

~~ENCLOSURE (B) 12~~

~~SYNTHESIS OF ACETONE
FROM ACETYLENE~~

by

~~CHEM. ENG. LT. COMDR.
T. YAMAMOTO~~

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SUMMARY

Acetone was synthesized from acetylene using a catalyst consisting of manganese dioxide and ferric oxide. A mixture of acetylene and steam was passed through the above catalyst at 450°C and 80 percent of the acetylene reacted and 80-85% of the reacted acetylene was converted to acetone.

The formation of acetaldehyde and acetic acid was below one percent of the acetylene reacted in each case. Pure acetone was easily separated from the product by fractionation.

I. INTRODUCTION

In general, acetone has been manufactured by the dry distillation of calcium acetate, the catalytic conversion of acetic acid and the catalytic reaction of acetaldehyde and steam. Since there was a possibility of using acetone as a raw material in the synthesis of high antiknocking iso-paraffine hydrocarbons, such as 2,3-dimethyl butane or neohexane through pinacone utilizing the pinacone rearrangement, this research was undertaken.

Although the synthetic method of preparing acetone by the catalytic reaction of acetylene and steam has been known previously, it has not been practiced commercially due to the lack of a good catalyst. Therefore, the effects of many catalysts in this reaction were tested, but the most simple mixed catalyst consisting of manganese dioxide and ferric oxide showed the best results.

Experiments were made using a pilot plant having a capacity of 5m³ acetylene per hour. Although the results obtained were satisfactory, the difficulty of the local overheating of the catalyst zone was encountered. While the plant was being reconstructed, it was ordered that the research be stopped because of the success of another method at the laboratory of Chosen Chisso Hiryo Co.

The catalyst used was prepared by the following procedure:

To a solution of manganous chloride an excess of caustic soda solution was added and, separately, to a solution of ferric chloride, a solution of ammonium hydroxide was added. The amounts of manganous chloride and ferric chloride were taken according to the weight ratio of MnO₂:Fe₂O₃=1:4.

The precipitates were mixed mechanically, filtered, washed, dried, and ignited at 500°C. The cake of catalyst was crushed, powdered, and shaped into cylinders 6mm x 6mm.

The research was begun in 1937 and stopped in 1940 by Naval Engineer G. ISHIDA.

II. DETAILED DESCRIPTION (See Figure 1(B)12)

In laboratory scale tests, catalysts having a composition of one part of manganese oxide and four parts of ferric oxide, with small added amounts of the oxides of zinc, cadmium, vanadium, molybdenum, tin, calcium or chromium, etc., were tried as catalyst promoters.

None of these promoters showed appreciable effects on the basic catalyst of MnO₂-Fe₂O₃. Hence, the use of the promoters was abandoned.

B. Apparatus and Procedure

A diagrammatic sketch of the apparatus is shown in Figure 1(B)12. Purified carbide acetylene was introduced by a steam injector (1) through a gas

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meter (2) into a preheater (3) which was heated by an electric furnace.

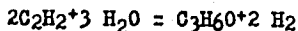
The amount of steam was measured by a steam flow meter (4). The mixture of acetylene and steam, heated to the reaction temperature, was passed through the catalyst layer of one of two reactors, (5) and (6). From the product the greater part of water was separated by an dephlegmator (7). Acetone and steam were condensed by a condenser (8) and collected in a receiver (9). The waste gas escaped through a gas meter (10). The weakened catalyst activity was recovered by passing hot air heated by an electric heater (11) into the reactor through a blower (12).

C. Analytical Procedure

Acetaldehyde was determined by an ammoniacal silver nitrate solution followed by weighing the deposited silver. Acetone was measured after the determination of acetaldehyde by the Messiger's method, and acetic acid by the titration of the original sample.

D. Calculation of the Experimental Results

The percentage yield of acetone was calculated from the following equation.



The percentage conversion of acetylene was calculated from the concentration of acetylene and the volume of the charge and the waste gas.

E. Experimental Results

Composition of the catalyst	1 MnO ₂ + 4 Fe ₂ O ₃
Volume of the catalyst	30 liters
Reaction temperature	420°C - 450°C
Velocity of acetylene	3m ³ /hr
Time of experiment	120 hours
Amount of steam used	10 times that of acetylene

Results Obtained

	The first day	The last day
Total volume of C ₂ H ₂ used	71.298m ³	75.621m ³
Average concentration of C ₂ H ₂ charged ..	95.4 %	96.2 %
Total volume of waste gas	65.798m ³	69.221m ³
Average composition of waste gas		
CO ₂	20.8 %	17.9 %
C ₂ H ₂	6.8 %	15.3 %
CO	7.9 %	8.2 %
H ₂	48.6 %	51.2 %
CH ₄	8.5 %	9.1 %
Average conversion of C ₂ H ₂	93.4 %	88.3 %
Total yield of acetone	73.09 kg	70.71 kg
Yield of acetone based on converted C ₂ H ₂ ..	83.0 %	87.9 %
Total yield of acetaldehyde	1.25 kg	1.15 kg
Average yield of acetaldehyde	1.0 %	0.9 %
Total yield of acetic acid	0.65 kg	0.39 kg
Average yield of acetic acid	0.4 %	0.4 %

F. Discussion

Since the catalyst activity decreased after five days, the catalyst was aerated at 450°C for 12 hours. The mean results obtained after restarting

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showed partial but not complete recovery of the catalyst activity. In repeating the reaction after recovery of the catalyst activity the yield and the percentage conversion decreased gradually.

After about 500 hour's use the average conversion of acetylene decreased to 70 percent even when the aeration had been continued for a day. It seemed that this was caused by the over heating of the catalyst during the reaction and the aeration, since no cooling device was installed to overcome the effects of the exothermic reaction.

III. CONCLUSIONS

This method is not yet successful because of the short life of the catalyst activity. Hence, additional improvements of the catalyst and the reaction apparatus are required for commercial operation.

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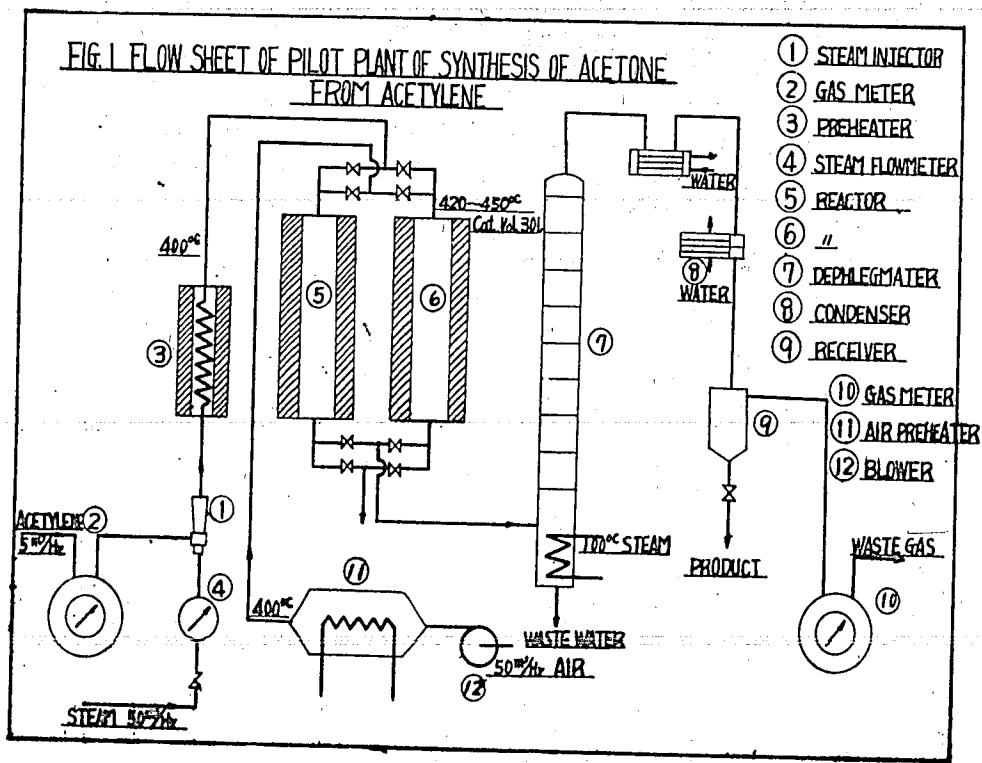


Figure 1(B) 12
FLOW SHEET OF PILOT PLANT OF SYNTHESIS OF ACETONE
FROM ACETYLENE