methane oxidation; there seemed to be evidence that both formaldehyde and methanol may be produced simultaneously by parallel routes. As early as 1923, Berl and Fischer<sup>(7)</sup> showed that formaldehyde was formed directly from methane. Investigating the kinetics of the initial stages of the methane oxidation, Karmilova, Enikolopyan, and Nalbandyan<sup>(8)</sup> showed that formaldehyde and alcohol were formed together at the very start of the oxidation. Using carbon labeled compounds, and  $\text{NO}_2$  as a catalyst, Moshkina, Galanina, and Nalbandyan<sup>(9)</sup> found that formaldehyde and methanol formed by two parallel routes and showed that under conditions where the intermediate products reach stationary values, the rate of the formation of formaldehyde from the methane is nine times greater than the rate of formation of methanol. The methyl alcohol is oxidized

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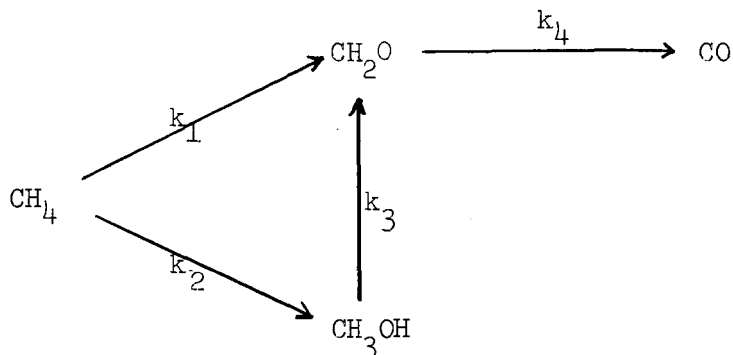
(6) Elworthy, Trans. Roy. Soc. Can. III, 16, 93 (1922)

(7) E. Berl and H. Fischer, Z. anorg. Chem. 36, 297 (1923)

(8) L.V. Karmilova, N. S. Enikolopyan, and A. B. Nalbandyan, Zhur. Fiz. Khim. 30, 798 (1956)

(9) R. I. Moshkina, N. L. Galanina, and A. B. Nalbandyan, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk. 1959, 1725

to formaldehyde which is oxidized further to give carbon monoxide. The results of this investigation may be represented by



where  $k_1 = 9 k_2$ ,  $k_2 = k_3$  and  $k_4 = k_1 + k_3$ . Thus, under given conditions a dynamic equilibrium is achieved where the rate of methane disappearance becomes equal to the formation of CO and the concentration of formaldehyde remains constant. Consequently, in a flow system, the concentration of formaldehyde in the product is increased by increasing its rate of formation and decreasing the rate of CO formation.

Numerous investigators have attempted to increase the yields of formaldehyde from the oxidation of methane by the use of heterogeneous or homogeneous catalysts, photochemical methods, electric discharge, and various combinations of these methods summarized in the following sections.

(b) Solid Catalysts

Table 1 summarizes processes for the formation of formaldehyde by the catalytic oxidation of methane using solid catalysts described in the literature. The descriptions of catalysts, conditions of reaction, and the amounts of formaldehyde formed, indicated in this and in subsequent Tables were expressed in the same manner as found in the literature. The proposed solid catalysts include many metals, metal oxides, and other mater-

ials which are general oxidation catalysts. In the presence of oxygen and at elevated temperatures, it is difficult to stop the oxidation at the formaldehyde stage; it has been shown that the process wherein methane and oxygen react in the presence of a catalytic surface is not only heterogeneous, but that a homogeneous process also occurs away from the catalyst surface.<sup>(10)</sup>

Most of the formaldehyde is formed on the catalyst surface, but some is formed in the gas phases. Some formaldehyde reacts further on the surface to form  $\text{CO}_2$ ; but an additional and possibly larger part can undergo oxidation by a chain reaction in the gas phase. It is conceivable that at high temperatures the solid catalyst or species adsorbed on its surface may act as chain reaction initiators. Therefore, it is thought<sup>(11)</sup> that even at short contact times the formaldehyde concentration in the product can increase only up to a certain limiting value. Generally, the concentration of formaldehyde in the product is low; overall production of formaldehyde can be increased by using recycle systems.

(c) Gaseous Catalysts

Processes utilizing gaseous catalysts, alone or in conjunction with solid catalysts, are listed in Table 2. The gaseous catalysts used include  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{HNO}_3$ ,  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{SO}_2$  and others; however, the most promising seem to be ozone and the nitrogen oxides. While single pass operation results in a low formaldehyde concentration, recycling increases

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(10) P.M. Stadnik and V.I. Gomonai, *Kinetika i Kataliz* 4 (3), 348 (1963)

(11) N.S. Enikolopyan and G.V. Koralev, *Doklady Akad. Nauk SSR* 118, 983 (1958)

the formaldehyde production considerably. The Guttehoffnungshutte process utilizing nitrogen oxide catalyst is being used on a pilot plant scale in Rumania.<sup>(12)</sup> A gas mixture consisting of 18% CH<sub>4</sub>, 9% O<sub>2</sub>, 68% N<sub>2</sub>, 3% CO, 1.6% CO<sub>2</sub> and containing 0.08% NO is recirculated through a tubular reactor at 600 - 620°C and contact time of 0.15 - 0.2 seconds. About 8% of the methane is converted into formaldehyde. A similar process is being used in the USSR producing 3000 tons/year of formaldehyde.<sup>(13)</sup>

The most promising appears to be the patent claim of the Hibernia process<sup>(14)</sup> utilizing a solid catalyst and ozonized oxygen or air. It is claimed that this process can convert up to 40% of the methane into formaldehyde. The advantages of this process are high conversion to formaldehyde, low operating temperature (106°C), ease of removal of the unreacted ozone, if any, from the product, and the absence of by-products.

(d) Miscellaneous Methods

Miscellaneous methods described for the production of formaldehyde are listed in Table 3. None of these methods, however, have achieved any significant success. The claims of formaldehyde production in the presence of an electric discharge may actually be due to the nitrogen oxides or ozone formed in the gas mixture.

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(12) N.S. Enikolopyan, N.A. Kleimenov, L.V. Karmilova, A.M. Markevich, and A.B. Nalbandyan, Zh. Prikl. Khim. 32, 913 (1959)

(13) S.F. Gudkov, Gazovaya Promischlennost 8, (9), 44 (1963)

(14) Ger.891, 687 (Oct. 1, 1953)

## 5. Future Activities

During the next quarter, the experimental set-up for the formation of formaldehyde from methane will be assembled and tested. The actual experimentation will be started by investigating etched quartz catalysts, ozone, nitrogen oxides, and then combinations of other solid and gaseous catalysts.

The experimental apparatus consists essentially of a vertical quartz tube surrounded by an electric heater which permits regulation of the temperature of the reaction zone. The tube can be used with either gaseous catalysts or solid catalysts. Solid catalysts will be tested in the tube by placing a support structure for the catalyst bed in the desired position. The metered reaction gases are admitted separately, preheated as required, and then passed through the reaction tube. The product gas stream is cooled rapidly to "freeze" the composition by blowing air over the bottom portion of the quartz tube extending below the heater. Sampling ports permit withdrawal of gases both from the reacting mixture and from the product for analysis. The gas mixture and the product will be analyzed by gas chromatographic methods. The entire system will be provided with thermocouples to measure inlet, catalyst bed, and outlet temperatures at various points in the system cross-section.

TABULAR LISTING OF REFERENCES AND CATALYSTS

Table 1. OXIDATION OF METHANE USING SOLID CATALYSTS

No. Abstract	Reference		Publication	Catalyst	Conditions		Formaldehyde Produced	Remarks
	Author	2			Temp., °C Pressure	Feed Composition		
1								
1	CA 2, 2979	M.C. von Unruh	U.S. 891,753 (June 23, 1908)	Tan bark	30 - 50	CH <sub>4</sub> or natural gas, air		
2	CA 10, 1911	Verein für chem. Ind. in Mainz	Ger. 286,731 (August 24, 1915)	Cu, Ag, or both	150 - 200	3 parts CH <sub>4</sub> and 100 parts moist air	A portion of CH <sub>4</sub> is conv. to CH <sub>2</sub> O	Mixture of formaldehyde, methanol, and formic acid is obtained.
3	CA 20, 970	K. Kaiser	Brit. 236,086 (October 17, 1924)	Cu, Fe, Mn, Cr oxides on pumice or other carriers				
4	CA 22, 2951	J.H. James	U.S. 1,675,029 (June 26, 1928) U.S. 1,941,010 (December 26, 1934)	Mo oxide	550	CH <sub>4</sub> and gas contg. O <sub>2</sub>		Gas velocity controlled to give partial oxidation products.
5	CA 23, 5308	E.H. Boomer	Can. 291,411 (July 16, 1929)	Unspecified	250 - 500	Natural gas; 1 g. mol. hydrocarbon mixed with 1 g. atom O		Conditions changed to favor desired oxygenated products.
6	CA 24, 5985	E.H. Boomer	U.S. 1,776,771 (September 30, 1930)	Pt, Pd, Cr, Mn, Fe, Cu, Ni, Au, Ag, oxides of Cu, Mn, Fe, Ni, V, Cr, Mo, Ce	60-300 atm			
7	CA 23, 846	J.C. Walker	Brit. 290,613 (May 17, 1927)					
7		G. Glock	Ger. 109,014 (1898)	Cu, pumice, asbestos	600	Equal volumes of CH <sub>4</sub> and air		
8		G. Hildebrandt	Ger. 214,155 (1906)	Bark	30 - 50	CH <sub>4</sub> , air, or oxygen		
9		Seliden	Brit. 170,022 (1921)	V <sub>2</sub> O <sub>5</sub>	500			
10		Wohl	Ger. 347,610 (June 23, 1916)	Vanadic or Molybdic acids				
11		F. Müller	Ger. 307,380 (March 26, 1916)	Cerous cobalt nitrate	150	CH <sub>4</sub> , air		
12		R. Hessen	Ger. 421,215 (December 9, 1922)	Porous pumice, brick, asbestos, quartz sand, slag wool	600 - 1000	CH <sub>4</sub> with excess air, oxygen, or ozonized air		Reaction temperature is below red heat.
13		Mittasch, Willforth, Balz	U.S. 1,487,020 (March 18, 1924)	P <sub>2</sub> O <sub>5</sub> or P <sub>2</sub> O <sub>5</sub> contg. materials	Above atmospheric			
14	CA 21, 2457	Medvedev	Trans. Karlov. Inst. Chem., No. 3, 54 (1924)	Glass surfaces, lead borates, lead phosphates	575	CH <sub>4</sub> , air or oxygen	5% of methane conv. to formaldehyde	Possible traces of chlorides in catalyst could account for relatively high conversion.

Table I Cont.

1	2	3	4	5	6	7	8
15	J.H. James	U.S. 1,588,836 (June 15, 1926)	Oxides of Mo, V, Mn, W, U, Cr, Ti, Zr, Th, Ag	550	CH <sub>4</sub> , air in ratio 1:1 but not over 1:3.5	6.75% based on weight of methane treated	Molybdic oxide is the most active catalyst
16	Medvedev	Trans. Karpov. Inst. Chem. No. 4, 117 (1925)	Phosphates or borates	600	CH <sub>4</sub> -26%, O <sub>2</sub> -26%, N <sub>2</sub> -8.7% H <sub>2</sub> -7%, HCl-0.13-0.3%	About 3% formaldehyde in the pro- duct gas	Higher conc. of HCl result in decrease of formaldehyde
17	R. Hasche (A.O. Smith Corp.)	U.S. 2,066,622 (1937)	Mo oxide, silica gel	415 - 500	C <sub>2</sub> H <sub>4</sub> , air	19.3 mg CH <sub>2</sub> O/l l. gas mixture	Partial oxidation to CH <sub>2</sub> O
18	S.S. Medvedev	Nat. Gases U.S.S.R. No. 4/5 29 (1932)	Iron borate, tin phosphate	600 - 610	CH <sub>4</sub> , air or O <sub>2</sub>		
19	H. Harter	Ger. 657,194 (1938)	Activated natural bleaching earths & silica gel, active C, Cu, Ag, Co, Mn		CH <sub>4</sub> , (air or O <sub>2</sub> )		
20	W. Bone, D. Newitt (Imp. Chem. Indus. Ltd.)	U.S. 2,196,188 (1940)	Porous portion of unglazed porcelain	400 - 600 1-20 atm	CH <sub>4</sub> , O <sub>2</sub> (1:1, vol.)	Ag <sub>2</sub> O, CuO - 30 mg CH <sub>2</sub> O/ 100 l gas;	CH <sub>2</sub> O separated by H <sub>2</sub> O scrubbing
21	A. Matui, M. Yasuda	J. Soc. Chem. Ind. Japan 43, 453 (1940)	Ag <sub>2</sub> O, CuO, Fe <sub>2</sub> O <sub>3</sub>	350 100 atm	Natural gas (94.95% CH <sub>4</sub> ), air (7:3 vol)	Fe <sub>2</sub> O <sub>3</sub> - 23 mg CH <sub>2</sub> O/ 100 l gas	Pressure and space velocity varied to determine effect on CH <sub>2</sub> O yield
22	E. Berl (Berl Chem. Corp.)	U.S. 2,270,779 (1942)	Fe oxide, antiknock reagent, e.g. Fe pentacarbonyl		Exothermically oxidi- zable hydrocarbons, O <sub>2</sub>		Controlled partial oxidation reaction employed
23	C. Hochwalt, et. al. (To Monsanto Chem. Co.)	U.S. 2,434, 850 (1948)	Products of reaction of Fe & H <sub>2</sub> O <sub>4</sub>		Aliphatic hydrocarbons, (air or O <sub>2</sub> )		The reaction products from Fe and H <sub>2</sub> PO <sub>4</sub> were found to prevent the decomposition of hydro- carbon oxidation products to CO <sub>2</sub> and H <sub>2</sub> O
24	E. Boomer, S. Waldrett	Can. J. Research 25B, 494 (1947)	Cu, Ag, Zn, Ni, MnO <sub>2</sub>		CH <sub>4</sub> , O, N		Ni and MnO <sub>2</sub> catalysts gave the best results. A massive catalyst gave better results than wire gauze.
25	C. Dewitt, L. Hein	Mich. St. Coll. Agr. Eng. Expt. Sta. Bull., 100 (1946)	Electrolytic Cu, SiO <sub>2</sub> gel, CuO-SiO <sub>2</sub> , V oxides on SiO <sub>2</sub> , Mo oxides on SiO <sub>2</sub> , bronze	350 - 650 739 mm Hg	CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , nat. gas, (air or O <sub>2</sub> )	Max. yield = 3% CH <sub>2</sub> O (based on input O <sub>2</sub> )	The most active catalysts were Mo oxide - SiO <sub>2</sub> which was better than V oxide - SiO <sub>2</sub>
26	P. Sherwood	Petroleum Processing 4, 794 (1949)	Steam; catalytic oxidation		CH <sub>4</sub> or C <sub>2</sub> H <sub>4</sub> (air or O <sub>2</sub> )	20% CH <sub>2</sub> O, 27% CH <sub>3</sub> CHO	Good yields were obtained from the catalytic oxidation, more than 90% aldehydes being ob- tained. Steam gave no significant yields.
27	Clark Bros. Co., Inc.	Brit. 606,967 (1948)	Ce, Ru, Pt, Pd, Pb, and their compounds	240 - 320	Nat. gas, 80-98% H <sub>2</sub> SO <sub>4</sub>		Liquid phase catalysis produced a mixture of MeOH, CH <sub>2</sub> O and AcH-H <sub>2</sub> SO <sub>4</sub> used as oxidizer.



Table I Cont.

1	2	3	4	5	6	7	8
28 CA 44, 5900	M.M. Kellogg Co.	Brit. 633,334 (1949)	Cu oxide; Cu, Cu oxide	330	CH <sub>4</sub> , CuO		A fluidized bed of CuO oxidized CH <sub>4</sub> to CH <sub>2</sub> O. The Cu produced was reoxidized to CuO in a regeneration zone.
29 CA 45, 3865	Clark Bros. Co., Inc.	Brit. 643,862 (1950)	Act. Al <sub>2</sub> O <sub>3</sub> , Co sulfate, 0.05% wt. AgNO <sub>3</sub>		97% CH <sub>4</sub> , 0.7% SO <sub>2</sub> , 0.5% SO <sub>2</sub> , 1.8% CO, CO <sub>2</sub>	80% Mol yield CH <sub>2</sub> O (based on CH <sub>4</sub> )	Other aliphatic hydrocarbons were oxidized. Group Ib metal oxides were also tested as catalysts. A recycle system was employed. The contact time was 0.72 sec.
30 CA 45, 3865	Clark Bros. Co., Inc.	Brit. 644,027 (1950)	Group Ib salts and oxides; transition elements	350-600 psi	67% CH <sub>4</sub> and inert, 2% SO <sub>2</sub> , 30% SO <sub>2</sub> , 0.8% O	95% Mol yield CH <sub>2</sub> O (based on CH <sub>4</sub> )	The CH <sub>2</sub> O yield was found to be influenced by concentration of free O. The space velocity used was 286 hr <sup>-1</sup> and the contact time was 12.6 sec.
31 CA 38, 3247	R. Schwarz, M. Ruhnke	Ger. 768, 957 (1943)	Fe sulfate, NH <sub>4</sub> dichromate, NH <sub>4</sub> vanadate	500-600 psi	C <sub>2</sub> H <sub>4</sub> , O <sub>2</sub> (9:1)	47% yield CH <sub>2</sub> O (based on C <sub>2</sub> H <sub>4</sub> converted)	Solid catalysts were found to decrease yield. Pure silite rod (heater element) gave best results.
32 CA 46, 9583	M. Marconi (To Societa per Azioni Polvere Metall)	Ital. 464,173 (1951)	Salts of Group I and 7, metals activated by salts of Group 6 on a porous carrier	500-600 psi	CH <sub>4</sub> , O <sub>2</sub>		These catalysts produced CH <sub>2</sub> O from CH <sub>4</sub> in quantitative yields.
33 CA 47, 11226	M. Hartig (To du Pont de Nemours & Co.)	U.S. 2,625,519 (1953)	Precipitated Mo oxide with Co or Ni oxide with Si, W, Ti, Be, Zr, Cr, U as promoters	500-600 psi			These catalysts are suggested as a possibility for oxidizing CH <sub>4</sub> to CH <sub>2</sub> O.
34 CA 61, 2878	V. Atroshchenko, Z. Shechedinskaya	Tr. Kharkovsk. Politekh. Inst. 32, 19 (1962)	MoO <sub>3</sub> , Ag <sub>2</sub> O, Pumice	375 - 500	Nat. gas (93% CH <sub>4</sub> , 2% O), (air or O <sub>2</sub> )	CH <sub>2</sub> O yield = 25% (CH <sub>4</sub> )	A wide range of materials was tested. Space velocity was varied from 1,000 to 50,000 hr <sup>-1</sup> . Many experimental parameters were varied.
35 CA 60, 5311	M. Baccaredda, et. al.	Chem. Age India 14, 250 (1963)	Glass	350 - 400	Butanes, O	Max. CH <sub>2</sub> O converted (based on O) = 10%	CH <sub>2</sub> O conversion was found to be strongly influenced by temperature and space velocity. Glass packing inhibits CH <sub>2</sub> O decomposition and conversion to acids at <350°, CH <sub>2</sub> O conversion increased with contact time.
36 CA 51, 7828	A. Egerton, et. al.	Combustion and Flame 1, 25 (1957)	HF treated SiO <sub>2</sub> and Pyrex vessels; soda-glass; NaCl & alkali treated vessels	450 - 500 mm	CH <sub>4</sub> , O		CH <sub>4</sub> oxidation was most rapid in HF-treated SiO <sub>2</sub> and Pyrex vessels. Py <sub>2</sub> coated surfaces gave results similar to Pyrex.
37 CA 55, 8002	T. Kormienko, M. Polyakov	Ukrain. Khim. Zhur. 26, 440 (1960)	MgCl <sub>2</sub> coated walls	Low temp.	CH <sub>4</sub> , (air or O <sub>2</sub> )		MgCl <sub>2</sub> found to be a negative catalyst for CH <sub>2</sub> O formation.
38 CA 55, 20400	M. Miyashiro	Mem. Fac. Eng. Hiroshima Univ. 1, 309 (1961)	Glass surfaces, metal oxides, sulfides; hexagonal surfaces; PbEt <sub>4</sub> ; Cu, Sn plated Al surfaces		Hydrocarbons with C > 4, (air or O <sub>2</sub> )		Hexagonal microcrystals catalyzed while PbEt <sub>4</sub> inhibited CH <sub>2</sub> O formation. Catalytic activity of glass indicated surface covered with a monolayer of hexagonal microcrystals.

Table I Cont.

1	2	3	4	5	6	7	8
39 CA 51, 18501	A. Anisonvan, et. al.	Gazovaya Prom. No. 6, 32 (1957)	K <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , porcelain	650	CH <sub>4</sub> , O, N (1:1:1 vol)	CH <sub>2</sub> O conc. in prod. gases=3.3%	K <sub>2</sub> B <sub>4</sub> O <sub>7</sub> found to promote CH <sub>2</sub> O formation while porcelain inhibited CH <sub>2</sub> O decomposition. A flow rate of 180 m/hr and a contact time of 0.4 sec was used.
40 CA 55, 8823	V. Atroschenko, et. al.	U.S.S.R. 132,623 (1960)	Pumice, Mo oxide; pumice, Ag <sub>2</sub> O; pumice, Ag <sub>2</sub> O, Cr <sub>2</sub> O <sub>3</sub>	375 - 390 25-75 atm	CH <sub>4</sub> contg. gases, O <sub>2</sub> (98.2 vol)		Ag <sub>2</sub> O and Ag <sub>2</sub> O + Cr <sub>2</sub> O <sub>3</sub> produced MeOH and CH <sub>2</sub> O. Mo oxide produced only CH <sub>2</sub> O. The volumetric velocity through the catalyst was 50,000 cc/m.
41 CA 51, 18023	B. Losev	Khim. Pere. Neft. Uglev., Trudy Vses. Sov. Kom. Khim. Pere. Neft. Gasov. 339 (1956)	BaCl <sub>2</sub> on kaolin	540	CH <sub>4</sub> , air (1:1 vol)	10.63 mg. CH <sub>2</sub> O/liter gas mixture	Product gas condensate contained 1% CH <sub>2</sub> O and 20% hydroperoxides.
42 CA 52, 2476	O. Zechetmayer (Gutthoffnungshutte Sterktrade A.-G.)	Ger. 765,968 (1953)	5 pts. Na silicate, 1 pt. ZnO, 0.1 pt. NaOH	620	CH <sub>4</sub> , O <sub>2</sub>	3 gms. CH <sub>2</sub> O/m <sup>3</sup> gas mixture	The catalyst is deposited as a thin coating on the walls of a heat exchanger to prevent CH <sub>2</sub> O decomposition.
43 CA 53, 222	P. Mashan (Gutthoffnungshutte Sterktrade A.-G.)	Ger. 861,242 (1952)	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	5-10 atm	CH <sub>4</sub> , (air or O <sub>2</sub> )		A process is described for controlled oxidation of CH <sub>4</sub> to CH <sub>2</sub> O.
44 CA 53, 12178	A. Zechetmayer (Gutthoffnungshutte Sterktrade A.-G.)	Ger. 845,505 (1952)	Hydrogenation extralysts, e.g. Fe or Co oxide with Ni or Co activators on kieselguhr	260	CH <sub>4</sub> , O <sub>2</sub> or air		These catalysts prevented dissociation of CH <sub>2</sub> O formed at higher temperatures.
45 CA 42, 13630	M. Miyawishi	J. Fuel Soc. Japan 34, 373 (1955)	Hexagonal crystals, PbEt <sub>4</sub>	150 - 400	Heptane, O		When glass vessel walls were coated with sublimed fibers of various metals, only metals forming hexagonal metal oxide crystals catalyzed CH <sub>2</sub> O formation. PbEt <sub>4</sub> inhibited CH <sub>2</sub> O formation.
46 CA 42, 5043	F. Laffer (Universal Oil Products Co.)	U.S. 2,689,210 (1954)	Solid particulate material, CuO	480 - 650	CH <sub>4</sub> , (air or O <sub>2</sub> )		An elongated tubular reactor was used.
47 CA 50, 5382	M. Miyawishi	Bull. Fac. Eng., Hiroshima Univ. 4, 353 (1955)	Glass surfaces		n - hydrocarbons, (air or O <sub>2</sub> )		Since glass surfaces catalyze CH <sub>2</sub> O formation in a Pb-lined combustion chamber, it was concluded that glass is composed of hexagonal microcrystals.
48 CA 50, 16829	M. Marconi	Ital. 485,052 (1953)	Oxidized copper chips	70 - 80	CH <sub>4</sub> , O or air		High CH <sub>2</sub> O yield was obtained when air and CH <sub>4</sub> was used freed of unsaturated hydrocarbons, H <sub>2</sub> O, CO <sub>2</sub> , and H <sub>2</sub> S. A detailed method is given for accomplishing this purification.
49 CA 42, 6822	M. Maki	J. Fuel Soc. Japan 32, 249 (1953)	FeHAsO <sub>4</sub> , WO <sub>3</sub> , MnO <sub>2</sub> , V <sub>2</sub> O <sub>5</sub> , ThO <sub>2</sub>	650 1 atm	CH <sub>4</sub> , (air or O <sub>2</sub> )	70-101 mg. CH <sub>2</sub> O/10 liters CH <sub>4</sub>	A number of other catalysts were also tested.

Table 2. OXIDATION OF METHANE USING GASEOUS CATALYSTS

No. Abstract	Reference		Catalyst	Conditions		Formaldehyde Produced	Remarks
	Author	Publication		Temp., °C Pressure	Feed Composition		
1			4	5	6	7	8
1 CA 22, 4333	T. E. Laying and R. Soukup	Ind. Eng. Chem. 20, 1052 (1928)	NO <sub>2</sub> , MnO <sub>2</sub>	100 - 700	CH <sub>4</sub> or natural gas with O <sub>2</sub>	15-30% of oxygenated derivatives were obtained	With gas catalysts shown Cu, Ag, their oxides, activated charcoal, Pt oxide, BaO <sub>2</sub> were found unsatisfactory.
2 CA 23, 1142	F. J. Carman and T. H. Chilton	U.S. 1,697,106 (January 1, 1929)	Halogenating agent such as Cl <sub>2</sub>	above 500	CH <sub>4</sub> , O <sub>2</sub>		
3 CA 23, 1142	F. J. Carman	U.S. 1,697,105 (January 1, 1929)	Halogenating agent such as Cl <sub>2</sub>		CH <sub>4</sub> , O <sub>2</sub>		
4 CA 25, 2156	H. Harter	Brit. 337,407 (June 24, 1929)	N oxides with solid catalysts Cu, Ag, Co, Mn, active C, silica gel		CH <sub>4</sub> , O <sub>2</sub> or air		N oxides are formed from air by an electric flaming arc.
5 CA 26, 1302	Guttenhoffnungshutte Oberhausen A.-G.	Fr. 709,823 (January 14, 1931)	N oxides with contact materials: Mg, Pt, W, Cr, Ni, Mn, Si, Cu, Ag or their oxides, quartz		CH <sub>4</sub> , O <sub>2</sub>		
6 CA 29, 1103	H. Harter	U.S. 1,985,875 (December 25, 1935) Ger. 657,194 (February 28, 1936)	Decomposing NO and bleaching (fullers) earth	100 - 500	CH <sub>4</sub> , air		Various solids used as additional catalysts.
7 CA 29, 480		Fr. 770,179 (September 10, 1934)	NO with oxides or carbonates of 2nd and 4th group; also of Al, Cr, V, Mo, W, Mn, Ni or Co	600 - 750	CH <sub>4</sub> , O <sub>2</sub>		
8	R. K. Bailey	U.S. 1,319,748 (1919)	N oxides	450	CH <sub>4</sub> , air		
9 CA 28, 1354	G. Egloff	U.S. 1,939,255 (December 12, 1934)	Pb(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>		Hydrocarbons with air		Fast cooling of product used to prevent formaldehyde decomp. Pb(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> controls the limit of oxidation to produce oxygenated products.
10	C. H. Bibb	U.S. 1,392,886 (October 4, 1921) Re. 15,789 (March 11, 1924)	1-2% nitric acid fumes	250 - 560	CH <sub>4</sub> or nat. gas, air		
11	C. H. Bibb and H. J. Lucas	Ind. Eng. Chem. 21, 633 (1929)	Nitrogen oxides obtained by bubbling feed through conc. HNO <sub>3</sub>	700 - 750	Nat. gas, air in ratios up to 1:4	Up to 3.6% of hydrocarbons in feed converted to CH <sub>2</sub> O	Feed mixture contained up to 7% of C <sub>2</sub> H <sub>6</sub>

Table II Cont.

1	2	3	4	5	6	7	8
12	D.F. Smith and R.T. Milner	Ind. Eng. Chem. <u>23</u> , 357 (1931)	Nitrogen oxides obtained by bubbling through conc. $\text{HNO}_3$	500 - 700	$\text{CH}_4$ , oxygen, various ratios	Up to 3.7% of the methane converted to $\text{CH}_2\text{O}$	
13	S.S. Medvedev	Nat. Gasses U.S.S.R. No. 4/5, 29 (1932)	HCl, Al, Fe phosphate	600 - 610	$\text{CH}_4$ , air or $\text{O}_2$ , 0.3% HCl	HCl improves $\text{CH}_2\text{O}$ yield only up to a limit. Air gives higher $\text{CH}_2\text{O}$ yield than $\text{O}_2$ .	
14	F. Nishan (Guthehoffnungshutte Oberhausen A.-G.)	U.S. 2,102,160 (1938)	N oxides, alkaline earth metal oxide, metal oxides (Co and Ti)	600 - 700	$\text{CH}_4$ , $\text{O}_2$ , N oxides < 1% (Vol.)	The Co as Ti oxide accelerates $\text{CH}_4$ oxidation while the oxide mixture prevents undesired oxidation of $\text{CH}_2\text{O}$ .	
15	A. Matui, M. Yasuda	J. Soc. Chem. Ind. Japan, <u>43</u> , 117 (1940)	$\text{UO}_2$ , BeO, $\text{NO}_2$	500 - 700	$\text{CH}_4$ (from nat. gas), air (7:3 vol.)	Fyrex, quartz, porcelain and copper tubes used as reactors.	
16	A. Kreshkov	J. Gen. Chem. (U.S.S.R.) <u>10</u> , 1605 (1940)	$\text{Cl}_2$ & superheated steam with $\text{CuCl}_2$ , $\text{BaCl}_2$ , $\text{V}_2\text{O}_5$ catalysts activated carbon, pumice carrier	500 - 700	$\text{CH}_4$ (air or $\text{O}_2$ )	Lower contact times found to give higher yields.	
17	Guthehoffnungshutte Oberhausen A.-G.	Brit. 520,480 (1940)	$\text{NO}$ , difficultly reducible solid oxides	500 - 700	Hydrocarbons (air or $\text{O}_2$ )	Lower molecular weight aliphatic aldehydes produced. Reaction gas was passed through numerous heated tubes.	
18	Guthehoffnungshutte Oberhausen A.-G.	Ger. 721,883 (1942)	N oxides, 2nd Group metal oxides, or Al, Mo, Ni oxides alone or mixed	500 - 800	Paraffins with > 1C, $\text{O}_2$ , 1% N oxides		
19	C. Thomas (Monsanto Chem. Co.)	U.S. 2,365,851 (1944)	Fe phosphate, "Proknocks" vapor	650	$\text{C}_3\text{H}_8$ , air (1.5:8.5); $\text{CH}_4$ air (3:7)	Recycle system employed. Reactants preheated to 300°. Fe phosphate inhibits $\text{CH}_2\text{O}$ decomposition.	
20	W. Derby (Monsanto Chem. Co.)	U.S. 2,376,668 (1945)	$\text{HNO}_3$		$\text{CH}_4$ , $\text{C}_2\text{H}_6$ , $\text{C}_3\text{H}_8$ , nat. gas, air	Reactor constructed of an alloy containing 55% Ni, 17% Mo, 15% Cr, 4% W, Fe, Si, Mn. The reaction was run isothermally.	
21	H. Harter	Ger. 737,418 (1943)	N oxides	500 - 600	$\text{CH}_4$ (and gases contg. $\text{CH}_4$ ) $\text{O}_2$ (and gases contg. $\text{O}_2$ )	The oxidant and N oxide were preheated to 500-600°, then mixed with the $\text{CH}_4$ immediately before the reaction	
22	M. Patry, P. Monceaux	Compt. Rend. <u>223</u> , 329 (1946)	Non-catalytic: $\text{P}_2\text{O}$	760 ; 570	$\text{CH}_4$ , 0 (8:2)	Non-cat., 760°, 1.7 sec, 0.6% yield $\text{CH}_2\text{O}$ $\text{P}_2\text{O}$ : 570° 15% yield $\text{CH}_2\text{O}$	
23	T. Sherwood (To Godfrey L. Cabot, Inc.)	U.S. 2,412,014 (1946)	2% (vol) $\text{NO}_2$	650 1 atm	Nat. gas, air (3 to 5: 7 to 5 vol)	Condensate conc-19% $\text{CH}_2\text{O}$ soln.	The reactor was a series of vertical alloy steel and silica tubes. The contact time varied from 0.25-0.5 sec.

Table II Cont.

1	2	3	4	5	6	7	8
24 CA 43, 5792	R. Rossman (To Godfrey I. Cabot, Inc.)	U.S. 2,476,993 (1949)	NO <sub>2</sub>	900; 1200	Net. gas, air (1:1 vol) 0.29 lb NO <sub>2</sub> /1000 cu ft CH <sub>4</sub>		The reactants were passed thru a steel tube at 900° then thru a silica tube at 1200°.
25 CA 43, 6159	P. Monceaux	Mem. Services Chim. Etat. 33, 423 (1947)	O <sub>3</sub>	650 - 700	CH <sub>4</sub> , O <sub>3</sub>		The O <sub>3</sub> had no effect on yield up to 600°. Between 650-700° the yield doubled.
26 CA 46, 10091	P. Luetic, I. Brihta	Archiv. Kem. 23, 104 (1951) (Eng. 117)	N oxides	650	CH <sub>4</sub> , air	Max. yield (>71%) at 2.4% conv., max. conv. of 28% corresp. to max. wt./vol yields=37 g. CH <sub>2</sub> O/m <sup>3</sup> CH <sub>4</sub>	The flow rate was found to greatly affect the yield but to have no effect on conversion. Substitution of O <sub>2</sub> for air gave both lower conversion and yield.
27 CA 46, 10191	J. Tebboth (To British Oxygen Co. Ltd.)	Brit. 664,741 (1952)	NO	570 - 650 0.17 atm	50% CH <sub>4</sub> , 10% O, 0.1-1% NO, CO, CO <sub>2</sub> , H <sub>2</sub> , H <sub>2</sub>	25-30 gm. CH <sub>2</sub> O/m <sup>3</sup>	The product CH <sub>2</sub> O was scrubbed with H <sub>2</sub> O to give a 40% solution. The contact time varied from 0.5-2 sec.
28 CA 46, 2781	J. Cech	Chemie (Prague) 5, 23 (1949)	O <sub>3</sub> , BaO <sub>2</sub>		CH <sub>4</sub> , O, O <sub>3</sub>		
29 CA 47, 5347	N. Zemlyanski, O. Prib, M. Sharypkina	Zhur. Obsh. Khim. 22, 1770 (1952)	Cl <sub>2</sub>	800	CH <sub>4</sub> , air, Cl <sub>2</sub> (12:36:1 vol)	0.27% CH <sub>2</sub> O yield	At lower temperatures Cl <sub>2</sub> is found to promote oxidation. The contact time was 0.11 min.
30 CA 48, 5208	Gutthoffmangshutte Oberhausen A.-G.	Brit. 686,424 (1953)	N oxides, NO tetra- borate	362	CH <sub>4</sub> , O (1:1 vol.), NO (0.2% vol.)	65% CH <sub>2</sub> O	A cyclic process was employed using two ovens in series. The flow rate used was 25 cm <sup>3</sup> /sec. Homologs of CH <sub>4</sub> were also tested
31 CA 48, 5469	A. McKinnis (To Union Oil Co. of Calif.)	U.S. 2,667,513 (1954)	NO <sub>2</sub>	450 - 700	CH <sub>4</sub> , NO <sub>2</sub> (2:1 mol)	40% conversion	The reaction is carried out in a small flame. The contact time varies from 0.001-0.5 sec.
32 CA 48, 6958	P. Luetic, I. Brihta	Archiv. Kem. 24, 123 (1952)	HNO <sub>3</sub>		CH <sub>4</sub> , air	40% yield	The influence of the ratio of fresh to recirculated gas on the yield was determined. An unsuccessful attempt was made to repeat the Hibernia results.
33 CA 48, 10057	Gutthoffmangshutte Oberhausen A.-G.	Brit. 692,840 (1953)	N oxides, NO tetraborate		CH <sub>4</sub> (homologs), O <sub>2</sub> or air	"High" yield	This process optimizes CH <sub>2</sub> O yields by using low flow rates and short contact times.
34 CA 52, 3436	H. Gertges, H. Heinze, W. Brocke	Ger. 1,050,752 (1959)	NO, fluidized pumice	470	CH <sub>4</sub> , air or O <sub>2</sub> (1:5 vol), 0.1% NO		The product gases were cooled in the presence of SiC to prevent CH <sub>2</sub> O decomposition.
35 CA 51, 7403	W. Reeder (To Dresser Operations, Inc.)	U.S. 2,776,317 (1957)	SO <sub>2</sub> , metal oxide and salts	175 - 450	Simple saturated hydro- carbons, O, SO <sub>2</sub>		A schematic is given of the process equipment used. Good yields of ROOH and ROOR reported.
36 CA 52, 9193	P. Mehan (Bergan Akt. Ges. Neuhofnung)	Ger. 872,202 (1953)	Solid catalyst and NO or NO <sub>2</sub>		CH <sub>4</sub> , O <sub>2</sub> , H <sub>2</sub> , CO		A procedure is described for inhibiting CH <sub>2</sub> O disproportionation.

Table II Cont.

1	2	3	4	5	6	7	8
37 CA 52, 6396	W. Brocke, et.al. (Hüttenwerk Oberhausen A.-G.)	Ger. 1,181,192	NO, pumice	670 - 85	CH <sub>4</sub> , O <sub>2</sub> , NO (6:30:0.11 vol)	188 gm. CH <sub>2</sub> O/m <sup>3</sup> CH <sub>4</sub>	A bed of hot fluidized pumice was used to catalyze CH <sub>2</sub> O formation while a bed of cold fluidized pumice together with a copper wire net was used for chilling the product gas.
38 CA 50, 10440	F. Dilleuth, C. Schubert	West. States Sect. Combust. Inst. Pap. WSS/OI 63 (1963)	O <sub>3</sub> (ozone)	150 - 285	CH <sub>4</sub> , O <sub>3</sub> (ozone)	0	O <sub>3</sub> was found to eliminate the induction time for the reaction. Major products from CH <sub>4</sub> oxida- tion by O <sub>3</sub> were CO, CH <sub>2</sub> O, CO <sub>2</sub> , and H <sub>2</sub> O.
39 CA 54, 4895	E. Otsuka, H. Metanabe	Nenryo Kyokaiishi, 42 (1938)	HNO <sub>3</sub> , NO <sub>2</sub> , NO	600	CH <sub>4</sub> , O, NO (90:10: 1 to 3 Mol)	For HNO <sub>3</sub> , 0 conversion= 60-70%; CH <sub>2</sub> O concentration =1.6-2.3%; CH <sub>2</sub> O yield= 30% (based on CH <sub>4</sub> )	Among the catalysts tested, per- formance decreased in the order HNO <sub>3</sub> > NO <sub>2</sub> > NO. Contact time varied from 0.1 to 0.3 sec.
40 CA 56, 7137	E. Magee (Esso Research & Eng. Co.)	U.S. 3,014,969	HCl, PbO	480 - 700	CH <sub>4</sub> , free O	"Economic" yield	The reactant gases were passed thru HCl before entrance to the reactor. The reactor wall was coated with PbO. A partial oxidation process was used. Contact time varied from 0.5- 1.5 sec.
41 CA 52, 5152	E. Otsuka, H. Metanabe	Nenryo Kyokaiishi, 43 (1942)	NO, solid catalyst	600 - 700	CH <sub>4</sub> , O, NO (90:10: 1 to 3 vol)	CH <sub>2</sub> O conc.= 2%; CH <sub>2</sub> O yield=30% CH <sub>4</sub>	CH <sub>2</sub> O yield as a function of catalyst concentration, pre- heating, solid catalysts, and contact time was studied. Con- tact time varied from 0.2- 0.6 sec.
42 CA 56, 8050	L. Karmlova, N. Ezhikolovyan, A. Naibandyan	Zhur. Fiz. Khim. 32, 1046 (1961)	H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> O	423 - 513	CH <sub>4</sub> , (air or O <sub>2</sub> )	H <sub>2</sub> O was found to prevent decom- position of CH <sub>2</sub> O. H <sub>2</sub> O <sub>2</sub> shorten- ed the induction period, but neither H <sub>2</sub> O nor H <sub>2</sub> O <sub>2</sub> increased the maximum yield.	H <sub>2</sub> O was found to prevent decom- position of CH <sub>2</sub> O. H <sub>2</sub> O <sub>2</sub> shorten- ed the induction period, but neither H <sub>2</sub> O nor H <sub>2</sub> O <sub>2</sub> increased the maximum yield.
43 CA 56, 10952	R. Maré, M. McLaussé, M. Dzierzynski	Bull. Soc. Lorraine Sci. 1, No. 4, 29 (1961)	Pyrex; silica, H <sub>2</sub> O		CH <sub>4</sub> , (air or O <sub>2</sub> )	(CH <sub>2</sub> O)/(CH <sub>4</sub> ) yield=5%	The rate of CH <sub>4</sub> oxidation was found to be affected by H <sub>2</sub> O vapor, and by the properties of container surfaces.
44 CA 56, 1331	S. Takahashi	Shinshi Kagaku 2, 55 (1961)	H <sub>2</sub> O, 40 megacycle discharge; H <sub>2</sub> ; CO <sub>2</sub>	1-9 cm.Hg	CH <sub>4</sub> , (air or O <sub>2</sub> )		H <sub>2</sub> was found to improve CH <sub>2</sub> O yield and inhibit CH <sub>2</sub> O decom- position. CO <sub>2</sub> was found to decrease CH <sub>2</sub> O yield.
45 CA 59, 11259	Hüttenwerk Oberhausen A.-G.	Brit. 880,873 (1960)	NO, (porcelain re- actor) 4 mm grain size, fluidized Feal. Pumice	670	CH <sub>4</sub> , air (1.5 vol), 0.1% NO	CH <sub>2</sub> O yield= 837 g/m <sup>3</sup> CH <sub>4</sub> (STP)	A 94% Cu-6% Sn alloy mesh screen containing SiC was placed before the quenching zone. A residence time of 0.35 sec. was used.

Table II Cont.

1	2	3	4	5	6	7	8
46 CA 29, 4428	Mitrokemia Ipartelepek	Hung. 137,268 (1962)	N oxides	400 - 750	CH <sub>4</sub> , O		Partial oxidation of CH <sub>4</sub> was carried out in enamel and glass-lined reactors.
47 CA 29, 10085	C. Heath (Esso Research & Eng. Co.)	U.S. 3,056,833 (1962)	O <sub>3</sub> , Cr-M alloy reactor	150	CO <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> (4:10), O <sub>3</sub>	19% CH <sub>2</sub> O	The reactor surface-volume ratio was 3 cm <sup>-1</sup> . The contact time was 2 sec. The products included 61% CH <sub>2</sub> O and 15% HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .
48 CA 29, 9800	C. Heath, W. Barton (Esso Research & Eng. Co.)	U.S. 3,086,995 (1959)	PbO, B <sub>2</sub> O <sub>3</sub> , MnO <sub>2</sub> , O <sub>3</sub>	315	O <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> (4:10), 0.3% O <sub>3</sub>	CH <sub>2</sub> O selectivity = 90%	The reactor was a PbO coated steel tube with a surface volume ratio of 5 cm <sup>-1</sup> . The contact time was 2 sec. The C <sub>2</sub> H <sub>6</sub> was preheated.
49 CA 29, 12551	E. Magee (Esso Research & Eng. Co.)	U.S. 3,232,991	N oxide, PbO	650 1-50 atm	CH <sub>4</sub> , O, NO <sub>2</sub> (4:1:0.12 vol)	CH <sub>2</sub> O yield = 1.6 mol-%; selectivity = 32%	Stainless-steel reactors coated with PbO, with surface-volume ratio of 2 to 37 cm <sup>-1</sup> were used. The contact time was 0.3 sec.
50 CA 29, 14431	S. Gudkov, et. al.	Vestn. Tekhn. i Ekon. Inform. Nauchn.-Issled. Inst. Tekhn.-Ekon. Issled. Gos. Kom. Khim. i Neft Prom. Pri. Gos. Plane S.S.S.R. (1963) (6), 13	N oxides	593 - 5	Nat. gas (96% CH <sub>4</sub> ), air (1:2 vol)	CH <sub>2</sub> O yield = 0.7%	Partial adiabatic oxidation was employed. The contact time was 0.17 sec.; the flow rates were 2145 m <sup>3</sup> /hr. nat. gas, 4265 m <sup>3</sup> /hr. air, 8 m <sup>3</sup> /hr. NO.
51 CA 29, 14445	F. Poulignon, B. Gourdon	Fr. 1,359,877 (1964)	NO <sub>2</sub>	570	Air, nat. gas, NO <sub>2</sub> (18:8:0.3 vol)	40 g CH <sub>2</sub> O/m <sup>3</sup> CH <sub>4</sub>	An inverse flame oxidation method was used. Air and gas were mixed in a burner then heated to 570° in a tube for 0.5 sec. Flow rates were 18.1/hr air, 8.1/hr nat. gas (96% CH <sub>4</sub> , 2.5% C <sub>2</sub> H <sub>6</sub> ), 0.3 l/hr. NO <sub>2</sub>
52 CA 29, 4202	E. Otsuka, H. Watanabe	Nenryo Kyoraisai, 42, 523 (1963)	O <sub>3</sub> ; silent discharge		CH <sub>4</sub> , O		An unsuccessful attempt was made to repeat the Hibernia results. CH <sub>2</sub> O decomposition was believed to be the cause. In a silent discharge tube a copper electrode gave 12 times the yield of CH <sub>2</sub> O that glass gave. The reactant gas was drawn through an electric furnace.
53 CA 29, 5862	N. Tsalaif	Khim. V Shtkole (6) (1964) 55	NO	600 - 50	CH <sub>4</sub> , air	CH <sub>2</sub> O yield = 2.55-2.82% (on CH <sub>4</sub> basis) 0.85-0.94% (on mixt. basis)	A pilot-plant operation is described which produces 3000 tons 37% CH <sub>2</sub> O/yr. Contact time varied from 0.1-0.15 sec.
54 CA 29, 2559	S. Gudkov, et. al.	Gazovaya Prom. 8, No. 4 35 (1963)	NO	590 - 610	Nat. gas, air (1:1 vol), 0.1% NO		
55 CA 29, 15100	S. Gudkov	Gas. Prom. 8, (9), 44 (1963)	N oxides		Nat. gas, (air or O <sub>2</sub> )		A recycle system reclaimed N oxides from waste gases from a CH <sub>2</sub> O converter.

Table II Cont.

1	2	3	4	5	6	7	8
56 CA 52, 419	E. Magee	J. Phys. Chem. 67, 938 (1963)	N oxides, Pb oxides	480 - 525 300 mm	CH <sub>4</sub> , (air or O <sub>2</sub> )		Presence of both oxides results in marked increase in CH <sub>2</sub> O yield which reaches a maximum one hundred degrees lower than in their absence. Surface vol ratio should be > 8 cm <sup>2</sup> .
57 CA 51, 7813	V. Urizko, M. Polyakov	Ukrain. Khim. Zhur. 22, 702 (1956)	NO		CH <sub>4</sub> , air (15:80 vol.), 0.2% NO		A static system with a quartz reactor was used. When only quartz was present the CH <sub>2</sub> O concentration first rises rapidly then falls off. With NO two $\Delta T$ maxima occurred; $\Delta T$ (wall temp.-center temp). The first resulted from homogeneous formation of CO and CH <sub>2</sub> O, and the second from CH <sub>2</sub> O decomposition to H and CO. At 480° t=1.3 min; at 525° t=1.5 min.
58 CA 51, 1829	B. Losev	Vsesoyuz. Zaochny. Pol. Inst. Sb. Stat. (1955) No. 12	0.1% Cl <sub>2</sub> , BaCl <sub>2</sub>	520 - 30	Nat. gas (>99% CH <sub>4</sub> ), air (1:1 vol)	10 mg. CH <sub>2</sub> O/ liter gas mixture	Natural gas with 91% CH <sub>4</sub> , 6% higher hydrocarbons, etc. tested but gave lower yield. CH <sub>4</sub> oxidation by O <sub>2</sub> was direct; CH <sub>2</sub> oxidation did not occur by decomposition of the O <sub>3</sub> to O and O <sub>2</sub> followed by reaction of the O with CH <sub>4</sub> .
59 CA 52, 6377	M. Morita (Moguchi Research Foundation)	Japan 7458 (1960)	Ag <sub>2</sub> O, HgO, HNO <sub>3</sub> , steam	150 - 350	CH <sub>4</sub> , air		The contact time was varied from 2-20 sec.
60 CA 52, 4965	L. Karmilova, et. al	Zhur. Fiz. Khim. 31, 851 (1957)	Thermal oxid.; N oxides	483 - 700 200 mm - 1 atm	CH <sub>4</sub> , (air or O <sub>2</sub> )		Reaction mechanisms were studied. Contact time varied from 0.02 sec. to 2 hrs.
61 CA 52, 17108	P. Hachen (Bergbau Akt.-Ges. Neuhoffnung)	Ger. 871, 445 (1953)	NO, Na <sub>2</sub> BuO <sub>2</sub>		CH <sub>4</sub> , air or O <sub>2</sub> , trace NO, CO or H <sub>2</sub> .		Gases in place of CO and H <sub>2</sub> may be used which have a greater affinity for O <sub>2</sub> than CH <sub>4</sub> . Combustion of such gases supplies heat for, and controls temperature of, CH <sub>4</sub> oxidation reactions.
62 CA 53, 21627	N. S. Enikolopyan, et. al.	Zhur. Priklad. Khim. 32, 913 (1959)	N oxide, K <sub>2</sub> BuO <sub>7</sub> treated porcelain	600 - 800 1 atm	33% CH <sub>4</sub> , 66% air, 1 mole NO, 10 moles CH <sub>2</sub> formed	70% CH <sub>4</sub> reacted form- ed CH <sub>2</sub> O	A pilot plant operation is described capable of processing 1.3 m <sup>3</sup> CH <sub>4</sub> and air/hr. A quartz reactor gave unreactable CH <sub>2</sub> O yields but when coated with K <sub>2</sub> BuO <sub>7</sub> gave both reproducible and higher yields. The contact time was 0.1 sec.
63 CA 53, 206	N. S. Enikolopyan, G. Korolev	Doklady Akad. Nauk. SSSR 118, 983 (1958)	Non-catalytic; 0.06% 0.53% NO; 0.3-0.5% Cl		CH <sub>4</sub> , (air or O <sub>2</sub> )		When initiators were not used CH <sub>2</sub> O yield depends on reaction conditions, e.g., wall effects, dilution with inert gas. When initiators were added yield was independent of conditions.



Table II Cont.

1	2	3	4	5	6	7	8
64 CA 53, 17892	N. Enikolopyan	Zhur. Priklad. Khim. 32, 1132, (1959)	NO		CH <sub>4</sub> , air, 0.1% NO	CH <sub>2</sub> O yield=30%	Three packed reactors were used in series. 20-30 moles CH <sub>2</sub> O were formed for every mole of NO. The product gases were continuously recycled.
65 CA 53, 3061	F. Mashan (Gutthoffnungshutte Oberhausen A.-G.)	Ger. 863,654 (1953)	N oxides, alkali borate		CH <sub>4</sub> , air (1:1 vol); (0.5:1 vol)	For 1:1 CH <sub>4</sub> air mixture, 82 gms. CH <sub>2</sub> O formed per hr. For 0.5:1 CH <sub>4</sub> air mixture, 99 gms. CH <sub>2</sub> O formed per hr.	A recycle system was used which operated at rate of 40 cm/sec.
66 CA 50, 7551	I. Antonova, et.al.	Izvest. Akad. Nauk. SSSR Otdel. Khim. Nauk (1955) 789	NO	670	CH <sub>4</sub> , air, NO, CO, C <sup>14</sup> H <sub>4</sub> O (33:66:0.1:0.5:0.07 vol)		A tracer method was used to establish the reaction mechanism.
67 CA 49, 10714	V. Urizko, M. Polyakov	Doklady Akad. Nauk SSSR 95, 1239 (1954)	K <sub>2</sub> B <sub>4</sub> O <sub>7</sub> , N oxides	525	CH <sub>4</sub> , air (15:85 vol), 1.37% N oxides (based on CH <sub>4</sub> )		N oxides lowered the reaction temperature and increased CH <sub>2</sub> O yield. Quartz reactor walls caused CH <sub>2</sub> O decomposition; however, K <sub>2</sub> B <sub>4</sub> O <sub>7</sub> wall coverings lowered the decomposition.
68 CA 53, 4116	N. Enikolopyan, G. Korolev	Doklady Akad. Nauk SSSR 116, 1138 (1958)	NO <sub>2</sub> quartz reactors washed with (1) H <sub>2</sub> P <sub>2</sub> (2) K <sub>2</sub> B <sub>4</sub> O <sub>7</sub> soln.	"High" 25 mm-53 mm	C <sub>2</sub> H <sub>6</sub> , O		CH <sub>2</sub> O yield was studied as a function of pressure and inlet composition.
69 CA 49, 2838	V. Urizko, M. Polyakov	Dopovidi Akad. Nauk. Ukr. R.S.S.R. (1953), 397	NO; non-catalytic	515 - 542 585 - 600	CH <sub>4</sub> , (air or O <sub>2</sub> )		In the presence of NO the CH <sub>4</sub> oxidation kinetic curve exhibited two maxima; the first being due to CH <sub>2</sub> O formation and the second being due to CH <sub>2</sub> O decomposition to CO and H <sub>2</sub> .
70 CA 50, 16315	L. Karmilova, et.al	Zhur. Fiz. Khim. 30, 798 (1956)	NO	"High"	CH <sub>4</sub> , (air or O <sub>2</sub> )		CH <sub>2</sub> O was the principal product formed within a wide range of experimental conditions.
71 CA 50, 7844	Gutthoffnungshutte Sterkrade A.-G.	Brit. 735,107 (1955)	N oxides, alkali-metal borates	"Normal" 1-10 atm	CH <sub>4</sub> , atomic O		Using a cyclic process maximum CH <sub>2</sub> O yield was obtained using a 0.5:1 volume ratio of O to CH <sub>4</sub> .
72 CA 50, 5019	S. Miller, et.al. (Brit. Oxygen Co. Ltd.)	Brit. 716,181 (1954)	NO	680	80% CH <sub>4</sub> , 10% O, 0.2-0.4% NO, N <sub>2</sub>	Production rates=35 to 59 gm CH <sub>2</sub> O/liter/hr. CH <sub>2</sub> O in exit gases=12 to 18 gm/m <sup>3</sup>	SiO <sub>2</sub> reactors with surface-volume ratios of 3.2 to 11.8 cm <sup>2</sup> were used. Contact time varied from 0.29-0.54 sec.
73 CA 49, 15430	M. Constantinesch	Rev. Chim. (Bucharest) 5, 537 (1954)	NO <sub>2</sub>	600 1 atm	CH <sub>4</sub> , air		Thermodynamic data is given for 26 CH <sub>4</sub> oxidation reactions.
74 CA 53, 4136	S. Gudkov, V. Fedulova	U.S.S.R. 112,633 (1958)	N oxides	500	Hydrocarbons, (air or O <sub>2</sub> )		Partial oxidation was carried out in a reactor where a short zone was heated to 500° while the remainder was kept below 100°.

Table II Cont.

1	2	3	4	5	6	7	8
75	M. Holm, E. Reichl	FLAF Final Report No. 1085, (31 March 1947)	NO	400 - 600	Nat. gas (99% CH <sub>4</sub> ), air (1:3.7 vol)	CH <sub>2</sub> O yield= 9.7% (Theoretical)	The Guttehoffnungshutte Process for industrial production is described. Information on this process was obtained in 1947 by interrogation of P. Neehan. The process is a low pressure, high temperature partial oxidation of CH <sub>4</sub> employing a recycle system.
76	M. Holm, E. Reichl	FLAF Final Report No. 1085 (31 March 1947)	O <sub>2</sub> , BaO <sub>2</sub> , 0.5% Ag <sub>2</sub> O, unglazed porcelain chips	80 - 120 1 atm	Coke oven gas (70% CH <sub>4</sub> ), O <sub>2</sub> (2:1 vol)	CH <sub>4</sub> conversion=27-30% CH <sub>2</sub> O yield=90% (Theoretical)	The Hibernia Process for industrial production is described. Information on this process was obtained in 1947 by interrogation of K. Schmitt. The process is a low temperature, low pressure catalytic means for converting CH <sub>4</sub> to CH <sub>2</sub> O by partial oxidation with O <sub>2</sub> or air. The catalyst preparation procedure and the operating conditions are given.
77	E. Rindtorff and K. Schmitt (To Hibernia A. G.)	Ger. 886,903 (August 17, 1953)	Ozone		CH <sub>4</sub> , ozonized oxygen or air	130-230 g. CH <sub>2</sub> O per cu. meter of CH <sub>4</sub>	Ozonized air gives better results than ozonized oxygen.
78	E. Rindtorff and K. Schmitt (To Hibernia A. G.)	Ger. 891,687 (October 1, 1953)	BaO <sub>2</sub> plus 1% Na <sub>2</sub> O, 0.5% Ag <sub>2</sub> O, O <sub>3</sub>	106	CH <sub>4</sub> -50%, C <sub>2</sub> H <sub>6</sub> -0.1%, C <sub>2</sub> H <sub>4</sub> - 0.2%, CO-12%, and 30% oxygen ozonized to 2%	320-350 g. CH <sub>2</sub> O per cu. meter of CH <sub>4</sub>	Process consists of three reactors connected in series.

Table 3. OXIDATION OF METHANE USING MISCELLANEOUS METHODS

No. Abstract	Reference		Catalyst	Conditions		Formaldehyde Produced	Remarks
	Author	Publication		Temp., °C Pressure	Feed Composition		
1							
1 CA 2, 355	J. Gruszkiewicz	Austr. 7, 279 (August 23, 1913)	None	CH <sub>4</sub> , air			Process consists of rapid cooling of a CH <sub>4</sub> burning flame.
2 CA 15, 1726	H. Plauson and J. A. Vielle	Brit. 156, 148 (December 21, 1920)	None	CH <sub>4</sub> or natural gas and CO <sub>2</sub> , or mixture diluted with inert gas such as N <sub>2</sub>			Heated momentarily in a restriction of tube made of various metals.
3 CA 18, 2494	H. Tropach and O. Roelen	Brennstoff-Chemie 2, 37 (1924)	None	CH <sub>4</sub> , air (16% CH <sub>4</sub> , 17% O <sub>2</sub> )	Product gas contains up to 0.19% CH <sub>2</sub> O		Low % of CH <sub>4</sub> in feed gives more CH <sub>2</sub> O per CH <sub>4</sub> reacted, but low total % of CH <sub>2</sub> O in product.
4 CA 12, 769	H. v. Wartenberg, A. Michlinski and G. Riedler	Z. angew. Chem. 37, 457 (1924)	None or PbCrO <sub>4</sub>	CH <sub>4</sub> , O <sub>2</sub>	2% based on CH <sub>4</sub>		Electric field with visible discharge of high frequency and very high voltage.
5 CA 24, 5241	Gutthoffnungshutte Oberhausen A.G.	Fr. 684, 969 (November 14, 1929)	None or Ag	CH <sub>4</sub> , O <sub>2</sub>			Electric field with visible discharge of high frequency and very high voltage.
6 CA 25, 1744	Gutthoffnungshutte Oberhausen A.G.	Fr. 694, 330 (April 23, 1930)	None	CH <sub>4</sub> , CO <sub>2</sub>			Silent electric discharge, 25-100 cycles, 10,000-100,000 volts.
7 CA 26, 1525	H. Dreyfus	Fr. 715, 031 (April 9, 1931)	None	CH <sub>4</sub> , CO <sub>2</sub>			Electric field of high frequency and high voltage.
8 CA 26, 3446	Gutthoffnungshutte Oberhausen A.G.	Brit. 353, 076 (April 29, 1929)	None or CaCO <sub>3</sub> , MeCO <sub>3</sub>	CH <sub>4</sub> , CO <sub>2</sub> . Conc. of CO <sub>2</sub> at least equal to that of CH <sub>4</sub>			Electric field with visible discharge of high frequency and very high voltage.
CA 28, 979	Gutthoffnungshutte Oberhausen A.G.	Ger. 580, 580 (July 15, 1933)	None	CH <sub>4</sub> , exceeding CO <sub>2</sub>			
CA 26, 3446	Gutthoffnungshutte Oberhausen A.G.	Brit. 353, 455 (April 29, 1929)	None	CH <sub>4</sub> , O <sub>2</sub>			
9 CA 27, 3675	P. Mashan	U.S. 1,909, 215 (May 16, 1933)	None	Natural gas, air or oxygen			Partial oxidation by burning.
CA 28, 2280	P. Mashan	Ger. 566, 516 (August 28, 1933)	None	CH <sub>4</sub> , hydrocarbons, O <sub>2</sub>			Heated hydrocarbon mixed with preheated CH <sub>4</sub> , O <sub>2</sub> mixture
10 CA 29, 480	Bellas Proc. Corp.	Fr. 770, 065 (September 6, 1934)	None	CH <sub>4</sub> , Nitrogen oxides	15-30% of the methane used		
11 CA 24, 625	P. L. Young	U.S. 1,735, 486 (November 12, 1930)	None				
12 CA 25, 2682	D. F. Smith and R. T. Milner	Ind. Eng. Chem. 23, 357 (1931)	None				

Table III Cont.

1	2	3	4	5	6	7	8
13	Morgan	Brit. 176,438 (1920)	None	350 - 400	58-80% CH <sub>4</sub> , 20-40% air		Bubbling through molten metals.
14	Elworthy	Trans. Roy. Soc. Can. III 16, 93 (1922)	None	100	Nat. gas and oxygen	Formaldehyde and formic acid were produced	Silent electric discharge
15	Otto	Ann. chim. phys. 13, 109 (1906)	None	100	CH <sub>4</sub> , ozone	Formaldehyde and formic acid were produced	
16	Drugman	J. Chem. Soc. 89, 939 (1906)	None	10 - 400	CH <sub>4</sub> , ozone	Up to 20% of CH <sub>4</sub> to formaldehyde	
17	R. V. Wheeler and Blair	J. Soc. Chem. Ind. 41, 331 (1922)	None	35	3% CH <sub>4</sub> in oxygen. Ozonized		Dark electric discharge, formation of ozone.
18	C. A. Kloppenburg	U.S. 1,500,080 (July 26, 1922)	Activated carbon	400 - 500	CH <sub>4</sub> , O <sub>2</sub>		CH <sub>4</sub> becomes chlorinated; then oxidized to formaldehyde.
19	F. J. Carman, T. H. Carman	U.S. 1,697,106 (January 1, 1929)	BaCl <sub>2</sub>		CH <sub>4</sub> , O <sub>2</sub> , Cl <sub>2</sub>		Economic and technical calculation for the prepn. of CH <sub>2</sub> O from natural gases.
20	CA 31, 3669	Nat. Gases U.S.S.R. No. 7, 12 (1933)		High	Nat. gas (air or O <sub>2</sub> )		An apparatus is described for forming CH <sub>2</sub> O from CH <sub>4</sub> and O <sub>2</sub> .
21	CA 31, 7882	Fr. 47,135 (1937)			CH <sub>4</sub> , O <sub>2</sub>		Partial oxidation. Hydrocarbon heated to below decomposition pressure by mixing with hot steam and air, then immediately mixed with gaseous O. Reaction time is 0.2-3.0 sec.
22	CA 32, 586	Fr. 811,866 (1937)			C <sub>2</sub> H <sub>6</sub> , hydrocarbons & O <sub>2</sub>		A review with 13 references.
23	CA 34, 4053	Industrie Chimique 26, 291 (1939)			CH <sub>4</sub> , O <sub>2</sub> (4% vol); higher hydrocarbons	16.6 g. CH <sub>2</sub> O/lv. hr.	Circulation system used. Higher hydrocarbons gave carbon black which interferred with arc.
24	CA 34, 6531	Helv. Chim. Acta 23, 800 (1940)	Electric arcs: 116-640 volts, 50-107 cycles/sec.	40-50 mm Hg	CH <sub>4</sub> , (air or O <sub>2</sub> )		Equilibrium data given for CH <sub>4</sub> oxidation reactions.
25	CA 36, 3777	Bull. Chem. Soc. Japan 16, 262 (1941)			Nat. gas (air or O <sub>2</sub> )		A review with 27 references.
26	CA 36, 2390	Chem. Industries 50, 204 (1942)			990 cc CH <sub>4</sub> , 550 cc free O atoms, O <sub>2</sub> , A	16 cc reaction prod. with 50% CH <sub>2</sub> O	O atoms are formed in a discharge tube but not O. CH <sub>4</sub> is oxidized by free O atoms.
27	CA 37, 1697	Compt. Rend. Acad. Sci. URSS, 32, 560 (1941)	Non-catalytic; discharge tube		Gas (pentane, hexane, heptane), air (16:6 vol)		Oxygenated compounds were obtained. The contact time was 0.1-1 sec.
28	CA 39, 4083	U.S. 2,369,710 (1945)	Non-catalytic	330 - 370 40-65 psi			

Table III Cont.

1	2	3	4	5	6	7	8
29 CA 40, 2453	M. Fastry, P. Monceaux	Compt. Rend. 221, 259 (1945)	Quartz tube reactor	575 - 800	CH <sub>4</sub> , air (1 to 7 : 9 to 3 vol)	0.01-1.05% yield CH <sub>2</sub> O	The CH <sub>2</sub> O yield was studied as a function of temperature, contact time and initial composition.
30 CA 41, 349	J. Hall	U.S. 2,384,028 (1945)	Non-catalytic	565 - 650 1 atm	CH <sub>4</sub> , air or O <sub>2</sub> (20 fold excess)		An apparatus is shown for partial oxidation of CH <sub>4</sub> using an elongated flame.
31 CA 41, 684	E. Audibert	Ann. Mines & Carburants, Mem. 2, 5 (1943)	Non-catalytic				A study was made of CH <sub>4</sub> burning mechanisms.
32 CA 41, 1598	J. Walker, H. Malakoff	Oil Gas J. 45, No. 33, 59 (1946)					A review was made of methods of producing oxygenated hydrocarbons.
33 CA 42, 5838	J. Bludworth	Oil Gas J. 46, No. 51, 99 (1948)			Lower aliphatic hydrocarbons (air or O <sub>2</sub> )	"Large amts." CH <sub>2</sub> O	A discussion was made of the importance of controlled oxidation. It was found that CH <sub>2</sub> O yield improved with decrease in temperature.
34 CA 43, 3993	A. Foster	Petroleum Engr. 216, No. 3, 7 (1949)			Mat. gas, (air or O <sub>2</sub> )	37% Aq-CH <sub>2</sub> O	MeOH, AcH and AcOH were also produced.
35 CA 45, 8740	J. Hightower	Chem. Eng. 56, No. 1, 92, 132 (1949)			Mat. gas, O <sub>2</sub> (90-95% pure)		Most of the CH <sub>2</sub> O produced was prepared from CH <sub>3</sub> OH which in was prepared from natural gas.
36 CA 45, 2157	G. Manfredi	Ingegneri (Milan) 24, 241 (1950)			Synthesis gas (air or O <sub>2</sub> )		A review was made of the use of synthesis gas in the CH <sub>2</sub> O industry.
37 CA 47, 12791	G. Minhoff, K. Salooja	Fuel, 32, 516 (1953)	Non-catalytic, Pyrex reactor	440 - 520	CH <sub>4</sub> (air or O <sub>2</sub> )	1% CH <sub>4</sub> converted to CH <sub>2</sub> O	Static conditions were employed. 1% of the CH <sub>4</sub> forms H <sub>2</sub> O <sub>2</sub> under normal reaction conditions; however, no H <sub>2</sub> O <sub>2</sub> is formed when reactive surfaces are present.
38 CA 48, 12790	Ruttenhoffnungshütte Oberhausen A.-G.	Ger. 811,230 (1951)			CH <sub>4</sub>		A cyclic process was employed. 2% aqueous K <sub>2</sub> CO <sub>3</sub> was found to absorb peroxide impurities and small amounts of CH <sub>2</sub> O and there-by improve CH <sub>2</sub> O yield by 50%.
39 CA 48, 1421	P. Keith (To M. W. Kellogg Co.)	U.S. 2,616,898 (1952)		540	CH <sub>4</sub> , CuO		Two reactors were employed with CuO in the first and with reduced CuO reoxidized and recycled in the 2nd reactor. High space velocities were used.
40 CA 54, 20440	L. Karmilova, N. Enkolovska, A. Balabanova	Zhur. Fiz. Khim. 34, 990 (1960)	HF-etched quartz vessels	423 - 513	CH <sub>4</sub> , O, N <sub>2</sub>		CH <sub>2</sub> O yield was found to increase with shorter contact times and higher temperatures. Maximum CH <sub>2</sub> O yield is a linear function of the initial pressure and of P <sub>CH<sub>4</sub></sub> , but is independent of P <sub>O<sub>2</sub></sub> .

Table III Cont.

1	2	3	4	5	6	7	8
41 CA 54, 9456	R. Moshkina, N. Galanina A. Malbandyan	Izvest. Akad. Nauk SSSR Otdel Khim. Nauk. (1959)	Non-catalytic	1 atm	CH <sub>4</sub> , O <sub>2</sub> , 0.03% C- labeled CH <sub>3</sub> OH		The kinetics of formation of CH <sub>2</sub> O and CH <sub>3</sub> OH from CH <sub>4</sub> oxidation were studied. At steady-state the rate of CH <sub>2</sub> O formation is nine times that of CH <sub>3</sub> OH formation. It was found that CH <sub>3</sub> OH and CH <sub>2</sub> O are formed from parallel reactions.
42 CA 54, 3264	A. Malbandyan, M. Neimab, M. Emanuel	Radioisotopies Sci. Res. Proc. Intern. Conf. Paris (1957) 2, 72	Non-catalytic	650 - 670	CH <sub>4</sub> , (air or O <sub>2</sub> )		CH <sub>4</sub> oxidation to CH <sub>2</sub> O and then to CO was studied by means of the "jet" method for short time periods.
43 CA 54, 2171	J. Bates (No Sun Oil Co.)	U.S. 2,908,622 (1959)	Hg vapor & U.V. (2537 A)	25 1 atm	O, H, CH <sub>4</sub> (8.6:16.7, 32.4)		For optimum yield reactants shall be in volume proportions such that O > H > CH <sub>4</sub> . The product gases were collected at -80° as a white solid. Flow rates were 8.6 cc/min O <sub>2</sub> , 16.7 cc/min H <sub>2</sub> , 32.4 cc/min CH <sub>4</sub> .
44 CA 54, 16386	E. Hausmann, et al. (Bergbau. Akt. Ges. Neue Hoffnung)	Ger. 1,031,776 (1958)		676 - 770 1 atm	CH <sub>4</sub> ; CH <sub>4</sub> homologs (air or O <sub>2</sub> )		A reaction vessel is described having numerous channels for gas and catalyst recycling. Maximum CH <sub>2</sub> O yield occurred after 90 sec. at 770° and after 200 sec. at 676°. Negligible amounts of MeOH and AcH were formed. The reactor was a quartz tube.
45 CA 60, 14301	I. Schneider	Acad. Rep. Pop. Rom. Stud. Cere. Chim. II, (1963)	HF etched quartz	500	CH <sub>4</sub> , O <sub>2</sub> (2:1 vol)		Cu, Brass, and Pt wall coatings on a quartz tube reactor decreased CH <sub>2</sub> O yield relative to pure quartz. It was concluded that quartz is a selective catalyst for CH <sub>2</sub> O formation. A flow rate of 3 l/min was used. The CH <sub>2</sub> O yield was proportional to magnitude of free SiO <sub>2</sub> surface.
46 CA 59, 5826	P. Stadnik, V. Gomoni	Kinetika i Kataliz I, (3), 348 (1963)			CH <sub>4</sub> , 5-20% O <sub>2</sub> inert gas, H <sub>2</sub> O		Partial localized burning was used to produce CH <sub>2</sub> O. Inert gas or H <sub>2</sub> O was used to limit the total O <sub>2</sub> volume to less than twice the CH <sub>4</sub> volume.
47 CA 59, 8596	A. Van Tiggelen	Fr. 1, 313,722 (1963)	Argon plasma jet	1000	Air, CH <sub>4</sub> (20:1 vol)	CH <sub>2</sub> O yield= 8 vol. % (based on CH <sub>4</sub> )	CH <sub>2</sub> O yield was increased by a factor of 3 to 4 when air was used in place of O <sub>2</sub> . Although N <sub>2</sub> was present no N oxides were formed.
48 CA 64, 3255	A. Ousyannikov, L. S. Folak	Kinetika i Term. Khim. Reaktsii v Nizkotemp. Pla - Akad. Nauk SSSR Inst. Nert. Sin. (1965)					

Table III Cont.

1	2	3	4	5	6	7	8
49 CA 60, 6712	J. Knox, C. Wells	Trans. Farad. Soc. 52, (1956) 2786 (1956)	Non-catalytic	300 - 400	O <sub>2</sub> , H <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> , O <sub>2</sub>	CH <sub>2</sub> O yield= from C <sub>2</sub> H <sub>4</sub> = 80%	C <sub>2</sub> H <sub>6</sub> ions oxidized to 80% C <sub>2</sub> H <sub>4</sub> yield. In C <sub>2</sub> H <sub>4</sub> oxidation, CH <sub>2</sub> O appears as an intermediate which later goes to CO.
50 CA 51, 199	A. Egerton, et. al.	Proc. Roy. Soc. (London) A235, 156 (1956)	HF etched Pyrex vessels	440 - 520 100-350 mm	CH <sub>4</sub> , O		CH <sub>2</sub> O concentration reaches a maximum near the stage where the pressure rise is a maximum, then falls off. The CH <sub>2</sub> O was formed during the induction period.
51 CA 55, 27005	L. Karmilova, et. al.	Zhur. Fiz. Khim. 32, 1435 (1956)	Non-catalytic	423 - 513 117-375 mm	CH <sub>4</sub> , O <sub>2</sub>		Flow rate and inlet composition studied as a function of CH <sub>2</sub> O yield.
52 CA 55, 80	E. Magee	J. A.C.S. 82, 355 (1960)	Non-catalytic	815	CH <sub>4</sub> , O <sub>2</sub>		A quartz reactor was used to study the effect of CH <sub>4</sub> concentration on CH <sub>2</sub> O yield. At low CH <sub>4</sub> concentration, CH <sub>2</sub> O concentration was proportional to CH <sub>4</sub> . At higher CH <sub>4</sub> concentration CH <sub>2</sub> O was independent.
53 CA 55, 8282	N. Kleimenov, A. Malbanbyan	Doklady Akad. Nauk SSSR 124, 119 (1959)			CH <sub>4</sub> , (air or O <sub>2</sub> )		Low temperature CH <sub>4</sub> oxidation was studied.
54 CA 55, 11033	F. Dillemath, et. al.	J. Phys. Chem. 64, 1496 (1960)	Non-catalytic		CH <sub>4</sub> , O <sub>3</sub>	CH <sub>2</sub> O yield negligible	The reaction was independent of glass and NaCl surfaces. Major products were CO, CO <sub>2</sub> , CH <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> O.
55 CA 55, 1149	N. Kleimenov, A. Malbanbyan	Doklady Akad. Nauk. SSSR 122, 420 (1958)	Non-catalytic		CH <sub>4</sub> , O <sub>3</sub>		CH <sub>2</sub> O yield was measured as a function of mixture composition, O <sub>3</sub> concentration and contact time. Free O initiation of CH <sub>4</sub> oxidation was studied.
56 CA 52, 9579	P. Mashen (Bergbau Akt.-Ges. Neue Hoffnung)	Ger. 904, 047 (1954)					A heating system is described for CH <sub>4</sub> and air mixtures in a CH <sub>2</sub> O converter.
57 CA 53, 10916	E. Magee	JACS; 81, 2781 (1959)	Non-catalytic	815	CH <sub>4</sub> , O		The time at which the maximum CH <sub>2</sub> O concentration appears in a linear function of 1/O <sub>2</sub> concentration; the maximum CH <sub>2</sub> O concentration is proportional to the O <sub>2</sub> concentration.
58 CA 53, 10913	A. Markevich, et. al.	Zhur. Fiz. Khim. 32, 2242 (1956)	Non-catalytic	25 6,000 kg/m <sup>2</sup>	Mat. gas (1-2% higher hydrocarbons), < 15% O <sub>2</sub>	Max. CH <sub>2</sub> O yield=2.2% of total mixt.	The reaction was carried out under adiabatic compression and expansion at 25 C.
59 CA 49, 5085	J. Burgoyne, H. Hirsch	Proc. Roy. Soc. (London) A 227, 73 (1954)	Non-catalytic	1000	CH <sub>4</sub> , air (5:95 vol)	CH <sub>2</sub> O yield= 36%	Studies with a flow system indicated that the reaction occurs in a few milliseconds, and is independent of surface effects at high temperatures, although dependent at lower temperatures.

Table III Cont.

1	2	3	4	5	6	7	8
60 CA 42, 13715	Y. Ryabinin	Doklady Akad. Nauk. SSSR 94, 1121 (1954)	Non-catalytic	4000 atm	Net. gas (94% CH <sub>4</sub> ), air or O <sub>2</sub>		Rapid heating and cooling of the reaction mixture was accomplished by means of adiabatic compression and expansion.
61 CA 42, 6701	L. Avramenko, R. Kolesnikova	Doklady Akad. Nauk. SSSR 91, 107 (1953)	Non-catalytic		CH <sub>4</sub> , O		Atomic oxygen was used primarily but when O <sub>2</sub> was added CH <sub>2</sub> O yield was improved.
62 CA 50, 5019	J. Tebboth (Brit. Oxygen Co. Ltd.)	Brit. 716,180 (1954)	Non-catalytic	350	CH <sub>4</sub> , (air or O <sub>2</sub> )		CH <sub>2</sub> O decomposition was prevented by passing the product gases over a non-metallic refractory material having a surface-volume ratio > 2 cm <sup>-1</sup> .
63 CA 50, 3500	J. Millen, J. Fenn (Chem. Const. Corp.)	U.S. 2,722, 553 (1955)			Net. gas, O		An apparatus is described for heating the reactants to high temperatures while maintaining a high flow rate (1000 Ft/sec.).
64 CA 53, 18851	J. Morita	Noguchi Kenkyusho Jiho 5, 32 (1957)			CH <sub>4</sub> , (air or O <sub>2</sub> )		A review was made of CH <sub>2</sub> O manufacture by direct oxidation of CH <sub>4</sub> gas.