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FURTHER STUDIES OF THE CATALYTIC OXIDATION OF ORTHO-XYLENE TO
PHTHALIC ANHYDRIDE USING A FLUIDIZED BED REACTOR

BY

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A

THESIS

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ABSTRACT

This investigation was conducted to further study the vapor-phase oxidation of o-xylene to phthalic anhydride in a fluidized bed catalytic reactor. Parameters investigated during the study were temperature, catalyst volume, and catalyst activated by use of different promoters. Two different vanadium pentoxide catalysts were used. One was a new catalyst (Catalyst I) supported on a silica base and diluted with potassium sulfate. The other catalyst (Catalyst II) was similar to the first one except that it had been used in a commercial fixed bed reactor operated by the Monsanto Company, St. Louis, Missouri, using naphthalene as a feed material. It had been suggested that this second catalyst would be "activated" whereas the fresh catalyst would not and the used catalyst would thus give higher yield of phthalic anhydride. Little difference in yield of phthalic anhydride was found, the used catalyst giving slightly lower yields. These studies were conducted on a laboratory scale in equipment similar to that used in earlier studies by Wang(12) but modified in several respects.

Phthalic anhydride, maleic anhydride, o-toluic aldehyde, carbon dioxide and water were obtained as oxidation products. Except water, they are all determined by quantitative analysis.

Two different amounts of Catalyst I (24 grams and 102 grams) were used at five different temperatures (320,400,450,490,520°C) to study the effect on the yield per cent of phthalic anhydride. It was found that the optimum reaction temperature is at 490°C when using

either amount of catalyst. The highest yields of phthalic anhydride obtained were 21.5 per cent when using 24 grams of Catalyst I and 24.3 per cent when using 102 grams. The highest yield of phthalic anhydride was 19.6 per cent when 137 grams of Catalyst II were used at 490°C and the lowest yield was 9.6 per cent at 320°C.

The effect of the addition of bromine, phenol bromide, and 1-3 dibromo-propane, as promoters, was also investigated. These promoters were introduced into the liquid o-xylene feed in separate tests. It was again found from a number of tests at different reactor temperatures that 490°C gave the highest yield of phthalic anhydride, 36.2 per cent. This yield was obtained using 5 per cent by volume of liquid bromine in the feed and 102 grams of Catalyst I.

TABLE OF CONTENTS

	Page
TITLE PAGE	i
ABSTRACT	ii
TABLE OF CONTENTS	iv
LIST OF FIGURES	vi
LIST OF TABLES	vii
I. INTRODUCTION	1
II. LITERATURE REVIEW	4
Vanadium Oxides as Oxidation Catalyst	4
Interaction of O-Xylene with Vanadium Pentoxide	5
Laboratory Oxidation of Ortho-Xylene in a Fluidized Bed Reactor	7
Patent References in Production of Phthalic Anhydride by Catalytic Oxidation of O-Xylene	12
Commercial Production of Phthalic Anhydride from Ortho-Xylene	17
III. EXPERIMENTAL	
Purpose of Investigation	19
Plan of Experimentation	19
Materials	20
Equipment Description and Operation	23
Air Feed Unit	23
Orifice Meter and Calibration	23
Xylene Vaporization Unit	23
Gas Mixer	24
Fluidized Reactor	24

Temperature Control Unit	28
Condensation Unit	28
Experimental Procedure	28
Oxidation of O-Xylene	28
Product Analysis	30
Data and Results	31
IV. DISCUSSION	53
The Results	53
Conclusions	56
V. RECOMMENDATIONS	57
VI. APPENDICES	58
A. Nomenclature	59
B. Calibration Data for the Air Flow Meter	60
C. Data for Fluidization of Catalyst	62
D. Sample Calculations	65
VII. BIBLIOGRAPHY	68
VIII. ACKNOWLEDGEMENTS	70
IX. VITA	71

LIST OF FIGURES

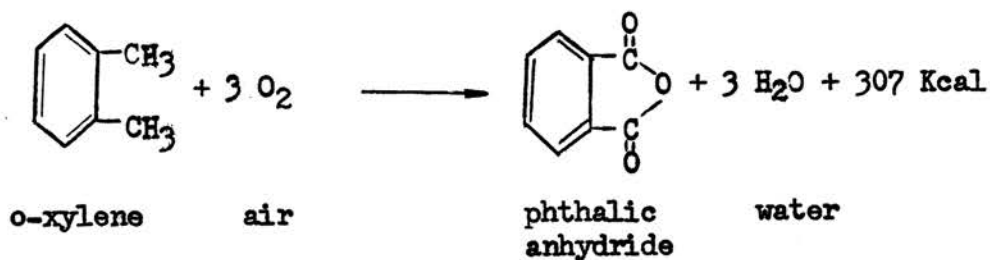
FIGURE		Page
1	Apparatus for Vapor-phase Oxidation of O-Xylene in a Fluidized Bed Reactor	26
2	Photograph of the Experimental Apparatus	27
3	Effect of Temperature at Various Molar Air/Xylene Ratios of Phthalic Anhydride Using Catalyst I ..	38
4	Correlation of Phthalic Anhydride Yield Per Cent and Molar Air/Xylene Ratio at Various Temperatures	41
5	Correlation of Phthalic Anhydride Yield Per Cent and Space Velocity at Various Temperatures	42
6	Effect of Temperature on Yield Using Bromine and Phenol Bromide Promoter and Catalyst I	51
7	Effect of Liquid Bromine as a Promoter and Catalyst II at Various Temperatures	52
B-1	Air Flow Meter Calibration Curve	61
C-1	Pressure Drop through Catalyst Bed (24 g of Catalyst I and 27 g of Catalyst II)	63
C-2	Pressure Drop through Catalyst Bed (102 g of Catalyst I and 137 g of Catalyst II)	64

LIST OF TABLES

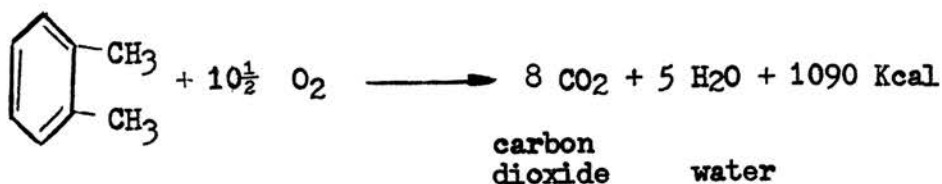
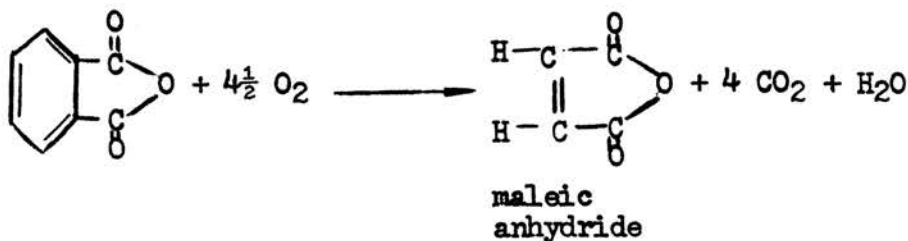
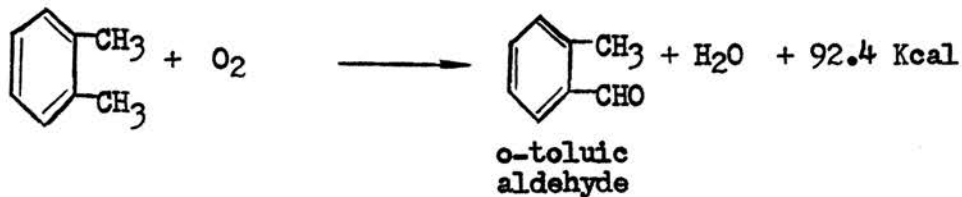
TABLE		Page
I	Oxidation of O-Xylene on Vanadium Pentoxide	6
II	Comparative Efficiencies of Vanadium Pentoxide Catalyst for Vapor-phase Oxidation of O-Xylene in Fixed and Fluidized Bed Reactors	9
III	Comparison of the Yield Per Cent of Phthalic Anhydride by Adding Various Bromides as Promoter.....	15
IV	Experimental Results Using 24 Grams of Catalyst I ..	33
IV A	Rearrangement of Table IV for Study	37
V	Experimental Results Using 24 Grams of Catalyst I and Two Bromide Promoters	44
VI	Experimental Results Using 102 Grams of Catalyst I or 137 Grams of Catalyst II with and without a Bromine Promoter	47
B-1	Calibration Data for the Air Flow Meter	60
C-1	Data for Fluidization of Catalyst	62

I. INTRODUCTION

Phthalic anhydride can be produced from o-xylene by the following chemical reaction:



Side reactions give other products, such as o-toluic aldehyde, maleic anhydride and carbon dioxide as shown by the following equations:



Phthalic anhydride is a very important raw material for the production of anthraquinone used in the manufacture of various vat dyes and in alizarin and alizarin derivatives.

It is used for alkyl resins, phthalate plasticizers and insecticides. Phthalic anhydride has experienced a steadily increasing demand for the past twenty years as new uses have been developed.

The commercial production of phthalic anhydride began in 1917 using the vapor phase oxidation of naphthalene in a fixed bed reactor. There are three suitable ways to make phthalic anhydride. They are: (a) Fluidized bed oxidation using petroleum naphthalene (b) Fixed bed oxidation using o-xylene (c) Fixed bed oxidation using naphthalene. Cost comparison(?) shows o-xylene to be the cheapest raw material for the production of phthalic anhydride.

As a large heat of reaction can not be dissipated quickly in a fixed bed reactor, it is difficult to control the operating temperature and the temperature distribution throughout the catalyst. On the other hand, a fluidized bed catalyst reactor has a high thermal conductivity, five to six times greater than that of a fixed bed, and also the temperature profile is uniform (1). These facts indicate the desirability of using a fluidized bed reactor if possible.

One of the important things that must be mentioned is that when o-xylene is mixed with air the mixture will be explosive if the mole fraction of o-xylene is more than one mole per cent. In the fluidized condition the explosion hazard reduces to a minimum because in the fixed bed reactor it is necessary to work with excess air in order to avoid explosive air-xylene mixtures but in the fluidized-catalyst bed the catalyst dust effectively, "stone dusts" (8), the interior of the

reactor and so eliminates the danger of explosion. In another words, it is safer to use a fluidized bed than a fixed bed operation.

So far, there is no fluidized bed reactor used commercially with o-xylene. Yet, in the light of the better control of the conditions and the course of reaction, the potentially high yields and the high purity of phthalic anhydride, and the absence of explosion hazard, the use of a fluidized bed reactor in the oxidation of o-xylene would seem to have greater promise than the fixed bed reactor. Even so, only fixed bed reactors have been used commercially to manufacture phthalic anhydride from o-xylene.

The aim of this work was to design and construct a bench scale laboratory apparatus to study the vapor-phase oxidation of o-xylene in a fluidized bed and the influence of using different catalysts, temperatures, catalyst volumes, molar air/o-xylene ratios, the effect of promoters, and space velocities on the yield of phthalic anhydride.

II. LITERATURE REVIEW

VANADIUM OXIDES AS OXIDATION CATALYSTS.

As an approach to the development of an oxidation catalyst a fundamental study of unpromoted vanadium oxides was undertaken by Simard and his coworkers (9). O-xylene was chosen as the hydrocarbon for oxidation because it permitted the use of a simple feed system. For the most part, the measurements were of bulk properties-- i.e., properties of more regular structures than would be expected of the catalyst surface. A qualitative picture of the surface must nevertheless be obtained since the arrangement of the surface atoms, although subject to considerable disorder, will tend toward the stable structures. The results have helped clarify the catalytic behavior of vanadium oxides.

The vanadium oxides formed in the oxidation of o-xylene were considered first. The properties of those oxides which are believed to determine the catalytic mechanism were then described.

The study by G.L. Simard and J.F. Steger, R.J. Arnott and L.A. Siegel (9), led them to the following general conclusions:

1. Vanadium in an unpromoted vanadium oxide catalyst during catalytic oxidation is in the V^{+4} and V^{+5} states.
2. In bulk, these states are associated with oxygen in three crystalline forms-- V_2O_4 , $V_2O_4.34$ and V_2O_5 .
3. The relative proportions of these oxides are dependent on the hydrocarbon concentration in the feed air; the changes

with time of operation observed were in a direction to establish the characteristic composition.

4. V_2O_4 and V_2O_3 are not catalytically active for the production of phthalic anhydride or intermediates. Further consideration of the active catalyst can therefore be limited to V_2O_4 , $V_2O_4.3H_2O$, and to intermediate structures which may exist on the surface.

INTERACTION OF O-XYLENE WITH VANADIUM PENTOXIDE.

The reduction of a catalyst charged as vanadium pentoxide during reaction suggested that oxygen ions of the catalyst might interact directly with the hydrocarbon. This would be of particular interest if the interaction formed phthalic anhydride. The study made by G.L. Simard and his co-workers(9) therefore included an examination of the products obtained on passing o-xylene in the absence of gaseous oxygen over the catalyst.

Weil and Klapproth (13) obtained a French Patent covering a catalyst for the preparation of phthalic anhydride which they assigned to the American Cyanamid Company. They studied the catalyst in a 23 inch converter using a feed of one mole per cent of o-xylene in a prepurified grade of nitrogen (less than 0.002 H_2 or O_2). The total amount of hydrocarbon fed was about that oxidizable to phthalic anhydride by the oxygen available in reducing V_2O_5 to $V_2O_4.3H_2O$. The duration of the run was 2 to 5 minutes, after which the hydrocarbon was shut off and the catalyst quenched. Other experimental conditions and the results are given in Table I. The acids produced were those normally

observed in catalytic oxidation-- phthalic and maleic. The CO_2/CO ratio was of the order usually found in the "break-in" period of catalyst. The conversion calculated from products was 30 per cent of the o-xylene fed.

TABLE I. Oxidation of o-Xylene on Vanadium Pentoxide. (9)

Catalyst: V_2O_5 on 6-to 8-mesh SiC

Feed: 1 % o-xylene (90-93 % purity) in nitrogen.
Contact time, 0.1-0.2 sec.; temp.; 463°C .

Oxide Surface area(total) sq m	Reduction		Products
	Chemical %	X-ray	
60-125	12-13	$\text{V}_2\text{O}_5 + \text{V}_2\text{O}_4$, 34 (trace V_2O_4)	84% phthalic 16% maleic CO_2/CO : 5.3

Recent experiments (by the same workers) with o-xylene using normal conditions and conversions below 20 per cent have shown o-tolualdehyde to be an isolatable intermediate. Accordingly, the transformation of o-xylene to phthalic anhydride does not necessarily occur only in one stage of adsorption. The question of whether and intermediate desorbs and then oxidizes further either in the gas phase or on readsorption is important to the mechanism. The described experiments in the absence of gaseous oxygen suggest that the gas phase need not be considered. There may, however, be successive desorptions of intermediates in the course of reaching phthalic anhydride, which is a product relatively stable over the catalyst. "Overoxidation" products such as maleic acid and carbon dioxide are evidence of variation in the activity of adsorption sites on the catalyst or in the

mode of breakdown of the hydrocarbon (13).

LABORATORY OXIDATION OF ORTHO-XYLENE IN A FLUIDIZED BED REACTOR.

Bhattacharyya and Krishnamurthy (1) studied the topic of "Catalytic Vapor-Phase Oxidation of Xylenes in Fluidized Bed". These workers carried out a systematic investigation of the vapor-phase oxidation of o-, m-, and p-xylenes with fluidized catalysts, both fused and unfused (see Table II). The influence of catalyst support and of promoters on the catalytic activity was studied. They reported the following results:

Effect of catalyst-- "The comparative efficiencies of five different catalysts for the oxidation of o-xylene in a fluidized bed showed that fused vanadium pentoxide was the best catalyst for this oxidation: under optimum conditions (490°C, air/xylene = 95:1, space velocity = 10,030 l/hr/l, catalyst volume = 17.3 cc), a maximum yield of 67.8 per cent of phthalic anhydride and 3.6 per cent of o-toluic aldehyde was obtained. Pumice served as a good support only up to a concentration of 29 per cent above which both the yield of phthalic anhydride and the selectivity of the catalyst were adversely affected."

Effect of space velocity-- "The effect of space velocity was studied by varying the feed rate of xylene, the catalyst volume being kept constant. Space velocity had a similar influence with the first two catalysts on the yields and distribution of the products, the yield of phthalic anhydride increasing with an increased space velocity but the effect with unfused catalysts was the reverse."

Effect of air/xylene ratio-- "The influence of air/xylene ratio on the performance of the first two catalysts was directly opposite to that observed with third and fourth, in other words the yield of phthalic anhydride was increased with an increase of air/xylene ratio with the first and second catalysts and a decrease of yield was observed with the third and fourth catalyst."

They pointed out five advantages of fluidized beds for air oxidation of o-xylene.

1. The catalyst charging and discharge problem is solved.
2. Temperature profile within the bed is very uniform.
3. Thermal conductivity is high, generally, 5 to 6 times greater than that of a fixed bed catalyst. This permits efficient recovery of the heat of reaction.
4. Higher output per unit of investment is obtained.
5. Higher product purity is obtained.

They explained these advantages of the fluidized beds by the following reasons:

1. Great available surface of the solid.
2. Circulation of particles within the entire bed.
3. High operating air velocity.

The catalytic vapor phase oxidation of xylenes in a fluidized bed differs from that in a fixed bed in several ways, although the most active catalyst in both cases is fused vanadium pentoxide. A comparison of the two methods is recorded in Table II.

TABLE II

Comparative Efficiencies of Vanadium Pentoxide Catalyst for
Vapor-phase Oxidation of Ortho-xylene in Fixed and Fluidized Bed Reactors (1)

Catalyst	Type of Bed	Volume of Catalyst ml	Space Velocity l/hr/l	Molar Air/Xylene Ratio	Catalyst Temperature °C	Yield Per Cent		
						Phthalic Anhydride	Maleic Anhydride	O-toluic Aldehyde
Fused V_2O_5	Fluidized	17.3	10030	95.1	490	67.8	-	3.6
	Fixed	20.0	5740	275.0	490	61.7	9.6	-
V_2O_5 - Pumice (fused) (V_2O_5 : Pumice = 243:100)	Fluidized	49.3	3700	635.0	470	61.2	-	3.1
	Fixed	20.0	5760	383.0	510	51.8	9.3	-
V_2O_5 -Kieselguhr (V_2O_5 :Kieselguhr = 31.1:100)	Fluidized	21.2	8500	430.0	380	40.1	11.9	7.3
	Fixed	20.0	6180	360.0	440	42.7	11.3	-

A most remarkable difference exists in the distribution of the oxidation products. As reported by Bhattacharyya & Gulati, (2) the products of oxidation of o-xylene in the fixed bed contained no trace of o-toluic aldehyde, but it was formed in appreciable quantity in the fluidized bed operations.

The optimum temperatures of oxidation of o-xylene was the same in both fixed and fluidized catalyst beds, and there was no reaction below 440°C in the fixed bed whereas appreciable conversion was obtained at 430°C in the fluidized bed.

Hence, it is concluded that by reason of better control of the conditions and course of reaction, higher yields and purity of desirable products, absence of explosion hazard and greater through-put per unit volume of the catalyst, the fluidized bed should have a higher efficiency in the yield of phthalic anhydride than the fixed bed.

Wang(12) performed exploratory experiments using bench scale equipment similar to that used in the present work. He studied the vapor-phase oxidation of o-xylene to phthalic anhydride in a fluidized bed reactor. Parameters investigated during the study were temperature, molar ratio of air to o-xylene vapor, and space velocity. His catalyst was the same material as Catalyst I described in the Experimental Section of this thesis.

He used the volumes of 20, 30, 40, and 50 ml of catalyst. It was pointed out that when temperature and molar air/xylene ratio were kept constant the yield per cent of phthalic anhydride increased

with an increase in catalyst volume until 30 ml was reached. He obtained a decreased yield with 40 ml and 50 ml of catalyst respectively.

The temperatures which he used were 470, 490, 520, and 535°C. At the same molar air/xylene ratio, the optimum reaction temperatures were 520°C when using 20 ml of catalyst and 490°C when using 30 ml of catalyst. The highest yield per cent of phthalic anhydride he obtained was 15.20 per cent of theoretical.

He reported the optimum molar air/xylene ratio (see Nomenclature Appendix A) was in the neighborhood of 300 and 500 to 1 corresponding to 20 and 30 ml of catalyst.

PATENT REFERENCES IN PRODUCTION OF PHTHALIC ANHYDRIDE BY CATALYTIC OXIDATION OF O-XYLENE.

Production of Maleic and Phthalic Anhydride.

An invention was patented on September 27, 1960. (assigned by Donald E. Burney, Hammond, and Melvern C. Hoff, Highland, Ind., assignors (3) to the Standard Oil Company, Chicago, Ill., U.S.A.). A 98 per cent pure ortho-xylene is oxidized to phthalic anhydride in a fluidized catalyst system using 10-100 micron size fused vanadium oxide microspheres both as the catalyst and as the source of oxygen. And the catalyst is regenerated with air in a separate vessel. This procedure is claimed to have the advantage that the product gas stream is substantially free from noncondensable oxygen or nitrogen, thus permitting the ready recovery of phthalic anhydride.

Eighty three and one half pounds per hour of ortho-xylene containing of 0.2 weight per cent dissolved ethylene dibromide was used by these experimenters. The vaporized stream throughout the catalyst bed was at a temperature of about 400°C and a flow rate of about 430 pounds per hour was used. The reactor size was 3 feet in diameter and 6 feet high. The residence time was said to be about one second. The catalyst is regenerated in the regenerator by re-oxidizing with air at the temperature of about 590°C.

Unfortunately, the patent did not point out the yield per cent of phthalic anhydride obtained in this operation. These inventors (3) claim a process for the catalytic vapor phase oxidation of o-xylene to phthalic anhydride which comprises reacting vaporized

o-xylene with oxygen in the presence of a metal oxide oxidation catalyst, the metal was a member of groups V-b and VI-b of the periodic table of elements, and in the presence of a small promotional amount of a volatile bromine compound free from metallic constituents.

Production of Phthalic Anhydride by Catalytic Oxidation of O-xylene.

Another invention (6) was patented on October 5, 1965. (assigned by Helmut Nonnenmacher, Max Appl, and Konstantin Andrussow, all of Ludwigshafen(Rhine), Germany, Assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany). It relates to the production of phthalic anhydride by catalytic oxidation of o-xylene in a fluidized bed.

Here is an example in this patent (U.S. No. 3,210,378) that shows the effect on the yield of phthalic anhydride of adding an amount of bromine or organic bromides during the oxidation of o-xylene.

A 0.7 per cent solution of nitrosyl bromide in o-xylene is prepared (equivalent to 0.5 per cent of bromide with reference to o-xylene). This solution is vaporized in an evaporator in the conventional way in a stream of air of 400 liters (S.T.P.) per hour and passed into the reaction chamber, 35 g of o-xylene per hour being thus metered in. The reaction chamber contained 7 liters of a catalyst consisting (in per cent) of 7.55 of V_2O_5 , 1.60 of MoO_3 , 0.15 of P_2O_5 , 0.10 of Ag_2O , 35.6 of $K_2S_2O_7$ and 55.0 of silica gel. The temperature in the fluidized bed was kept at $310^{\circ}C$. The residence period at the

catalyst is 33 seconds.

They reported that they obtained per hour:

29.0 g of phthalic anhydride (59.3 mole per cent)

0.78 g of maleic anhydride (1.2 mole per cent)

21.4 liters (S.T.P.) of carbon dioxide and carbon
monoxide (36.3 mole per cent)

1.12 g of residual xylene (3.2 mole per cent)

Using hydrogen bromide instead of nitrosyl bromide, by vaporizing a 0.5 per cent solution of hydrogen bromide in o-xylene as the initial material, the following results were claimed with an hourly throughput of 35 g of o-xylene at 310°C.

29.3 g of phthalic anhydride (60.1 mole per cent)

0.81 g of maleic anhydride (1.25 mole per cent)

21.3 liters (S.T.P.) of carbon dioxide and carbon monoxide
(36.0 mole per cent)

0.93 g of residual xylene (2.65 mole per cent)

Nitrosyl bromide and other organic bromides were also used in small percentages as promoters. The results of using these bromides as reported in the patent are shown in Table III.

TABLE III

Comparison of the Yield Per Cent of Phthalic Anhydride by Adding Various Bromides as Promoters (6)

Additive	Wt % supplied with reference to xylene	Wt % of Chromium supplied with reference to xylene	Yield per cent of phthalic anhydride
4-bromoxylene	1.16	0.5	57.6
Ethyl bromide	0.68	0.5	60.5
Cyclohexyl bromide	1.02	0.5	59.1
Acetyl bromide	0.77	0.5	60.3
Benzoic acid bromide	1.16	0.5	58.9
Phenylacetic acid bromide	1.25	0.5	59.2

These investigators reported that they obtained the following amounts of products per hour when no promoters were used.

20.1 g of phthalic anhydride (41.2 mole per cent)

1.49 g of maleic anhydride (2.3 mole per cent)

24.2 liters (S.T.P.) of carbon monoxide and carbon dioxide (41.0 mole per cent)

3.3 g of residual xylene (about 9.5 mole per cent) and o-tolualdehyde (about 6 mole per cent) making a total of 15.5 mole per cent.

Nonnenmacher, Appl, and Andrussow (6) essentially claim a process for the catalytic vapor phase oxidation of o-xylene to phthalic anhydride using a fluidized catalyst in a temperature range of 250 to 380°C. They report using a residence period of 5 to 50 seconds. Their catalyst was disclosed as 5 to 30 per cent by weight of vanadium pentoxide supported on an inert carrier. The catalyst was applied to the carrier in solution form. The solution contained either potassium pyrosulfate or a mixture of the potassium pyrosulfate and sodium pyrosulfate in a ratio by weight of 1:1. They also used bromine and bromine containing compounds in amounts of 10^{-3} to 2 per cent by weight. They also report using sulfur dioxide to restore catalyst activity after prolonged use of the catalyst. Table III indicates that these investigators also supplied 0.5 weight per cent of chromium with reference to xylene but no mention seems to be made in the patent as to how or in what form this chromium was introduced.

COMMERCIAL PRODUCTION OF PHTHALIC ANHYDRIDE FROM ORTHO-XYLENE

Phthalic anhydride has been produced commercially (11) from o-xylene since 1945. The production increased steadily from 123 million pounds in 1945 (5) to 550 million pounds in 1965 (7). Sales value of phthalic anhydride, on the contrary, dropped steadily: \$ 0.125 per pound in 1945 (5) and \$ 0.095 per pound in 1965 (7).

The advantage of using o-xylene is apparent because of its low sales value (7) of 2.5 to 3.0 cents per pound less than naphthalene. If phthalic anhydride prices remain low, small producers and those with an advantageous position in raw-material naphthalene would be forced either to halt manufacture or replace existing units with larger more efficient plants. The feedstock of choice would be o-xylene.

The Oronite Chemical Company division of the Standard Oil Company of California (5) built the first plant to use o-xylene as a feed material for the production of phthalic anhydride at Richmond, California in 1945. This was a fixed bed reactor plant with a rated capacity of 4,000 tons per year. This plant was reported to have been closed in June 1963 when Oronite opened its new 6,000 tons per year plant at Perth Amboy, New Jersey.

The o-xylene based plants now operating in the continental United States are:

1. Allied Chemical and Dye Corporation,
El Segundo, California
2. Stepan Chemical Company,
Millsdale, Illinois
3. Oronite Chemical Company,
Perth Amboy, New Jersey
4. Heyden Newport Chemical Corporation,
Fords, New Jersey

All of these plants are of the fixed bed reactor type. The first two use the Chemiebau process.

An up-to-date plant was built by the Puerto Rico Chemical Company at Arecibo, Puerto Rico in 1965. It went on stream in early 1966. This plant has a capacity of 25,000 tons per year, half of which is slated for shipment to markets outside the United States. The feedstock is o-xylene and the plant uses a Chemiebau catalyst to produce what is reported to be an exceptionally high quality phthalic anhydride (4).

III. EXPERIMENTAL

The purpose of the investigation, plan of experimentation, materials used, equipment construction, experimental procedure, data, results and calculations are included in this section. They are individually described below.

Purpose of Investigation

The purpose of this investigation was to conduct further studies on the vapor phase air oxidation of o-xylene to phthalic anhydride in a fluidized bed catalyst. An effort was made to construct a better reactor, and the operating variables such as temperature, catalyst volume, space velocity, and molar ratio of air to o-xylene vapor of this process were studied. The nature of the catalyst is an important variable. A study of the effects of some of the same variables as were investigated by Wang (12) was carried out. However, some different ranges of the variables were used. Two kinds of catalysts were employed in this investigation. The overall purpose was to try to increase the yield of phthalic anhydride with a fluidized reactor and to study the variables affecting the yield.

Plan of Experimentation

The investigation was initiated by a review of the literature, including the catalytic oxidation of hydrocarbons in general and of o-xylene in particular. After the characteristics of oxidation catalysts and fluidized beds were studied to find practical approaches to this topic, the equipment was then constructed and the materials to be used in the experiments were obtained. Actual experimentation

was started after the experimental setup had been found to operate satisfactorily. Finally, the correlation of the data and the calculation of the results were made.

Materials

The materials used during this investigation are listed below.

Catalysts.

(a) Catalyst I (same lot as used by Wang)

Davison Grade 906. Manufactured and distributed by Grace Davison Chemical Company, Baltimore 3, Maryland. The catalyst has the following properties as reported by the supplier (10):

1. Typical physical analysis.

Bulk density -----	39 lb/cu ft
Surface area -----	200 sq m/gm
Pore diameter -----	95 angstroms

2. Typical chemical analysis.

Volatile at 750°F, wt % -----	1.0
V ₂ O ₅ , wt % (dry basis at 750°F) -----	4.0
SO ₃ , wt % (dry basis at 750°F) -----	6.7
K ₂ SO ₄ , wt % (dry basis at 750°F) -----	14.9
SiO ₂ , wt % (dry basis at 750°F) -----	73.0

3. Typical particle size analysis.

On 50 mesh, wt % -----	0.5
On 200 mesh, wt % -----	93.0
0 to 20 micron, wt % -----	0.5

(b) Catalyst II

This catalyst was a lot received from the Monsanto Company, St. Louis, Missouri. It had been withdrawn from a fixed bed reactor in commercial production. It was reported that this catalyst initially was about the same as Davison Grade 906. It was observed to have more fine material than the other catalyst. A screen analysis of this used catalyst follows:

On 50 mesh, wt % -----	3.6
On 100 mesh, wt % -----	23.7
On 200 mesh, wt % -----	63.4
Below 200 mesh, wt % -----	36.6

Air. Compressed. Supplied by the University. Used as the source of oxygen needed for oxidizing o-xylene.

o-Xylene. Obtained from the Monsanto Company, St. Louis, Missouri, Used as raw material for producing phthalic anhydride. The following typical analysis was reported by the supplier:

Specific gravity -----	0.883
Initial boiling point -----	144.0°C
Dry point -----	145.5°C
Acidity (no free acid) -----	pass
Isomer compounds:	
Volume per cent of o-xylene -----	96.4 (95.0 % minimum)
Olefins and saturates -----	0.3
Sulfur compounds (Free H ₂ O & SO ₂) -----	pass

Filter Paper. White Label, No. 589. Manufactured and dis-

tributed by Carl Schleicher & Schuell Co. Eleven cm in diameter. Used to filter the insoluble reaction product.

Sodium Bisulfite. Lot No. 763359. Obtained from Fisher Scientific Co., Fair Lawn, N.J. Used to determine o-toluic aldehyde.

Calcium Hydroxide. Lot No. 23436. Manufactured and distributed by J.T. Baker Chemical Co., Phillipsburg, N.J. A saturated solution was prepared to precipitate carbon dioxide as calcium carbonate.

Sodium Hydroxide. Manufactured and distributed by the Matheson Coleman Copmany. A ten normal solution was used to purify the compressed air by removing carbon monoxide and carbon dioxide; a standardized solution (0.91 N) was prepared as the reagent for determining the total acidity of the oxidation product.

Sulfuric Acid. Manufactured and distributed by the E.I. Du Pont de Nemours Co. A 50 per cent solution was used in drying the air and a 1:8 solution was employed to acidify the filtrate from the total acidity determination for the titration of maleic anhydride.

Calcium Chloride. Purified, anhydrous, granulated. Manufactured and distributed by J.T. Baker Chemical Co., Phillipsburg, New Jersey. Used in drying the air.

Distilled Water. Conventional for ordinary laboratory purposes. Supplied by this University. Used for dissolving oxidation product.

Potassium Permanganate. Pure grade, Lot No. 90389. Obtained from J.T. Bader Chemical Co., Phillipsburg, New Jersey. A 0.192 N solution was prepared for the quantitative analysis of maleic anhydride.

Equipment Description and Operation

The equipment used in these experiments is shown schematically in Figure 1 and Figure 2 is a photograph of this apparatus.

Air Feed Unit. The air purifying train consisted of three one liter flasks in series, the first of which contained sulfuric acid, the second sodium hydroxide, and the third anhydrous calcium chloride. The purpose of this train was to remove dust, carbon dioxide, carbon monoxide and moisture if any of these were contained in the compressed air. The purified air was then passed through the orifice meter.

Orifice Meter and Calibration. A 1/16 inch-diameter orifice meter was used to determine the total air flow rate. A wet test meter (made by Precision Scientific Company, Chicago, U.S.A. No. 12683) was used to calibrate the orifice meter. The calibration curve of this orifice is shown in Figure B-1. The purified dry air was then distributed into two streams, one going into the o-xylene evaporator and the other directly to the gas mixer.

Xylene Evaporation Unit. The vaporizer was a 500 ml three neck pyrex glass flask which was heated by a heating mantle. The

temperature was controlled by a Variac. The amount of o-xylene evaporated in a given time was found to be dependent upon the temperature of the liquid and the flow rate of the air. The central neck of the flask was the inlet for the air stream, and a long glass tube extended down to the bottom of the flask to introduce the air below the o-xylene liquid surface. The left neck was fitted with a thermometer to measure the temperature of the vapor. The right neck was the outlet for the mixed gases which passed to the gas mixer.

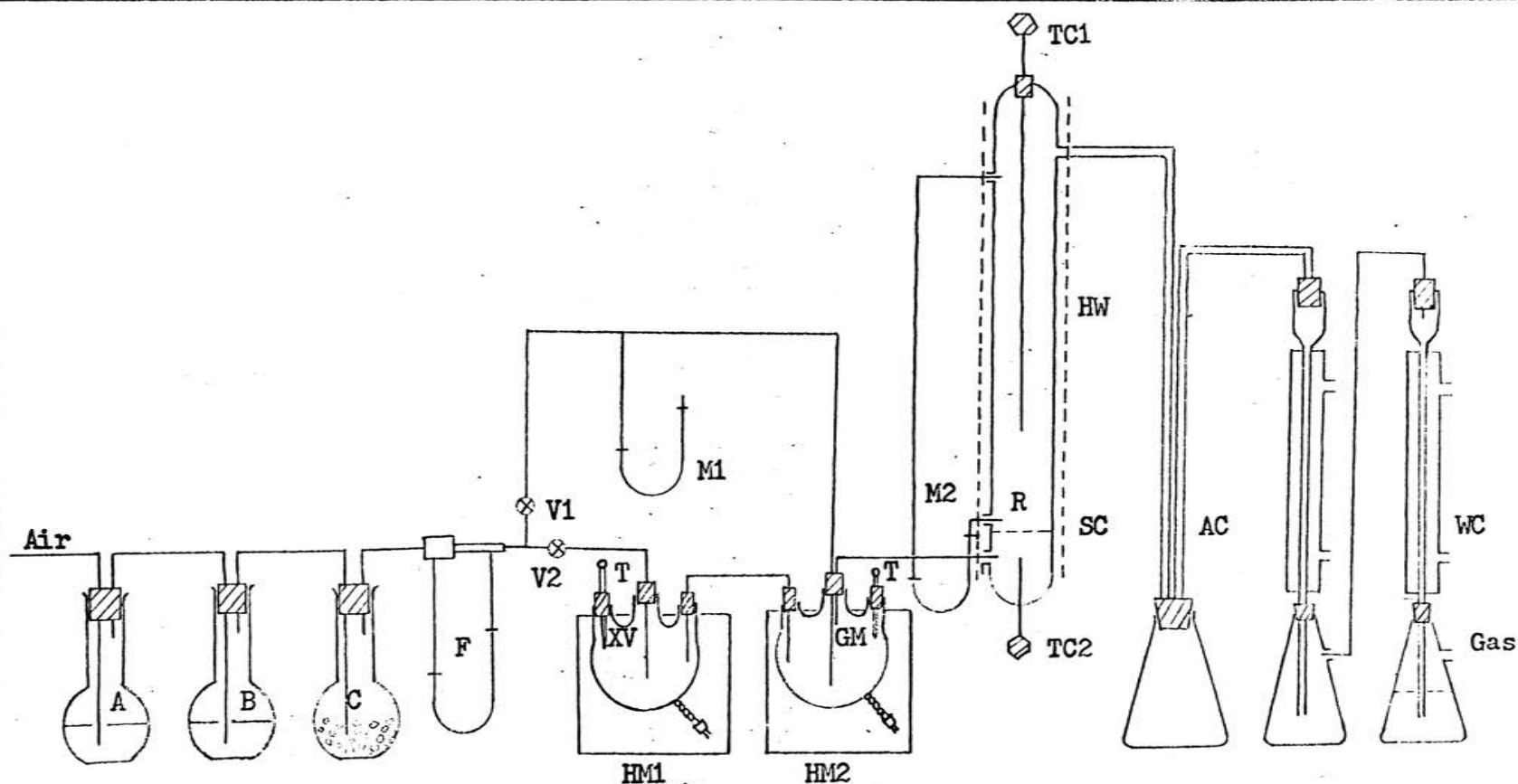
Gas Mixer. The gas mixer was also a 500 ml three neck pyrex glass flask covered with a heating mantle. The temperature of the mixed gases was controlled by another Variac. Gas from the evaporator was introduced at the left neck. The central neck of the gas mixer was the inlet of the secondary air stream coming from the orifice. The mixed gases left the gas mixer through the right neck and passed into the preheater (the temperature of gas leaving the gas mixer was no less than 200°C).

Fluidized Reactor. This unit is shown schematically in Figure 1. The total length of the preheater and the reactor was 3 feet. It was made of one inch, Schedule 40 steel pipe mounted vertically. The bottom six inches of the pipe was the preheater. The preheater was wrapped with two heating tapes (Cat. No. Sc-C4; U.S. Patent, 2,989,613; maximum temperature 600°C; diameter 3/16 inch; length 4 feet each; watts 400; voltage 115 ac; covering material quartz fabric). The heat supply was controlled by another

Variac, and the temperature was measured with a thermocouple (Iron-constantan Cat. No. SS12J-U-B2-MK22-10) connected with a potentiometer which will be described later. It was possible to raise the temperature of the air-xylene mixture from about 200°C to 350°C in the preheater section. There was an iron-constantan thermocouple (same as used in preheater) fitted in the top of the reactor. It extended straight down to the middle of the catalyst bed. The temperature of the reactor was controlled with a Variac, heat input supplied by a 1000 watt tungsten heating coil wrapped uniformly around a layer of 5 mm diameter glass rods. The input to the heating coil was controlled with a Variac and the temperature was measured with a thermocouple and potentiometer. Both the preheater and the reactor were then covered with a two inch layer of 85 per cent magnesia insulation wrapped with asbestos paper.

The differences in construction of the reactor used in this work from the reactor used by Wang (12) were:

1. The 200 mesh screen used to support the catalyst was inserted between two flanges. This was done to insure that the screen remained stable and was not disturbed by the mixed gases passing upward through the catalyst bed. Thus the cross-section of the bed would remain constant during fluidization.
2. The thermocouple used to measure the catalyst temperature extended down into the fluidized bed. Thus the catalyst temperature could be obtained with more accuracy than in the construction used by Wang (12) who measured a wall temperature.



A Sulfuric Acid
 B Sodium Hydroxide
 C Anhydrous CaCl_2
 AC Air Condenser
 F Flow Meter
 M1, M2 Manometers

GM Gas Mixer
 HW Heating Wires
 R Reactor
 SC Screen
 T Thermometers
 XV O-xylene Vaporizer

HM1, HM2 Heating Mantles
 TC1, TC2 Thermocouples
 V1, V2 Valves
 WC Water Condenser

FIGURE 1. APPARATUS FOR VAPOR-PHASE OXIDATION OF O-XYLENE IN A FLUIDIZED BED REACTOR

• FEB • 66

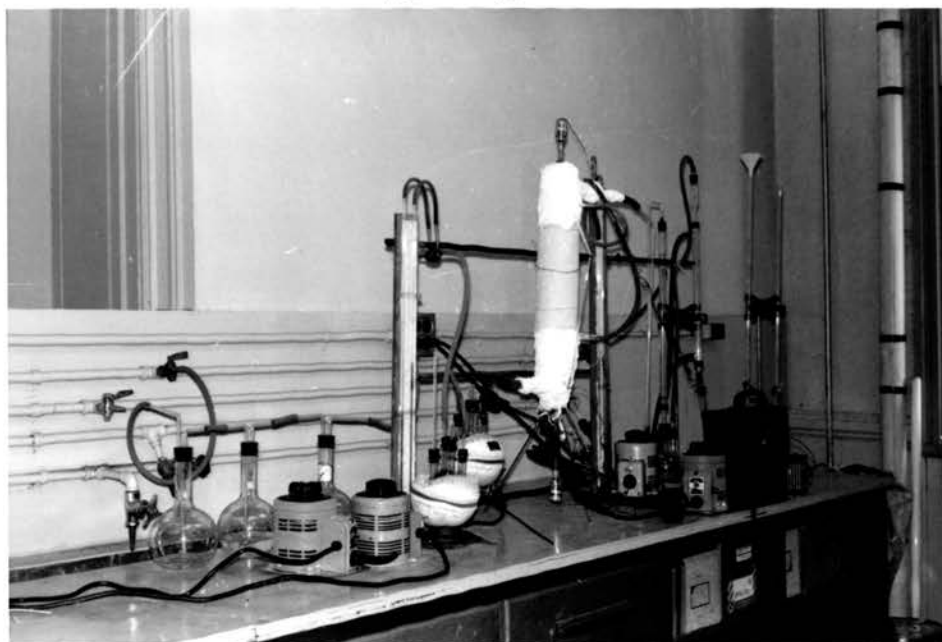


FIGURE 2. PHOTOGRAPH OF THE EXPERIMENTAL APPARATUS

3. The use of the 1000 watt tungsten heating coil, in place of the heat tapes, permit a greater temperature range to be used. A temperature of 600°C could be obtained with this tungsten coil.

4. Water colored with a few drops of ink was used as a manometer fluid to measure the pressure drop through the catalyst because it gave larger readings than the mercury used by Wang in his work.

Temperature Control. The temperatures in the reactor and preheater were measured by a Foxboro Potentiometer (model 8105, Serial No. 47456). The variation of the temperature readings was $\pm 2^{\circ}\text{C}$. The temperatures in the vaporizer and gas mixer were measured with mercury thermometers and all heat supplies were controlled by Variacs.

Condensation Unit. The condensation unit consisted of three pyrex glass condensers connected in series. The first one was an air cooled condenser, four feet in length and one quarter inch inside diameter. The second and third condensers were water cooled. Each was $\frac{1}{2}$ inch I.D. and 23 inches in length. Three 500 ml flasks were used to collect the condensate. The exhaust gas was passed into a saturated calcium hydroxide solution to form calcium carbonate to measure the amount of carbon dioxide formed during the test period.

Experimental Procedure

Oxidation of O-Xylene. The experimental apparatus was closely checked to detect any possible leakage by passing compressed air

through it and painting it with a soap solution and looking for bubbles. The catalyst was measured in a 100 ml graduated cylinder and then weighed on an Ohaus triple beam balance. It was charged into the reactor from the top. The reactor was then tightly closed and the current was turned on in the heating tapes and heating coil. The reactor was heated to a temperature 5°C above the desired test temperature. The compressed air valve was opened and the air flow rate was held constant by observing the air flow meter reading. The pressure drop through the reactor was noted, making sure the catalyst was really in a fluidized condition. Cooling water was turned on in the condensers. Xylene was measured and introduced into the vaporizer through the neck of the flask where the thermometer had been inserted. The thermometer was then tightly replaced. Air was introduced into both the vaporizer and the gas mixer as shown in Figure 1. The temperature of the o-xylene in the vaporizer was generally held at room temperature (25°C) but it could be increased by use of the heating mantle. Generally, sufficient o-xylene was vaporized by the air passing through it and it was not necessary to use the heating mantle. The temperature of the air xylene mixture was increased by another heating mantle covering the gas mixer to 200°C or slightly above. The final temperature increase of the gas mixture to the desired test temperature took place in the preheater. One or two hours were required to complete a test. At the end of each test, the weight of unvaporized o-xylene was obtained with an Ohaus triple beam scale. The difference between this weight and that of the o-xylene charged was recorded as the

amount of vaporized o-xylene. The time of the test was also recorded.

The needle crystals which accumulated in the air condensers and any other material that may have adhered to the inside of the condensers were washed into a 500 ml flask with boiling distilled water. The total amount of materials that had been washed from the condensers were analyzed for phthalic anhydride, maleic anhydride, and o-toluic aldehyde. The last flask in the products collection train containing calcium hydroxide solution, was analyzed for carbon dioxide.

The catalyst, after three to five tests, changed its color from the normal orange to a blue-black or dark green color indicating the presence of V_2O_4 and V_2O_3 , respectively. This reduced catalyst was discharged and fresh catalyst added for future tests, because the reduced catalyst is not as active as V_2O_5 (9).

Product Analysis. The methods of analysis used to obtain the yields of phthalic anhydride, maleic anhydride and ortho toluic aldehyde were practically the same as those used by Wang (12). He reported that he analysed a portion of the product for the phthalic tests while the whole amount of the product was analysed in this work. Summarized below are the equations used to calculate the amount of phthalic anhydride, maleic anhydride and ortho toluic aldehyde.

Weight of maleic anhydride:

$$(\text{ml } KMnO_4 \times \text{normality}) \times 98/2000$$

Weight of phthalic anhydride:

$$(\text{ml NaOH} \times \text{normality} - \text{ml KMnO}_4 \times \text{normality}) \times 148/2000$$

Where:

98: molecular weight of maleic anhydride

148: molecular weight of phthalic anhydride

Weight of o-toluic aldehyde:

$$(\text{ml NaHSO}_3 \times \text{normality} - \text{ml NaOH} \times \text{normality}) \times 120/1000$$

Where:

120: molecular weight of o-toluic aldehyde

An additional analysis of the products was the determination of carbon dioxide. It was calculated from the CO₂ contained in the saturated calcium hydroxide solution when this solution had become neutralized at room temperature.

Sample calculations are described in the Appendices.

Data and Results

A total of sixty nine tests were performed during this investigation. These were divided into three groups. Group one consisted of Tests Number 1 through 24. In these tests 30 ml (24 grams) of Catalyst I were used and oxidation was carried out at various temperatures from 350 to 520°C. Also the molar air/xylene was varied from 242.5 to 590. No promoter was used in this group of tests. Results of the tests of Group one are presented in Table IV.

Group two, Tests Number 25 through 45, used the same weight of Catalyst I over the same temperature range, except that the majority of the tests were made at an apparent catalyst temperature of 490°C

which was found to give the highest yield of phthalic anhydride during the tests in Group one. In Group two different small percentages of several organic bromine compounds were used as promoters. Results of this group of tests are shown in Table V.

The tests of Group three, No. 46 through 69, were made either with 102 grams of Catalyst I or 137 grams (approximately 150 ml) of Catalyst II. In addition in this group of tests various volume percentages of liquid bromine (1 to 5 %) were added to the o-xylene in the evaporator to serve as a promoter. The results of this group of tests have been tabulated in Table VI.

In order to better study the results of the twenty four tests of Group one they are divided into four subgroups(I-IV). These are shown in Table IV A. Tests having nearly the same amount of o-xylene evaporated, about the same air flow rate, nearly the same air/xylene ratio and roughly the same space velocity were grouped together in the same subgroup. These results are also shown graphically in Figure 3, which is a plot of the yield of phthalic anhydride as a function of the reactor temperature in the catalyst.

Examination of Table IV A and Figure 3 indicates that the highest yields of phthalic anhydride were obtained at 490°C. This confirms the optimum temperature obtained by Wang (12) and Bhattacharyya and Krishnamurthy (1). This is higher than the temperature reported by Nonnmacher, Appl, and Andrussow (6). It may also

TABLE IV

Experimental Results Using 24 Grams of Catalyst I

Test No	Time of Test hr	O-xylene Vaporized gm (Total)	Apparent Catalyst Temp °C	Air Flow Rate at S.C. l/hr	Molar Air/Xylene Ratio	Space Velocity l/hr/l *
1	1.0	2.11	490	244	547	8130
2	1.0	5.68	490	292	242.5	9740
3	1.0	3.67	490	324	417.5	10800
4	1.0	6.10	490	390	303	13000
5	1.0	2.05	550	243	565	8100
6	1.0	3.53	550	291	390	9700
7	1.0	5.52	550	322	277	10780
8	1.0	5.97	550	388	308	12920
9	1.0	2.07	520	244	558	8130
10	1.0	3.32	520	292	416	9740
11	1.0	6.03	520	324	254	10800
12	1.0	6.13	520	390	301	13000

* l/hr/l = Space Velocity of liters per hour per liter of catalyst

TABLE IV
(Continued)

Test No	Percentage Yield				Total hr Catalyst Previously Used
	Maleic Anhydride	O-Toluic Aldehyde	Carbon Dioxide	Phthalic Anhydride	
1	9.1	8.2	18.65	12.5	0.0
2	8.3	9.0	17.35	21.5	1.0
3	10.4	10.2	18.3	20.1	2.0
4	9.7	12.3	20.4	17.3	3.0
5	15.0	7.7	23.8	11.8	0.0
6	14.1	8.8	21.6	19.2	1.0
7	12.3	9.2	21.2	18.9	2.0
8	11.0	11.0	18.2	15.6	3.0
9	9.3	6.7	20.3	10.1	0.0
10	7.6	7.6	17.0	14.6	1.0
11	6.3	8.2	13.47	17.1	2.0
12	8.2	9.1	15.3	13.2	3.0

TABLE IV
(Continued)

Test No	Time of Test hr	O-xylene Vaporized gm (Total)	Apparent Catalyst Temp °C	Air Flow Rate at S C l/hr	Molar Air/Xylene Ratio	Space Velocity l/hr/l
13	1.0	2.10	450	242	546	8070
14	1.0	3.45	450	291	400	9700
15	1.0	5.70	450	322	267	10720
16	1.0	6.05	450	387	303	12900
17	1.0	1.96	400	244.5	590	8150
18	1.0	3.47	400	293	400	9770
19	1.0	5.58	400	325.5	276	10830
20	1.0	5.97	400	391	310	13000
21	1.0	2.35	350	244	492	8130
22	1.0	4.03	350	292	344	9740
23	1.0	5.56	350	324	276	10800
24	1.0	6.37	350	390	290	13000

TABLE IV
(Continued)

Test No	Percentage Yields				Total hr Catalyst Previously Used
	Maleic Anhydride	O-toluic Aldehyde	Carbon Dioxide	Phthalic Anhydride	
13	7.6	4.3	13.0	10.3	0.0
14	8.7	5.2	16.65	15.1	1.0
15	10.5	4.6	18.35	17.1	2.0
16	11.2	2.6	16.1	13.4	3.0
17	5.6	3.2	11.0	9.6	0.0
18	6.4	8.9	12.8	12.3	1.0
19	10.0	6.2	18.2	16.5	2.0
20	9.1	7.2	12.85	11.7	3.0
21	4.6	6.2	9.9	5.2	0.0
22	8.2	5.2	12.4	7.8	1.0
23	9.1	4.6	14.15	11.3	2.0
24	8.2	1.2	13.7	11.5	3.0

TABLE IV A

Sub Group	Test No	O-Xylene Vaporized gm	Apparent Catalyst Temp °C	Air Flow Rate l/hr	Molar Air/Xylene Ratio	Space Velocity l/hr/l	Percentage Yield			
							Maleic Anhydride	O-Toluic Aldehyde	Carbon Dioxide	Phthalic Anhydride
I	1	2.11	490	244	547	8130	9.1	8.2	18.65	12.5
	5	2.05	550	243	565	8100	15.0	7.7	23.8	11.8
	9	2.07	520	244	558	8130	9.3	6.7	20.3	10.1
	13	2.10	450	242	546	8070	7.6	4.3	13.0	10.3
	17	1.96	400	244.5	590	8150	5.6	3.2	11.0	9.6
	21	2.35	350	244	492	8130	4.6	6.2	9.9	5.2
II	3	3.67	490	324	417.5	10800	10.4	10.2	18.3	20.1
	6	3.53	550	291	390	9700	14.1	8.8	21.6	19.2
	10	3.32	520	292	416	9740	7.6	7.6	17.0	14.6
	14	3.45	450	291	400	9700	5.2	5.2	16.65	15.1
	18	3.47	400	293	400	9770	8.9	8.9	12.8	12.3
	22	4.03	350	292	344	9740	5.2	5.2	12.4	7.8
III	2	5.68	490	292	242.5	9740	8.3	9.0	17.35	21.5
	7	5.52	550	323	277	10780	12.3	9.2	21.2	18.9
	11	6.03	520	324	254	10800	6.3	8.2	13.47	17.1
	15	5.70	450	322	267	10720	10.5	4.6	18.35	17.1
	19	5.58	400	325.5	276	10830	10.0	6.2	18.2	16.5
	23	5.56	350	324	276	10800	9.1	4.6	14.15	11.3
IV	4	6.10	490	390	303	13000	9.7	12.3	20.4	17.3
	8	5.97	550	388	308	12920	11.0	11.0	18.2	15.6
	12	6.13	520	390	301	13000	8.2	9.1	15.3	13.2
	16	6.05	450	387	303	12900	11.2	2.6	16.1	13.4
	20	5.97	400	391	310	13000	9.1	7.2	12.85	11.7
	24	6.37	350	390	290	13000	8.2	1.2	13.7	11.5

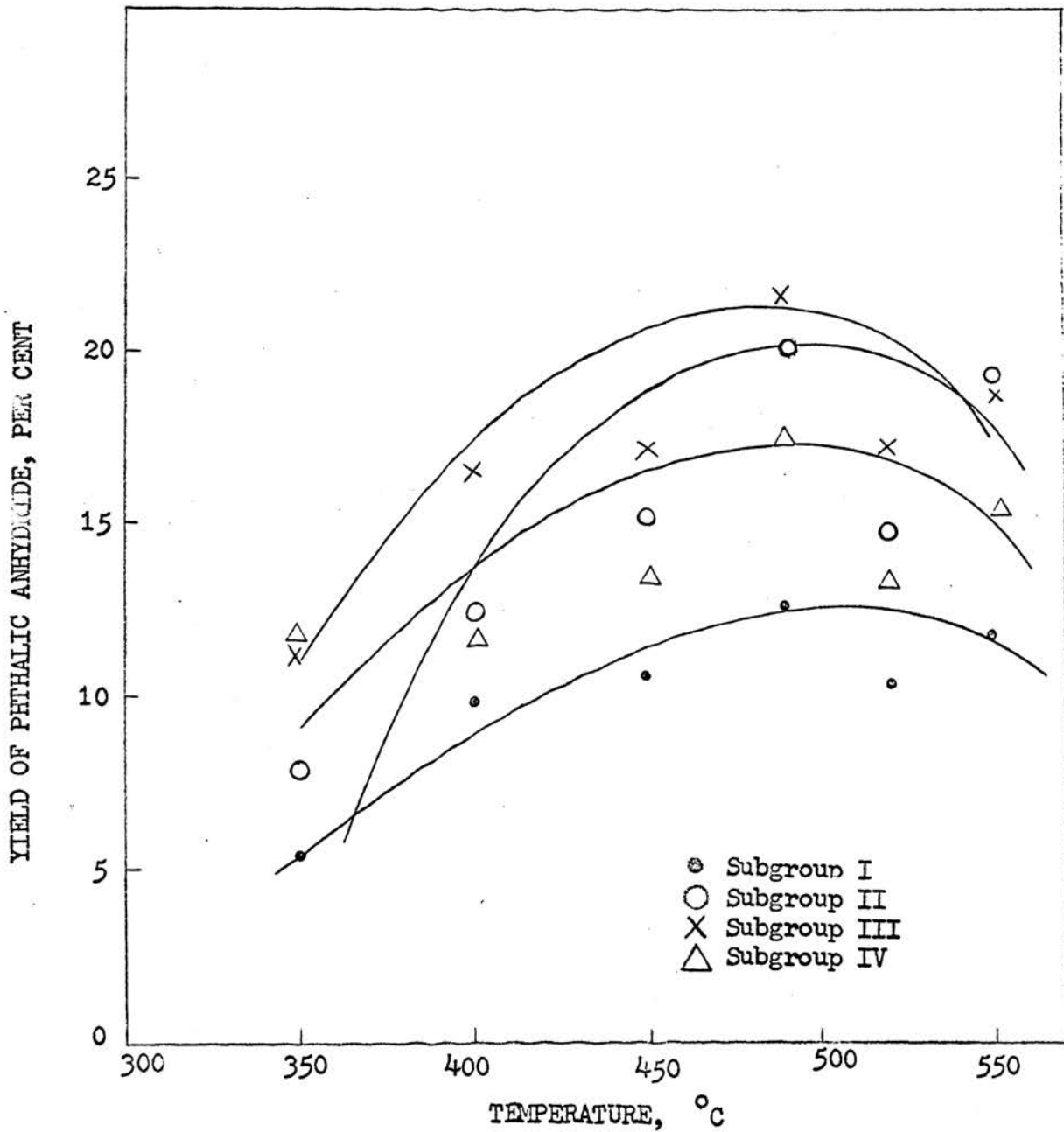


FIGURE 3 EFFECT OF TEMPERATURE AND MOLAR AIR/XYLENE RATIO ON YIELD OF PHTHALIC ANHYDRIDE USING CATALYST I

be noted that the largest production of maleic anhydride takes place at 550°C, as well as, the greatest production of carbon dioxide with one exception. In general, the tests using the smaller molar air/xylene ratios (approximately 260:1) gave the highest yield of phthalic anhydride at all temperature. The curve for subgroup II seems to be an exception to this as it crosses the other curves.

Comparing the yields of phthalic anhydride (Tests 1 to 24) with those obtained by Wang (12), it can be noted that, in general, the results of this investigation were higher than those he obtained. For example he obtained 15.2 per cent (highest) and 0.86 per cent (lowest) when using 30 ml Catalyst I, while 21.5 per cent (highest) and 5.2 per cent (lowest) were obtained in this work.

Examination of Table IV shows that Test No. 2 gave the highest yield of phthalic anhydride 21.5 per cent at 490°C with an air/xylene ratio of 242.5 and a space velocity 9740 liter per hour per liter of catalyst. The yield per cent of maleic anhydride, o-toluic aldehyde and carbon dioxide were 8.3, 9.0 and 17.35 per cent respectively. The use of temperatures either above or below 490°C decreased the yield per cent of phthalic anhydride.

Figure 4 is a correlation of the yield of phthalic anhydride with molar air/xylene ratio. This plot shows that ratios between 200 and 300 give the higher yields at all temperatures investigated.

Figure 5 shows the effect of space velocity on yield of phthalic anhydride. Space velocities between 9500 and 11,000 give the maximum yields of phthalic anhydride at temperatures from 350 to 550°C.

It has been reported in Patent No. 3,210,378, Badische Anilin- & Soda-Fabrik Aktiengesellschaft Company (6), Germany dated October 5, 1965 that the use of bromine or bromine compounds improved the yield of phthalic anhydride. It was decided to investigate this claim using 24 grams of Catalyst I. Four tests (No. 25 - 28) were made using one per cent *o*-phenol bromide as a promoter at four different oxidation temperatures. The promoters in all cases were introduced in solution in the *o*-xylene. It was found that the use of phenol bromide increased the yield of phthalic anhydride at all temperatures tested under approximately equal conditions of space velocity. The highest yield of phthalic anhydride, 25.2 per cent, was obtained at a catalyst temperature of 490°C. This was also the temperature at which the best yield had been obtained without a promoter.

Nine additional tests (No. 29 to 37) were made using 1, 2, and 5 per cent of 1-3 dibromo-propane as a promoter with Catalyst I at 490°C. The yields obtained with this promoter were in some cases less than when unpromoted Catalyst I was used. However, the percentage yield of phthalic anhydride increased from approximately

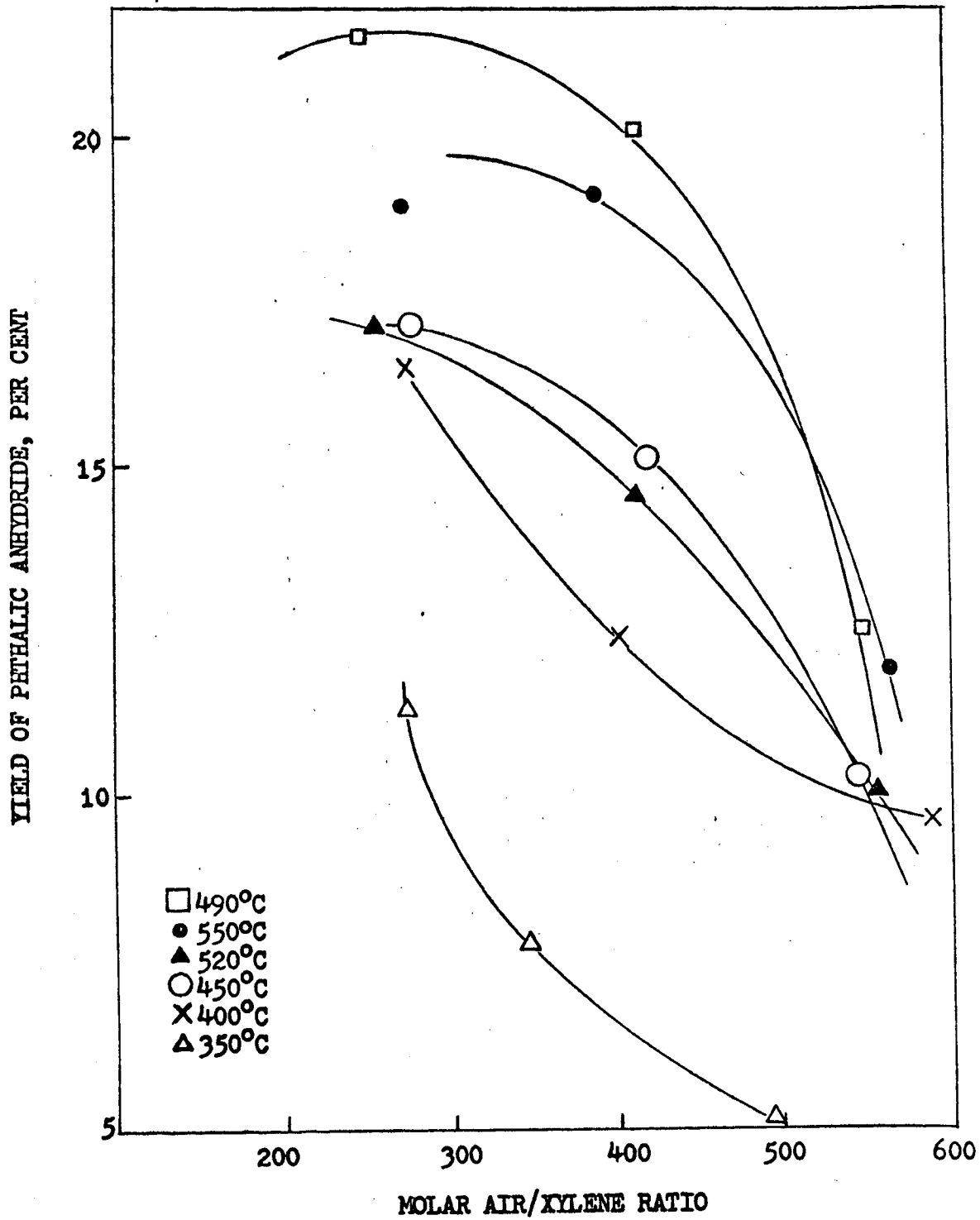


FIGURE 4 CORRELATION OF PHTHALIC ANHYDRIDE YIELD PER CENT AND MOLAR AIR/XYLENE RATIO AT VARIOUS TEMPERATURES (Data from Table IV)

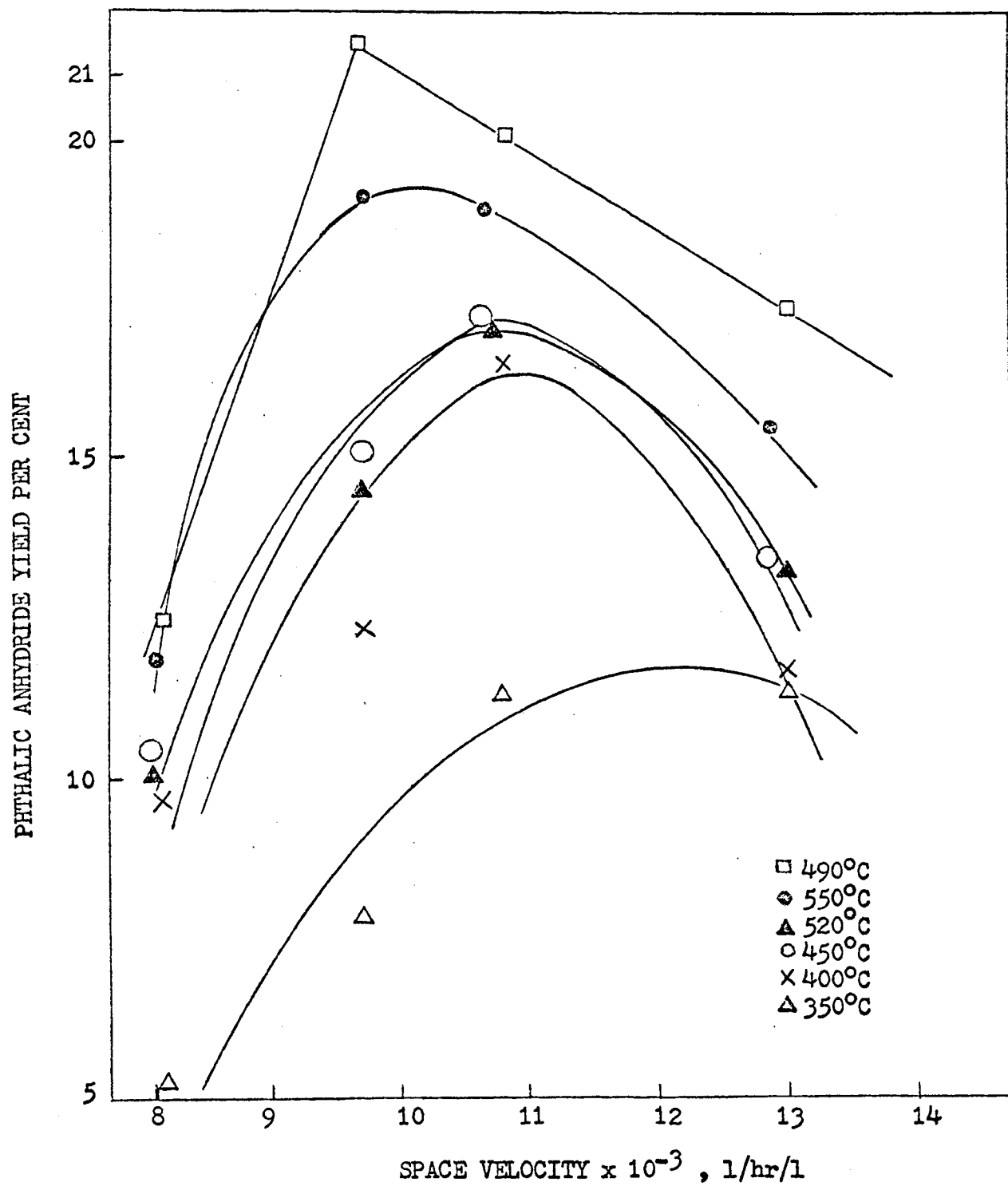


FIGURE 5 CORRELATION OF PHTHALIC ANHYDRIDE YIELD PER CENT AND SPACE VELOCITY AT VARIOUS TEMPERATURES (Data from Table IV)

12 per cent when one per cent 1-3 dibromo-propane was used to a high of 17.6 per cent when 5 per cent of this promoter was used. The results of tests 25 to 37 are given in Table V.

Some of tests shown in Table VI were made with 102 grams of Catalyst I and others were performed with 137 grams of Catalyst II. Tests No. 38 through 41 used Catalyst I and Tests No. 42 through 45 used Catalyst II. The highest yield per cents of phthalic anhydride obtained without any promoter were 24.3 in Test No. 38 and 19.6 in Test No. 42, both at the reaction temperature of 490°C.

Tests No. 46 through 69 used different percentages of bromine as a promoter at several temperatures (320,400,490,520°C). The results which are tabulated in Table VI show the usefulness of bromine as a promoter. The highest yield per cent of phthalic anhydride obtained in this investigation (Test No. 50) was 36.2 per cent when using 5 per cent bromine with Catalyst I at a reaction temperature of 490°C.

Figure 6 shows the effect of temperature on phthalic anhydride yield per cent when different volume percentages of bromine or bromide were used. It was found, for each group of tests (as shown in Figure 6) the phthalic anhydride yield per cent increased with an increase in temperature until it reached 490°C. When the temperature was increased above 490°C the phthalic anhydride yield per cent decreased with an increase in temperature. This plot also shows that in each group of tests the optimum reaction temperature was 490°C.

TABLE V

Experimental Results Using 24 Grams of Catalyst I and
Two Bromide Promoters

Test No	Time of Test hr	O-xylene Vaporized Grams (Total)	Apparent Catalyst Temp °C	Air Flow Rate at S C l/hr	Molar Air/Xylene Ratio	Space Velocity l/hr/l
25	1.5	5.420	490	254	222	8470
26	1.0	3.815	400	254	315	8470
27	1.5	4.652	520	254	258	8470
28	1.0	3.600	450	182	384	6100
29	1.0	2.613	490	254	461	8470
30	1.0	3.545	490	254	339	8470
31	1.5	4.554	490	254	264	8470
32	1.5	5.235	490	253	229	8440
33	1.5	6.072	490	253	198	8440
34	1.5	4.334	490	253	277	8440
35	1.0	2.555	490	254	469	8470
36	1.0	3.671	490	254	326	8470
37	1.5	4.545	490	254	264	8470

TABLE V
(Continued)

Test No	Percentage Yield				Total hr Catalyst Previously Used
	Maleic Anhydride	O-Toluic Aldehyde	Carbon Dioxide	Phthalic Anhydride	
25	9.95	10.8	11.05	25.2	0.0*
26	11.1	11.0	13.25	11.5	1.5*
27	6.6	8.0	10.25	12.6	2.5*
28	9.8	8.4	14.5	20.1	4.0*
29	4.87	5.4	7.56	12.35	0.0**
30	4.93	5.35	7.6	12.60	1.0**
31	4.50	5.43	8.0	11.30	2.0**
32	5.96	6.5	9.85	15.10	3.5#
33	6.10	6.45	10.3	15.40	5.0#
34	5.94	6.53	8.22	15.50	0.0#
35	6.95	7.5	8.10	17.60	1.5##
36	6.87	7.4	8.16	17.10	2.5##
37	7.02	7.3	7.86	17.52	3.5##

* 1 % Phenol Bromide added in O-xylene

** 1% 1-3 Dibromo-Propane added in O-xylene

2 % 1-3 Dibromo-Propane added in O-xylene

5 % 1-3 Dibromo-Propane added in O-xylene

Figure 7 shows the effect of temperature on phthalic anhydride yield per cent at different temperatures when Catalyst II was used. Bromine was used as a promoter in these tests and again the highest yield per cent of phthalic anhydride was obtained at the reaction temperature of 490°C.

Maleic anhydride was found to be produced in all experiments and it was found, generally, that the yield of maleic anhydride from o-xylene increased with an increase in yield of phthalic anhydride.

Carbon dioxide was measured in each test run. In some cases it increased with an increase in yield of phthalic anhydride, but in other cases it did not.

TABLE VI

Experimental Results Using 102 Grams of Catalyst I or 137 Grams of Catalyst II with and without a Bromine Promoter

Test No	Time of Test hr	O-xylene Vaporized Grams (Total)	Apparent Catalyst Temp °C	Air Flow Rate at S C l/hr	Molar Air/Xylene Ratio	Space Velocity l/hr/l
38	1.0	3.040	490	290.1	451	1935
39	1.0	2.954	490	290.1	465	1935
40	1.0	3.252	320	284	413	1891
41	1.0	3.103	320	284	433	1891
42	1.0	2.861	490	354	585	2360
43	1.0	3.135	490	354	535	2360
44	1.0	2.562	320	343.2	634	2282
45	1.0	2.953	320	343.2	550	2282
46	1.0	4.385	490	198	214	1320
47	1.0	4.549	490	226	236	1500
48	1.0	3.061	320	254	393	1130
49	1.0	2.513	320	203	383	1350
50	1.0	4.345	490	283	309	1890
51	1.0	4.216	490	226	251	1500
52	1.0	3.130	490	198	214	1320
53	1.0	3.952	490	226	236	1500
54	1.0	2.831	320	254	393	1130

TABLE VI
(Continued)

Test No	Percentage Yields				Total hr Catalyst Previously Used
	Maleic Anhydride	O-Toluic Aldehyde	Carbon Dioxide	Phthalic Anhydride	
38	10.3	9.3	15.3	24.3	0.0*
39	9.8	9.4	14.7	23.8	1.0*
40	4.2	5.6	6.1	10.5	2.0*
41	4.6	4.5	6.4	11.8	3.0*
42	5.6	5.8	10.4	19.6	0.0**
43	4.8	5.7	9.9	17.3	1.0**
44	4.2	4.3	8.6	9.6	2.0**
45	4.0	5.0	7.2	10.1	3.0**
46	9.0	10.11	15.5	29.7	0.0*#
47	9.0	11.0	15.1	28.5	1.0*#
48	8.0	10.12	13.0	12.5	2.0*#
49	8.5	12.0	13.3	13.4	3.5*#
50	12.0	15.0	19.0	36.2	4.5*###
51	14.0	14.2	19.7	34.1	5.0*###
52	11.0	6.05	13.8	26.3	0.0***#
53	10.1	7.0	12.6	27.5	1.0***#
54	7.0	5.5	10.1	15.2	2.0***#

* Catalyst I
 ** Catalyst II
 # 1 % by volume of bromine
 ## 3 % by volume of bromine
 ### 5 % by volume of bromine

TABLE VI
(Continued)

Test No	Time of Test hr	O-xylene Vaporized Grams (Total)	Apparent Catalyst Temp °C	Air Flow Rate at S C l/hr	Molar Air/Xylene Ratio	Space Velocity l/hr/l
55	1.33	2.965	320	203	383	1350
56	1.0	4.065	490	283	309	1890
57	1.0	3.976	490	226	251	1500
58	1.0	4.251	400	264	277	1760
59	1.0	4.373	520	283	290	1890
60	1.0	3.968	400	261	294	1740
61	1.0	3.877	520	254	293	1690
62	1.0	4.046	400	305	337	2030
63	1.0	4.581	520	314	307	2100
64	1.0	4.366	400	274	280	1825
65	1.0	4.207	520	294	312	1960
66	1.0	3.991	400	270	303	1800
67	1.0	4.005	520	252	281	1680
68	1.0	4.131	400	313	339	2080
69	1.0	3.967	520	298	336	1985

TABLE VI
(Continued)

Test No	Percentage Yields				Total hr Catalyst Previously Used
	Maleic Anhydride	O-Toluic Aldehyde	Carbon Dioxide	Phthalic Anhydride	
55	13.1	7.6	14.6	24.3	0.00***##
56	14.0	8.5	16.05	32.6	1.33***##
57	13.5	9.0	18.8	31.8	2.33***##
58	9.5	10.2	13.95	23.2	0.00*#
59	9.6	11.1	15.1	25.3	1.00*#
60	9.2	12.1	16.7	23.8	2.00*##
61	10.1	13.5	15.55	24.2	3.00*##
62	13.5	12.5	21.3	27.1	4.00*###
63	12.0	14.2	19.5	25.7	5.00*###
64	10.0	9.1	12.5	24.3	0.00***#
65	8.5	8.9	12.95	23.1	1.00***#
66	7.9	10.5	11.2	23.2	2.00***##
67	9.7	8.7	14.5	25.3	3.00***##
68	13.0	9.3	15.6	26.5	4.00***###
69	14.1	12.1	20.15	27.3	5.0***###

* Catalyst I
 ** Catalyst II
 # 1 % by volume of bromine
 ## 3 % by volume of bromine
 ### 5 % by volume of bromine

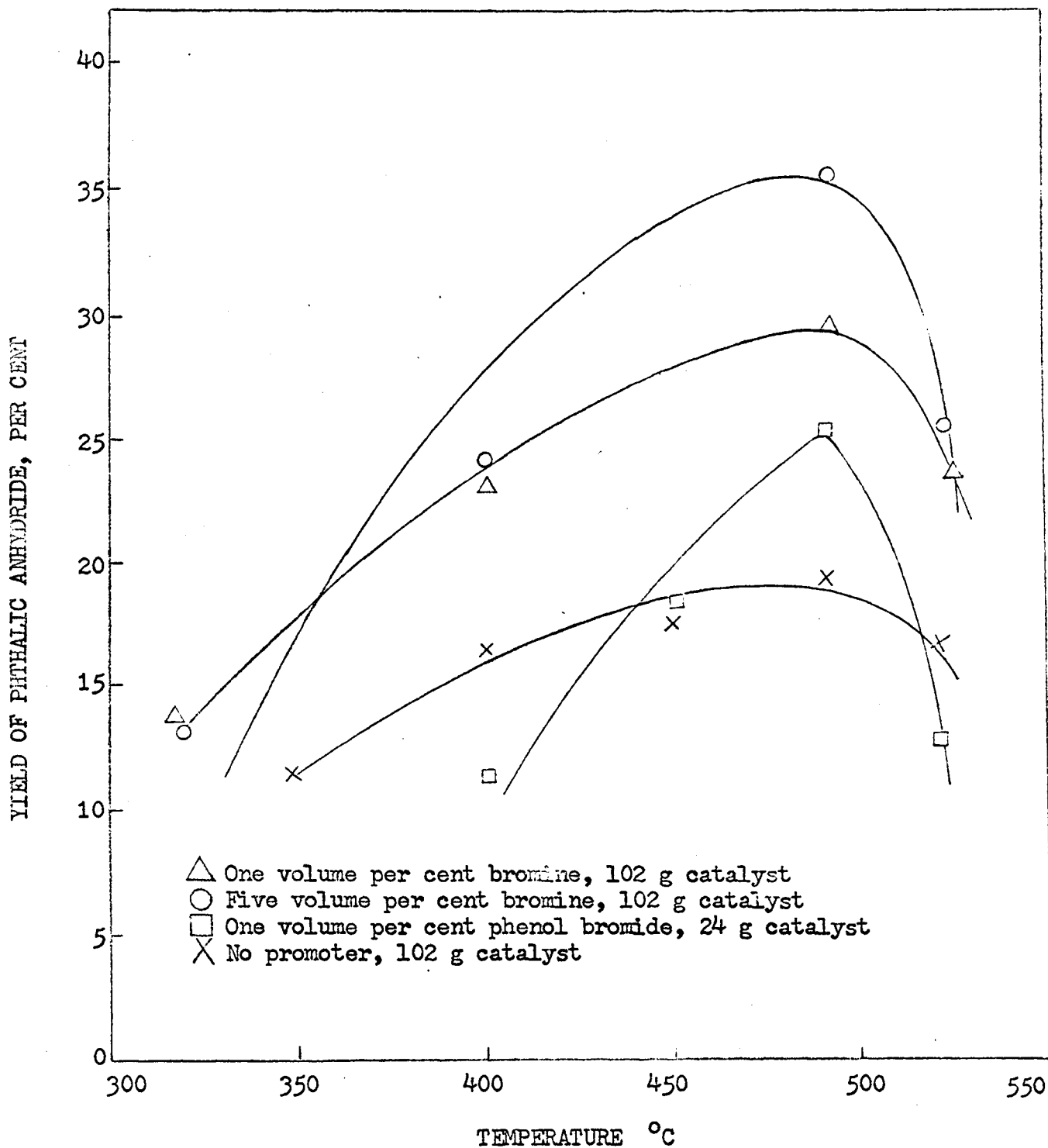


FIGURE 6 EFFECT OF TEMPERATURE ON YIELD USING BROMINE AND PHENOL BROMIDE PROMOTERS AND CATALYST I

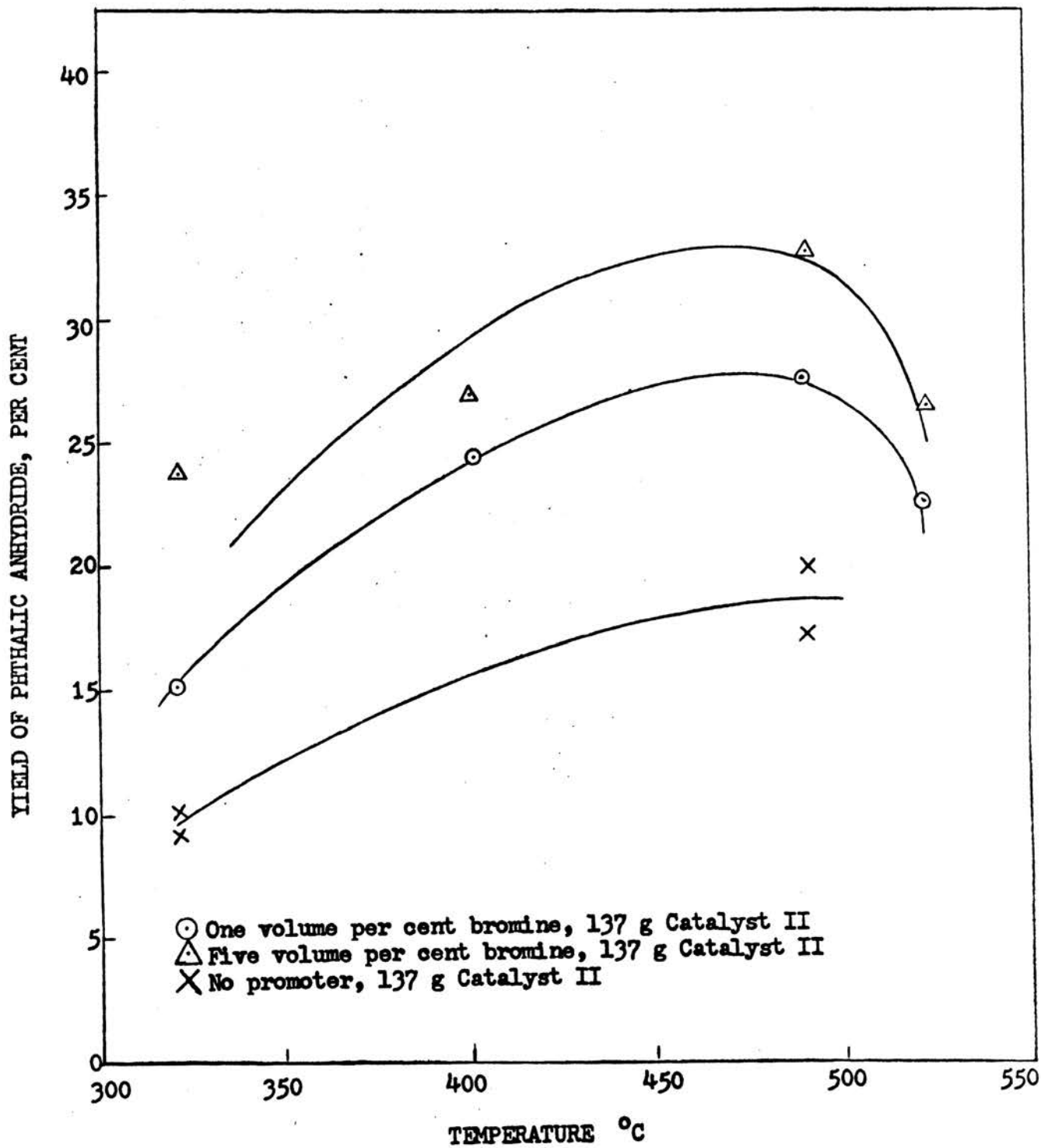


FIGURE 7 EFFECT OF LIQUID BROMINE AS A PROMOTER WITH CATALYST II AT VARIOUS TEMPERATURES

IV. DISCUSSION

THE RESULTS

Ideally it would be desirable to obtain a one hundred per cent yield of phthalic anhydride by the oxidation of o-xylene in a fluidized bed reactor. Yields of phthalic anhydride ranged from 5.2 per cent to 36.2 per cent. The highest yield of this desired product was obtained at 490°C apparent catalyst temperature and using five per cent liquid bromine dissolved in the o-xylene as a promoter.

Yields of phthalic anhydride were greater in almost all tests when using bromine or an organic bromide as a promoter. The results obtained with Catalyst I and II were not significantly different when the tests were made under like conditions either with or without a promoter.

Yields of 67.8 per cent phthalic anhydride have been reported by Bhattacharyya and Krishnamurthy (1) using fused vanadium pentoxide catalyst in a fluidized bed reactor. Helmut Nonnermacher and his coworkers (6) in U.S. Patent No. 3,210,378 claim to have obtained a 63.3 per cent yield of phthalic anhydride when using o-xylyl bromide as a promoter with a fluidized vanadium pentoxide-molybdenum oxide catalyst. They state that a temperature of only 320°C was required.

Although an increase in yield of phthalic anhydride has been obtained in this work over that obtained by Wang (12), it has not been possible to obtain the yields reported by the investigators mentioned above.

Concerning the effect of promoters, three kinds of promoters have been used. When o-phenol bromide ($\text{BrC}_6\text{H}_4\text{OH}$, Boiling point 194°C) was used as a promoter in Tests No. 25 through No. 28 at four different temperatures, it was found that yields of phthalic anhydride were greater in all tests than without using this promoter. The use of 1-3 dibromo-propane as a promoter in Tests No. 29 through No. 37 gave a yield of phthalic anhydride that was less in almost all cases than without using this promoter, even though the boiling point of this promoter is 165°C which is pretty close to the boiling point of o-xylene (144.4°C). A possible explanation of why o-phenol bromide gave an increased yield of phthalic anhydride and 1-3 dibromo-propane did not may be that o-xylene and phenol bromide are ring structure compounds. The use of bromine as a promoter seems to show promise. It was the most effective of three substances tried. No attempt was made to determine the actual percentage of bromine in the feed mixture or whether it carried over into the reaction products.

The effect of space velocity on the yield of phthalic anhydride may be seen from a study of Table IV. The yield of phthalic anhydride increased with an increase in space velocity at various constant reaction temperatures up to a range of 9000 to 11,000 l/hr/l when the amount of catalyst used was held constant. Above or below this range of space velocities the yield decreased.

An examination of certain of the results of the tests given in Table VI also indicates an increased yield of phthalic anhydride with an increase in space velocity. A comparison may be made between Tests 50 and 51, for example. Both of these tests used

5 per cent bromine as a promoter, the same reaction temperature and approximately the same molar air/xylene ratio. Test 50 with a space velocity of 1890 gave a yield of 36.2 per cent while Test 51 with a space velocity of 1500 yielded 34.1 per cent phthalic anhydride. Similar observations may be made for Tests 44, 45, 52, 53, 56, 57, 58 and 59. Several of the tests such as 46 and 47 showed the reverse so that no firm conclusion can be made as to the affect of space velocity.

The difference in range of the space velocity values shown in Tables IV and VI may be explained by the large amount of catalyst used in the tests in Table VI.

V. CONCLUSIONS

On the basis of the findings in this study of the oxidation of o-xylene by air in the fluidized bed of V_2O_5 catalyst, the following conclusions have been drawn:

1. It has been found possible to increase the yield of phthalic anhydride to 36.2 per cent of theoretical, which is some 21 per cent over that obtained by Wang (12); but so far it has not been possible to attain the yields reported by other workers (1) (6).

2. The optimum apparent catalyst temperature (reaction temperature) for the equipment and catalysts used was found to be 490°C.

3. The molar air/xylene ratio affects the yield of product. Values between 200 and 300 generally gave the higher yields.

4. Bromine and phenol bromide when used in small percentages as promoters increased the yield of phthalic anhydride. A maximum increase of approximately 14 per cent in yield was obtained with the use of 5 per cent bromine solution in o-xylene.

V. RECOMMENDATIONS

1. Since the yields of phthalic anhydride in this investigation were all below the range of commercial interest it is suggested that in future work other types of catalyst be tried. Some other catalysts have been reported by other workers (1) (6) to give much higher yield of phthalic anhydride.
2. Further study should be made of the use of bromine, bromine compounds and possibly other promoters. Equipment should be modified in order to be able to measure the actual content of the promoters in the feed stock. Also an investigation should be conducted to determine what happens to the promoters.
3. Three suggested modifications of equipment for additional study are as follows:
 - (a) Provisions should be made to preheat the mixed gases to a higher temperature before they enter the catalyst chamber.
 - (b) The catalyst chamber of the reactor should be increased in length to permit a longer residence time. It has been reported (6) that a residence period of 13 seconds at the catalyst gave high yields with an operating temperature of 320°C.
 - (c) The use of a glass reactor in place of a steel pipe is suggested in order to be able to observe the operation of the catalyst bed.

VI. APPENDICES

APPENDIX ANomenclature

1. S.C.: It is the abbreviation for standard conditions. (0°C and 760 mm or 29.92 inch Hg).
2. Space Velocity: It is defined as liters of air at standard conditions passed per hour per liter of catalyst.
3. Molar Air/Xylene Ratio: This ratio is calculated as liters of air per liter of xylene vapor, both measured at standard conditions.
4. Air Flow Rate: It is expressed in liters per hour at standard conditions.
5. Yield Per Cent of Phthalic Anhydride: This is the per cent of the total weight of phthalic anhydride obtained to that theoretically possible.

APPENDIX B

TABLE B-1 Calibration Data for the Air Flow Meter

AIR FLOW RATE (Wet test gas meter)		FLOW METER READING		DIFFERENCE
cu ft/hr	liter/hr	Observed cu ft/hr	Calculated liter/hr	
0.0	0.0	0.0	0.0	0.0
1.54	43.5	0.75	47.07	3.57
2.10	59.5	1.50	61.57	2.07
3.60	101.1	3.00	89.96	-11.04
4.30	122.0	4.70	121.67	-0.33
5.43	153.5	6.80	161.2	7.67
8.20	232.0	10.30	229.36	-2.64
9.70	274.5	12.50	280.93	-6.43
12.50	354.0	15.00	344.39	-9.61
14.60	414.0	17.50	417.84	3.84

The standard deviation is 9.24

The average per cent error is 7.71

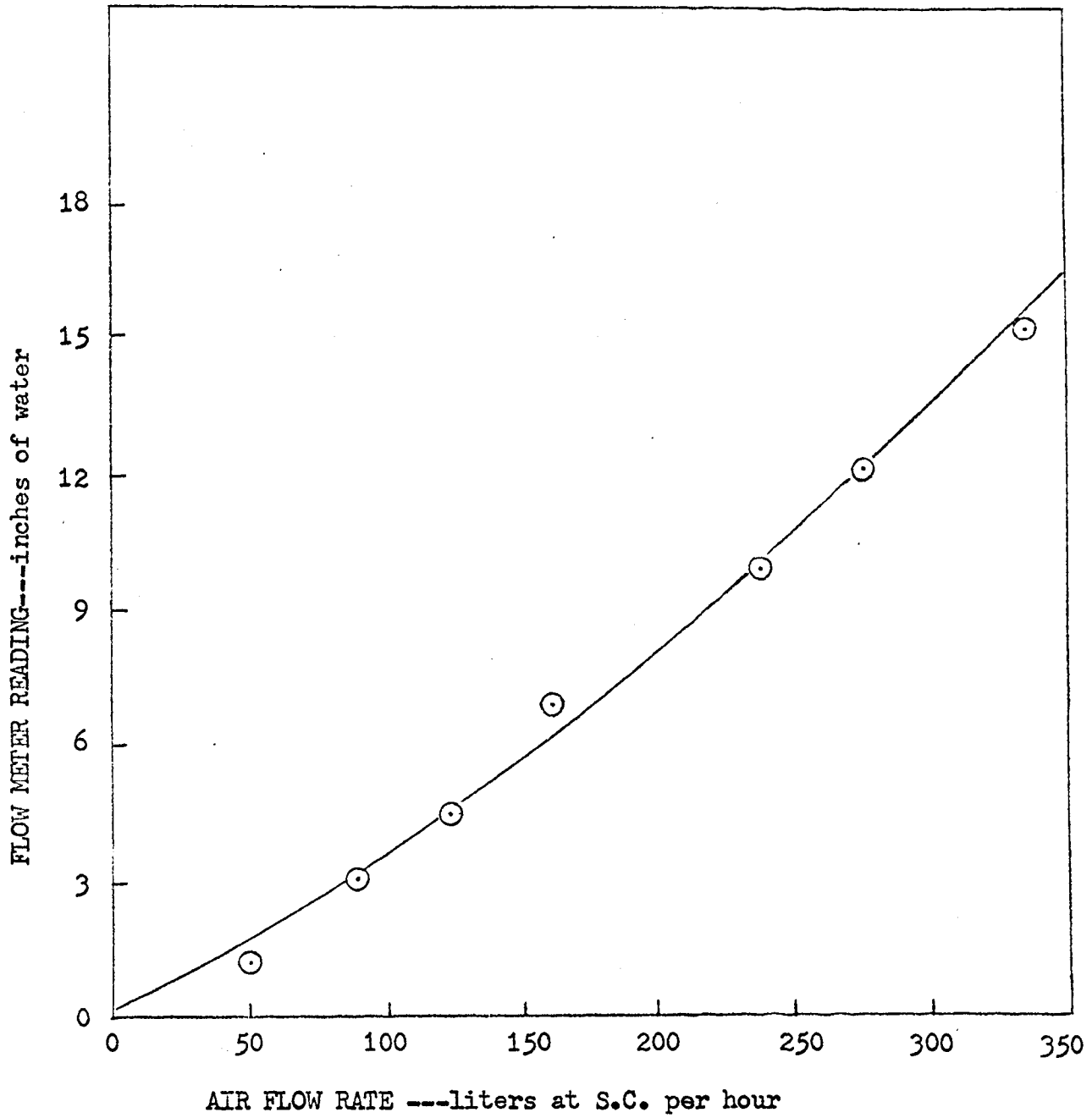


FIGURE B-1

AIR FLOW METER CALIBRATION CURVE

APPENDIX C

TABLE C-1 Data for Fluidization of Catalyst

Catalyst I 24 g Catalyst		Catalyst II 27 g Catalyst		Catalyst I 102 g Catalyst		Catalyst II 137 g Catalyst	
Air Flow Rate l/hr	Pressure Gradient inch H ₂ O	Air Flow Rate l/hr	Pressure Gradient inch H ₂ O	Air Flow Rate l/hr	Pressure Gradient inch H ₂ O	Air Flow Rate l/hr	Pressure Gradient inch H ₂ O
30.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0
60.1	0.5	50.0	0.2	50.0	5.0	50.0	1.3
90.2	0.6	70.6	0.3	92.0	6.6	92.0	2.3
127.0	0.8	92.0	0.5	127.0	8.1	127.0	3.1
177.0	1.0	112.0	0.5	163.0	11.4	163.0	3.8
268.0	1.0	127.0	0.5	198.0	12.7	198.0	4.5
347.0	1.0	145.0	-	219.0	14.0	219.0	4.8
430.0	1.0			240.0	14.8	240.0	5.1
				254.0	14.5	268.0	5.1
				268.0	15.0	290.0	5.1
				290.0	15.0	319.0	5.1
				319.0	15.0		

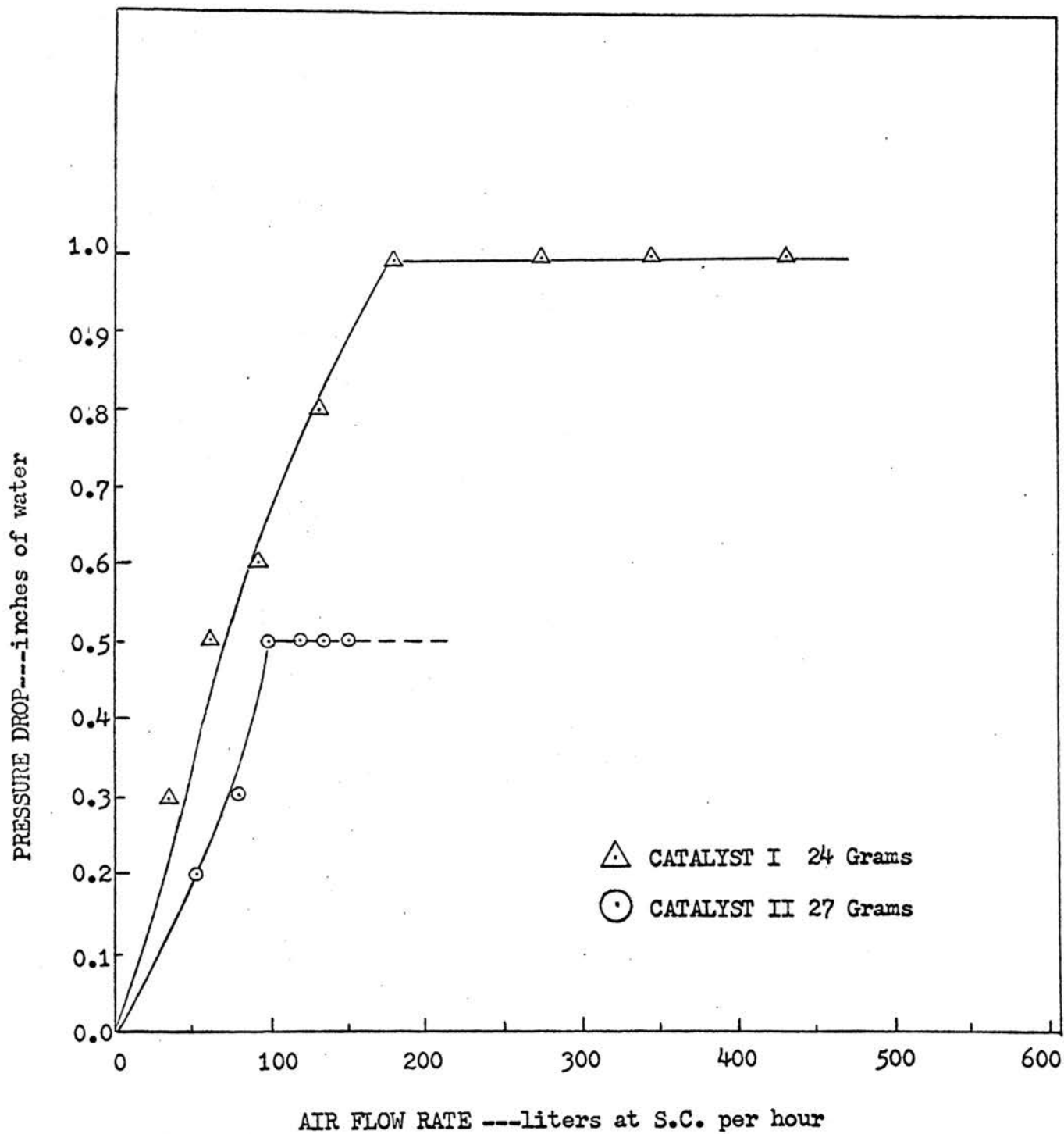


FIGURE C-1 PRESSURE DROP THROUGH CATALYST BED

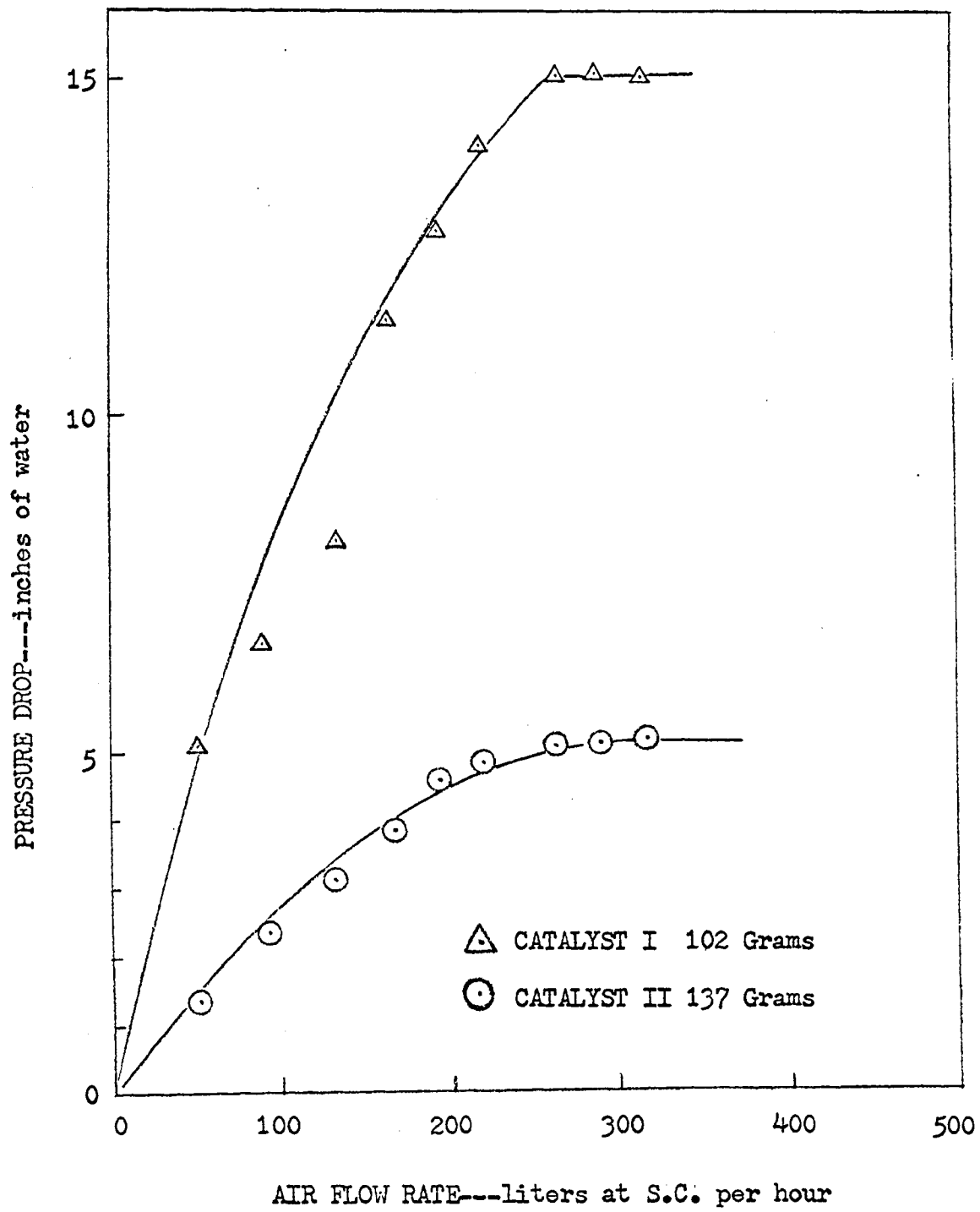


FIGURE C-2 PRESSURE DROP THROUGH CATALYST BED

APPENDIX D

Sample Calculations

Test No. 1 was taken as the example to show how to calculate the molar air/xylene ratio and the space velocity in liters of air/hr/liter of catalyst at standard conditions.

Data Sheet

Volume of Catalyst	30	ml
Catalyst temperature	490	°C
Air flow rate at room temperature	266	l/hr
Room temperature	25	°C
O-xylene charged	20	ml
Specific gravity of o-xylene	0.88	
Time of test	1	hr
Volume of NaOH Consumed for total acid	9.45	ml
KMnO ₄ consumed	18.87	ml
NaHSO ₃ added	30.0	ml
Normality of NaOH	0.91	N
NaOH consumed for back titration	3.15	ml
Normality of KMnO ₄	0.192	N
Normality of NaHSO ₃	0.15	N
Volume of saturated Ca(OH) ₂ used	1380	ml

CalculationAir Flow Rate Calculated at Standard Conditions

$$(266)(273/298)(755/760) = 244 \text{ l/hr}$$

Molar Air/O-xylene Ratio

$$\frac{(244)(106)}{(22.4)(2.11)} = 547$$

Space Velocity

$$244\left(\frac{1000}{30}\right) = 8130$$

Weight of Products :Phthalic Anhydride

$$\left[(9.45)(0.91) - (18.87)(0.192) \right] \left(\frac{148}{2000} \right) = 0.368 \text{ gm}$$

Where 148 is the molecular weight of Phthalic Anhydride

Yield Phthalic Anhydride Per Cent of Theoretical. Ideally,

2.11 gm of O-xylene can produce:

$$(2.11/106)(148) = 2.941 \text{ gm}$$

Actual weight of Phthalic Anhydride obtained was 0.368 gm

Yield % of Phthalic Anhydride:

$$(0.368/2.911)(100) = 12.5 \%$$

Maleic Anhydride

$$(18.87)(0.192)\left(\frac{98}{2000}\right) = 0.178 \text{ gm}$$

$$\% = \left(\frac{0.178}{98}\right)/(2.11/106)(100) = 9.1$$

O-Toluic Aldehyde

$$= [(30)(0.15) - (3.15)(0.91)](120/1000) = 0.196 \text{ gm}$$

$$\% = (0.196/120)/(2.11/106)(100) = 8.2$$

Carbon Dioxide

Solubility of $\text{Ca}(\text{OH})_2$ in H_2O at 25°C :

0.159 gm/100 ml

$$\text{CaCO}_3 = 1380(0.00159)\left(\frac{100}{74}\right) = 2.97 \text{ gm}$$

$$\text{CO}_2 = (2.97)(44/100) = 1.307 \text{ gm}$$

$$\% \text{ CO}_2 = (1.307)/(2.11)(8)(44)/106 = 18.65 \%$$

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X VITA

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He entered the University of Missouri at Rolla in September 1964 as a graduate student in the Department of Chemical Engineering.