ENCLOSURE (B) 7

SYNTHESIS OF METHANOL

(In Two Parts)

by

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LIST OF TABLES AND ILLUSTRATIONS

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PART I

by

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Research Period: 1943-1944

SUMMARY

Some experiments were made to find a good catalyst and conditions for the synthesis of CH_3OH from CO_2 and H_2, for utilization of the waste gas in the butanol fermentation industry. The catalyst to be used for the industry was Zn-Cu-chromite (atomic ratio of Zn:Cu:Cr = 8:3.2:2) or Zn+Cu+aluminate (atomic ratio of Zn:Cu:Al = 7:2:1). The duration of catalytic activity is 400 hours and 260 hours, respectively. The experimental conditions which afford good results, are: pressure 200 kg/cm^2, temperature 250 - 270°C, for the chromite catalyst; and pressure 150 kg/cm^2, temperature 250 - 270°C, for the aluminate catalyst. The space time yield of pure methanol under these conditions is 0.4 - 0.5.

I. INTRODUCTION

A. History of Project

It is well known that in the n-butanol fermentation of starchy materials, a large quantity of CO_2 and H_2 is produced. For utilizing the waste gas of this fermentation industry, the present experiments to study the fundamental conditions of the methanol synthesis were undertaken from April, 1943 to March, 1944. A larger scale pilot plant was established in the Depot in May, 1944. But the project was discontinued after March, 1944; therefore, there is no data of a larger scale experiment. A flow sheet for this pilot plant is shown in Figure 4(B)7. The important references for the methanol synthesis from CO_2 and H_2 are mentioned in the following literature:

J. C. Woodruff, Ind. Eng. Chem., 19, 1147 (1927)
J. C. Woodruff, U.S.P. 1695447
B. N. Dolgow, Chem. Zentr., 105, 2653 (1934)
B. N. Dolgow, Chem. Abs., 28, 5805
A. Z. Karpov, Chem. Abs., 34, 5047 (1940)
E. M. Bocharova, Chem. Abs., 32, 4518 (1938)
FUJII, J. P. 154358

B. Key Research Personnel

Chem. Eng. Lieut. Comdr. A. YAMAOKA
Chem. Eng. Lieut. M. YOSHIDA
Chem. Eng. Lieut. S. ENDO
Engineer INOUE

II. DETAILED DESCRIPTION

A. Description of Test Apparatus

The flow sheet of the pilot plant is shown in Figure I(B)7.

B. Description of Test Procedures

1. Preparation of Catalysts. Solutions of 0.5 N $Cu(NO_3)_2$, $Zn(NO_3)_2$, and $Cr(NO_3)_3$ or $Al(NO_3)_3$ were mixed in definite proportions and heated to 80°C. The solution was poured into an equivalent amount of 0.5 N.NaOH, and the precipitate formed was washed with hot water and filtered. It was dried at 350°C, powdered in a ball-mill, and made into tablets.

2. The Raw Material Gases. CO_2 from market and H_2 produced in the Depot were mixed in a ratio of 1:3.

3. Procedure of the Operation. To the reaction vessel, which contained 50cc of catalyst, the mixed gas was passed at a rate of 4lit/hr and heated slowly to 200°C during 7 hours. Maintaining the reaction vessel at a definite temperature and pressure, the reaction products were obtained and their composition determined. The gas composition was determined by the Hempel method and the composition of liquid product, being composed of CH_3OH and H_2O, was determined by the specific gravity. From these data, the volume of the charged gas, specific velocity in the reaction vessel, and space time yield of CH_3OH were calculated by the following formula:

The volume of charged gas = The equivalent gas volume of the liquid products + The volume of waste gas.

$$\text{Space velocity (SV)} = \frac{\text{The volume of charged gas (lit/hr)}}{\text{The volume of the catalyst (lit)}}$$

$$\text{Space time yield of } CH_3OH \text{ (S.T.Y.)} = \frac{\text{The quantity of produced } CH_3OH \text{ per one hour (gm)}}{\text{The volume of the catalyst (cc)}}$$

C. Experimental Results

The effect of temperature and the chemical composition of the catalyst on the yield of methanol is shown in Table I(B)7 and Figure 2(B)7. The duration of catalyst activity was investigated by determining the temperature necessary to maintain the S.T.Y. of CH_3OH at 0.4 - 0.6. The results were shown in Table II(B)7 and Figure 3(B)7.

III. CONCLUSIONS

The atomic ratio of a good mixed catalyst is as follows:

Zn : Cu : Cr = 8 : 3.2 : 2
Zn : Cu : Al = 7 : 2 : 1

Using these catalysts the following S.T.Y. of CH_3OH were obtained at the indicated temperature.

Cat.	Temp.	S.T.Y.
Zn:Cu:Cr = 8:3.2:2	250 - 320°C	1.3 - 1.4
Zn:Cu:Al = 7:2:1	300 - 325°C	1.2 - 1.3.

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The activity of the catalyst depends largely on the Cu-content. As Cu-content increases, the catalyst becomes more active at low temperatures.

The conditions under which these catalysts show durability in regard to catalyst activity are:

	Zn:Cu:Cr	Zn:Cu:Cr	Zn:Cu:Al
Catalyst composition	8:3.2:2	8:3.2:2	7:2:1
Reaction pressure	150 kg/cm^2	200	150
Reaction temperature	275-400^{o}C	260-355	250-310
Space velocity	15000-16000	15000-16000	15000-16000
S.T.Y. of CH_3OH	0.4-0.5	0.4-0.6	0.4-0.5
Life of catalyst	150 hrs	400	260.

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Table I(B)7-a
CATALYST ACTIVITY IN SYNTHESIS OF CH_3OH

Exp.No.	Condition*			Product		
	Temp. (°C)	SV	Total (gm)	% of CH_3OH (%)	CH_3OH (gm)	STY of CH_3OH
No. 1	230	14650	13	40	5	0.05
	250	14860	27	39	11	0.11
	275	14035	44	30	13	0.13
	300	15350	80	39	31	0.31
	325	15800	105	39	41	0.41
	350	16190	118	39	46	0.46
	375	16248	151	38	51	0.51
	400	16340	181	36	65	0.65
	425	16355	178	30	53	0.53
No. 3	225	14380	27	32	9	0.09
	250	14745	45	48	22	0.22
	275	15160	89	51	45	0.45
	300	15760	120	49	59	0.59
	325	15870	143	47	66	0.66
	350	16900	143	40	57	0.57
	375	16270	142	37	53	0.53
	400	15890	129	33	42	0.42
No. 4	230	14800	58	38	20	0.20
	250	15400	85	44	37	0.37
	275	16700	162	46	75	0.75
	300	16710	200	51	102	1.02
	325	17230	192	43	84	0.84
	350	16210	192	42	81	0.81
	375	18860	201	38	76	0.76
	400	16920	177	31	55	0.55

* In all cases: pressure was 200 Kg/cm^2, time was 2 hours. The catalyst was 50cc of Zn:Cu:Cr in the following ratios: Experiment No. 1 7:1:3, Experiment No. 3 7:5:3, Experiment No. 4 7:6:3.

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Table I(B)7-b
CATALYST ACTIVITY IN SYNTHESIS OF CH_3OH

Exp.No.	Catalyst Zn:Cu:Cr	Condition* Temp. (°C)	Condition* SV	Total (gm)	Product % of CH_3OH (%)	CH_3OH (gm)	STY of CH_3OH
No. 7	7:9:3	230	15470	100	47	47	0.47
	50cc	250	16830	151	51	77	0.77
		275	17003	203	51	104	1.04
		300	18235	248	51	126	1.26
		325	16290	197	49	96.5	0.97
		350	16830	195	44	85.8	0.86
		375	16214	159	38	60	0.60
		400	16430	176	32	56	0.56
No.11	Zn:Cu:Cr	225	15810	108.7	57.7	62.7	0.68
	8:32:2	250	17657	229	61	139.7	1.40
	50cc	275	18335	236	55	130	1.30
		300	18750	260.5	51.5	134	1.34
		325	17501	248	46	114	1.14
		350	16805	223	46	103	1.03
		375	16895	194	42	81	0.81
No.13	Zn:Cu:Al	225	15240	64	49	31	0.31
	7:2:1	250	15220	87	44	38	0.38
	50cc	275	17030	154	46	71	0.71
		300	18700	242	50	121	1.21
		325	18330	272	47	128	1.28
		350	17260	246	41	101	1.01
		375	17380	217	32	69	0.69
		400	16390	181	20	36	0.36

* In all cases: pressure was 200 Kg/cm^2, time was 2 hours.

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Table II(B)7-a
THE RESULTS OF THE DURATION TEST

Duration Time (hr)	Condition*			Produot		S. T. Y. of CH_3CH
	Temp (°C)	S.V.	Total (gm)	% of CH_3OH (gm)	CH_3OH (gm)	
14	250-270	15650	103	39	40	0.40
34	270	15440	115	40	46	0.46
54	270	15430	104	39	40	0.40
64	270	15380	99	38	37	0.37
74	280	15540	119	40	48	0.48
94	280	15490	109	36	39	0.39
104	280	15610	106	38	40	0.40
124	290	15830	126	38	47	0.47
148	290	15570	120	41	49	0.49
160	300	15970	131	44	58	0.58
180	300	15680	124	38	47	0.47
200	300	16050	127	38	49	0.49
220	300	15510	124	36	44	0.44
234	300	15780	118	37	44	0.44
258	310	15640	124	36	45	0.45
268	310	15860	123	39	48	0.48

* Pressure: 150 kg/cm^2;
Time: 2 hrs.
Catalyst: Zn:Cu:Al::7:2:1; 50°°

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Table II(B)7-b
THE RESULTS OF THE DURATION TEST

Duration Time (hr)	Condition*		Product			S. T. Y. of CH_3CH
	Temp. 230°C	S.V.	Total (gm)	% of CH_3OH	CH_3OH (gm)	
10	275	15420	65	35	22	0.22
14	275	15480	94	40	38	0.38
40	300	16108	137	40	55	0.55
60	300	15860	125	48	60	0.60
80	300	15637	107	49	53	0.53
100	300	15637	118	45	54	0.54
126	300	15283	79	51	41	0.41
146	310	15320	90	49	44	0.44
160	310	16520	100	39	39	0.39
180	320 340	15230	82	43	35	0.35
190	340 360	15660	74	37	27	0.27
208	360 400	15100	73	25	19	0.19

* Pressure: 150 kg/cm^2
Time: 2 hrs.
Catalyst: Zn:Cu:Cr::8:3.2:2; 50cc

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Table II(B)7-c
THE RESULTS OF THE DURATION TEST

Duration Time (hr)	Condition*		Product			S. T. Y. of CH_3OH
	Temp. (°C)	S.V.	Total (gm)	% of CH_3OH	CH_3OH (gm)	
4	230	14680	56	42	23	0.23
14	250	14730	78	49	38	0.38
28	260	15350	105	50	53	0.53
46	270	15740	115	49	56	0.56
66	270	15770	118	50	59	0.59
82	270	15810	100	51	51	0.51
90	275	15790	120	51	61	0.61
110	280	16230	129	49	63	0.63
124	280	16000	98	49	48	0.48
144	285	16460	145	49	71	0.71
164	285	15930	117	51	60	0.60
184	285	15620	109	46	50	0.50
192	285	15760	110	43	47	0.47
196	290	16185	111	45	50	0.50
216	300	15340	98	46	45	0.45
222	300	15380	85	45	38	0.38
230	305	15375	93	46	43	0.43
250	310	15660	107	45	48	0.48
268	310	15570	99	46	46	0.46
274	315	15270	84	44	37	0.37
276	320	15030	99	45	45	0.45
298	325	15670	107	42	45	0.45
318	330	15840	123	43	53	0.53
338	330	15250	140	27	38	0.38
346	330	15280	91	40	36	0.36
352	335	14980	90	42	38	0.38
364	340	15090	91	39	35	0.35
370	345	14950	97	40	39	0.39
378	350	15625	102	39	40	0.40
396	355	15320	115	38	44	0.44
400	355	12615	102	30	30	0.30

* Pressure: 200 kg/cm^2
Time: 2 hrs.
Catalyst: Zn:Cu:Cr::8:3.2:2 ; 5000

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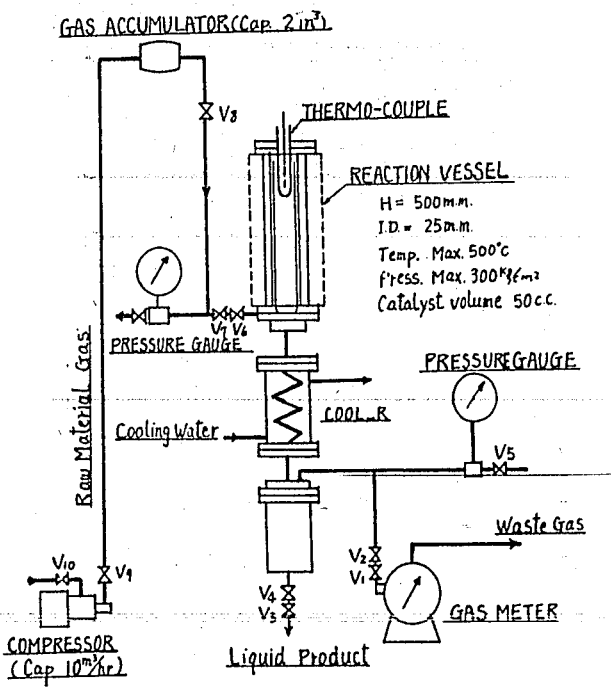

Figure 1 (B)7
FLOW SHEET OF THE PILOT PLANT FOR METHANOL SYNTHESIS

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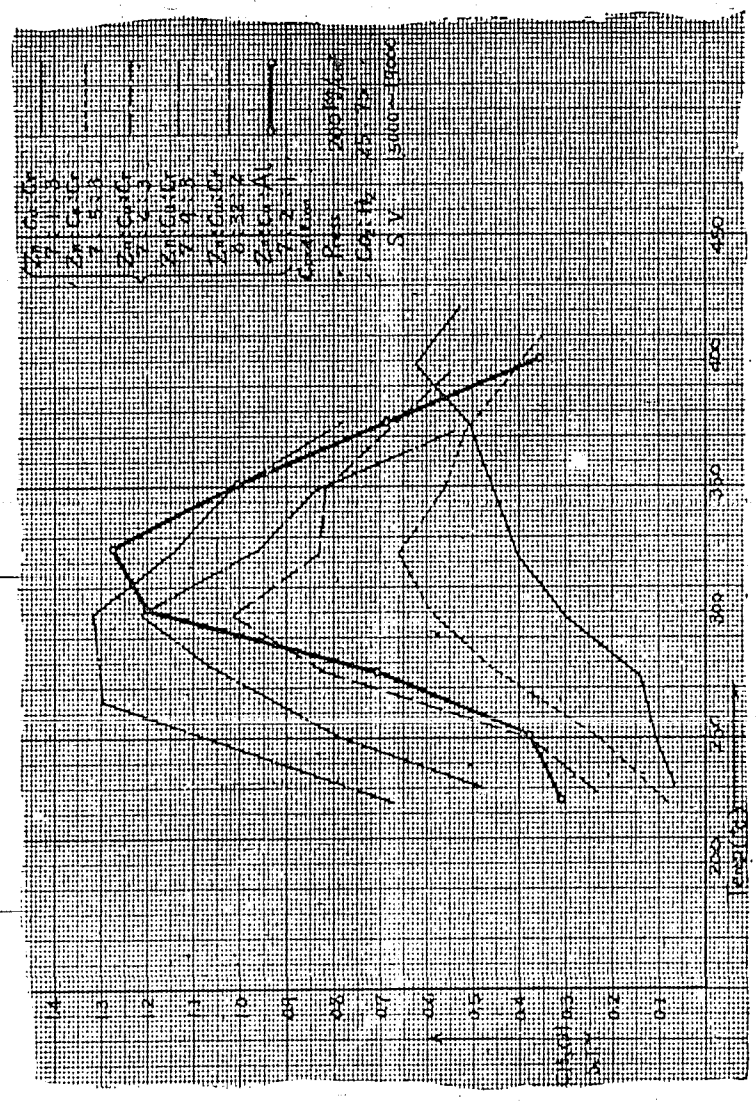

Figure 2 (B)7
CATALYST ACTIVITY IN SYNTHESIS OF CH3OH

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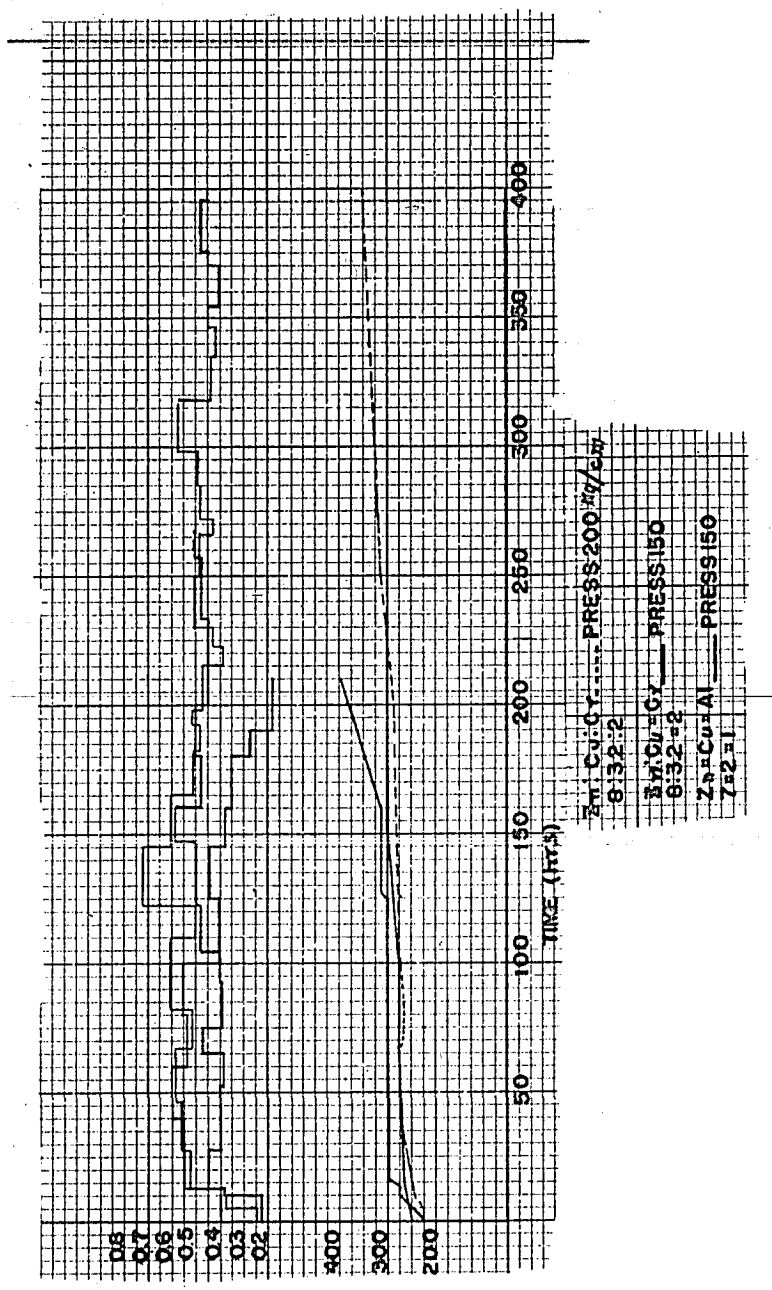

Figure 3 (B)7
THE RESULTS OF THE DURATION TEST

ENCLOSURE (B)7

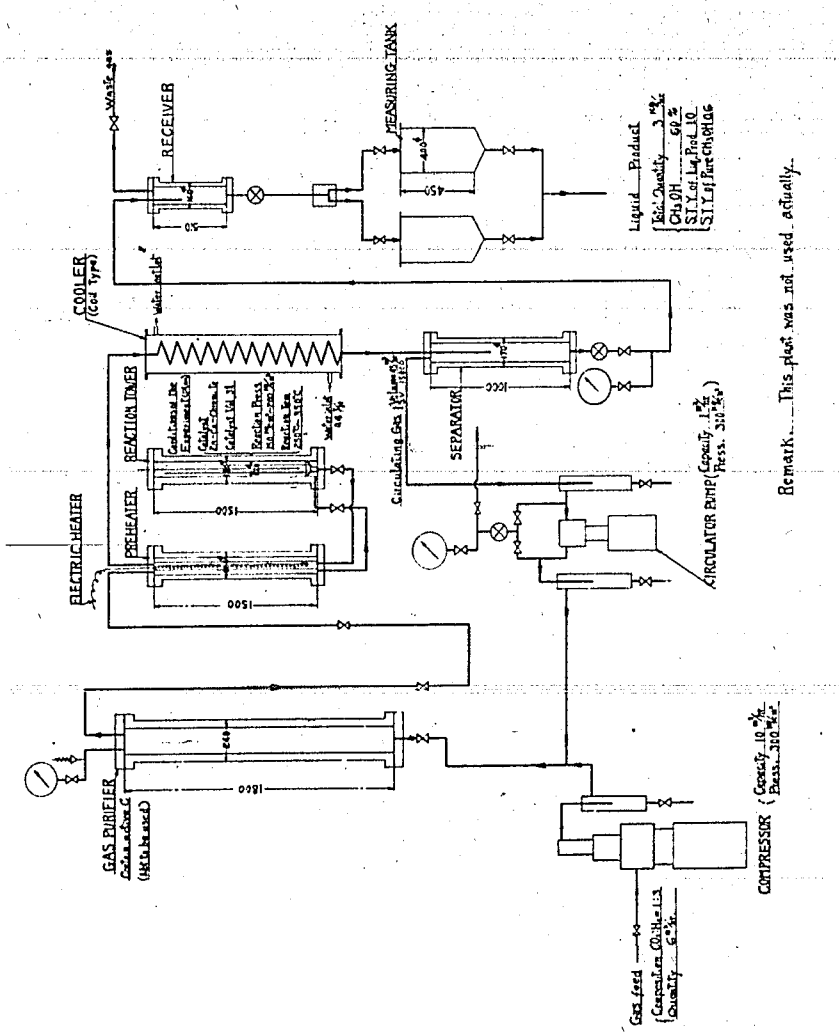

Figure 4 (B)7
FLOW SHEET OF THE PILOT PLANT
FOR CH_3OH SYNTHESIS FROM CO_2 AND H_2

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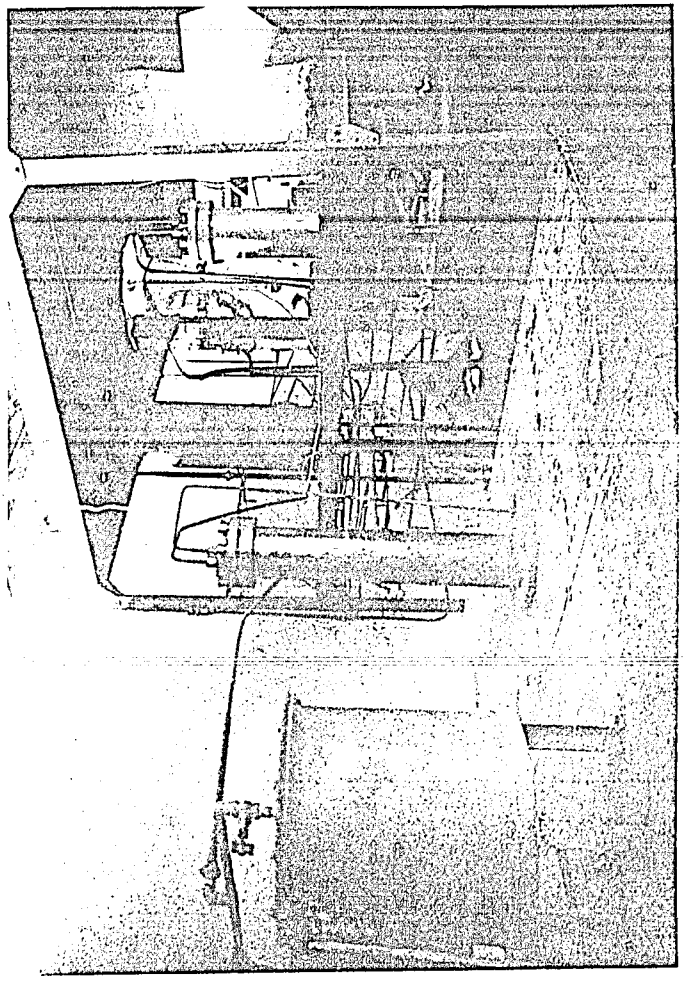

Figure 5 (B)7
PILOT PLANT FOR SYNTHESIS
OF METHANOL FROM WATER GASES

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PART II

by

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Research Period: 1943-1944

SUMMARY

This study was made to find a new catalyst for the methanol synthesis from water gas. The result of the experiments was as follows:

The Zn-Cu-chromite catalyst, having the composition Zn:Cu:Cr = 8:3.2:2, was found to be a good one. Its catalytic activity was kept for 20 days under the following conditions:

Reaction temperature .....250-350°C
Reaction pressure .....150 kg/cm^2
S.V. 10,000-15,000
S.T.Y. .....0.5-1.0.

I. INTRODUCTION

A. History of Project

Previously, a Cu-uranium catalyst was used in the methanol synthesis plant because of its strong activity at low temperatures and low pressures. However, its activity was impaired by overheating and the poisonous action of sulfur in the gas. The Zn-Cu-chromite catalyst, mentioned in Part I, was therefore studied.

B. Key Research Personnel

Chem. Eng. Lt. Comdr. A. YAMAOKA
Chem. Eng. Lt. S. ENDO
Chem. Eng. T. INOUE

II. DETAILED DESCRIPTION

The gas used for this experiment was a mixture of 1 mol of CO and 2 mols of H_2. CO was prepared by burning charcoal and the CO_2 was removed with caustic. The details of the experiment and the apparatus used are the same as those described in Part I.

The experimental results: Using the previously studied Zn-Cu-chromite catalyst, similar results for the experiments made in Part I were obtained. The Zn-Cu-chromite catalyst, having the composition Zn:Cu:Cr= 8:3.2:2, was found to be a good one. Its catalytic activity was kept for 20 days under the following conditions:

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Reaction temperature	250-350°C
Reaction pressure	150 kg/cm^2
S.V.	10,000-15,000
S.T.Y.	0.5-1.0.