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EVALUATION OF CATALYSTS FOR THE
OXIDATIVE AMMONOLYSIS OF m-XYLENE

A Thesis
Submitted to the Faculty of Graduate Studies Through the
Department of Chemical Engineering in Partial Fulfilment
of the Requirements for the Degree of
Master of Applied Science at the
University of Windsor

by

Raj K. Dhawan

Windsor, Ontario
September, 1972

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ABSTRACT

An experimental investigation into the effectiveness of various catalytic formulations for the oxidative ammonolysis of m-xylene in the temperature range of 300-500°C was carried out. Catalysts were based upon vanadium oxide, deposited on highly activated γ -alumina. Catalyst evaluation was made on the basis of the selectivity for the formation of nitriles, for each catalyst. Activity of the carrier, its pretreatment and the method of preparing the catalyst were found to effect the selectivity of nitriles. Incorporation of oxides of transition metals to the base oxide- V_2O_5 , showed varying influence on the selectivity for nitriles of the catalyst. Presence of the water vapour in the reaction mixture was also found to have an important effect on the selectivity for the nitriles. Of all the catalysts tried out under identical conditions of temperature, concentrations and contact times, a co-precipitate of tin chloride and ammonium vanadate showed the best yield and selectivity for nitriles.

ACKNOWLEDGEMENTS

It is indeed a pleasure for me to take this opportunity to express my sincere appreciation of the constructive guidance offered so readily by Dr. G.P. Mathur. During the course of this research, the valuable criticism and suggestions offered by Dr. M. Adelman are graciously acknowledged.

I am also thankful to Mr. W. Eberhart for helping me in the construction of the experimental equipment.

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CHAPTER 1

INTRODUCTION

As early as 1832, Wohler and Liebig synthesized benzoyl-cyanide and benzonitrile, but the toxicity of nitriles and the limited availability of the raw materials that go into the production of these compounds hampered further work in this field for many years. It was only during 1920-35 that large tonnages of acrylonitrile, phthalonitriles, acetonecyanohydrin, adiponitriles and trichloroacetonitriles were produced. These compounds found unlimited applications in the manufacture of plastics, synthetic rubbers and fibres, dyestuffs and fumigants. Other applications for these nitriles and others prepared more recently have been in the field of synthetic resins, war-gases, insecticides, speciality solvents and most important of all as intermediates in the synthesis of pharmaceuticals, vitamins and plastics. Increased demand for aromatic nitriles, used as intermediates and in the synthetic resin field has necessitated search for economically optimum methods for producing these compounds.

Vapor phase catalytic oxidative ammonolysis of benzene, toluene xylenes and other aromatic compounds has been successfully carried out in the past. In the present work, effectiveness of various catalyst formulations for forming

m-phthalonitrile from m-xylene in the presence of ammonia and oxygen (air) in the temperature range of 300-500°C was studied. Reaction was carried out in an isothermal fixed bed catalytic reactor. High effectiveness of a specific catalyst was interpreted as formation of dinitrile with side reactions and carbonization of m-xylene occurring to an insignificant degree only. Catalysts screened for their effectiveness were based on either vanadium oxide or vanadium oxide modified with oxides of Mn, Cr, B, Co, Mo and Sb. Binary catalysts, tin vanadate and manganese p-tungstate were also tested. The influence of following parameters on yield and selectivity of nitriles was studied for the catalyst formulations mentioned above.

1. Surface area of the catalyst.
2. Precalcining of carrier at 900°C and 1250°C over prolonged periods whereby crystal structure was so modified that increased catalytic activity was achieved.
3. Percentage of oxide deposited on the catalyst.
4. Water vapor in the reaction mixture.
5. Contact time for the reaction mixture in the reaction zone.

The objective of the study was primarily to choose the most promising catalyst for further studies into the kinetics and mechanism of this complex reaction. The latter will facilitate the design of an efficient reactor set up for obtaining high yields of nitriles in the oxidative ammonolysis of xylenes.

CHAPTER II

LITERATURE SURVEY

A. Nitriles

Because of their industrial applications as intermediates in the manufacture of synthetic rubbers and fibres, dyestuffs, pharmaceuticals, fumigants and insecticides, nitriles were prepared as early as 1832 by Wohler and Liebig (1). Historical background, natural occurrence, preparation by various chemical methods and industrial applications for nitriles have been exhaustively covered by Mowrey (2). Because of the inherent limitations of these methods for the manufacture of nitriles, vapor-phase catalytic oxidative ammonolysis of various hydrocarbons-paraffins, aromatics, olefins and substituted unsaturated molecules, aldehydes, acids and esters, alcohols, and ethylene oxide was suggested (3). This one step procedure of contacting in the vapor-phase the hydrocarbon, ammonia, and oxygen with a suitable catalyst was found to be in marked contrast with the previously known methods, such as reaction of aromatic halides or sulfate with alkali-cyanide, decomposition of diazonium-halides with potassium-cuprous-cyanide, decomposition of isothiocyanates with copper or zinc dust.

B. Amoxidation of Aromatics

Oxidative ammonolysis of xylene, toluene, and trimethyl

benzene was carried out successfully in the presence of a catalyst (consisting of mixed oxides of molybdenum and phosphorous deposited on alumina) in the temperature range 496-580°C, with yields of nitriles of the order of 10%, based upon the moles of hydrocarbon charged (3). O-phthalonitrile was prepared from phthalic anhydride in the presence of oxides of tungsten, chromium, and/or vanadium at 400°C with yields of 61.9-72% (4). Klinitas et al. (5) reported activated carbon effective between 310-425°C and silica supported on activated alumina effective between 900-1075°C, as catalysts for the oxidative ammonolysis of toluene. They observed a marked improvement in the yield of benzonitrile from toluene in an adiabatic reactor as compared to an isothermal one. They, however, could not find any beneficial effect of water vapor in the reaction mixture upon the yield of mononitrile for isothermal operation of the reactor. Nitrosation of toluene, xylenes, and p-picoline ($(C_5NH_4)CH_3$) with nitric oxide between 400-700°C in the presence of dehydrating catalysts, such as silver extended on inert support was reported to give high yields and conversions and the carbonization of hydrocarbon and side-product formation was low (6). Liquid-phase ammoxidation of m-xylene in the presence of manganese bromide as a catalyst gave a yield of 31% for m-phthalonitrile with predominant product being a mixture of m-cyanobenzamide ($C_8H_6N_2O$) and 1,3 $C_6H_4(CN)(CO_2NH_4)$ (7). Most of the work on the oxidative ammonolysis of hydrocarbons in Russia has been carried out with vanadates

as the catalysts (8-10). In their work, Suvorov et al. (11, 45) found that water vapor in the reaction mixture has an important influence on the yield of nitriles besides providing a means of efficient control of reaction temperature. The reaction has been carried out in fluidized bed reactors with both the single and multi-oxides as catalysts (12-16). Fluidized beds offer but marginal improvement in the yield of dinitriles. Many papers have appeared on the simultaneous ammoxidation of xylene isomers (o-, m-, p-) and the influence of presence of one on the yield of other isomer's dinitrile (9,15, 17,18). Ohta et al. (19) studied the activity of X-Mo (where X is ferrous, nickel or cobalt oxide and Mo is oxide of molybdenum) for ammoxidation of p-xylene for various percentages of X in the binary oxide catalyst. They reported the formation of complete oxidation products-CO, CO₂, HCN with single oxides of ferrous, nickel, and cobalt. For the ammoxidation of o-xylene where o-phthalamide is the primary product with conventional catalysts based on vanadium pentoxide, Nakamura et al. (20) found that manganese p-tungstate gives very good yields of o-phthalonitrile around 470°C.

In the past twenty years, numerous papers on the ammoxidation of aromatic hydrocarbons in the presence of a variety of catalysts have appeared. The literature in this field is mostly in the form of patent specifications. Some of the more important references along with whatever data is available from these appear in Appendix I.

CHAPTER III

EXPERIMENTAL AND THEORETICAL CONSIDERATIONS

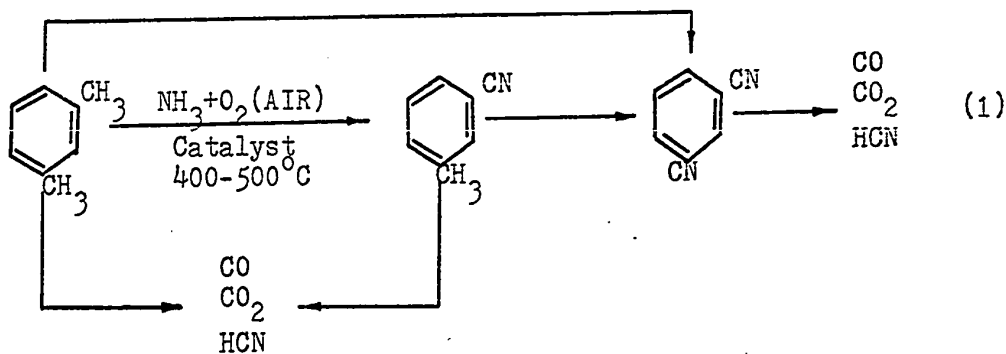
A. Experimental Consideration for Scientific Selection of Catalysts

Considerable efforts have been expended in the past to evolve scientific principles for catalyst selection. Development of 'Multiplet Theory' in this connection has been one of the major successes. In brief, this theory postulates that catalysis proceeds under the action of chemical forces which are characterized by bonds of specific, closely defined length and of specific energy of dissociation. Catalysis is a chemical phenomenon, i.e., intermediate interactions of chemical nature occur between the catalyst and the reacting atoms. This being so and the fact that chemical valence forces are effective over a short range, the atoms will react only upon contact with the catalyst. From the known valence bond angles, lengths and energies, energy of formation and dissociation of the intermediate complexes can be calculated and thus the occurrence of specific reactions can be ascertained. This theory has been successfully applied in many hydrogenation, dehydrogenation, hydrogenolysis and dehalogenation reactions. But the theory in the present state can not be applied to oxidation reactions and acid base catalysis (21).

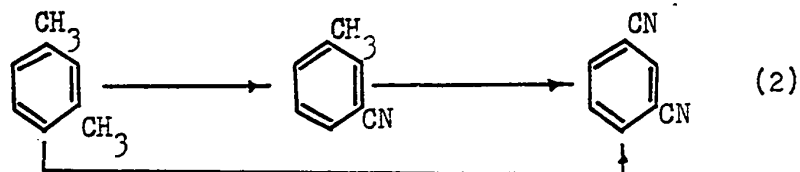
Selection of catalysts includes finding both the suitable catalysts for a reaction as well as the reactions which would occur on such a catalyst. Multiplet theory has been of immense help in solving the latter part of the problem as evidenced by experimental verifications of predictions made about the comparative ease with which hydrogenolysis of different bonds in polyfunctional molecules on nickel can be carried out. In this connection, preparation of α -decalol from decaline ($C_{10}H_{18}$) peroxide hydrogenation on nickel and previously unknown transformations of furan (C_4H_4O) derivatives are worth mentioning. Lack of data on bond (between the catalyst and reacting atoms) energies at present precludes wide-spread usage of the theory for a scientific selection of a catalyst for a specific reaction.

B. Selectivity Considerations

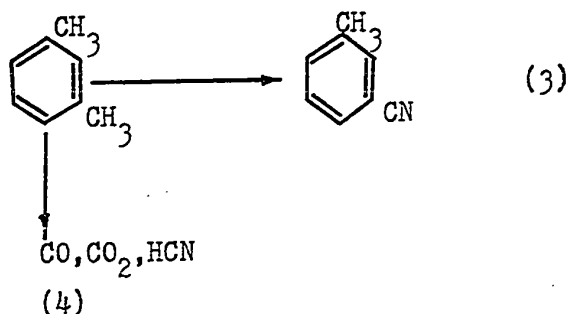
Oxidative ammonolysis, also referred to as ammoxidation, of xylenes is a complex set of consecutive and simultaneous reactions as outlined below.



Function of the catalyst in this set of reactions is to selectively accelerate the main consecutive reaction till $C_6H_5(CN)_2$, i.e.,



Selectivity is controlled by suitable control of the relative rates of the independent parallel reactions (3) and (4), shown below.



The simultaneous and independent formation of m-phthalonitrile and CO , CO_2 , HCN is favoured by catalytically heterogeneous surfaces. A Heterogeneous Surface is defined as:

If, for individual types of surface areas, the adsorption coefficients of a given species are a_1, a_2, a_3, \dots and of another species are a'_1, a'_2, a'_3, \dots , the surface is heterogeneous if

$$a_1 \neq a_2 \neq a_3 \dots \dots \dots (5)$$

$$a'_1 \neq a'_2 \neq a'_3 \dots \dots \dots (6)$$

Thus, reduction of non-homogeneity of a surface, either during the preparation of the catalyst, or by selective poisoning of certain sections should increase the selectivity of the catalyst for the desirable nitriles vis-a-vis products

of complete amoxidation, viz., CO, CO₂, HCN.

It is widely recognized that the method of preparation of a catalyst has a marked influence on its catalytic activity, upon the energy of activation of a specific reaction and surface non-homogeneity.

Selection of a carrier is of equal, if not more importance in determining the activity of a catalyst for either the laboratory or industrial use. A carrier besides providing the conventionally recognized properties, viz., surface area for the reactants to come in contact with the catalyst and undergo reaction, mechanical strength for the catalyst deposited on it, increased resistance to sintering at high temperatures and an outlet for heat for exothermic reactions, is not catalytic-activity-wise inert in some reactions. In other words, it exerts strong influence on the activity and selectivity of a catalyst for certain reactions. One of the most important carriers γ -alumina became especially important when used with outstanding success in the hydrogenation of aromatic rings, dehydrogenation of alicyclic compounds and dehydrocyclization reactions (21).

In short, in spite of extensive work into developing reliable and simple relationship between catalytic activity of a substance and its physio-chemical properties such as structure, electric-conductance (Electronic Theory of Catalysis for semi-conductors), electron work-function and magnetic susceptibility, the theory has not advanced to a stage where catalysts for specific reactions could be predicted with 100%

accuracy. Under the circumstances, one has to compromise to obtaining empirical data on various catalysts, chosen by applying known scientific principles to a greater or lesser extent. From this data, one could make conclusions as to the optimum catalyst for a certain reaction.

C. Criteria for Optimum Catalyst

Optimum catalyst is one whose surface comprise a large number of active sites that are optimal under the given reaction conditions. Such a catalyst may be far from optimal under marginally different reaction conditions. Hence, a catalyst with homogeneous surface (from the standpoint of energetic and structure correspondence) may be less advantageous under changing reaction conditions. In heterogeneous surfaces, range of energetic variations of various sections is fairly wide, so that changed reaction conditions will still meet sufficiently large number of active sites which are optimal.

In order to select the best catalyst, it is imperative to consider reaction rates for various catalysts under their optimal conditions of performance-starting composition of reactants, temperature and pressure. The latter are determined by the thermodynamics and kinetics of a reaction.

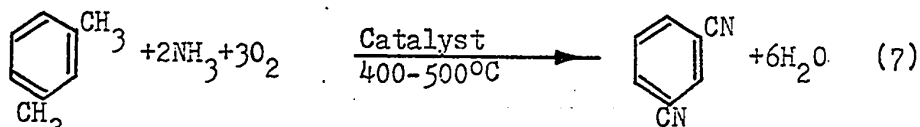
Transition from one catalyst to another one may result in a change in reaction kinetics and mechanism. Certain conditions may be optimal for one catalyst but far removed from optimal performances for another catalyst. Thus, study of reaction kinetics is essential to decide the optimal conditions for

a catalyst.

Comparison of reaction rate through its rate constant should be made only if reaction kinetic's equations are identical. One can use initial rates for activity comparison, again for identical kinetics only. It is erroneous to compare various catalysts by the temperature needed by them to reach prespecified conversion since temperature coefficients may be different for different catalysts. Thus, the most suitable criterion for deciding optimum catalyst formulation would be to find the amount of desirable products formed per unit surface area of the catalyst under its optimal reaction conditions.

D. Heat of Reaction Considerations

Overall reaction can be put as,



Below are tabulated the standard heat of formation

($\Delta H_{f,298.1}^\circ$) of various components in (7) above, along with the standard entropy ($S_{298.1}^\circ$).

Table I

Heat of Reaction Data		
Component(phase)	$\Delta H_{f,298.1}^\circ$ (Kcal/g.mole)	$S_{298.1}^\circ$ (Kcal/g.mole)
m-xylene (g)	4.12	84.31
ammonia (g)	-11.04	46.01
oxygen (g)	0.00	49.00
m-phthalonitrile (g)	82.54	88.31
water (g)	-57.80	45.11

$$\begin{aligned}
 \Delta H_{298.1}^{\circ} &= \text{Heat of reaction at } 298.1^{\circ}\text{K} \\
 &= \Delta H_{298.1}^{\circ}(\text{g}) \left[\text{products} - \text{reactants} \right] \quad (8) \\
 &= [82.54 + 6(-57.80)] - [4.12 + 2(-11.04) + 3(0.0)] \\
 &= -246.3 \text{ Kcal/g.mole}
 \end{aligned}$$

$$\begin{aligned}
 \Delta S_{298.1}^{\circ} &= S_{298.1}^{\circ}(\text{g}) \left[\text{products} - \text{reactants} \right] \quad (9) \\
 &= 88.31 + 6(45.11) - 84.31 - 2(46.01) - 3(49.00) \\
 &= 35.64 \text{ Kcal/g.mole}
 \end{aligned}$$

$$\begin{aligned}
 \Delta G_{298.1}^{\circ} &= (-246.30 - 35.64) \\
 &= -281.94 \text{ Kcal/g.mole}
 \end{aligned}$$

Heat of reaction can be calculated from the equation (10) for any temperature other than 298.1°K .

$$\Delta H_T^{\circ} = I_H + \Delta aT + \frac{\Delta b}{2}T^2 + \frac{\Delta c}{3}T^3 \quad (10)$$

Parameters a, b, c are tabulated in Table II.

Table II

Values of parameters for Equation (10)			
Component	a	b	c
m-xylene	0.85	117.7	-43.91
m-phthalonitrile	4.49	163.78	39.38
water	8.22	0.15	1.34
ammonia	6.70	6.30	-
oxygen	0.00	0.00	0.00

Therefore,

$$\Delta a = 39.56$$

$$\Delta b = 35.36 \times 10^{-3}$$

$$\Delta c = -75.85 \times 10^{-6}$$

$$\begin{aligned}
 \text{and, } I_H &= -246.30 - 11.80 - 1.56 + 0.66 \\
 &= -259.00 \text{ Kcal/g.mole}
 \end{aligned}$$

Since the reaction is carried out in the temperature range of $400-500^{\circ}\text{C}$. we will calculate ΔH° at an average

temperature of 450°C (= 748.1°K).

$$\begin{aligned}\Delta H_{748.1^\circ\text{K}}^{\circ} &= -259.00 + \frac{39.56 \times 748.1}{1000} + \frac{35.35(10^{-3}) \times 748.1^2}{2 \times 1000} \\ &\quad - \frac{75.85(10^{-6}) \times 748.1^3}{3 \times 1000} \\ &= -259.00 + 29.6 + 9.99 - 10.62 \\ &= -230.12 \text{ Kcal/g.mole}\end{aligned}$$

E. Heat Transfer Calculations

(Ref.: Chem. Eng. Kinetics, 2nd Ed., Smith, M.J., p.446
Equation 11-77)

$$\begin{aligned}(T_c - T_s)_{\text{max}} &= -\frac{\Delta H D_e}{K_e} C_s \quad (11) \\ &= \frac{(-230.12 \text{ Kcal/g.mole})(0.166 \text{ cm}^2/\text{sec}) \times}{\left(\frac{0.015}{22400} \text{ g.mole/cm}^3\right)} \\ &= \frac{\quad}{(6.2 \times 10^{-4} \text{ cal/sec.cm.}^\circ\text{C})} \\ &= 41.4^\circ\text{C}\end{aligned}$$

Temperature increase of catalytic bed due to heat of reaction, assuming no heat carry-away by the reaction mixture:

Flow rate of m-xylene (average) = 1.5 g./Hr = (1.5/106) gmole/Hr

Heat liberated = (1.5/106)(230.38)(1/3600)(1000) cal/sec.
= 0.9 cal/sec.

Heat capacity of catalytic mass = 4(0.94)(0.186) cal/°C
= 0.7 cal/°C

Temperature increase per second of reaction contact
time = (0.9/0.7) = 1.3°C.

CHAPTER IV
EXPERIMENTAL APPARATUS

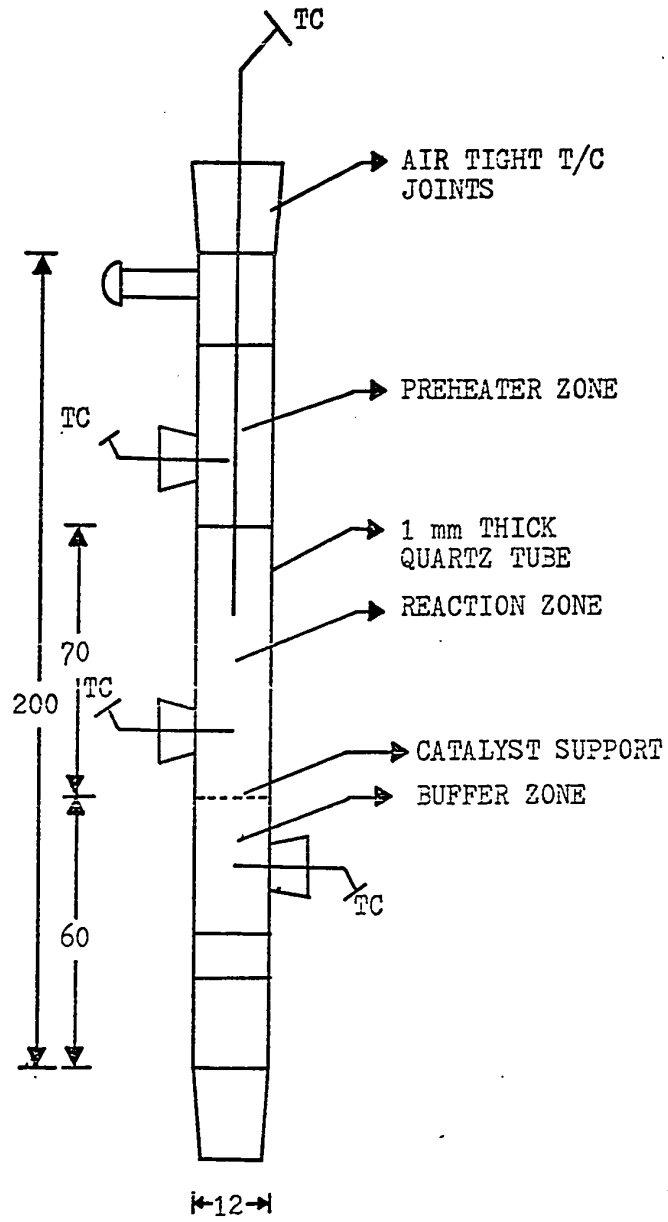
The oxidative ammonolysis of m-xylene (BP 138-39, MW 106.17, Highest purity, supplied by Fisher Scientific Ltd.) was carried out in an all quartz reactor tube, 13 mm in diameter and 200 mm long, wrapped on the outside with nichrome wire for heating. The reactor was divided into three sections as follows:

- (a) Preheater zone - packed with inert support.
- (b) Reaction zone - packed with catalyst.
- (c) Buffer zone - packed with glass wool.

Each section was heated separately with nichrome heater around it. The maximum voltage of nichrome wire around each section was as follows:

- (a) Preheater zone 500 W
- (b) Reaction zone 250 W
- (c) Buffer zone 500 W

The power input to each section was controlled with variable auto-transformer (0-120/140 V, Maximum amperage 10). For details of reactor see Fig.1. Temperature in various sections was measured with chromel-alumel thermocouples (ungrounded welded measuring junction sheathed in stainless steel 304 tube of diameter 1/16", probe length 6"). The temperature



ALL DIMENSIONS IN MM

FIGURE 1 DETAILS OF REACTOR

of the catalyst bed was measured both at the top and the bottom surfaces so as to know the temperature distribution across the length of the bed.

Nitrogen (purity 99.99 % minimum) from a cylinder (Matheson Co. Ltd.) with a 0-100 psig outlet pressure regulator, was controlled with Milli-Mite forged needle valve CV.1 (flow range: 0-20,000 ccpm at inlet pressure of 25 psig, Cv factor: 0.28, micrometer vernier handle, manufacturer: Hoke Controls Ltd.) and the flow was monitored with flowmeter FM 2 (capacity: 0-700 ccpm air @ 14.7 psig and 70°F). Anhydrous ammonia from cylinder (pressure: 114 psig @ 70°F), supplied by Matheson Ltd. was passed through control valve CV.2 (Milli-mite needle valve) followed by a 'Lo-Flo' flowmeter FM 2 (capacity: 200 ccpm of air @ 14.7 psig, 70°F) supplied by Schutte-Koerting Co. Ltd.). Ammonia flow was regulated with a corrosion resistant line regulator (series 71, supplied by Matheson Ltd.) for an outlet pressure of 0-15 psig. Air supply was taken from laboratory facilities of low pressure air line (outlet pressure: 20 psig) provided with an oil trap. The outlet pressure was regulated with a Barrie-DevilBiss Ltd. regulator (0-100 psig). Flow of air into the system was controlled with CV.3 (Milli-Mite needle valve) and flow was measured with flowmeter FM 3 (capacity: 2270 ccpm of air @ 14.7 psig and 70°F).

Products of ammoxidation, unconverted reactants and nitrogen were passed through a two way stop-cock into the condenser system or the vent. The former consisted of air

cooled and ice cooled condensers. The exit gases were passed over ascarite (sodium hydroxide impregnated on asbestos) bulb to determine the CO_2 content of the exit gases. The exit gases were vented into fume-hood.

Temperature of the catalytic bed was controlled with a Thermo Electric 400 controller of the following specifications:

Range:	0-675°C
ISA Calibration:	K (Chromel-alumel)
Type of Control:	ON-OFF proportional output
Proportional band width:	10 ⁰ -50 ⁰ F adjustable
Reset:	Manual, adjustable

Products of oxidative ammonolysis of m-xylene were analysed on GLC -Series 1520C (Varian Aerograph) with the following specifications:

Detectors:	Thermal conductivity-four filaments, tungsten-rhenium WX, Hot Wire Hydrogen flame ionization
Column oven temperature control:	Linear temperature programmer
Carrier gas:	Helium at 40 psig
Recorder:	Varian Aerograph (1 mv span) Model 30
Disc Chart Recorder:	Model 607

Dual/Differential Electrometer available.

Surface area measurements for various catalysts were made with Perkin-Elmer Shell Model 212D Sorptometer through measurements of nitrogen adsorbed on these materials at the temperature of liquid nitrogen. Calculation of specific surface area is based on the BET equation.

CHAPTER V

EXPERIMENTAL PROCEDURE

The apparatus has been shown in Fig.2 as a flow diagram. Independent flow systems were provided for nitrogen, oxygen and ammonia with precision flow control valves and flowmeters. Dry oxygen and nitrogen from cylinders were fed directly to the reactor with a controlled flow of nitrogen via a side stream going through the xylene vaporizer. Xylene vaporizer was enclosed in a constant temperature oil bath and insulated completely with glass wool. Nitrogen flowing through the vaporizer was saturated with xylene vapor and was mixed with oxygen and ammonia streams. The tubing carrying the reaction mixture was kept warm by winding nichrome heater wire around it and wrapping it with glass wool. This was necessary to avoid condensation of the xylene from the reaction mixture. The reaction mixture flowed through the reactor tube wherein it was raised to a temperature 10-20°C below the desired reaction temperature in the preheating zone, packed with inert alumina granules. The temperature of the exit stream from preheating zone was monitored via thermocouple T/C 2. The heat input through the preheater was controlled with a standard variac. After flowing through the catalyst bed, the reaction mixture was led through the condenser system.

- CV CONTROL VALVES
- FM FLOW METERS
- PR PRESSURE REDUCERS
- TC THERMOCOUPLES
- AC AIR COOLED CONDENSER
- IC ICE COOLED CONDENSER

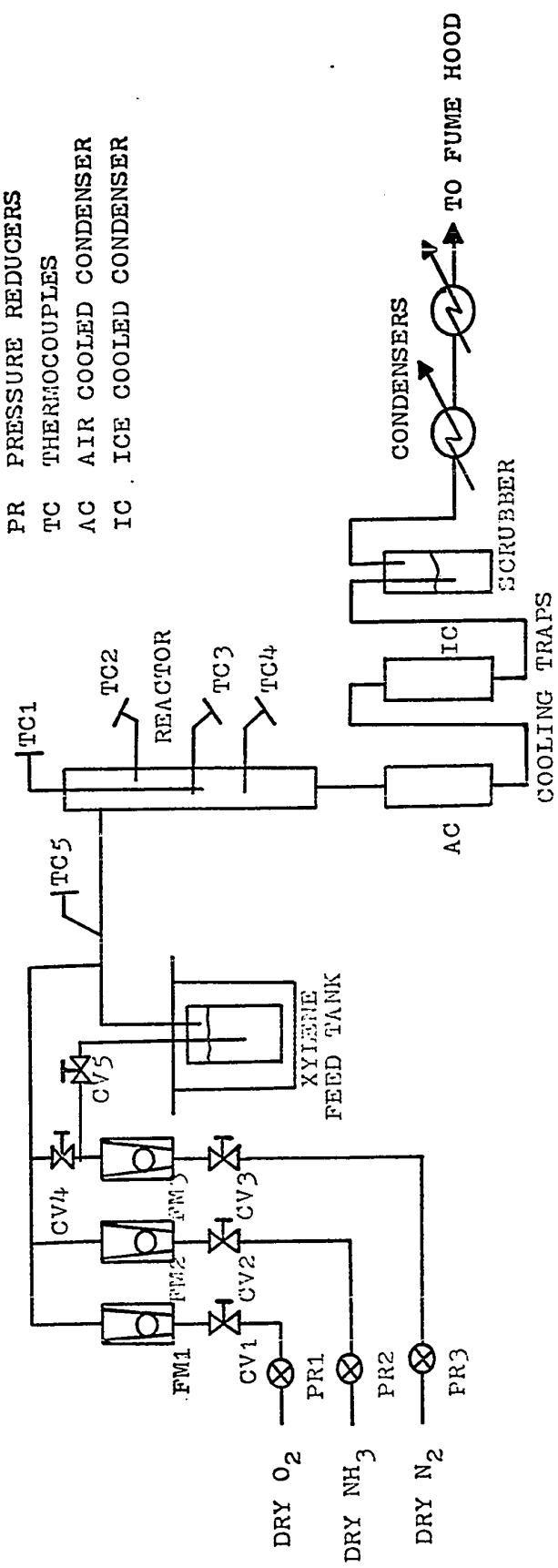


FIGURE 2 SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS

Condenser system consisted of air cooled condenser AC, ice cooled condensers IC and CO₂ absorber. The uncondensed gases were exhausted into fume hood.

Catalyst under screening studies was held in the reaction zone, surrounding the thermocouple's tips. With glass wool plug on the top surface of the catalyst, inert carrier was filled in the remaining length of reactor. System was warmed up slowly by supplying controlled voltages through coil heaters, to avoid undue stresses in the glass set up.

Oil bath temperature was increased and maintained constant at 90°C. Xylene vaporizer was immersed in the oil bath after noting its initial weight. Carrier gas nitrogen was introduced in the vaporizer (xylene bubbler) at such a flow rate that the maximum concentration of xylene in the reaction mixture did not exceed 2% as beyond this concentration of xylene in the feed mixture, possibilities of occurrence of explosion existed (23). Saturated nitrogen passed through the reactor reaction zone where xylene was ammoxidized in the presence of ammonia and oxygen. Time of commencement of xylene feeding was noted.

Temperature indicated by thermocouple T/C 3 was continuously monitored with a potentiometer. When temperature reached 200°C, controlled amounts of oxygen, nitrogen and ammonia were introduced into the system. Flow rates of oxygen, ammonia and nitrogen were such that molar ratios

of NH_3 to xylene was 3-4. This is the suggested range by Gasson et al. (23). Minimum concentration of O_2 was 5% and that of oxylene 3%.

Flow of nitrogen was decided by the bed length provided and the desired contact time for the feed mixture. Flow rate of the key reactant viz. m-xylene was varied independent of other reaction conditions by appropriate adjustment of oil bath temperature and flow rate of nitrogen through the vaporizer. By increasing oil bath temperature and flow rate of nitrogen, flow of m-xylene could be increased and vice-versa. Depending upon the temperature of the feed mixture leaving the preheater zone, power was readjusted so that temperature was $10\text{-}20^\circ\text{C}$ below the temperature at which ammoxidation was desired to be carried out. Temperature of reaction zone as monitored by T/C 1 was fed to the controller where error between set point (desired temperature of reaction $300\text{-}500^\circ\text{C}$) and existing temperature decided the power input into HW 3.

During the unsteady temperature period (normally 1 hour) the products formed were vented into fume-hood. Once controller shows a reasonably (5°C) constant temperature of the bed over a period of 1/2 hour, quantitative sampling of the reaction products were commenced by letting the products, unconverted xylene, N_2 , O_2 , NH_3 flow through the condenser system. Any solid product formed during reaction was deposited in the air condenser while unconverted xylene and intermediate products were condensed in liquid form in the ice cooled condenser tube. The uncondensed components flowed through

a bulb filled with preweighed amount of ascarite (NaOH on asbestos) wherein CO_2 absorbed. HCN would also absorb.

Sampling was continued for a period of 1 hour after which the xylene left in the vaporizer was weighed to know the xylene fed during the period of run (1 hour). Supply of O_2 , ammonia and N_2 for xylene vaporizer was stopped. Nitrogen was allowed to flow through the system for 1 hour after the sampling was over.

The products formed along with unconverted xylene were dissolved in methanol. The sample so obtained was analysed with gas chromatograph for xylene (unconverted), m-tolunitrile and m-phthalonitrile.

ANALYTICAL PROCEDURE

Unreacted m-xylene and products of ammoxidation viz. m-tolunitrile and m-phthalonitrile were separated gas chromatographically.

By injecting standard solution of m-xylene, m-TN and m-PN, retention times of these components under the conditions of chromatography were determined for later identifications.

Calibration charts were prepared for known but varying concentrations of m-xylene, m-TN and m-PN in methanol to know the calibration coefficients.

Sample was made by dissolving the products in methanol. To know the amounts of various products, 'Internal Standard Method' was adopted. In this method, known amounts of suitably chosen internal standards were added. The product's weight in the sample was known from the formula:

Weight of the product = (Weight of Internal standard)x
 (Calibration coefficient)x(Area of the product
 peak/Area of the Internal Standard peak)

The other pertinent details for the gas chromatographic analysis of product's sample were:

Sample size: 0.5 μ l
 Column: 10.0' x 0.125" OD SS
 8% FFAP deposited on AW(DMCS)
 Chromosorb W 60/70
 Detector: Thermal conductivity
 Program: Isothermal at 110°C for 5 min.
 110-175°C at 40°/min.
 175-250°C at 40°/min.
 Temperature: Injector 250°C, Detector 285°C
 Flow rates: Column A 15 ml/min. (Helium)
 Column B 30 ml/min. (Helium)
 Chart Speed: 20"/Hr
 Internal
 Standard: pseudo-cumene for m-xylene and
 m-tolunitrile, o-toluamide for
 m-phthalonitrile.

For the products of complete oxidation, the following procedure was adopted.

For HCN, titration of an alkali solution in which the gas had been dissolved against a standard N/50 H₂SO₄ solution gave the amount of HCN formed during the sampling period.

For CO₂, ascarite bulb increase in weight during sampling was equivalent to the CO₂ formed.

CHAPTER VI
CATALYSTS INVESTIGATED

The catalysts subjected to screening tests to ascertain their effectiveness for accomplishing oxidative ammonolysis of m-xylene are tabulated in Table III on page 25. In the table also appear the physical properties of the catalysts - surface area in m^2/g and bulk density in g/cc .

The method of preparation of various catalysts is outlined next.

PREPARATIONS:

CATALYST #1. Vanadium oxide (0.5 parts) was suspended in distilled water (5), heated to $90^{\circ}C$, and oxalic acid (1.5-2) gradually added until vanadium oxide was completely reduced to give a clear blue solution of vanadyl oxalate this solution was poured over 8-14 mesh inert alundum (9) and evaporated to dryness at $100^{\circ}C$ with constant stirring of the mass. The impregnated carrier was calcined at $400^{\circ}C$ for 12 hours in a stream of air to give 5% V_2O_5 on alundum. This catalyst was aged under catalytic conditions for a day before use.

CATALYST #2. Preparation procedure outlined above for catalyst #1 was repeated except that 8-14 mesh activated γ -alumina (9 parts) was used.

CATALYST #3. Preparation procedure outlined above for catalyst #2 was repeated except that 8-14 mesh activated

Table IV
Catalysts Investigated And Their Method Of Preparation

Cat. #	Carrier (Pretreatment)	Compound Impregnated on the Carrier	Percentage of the Compound Impregnated (g/g)	Method of Impregnation	Surface Area of the Catalyst (m ² /g)	Bulk Density of the Catalyst (g/cc)
1	8-14 mesh Inert γ -alumina (Nil)	V ₂ O ₅	5	Precipitation	0.3	1.60
2	8-14 mesh Activated γ -alumina (Nil)	V ₂ O ₅	5	Precipitation	52	0.88
3	8-14 mesh Activated γ -alumina (900°C, 12hrs)	V ₂ O ₅	5	Precipitation	67	0.99
4	8-14 mesh Activated γ -alumina (1250°C, 12hrs)	V ₂ O ₅	5	Precipitation	93	0.90
5	8-14 mesh Activated γ -alumina (1250°C, 12hrs)	V ₂ O ₅	10	Precipitation	99	0.95
6	8-14 mesh Activated γ -alumina (1250°C, 12hrs)	V ₂ O ₅	20	Precipitation	108	1.05 (contd.)

Table IV (contd.)

Cat. #	Carrier (Pretreatment)	Compound Impregnated on the Carrier	Percentage of the Compound Impregnated (g/g)	Method of Impregnation	Surface Area of the Catalyst (m ² /g)	Bulk Density of the Catalyst (g/cc)
7	8-14 mesh Activated γ -alumina (1250°C, 12hrs)	5% V ₂ O ₅ 5% MoO ₃	10	Co-precipitation	91	1.00
8	8-14 mesh Activated γ -alumina (1250°C, 12hrs)	V ₂ O ₅ :MoO ₃ :CrO ₃ 10:10:1	10	Co-precipitation	103	0.95
9	8-14 mesh Activated γ -alumina (1250°C, 12hrs)	V ₂ O ₅ :MnO ₃ :CrO ₃ 10:10:1	10	Co-precipitation	113	0.95
10	8-14 mesh Activated γ -alumina (1250°C, 12hrs)	V ₂ O ₅ :CrO ₃ :PbO 10:10:1	10	Co-precipitation	85	0.95
11	8-14 mesh Activated γ -alumina (1250°C, 12hrs)	V ₂ O ₅ :CrO ₃ :CoO 10:10:1	10	Co-precipitation	100	0.95
12	8-14 mesh Activated γ -alumina (1250°C, 12hrs)	V ₂ O ₅ :CrO ₃ :B ₂ O ₃ 10:10:1	10	Co-precipitation	110	0.95

(contd.)

Table IV (contd.)

Cat.#	Carrier (Pretreatment)	Compound Impregnated on the carrier	Percentage of the compound Impregnated (g/g)	Method of Impregnation	Surface Area of the Catalyst (m ² /g)	Bulk Density of the Catalyst (g/cc)
13	8-14 mesh Activated -alumina (1250°C, 12 hrs)	V ₂ O ₅ :CrO ₃ :Sb ₂ O ₃	10	Co-precipi- tation	95	0.95
14	-nil-	Tin Vanadate	-na-	Precipi- tation	45	1.3
15	-nil-	Manganese p-tungstate	-na-	Precipi- tation	48	1.9
16	8-14 mesh Activated -alumina (1250°C, 12hrs)	MoO ₃	10	Precipi- tation	85	0.95

alumina used was precalcined at 900°C for 12 hours.

CATALYST #4. Preparation procedure outlined above for catalyst #2 was repeated except that 8-14 mesh activated alumina used was precalcined at 1250°C for 12 hours.

CATALYST #5. Preparation procedure outlined in the case of catalyst #4 was repeated except that 8-14 mesh pre-activated alumina (4.5 parts) was impregnated with the solution of vanadyl oxalate to give 10% V_2O_5 on alumina.

CATALYST #6. Preparation procedure outlined in the case of catalyst #4 repeated except that 8-14 mesh pre-activated alumina (2.25 parts) was impregnated with the solution of vanadyl oxalate to give 20% V_2O_5 on alumina.

CATALYST #7. Vanadium oxide (1.5 g) was suspended in water (20 g) and reduced to a blue solution of vanadyl oxalate at 90°C with oxalic acid (5.2 g). Ammonium molybdate (1.94 g equivalent to 1.5 g MoO_3) was added to the above solution. Pre-activated alumina (8-14 mesh) (27 g) was added to the solution. Water was evaporated at 100°C with constant stirring of the mass. The impregnated carrier having 5% V_2O_5 and 5% MoO_3 was calcined at 400°C for 12 hours in a stream of air and finally aged for a day under catalytic conditions before screening tests were performed on it.

CATALYST #8. To a hot (90°C) suspension of V_2O_5 (2.69g) in water (30g) oxalic acid (6.73g) was added. The resulting blue solution of vanadyl oxalate was mixed with a solution of CrO_3 (2.97g) in water (30g) reduced with oxalic acid (11.42g). The solution thus obtained was further mixed with

ammonium molybdate (0.53g) and preactivated alumina (33g).

Water was evaporated with constant stirring of the mass and the impregnated carrier was calcined at 400°C for 12 hours in a stream of air to give a composition of V:Cr:Mo :: 10:10:1.

CATALYST #9. Added manganese nitrate (0.8g) instead of ammonium molybdate as outlined above for catalyst #8, to give a composition of V:Cr:Mn :: 10:10:1.

CATALYST #10. Added lead nitrate (0.98g) instead of ammonium molybdate as outlined above for catalyst #8, to give a composition of V:Cr:Pb :: 10:10:1.

CATALYST #11. Added cobalt nitrate (0.87g) instead of ammonium molybdate as outlined above for catalyst #8, to give a composition of V:Cr:Co :: 10:10:1.

CATALYST #12. Added o-boric acid (1.82g) instead of ammonium molybdate as outlined above for catalyst #8, to give a composition of V:Cr:B :: 10:10:1.

CATALYST #13. Added antimonyl oxide (0.36g) in the form of antimonyl tartrate instead of ammonium molybdate as outlined above for catalyst #8, to give a composition of V:Cr:Sb :: 10:10:1.

CATALYST #14. Ammonium vanadate (25g) was dissolved in water (400 cc) at 85°C. To the solution thus obtained was added gradually stannic chloride (13.8g)-highly diluted. The orange colored precipitate of tin vanadate obtained was washed several times with distilled water to dissolve out ammonium chloride formed during precipitation of tin vanadate. The precipitate was filtered and dried in an oven at 100°C

for 6 hours with occasional stirring to give 27.5g of tin vanadate. It was calcined in the reactor at 400°C for 4 hours in a stream of air.

CATALYST #15. Ammonium p-tungstate (13.4g) was dissolved in hot (80°C) water (170 cc) with stirring. To this solution was added dropwise over a period of 5 minutes another solution obtained by dissolving manganese nitrate (6.1g) in water (20 cc). The precipitate of manganese p-tungstate obtained was washed and magnesium nitrate (5.7g) dissolved in water (5 cc) added. Water was evaporated by heating in a water bath, paste was shaped into small globules (1/8") and left for drying in an oven at 100°C for 6 hours. The granules obtained were calcined at 450°C for 4 hours before use.

CATALYST #16. Preactivated alumina (23 parts) was mixed with a solution of ammonium molybdate (1.5) in water (8) and concentrated ammonium solution (1). The mixture was dried with stirring and calcined at 450°C for 6 hours to give 10% MoO₃ on alundum.

CHAPTER VII

RESULTS AND DISCUSSION

The objective of this study was to obtain data on catalyst performance under high conversion conditions so that commercial conditions of reactor operation were approached as closely as possible. The reactor was thus operated as an integral one.

The kinetic equation for an integral reactor is given by,

$$r = dN_i'/dV \quad (12)$$

where r is the point rate of reaction in moles/(sec.)(cc), dN_i' is the change in molal rate of flow of a component i in (moles/sec.), and dV is the differential element of reactor volume.

Yield of the reaction for a product P (η_p) has been defined as follows.

$$\eta_p = \sigma_p \zeta_A \quad (13)$$

where σ_p : fraction of product P in the reaction products, in other words selectivity for P (dimensionless number)

ζ_A : fraction of key reactant A converted into products - i.e., relative degree of conversion of A (dimensionless number)

Selectivity of the reaction for the product P (σ_p) when expressed on molar basis and the stoichiometry of the reaction equation is taken into account, ranges from 0 to 1.0. The following definition for σ_p is used.

$$\sigma_P = \xi_P \mathcal{J}_A^{M_A} / \xi_A \mathcal{J}_P^{M_P} \quad (14)$$

where ξ_P, ξ_A : degree of conversion to product P and of key reactant A, respectively (dimensionless number)

$\mathcal{J}_P, \mathcal{J}_A$: stoichiometric coefficients for species P and A, respectively (dimensionless number)

M_P, M_A : molar mass of species P and A, respectively (g/g mols)

Degree of conversion ξ_J of a component J is so defined that it is positive always. Thus,

$$\xi_J = \frac{W_{J_0} - W_J}{W_{J_0}} \quad (15)$$

where W_{J_0}, W_J are the mass fractions of any component J initially and finally, respectively.

Rating of a catalyst is defined as an arbitrary number below.

$$R_i = 100x \left(\frac{\sigma_{P_i}}{T_i} x \bar{\tau}_i \right) \quad (16)$$

where R_i : Rating of catalyst i ($^{\circ}\text{C} \cdot \text{sec.}$)⁻¹

σ_{P_i} : Selectivity of the reaction for product P with catalyst (dimensionless number)

T_i : Average catalyst (i) bed temperature ($^{\circ}\text{C}$)

$\bar{\tau}_i$: Average residence time for the feed mixture in the catalyst (i) bed (sec.)

Average residence time ($\bar{\tau}$) - also termed as contact time has been calculated as follows.

$$\bar{\tau} = \frac{V_c}{Q_R} \quad (17)$$

where V_c : volume of the catalyst in the reaction zone (cc)

Q_R : volumetric flow rate of the feed mixture at
NTP (cc/sec.)

Space Velocity (SV) is the inverse of contact time in
hours. Thus,

$$SV = Q_R' / V_c \quad (18)$$

where Q_R' : volumetric flow rate of the feed mixture at
NTP (cc/hr)

The reaction products obtained in significant yields were

1. meta-phthalonitrile
2. meta-tolunitrile
3. hydrocyanic acid
4. CO_2, H_2O

The temperature range studied was, as stated earlier
250-500°C. Yield of m-phthalonitrile ranged from 0 to 86%,
depending upon the reaction conditions employed and the catalyst
in use. Yield of m-tolunitrile ranged from 0 to 50%. Influence
of presence of water vapor in the reaction mixture upon the
yields of various ammoxidation products was studied over a
range of 0 to 70% water vapor in the feed mixture. Influence
of contact time over yield was studied by varying $\bar{\tau}$ over 0.1-1.0
second.

The major product of oxidative ammonolysis of m-xylene
was m-phthalonitrile though significant quantities of m-tolu-
nitrile were obtained at low temperatures and contact times.

At temperatures $\geq 500^{\circ}\text{C}$, substantial proportion of m-xylene was oxidized completely into CO_2 , H_2O .

The exact kinetics of the reaction - oxidative ammonolysis of m-xylene, are not known. The present work does not aim at investigating the kinetics of this reaction system; its primary objective was to analyse the data to ascertain the relative effectiveness of various catalysts on the basis of yield and selectivity in the outlet stream.

The criterion for comparison of catalysts has to be arrived at rationally so that commercial importance of various products - specially mono and dinitriles, is appropriately accounted for. The combined selectivity for m-tolunitrile and m-phthalonitrile is a satisfactory criterion if the objective is to maximize production of nitriles - mono and di. This would be the case if facilities for recycling intermediate product m-tolunitrile, exist. Of course, if the primary interest is in commercial value of m-phthalonitrile alone, selectivity should be based upon m-phthalonitrile only. However, m-tolunitrile as an end product has been found to possess important industrial applications, such as in the preparation of polymers useful for coatings, goes into the production of nail lacquers, photochromic paper for ultra-violet pulse lasers, heart-affecting pharmaceuticals and exhibits fungicidal activity. Besides, the mono - (B.P. 213°C) and di-nitrile (M.P. 162°C) can be easily separated as pure compounds. Thus it is justifiable from the

standpoint of commercial exploitation value of each product that the evaluation of a catalyst be based on selectivity for total nitriles.

The implication of the criterion for catalyst evaluation stated above, is that a catalyst with a high selectivity converts substantial fraction of m-xylene into the desired products; nitriles. A low selectivity signifies poor activity of the catalyst for nitriles - i.e., majority of the key reactant; m-xylene, is being converted into undesirables; CO, CO₂, etc.

Ultimately, the merits of a complex reaction operation are intimately related to the amount of a desired product obtained with respect to the amount of a key reactant fed - i.e., yield of the reaction. However, a low yield but high selectivity is generally acceptable since the unconverted m-xylene could be separated from the products and recycled.

A. Data Compilation

The data obtained has been tabulated in Appendix II. Reliability of the data was assured by using suitable precautions in taking readings during the course of experimental runs. Thus, weight of m-xylene fed was measured to an accuracy of .01 g (maximum error 4%). GC analysis of product samples was repeated for random runs to ensure reproducible results, temperature of the reaction was measured with fast response and extremely sensitive chromel/alumel thermocouples (maximum error $\pm 1^{\circ}\text{C}$, and flow rates of NH₃, O₂ and N₂ were determined with precision rotameters (maximum error 2%). A maximum cumulative error of 10% is estimated in the data reported, on the basis of errors in readings.

In order to study the effect of activity of carrier on the yield and selectivity of nitriles, runs (#1-13) were made with 5% V₂O₅ deposited on 1. Inert and 2. Activated alumina (no precalcination).

Precalcination of the carrier was performed at two temperatures - 900° and 1250°C . Beneficial effects of precalcination of the carrier were studied (runs # 14-25) by screening the following catalysts:

3. 5% V_2O_5 deposited on activated alumina (precalcined at 900°C for 12 hours).
4. 5% V_2O_5 deposited on activated alumina (precalcined at 1250°C for 12 hours).

Optimum concentration of the catalyst on the activated carrier (precalcined at 1250°C for 12 hours) was studied (run # 26-33) by screening the following catalysts:

5. 10% V_2O_5
6. 20% V_2O_5
7. MoO_3 as a catalyst was tried out (run # 34-37) by depositing 10% of it on activated alumina (precalcined at 1250°C for 12 hours).

The following binary catalysts were subjected to ammoxidation runs to study the influence of incorporation of other metallic compounds (deposited on activated, precalcined alumina) on yield and selectivity of nitriles.

8. $\text{V}_2\text{O}_5 - \text{MoO}_3$ (runs # 38-41)
9. $\text{SnCl}_4 - \text{NH}_4\text{VO}_3$ (runs # 70-75)
10. ammonium-paratungstate - $\text{Mn}(\text{NO}_3)_2$ (runs # 42-46)

Mixed oxides V-Cr-X, where X denotes the following oxides were also studied for their selectivity for nitriles.

11. Pb (II) (runs # 63-66)
12. Mo (VI) (runs # 51-54)

13. Sb (III) (runs # 55-58)
14. Co (II) (runs # 67-70)
15. Mn (II) (runs # 47-50)
16. B (III) (runs # 59-62)

The influence of contact time (0.1, 0.4, 0.8, 1.0 sec.) on yield of mono-nitrile, dinitrile and total ammoxidation products was studied (runs # 76-91) on tin vanadate as the catalyst.

The influence of water vapour in the reaction mixture (moles of water vapour per mole of mOxylene fed = 4, 40, 85) on the yields of nitriles was studied (runs # 92-104) on tin vanadate as the catalyst.

B. Discussion of Results

Results of the runs made on various catalysts mentioned above have been tabulated in Appendix III.

I. Inert Alumina as Carrier for V_2O_5

Figure 3 is a plot of yield and selectivity for total nitriles (m-tolunitrile and m-phthalonitrile) in the temperature range 350-550°C with 5% V_2O_5 deposited on inert alumina as the catalyst. Due to a low surface area for the catalyst ($0.3 \text{ m}^2/\text{g}$), it had a very poor yield for nitriles (maximum of 8% at 500°C). Of the xylene converted into products, a maximum of 40% was converted into nitriles in the temperature range 350-400°C and a space velocity of 7160 hrs^{-1} . The low yields and selectivities obtained in the reaction with catalyst on inert carrier was due to a lack of pore structure of the carrier which allowed but very short contact time between the catalyst and reaction mixture.

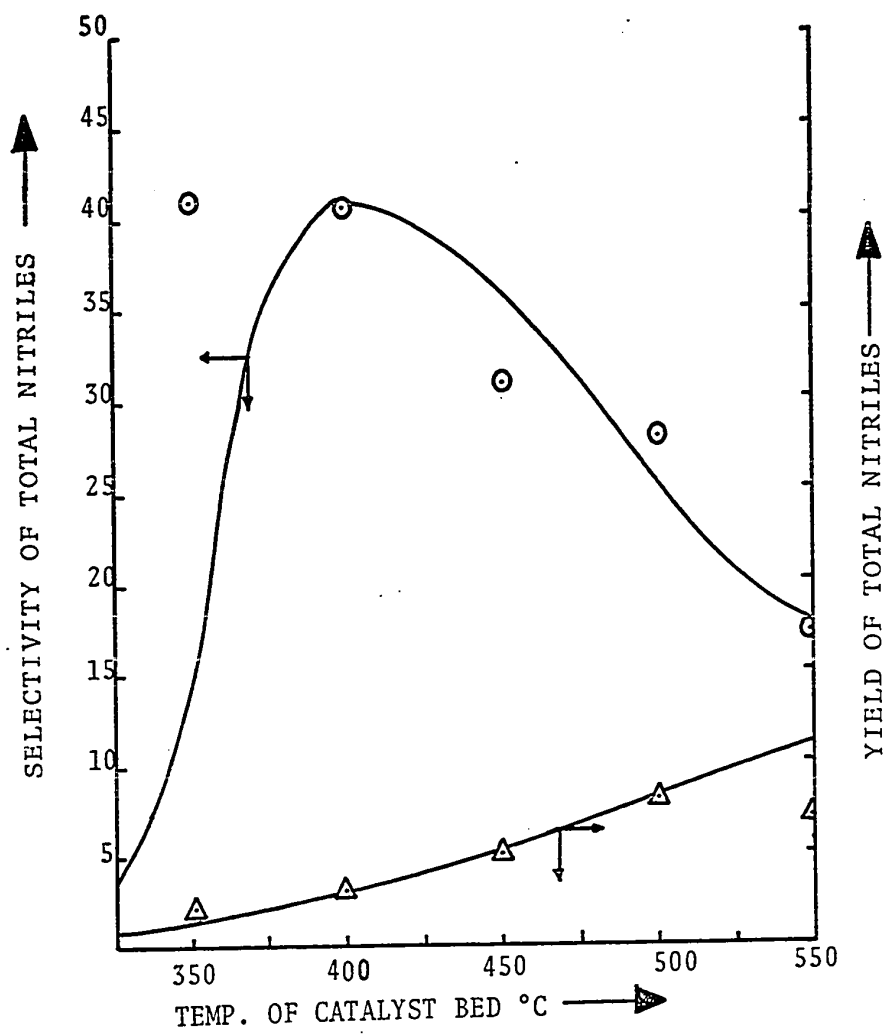


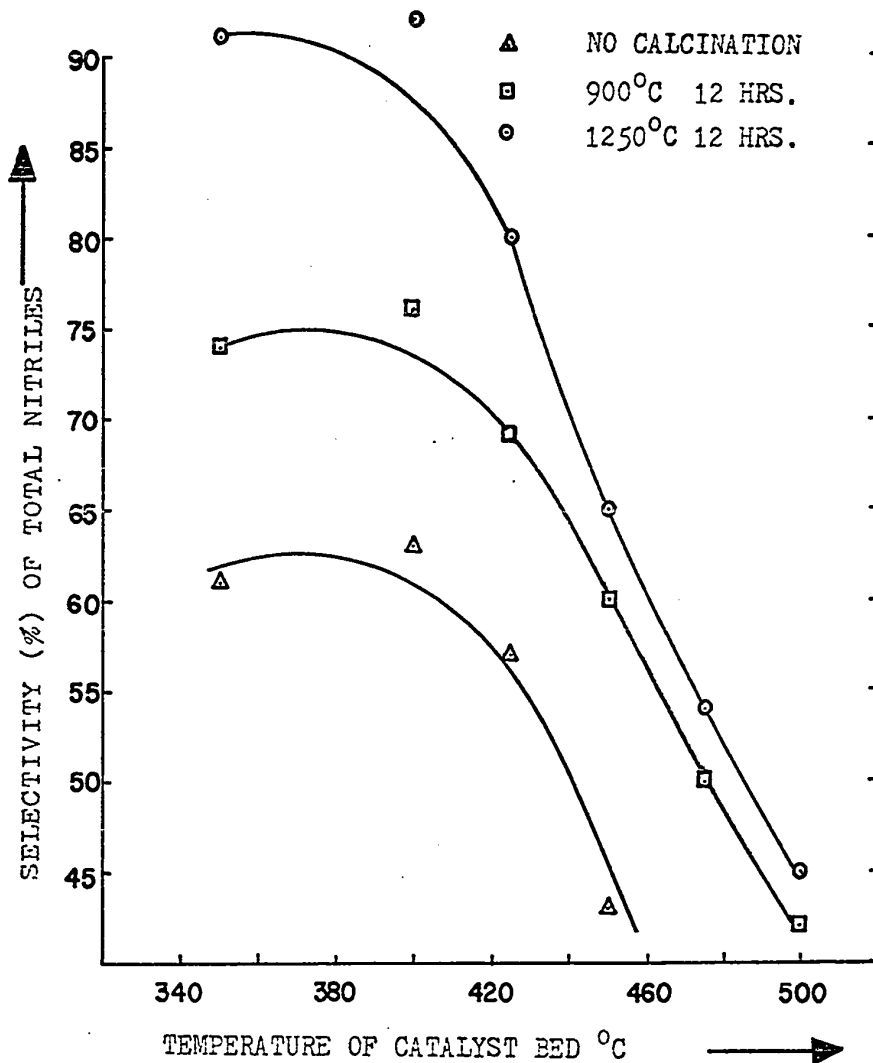
FIGURE 3. V_2O_5 DEPOSITED ON INERT CARRIER
EFFECT OF REACTION TEMPERATURE ON
YIELD AND SELECTIVITY FOR TOTAL
NITRILES

The arbitrarily defined Rating of the catalyst is very low (Appendix III - VANADIA-I) showing the catalyst to possess poor performance characteristics.

II. Effect of Activity of the Catalyst Carrier

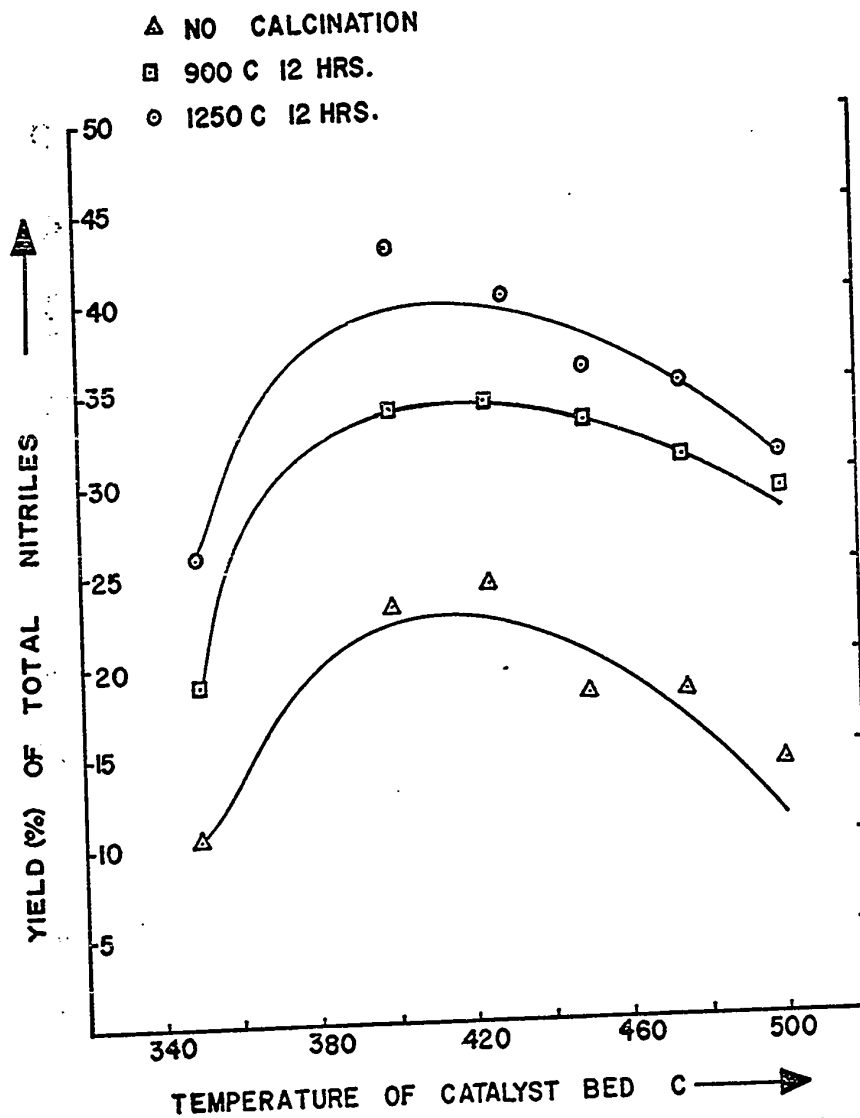
The selectivity of the catalyst is considerably improved by impregnation of the oxide of vanadium on activated alumina. Alumina was activated by precalcination, heating in a muffle furnace at 900 and 1250°C for 12 hours. The results of the runs made with this catalyst are shown in figures 4A, 4B where yields and selectivities for total nitriles have been plotted against temperature of the catalyst bed for no calcination and precalcination at 900 and 1250°C of the carrier. Under identical conditions of reactor operation, yield for nitriles is improved to about 20% for the catalyst impregnated on a carrier which is precalcined at 1250°C for 12 hours. The catalyst shows good selectivity for nitriles (a maximum of 92% at 400°C) in the temperature range 380-410°C but it drops significantly at higher temperatures. Thus higher the temperature of precalcination of the carrier better is the selectivity for nitriles. This is due to the fact that precalcination opens up the porous structure of the catalyst by expelling entrapped gases and thus exposing more area for contact with the reactants. However, a temperature of precalcination beyond 1250°C can only achieve little improvement in the selectivity for nitriles beyond the 92% obtained for precalcination at 1250°C.

III. Effect of per cent V_2O_5 deposited on precalcined (1250°C for 12 hours) carrier



OXIDATIVE AMMONOLYSIS OF *m*-XYLENE ON 5% VAN. OXIDE
DEPOSITED ON ACTIVATED ALUMINA

FIGURE 4A EFFECT OF PRETREATMENT OF CARRIER ON
SELECTIVITY FOR NITRILES AT VARIOUS TEMPS.



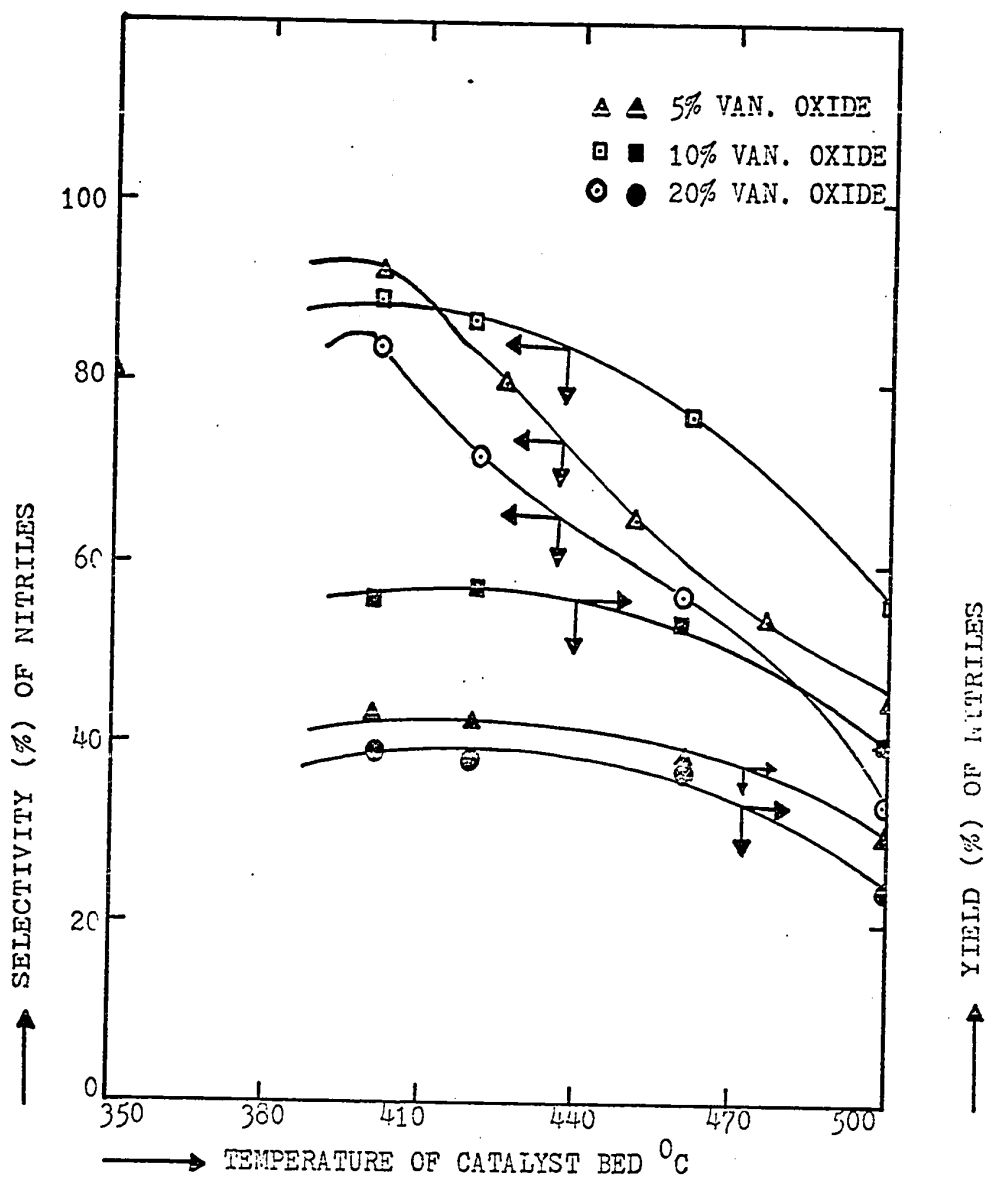
OXIDATIVE AMMONOLYSIS OF M-XYLENE ON 5% VAN. OXIDE
DEPOSITED ON ACTIVATED ALUMINA
FIGURE 4B EFFECT OF PRETREATMENT OF CARRIER ON
YIELD OF NITRILES AT VARIOUS TEMPERATURES

Figure 5 shows the influence of impregnation of various percentages of V_2O_5 -5,10,20 on the yield and selectivity for nitriles. The overall activity is marginally increased for 10% V_2O_5 as compared to that for 5% V_2O_5 (maximum of 57% yield at 420°C for 10% V_2O_5 compared to a maximum of 43% at 400°C for 5% V_2O_5). Selectivity for nitriles is not significantly affected by higher percentages of oxide on the carrier. Yield and selectivity for nitriles for 20% V_2O_5 were uniformly lower than that for 5% V_2O_5 in the temperature range investigated. This could probably be due to the fact that the deposition of 20% V_2O_5 causes formation of more than monolayer of V_2O_5 - whereby layers underneath the outermost layer are not exposed to the reaction mixture. However, surface area determinations showed 20% V_2O_5 catalyst having a higher surface area than 5% V_2O_5 (see Table IV, pp 25).

Figure 6 shows the yield and selectivity for nitriles - m-tolunitrile and m-phthalonitrile separately, for 10% V_2O_5 on precalcined (1250°C for 12 hours) alumina. Selectivity for m-phthalonitrile is fairly constant over the temperature range 400-460°C while that for m-tolunitrile decreases gradually in this temperature range.

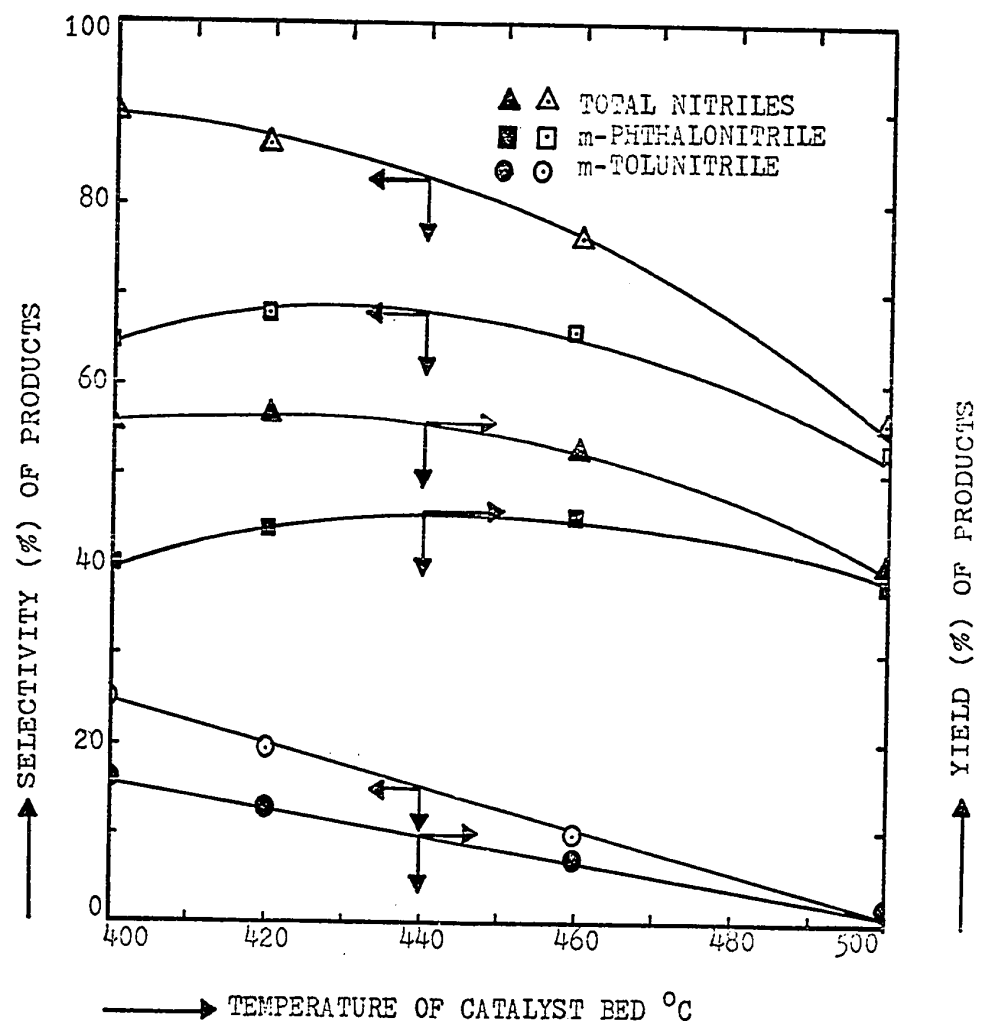
IV. MoO_3 on Activated Precalcined Alumina

Figure 7 shows the yields and selectivities for total nitriles obtained with 10% MoO_3 deposited on precalcined alumina in the temperature range of 350-500°C. At a space velocity of 3870 hrs⁻¹ with 4 moles of ammonia and 20 moles of oxygen for each mole of m-xylene in the reaction mixture, a maximum



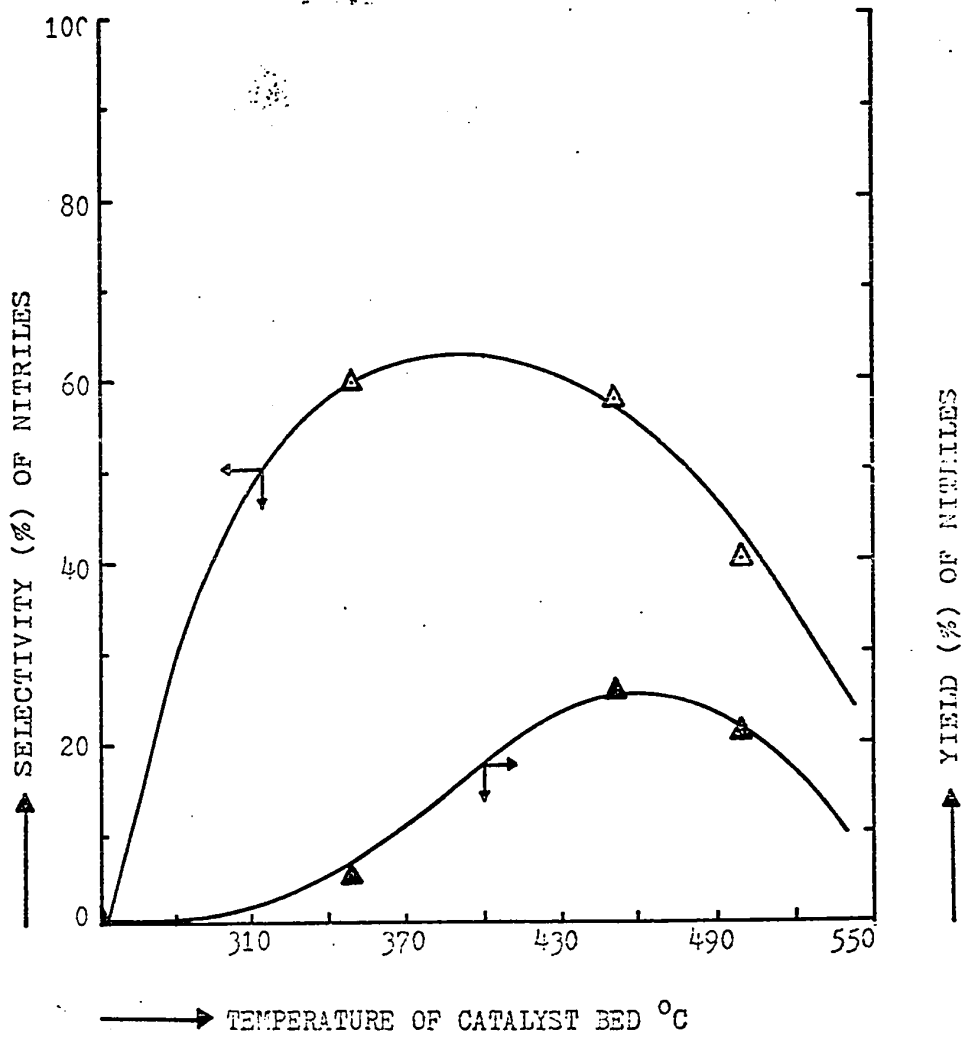
OXIDATIVE AMMONOLYSIS OF *m*-XYLENE ON VAN. OXIDE
DEPOSITED ON PRECALCINED ALUMINA CARRIER

FIGURE 5 EFFECT OF % OF VAN. OXIDE DEPOSITED ON
SELECTIVITY AND YIELD OF NITRILES



OXIDATIVE AMMONOLYSIS OF m-XYLENE ON 10% VAN. OXIDE DEPOSITED ON PRECALCINED ALUMINA CARRIER

FIGURE 6 EFFECT OF TEMPERATURE ON PRODUCT DISTRIBUTION



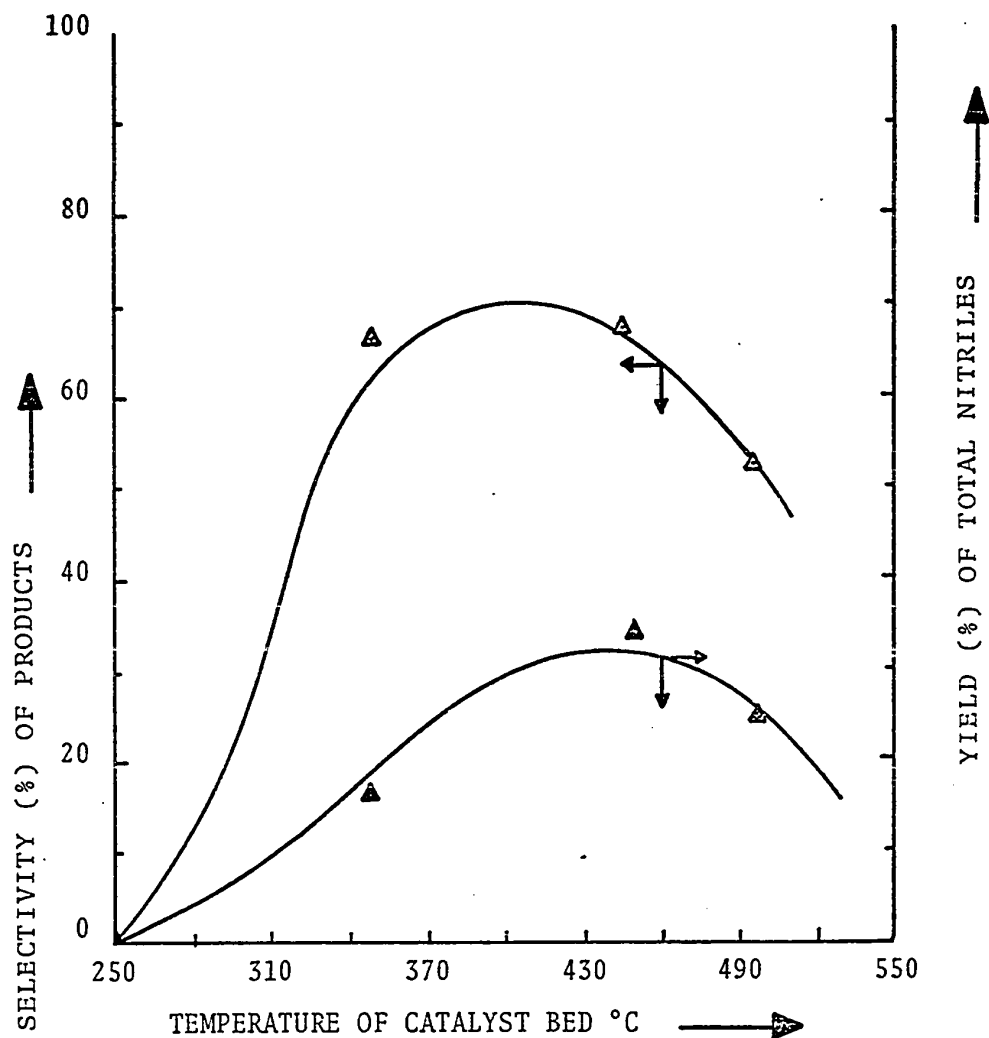
OXIDATIVE AMMONOLYSIS OF *m*-XYLENE ON 10% MoO₃
ON PRECALCINED ALUMINA CARRIER

FIGURE 7 EFFECT OF TEMPERATURE ON PRODUCT DISTRIBUTION

selectivity of 60% (yield 25%) for total nitriles is obtained in the temperature region of 350-450°C. The catalyst shows lower activity for ammoxidation of m-xylene even at a contact time of 0.93 secs as compared to 0.5 secs for V₂O₅.

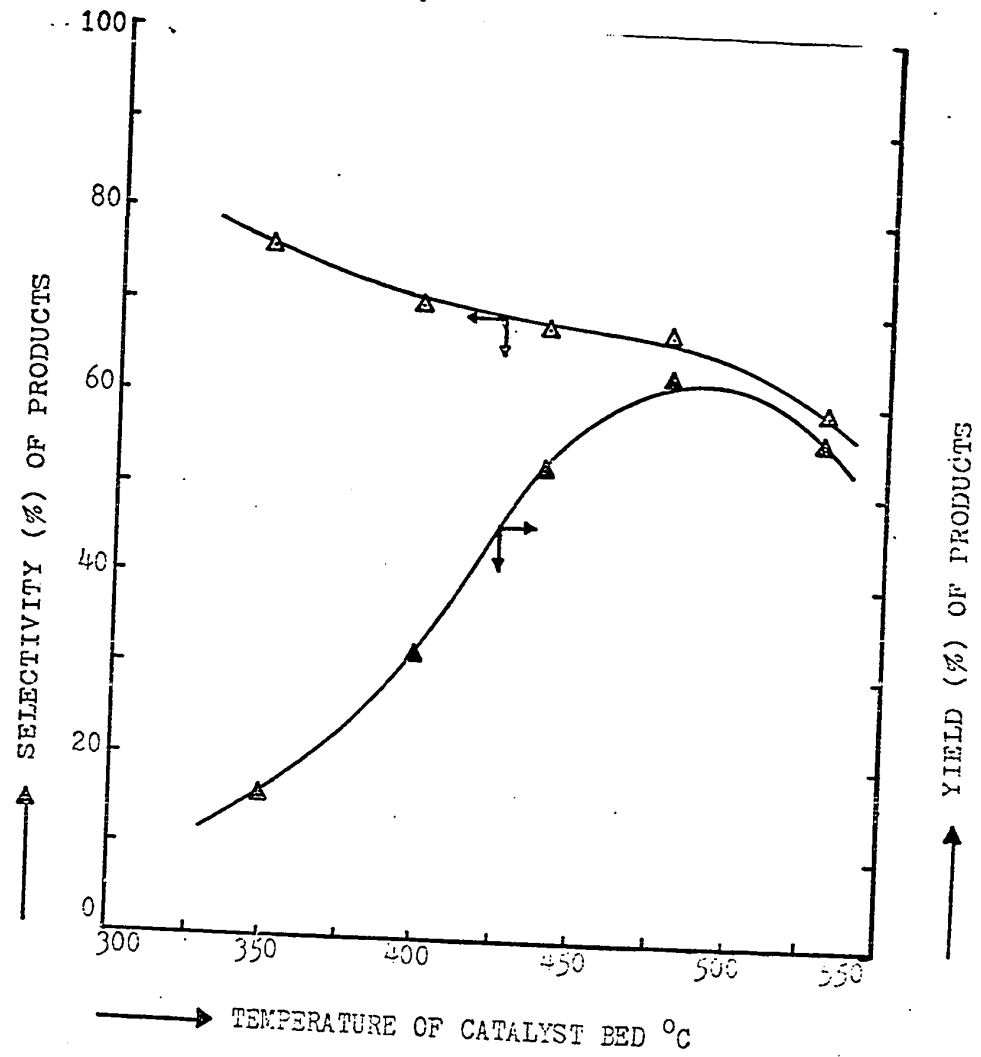
V. Binary Catalysts

The influence of incorporation of Mo, W, Mn and Sn oxides to catalysts based upon V₂O₅ on the yield and selectivity for total nitriles are plotted in Figures 8 to 11. Catalyst based upon 5% MoO₃-5% V₂O₅ shows marginal improvement in the yield and selectivity for total nitriles as compared to those for 5% MoO₃ (Figure 8). Figure 9 shows the yields and selectivities for total nitriles over manganese p-tungstate as the catalyst at a space velocity of 1370 hrs⁻¹ in the temperature range of 300-550°C. The maximum yield (65%) and selectivity (75%) for nitriles are obtained at a temperature of 480°C. The comparative evaluation of this catalyst shows it to possess a low rating for nitriles (see Appendix III). Perhaps the catalyst has its importance in the selective conversion of o-xylene to o-phthalonitrile as compared to m-xylene. Figure 10 shows the effect of temperature on the yield and selectivity for nitriles, on total conversion of m-xylene and conversion of xylene to CO, CO₂, HCN. Conversion of m-xylene to complete ammoxidation products increases with temperature and becomes a predominant product beyond 500°C.



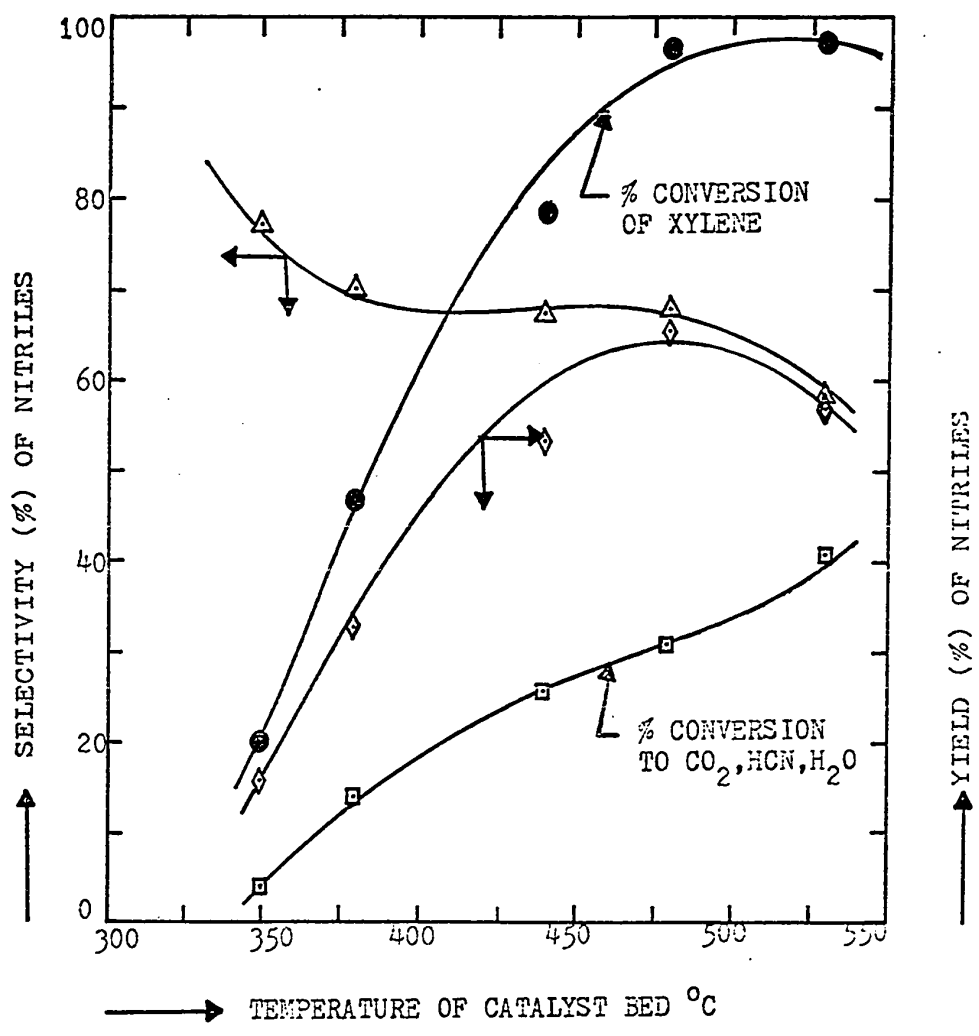
OXIDATIVE AMMONOLYSIS OF M-XYLENE ON 5% MoO_3 -5% V_2O_5
ON PRECALCINED ALUMINA

FIGURE 8 EFFECT OF TEMPERATURE ON SELECTIVITY OF PRODUCTS



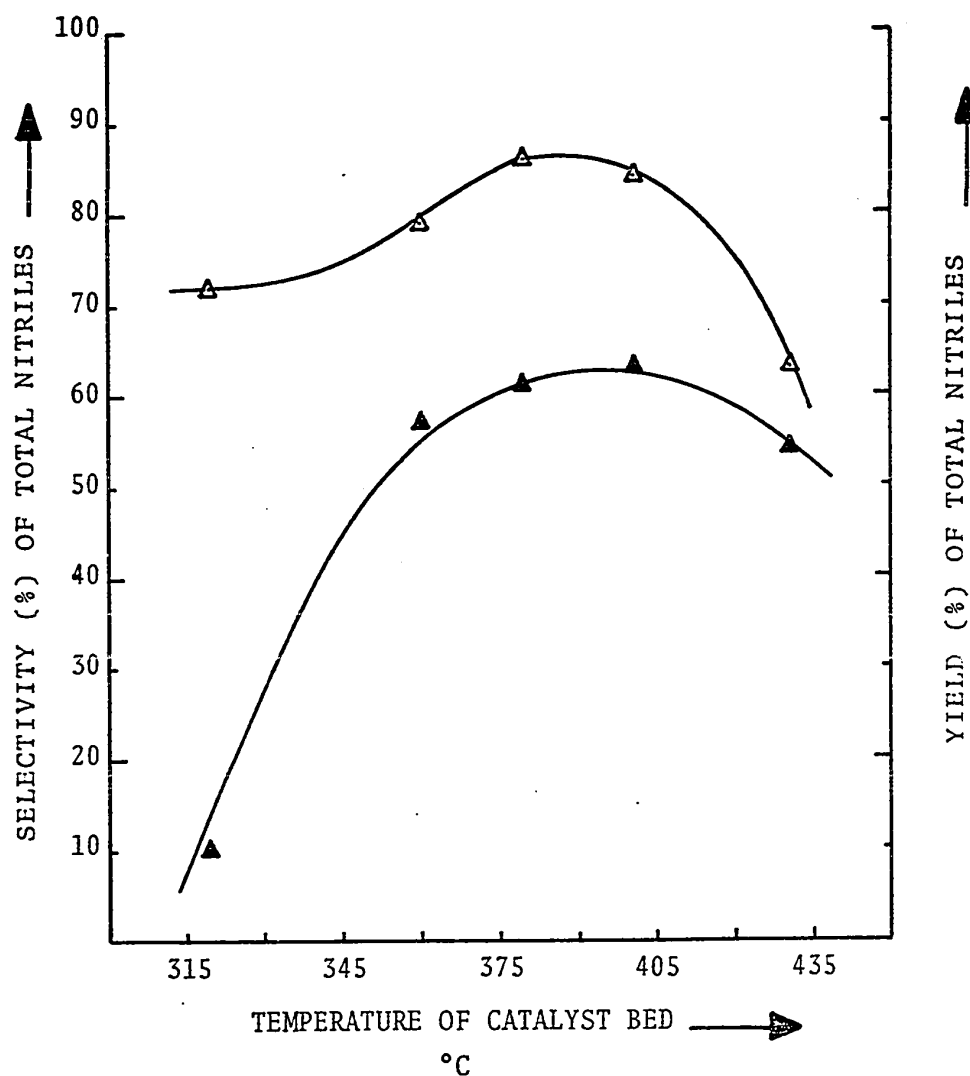
OXIDATIVE AMMONOLYSIS OF m-XYLENE ON MANGANESE p-TUNGSTATE

FIGURE 9A EFFECT OF TEMPERATURE ON SELECTIVITY AND YIELD OF PRODUCTS



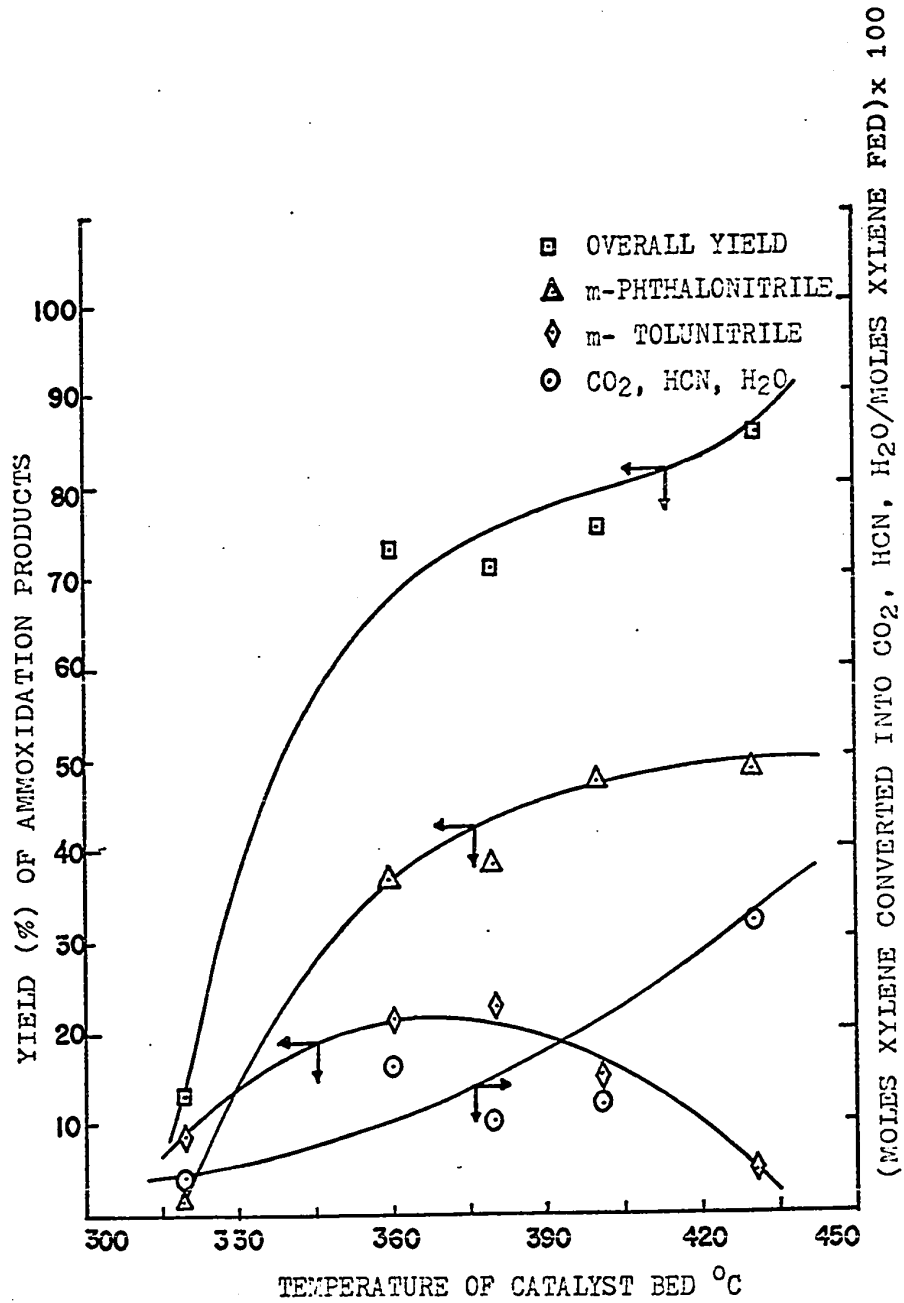
OXIDATIVE AMMONOLYSIS OF *m*-XYLENE ON MANGANESE *p*-TUNGSTATE

FIGURE 9B EFFECT OF TEMPERATURE ON TOTAL YIELD AND SELECTIVITY OF NITRILES



OXIDATIVE AMMONOLYSIS OF M-XYLENE ON
TIN VANADATE

FIGURE 10 EFFECT OF REACTION TEMPERATURE
ON SELECTIVITY OF TOTAL NITRILES



OXIDATIVE AMMONOLYSIS OF m-XYLENE ON TIN VANADATE

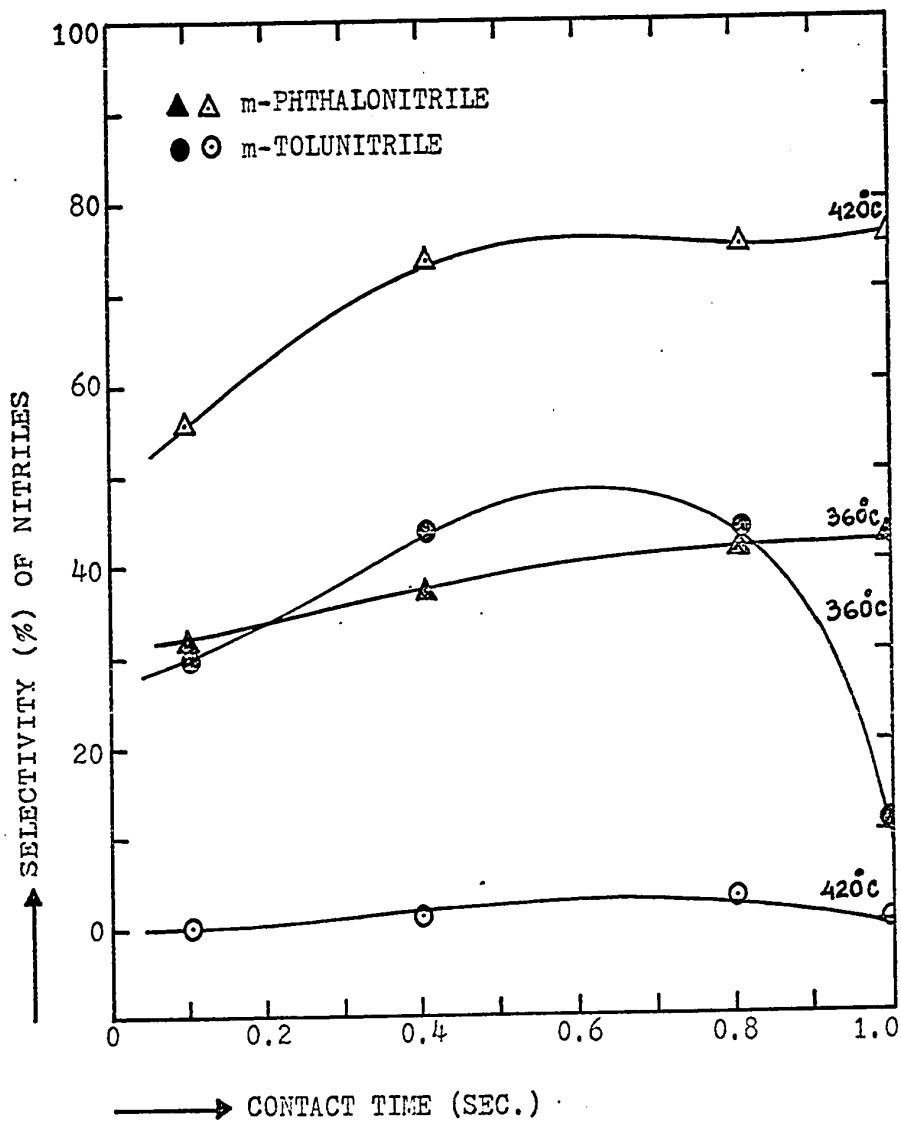
FIGURE 11 PRODUCTS DISTRIBUTION AS A FUNCTION OF TEMPERATURE

Figure 10 shows the equivalent plot for tin vanadate as the catalyst. The temperature of the catalyst was varied over the range 325-425°C and the space velocity was maintained constant at 8000 hrs⁻¹. A maximum yield of 65% at 400°C for total nitriles is obtained with a corresponding selectivity of 85%. Comparative evaluation of the catalysts shows it to possess very good rating for nitriles (Appendix III). Rating of the catalyst - manganese p-tungstate for m-phthalonitrile is 0.05 while that for tin vanadate is 0.36.

Figure 11 shows the overall yield and selectivity for mono and dinitriles as a function of temperature for tin vanadate as the catalyst. This catalyst shows a broad temperature range (330-420°C) over which the yield for m-phthalonitrile is fairly constant. Conversion to complete ammoxidation products is marginal only in this temperature range.

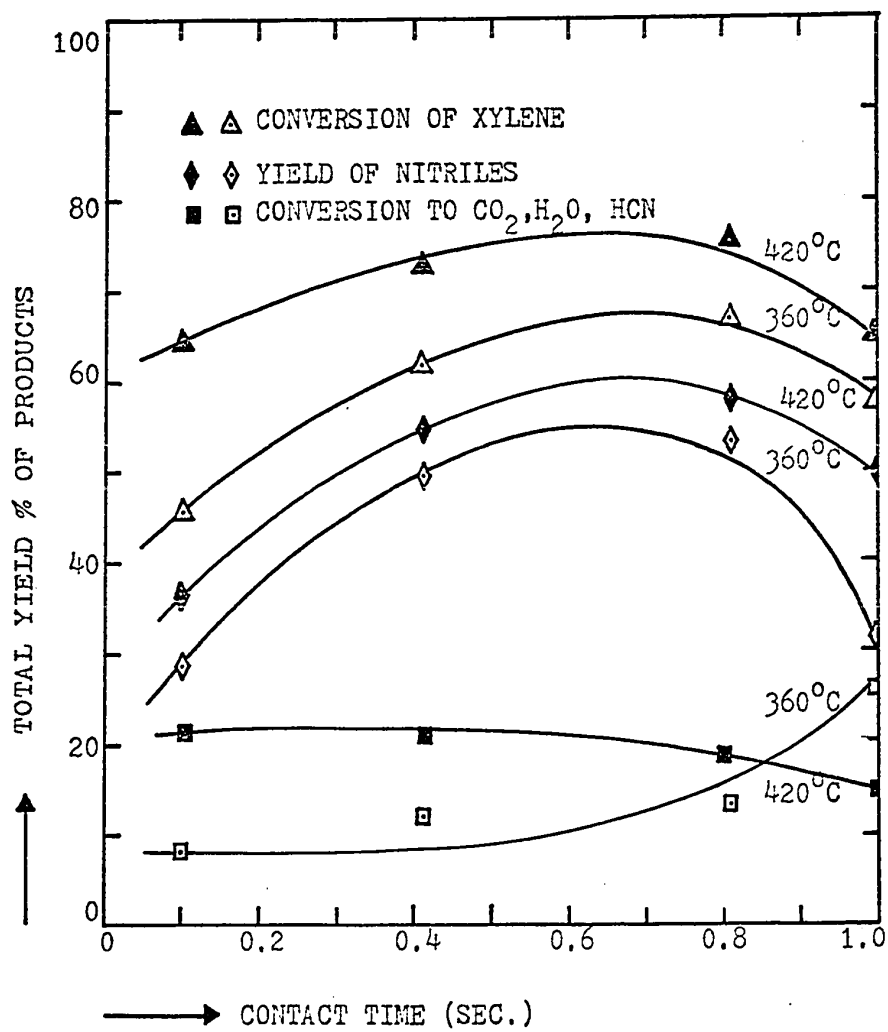
VI. Effect of Contact Time on Yield

Figures 12 and 13 show the influence of contact time on yield and selectivities of various products at the reaction temperatures of 360 and 420°C with tin vanadate as the catalyst. Contact time has an important influence on the yield of various products. Higher contact times result in formation of larger proportion of CO, CO₂, HCN in the products. The rating of the



OXIDATIVE AMMONOLYSIS OF m-XYLENE ON TIN VANADATE

FIGURE 12 EFFECT OF CONTACT TIME ON SELECTIVITY FOR NITRILES



OXIDATIVE AMMONOLYSIS OF *m*-XYLENE ON TIN VANADATE

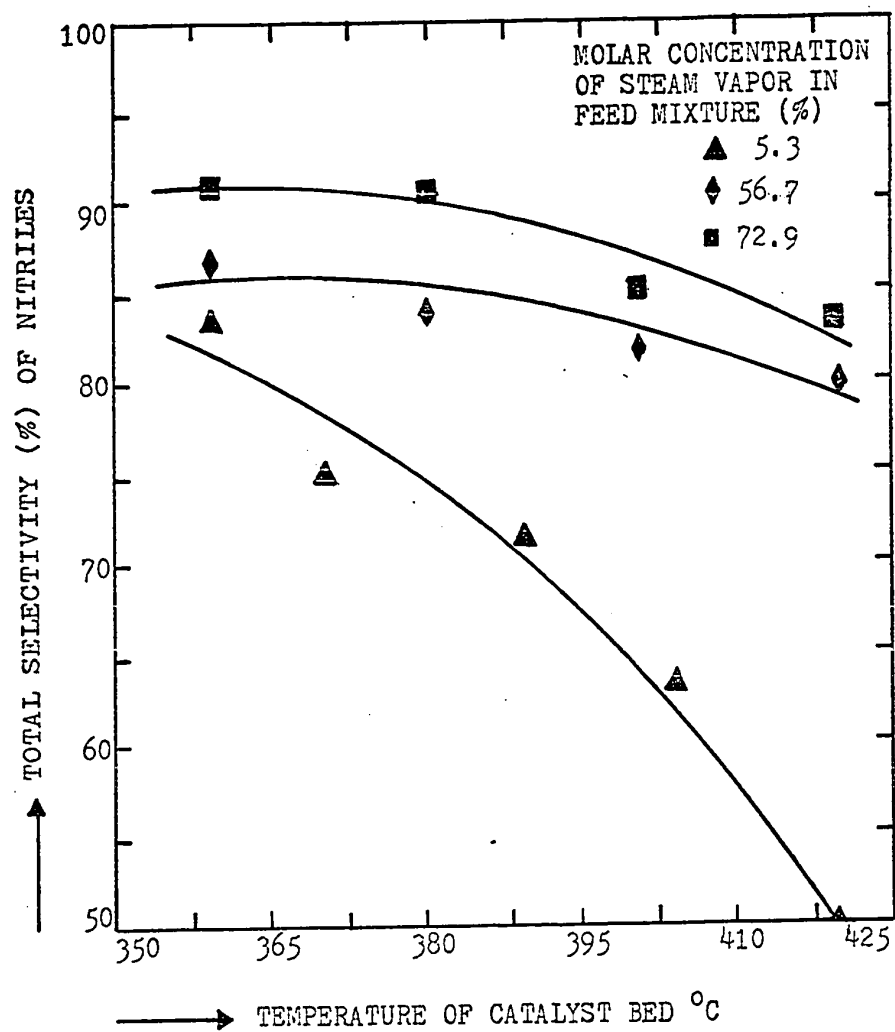
FIGURE 13 EFFECT OF CONTACT TIME ON YIELD OF PRODUCTS

catalyst drops at higher contact times exhibiting the necessity to carry out this reaction at lower contact times so as to obtain appreciable yields of nitriles. Over the contact times investigated, temperature has little influence on yields; the reaction can be safely carried out with more or less constant yields of desirable products over wide temperature range (50°C).

VII. Effect of Water Vapor in Reaction Zone:

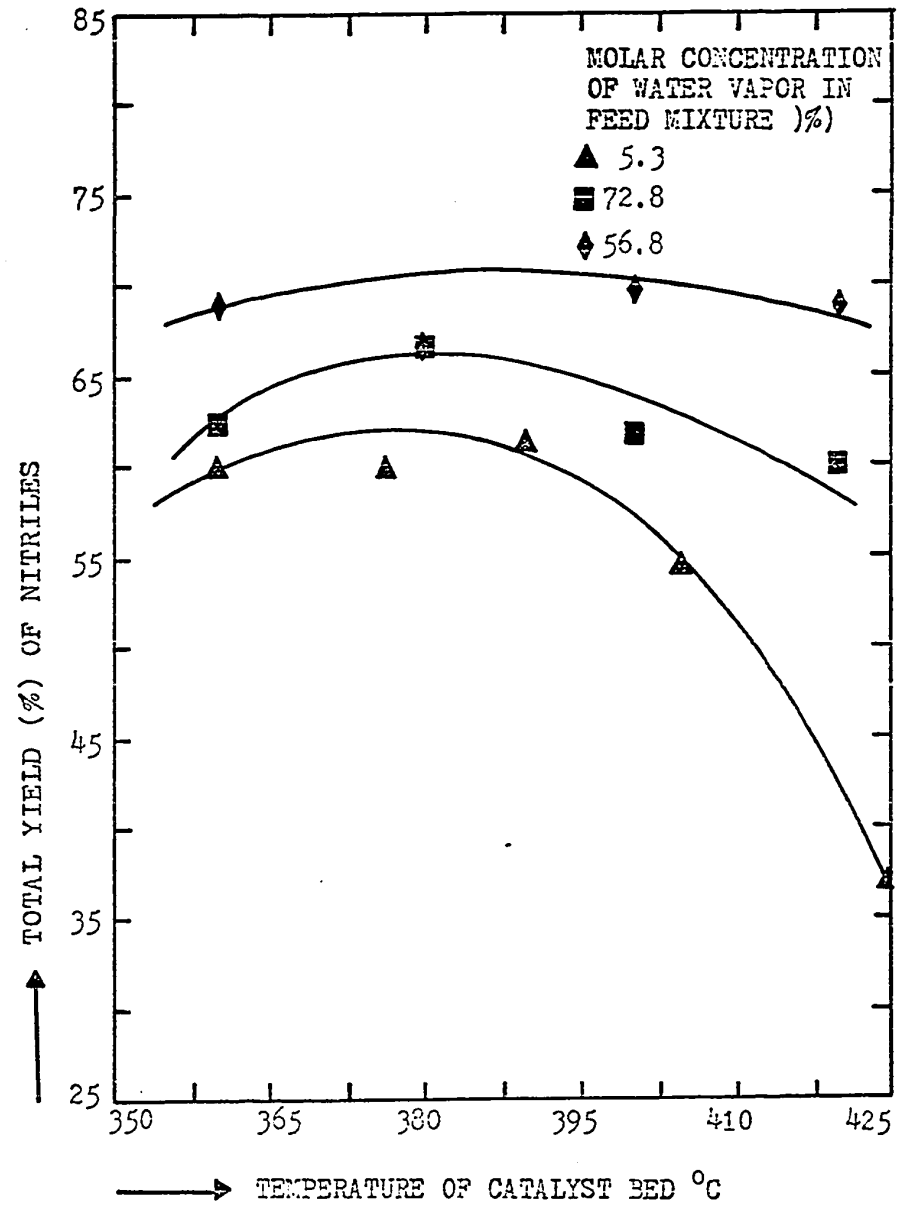
Figures 14-16 show the effect of various percentages of water vapor in the reaction mixture upon the yields and selectivities of nitriles.

Kostromin et al. (45) have established that aromatic carbonyl and carboxyl compounds are obtained in improved yields in the vapor-phase catalytic oxidation of alkylbenzene if water vapor were introduced in the reaction zone. In our experiments with various percentages of water vapor in the reaction zone, the yield of m-phthalonitrile is considerably increased whereas the amount of side reaction causing the splitting of α -carbon atom of the side chain is reduced. The catalyst shows a uniform 'rating' of the order of 0.2 over a widened temperature range ($360-430^{\circ}\text{C}$) i.e. optimum temperature range of the reaction is extended. The beneficial influence exerted by water in the reaction mixture is explained by the fact that it takes part in the reaction as a donor of H^+ and $(\text{OH})^-$ groups. Suvorov (46) put forth the following mechanism for the transfer of $(\text{OH})^-$ groups to the molecules of the organic compounds and on the path for the formation of nitriles.



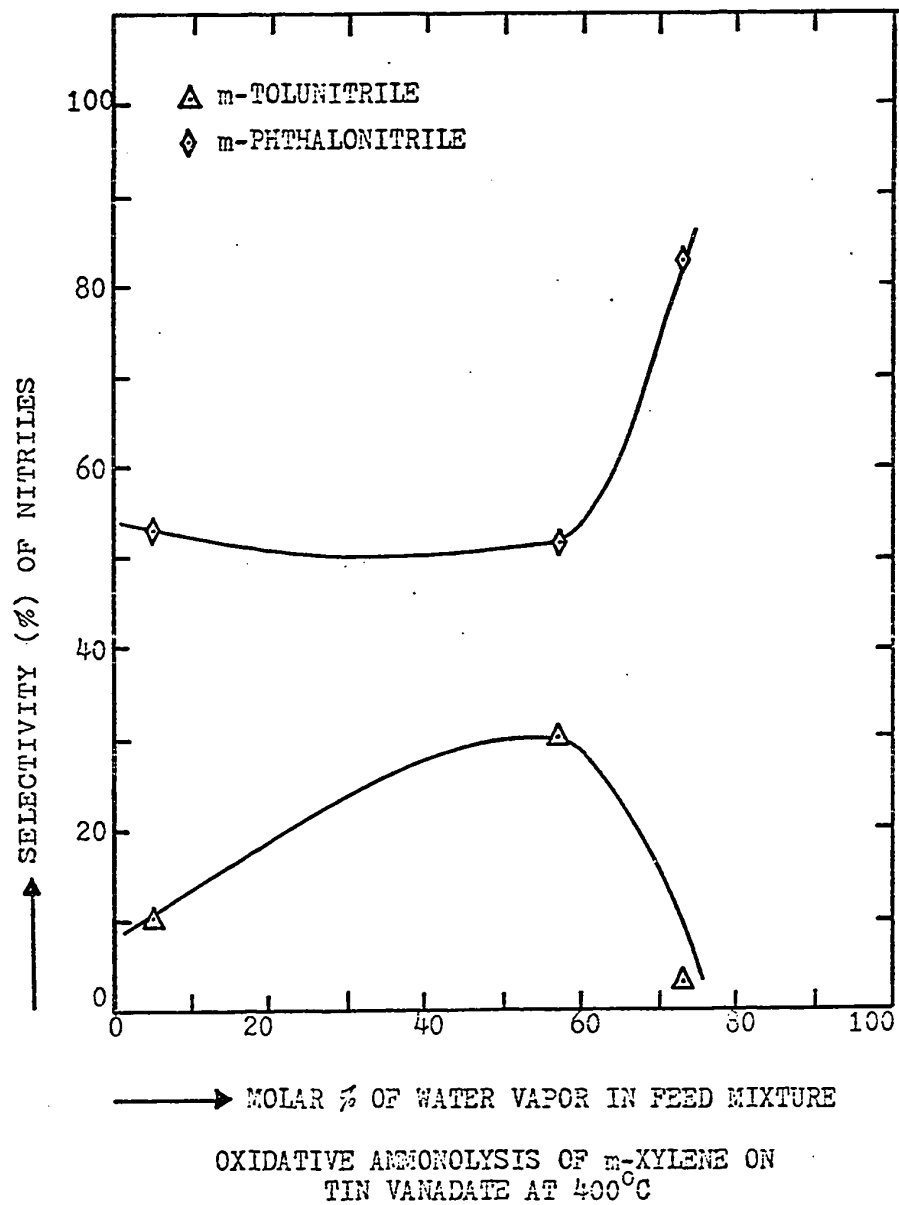
OXIDATIVE AMMONOLYSIS OF *m*-XYLENE ON TIN VANADATE

FIGURE 14 INFLUENCE OF VARYING MOLAR CONCENTRATION OF WATER VAPOR IN FEED MIXTURE ON SELECTIVITY OF NITRILES



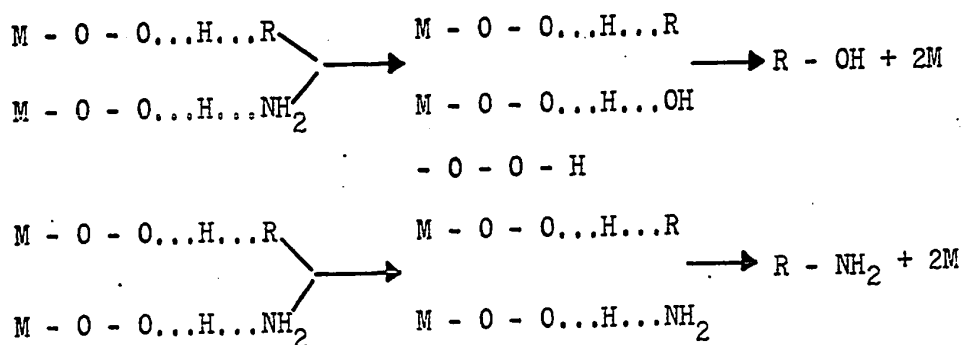
OXIDATIVE AMMONOLYSIS OF *m*-XYLENE ON TIN VANADATE

FIGURE 15 INFLUENCE OF VARYING MOLAR CONCENTRATION OF WATER VAPOR IN FEED MIXTURE ON TOTAL YIELD OF NITRILES



OXIDATIVE AMMONOLYSIS OF *m*-XYLENE ON
TIN VANADATE AT 400°C

FIGURE 16 EFFECT OF WATER VAPOR IN FEED MIXTURE
ON SELECTIVITY OF NITRILES



M: Catalyst - metallic part

VIII. Mixed Oxides:

Figures 17 and 18 show the influence of addition of oxides of Mn, B, Pb, Co, and Sb to $\text{V}_2\text{O}_5\text{-CrO}_3$. The mixed catalyst shows varying yields and selectivities for nitriles. Smooth curves can not be drawn through the data points as the curves intermingle and spread out as function of temperature of the reaction. The only inference that could be made is that addition of various oxides has a random effect on the selectivity of the catalyst for nitriles in other words the data points show no set trend. Addition of MnO , however, has the most favourable influence on the selectivity for nitriles while the oxide of Pb shows the most dampening effect on the activity of the catalyst.

Presence of unpaired electrons in the d- shell of the electronic configuration of the transition metals has been proposed to influence the relative catalytic activity of nickel-cobalt alloys (14). This hypothesis does not satisfactorily explain the data obtained in the present investigation as shown in the next page.

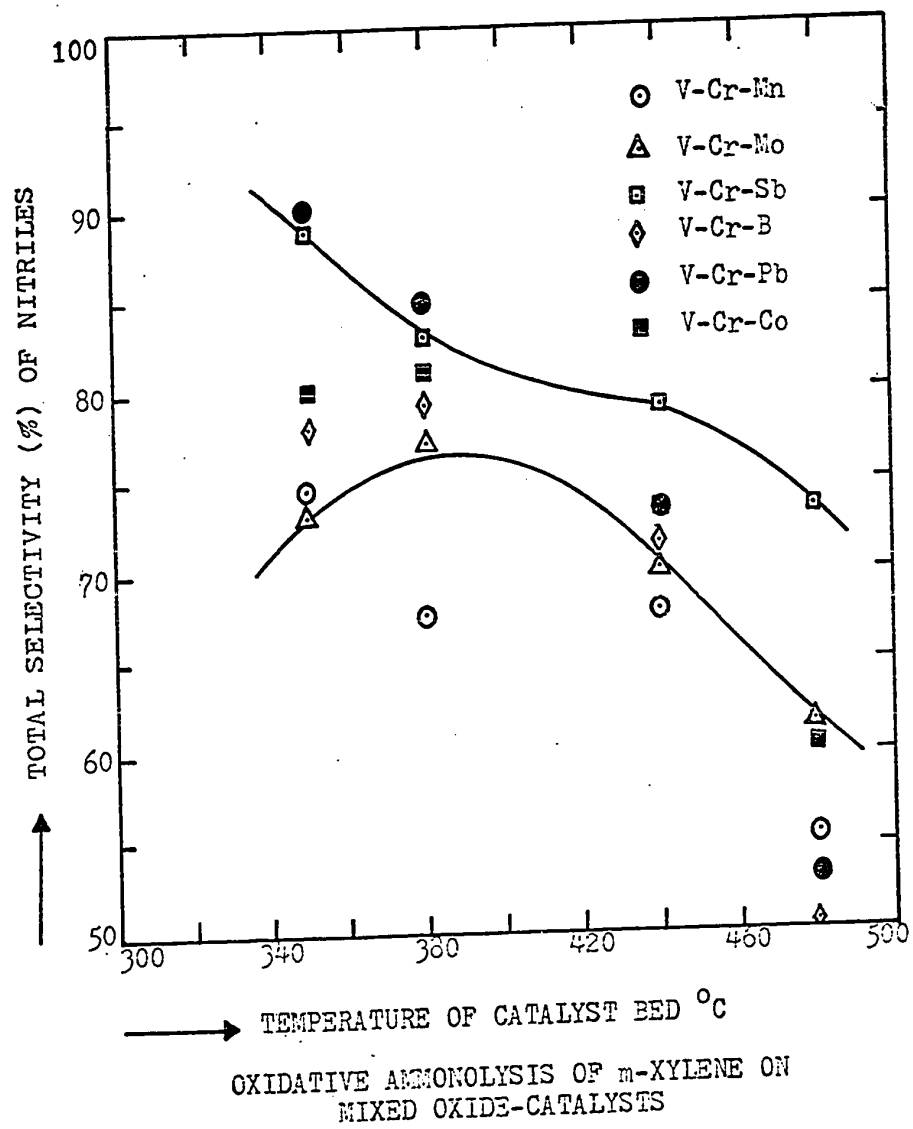
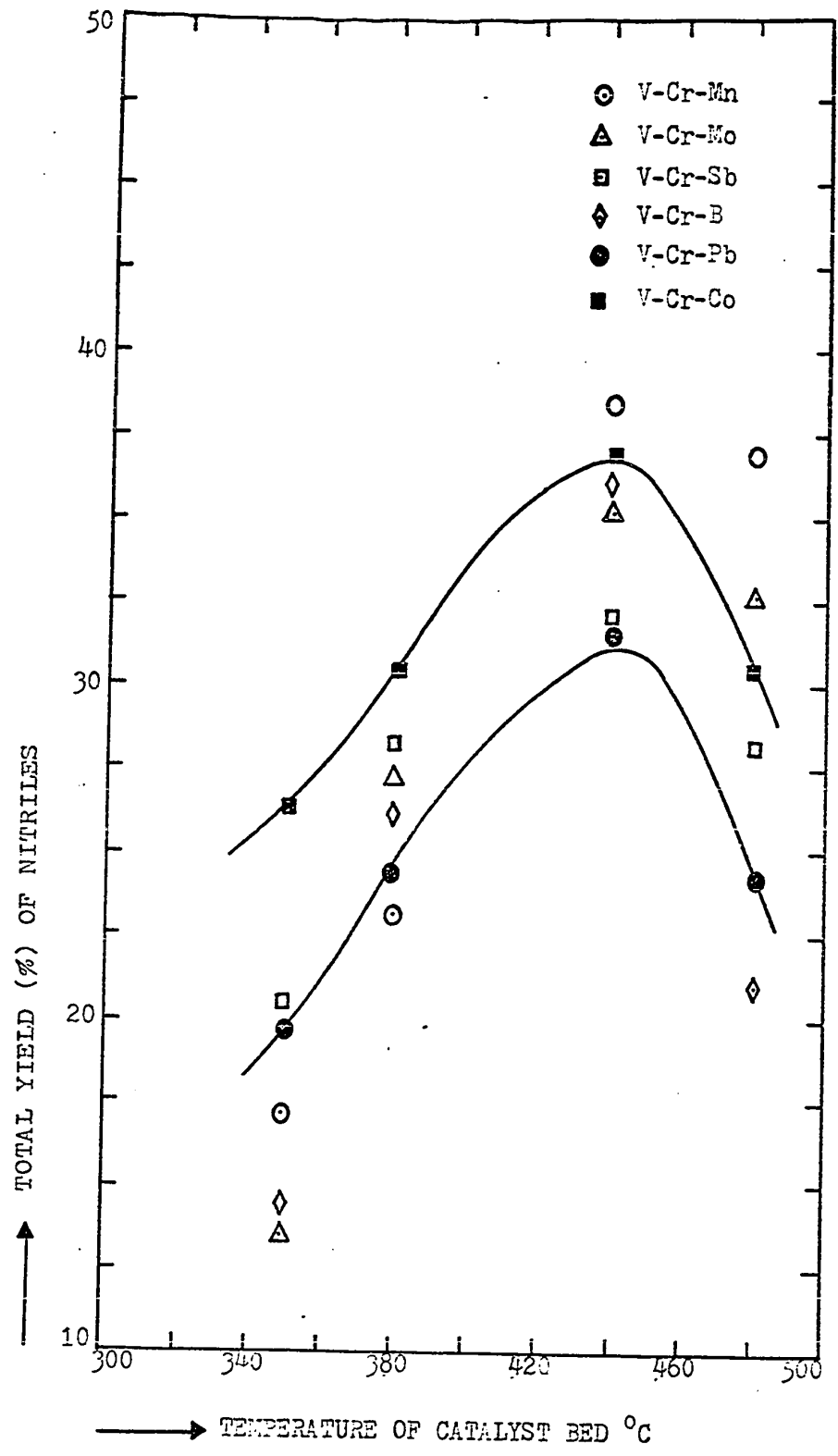


FIGURE 17 PRODUCT DISTRIBUTION AS A FUNCTION OF TEMPERATURE



OXIDATIVE AMMONOLYSIS OF *m*-XYLENE ON MIXED OXIDE CATALYSTS

FIGURE 18 PRODUCT DISTRIBUTION AS A FUNCTION OF TEMPERATURE

Table IV

Element	Atomic Number	Group	Unpaired d-electrons	Rating of the Catalyst under Identical Condition
B	5	3a	No d-shell occupied	.082
Co	27	8	Md ₇ (7)	.060
Mo	42	6	Md ₁₀ (10) Nd ₅ (5)	.070
Pb	82	4a	Md ₁₀ (10) Nd ₁₀ (10) Od ₁₀ (10)	.046
Mn	25	7b	Md ₍₅₎	.095
Sb	51	5a	Md ₁₀ (10) Nd ₁₀ (10)	.053

Thus the co-precipitated tin vanadate shows the best promise as a catalyst with the most favourable selectivity for m-phthalonitrile in the ammoxidation of m-xylene. Water vapor in the reaction zone is essential to reduce the side reactions whereby the yield of nitriles is increased as also the optimum temperature range of the reaction for the catalyst under investigation. The selectivity of the nitriles for this catalyst is much higher than that for any other catalyst tried in the present study. Vanadium oxide shows excessive activity for complete oxidation products and this is not suitably modified so as to increase the selectivity of nitriles by the inclusion of various oxides of transition metals.

C. Comparison with Previous Work

A brief comparison of the present work with available literature from the past has been tabulated in Table V.

Following are some of the important observations that emerge from this comparison.

1) Addition of various metallic oxides to vanadium oxide influenced the resulting performance characteristics of the impregnated catalysts to varying degrees. In this connection, MnO improves the selectivity considerably while PbO causes a sharp decrease in the selectivity for m-phthalonitrile and m-tolunitrile. This is in disagreement with the data obtained by Yoshio, et al., (32-38).

2) Manganese paratungstate, claimed in the literature as a versatile catalyst for ammoxidation of a wide variety of aromatic hydrocarbons (20), does not show better selectivities than V_2O_5 for m-xylene ammoxidation. Catalyst also shows poor life if subjected to prolonged reaction conditions.

3) Tin vanadate shows steady selectivities over wide temperature range (350-425°C) whereby by operating the reactor on lower side of temperature range, high yields of m-tolunitrile can be obtained. The yield of m-phthalonitrile is satisfactorily high over this temperature range.

Table V

# Catalyst	Present Work Results	Previous Work Ref.	Comparison with Previous Work
1 Vanadium oxide	Shows excessive selective activity for complete oxidation products making temperature control difficult. A maximum of 47% yield for m-phthalonitrile is obtained with 10% V ₂ O ₅ on precalcined alumina at a contact time of 0.5 sec	(22)	At a contact time of 6 sec and 360°C, a maximum of 66% yield of m-PN was obtained. At such high contact times very large percentage of xylylene converted to CO ₂ , HCN.
2 Tin Vanadate	Shows good selectivity for m-phthalonitrile at moderate temperatures and low contact times. The highest selectivity obtained is 82% at a contact time of 0.5 sec. in presence of water vapor in the feed mixture.	(8)	A yield of 60% is achieved at 0.4 sec contact time in presence of moist air. Catalyst shows good selectivity for nitriles from other aromatics-toluene, p-xylene, mesitylene etc.
3 Mixed Catalysts V-Cr-X, where X(Mo, Pb, Li, Na, B, Co, Sb, Mn)	Addition of Cr-X to V shows little improvement in selectivity of the catalyst. Addition of various metals have differing influence on yield of dinitriles. A maximum of 42.5% (cf 47% with V ₂ O ₅) yield of m-phthalonitrile is obtained with Mn.	(33-40)	Only at a larger contact times a yield of 70% is reported for various elements under identical reaction conditions.

(contd.)

Table V (contd.)

#	Catalyst	Present Work Results	Previous Work Ref.	Comparison with Previous Work
4	Manganese p-tungstate	Considerably higher yields for m-phthalonitrile are obtained than that for Vanadium oxide. Catalyst powders upon prolonged exposure to reaction conditions causing handling problem.	(20)	Catalyst shows low activity whereby predominantly mononitrile is formed.
5	MoO ₃	Shows as good properties as V ₂ O ₅ . A maximum yield of 25% is achieved.	(23)	At 6 sec contact time, predominantly CO ₂ with 39% dinitrile is reported.

CHAPTER VIII

CONCLUSIONS

Vapor phase catalytic oxidative ammonolysis of the meta isomer of xylene was performed in the presence of ammonia for the screening studies on various promising catalysts. Catalysts subjected to screening tests consisted of those based upon either Vanadium oxide or Stannic oxide. Reaction was carried out in fixed bed quartz reactor.

1. V_2O_5 deposited on inert carrier showed very little activity proving the importance of large surface areas for the activity of oxide impregnated catalysts.

2. Major work was done on the V_2O_5 deposited on activated alumina where carrier was pretreated by heat treatment at 900°C and 1250°C over extended periods of time. Pretreatment had a favourable influence on the overall activity of the catalyst though selectivity for the desirable product - m-phthalonitrile is not improved substantially.

3. Most of the catalysts based upon V_2O_5 show significant activity for the oxidative ammonolysis of aromatic hydrocarbons at temperatures higher than 400°C . As a consequence the data was collected for the study of various parameters over a temperature range of $350-500^\circ\text{C}$.

4. The percentage of V_2O_5 impregnated on the carrier

has an important influence on the overall activity of the catalyst (based upon per gm. of catalyst). Enough V_2O_5 should be impregnated so that monolayer of V_2O_5 is deposited on the whole of pore structure of the carrier whereby the whole of the pore surface is available for reaction. In this connection it was found that 20% V_2O_5 on activated carrier showed an activity which was lower than that for 5% V_2O_5 .

5. Contact time improves the yield of complete ammoxidation products. A contact time of 0.5 sec. for tin vanadate is optimum for good yields of m-phthalonitrile.

6. Water vapor improves the yield of intermediate products. It also extends the optimum range of catalyst operation.

7. Tin Vanadate shows the most optimum selectivity for m-phthalonitrile.

8. Mixed triple oxides (V_2O_5 - CrO_3 -M) do not result in significant improvement of the selectivity for dinitrile.

It may be concluded that the present investigation has improved and extended the available knowledge on the behaviour of various catalysts for the oxidative ammonolysis of m-xylene under wide temperature conditions.

The results show that for catalysts based upon V_2O_5 a temperature range of 400-430°C is to be recommended on the basis of combined selectivity for nitriles. If m-phthalonitrile is the only product of interest, the temperature range of 420-460°C is optimum.

The catalyst showing the best promise on the basis of selectivity for nitriles is tin vanadate. Catalysts based upon vanadium oxide show excessive activity for products of complete oxidation.

The results of this investigation should prove to be of much value in the selection of a catalyst and the reaction conditions most favourable for achieving optimum selectivities of nitriles.

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APPENDIX I
DATA FROM LITERATURE ON
AMMOXIDATION OF AROMATIC HYDROCARBONS

A. SINGLE OXIDES

Raw Material	Catalyst	Reaction Conditions	Results
Toluene, o-, p-xylene	V ₂ O ₅ on Activated Alumina	375-400°C, O ₂ /toluene(molar): 1.5-2, O ₂ /o-, p-xylene: 6	Yield of benzonitrile from toluene decreased above 400°C. (Ref. 21)
Toluene, ethylbenzene, mesitylene, o-, p-, m-xylene, p-diisopropylbenzene	10% V ₂ O ₅ on precalcined (1250°C for 22 hours) Alumina	360°C, CT: 6 sec. Feed Composition: 1.5:6:92.5(Air)	Yields reported are, p-PN (66%), p-TN (1%), CO ₂ (18%) from p-xylene; m-PN (70%) from o-xylene; PA (72%) from p-diisopropylbenzene; p-PN (26%) from p-dicyanotoluene (26%), dimethylbenzonitrile (10%) from mesitylene; benzonitrile (53%) from ethylbenzene; benzonitrile (44%) from toluene. (Ref. 22)
p-xylene	10% V ₂ O ₅ on precalcined (1000-1500°C for 3 hours) Alumina	360-95°C CT: 2-6 sec. Feed Composition: 1.5:7.5-9:91-89.5- (Air)	Yield of p-PN reported is 70%. (Ref. 23)
p-, m-xylene	V ₂ O ₅ on Activated Alumina	385°C CT: 6 sec. Feed Composition: 1.6:6.5:91.9(Air)	Yield of p-, m-PN (75%), p-, m-TN (2%), CO ₂ (9%) (Ref. 17)

(contd.)

APPENDIX I (contd.)

Raw Material	Catalyst	Reaction Conditions	Results
p-TN	V ₂ O ₅ on TiO ₂	380°C Feed Composition: NH ₃ (45.1kg) Water (350g) p-TN (2400 1/1 catalyst/hr.)	Selectivity for p-PN from p-TN was higher than the same from p-xylene. (Ref. 24). Yield of p-PN was 39%. (Ref. 23)
p-xylene	10% MoO ₃ on precalcined (1000-1500°C for 3hrs) Alumina	380°C CT: 6 sec. Feed Composition: 1.5:7.4:91.1	
m-xylene	MnBr ₂ suspended in m-TN (solvent)	170-200 (183°C) 50 psi Feed composition: m-xylene (25%) in m-TN(solvent)	Liquid-phase ammoxidation. For o-TN ammoxidation, total conversion reported is 60-90% out of which PA (46%), o-TN (18%). (Ref. 7)

B. BINARY OXIDES

m-xylene	Tin Vanadate	390°C CT: 0.9 sec. Feed Composition: 1:3:80(moist air)	Yield of m-PN (60%) with CO, CO ₂ , HCN and isophthalic acid as side products. (Ref. 8)
m-, p-xylene	Tin Vanadate	not available	Conversion to nitriles decreased with more of p-xylene in reaction mixture. (Ref. 9)
o-xylene	Tin Vanadate	350-400°C CT: 0.6 sec. Feed Composition: o-xylene (55-66g), air (2500 l), NH ₃ (35-40g), Water vapor(40g/l catalyst)	Yield of PA (45-50%). Moles NH ₃ /Moles O ₂ decides the product. 4 moles of NH ₃ per mole of O ₂ give PA while 15 moles give o-PN as the major product. (Ref. 10)

(contd.)

APPENDIX I (contd.)

Raw Material	Catalyst	Reaction Conditions	Results
m-xylene, m-TN, and their mixture	2% V ₂ O ₅ and 6% MoO ₃ on Alumina	380°C CT: 1.5 sec. Feed Composition: m-xylene:1:7:10(O ₂) m-TN: 1:3:4 (O ₂) m-TN/m-xylene:10-50%	Yield of m-PN, for pure m-xylene feed: 49.5% for mixed feed: 71.5% Fluidized bed reactor. (Ref. 13)
o-(and/or)p-xylene	V ₂ O ₅ and MoO ₃ on Alumina	300-400°C CT: 1.6-2 sec. Feed Composition: 1:10:20(O ₂)	Yield of p-PN (69.3-73.9%), o-PN (59.6-62.3%) in Fluidized bed reactor. (Ref. 15)
m-xylene	0.13% Pt. on a heavy metal oxide or V ₂ O ₅ on SiC	440°C Feed Composition: 1:3.46:69.5(Air)	Yield of m-TN and m-PN was 51.5%. (Ref. 25)
o-xylene	16% MoO ₃ 2% V ₂ O ₅ on Alumina	380°C CT: 1.5 sec. Feed Composition: 1:10:50(O ₂)	Yield of PA(95-98%), o-PN (5-2%). Total conversion of o-xylene - 60.3%. (Ref. 27)
m-xylene	15% V ₂ O ₅ K ₂ SO ₄ on Alumina	400°C SV: 355 cc/min. Feed Composition: 1.5:11:23(O ₂)	Yield of m-TN (20%), m-PN (40%). Yield of m-TN is not affected by temperature while that of m-PN depends upon temperature. (Ref. 28)
m-xylene	V ₂ O ₅ , CrO ₃ on Alumina	420°C CT: 3 sec.	Yields were m-PN (80%), m-TN (1%), HCN (4%), CO, CO ₂ (7%) in a fluidized bed reactor. (Ref. 29)

(contd.)

APPENDIX I (contd.)

Raw Material	Catalyst	Reaction Conditions	Results
p-xylene	Fe(Ni or Cr)-Mo on pumice	450°C 0.88-1.57 sec. Feed Composition: 1:5-8:120-180 (moles of air)	Yield of p-TN (50%), p-PN (65%). Influence of various percentages of Fe in Fe-Mo, Ni in Ni-Mo, Co in Co-Mo on yields on nitriles was studied. (Ref. 19)
o-, p-xylene	V ₂ O ₅ and/or MoO ₃ on Alumina	460°C CT: 3.13-3.18 sec. Feed Composition: p-xylene (0.0421-0.0496), ammonia (0.25), N ₂ (1.25 l/mt)	Yield of p-TN (16%), p-PN (39%). (Ref. 31)
m-TN	2% MoO ₃ 6% V ₂ O ₅ on Alumina	352-412°C partial pressure of m-TN: .05-.21 atm	Rate constant reaches a maximum at a SV of 2400 hr ⁻¹ . Activation energies for formation of m-TN, HCN and CO ₂ are respectively 9.6, 9.4, 17.5 kcal/mole. (Ref. 30)

C. TRIPLE OXIDES

Toluene o-, m-, p-xylene	Manganese p-tungstate promoted by Al(OH) ₃ , nickel p-tungstate, Cobalt Chromate	350-600°C CT: 6 sec. Feed Composition: 2:6:92(Air)	Yield of benzonitrile (86.7). With o-xylene, o-PN rather than PA is the major product. (Ref. 20)
m-xylene	V ₂ O ₅ , CrO ₃ , Mn(NO ₃) ₂ on Activated Alumina	400°C CT: 3.2 sec. Feed Composition: 0.91:7.28:91.81(Air)	Yield of m-TN (3.1%), m-PN (78.8%) (Ref. 32)

(contd.)

APPENDIX I (contd.)

Raw Material	Catalyst	Reaction Conditions	Results
m-xylene	V ₂ O ₅ , CrO ₃ , Pb(NO ₃) ₂ on Activated Alumina	404°C CT: 3 sec. Feed Composition: 0.91:7.28:91.81(Air)	Yield of m-TN (2.2%), m-PN (79.3%). (Ref. 33)
m-xylene	V ₂ O ₅ , CrO ₃ , H ₃ BO ₃ on Activated Alumina	437°C CT: 1.4 sec. Feed Composition: 0.59:5.74:93.67(Air)	Yield of m-PN (80.9%). (Ref. 35)
m-xylene	V ₂ O ₅ , CrO ₃ , MnO ₃ on Activated Alumina	440°C CT: 1.5 sec. Feed Composition: 0.6:7.75:91.65(Air)	Yield of m-PN (79.8%). (Ref. 34)
m-xylene	V ₂ O ₅ , CrO ₃ , Co(NO ₃) ₂ on Activated Alumina	419°C CT: 0.7 sec. Feed Composition: 0.6:7.75:91.65(Air)	Yield of m-PN (78.6%). (Ref. 36)
m-xylene	V ₂ O ₅ , Na ₂ SO ₄ , H ₂ SO ₄ on TiO ₂	370°C CT: 2 sec. Feed Composition: 1:8:91(Air)	Yield of m-PN (79%). (Ref. 37)
m-xylene	V ₂ O ₅ , Li ₂ SO ₄ , H ₂ SO ₄ on TiO ₂	400°C CT: 1 sec. Feed Composition: 1:8:91(Air)	Yield of m-PN (74%). (Ref. 38)
p-xylene	Mixed oxides of V, Mo, Mn on Alumina	380°C CT: 0.91 sec. Feed Composition: 1:16:30(O ₂)	Yield of m-PN (71.2%). (Ref. 39)

APPENDIX I (contd.)

Raw Material	Catalyst	Reaction Conditions	Results
p-, m-xylene mixture	Mixed oxides of Mo, Mn on Alumina	380°C Ct: 1.5 sec. Feed Composition: 1:7:10(O ₂) p-xylene:m-xylene: 30:70	Yield of m-PN (60%), p-PN (40%). Yield of corresponding dinitrile increases with increasing mole fraction of an isomer. (Ref. 40)
p-xylene	MoO ₃ -Iron molybdate-V ₂ O ₅ on Alumina	400-420°C ammonia/p-xylene (molar):5 air/p-xylene:40-60	Conversion of p-xylene 70%. (Ref. 41)
p-xylene	V ₂ O ₅ , CrO ₃ MoO ₃ on TiO ₂	380°C p-xylene: 34 g/hr air: 1600 l/hr ammonia: 135 l/hr	Yield of p-PN (71.2%). Only traces of p-TN were formed. (Ref. 42)
p-xylene	V ₂ O ₅ , SnO on TiO ₂	380-450°C ammonia/p-xylene (molar):5-8 air/p-xylene:30-45	Yield of p-TN (3-5%), p-PN (75%). At low temperatures p-toluamide and terephthalic acid diamide were pre-dominantly formed. (Ref. 43)
o-, m-, p-xylene	V ₂ O ₅ , MoO ₃ P ₂ O ₅ on Alumina	450°C SV: 2150 Hr ⁻¹ Feed Composition: 1:2:75	Yield of dinitriles (75%) with total conversion of xylenes (40%). (Ref. 44)

(contd.)

APPENDIX I (contd.)

Raw Material	Catalyst	Reaction Conditions	Results
m-xylene	V ₂ O ₅ , Cr ₂ O ₃ on Alumina	420±4°C CT: 3 sec. Flow Velocity: 15 cm/sec. m-xylene: 35.4 g/hr ammonia/m-xylene (molar): 6	Yield of m-PN (8%) in a Fluidized bed reactor. (Ref. 29)
p-xylene	V ₂ O ₅ -SnO ₂ - P ₂ O ₅ on Si ₃ N ₄	500-520°C CT: 3-5 sec. p-xylene (10), ammonia (20-24), air (200), steam (0-10 moles/hr)	Yield of p-PN (50%) in a Fluidized bed reactor. Total conversion of p-xylene (75-80%). (Ref. 16)

Notes: 1. Composition: Reaction mixture composition (Hydrocarbon: NH₃:Air/O₂) is on molar basis.

2. Rating is based on the severity of reaction conditions. It is defined as, Selectivity of dinitrile (%)

Rating: $\frac{\text{Contact time (sec)} \times \text{temperature (}^\circ\text{C)}}{\text{Selectivity of dinitrile (\%)}}$

3. o-, m-, p-TN: ortho-, meta-, para-tolunitrile
o-, m-, p-PN: ortho-, meta-, para-phthalonitrile
PA: phthalimide
CT: Contact time for the reaction mixture with the catalytic mass (sec)
SV: Space velocity (hr⁻¹)

APPENDICES
(I, II, III, IV)

APPENDIX II
DATA

GC ANALYSIS OF PRODUCTS, G./HR. OF
M-TN M-PN

RUN CATALYST VOL., CC. AVG. L1 TEMP. L2 FLOW AT 25 C, CC./MT. M-XY NH3 O2 N2 H2O M-XY M-TN M-PN

CATALYST 5% VANADIUM OXIDE DEPOSITED ON INERT ALUMINA-NO PREACTIVATION

Run	Catalyst Vol., CC.	Avg. L1	Temp. L2	Flow at 25 C, CC./MT.	M-XY	NH3	O2	N2	H2O	M-XY	M-TN	M-PN
1	5.8	250.	249.	6.2	30	65	575	0	1.760	0.000	0.000	0.000
2	5.8	300.	297.	6.0	30	65	585	0	1.666	0.000	0.000	0.000
3	5.8	350.	348.	6.2	30	65	585	0	1.672	0.038	0.000	0.000
4	5.8	400.	391.	6.2	30	65	585	0	1.602	0.019	0.032	0.000
5	5.8	453.	442.	6.2	30	65	585	0	1.443	0.020	0.095	0.000
6	5.8	500.	487.	6.1	30	65	585	0	1.326	0.000	0.163	0.000
7	5.8	550.	531.	6.1	30	65	585	0	1.020	0.000	0.143	0.000

CATALYST 5% VANADIUM OXIDE DEPOSITED ON ACTIVATED ALUMINA-NO PREACTIVATION

8	5.8	350.	344.	6.2	30	65	585	0	1.443	0.097	0.127	0.000
9	5.8	400.	396.	6.2	30	65	585	0	1.100	0.300	0.174	0.000
10	5.8	425.	417.	6.1	30	65	585	0	1.020	0.206	0.265	0.000
11	5.8	450.	443.	6.1	30	65	585	0	1.037	0.056	0.306	0.000
12	5.8	475.	464.	6.1	30	65	585	0	0.918	0.019	0.347	0.000
13	5.8	500.	492.	6.2	30	65	585	0	0.933	0.000	0.296	0.000

CATALYST 5% VANADIUM OXIDE DEPOSITED ON ACTIVATED ALUMINA-PREACTIVATION AT 900 C FOR 12 HOURS

14	5.8	350.	348.	6.1	30	65	585	0	1.292	0.149	0.224	0.000
15	5.8	400.	399.	6.1	30	65	585	0	0.952	0.224	0.469	0.000
16	5.8	425.	423.	6.2	30	65	585	0	0.898	0.058	0.655	0.000
17	5.8	450.	447.	6.1	30	65	585	0	0.765	0.021	0.673	0.000
18	5.8	475.	473.	6.1	30	65	585	0	0.646	0.000	0.653	0.000
19	5.8	500.	495.	6.2	30	65	585	0	0.546	0.000	0.612	0.000

APPENDIX II (CONTD.)

RUN CATALYST VOL., CC. AVG. TEMP. L1 L2 M-XY NH3 Q2 N2 H2O GC ANALYSIS OF PRODUCTS, G./HR. OF M-TN M-PN

CATALYST 5% VANADIUM OXIDE DEPOSITED ON ACTIVATED ALUMINA-PREACTIVATION AT 1250 C FOR 12 HOURS:

20	5.8	350.	348.	6.2	30	65	585	0	1.197	0.271	0.253
21	5.8	400.	392.	6.2	30	65	585	0	0.950	0.252	0.634
22	5.8	425.	423.	5.9	30	65	585	0	0.839	0.127	0.671
23	5.8	450.	449.	5.9	30	65	585	0	0.757	0.028	0.734
24	5.8	475.	472.	6.1	30	65	585	0	0.612	0.000	0.734
25	5.8	500.	498.	6.0	30	65	585	0	0.533	0.000	0.632

CATALYST 10% VANADIUM OXIDE ON ACTIVATED ALUMINA-PREACTIVATION AT 1250 C FOR 12 HOURS

26	5.8	400.	396.	6.1	30	65	585	0	0.663	0.299	0.836
27	5.8	420.	418.	5.9	30	65	585	0	0.612	0.243	0.918
28	5.8	460.	456.	5.8	30	65	585	0	0.517	0.129	0.912
29	5.8	500.	496.	6.0	30	65	585	0	0.500	0.037	0.780

CATALYST 20% VANADIUM OXIDE ON ACTIVATED ALUMINA-PREACTIVATION AT 1250 C FOR 12 HOURS:

30	5.8	400.	395.	6.2	30	65	585	0	0.950	0.213	0.591
31	5.8	420.	411.	6.2	30	65	585	0	0.827	0.097	0.697
32	5.8	460.	450.	6.3	30	65	585	0	0.603	0.055	0.700
33	5.8	500.	493.	6.1	30	65	585	0	0.544	0.000	0.489

APPENDIX II (CONTD.)

RUN	CATALYST VOL., CC.	AVG. TEMP.			FLOW AT 25 C, CC/MT.			GC ANALYSIS OF PRODUCTS, G./HR.			
		L1	L2	M-XY	NH3	D2	N2	H2O	M-TN.	M-XY	M-PV
CATALYST 10% MOLYBDENUM(6)OXIDE DEPOSITED ON ACTIVATED ALUMINA											
-PREACTIVATION AT 1250 C FOR 12 HOURS											
34	5.0	250.	248.	4.5	18	90	210	0	1.278	0.000	0.000
35	5.0	350.	341.	4.3	18	90	210	0	1.087	0.073	0.012
36	5.0	450.	446.	4.3	18	90	210	0	0.683	0.134	0.232
37	5.0	500.	492.	4.4	18	90	210	0	0.600	0.050	0.262
CATALYST 5% VANADIUM(5)OXIDE, 5% MOLYBDENUM(6)OXIDE DEPOSITED ON ACTIVATED ALUMINA											
-PREACTIVATION AT 1250 C FOR 12 HOURS											
38	5.0	250.	247.	4.4	20	95	210	0	1.249	0.000	0.000
39	5.0	350.	348.	4.4	20	95	210	0	0.949	0.150	0.087
40	5.0	450.	439.	4.4	20	95	210	0	0.625	0.150	0.350
41	5.0	500.	487.	4.5	20	95	210	0	0.677	0.038	0.345
CATALYST MANGANESE PARATUNGSTATE											
42	12.0	350.	348.	4.3	20	95	155	0	0.972	0.125	0.092
43	12.0	400.	397.	4.5	20	95	155	0	0.682	0.221	0.268
44	12.0	440.	439.	4.5	20	95	155	0	0.280	0.142	0.668
45	12.0	480.	471.	4.4	20	95	155	0	0.045	0.095	0.888
46	12.0	530.	523.	4.4	20	95	155	0	0.034	0.000	0.862

APPENDIX II (CONTD.)

RUN	CATALYST VOL., CC.	AVG. TEMP.		FLOW AT 25 C, CC/MT.			GC ANALYSIS OF PRODUCTS, G./HR. OF				
		L1	L2	M-XY	NH3	O2	N2	H2O	M-XY	M-TN	M-PN
<p>CATALYST VANADIUM(5)OXIDE-CHROMIUM(6)OXIDE-MANGANESE(2)OXIDE DEPOSITED ON ACTIVATED ALUMINA-PREACTIVATION AT 1250 C FOR 12 HOURS</p>											
47	3.0	350.	345.	3.4	18	65	105	0	0.738	0.068	0.125
48	3.0	380.	375.	3.4	18	65	105	0	0.647	0.075	0.188
49	3.0	440.	437.	3.4	18	65	105	0	0.418	0.055	0.389
50	3.0	480.	479.	3.4	18	65	105	0	0.351	0.020	0.410
<p>CATALYST VANADIUM(5)OXIDE-CHROMIUM(6)OXIDE-MOLYBDENUM(6)OXIDE DEPOSITED ON ACTIVATED ALUMINA-PREACTIVATION AT 1250 C FOR 12 HOURS</p>											
51	3.0	350.	347.	3.4	18	65	105	0	0.789	0.082	0.069
52	3.0	380.	378.	3.3	18	65	105	0	0.607	0.118	0.178
53	3.0	440.	433.	3.3	18	65	105	0	0.468	0.118	0.269
54	3.0	480.	471.	3.5	18	65	105	0	0.465	0.097	0.287
<p>CATALYST VANADIUM(5)OXIDE-CHROMIUM(6)OXIDE-ANTIMONY(3)OXIDE DEPOSITED ON ACTIVATED ALUMINA-PREACTIVATION AT 1250 C FOR 12 HOURS</p>											
55	3.0	350.	345.	3.3	18	65	105	0	0.721	0.129	0.087
56	3.0	380.	379.	3.3	18	65	105	0	0.614	0.157	0.146
57	3.0	440.	437.	3.5	18	65	105	0	0.597	0.150	0.219
58	3.0	480.	473.	3.4	18	65	105	0	0.596	0.106	0.212

APPENDIX II (CONTD.)

RUN	CATALYST VOL., CC.	AVG. TEMP.		FLOW AT 25 C. CC/MT.			GC ANALYSIS OF PRODUCTS, G./HR. OF			
		L1	L2	M-XY	NH3	O2	N2	H2O	M-TN	M-PN
CATALYST VANADIUM(5)OXIDE-CHROMIUM(6)OXIDE-BORON(3)OXIDE DEPOSITED ON ACTIVATED ALUMINA-PREACTIVATION AT 1250 C FOR 12 HOURS										
59	3.0	350.	344.	3.3	18	65	105	0	0.053	0.102
60	3.0	380.	374.	3.3	18	65	105	0	0.093	0.193
61	3.0	440.	436.	3.3	18	65	105	0	0.076	0.319
62	3.0	480.	477.	3.6	18	65	105	0	0.031	0.224
CATALYST VANADIUM(5)OXIDE-CHROMIUM(6)OXIDE-LEAD(2)OXIDE DEPOSITED ON ACTIVATED ALUMINA-PREACTIVATION AT 1250 C FOR 12 HOURS										
63	3.0	350.	347.	3.4	18	65	105	0	0.167	0.048
64	3.0	380.	372.	3.4	18	65	105	0	0.166	0.102
65	3.0	440.	430.	3.3	20	65	105	0	0.131	0.181
66	3.0	480.	475.	3.3	20	65	105	0	0.165	0.068
CATALYST VANADIUM(5)OXIDE-CHROMIUM(6)OXIDE-CORALY(2)OXIDE DEPOSITED ON ACTIVATED ALUMINA-PREACTIVATION AT 1250 C FOR 12 HOURS										
67	3.0	350.	348.	3.4	20	65	105	0	0.122	0.136
68	3.0	380.	371.	3.6	20	65	105	0	0.149	0.173
69	3.0	440.	433.	3.4	20	65	105	0	0.129	0.237
70	3.0	480.	470.	3.6	20	65	105	0	0.044	0.264

APPENDIX II (CONTD.)

RUN	CATALYST VOL., CC.	AVG. LI	TEMP. L2	FLOW AT 25 C., CC./MT.			GC ANALYSIS OF PRODUCTS, G./HR.				
				M-XY	NH3	O2	N2	H2O	M-TN	M-PN	
71	4.0	320.	314.	7.0	40	185	0	300	1.720	0.177	0.036
72	4.0	360.	356.	7.2	40	185	0	300	0.550	0.462	0.912
73	4.0	380.	371.	7.0	40	185	0	300	0.580	0.495	0.924
74	4.0	400.	393.	6.8	40	185	0	300	0.480	0.319	1.116
75	4.0	430.	425.	7.2	40	185	0	300	0.300	0.110	1.200
76	1.0	360.	358.	7.1	28	135	250	200	1.080	0.308	0.360
77	1.0	390.	387.	7.0	28	135	250	200	0.940	0.242	0.480
78	1.0	400.	398.	7.1	28	135	250	200	0.840	0.066	0.768
79	1.0	420.	417.	7.0	28	135	250	200	0.700	0.011	0.864
80	4.0	360.	356.	7.0	28	135	220	200	0.760	0.594	0.552
81	4.0	390.	383.	7.0	28	135	220	200	0.640	0.308	1.104
82	4.0	400.	395.	7.1	28	135	220	200	0.600	0.088	1.224
83	4.0	420.	416.	7.0	28	135	220	200	0.540	0.017	1.296
84	5.0	360.	356.	7.2	28	135	0	200	0.760	0.616	0.648
85	5.0	390.	387.	7.2	28	135	0	200	0.600	0.264	1.128
86	5.0	400.	397.	7.2	28	135	0	200	0.540	0.132	1.296
87	5.0	420.	416.	7.1	28	135	0	200	0.500	0.044	1.368
88	6.1	360.	358.	7.0	28	135	0	200	0.840	0.132	0.600
89	6.1	390.	384.	7.0	28	135	0	200	0.840	0.088	0.960
90	6.1	400.	395.	7.0	28	135	0	200	0.760	0.033	1.056
91	6.1	420.	413.	7.1	28	135	0	200	0.700	0.011	1.200
92	4.0	360.	356.	7.0	40	185	220	25	0.560	0.748	0.624
93	4.0	376.	374.	7.3	40	185	220	25	0.400	0.484	0.984
94	4.0	390.	386.	7.3	40	185	220	25	0.300	0.308	1.200
95	4.0	405.	400.	7.2	40	185	220	25	0.280	0.198	1.128
96	4.0	420.	417.	7.0	40	185	220	25	0.520	0.110	0.768
97	4.5	360.	350.	7.3	40	185	0	305	0.420	1.144	0.480
98	4.5	380.	372.	7.3	40	185	0	305	0.420	0.748	0.864
99	4.5	400.	391.	7.3	40	185	0	305	0.300	0.594	1.104
100	4.5	420.	415.	7.2	40	185	0	305	0.280	0.396	1.272
101	7.0	360.	352.	7.1	40	180	0	610	0.640	0.286	1.200
102	7.0	380.	372.	7.1	40	180	0	610	0.520	0.176	1.440
103	7.0	400.	390.	7.2	40	180	0	610	0.560	0.044	1.480
104	7.0	420.	412.	7.2	40	180	0	610	0.580	0.032	1.440

APPENDIX III
RESULTS*

CATALYST	MC	CT	SV	AVGT	MXF	MXC	FC	YMTN	YMPN	SMTN	SMPN	RMPN			
VANADIA-I	0.90:4.37:9.47:0.00	0.50	7160	250	16.6	0.0	0.00	0.00	0.00	0.00	0.00	0.00			
				300	16.1	0.4	0.02	0.00	0.00	0.00	0.00	0.00	0.00		
				350	16.6	0.8	0.05	0.02	0.00	0.00	0.00	0.00	0.00	0.00	
				400	16.6	1.0	0.09	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00
				450	16.6	3.0	0.18	0.01	0.04	0.00	0.00	0.00	0.00	0.00	0.00
VANADIA-II	0.90:4.37:9.47:0.00	0.50	7160	500	16.3	4.6	0.28	0.00	0.08	0.00	0.00	0.00			
				550	16.3	6.7	0.41	0.00	0.07	0.00	0.00	0.00	0.00	0.00	
				350	16.6	3.0	0.18	0.05	0.06	0.00	0.00	0.00	0.00	0.00	
				400	16.6	6.2	0.38	0.15	0.09	0.00	0.00	0.00	0.00	0.00	0.00
				425	16.3	6.7	0.41	0.11	0.13	0.00	0.00	0.00	0.00	0.00	0.00
VANADIA-III	0.90:4.37:9.47:0.00	0.50	7160	450	16.3	6.6	0.40	0.03	0.15	0.00	0.00	0.00			
				475	16.3	7.7	0.47	0.01	0.17	0.00	0.00	0.00	0.00	0.00	
				500	16.6	7.8	0.47	0.00	0.14	0.00	0.00	0.00	0.00	0.00	
				350	16.3	4.1	0.25	0.08	0.11	0.00	0.00	0.00	0.00	0.00	0.00
				400	16.3	7.4	0.45	0.12	0.22	0.00	0.00	0.00	0.00	0.00	0.00
VANADIA-IV	0.90:4.37:9.47:0.00	0.50	7160	425	16.6	8.1	0.49	0.03	0.31	0.00	0.00	0.00			
				450	16.3	9.1	0.56	0.01	0.32	0.00	0.00	0.00	0.00	0.00	
				475	16.3	10.2	0.63	0.00	0.31	0.00	0.00	0.00	0.00	0.00	
				500	16.6	11.5	0.69	0.00	0.29	0.00	0.00	0.00	0.00	0.00	0.00
				350	16.6	5.3	0.32	0.14	0.12	0.00	0.00	0.00	0.00	0.00	0.00
VANADIA-V	0.90:4.37:9.47:0.00	0.50	7160	400	16.6	7.7	0.46	0.13	0.30	0.00	0.00	0.00			
				425	15.8	7.9	0.50	0.07	0.33	0.00	0.00	0.00	0.00	0.00	
				450	16.3	9.2	0.56	0.01	0.35	0.00	0.00	0.00	0.00	0.00	
				475	16.3	10.6	0.65	0.00	0.35	0.00	0.00	0.00	0.00	0.00	0.00
				500	16.1	11.0	0.69	0.00	0.31	0.00	0.00	0.00	0.00	0.00	0.00
				400	16.3	10.1	0.62	0.16	0.40	0.00	0.00	0.00	0.00		
				420	16.3	10.6	0.65	0.13	0.44	0.00	0.00	0.00	0.00	0.00	
				460	15.5	10.7	0.69	0.07	0.46	0.00	0.00	0.00	0.00	0.00	
				500	16.1	11.4	0.71	0.02	0.38	0.00	0.00	0.00	0.00	0.00	0.00

*NOTATION USED IS EXPLAINED AT THE END OF APPENDIX III.

APPENDIX III (CONTD.)

CATALYST	MC	CT	SV	AVGT	MXF	MXC	FC	YMTN	YMPN	SMTN	SMPN	RMPN
VANADIA-VI	0.90:4.37:9.47:0.00	0.50	7160	400	16.6	7.7	0.46	0.11	0.28	0.24	0.60	0.30
				420	16.6	8.8	0.53	0.05	0.33	0.09	0.62	0.30
				460	16.1	10.4	0.65	0.03	0.34	0.05	0.53	0.23
				500	16.1	11.4	0.71	0.00	0.24	0.00	0.34	0.14
MoO ₃	1.36:5.58:27.9:0.00	0.93	3870	250	12.1	0.0	0.00	0.00	0.00	0.00	0.00	0.00
				350	11.5	1.2	0.10	0.05	0.01	0.52	0.08	0.02
				450	11.5	5.1	0.44	0.10	0.16	0.22	0.36	0.09
				500	11.8	6.1	0.52	0.04	0.17	0.07	0.34	0.07
V ₂ O ₅ -MoO ₃	1.34:6.07:28.8:0.00	0.91	3960	250	11.8	0.0	0.00	0.00	0.00	0.00	0.00	0.00
				350	11.8	2.9	0.25	0.11	0.06	0.44	0.23	0.07
				450	11.8	5.9	0.50	0.11	0.23	0.22	0.46	0.11
				500	12.1	5.7	0.47	0.03	0.22	0.06	0.47	0.10
MANGANESE	1.60:7.29:34.6:0.00	2.63	1370	350	11.5	2.3	0.20	0.10	0.06	0.46	0.31	0.03
p-TUNGSTATE				400	12.1	5.7	0.47	0.16	0.17	0.33	0.37	0.03
				440	12.1	9.5	0.79	0.10	0.43	0.13	0.55	0.05
				480	11.8	11.4	0.97	0.07	0.59	0.07	0.61	0.05
V-Cr-Mn	1.78:9.40:33.9:0.00	0.94	3830	530	11.8	11.5	0.98	0.00	0.57	0.00	0.59	0.04
				350	9.1	2.1	0.23	0.06	0.11	0.28	0.47	0.14
				380	9.1	8.0	0.33	0.07	0.16	0.08	0.18	0.05
				440	9.1	5.2	0.57	0.05	0.33	0.09	0.58	0.14
				480	9.1	6.1	0.67	0.02	0.35	0.03	0.53	0.12
V-Cr-Mo	1.78:9.40:33.9:0.00	0.94	3830	350	9.1	1.7	0.19	0.08	0.06	0.41	0.32	0.10
				380	8.8	3.1	0.35	0.11	0.16	0.33	0.45	0.13
				440	8.8	4.4	0.50	0.11	0.24	0.23	0.48	0.12
				480	9.4	5.0	0.53	0.09	0.24	0.17	0.45	0.10

APPENDIX III (CONTD.)

CATALYST	MC	CT	SV	AVGT	MXF	MXC	FC	YMTN	YMPN	SMTN	SMPN	RMPN
V-Cr-Sb	1.78:9.40:33.9:0.00	0.94	3830	350	8.8	2.0	0.23	0.13	0.08	0.55	0.34	0.10
				320	8.8	3.0	0.34	0.15	0.13	0.45	0.38	0.11
				440	9.4	3.8	0.40	0.14	0.18	0.34	0.45	0.11
				480	9.1	3.5	0.38	0.10	0.18	0.26	0.47	0.10
V-Cr-B	1.78:9.40:33.9:0.00	0.94	3830	350	8.8	1.6	0.18	0.05	0.09	0.28	0.50	0.15
				380	8.8	2.9	0.30	0.10	0.17	0.27	0.52	0.15
				440	8.8	4.4	0.50	0.07	0.28	0.15	0.57	0.14
				480	9.6	4.0	0.42	0.03	0.18	0.07	0.44	0.10
V-Cr-Pb	1.78:9.40:33.9:0.00	0.94	3830	350	9.1	2.0	0.22	0.16	0.04	0.71	0.19	0.06
				380	9.1	2.6	0.29	0.16	0.09	0.55	0.31	0.09
				440	8.0	3.5	0.44	0.14	0.18	0.32	0.40	0.10
				480	8.0	3.7	0.46	0.18	0.07	0.38	0.14	0.03
V-Cr-Co	1.76:10.3:33.6:0.00	0.93	3870	350	8.0	2.6	0.32	0.13	0.13	0.41	0.42	0.13
				380	8.0	3.2	0.41	0.16	0.17	0.40	0.42	0.12
				440	8.0	3.9	0.49	0.14	0.23	0.28	0.47	0.11
				480	8.0	4.0	0.50	0.05	0.26	0.10	0.52	0.12
TIN	1.32:7.56:34.9:56.7	0.45	8000	320	18.8	2.5	0.13	0.08	0.02	0.61	0.11	0.08
VANADATE				360	19.3	14.1	0.73	0.20	0.37	0.28	0.51	0.31
				380	18.8	13.3	0.71	0.23	0.38	0.32	0.54	0.32
				400	18.2	13.7	0.75	0.15	0.48	0.20	0.64	0.36
				430	19.3	16.5	0.86	0.05	0.49	0.06	0.57	0.29
	1.13:4.5:21.8:32.32	0.10	36000	360	19.0	8.8	0.46	0.14	0.15	0.30	0.32	0.89
				390	18.8	9.9	0.53	0.11	0.20	0.21	0.38	0.97
				400	19.0	11.1	0.58	0.03	0.32	0.05	0.54	1.35
				420	18.8	11.6	0.62	0.01	0.36	0.01	0.56	1.33
	1.19:4.75:22.8:33.9	0.41	8780	360	18.8	11.6	0.62	0.27	0.23	0.44	0.37	0.25
				390	18.8	12.7	0.68	0.14	0.46	0.21	0.68	0.43
				400	19.0	13.4	0.71	0.04	0.50	0.06	0.71	0.43
				420	18.8	13.7	0.73	0.01	0.54	0.01	0.74	0.43

APPENDIX III (CONTD.)

CATALYST	MC	CT	SV	AVGT	MXF	MXC	FC	YMTN	YMPN	SMTN	SMPN	RMPN
TIN	1.95:7.57:36.5:54.1	0.81	4440	360	19.3	12.1	0.63	0.27	0.26	0.44	0.42	0.14
VANADATE				390	19.3	13.6	0.71	0.12	0.46	0.17	0.65	0.21
				400	19.3	14.2	0.74	0.06	0.52	0.08	0.71	0.22
				420	19.0	14.3	0.75	0.02	0.56	0.03	0.75	0.22
	1.89:7.57:36.5:54.1	1.00	3600	360	18.8	10.8	0.57	0.06	0.25	0.10	0.43	0.15
				390	18.8	10.8	0.57	0.04	0.40	0.07	0.69	0.22
				400	18.8	11.6	0.62	0.02	0.44	0.02	0.71	0.22
				420	19.0	12.4	0.65	0.01	0.49	0.01	0.76	0.22
	1.47:8.39:38.8:5.24	0.50	7200	360	18.8	13.5	0.72	0.34	0.26	0.47	0.36	0.20
				376	19.6	15.8	0.81	0.21	0.39	0.26	0.49	0.26
				390	19.6	16.7	0.85	0.13	0.48	0.16	0.56	0.29
				405	19.3	16.6	0.86	0.09	0.46	0.10	0.53	0.26
				420	18.8	13.8	0.75	0.05	0.32	0.07	0.43	0.20
	1.36:7.45:34.5:56.8	0.50	7200	360	19.6	15.6	0.80	0.50	0.19	0.63	0.24	0.13
				380	19.6	15.6	0.80	0.33	0.34	0.41	0.43	0.23
				400	19.6	16.7	0.85	0.26	0.44	0.30	0.52	0.26
				420	19.3	16.6	0.86	0.18	0.51	0.20	0.60	0.29
	0.85:4.78:21.5:72.9	0.50	7200	360	19.0	13.0	0.68	0.13	0.49	0.19	0.72	0.42
				380	19.0	14.1	0.74	0.08	0.59	0.11	0.80	0.42
				400	19.3	14.0	0.73	0.02	0.60	0.03	0.83	0.41
				420	19.3	13.8	0.72	0.01	0.58	0.02	0.82	0.39

NOTATION USED IS

- MC.....MOLAR COMPOSITION OF THE REACTION MIXTURE (AVG. %)
- CT.....CONTACT TIME IN SECONDS
- SV.....SPACE VELOCITY IN HOURS INVERSE
- AVGT.....AVERAGE TEMPERATURE OF THE CATALYTIC BED IN DEGREES C
- MXF.....MMOLS./HR. OF M-XYLFNE FED
- MXC.....MMOLS./HR. OF M-XYLFNE CONVERTED INTO PRODUCTS
- FC.....FRACTIONAL CONVERSION OF M-XYLFNE TO THE AMOXIDATION PRODUCTS
- YMPN.....FRACTIONAL YIELD OF M-PHTHALONITRILE
- SMPN.....SELECTIVITY OF THE CATALYST FOR FORMING M-PHTHALONITRILE
- RMPN.....RATING OF THE CATALYST FOR FORMING M-PHTHALONITRILE

APPENDIX IV

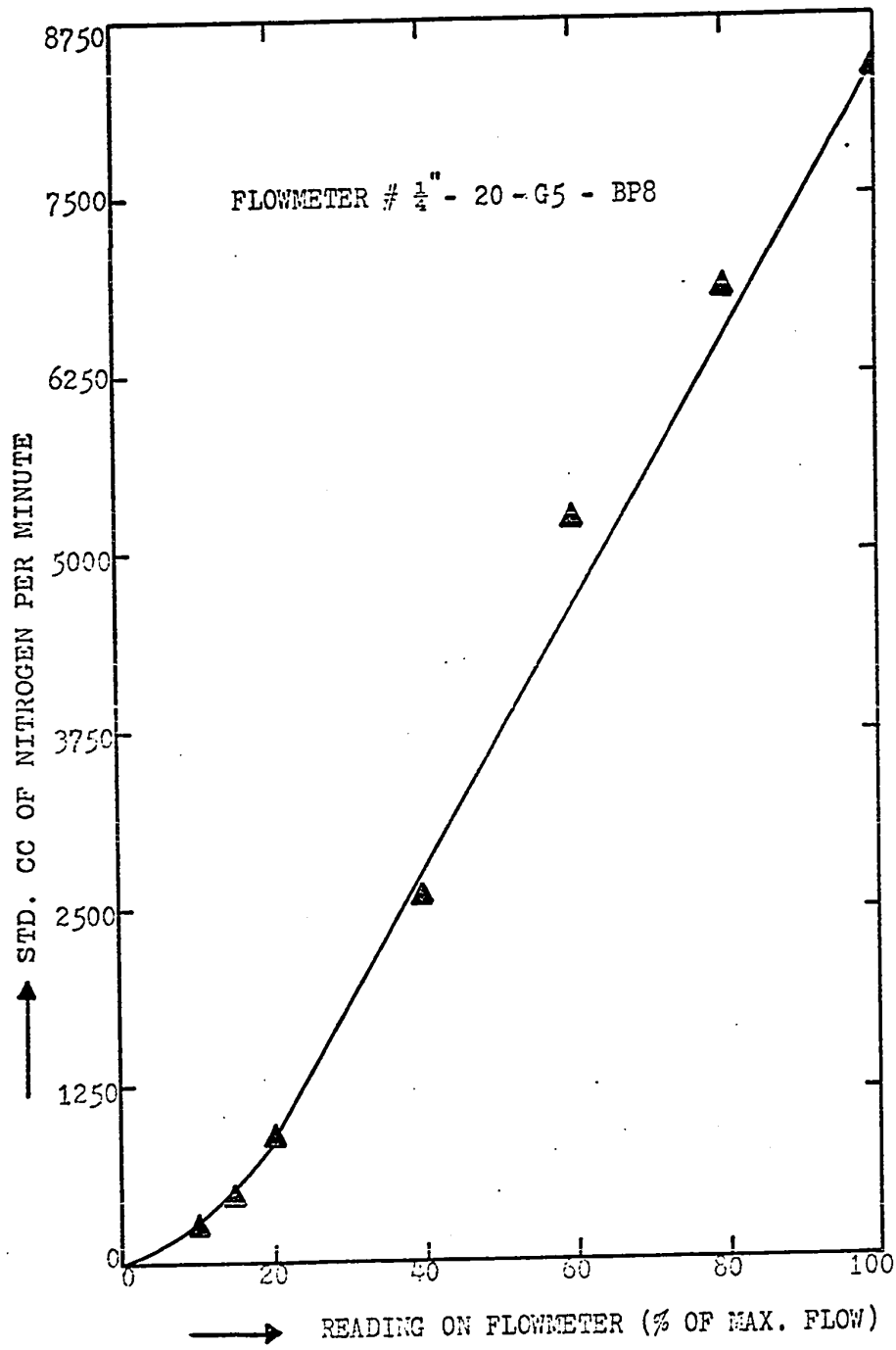


FIGURE 19 CALIBRATION PLOT FOR NITROGEN FLOWMETER I

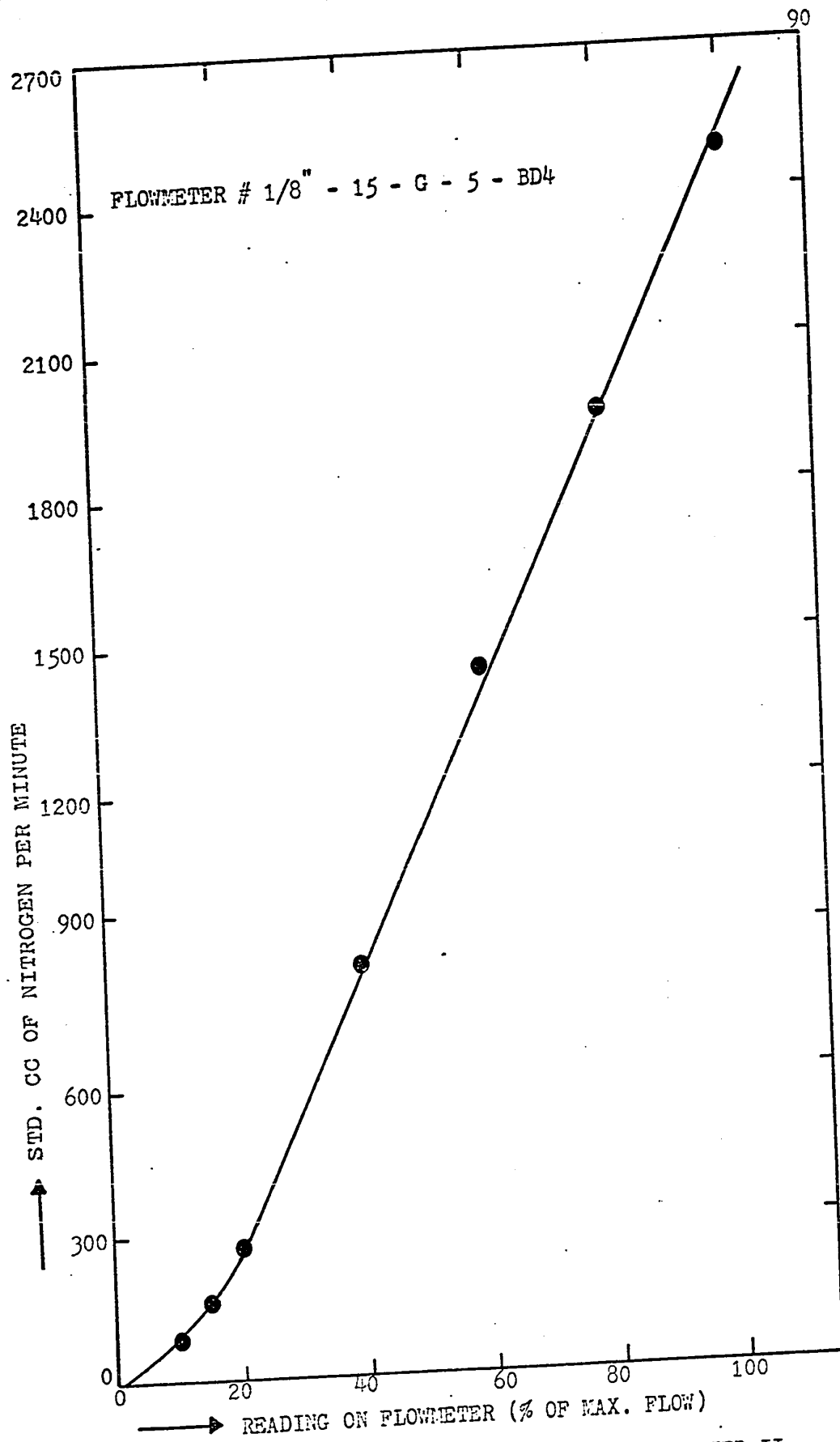


FIGURE 20 CALIBRATION PLOT FOR NITROGEN FLOWMETER II

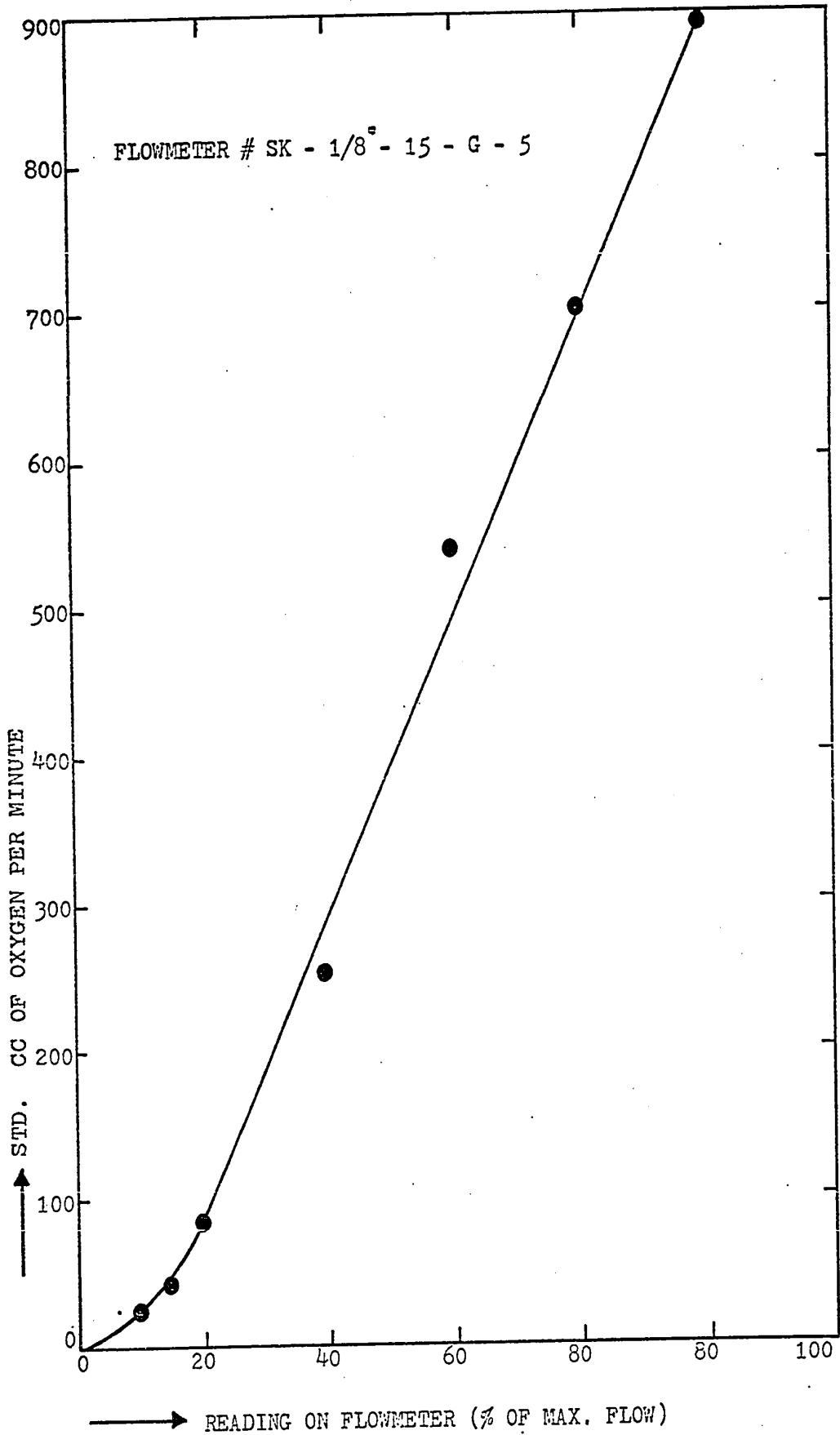


FIGURE 21 CALIBRATION PLOT FOR OXYGEN FLOWMETER

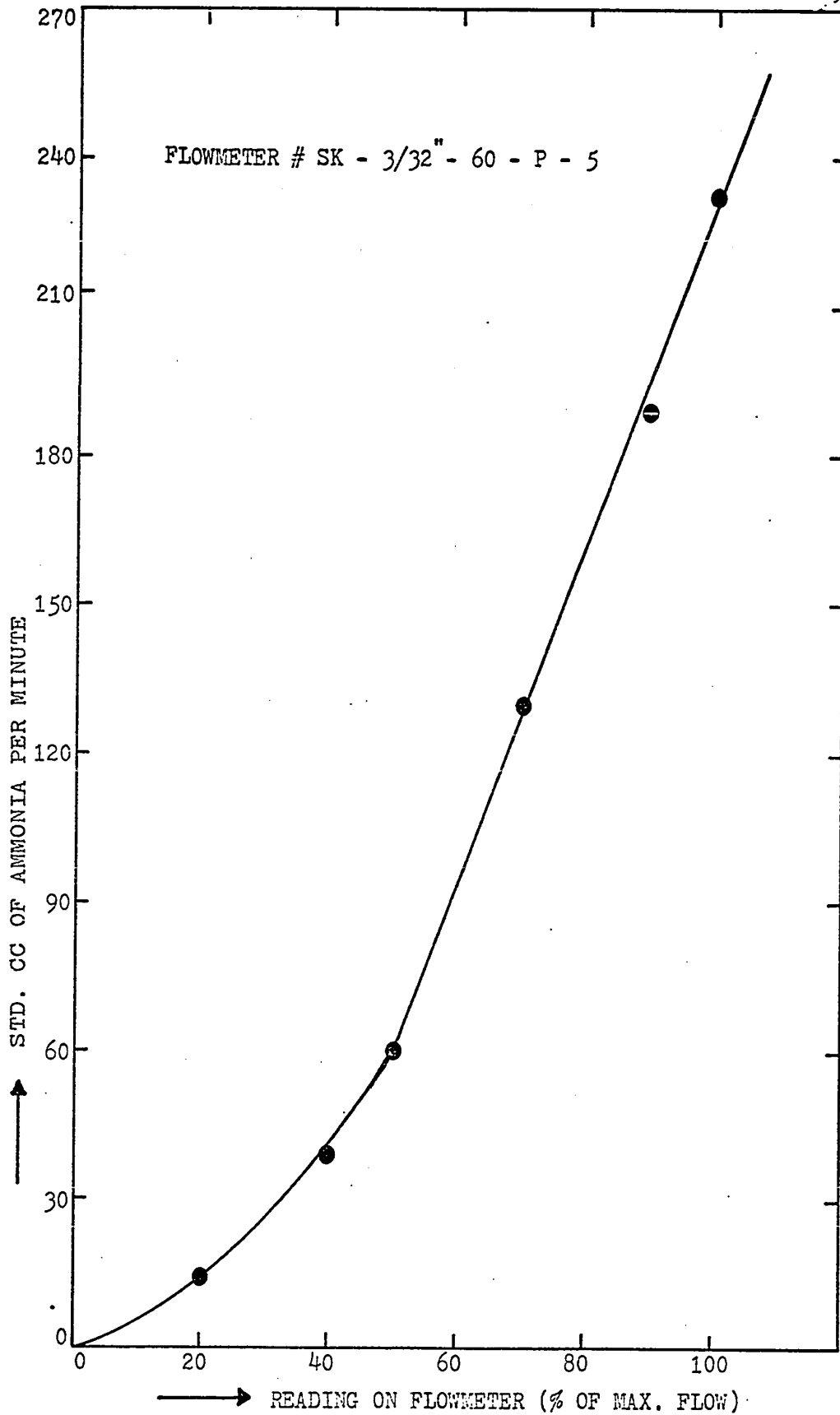


FIGURE 22 CALIBRATION PLOT FOR AMMONIA FLOWMETER

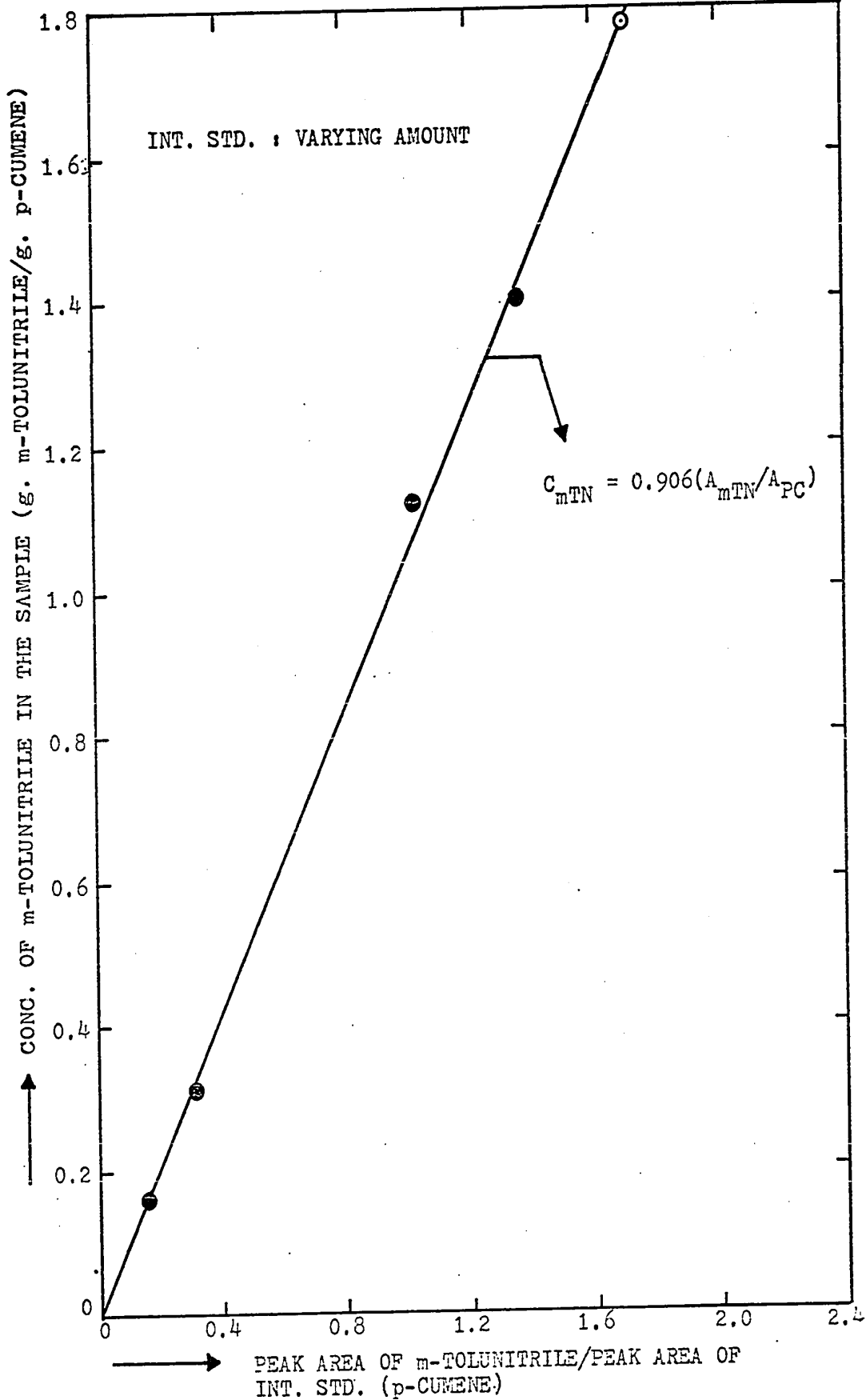


FIGURE 23 CALIBRATION CURVE FOR THE DETERMINATION OF SMALL CONC. OF m-TOLUNITRILE IN A MIXTURE

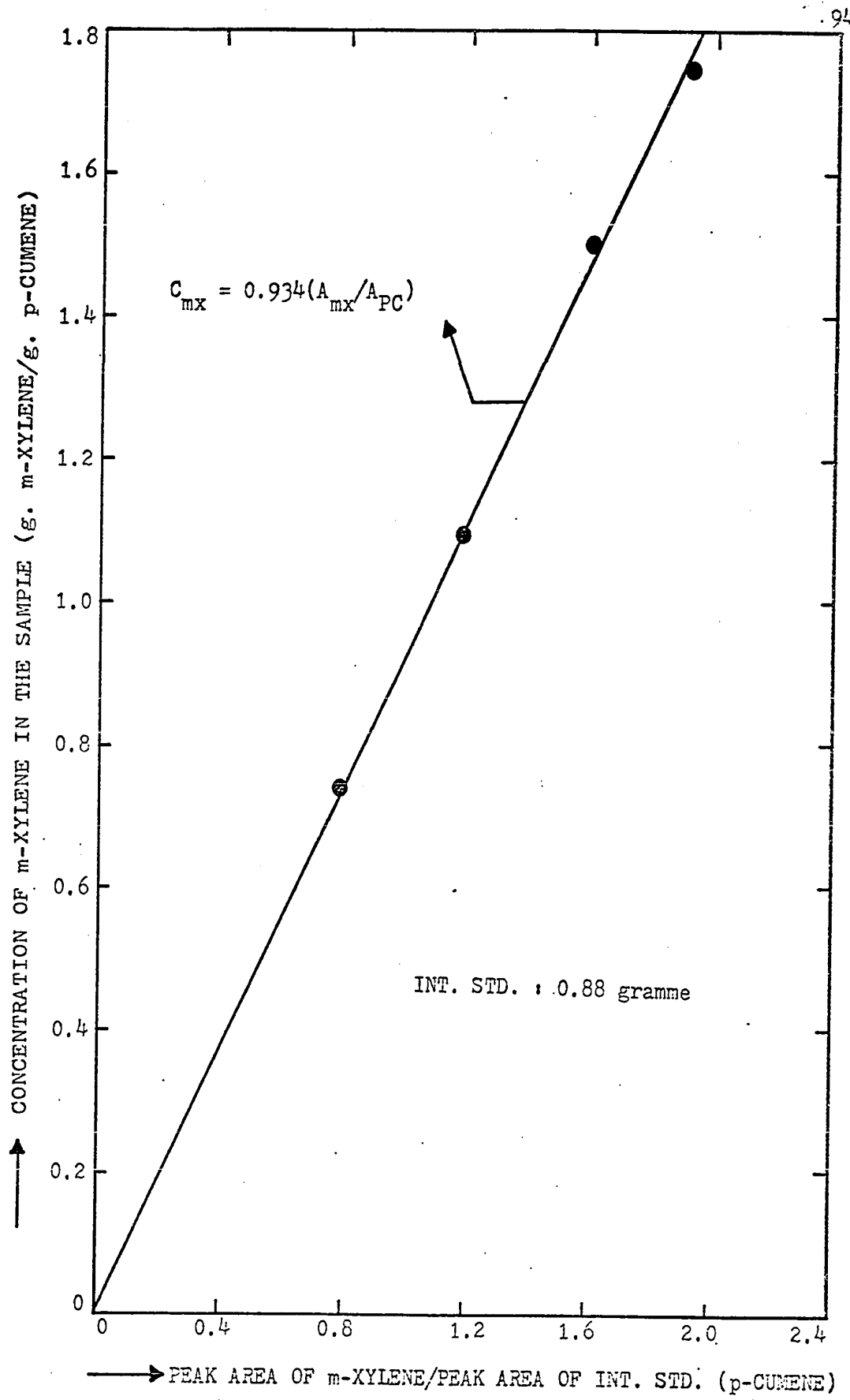


FIGURE 24 CALIBRATION CURVE FOR THE DETERMINATION OF m-XYLENE CONCENTRATIONS IN A SAMPLE

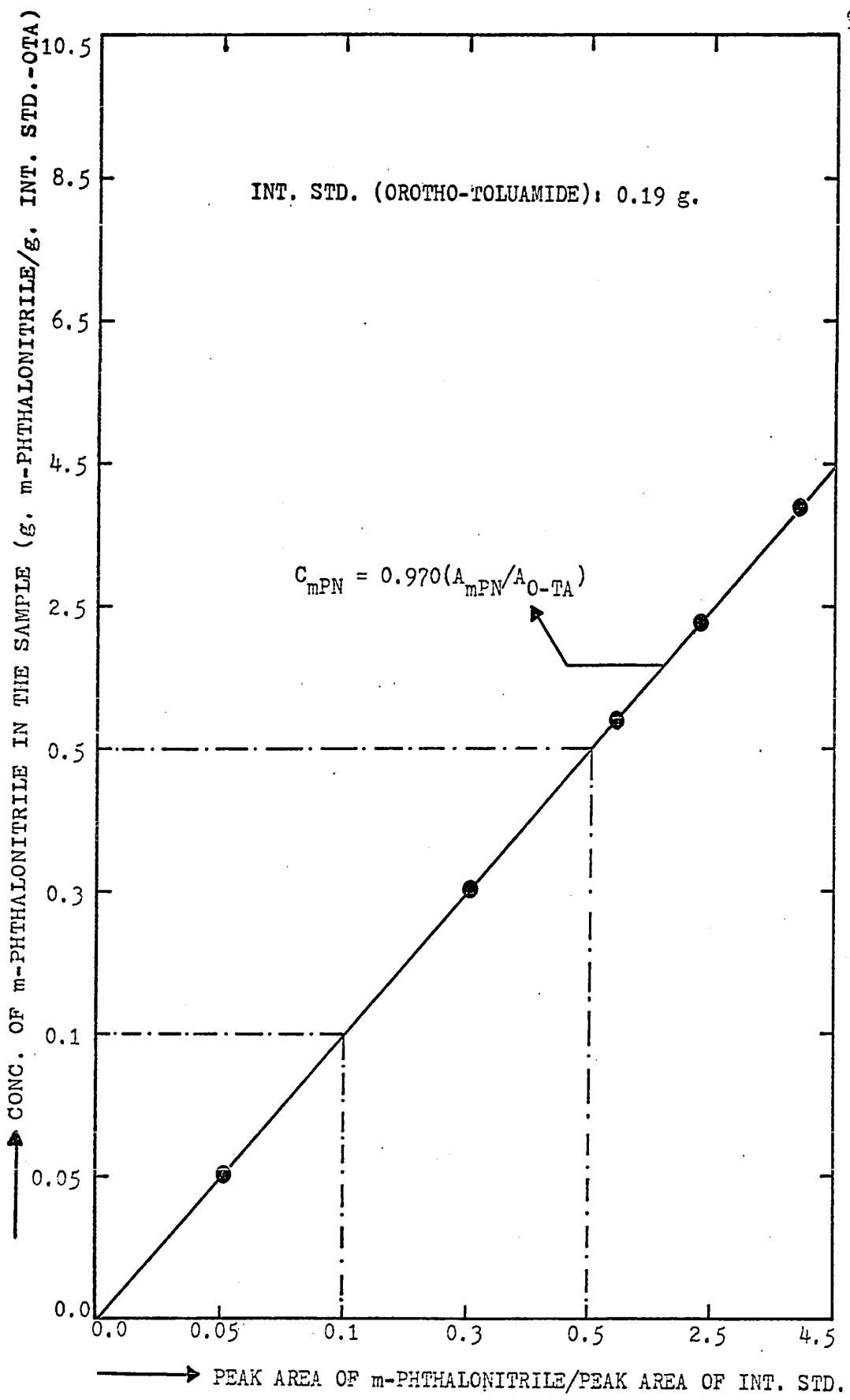


FIGURE 25 CALIBRATION OF SMALL CONCENTRATIONS OF m-PHTHALONITRILE IN A MIXTURE

VITA AUCTORIS

- 1944 Born at Abbatabad, N.W.F.P., India.
- 1967 Received Bachelor of Technology (Chemical Engineering) from Indian Institute of Technology, Kharagpur, India.
- 1967 Worked as a Commissioning Engineer, Rajasthan Atomic Power Station, Kota, India.
- 1971 Accepted into the Graduate School of the University of Windsor, Windsor, Ontario as a candidate for the Degree of Master of Applied Science in Chemical Engineering.