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BACKMIX MOLTEN SALT REACTOR.

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VAPOR PHASE NITRATION OF ETHANE IN A  
BACKMIX MOLTEN SALT REACTOR

by

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## TABLE OF CONTENTS

	Page
ABSTRACT	iv
INTRODUCTION	1
Motivation	1
Objectives	2
REVIEW OF LITERATURE	3
Nitration of Paraffin Hydrocarbons	3
Nitration of Ethane	5
Analytical Techniques	7
REACTION MECHANISM	10
Free Radical Reaction	10
Free Radical Nitration Mechanisms	11
Decomposition of Nitric Acid	12
Alkyl Radical Formation	13
Nitroparaffin Formation	14
Simplified Reaction Scheme	15
EXPERIMENTAL	18
Description of Pilot Plant	18
Analytical Method	37
Design of Experiments	44
Operation of Pilot Plant	50
Results	54
DISCUSSION OF RESULTS	58
Reactor Operation	58
On-Line Analysis	60

## TABLE OF CONTENTS, CONTINUED

	Page
Product Distribution	61
Yields and Conversions	62
Residence Time	70
Temperature Effects	71
Mole Ratio Effects	81
Discussion of Mechanism	81
CONCLUSIONS	88
RECOMMENDATIONS	89
LITERATURE CITED	90
ACKNOWLEDGEMENTS	96
APPENDIX	97

## ABSTRACT

Nitration of ethane with nitric acid in the vapor phase has been investigated in a molten salt reactor in which the reactants are ejected directly into the molten salt. Molten salt temperature was varied from 400° to 500° and mole ratio of hydrocarbon to nitric acid was varied from 3:1 to 17:1.

Gas chromatography techniques were developed which provide on-line quantitative analysis of the reaction products. Complete product distributions were obtained for all experiments. The oxidation products, including formaldehyde, acetaldehyde, methanol, ethanol, carbon monoxide and carbon dioxide, were present in greater quantity than the nitro-paraffins formed.

Yields based on nitric acid ranged up to 76.08% while conversions based on nitric acid were obtained up to 8.37%. Maximum hydrocarbon yield and conversion were 68.54% and 1.18% respectively.

A proposed free radical reaction mechanism including both nitration and oxidation reactions is discussed with reference to product distribution.

## INTRODUCTION

Nitroparaffins have attained important commercial significance in recent years. There are many commercial uses of nitroparaffins and promises of a great number of future applications. Over 2,000 derivatives of nitroparaffins had been produced in the laboratories of the Commercial Solvents Corporation alone by 1955 (19). Used as solvents and components of rocket fuels in nitroparaffin form, their derivatives include amino alcohols, nitroalcohols, nitroolefins, amines, oximes and hydroxylammonium salts. And yet the uses for nitroparaffin derivatives have been only partially explored emphasizing the long range prospects for continued growth and increased importance.

## Motivation

Nitration of the paraffin hydrocarbons has been carried out in both the liquid and vapor phases. Where low molecular weight paraffins are concerned it has been found that the vapor phase reaction is the most desirable (49). Vapor phase nitration of the low molecular weight paraffins has been investigated for a number of combinations of the possible hydrocarbons, nitrating agents and reactor designs. The method chosen for this investigation was selected for the following reasons: (a) the work is a continuation of that initiated by Adams (1) and continued by Fear and Burnet (22) and Hankinson (25), (b) the factors which led these investigators to choose

this system are still valid, (c) ethane has not previously been nitrated by this method and (d) the improved analysis provides complete product distributions which have never been reported.

At the present time a large demand exists for nitroethane for use as a chemical intermediate and a solvent. Nitroethane is a principle product of the commercial nitration of propane by the Commercial Solvents Corporation. Thus, the nitration of ethane takes on economic significance as the cost of the raw materials decreases, and at the same time is of theoretical interest in determining a suitable reaction mechanism for the vapor phase nitration of alkanes of higher carbon number.

#### Objectives

The specific objectives of this investigation were:

(a) to adapt an on-line gas chromatography system to analyze the products of the nitration of ethane, (b) to determine the optimum operating conditions for the vapor phase nitration of ethane in a backmix, molten salt reactor, (c) to determine the complete product distribution obtained in this reaction and (d) to obtain information which would shed light on the reaction mechanism for nitration of paraffin hydrocarbons in the vapor phase.

## REVIEW OF LITERATURE

Nitration of saturated hydrocarbons has been conducted in both the liquid phase and the gas phase. Liquid phase nitration reactions are comparatively slow with reaction times ranging from a few seconds to several days (54). Vapor phase nitration of paraffins has been accomplished using both nitric acid and nitrogen dioxide as nitrating agents, but the reaction rates and yields are both lower when nitrogen dioxide is used (33). The most modern method of nitrating lower molecular weight paraffin hydrocarbons is considered to be nitration with nitric acid in the vapor phase (49).

Complete summaries of the literature concerning vapor phase nitration of paraffin hydrocarbons have been assembled by Adams (1), Fear (21) and Albright (3). Therefore this review will cover in detail only recent work and that specifically related to ethane nitration.

## Nitration of Paraffin Hydrocarbons

Nitration of the lower molecular weight paraffins in the vapor phase has been carried out primarily in tubular flow reactors (7, 23, 30, 34, 35, 49, 58) and fused salt bed reactors (1, 18, 25, 36). Variables which have been considered to have an effect on product distributions include temperature, mole ratio of reactants, reaction time and pressure.

Vapor phase nitration of paraffins has been successfully

carried out at temperatures from 250 to 600°C, but 375 to 450°C is generally considered the optimal range (55). It has been shown that as the temperature is increased the formation of higher nitroparaffins is decreased and the formation of the nitroparaffins of lower molecular weight is increased (33, 46). It is thought that to insure good yields of nitroparaffins and to avoid the risk of explosion it is important to keep the mole ratio of hydrocarbon to acid at least 2:1 (55). Very short reaction times are required in vapor phase nitration of hydrocarbons and for pilot scale reactions of tubular or salt bath type retention times are limited to a maximum of a few seconds. The rate of reaction is increased with increasing pressure but the effects of pressure on yield of nitroparaffins is considered minimal (34). Thus, nitration in the vapor phase is usually conducted at temperatures between 375 and 450°C, mole ratios of hydrocarbon to acid between three and ten, reaction times between 0.1 and 1.0 sec. and pressures between 1 and 10 atmospheres.

A variety of products are formed in the vapor phase nitration of saturated hydrocarbons. Since pyrolytic temperatures are often exceeded carbon skeletal rearrangements can occur resulting in formation of lower molecular weight substitution products. These temperatures may also result in the considerable decomposition of the nitrated and oxidized compounds (33). Thus in addition to substitution products all manner of decomposition products may be expected including

olefins, aldehydes, ketones, fixed gases, cyanogens and nitrates. Simple alkanes nitrated under vapor phase conditions, however, do not generally yield products with more than one nitro group (33). Total yields of nitroparaffins do not vary greatly over wide temperature ranges but there is an optimum temperature for producing a maximum of a given nitroparaffin at a given pressure (33).

Nitration of the lower paraffin hydrocarbons has been investigated extensively by several researchers. The most extensively investigated nitration is that of propane (3, 4, 5, 8, 10, 12, 13, 16, 18, 20, 27, 28, 36, 46, 60). Although some difficulty has been experienced in nitrating methane (2, 30), several successful results have been reported (15, 27, 34, 42, 43, 48, 49, 50, 52, 55, 56, 57, 58). The first vapor phase nitration work in this country was done with butane (30) and this work has been extended since that time (1, 2, 9, 21, 22, 25, 26, 31, 33, 44, 45). A relatively small amount of work has been reported on nitrating ethane (23, 29, 30, 35).

#### Nitration of Ethane

Nitration of ethane with nitric acid was first carried out in a glass reactor immersed in a salt bath at  $420^{\circ}\text{C}$  by Hass, Hodge, and Vanderbilt (30) in 1936. The gaseous hydrocarbon was passed through hot concentrated nitric acid, heated to  $108^{\circ}\text{C}$ , to pick up nitric acid vapors. The mixed vapors in a mole ratio of about 2:1 of hydrocarbon to acid were reacted

and collected by a condenser immersed in an ice bath. The product separated into two layers, the lower layer containing dilute nitric acid and the upper layer the nitroparaffins. Excess nitric acid was determined by titration of the aqueous layer and the nitroparaffins were separated by distillation. Nitroethane and nitromethane were obtained in a ratio of between 4 and 9 to 1 and a 9% conversion per pass was found. Nitromethane was identified by its boiling point and nitroethane by its physical constants and starting materials.

Hibshman, Pierson, and Hass (35) followed up this work using a stainless steel reactor immersed in a salt bath. Ethane was preheated to 500°C and contacted with nitric acid in a mixing tee. The products were condensed and the lower layer containing the nitroparaffins was distilled in a packed column. In this investigation a retention time of 0.33 sec. gave maximum conversion of 33% at 455°C, while for a retention time of 0.23 sec. a maximum conversion of 32% was obtained at 475°C. Dilute nitric acid (50%) containing 3 gm./l. of dissolved  $\text{KNO}_3$  was used and conversion of acid appeared to increase with coating of the reactor by the salt. Conversion increased with mole ratio up to hydrocarbon to acid ratio of 10:1. Nitroethane to nitromethane ratio found in the product was about 2.5:1. A second reactor was designed to give a larger range of temperature and retention time variation but optimum operating conditions were not reported. The researchers concluded that nitration of ethane was a suitable

source of nitromethane only if a large demand for nitroethane existed.

The most recent work found on vapor phase nitration of ethane was carried out by Geiseler and Reinhardt (23) in a glass tubular reactor. An ethane preheater was immersed in the molten salt bath. The 65% nitric acid used was fed through a hair capillary tube to the wall of a hot evaporation coil where it evaporated as a thin film. Ethane at reaction temperature was mixed with the nitric acid vapor at 280°C. Considerable reaction was observed to occur at the mixing place when high temperature acid vapors were fed. It was visible as a bluish luminescent light. The rates of nitration of ethane were measured and found to be 1st order with respect to  $\text{HNO}_3$ . The rate determining step was concluded to be the decomposition of  $\text{HNO}_3$  and the thermal decomposition of the nitroparaffins was found to be unimportant. A maximum conversion of 31% was obtained at 445°C for a retention time of 0.5 sec.

#### Analytical Techniques

The early investigations of vapor phase nitration were hampered by lack of a satisfactory method of analyzing the product composition. In several cases only the nitroparaffin portion of the product was analyzed (3) and even then it was assumed that the organic phase contained only nitroparaffins. This has since been disproven by Adams (1) and Fear and

Burnet (22) who found significant quantities of oxygenated materials by the use of gas-liquid chromatography analysis.

The analytical technique used in early investigations (30, 35) relied on distillation of the organic phase and construction of a rectification curve from which the nitro-paraffins were quantitatively determined by their boiling points. Unreacted nitric acid was quantitatively determined by titration of the aqueous layer.

In a more recent attempt to analyze the products of ethane nitration (23), the liquid product was neutralized with bicarbonate, steam distilled, and the nitroparaffins separated quantitatively from the distillate by saturation with sodium chloride. The gaseous product was scrubbed with sodium bicarbonate solution to combine the nitric acid and nitrogen dioxide. A quantitative portion of the gas was analyzed for nitric oxide. A portion of the scrubber solution was vacuum distilled to remove the nitroparaffins and formaldehyde and the residue tested for total nitrogen and titrated for nitrite. The difference gave the unreacted nitric acid.

The problems involved in chemical analysis of a complicated spectrum of nitration products are apparent. As modern analytical techniques became more readily available, a method of analyzing the products by gas-liquid chromatography was sought. The first significant quantitative method of determining product distribution was reported by Bethea and Adams (14). The entire cooled product was separated into four parts

and each fraction analyzed by suitable gas chromatography columns. This analytical technique was refined by Fear (21) and further by Ives (37) who was able to overcome the problem of large quantities of water.

Following the investigation of Ives, an on-line analysis of the products of butane nitration was developed by Johnnie (38) and Hankinson (25). This method utilized four columns in series with provisions for bypassing any given column after the initial separation on the first column. Quantitative separation of nearly all the products of butane nitration in an on-line sample was achieved in about one hour. Separation of nitric oxide and nitrogen dioxide, however, was not achieved.

Nitric oxide-nitrogen dioxide separation by gas chromatography has proved to be a significant problem. A technique of freezing the nitrogen dioxide out on glass beads has been reported by Trowell (59) and a chromatographic separation at 22°C has been reported (1, 14). Investigations of the later method by this author, however, failed reproduce this result.

Gas chromatography analytical methods have not previously been applied to ethane nitration. Complete product distributions for this system are not available in the literature.

## REACTION MECHANISM

Comparatively little is known about the reaction mechanism by which vapor phase nitration of saturated hydrocarbons takes place. At least two proposed mechanisms have been considered acceptable and a few general conclusions have been confirmed experimentally.

## Free Radical Reaction

Experimental evidence as well as intuition supports the theory that the reaction proceeds through a series of free radical rather than ionic reactions. The reasons for this are the following: (a) Addition of a small amount of oxygen (9, 10, 13, 23) or a halogen (11, 12, 13) to the reactants increases the number of free alkyl radicals and results in increased conversions to nitroparaffins. (b) Increasing the surface to volume ratio of the reactor results in smaller conversions (9). Excessive addition of oxygen (9, 10, 13) or halogen (11, 12, 13) and addition of nitric oxide (27, 51) also reduce conversion to nitroparaffins. All of these factors tend to reduce free alkyl radical concentration. (c) The use of reactors with surfaces of metallic oxides and salts (4), which would catalyze an ionic reaction, often decrease but do not increase yields over those which are obtained in glass reactor vessels. (d) Tetraethyl lead, which produces free alkyl radicals when heated, yields nitroparaffins on vapor phase nitration with nitric acid (32, 46). (e) The fact

that the reaction occurs in the gas phase is good evidence that it is a free radical reaction.

Another theory is based on the assumption that when combining with nitric acid, hydrocarbons form two types of intermediate complexes (56). The breakdown of the first gives alcohols and nitroparaffins of lower order than the original hydrocarbon while breakdown of the second yields water and nitroparaffins of the same order as the original hydrocarbon. However, the free radical chain reaction theory has the most support.

#### Free Radical Nitration Mechanisms

Two possible types of free radical reaction mechanisms have been suggested for the formation of nitroparaffins in vapor phase nitration with nitric acid. The first is a radical step mechanism and the second a short chain reaction mechanism.

The radical step reaction mechanism proposed consists of the following reactions (7).



The decomposition of nitric acid to form nitrogen dioxide and hydroxyl radicals is shown in reaction [1]. Hydroxyl radicals

then extract a hydrogen atom from the paraffin hydrocarbon, indicated by reaction [2], to form alkyl radicals which combine with the nitrogen dioxide formed in reaction [1] to yield nitroparaffins by reaction [3]. There is some doubt that the rate of decomposition of nitric acid by reaction [1] is sufficient to supply the nitrogen dioxide required by reaction [3] to form nitroparaffins at the experimental rate observed (41). For this reason a short chain mechanism was suggested.

The short chain reaction mechanism proposed consists of the following reactions (4, 6, 46).



Here the decomposition of nitric acid to form nitrogen dioxide and hydroxyl radicals, reaction [1], is the initiation step. Reactions [2] and [4] propagate the chain and result in nitroparaffin formation. Reaction [4] can also be thought of as a chain termination step. Reaction [4] provides for incomplete decomposition of the nitric acid.

#### Decomposition of Nitric Acid

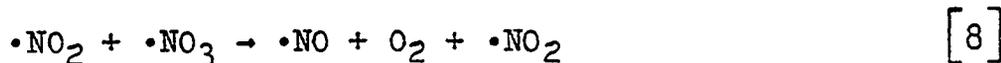
At one atmosphere and 400°C the primary decomposition reaction for  $\text{HNO}_3$  is a homogenous first order reaction (40).



The net rate of decomposition falls off as the reaction proceeds which indicates inhibition by the decomposition products. Inhibition by  $\text{NO}_2$  is further implied by the slower rate of decomposition in the presence of  $\text{NO}_2$  (41). It is suspected that the nitrogen dioxide and nitric acid compete for hydroxyl radicals (41), suggesting the formation of  $\text{NO}_3$ .



The  $\text{NO}_3$  radical decomposes rapidly and the relative significance of the reactions depends on the concentrations of  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_3$  and the reaction rates.



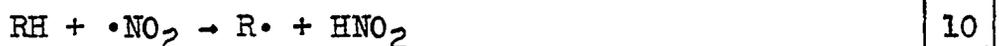
At room temperature reaction [7] is  $10^5$  times faster than reaction [8] (39), and at  $1000^\circ\text{K}$  it is two or three orders of magnitude faster (53).

#### Alkyl Radical Formation

Probably the most important source of alkyl radicals in nitration of paraffins is by reaction with hydroxyl radicals.



Since  $\text{NO}_2$  can also be used as the nitrating agent it has been suggested that free radicals may be formed by its reaction with the hydrocarbon forming nitrous acid.



Lower conversions and longer reaction times necessary when  $\text{NO}_2$  is used indicate that it is less important in forming alkyl radicals than is the hydroxyl radical from  $\text{HNO}_3$  decomposition.

#### Nitroparaffin Formation

It is assumed that the actual nitroparaffin formation is by combination of the alkyl and  $\text{NO}_2$  free radicals (7).



This assumption is adapted with ease to the proposal of alkyl nitrite formation since the  $\text{NO}_2$  radical is a resonance hybrid which can be represented by two forms.



If an alkyl radical reacts with  $\text{NO}_2$  in form A, a nitroparaffin is formed whereas if it reacts with form B, the product is an alkyl nitrite. Alkyl nitrites are unstable at elevated temperatures and would rapidly decompose at the temperatures under which nitration is accomplished. The products are an alkoxy radical and nitric oxide.



Reactions involving the alkoxy radical are then assumed to lead to the oxidation products observed in nitration. The primary step in decomposition of the alkyl nitrite at high temperatures is the breaking of the oxygen nitrogen bond. Rearrangement of RONO to RNO<sub>2</sub> is not believed to occur.

It has been suggested that nitroparaffin formation can also occur by the short chain reaction mechanism (4, 6, 46).



If this is the case the rate of nitroparaffin formation can be faster than would be allowed by thermal decomposition of nitric acid. There is reason to expect that this attack of an alkyl radical on a nitric acid molecule could also result in the removal of the hydrogen to form the NO<sub>3</sub> radical and an alkane.

#### Simplified Reaction Scheme

Derivation of the experimentally determined reaction rate on a theoretical basis can only be done with great difficulty when all the partial reactions are considered. The mathematical complexities of the system of differential equations dictate that a practical solution is possible only if one uses a simplified fundamental reaction mechanism that is

characteristic of the actual mechanism. This simplified scheme must be selected on the basis of thermodynamic and kinetic data from the wide range of reactions thought possible. A summary reaction scheme which contains the reactions thought to be important by various authors follows:

1.  $\text{HNO}_3 \rightarrow \cdot\text{OH} + \cdot\text{NO}_2$  (4,6,7,23,46,51)
2.  $\text{RH} + \cdot\text{OH} \rightarrow \text{R}\cdot + \text{H}_2\text{O}$  (4,6,7,23,46,51)
3.  $\text{R}\cdot + \cdot\text{NO}_2 \rightarrow \text{RNO}_2$  (7,23,51,55)
4.  $\text{R}\cdot + \text{HNO}_3 \rightarrow \text{RNO}_2 + \cdot\text{OH}$  (4,6,23,46)
5.  $\cdot\text{OH} + \text{HNO}_3 \rightarrow \cdot\text{NO}_3 + \text{H}_2\text{O}$  (51)
6.  $\text{R}\cdot + \cdot\text{NO}_2 \rightarrow \text{RONO}$  (7,23,24,51,55)
7.  $\text{RH} + \cdot\text{NO}_2 \rightarrow \text{R}\cdot + \text{HNO}_2$  (7,55)

The alkyl nitrite formed in reaction 6 and the  $\text{NO}_3$  formed in reaction 5 are assumed to lead to the decomposition products found in the product gas.

In formulating a reaction mechanism the following types of reactions must be considered:

1. Decomposition of nitric acid and decomposition products.
2. Alkyl radical formation by reaction between products of nitric acid decomposition and alkanes.
3. Nitroparaffin formation.

4. Alkyl nitrite formation and decomposition.
5. Decomposition of nitroalkanes.
6. Decomposition of aldehydes.
7. Decomposition of alcohols.
8. Decomposition of formyl, acetyl, and nitroso radicals.
9. Inhibiting effect of nitric oxide.
10. Competitive oxidation and decomposition reactions.
11. Radical combination reactions.

Considering these types of reactions and using the seven reactions previously stated as a basis, an analysis of the product distribution should enable one to determine the relative importance of each reaction step and the importance of the succeeding reactions of  $\text{RONO}$  and  $\text{NO}_3$  to form decomposition products. If kinetic data were not available it would be difficult to do more than check the validity of a proposed mechanism and make inferences about a few of the reactions.

## EXPERIMENTAL

Nitration in the vapor phase has been successful in tubular reactors immersed in a constant temperature bath and by mixing the reactants below the level of a molten salt bath and allowing them to bubble up through it. Ethane, however, has not previously been nitrated by the latter method. The reactor used in this investigation is of the second type. A gas chromatography analysis has been developed for the products of ethane nitration. Experiments have been statistically designed to gain the most information from a minimum number of runs. Pilot plant operation has been programmed to eliminate errors due to inconsistent experimental techniques.

## Description of Pilot Plant

The primary systems of the experimental apparatus are shown in the schematic block diagram of Figure 1. Liquid nitric acid and gaseous ethane are fed to the reactor which operates up to 500°C. The gaseous products are cooled and condensed and the liquid collected. Analysis of the product is accomplished by taking a small sample of the effluent and separating it into its components by gas chromatography.

The nitric acid feed system shown in Figure 2 provides excellent control of acid flow rate by use of a constant pressure acid egg. Pressure on the acid in the acid egg is provided by a helium cylinder with standard dual pressure gauge control valve. The flow of the 71% (wt) nitric acid is

Figure 1. Schematic block diagram of experimental apparatus

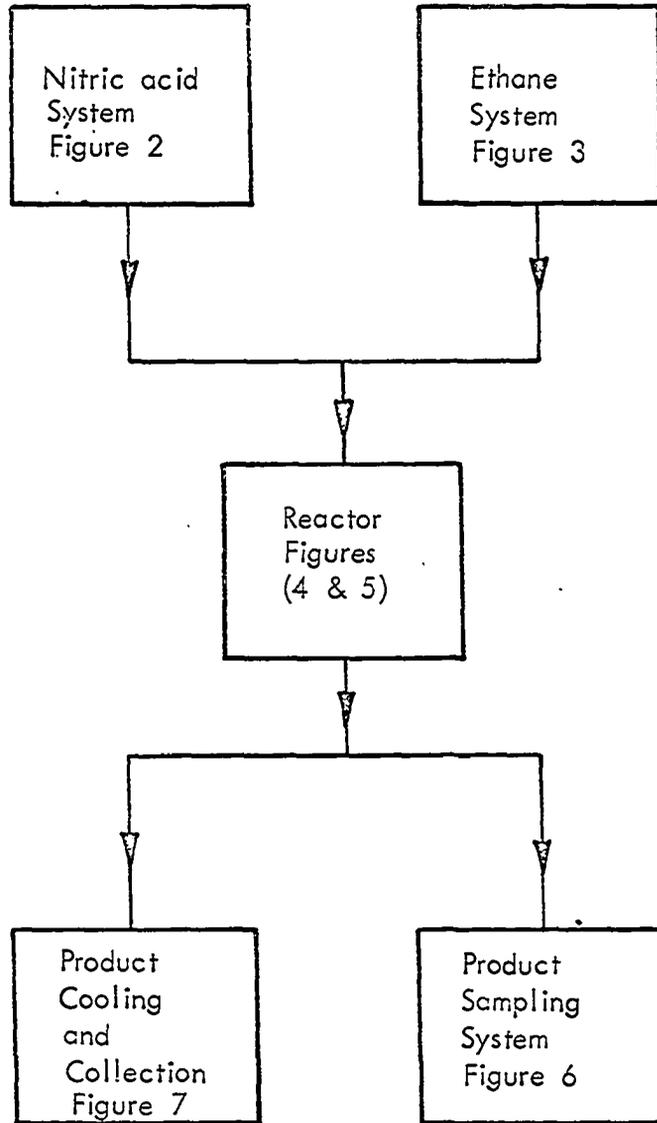
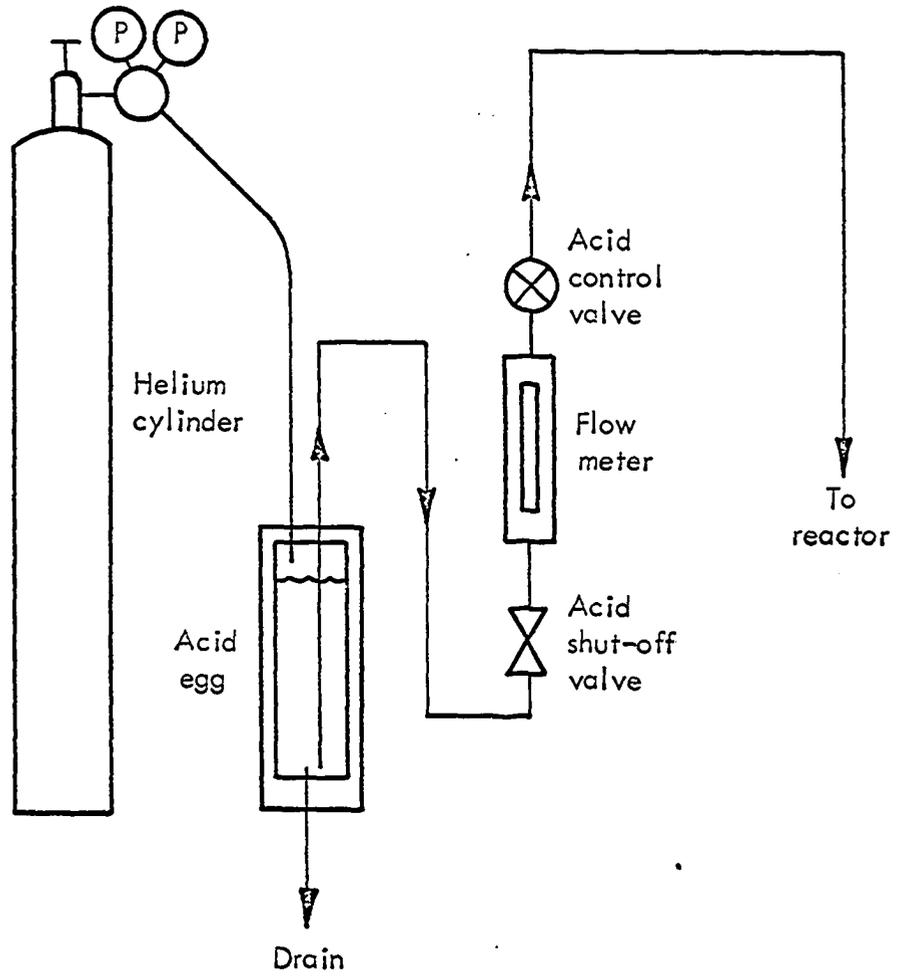


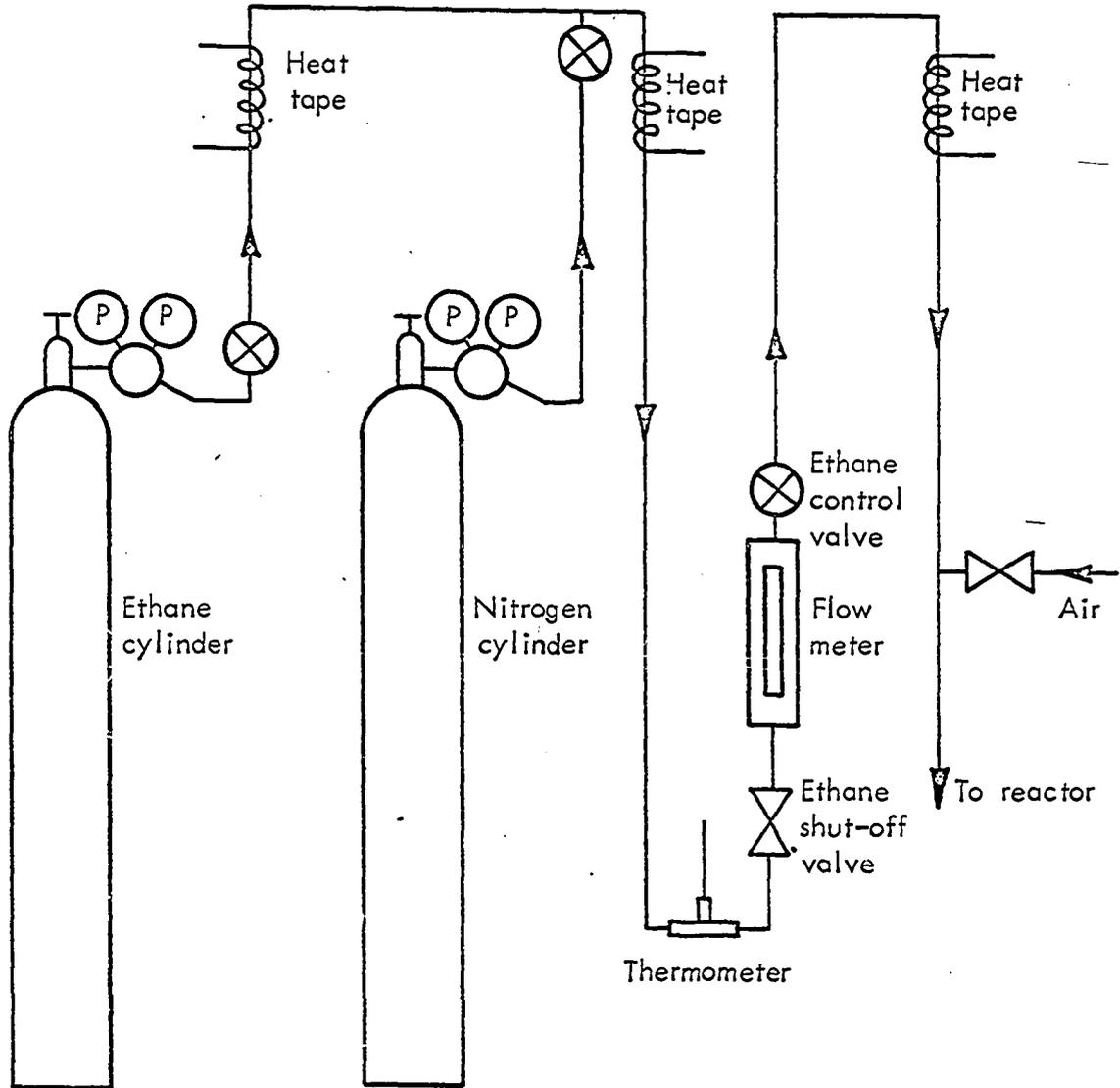
Figure 2. Nitric acid feed system



controlled by a needle valve and a flowmeter. The acid egg is constructed of 24 inches of 2.5 inch stainless steel pipe, 0.25 inches wall thickness, with stainless steel plates welded on both ends. Two ports on the top and the drain port at the bottom are sealed with 1/4 inch Swagelock fittings to 1/4 inch stainless steel tubing. The entire acid egg is enclosed in a plywood box. A Brooks rotometer (number R-2-15-A) containing glass and stainless steel floats is used to monitor the flow rate and a 1/8 inch Swagelock stainless steel needle valve with Teflon packing provides flow control. Acid can be fed accurately up to about 30 ml/min. The acid flows through 1/8 inch stainless steel tubing to the reactor.

The ethane feed system shown in Figure 3 allows ethane to be fed to the reactor at a constant rate from a cylinder of Phillips 99% pure ethane. Heat tapes installed around the feed lines keep the gas at a constant temperature. The 1/4 inch copper tubes are insulated with 1/2 inch fiberglass pipe insulation. A thermometer very near the flowmeter gives the temperature of the ethane in the line. A Brooks rotometer (number R-6L-500-G1) containing both glass and stainless steel floats, and a stainless steel needle valve provide careful control of the ethane to the reactor. Ethane can be fed up to 0.85 ft<sup>3</sup>/min. at 25°C. Referring to Figure 3, the nitrogen supply is used to flush out the lines and reactor following each run. Bubbling nitrogen through the reactor keeps the lines free of salt when reactants are not being fed. For

Figure 3. Ethane feed and nitrogen purge system



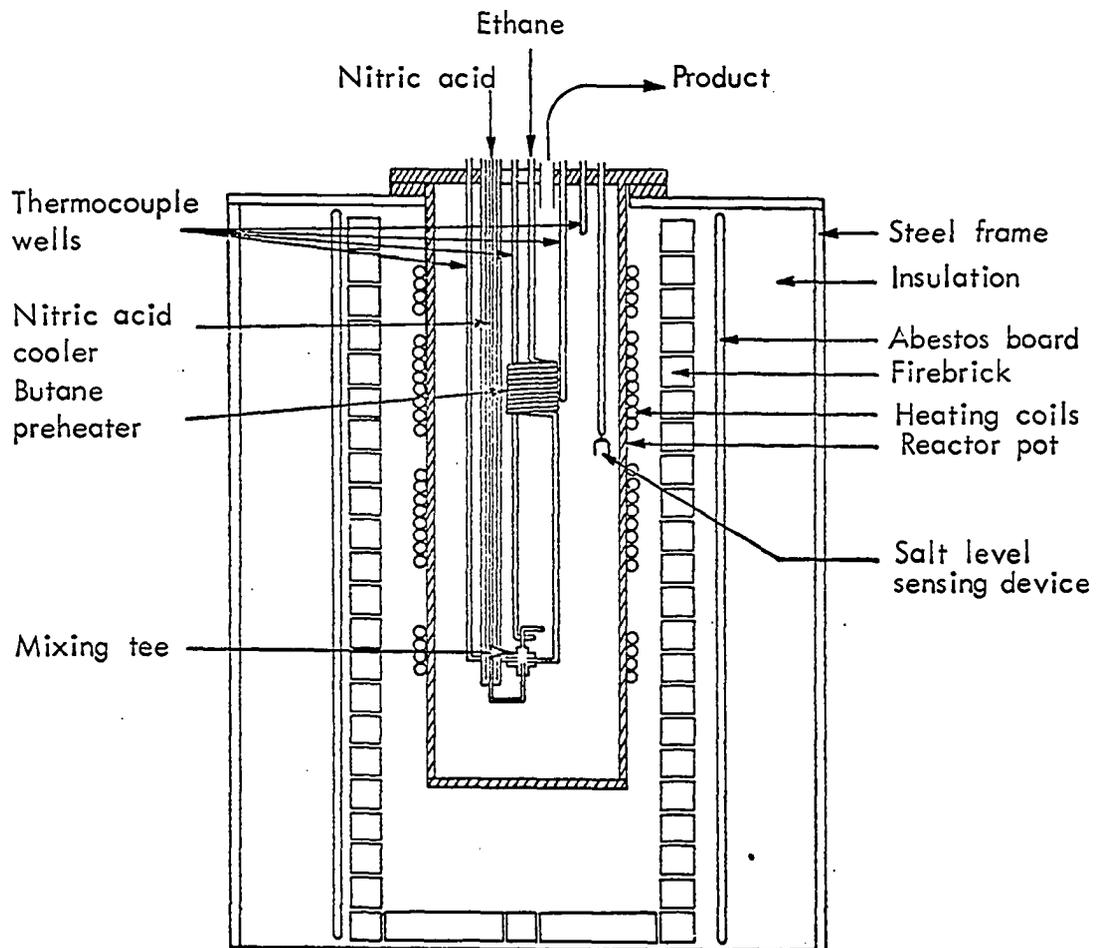
longer periods of time, air can be bubbled through the reactor to conserve nitrogen.

A two foot square and 3 foot high box of 1/4 inch asbestos board supported by a frame of one inch angle iron encloses the reactor shown in Figure 4. The box is lined with firebrick both on the sides and bottom. The reactor pot is constructed from 24 inches of 8 inch steel pipe, 3/8 inch wall, welded at the bottom to a 1/4 inch steel dish and at the top to a 1/2 inch steel flange. To the flange are welded six 5/8 inch bolts to secure the reactor head plate.

Four separate heating coils are wrapped around the reactor pot. The two middle heating coils are calrods controlled by 2000 watt powerstats and the top and bottom coils are ceramic insulated nichrome wire filaments controlled by 1000 watt powerstats. A Brown indicating pyrometer is connected to the bottom coil to provide temperature control while two of the other three coils are used to maintain the temperature. The fourth heater is used for auxiliary power if one of the others should fail. Twenty-two pounds of a eutectic mixture of sodium nitrate and potassium nitrate provide a salt depth of about 12 inches in the reactor pot when melted.

A 9 inch diameter steel plate, one inch thick, with six 5/8 inch bolt holes fitted to the bolts on the reactor pot flange and 8 ports in a circular arrangement within the radius of the reactor pot describes the reactor head plate. Six of the ports are 1/4 inch extension Swagelock fittings while the

Figure 4. Reactor



product exit and nitric acid entrance are  $3/4$  inch pipe unions. All fittings are welded to the reactor head plate. The acid entrance to the reactor is constructed of three concentric stainless steel tubes of  $1/8$  inch,  $3/8$  inch and  $5/8$  inch outside diameter extending to a depth of 20 inches into the reactor. Acid flows through the center  $1/8$  inch tube to the mixing tee and cool air circulates cocurrent to the acid in the smaller annulus, reverses direction at the depth of 20 inches and flows countercurrent to the acid in the outer annulus. Liquid nitric acid can thus be delivered to the mixing tee at a distance of 20 inches below the head plate. Ethane enters the reactor through a  $1/4$  inch steel tube and is heated to reaction temperature in a heating coil before being mixed with the liquid nitric acid at the mixing tee.

A  $1/4$  inch stainless steel Swagelock cross fitting serves as the mixing tee as shown in Figure 5. Liquid nitric acid and ethane are mixed and ejected downward into the molten salt through four  $1/32$  inch holes in a sealed length of  $1/4$  inch steel tubing. Thermocouples in the mixing tee and directly below the jet in the salt give the temperatures at these two positions. Two other thermocouples, one in the upper portion of the salt and one in the dead space above the salt, and a salt level sensing device are also installed through the reactor head plate.

The sampling system is shown in Figure 6. To sample the product flowing from the reactor during nitration, a vacuum

Figure 5. Cross section of mixing tee

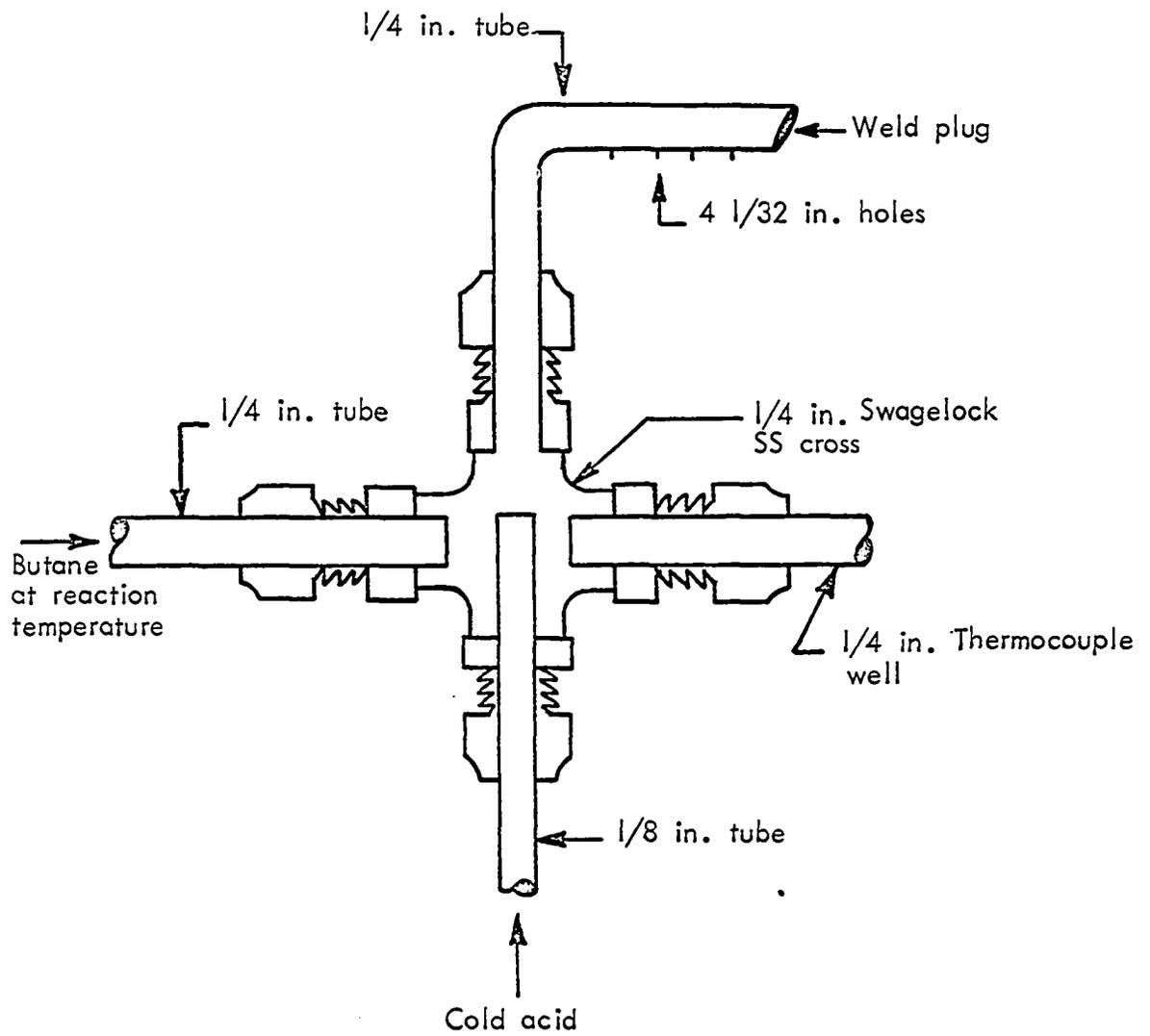
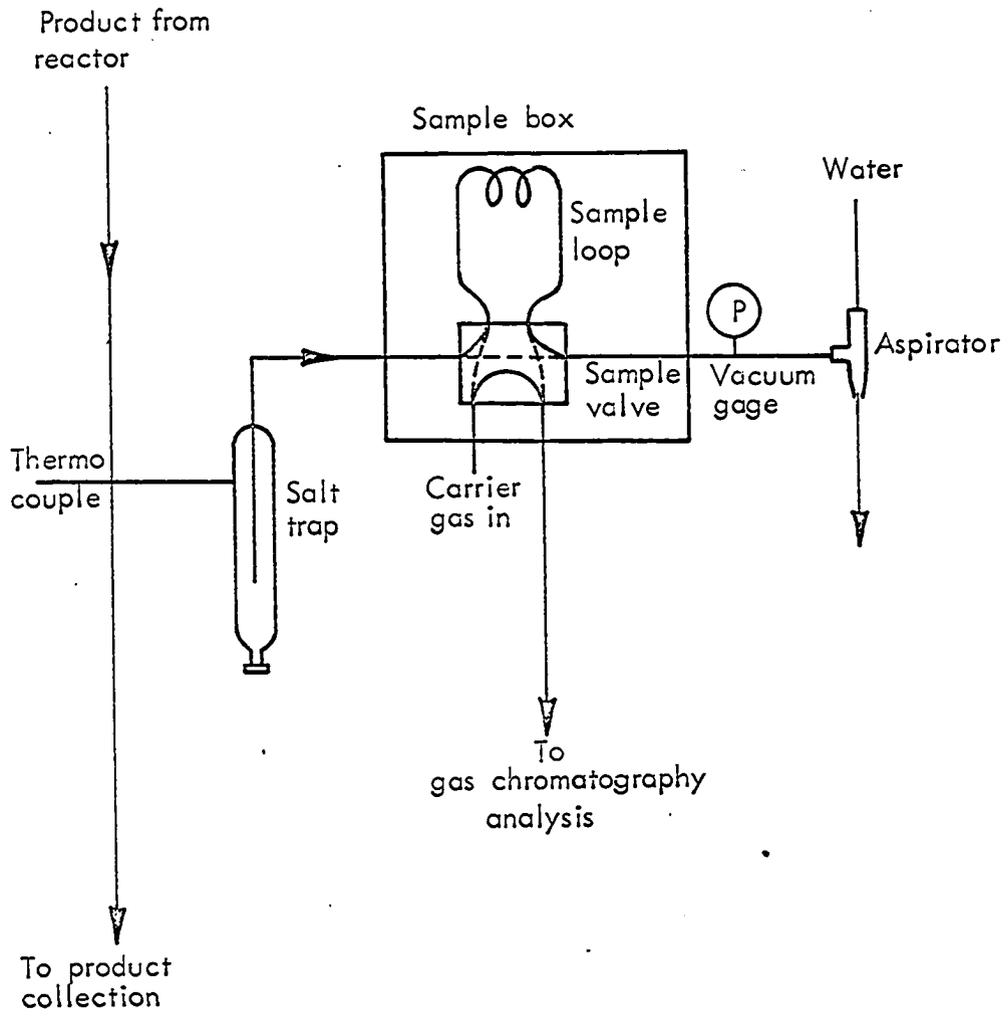


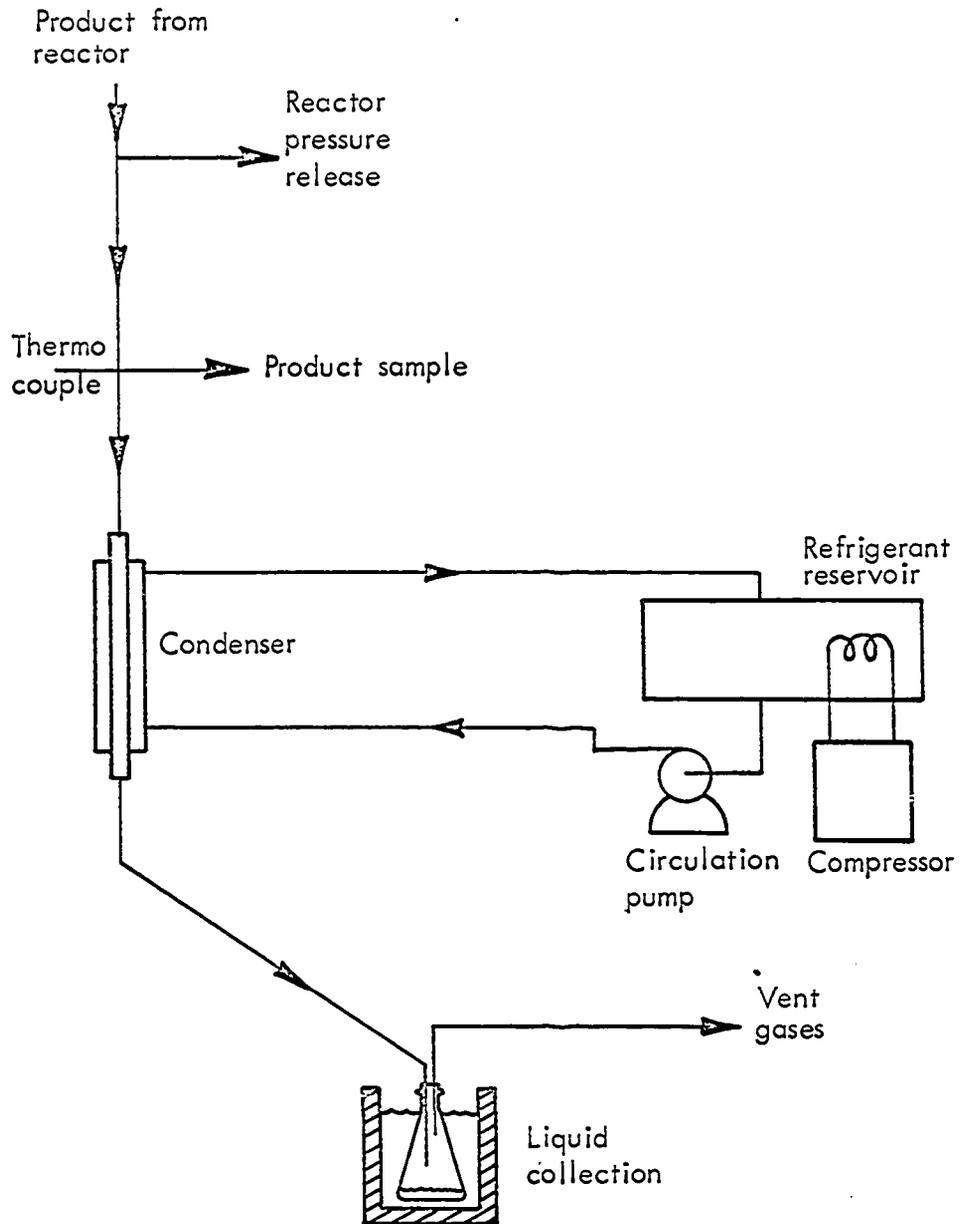
Figure 6. Sampling system



produced by an aspirator is applied to a line connected to the product exit stream. A stainless steel salt trap with a tangentially located entrance removes, by centrifugal force, any salt from the sample being drawn through it. This prevents salt from freezing in and clogging the sample valve. In the closed position a continuous stream of sample is drawn through an 8-port, single throw, stainless steel sampling valve and through a 3 cc. sample loop. With the valve in this position, helium carrier gas flows through the other side of the valve. When the air operated valve is switched, the carrier gas flows through the sample loop and the sample is transferred to the gas chromatography analytical system through a short length of 1/8 inch stainless steel tubing wrapped in insulation and heating tape. An insulated aluminum box heated by an inverted hot plate controlled by a 1000 watt powerstat encloses the sample valve and loop. This box is located on the top of the reactor and is easily maintained at 200°C to prevent condensation of any of the reaction products.

The majority of the product leaving the reactor is cooled in a countercurrent heat exchanger with a 50% ethylene glycol-water coolant as shown in Figure 7. A compressor, circulation pump and refrigerant reservoir supply the coolant at -15°C. Those portions of the product which are liquids at room temperature are collected in a flask and the gases are vented.

Figure 7. Product cooling and collection system



### Analytical Method

Gas chromatography analysis of the products of vapor phase nitration has previously been accomplished by collecting the product and separating it into three phases (gases, oil and water) for separation on suitable chromatography columns. On-line analysis of a sample has proved difficult because of the large spectrum of products ranging from fixed gases to the high boiling nitroparaffins. Work by Ives (37), Johnnie (38) and Hankinson (25) has resulted in an analytical technique for separating the components found in a single sample of the total product stream from butane nitration as it leaves the reactor. This technique has been adapted to the separation of the fifteen compounds found in the nitration of ethane.

#### Gas chromatography system

Four columns in series with bypasses for each and two thermal conductivity detectors connected to two chromatographs are required to separate the product. The first chromatograph, an F&M 500-A (F&M Scientific Corporation) equipped with a 0-5 mv strip chart recorder (Model K 1436(58)-(UB)-II-III-IV, Minneapolis Honeywell Company), records all the peaks eluding from the first column. The second chromatograph, a PE 154D Vapor Fractometer (Perkin Elmer Corporation) equipped with a 0-1 mv strip chart recorder (Model 69800, Leeds and Northrup Company) records the peaks eluding from the other three columns.

Helium carrier gas, supplied to each chromatograph, is first dried in a small column of 4A molecular sieves (Linde Company). The pressure at each of the two helium sources is controlled by a two stage regulator. A flow rate of 40 ml/min of helium at 72°F and 1 atmosphere is maintained.

The four columns used are as follows. Column I consists of 5 grams of Celanese ester 9 Tripelargonate (F&M Scientific Corporation) per 100 grams of Haloport F (F&M Scientific Corporation) in 20 feet of 1/4 inch o.d., 0.035 inch wall, copper refrigeration tubing. The ends are packed with glass wool to keep the packing in the column. Column I is operated isothermally at 105°C. Column II consists of 5 grams of Celanese 9 on Haloport F in 12 feet of 1/4 inch copper refrigeration tubing. It is operated isothermally at 50°C. Column III consists of 20-35 mesh silica gel (refrigeration grade, Eagle Chemical Company) in 2 feet of 1/4 inch copper refrigeration tubing and is operated isothermally at 72°F. Column IV consists of 14-30 mesh 13X molecular sieves (Linde Company) in 6 feet of 1/4 inch copper refrigeration tubing and is also operated at 72°F.

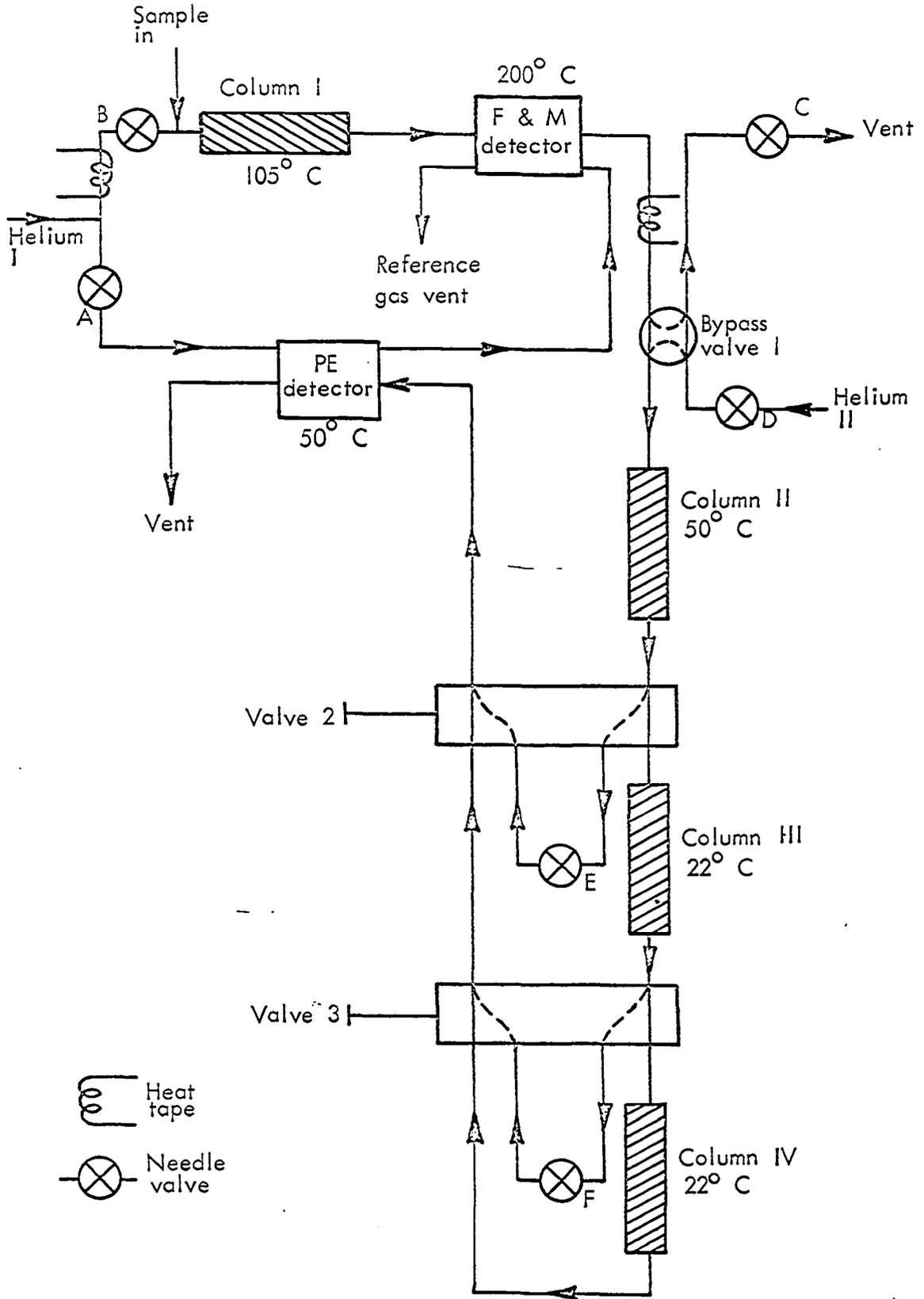
The entire effluent of column I passes through the detector of the F&M Chromatograph operated at 200°C. At a specific time a bypass valve downstream from the F&M detector is switched to vent those components yet to pass by the valve. The components which had already passed the valve have been sent to the other three columns and detected on the PE

detector which is operated at 50°C. A schematic flow diagram of the analytical system is shown in Figure 8.

Before a sample can be analyzed, the system of columns and chromatographs must be balanced so that pressure surges do not occur when a valve is switched. A change in pressure causes a change in mass flow rate which shows up as a jump in baseline on the chromatograph. The jump is due to the change in relative thermal conductivity of the two streams flowing through the detector. During the analysis of a sample, three valves must be switched to channel the components through the proper columns.

Balancing the system is accomplished by first turning on both helium supplies to about 30 psig. The reference gas needle valve A is adjusted so that a flow of about 40 ml/min is obtained on the reference side of the two thermal conductivity detectors. After all parts of the equipment have come to equilibrium, and with helium from source I flowing through all four columns, the flow of helium from the PE detector is adjusted to 40 ml/min using the needle valve B near column I. Then bypass valve 1 is switched and the system resistance needle valve C is adjusted to equal the combined resistance of columns II, III and IV so that no change in baseline on the F&M Chromatograph occurs when valve 1 is switched. At the same time the needle valve D controlling helium from source II is adjusted to obtain 40 ml/min of helium from the PE detector. Fine adjustment is made by insuring no baseline jump on

Figure 8. Gas chromatography analytical system



the PE chromatograph when valve 1 is switched. Similarly, with helium at 40 ml/min flowing through columns II, III and IV, valve 2 is switched and needle valve E is adjusted so that no baseline change occurs on the PE chromatograph. Finally, with valve 2 open and helium flowing through columns III and IV valve 3 is switched. Needle valve F is adjusted so that no baseline jump occurs on the PE chromatograph when valve 3 is switched.

#### Analytical procedure

In a typical analysis, a 3 cc. sample from the sample loop is carried by preheated helium carrier gas into column I. The helium is preheated by a heat tape wrapped around the 1/8 inch stainless steel line leading to the sample box. The 1/8 inch stainless steel line from the sample box to column I is insulated to prevent condensation.

The compounds eluding from column I are recorded by the F&M detector with the bypass valve 1 in the load position. About 7.0 minutes after sampling, valve 1 is switched to bypass allowing the nitromethane and nitroethane, which have not yet eluded from column I, to be vented. The gases and low boilers have, by this time, been loaded onto the remaining three columns. Nitromethane and nitroethane are well separated from the other components by column I and are resolved on the first chromatograph. When valve 1 is switched the second supply of helium carries the unresolved portion of the

sample through the remaining columns. The second supply of helium provides uninterrupted flow in both systems.

The components not vented after column I are loaded onto columns II, III and IV. At 5.5 minutes after sampling, valve 2 is pushed and flow is stopped to columns III and IV. By this time, hydrogen in the sample has passed through all four columns and been detected on the PE chromatograph. When valve 2 is pushed, those components which have not yet passed valve 2 are sent to the PE detector as they elude from column II. Thus, formaldehyde, acetaldehyde, water, methanol and ethanol are recorded on the PE chromatograph. At 12.5 minutes after sampling, valve 2 is pulled and flow of pure helium carrier gas is resumed to columns III and IV.

Shortly after flow is resumed to columns III and IV, oxygen eludes from column IV and is detected on the PE chromatograph. At 14.5 minutes after sampling, valve 3 is pushed and flow is stopped to column IV. Those gases which have not yet passed valve 3 are sent to the PE detector. Thus, ethane and carbon dioxide are recorded on the PE chromatograph. At 19.5 minutes after sampling valve 3 is pulled and flow of pure helium gas is resumed to column IV. The gases which have been stopped on column IV are detected by the PE detector as they elude from column IV. These remaining gases, nitrogen, NO-NO<sub>2</sub>, methane and carbon monoxide, are recorded on the PE chromatograph. A total of 15 components are thus separated on the two chromatographs in an analysis time of 30 minutes.

Example chromatograms from an actual run appear in Figure 9 and Figure 10.

The nitric oxide-nitrogen dioxide peak, which is not resolved on the chromatograph, is trapped in an infrared cell as it eludes from the PE detector. A bubble meter is connected at the outlet in a tee arrangement with the evacuated infrared cell. As the peak eludes from the chromatograph, a valve on the cell is opened slowly allowing the vacuum in the cell to draw the effluent from the chromatograph into the cell. The rate is maintained by continuously opening the valve on the cell such that a bubble in the meter is held motionless. When the cell has been filled in this manner it contains the nitric oxide-nitrogen dioxide peak diluted with helium carrier gas. Nitrogen dioxide absorbs strongly around  $1300\text{ cm}^{-1}$  while nitric oxide absorbs at about  $1900\text{ cm}^{-1}$  (47). Infrared analysis of this sample gives the relative amounts of nitric oxide and nitrogen dioxide and completes the product distribution.

#### Design of Experiments

Vapor phase nitration of ethane has been studied previously by three groups of investigators. No product distribution data have been published but maximum conversions and optimum operating conditions for production of nitroparaffins have been reported. In the 1930's, Hass, Hodge, and Vanderbilt (30) contacted nitric acid and ethane in a tubular

Figure 9. Actual chromatogram from F&M chromatograph

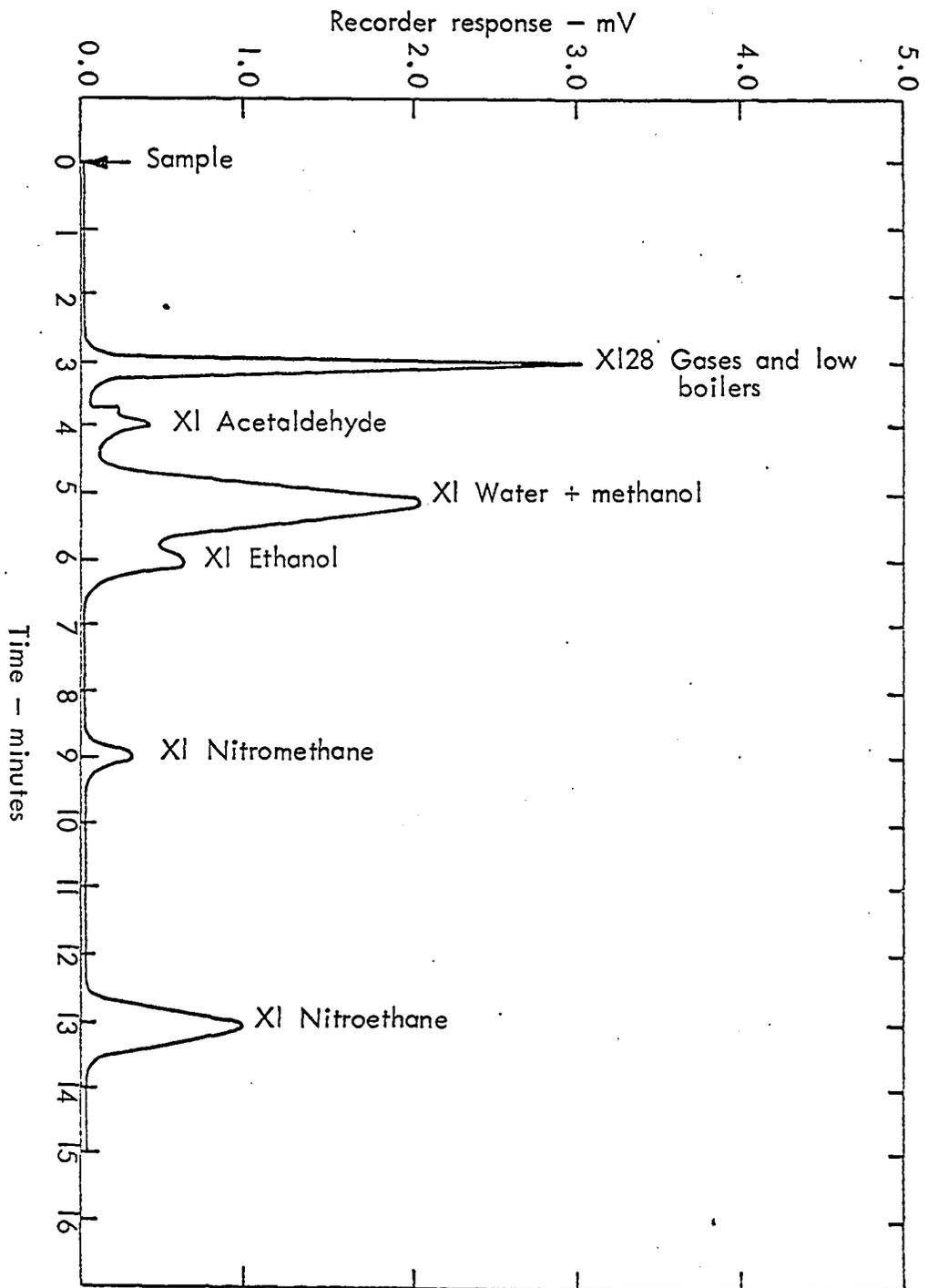
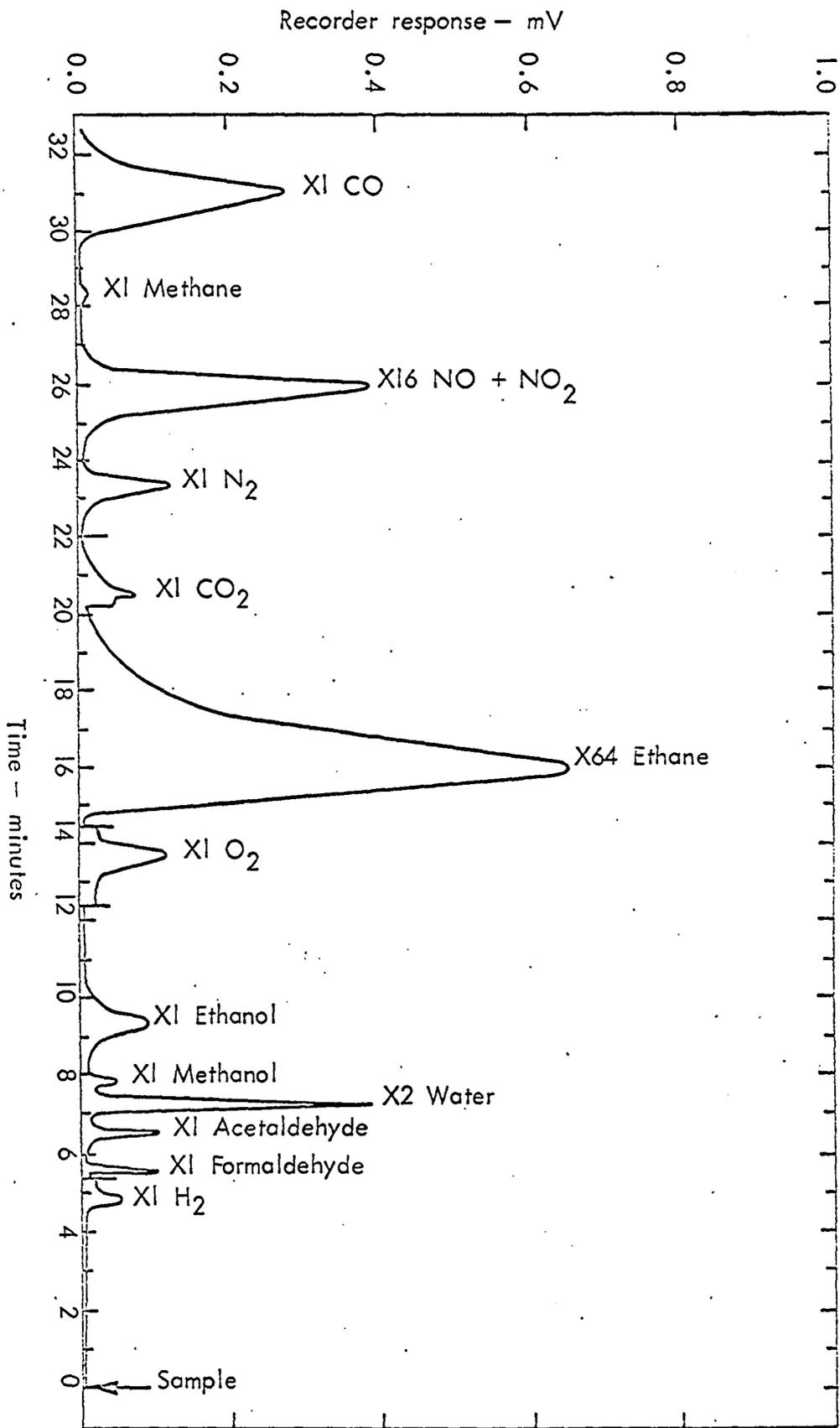


Figure 10. Actual chromatogram from PE chromatograph



glass reactor and obtained 9% conversions at 420°C and a mole ratio of 2:1 hydrocarbon to acid. Hibshman, Pierson and Hass (35) followed up this work in a stainless steel tube and obtained 33% conversions at 450 to 475°C and mole ratios of 10:1. They reported residence times about 0.25 sec. Again in a glass tubular reactor, Geiseler and Reinhardt (23) in 1956 obtained 31% conversions at 445°C and a mole ratio of 10:1. They reported best conversions at a residence time of 0.5 seconds. These data are summarized in Table 1. Ethane has not been nitrated in other than a tubular reactor. Butane was nitrated in a bubbling salt bath reactor by Hankinson (25). He found little effect of residence time on conversion, but strong correlation with temperature and mole ratio. Pressure has been found to have little effect on the nitration of methane (34).

Because of the above information, it was decided to limit experiments to the investigation of the effects of temperature and mole ratio on product distribution at a single residence time and atmospheric pressure. The temperature range selected was from 400 to 500°C and mole ratio range from 3:1 to 17:1 hydrocarbon to acid. It was intended to use the minimum possible residence time reasonably obtainable with the reactor.

To accomplish investigation of these two variables, a central composite rotatable design in two variables (17) was selected to facilitate statistical analysis of the data. This design for location of experimental points allows one to fit a quadratic response surface to the two dimensional range and

Table 1. Summary of literature data on nitration of ethane

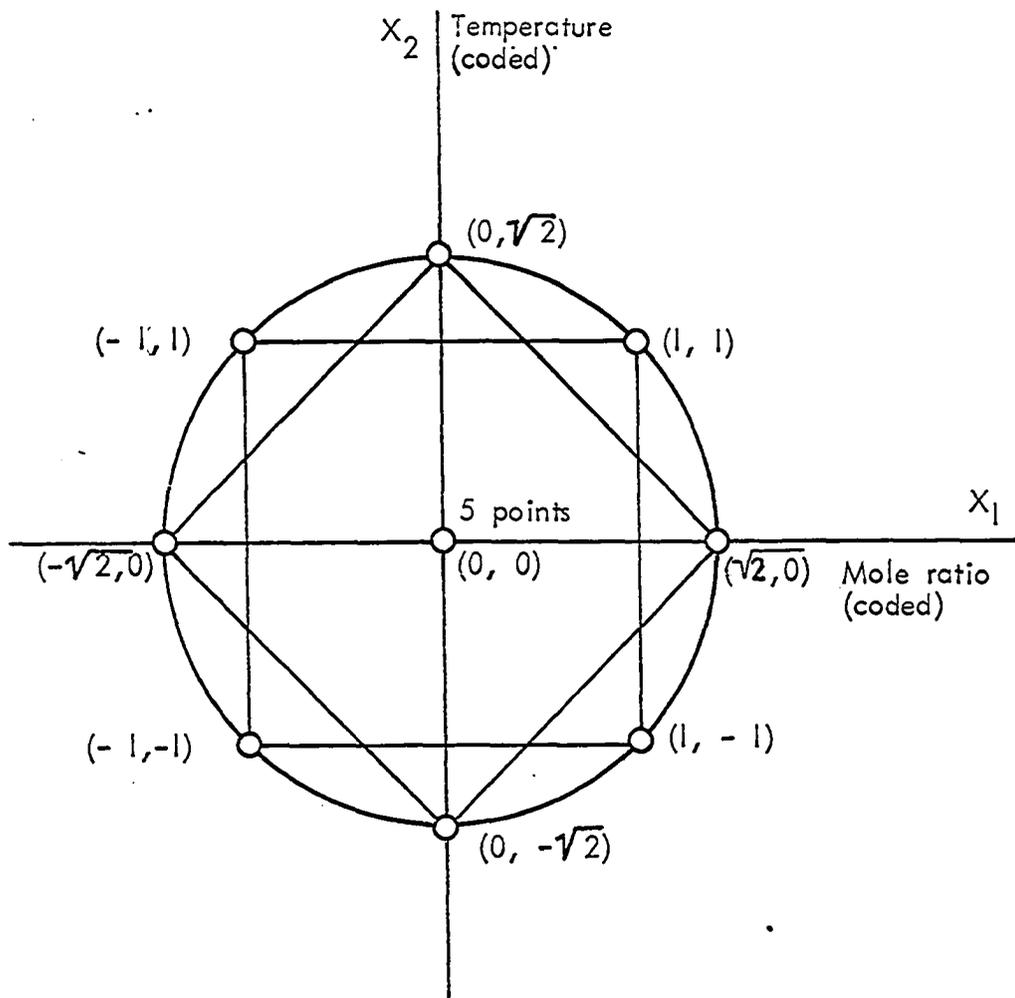
	Hass et al. (30)	Hibshman et al. (35)	Geiseler and Reinhardt (23)
Optimum temperature	420°C	455°C	445°C
Residence time	-	0.33 sec.	0.50 sec.
Mole ratio hydrocarbon/acid	2:1	10:1	10:1
Pressure	1 atm.	1 atm.	1 atm.
Maximum conversion based on nitric acid	9%	33%	30%

determine goodness of fit and experimental errors. Figure 11 shows the design in two variables for locating experimental points. It can be seen that a quadratic can be put through any of the four combinations of 3 points in a straight line. This fact provides sufficient information for the regression coefficients of a second order response surface to be calculated. Experimental error is obtained by replication of the center point. Nine different data points and four replications of the center point must be taken requiring thirteen runs.

#### Operation of Pilot Plant

In a typical run nitrogen is bubbled through the reactor to prevent salt from backing up into the tubes while the

Figure 11. Central composite rotatable design



$T = 450 + 35.4 X_2$ , Degrees centegrade  
 $MR = 10 + 4.95 X_1$ , Hydrocarbon to acid

reaction temperature is being reached. The temperatures are recorded continuously on a multipoint temperature recorder. Reactor pressure is indicated continuously by a manometer on the product exit stream. The cooling system is turned on and coolant is pumped through the product condenser.

When the reactor reaches reaction temperature, the ethane is fed at a predetermined rate into the reactor. Nitric acid flow is begun five minutes later and increased slowly until the desired mole ratio of reactants is reached. Reaction time is controlled by selecting the appropriate volumetric flow rate at the reactor and back calculating to determine the ethane and nitric acid feed rates at their feed temperatures. Conversion of flow rates to rotameter readings is made by means of calibration curves.

Equilibrium is reached almost immediately according to the steady state monitor which records the thermal conductivity of the product stream. Reactants are allowed to enter the reactor steadily for 10 minutes to insure that a representative sample will be obtained. After a few minutes has elapsed the aspirator near the sample box is turned on and a continuous stream of product is drawn through the sample valve and loop. At a convenient time (approximately 10 minutes after the reaction has begun) the air operated sample valve is switched on and a sample is carried by the helium carrier gas into the gas chromatography analytical system. During the 30 minute analysis of the sample the nitric acid flow is

stopped and the line closed at the reactor head. Nitrogen is fed into the ethane line at a reasonable rate and ethane flow is stopped. This procedure conserves reactants and keeps the lines immersed in the salt of the reactor from plugging with salt. When the analysis is completed the above procedure is repeated for new reaction conditions.

The bulk of the product which passes through the condenser separates into a gas phase and two liquid phases. Provisions are made for collecting a gas sample which may be analyzed separately or vented to the outside. The liquid product collected in an ice bath may be analyzed separately by gas chromatography or destroyed in an appropriate manner.

According to the central composite rotatable design, data are taken at five different temperatures ( $500^{\circ}\text{C}$ ,  $485.4^{\circ}\text{C}$ ,  $450^{\circ}\text{C}$ ,  $414.6^{\circ}\text{C}$ ,  $400^{\circ}\text{C}$ ) and 5 different mole ratios (3:1, 5.05:1, 10:1, 14.95:1, 17:1). The mole fraction of each component in the product may be calculated and the complete product distribution tabulated at each combination of temperature and mole ratio.

### Results

Analysis of the products of vapor phase nitration of ethane in an on-line sample by gas chromatography generates data in the form of complete product distributions. Product distributions for all significant runs are tabulated in the appendix. The experimental ranges of temperature and mole

ratio were covered according to the statistical design in a preliminary set of thirteen runs indicated by numbers 1 to 13 in the appendix. For these initial experiments, a uniform residence time of 5.0 seconds was maintained. From the product distribution, yields and conversions based on hydrocarbon and acid may be calculated. These appear in Table 2.

Following the preliminary set of experiments a number of replications of single points were made to check for time trends and see what effects bubbling air through the reactor between runs might have on subsequent conversions. Product distributions for these runs, numbered 21-27 and 31-36, also appear in the appendix.

The results of the first experiments indicated that the range of variables investigated adequately covered the area of interest. Conversion attained a maximum with respect to both mole ratio and temperature in the selected range. The five replications of the center point showed a decrease in conversion with time. However, no such time trend was found in subsequent replications and bubbling of air through the reactor between runs did not affect conversion. Therefore, another set of thirteen runs covering the same range of variables was made to check the reproducibility of the results and to see if the time trend reappeared. Product distributions for these runs, numbered 41-53, also appear in the appendix. Residence time was maintained at 4.0 seconds for all runs. Yields and conversions are tabulated in Table 2. The results of this

Table 2. Yields and conversions

Run	T °C	MR Hydro- carbon to acid	HNO <sub>3</sub> <sup>(1)</sup> conv. %	HNO <sub>3</sub> <sup>(2)</sup> yield %	Ethane <sup>(3)</sup> conv. %	Ethane <sup>(4)</sup> yield %	% NE <sup>(5)</sup> of NP's
1	500	10	2.30	20.44	0.26	11.37	69.50
2	485.4	5.05	3.35	32.39	0.95	15.66	70.41
3	450	3	3.67	56.15	6.50	10.39	74.66
4	450	10	8.37	42.50	1.18	33.84	77.04
5	450	10	6.74	63.40	1.07	39.29	85.15
6	485.4	14.95	7.06	71.15	0.96	68.54	87.13
7	450	10	5.66	69.74	0.74	46.69	81.46
8	414.6	5.05	6.43	76.08	0.46	33.86	89.52
9	450	10	4.90	31.43	0.11	36.22	86.36
10	450	10	4.02	26.83	0.09	27.88	89.77
11	450	17	0.39	34.13	0.16	3.24	80.70
12	414.6	14.95	21.90	84.89	0.46	63.02	87.71
13	400	10	0.00	0.00	0.00	0.00	-
41	500	10	2.39	15.70	0.15	13.31	68.21
42	485.4	5.05	1.32	10.92	0.15	8.04	79.86
43	450	3	1.66	21.33	0.23	22.87	75.12
44	450	10	3.20	22.33	0.16	35.62	77.02
45	450	10	2.52	20.33	0.14	22.87	70.27
46	485.4	14.95	5.35	22.80	0.12	35.62	77.86
47	450	10	4.41	28.62	0.29	30.09	80.00
48	414.6	5.05	0.95	12.46	0.09	10.14	82.89
49	450	10	3.50	30.77	0.23	27.51	81.25
50	450	10	7.34	57.14	0.40	33.70	75.72
51	450	17	4.46	35.53	0.14	28.94	72.85
52	414.6	14.95	2.53	30.77	0.10	25.85	75.00
53	400	10	0.62	2.63	0.03	6.83	85.29

(1) HNO<sub>3</sub> conv. = molar ratio of nitroparaffins to HNO<sub>3</sub> charged

(2) HNO<sub>3</sub> yield = molar ratio of nitroparaffins to HNO<sub>3</sub> consumed - assumes NO-NO<sub>2</sub> recoverable

(3) Ethane conv. = molar ratio of carbon in NP's to carbon charged

(4) Ethane yield = molar ratio of carbon in NP's to carbon consumed - assumes ethane recoverable

(5) % Nitroethane = mole % nitroethane of total NP's produced

second set compare very favorably with the first set and seem to show the same mole ratio and temperature dependence. In this set of runs no time trend was apparent.

## DISCUSSION OF RESULTS

The pilot plant equipment and the analytical system operated very satisfactorily. A few mechanical problems which did arise were quickly corrected and operation as a whole was very smooth.

## Reactor Operation

The reactor and its auxiliaries performed very well. Problems with metering and control of feed streams reported by other authors (1, 21) were not encountered with the equipment used. The use of an acid egg to feed nitric acid and the practice of feeding cold liquid acid directly to the mixing tee have eliminated the problem of pulsating flow reported by Adams (1) and Fear (21). Ethane feed rates were steady and uninterrupted.

With ethane flowing into the reactor the acid flow was begun and increased slowly to the desired rate. As the reaction began a distinct bumping was often observed but no violent reaction was encountered. At low mole ratios of hydrocarbon to acid the bumping was more apparent. In a very short time, however, the reaction would stabilize and smooth operation would follow.

Temperature control was found to be adequate. The reactor temperature was relatively slow in responding to a change in power input, but for this reason held a steady temperature easily during the reaction period. When the reactants were

first introduced into the reactor, a few degrees drop in temperature occurred. With experience this was compensated for and reaction temperatures were easily held at the desired level. A significant drop in temperature occurred between the salt bath and the product exit indicating that the products cooled very quickly on leaving the reactor. No hot spots or temperatures higher than that of the salt bath were observed indicating that the exothermic reaction was well under control.

A small amount of very fine particles of salt were observed to leave the reactor through the exit port and deposit in the exit tubing. The inside of the tubing became coated with a layer of salt which continued to increase during operation. A slight increase in reactor pressure was observed from run to run due to the growth of this salt layer. This limited the rate at which reactants could be fed to the reactor and thus limited the minimum residence time obtainable. In only one instance, however, did the exit tubing become clogged. When this happened it was removed and cleaned and replaced in a short time.

A steady state monitor installed in the exit stream and maintained at 200°C operated well for short periods of time. Feed ethane was passed through one side of the thermal conductivity cell as a reference and the reaction product gas through the other side. The thermal conductivity filament in the product line was destroyed by the corrosive product mixture

after several runs. During operation the relative thermal conductivity of the two streams became constant very quickly indicating that steady state was reached in a very short time.

#### On-Line Analysis

The on-line chromatographic analysis of the reaction products for the nitration of ethane was found to operate successfully. The sample box containing the air operated sample valve and 3 cc. sample loop was easily maintained at 200°C. A 3 cc. sample gave the best detection of components present in small amounts and gave good resolution of all peaks with a minimum amount of "tailing". The salt trap installed in the sample line effectively removed all salt from the sample and the 1/8 inch sample lines were never clogged.

Once the helium flow rates and resistance settings were carefully balanced, the chromatographs performed exceptionally well. No baseline drift was encountered and only small shifts occurred when a bypass valve was switched. There were no unidentified peaks obtained and only the nitric oxide-nitrogen dioxide peak was unresolved. This problem was solved by trapping this peak for infrared analysis. Since an infrared analyzer was not readily available, all of the chromatograms were not supplemented with this information. However, all of the nitrogen oxide peaks analyzed showed little or no nitric oxide and it may be assumed that very little nitric oxide is present in the product gases. The value of gas chromatography

in obtaining product distributions for the vapor phase nitration of ethane has been proven by these experiments.

#### Product Distribution

Complete product distribution data for all significant runs are tabulated in the appendix. Runs numbered 1 to 13 and 41 to 53 are complete sets covering the experimental ranges of mole ratio and temperature investigated. Runs 1 to 13 were made at a residence time of 5.0 seconds and runs 41 to 53 were made at a residence time of 4.0 seconds. Infrared analysis of an NO-NO<sub>2</sub> peak indicates that only a comparatively small amount of NO is present and the mole fraction designated NO-NO<sub>2</sub> may be considered mostly NO<sub>2</sub>.

Higher order nitroparaffins and dinitroparaffins were not found in the product. This has been characteristic of all vapor phase nitrations in the past. Only trace amounts of methane were found and not in all of the runs. There were no ketones but significant amounts of ethanol, acetaldehyde and formaldehyde which increased with increasing temperature. Carbon monoxide appeared in all experiments in relatively large quantities. This indicates that the breakdown of larger molecules is extensive. It appears that of those molecules of ethane that do take part in the reaction a good share are split and stripped of their hydrogen atoms and end up as CO. Ethane is the only source of carbon atoms in the reaction.

### Yields and Conversions

Yields and conversions were presented in Table 2. Calculations were based on the amounts of ethane and nitric acid actually fed. This is determined by summing the moles of carbon and nitrogen appearing in the product and calculating the amounts of the starting materials. There has been some confusion associated with the definitions of yield and conversion in the literature. Conversion is used here to relate product to feed materials charged. Definitions of these terms appear as footnotes to Table 2 and are consistent with the majority of the published nitration data.

Conversion based on nitric acid has been most commonly used to measure the extent of nitration. Figures 12 and 13 indicate the form of the response surfaces obtained for nitric acid conversion by showing the location of data points on the two dimensional range of temperature and mole ratio and the conversion obtained at each combination of the two variables. Figure 12 represents the data taken at a residence time of 5.0 seconds while Figure 13 is for a residence time of 4.0 seconds. The conversion obtained at 414.6°C and 14.95:1 mole ratio for the first set of runs is inconsistent with the rest of the data. In general, conversions at 4.0 seconds residence time appear slightly lower than at 5.0 seconds, but the form of the surface seems to be nearly the same.

The response surface which can be fitted to each of these sets of data is of the form:

Figure 12. Conversion of nitric acid for runs 1-13  
at residence time = 5.0 sec.

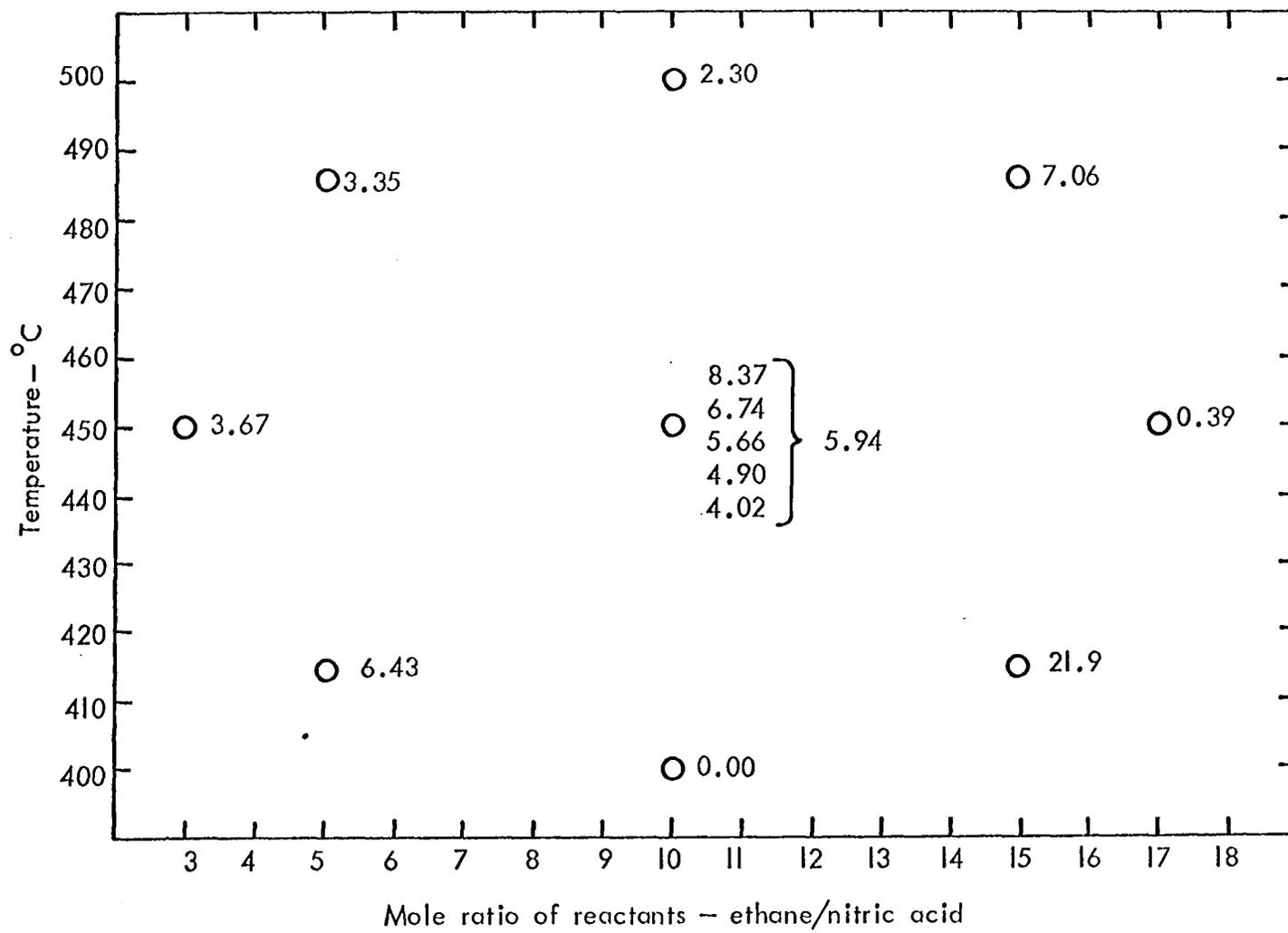
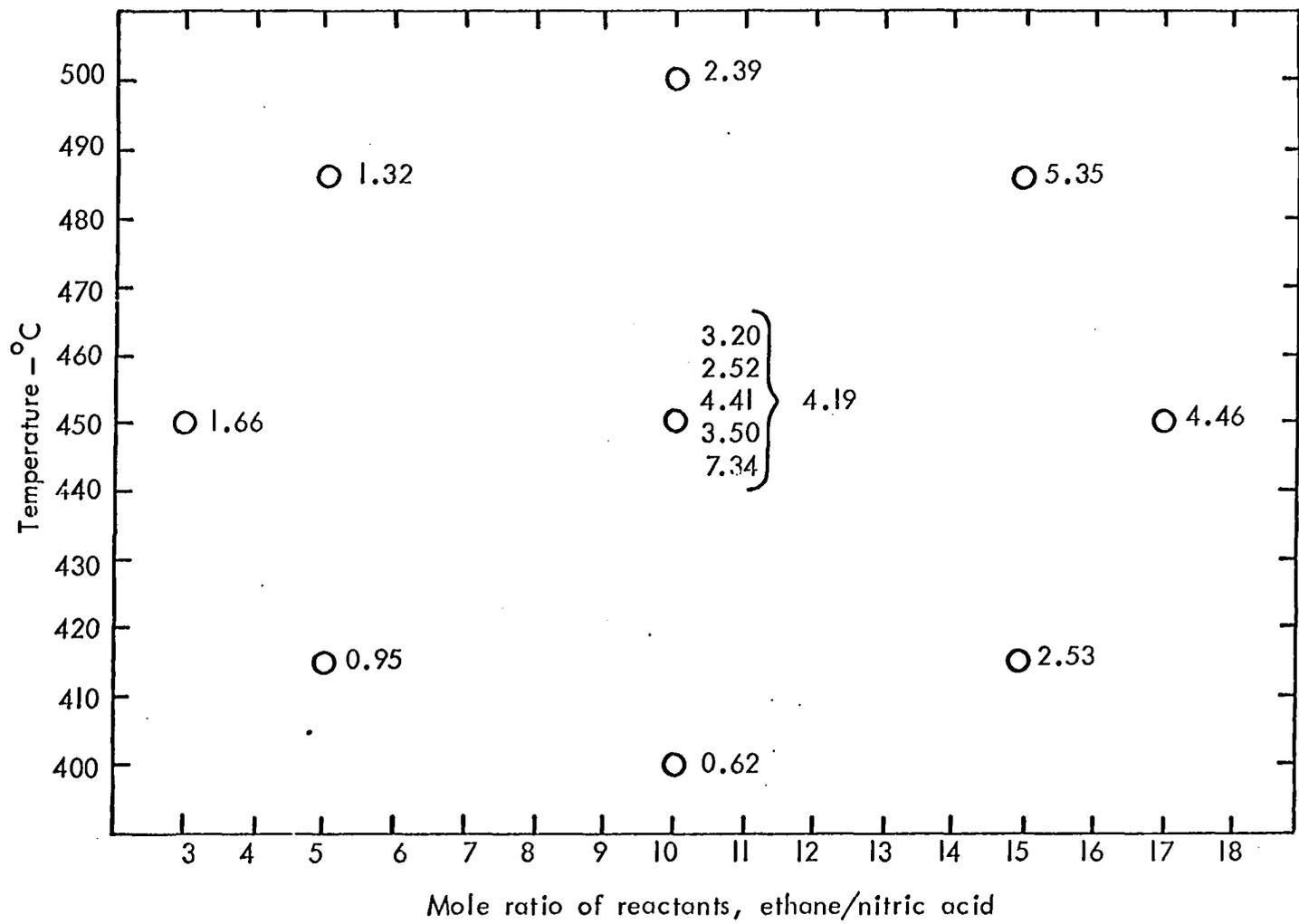


Figure 13. Conversion of nitric acid for runs 41-53  
at residence time = 4.0 sec.



$$y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{22} x_2^2 + b_{12} x_1 x_2$$

where:  $y$  = the %  $\text{HNO}_3$  conversion

$$x_1 = \frac{\text{M.R.} - 10.0}{4.95} \quad (\text{coded mole ratio})$$

$$x_2 = \frac{T - 450}{35.4} \quad (\text{coded temperature})$$

M.R. = Mole ratio (dimensionless)

T = Temperature ( $^{\circ}\text{C}$ )

Calculation of the best estimates of the coefficients in the above equation for runs 1-13 at a residence time of 5.0 seconds results in the following values:

$$b_0 = 5.938$$

$$b_1 = 1.8178$$

$$b_2 = -1.8335$$

$$b_{11} = 0.0698$$

$$b_{22} = -0.3702$$

$$b_{12} = -2.9400$$

An analysis of variance for this surface is found in Table 3.

The equation of the response surface which results from the  $\text{HNO}_3$  conversions obtained does not adequately fit the data. The coefficients  $b_1$  and  $b_2$  show the relatively strong dependence of yield on mole ratio and temperature respectively. A large interaction effect is indicated by the size of coefficient  $b_{12}$ . Analysis of variance shows the lack of fit to be significant. The 21.9% conversion obtained at  $414.6^{\circ}\text{C}$  and 14.95:1 mole ratio is not consistent with the rest of the data and probably contributes a great deal to the lack of fit of

Table 3. Analysis of variance for runs 1-13

Source of variation	Sum of squares	Degrees of freedom	Mean square	F statistic	Test statistic
First order	53.32822	2	26.66	9.35*	6.94
Second order	35.62665	3	11.88	4.17	6.59
Lack of fit	278.00373	3	86.00	30.18*	6.59
Error	11.39128	4	2.85		
Total	358.34988	12			

\*Significant at the 95% level of significance

the second order response surface.

Calculation of the best estimates of the coefficients for the response surface for runs 41-53 at a residence time of 4.0 seconds results in the following values:

$$b_0 = 4.194$$

$$b_1 = 1.196$$

$$b_2 = 0.711$$

$$b_{11} = -0.503$$

$$b_{22} = -1.281$$

$$b_{12} = 0.6125$$

An analysis of variance for this surface is found in Table 4.

The response surface resulting from the second set of experiments is found to fit the data adequately at the 75% level of significance. At the 95% level of significance none

Table 4. Analysis of variance for runs 41-53

Source of variation	Sum of squares	Degrees of freedom	Mean square	F statistic	Test statistic
First order	15.490	2	7.74	2.18**	2.00
Second order	13.753	3	4.58	1.29	2.05
Lack of fit	0.485	3	0.16	0.046	2.05
Error	14.212	4	3.55		
Total	43.94	12			

\*\*Significant at the 75% level of significance

of the F statistics are significant. This indicates that there is a tendency toward a second order surface but at the 95% level of significance the first order terms are sufficient. This is due to the relatively large scatter in replications at the center point. The error mean square obtained in both sets of data are comparable.

The coefficients  $b_1$  and  $b_2$  again show the relatively strong dependence on mole ratio and temperature and the coefficient  $b_{22}$  shows the temperature effect to be strongly second order. The interaction effect is again important as shown by the coefficient  $b_{12}$ .

A decay of reactor efficiency has been noted by other authors using tubular reactors for vapor phase nitration. It should be noted here that tests of this reactor by

replications of a single point showed no such time trend and that flushing of the reactor with only nitrogen and flushing with air between runs had no effect on conversions. Product distribution data for these runs are included in the appendix. The error mean square for nitric acid conversion was 2.19, about the same size as that obtained in the above designs. The reactor was in no way poisoned by the products of ethane nitration.

The substantial improvement in analytical technique may partially account for the difference in conversions and yields from those previously reported. However, reaction time may have a significant effect on the results. The longer residence times used in this molten salt reactor may allow increased decomposition of the nitroparaffins.

#### Residence Time

The bubbling molten salt reactor is not particularly well suited to control of residence time. Minimum residence times were limited in this case by clogging of exit tubing with salt that left the reactor with the reaction products and by the rate at which the reactants could be forced into the reactor. Residence time in this reactor is more accurately described as residence time distribution.

For runs 1-13, 21-27 and 31-35, the level of the molten salt was 10 inches below the reactor headplate leaving a dead space of  $0.165 \text{ ft}^3$ . The volumetric flow rate of reactants

into the reactor was constant for all of these runs at 2.00 ft<sup>3</sup>/min. at the temperature and pressure of the reaction. This results in an average residence time of about 5.0 seconds assuming no molar change on reaction.

For runs 41-53 the level of the molten salt was raised to 6" below the headplate leaving a dead space of 0.099 ft<sup>3</sup>. A lower volumetric flow rate of 1.5 ft<sup>3</sup>/min. was used to minimize the amount of salt carried out the exit. This results in an average residence time of about 4.0 sec. The flow rates were maintained by proper feed rates of reactants and checking the exit gas rate with a wet test meter. The ethane flow rate measured was within 3% of the desired rate.

In general, very slightly lower conversions were obtained at a residence time of 4.0 seconds than at 5.0 seconds. The amounts of oxidation products increased more rapidly with temperature at the longer residence time as shown in Figure 14. At lower temperatures, however, the oxidation products were comparable. On the other hand, the ratio of CO to CO<sub>2</sub> increased more rapidly with temperature at the lower residence time as shown in Figure 15. These facts indicate that oxidation is more extensive at longer residence times as well as higher temperatures.

#### Temperature Effects

In spite of the fact that conversion is low compared to tubular reactors, some reassuring trends are evident.

Figure 14. Oxidation products as a function  
of temperature and residence time

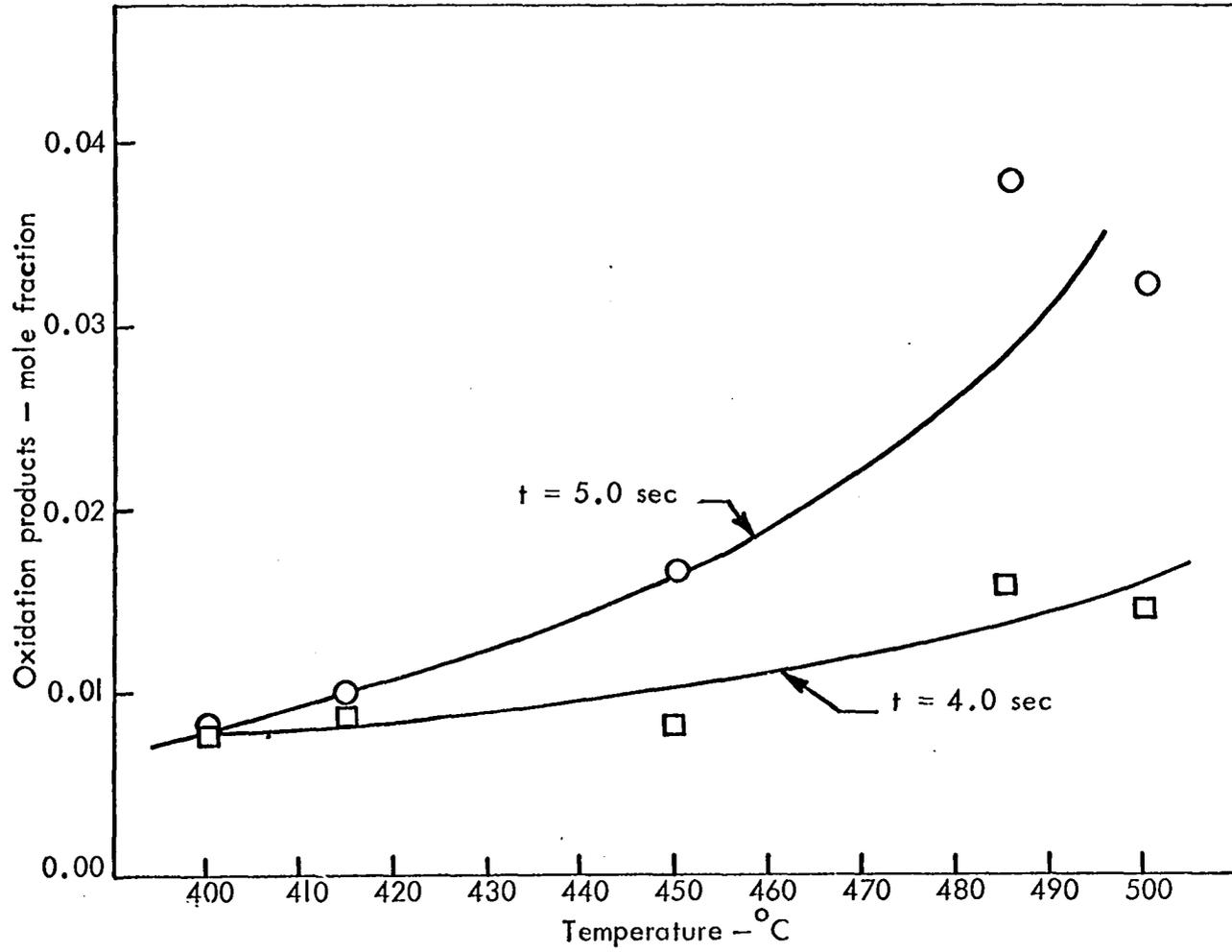
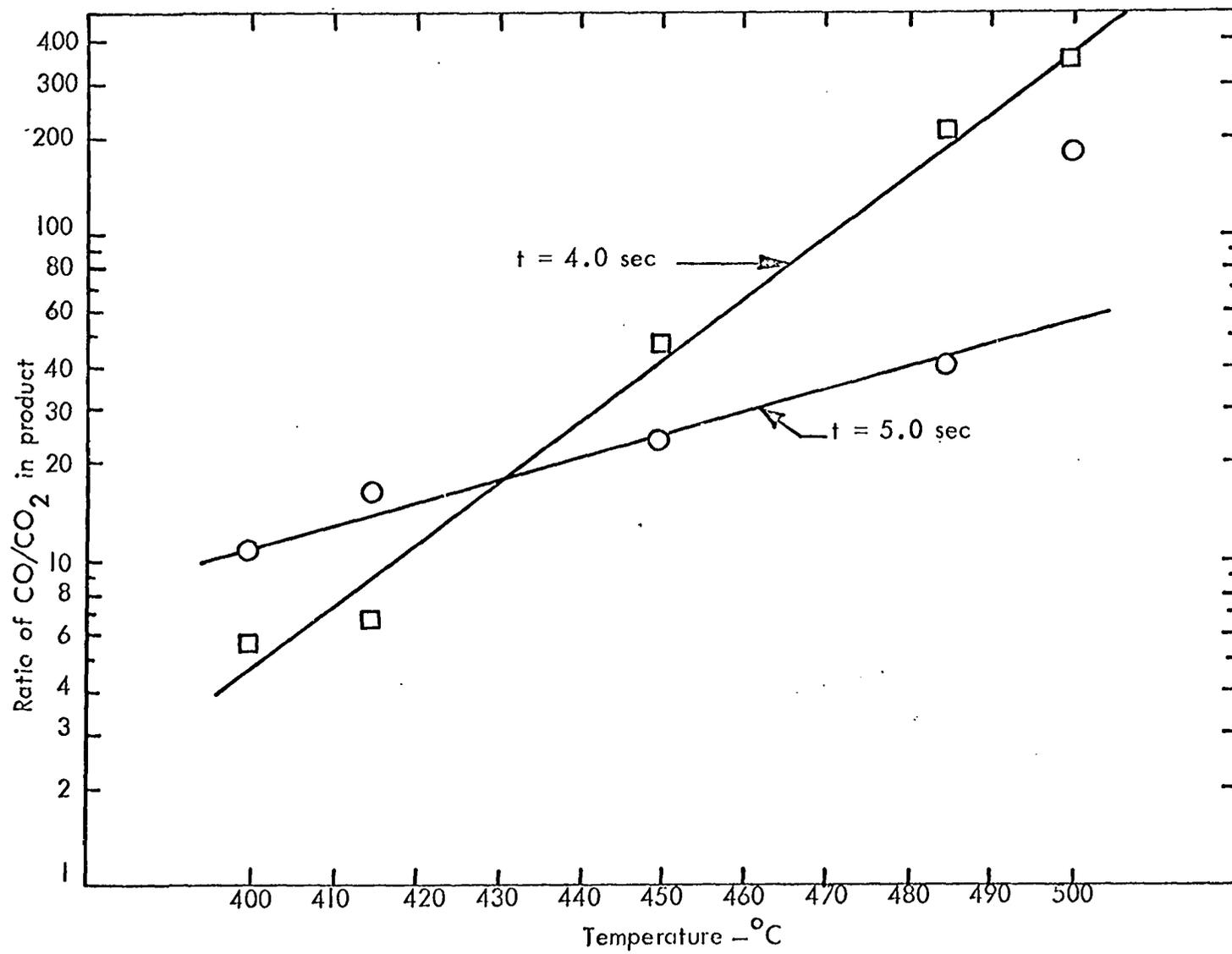


Figure 15. Ratio of CO to CO<sub>2</sub> as a function  
of temperature and residence time



Conversions and yields assume a maximum with respect to temperature in the experimental range at a mole ratio of 10:1. This is shown in Figure 16 and Figure 17 for residence times of 5.0 and 4.0 seconds respectively and is consistent with the findings in all other reports of nitration of ethane. It indicates that maximum nitration is obtained within the investigated range. Also shown in Figures 16 and 17 is the temperature dependence of the per cent nitroethane of the nitroparaffins produced. Since only nitroethane and nitromethane are produced, the decrease in per cent nitroethane with increasing temperature shows that more ethane is pyrolyzed at higher temperature. This too, is consistent with other findings and is a predictable result.

Oxidation products found in the product mixture increase rapidly with increasing temperature. This was shown in Figure 14. The increase seems to be faster with longer residence time. As would be expected, the amount of oxidation products formed increases with both higher temperature and longer exposure to higher temperature. The extent to which the oxidation reactions occur is evidenced not only by the amount of oxidation products present in the product but also by the relative amounts of more highly oxidized products. The temperature dependence of the ratio of CO to CO<sub>2</sub> was shown in Figure 15. For both residence times this ratio increases rapidly with temperature indicating that at high temperature decomposition becomes more extensive relative to oxidation;

Figure 16. Temperature dependence of conversions, yields and mole per cent nitroethane for mole ratio of 10:1 and residence time of 5.0 seconds

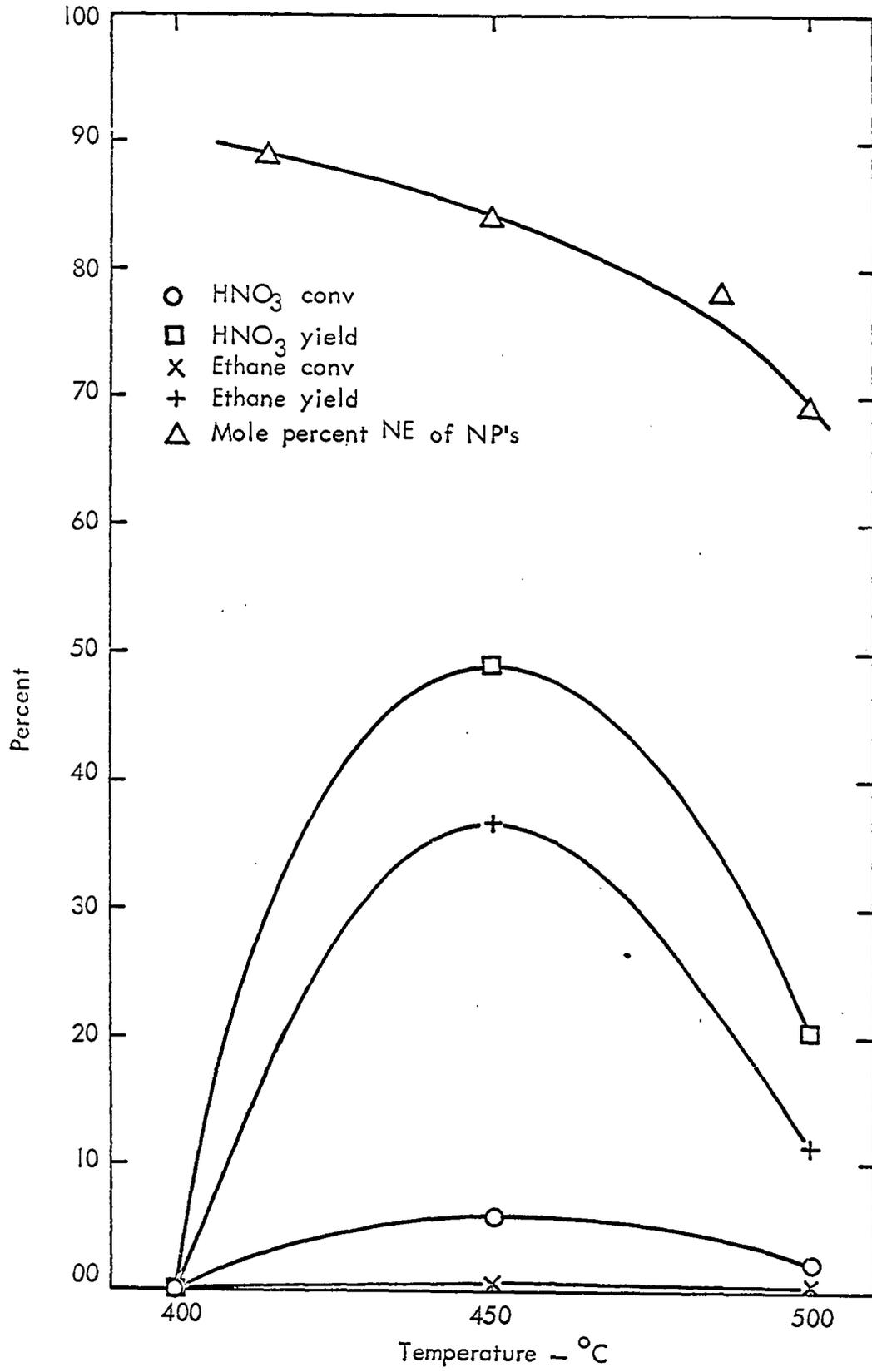
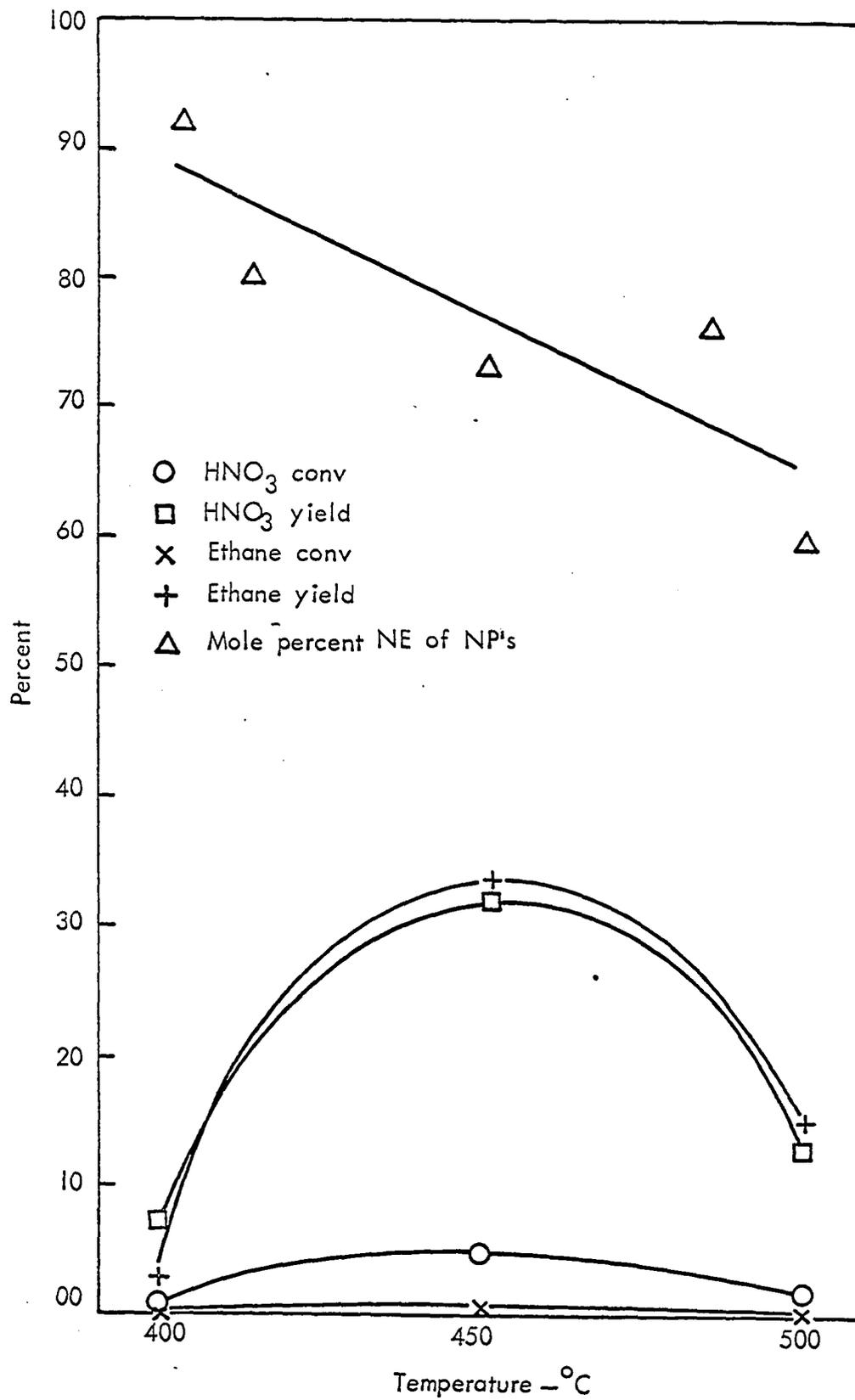


Figure 17. Temperature dependence of conversions, yields and mole per cent nitroethane for mole ratio of 10:1 and residence time of 4.0 seconds



and, as might be expected, the rate of increase of the ratio of CO to CO<sub>2</sub> is less at longer residence times showing that longer exposure allows more complete oxidation.

It has been suggested that at the high temperatures involved the nitrate salt mixture used in the salt bath might form nitrites and liberate oxygen. However, tests of the melting points of unused salt and salt which had been in the reactor for all runs gave identical results indicating no change in salt composition.

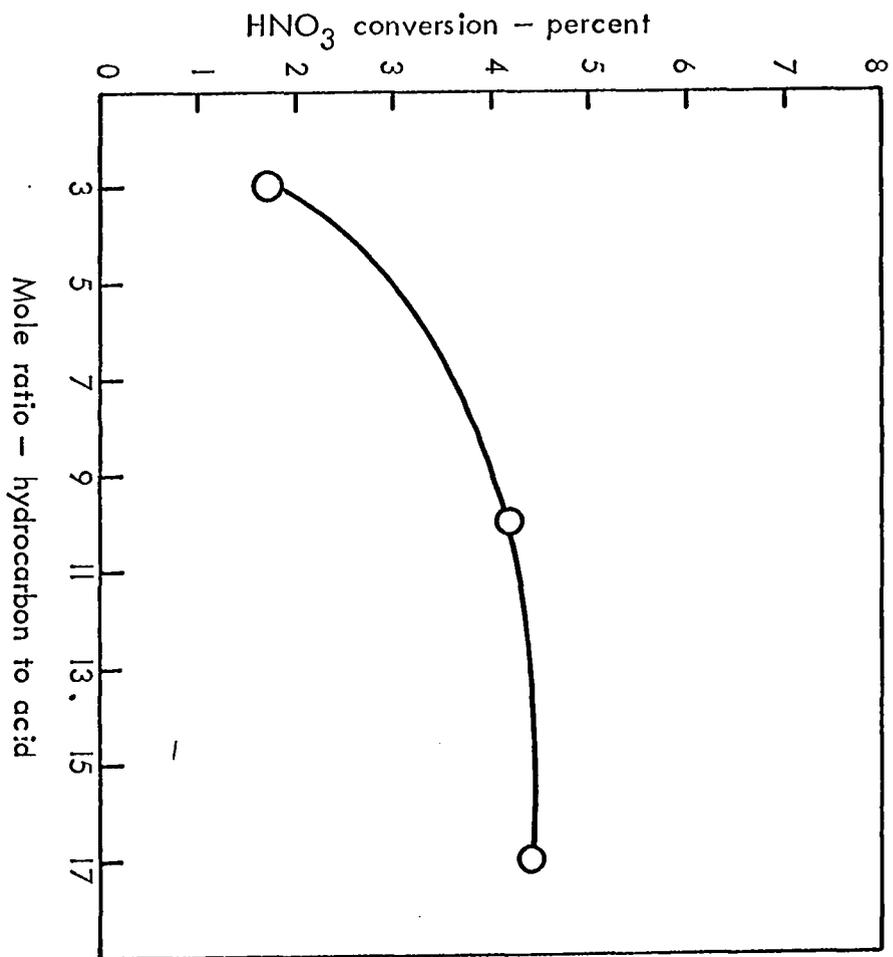
#### Mole Ratio Effects

Although yields and conversions were not affected by mole ratio of reactants as extensively as by temperature, it was noted that nitric acid conversion went through a maximum in the range investigated for runs 1-13. For runs 41-53, nitric acid conversion increased to a mole ratio of 10:1 and then leveled off for higher mole ratios. This latter result, shown in Figure 18, has been noted by other investigators of ethane nitration (35). The amounts of oxidation products generally increased with decreasing mole ratio for both sets of experiments.

#### Discussion of Mechanism

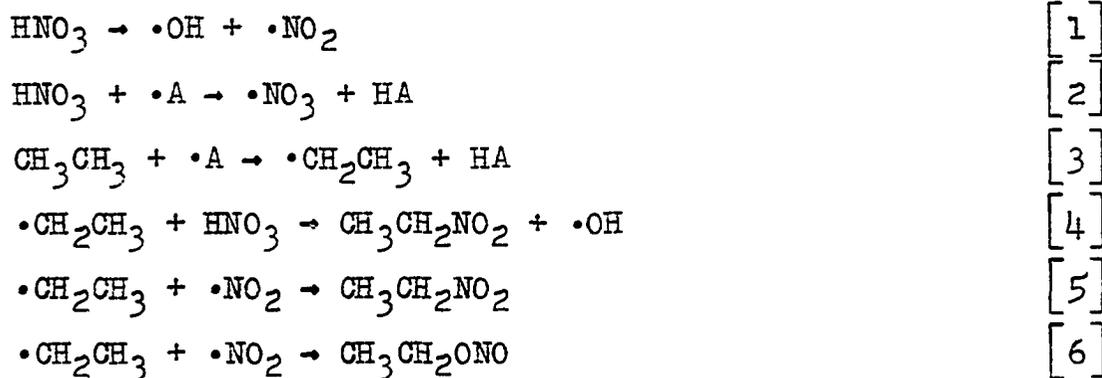
The product distribution data indicate that the reaction mechanism must include alkyl nitrite formation leading to alkoxy radicals and nitric acid decomposition leading to NO<sub>3</sub> radicals. A possible reaction mechanism, based on the review

Figure 18. Mole ratio dependence of nitric acid conversion at 450°C and residence time of 4.0 seconds

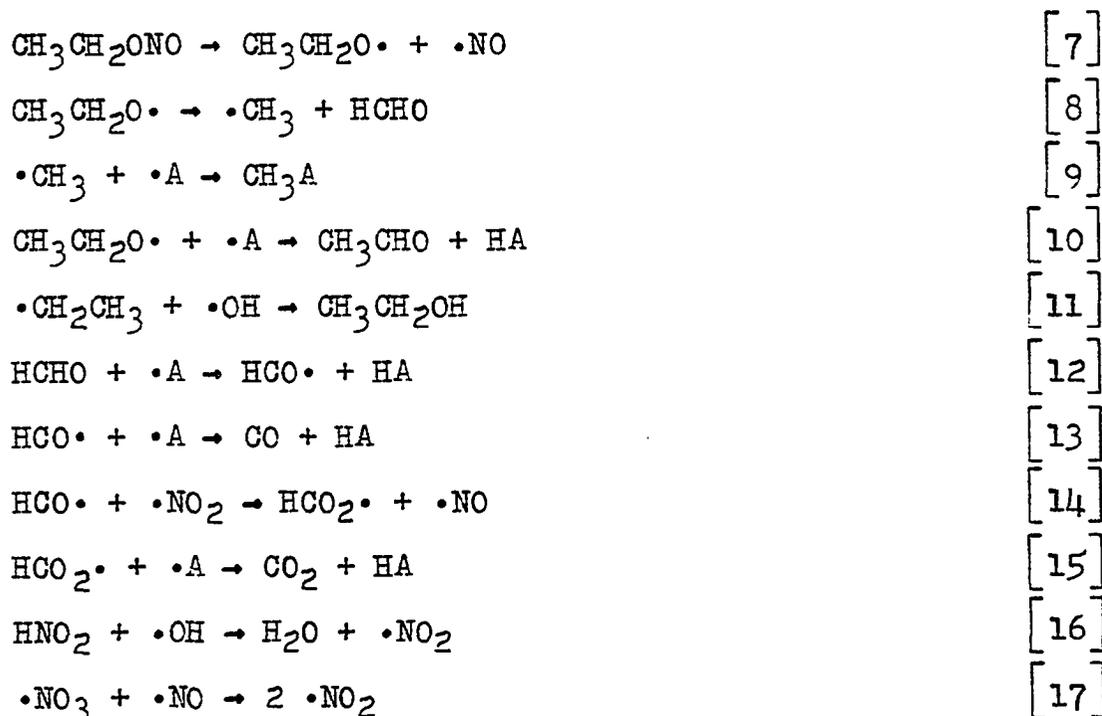


of literature on the reaction mechanism, is shown in reactions 1-17 and a qualitative discussion in view of product distribution follows.

Nitration:



Oxidation:



The symbol  $\cdot\text{A}$  represents a hydrogen acceptor and might be  $\cdot\text{OH}$ ,  $\cdot\text{NO}_2$  or an alkyl radical.

Decomposition of nitric acid is presumed to be the rate determining step (7). It probably occurs both by direct

decomposition, reaction [1], and a short chain step, reaction [4], to allow faster nitroparaffin formation. Nitric acid decomposition may also include  $\cdot\text{NO}_3$  radical formation by reaction [2] since this radical has been observed while the decomposition was taking place (41).

Nitroethane formation presumably occurs both by the short chain step mentioned above and by direct combination of  $\cdot\text{NO}_2$  with an alkyl radical as shown in reaction [5]. Alkyl radicals result from removal of a hydrogen from the paraffin hydrocarbon by one of the hydrogen acceptors in reaction [3].

Combination of the alkyl radical with  $\cdot\text{NO}_2$  in its resonance form by reaction [6] gives the alkyl nitrite which decomposes rapidly by reaction [7] and leads to the oxidation products formed. The fact that the oxidation products account for a larger part of the product than do nitroparaffins supports the idea that alkyl nitrite formation is more frequent than nitroparaffin formation when an  $\cdot\text{NO}_2$  radical is encountered by an alkyl radical. This might well be expected simply from the geometry of the  $\cdot\text{NO}_2$  radical. Decomposition of the nitroparaffin has been considered negligible (23) but may be somewhat more extensive where longer residence times are involved.

The ethoxy radical formed by decomposition of the ethyl nitrite may itself decompose by reaction [8] yielding formaldehyde and a methyl radical. Both nitromethane and methanol may be formed by reaction [9] depending on the relative

concentrations of the respective hydrogen acceptors  $\cdot\text{NO}_2$  and  $\cdot\text{OH}$ . The fact that little methanol is found in the product while a significant amount of nitromethane is present indicates that  $\cdot\text{OH}$  radicals are in relatively low concentration. Methyl nitrite is probably also formed in the same manner as ethyl nitrite and undergoes similar decomposition. Removal of a hydrogen from the ethoxy radical by reaction [10] results in acetaldehyde which is found in appreciable quantities in the product mixture.

Another significant product is ethanol which may be formed by reaction [11]. Ethanol is found in quantities comparable to nitroethane and it has already been shown that  $\cdot\text{OH}$  concentration may be low in relation to  $\cdot\text{NO}_2$  concentration. This further supports the idea that combination of an ethyl radical with  $\cdot\text{NO}_2$  does not always produce a nitroparaffin.

The large amounts of carbon oxides found in the product point to further decomposition of the oxidation products already formed. Carbon monoxide may be most easily accounted for by extraction of hydrogens from HCHO in reactions [12] and [13]. Hydrogen acceptors are evidently in abundance throughout the course of the nitration reaction. Carbon dioxide, found in much smaller concentration, may be formed by reactions [14] and [15]. Reaction [14] is less likely to occur than reaction [13] but the large concentration of  $\cdot\text{NO}_2$  increases the possibility. As temperature is increased the occurrence of reaction [14] is even less frequent since the ratio of CO to  $\text{CO}_2$

found increases rapidly. Hydrogen extraction from  $\text{HCO}\cdot$  is dominant at all temperatures investigated and considerably more likely as temperature is increased.

The hydrogen acceptor in several of these reactions may be either  $\cdot\text{OH}$ ,  $\cdot\text{NO}_2$  or an alkyl radical. Water is formed directly with  $\cdot\text{OH}$  and  $\cdot\text{NO}_2$  forms  $\text{HNO}_2$  which may combine with a hydroxyl radical by reaction [16] to form water and  $\cdot\text{NO}_2$ . Should the hydrogen acceptor be an alkyl radical, a paraffin hydrocarbon would, of course, be formed.

Nitric oxide, produced by reactions [7] and [14], was not found in significant quantities relative to nitrogen dioxide. This may be accounted for by combination with  $\cdot\text{NO}_3$  by reaction [17] to form nitrogen dioxide. It also indirectly supports the suggestion of  $\cdot\text{NO}_3$  formation by reaction [2].

This qualitative discussion has not attempted to present a comprehensive picture of the nitration mechanism. Indeed, several results are as yet unexplained. For example, from the above outlined mechanism one would expect large quantities of water to be produced. But this was not found in the product distribution. Also, the production of  $\text{N}_2$  found in the product is not explained by the above mechanism. However, reactions of the type listed above can be expected to occur during vapor phase nitration and seem quite likely for the reasons cited.

## CONCLUSIONS

1. Vapor phase nitration of ethane with nitric acid can be carried out in a molten salt reactor by bubbling the reactants up through the salt.
2. An on-line gas chromatographic method of analysis has been developed which provides quantitative analysis of all the products resulting from the vapor phase nitration of ethane with nitric acid.
3. Conversions and yields are lower in a bubbling molten salt reactor than in a tubular reactor under the same conditions of mole ratio and temperature.
4. Conversion is a function of both temperature and mole ratio. Temperature has the greatest effect and conversion goes through a maximum with respect to temperature in the range from 400°C to 500°C. As temperature is increased the amount of oxidation products increases. Conversion also assumes a maximum with respect to mole ratio in the range from 3:1 to 17:1 hydrocarbon to acid.
5. The performance of the reactor and analytical equipment did not change significantly with time. There was no time dependent catalytic effect of metal surfaces and the salt composition remained the same.
6. Alkyl nitrite formation as an intermediate during the reaction is supported by the large amounts of oxidation products formed.

## RECOMMENDATIONS

1. Ethane nitration should be studied at very short retention times. This is not practical in the molten salt reactor. Perhaps a venturi type of reactor with an immediate quench would allow nitration to occur and eliminate further oxidation and decomposition.
2. The on-line analysis developed should be applied to ethane nitration in tubular reactors to obtain complete product distributions for the reaction when higher conversions result.

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**APPENDIX**

Table 5. Product distributions, mole fractions

Run	1	2	3	4	5	6	7	8	9	10
T °C	500	485.4	450	450	450	485.4	450	414.6	450	450
Hydrocarbon to acid, MR	10	5.05	3	10	10	14.95	10	5.05	10	10
C <sub>2</sub> H <sub>6</sub>	.83936	.67220	.10596	.82475	.80890	.84233	.83704	.89095	.92223	.93230
NO-NO <sub>2</sub>	.10014	.21422	.53693	.10915	.12779	.11182	.11300	.06355	.01894	.01862
H <sub>2</sub> O	.02096	.02824	.01731	.00953	.02578	.02847	.02920	.02532	.05316	.04324
CH <sub>3</sub> NO <sub>2</sub>	.00079	.00237	.00533	.00261	.00143	.00113	.00129	.00046	.00015	.00009
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	.00180	.00564	.01570	.00876	.00820	.00765	.00567	.00393	.00095	.00079
HCHO	.00036	.00084	.00171	.00031	.00004	.00012	.00005	.00005	.00002	.00006
C <sub>3</sub> CHO	.00208	.00435	.00604	.00169	.00219	.00062	.00196	.00080	.00030	.00053
CH <sub>2</sub> OH	trace	t	t	t	t	t	t	t	t	t
C <sub>2</sub> H <sub>5</sub> OH	.00025	.00024	.00060	.00031	.00029	.00015	.00019	.00039	.00000	.00009
CO	.02668	.05966	.30187	.03505	.02074	.00558	.00945	.01359	.00267	.00270
CO <sub>2</sub>	.00252	.00384	.00000	.00000	.00181	.00030	.00062	.00023	.00032	.00032
CH <sub>4</sub>	trace	t	t	t	t	.00000	.00000	.00000	.00000	.00000
H <sub>2</sub>	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
O <sub>2</sub>	.00000	.00003	.00030	.00015	.00004	.00006	.00002	.00002	.00005	.00006
N <sub>2</sub>	.00504	.00836	.00821	.00769	.00278	.00178	.00151	.00069	.00120	.00120

Table 5. (Continued)

Run	11	12	13	21	22	23	24	25	26	27
T °C	450	414.6	400	450	450	450	450	450	450	450
Hydrocarbon to acid, MR	17	14.95	10	10	10	10	10	10	10	10
C <sub>2</sub> H <sub>6</sub>	.62355	.96306	.95457	.85020	.92508	.89640	.89227	.89481	.87675	.87536
NO-NO <sub>2</sub>	.28518	.01597	.02649	.08951	.05018	.05875	.05867	.05210	.06156	.05412
H <sub>2</sub> O	.02804	.01136	.01072	.03279	.00760	.02524	.03333	.03485	.03846	.04820
CH <sub>3</sub> NO <sub>2</sub>	.00022	.00058	.00000	.00133	.00076	.00110	.00026	.00042	.00047	.00067
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	.00092	.00414	.00000	.00295	.00127	.00262	.00039	.00084	.00095	.00188
HCHO	.00004	.00000	.00000	.00009	.00010	.00008	.00005	.00011	.00025	.00011
C <sub>3</sub> CHO	.00059	.00067	.00020	.00298	.00193	.00185	.00144	.00135	.00139	.00188
CH <sub>3</sub> OH	trace	t	t	t	t	t	t	t	t	t
C <sub>2</sub> H <sub>5</sub> OH	.00004	.00013	.00020	.00221	.00152	.00138	.00079	.00098	.00111	.00121
CO	.05963	.00338	.00727	.01037	.00715	.00765	.00837	.01082	.01481	.01360
CO <sub>2</sub>	.00066	.00022	.00004	.00100	.00046	.00055	.00066	.00065	.00082	.00062
CH <sub>4</sub>	.00000	.00000	.00000	trace	t	.00000	.00000	t	.00000	.00000
H <sub>2</sub>	.00000	.00000	.00000	.00003	.00000	.00000	.00000	.00000	.00000	.00000
O <sub>2</sub>	.00004	.00006	.00002	trace	t	.00000	t	t	t	t
N <sub>2</sub>	.00110	.00042	.00050	.00656	.00395	.00441	.00386	.00306	.00342	.00234

Table 5. (Continued)

Run	31	32	33	34	35	41	42	43	44	45
T °C	450	450	450	450	450	500	485.4	450	450	450
Hydrocarbon to acid MR	5.05	5.05	5.05	5.05	5.05	10	5.05	3	10	10
C <sub>2</sub> H <sub>6</sub>	.79098	.78797	.79673	.80332	.77593	.88490	.82820	.82183	.90423	.90390
NO-NO <sub>2</sub>	.11167	.11053	.11354	.11373	.11199	.05321	.09576	.12075	.04545	.05142
H <sub>2</sub> O	.05355	.05146	.04252	.03958	.06015	.04168	.04141	.03993	.04115	.03358
CH <sub>3</sub> NO <sub>2</sub>	.00034	.00050	.00045	.00015	.00049	.00048	.00029	.00054	.00039	.00044
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	.00101	.00116	.00075	.00015	.00065	.00103	.00115	.00164	.00131	.00104
HCHO	.00030	.00096	.00063	.00071	.00072	.00086	.00124	.00016	.00002	.00003
CH <sub>3</sub> CHO	.00226	.00321	.00212	.00124	.00244	.00143	.00201	.00108	.00068	.00121
CH <sub>3</sub> OH	trace	.00003	.00003	t	t	t	t	t	t	t
C <sub>2</sub> H <sub>5</sub> OH	.00128	.00139	.00080	.00041	.00117	.00034	.00029	.00054	.00026	.00041
CO	.03244	.03657	.03566	.03413	.03893	.01005	.02059	.00915	.00335	.00488
CO <sub>2</sub>	.00236	.00215	.00292	.00247	.00297	.00177	.00319	.00032	.00016	.00015
CH <sub>4</sub>	trace	.00000	.00000	t	t	t	t	t	.00000	t
H <sub>2</sub>	trace	.00000	t	.00000	t	.00000	.00000	.00000	.00000	.00000
O <sub>2</sub>	trace	t	t	t	t	.00003	t	.00002	.00002	.00003
N <sub>2</sub>	.00378	.00407	.00385	.00412	.00456	.00422	.00587	.00402	.00295	.00290

Table 5. (Continued)

Run	46	47	48	49	50	51	52	53
T °C	485.4	450	414.6	450	450	450	414.6	400
Hydrocarbon to acid MR	14.95	10	5.05	10	10	17	14.95	10
C <sub>2</sub> H <sub>6</sub>	.93649	.88290	.83679	.89113	.90737	.91966	.92726	.91848
NO-NO <sub>2</sub>	.01847	.05522	.07847	.05680	.04943	.02958	.02768	.04201
H <sub>2</sub> O	.03760	.04608	.06791	.03861	.02680	.04344	.03844	.02505
CH <sub>3</sub> NO <sub>2</sub>	.00029	.00058	.00014	.00042	.00101	.00041	.00026	.00005
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	.00102	.00230	.00067	.00182	.00315	.00110	.00078	.00029
HCHO	.00029	.00003	.00000	.00000	.00002	.00000	.00000	.00000
CH <sub>3</sub> CHO	.00029	.00190	.00008	.00140	.00257	.00135	.00047	.00047
CH <sub>3</sub> OH	.00000	trace	t	t	t	t	t	t
C <sub>2</sub> H <sub>5</sub> OH	.00023	.00086	.00021	.00062	.00116	.00066	.00039	.00034
CO	.00261	.00636	.01286	.00658	.00684	.00234	.00347	.00697
CO <sub>2</sub>	.00029	.00015	.00002	.00008	.00005	.00005	.00003	.00003
CH <sub>4</sub>	trace	t	t	t	t	t	t	.00000
H <sub>2</sub>	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
O <sub>2</sub>	.00006	.00003	.00002	.00003	.00002	.00003	.00005	.00003
N <sub>2</sub>	.00235	.00359	.00283	.00252	.00156	.00137	.00117	.00629

