OPTIMUM TECHNIQUES APPLIED TO CATALYTIC OXIDATION OF NAPHTHALENE

by

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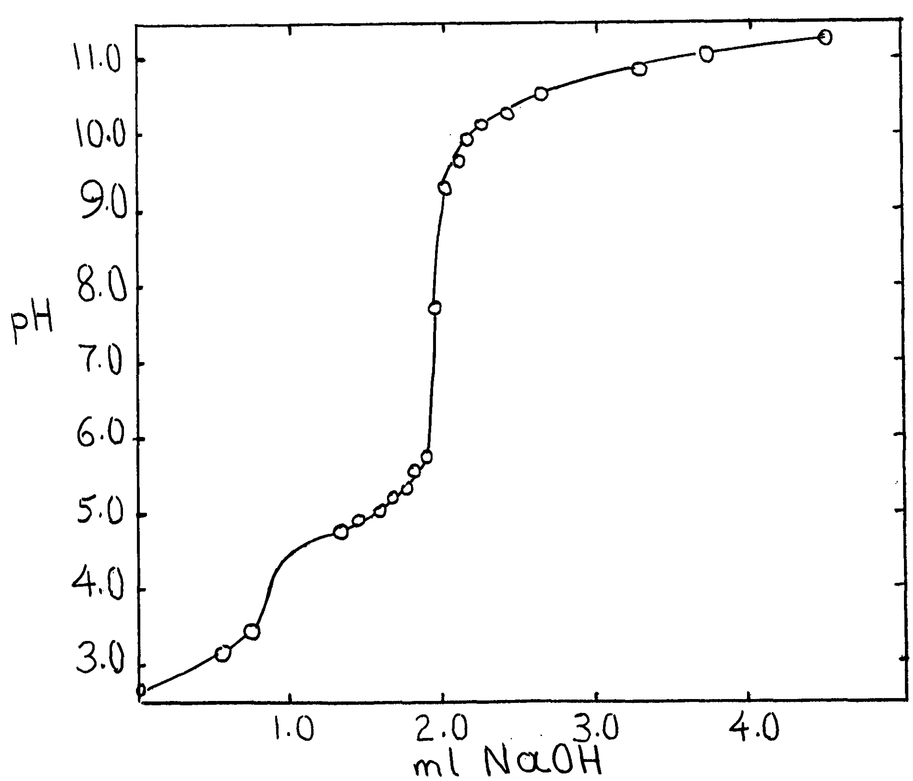
ABSTRACT

The object of this investigation was to apply optimization techniques to determine the performances of deposited barium chromate and peroxide prepared vanadium pentoxide catalysts. These were compared to commercial vanadium pentoxide catalyst on vapor-phase oxidation of naphthalene in a fixed-bed laboratory scale flow equipment. In the commercial 8 to 14 mesh vanadium pentoxide catalyst, contour tangent elimination methods were used in the determination of the optimum region of phthalic anhydride yields the dependent variable taken as the basis of comparison. For the placement of the first two experiments the unidimensional minimax techniques were used to determine the values of the two independent variables: flow rate and reaction temperature. The maximum phthalic anhydride yield was found to be 89.5 w. % at an average temperature of 863°F and 0.0210 ft^3/min flow rate on 30 ml of 8 to 14 mesh commercial vanadium pentoxide catalyst.

The deposited barium chromate and peroxide prepared vanadium pentoxide catalysts, in the range of 650-1100°F and 0.0175-0.050 ft^3/min flow rates used, were found to be complete combustion catalysts for vapor-phase oxidation of naphthalene.

ERRATA

Phthalic anhydride yield values presented in this thesis should be divided by a factor of two since pH end points showed that phthalic acid has two equivalents being titrated to the phenolphthalein end point. A pH vs. ml NaOH (0.400 N) plot, obtained by titrating 0.065 gm phthalic anhydride in water, is presented below:



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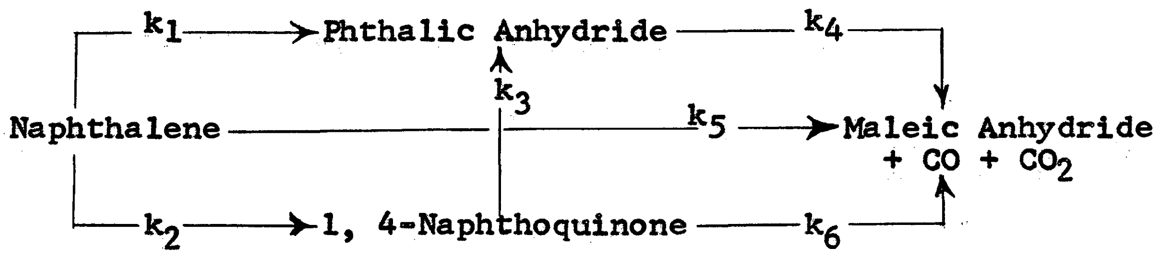
INTRODUCTION

The catalytic vapor phase oxidation of naphthalene for the production of phthalic anhydride has been known since 1917. Numerous experiments have been carried out during the past 40 years, and a large number of these experiments were concerned with the catalytic properties of various preparations and with the determination of conditions for producing phthalic anhydride. Nowadays tens of millions of pounds of highly refined phthalic anhydride per year is produced in numerous commercial plants by the oxidation of naphthalene in the vapor phase over a contact catalyst.

Kinetics

Most workers who have studied the catalytic oxidation of naphthalene agree that the principal reaction to be considered are those indicated below (2, 3)



Reactions k_1 and k_2 are the most important reactions involved in the oxidation of naphthalene. Their rates are approximately equal and considerably greater than that of reaction k_5 (1, 2, 3, 7, 8). Of the 1, 4-naphthoquinone initially formed, a large fraction is oxidized further to phthalic anhydride and some to maleic anhydride, CO and CO_2. A portion of the phthalic anhydride formed by reactions k_1 and k_3 is subsequently oxidized according to reaction k_4. A summary of the kinetics of the major reactions in naphthalene oxidation is presented in Table I. The catalysts used for the development of this kinetic scheme were more or less similar in composition -- namely, V_2O_5 and $K_2S_2O_7$, or K_2SO_4 supported on SiO_2.

Based on the foregoing analysis, one may simplify the kinetic scheme originally advanced to that shown below (1, 2, 8):

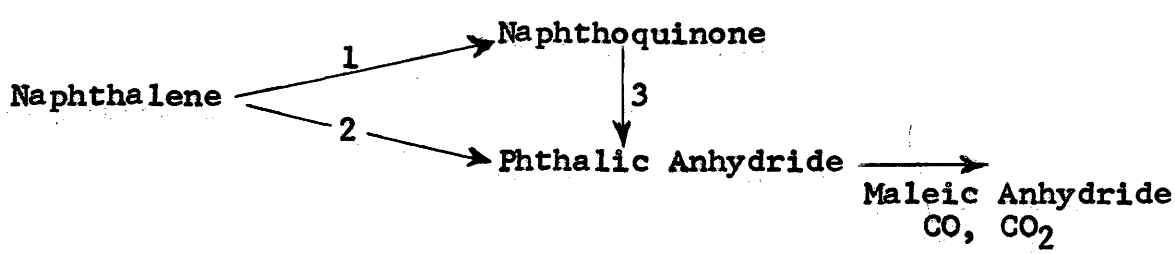


TABLE I. Major Reactions in the Catalytic Oxidation of Naphthalene (2).

Reaction		Kinetic Order Organic	Kinetic Order O_2	Relative Rate
Naphthalene	Naphthoquinone (k_1)	0.5-1.0	1.0	Important k_1 k_2
Naphthalene	Phthalic Anhydride (k_2)	0.5-1.0	1.0	Important
Naphthoquinone	Phthalic Anhydride (k_3)	1.0	---	Important
Phthalic Anhydride	MAA, CO, CO_2 (k_4)	1.0 (or less)	0.8	Important (k_4 k_1, k_2 & k_3)
Naphthalene	MAA, CO, CO_2 (k_5)	---	---	Small
Naphthoquinone	MAA, CO, CO_2 (k_6)	---	---	Small

On assuming that each of the reactions involved is first order with respect to both the organic reactant and the oxygen concentrations, the following kinetic equations are obtained (2):

$$- \frac{d}{dt} (\rho C_W) = (k_1+k_2)\rho^2 \; C_W \; C_{O_2}$$

$$- \frac{d}{dt} (\rho C_Q) = - k_1\rho^2 C_W \; CO_2 \; + k_3\rho^2 \; C_Q C_{O_2}$$

$$- \frac{d}{dt} (\rho C_P) = - k_2 \rho^2 C_W \; CO_2 \; - k_3 \rho^2 \; C_Q CO_2 \; + k_4\rho^2 C_\rho C_{O_2}$$

where C_W = naphthalene concentration

C_Q = naphthaquinone concentration

C = phthalic anhydride concentration

this scheme is probably quite good for relatively low naphthalene feed concentrations, but not at all valid for naphthalene concentrations much greater than 1 mole % (1, 2, 8).

Naphthalene to phthalic anhydride

The manufacture of phthalic anhydride from naphthalene can be accomplished by a number of different process variations (9), which basically divide themselves into fixed-bed and fluid-bed operations. Fixed-bed reactors have certain unavoidable deficiencies. Tube diameters must be kept small in order to avoid excessive radial temperature gradients, and the charging of the catalyst can be an exacting and tedious task. Feed concentrations of naphthalene in air must normally be maintained below about 1 mole % in order to avoid an excessively high temperature leading to low yields of phthalic anhydride and excessively rapid catalyst deterioration.

The advent of the fluidized bed technique for carrying out catalytic reactions has offered a solution to several of these problems, but has raised others peculiar to fluidized bed processing. Catalyst charging problems are eliminated; temperatures within the bed are very uniform; and heat-transfer coefficients are such as to permit efficient recovery of the heat of reaction. However, problems associated with the scale-up of the fluid process are much greater than with fixed beds. These problems arise largely from the fact that the gases flowing through a fluid bed do not proceed in plug flow from the inlet to the outlet, but rather undergo varying degrees of backmixing and/or bypassing. As a result, the gases leaving the fluid bed have a broad distribution of residence times rather than a single residence time. A comparison of operating conditions and yields in phthalic anhydride manufacture from naphthalene by different processes is summarized in Table II (9):

TABLE II. Phthalic Anhydride Production-Operating Conditions and Yields*.

Reactor	Fixed Bed Conventional	Fixed Bed German
Catalyst	V_2O_5 on inert support (alkali-free)	V_2O_5/SiO_2 20-30% K_2SO_4
Oper. temp., °F	750-885	645-705
press., psi	25	7.5
lbs. catalysts/lb. charge/hr.	5.9	13.4
lbs. air/lb. $C_{10}H_8$	25-30	30
Yield*, crude Phthalic Anhydride	80	104

TABLE II. (continued)

Reactor	Fluidized Conventional	Fluidized German
Catalyst	V_2O_5 on inert support (alkali-free)	V_2O_5/SiO_2 20-30% K_2SO_4
Oper. temp., °F	680	700
press., psi	15	15
lbs. catalysts/lb. charge/hr.	37.5	37.5
lbs. air/lb. $C_{10}H_8$	15.0	15.0
Yield*, crude Phthalic Anhydride	80	100

*Yield expressed by industry custom, as pounds of phthalic per 100 pounds of naphthalene; the maximum possible is about 125.

Present Research

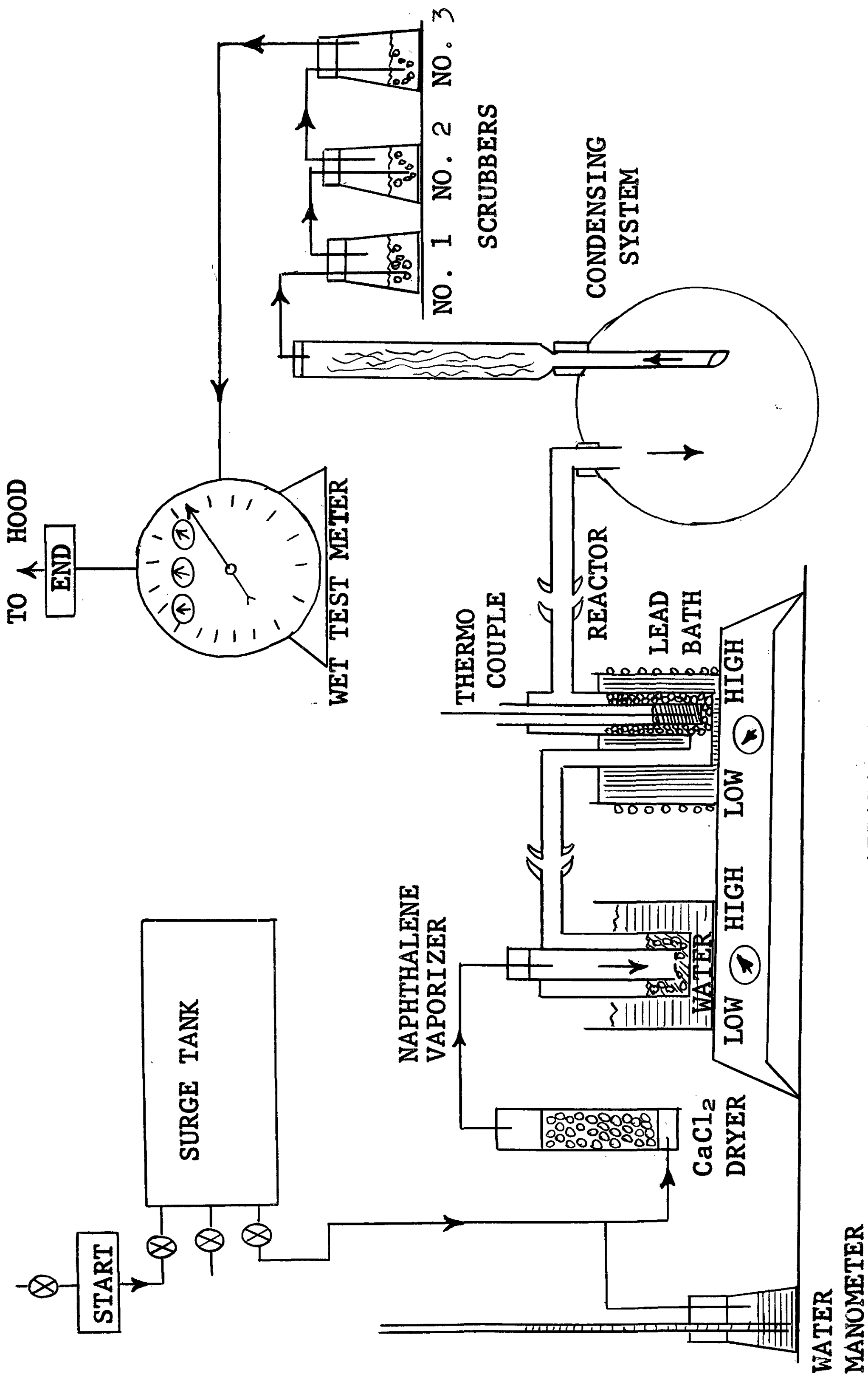
Use of optimization techniques for an engineering comparison of deposited V_2O_5 and $BaCrO_4$ catalysts on the continuous vapor-phase oxidation of naphthalene was the purpose of this research. Use of chromates, dichromates, and chromic acid as oxidizing agents is well known in the literature, and they find many applications as in the preparation of anthraquinone, benzoic acid, saccharin, etc. The high thermal stability of alkali and alkaline earth chromates is particularly interesting in the current search for oxidation catalysts to use in the vapor-phase oxidation of hydrocarbons in the temperature range of 300 to 800°C. Barium chromate was selected for use in the supported catalyst form for the oxidation of naphthalene because of the high thermal stability (1100°C) and low solubility in water (3 ppm), (4, 5). Optimization techniques were utilized to decrease the amount of data required to compare commercial V_2O_5 catalyst vs. supported $BaCrO_4$ and peroxide prepared V_2O_5 catalysts. The contour tangent elimination method (10) was used to optimize the yield of phthalic anhydride with respect to reaction temperature and flow rate (space velocity and naphthalene concentration). The evaluation of each catalyst was based on the comparison of regions determined by temperature and flow-rate combinations for optimal phthalic anhydride yields which were based on the amount naphthalene sent to the reactor. No quantitative product analysis was made for naphthalene, maleic anhydride, naphthoquinone, and CO, CO_2.

A fixed-bed plug flow glass reactor was employed in this study. The advantages of fixed-bed reactors over fluid-bed reactors for scale-up and reaction comparison purposes has been established in the foregoing discussion (2).

EXPERIMENTAL PROCEDURE AND RESULTS

Apparatus

Figure 1 is a flow diagram of the apparatus used for the catalytic vapor-phase oxidation experiments. The tap compressed air, used as process air, was passed through a 25-liter metal surge tank equipped with a purge valve and a process-air inlet valve. A surge tank was necessary in order to prevent surging due to pressure variations in compressor tank. A small bed packed with about 250 ml of anhydrous $CaCl_2$ was placed after the process-air inlet valve to remove any possible oil and water mixed with the tap-compressed air. From the dryer, the process air went to the naphthalene vaporizer, and a water manometer connected to the air stream was useful to check the system pressure and flow fluctuations. The naphthalene vaporizer consisted of 35 mm. O. D., 28 cm. high, pyrex liquid naphthalene storage tube through which process air was bubbled. The air was introduced through a 40-cm.-long 10-mm. O. D.



APPARATUS
FIG. 1

tube extending to the bottom of the naphthalene storage tube and fitted into it with a leakproof 24/40 ground-glass pyrex joint. Bubbling action was increased by adding constrictions at the bottom of this tube. The naphthalene vaporizer was immersed in a 600-ml beaker in which water was boiled to melt the naphthalene. The vaporized naphthalene and air mixture was taken out of the vaporizer through a small tube in the side of the vaporizer and connected with a leak-proof ground-glass ball joint to the reactor inlet tube.

All glass connection tubes, 12 mm. O. D. Pyrex, were wrapped with resistance wires connected in series. Heat, which was supplied by means of a variac in order to maintain the lines at 150°C, prevented plugging of the lines due to solidification. This system also worked as a preheater.

The reactor, vertically placed, was a plug-flow tubular reactor, 25 cm. high 2.5 cm. O. D., made of high-temperature Vycor glass, and equipped with a thermocouple well. It was packed with a small glass wool plug, and 30 ml. of known mesh catalyst to be used. The purpose of the glass wool was to support the catalyst bed. The reactants were fed into the reactor at the bottom; and the naphthalene, excess air and products were taken off at the top by a side glass connection, made of 12 mm. O. D. pyrex tubing and wrapped with resistance wires, series connected with the others. Clamps were used to support the ball-joint connections of the side tubes of the reactor, naphthalene vaporizer, and condenser system. A bigger screw-tightened clamp was used to secure the ground-joint fit of the reactor and thermowell. The thermowell, made of 12-mm. O. D., 32-cm.-long pyrex glass tubing, was extended to the bottom of the reactor. A Calomel-alumel calibrated thermocouple was immersed into 3 cm. high pure molten tin placed in thermowell. The purpose of tin in the thermowell was to prevent convection heat transfer around thermocouple, to secure a better connection with reactor medium, and to provide a one-measurement nominal temperature of the catalytic bed. A model 80237 Thermo Electric Co., Inc. Potentiometer Pyrometer with a range of 0-2400°F was used to measure reaction temperature. The whole reactor system was immersed into a molten lead bath up to the top of the catalyst bed to maintain reactor temperature. Lead bath temperature was regulated and the initial reaction heat was supplied by resistance wires wrapped around the bath and controlled by a variac transformer. About 200 ml. of powdered graphite was used to cover lead in order to diminish poisonous lead vapors.

The exit gases from the reactor were then trapped and solidified by a condensing and scrubbing system consisting of a 2-holed 5-liter air cooled, round-bottom flask, a 50 cm.

long 3 cm. O. D. vertically placed glass wool filled, air cooled glass tube and three 500 ml flask scrubbers. Round bottom flask holes were 29/42 Pyrex ground joints tightly fitted with reactor outlet and vertical cooling tube. Rubber hose was used to connect the scrubbers, vertical tube and wet test meter. The first scrubber was filled with 150 ml. of benzene and anthracene solution, and the next two with 100 ml. of 0.02 N NaOH. The purpose of the first scrubber was to knock out any possible product gases not solidified in the round-bottom flask and glass wool packed vertical tube; whereas the NaOH scrubbers were aimed at removing CO_2 evolved during the reaction. The scrubbed gases were then sent to a wet-test meter before they were vented in the hood. Since all reaction gases were removed and air was in a very large excess compared to naphthalene, it was assumed that the flow measured by the meter was the same as that which went into the process. The wet-test meter used was a calibrated "Precision" model of Precision Instrument Company with 0.001 ft^3 scale divisions.

<u>Materials Employed</u>

Naphthalene was chemically pure, with a melting point of $80^{\circ}C$.

Benzene was commercial grade.

Anthracene was the Coleman & Bell Co. certified chemical.

NaOH solutions were prepared from pure NaOH quantitatively with 0.02 and 0.4 normalities. 0.0154 N HCl was standardized against 0.02 N NaOH.

The catalyst A was obtained from Davison Chemical Corporation as 900-08-x1949 pelletized 3/16". This V_2O_5 catalyst was then crushed to have 8-14 mesh size.

Catalyst B was deposited $BaCrO_4$ on the Aluminum Company of America's Grade F-10, 8-14 mesh activated alumina. It was prepared by a method described in Appendix III; contained 1.75 wt. % $BaCrO_4$.

Catalyst C, supplied by the Carborundum Company, contained 3.7 wt. % $BaCrO_4$ deposited on a gamma-alumina support of AlO10NT 1/8" cylindrical pellets with 94 m^2/gm surface area.

Catalysts D and E were prepared by a method described in Appendix III. They were deposited V_2O_5 catalysts on the Aluminum Company of America's Grade F-10, 8-14 mesh activated alumina. Catalyst D contained 2.14 wt. % V_2O_5, and catalyst E 2.56 wt. % V_2O_5 (Appendix III).

<u>Analytical Methods</u>

The reaction products accumulated in the 5-liter round bottom flask, its inlet joint and glass wool filled vertical tube were washed out with saturated benzene-anthracene solution. It was assumed that all maleic anhydride would react with anthracene to form a water insoluble complex. Scrubbers 2 and 3, originally each a known volume of 0.02 N NaOH, after reaction were usually acidic. If not, they were first acidified with a known volume of 0.0154N HCl. The benzene and scrubbing solutions were combined in a 1-liter separatory funnel, shaken and the phthalic acid extracted into the aqueous phase. The aqueous layer was separated, boiled to expel CO_2, cooled then titrated with 0.4 N NaOH to the phenolphthalein end point. No analyses for unreacted naphthalene, maleic anhydride, 1-4 naphthoquinone and $CO+CO_2$ were made.

<u>Operating Procedure</u>

The operating procedure involved, in the first place, a preliminary run of passing air through the system for 1 to 2 hours at the desired operating temperature and flow rate of the run. The purpose was to permit the system temperature, particularly the catalyst and bed temperature, to attain a steady-state condition. The current to the resistance wires around the lead bath was turned on at least 30 minutes prior to the preliminary run. Twenty minutes was enough to melt all the lead in bath. During the preliminary run, the naphthalene vaporizer was cleaned with benzene and acetone after two successive runs and filled with 5 to 10 gm. of fresh unmelted naphthalene and weighed. Glass wool was placed into the vertical tube, no. 2 and no. 3 scrubbers were filled with 100 ml. 0.02 N NaOH in each, and 150 ml. of benzene-anthracene solution were put into the no. 1 scrubber. A run was then started by placing the naphthalene vaporizer and condensing apparatus into the system and applying current to the wires around connection lines. After the initial temperature was noted, current to the lead bath was turned off temporarily. Total flow, flow rate, and temperature were noted at 5- to 30-minute intervals, but kept under close control to prolong the steady-state conditions. Experience with the lead-bath variac setting was necessary to keep temperatures under close control. The time for these runs varied from 50 minutes to two hours. Flow-rate regulation by the inlet process air valve on the surge tank was satisfactory. The water monometer level was checked continuously to find out possible solid plug-up of lines. A bunsen-burner was kept ready to heat up such points if any happened to form. At the end of each run, air was passed through the reactor for at least 30 minutes before the current to the electrical heaters was turned off and the condensing system disconnected from the reactor, in order to burn any carbon deposits on catalyst particles and to remove any products accumulated in the pores of the catalyst. The naphthalene vaporizer was weighed after it cooled to room temperature, and product analysis for phthalic anhydride was made at the end of each run.

Experiments and Results

"Search by golden section" and "lattice search" techniques (11) were employed to determine optimum flow rates and temperatures of the first two runs proper, no. 5 and no. 6. Runs no. 1 - no. 4 were discarded due to the large reaction temperature fluctuations, plug-up problems in connection tubes, and unsteady flow rates.

The temperatures for runs 5 and 6 had been determined by the golden section search method to be at 750°F and 850°F (Appendix II). Optimum flow rates of these two runs were determined to be about 0.015 ft^3/min for run 5 and 0.030 ft^3/min for run 6, by the lattice search method.

Naphthalene concentration in the air flow was always kept at approximately 1 mole %. The phthalic anhydride yields based on weight of naphthalene vaporized during the run were 22.5 wt. % for run 5 and 57.0 wt. % for run 6 (Table III). Since yield increased as temperature and flow rate increased, no experiments were run in the region where the temperature was lower than 759°F and flow rate was less than 0.0159 ft^3/min. Runs 7 and 13 were made to determine the promising region of optimal phthalic anhydride yields. Run 7 gave 35.5% phthalic anhydride yield at any 930°F and 0.0224 ft^3/min flow rate whereas run 13 gave a yield of 61.3 wt % at avg. 887°F, and 0.0209 ft^3/min flow rate with a contact time of 3.04 seconds, which indicated that the yield would be smaller than 61.3% in the regions where the average reaction temperature was greater than 890°F, and the flow rates were larger than 0.0224 ft^3/min. In run 14, the temperature was decreased to avg. 863°F while the flow rate and contact time was held constant at 0.0210 ft^3/min and 3.04 sec. This run gave the overall maximum phthalic anhydride yield of 89.5 wt %. Runs 15, 16, and 17 were placed relatively close to run 14, in order to have a better definition of the promising region, and to have enough data to apply the contour tangent elimination method (10) for its determination. Run 18 was placed at avg. 860°F and 0.0215

TABLE III.

CATALYST A

Run	Av. Temp. °F	%Yield	%Max. Tamp. Dev.	Average Flow Rate ft^3/min	Contact Time sec.	Total Run Time min	Mole Ratio Naphthalene to air
5	759	27.5	1.45	0.01590	4.1	120	0.085
6	890	57.0	6.65	0.03308	1.93	90	0.0124
7	930	35.5	6.45	0.02240	2.76	90	0.0147
13	887	61.3	3.05	0.02090	3.04	60	0.0198
14	863	89.5	2.66	0.02100	3.04	50	0.0154
15	866	72.0	1.85	0.02120	3.0	75	0.0208
16	848	55.0	2.7	0.02346	2.71	60	0.0216
17	840.5	52.0	1.13	0.01750	3.64	90	0.0180
18	860	88.5	1.16	0.02150	2.96	90	0.0170

ft^3/min as a double check of the maximum 89.5 % yield of run 14. In run 18, an 88.5 % yield was obtained.

Runs 8 through 12 were discarded because, when naphthalene in a storage tube is subjected to melting, cooling, and recrystallization, it changes its structure and gives poor phthalic anhydride yields. All through runs 1 to 18, catalyst A, 8-14 mesh commercial V_2O_5 catalysts was used. By the contour tangent elimination method, the boundaries of the optimum phthalic anhydride yield region were determined as shown on fig. 2.

Runs 19 through 23 were made for evaluation of catalysts B, C, D, E. 30 ml of catalyst B, 8-14 mesh deposited $BaCrO_4$, was used for run 19. No phthalic anhydride, naphthaquinone, nor maleic anhydride was formed during the run. Some unreacted naphthalene was seen in the condensing system. The heat of reaction was high enough to maintain bed temperature at about 775°F, while the current to the lead heating media was turned off; indicating that the oxidation of naphthalene was taking place. Some NaOH additions to the scrubbing during the run were neutralized in relatively short times, showing that there was complete oxidation to CO_2. Run 20 was discarded because naphthalene had plugged up the connection tubings. In run 21, 15 ml. of catalyst C was used. The heat of reaction was enough to raise the reactor temperature from 625°F to 695°F in five minutes. The reaction had started rapidly after the bed temperature had reached 720°F, and the bed temperature then increased to 1100°F.

When temperature was lower than 700°F, the solid formation in the condensing system, qualitatively indicated by crystal structure and color, was unreacted naphthalene. At temperatures of 720°F and higher, no additional solid formation was noticed in the condensing system. The collected solids were completely soluble in benzol, showing that no phthalic anhydride, maleic anhydride, or naphthoquinone was produced. There was complete oxidation of reacted naphthalene to CO, CO_2, the rate of naphthalene conversion depending on the severity of reaction conditions.

Thirty ml of catalyst D, 8-14 mesh, V_2O_5 catalyst prepared from ammonium vandadate by hydrogen peroxide (Appendix III), was evaluated in run 22. During this run, which took 60 minutes, no solid formation was noticed in the product condensing system. Starting with an initial temperature of 760°F, the bed temperature increased to a maximum of 800°F after ten minutes, while the current to the outside heating media was turned off. The temperature was decreased gradually to 660°F, at which point the lead bath started to solidify. It was established by neutralization of additional

NaOH placed in the scrubbers that there was 100% conversion of 5.4 gm. naphthalene evaporated during the run, to complete oxidation products of CO_2 and possible CO, all through the temperature and flow rate combinations of 800 to 660°F, and 0.0182 to 0.0292 ft^3/min.

Run 23 was used for the comparative evaluation of 30 ml. of 8 to 14 mesh catalyst E (Appendix III). The bed temperature had increased from 738°F initial to 800°F in 5 minutes. During the run time of 60 minutes, the bed temperature was gradually decreased to 700°F, while the flow rate was increased from 0.0260 ft^3/min to 0.0391 ft^3/min, and 5.0 gm. of naphthalene was sent to reactor. No solid formation was observed in the condensing system throughout this run. There was 100% conversion of naphthalene to its complete oxidation products of CO_2 and possible CO, as CO_2 formation was established by the neutralization of NaOH added to the scrubbers during the run.

No optimization techniques were used for the evaluation of oxidation of naphthalene in runs 19 through 23, because of no visible amounts of phthalic anhydride, naphthoquinone or maleic anhydride formations in solid condensing systems at any temperature -- flow rate combinations used in these runs.

INTERPRETATION OF RESULTS

The tests described in the preceding chapter may be divided into two groups: (1) the group upon which the deductions about catalyst A performance on the oxidation of naphthalene as to the optimum yields of phthalic anhydride are based, and (2) the group from which limited information has been obtained relative to the performance of catalysts B, C, D, E on complete oxidation of naphthalene to CO, CO_2. This group is not strictly within the scope of the present work. Thus, group (1) would comprise most tests dealing with:

(a) Utilization of optimum techniques in order to determine optimum flow and temperature conditions for optimum phthalic anhydride yields.

(b) Comparison of optimum operating conditions with literature values.

All the remaining tests are included in the second group and are discussed later. It should be pointed out, at the outset, that no significant errors in data presented are apparent from Table III and Fig. 2.

Utilization of Optimum Techniques

Search problems can be classified according to their number of independent variables, to whether or not experimental error is present, and to whether the system is unimodal. In this problem are two independent variables: reaction temperatures and system flow rate. The phthalic anhydride yield, as calculated directly on the amount of naphthalene sent to the reactor, is the dependent variable. The assumptions made are that the data are error-free and that the function is unimodal. The unimodality assumption holds in a large number of practical search problems. A unimodal function does not have to be smooth, or continuous; it can be broken, discontinuous, and even undefined in certain intervals (10). Unimodality means that, if two experiments are run on the same side of the optimum point, then the one nearer the optimum gives a higher value of dependent variable, i.e., the phthalic anhydride yield.

In this search we were not particularly interested in finding out all there is to know about the oxidation of naphthalene. We merely wished to determine what settings of the independent variables would yield the maximum value of phthalic anhydride yield taken as a criterion of effectiveness. From another point of view, the problem was to reach a specified minimum acceptable level of performance in as few trials as possible. Thus, each experiment had two purposes, not only to attain a good value of the criterion, but also to give information useful for locating future experiments where desirable values of the criterion are likely to be found.

Contour tangent elimination methods, which use contour tangents determined by successive local explorations of strongly unimodal response surfaces to eliminate parts of the experimental region from all further consideration, are convenient to be used on strongly unimodal functions. The contour tangent computations are straightforward for three dimensional response surfaces.

The foregoing assumptions and theory did not contradict the outcome of the experimentation. The contour tangent elimination method has worked successfully in the determination of the optimal phthalic anhydride yield regions. The effectiveness of the method is indicated by the size of uncertainty remaining in the area. Eight sequential experiments reduced the size of this area from 252 unit^2 to 8 unit^2 (Fig. 2). The response surface was strongly unimodal. Although no contours were attempted to be drawn on fig. 2, the final region of uncertainty showed that the maximum lies in the middle of this region; the almost equidistant boundaries of the region around the maximum yield had yields 22 to 45% lower than the maximum. Although the placing of the first two experiments were according to the unidimensional minimax techniques (golden search on temperature and lattice search on flow rates), the remaining runs were all placed randomly from three-dimensional, two-variable search strategies. The randomness of the sequential experiments did not decrease the effect of the contour tangent elimination method, only because each experiment was sequentially placed to reach the maximum in as few trials as possible.

Optimum Operating Conditions

The equipment and the process used in this research can be compared with the commercial fixed-bed conventional process shown in Table II, gives the operating conditions of the process mentioned as 80% crude phthalic anhydride yield at 25 psi pressure and the temperature range of 750 to 885^{o}F on a V_2O_5 on inert support (alkali-free) catalyst. In this research, a maximum yield of 89.5% phthalic anhydride was obtained at an average reaction temperature of 863^{o}F and a contact time of 3.04 sec. (Table III). The pressure on the system had about 3 in of water. The mole ratio of naphthalene to air was 1.54%, which was analogous to the naphthalene concentration employed in industrial fixed-bed processes. The operating conditions do not contradict each other, as 25 psi pressure applied in commercial systems would bring the reaction conditions to the same level obtained in this research, although the optimum temperature range is lower in the former.

Runs 14 and 15, having almost equal flow rates of 0.0210 ft^3/min and 0.0212 ft^3/min respectively with contact times of 3.04 sec and 2.96 sec had largely different phthalic anhydride yields, 89.5% and 72.0%. Although there are 3°F difference between their reaction temperatures, the drop in yield was probably due to the fact that the molar ratio of naphthalene in run 15 was 2.08% whereas in 14 it was 1.54% which was approximately the optimum naphthalene concentration in commercial operations (2). Within the optimum region, correlations of yield with average temperature, contact time or naphthalene concentration were not attempted.

Contact times, calculated in Appendix I and presented in Table III, are not true contact times since they were not calculated at reactor temperature and pressure, but at S.T.P. Thus, contact times presented were a linear function of flow rate as catalyst volume was kept constant at 30-ml.

Feed naphthalene concentration to air was a function of amount of naphthalene in the vaporizer and flow rate; and was held approximately constant at 1.5±0.6 mole % all through the experiments.

The optimum contact time of 3.04 sec obtained in this research corresponds to 1.2 sec as true contact time calculated at 863°F average reactor temperature. The contact times in commercial processes working at optimum conditions are lower than 1.2 sec (3). Contact time and flow rate being inversely proportional to each other, lower contact times render high flow rates increasing the economic feasibility of the process, if the amount of catalyst charged is constant. It would probably be possible to make an optimization study by changing the volume of catalyst charged to the reactor as an independent variable. This was considered to be a separate research in itself and was out of the present study of the catalyst comparison.

Performances of Catalysts B, C, D, E

No success was obtained in producing phthalic anhydride by vapor-phase oxidation of naphthalene on catalysts B, C, D, E. On catalysts B and C, the only solid product collected in the condensing system was unreacted naphthalene which decreased in amount with increasing severity of reaction conditions. The balance of reaction products were gaseous (CO, CO_2). Catalysts D and E gave complete oxidation products of CO_2 and CO in the possible temperature and flow rate ranges. As a result it can be said that deposited barium chromate catalysts B and C and peroxide-prepared vanadium pentoxide catalysts D and E were more active in the oxidation of naphthalene than commercial vanadium pentoxide. Catalysts D and E were more active than catalysts B and C if the activity of a catalyst is considered to be its complete or destructive oxidation power rather than its selectivity. It would be possible to make a study of adding inhibitors, promoters, and poisons to these catalysts to change their effectivity in favor of oxidation to phthalic anhydride. However, no such study was attempted since it was considered to be outside the scope of the present research. The activity of the supported barium chromate catalyst is undoubtedly associated with the formation of small amounts of lower valent states of chromium resulting in lattice defects (5), which are very mobile, particularly once catalytic temperatures are reached. The same is valid for vanadium pentoxide catalyst which was observed to have a mixture of valance states in the active catalyst which results in the lattice defects necessary for catalytic activities (3, 5, 6). It is probably the nature of these lattice defects, which were characteristics of barium chromate crystals and which were different in peroxide prepared vanadium peroxide (catalyst D and E) than in commercial grade catalyst A, that caused the complete oxidation of naphthalene. One may speculate that the products of oxidation depended on the point of attack on the ring which were determined by lattice defects of catalyst crystals; an attack on an α-carbon may lead to mapthaquinone, and a β-carbon to phthalic anhydride and on a bridge carbon to complete combustion (3).

As a result, the catalytic oxidation of naphthalene on catalysts B, C, D, and E were in complete disagreement with the kinetic scheme presented in the Introduction, because the only reaction that took place during the oxidation was the least probable, the complete combustion to CO and CO_2.

CONCLUSIONS

An attempt made to use deposited barium chromate and peroxide-prepared vanadium pentoxide as contact catalysts for vapor-phase oxidation of naphthalene showed that the kinetic scheme of oxidation reactions found in the literature was apparently not valid for catalysts in which the lattice defects were different from those of the classical commercial vanadium pentoxide catalysts, although they showed excellent oxidizing properties.

An investigation concerning the feasibility of using these catalysts for low-temperature combustion of hydrocarbon and CO to CO_2, for example in automobile exhausts, should be made; and the thermal stability of peroxide-prepared vanadium pentoxide catalysts should be determined.

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APPENDIX I

<u>Run No. 5</u>

Initial temperature = 750°F

Naphthalene + Vaporizer (initial) = 190.0 gm

50 ml 0.02 N NaOH each in scrubbers 2 and 3.

Time (min)	Temp. (°F)	(ft^3)	(ft^3)	(min)	V= ft^3/min
0	750	0	0	0	0
5	755	0.0775	0.0775	5	0.0155
10	768	0.1565	0.0790	5	0.0158
15	762	0.2328	0.0763	5	0.01526
20	755	0.3070	0.0742	5	0.01481
30	752	0.4700	0.1630	10	0.01630
35	750	0.5475	0.0775	5	0.01550
40	750	0.6285	0.0810	5	0.01602
45	755	0.7145	0.0860	5	0.01702
50	760	0.7985	0.0840	5	0.01680
55	765	0.8770	0.0785	5	0.01570
60	762	0.9620	0.0850	5	0.01700
70	760	1.0290	0.1670	10	0.01670
80	770	1.2835	0.1545	10	0.01537
90	760	1.4372	0.1537	10	0.01539
100	752	1.5955	0.1583	10	0.01583
110	755	1.7527	0.1572	10	0.01572
120	770	1.9185	0.1658	10	0.01658

Naphthalene flow was cut.

180 stop air flow.

Napthalene + Vaporizer = 188.1 gm.

Amount naphthalene evaporated = 190.0 - 188.1 = 1.9 gm.

$$\frac{\text{Naphth.}}{\text{air}} = \frac{1.9 \text{ gm.}}{1.9185 \text{ ft}^3 \text{ air}} = 0.9 \text{ gm.} \frac{\text{gm. naphthalene}}{\text{ft}^3 \text{ air}}$$

$$\frac{\text{Naphth.}}{\text{Oxygen}} = \frac{1.9}{(1.9185)(0.21)} = 4.74 \frac{\text{gm. naphth}}{\text{ft}^3 \text{ oxygen}}$$

Mole ratio naphth. to air $= \frac{(1.9)(22.4)}{(1.9185)(28.32)(128.16)}$

$$\times \frac{760}{620} \times \frac{535}{492} = 0.0085$$

$$v\ (ft^3/min) = \frac{1.9185}{120} = 0.0159\ ft^3/min\ avg.$$

Contact time $= \frac{(0.03)(60)}{(0.0159)(28.32)} = 4.1$ sec.

Analysis:

Initial NaOH = 0.02 N (100+13) = 113 ml.

NaOH burette

13.7 - 50 = 36.30

41.0 - 15.2 = $\frac{25.8}{62.1}$ 0.02 N

Contact time $= \frac{(0.03)(60)}{(0.0159)(28.32)} = 4.1$ sec.

Analysis:

Initial NaOH = 0.02 N (100 + 13) = 113 ml.

NaOH burette

13.7 - 50 = 36.30

41.0 - 15.2 = $\frac{25.8}{62.1}$ 0.02 N

Total NaOH = 113 + 62.1 = 175.1 ml. 0.02 N

gm - moles phthalic anhydride $= \frac{(175.1)(0.02)}{1000} = \frac{3.502}{1000}$

wt. phthalic anhydride $\frac{(3.502)(148.11)}{1000} = \frac{521}{1000}$

% yield $= \frac{521}{1.9} \times \frac{100}{1000} = 27.5\%$

No visible amount of naphthoquinone had been formed. Carry the next run at 850°F and larger flow rate. If yield percentage decreases, decrease the temperature to less than 750°F for the following run.

Run No. 6

Initial Temperature = 850°F

Naphthalene + Vaporizer (initial) = 188.1 gm.

50 ml. of 0.02 N NaOH each in scrubbers 2 and 3.

Time (min.)	Temp. (°F)	(ft^3)	(ft^3)	(min)	v= ft^3/min
0	850	0	0	0	0
5	915	0.164	0.164	5	0.0328
10	920	0.326	0.162	5	0.0328
15	950	0.492	0.166	5	0.0332
30	885	0.973	0.481	15	0.0320
40	875	1.305	0.332	10	0.0332
45	900	1.465	0.160	5	0.0320
60	850	1.964	0.499	15	0.0333
90	900	2.977	1.013	30	0.0337

Naphthalene flow was cut.

150 cut air flow.

Naphthalene + Vaporizer = 183.7 gm.

Naphthalene evaporated = 188.1 - 183.7 = 4.4 gm.

$$\frac{\text{Naphth.}}{\text{air}} = \frac{4.4 \text{ gm.}}{2.977 \text{ ft}^3} = 1.475 \frac{\text{gm.}}{\text{ft}^3 \text{ air}}$$

$$\frac{\text{Naphth.}}{\text{air}} = \frac{1.475}{0.21} = 7.04 \frac{\text{gm.}}{\text{ft}^3 O_2}$$

$$\text{Mole ratio naphth. to air} = \frac{(4.4)(22.4)}{(2.977)(28.32)(128.16)} = 0.0093$$

at S.T.P.

$$= (0.0093)(1.34) = 0.0124$$

$$v\ (\text{ft}^3/\text{min}) = \frac{2.977}{90} = 0.03308 \text{ ft}^3/\text{min.}$$

Contact time = $\frac{(0.03)(60)}{(0.03308)(28.32)}$ = 1.93 sec.

Analysis

Initial 0.02 N NaOH = 100 ml.

From burette:

0.02 N NaOH	0-50 =	50 ml.
	0-50 =	50 ml.
	0-50 =	50 ml.
	0-50 =	50 ml.
		200 ml.
0.400 N NaOH	20-46.7 =	26.7 ml.

gm. moles phthalic anhydride = $\frac{(300)(0.02)+(26.7)(0.4)}{1000} = \frac{16.68}{1000}$

wt. phthalic anhydride = $\frac{(16.68)(148.11)}{1000} = \frac{2500}{1000}$ gm.

% yield = $\frac{25}{10} \times \frac{100}{4.4} = 57$

Run No. 7

Initial Temperature = 845°F

Naphthalene + Vaporizer (initial) = 188.0 gm.

100 ml. of 0.02 N NaOH each in scrubbers 2 and 3.

Time (min)	Temp. (°F)	(ft^3)	(ft^3)	(min)	(ft^3/min)
0	845	0	0	0	0
5	870	0.116	0.116	5	0.0232
10	890	0.226	0.110	5	0.0220
20	915	0.4420	0.216	10	0.0216
30	920	0.661	0.219	10	0.0219
60	950	1.3315	0.6705	30	0.02235
90	955	2.013	0.6805	30	0.02268

Naphthalene flow was cut.

Naphthalene + Vaporizer = 184.4 gm.

Naphthalene Vaporized = 188-184.4 = 3.6 gm.

$$\frac{\text{Naphth.}}{\text{air}} = \frac{3.6 \text{ gm.}}{2.013 \text{ ft}^3} = 1.79 \text{ gm/ft}^3$$

$$\frac{\text{Naphth.}}{\text{oxygen}} = \frac{1.79}{0.21} = 8.55 \text{ gm/ft}^3$$

$$\text{Mole Ratio to air} = \frac{(3.6)(22.4)(1.34)}{(2.013)(28.32)(128.16)} = 0.0147$$

$$v \text{ (ft}^3\text{/min)} = \frac{2.013}{g\ 0} = 0.0224$$

$$\text{Contact time} = \frac{(0.03)(60)(90)}{(2.013)(28.32)} = 2.76 \text{ sec.}$$

Analysis:

200 ml. 0.02 N NaOH initial

$21.0 - 32.3 = 11.3$ ml. 0.400 N NaOH

$$\text{gm-moles phthalic anhydride} = \frac{(0.02)(200)+(11.3)(0.4)}{1000} = \frac{8.52}{1000}$$

$$\text{wt. phthalic anhydride} = \frac{(8.52)(148.11)}{1000} = \frac{1270}{1000}$$

$$\%\ \text{yield} = \frac{1270}{1000} \times \frac{100}{3.6} = 35.5$$

Run No. 13

Initial Temperature = 800°F

Naphthalene + Vaporizer (initial) = 188.3 gm.

100 ml. of 0.02 N NaOH each in 2 and 3 scrubbers.

Time (min)	Temp. (°F)	(ft³)	(ft³)	(min)	(ft³/min)
0	800	0	0	0	0
5	875	0.1085	0.1085	5	0.0217
10	895	0.2125	0.1040	5	0.0208
15	900	0.315	0.1025	5	0.0205
25	880	0.524	0.209	10	0.0209
30	880	0.630	0.106	5	0.0212
35	895	0.738	0.108	5	0.0216
45	875	0.922	0.184	10	0.0184
55	900	0.1435	0.2215	10	0.02215
60	880	1.255	0.1125	5	0.02250

Cut the naphthalene flow.

90 air flow was cut.

Naphthalene + Vaporizer = 185.3 gm.

Naphthalene Vaporized = 188.3 - 185.3 = 3.0 gm.

$$\frac{\text{Naphth.}}{\text{air}} = \frac{3 \text{ gm.}}{1.255 \text{ ft}^3} = 2.4 \text{ gm/ft}^3$$

$$\frac{\text{Naphth.}}{\text{Oxygen}} = \frac{2.4}{0.21} = 11.5 \text{ gm/ft}^3$$

$$\text{Mole ratio to air} = \frac{(3)(22.4)(1.34)}{(28.32)(128.16)(1.255)} = 0.0198$$

$$\text{Contact time} = \frac{(0.03)(60)(60)}{(28.32)(1.255)} = 3.04 \text{ sec.}$$

$$\text{Average Flow Rate} = \frac{1.255}{60} = 0.0209 \text{ ft}^3/\text{min.}$$

Analysis:

200 ml. 0.02 N NaOH initial

4.6 - 25.6 = 21 ml. 0.400 N NaOH added

$$\text{gm-moles phthalic anhydride} = \frac{(0.02)(200)+(0.4)(21)}{1000} = \frac{12.4}{1000}$$

$$\text{wt. phthalic anhydride} = \frac{(12.4)(148.11)}{1000} = \frac{1840}{1000}$$

$$\%\ \text{yield} = \frac{1840}{1000} \times \frac{100}{3.0} = 61.3$$

Run No. 14

Initial Temperature = 770°F

Naphthalene + Vaporizer (initial) = 196.9 gm.

100 ml. 0.02 N NaOH each in scrubbers 2 and 3.

Time (min)	Temp. (°F)	(ft^3)	(ft^3)	(min)	(ft^3/min)
0	770	0	0	0	0
5	840	0.1175	0.1175	5	0.0235
10	860	0.2185	0.1010	5	0.0202
15	875	0.3220	0.1045	5	0.0209
20	870	0.4255	0.1035	5	0.0207
30	850	0.6285	0.2030	10	0.0203
40	805	0.8370	0.2085	10	0.02085
50	880	1.0480	0.2110	10	0.0211

Naphthalene flow was cut.

80 air flow was cut.

Naphthalene + Vaporizer = 194.95 gm.

Naphthalene Vaporized = 196.9 - 194.95 = 1.95 gm.

$$\frac{\text{Naphth.}}{\text{air}} = \frac{1.95 \text{ gm.}}{1.048 \text{ ft}^3} = 1.85 \text{ gm/ft}^3$$

$$\frac{\text{Naphth.}}{\text{Oxygen}} = \frac{1.85}{0.21} = 8.8 \text{ gm/ft}^3$$

$$\text{Average Flow Rate} = \frac{1.0480}{50} = 0.0210 \text{ ft}^3\text{/min.}$$

$$\text{Mole Ratio to air} = \frac{(22.4)(1.95)(1.34)}{(28.32)(128.16)(1.048)} = 0.0154$$

$$\text{Contact time} = \frac{(0.03)(60)(50)}{(28.32)(1.048)} = 3.04 \text{ sec.}$$

Analysis:

200 ml. 0.02 N NaOH initial

0.400 N NaOH	0.015 N HCl
3.0-23.0	11-2216 = 11.6 ml.
23 - 23.4	
= 20.4 ml.	

gm-moles phthalic anhydride = (0.02)(200)+(20.4)(0.4)-(11.6)

(0.015) = 11.986 m. moles

wt. phthalic anhydride = $\frac{(11.986)(148.11)}{1000} = \frac{1780}{1000}$

wt. phthalic anhydride = $\frac{(11.986)(148.11)}{1000} = \frac{1780}{1000}$

% yield = $\frac{1780}{1000} \times \frac{100}{1.95} = 89.5$

Run No. 15

Initial Temperature = 780°F

Naphthalene + Vaporizer (initial) = 194.8 gm.

100 ml. 0.02 N NaOH each in scrubbers 2 and 3.

Time (min)	Temp. (°F)	(ft³)	(ft³)	(min)	(ft³/min)
0	780	0	0	0	0
5	880	0.1305	0.1305	5	0.02601
10	870	0.2395	0.1090	5	0.02180
20	860	0.453	0.2135	10	0.02135
30	850	0.662	0.209	10	0.0209
40	870	0.865	0.203	10	0.0203
50	870	1.070	0.205	10	0.0205
60	870	1.276	0.206	10	0.0206
70	870	1.4825	0.20625	10	0.0206
75	870	1.5855	0.103	5	0.0206

90 Naphthalene flow was cut.

120 cut air flow.

$$\frac{\text{Naphth.}}{\text{air}} = \frac{4 \text{ gm.}}{1.5855 \text{ ft}^3} = 2.52 \text{ gm/ft}^3$$

$$\frac{\text{Naphth.}}{\text{Oxygen}} = \frac{2.52}{0.21} = 12 \text{ gm/ft}^3$$

$$\text{Average flow rate} = \frac{1.5855}{75} = 0.0212 \text{ ft}^3/\text{min.}$$

$$\text{Contact time} = \frac{(0.02)(60)(75)}{(28.32)(1.5855)} = 3 \text{ sec.}$$

$$\text{Mole ratio to air} = \frac{(4)(22.4)(1.34)}{(28.32)(128.16)(1.5855)} = 0.0208$$

Analysis:

200 ml. 0.02 N NaOH initial

0.400 N NaOH   2.00-40.1 = 38.1 ml.

gm-moles phthalic anhydride = $\frac{(0.02)(200)+(38.1)(0.4)}{1000} = \frac{19.24}{1000}$

wt. phthalic anhydride = $\frac{(19.24)(148.11)}{1000} = \frac{2880}{1000}$

% yield = $\frac{2880}{1000} \times \frac{100}{4.0} = 72.0$

Run No. 16

Initial Temperature = 755°F

Naphthalene + Vaporizer (initial) = 190.8 gm.

100 ml. 0.02 N NaOH each in scrubbers 2 and 3.

Time (min)	Temp. (°F)	(ft^3)	(ft^3)	(min)	(ft^3/min)
0	755	0	0	0	0
5	855	0.107	0.107	5	0.02014
10	865	0.212	0.105	5	0.02010
15	845	0.325	0.113	5	0.02260
20	840	0.440	0.115	5	0.0230
30	825	0.675	0.235	10	0.0235
40	850	0.903	0.228	10	0.0228
50	850	1.142	0.239	10	0.0239
60	850	1.408	0.266	10	0.0266

Naphthalene flow was cut.

90 cut air flow.

Naphthalene + Vaporizer = 187.1 gm.

Naphthalene Vaporized = 190.8 - 187.1 = 3.7 gm.

$$\frac{\text{Naphth.}}{\text{air}} = \frac{3.7 \text{ gm.}}{1.408 \text{ ft}^3} = 2.64 \text{ gm/ft}^3$$

$$\frac{\text{Naphth.}}{\text{Oxygen}} = \frac{2.64}{0.21} = 12.5 \text{ gm/ft}^3$$

$$\text{Average Flow Rate} = \frac{1.408}{60} = 0.02346 \text{ ft}^3\text{/min.}$$

$$\text{Mole ratio to air} = \frac{(3.7)(22.4)(1.34)}{(28.32)(128.16)(1.408)} = 0.0216$$

$$\text{Contact time} = \frac{(0.03)(60)(60)}{(28.32)(1.408)} = 2.71 \text{ sec.}$$

Analysis:

200 ml. 0.02 N NaOH initial

0.400 N NaOH = 0-30 = 30 ml.

0.0154 N HCl = 150 ml.

$$\text{gm-moles phthalic anhydride} = \frac{(0.02)(200)+(30)(10.4)-(150)(0.0154)}{1000}$$

$$= \frac{13.7}{1000}$$

$$\text{wt. phthalic anhydride} = \frac{(13.7)(148.11)}{1000} = \frac{2040}{1000} \text{ gm.}$$

$$\% \text{ yield} = \frac{2040}{1000} \times \frac{100}{2.7} = 55.0$$

Run No. 17

Initial Temperature = 800°F

Naphthalene + Vaporizer (initial) = 194.6 gm.

100 ml. 0.02 N NaOH each in scrubbers 2 and 3.

Time (min)	Temp. (°F)	(ft^3)	(ft^3)	(min)	(ft^3/min)
0	800	0	0	0	0
5	820	0.0870	0.0870	5	0.0174
10	840	0.1745	0.0875	5	0.0175
20	850	0.3545	0.180	10	0.0180
30	835	0.5235	0.179	10	0.0179
40	840	0.8655	0.342	20	0.0171
70	840	0.2005	0.345	20	0.01725
90	843	1.575	0.3745	20	0.018725

Naphthalene flow was cut.

120 cut air flow.

Naphthalene + Vaporizer = 191.2 gm.

Naphthalene Vaporized = 194.6 - 191.2 = 3.4 gm.

$$\text{Mole ratio to air} = \frac{(3.4)(22.4)(1.34)}{(28.32)(128.16)(1.575)} = 0.018$$

$$\text{Contact time} = \frac{(0.03)(60)(90)}{(28.32)(1.575)} = 3.64 \text{ sec.}$$

$$\text{Average flow rate} = \frac{1.575}{90} = 0.0175 \text{ ft}^3/\text{min.}$$

Analysis:

200 ml. of 0.02 N NaOH each in scrubbers 2 and 3.

0.400 N NaOH 0.20 = 20 ml.

$$\text{wt. phthalic anhydride} = \frac{(20)(0.4)+(0.02)(200)\ 148.11}{1000} = 1.78 \text{ gm.}$$

$$\%\ \text{yield} = \frac{1.78}{3.4} \times 100 = 52.0$$

Run No. 18

Initial Temperature = 770°F

Naphthalene + Vaporizer = 194.0 gm.

100 ml. 0.02 N NaOH each in scrubbers 2 and 3.

Time (min)	Temp. (°F)	(ft³)	(ft³)	(min)	(ft³/min)
0	770	0	0	0	0
5	840	0.1176	0.1176	5	0.02352
10	865	0.2350	0.1174	5	0.02348
20	870	0.4550	0.220	10	0.0220
30	860	0.6700	0.215	10	0.0215
50	855	1.095	0.425	20	0.02125
70	860	1.525	0.430	20	0.02150
90	860	1.935	0.410	20	0.0205

Cut the naphthalene flow.

120 cut air flow.

Naphthalene + Vaporizer = 190.1 gm.

Naphthalene Vaporized = 194.0 - 190.1 = 3.9 gm.

Average flow rate = $\frac{1.935}{90} = 0.0215$

Mole ratio to air = $\frac{(4.0)(22.4)(1.34)}{(28.32)(128.16)(1.935)} = 0.0170$

Contact time = $\frac{(0103)(60)(90)}{(28.32)(1.935)} = 2.96$ sec.

Analysis:

200 ml. 0.02 N NaOH initial.

0.400 N NaOH 0-48.3 = 48.3 ml.

$$\text{gm-moles phthalic anhydride} = \frac{(48.3)(0.4)+(0.02)(200)}{1000} = \frac{23.32}{1000}$$

$$\text{wt. phthalic anhydride} = \frac{(23.32)(148.11)}{1000} = 3.45 \text{ gm.}$$

$$\%\ \text{yield} = \frac{3.45}{3.9} \times 100 = 88.0$$

APPENDIX II

Run No. 19

30 ml. of catalyst B.

Initial Temperature = 670°F.

Naphthalene + Vaporizer (initial) = 191.5 gm.

100 ml. 0.02 N NaOH in each no. 2 and no. 3 scrubbers.

Time (min)	Temp. (°F)	(ft^3)	(ft^3)	(min)	(ft^3/min)
0	670	0	0	0	0
5	790	0.128	0.128	5	0.0256
10	800	0.241	0.113	5	0.0226

Very little phthalic anhydride formation. No visible napthoquinone was formed. It seems that there is complete oxidation. Decrease the temperature. The variac was turned to zero rate at 12th minute, but the temp. is still 800°F at 25th minute. For next run, decrease the initial temperature.

30	760	---	---	---	---

no trace of naphthoquinone was seen.

40	765	1.000	0.759	30	0.2518
50	775	1.276	0.276	10	0.02760
60	760	1.515	0.239	10	0.02390

Cut air and naphthalene flow.

There is no phthalic anhydride produced. Since the heat of reaction was high, we can assume that there was complete oxidation.

Run No. 21

15 ml. of catalyst C.

Initial Temperature = 625°F.

Naphthalene + Vaporizer = 210.3 gm.

100 ml. 0.02 N NaOH in scrubbers 2 and 3.

Time (min)	Temp. (°F)	(ft^3)	(ft^3)	(min)	(ft^3/min)
0	625	0	0	0	0
5	695	0.151	0.151	5	0.0302
10	695	0.295	0.144	5	0.0288

No phthalic anhydride formation, all solids seem to be naphthalene. Increase flow rate.

15	650	0.536	0.241	5	0.0482

The reaction is very small. Increase the temperature. The reaction has started strongly after 720°F. It jumped to 1100°F.

60	800	---	---	---	---

Stop the flow.

All of the products were soluble in benzol. No phthalic anhydride or maleic anhydride whatsoever.

Run No. 22

30 ml. of Catalyst D.

Initial Temperature = 755°F.

Naphthalene + Vaporizer = 203.4 gm.

100 ml. 0.02 N NaOH + 4 ml. 0.400 N NaOH in scrubbers 2 and 3.

Time (min)	Temp. (°F)	(ft³)	(ft³)	(min)	(ft³/min)
0	760	0	0	0	0
5	795	0.091	0.091	5	0.0182
10	800	0.216	0.125	5	0.0250

No solid formation. All is going to CO_2. At 20th minute, NaOH in scrubbers was neutralized. Decrease temperature to find the lower boundary of CO_2 formation.

34	760	no solid formations
39	745	" " "
43	720	" " "
64	660	" " "
70	650	" " "
75	660	" " "

Lead bath started to solidify, stop the run.

A very possible complete combustion catalyst for hydrocarbons. 100% conversion to complete combustion products.

Run No. 23

30 ml. of Catalyst E.

100 ml. 0.02 N NaOH each in scrubbers 2 and 3.

Initial Temperature = 730°F.

Naphthalene + Vaporizer = 198.0 gm.

Time (min)	Temp. (°F)	(ft^3)	(ft^3)	(min)	(ft^3/min)
0	730	0	0	0	0
5	800	0.130	0.130	5	0.0260
		No solid formation			
10	795	0.258	0.128	5	0.0256
		No solid formation			
15	795	0.392	0.134	5	0.0268
		No solid formation			
20	775	0.509	0.117	5	0.0234
		No solid formation			
30	760	0.733	0.224	10	0.0224
		No solid formation, increase flow rate.			
40	810	1.096	0.363	10	0.0363
		No solid formation, decrease temperature.			
60	700	1.857	---	---	---

Stop the run. No solids were seen in condensing system; all is going to the complete combustion products.

This is a very possible complete oxidation catalyst for hydrocarbons.

APPENDIX III

Preparation of Catalyst B

1. 40 gm. of 8-14 mesh alumina pellets was left in vacuum for 45 minutes.
2. A solution was made by 12 gm. of barium acetate and 5 gm. of chromic acid in 100 ml. of distilled water and readily sent into the vacuum flask.
3. The catalyst carrier was soaked in this solution for one and a half hours while the vacuum was on.
4. The vacuum was turned off, the excess solution decanted.
5. The catalyst in a porcelain crucible was dried in oven at 200°C for 16 hours.
6. % $BaCrO_4$ deposited $= \frac{40.7-40}{40} \times 100 = 1.75.$
7. 30 ml. of this catalyst was placed in reactor, and air at 0.4 ft^3/min was passed through at 800°C for two hours, in order to complete calcination and activation.

Preparation of Catalyst D

1. 50 ml. of 8 to 14 mesh alumina pellets were put into the vacuum flask, and left in vacuum for one hour.
2. A solution was made with 5 gm. of ammonium vandadate and 75 ml. of 30% hydrogen peroxide, and was put into the vacuum flask.
3. The pellets were soaked in this solution for one hour under the vacuum.
4. The vacuum was turned off, the excess solution was decanted.
5. The prepared catalyst in a porcelain crucible was put in the oven at 330°C for 20 hours.
6. The calcination and activation were done in the reactor at 800°F by passing air through for two hours.
7. % V_2O_5 deposited $= \frac{51.07-50}{50} \times 100 = 2.14$

Preparation of Catalyst E

1. 42.92 gm. of 8 to 14 mesh alumina was put into the vacuum flask and left in vacuum for 45 minutes.
2. A solution was made of 5 gm. vanadium pentoxide powder and 75 ml. 30% hydrogen peroxide, and sent into the vacuum flask.
3. The pellets were soaked in this solution for two hours under the vacuum.
4. The vacuum was turned off, the excess solution decanted.
5. The prepared catalyst in a porcelain crucible was left in the oven for 48 hours at 180°C.
6. Air was blown through dried pellets to remove excess V_2O_5 dust. % V_2O_5 deposited = $\frac{44.02-42.92}{42.92} \times 100 = 2.56.$
7. For calcination and activation, 30 ml. of prepared catalyst was placed in reactor, and air passed through for two hours at 800°F.

CONTOUR TANGENT ELIMINATION (10)

Sample Calculation:

BLOCK I

Run	Yield	Temperature	Flow Rate
17	$y_0=52$	$x_{01} = 840$	$x_{02} = 0.0175$
16	$y_1=55$	$x_{11} = 848$	$x_{13} = 0.02346$
15	$y_2=72$	$x_{21} = 866$	$x_{22} = 0.0212$

$$y_i = m_1 \triangle x_i + m_2 \triangle x_i \quad 0$$

to reach a maximum value for y.

Where

$$m_1 = \frac{\triangle y_1}{\triangle x_{11}} \qquad \begin{aligned} \triangle y_1 &= y_1 - y_0 = 55 - 52 = 3 \\ \triangle x_{11} &= x_{11} - x_{01} = 848 - 840 = 8 \end{aligned}$$

and

$$m_2 = \frac{\triangle y_2}{\triangle x_{22}} \qquad \begin{aligned} \triangle y_2 &= y_2 - y_0 = 72 - 52 = 20 \\ \triangle x_{22} &= x_{22} - x_{02} = 0.0212 - 0.0175 = 0.0037 \end{aligned}$$

therefore

$$m_1 = \frac{3}{8} = 0.375 \qquad m_2 = \frac{20}{0.0037} = 0.54 \times 10^4,$$

and

$$0.375 \triangle x_1 + 0.54 \times 10^4 \triangle x_2 = 0$$

The slope of this line is:

$$\frac{x_2}{x_1} = - \frac{0.375 \times 10^4}{0.54} = - 0.695 \times 10^4$$

Since the slope is negative, the area over this line will give negative values of y, i.e., the yield will be smaller than 52% and is cancelled from further experimentation.

BLOCK II

Run			
13	$y_0 = 61.3$	$x_{01} = 887$	$x_{02} = 0.0209$
6	$y_1 = 57$	$x_{11} = 890$	$x_{12} = 0.03308$
7	$y_2 = 35.5$	$x_{21} = 930$	$x_{22} = 0.0224$

$$\Delta y_1 = 0 = -1.435 \quad \Delta x_1 - 1.73 \times 10^4 \Delta x_2$$

BLOCK III

Run			
16	$y_0 = 55$	$x_{01} = 848$	$x_{02} = 0.02346$
17	$y_1 = 52$	$x_{11} = 840$	$x_{12} = 0.0175$
13	$y_2 = 61.3$	$x_{21} = 887$	$x_{22} = 0.0209$

$$\Delta y_1 = 0 = 0.375 \quad \Delta x_1 - 0.251 \times 10^4 \Delta x_2$$

BLOCK IV

Run			
13	$y_0 = 61.3$	$x_{01} = 887$	$x_{02} = 0.0209$
16	$y_1 = 55$	$x_{11} = 848$	$x_{12} = 0.02346$
6	$y_2 = 57$	$x_{21} = 890$	$x_{22} = 0.03308$

$$\Delta y_1 = 0 = 0.162 \quad \Delta x_1 - 0.0456 \times 10^4 \Delta x_2$$

BLOCK V

Run			
15	$y_0 = 72$	$x_{01} = 866$	$x_{02} = 0.0210$
13	$y_1 = 61.3$	$x_{11} = 887$	$x_{12} = 0.0209$
6	$y_2 = 57$	$x_{21} = 890$	$x_{22} = 0.03308$

$$\Delta y_1 = 0 = -0.51 \quad \Delta x_1 - 0.1245 \times 10^4 \Delta x_2$$

BLOCK VI

Run			
15	$y_0 = 72$	$x_{01} = 866$	$x_{02} = 0.0212$
6	$y_1 = 57$	$x_{11} = 890$	$x_{12} = 0.03308$
16	$y_2 = 55$	$x_{21} = 848$	$x_{22} = 0.02346$

$$\Delta y_1 = 0 = -0.625 \quad \Delta x_1 - 0.75 \times 10^4 \Delta x_2$$

BLOCK VII

Run			
17	$y_0 = 52$	$x_{01} = 840$	$x_{02} = 0.0175$
13	$y_1 = 61.3$	$x_{11} = 887$	$x_{12} = 0.0209$
14	$y_2 = 89.5$	$x_{21} = 863$	$x_{22} = 0.0210$

$$\Delta y_1 = 0 = 0.198 \quad \Delta x_1 + 1.07 \times 10^4 \Delta x_2$$

BLOCK VIII

Run			
16	$y_0 = 55$	$x_{01} = 848$	$x_{02} = 0.02346$
13	$y_1 = 61.3$	$x_{11} = 887$	$x_{12} = 0.0209$
14	$y_2 = 89.5$	$x_{21} = 863$	$x_{22} = 0.0210$

$\Delta y_1 = 0 = 0.3 \qquad \Delta x_1 - 1.4 \times 10^4 \, \Delta x_2$

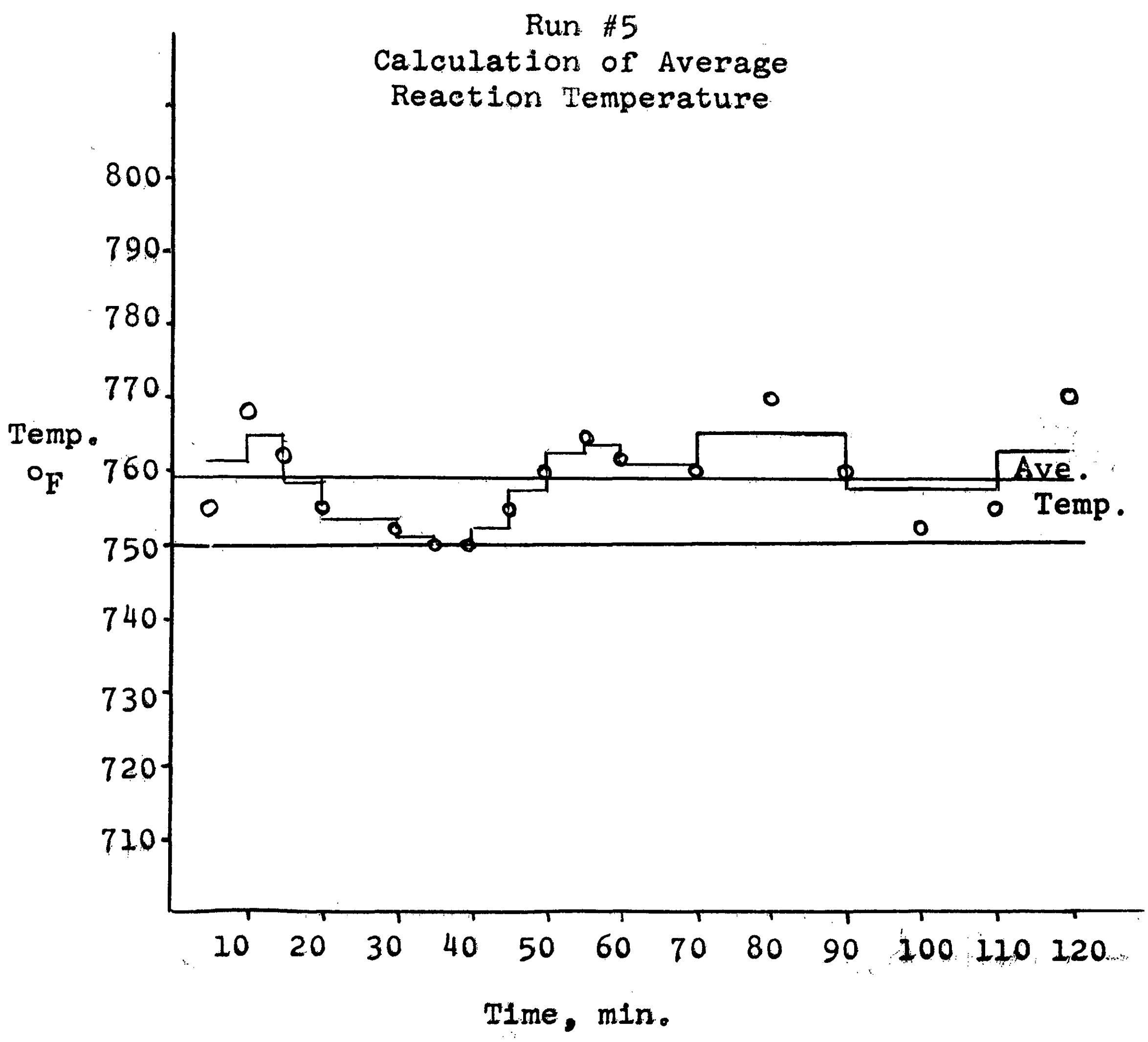
Run #5
Calculation of Average
Reaction Temperature
Temp. °F
800
790
780
770
760
750
740
730
720
710
Ave. Temp.
10
20
30
40
50
60
70
80
90
100
110
120
Time, min.

Fig. 3

Calculation of Average Reaction Temperature

Sample Calculation (run 5)

1. Time vs. Temperature was plotted (fig. 3).
2. Draw a straight line through the lowest temperature parallel to the abcissa.
3. Draw straight lines through the mid-point of distance between each consecutive temperature for the length of their time interval.
4. Connect these lines by vertical lines and count the number of square centimeters this curve covers over the line passing through the lowest temperature (for run 5, = 42 cm^2).
5. Divide this number by the length of abcissa in cm.

   (for run 5, = $\frac{42}{33}$ = 1.83 cm)
6. Add this length vertically to the lowest temperature and draw a straight line which divides area of section 4 into two equal parts. This gives us the averaged reaction temperature, which was 759°F for run 5.

   Av. Temp. = 759°F

   Max. Temp. = 770°F % Dev. = $\frac{770-759}{759}$ x 100 = 1.45

   Min. Temp. = 750°F % Dev. = $\frac{750-759}{759}$ = 1.19

% Max. Temp. Deviation = 1.45

% Max. Temp. Deviations for run proper on catalyst A are presented on Table III.