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VAPOR PHASE NITRATION OF BUTANE
IN A MOLTEN SALT REACTOR: PROCESS
AND ECONOMIC OPTIMIZATION

by

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1967

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ABSTRACT

A molten salt reactor for continuously nitrating butane with nitric acid in the vapor phase was designed, constructed, and successfully operated. The reactor was designed to use the exothermic heat of reaction to vaporize liquid nitric acid thereby providing excellent temperature control in the reaction zone and reducing the possibility of explosions. Molten salt temperature was varied from 385°C to 455°C; mole ratio of hydrocarbon to nitric acid from 3 to 7; and reactant flow rate from 0.433 gram moles/min. to 1.235 gram moles/min. A central composite statistical design in three orthogonal blocks was used to reduce the number of experimental points required to adequately cover the range of variables, to supply an estimate of experimental error, and to prevent the presence of a linear time trend from affecting comparisons between different levels of each variable. However, no measurable time trend existed.

Gas chromatography techniques were developed which provide on-line quantitative analysis of the reactor products.

Nitroparaffin yields based on hydrocarbon consumed ranged from 33.5 per cent to 67.3 per cent while conversions based on hydrocarbon fed ranged from 1.46 per cent to 4.71 per cent. Yields based on nitric acid ranged from 20.8 per cent to 34.7 per cent.

The mole per cent distribution of the nitroparaffins produced ranged as follows: nitromethane, 9.26 - 16.18;

nitroethane 17.32 - 27.48; 1-nitropropane, 7.14 - 12.90; 2-nitrobutane, 12.54 - 46.97; 1-nitrobutane, 14.47 - 31.60. For six replicated experiments the standard deviations of the mean varied from 0.38 on a mean of 23.61 for nitroethane to 1.83 on a mean of 23.84 for 1-nitrobutane.

An economic profit model was constructed for a 15,000,000 lb./year nitroparaffin plant and then optimized to determine the most favorable set of operating conditions. The optimum per cent return on investment after taxes was 7.65 per cent which occurred at the following operating conditions: 445.7°O, 4.51 moles butane/mole acid, and 0.833 gram moles of reactant/min. The nitroparaffin distribution under these conditions was: 14.9 mole per cent NM, 23.6 mole per cent NE, 12.0 mole per cent 1-NP, 16.6 mole per cent 2-NB, and 32.9 mole per cent 1-NB.

INTRODUCTION

At this time there are both numerous commercial uses for and high promise of many future applications of the lower nitroparaffins. Because these chemicals are miscible with most organic substances, they have value as industrial solvents. In addition to this direct application, a large number of commercially desirable compounds are derived from the nitroparaffins. Of importance are hydroxylammonium salts, amines, nitroolefins, and nitroalcohols. They are also potentially useful as components in rocket fuels. The long-range promise of the nitroparaffin derivatives has been but partially explored, for there have been over 2,000 derivatives produced on an exploratory basis in the laboratories of the Commercial Solvents Corporation alone (25). This versatility assures further extension of their already proven applications.

The Commercial Solvents Corporation is the only major U. S. producer of nitroparaffins. Their plant, which uses the vapor phase contacting of propane with 67 per cent nitric acid in spray nitration chambers, has a rated capacity of 10,000,000 pounds of nitroparaffins per year (25). This commercially successful nitration of propane gave good reason to believe that butane nitration could also be a profitable operation. A preliminary economic evaluation for a nitroparaffin plant using butane and nitric acid as the feed materials was recently reported by Fear (31). He showed that the raw material cost

was approximately 28 per cent of the value of the nitrated product and that an estimated investment return for a 14,000,000 lb./yr. plant would be approximately 9 per cent.

General

The vapor phase nitration of the lower molecular weight paraffinic hydrocarbons may be conducted by numerous permutations of the possible reactants, nitrating agents, and reactor designs. The choice of the particular systems investigated in this research was influenced by two considerations: (1) the work is a continuation of that initiated by Adams (1) and Fear and Burnet (32) and (2) the factors which led these investigators to choose the system under consideration are still valid.

Nitrating agents

Nitrating agents which have been used by previous investigators of vapor phase nitrations are nitrogen dioxide (10, 29, 38, 61), nitric oxide (37), and nitric acid (1, 13, 31, 32, 40). Some difficulty has been reported with corrosion of equipment used to vaporize nitric acid (25, 50, 53), and several problems have been encountered in the controlled metering of the liquid acid (1, 31, 39). Moreover, the addition of water with the nitric acid increases, in no small measure, the difficulties encountered in product analysis. However, the following reasons were sufficient impetus to overcome these problems and use nitric acid as the nitrating agent in this research: (1) both conversion (based on nitrating agent) and

yields (based on alkane) are generally higher when nitric acid rather than nitrogen dioxide is employed, (2) liquid nitric acid is used in the commercial process, and (3) the in-reactor vaporization of the nitric acid could be used to control the highly exothermic reaction.

Analytical

Through the combined efforts of Ives (46), Johnnie (47), and this author (48), the analytical problems have been considerably reduced by the development of a chromatographic column which will handle the quantities of water that occur in the reactor effluent because of the use of nitric acid feed. The operating conditions for a gas-liquid chromatographic unit using this column have been determined, which allow the quantitative separation of the bulk of the reaction products by a 25 minute isothermal analysis. The mechanical hook-up for this multiple-column, on-line analysis was reported by Johnnie (47, 48).

Metering and control

The acid metering and control problems were solved by the use of an acid egg as the prime mover for the liquid nitric acid. To minimize the difficulties previously encountered with acid vaporization in the feed lines the acid was kept in liquid form until it reached the reaction zone where its heat of vaporization was then used to help control the temperature of the highly exothermic reaction. In this way the reaction

was conducted at low mole ratios of hydrocarbon to acid without the explosions or extremely high temperatures previously reported (1).

Hydrocarbon

Butane, which frequently has a price advantage over propane but which has not been as fully investigated, was selected for the hydrocarbon. The same nitroparaffins which are obtained from propane plus four additional ones, 1-nitrobutane, 2-nitrobutane, 2-nitro-2-methylpropane, and 1-nitro-2-methylpropane, are obtained from the nitration of butane. Previous studies of butane were made in tubular reactors by Hass, Hodge, and Vanderbilt (39) in 1936, by McCleary and Degering (54) in 1938, and by Bachman, Hass, and Addison (9) in 1952. In these studies the quantitative analysis was based on average molecular weights. Recently Adams (1) and Fear and Burnet (32) applied gas-liquid chromatographic techniques to aliquot samples from the effluent of a vapor phase nitrator and determined, with relatively good success, the distribution of the nitroparaffinic products. These previous results are shown in Table 1. However, because of differences in feed stream compositions, analytical techniques, and in some cases doubtful product collection systems, the data are hardly comparable.

Reactor designs

The two major types of reactors of importance in bench and pilot scale nitration studies are: (1) tubular reactors

Table 1. Product distribution of nitroparaffins in mole per cent formed during the nitration of butane

	*Adams (1)	**McCleary et al. (54)	**Addison ^a (2)	**Hass et al. (39)	*Fear (31)
NM	8-14	2-9	19	6-10	5.7-14.3
NE	20-26	11-25	32	12-13	14.4-38.7
2-NP	0.04-0.29	- - -	--	- - -	0-0.12
2-M-2-NP	0-0.34	- - -	--	- - -	0-3.0
1-NP	5-9	5-7	11	5-8	2.4-13.4
2-NB	36-51	23-49	21	45-50	5.9-64.7
2-M-1-NP	0-0.04	- - -	--	- - -	0-1.1
1-NB	14-20	27-32	17	24-27	10.4-40.9
Yield ^b	60-82	- ^c	17.4	- ^c	26.7-84.3 ^e
Conversion	20-40	18-20	33	28 ^d	8.8-30.7

^aWith oxygen added: 2 moles per mole HNO_3 .

^bBased on hydrocarbon consumed.

^cInsufficient data available.

^dBased on HNO_3 consumed.

^eBased on assumption propane, isobutane, and n-butane are recoverable hydrocarbon.

*Adams and Fear both used the same range of temperatures (370 to 480°C) and mole ratios (3 to 8). However, their residence times are not directly comparable as Adams reported his on the basis of space velocity in the tube to the bottom of reactor while Fear reported total time in the reactor.

**All work performed at mole ratios of butane to nitric acid of 14 or higher.

and (2) molten salt bath reactors. The Commercial Solvents industrial reactor is of the continuous, multi-stage spray type.

Tubular reactors The majority of all vapor phase nitration studies have been conducted in tubular reactors of one type or another. Extreme wall effects and catalytic activity which prevent the formation of nitroparaffins were reported by Albright (5) and again observed by Johnnie (47). Dr. R. L. Abbott reports that, although fairly reproducible composite products have been obtained for propane nitration in tubular reactors, the instantaneous effluent concentrations vary in a random fashion for a test under a given set of conditions. To avoid these undesirable effects, gold-lined, and platinum-clad apparatus have been used; but these would be expensive for large scale use. At low mole ratios (hydrocarbon to acid), explosions have been reported which were thought to be caused by poor temperature control in the tubular reactor. During some preliminary tests with stainless steel tubular reactors at low mole ratios, the author and Johnnie noted a violent initiation period for the reaction even when the temperatures were under control. This violent action precludes the use of pyrex reactors under these conditions.

Salt bath reactors To effect better mixing and temperature control and at the same time avoid the catalytic effect of metal surfaces, some work has been done with molten salt reactors (1, 5, 24, 31, 32, 38). These investigators

have successfully conducted the continuous vapor phase nitration of butane and propane with nitric acid and have demonstrated the flexibility and potential of this type reactor as an experimental tool. However, because of the exploratory nature of the initial designs, precise control and measurement of the salient variables (temperature, residence time, mole ratio) were not obtained.

In addition to design and operational problems, these early studies were hindered by the lack of suitable analytical methods. Propane was the hydrocarbon feedstock for the early studies, and once again average molecular weight techniques were used for analysis. While more recent investigators using butane reported product distributions, they encountered certain problems in collecting the product for subsequent analysis. Specifically, the products were collected, refrigerated, and stored for up to 14 days prior to analysis. Since this time it has been noted that even at low temperatures the nitrous acid formed in the condensate can destroy the primary and secondary nitroparaffins (18). The occurrence of the "wild" nitration products through the destructive action of nitrous acid was further confirmed by Dr. R. L. Abbott. Because of these problems, optimum nitration conditions and the resulting product distributions for the reaction conducted completely in a molten salt reactor were yet to be determined.

Choice of design Based on the exploratory work of these previous researchers, particularly that of Fear and

Burnet (32), a nitration pilot unit utilizing a back-mix salt bath reactor was designed and constructed for use in this investigation. The items of primary concern in this design were: (1) increased accuracy in the control of acid and butane flow rates, thereby allowing the investigator to better set the mole ratios to be studied, (2) improved control of the reactor temperature and elimination to the extent possible of the 1,800°F hot spots reported by Adams (1), (3) minimum exposure of the reactant mixture to any surface other than the salt, thereby reducing possible catalytic and tubular reactor effects, (4) utilization of the latent heat of vaporization of the acid to control the reaction thus minimizing the chance of explosions at low mole ratios, and (5) elimination of conditions which would cause destruction of the product during the collection.

Objectives of the Research

The specific objectives of this research were: (1) to determine the optimum nitration conditions for the vapor phase nitration of butane by nitric acid in a molten salt reactor, (2) to aid in the development of an on-line gas chromatographic analysis for the effluent nitration product stream, and (3) obtain any information which will lead to a better insight as to the reaction mechanism.

REVIEW OF LITERATURE

Very complete summaries of both the historical and contemporary nitration literature have been recently compiled and reported by Adams (1), Fear (31), and Albright (3). Therefore, this review presents only that work relevant to the current research project.

Reaction Mechanisms

General

At present, comparatively little is known of the mechanism by which the vapor phase nitration of aliphatic hydrocarbons takes place. In general, it is thought that the reaction proceeds by a free radical mechanism since: (1) most gas phase reactions do proceed by this type of mechanism (33), (2) experimental evidence has shown that materials, such as metallic oxides, which normally catalyze ionic reactions usually decrease the yield from a nitration reaction (10, 39), and (3) the nitration of higher paraffins produces not only nitroparaffins of the same carbon chain number, but also produces significant quantities of both lower nitroparaffins and oxygenated products such as aldehydes. This product mix agrees with that predicted by free radical mechanisms.

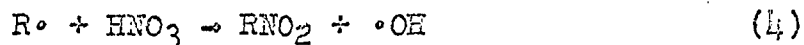
Bachman, et al., (7) have proposed the following free radical mechanism:





It since has, however, been questioned as to whether the decomposition of nitric acid, Reaction 1, is rapid enough to supply the NO_2 radicals consumed in Reaction 3. Experimentally it has been shown that the normal rate of thermal decomposition of nitric acid is much slower than the rate of nitration.

An alternate mechanism has been suggested by Albright, et al., (5) which involves the entrance of molecular nitric acid into a short chain mechanism.



Beach¹ feels that both Reactions 3 and 4 are probably involved in the actual nitration.

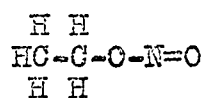
Production of lower nitroparaffins

The formation of the lower nitroparaffins cannot be explained by pyrolysis at the temperatures and retention times normally used in nitration (5). In addition, it is highly

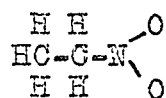
¹Beach, A. B., Instructor of Chemical Engineering, Iowa State University of Science and Technology, Ames, Iowa. Private communication. March, 1966.

unlikely that there is a direct cleavage of the C-C bond by NO₂ attack (19). Therefore, the most satisfactory explanation of the formation of the lower nitroparaffins is that alkyl nitrites are formed, then decomposed to yield lower alkyl radicals. The lower alkyl radicals are then nitrated to produce nitroparaffins.

The structural relation of the alkyl nitrites to the nitroparaffins can be seen from the following formulas. Particular attention is called to the fact that the nitrogen atom of a nitro compound is joined directly to the carbon.



ethyl nitrite

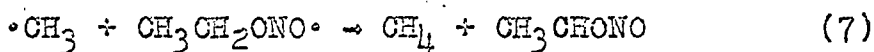
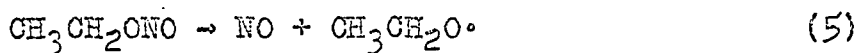


nitroethane

Pauling (55) represents nitrogen dioxide as a resonance hybrid where an electron is distributed between the oxygen atoms and the nitrogen atoms. If an alkyl radical reacts with nitrogen dioxide when the electron density about the nitrogen atom is low, a nitroparaffin is formed. On the other hand, if the reaction occurs when the electron density about the nitrogen is high, an alkyl nitrite results.

The alkyl nitrites are unstable at nitration temperatures and their decomposition mechanism as suggested by Grey (34) adequately accounts for the vapor phase production of the lower nitroparaffins. This decomposition is a two-step mechanism: (1) the alkyl nitrite breaks into a NO molecule and

an alkoxide radical and (2) the alkoxide radical breaks into a lower alkyl radical and an aldehyde. The second step is thought to be the faster so that the overall reaction would give a satisfactory representation of the decomposition process. This mechanism is illustrated by the decomposition of ethyl nitrite.



Any available alkyl radical could react with an alkyl nitrite in a reaction similar to Reaction 7. This mechanism also helps account for the oxidation products found in such reaction products.

Decomposition of nitroparaffins

The thermal decomposition of nitroethane and 1-nitropropane was investigated by Grey, et al., (35). At 430°C nitroethane was 13 per cent decomposed in 2.1 seconds, while 1-nitropropane was 20 per cent decomposed in 4.2 seconds. As compared with the retention times used in nitration, 0.5 to 1.5 seconds, these rates are large enough to account for the loss in nitroparaffins when the temperature exceeds some optimum value.

Basis for Computation

The results of nitration experiments have been reported in terms of conversion and yield; however, several different definitions of these quantities have been used. Both terms can be based on either input quantities or reacted quantities of either hydrocarbon or nitrating agent. To add to the confusion, some reports do not clearly state which definitions were used. In the usual case conversion meant the molar ratio of nitrogen in the nitroparaffin product to nitrogen charged, while yield implied carbon in the nitroparaffin product to carbon in the hydrocarbon consumed. These general usage conventions will be followed in this work so the results will be, in the main, comparative with some of the previous work.

Effect of Variables

Temperature effects

Work on isobutane by Hass, Hodge, and Vanderbilt (39) showed that the yield of primary nitroparaffins was greatly increased by raising the reaction temperature from 150°C to 420°C. It was later shown by Bachman, et al., (8) that, as the nitration temperature for propane is raised, the percentage of nitroethane produced increases, that of 2-nitropropane decreases, and those of nitromethane and 1-nitropropane remain the same. This observation is interesting in that the half-life of nitromethane under thermal decomposition at 420°C is 4 minutes, while Grey, et al., (35) found that 20 per cent

of the 1-nitropropane was decomposed in 4.2 seconds. This would lead one to believe that the 1-nitropropane percentage should decrease significantly faster than that of nitromethane under increasing temperature. However, Fear (31) reporting on the nitration of butane further substantiated the increase of nitroethane with temperature and the relative insensibility of 1-nitropropane and nitromethane percentages to temperature. As his 2-nitropropane figures scattered badly (0.063 ± 0.033 mole per cent on the average), he was unable to note a trend in this compound.

Hass and Shechter (42) used the previously published data to draw some general conclusions about the effect of temperature: (1) conversion increases with temperature until some optimum temperature is reached for each hydrocarbon, then decreases with further increase in temperature, (2) if contact time is matched with temperature, total yield of nitroparaffins will be approximately the same, and (3) the rate of substitution of primary, secondary, and tertiary position approaches equality as the temperature increases. Fear (31), on the other hand, found that, as temperature increased, the amount of 1-nitrobutane increased from an average of 12 mole per cent at 371°C to an average of 32 mole per cent at 482°C , while over the same temperature range the amount of 2-nitrobutane correspondingly decreased from 56 mole per cent to 9 mole per cent. In addition, over the range studied (0.5 to 0.7 seconds) he found no significant effect of residence time

on nitroparaffin production in his molten salt bath reactor study of butane nitration.

Pressure effects

At this writing there is very little data available on this subject. It was shown by Hass, et al., (39) that during the nitration of methane a moderate pressure (100 psig) increased conversion based on nitric acid. At both 100 psig and 1,000 psig optimum temperature and contact times decreased although the conversion had decreased from the 100 psig level to the 1,000 psig level.

Catalysis

Both homogeneous and heterogeneous catalysis have been studied in some detail. The general result of these studies was to find materials that either inhibited the reaction or that increased conversions based on nitrating agent at the expense of yields based on hydrocarbon.

Heterogeneous Although a considerable amount of work has been done in this area and several materials (particularly borosilicate glass) seemed, for a short time, to have positive catalytic effect on nitration, all of the concrete results obtained indicate either a negative or neutral effect. The highly detrimental effects of copper, mild steel, and to a lesser degree stainless steel are discussed in the section on Tubular Reactors. Of importance, however, is the evidence of the noncatalytic character of sodium and potassium nitrate

salts (4, 5, 24, 44). In general, at this time there is no published evidence of the existence of a heterogeneous catalyst that accelerates nitration or improves the yields or product distribution. The catalysts that show any activity have increased the competing oxidation reactions at the expense of the nitration reaction.

Homogeneous Nitric oxide has been shown to decrease conversion (12, 37), presumably by action as a chain stopper. In a tubular reactor, the addition of bromine or chlorine to the vapor phase nitration mixture can increase both yield and conversion (12, 13, 14), while the addition of oxygen can increase the conversion (9). These compounds, however, increase the conversion based on nitrating agent at the expense of yields based on hydrocarbon. This occurs because there is a correspondingly greater increase in the competing oxidation reactions.

Mole ratio effects

Coldiron (23, 24) reported that the maximum conversions based on nitric acid were essentially independent of mole ratio during the nitration of propane; however, the apparent best operating temperature decreased with decreasing mole ratio. Fear (31) also found that conversions were not appreciably affected by changes in mole ratio during the nitration of butane.

Reactors and Auxiliaries

Tubular reactors

Tubular reactors have been used to conduct the majority of the vapor phase nitration studies. Glass has been used most often as the material of construction, and stainless steel has been used occasionally (4, 5, 43). Albright, et al., (5) investigated the surface effects of glass, stainless steel, copper, and carbon steel. He encountered considerable difficulty in reproducing results from the metal reactors. However, when the relative conversions were calculated by dividing nitroparaffin conversion in the metal reactor by conversion in the glass reactor at the same temperature, a trend was evident. The relative conversion in the carbon steel reactor increased from 58 per cent to 100 per cent in six hours of operation, that in the stainless steel reactor decreased from 100 per cent to 82 per cent in the same time span, while after less than three hours of operation almost no product was being formed in the copper reactor. The glass surface itself did not seem to change as a function of time. His additional studies with surfaces involving molten salt showed that surfaces favoring nitration reactions minimize oxidation reactions and vice versa.

Molten salt reactors

Reactors using a molten mixture of sodium and potassium nitrates as the heat transfer medium have been developed

recently in an effort to both provide better temperature control of the highly exothermic nitration reactions and to minimize contact of the reacting mixture with possible inhibiting surfaces. This effort was the outgrowth of the work by Hodge (45) who noted that these salts prevented the increase of oxidation that occurs at the expense of nitration in stainless steel reactors.

In 1952, Hill (44) first applied the technique of allowing the reaction mixture to bubble through these salts. Following this general technique, Coldiron, et al., (24) were able to nitrate propane at hydrocarbon to acid ratios of one to one without experiencing the explosions previously reported (40) at mole ratios lower than two to one in tubular reactors. They attribute this to better temperature control. Albright, et al., (5) showed qualitatively that, when no heated void space existed above the salt level in a glass salt bath reactor, only insignificant amounts of oxidation occurred; while, if several inches of heated void space were available, a considerable quantity of aldehyde was produced. He attributed this to a possible surface effect. Adams (1) and later Fear (31), working with a metal reactor pot filled with molten salt, demonstrated the flexibility of the reactor as an experimental tool and reported the first sets of product distribution data available for the nitration of butane.

The method of mixing the reactants varied widely between these studies. The earlier investigators vaporized the acid

in a flask and contacted the butane and acid in the vapor phase outside of the reactor, then ran this mixture through a vertical tube to the bottom of the molten salt bath where it was allowed to bubble through the salt (5, 24). Adams (1) sprayed liquid acid through a 0.008 in. hole into a concentrically flowing stream of butane about three to four in. above the reactor head, then allowed the mixture to flow through 13 in. of tube to the bottom of the salt bath and bubble up through the molten mixture. Fear¹ attempted to contact liquid acid with preheated butane below the salt level but reported, "when the tip of the acid spray was below the salt level, excessive pressures were required to pump the nitric acid and the flow rate was erratic. I am still not quite sure why this happened but perhaps acid was vaporizing in the spray tube causing high pressure drop at the spray holes." Consequently, he contacted the acid and butane in a manner similar to that reported by Adams.

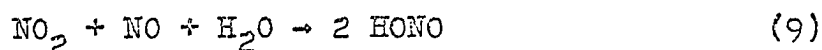
Product collection

In the bulk of the vapor phase nitration studies, the effluent product has been cooled to the extent of forming a two-phase liquid layer and an off gas product. The liquid layers have then been separated and either further fractionated by distillation prior to molecular weight determinations or

¹Fear, D. L.; Engineer, Dow Corning Chemical Company, Midland, Michigan. Private communication. July, 1965.

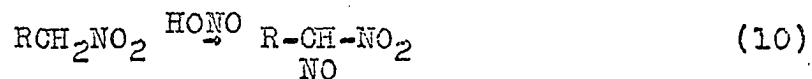
analyzed directly by gas chromatography. In at least one case the liquid layers were stored at refrigerator temperatures for several days prior to analysis (31). Both Coldiron (23) and Albright, et al., (4, 5) collected their liquid condensate in saturated solutions of sodium bisulfite for the purpose of removing the aldehydes. Coldiron noted that a higher amount of nitration product could be obtained if sodium bisulfite solutions were used instead of sodium bicarbonate. Fear (31), who collected his product by direct condensation, observed the following occurrence in his collection flask: "The reaction of nitric acid with other compounds caused boiling and evolution of CO₂ and NO₂. Nitrogen loss from these reactions possibly explains the low accountability."

In work to suppress the oxides of nitrogen, Kerns (49) showed that the active effect of the oxides of nitrogen in an aqueous medium occurred through the intermediate, nitrous acid, which is formed in the following manner:



This nitrous acid is stable in aqueous solutions below 20°C. When heated, the reverse of the above reaction occurs. As shown by Brewster (18), nitrous acid in solution is quite reactive towards organic compounds containing active hydrogens, such as the nitroparaffins. For example, by reaction with nitrous acid, primary nitroparaffins are converted into nitroso compounds known as nitrolic acids. The following

equation is an example of this reaction.



By a similar reaction, secondary nitroparaffins give nitroso derivatives called pseudo-nitroles.

In an effort to eliminate nitric oxide and nitrogen dioxide from the off gas during a metal processing operation, Kerns (49) found that urea was an excellent suppressor of the nitrogen oxides. Also, one of the standard techniques to quantitatively determine urea is to measure the nitrogen evolved when it is treated with nitrous acid (18).

Chromatographic Analysis

The study of the vapor phase nitration has been continually hampered by the lack of a rapid, reproducible quantitative analysis for the reactor effluent. The first satisfactory method of determining quantitatively the nitroparaffin distribution resulting from a vapor phase nitration was reported by Bethea and Adams (1, 15, 16, 17). In their method, the reactor product stream was cooled and separated into three phases: an oil layer containing mostly nitroparaffins and oxygenated organics, an aqueous phase containing mostly water, and an off gas containing butane, propane, water vapor, and the oxides of carbon and nitrogen. These phases were then analyzed using gas chromatography with three different columns, one of Armeen SD and Apiezon N on C-22 firebrick, one of

squalane on activated charcoal, and one of squalane on Fluoropak. Aliquot samples of the oil layer were analyzed on each of these columns, while samples of both the liquid layer and the gas phase were analyzed once on the activated charcoal column and twice on the Fluoropak column at different conditions. By the use of the substances appearing on each column, they were able to quantitatively identify the major oxygenated compounds, some of the gases, and all of the nitroparaffins. Initially they reported that the squalane, activated charcoal column would separate the oxides of nitrogen (1, 17); however, later this technique could not be replicated.

This general analytical technique was much refined by Fear (31), who found that bis (2-ethyl hexyl) adipate on Chromsorb W resulted in a more satisfactory analysis. He also separated the oxides of nitrogen by cooling the off gas below the freezing point of nitrogen dioxide and assuming only nitric oxide remained behind in the gas phase. Some difficulty was encountered with water tailing on the Chromsorb W column.

One interesting result of these chromatographic analyses was to show that the organic or oil layer contained significant quantities of the oxygenated materials. The earlier investigators of salt bath nitrations all made the same assumption, "Molecular weight of the organic layer, assumed to be only nitroparaffins, was determined by the Victor Meyer method" (24).

To date no satisfactory quantitative analysis by gas chromatographic techniques has been found for the oxides of nitrogen. In 1964, Bethea (15) reported, "In a recent attempt to obtain a satisfactory quantitative analysis of the oxides of nitrogen, over 30 chromatographic systems reported in the literature as effective for this separation problem were investigated. The results were uniformly poor; no acceptable quantitative analysis was obtained even though some qualitative results were marginally acceptable." More recently, Trowell (62) performed a quantitative analysis of the oxides of nitrogen in the presence of nitrogen and water vapor by first freezing out the nitrogen dioxide and water vapor on glass beads. Frossard, Rinker, and Corcoran (26) were able to quantitatively separate the oxides of nitrogen in the presence of nitrogen on a special silica gel column. However, while the nitrogen dioxide and nitrogen peaks appeared immediately, the nitrogen dioxide peak tailed for twenty minutes.

EXPERIMENTAL

This section consists of: (1) a description of the pilot plant, (2) a discussion of the operating procedure, (3) a study of the chromatographic analysis used and (4) a development of the experimental plan.

Description of the Pilot Plant

The equipment was designed to allow the maximum control of input flow rates and reactor temperature. All design calculations were based upon the assumption of ideal gas behavior for the vapor phase and reactant properties shown in Table 2.

The pilot plant which was constructed for this investigation consists of five major sections: (1) the nitric acid system, (2) the butane system, (3) the furnace group, (4) the reactor assembly, and (5) the product sampling system. Figure 1 shows a schematic flow diagram for the entire pilot plant.

General

The pilot unit was designed for continuous operation up to a maximum of three hours. The length of the period of continuous operation was limited by the capacity of the acid egg which held sufficient acid for a three hour run at the maximum possible butane flow rate and a one to one mole ratio of butane to acid.

The entire pilot unit was installed behind a 3/4 in. plywood enclosure which served both as panel board and secondary

Figure 1. Flow diagram of pilot plant

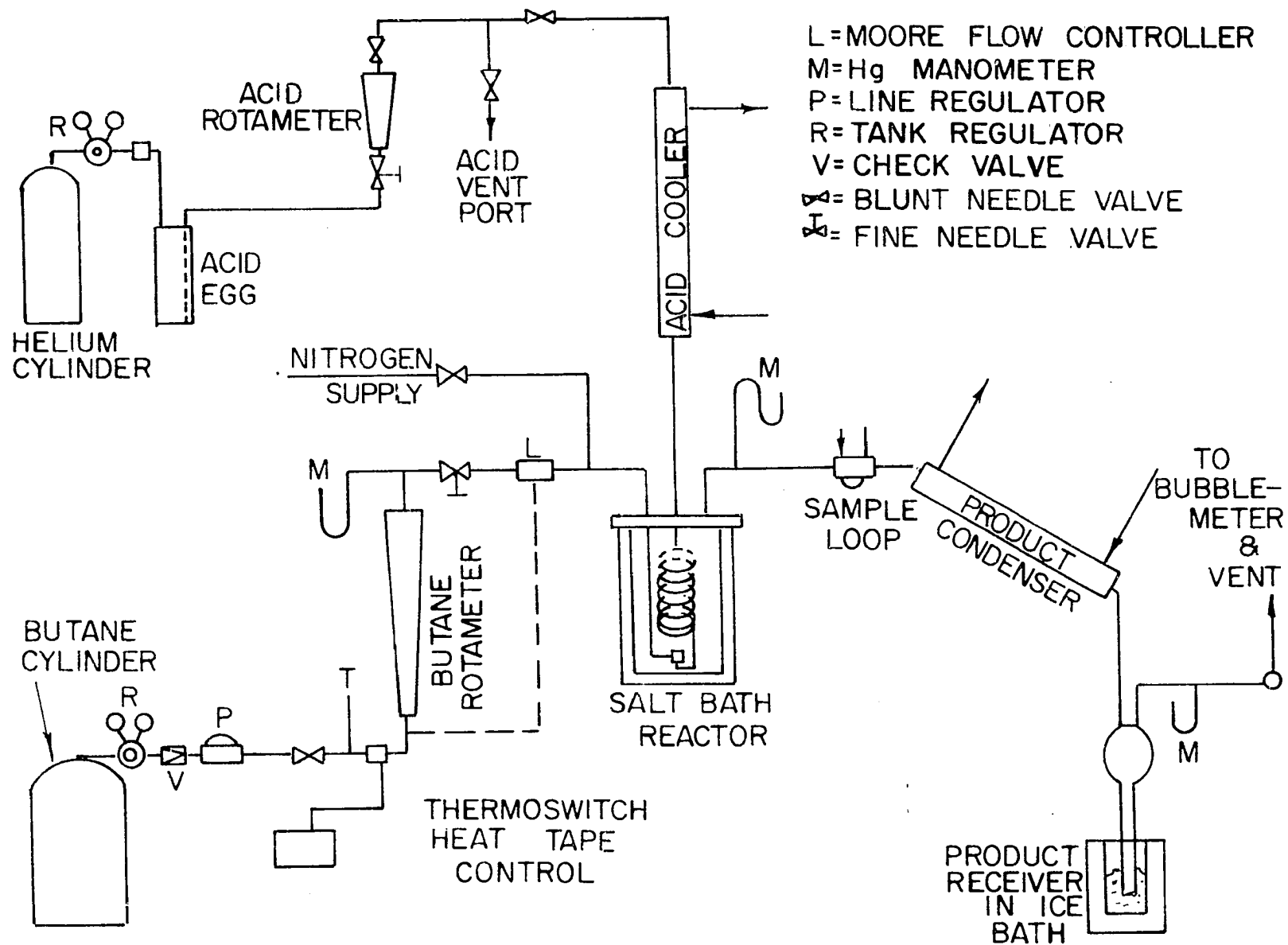


Table 2. Butane and nitric acid physical properties used in equipment design (56)

Butane Vapor

Heat capacity

Computed from empirical equation for hydrocarbon vapor

at 100°F 24.12 Btu/lb. mole °F

at 842°F 43.9 Btu/lb. mole °F

Thermal conductivity

Plot of log k versus t used to extrapolate outside the given range of data

at 32°F 0.0078 Btu/hr. ft. °F

at 212°F 0.0135 Btu/hr. ft. °F

Critical values

Temperature 425.2°K

Pressure 37.5 atm.

 μ (viscosity) 239×10^{-6} gram cm⁻¹sec⁻¹

Viscosity (1 atm.)

Computed from reduced correlation

at 100°F 0.0081 C_p at 842°F 0.0179 C_p

Enthalpy

at 100°F sat. vapor: 52 psia 306 Btu/lb.

sat. liquid: 52 psia 155 Btu/lb.

at 80°F sat. vapor: 40 psia 302 Btu/lb.

sat. liquid: 40 psia 146 Btu/lb.

Table 2. (Continued)

Nitric Acid (70% Liquid)

Density

at 20°C	1.4134 C_p
at 25°C	1.4067 C_p
at 30°C	1.3983 C_p

Specific heat

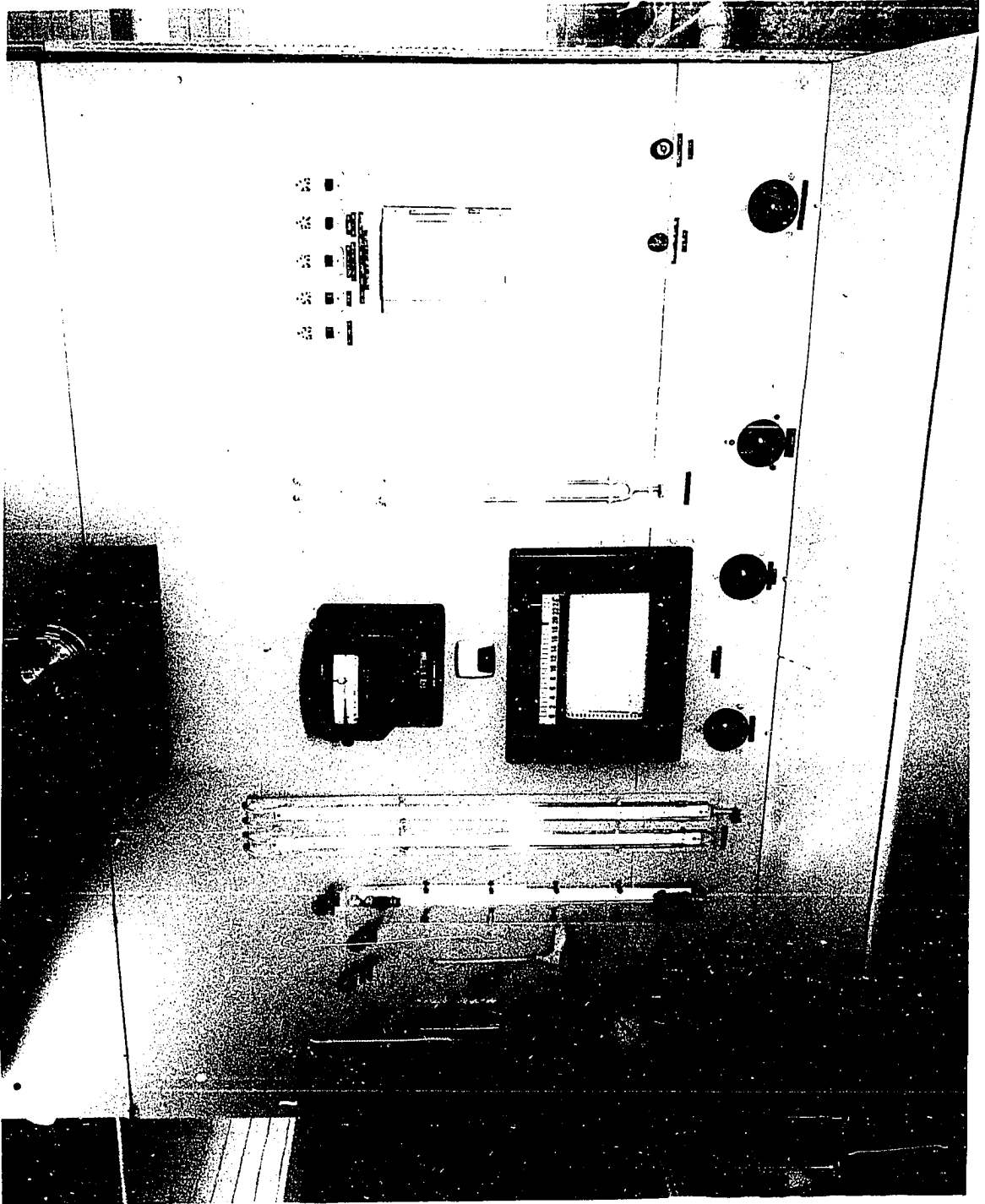
at 20°C	0.615 cal./g. °C
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and secondary blast shield. The plywood was bolted securely to three tubular steel uprights which were anchored to both the floor and ceiling of the laboratory. Because of previous reports of occasional explosions occurring during vapor phase nitration, an additional three-sided enclosure of 1/4 in. aluminum plate was bolted to the floor between the boiler plate frame of the reactor furnace and the plywood enclosure. One common side of both the plywood and aluminum enclosures opened toward a window which provided pressure relief in case of an emergency.

All instrumentation and controls required to operate the unit once the reaction was initiated were placed on the plywood panel board. A photograph of the panel board is shown in Figure 2.

The physical properties of the products, reactants, and

Figure 2. Photograph of control panel



materials of construction required to perform the design computations were, where possible, obtained from the literature or, where necessary, estimated by standard empirical methods. The values of the properties used and their sources are shown in Table 2.

Nitric acid system

The nitric acid system used an acid egg connected to the regulator of a helium cylinder to pump the acid. The acid egg, which had a capacity of 79.5 cu. in., was constructed of 1.5 ft. of 2.5 in. outside diameter, 0.065 in. wall, type 306 stainless steel tubing with 1/4 in. stainless steel plates welded to close each end. Swagelok 1/4 in. tube fittings were welded on the end plates to provide the helium in, acid out, and drain ports. A check valve was installed to prevent acid vapors from backing up to the cylinder regulator when the pressure was released. Although both the cylinder and acid egg were behind the plywood enclosure, the pressure in the acid egg could be observed and controlled by a pressure gage and valve mounted on the panel board.

The nitric acid flow system is included in Figure 1. The acid was forced from the acid egg through 1/4 in. tubing to a blunt needle valve and a calibrated Brooks rotameter. From the rotameter, the acid passed through a Whitely micro-regulator control valve, and then either to the acid vent port while the flow rate was being adjusted or to the reactor. The acid,

while flowing from the rotameter to the reactor, passed through a six foot counter-current double-pipe heat exchanger in which the annular space was filled with flowing Prestone antifreeze at -15°C . Cooling the acid was one of the things done to aid in the prevention of premature acid vaporization which could have led to vapor locking in the acid spray device, reduced nitroparaffin yields or explosions at low mole ratios. The acid line was reduced from 1/4 in. to 1/8 in. immediately prior to entering the reactor.

Controllable flow rates from 3×10^{-4} to 100×10^{-4} gram moles of 70 per cent nitric acid per second were obtained by use of this system. Commercial grade (Mallinckrodt Chemical Works) 70 per cent acid was used exclusively for this research.

Butane system

The butane system is also included in Figure 1. The butane cylinder was heated by a hot water bath and insulated to maintain a supply pressure of 60 psig. The downstream pressure was set first by a two-stage regulator on the cylinder and then by a low pressure pancake regulator set at 20 psig. After flowing through 20 feet of 1/4 in. copper tubing and a Moore constant differential pressure flow controller, the gas was metered in a calibrated Brooks 600 mm. rotameter. The butane temperature at the rotameter entrance was controlled by means of a Fenwall thermostwitch connected to 20 feet of electrical heating tape which was placed outside the insulated

line from the source cylinder. By use of a fine Hoke needle valve sized according to specifications for use with the Moore controller, constant and highly reproducible flow rates were obtained, and because of the controller, were independent of downstream pressure fluctuations. The butane pressure was measured at the rotameter with a mercury manometer.

The rotameter was calibrated with a precision wet test meter. The system delivered butane at rates from 0.04 to 0.35 gram moles per minute. The butane used in this calibration was Phillips Petroleum Company technical grade butane with a minimum purity of 95 mole per cent n-butane.

Reactor furnace group

The reactor furnace group was both a support for the reactor pot and a heat source for the molten salt. The furnace frame was a 19 x 19 x 30 in. shell formed from angle iron with 1/4 in. boiler plate on the top, bottom, and three sides. The angle iron junctions were first securely bolted together, then the edges were sealed with a bead of weld. The boiler plate sides were bolted to the inner face of the angles, thereby creating a firm structure. The outer faces of the reactor frame were covered with 1/4 in. transite. The inner walls of the cavity were lined with a double layer of fire-brick while the remainder of the cavity, with the exception of sufficient space in the center to accommodate the reactor pot, was filled with asbestos blocks. The side of the frame not

covered with boiler plate was covered with a sheet of transite and faced toward the window.

The reactor pot was wrapped in a spiral with three ceramic-covered heaters. Then the pot and heaters were encased in thermal setting ceramic. Two of the heaters are rated at 1,500 watts, the third at 1,000 watts. The power output of the heaters was controlled by powerstat variable transformers mounted on the panel board. To control the temperature of the molten salt at the desired set point, a Brown Electric Pyrometer was connected in series with one of the 1,500 watt heaters.

Reactor assembly

The reactor assembly consisted of two separate groups, the reactor head and the reactor pot. These sections were bolted together using five 3/4 in. bolts and were supported in the furnace by the upper boiler plate of the furnace frame.

The reactor pot, shown in Figure 3, was 24 inches deep and six inches in internal diameter. It was constructed of Schedule 40, six inch iron pipe with a 1/2 in. mild steel plate for the bottom. Three baffles of 1/2 x 1/8 in. stainless steel plate were installed at 120° separations. The pot was filled with 21 pounds of a eutectic mixture which melts at 222°C and consists of 54 weight per cent KNO_3 and 46 weight per cent NaNO_3 . The reactor contents were agitated by means of a two-inch stainless steel impeller of the turbine type

Figure 3. Reactor pot and head assembly

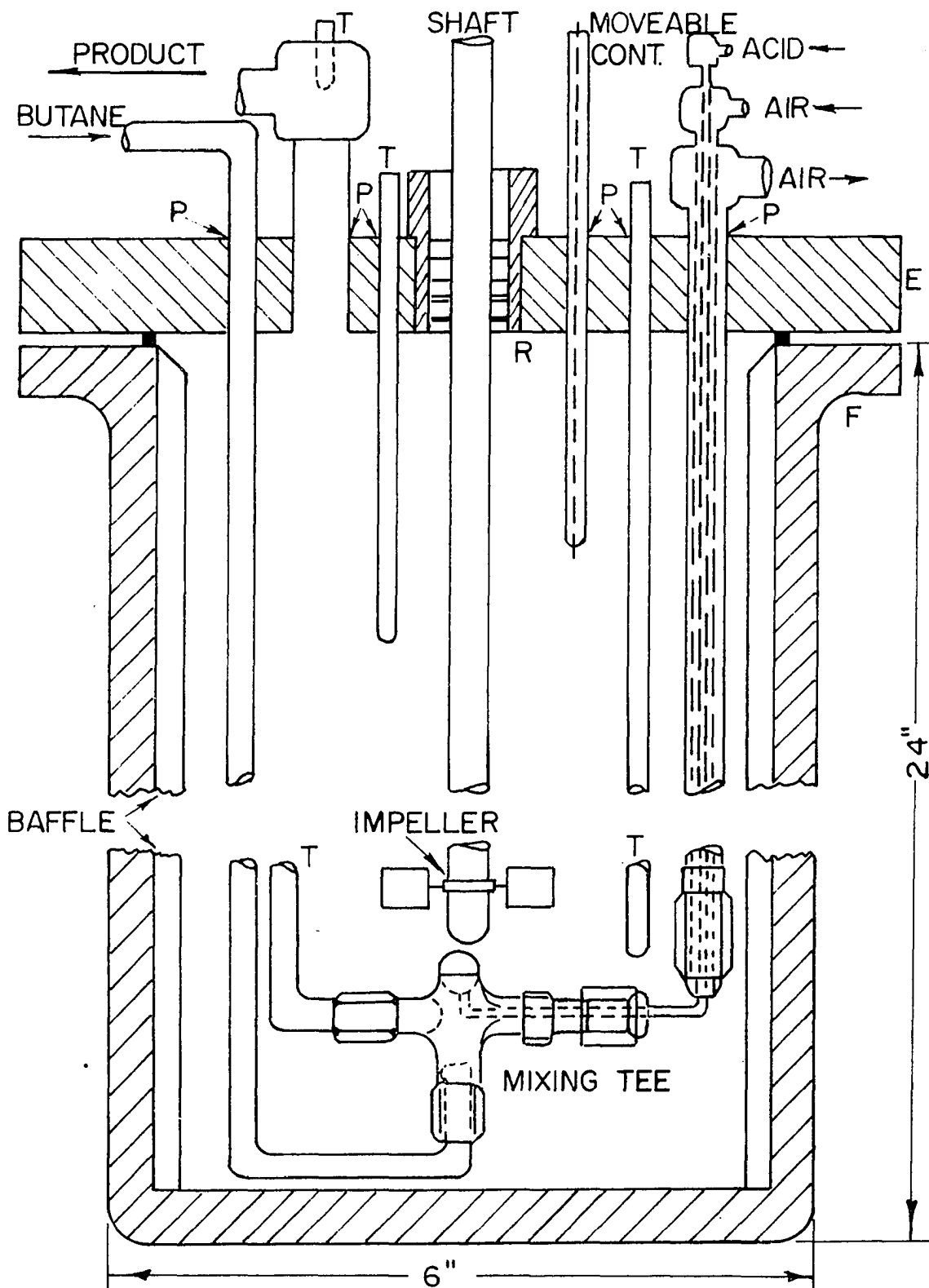
E: 1/2 in. mild steel plate

F: schedule 40, 6 in. iron pipe

P: packing gland

R: compression ring

T: thermocouple



mounted on a shaft driven by a 1/20 hp., 115 volt, fan-cooled motor at 1,000 rpm. The stirrer was capable of producing a local Reynolds number of approximately 30,000 (56).

The reactor head was constructed of 1/2 in. mild steel plate with stainless steel fittings. Figure 3 is a cross-sectional drawing of the assembly reactor head, modified by rotation of several items to permit all components to be shown in one plane. Photographs of the reactor head are shown in Figures 4 and 5.

The acid entered the reactor assembly through the inner tube of a concentric assembly which consisted of 1/8 in., 1/4 in., and 1/2 in. tubes. Air flowed down the inner annular space to the point where the acid line entered the mixing tee, then up through the outer annular space to be vented. The purpose of this concentric tube arrangement was to prevent premature vaporization of the nitric acid.

The butane entrance line and preheater consisted of a 13 ft. long, 4 in. diameter coil of 1/4 in. stainless tubing. The coil was sized to bring the butane approach temperature to approximately 25°C at a butane flow rate of 0.13 gram moles per minute. The reactants entered the mixing tee where the acid sprayed radially into the concentric stream of butane and once the reaction started, the acid was vaporized by the heat of reaction. The mixture then flowed from the tee, through a two-inch section of 1/4 in. tubing, and sprayed through four 0.032 in. holes into the highly turbulent salt bath. Figure 6

Figure 4. Photograph of reactor head plate

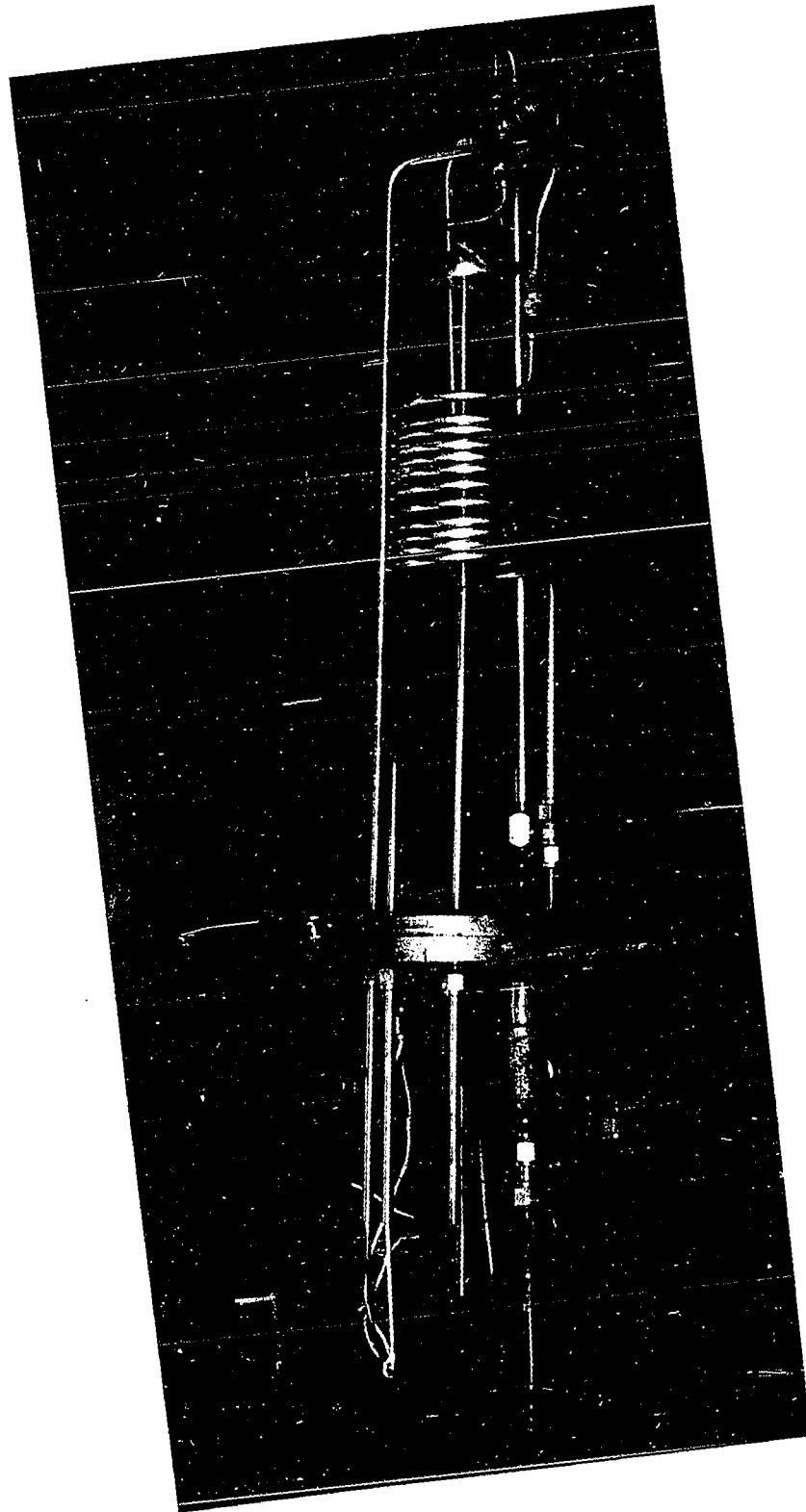


Figure 5. Photograph of the assembled reactor

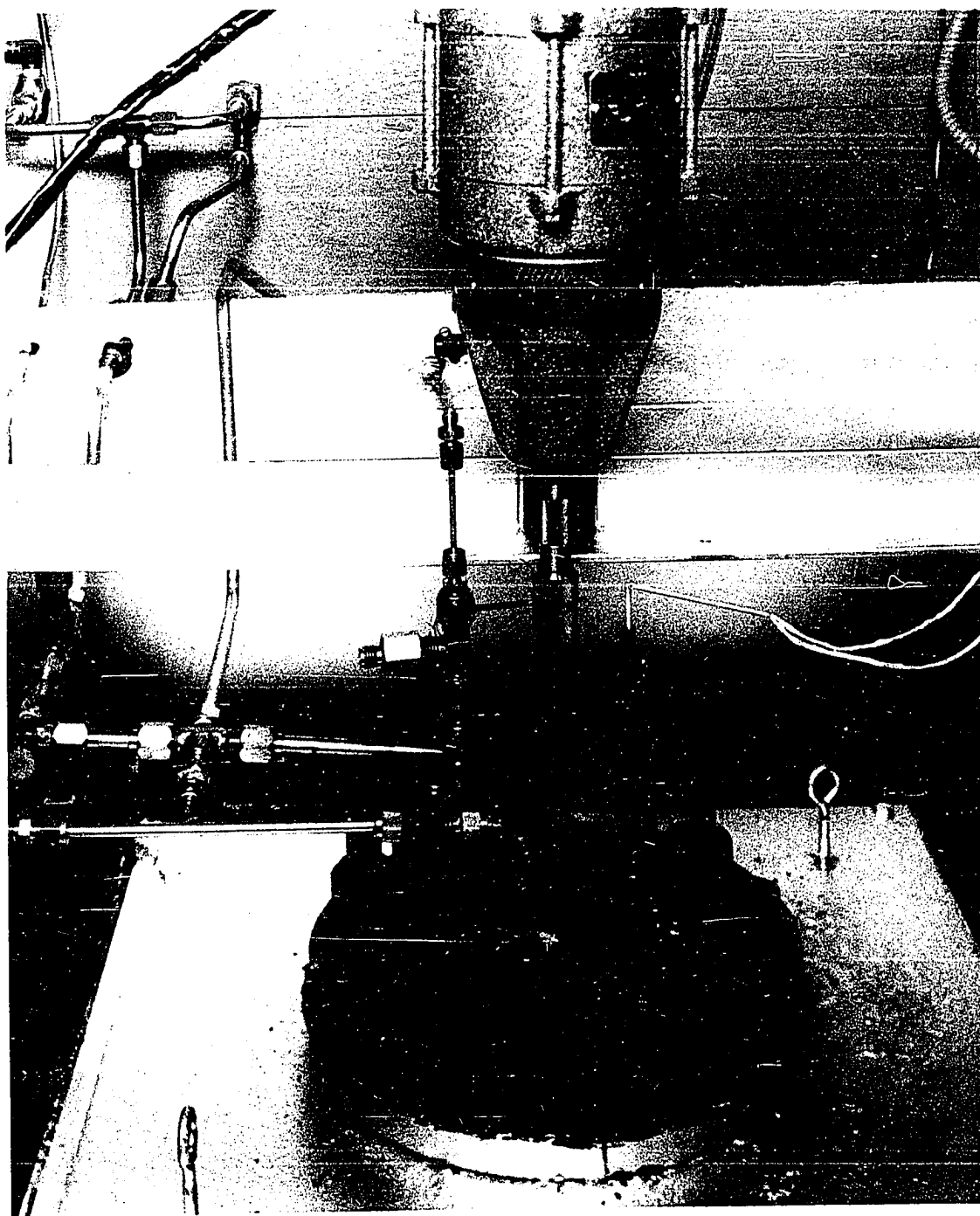
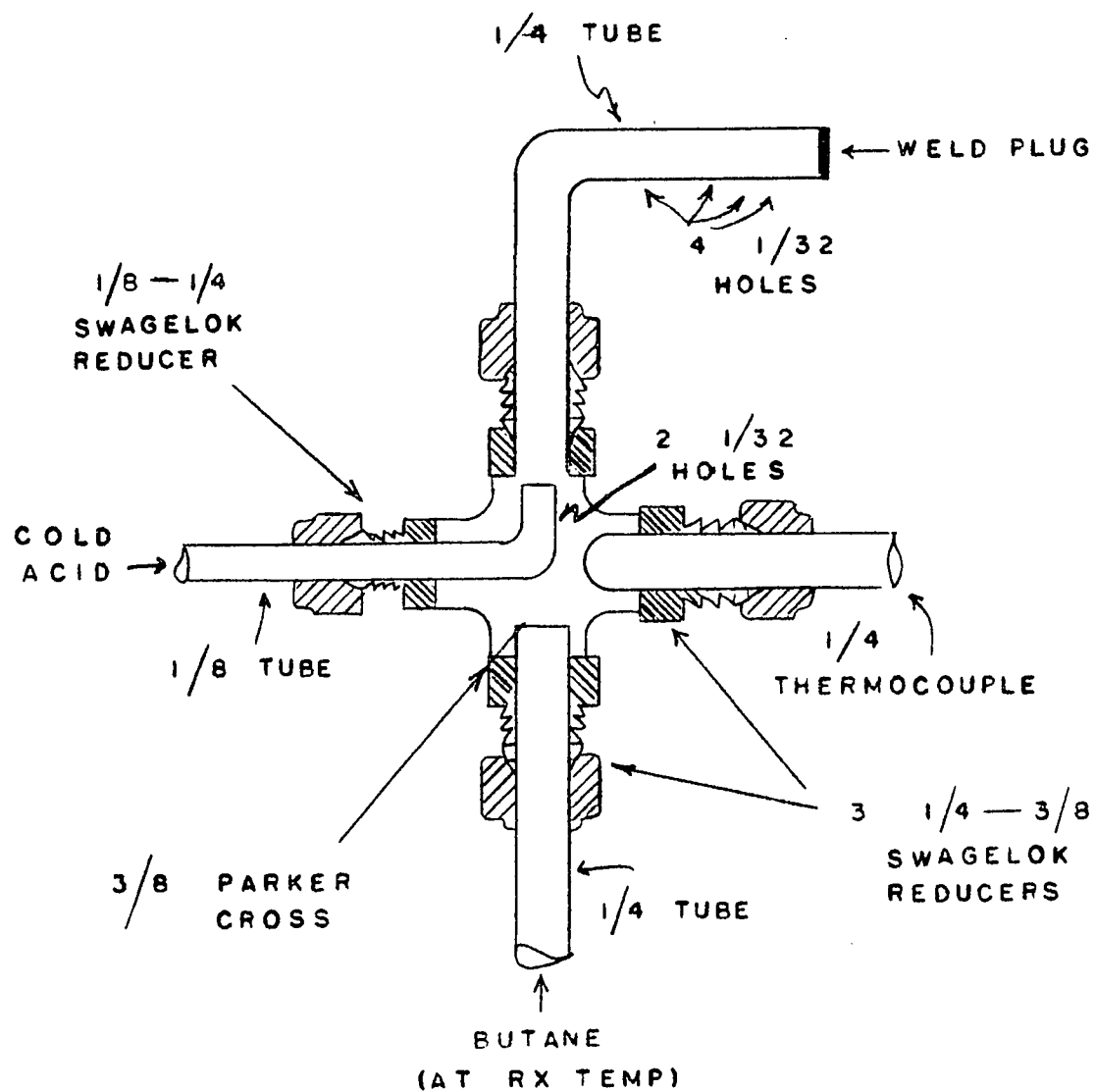


Figure 6. Cross-section of mixing tee



shows a diagram of the mixing tee assembly.

The agitator shaft passed through a compression ring packing gland in the reactor head plate stuffed with asbestos packing rings. The thermocouple wells contained 28 gauge chromel alumel thermocouples welded into the tips of 1/4 in. stainless steel tubes which made up the wells themselves and passed through drilled-out Swagelok fittings mounted in the head plate. Two of the four thermocouples measured the salt bath temperature, one the freeboard gas temperature, and one the temperature in the mixing tee. An additional thermocouple was installed in the product exit line just above the reactor head. The salt bath thermocouple in the neighborhood of the mixing tee sent its signal to the Brown Electric Controlling Pyrometer, while the signals from the others went to a Brown Elektronik multiport recorder. A mercury manometer was connected by a tap to the product exit line.

A movable electric probe, which closed a 10 volt circuit in series with a panel light on touching the salt level, extended through a packing gland constructed from a Swagelok fitting. The probe was fabricated from a 1/4 in. stainless steel tube containing two electrically insulated silver wires. At the terminal end of the probe in the reactor, the ends of the wire were bare and slightly protruding from the tube. By use of the probe the level of the molten salt could be measured, although under operating conditions the entire reactor was filled with salt.

Product sampling system

The product sampling system consisted of two major parts; an on-line and a total product system. The first was used in the collection of an aliquot sample of the product gases in a heated sampling valve and subsequent analysis by gas chromatography. The second in the cooling and collection of the total product followed by its subsequent separation and analysis by gas chromatography.

For the on-line collection and analysis the product was sampled for analysis by a Beckman sampling valve (Model 102396, Beckman Instruments, Incorporated) with a 3 cc sample loop. The valve was operated pneumatically from the panel board by a solenoid with 50 psig air used to actuate the valve. Because salt carry over built up in the sample loop and prevented the obtaining of a full size sample, reactor effluent could not be allowed to pass thru the sample loop on a continuous basis. Consequently a water operated aspirator was used to draw a portion of the effluent thru the device for a few minutes prior to sampling. The bulk of the effluent went to the product collection system directly.

To prevent sample condensation in the sampling device, the valve was installed in an insulated aluminum box which was kept at 250°C. The temperature was maintained by a hot plate (700 watt, Model HP-A1915B, Type 1900, Thermolyne Corporation) controlled by a Model 117, Superior Electric Company powerstat. The temperature in the sample box was measured by

2 iron-constantan thermocouples mounted in stainless steel thermowells.

The sample box was mounted directly on top of the reactor body so a minimum amount of additional tubing was required to send the sample from the effluent tube to the valve. The sample was picked up by helium in the valve and sent to the first chromatograph for analysis.

The cooling and collection system involved a major product exit line of 3/8 in. stainless tubing which formed the inner shell of a double pipe heat exchanger. The outer shell was of 1/2 in. pipe. Prestone antifreeze at about -15°C entered the annular space and flowed countercurrent to the product stream. The condensed portion of the nitration effluent passed through a dry-ice liquid trap into a flask. The uncondensed portion passed through a gas sampling flask then to a vent. The rate of flow from the vent was measured by a calibrated bubblemeter as described in detail by Ives (46).

The coolant was supplied by a small gear pump from a 50 gallon reservoir which contained a 1:1 mixture by volume of water and Prestone antifreeze. The refrigeration mixture was cooled to a minimum of -15°C by a double pipe heat exchanger device using expanding Freon 12 supplied from a Mills two-cylinder gas compressor driven by a 220 volt, 3 hp. motor.

Chromatographic Analysis

General

Butane nitration products may, in general, be considered to consist of three distinct groups of substances, each group possessing unique characteristics which allow it to be separated by a particular combination of packing and partitioning agent. The groups are: (1) the nitroparaffins and higher alcohols, (2) the oxygenated aliphatics and water, and (3) the fixed gases and paraffins. An acceptable degree of component resolution is required to obtain quantitative results but this must be obtained at a minimum retention time when the analytical system is to be used on-line. It was believed that, if a suitable chromatographic analysis could be developed for each of the three major groups occurring in the nitration effluent stream, an effective on-line analysis could be developed by using a valving arrangement to hook the three chromatographic columns in series. The concept was that, if the first column were operated at a relatively high temperature and flow rate, the low and middle boilers would pass through rapidly and unresolved and could then be sent to the second column. The high boilers would be quantitatively separated on column one, then through the use of a multiport valve, sent to vent to prevent their contaminating the second column which would be operated at a lower temperature.

The particular type of column used during this

investigation consisted of a packing of powdered teflon which was marketed under the name Halleport F and a partitioning agent of Celanese No. 9 ester. This combination of packing and partitioning agent was used because Ives (46) had earlier shown that the non-porous surface of the teflon reduced the possibility of serious water tail and that the ester would quantitatively separate the nitroparaffins.

Initial work showed that the time controlling analysis would be that of group (1), the nitroparaffins and higher alcohols. The approach then taken was to develop an analysis for this group which could be performed in a reasonable time, then to mesh the remainder of the groups in series. In this way all group analyses were complete by the time group (1) was finished.

Exploratory study

Since the problem was, in essence, one of minimizing a retention time function subject to a set of constraints which insured acceptable resolution between all important peaks, it was necessary to first mathematically define the term acceptable resolution.

$$R = \frac{t_2 - t_1}{W_{avg}} \quad (11)$$

R = resolution between two adjacent peaks

t_1 = retention time in minutes for first peak

t_2 = retention time in minutes for second peak

W_{avg} = average base width for adjacent peaks, scale units

It was then necessary to determine the smallest value of R which would, in the case of all adjacent peaks, insure quantitative separation, then to make an initial estimate of the best set of operating conditions.

The first part of the work was carried out using a 12 ft., 3/16 in. diameter, 5 per cent Celanese No. 9 on Halleport F column and a second column six ft. in length, 1/4 in. in diameter, and containing 15 per cent agent.

- (a) Two 2.0 μ l samples of each expected reaction product (except NO , NO_2 , and fixed gases) were run individually through each of the above two columns at 60 ml./min. helium and 78°C.
- (b) For each column the retention time and peak width were determined for each individual component. The components were then ordered for each column according to retention time and a resolution factor (R) calculated for all adjacent pairs of peaks. The following actual data are given as an example of the type of results observed.

Table 3. Resolution factors

Component	Retention Time (min.)	Peak Width (in.)	Resolution Factor (R)
Nitromethane	1.9	0.4	$\frac{2.0 - 1.9}{0.5} = 0.20$
n-butanol	2.0	0.5	

Table 3. Continued

Component	Retention Time (min.)	Peak Width (in.)	Resolution Factor (R)
Isobutanol	3.0	0.6	$\frac{3.0 - 2.0}{0.6} = 1.65$
Nitroethane	3.3	0.7	$\frac{3.3 - 3.0}{0.7} = 0.43$

- (c) To confirm that the expected separations could be made, two-component mixtures of each adjacent pair of possible products were run in the two columns at the same conditions, viz., 60 ml./min. helium and 78°C.
- (d) From a knowledge of the value of the resolution factor (R) between adjacent peaks as determined in (b) and confirmed in (c) above, the minimum (smallest) value of R that will assure a quantitative separation of all peaks was identified for each column. As anticipated, this value was the same for each column, 0.8. This minimum resolution value was used later as one optimization criterion.

The next portion of the work was necessary to obtain an initial estimate of the optimum operating conditions to give the desired quantitative resolution in minimum time. The values thus obtained were used as a starting point for the final experimental design.

- (a) The overall experiment involved the following values:

Column length (2 levels), ft.	6	12
Column diameter (2 levels), in.	3/16	1/4
Per cent agent (2 levels)	5	15
Temperature (2 levels), °C	50	100
Helium rate (2 levels), ml./min.	30	90

The values selected were for the most part based on practical limitations. As examples, the Teflon support packing will not fit in a column less than 3/16 in. in diameter, partitioning agent concentrations greater than 15 per cent lead to stickiness, and at 120° a slow bleed of the agent can be detected. To decrease the number of experiments required, a one-half replicate was used. This confounded any interaction between column length, diameter, and per cent agent. It was equivalent to assuming these factors are independent, which was quite likely.

- (b) The experiments were statistically scheduled using the following nomenclature:

<u>Treatment</u>	<u>Code Letter</u>	<u>First Level</u>	<u>Second Level</u>
Column length, ft.	E	12	6
Column diameter, in.	D	3/16	1/4
Per cent agent	C	15	5
Temperature	B	100	50
Helium rate, ml./min.	A	90	30

When the nomenclature was used to designate combinations, the absence of a letter meant first level of treatment. Conversely, the presence of a letter meant second level. The symbol, (1), indicated the first level for all treatments. For example:

BE meant 90 ml./min., 50°C, 15%, 3/16 in., 6 ft.

ACDE meant 30 ml./min., 100°C, 5%, 1/4 in., 6 ft.

The experiments were performed in four blocks to eliminate random variation according to the sequence shown in Table 4. Run 5 in each block was included to supply a replicate point to allow the determination of error variance.

Table 4. Experimental design for initial chromatographic experiment

Run	Block 1	Block 2	Block 3	Block 4
1	(1)	AC	AE	AD
2	AB	BC	BE	BD
3	ACDE	DE	CD	CE
4	BCDE	ABDE	ADCD	ABCE
5	AB	BC	BE	BD

- (c) The experiment performed under each treatment combination consisted of the following:

- i. Run individually a 2 μ l sample of each of the five components listed below at each combination of conditions (total of 20) listed immediately above.
- ii. Record the retention time and peak width for each component.
- iii. Calculate the following:

<u>Component</u>	<u>Calculate</u>
n-butanol	Resolution Factor
2-nitropropane	
Nitromethane	Resolution Factor
2-butanol	
1-nitropropane	Retention Time

Previous work had indicated that the first two pairs would probably be the most difficult to separate and that 1-NP would probably exhibit the longest retention time.

- (d) From the 20 tests required in (b) above, the initial estimate of the optimum operating conditions was estimated.

Results of exploratory study

From the study thus far described, the following conclusions were reached.

- (1) In each case a minimum value of the resolution factor, R, of 0.8 resulted in a quantitative separation.
- (2) The resolution factor, R, measured not only the retention time differences but also the peak spread and tailing.

These qualities make the R value superior to the standard measure, the height equivalent to a theoretical plate (HETP), for determining the operating conditions of a column.

- (3) A 15 per cent column increased both the peak widths and tailing and decreased column efficiency.
- (4) The only effect of the 3/16 in. column was to increase the effective flow rate.
- (5) That a column of length greater than 12 ft. would be required to perform the separations. An extrapolation of R values indicated that an 18 to 20 ft. column would do and that the low boiler separation would require a temperature in excess of 70°C.

Second experiment

A 20 ft., 1/4 in. diameter, 5 per cent Celanese No. 9 on Halleport F column was constructed and a ten-component mixture containing possible products in the low boiler range was prepared. The components were t-butanol, isobutyraldehyde, n-butyraldehyde, 2-butanone, 1-propanol, nitromethane, 2-butanol, nitroethane, isobutanol, n-butanol, and 2-nitropropane. This mixture included all reactor products previously reported in this range except 2-methyl-2-nitropropane, 1-nitropropane, 2-nitrobutane, 1-nitrobutane. These four components have the longest retention times, and previous experiments indicated that they are very easy to separate quantitatively. Therefore,

to shorten the time required to complete this block of tests, they were omitted from the test mixture.

A second-order central composite design (20, 22) was set up and 2 μ l samples of the test mixture analyzed. Figure 7 shows the pictorial representation of the design and the test levels. The results of this experiment were expressed in quadratic polynomials by multiple regression analysis.

$$(RT)_i = b_0 + b_1x_1 + b_2x_2 + b_{11}x_1^2 + b_{22}x_2^2 + b_{12}x_1x_2 \quad (12)$$

$$i = 1, 2, 3, \dots, 10$$

$$R_{ij} = a_0 + a_1x_1 + a_2x_2 + a_{11}x_1^2 + a_{22}x_2^2 + a_{12}x_1x_2 \quad (13)$$

$$i, j = 1, 2, 3, \dots, 10$$

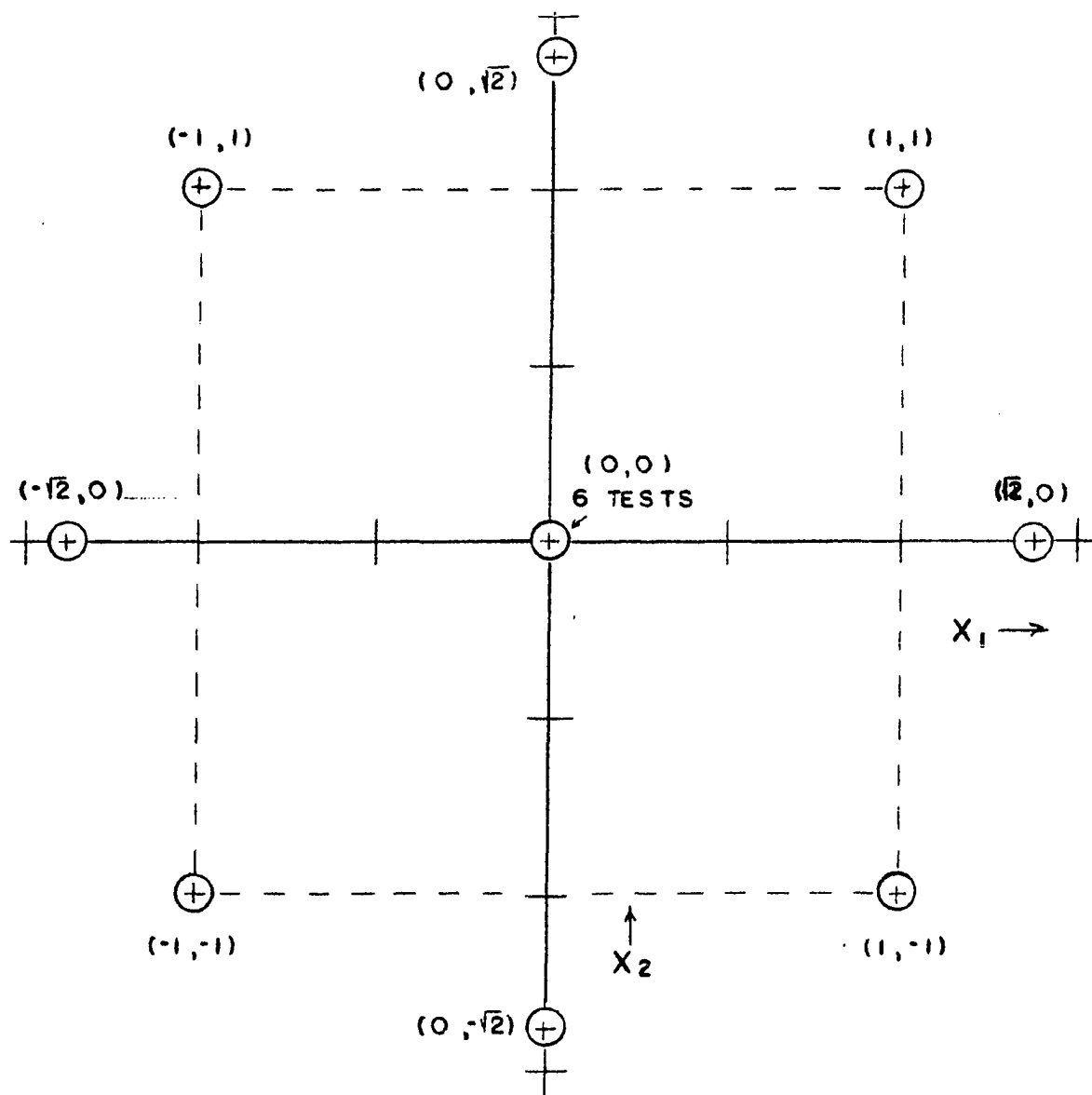
where: $(RT)_i$ = retention time of the i th component, min.
 R_{ij} = resolution between adjacent peaks
 x_1 = flow rate helium, ml./min.
 x_2 = column temperature, $^{\circ}$ C

All of the correlation coefficients were greater than 0.9, thus indicating an acceptable fit of the data by the quadratic expressions.

From the least squares equation the following plots were produced:

- (1) for each pair of adjacent components a plot of resolution, R , versus flow rate at parameters of constant temperature
- (2) for the component of each pair with the greatest retention time, a plot of retention time, RT , versus flow rate

Figure 7. Experimental design for chromatographic experiment



HELIUM RATE
(ML MIN)

X_1	HR
$+\sqrt{2}$	76
$+1$	70
0	55
-1	40
$-\sqrt{2}$	34

COLUMN
TEMPERATURE
(°C)

X_2	T
$+\sqrt{2}$	105
$+1$	100
0	90
-1	80
$-\sqrt{2}$	75

at parameters of constant temperature.

It was noted that for each individual pair of components there was a true optimum or best set of operating conditions. The best set was not the same, however, for all adjacent pairs. Thus, the problem became one of matching ranges of conditions to arrive at a set of conditions that would give a resolution value of at least 0.8 for all pairs at a minimum overall retention time. For example, it can be seen from Figure 8 that the optimum resolution in the operating range is 1.1 at 105°C and 44 ml./min. for the 1-butanol, 2-nitropropane pair, while Figure 9 shows that the minimum retention time for 2-nitropropane occurs at 105°C and 70 to 75 ml./min.

Data analysis and results

The method developed to minimize the total retention time while keeping all R values greater than 0.8 is outlined below:

- (a) Contour plots of resolution as a function of temperature and flow rates were prepared for each adjacent peak pair. Figure 10 shows an example of the contour plots. At increments of coded flow rate, coded temperature ranges which bounded the criterion $R \geq 0.8$ were read from the plots for each pair of peaks.
- (b) A table of flow rates and temperature boundaries for each peak pair was constructed and examined. It was observed that the criterion of $R \geq 0.8$ for all peak pairs was obtainable for only a limited range of flow rates.

Figure 8. Resolution of 1-butanol and 2-nitropropane on a 20 ft., 1/4 in. diameter, 5 per cent Celanese No. 9 on Halleport F column as a function of flow rate and temperature

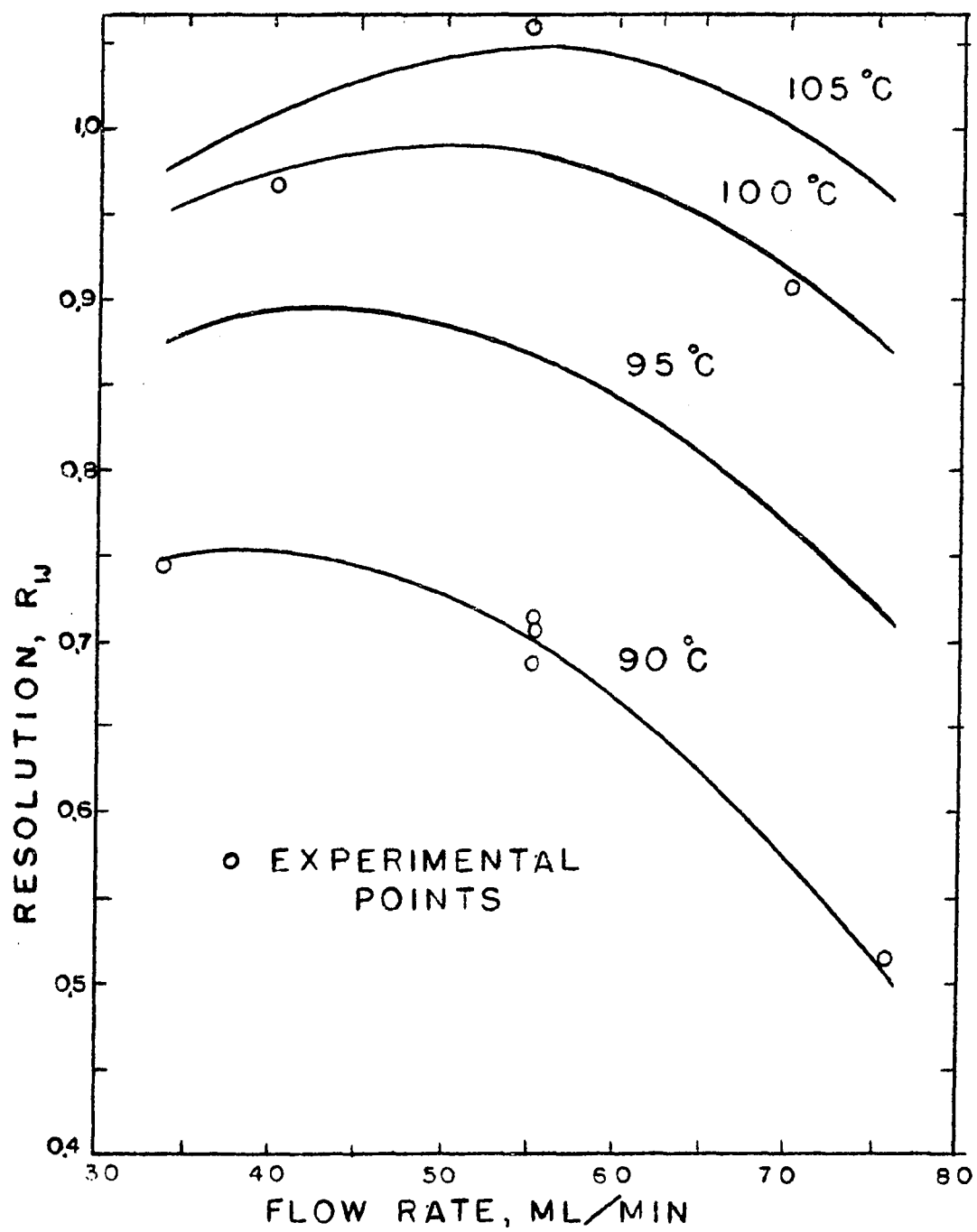


Figure 9. Retention time of 2-nitropropane on a 20 ft.,
1/4 in. diameter, 5 per cent Celanese No. 9 on
Halleport F column as a function of flow rate
and temperature

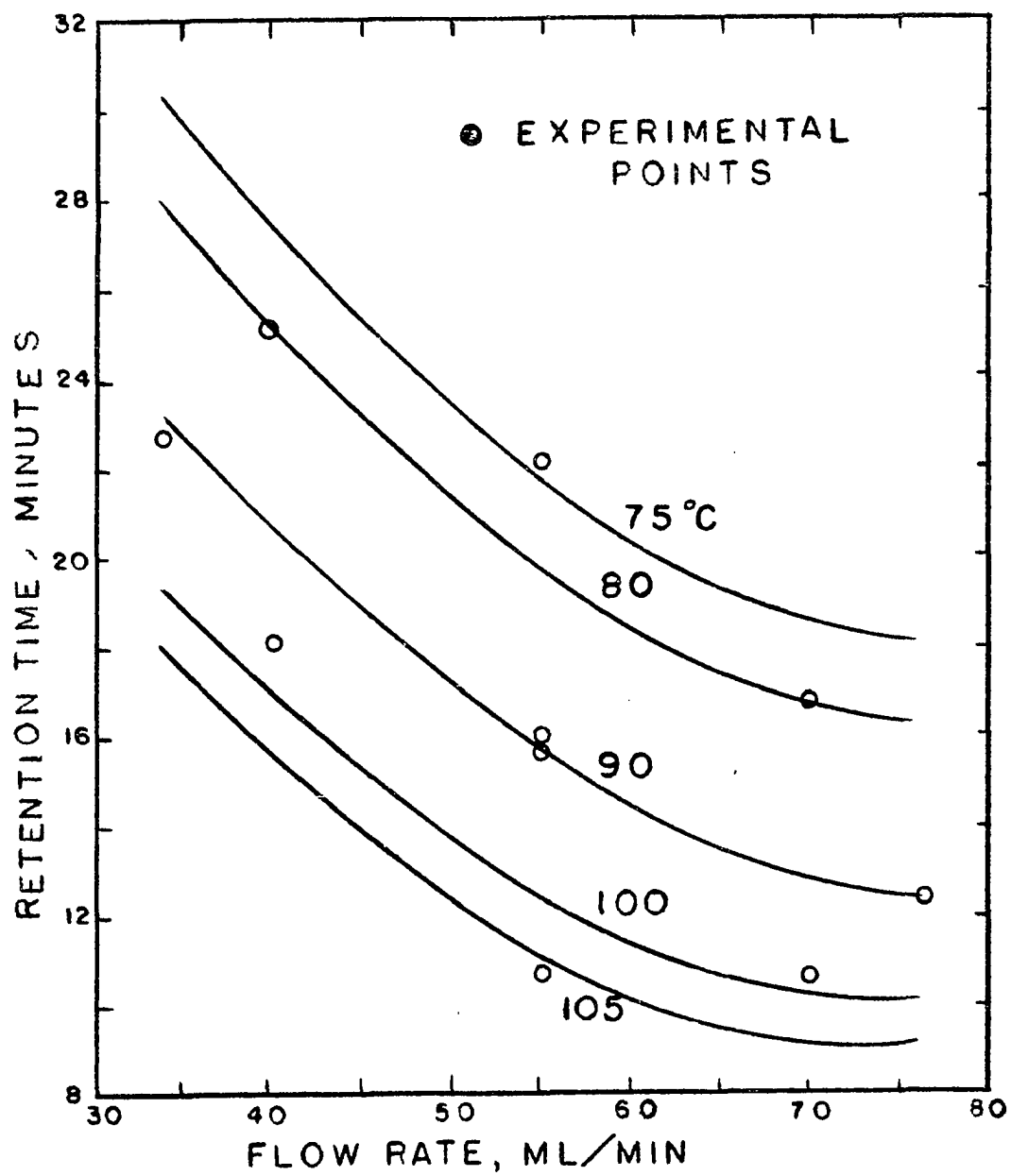


Figure 10. Plot of resolution value contours for 2-butanol, nitromethane on a 20 ft., 1/4 in. diameter, 5 per cent Celanese No. 9 on Halloport F column as a function of temperature and flow rate

Resolution values start at 0.9 (A) and increase in steps of 0.1 to 1.9 (K).

(c) Those acceptable temperature, flow rate combinations were then used to compute, from the appropriate quadratic equation, the retention time of 2-nitropropane which was the time controlling component. The temperature-flow rate combination which resulted in the shortest computed residence time was picked as the operating condition. An example of this procedure is shown in Table 5. The best set of operating conditions was found to be at 105°C and 55 ml./min. helium flow.

In addition to being useful in determining operation conditions, the contour plots were helpful in obtaining a better appreciation of the relationships between the controlled variables and the analytical response. For example, the 1-butanol, 2-nitropropane system results in a retention time plot as shown in Figure 11. This plot showed that a low-level retention time could be obtained over a rather wide range of temperature-flow rate combinations.

By utilizing the concept described in this section, of using boiling points to make initial separations then running each resulting cut thru an appropriate column, Johnnie (47, 48) developed the mechanical procedures for a complete on-line analytical system. He used the operating conditions developed herein to separate the first two groups of products, and standard analytical procedures from the literature to separate the fixed gases. The final tool was a complicated, but very workable combination of chromatographs, multiport valves, and

Figure 11. Plot of retention time contours for 2-nitropropane on a 20 ft., 1/4 in. diameter, 5 per cent Celanese No. 9 on Halleport F column as a function of temperature and flow rate

Retention times start at 12 min. (A) and increase in steps of 1.0 min. to 29 min. (R).

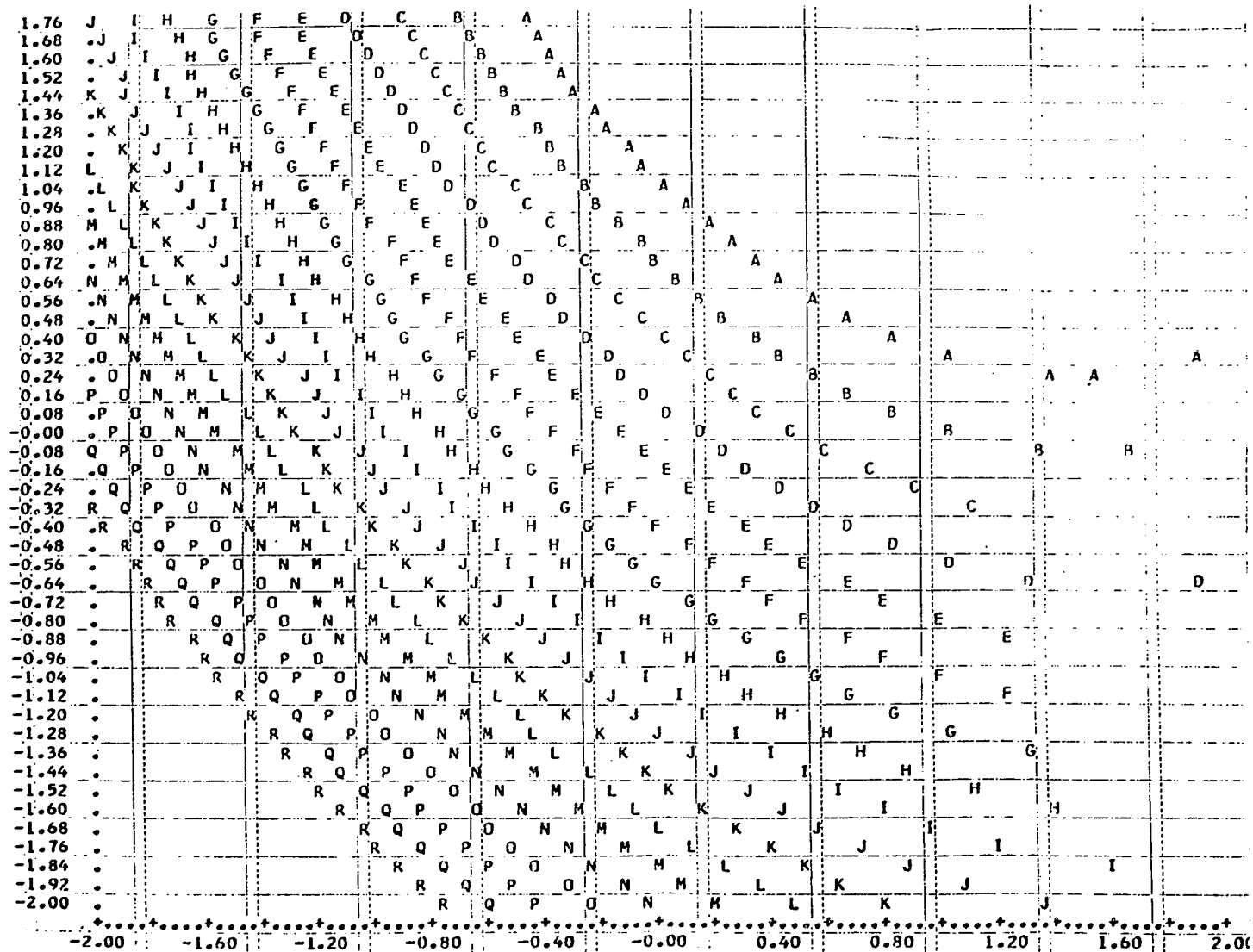


Table 5. Example of method used to determine the best set of operating conditions for a gas chromatographic analytical procedure

Temperature values which bound acceptable resolution for each peak pair, coded

Flow rate, coded	1,1 (max.)	1,2 (min.)	2,3 (range)	3,4 (min.)	8,9 (min.)
-2.0	-	-0.64	-1.44 0.24	-1.20	0.32
-1.6	-	-0.80	-1.44 0.24	-1.04	0.24
-1.2	1.36	-0.88	-1.44 0.20	-0.96	0.16
-0.8	0.96	-0.80	-1.44 0.16	-0.80	0.16
-0.4	0.72	-0.72	-1.44 0.08	-0.64	0.24
0.0	0.50	-0.56	-1.44 0.08	-0.48	0.32
:	:	:	:	:	:	:
:	:	:	:	:	:	:
:	:	:	:	:	:	:

Limiting values of temperature for all peak pairs

Flow rate, coded	Minimum	Maximum	
-2.0	0.32	0.24	
-1.6	0.24	0.24	} possible operating range
-1.2	0.16	0.20	
-0.8	0.16	0.20	
-0.4	0.24	0.16	

From Retention times for 2-NP

At flow rate = -0.8
temperature = 0.16 RT = 17 min.

pressure control valves which gave an on-line product analysis in less than 30 minutes. This tool was incorporated into the pilot plant scheme and used the sampling system described earlier.

Operating Procedure

Start up

On the day prior to start-up, the reactor furnace was turned on and the power adjusted to approximately 50 per cent total capacity with the set point controller at 300°C. This type of adjustment melted the salt and brought the reactor to within 100°C of reaction temperature in 12 hours. The chromatographic system was turned on and all flows and valve resistances set at appropriate levels. The sample valve was in the "off" position so that the products would purge the sample loop once the flow of reactants was started.

On the morning of start-up, the reactor furnace was adjusted to 80 per cent total capacity and the set point moved to the initial reaction temperature. The flange plate on the reactor pot was covered with silicone grease to insure a proper seal between it and the headplate. A flexible hose was connected to the inlet lines on the reactor headplate, and nitrogen flow started thru the hose. This was to keep a positive pressure on the reaction tee so the salt would not plug the bubbler when the headplate was lowered into the molten salt bath. The reactor head plate was then lowered and

secured to the reactor pot. All piping and thermocouple connections were then made and the refrigeration unit started up. The multipoint temperature recorder and chromatographic equipment were checked to insure that they were functioning properly and had sufficient chart paper and ink.

The acid line was disconnected from the reactor head and the entire acid system was washed with two 500 cc portions of acid to remove any residual wash water. The acid egg was then filled with 1,000 cc of acid, all connections completed, and the egg pressurized to 20 psig with helium.

The product recovery system was flushed with water to remove any salt deposits left from a previous run. The product exit line and sample box system were connected to the reactor head plate. Dry ice was packed around the product recovery flask.

Nitrogen was purged through the butane and reactor system for at least 20 minutes to remove any air that was present. This was extremely important in preventing fires resulting from butane flash. After the purging, the butane flow was set at the desired level and the final adjustments on the reactor furnace made. The butane was allowed to flow into the reactor for approximately 20 minutes. In this time interval the reactor temperature leveled off at the required set point.

After the temperatures had leveled out, the acid flow was slowly initiated. It was mandatory that the final flow rate be approached very slowly to allow the mixing-tee to reach

thermal equilibrium. When this was not done the reaction was very violent. The large bubble meter was then switched into the product vent line to measure the off gas flow rate.

Operation and sampling

After approximately 15 min. of reaction, the water induced vacuum was started in order to pull a sample thru the sample loop. A 500 cc off gas sample was collected from the product exit line by the opening and closing of appropriate stop cocks. The on-line sample was taken by flipping the sample switch to "on". As soon as the sample switch was "on", a synchronous timer was started to indicate valve switching times to the individual controlling the on-line device. The liquid product from the collection system was separated into two phases, the aqueous phase and the organic phase. Each phase was drained into a tared flask, weighed and stored under refrigeration. The off gas sample was analyzed as soon as the on-line sample cleared the chromatographs. The liquid samples were analyzed at the end of each day of operation.

It required between one and two hours to attain equilibrium at a new set of conditions. During this period, the product collection and sample box systems were disconnected and flushed with water to prevent salt build up.

Shut down

The acid and butane flows were turned off completely and the system purged for 20 minutes with nitrogen. After purging,

the acid line was disconnected and the entire acid system was washed with two 1,000 cc portions of water. If the system was not properly washed, the acid tended to swell the packing around the controlling needle valves which consequently made them useless.

The reactor head was removed while maintaining a nitrogen flow to prevent plug-up. The furnace, refrigeration system and all heating elements were then turned off.

Experimental Plan

General

The term "optimum operating conditions" for the butane nitration process encompasses numerous criterion such as the following:

- (a) To maximize the mole ratio of the nitroparaffins produced per mole of butane consumed in the reaction (i.e. hydrocarbon yield).
- (b) To maximize the total moles of butane reacting per mole of butane fed (i.e. hydrocarbon conversion).
- (c) To restrict the mole ratio of butane to acid to a minimum value in order to keep the quantities of butane and acid that would have to be recycled in an industrial process at a reasonable level.
- (d) To produce the most desirable nitroparaffin distribution.

It was realized that these constraints and the ones concerning nitric acid would probably be conflicting, but this is

not unique in a practical situation. In Cochran's words, "Frequently, more than one characteristic of a product is important. A shift in the X_1 away from the true optimum may be preferable because of its effect on one of these other characteristics" (22). In the nitration work, however, all desirable constraints were linked to a common denominator, the profit function.

Optimization

Many general methods of obtaining optimum conditions from experimental data are available (6, 20, 22, 28). Some of these, however, like the Method of Steepest Ascent require that the results of an experiment become known quickly, since each experiment in the method awaits the completion and analysis of the previous one. These sequential methods, in general, attain optimum points in less total experimentation than other methods. Because of the length of time required to start-up the pilot plant then to evaluate the resulting chromatographs, such sequential strategies were not practicable so the "Single Large" experiment technique was used (22). In this case, because the exploratory work of previous investigators had already bracketed reasonable starting conditions this technique was applicable.

The results of the experimental work in terms of yields, conversions, and nitroparaffin distribution were fit to quadratic polynomials by multiple regression analysis. The

polynomials were of the form

$$Y_i = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 \\ + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 \quad (14)$$

$$i = 1 \cdots 8$$

where: Y_i = response in terms of yield, conversion or nitro-paraffin distribution

x_1 = temperature, coded

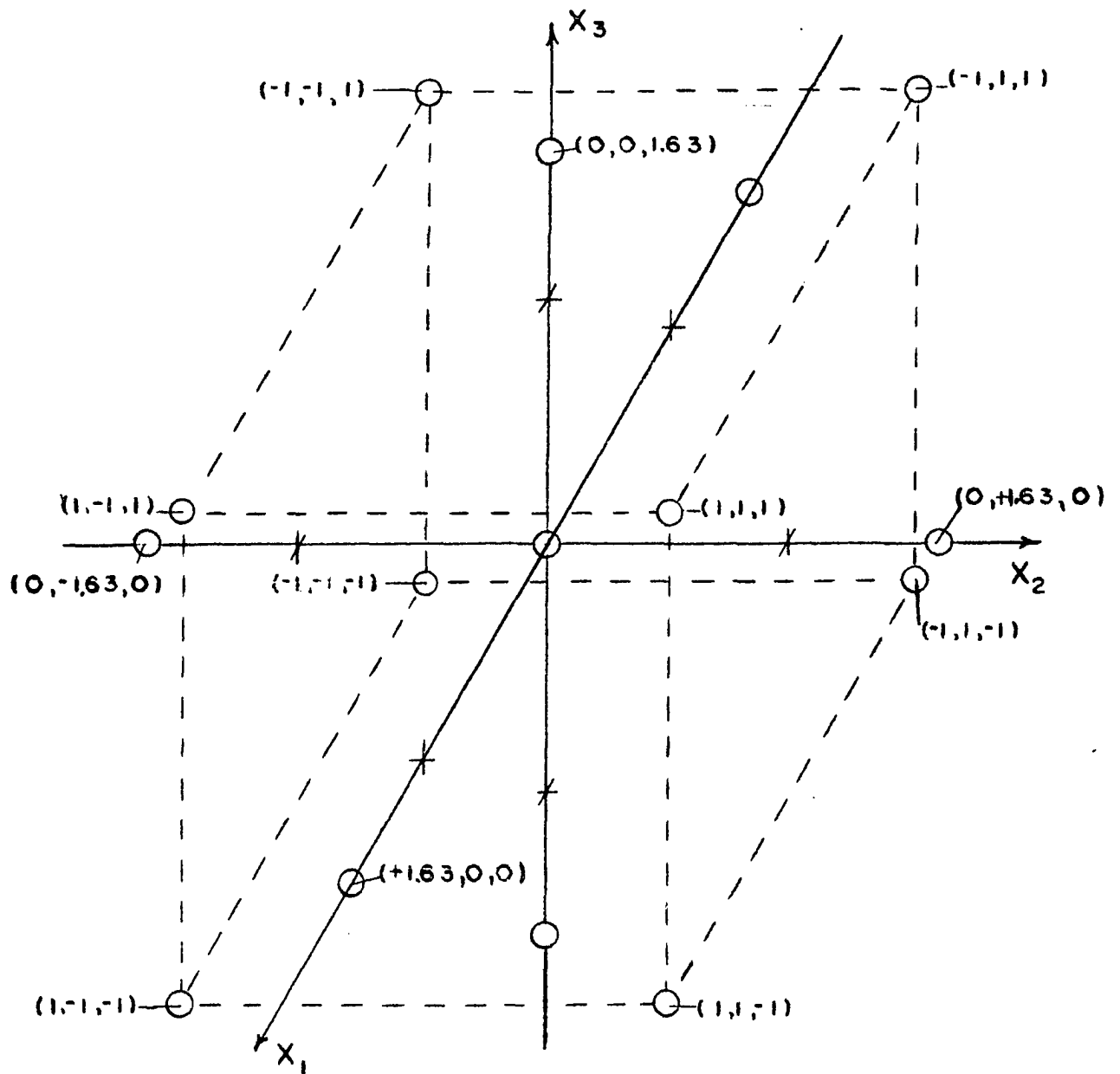
x_2 = mole ratio, coded

x_3 = molar flow rate of reactants, coded

Experimental design

The experiment was performed in a central composite second-order design in three incomplete orthogonal blocks (20, 22). The variable levels were coded to range from -1.633 to +1.633 in order to maintain the orthogonal features of the design. Table 6 shows the effect levels, coded values, and block design. The design itself is shown pictorially in Figure 12. The center point was replicated six times to obtain an estimate of the experimental error and the blocks were made on days. A design of this nature: (1) reduces the amount of experimentation required to study a response surface, (2) provides a measure of the lack of fit of the quadratic surface, (3) provides an estimate of the experimental error, and (4) indicates any time trend which could result from the slow poisoning of the reactor.

Figure 12. Experimental design for reactor optimization



<u>CODED VARIABLES</u>	X_1 : MOLE RATIO	C4/ACID
	X_2 : TEMPERATURE	$^{\circ}\text{C}$
	X_3 : FLOW RATE	G-MOLE/MIN

Table 6. Experimental design for reactor optimization

Mole Ratio x1	Cl ₂ /Acid M.R.	Temperature x2 °C	Flow Rate x3 g. moles/min.
-1.633	3.0	-1.633	385
-1	3.77	-1	398.5
0	5.0	0	420
+1	6.23	+1	441.5
+1.633	7.0	+1.633	455

Central composite second-order design in three incomplete blocks. (A block was a day)

Block I			Block II			Block III		
x1	x2	x3	x1	x2	x3	x1	x2	x3
-1	-1	1	-1	-1	-1	-1.633	0	0
1	-1	-1	1	-1	1	+1.633	0	0
-1	1	-1	-1	1	1	0	-1.633	0
1	1	1	1	1	-1	0	+1.633	0
0	0	0	0	0	0	0	0	-1.633
0	0	0	0	0	0	0	0	+1.633
						0	0	0
						0	0	0

DISCUSSION

Reactor Operation

The reactor and its auxiliary equipment performed, in general, very satisfactorily. The significant problems associated with metering and control of reactant streams were overcome. The pulsing acid flow reported by Adams (1) and Fear (31) was prevented by the use of the acid egg which produced a steady, reproducible acid flow rate. The Moore Flow Controller in the butane line was successful in preventing downstream pulsations from effecting the butane rotameter settings.

The concept of using cold acid feed as an aid in controlling the reaction was quite successful, for the reactor was operated at low mole ratios of hydrocarbon to acid without the occurrence of excessively violent reactions. Although a series of very distinct "bumps" were often felt when the acid flow was initiated, it was found that this undesirable effect could be reduced by bringing the acid to the final flow rate very slowly. Within a few minutes after the final flow rate was reached, the reaction would level out, and any initial tendency toward irregular behavior would disappear.

No problem was encountered in obtaining and maintaining operational salt bath temperatures. As with the acid flow start up problem, an experience factor soon became a significant aid in obtaining the desired temperatures quickly. For

example, when operating at mole ratios of less than 5 to 1 it was advantageous to have the salt bath a few degrees above the set point value prior to starting the acid flow. In this way the initial heat absorption required for acid vaporization before the reaction started did not result in a temperature drop below the desired reaction value. During operation, no temperatures exceeding those of the salt bath were ever observed. This was another indication that the highly exothermic reactions were under control at all times. The product temperatures at the outlet above the reactor head were on the average 100°C below the salt bath temperature indicating that the product cooled rapidly after leaving the reactor.

Analytical Results

General

The on-line analytical method which was earlier tested on simulated nitration products (47, 48) proved to be quite satisfactory in actual operation. There were, however, several mechanical problems with the sampling system which were not completely solved.

The main problems encountered with the analysis resulted from the very delicate balance between sufficient sample size and excess sample size. In order to quantitatively detect the small quantities of some components, a sample size of 5 cc was required. However, with the available sampling technique, a sample this large resulted in a decrease in component

resolution because of peak "tailing". The shape of a chromatographic peak is strongly influenced by the flow characteristics of the sample "plug" (59). Any diffusion or backmixing will result in tailing of the leading or trailing edge of the sample plug and consequently result in analogous tailing of the individual peaks on the recorder chart. This tailing effect becomes more and more significant as analysis times are decreased and as the column efficiency is maximized.

Commercial sample valves are available with $1/8$ to $1/16$ in. entrance and exit ports. The one used during this research had $1/8$ in. ports, and the supplied 5 cc sample collection loop was consequently $1/8$ in. o.d. A $1/8$ in. o.d. loop with a 5 cc capacity is 3 feet long. Therefore, the 5 cc sample carried by a helium stream was already "tailed" for 3 feet before arrival at the analytical device. It was also found that a $1/4$ in. o.d. loop with a 5 cc capacity resulted in a different type of, but equally unacceptable, tail. This occurred because the helium stream from a $1/8$ in. port was unable to sweep a larger sample loop while maintaining a true plug flow condition. The resulting diffuse and backmix flow then caused the sample tail.

An acceptable, but not ideal, compromise was obtained by constructing a $1/8$ in. o.d. sample loop with a 3 cc capacity. Some sensitivity was lost, but the resulting analysis was quantitative for the major components. This system would be ideal for the analysis of ethane nitration products where the

number of components present would be considerably smaller and sensitivity would not then be a problem.

Another difficulty with the sample collection system which resulted in lost results during the early runs was salt carryover. During the early stages of experimentation, a portion of the product was allowed to continuously purge the sample loop. With this type of operation, salt build up in the loop resulted in, first smaller samples, and ultimately no samples. This problem was eliminated by the installation of the aspirator system which pulled a portion of the reactor effluent thru the loop prior to sampling.

Product analysis

The complete analysis of the nitration products for the final experiment, runs 20 to 39, is given in Table 19, Appendix A. Of the possible nitroparaffins, only NM, NE, 1-NP, 2-NB and 1-NB were found in significant quantities. Of interest is the fact that appreciable quantities of methanol, ethanol, and 1-propanol were present while no ketones were observed. Quantities of propionaldehyde, n-butyraldehyde, acetaldehyde and formaldehyde were present in varying proportions. In general, the quantity of oxidation and decomposition products such as the alcohols, aldehydes, low molecular weight hydrocarbons, and the oxides of carbon increased with increased reaction temperatures. This is seen in Figure 13. Also shown in the same figure are the ethane/butane and propane/butane


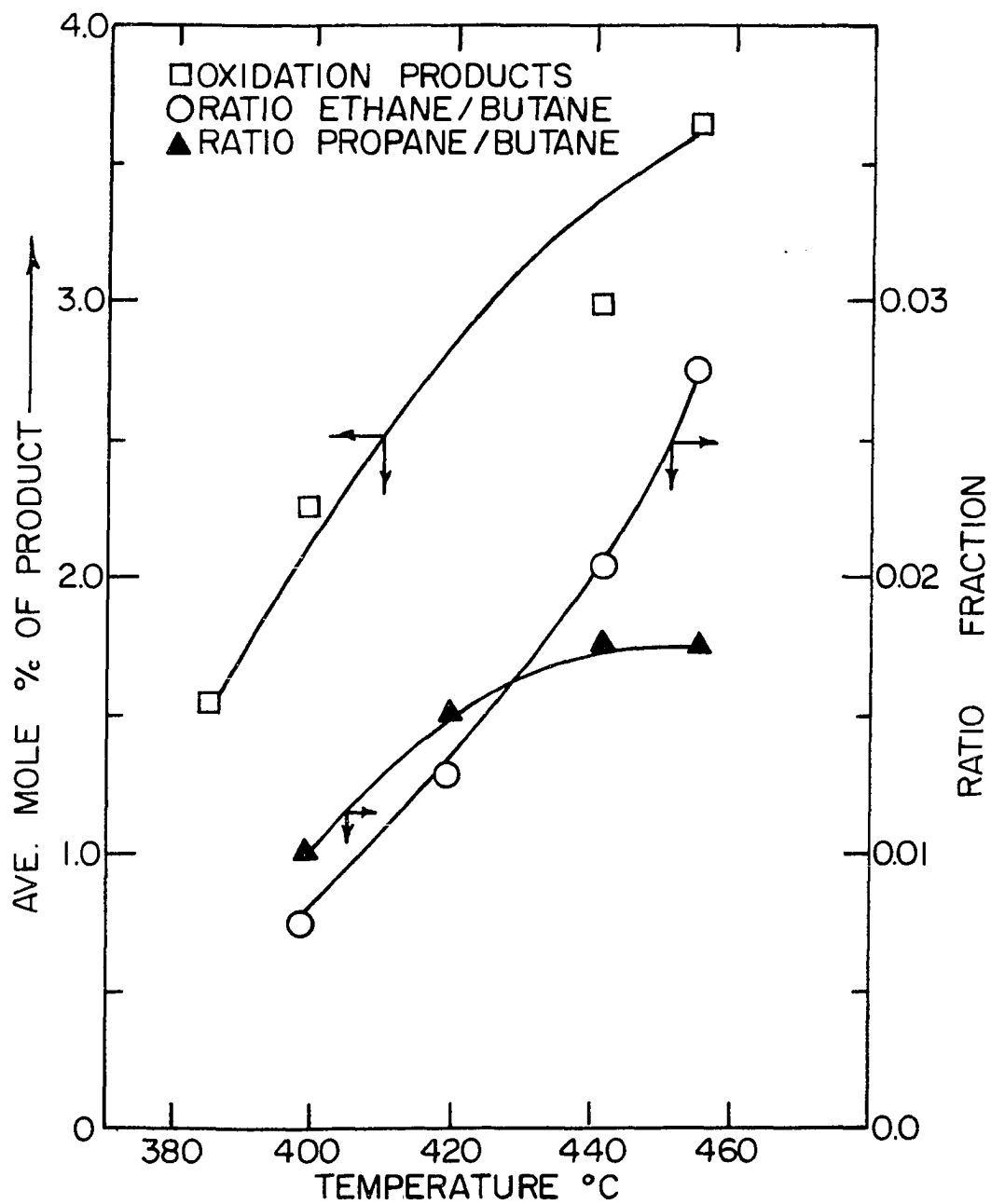


Figure 13. Plot of average mole per cent of oxidation products and mole fractions of hydrocarbon decomposition products as a function of temperature



mole ratios vs. temperature. It is seen that the quantity of light hydrocarbons formed increased with temperature. The amount of nitrogen formed also increased from an average mole per cent of 0.135 at 398.5°C to 0.375 mole per cent at 441.5°C. The ratio of carbon monoxide to carbon dioxide increased markedly both with increases in temperature and with decreases in mole ratio.

Product Results

General

Conversion, yield, and nitroparaffin distribution are of direct importance in determining the economic feasibility of the nitration process. The conversion values, which indicate the total extent of the reaction, determine the magnitude of recycle streams required for a given product output rate. The yield values give information on the quantity of raw materials lost to undesirable side reactions. Together these two parameters fix, for a given production rate, the sizes of the clean-up and separation equipment, the quantities of chemicals consumed in this equipment, and certain utility requirements. The nitroparaffin distribution is of marketing importance in that it is desirable to produce the largest quantities of the most salable materials.

In order to obtain the functional relationship between these three economically important variables and the controllable reaction variables: temperature, flow rate and mole

ratio, the data from the final, complete, central composite design were fit to quadratic polynomials by multiple regression analysis techniques. The actual multiple regression analysis was performed on an I.B.M. 360 series digital computer.

The experimental design used permitted not only the extraction of a maximum amount of information from a minimal number of data points, but also allowed the use of statistical methods to evaluate the results. If a factorial experiment had been used, it would have required 125 runs to cover the possible treatment combinations for 5 levels of three variables. Additional runs would have been required to obtain an estimate of the experimental error. The central composite design permitted the study of five levels of three variables in 19 runs which included an estimate of the experimental error. The design was split into three incomplete blocks (20, 22) to prevent a linear time trend from affecting the comparisons between the different levels of each variable. It was thought that such a trend might be caused by a gradual poisoning of the reactor or of the chromatographic columns.

The blocks were performed as days, and if, due to equipment failure, the process was shut down in the middle of a block, that block was started over on another day. Approximately 20 preliminary runs were made to obtain the switching times required to operate the on-line analytical equipment and to generally shakedown the equipment. After these preliminary

runs, the numbered runs were started and data collected. However, due to failures in the sampling valve and the heaters, blocks were not completed in the required time and some results were lost for the first 19 runs. The policy was then instituted of running a block, completely shutting down the equipment, checking every major piece for proper functioning, readjusting the chromatographic flow rates and pressures, and starting up again in five days. In this way runs 20 to 39 were successfully collected in three blocks over a 15 day period.

Yields and conversions

The experimental conditions and the results in terms of yields and conversions for runs 20 to 39 are presented in Table 20, Appendix A. The regression coefficients for the smoothed yield and conversion data are in Table 21, Appendix A. An analysis of variance (62) and subsequent F-ratio test was used on the yield and conversion data to determine: (1) if the data were adequately fit by the quadratic equations, (2) if the quadratic terms were required or if a linear equation would have been equally satisfactory, and (3) if a block effect indicating a time trend was present. Tables 7, 8, 9 show the analysis of variance for hydrocarbon conversion, hydrocarbon yield and acid yield. The levels of statistical significance used were 90% indicated by one asterisk and 95% indicated by two asterisk in the tabular values. The error

Table 7. Analysis of variance for hydrocarbon conversion

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-ratio
(Regression)	(9)	(18.6116)	(2.067)	(17.5)**
Linear	3	11.0388	3.679	30.359**
Quadratic	6	7.5719	1.262	10.398**
Blocks	2	0.7897	0.395	3.257 ¹
Lack of fit	5	3.0838	0.617	5.089
Error (pooled)	3	0.3638	0.1212	
Total	19	22.848		

Table 8. Analysis of variance for hydrocarbon yield

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-ratio
(Regression)	(9)	(1598.14)	(177.57)	(6.71)*
Linear	3	464.37	154.79	5.85*
Quadratic	6	1133.77	188.96	7.14*
Block	2	75.8	37.9	1.44
Lack of fit	5	143.779	28.756	1.09
Error	3	79.390	26.463	
Total	19	1897.11		

Table 9. Analysis of variance for acid yield

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-ratio
(Regression)	(9)	(337.228)	(37.469)	(9.37)*
Linear	3	81.375	27.125	6.78*
Quadratic	6	255.854	42.642	10.66**
Block	2	17.354	8.677	2.17
Lack of fit	5	30.516	6.103	1.526
Error	3	11.993	3.998	
Total	19	397.098		

terms were obtained from the two replicate values in each block and were pooled among blocks.

The individual regression coefficients of the regression model were then separately tested for significant departure from zero by the student-t test (60). It must be emphasized that this test was performed to obtain an insight as to the relationships among the variables, not to eliminate terms from the model. Although a number of the coefficients were not, in a statistical sense, significantly different from zero, they could not be replaced with zeros, for regardless of their magnitudes they were the best estimates of unknown coefficients. To replace a best estimate estimate by a zero would in effect be replacing a best estimate by a biased one.

An examination of the analysis of variance shows, in all three cases, that the data are fit significantly well by the quadratic form and that the linear form would not have been adequate. In every case, the mean square for blocks is of the same order-of-magnitude as the error term, thus indicating no significant time trend. The lack of fit terms are all insignificant in a statistical sense thus again showing that the total sum of squares was adequately accounted for by the quadratic fit.

Nitroparaffin yields based on hydrocarbon consumed ranged from 33.5% to 67.3%, while conversions based on hydrocarbon fed ranged from 1.46% to 4.71%. The yields based on nitric acid ranged from 20.8% to 34.7%. The results of this section

are generally summarized in Figure 14 which shows the effect of temperature on conversions and yields. The mole per cent nitromethane and the mole of nitroethane in the nitroparaffin product are plotted against temperature in Figure 14. Since nitromethane and nitroethane are normally the higher priced nitroparaffins, this figure shows that while increasing temperature adversely effects conversions and yields it improves the economic worth of the product. This conflicting temperature criterion demonstrates both the importance and the difficulty of choosing the most economically favorable operating conditions.

Nitroparaffin distribution

Replicated values for nitroparaffin distribution at the design center point and the statistical estimate of their reliability are presented in Table 10. The error mean square or variance term is a measure of the dispersion of the individual points. The standard deviation of the mean and the 90% student-t value were used to place the confidence limits on each mean value. The nitromethane data have a large random effect while the nitroethane and 1-nitropropane data are very consistent. The confidence limits on the 1-nitrobutane data are rather large. However, the entire analysis was effected by the 18.09% value which is the unique and inconsistent point.

The experimental values of the nitroparaffin distribution for runs 20 thru 39 are presented in Table 22, Appendix A.

Figure 14. Plot of nitration yields and conversions as a function of temperature

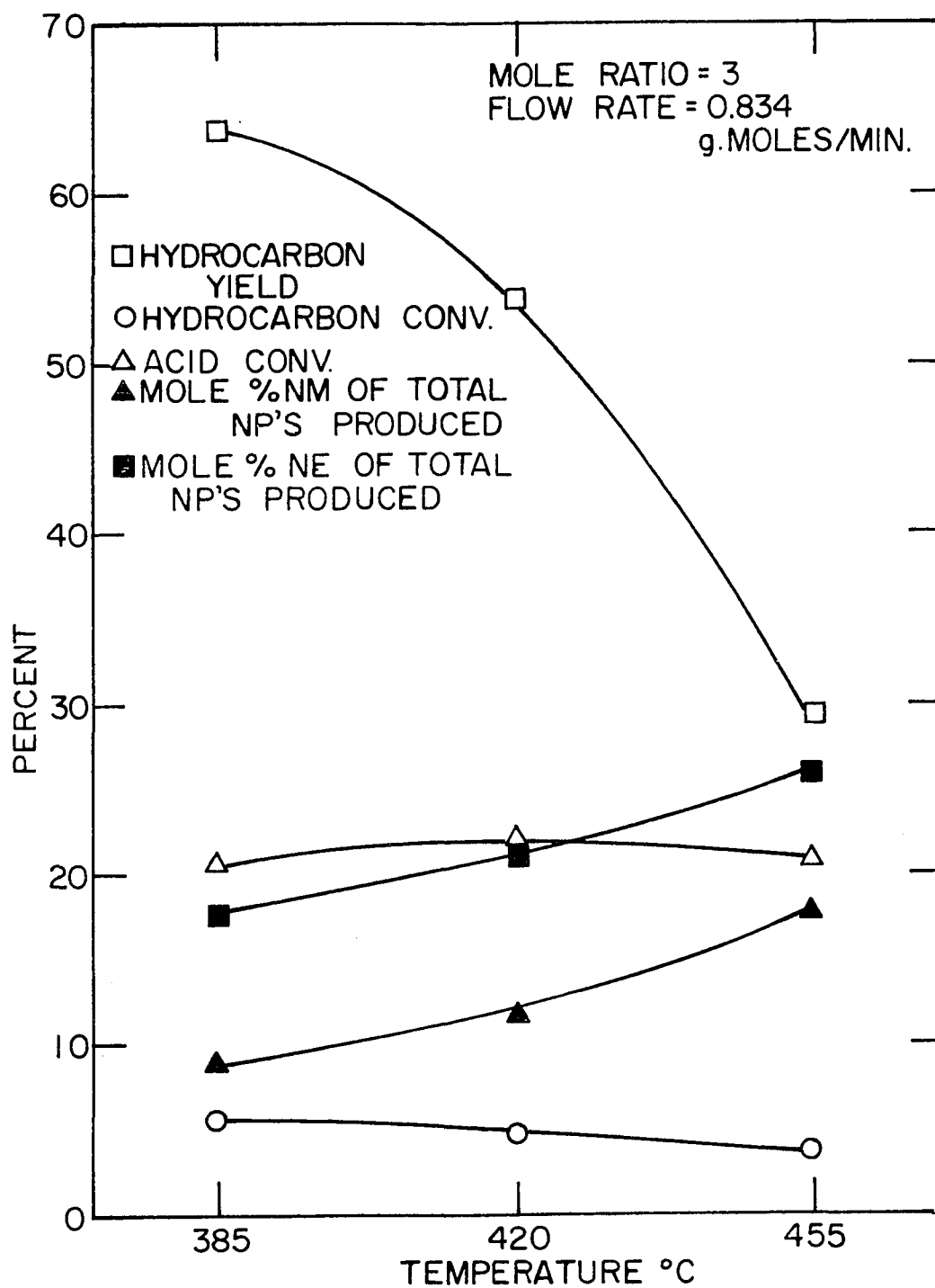


Table 10. Replicate values for nitroparaffin distribution at center point

Component	NM	NE	1-NP	2-NB	1-NB
Mole % of total nitro-paraffins produced	14.145	24.444	10.239	33.081	18.091
	9.672	22.092	11.064	30.647	26.524
	14.543	24.672	10.137	26.162	24.489
	12.953	23.594	10.946	24.772	27.730
	12.926	23.714	10.617	29.626	23.121
	13.189	23.157	10.954	29.617	23.083
Mean value	12.904	23.612	10.659	29.108	23.839
Error mean square	2.952	0.8686	0.1568	9.207	20.05
Standard deviation of the mean	0.7014	0.3804	0.5110	1.239	1.828
t value (90%)	2.015	2.015	2.015	2.015	2.015
90% confidence limits	11.491,	22.845,	9.629	26.612,	20.156
	14.317	24.379	11.689	31.604	27.522

The regression coefficients which were determined for each of the five significant nitroparaffins are found in Table 21, Appendix A, while the analysis of variance for each of the nitroparaffins is in Tables 11, 12, 13, 14 and 15. The F-ratio tests showed each of the nitroparaffins with the exception of nitromethane were significantly fit by the quadratic equations. The size of the nitromethane error term which

Table 11. Analysis of variance for nitromethane distribution

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-ratio
(Regression)	(9)	(71.9856)	(7.9984)	(2.7)
Linear	3	12.5787	4.1929	1.37
Quadratic	6	59.4069	9.9011	3.35
Lack of fit	5	18.8035	3.7607	1.28
Error	5	14.7563	2.9513	
Total	19	105.5454		

Table 12. Analysis of variance for nitroethane distribution

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-ratio
(Regression)	(9)	(128.635)	(14.292)	(16.5)**
Linear	3	37.601	12.534	14.6**
Quadratic	6	91.034	15.172	17.6**
Lack of fit	5	11.213	2.243	2.6
Error	5	4.343	0.8686	
Total	19	144.1906		

Table 13. Analysis of variance for 1-Nitropropane distribution

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-ratio
(Regression)	(9)	(37.974)	(4.219)	(27.1)**
Linear	3	16.229	5.409	34.6**
Quadratic	6	21.745	3.624	22.2**
Lack of fit	5	1.687	0.3374	2.6
Error	5	0.7841	0.1568	
Total	19	40.445		

Table 14. Analysis of variance for 2-Nitrobutane distribution

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square	F-ratio
(Regression)	(9)	(1359.84)	(151.093)	(16.4)**
Linear	3	493.39	164.464	17.8**
Quadratic	6	866.45	144.408	15.6**
Lack of fit	5	60.142	12.028	1.31
Error	5	46.035	9.2069	
Total	19	1466.017		

Table 15. Analysis of variance for 1-Nitrobutane

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-ratio
(Regression)	(9)	(351.42)	(39.047)	(9.75)**
Linear	3	134.01	44.67	11.1**
Quadratic	6	217.41	36.22	9.00**
Lack of fit	5	56.88	11.376	2.83
Error	5	20.05	4.01	
Total	19	428.35		

resulted from the data scatter was the reason for the failure of fit in this case.

None of the nitroparaffins were found to be time dependent to the first power. Temperature was in every case the most significant factor in fixing the distribution, however, mole ratio was significant in the nitroethane equation. The temperature effect is shown graphically in Figure 15. The amount of lower nitroparaffins increased with increasing temperature. The increase in the 1-nitropropane was small but the amount of nitroethane increased from 18 to 26 mole per cent and the amount of nitromethane increased from 8 to 17 mole per cent over the 70°C range. The amount of 2-nitrobutane fell off drastically as temperature was increased while the 1-nitrobutane increased. The effect of both temperature and mole ratio on the nitroethane produced is shown by a contour plot, Figure 16. From this plot it is easy to see that there is an optimum per cent nitroethane at any given temperature. This in each case occurs at a mole ratio of close to four. At a fixed mole ratio the per cent nitroethane increases with increasing temperature. The general results of this section show that the product distribution can be controlled by controlling temperature and mole ratio. The greatest control exists in the relative amounts of 1-nitrobutane to 2-nitrobutane that can be obtained.

Figure 15. Plot of nitroparaffin distribution as a function of temperature

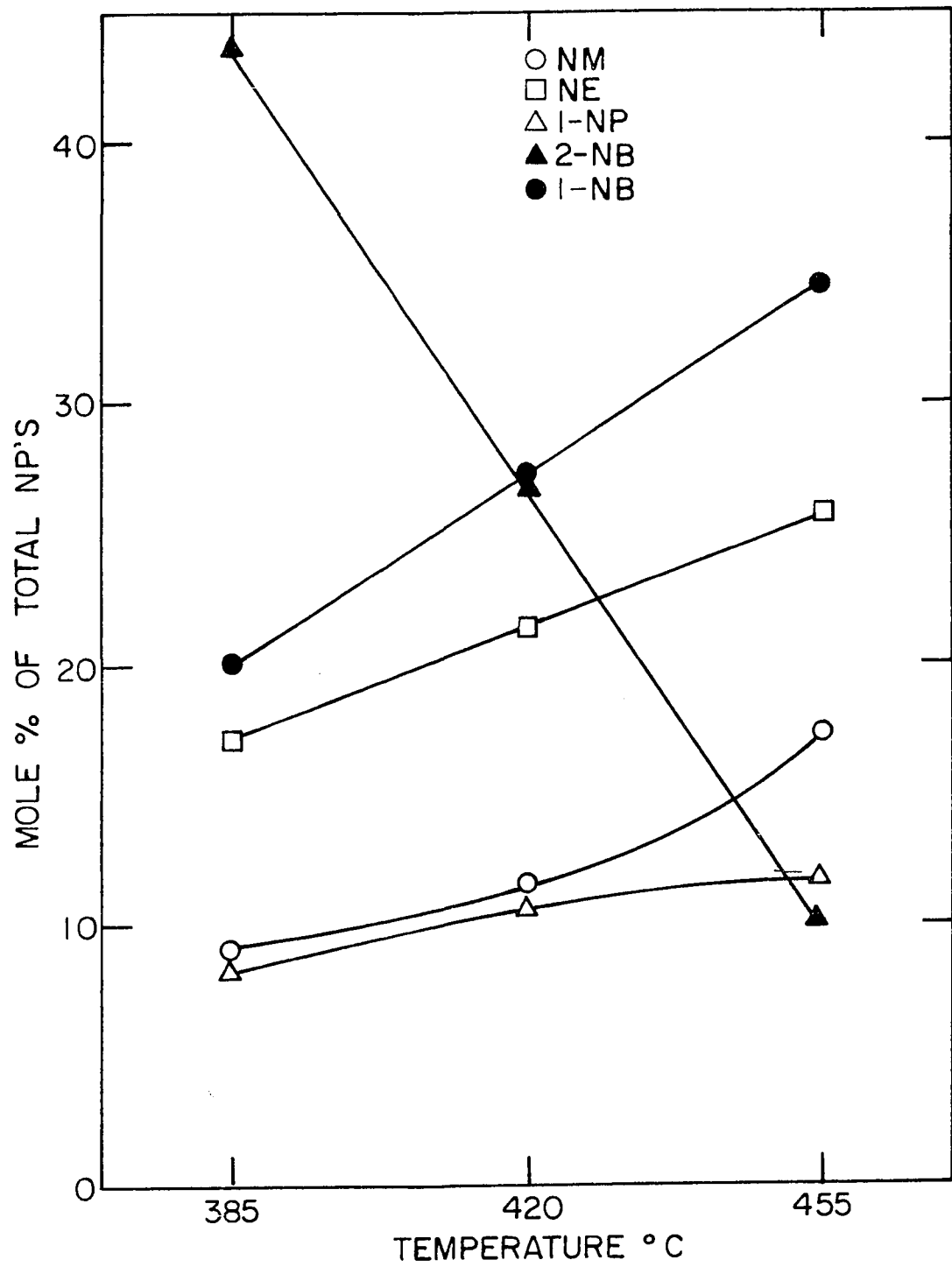
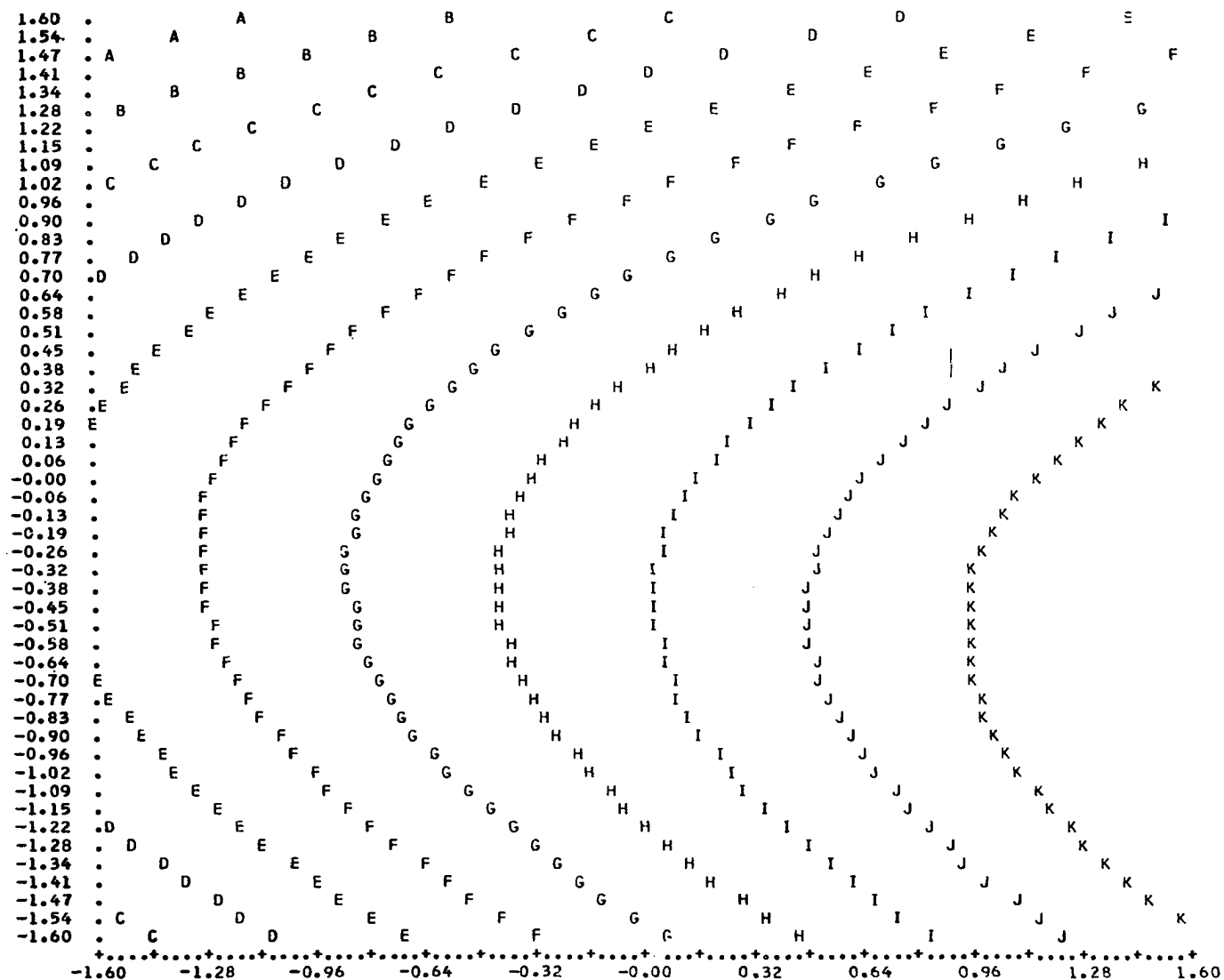


Figure 16. Contour plot of mole per cent nitroethane in the nitroparaffin distribution as a function of temperature and mole ratio at a reactant flow rate of 0.834 g. moles/min.

Mole per cent nitroethane starts at 18.0 (C) and increases in steps of 1.0 to 26.0 (K). Coded temperature is the horizontal axis and coded mole ratio is the vertical axis.



Economic Optimization

General

As shown in Figure 14 each of the important properties of the process, yield, conversion, and product distribution has a different functional dependence on the controlled variable, temperature, mole ratio, and reactant flow rate. If a single criterion, for example acid conversion, were picked to determine the best set of operating conditions, then the resulting product distribution or hydrocarbon conversion would not necessarily be the most favorable. The process properties or state variables and the controlled or decision variables are, however, related by one common denominator, economics. An economic model for a nitroparaffin plant using butane and nitric acid as the feed materials was constructed. From the model an objective function which explicitly described the relationship between per cent return on investment and the state variables was written. The objective function implicitly was dependent upon the decision variables thru the quadratic equations obtained from the experimental data. The objective function was then optimized to produce a maximum return on investment, and the values of the decision variables which produced this result were determined. In this manner a set of optimum operating conditions was obtained.

Objective function

The profit model and resulting objective function was constructed using the definition of profit and the general

guidelines set forth by Villbrandt and Dryden (63). The criterion for optimization was chosen as per cent return on investment.

$$r_a = \frac{(100) E}{I} \quad (15)$$

r_a = annual per cent return on investment after tax

I = capital investment, dollars

E = annual new earnings, dollars

$$E = Px \quad (16)$$

P = annual gross profit before tax, dollars

x = (1 - fraction for tax) = 1 - a

a = fraction for tax

The annual gross profit was in turn related to production rate, production selling price and total production cost.

$$P = V(S - C_T) \quad (17)$$

V = annual units of production, lbs.

S = selling price per unit of production,
dollars/lb.

C_T = total production cost per unit of production,
dollars/lb.

The total production cost was then defined in terms of costs which were later related to the process state variables.

$$C_T = R + (b + c + o + l) L + P_s + (m + d + t)(F/V) \quad (18)$$

R = cost of raw materials per unit of product,
dollars/lb.

L = cost of operating labor per unit of product,
dollars/lb.

P_s = cost of services per unit of product, dollars/lb.

F = fixed plant investment, dollars

V = annual units of production, lbs.

b = operating supervision as fraction of operating
labor

c = control lab as fraction of operating labor

o = overhead as fraction of operating labor

m = maintenance as annual fraction of fixed investment

d = depreciation as annual fraction of fixed investment

t = taxes as annual fraction of fixed investment

Equations 15, 16, and 17 were combined to give:

$$r_a = \frac{E(100)}{I} = \frac{Px(100)}{I} = \frac{V(S - C_T)(x)(100)}{I} \quad (19)$$

The final objective function was then obtained from a combination of Equations 18 and 19.

$$r_a = \frac{V(x)(100)}{I} [S - R - (b + c + o + l) L - P_s - (m + d + t)(F/V)] \quad (20)$$

Relationship to process variables

The product selling price, S , and the raw materials costs, R , were related to the process state variables which then made them functions of the decision variable thru the quadratic equations. In the preparation of the following equations, it was assumed that the nitric acid would be manufactured at the plant site and sold at cost to the nitroparaffin plant. It was further assumed that the cost of the recycle acid would be 68 per cent of the original manufacturing cost. This figure was based on the fact that the recycle acid will be reprocessed at a fraction of the original cost and that the raw materials will be available in the recycle stream. The exact fraction was estimated from information available in Chilton (21).

From the nitroparaffin distribution as a function of temperature, mole ratio, and flow rate, the following values may be computed directly for any choice of operating conditions within the experimental range:

A_m = average molecular weight of the nitroparaffins
(NP)

$(W_n)_i$ = weight fraction of the i^{th} nitroparaffin in the
total nitroparaffin product

C/mole = moles carbon per mole of nitroparaffin product

N/mole = moles nitrogen per mole of nitroparaffin product
= 1.0

The equation giving the cost of acid per lb. of

nitroparaffin product produced was obtained then simplified by assuming an average recycle. The experimental data show that on the average 50 per cent of the input acid will be recycled.

$$\frac{\text{mole acid fed}}{\text{mole NP produced}} = \frac{N/\text{mole}}{\text{acid yield}} \quad (21)$$

$$\frac{\text{lb. acid}}{\text{lb. NP}} = \frac{\text{mole wt. acid}}{A_m} \left(\frac{\text{mole acid fed}}{\text{mole NP produced}} \right) \quad (22)$$

$$\begin{aligned} \frac{\text{cost of acid}}{\text{lb. NP}} = \frac{\text{lb. acid}}{\text{lb. NP}} & \left[\left(\frac{\text{mgf. cost}}{\text{lb. acid}} \times \frac{1}{2} \right) \right. \\ & \left. + \left(\frac{\text{mgf. cost}}{\text{lb. acid}} \times \frac{0.68}{2} \right) \right] \end{aligned} \quad (23)$$

By combining Equations 21, 22 and 23 and inserting numerical values, the acid cost equation was obtained as a function of the state variables.

$$\frac{\text{cost of acid}}{\text{lb. NP}} = \frac{(88.2)}{(\text{acid yield})(A_m)} \quad (24)$$

cost of acid/lb. NP in cents/lb.

The cost of the butane per pound of product was obtained by a similar derivation.

$$\frac{\text{moles butane used}}{\text{moles NP formed}} = \frac{C/\text{mole}}{4(\text{hydrocarbon yield})} \quad (25)$$

$$\frac{\text{lb. butane}}{\text{lb. NP}} = \frac{\text{moles butane}}{\text{moles NP}} \left(\frac{\text{mole wt. butane}}{A_m} \right) \quad (26)$$

$$\frac{\text{cost of butane}}{\text{lb. NP}} = \frac{\text{cost}}{\text{lb. butane}} \left(\frac{\text{lb. butane}}{\text{lb. NP}} \right) \quad (27)$$

From Equations 25, 26 and 27 and the appropriate numerical values the butane cost was found to be:

$$\frac{\text{cost of butane}}{\text{lb. NP}} = \frac{43.21 \text{ (C/mole)}}{(\text{hydrocarbon yield})} \quad (28)$$

cost of butane/lb. NP in cents/lb.

The recycle cost was obtained by first setting up a balance to compute the moles of butane recycled per mole of nitroparaffin produced, then estimating the material costs per pound of recycle. The material costs were based on estimates of make-up kerosene and soda ash used in the product recovery system. These estimates were made by considering the recovery system in the existing propane nitration plant (25).

$$\frac{\text{cost of recycle}}{\text{lb. NP}} = 0.0415 \left[\frac{3.0(\text{mole ratio})}{\text{acid yield}} \left(1 - \frac{\text{butane conv.}}{\text{butane yield}} \right) \right] \quad (29)$$

The selling price of the product was very simply related to the nitroparaffin distribution by:

$$S = \sum_{i=1}^5 (W_n)_i \left(\frac{\text{selling price}}{\text{lb.}} \right)_i \quad (30)$$

$$i = 1 \dots 5$$

The selling price per lb. of the individual nitroparaffins were obtained from the literature for NM, NE, 2-NP, and 1-NP (58).

The prices per lb. of the nitrobutanes were estimated to be the same as those for the nitropropanes. The prices in dollars per lb. were: NM, 0.31; NE, 0.29; 1-NP, 0.27; 2-NP, 0.18; 2-NB, 0.18 and 1-NB, 0.27.

The fixed capital cost of the plant was estimated by scaling up a cost estimate for the 10,000,00 lb./yr. nitro-paraffin plant built by the Commercial Solvents Corporation in 1954. Assuming that numerous process improvements have been made over the years so that the present plant capacity is greater than the initial rated capacity, and that the current demand for nitroparaffin is increasing, the butane nitration process was sized for 15,000,000 lb./yr. The original cost of the propane nitration plant was \$4,200,000. This was scaled to current costs by the ratio of the Marshall and Stevens index for 1967 (30) to the index for 1954 (27). This resulted in a capital cost estimate of \$5,704,000. The cost was then increased by a factor to account for the extra purification equipment required when additional nitropareffins are produced. This additional factor was obtained by sizing and costing a distillation tower then relating its input capacity to reactor mole ratio by average yield and conversion figures.

F = fixed plant investment

$$\begin{aligned}
 &= 5.704 \times 10^6 \\
 &+ \left[0.10 \times 10^6 + (\text{mole ratio} - 2)(0.04 \times 10^6) \right] \quad (31)
 \end{aligned}$$

The minimum possible mole ratio was fixed at 2 and used as a base in the cost estimates. This was reasonable because of the safety and control problems that become significant when operating at low mole ratios.

Profit equation

All factors and costs required for the basic objective function were obtained from Chilton (21) and Villbrandt (63). The values used and notes on judgements made in their estimation are given in Table 16. With these numerical values inserted in Equation 20, the final profit equation became:

$$r_a = \frac{6.594 \times 10^6}{F} [S - R - 2.23 - (1.066 \times 10^{-6})F] \quad (32)$$

Equation 32 was subject to the definitions of S and R given by Equations 24, 29, 30, and 31. The entire profit equation was restricted by the quadratic equations relating the state and decision variables.

Optimum operating conditions

The profit function, Equation (32), was optimized over temperature and mole ratio at a fixed reactant flow rate by exhaustive search technique. This technique was used because profit equation is a nonlinear function of highly nonlinear constraints and without simplification, direct methods would not be feasible. Such a simplification was, however, attempted and the resulting equation optimized by Jacobian

Table 16. Estimates** of economic factors used in profit model

a:	tax on gross profit	a = 0.49
b:	operating supervision as fraction of operating labor (assume average instrumented chemical plant)	b = 0.25
c:	control lab as fraction of operating labor (assume average value of given range)	c = 0.20
o:	overhead as fraction of operating labor (Chilton gives 0.50 but assume added social security and benefits have increased it)	o = 0.60
m:	maintenance, 6 per cent of fixed investment	m = 0.06
d:	depreciation, 8 per cent of fixed investment	d = 0.08
t:	taxes and insurance, 2 per cent of fixed investment	t = 0.02
L*:	operating labor, 6 per cent of estimated mgf. costs	L = 0.6
P_s^*	= cost of services per unit cost of product, 10 per cent of estimated mgf. costs	P = 1.0
I	= capital investment = $F(1 + 0.1)$ This assumes operating capital is 10 per cent of fixed capital.	

*Estimated mgf. costs obtained from Fear (31)

**Values and estimates obtained from Chilton (21)

elimination. As might have been anticipated the simplifications were too stringent and the resulting answers were nonsensical. The flow rate was not considered in the optimization because an examination of the physical data indicates that the nitroparaffin distribution is not a first power function of flow rate and that the yields and conversions are lowered by long residence times. Therefore the flow rate was fixed at the center point of the design.

A program was written for the I.B.M. 360 digital computer to perform the exhaustive search. The computer incremental temperature and mole ratio over the experimental range with a 19 x 19 matrix and printed out complete results on a card deck and partial results on paper. The results printed out included product distribution, yields, conversions, selling price, materials and recycle costs and per cent return on investment. Table 23 and Figure 19 in Appendix B show and explain the computer program. The complete search routine and subsequent printout took 22.6 seconds of computer time.

Pictorial representations of how the profit response surface changes with temperature and mole ratio are given in Figures 17 and 18. These figures represent the same response surface looked at from two different angles. The first shows best the existence of the optimum, while the second demonstrates more clearly the degree of curvature of the surface.

From an examination of the computer printout, the optimum profit was found to be 7.65 per cent which occurred at a

Figure 17. Response surface of per cent return on investment, ra , as a function of temperature, x_1 , and mole ratio, x_2

Temperature and mole ratio in coded units over range from -1.8 to 1.8

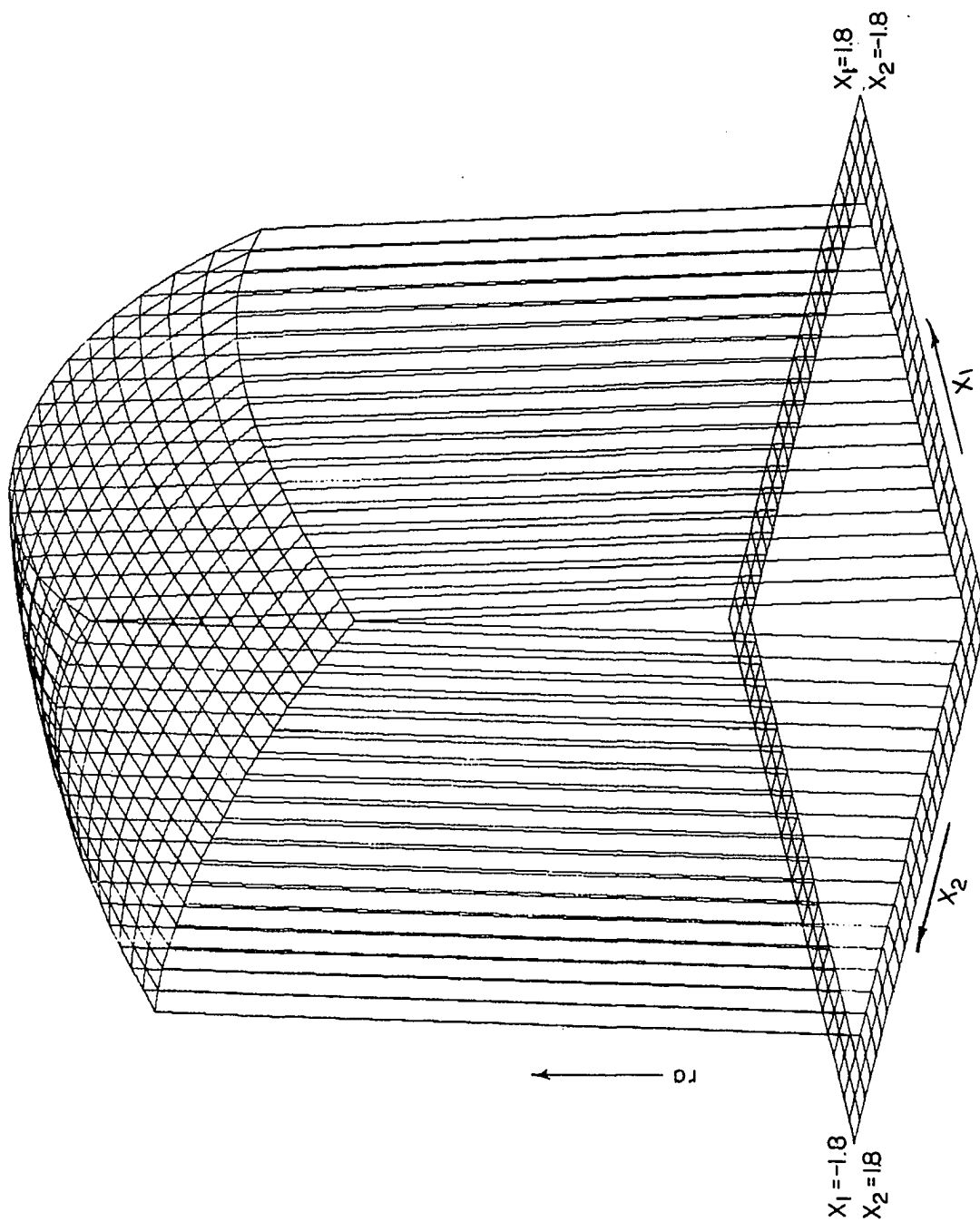
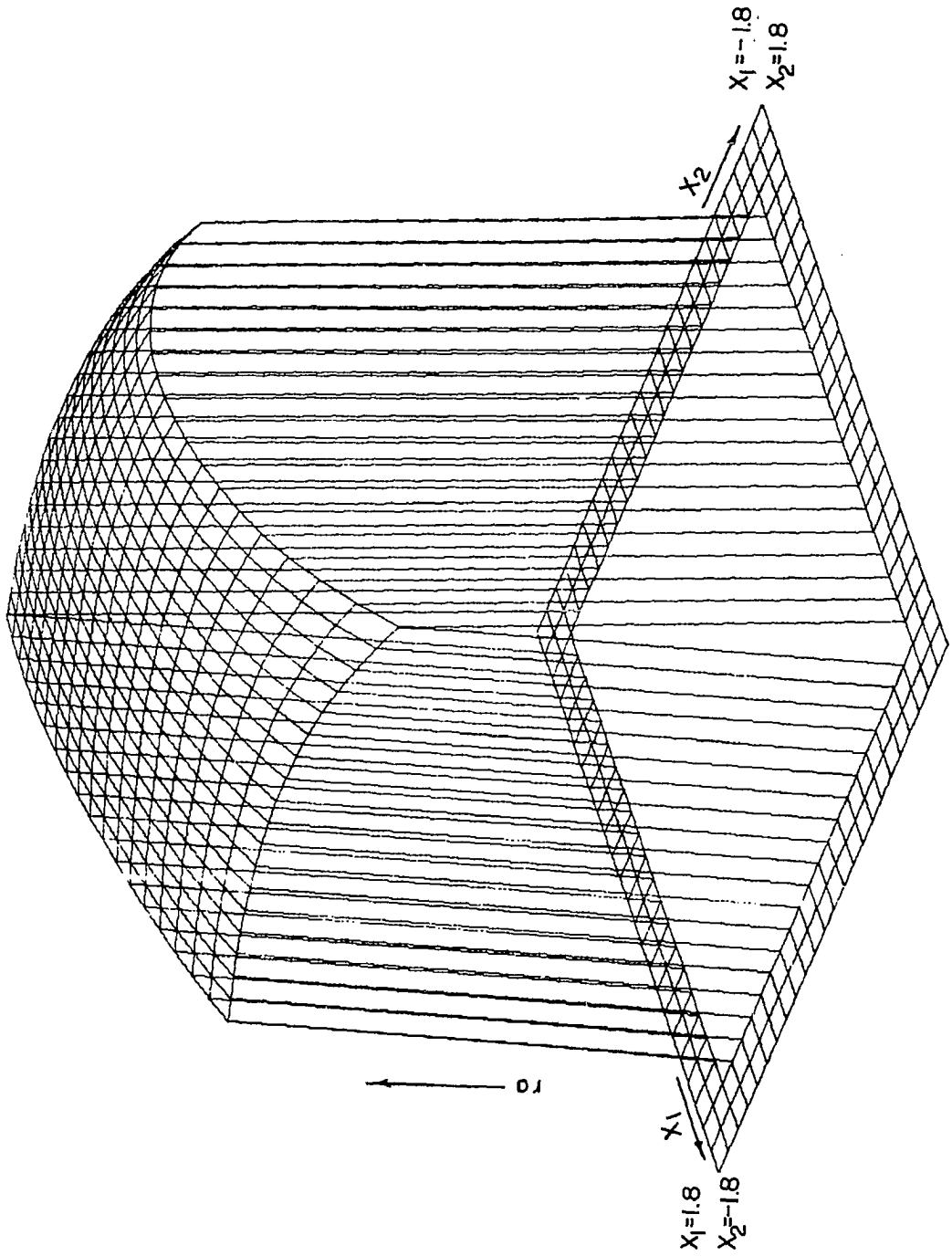


Figure 18. Response surface of per cent return on investment, ra , as a function of temperature x_1 , and mole ratio, x_2

Temperature and mole ratio in coded units over range from -1.8 to 1.8



temperature of 445.7°C and a mole ratio of 4.51. The optimum results are shown in Table 17. From a study of Table 17 it was concluded that the product selling price is one of the controlling factors in the optimum conditions. The temperature was pushed upward to the point of a very low hydrocarbon yield which would indicate a high formation of oxidation products. This was, however, compensated for by a low hydrocarbon conversion so the total quantity of reactant lost to byproduct was kept low. In exchange for the low yield the product distribution was quite favorable in terms of the higher priced nitroparaffins. In general, it was observed that for the economic data used, it is better to accept low conversions and yields, recycle large quantities of material, and produce a more favorable distribution. The absolute accuracy of this picture depends to a great extent on the estimation of recycle cost. Pilot plant data or actual plant data on such a recovery system would be required to greatly improve the value used.

No true optimum minimum or maximum for the selling price or material and recycle costs existed in the range studied. In each case the most favorable value observed, lowest for cost or highest for selling price, existed at one of the experimental boundaries. These favorable values and conditions are shown in Table 18.

Three of the cost figures were the lowest at 385°C , however, the mixture does not react significantly below this

Table 17. Optimum economic values for butane nitration

Conditions: 445.7°C and 4.51 moles hydrocarbon/mole acid

Per cent return on investment: 7.65 per cent

Economic values, cents/lb. product

Selling price:	26.1
Acid cost:	4.8
Butane cost:	3.5
Recycle cost:	2.4

Nitroparaffin distribution, mole per cent

NM:	14.9
NE:	23.6
1-NP:	12.0
2-NB:	16.6
1-NB:	32.9
	100.0

Yields and conversions, per cent

Hydrocarbon yield:	40.41
Acid yield:	21.28
Hydrocarbon conversion:	1.93

Table 18. Most favorable values of economic cost factors found in the experimental range

Per lb. of Nitroparaffin Product	
Selling price	26.9 cents/lb. at 455°C and 3 M. R.
Acid cost	3.2 cents/lb. at 385°C and 7 M. R.
Butane cost	2.3 cents/lb. at 385°C and 5 M. R.
Recycle cost	1.5 cents/lb. at 385°C and 3 M. R.

temperature. The best selling price and lowest recycle cost were found to occur at a mole ratio of 3, however, below this value the reaction is dangerous and quite difficult to control.

The optimum profit obtained, 7.65 per cent, is low and would not generally make the butane nitration attractive for a new venture. However the following points are made:

(1) the total profit estimate was made from conservative estimates of ranges taken from text books, (2) the butane was priced at the current market price 14.5 cents/gal. (57) and could vary widely depending on plant location and quantity purchased, (3) the selling prices of the nitrobutane were estimated for lack of true values, (4) the plant volume was fixed, and (5) nitration of hydrocarbon is not a new venture and an existing propane facility would have to make but a few modifications to use butane. The selling price and volume estimates are marketing problems which could substantially

increase the estimated profit. More exact values on points (1) to (4) would be available in a corporation considering butane nitration as a venture, and the possibility or desirability of changing feed stream in an existing plant would depend on the propane to butane price ratio. In general the success of a commercial butane nitration process will depend both on the ability of a corporation to produce desirable products from the nitrobutanes and in its marketing ability to create an over-all demand for the nitroparaffin.

CONCLUSIONS

Investigation of the vapor phase nitration of butane with 67% nitric acid in a molten salt bath reactor at temperatures from 385°C to 455°C, mole ratios of butane to nitric acid from 3 to 7, and reactant flow rates from 0.433 g. moles/min. to 1.235 g. moles/min. resulted in the following conclusions:

1. An on-line gas chromatographic method has been developed which provides a reproducible quantitative analysis of the major products resulting from the vapor phase nitration of butane. Based on a replicate of six experiments, the standard deviations of the mean per cent nitroparaffin in the total nitroparaffin distribution varies from a minimum of 0.380 on a mean of 23.612 mole per cent nitroethane to a maximum of 1.828 on a mean of 23.839 mole per cent 1-nitrobutane.

2. Nitroparaffin distributions are not significantly dependent on the first power of reactant flow rate, but are significant functions of both temperature and mole ratio. The greatest dependence is on temperature, and the amount of lower nitroparaffins formed increases with increasing temperature. The ratio of the quantities of 1-nitrobutane to 2-nitrobutane produced varies greatly with changes in the controlled variables.

3. Yields and conversions are functions of all three controlled variables. The greatest dependence is on temperature, and increasing temperature adversely affects the yields

and conversions. The quantities of decomposition and oxidation products formed increases with an increase in temperature.

4. There was no significant change in the performance of either the reactor or analytical equipment with time. The time dependent catalytic effect of metal surfaces on vapor phase nitration is effectively eliminated by the reactor design used.

5. The optimum per cent return on investment after tax for a hypothetical plant designed to produce 15,000,000 lbs. of nitroparaffins per year by the vapor phase nitration of butane is 7.65 per cent. This optimum value was obtained at the following values of the controlled variables: 445.7°C, 4.51 moles butane per mole nitric acid, 0.833 moles of reactant per min. The nitroparaffin product has a selling price of 26.1 cents per lb. while the raw materials cost 10.7 cents per lb. of product.

RECOMMENDATIONS

1. Development of an improved on-line sample valve should be investigated. The ideal valve would collect a five cc sample, thereby improving the sensitivity of the analysis and would allow the sample to be swept to the chromatographs in true plug flow to reduce tailing.

2. Butane nitration should be further studied in a reactor with very short retention times in order to isolate the nitration portion of the mechanism from the oxidation and decomposition portions. It is suggested that a venturi or monotube mixer reactor similar to an acetylene converter may be appropriate.

3. The effect of pressure on the vapor phase nitration of butane should be studied.

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APPENDIX A

Table 19. Complete analysis of reactor products for runs 20 to 39, mole per cent

	20	21	22	23	24
CO ₂	1.827	1.402	2.357	1.900	1.665
CO	0.598	0.966	2.286	1.349	2.229
C ₂ H ₆	0.897	0.880	1.532	0.874	0.688
C ₃ H ₈	0.629	0.832	1.163	0.574	0.449
C ₄ H ₁₀	79.105	78.346	77.855	79.694	76.124
N ₂	0.088	0.165	0.399	0.261	0.238
NO-NO ₂	7.822	7.743	8.375	6.894	12.322
HCHO	0.118	0.127	0.024	0.250	0.076
CH ₃ CHO	-	-	-	-	-
H ₂ O	2.755	2.001	2.253	3.209	1.351
CH ₃ OH	0.129	0.417	-	-	0.135
C ₂ H ₅ CHO	1.537	0.923	0.761	0.752	0.490
C ₂ H ₅ OH	0.646	0.633	0.349	0.573	0.317
(CH ₃) ₂ CHCHO	-	-	-	-	-
(CH ₃) ₂ CHOH	-	-	-	-	-
C ₃ H ₇ CHO	0.150	0.196	0.153	0.188	0.150
C ₃ H ₇ OH	0.027	0.151	0.025	-	0.006
NM	0.398	0.521	0.325	0.399	0.527
NE	0.635	1.075	0.632	0.815	0.921
2-NP	0.027	Trace	Trace	Trace	Trace
1-NP	0.302	0.477	0.318	0.425	0.386
2-NB	1.422	1.599	0.494	0.813	1.246
1-NB	0.882	0.982	0.699	1.032	0.682

Table 19. Continued

	25	26	27	28	29
CO ₂	2.022	1.931	1.310	1.597	2.308
CO	1.757	1.889	1.354	1.876	3.543
C ₂ H ₆	0.379	0.879	0.048	1.564	2.316
C ₃ H ₈	0.638	0.947	-	1.494	2.099
C ₄ H ₁₀	76.941	76.090	81.164	82.036	69.728
N ₂	0.209	0.168	0.138	0.254	0.595
NO-NO ₂	10.080	8.928	6.772	6.078	9.419
HCHO	0.155	0.147	0.216	0.278	0.136
CH ₃ CHO	-	-	-	-	-
H ₂ O	2.907	1.934	2.503	1.843	3.265
CH ₃ OH	1.058	0.547	0.139	-	0.816
C ₂ H ₅ CHO	0.772	0.729	0.946	0.686	1.266
C ₂ H ₅ OH	-	0.548	0.448	0.373	0.599
(CH ₃) ₂ CHCHO	-	-	-	-	-
(CH ₃) ₂ CHOH	-	-	-	-	-
C ₃ H ₇ CHO	0.204	0.170	0.139	0.183	0.211
C ₃ H ₇ OH	0.007	0.148	0.040	-	0.019
NM	0.277	0.457	0.566	0.305	0.620
NE	0.634	1.184	1.005	0.369	0.982
2-NP	Trace	Trace	Trace	Trace	Trace
1-NP	0.317	0.479	0.389	0.200	0.380
2-NB	0.879	1.799	1.888	0.272	0.681
1-NB	0.761	1.024	0.935	0.592	1.015

Table 19. Continued

	30	31	32	33	34
CO ₂	1.383	1.492	1.266	1.499	1.699
CO	1.074	2.799	1.472	0.657	2.161
C ₂ H ₆	0.999	1.139	0.710	0.695	1.225
C ₃ H ₈	0.959	1.202	0.441	0.441	1.455
C ₄ H ₁₀	82.094	77.667	84.931	83.627	74.886
N ₂	0.369	0.309	0.128	0.098	0.232
NO-NO ₂	7.435	7.232	4.826	6.532	9.204
HCHO	0.144	0.123	0.146	0.116	0.208
CH ₃ CHO	-	-	-	-	-
H ₂ O	2.117	3.657	2.258	2.549	2.475
CH ₃ OH	-	-	0.109	-	-
C ₂ H ₅ CHO	0.521	0.824	1.737	0.338	0.667
C ₂ H ₅ OH	0.389	0.477	0.579	0.242	0.479
(CH ₃) ₂ CHCHO	-	0.153	0.439	-	-
(CH ₃) ₂ CHOH	0.128	-	-	-	-
C ₃ H ₇ CHO	0.059	0.222	0.167	0.078	0.159
C ₃ H ₇ OH	0.026	0.019	0.099	0.029	-
NM	0.334	0.347	0.283	0.287	0.637
NE	0.567	0.633	1.188	0.575	1.348
2-NP	Trace	Trace	Trace	Trace	Trace
1-NP	0.233	0.294	0.734	0.327	0.476
2-NB	0.602	0.665	3.207	1.095	1.563
1-NB	0.563	0.744	2.970	0.815	1.132

Table 19. Continued

	35	36	37	38	39
CO ₂	1.840	2.362	1.928	1.348	1.867
CO	3.422	2.157	1.879	2.542	2.164
C ₂ H ₆	1.845	2.126	0.088	0.479	0.832
C ₃ H ₈	3.095	0.940	-	0.599	0.874
C ₄ H ₁₀	64.093	76.806	79.779	75.039	75.197
N ₂	0.463	0.229	0.589	0.248	0.262
NO-NO ₂	15.943	8.195	7.178	11.448	10.389
HCHO	0.191	1.782	0.332	0.163	0.023
CH ₃ CHO	-	0.754	0.877	-	-
H ₂ O	2.757	0.839	1.146	3.472	3.113
CH ₃ OH	-	-	-	0.165	0.567
C ₂ H ₅ CHO	0.701	0.858	0.701	0.613	0.702
C ₂ H ₅ OH	0.393	0.217	0.347	0.389	0.479
(CH ₃) ₂ CHCHO	-	-	-	-	-
(CH ₃) ₂ CHOH	0.0786	-	-	-	-
C ₃ H ₇ CHO	0.121	0.201	0.177	0.222	0.181
C ₃ H ₇ OH	0.053	-	-	0.034	0.011
NM	0.624	0.410	0.582	0.364	0.342
NE	1.053	0.697	0.982	0.665	0.723
2-NP	Trace	Trace	Trace	Trace	Trace
1-NP	0.545	0.309	0.356	0.442	0.372
2-NB	1.328	0.318	2.339	0.788	0.937
1-NB	1.450	0.801	0.720	0.898	0.970

Table 20. Experimental conditions and yield and conversion results for runs 20 to 39

	20	21	22	23	24
Temperature °C	398.5	398.5	441.5	441.5	420.0
Mole ratio butane to acid	6.23	3.77	3.77	6.23	5.0
Input flow rate 2 moles/min.	0.590	1.079	0.590	1.079	0.834
Coded temp. x1	-1.0	-1.0	1.0	1.0	0.0
Coded mole ratio x2	1.0	-1.0	-1.0	1.0	0.0
Coded flow rate x3	-1.0	1.0	-1.0	1.0	0.0
% hydrocarbon ^a conversion	3.277	3.916	2.192	1.996	3.453
% hydrocarbon ^b yield	50.54	57.896	39.142	53.867	58.043
% acid yields ^c	31.427	24.001	21.191	31.953	22.712

^aMolar ratio of carbon in NP's to carbon fed

^bMolar ratio of carbon in NP's to carbon consumed. The carbon consumed is based on the assumption that propane and butane in the exit stream can be recovered.

^cMolar ratio of nitrogen in the NP's to nitrogen fed

Table 20. Continued

	25	26	27	28	29
Temperature °C	420.0	398.5	398.5	441.5	441.5
Mole ratio butane to acid	5.0	3.77	6.23	6.23	3.77
Input flow rate 2 moles/min.	0.834	0.590	1.079	0.590	1.079
Coded temp. x1	0.0	-1.0	-1.0	1.0	1.0
Coded mole ratio x2	0.0	-1.0	1.0	1.0	-1.0
Coded flow rate x3	0.0	-1.0	1.0	-1.0	1.0
% hydrocarbon conversion	2.749	4.659	4.321	1.461	3.352
% hydrocarbon yield	47.289	59.628	67.285	33.466	37.925
% acid yields	21.455	25.628	28.796	20.885	25.742

Table 20. Continued

	30	31	32	33	34
Temperature °C	420.0	420.0	420.0	420.0	420.0
Mole ratio butane to acid	5.0	5.0	5.0	7.0	5.0
Input flow rate 2 moles/min.	0.834	0.834	0.433	0.834	1.235
Coded temp. x1	0.0	0.0	0.0	0.0	0.0
Coded mole ratio x2	0.0	0.0	0.0	1.633	0.0
Coded flow rate x3	0.0	0.0	-1.633	0.0	1.633
% hydrocarbon conversion	1.971	2.4301	2.345	2.858	4.706
% hydrocarbon yield	56.264	41.297	53.012	64.89	61.073
% acid yields	21.954	26.754	34.406	31.53	34.783

Table 20. Continued

	35	36	37	38	39
Temperature °C	420.0	455.0	385.0	420.0	420.0
Mole ratio butane to acid	3.0	5.0	5.0	5.0	5.0
Input flow rate 2 moles/min.	0.834	0.834	0.834	0.834	0.834
Coded temp. x1	0.0	-1.633	-1.633	0.0	0.0
Coded mole ratio x2	-1.633	0.0	0.0	0.0	0.0
Coded flow rate x3	0.0	0.0	0.0	0.0	0.0
% hydrocarbon conversion	5.254	2.128	4.571	2.657	2.512
% hydrocarbon yield	54.889	33.840	60.405	54.712	50.722
% acid yields	22.888	22.654	24.215	21.919	24.154

Table 21. Regression coefficients for yields, conversions, and nitroparaffin distributions from runs 20 to 39

	Hydrocarbon Conversion	Hydrocarbon Yield	Acid Yield	Nitromethane Distribution
b_0	2.6670**	51.7029**	23.333*	12.8647
b_1	0.8371**	-8.5747**	-0.9464	1.7749
b_2	0.5232**	2.0174	2.2967**	-0.2692
b_3	0.4388**	3.5520*	0.8991	0.1796
b_{11}	0.1264	-2.7823	-0.5575	0.5358
b_{22}	0.3913*	2.0046	0.8577	-0.6117
b_{33}	0.1924	0.9371	3.6269**	-0.3228
b_{12}	0.1388	1.2456	-0.5875	-0.4661
b_{13}	0.1742	0.5214	2.4832**	-0.6024
b_{23}	0.1452	5.0119**	0.6878	-1.284

**90 per cent significance level

*95 per cent significance level

Table 21. Continued

	Nitroethane Distribution	1-Nitropropane Distribution	2-Nitrobutane Distribution	1-Nitrobutane Distribution
b_0	23.6224**	10.6330**	29.1084**	23.7740**
b_1	2.0869*	1.5132*	-9.9602*	4.6221*
b_2	-1.2521*	-0.1793	1.2975	0.3413
b_3	0.5716	-0.2316	0.4313	-0.9129
b_{11}	-0.04241	-0.2722*	-0.1741	-0.05776
b_{22}	-1.4847*	0.1272	0.2674	1.6739*
b_{33}	0.3044	-0.3948*	0.4841	-0.08119
b_{12}	-0.3240	0.3534*	-0.2586	0.8206
b_{13}	0.5175	-0.1279	0.3461	-0.1929
b_{23}	1.1700*	0.4911*	0.8804	-1.1351

Table 22. Nitroparaffin distribution for runs 20 to 39
obtained by on-line analysis, mole per cent

	20	21	22	23	24
NM	10.846	10.714	13.141	11.444	14.145
NE	17.316	19.415	25.607	23.393	24.444
2-NP	0.742	Trace	Trace	Trace	Trace
1-NP	8.224	8.963	12.963	12.209	10.239
2-NB	38.822	39.281	20.004	23.333	33.081
1-NB	24.051	21.627	28.335	29.627	18.091

Table 22. Continued

	25	26	27	28	29
NM	9.672	9.263	11.840	17.539	16.862
NE	22.092	24.004	21.016	21.232	26.697
2-NP	Trace	Trace	Trace	Trace	Trace
1-NP	11.064	9.729	8.133	11.522	10.336
2-NB	30.647	36.490	39.469	15.636	18.514
1-NB	26.524	20.759	19.540	34.071	27.593

Table 22. Continued

	30	31	32	33	34
NM	14.543	12.953	10.932	9.257	12.355
NE	24.672	23.594	22.921	18.557	26.142
2-NP	Trace	Trace	Trace	Trace	Trace
1-NP	10.137	10.946	9.449	10.566	9.234
2-NB	26.162	24.776	32.705	35.322	30.320
1-NB	24.489	27.730	23.994	26.297	21.947

Table 22. Continued

	35	36	37	38	39
NM	12.489	16.182	11.685	12.926	13.189
NE	20.963	27.479	19.734	23.711	23.157
2-NP	Trace	Trace	Trace	Trace	Trace
1-NP	10.901	12.196	7.141	10.617	10.954
2-NB	26.547	12.541	46.973	29.626	29.617
1-NB	29.006	31.600	14.466	23.121	23.083

APPENDIX B

Table 23. Explanation of program to compute economic values including profit as a function of temperature, mole ratio and reactant flow rate

NOMENCLATURE

PROFIT (I,J):	Per cent return on investment after taxes
SELLPR (I,J):	Product selling price, cents/lb.
ACCCOST (I,J):	Cost of nitric acid per lb. product produced, cents/lb.
C4CCOST (I,J):	Cost of butane per lb. product produced, cents/lb.
RCCOST (I,J):	Cost of recycle stream per lb. product produced, cents/lb.
MOLPNP (I):	Mole per cent of the i^{th} nitroparaffin in the nitroparaffin distribution
HCYIEL:	Hydrocarbon yield
HCCONV:	Hydrocarbon conversion
ACYIEL:	Acid yield
AVMVT:	Average molecular weight of the nitroparaffin product
WTFNM:	Weight fraction nitromethane in the nitroparaffin distribution
WTFNE:	Weight fraction nitroethane in the nitroparaffin distribution
WTFNP:	Weight fraction 1-nitropropane in the nitroparaffin distribution

Table 23. Continued

NOMENCLATURE

WTF2NB: Weight fraction 2-nitrobutane in the nitro-
paraffin distribution

WTF1NB: Weight fraction 1-nitrobutane in the nitro-
paraffin distribution

Other terms are used in the program in a built in regression analysis and analysis of variance.

INPUT

Coded flow rate in Format (F5.2)

OUTPUT (19 x 19 matrix over temperature and mole ratio range)

REGRESSION COEFFICIENTS

ANALYSIS OF VARIANCE

SELLPR (I,J)

ACCCOST (I,J)

CH₄COST (I,J)

RCCOST (I,J)

PROFIT (I,J)

All outputs are on output paper, PROFIT (I,J) is also output on card deck. The output rows are at various mole fractions, the columns at various temperatures.

Figure 19. Fortran IV program to compute economic values including profit as a function of temperature, mole ratio and reactant flow rate

```

/JOE      US906 HANK      1
C      RETURN ON INVESTMENT FOR A 15M LB PER YEAR NITROPARAFFIN PLANT
C      USING      COST DATA AT CENTER FLOW RATE
C
1  FORMAT (F5.2)
   REAL MOLPNP(5)
   DIMENSION PROFIT(19,19),SELLPR(19,19),ACCCOST(19,19),C4COST(19,19),
   INCCOST(19,19),FIXINV(19,19)
   READ (1,1)X3
   X1=10.2 - 2.0
   X2=10.2 - 2.0
   I = 1
   J = 1
   L = 1
   JOB = 19
C      COMPUTE NP OISTN AND YIELDS AND CONVERSIONS OF THE
C      ACIO AND THE BUTANE
3  DO 100 I=1,19
   2  MOLPNP(1) = 12.865 + (1.775 * X1) - (1.284 * X2 + X3)
   MOLPNP(2) = 23.622 + (2.087 * X1) - (1.252 * X2) -
   I(1.485 * X2 + X2) + (1.170 * X2 + X3)
   MOLPNP(3) = 10.633 + (1.513 * X1) - (0.272 * X1 + X1) -
   I(0.395 * X3 + X3) + (0.401 * X2 + X3)
   MOLPNP(4) = (-9.96 * X1) + (1.298 * X2) + 29.108
   MOLPNP(5) = 100.0 - (MOLPNP(1) * MOLPNP(2) + MOLPNP(3) + MOLPNP(4))
   HCCONV = 2.667 - (0.837 * X1) - (0.823 * X2) + (0.439 * X3) +
   I(0.391 * X2 + X2)
   HCYLEL = 51.702 - (8.575 * X1) + (3.552 * X3) - (2.782 * X2 * X2) +
   I(5.012 * X2 + X3)
   ACYLEL = 23.333 - (0.946 * X1) + (2.297 * X2) + (3.626 * X3 + X3) +
   I(2.483 * X1 + X3)
C      COMPUTE WEIGHT FRACTION AND AVE MOL WT AND CARBON PER MOL
   FNM = (0.61 * MOLPNP(1))
   FNE = (0.75 * MOLPNP(2))
   FNP = (0.89 * MOLPNP(3))
   F2NB = (1.03 * MOLPNP(4))
   F1NB = (1.03 * MOLPNP(5))
   AVHWT = FNM + FNE + FNP + F2NB + F1NB
   WTFNM = (FNM/AVHWT)
   WTFNE = (FNE/AVHWT)
   WTFNP = (FNP/AVHWT)
   WTF2NB = (F2NB/AVHWT)
   WTF1NB = (F1NB/AVHWT)
   CPMOL = (MOLPNP(1)/100.0) + ((MOLPNP(2)/100.0) + 2.0) +
   I((MOLPNP(3)/100.0) + 5.0) + ((MOLPNP(4) + MOLPNP(5))/100.0) + 4.0
C      COMPUTE PRODUCT SELLING PRICE
   SELLPR(I,J) = (31.0 * WTFNM) + (29.0 * WTFNE) + (18.0 * WTF2NB) +
   I(27.0 * WTFNP + WTF1NB)
C      COMPUTE ACIO COST, BUTANE COST AND RECYCLE COST
   ACCOST(I,J) = (8820.0 / (ACYLEL * AVHWT))
   C4COST(I,J) = (2430.0 * CPMOL) / (HCYLEL * AVHWT)
   THEMR = (1.224 * X2) + 5.0
   RCCOST(I,J) = 0.1245 * (THEMR + 100.0 / ACYLEL) - 1.0 - (HCCONV / HCYLEL)
58  FORMAT (1H,7F10.4)
   WRITE(3,58) CPMOL,HCYLEL,AVHWT,MOLPNP(1),MOLPNP(2),MOLPNP(3)
C      COMPUTE FIXED INVESTMENT IN MILLIONS OF DOLLARS
   FIXINV(I,J) = 5.704 * (0.1 * (THEMR - 2.0) + (0.04))

   WRITE (3,54)ALACK      TOTAL)
57  FORMAT (16H
   WRITE (3,57)
   WRITE (3,54)TOTAL
   I=1
   J=1
   JOB=7
126  WRITE(3,58)(SELLPR(I,J),J=1,19,3)
125  CONTINUE
   I=I+3
   JOB=JOB+1
   IF (JOB)127,127,126
127  JOB=7
   I=1
130  WRITE(3,58)(ACCCOST(I,J),J=1,19,3)
128  CONTINUE
   I=I+3
   JOB=JOB+1
   IF (JOB)129,129,130
129  JOB=7
   I=1
132  WRITE(3,58)(C4COST(I,J),J=1,19,3)
131  CONTINUE
   I=I+3
   JOB=JOB+1
   IF (JOB)133,133,132
133  JOB=7
   I=1
135  WRITE(3,58)(RCCOST(I,J),J=1,19,3)
134  CONTINUE
   I=I+3
   JOB=JOB+1
   IF (JOB)136,136,135
136  JOB=19
   I=1
59  FORMAT (1H,7F10.4)
141  DO 139 J=1,19
   WRITE(12,59)PROFIT(I,J)
139  CONTINUE
   WRITE(3,59)(PROFIT(I,J),J=1,19,3)
   I=I+1
   JOB=JOB+1
   IF (JOB)140,140,141
140  END
C      COMPUTE RETURN
   COSTTO = ACCOST(I,J) + C4COST(I,J) + RCCOST(I,J)
   CON1 = 0.740 / FIXINV(I,J)
   CON2 = 1.265 * FIXINV(I,J)
   PROFIT(I,J) = CON1 * (SELLPR(I,J) - COSTTO - 2.28 - CON2)
   X2 = X2 + 0.2
100  CONTINUE
   J = J + 1
   JOB = JOB - 1
   X1 = X1 + 0.2
   X2 = (0.2 - 2.0)
   IF (JOB)4,4,3
4  CONTINUE
C      COMPUTE LEAST SQUARES EQUATION
   Y1 = PROFIT(5,5)
   Y2 = PROFIT(5,15)
   Y3 = PROFIT(15,5)
   Y4 = PROFIT(15,15)
   Y5 = PROFIT(10,3)
   Y6 = PROFIT(10,17)
   Y7 = PROFIT(3,10)
   Y8 = PROFIT(3,17)
   Y9 = PROFIT(10,10)
   SX1 = Y2 - Y1 - Y3 + Y4 - (1.414 * Y5) + (1.414 * Y6)
   SX2 = Y3 + Y4 - Y1 - Y2 + (1.414 * Y6) - (1.414 * Y7)
   SX11 = Y1 + Y2 + Y3 + Y4 + (Y5 + Y6) + 2.0
   SX22 = Y1 + Y2 + Y3 + Y4 + (Y7 + Y8) + 2.0
   SX12 = Y1 - Y2 - Y3 + Y4
   GSUM = Y1 + Y2 + Y3 + Y4 + Y5 + Y6 + Y7 + Y8 + Y9
   B0 = GSUM - 0.5 * (SX11 + SX22)
   B1 = 0.125 * (SX1)
   B2 = 0.125 * (SX2)
   B11 = 0.2187 * (SX22) + 0.3437 * (SX11) - 0.5 * (GSUM)
   B22 = 0.2187 * (SX11) + 0.3437 * (SX22) - 0.5 * (GSUM)
   B12 = 0.25 * (SX12)
C      COMPUTE SUM OF SQUARES
   TOTAL = (Y1 - Y1) + (Y2 - Y2) + (Y3 - Y3) + (Y4 - Y4) + (Y5 - Y5) + (Y6 - Y6) +
   I(Y7 - Y7) + (Y8 - Y8) + (Y9 - Y9) - ((GSUM - GSUM) / 9.0)
   FIRST = (B1 * SX1) + (B2 * SX2)
   SECOND = (B0 - GSUM) + (B11 * SX11) + (B22 * SX22) + (B12 * SX12) -
   I((GSUM - GSUM) / 9.0)
   ALACK = TOTAL - FIRST - SECOND
C      WRITE RESULTS
50  FORMAT (24H REGRESSION COEFFICIENTS)
51  FORMAT (1H0,F18.5)
   WRITE (3,50)
   WRITE (3,51) B0,B1,B2,B11,B22,B12
52  FORMAT (15H      ANOV)
53  FORMAT (16H      FIRST ORDER)
   WRITE (3,52)
   WRITE (3,53)
54  FORMAT (1H0,F25.5)
   WRITE (3,54)FIRST
55  FORMAT (17H      SECOND ORDER)
   WRITE (3,55)
   WRITE (3,54)SECCND
56  FORMAT (16H      LACK OF FIT)
   WRITE (3,56)

```