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Catalytic Vapor Phase Oxidation of Crotonaldehyde to Maleic Acid in a Fluidized Bed

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The oxidation of crotonaldehyde to maleic acid has been thoroughly studied in the presence of a large number of solid catalysts in a fluidized bed. Using V_2O_5: MoO_3: Pumice(33.06:5.83:100) as the catalyst a maximum conversion to 56.4% maleic acid was obtained at a temperature of 325°C, an air/aldehyde ratio of 171, and a space velocity of 9057.

INTRODUCTION

Maleic acid finds wide application in the chemical industry. In view of its highly reactive nature and of the reactivity of its anhydride and amide, the possibilities of finding new uses are unlimited. At present it is produced on a commercial scale mainly by the oxidation of benzene.

Crotonaldehyde can now be obtained quite cheaply from the petroleum refineries and the acetylene industry and hence its use as a starting material for the preparation of maleic acid seems to be quite promising and economical too.

The most important publication in this field in recent years is that of Bhattacharyya and Venkataraman (*1*), who have reported the results of their systematic and exhaustive study on the oxidation of crotonaldehyde in the presence of a large number of supported and unsupported catalysts in the fixed bed.

Using V_2O_5—MoO_3—kieselguhr (38.9: 6.86:100) as the catalyst, which was found to be the most active one, conversions of 50.9, 53.8, and 60.2% crotonaldehyde to maleic acid have been achieved at 400°C, a space velocity of 11,800 liter/hr/liter of catalyst and air/aldehyde ratios of 292, 433, and 865, respectively.

The oxidation of crotonaldehyde is a highly exothermic reaction, ($\Delta H = -176.4$ kcal/mole). Anticipating that effective heat dissipation, which is essential for the proper maintenance of isothermal conditions in the reaction zone, would probably improve the yield of maleic acid, this reaction has been studied in the fluidized catalyst bed. Performances of a large number of catalyst compositions consisting of the oxides of vanadium, molybdenum, tungsten, uranium, cobalt, titanium and phosphorus under different operating conditions have been studied. It has been observed that under experimental conditions, the total conversion of crotonaldehyde to the different products is well above 90%, leaving little numerical difference between the percentage conversion and selectivity. For all practical purposes, percentage conversion may be considered as synonymous with selectivity.

EXPERIMENTAL

Materials

Crotonaldehyde supplied by Eastman Kodak Co. was distilled over anhydrous sodium sulfate and the distilled sample (b.p. 99°C–101°C) analyzed as 99.5% crotonaldehyde.

Pumice supplied by the B.D.H. Ltd., was purified by boiling with 3–4 *N* nitric acid for about 2 hours and was washed free of acid, dried, and powdered to −120 to +240 mesh size.

Natural quartz −120 to +240 mesh size was purified in the same way as the pumice.

Calcined alumina supplied by B.D.H. Ltd. was sieved and the −120 to +240 mesh size fraction was used in the present investigation.

Apparatus

A diagrammatic flow sheet for the apparatus used in the investigation is shown in Fig. 1.

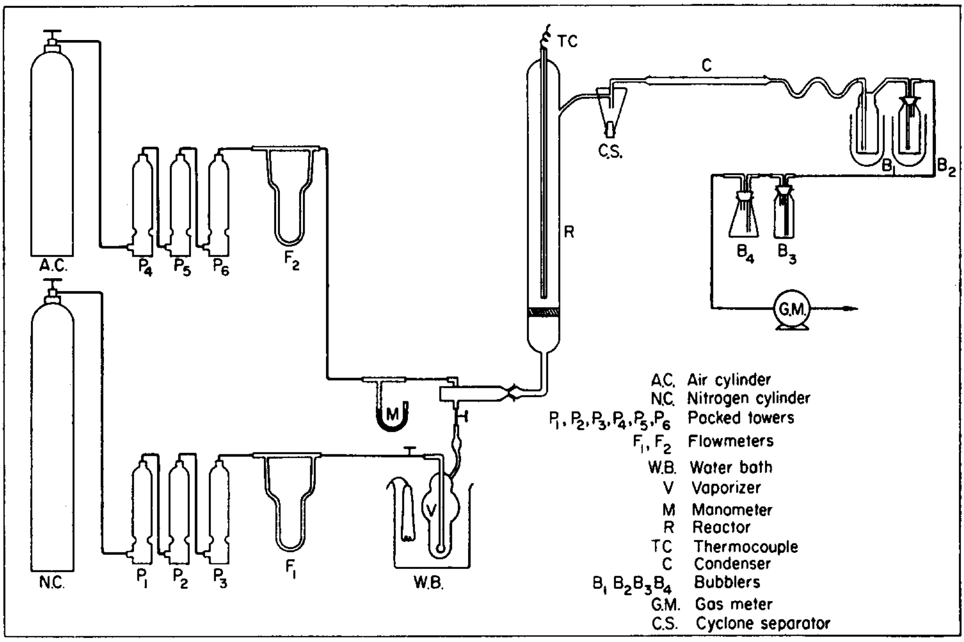

FIG. 1. Apparatus for the oxidation of crotonaldehyde in the fluidized bed.

The reactor is shown in Fig 2. The reactor with the preheater was made of Pyrex glass tube of 20-inch length and $1\frac{5}{8}$-inch ID. The preheater was $2\frac{1}{2}$ inches in length and was packed with broken glass pieces. The preheater and the reactor were electrically heated with Kanthal ribbons and the temperatures of the above two and the water bath were controlled by Variacs. The thermocouple pocket of $\frac{3}{8}$-inch glass tube extended up to $^{13}/_{16}$ inch from the bottom of the sintered disk. The catalyst was introduced before starting the experiment through the outlet tube for the product gases in the reactor.

Operational Procedure

The catalyst was charged in the reactor. Crotonaldehyde vapor obtained by passing nitrogen through crotonaldehyde contained in a thermostatically controlled vaporizer was mixed with secondary air in a mixer, preheated in the preheater zone of the reactor, and passed over the catalyst mass at the requisite temperature. Both the nitrogen and air were metered and purified before passing through the bubbler and mixer.

The exit gas from the side tube at the top of the reactor was passed through a cyclone separator (to remove the catalyst particles), air condensers, two ice-cooled bubblers, and two water bubblers and metered finally through a wet gas meter. Duration of each experiment was 1 hr.

Catalysts

The basic types of catalysts used in this

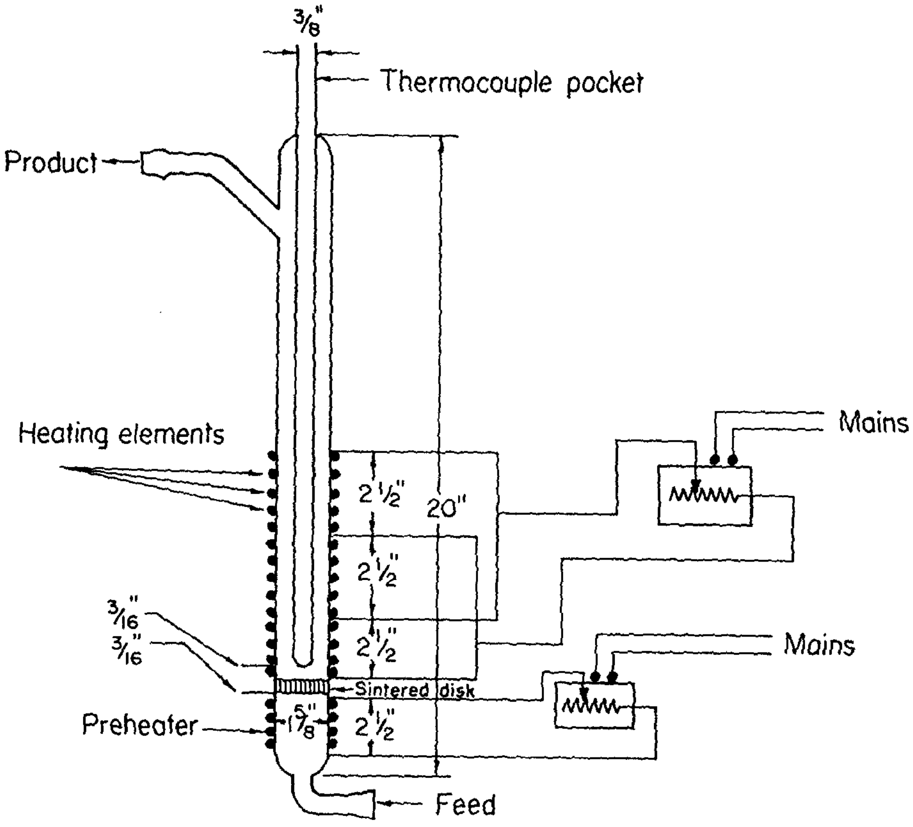

FIG. 2. Reactor.

investigation, their methods of preparation, and physical characteristic are given below. The catalysts used and their performances are presented in Table 1.

Catalysts A to T were prepared by methods analogous to those used by Bhattacharyya and Venkataraman (*1*). Catalyst U and catalyst V were prepared by adding pure titanium dioxide and the required amount of phosphoric acid, respectively, to the solution prior to impregnation on the carrier.

Catalyst E_1 was prepared by dissolving the requisite quantity of vanadium pentoxide in a mixture of hydrochloric acid and ethyl alcohol, 10:1 ratio, under reflux and mixing with ammonium molybdate dissolved in hydrochloric acid (1 in 4 parts). The solution was concentrated, the support added, evaporated to dryness on a water bath, dried in an air oven at 100°C, and finally heated in a furnace in the presence of air for 12 hours at 400°C. Catalyst E_2 was prepared in the same way as E but no oxalic acid was added.

The fused catalysts were prepared by heating ammonium vanadate and/or ammonium molybdate in an open china dish till all ammonia ceased to evolve, and finally by fusion in a muffle furnace. In the case of catalyst Y requisite amounts of ammonium vanadate and ammonium molybdate were taken in water and purified dried pumice was added. The mixture was dried over a water bath, heated in an open china dish till ammonia ceased to exit, and finally fused in a muffle furnace. Each catalyst was pretreated by passing a mixture of crotonaldehyde and air (air/aldehyde = 100 to 180:1) for at least 4 hours at 250–300°C before using it for oxidation.

TABLE 1
COMPARATIVE ACTIVITY DATA OF VARIOUS CATALYSTS[a]

Catalyst	Catalyst composition	Space velocity (l/hr/l)	Temp. (°C)	Air/crotonaldehyde (mole/mole)	Conversion to maleic acid (%)	S.T.Y. of maleic acid (g/hr/l)
A	V_2O_5:Pumice (51.84:100)	9092	325	300	46.2	71.0
		11750	325	140	43.6	183.0
B	MoO_3:Pumice (48.72:100)	9210	375	320	13.5	19.6
C	V_2O_5:MoO_3:Pumice (11.75:2.05:100)	9000	325	320	48.0	70.8
D	V_2O_5:MoO_3:Pumice (23.97:4.23:100)	9094	325	300	48.1	82.0
		11801	325	160	45.2	166.8
E	V_2O_5:MoO_3:Pumice (33.06:5.83:100)	9000	325	286	66.9	100.9
		9057	325	171	56.4	146.3
		11800	325	170	55.2	191.7
E_1	V_2O_5:MoO_3:Pumice (33.06:5.83:100)	9098	325	285	48.7	85.4
E_2	V_2O_5:MoO_3:Pumice (33.06:5.83:100)	9010	325	300	51.6	82.0
F	V_2O_5:MoO_3:Pumice (36.4:6.4:100)	9005	325	295	63.1	97.8
		11800	325	147	52.9	212.4
G	V_2O_5:MoO_3:Pumice (33.06:16.64:100)	9149	325	292	62.3	98.2
		11799	325	150	50.2	197.4
H	V_2O_5:MoO_3:Pumice (33.06:33.06:100)	9203	325	320	59.2	82.8
		11800	325	150	43.6	171.6
I	V_2O_5:MoO_3:Pumice (12.97:33.06:100)	9170	325	300	17.4	28.3
		9204	375	299	42.6	66.1
		11270	375	300	28.2	55.7
J	WO_3:Pumice (50.17:100)	9082	400	316	12.0	23.2
K	V_2O_5:WO_3:Pumice (33.06:4.32:100)	9170	325	316	49.6	71.7
		11800	325	145	45.5	185.2
L	V_2O_5:WO_3:Pumice (33.06:16.64:100)	9143	325	310	45.0	66.1
M	V_2O_5:UO_3:Pumice (33.06:4.32:100)	9141	325	309	49.2	73.3
		11760	325	150	46.5	182.4
N	V_2O_5:UO_3:Pumice (33.06:16.64:100)	9120	325	293	46.4	71.3
O	V_2O_5:Co_2O_3:Pumice (33.06:3.89:100)	9016	325	320	34.1	48.3
P	V_2O_5:Co_2O_3:Pumice (33.06:8.8:100)	9086	325	299	48.2	63.8
		11320	325	300	32.5	48.0
Q	V_2O_5:Co_2O_3:Pumice (33.06:12:100)	9083	325	293	45.0	69.5
R	V_2O_5:MoO_3:Quartz (23.97:4.23:100)	9090	325	298	8.5	13.9
S	V_2O_5:MoO_3:Alumina (23.97:4.23:100)	9062	325	315	47.3	76.5
T	V_2O_5:MoO_3:Co_2O_3:Pumice (33.06:5.83:8.8:100)	9000	325	300	49.2	86.4
U	V_2O_5:MoO_3:TiO_2:Pumice (33.06:5.83:2.8:100)	9084	325	307	51.2	90.0
V	V_2O_5:MoO_3:P_2O_5:Pumice (33.06:5.83:1.5:100)	9100	325	299	47.4	82.5
W	V_2O_5(Fused)	9101	400	250	36.0	65.6
X	V_2O_5:MoO_3(Fused) (85:15)	9035	400	255	38.9	67.9
Y	V_2O_5:MoO_3:Pumice(Fused) (33.06:5.83:100)	9035	400	261	26.4	46.3

[a] Apparent volume of the catalyst = 20 cc.

Analysis of the Product

The method of analysis was the same as followed by Bhattacharyya and Venkataraman (*1*).

Nomenclature

In this paper, space velocity is given as liters of gas, measured at NTP, passed per hour per liter of catalyst space. Air/crotonaldehyde ratio is calculated as liters of air/liters of crotonaldehyde vapor, both measured at NTP. The conversion is expressed as the percentage of the weight of maleic acid formed to that theoretically possible.

Space time yield (S.T.Y.) is obtained by determining the amount of maleic acid formed per hour per liter of catalyst volume.

RESULTS AND DISCUSSION

Comparative Activity of the Catalysts

The results on the comparative activities of different catalysts, single, binary and ternary oxide systems, supported and unsupported are presented in Table 1. The salient features of the table may be summed up as follows:

Vanadium pentoxide is the main active component, which is responsible for the oxidation of crotonaldehyde to maleic acid, though this activity can be enhanced considerably by the incorporation of other oxides.

A conversion of 46.2% is obtained when V_2O_5:pumice (51.8:100) (catalyst A) is used. But on using a small quantity of MoO_3 (catalyst E), the conversion is increased to nearly 66.0%.

Using catalyst E $V_2O_5:MoO_3$:pumice = 33.06:5.83:100 a conversion of 56.4% is obtained at a temperature of 325°C, an air/aldehyde ratio of 171, and a space velocity of 9057. The activity of the catalyst system increases with the increasing air/aldehyde ratio.

Bhattacharyya and Venkataraman (*1*) had earlier reported a conversion of 46.2% at a temperature of 400°C, air/aldehyde ratio of 145–165 and at a space velocity of 11,800, using the catalyst $V_2O_5:MoO_3$: kieselguhr (38.9:6.86:100) in a fixed bed.

Thus, in a fluidized bed much higher conversion of crotonaldehyde to maleic acid can be obtained at a much lower temperature and with lower concentration of oxides.

Fused vanadium pentoxide which was reported by Bhattacharyya and Gulati (*2*) to be an excellent catalyst for the oxidation of xylenes, gives poor conversion of crotonaldehyde to maleic acid. The optimum temperatures in the case of fused catalysts were also higher than with unfused catalysts.

Incorporation of the oxides of cobalt, uranium, tungsten, phosphorus, and titanium to the V_2O_5-pumice system does not materially increase the yield of maleic acid to any appreciable extent. The catalyst P containing 6.20% cobalt oxide gives a conversion of 48.2% maleic acid, the catalysts M and K containing 3.15% uranium oxide and 3.15% tungstic oxide give conversions of 49.2% and 49.6% maleic acid, respectively, compared to a conversion of 46.2% maleic acid obtained with V_2O_5:pumice catalyst (catalyst A). Cobalt oxide does not exercise any promoting effect on the vanadium pentoxide–molybdenum trioxide–pumice catalyst. Titanium dioxide and phosphorus pentoxide are found to be inactive for the oxidation of crotonaldehyde.

The comparative efficiencies of various catalysts for the vapor phase oxidation of crotonaldehyde to maleic acid in the fixed and fluidized beds are given in Table 2. Figure 3 shows the effect of air/aldehyde ratio on the activity of the catalysts $V_2O_5:MoO_3$:pumice (33.06:5.83:100) and $V_2O_5:MoO_3$:kieselguhr (38.9:6.86:100) in fluidized and fixed beds, respectively.

The catalyst composition, $V_2O_5:MoO_3$: pumice (33.06:5.83:100), having been found to exhibit maximum activity, a detailed study was made to find out the effect of various process variables on the conversion of crotonaldehyde to maleic acid in the fluidized bed. The results are shown in Table 1.

TABLE 2

COMPARATIVE EFFICIENCIES OF VARIOUS CATALYSTS FOR VAPOR PHASE OXIDATION OF CROTONALDEHYDE IN THE FIXED BED[a] AND FLUIDIZED BED

Sl. No.	Catalyst	Type of bed	Volume of catalyst (cc)	Space velocity (l/hr/l)	Molar air/aldehyde ratio	Temp. (°C)	Conversion to maleic acid (%)	S.T.Y. of maleic acid, (g/hr/l)
1.	V_2O_5:Pumice (51.84:100)	Fluidized	20	11750	140	325	43.6	183
	V_2O_5:Kieselguhr (51.84:100)	Fixed	19	11800	145	425	36.4	176
2.	V_2O_5:MoO_3:Pumice (33.06:5.83:100)	Fluidized	20	9057	171	325	56.4	146.3
	V_2O_5:MoO_3:Kieselguhr (38.9:6.86:100)	Fixed	19	11800	145	400	46.2	193.5
3.	V_2O_5:WO_3:Pumice (33.06:4.32:100)	Fluidized	20	9109	170	325	46.5	118.5
	V_2O_5:WO_3:Kieselguhr (38.9:4.32:100)	Fixed	19	11800	145	415	44.3	184.4
4.	V_2O_5:UO_2:Pumice (33.06:4.32:100)	Fluidized	20	9059	180	325	48.5	114.4
	V_2O_5:UO_2:Kieselguhr (38.9:4.32:100)	Fixed	19	11800	145	440	41.9	177.4
5.	V_2O_5:Co_2O_3:Pumice (33.06:8.8:100)	Fluidized	20	9083	144	325	46.2	145.5
	V_2O_5:Co_2O_3:Kieselguhr (38.9:3.89:100)	Fixed	19	11800	145	400	44.9	179.6

[a] Data of optimal conversions to maleic acid given in the paper published by Bhattacharyya and Venkataraman (*1*).

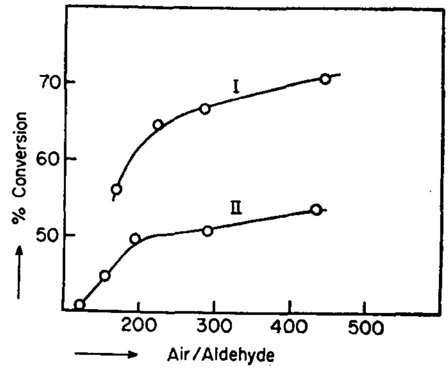

FIG. 3. The effect of air/aldehyde ratio on the conversion to maleic acid in the fixed and the fluidized beds with the best catalysts. Curve I: fluidized bed; S.V., 9022–9042; temp., 325°C. Curve II: fixed bed; S.V., 11800; temp., 400°C.

Effect of Vanadium Pentoxide–Molybdenum Trioxide Ratio

As shown in Fig. 4 the activity of vanadium pentoxide–molybdenum trioxide–pumice catalyst varied with the weight ratio of the two constituents. The data plotted relate to catalysts A to I. Maximum conversion of approximately 66.9% was obtained when the ratio of V_2O_5: MoO_3 was 85:15.

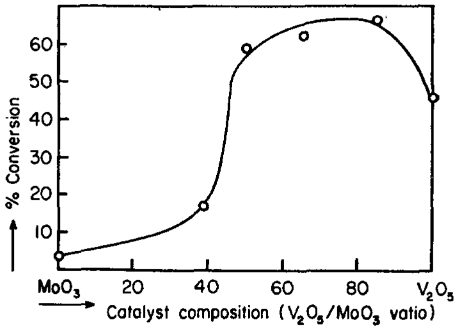

FIG. 4. The effect of catalyst composition (V_2O_5/MoO_3 ratio) on the conversion to maleic acid. S.V., 9022–9042; temp., 325°C; air/aldehyde ratio, 290–300.

Effect of Oxide Concentration

Figure 5 shows the effect of catalyst concentration on the activity of vanadium pentoxide–molybdenum trioxide–pumice catalyst. The conversion to maleic acid increased with increasing concentration of metal oxides (catalysts C to F) up to about 28%. Further increase of concentration had little effect.

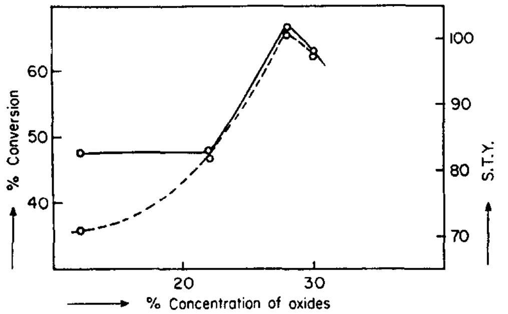

FIG. 5. The effect of total concentration ($V_2O_5 + MoO_3$) of the oxides on the conversion to maleic acid. S.V., 9022–9042; temp., 325°C; air/aldehyde ratio, 290–310; solid line, percentage conversion to maleic acid; broken line, S.T.Y. of maleic acid.

Effect of Catalyst Support

The efficiency of the catalyst for the oxidation of crotonaldehyde to maleic acid depends on the type of support employed. Pumice was found to be the best among the three supports tried (catalysts D, R, and S). While the support D gave a conversion to the acid of about 48%, the respective figures for other supports were 8.5% for quartz and 47.3% for alumina.

Effect of Mode of Preparation of Catalyst

Catalyst E_1 and E_2 containing the same proportions of vanadium pentoxide, molybdenum trioxide and pumice as E but prepared by different methods had widely different activity. When the catalyst was prepared by thermal decomposition of ammonium salt (catalyst E_2) and from vanadium pentoxide (catalyst E_1), the conversions were 51.6% and 48.7%, respectively, as compared with the value of 66.9% obtained with catalyst E (by decomposition of oxalates).

Effect of Temperature

The influence of temperature on the activity of the catalyst E is graphically represented in Fig. 6. The optimum temperature obtained in this was 325°C. With increase of temperature the yield of maleic acid decreased.

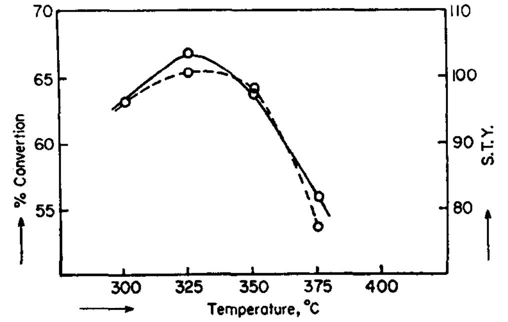

FIG. 6. The effect of temperature on the conversion to maleic acid with catalyst E. S.V., 9022–9042; air/aldehyde ratio, 290–300; solid line, percentage conversion to maleic acid; broken line, S.T.Y. of maleic acid.

Effect of Aldehyde Concentration

The ratio of air to aldehyde has a profound bearing on the yield of maleic acid. Figure 7 represents the results with the

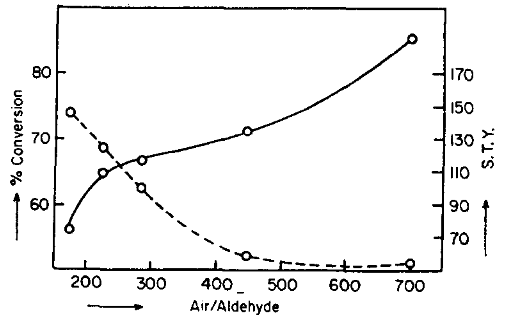

FIG. 7. The effect of air/aldehyde ratio on the conversion to maleic acid in the presence of catalyst E. S.V., 9000–9042; temp., 325°C; solid line, percentage conversion to maleic acid; broken line, S.T.Y. of maleic acid.

catalyst E. The percentage conversion to the acid progressively diminished from 85% (air: aldehyde = 700), to about 56.3% (air: aldehyde = 171), with an increase in the aldehyde concentration.

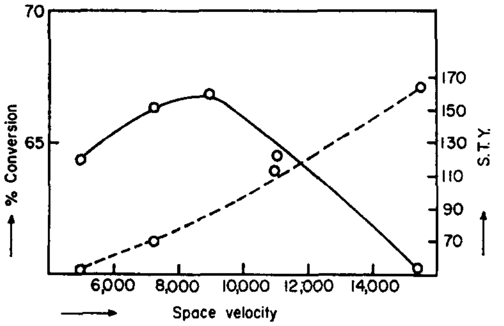

FIG. 8. The effect of space velocity on the conversion to maleic acid in the presence of catalyst E. Temp., 325°C; air/aldehyde ratio, 280–300; solid line, percentage conversion to maleic acid; broken line, S.T.Y. of maleic acid.

Effect of Space Velocity

The effect of space velocity on the yield of maleic acid with catalyst E is given in Fig. 8. A space velocity of near about 9022 was found to be optimum. With increase of space velocity, space time yield (S.T.Y.) of maleic acid increased from 54.0 at a space velocity of 4997 to 164.5 at a space velocity of 15568.

Effect of Steam on the Activity of the Catalyst E

It was found that when water vapor was mixed with the inlet aldehyde vapor up to a ratio, aldehyde: steam = 100: 34.2, the activity of the catalyst remained practically the same.

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2. BHATTACHARYYA, S. K., AND GULATI, I. B., *Ind. Eng. Chem.* **50**, 1719 (1958).