

ENCLOSURE (B) 13

STUDIES ON THE SYNTHESIS OF
ACETALDEHYDE WITHOUT THE
USE OF MERCURY CATALYST

by

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ENCLOSURE (B)13

LIST OF TABLES
AND ILLUSTRATIONS

Table I(B)13 Effect of the Velocity of Acetylene Page 186

Table II(B)13 Effect of the Reaction Temperature Page 187

Table III(B)13 Effect of the Concentration of Hydrochloric
Acid Page 187

Table IV(B)13 Effect of the Addition of Leucine
Hydrochloride Page 188

Table V(B)13 Effect of the Concentration of the Catalyst
Solution Page 188

Table VI(B)13 Vapor Phase Hydration of Acetylene Page 192

Figure 1(B)13 Flow Sheet of Vapor Phase Hydration of
Acetylene Page 191

Figure 2(B)13 Flow Sheet of Vapor Phase Hydration of
Acetylene to Acetaldehyde Page 194

Figure 3(B)13 Flow Sheet of Synthesis of Vinyl Methyl Ether ... Page 196

Figure 4(B)13 Vapor Phase Hydration Plant of Acetylene to
Acetaldehyde Page 197

Figure 5(B)13 Synthesis Plant of Vinyl-Methyl-Ether by
Means of Methylation of Acetylene Page 198

ENCLOSURE (B)13

SUMMARY

Acetaldehyde was synthesized from acetylene without mercury catalyst by three methods.

1. A dilute hydrochloric acid solution of a complex salt of cuprous chloride and ammonium chloride, which was a modification of the catalyst used in the synthesis of vinylacetylene from acetylene, was used as the catalyst for the liquid phase reaction. At the optimum conditions nearly 10 % of the acetylene used reacted and 9 % of the reacted acetylene was converted to acetaldehyde.

2. The vapor phase hydration of acetylene using a solid catalyst consisting of a mixture of cadmium phosphate and calcium phosphate was tested. Acetylene and steam were passed through the catalyst heated at 350-400°C. Nearly 40 % of the acetylene charged was hydrated, and a 90 % yield of acetaldehyde was obtained. The activity of the catalyst was maintained for 60 hours. The activity was recovered by aeration for five hours. The results obtained was satisfactory.

3. Acetylene was methylated by methanol using caustic soda as a catalyst, then the vinyl methyl ether obtained was hydrolysed to acetaldehyde and methanol. The yield of vinyl methyl ether was 94 %. Although, the investigation of the hydrolysis of vinyl methyl ether was not completed, a very high yield of acetaldehyde was obtained on the preliminary test.

I. INTRODUCTION

Isocotane is synthesized from acetylene commercially. However, the synthesis of acetaldehyde from acetylene, the first step of the isocotane synthesis, requires the use of mercury as the catalyst. Since some of the mercury is lost in the process and since the production of mercury in Japan is small, research on the synthesis of acetaldehyde from acetylene without using a mercury catalyst was ordered in 1940 for the isocotane synthesis. The research was begun by Chem. Eng. Capt. Dr. C. FUJIO and Chem. Eng. Lt. Comdr., T. YAMAMOTO and several other collaborators, and continued until the end of the war. The data in this report was collected from the notes of the above investigators by the author.

II. DETAILED DESCRIPTIONA. Liquid Phase Hydration of Acetylene Using the Complex Salt Solution of Cuprous Chloride and Ammonium Chloride as the Catalyst1. Introduction

In the synthesis of vinylacetylene from acetylene using a cuprous chloride complex salt solution, the formation of acetaldehyde as a byproduct was observed. In order to increase the yield of acetaldehyde, the relation between the composition of the catalyst solution, the yield of acetaldehyde, and the conditions of reaction were studied.

ENCLOSURE (B)13

2. Apparatus and Procedure

Purified acetylene from a pressure vessel was introduced continuously into a reaction vessel containing about 100cc of the catalyst solution placed in a thermostat. The gas volume was measured with a gas-meter. The gas from the reaction vessel was first cooled with an ice-cooled condenser, then by contact with crushed ice, and finally with a condenser cooled by dry ice. The reaction product from each condenser was analysed. The volume of the unreacted acetylene was measured with another gas-meter. The reaction products collected from the two ice coolers were fractionated exactly and acetaldehyde was determined as the fraction distilling from 19°C to 25°C. The product separated from the dry ice cooler was fractionated with the Podbielniak's apparatus into two fractions -20°C to -10°C and 0 to 10°C. The former was regarded as vinyl chloride and the latter as vinyl acetylene. When no vinylchloride was formed the product from the dry ice cooler was evaporated and vinyl acetylene was determined by absorption in 91 % sulfuric acid. The acetylene concentrations in the charging gas and the unreacted gas were determined by absorption in alkaline mercurous cyanide solution.

3. Experimental Resultsa. Acetaldehyde formation in the manufacture of vinyl acetylene

A catalyst solution having the following composition was used. This composition was obtained from the literature.

Cuprous chloride	40 grams
Ammonium ohloride	23 grams
Water	45 grams
Hydrochloric acid (38%)	5 grams

The experimental results are shown in Table I(B)13, II(B)13, and III(B)13. In these tables, the difference between the quantity of acetylene reacted and the acetylene converted to acetaldehyde is considered as being due to loss and the formation of higher polymers.

Table I(B)13
EFFECT OF THE VELOCITY OF ACETYLENE

Vol. of C ₂ H ₂ lit/hr	Reacted C ₂ H ₂ (%)	Yield of CH ₃ COH ₂ (%)	Yield of C ₄ H ₄ * (%)
2.0	18.6	2.0	38.2
4.3	13.5	9.5	34.3
6.5	11.1	10.8	35.0
8.7	5.3	15.5	34.8

*C₄H₄ is vinyl acetylene.

Note. The percent of reacted C₂H₂ and percent yield was calculated as follows:

$$\text{Percent yield} = 100 \times \frac{\text{measured wt. of CH}_3\text{OH}}{\text{vol. of reacted C}_2\text{H}_2 \times 44/22.4}$$

$$\text{Percent of reacted C}_2\text{H}_2 = 100 \times \frac{(\text{vol. of C}_2\text{H}_2 \text{ used} - \text{vol. of unreacted C}_2\text{H}_2)}{\text{vol. of C}_2\text{H}_2 \text{ used}}$$

ENCLOSURE (B)13

The gas volume was indicated as that at N.T.P.

Table II(B)13

EFFECT OF THE REACTION TEMPERATURE

React. temp. °C	Reacted C ₂ H ₂ (%)	Yield of CH ₃ OH (%)	Yield of C ₄ H ₄ (%)
90	6.3	7.0	28.1
78	11.1	10.8	35.0
70	13.6	9.9	36.1
60	14.0	3.1	29.3

Wt. of the catalyst solution used 113 grams
 Vol. of acetylene 6 lit/hr
 Time of experiment 5 hrs

Table III(B)13

EFFECT OF THE CONCENTRATION OF HYDROCHLORIC ACID

Vol. of 38% HCl added cc	Reacted C ₂ H ₂ (%)	Yield of CH ₃ COH (%)	Yield of C ₄ H ₄ (%)	Yield of C ₂ H ₃ Cl* (%)
oo	19.0		44.4	
5	11.1	10.8	35.0	2.3
10	5.0	25.6	23.3	10.0
15	4.3	14.5	10.6	13.5
20	2.8	9.5	8.1	14.1

*C₂H₃Cl is vinyl chloride.

Wt. of the catalyst solution used 108 grams
 Vol. of acetylene 6 lit/hr
 Reaction temperature 78 °C
 Time of the experiment 5 hrs

From these data it is concluded as follows:

- (1) Increase of the velocity of acetylene lowers the quantity of reacted acetylene and increases the percentage yield of acetaldehyde.
- (2) The maximum percentage yield of acetaldehyde was obtained at 78°C.
- (3) Increasing reaction temperature increases the rate of the reaction.
- (4) The percentage yield of vinyl acetylene did not vary with changes in temperature and gas velocity.
- (5) Though the high concentration of hydrochloric acid suppressed the rate of the reaction, the formation of vinyl chloride increased.
- (6) For the production of acetaldehyde there is an optimum concentration of hydrochloric acid, which is nearly 10% of 38% HCl in the catalyst solution.

ENCLOSURE (B)13

b. Effect of the addition of leucine hydrochloride

Many kinds of additives to increase the yield of acetaldehyde ~~in this reaction were tried, among them the best results were obtained when leucine hydrochloride was used.~~

The leucine hydrochloride was separated from the waste of glutamic acid manufacture which is the raw material of the Japanese seasoning "Ajinomoto". The experimental results are shown in Table IV(B)13. As shown in Table IV(B)13, the maximum yield of acetaldehyde was obtained and the formation of vinyl acetylene and vinyl chloride was minimized when 10 % of leucine hydrochloride was present in the catalyst solution. The effect of leucine hydrochloride in the catalyst solution was considerable.

c. Effect of the concentration of the catalyst solution

Various catalyst concentrations were tested maintaining constant acidity by dilution with dilute hydrochloric acid.

Table IV(B)13
EFFECT OF THE ADDITION OF LEUCINE HYDROCHLORIDE

Composition of Catalyst Solution				HCl (38%) (g)	C ₂ H ₂ Reacted (%)	Yield of Product		
Cu ₂ Cl ₂ (g)	NH ₄ Cl (g)	Leu-HCl (g)	H ₂ O (g)			CH ₃ OH (%)	C ₄ H ₄ (%)	C ₂ H ₃ Cl (%)
30	15	10	45	10	5.3	75.7	8.1	8.3
30	15	12	45	10	5.1	79.0		
30	15	14	45	10	6.5	52.0	5.5	10.2
30	15	16	45	10	7.6	49.0	2.3	11.0

Reaction Temperature 78 °C
Velocity of acetylene 6 l/hr
Time of experiment 5 hrs

The catalyst composition ratio which showed the best results in previous experiments was maintained constant. The results obtained are shown in Table V(B)13.

Table V(B)13
EFFECT OF THE CONCENTRATION OF THE CATALYST SOLUTION

Cu ₂ Cl ₂ (g)	NH ₄ Cl (g)	Leu-HCl (g)	H ₂ O (g)	HCl (38%) (g)	Reacted C ₂ H ₂ (%)	Yield of CH ₃ CHO (%)
15	7.5	6	45	10	4.2	45.4
22.5	11.25	9	45	10	5.3	47.5
30.0	15.0	12	45	10	6.1	79.6
37.5	18.75	15	45	10	8.0	91.3
52.5	26.75	21	45	10	5.7	85.8
56.25	28.12	22.5	45	10	4.7	53.2

Reaction Temperature 78 °C
Velocity of charged acetylene 6 lit/hr
Time of the experiment 5 hrs

ENCLOSURE (B)13

8.0 % of the acetylene used was reacted and 91 % of the reacted acetylene was hydrated to acetaldehyde by the catalyst having the following composition.

Cuprous chloride	37.5	grams
Ammonium chloride	18.75	grams
Leucine hydrochloride	15.0	grams
Water	45.0	grams
Hydrochloric acid (38%)	10.0	grams

When the concentration of the catalyst is too high, a part of the constituents are deposited as solids even at 80°C. The above composition is the maximum concentration which is completely soluble at 80°C.

d. Durability of catalyst solution

In order to determine the life of the catalyst a continuous experiment was carried out at 80°C and 60 lit/hr velocity of acetylene. Though the apparatus used was larger, the principle was the same as before. The catalyst solution consisted of:

Cuprous chloride	495	grams
Ammonium chloride	240	grams
Leucine hydrochloride	189	grams
35% hydrochloric acid	128	cc
Water	600	cc

The product was collected at 5 hour intervals, and the concentration of water and hydrochloric acid in the catalyst was maintained constant. The results, calculated from the 130 hours experimental data, were as follows:

The percentage of acetylene reacted was 13 % and 80-90 % of the reacted acetylene was converted to acetaldehyde. After 130 hours the rate of the reaction decreased due to the diminishing of the catalyst volume by withdrawing for analysis.

e. Conclusions

The optimum conditions are as follows:

- (1) The best reaction temperature is 70-80°C.
- (2) The best catalyst composition is:

Cuprous chloride	38	grams
Ammonium chloride	19	grams
Leucine hydrochloride	15	grams
38% hydrochloric acid	11	grams
Water	45	grams

- (3) The velocity of acetylene must be controlled as 10% of the used acetylene is reacted.

- (4) During the operation water and hydrochloric acid must be supplied to replace that which has been consumed and evaporated.

ENCLOSURE (B)13

(5) The life of the catalyst solution is at least 7 to 10 days. Accumulation of resinous higher polymers may interfere by decreasing catalyst activity if used for longer periods.

B. Vapor Phase Hydration of Acetylene on a Solid Catalyst

1. Introduction

A mixture of acetylene and steam was passed through the catalyst heated 300° to 400°C. Although many kinds of catalysts were tried, catalysts having strong activity such as phosphoric acid supported on diatomaceous earth lost their activity in a short time, and the activity could not be recovered. It was found that some phosphates, such as cadmium phosphate, also have good activity which could be easily recovered. This report is on the experiments using the mixed catalyst of cadmium phosphate and calcium phosphate which showed the best results.

2. Catalyst

The catalyst used was prepared as follows: A solution containing 0.1 mol of cadmium nitrate and 0.3 mol of calcium nitrate was warmed to 85°C, and a solution of sodium biphosphate (pH. adjusted to 7) was added until the precipitation was complete. Separately, the precipitate prepared from 0.3 mol of calcium nitrate solution by the same method was mixed with the above precipitate, washed, dried and shaped into 4mm x 1mm cylinders. This catalyst had an activity as shown below.

Diameter of the reaction tube	20mm
Volume of catalyst taken	50cc
Reaction temperature	350°C
Space velocity of acetylene only	250
Amount of steam used	6 times of the theoretical
Reacted acetylene	65% of charge
Yield of acetaldehyde	97.8% to reacted acetylene

This catalyst was used and a durability test was carried out on the apparatus shown in Figure 1(B)13.

3. Apparatus and Procedure

Purified carbide acetylene was introduced through a gas meter (1) with a blower (2) and was mixed with steam at an evaporator (3). Water was pumped from a measuring cylinder (5) by a small bellows pump (4) and evaporated in the evaporator, which was heated by steam. The mixture was heated in the preheater (6) and passed through the catalyst tube of the reactor (7). The product was condensed by a condenser (10) and unreacted acetylene was separated from the product at a receiver (14). Acetaldehyde vapor remaining in the gas was washed with water in a washing tower (11). The volume of the unreacted acetylene was measured with a gas meter (15).

The recycling pump and the receiver of the dilute solution of acetaldehyde are indicated by (12) and (13), respectively.

The catalyst tubes of the reactor were immersed in a liquid mixture of diphenyl and diphenyl oxide known as "dowtherm" which was heated with a heater (8) and a regulating transformer (9). The reaction

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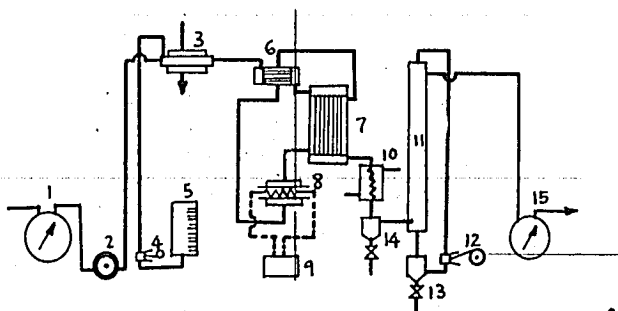


Figure 1 (F) 13

FLOW SHEET OF VAPOR PHASE HYDRATION OF ACETYLENE

ENCLOSURE (B)13

heat was conducted from the catalyst to the dowtherm, and the evaporated vapor of the dowtherm at the outside of the catalyst tubes was condensed at the preheater (6) and the condensate returned to (8). The reactor had 19 catalyst tubes, 500mm in length and 25mm in dia. The temperature was measured at the top and the bottom of one of the catalyst tubes and the inlet of the reactor by three thermocouples.

The catalyst was reactivated in the reactor by aerating at 350°C for 10 hours. After the air was expelled by steam, water and acetylene were introduced. The reaction product from each 12 hour interval was collected and analyzed.

4. Experimental Result

A durability test of the catalyst was carried out for 480 hours. The reaction conditions were as follows:

The space velocity of acetylene only 250
 The velocity of steam used 6 times theoretical
 The reaction temperature at the top of the reactor 340-390°C

The results obtained during the first 66 hours are shown in Table 6(B)13. After 66 hours the reaction temperature necessary for maintaining 30% conversion of acetylene reached 400°C.

The reaction was stopped and the activity of the catalyst was recovered by aeration at 350°C for five hours. At the beginning of the aeration the temperature at the top of the reactor rose suddenly to 500°C and then the catalyst zone indicating the maximum temperature gradually descended to the bottom of the reactor. After recovering the catalyst activity the reaction was resumed as before. For 60 hours there was but little change over the previous results.

After the 60 hours of reaction followed by the five hours of recovering the catalyst activity had been repeated eight times, the catalyst was removed and its activity was tested in a glass tube as had been done originally.

The result obtained showed no change in the catalyst activity. The reacted acetylene was 58.8% of the used acetylene and 91.3% of the reacted acetylene was hydrated.

Table VI(B)13
 VAPOR PHASE HYDRATION OF ACETYLENE

Time elapsed, hours	Reaction temp. (°C)		A C ₂ H ₂ used, l	B C ₂ H ₂ consumed lit	B/A	Yield of CH ₃ COH (%)
	top	bottom				
	357	359				
12	385	376	13.725	5.192	37.0	
24	390	380	14.840	4.787	32.2	99.3
36	390	380	13.280	4.629	34.9	90.0
48	400	390	13.700	4.512	33.0	81.0
60	395	390	13.408	4.304	32.1	96.2
66	400	400	7.293	2.247	30.9	99.6

ENCLOSURE (B)13

5. Conclusions

In the vapor phase hydration of acetylene using the mixed catalyst of ~~cadmium phosphate and calcium phosphate at reaction temperatures of 350° to 400°C~~, space velocity of acetylene 250, and a quantity of of steam six times the theoretical, 30 to 40% of the acetylene used reacted and 90% of the reacted acetylene was converted to acetaldehyde. The catalyst activity continued for about 60 hours, and the loss in activity of the catalyst could be recovered by aeration at 350°C for five hours.

Repetition of the running and the recovering of the catalyst activity six times over a period of three weeks shows no change in the catalyst activity.

C. Synthesis of Acetaldehyde by the Hydrolysis of Vinyl Methyl Ether and Synthesis of Vinyl Methyl Ether from Acetylene

1. Introduction

Previously the possibility of the synthesis of acetaldehyde by the hydrolysis of vinyl methyl ether and the synthesis of vinyl methyl ether from acetylene and methanol were known.

Experiments were carried out to clarify the reaction conditions. Since there were many difficulties in the use of high-pressure acetylene and methanol at high temperatures on the laboratory scale. A pilot plant having a capacity of several cubic meters of acetylene was erected without exact preliminary tests. Though the experiments on the synthesis of vinyl methyl ether were carried out successfully, the experiments on the hydrolysis of vinyl methyl ether had not yet been started.

2. Apparatus and Procedure

The flow sheet of the pilot plant is shown in Figure 2(B)13. Carbide acetylene purified by a mixture of ferric chloride, cupric acetate, mercuric chloride and diatomaceous earth, was introduced through a gas meter and compressed with a specially designed acetylene compressor in a reactor containing a caustic soda solution of methanol.

The methanol solution was circulated from the bottom to the top of the reactor through a heater heated by steam.

Acetylene was absorbed in the methanol solution under pressure and forms vinyl methyl ether by the catalytic action of caustic soda. The methanol solution containing ether was introduced through a cooler to a fractionating tower by releasing the pressure. Vinyl methyl ether was separated and condensed in a receiver. The methanol solution at the bottom of the fractionating tower was returned to the bottom of the reactor.

The methanol consumed by the reaction was supplied from a tank, and serves to dissolve caustic soda at the beginning of the run.

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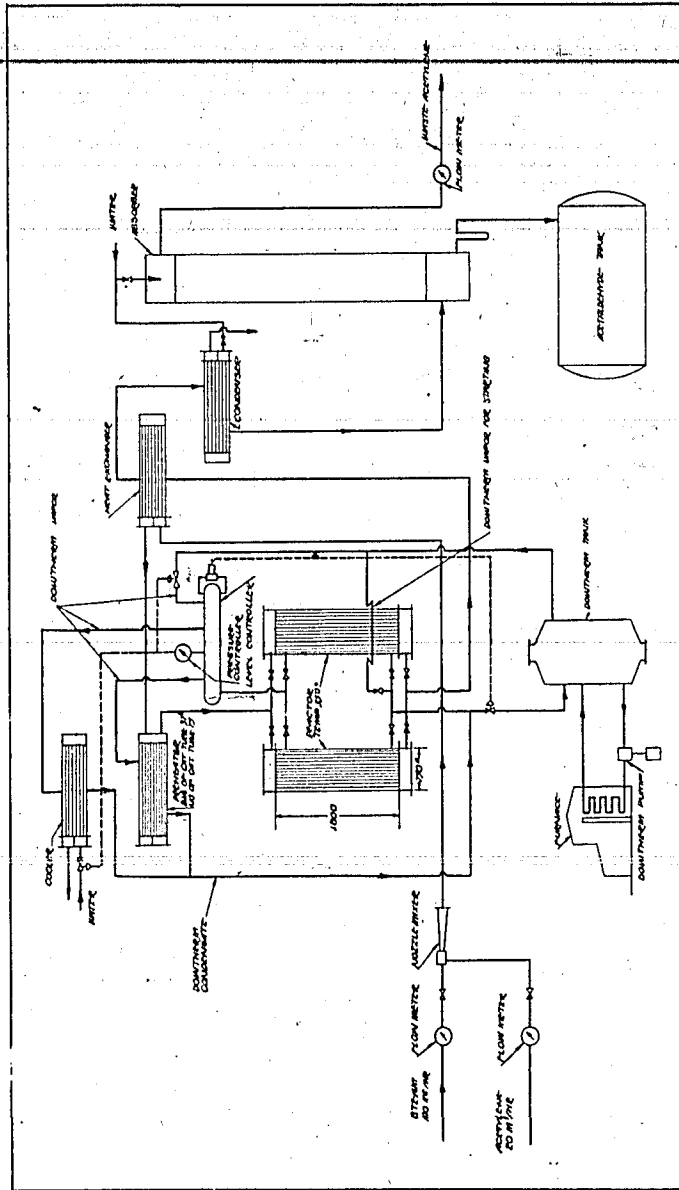


Figure 21113
FIG. SHEET OF LIQUID MASS FRACTIONATION OF ACETYLENE TO HYDRIFFER

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3. Experimental Results

Reaction temperature at the bottom of the reactor	150°C
Pressure of the reaction tower	15 atms
Velocity of acetylene charged	7.7m ³ /hr
Circulating velocity of methanol solution from the bottom to the top of the reactor	2m ³ /hr
Circulating velocity of methanol solution from the reactor to the fractionating tower	0.5m ³ /hr
Pressure of the fractionating tower	2.5 atms
Temperature of the distilling tower, top	50°C
bottom	120°C
Vinyl methyl ether obtained per hour	235kg
The purity of the product	96.4%
The percent yield of the product to theoretical	94.4%

The product contained no impurities except methanol and there were no side reactions. The releasing valve at the top of the reaction tower was prepared for the inert gas contained in acetylene which might be accumulated in the reaction tower, but the opening of the valve was not necessary during 50 hours of running. It seemed that the inert gas contained in acetylene was dissolved in methanol and was ejected at the releasing valve of the receiver.

There is but little data pertaining to the properties of vinyl methyl ether in the literature. Redistilled vinyl methyl ether had the following properties.

Sp. gr. 15/4	0.783 (under pressure)
B.P.	5.7°C
Solubility	partly soluble in water

It has no tendency to polymerize on standing under pressure in a glass pressure bottle at room temperature.

Vinyl methyl ether was easily hydrolysed by mixing with an equal volume of 0.1 N. sulphuric acid and heating in a pressure bottle at 80°C for five minutes. After neutralizing the acid, the acetaldehyde produced was determined by the hydroxylamine method. The hydrolysis was completed under the above conditions.

4. Comparison of Three Methods and Conclusions

There is but little difference in the yield of acetaldehyde by the three methods.

In the author's opinion, the first method is difficult to expand to a commercial scale because of the low rate of the reaction and the necessity of using material resistant to hot hydrochloric acid. The second method may be practiced when the design of the reactor for elimination of the reaction heat is perfected. The last method is suitable only for a small scale commercial plant because of the difficulty of the use of an acetylene compressor having a large capacity.

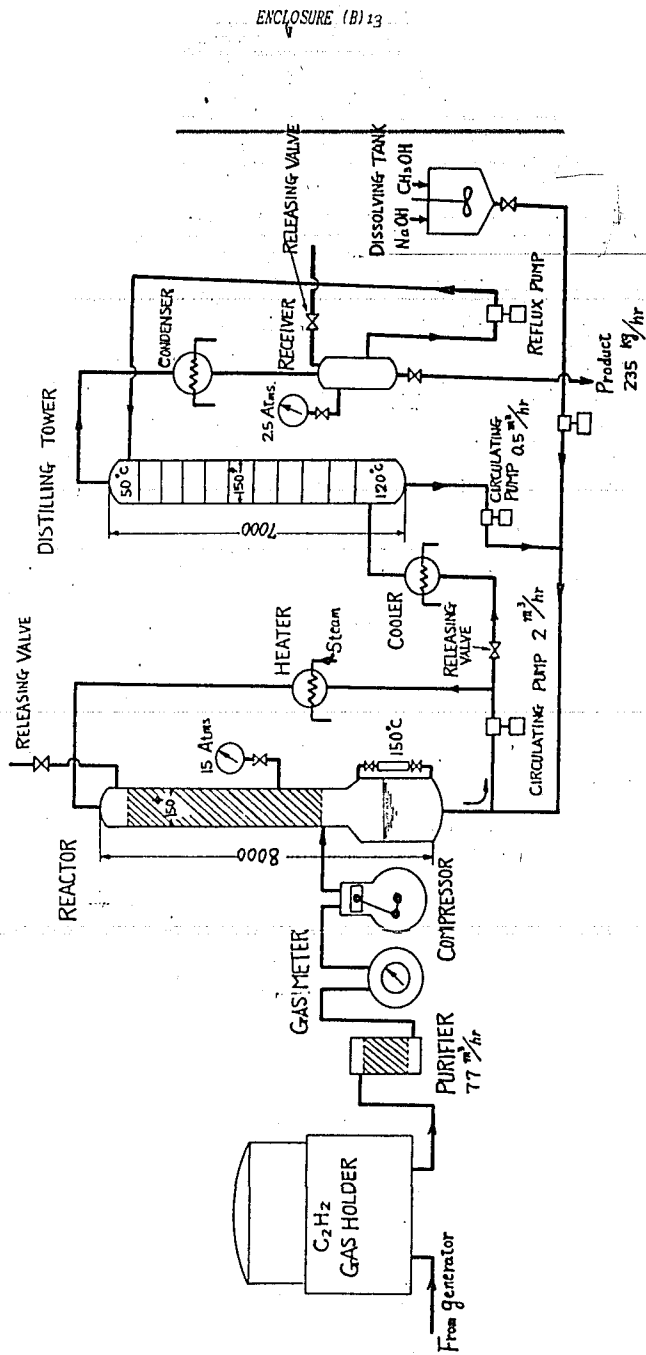


Figure 3(1)13
1 FLOW SHEET OF SYNTHESIS OF VINYL METHYL ETHER

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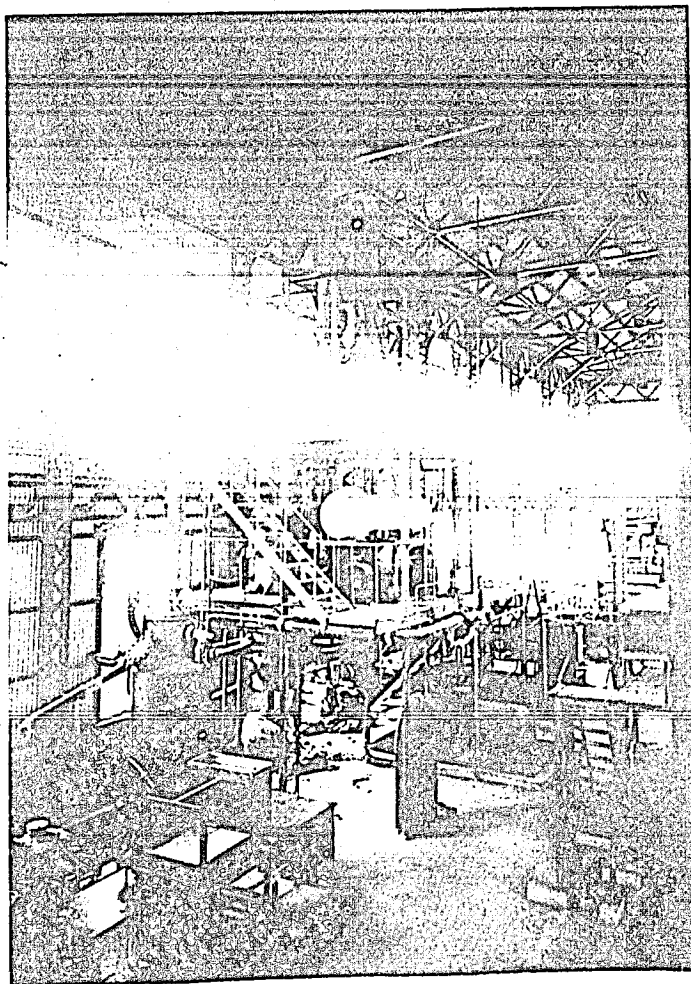


Figure 4(b)13

VAPOR PHASE HYDRATION PLANT OF ACETYLENE TO ACETALDEHYDE

This plant was erected for semi-commercial use but was never erected.

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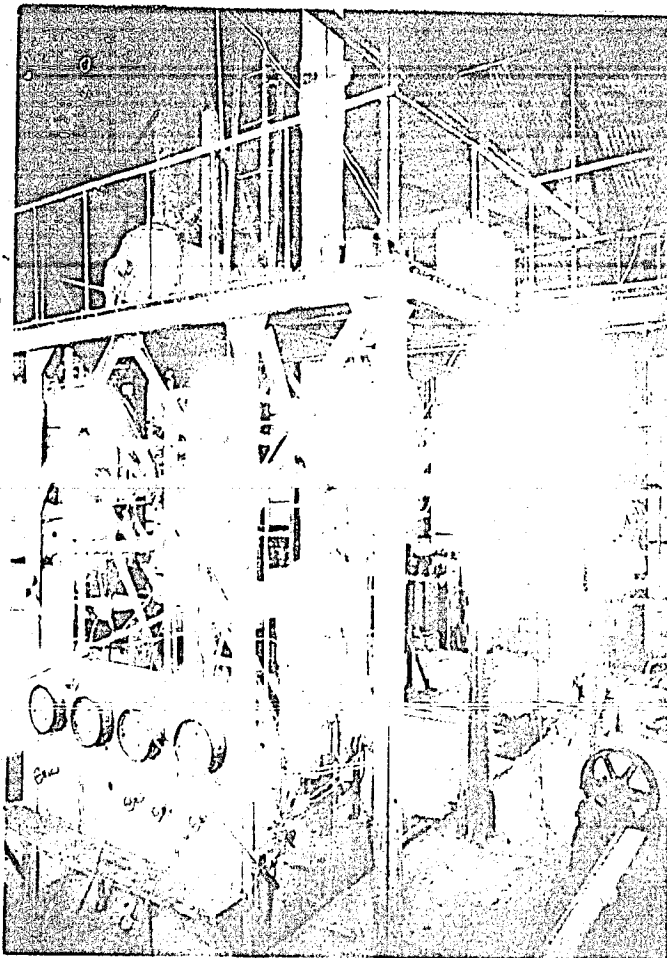


Figure 5(f)-115
SYNTHESIS PLANT OF VINYL-METHYL-ETHER BY MEANS
OF METHYLATES OF ACETYLENE