Vapor phase nitration of butane in a molten salt reactor

Dennis Lee Fear
Iowa State University

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Iowa State University of Science and Technology
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VAPOR PHASE NITRATION OF BUTANE IN A MOLTEN SALT REACTOR

by

Dennis Lee Fear

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

Approved:

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In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

Iowa State University Of Science and Technology Ames, Iowa

1964
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ABSTRACT

In this work, butane was nitrated continuously in the vapor phase using a molten salt reactor. Molten salt temperature was varied from 371°C to 482°C; mole ratio of hydrocarbon to nitric acid from 3.4 to 7.8; and residence time from 0.5 to 0.7 seconds. A statistical design was used to prevent the presence of a linear time trend from affecting comparisons between the different levels of each variable.

Nitroparaffin yields based on hydrocarbon consumed ranged from 26.7% to 84.3%, while conversions based on hydrocarbon fed ranged from 0.86% to 7.3%.

Nitroparaffin yields based on nitric acid consumed ranged from 38.7% to 74.4%, while conversions based on nitric acid fed ranged from 8.8% to 30.7%.

The mole per cent distribution of the nitroparaffins produced ranged as follows: nitromethane, 5.7 - 14.3; nitroethane, 14.4 - 38.7; 2-nitropropane, 0 - 0.12; 2-methyl-2-nitropropane, 0 - 3.0; 1-nitropropane, 2.4 - 13.4; 2-nitrobutane, 5.9 - 64.7; 2-methyl-1-nitropropane, 0 - 1.1; 1-nitrobutane, 10.4 - 40.9.

Gas chromatography techniques were developed which provided accurate quantitative analyses of the products. Material balances based on these analyses accounted for 99.1% (average) of the nitrogen fed and 96.5% (average) of the carbon fed.

An economic evaluation was made for a 14,000,000 lb./yr.
nitroparaffin plant. The estimated production cost per pound of product and per cent return on investment were determined as a function of butane cost. As the cost of butane decreased from $14.5\$/gal. to $5\$/gal., the production cost decreased from $14.43\$/lb. to $12.87\$/lb., while the return on investment increased from 7.53\% to 9.24\%.
INTRODUCTION

The nitroparaffins have been known and studied since 1872 when Meyer and Stüber (66) prepared a nitro derivative of isopentane by reacting amyl iodide and silver nitrite. Commercial prospects for the nitroparaffins were not realized until the early work of Hass, Hodge, and Vanderbilt on the vapor phase nitration of hydrocarbons appeared in 1936 (36). Several economic considerations in support of this work were: (1) the abundance and low cost of high purity, low molecular weight paraffinic hydrocarbons, (2) low cost tonnage nitric acid, and (3) relatively valuable nitration products.

A brief cost estimate of the raw materials needed to produce one pound of the lowest priced commercial nitroparaffin, 2-nitropropane, shows the economic feasibility of the nitration process. It is assumed in these calculations that nitric acid and propane react with 100% yield to produce 2-nitropropane. The calculations are summarized below:

\[
\text{Reaction: } \text{HNO}_3 + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_7\text{NO}_2 + \text{H}_2\text{O}
\]

<table>
<thead>
<tr>
<th></th>
<th>Moles</th>
<th>Lbs.</th>
<th>Lbs./lb. NP</th>
<th>Cost/lb. NP</th>
<th>Selling price/lb. NP</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>63</td>
<td>1.026</td>
<td>$0.040^a</td>
<td>$0.16</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>44</td>
<td>0.494</td>
<td>$0.00582^b</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>89</td>
<td>1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>18</td>
<td>0.206</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

\(^a\)Calculated at current cost, $3.90/100 lbs. of 100% acid (72).

\(^b\)Calculated at current cost, $0.05/gal. of 100% propane (71) using 4.2 lbs./gal. (23 p. 46).
This shows a profit of $0.160 - $0.046 or $0.114 per pound of 2-nitropropane produced not counting conversion costs.

The approximate distribution of the products produced from the commercial nitration of propane and their current market prices are shown in Table 1. It can be seen from the table that the production of nitroparaffins other than 2-nitropropane will further increase profits.

Table 1. Current prices and typical nitroparaffin product distribution from the nitration of propane

<table>
<thead>
<tr>
<th>Nitroparaffin (NP)</th>
<th>Distribution, a weight %</th>
<th>Current price, b cents per lb. in carload lots</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitromethane (NM)</td>
<td>19</td>
<td>28</td>
</tr>
<tr>
<td>Nitroethane (NE)</td>
<td>9</td>
<td>29</td>
</tr>
<tr>
<td>1-Nitropropane (1-NP)</td>
<td>28</td>
<td>27</td>
</tr>
<tr>
<td>2-Nitropropane (2-NP)</td>
<td>44</td>
<td>16</td>
</tr>
</tbody>
</table>

a Approximate, typical, calculated from (12).

b As of May 4, 1964 (72).

The only major U. S. producer of nitroparaffins using vapor phase nitration is the Commercial Solvents Corporation. Their plant started in 1955 has a rated capacity of 10,000,000 pounds of nitroparaffins per year (21). Propane and constant boiling (67%) nitric acid are the feed materials.
Since nitroparaffins have become available commercially, many new uses have been developed for these compounds, and it seems certain that many more will be adopted. Nitroparaffins are of value as industrial solvents since they are miscible with most organic substances. They are potentially useful as components in engine and rocket fuels. A large number of useful compounds are derived from the nitroparaffins. Among these are the aminoalcohols, nitroalcohols, nitroolefins, hydroxylammonium salts, amines, alkaterges and oximes.

A great many combinations of hydrocarbon, nitrating agent, and reactor design are possible in the vapor phase nitration of the lower paraffinic hydrocarbons. Several considerations led to the choice of the particular system used in this research.

Butane was selected for use as the hydrocarbon. One advantage of using butane instead of propane is that the same nitroparaffins are obtained from butane as from propane plus four additional nitroparaffins. These additional products are: 1-nitrobutane (1-NB), 2-nitrobutane (2-NB), 2-methyl-1-nitropropane (2-M-1-NP), and 2-methyl-2-nitropropane (2-M-2-NP). The nitrobutanes thus produced may be very useful as chemical intermediates. Studies of butane nitration in tubular reactors have been made by Hass, Hodge, and Vanderbilt (36) and by Bachman, Hass, and Addison (8), and a study of butane nitration in a molten salt reactor has been made by
Adams (1). These provide data for comparison purposes.

Butane has not been as fully investigated as propane presumably because of the difficulties involved in analyzing the nitrination products. In some of the previously published research only the average molecular weight of the bulk nitro-products has been reported because of the difficulty of separation, identification, and quantitative determination of individual compounds. Adams (1) determined the distribution of nitroparaffin products with good success by employing gas-liquid partition chromatography techniques. A portion of the present work has been devoted to developing highly sensitive chromatography techniques which will permit the complete quantitative analysis of all possible reaction products from the nitrination of butane. Such an analysis could also provide suitable information for determining some of the reaction mechanisms.

Nitrating agents which have been used by previous investigators are nitrogen dioxide (9, 24, 34, 89), nitric oxide (33), and nitric acid (12, 38). Some difficulty has been experienced with corrosion of equipment used to vaporize nitric acid (21, 50, 62). To avoid this problem the acid can be vaporized in the reaction zone where its heat of vaporization can be used to help control the reaction temperature. This technique is used successfully in commercial production of the nitroparaffins (21). The water introduced with the
nitric acid adds to the analytical difficulties and complicates the calculations. However, conversions based on nitrating agent are higher when nitric acid is employed. This information along with the facts that nitric acid is used in the commercial process and is readily available in the laboratory led to its selection as the nitrating agent to be used in this research.

Tubular reactors constructed from ordinary materials have exhibited corrosion and a gradual poisoning effect (3). To avoid these effects, pyrex, gold-lined, platinum-clad, and silica apparati have been used but these materials are expensive for large scale vessels. The majority of the laboratory scale vapor phase nitration studies have utilized pyrex tubular reactors. Several patents describe the use of alkali and alkaline earth materials which, when introduced into the reaction vessel, prevent reaction inhibiting effects from occurring (44, 45, 61).

To avoid catalytic effects and at the same time better temperature control, some work has been done with molten salt filled reaction vessels (1, 3, 20, 43). The molten nitrate salts employed are presumed to be noncatalytic. In the commercial plant temperature control is maintained by introducing nitric acid into a preheated hydrocarbon stream either at multiple points (75) or in stages (21).
The objectives of this research were threefold. These were: (1) to determine the specific effects of temperature, residence time, and mole rates of hydrocarbon to nitric acid on the vapor phase nitration of butane using a molten salt reactor, (2) to develop an analytical method for the complete and accurate analysis of products resulting from vapor phase butane nitration, and (3) to obtain information about the mechanisms of reaction for butane nitration by using the product analysis data.
The nitro alkanes were known for a very long time before they became industrially important. As early as 1844, 1, 1-dinitro alkanes were prepared from nitric acid and ketones (80, p. 429), but it was much later before the correct structure of these compounds was determined. Chloropicrin, or trichloronitromethane, the first mononitro alkane to be described, was prepared by Stenhouse (86) in 1848 by the chlorination of picric acid. Bromopicrin was synthesized in 1854 (87) by a similar method. Mills (67), in 1871, reported the first successful nitration of an aliphatic compound when he obtained chloropicrin from chloroform and nitric acid. Research in the chemistry of nitroparaffins received its greatest stimulus in 1872 when Meyer and Stüber (64, 65, 66) reacted amyl iodide with silver nitrite and obtained a mixture of nitropentane and amyl nitrite.

Along with the development of many chemical industries based on the nitration of aromatic compounds came an ever increasing interest in the nitration of aliphatic hydrocarbons. In 1880, Beilstein and Kurbatov (14, 15) performed the first direct nitration of a paraffin. This occurred as a by-product of a purification technique in which a heptane fraction was treated with nitric acid producing a mixture of
mononitroheptanes. Many stimulating papers describing the nitrination of paraffins were subsequently reported by Konovalov, Markovnikov, Worstall, Francis and Young, Nametkin and others. An excellent review of these papers is given by Hass and Riley (39) so no detailed discussion is given here. However, two of the many researchers established important points. Konovalov (51, 52) working with hexane in a sealed tube showed that increasing the temperature increased the yield. Markovnikov, working in a different direction, compared the effect of mixed sulfuric-nitric acid to that of nitric acid alone. His work (59, 60) indicated that the mixed acid approach customarily used for the nitrination of aromatic hydrocarbons caused considerable degradation of the nitroparaffins produced. This emphasized the need for a new method, not an extension of an old one.

From the variety of liquid phase studies carried out in this period some generalizations can be made: polynitro-paraffins are predominant; hydrogen atom substitution rates are in the order tertiary, secondary, primary; there is severe oxidation; and reaction is slow.

In the 1930's with the advent of large quantities of the lower molecular weight paraffinic hydrocarbons becoming available from the developing petroleum industry and cheap nitric acid from the ammonia oxidation process, Dr. H. B. Hass (21)
at Purdue University started an investigation of the vapor
phase nitration of the lower alkanes. The initial projects
by Hodge and Vanderbilt working with isobutane showed the
practicality of vapor phase nitration (36). Later work with
butane in a vapor phase reaction showed that all eight possible
mononitroparaffins were obtained (37), which was contrary to
liquid phase results. Since these initial investigations,
vapor phase nitration has been studied by many persons who
have investigated various alkanes, nitrating agents, catal-
ysts, and types of reactors. These are further discussed un-
der the appropriate headings in the remainder of this section.

Conversion and Yield

The results of most vapor phase nitration research are
reported in terms of conversion and yield. These terms can
be confusing since both can be based on either hydrocarbon
or nitrating agent. In some cases, it is not made clear
whether the reactants are considered the input quantities or
only the amount of material undergoing reaction. In this work,
the term conversion will mean the molar ratio of product pro-
duced/reactant charged.

Conversion of nitrating agent in tubular reactors has
been found to increase with increased mole ratio of paraffinic
hydrocarbon to nitrating agent (41). With methane and nitric
acid, for example, a mole ratio of 7 produces a nitric acid
conversion of 14%, while a mole ratio of 13 produces a conversion of 26% (36). However, extrapolation to infinite ratio does not result in 100% conversion.

The term yield, in this work, will mean the molar ratio of product produced/reactant consumed which is the usual meaning used in previously published vapor phase nitration research. The reason for this distinction between conversion and yield in vapor phase nitration work is inherent in the chemistry of the process. Conversions based on hydrocarbon introduced would not be very descriptive by themselves since a large excess of hydrocarbon to nitrating agent is used to increase the conversion of nitrating agent. For example, many of the hydrocarbon yields reported to have been 30-50% would correspond to conversions of 1% or less.

Types of Reactors

**Tubular**

The majority of vapor phase nitration studies have been conducted in tubular reactors. Most of these were constructed of glass but stainless steel has been used on occasion (3, 34, 42). Copper and carbon steel reactors each have been tested by Albright et al. (3). Conversions rapidly dropped with time of operation to zero in a copper reactor while in a mild steel reactor they gradually increased to those obtained in glass reactors. In stainless steel reactors, conversions
gradually decreased from those obtained in glass reactors. Although this phenomenon is not understood, it can be arrested by treating the reactor surfaces with solutions of alkali or alkaline earth salts (44, 45).

The effects of surface to volume ratio have been investigated in glass reactors by Bachman and co-workers (7, 9, 11). Surface to volume ratios from 4 cm$^{-1}$ to 300 cm$^{-1}$ produced no observable trends in the distribution of nitroparaffin products.

**Molten salt**

Molten salt reactors were developed in an effort to provide better temperature control of the reaction and to avoid the catalytic effects observed in metallic tubular reactors. The use of nitrate salts stems from the earlier work of Hodge (44) and Swallen (45) who found that these salts prevented the gradual poisoning effects occurring in stainless steel nitration vessels.

In 1952 Hill (43) first used the technique of bubbling the reaction mixture through a mixture of molten sodium and potassium nitrate salts. A maximum conversion of 15.3% was reported using propane and nitric acid. Albright et al. (3) found tubular reactors gave slightly higher conversions than did molten salt reactors. Coldiron et al. (20) report that they were able to run at propane to nitric acid ratios of one to one in a molten salt reactor without explosions previously
reported (38) at ratios below two to one in tubular reactors. This was attributed to better temperature control. Varying the mole ratios between two to one and twenty to one had little effect on conversion. Adams (1) nitrated butane in a molten salt reactor of the type used in the present investigation.

Paraffins Nitrated in the Vapor Phase

Methane

Although difficulty has been experienced by several researchers in nitrating methane (2, 36), two patents by Landon (54, 55) in 1939 claim successful nitration of methane in either ferrous or non-ferrous tubular reactors. A high temperature-short contact time process was employed which is typical of successful vapor phase nitration. The maximum reported conversion of nitrating agent was only 8.8%. Boyd and Hass (16) later investigated methane nitration and were able to improve the conversion to 13%. In subsequent work Hass et al. (41) obtained a maximum conversion of 26%. Methane was further studied by Alexander (4, 33) in work which emphasized the effect of additives. More recently, in 1959, Schay and Giber (77) made a very close study on the nitration of methane and reported a maximum conversion of 15.8%.

Ethane

Ethane was the object of a study by Hibshman et al. (42) in which the nitrated products were 27% nitromethane, the
balance being nitroethane. This aroused great interest at the time since the originally proposed mechanism (63) did not account for cleavage of the carbon chain to produce lower nitroparaffins. Ethane was also briefly studied by Hass et al. (36), and was the subject of a patent (35).

Propane

Propane has been studied the most extensively of all the hydrocarbons nitrated in the vapor phase. In all of the studies the first four mononitroparaffins were always produced. Urbánski and Slón (90), using a low temperature process, found some dinitroparaffins. Hass et al. (34) nitrated propane under similar conditions but at a higher temperature several years later and were unable to find any polynitroparaffins.

Nitration of propane using nitrogen dioxide as a nitrating agent has been reported by Hass et al. (34) and Hass and Alexander (33). Bachman et al. (9) and Chupp (19) nitrated propane with nitrogen dioxide using chlorine as a catalyst.

Using nitric acid, Bachman et al. (7) studied the effect of adding chlorine and Alexander (4) studied the effect of adding oxygen. Bachman and Pollack (12) and Bachman and Kohn (11) checked the effects of adding both oxygen and chlorine. All of these investigators used tubular reactors but differ-
ent reaction conditions.

Propane has also been nitrated in molten salt reactors. Coldiron et al. (20) used propane alone while Hill (43) and Albright et al. (3) added oxygen to the reaction mixture.

**Butane**

The initial vapor phase experiment (36) in this country was directed toward producing only a single mononitroparaffin. Inasmuch as in liquid phase nitrations, tertiary hydrogen atoms were most readily replaced, attempts were made to nitrate isobutane in a sealed tube. No reaction occurred at 115°C but a smooth reaction occurred at 150°C to give the expected tertiary nitrobutane. Conversions of nitrating agent were about 22%. A flow process was then tried on isobutane and at least four mononitroparaffins (32) were produced which was most unexpected.

The importance of the tertiary hydrogen atom in vapor phase reactions was then tested by nitrating n-butane. This time five mononitroparaffins were found showing that the order of attack was quite different from that of the liquid phase reactions. This new process was patented (37) in 1934. Tests runs on propane and ethane, though with diminishing yields, confirmed that derivatives of the lower homologs were obtained in each case. This was also evidence that nitration becomes easier as the homologous series is ascended.
A mixture of isobutane and n-butane was nitrated by Levy (57, 58) using catalysts. He reported the presence of 2,3-dinitrobutane in the reaction products but Hass and Shechter (40) were unable to verify this result.

The first work on n-butane in which any of the oxygenated by-products were even qualitatively identified was by Addison (2, 8). More recently Adams (1) nitrated n-butane in a molten salt reactor and obtained quantitative data on some of the oxygenated by-products.

Pentane

Hass and Patterson (38) nitrated n-pentane in 1938 and a year later isopentane data were published by Seigle and Hass (79). The primary concern of these researchers was the qualitative identification of the nitro compounds. In each case seven mononitroparaffins were obtained. Several generalizations were noted which distinguish vapor phase from liquid phase nitration of paraffinic hydrocarbons. They were:

1. Either any hydrogen or any alkyl group may be replaced by a nitro group.
2. At high temperatures (above 250°C), polynitroparaffins are generally not produced.

Neopentane and neohexane

These two substances were nitrated in the vapor phase by Howe and Hass (46) at temperatures of 406°C - 418°C. The neohexane (2, 2-dimethylbutane) study produced products quite
different from those found by Markovnikov (60) who nitrated the compound at 100-125°C and reported 2, 2-dimethyl-3-nitrobutane to be the only nitroparaffin found. A total of eight mononitroparaffins were found in this study. The ratio of fissioned to hydrogen substituted products was 4:1. In the neopentane (2, 2-dimethylpropane) study this ratio was only 1.63:1.

Pressure Effects

Very little data exists on this subject. Hass et al. (41) working with methane and nitric acid obtained increased conversions at 100 psig. over those obtained at one atmosphere. When the pressure was increased from 100 psig. to 1000 psig. the conversion decreased. The rate of reaction increased at both pressures as evidenced by lower optimum temperatures and contact times. Temperature control became more critical as the pressure increased.

Temperature Effects

From the data that have been published it is possible to draw several general conclusions about the effects of temperature (40). Conversions increase with temperature until some optimum temperature is reached (about 425°C for propane) and then decrease with further increases in temperature. If contact time and reaction temperature are carefully matched,
the conversion will be approximately the same. The rate of substitution of the primary, secondary, and tertiary positions approaches equality as the temperature increases and the ratio of fission products to substitution products increases. Oxidation and decomposition become increasingly important at higher temperatures.

Catalysts

Heterogeneous

From the materials used in reactors, it may be presumed that pyrex glass, silica, platinum, and gold are essentially non-catalytic with respect to either nitration or oxidation. Copper has been found to be very detrimental to nitration while mild steel gives poor nitration conversions that improve with time (3). Stainless steels gradually become catalytic with respect to oxidation (3) unless protected by nitrate salts (44, 45).

Several patents by Levy (56, 57, 58) claim the use of borosilicate glass containing antimony and/or arsenic catalyzes the formation of nitroparaffins. However, attempts to verify this work have been unsuccessful (40). Bachman et al. (9) have shown that ferric oxide, boric oxide, and 1-propanol do not have a beneficial effect on nitration. Hass et al. (36) report that aluminum nitrate has no effect while silica gel and platinum oxide promote oxidation.
In summary, the literature examined indicates that no satisfactory heterogeneous catalysts have been found for vapor phase nitration reactions. Those catalysts that show any activity have increased the competing oxidation reactions as much or more than the nitration reaction.

**Homogeneous**

In this class of catalysts oxygen, chlorine, and bromine are the most important. These compounds generally increase conversions based on nitrating agent at the expense of yields based on hydrocarbon. Oxygen added to a butane reaction mixture in a tubular reactor increases the amount of lower nitro-paraffins formed (8). A great deal of work has been done using these catalysts and they will be discussed in more detail later in this section.

Nitric oxide decreases conversion (11, 33), probably by action as a chain stopper. This effect has been nullified by the use of halogens or oxygen.

The use of ozone, peroxides, ultraviolet irradiation, and silent electric discharge in the nitration of propane has been recently studied by Bachman and Standish (13). Conversions of nitrating agent as high as 69.8% were reported when oxygen and ozone were added to the reaction mixture. However, yields based on hydrocarbon were considerably lower than those obtained when oxygen and ozone were not used. The
use of peroxides, ultraviolet irradiation, and silent electric discharge, decreased conversions and caused severe oxidation and degradation of the products.

The use of gamma radiation has been found to increase conversions of nitric acid in the nitration of propane (73). Exposure of liquid propane to gamma radiation for 40 to 50 hours before vaporization and reaction increased nitric acid conversion to 31% from 27% under optimum conditions without radiation. Addition of oxygen to the mixture raised nitric acid conversion to 36% in nonirradiated runs. Combining oxygen addition with irradiation gave conversions as high as 39.5%.

Mechanism of Reactions in Vapor Phase Nitration

General

Partial mechanisms for the vapor phase nitration of paraffin hydrocarbons have been proposed but the exact mechanism is uncertain. Experimental evidence supports the theory that vapor phase nitration proceeds by free radical mechanisms rather than by ionic reactions. Substances which normally catalyze ionic reactions, such as metallic oxides, do not increase the conversion over that obtained in glass reactors. In fact their presence usually decreases the yield (9, 36). Tetraethyl lead, which generates ethyl radicals when heated,
undergoes vapor phase nitration with nitric acid to produce nitroethane (39, 63). In addition, most gas phase reactions proceed by free radical mechanisms.

Two possible types of free radical mechanisms have been proposed for the vapor phase nitration of paraffin hydrocarbons using nitric acid. Bachman et al. (6) have proposed a radical step reaction mechanism consisting of the following reactions.

\[
\begin{align*}
HNO_3 & \rightarrow \cdot OH + NO_2 \\
RH + \cdot OH & \rightarrow R\cdot + H_2O \\
R\cdot + NO_2 & \rightarrow RNO_2
\end{align*}
\]

It has been questioned if the rate of decomposition of nitric acid (48) in reaction 1 is sufficient to supply the NO₂ radical consumed in reaction 3 at the experimental rate of nitroparaffin formation.

A short chain reaction has been proposed by Albright et al. (3), Alexander (4), and McCleary and Degering (63). 

\[
\begin{align*}
HNO_3 & \rightarrow \cdot OH + NO_2 \\
RH + \cdot OH & \rightarrow R\cdot + H_2O \\
R\cdot + HNO_3 & \rightarrow RNO_2 + \cdot OH
\end{align*}
\]

Reaction 1 is the starting step, and reactions 2 and 4 make up the chain. Reaction 4 probably proceeds via an addition
complex of nitric acid and the alkyl radical.

**NO₂ as a nitrating agent**

The basic reactions for the nitration of hydrocarbons using NO₂ are given by Topchiev (89).

\[
\begin{align*}
\text{RH} + \text{NO}_2 & \rightarrow \text{R}^* + \text{HNO}_2 \quad (5) \\
\text{R}^* + \text{NO}_2 & \rightarrow \text{RNO}_2 \quad (3)
\end{align*}
\]

Reactions 3 and 5 show that two moles of NO₂ are required for each mole of nitroparaffins produced. The nitrous acid formed in reaction 5 will decompose under nitrating conditions according to reaction 6 (6).

\[
2\text{HNO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \quad (6)
\]

These reactions probably account for the fact that nitric acid is a better nitrating agent than nitrogen dioxide.

**Production of lower nitroparaffins**

The vapor phase nitration of hydrocarbons produces significant quantities of lower nitroparaffins. At nitrating temperatures and reaction times used, the formation of alkyl radicals by pyrolysis of saturated hydrocarbons is negligible (3, 83). Also the direct cleavage of the C-C bond by NO₂ attack under these conditions is extremely unlikely (17).

The best explanation for the production of lower nitro-
paraffins is that alkyl nitrites are formed and then decomposed to yield lower alkyl radicals. The lower alkyl radicals are then nitrated to produce lower nitroparaffins. A mixture of nitroparaffins and alkyl nitrites are formed in the reaction between alkyl halides and silver nitrite (53, 70). It seems likely that alkyl nitrites are also formed in vapor phase nitration reactions.

Nitrogen dioxide can be represented by resonance hybrids. Those given by Pauling (69, p. 348) are shown below.

\[
\begin{align*}
\overset{\circ}{O} & \quad N \quad \overset{\circ}{O} \\
\overset{\circ}{O} & \quad N \quad \overset{\circ}{O}
\end{align*}
\]

These resonance hybrids show that an electron is well distributed between the oxygen atoms and the nitrogen atom. If an alkyl radical reacts with NO\textsubscript{2} when the electron density about the nitrogen atom is low, a nitroparaffin will be formed. However, if the alkyl radical reacts with NO\textsubscript{2} when the electron density about the nitrogen is high, an alkyl nitrite results. It is also possible that alkyl radicals react with nitric acid to form alkyl nitrites in a manner similar to reaction 4.

Alkyl nitrites are unstable at nitration temperatures. At low nitrite concentrations the alkyl nitrites decompose into lower hydrocarbons, aldehydes, and nitric oxide (29, 74, 84, 85). Rice and Rodowskas (74) suggest the following
reaction mechanism for the decomposition of ethyl nitrite at higher concentrations.

\[ \text{CH}_3\text{CH}_2\text{ONO} \rightarrow \text{NO} + \text{CH}_3\text{CH}_2\text{O}^* \]  
\[ (7) \]

\[ \text{CH}_3\text{CH}_2\text{O}^* + \text{CH}_3\text{CH}_2\text{ONO} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CHONO} \]  
\[ (8) \]

\[ \text{CH}_3\text{CHONO} \rightarrow \text{NO} + \text{CH}_3\text{CHO} \]  
\[ (9) \]

If the decomposition of ethyl nitrite occurs at low concentrations, the following reaction scheme is suggested.

\[ \text{CH}_3\text{CH}_2\text{ONO} \rightarrow \text{NO} + \text{CH}_3\text{CH}_2\text{O}^* \]  
\[ (7) \]

\[ \text{CH}_3\text{CH}_2\text{O}^* \rightarrow \text{HCHO} + \text{CH}_3^* \]  
\[ (10) \]

\[ \text{CH}_3^* + \text{CH}_3\text{CH}_2\text{ONO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CHONO} \]  
\[ (11) \]

\[ \text{CH}_3\text{CHONO} \rightarrow \text{NO} + \text{CH}_3\text{CHO} \]  
\[ (9) \]

When the partial pressure of ethyl nitrite is greater than one third atmosphere, reaction 8 occurs to the almost complete exclusion of reaction 10. At ethyl nitrite pressures of about 1 millimeter of mercury reaction 10 predominates.

Any alkyl radical could react with an alkyl nitrite in a reaction similar to reaction 11. This mechanism also accounts for some of the oxidation products formed by side reactions.

Gray (30) suggests the following mechanism for the decomposition of propyl and butyl nitrites.
The direct decomposition of higher alkyl radicals, such as reactions 21, 22, and 23, below, possibly accounts for some of the production of lower alkyl radicals at high temperatures.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{ONO} & \rightarrow \text{NO} + \text{CH}_3\text{CH}_2\text{CH}_2\text{O}^\cdot & (12) \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^\cdot & \rightarrow \text{CH}_3\text{CH}_2^\cdot + \text{HCHO} & (13) \\
\text{CH}_3\text{CH}(\text{ONO})\text{CH}_3 & \rightarrow \text{NO} + \text{CH}_3\text{CH}(\text{O})\text{CH}_3 & (14) \\
\text{CH}_3\text{CH}(\text{O})\text{CH}_3 & \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3^\cdot & (15) \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{ONO} & \rightarrow \text{NO} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}^\cdot & (16) \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}^\cdot & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^\cdot + \text{HCHO} & (17) \\
\text{CH}_3\text{CH}_2\text{CH}(\text{ONO})\text{CH}_3 & \rightarrow \text{NO} + \text{CH}_3\text{CH}_2\text{CH}(\text{O})\text{CH}_3 & (18) \\
\text{CH}_3\text{CH}_2\text{CH}(\text{O})\text{CH}_3 & \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{CH}_2^\cdot & (19) \\
\text{CH}_3\text{CH}_2\text{CH}(\text{O})\text{CH}_3 & \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{CH}_3^\cdot & (20)
\end{align*}
\]

McCleary and Degering (63) examined the gases produced from the nitration of propane, butane, pentane, and isopentane for the presence of olefins. In each case studied, all the olefins were found that would be predicted if it is assumed that
the free alkyl radicals decompose. However, Adams (1) was unable to detect the presence of any olefins in the products of the vapor phase nitration of butane.

Decomposition of nitric acid

Johnson et al. (47, 48, 49) have studied the decomposition of nitric acid vapor at 400°C and propose the following mechanisms.

\[
\begin{align*}
\text{HNO}_3 & \rightarrow \cdot \text{OH} + \text{NO}_2 \quad (1) \\
\cdot \text{OH} + \text{NO}_2 & \rightarrow \text{HNO}_3 \quad (24) \\
\cdot \text{OH} + \text{HNO}_3 & \rightarrow \text{H}_2\text{O} + \cdot \text{NO}_3 \quad (25) \\
2\cdot \text{NO}_3 & \rightarrow 2\text{NO}_2 + \text{O}_2 \quad (26) \\
\cdot \text{NO}_3 & \rightarrow \text{NO} + \text{O}_2 \quad (27) \\
\cdot \text{NO}_3 + \text{NO} & \rightarrow 2\text{NO}_2 \quad (28)
\end{align*}
\]

At nitration temperatures the decomposition of NO\textsubscript{2} by reaction 29 is fairly slow compared to the initial rate of decomposition of nitric acid (76).

\[
2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2 \quad (29)
\]

Inhibiting effect of nitric oxide

The vapor phase nitration reaction is strongly inhibited by the addition of nitric oxide (33, 78). At low nitric oxide
concentrations the inhibiting effect increases with increasing nitric oxide concentrations. Above a certain concentration further increases in the nitric oxide concentration do not increase the inhibiting effect.

Nitric oxide reacts readily with alkyl radicals removing them from the system and breaking the chain reactions in which they are involved (25, 27, 81) as shown in reaction 30. The reaction with hydroxy radicals, as shown in reaction 31, also accounts for the inhibiting effect of nitric oxide.

\[
\begin{align*}
\text{R}^* + \text{NO} & \rightarrow \text{RNO} \quad (30) \\
\cdot\text{OH} + \text{NO} & \rightarrow \text{HNO}_2 \\
\end{align*}
\]

The RNO compounds probably rearrange and decompose. Bachmann and Standish (13) suggest the following mechanism.

\[
\begin{align*}
\text{RCH}_2^* + \text{NO} & \rightarrow \text{RCH}_2\text{NO} \quad (32) \\
\text{RCH}_2\text{NO} & \rightarrow \text{RCH} = \text{NOH} \quad (33) \\
2\text{RCH} = \text{NOH} + \text{NO}_2 & \rightarrow 2\text{RCH} = \text{O} + \text{NO} + \text{N}_2 + \text{H}_2\text{O} \quad (34)
\end{align*}
\]

**Decomposition of aldehydes**

Formaldehyde and acetaldehyde are produced in vapor phase nitration reactions as previously shown. The aldehydes, particularly formaldehyde, are very reactive and could form other products under nitration conditions. A reaction for the combination of acetaldehyde and formaldehyde is given by
Walker (92, p. 223).

\[ \text{HCHO} + \text{CH}_3\text{CHO} \xrightarrow{300^\circ C} \text{CH}_2\text{CHCHO} + \text{H}_2\text{O} \]  \hspace{1cm} (35)

Topchiev (89) studied the nitration of alkanes with nitrogen dioxide and proposed the following reactions for the decomposition of formaldehyde.

\[ \text{HCHO} + \text{NO}_2 \rightarrow \text{HCO} + \text{HNO}_2 \]  \hspace{1cm} (36)

\[ \text{HCO} + \text{NO}_2 \rightarrow \text{H} \cdot + \text{CO}_2 + \text{NO} \]  \hspace{1cm} (37)

\[ \text{HCO} + \text{NO}_2 \rightarrow \text{HCO} \cdot + \text{CO} + \text{NO} \]  \hspace{1cm} (38)

With nitric acid present, reaction 39 could be added to this series due to the production of hydroxyl radicals via reaction 1.

\[ \text{HCHO} + \cdot\text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O} \]  \hspace{1cm} (39)

Giddings and Shin (28) give the following mechanism for the thermal decomposition of acetaldehyde at 400\(^\circ\)C.

\[ \text{CH}_3\text{CHO} \rightarrow \text{CH}_3 \cdot + \cdot\text{CHO} \]  \hspace{1cm} (40)

\[ \text{CH}_3 \cdot + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO} \cdot \]  \hspace{1cm} (41)

\[ \text{CH}_3\text{CO} \cdot \rightarrow \text{CH}_3 \cdot + \text{CO} \]  \hspace{1cm} (42)

In the presence of nitric acid, decomposition would probably be accelerated by reaction 43.
Decomposition of nitroparaffins

The optimum temperature effect observed in the production of nitroparaffins has sometimes been explained by the fact that the decomposition of nitroparaffins becomes significant at temperatures above the optimum. Taylor and Vesselovsky (88) found that the half-life of nitromethane at 420°C is 4 minutes and suggested the following mechanism.

$$\text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3\text{NO}^- + \text{O}^- \quad (44)$$

$$\text{CH}_3\text{NO}^- \rightarrow \text{CH}_3^- + \text{NO} \quad (45)$$

Even assuming a correspondingly greater degree of instability for the higher members of the series, pyrolysis should be negligible at contact times generally used in the vapor phase nitration of hydrocarbons. However, Taylor and Vesselovsky also found that the addition of oxygen greatly increased the rate of decomposition of nitromethane to yield carbon dioxide, water, and nitrogen. Since the nitrating agents employed in nitroparaffin production are also strong oxidizing agents, the rate of decomposition of nitroparaffins by oxidation is probably much greater than the rate of decomposition by pyrolysis.

Gray et al. (31) investigated the thermal decomposition of nitroethane and 1-nitropropane. At 430°C nitroethane was
13% decomposed in 2.1 seconds while 1-nitropropane was 20% decomposed in 4.2 seconds. These rates are large enough to account for some of the loss in nitroparaffin production when the temperature is above the optimum. No less than ten different reaction products were found in the decomposition of nitroethane which indicates a very complex reaction mechanism.

**Effect of adding oxygen**

The addition of oxygen to vapor phase nitration mixtures increases the conversion. As the amount of oxygen added to the mixture is increased, the conversion increases to a maximum and then decreases (8, 9, 12). When nitric acid is the nitrating agent, the addition of oxygen decreases the yield of nitroparaffins based on hydrocarbon consumed (8). When nitrogen dioxide is the nitrating agent, the addition of oxygen increases the yield (9).

Bachman et al. (6) have suggested that oxygen may promote the formation of free radicals by a mechanism similar to one suggested by Walsh (93) for the vapor phase oxidation of propane.

\[
(CH_3)_2CH_2 + O_2 \rightarrow (CH_3)_2CHOOH
\]  
(46)

\[
(CH_3)_2CHOOH \rightarrow (CH_3)_2CHO \cdot + \cdot OH
\]  
(47)

\[
(CH_3)_2HCOOH \rightarrow (CH_3)_2CO + H_2O
\]  
(48)

\[
(CH_3)_2CHO \cdot \rightarrow CH_3CHO + CH_3 \cdot
\]  
(49)
The maximum in the conversion can be accounted for by the reaction of alkyl radicals with the increased amount of oxygen according to reaction 51.

**Effect of adding bromine or chlorine**

The addition of bromine or chlorine to the vapor phase nitration mixture can increase both yield and conversion (10, 11, 12). Optimum concentrations exist for bromine and chlorine which give a maximum conversion and yield.

Bachman et al. (10) suggest the following mechanism when bromine or chlorine are added to the reaction mixture where X is a molecule of either chlorine or bromine.

\[ X_2 \rightarrow 2X^* \]  \hspace{1cm} (53)

\[ RH + X^* \rightarrow HX + R^* \]  \hspace{1cm} (54)

\[ R^* + X_2 \rightarrow RX + X^* \]  \hspace{1cm} (55)

The hydrogen halides and alkyl halides are probably oxidized by the nitrating agent thus regenerating the halogen catalyst (11).
EXPERIMENTAL

Description of the Pilot Plant

General

The pilot plant used for this study consisted of five basic sections which were: (1) the butane system, (2) the nitric acid system, (3) the reactor, (4) the product recovery system, and (5) the refrigeration system. Figure 1 and Figure 2 present different views of the pilot plant. A schematic flow diagram is shown in Figure 3.

All of the systems in the pilot plant operated on a continuous basis. Production was limited by the capacity of the nitric acid system which had a maximum controllable output of 220 grams per hour of 70% nitric acid. Assuming a 40% conversion based on nitric acid, this would correspond to a maximum production rate of about 90 grams per hour of nitroparaffin product.

Stainless steel and glass were the major materials of construction for the nitric acid and product recovery systems. Tygon tubing was used in the product recovery system for the transport of gaseous products. Brass and copper were used in the butane system. The reactor was made of cast iron and mild steel.

For safety reasons, the reactor section of the pilot plant was enclosed on three sides by a blast shield. One
Figure 1. Photograph of the control panel
Figure 2. Photograph of the product collection system
Figure 3. Schematic flow diagram of the pilot plant

Legend and symbols

| A | Glass Funnel          | R | Product condenser     |
| B | Graduated Acid Reservoir | S | Separatory Funnel     |
| C | Centrifugal pump       | T | Liquid product        |
| D | Filter                 | U | Pyrex condenser       |
| E | Air column             | V | Flask                 |
| F | Rotameter              | W | Hg manometer          |
| G | Heat exchanger         | X | Plastic balloon       |
| H | Butane Tank            | Y | Glass bottle          |
| J | Tank Regulator         | Z | Water overflow        |
| K | Line Regulator         |   |                        |
| L | Rotameter              |   |                        |
| M | Hg Manometer           |   |                        |
| N | Reactor                |   |                        |
| P | Thermocouple           |   |                        |
| Q | Hg manometer           |   |                        |

Legend and symbols (continued):

- Blunt needle valve
- Fine needle valve
- 2 way stopcock
- 3 way stopcock
- Hg thermometer
- Bourdon gauge
side opened toward a window to provide pressure relief if ever needed. The main portions of the shield were made of 1/4 in. steel plate bolted to a frame which was securely anchored to the floor, ceiling, and wall of the laboratory. Plexiglass sections permitted observation inside the shield. Aluminum plate enclosed the remainder.

Instrumentation and controls were centralized as much as possible either on or near the main steel blast plate. This was the control panel which is shown in Figure 1.

**Butane system**

The butane system is shown schematically in Figure 3. Butane was supplied by the tank regulator to a low pressure pancake regulator in the laboratory. The gas was metered in a 600 mm. rotameter where pressure and temperature were measured. Needle valves on both sides of the rotameter permitted both flow rate and pressure adjustment.

The rotameter was calibrated with a precision wet test meter. The system measured and delivered butane at rates from 2 to 30 gram moles per hour.

All butane used in this research was Phillips Petroleum Company technical grade butane with a minimum purity of 95 mole % n-butane.

**Nitric acid system**

The nitric acid system consisted of a reservoir, centrifu-
gal pump, rotameter, and assorted piping as shown in Figure 3. The acid reservoir, B, was a 5 ft. length of 1 in. glass pipe with saran end fittings. Acid was withdrawn from the reservoir by a small centrifugal pump, C, and was delivered through a glass wool filter, D, and fine needle control valve, 5, to the rotameter, F. The voltage input to the pump motor was controlled by a Powerstat variable transformer. This permitted control of the pump speed. Reducing the pump speed and recycling most of the flow back to the reservoir prevented the acid from getting too hot in the pump and also provided better flow control. The air column, E, tended to smooth out flow by increasing the hydraulic capacitance of the system. From the safety shield rotameter the acid flowed past the sampling point, where the system pressure was measured, to a double pipe heat exchanger, G. The exchanger was constructed from 1/4 in. tubing and 3/8 in. pipe and was 2 ft. long. All parts were of stainless steel. Coolant flowed into the annulus of the exchanger at a temperature of about $-10^\circ$C. Acid flowed through the 1/4 in. tubing and into the reactor.

The rotameter was calibrated and delivered acid at controllable rates from 0.2 gram moles per hour to 2.4 gram moles per hour using 70% acid.

Reactor

The reactor was made up of two separate parts, the reactor headplate and the reactor pot. To assemble the two, an asbes-
tos gasket, 12 mm. thick, was placed between them and they were bolted together. Dow Corning silicone stopcock grease was applied to the gasket surface to insure a tight seal.

The reactor pot was made of cast iron with 1/2 in. thick walls. It contained a molten salt mixture consisting of 54 wt. % potassium nitrate and 46 wt. % sodium nitrate. This is an eutectic mixture which melts at 222°C. The space within the pot was 6 in. in diameter and 12 in. deep. The pot was supported in an electric furnace which was an 18 in. hollow cube of asbestos blocks in an angle iron frame with steel top and bottom plates. The other four sides of the cube had an outer layer of transite board. The reactor pot extended down into the furnace through a close fitting hole in the top steel plate.

Heat was supplied by three sheathed immersion heaters which were wrapped around the reactor pot. Two of the heaters were rated at 750 watts and the third was rated at 1500 watts. Powerstat variable transformers, located on the control panel, controlled the power output of the 750 watt heaters and an ammeter indicated the total power consumption of the furnace. A Brown electric pyrometer was connected in series with one of the 750 watt heaters and provided temperature control. The pyrometer monitored the output of a thermocouple immersed in the molten salt and opened the circuit when the temperature rose above the set point. When the temperature fell below the
set point the circuit was again closed. Molten salt temperatures were controlled to within $\pm 2^\circ C$ of the set point.

A cross-section of the reactor headplate is shown in Figure 4. The figure has been modified slightly to permit all the important components to be shown in one plane. The main plate was made of mild steel. The other parts were made of stainless steel. Nitric acid passed through the center of the plate in a 1/4 in. tube and sprayed from four 0.005 in. diameter holes into the reaction tube. The acid tube was enclosed by a 3/8 in. tube and a 1/2 in pipe. Air flowed through the annular spaces within the pipe to keep the acid cool until it entered the reaction tube. A 1/8 in. diameter thermocouple was located inside the acid tube to measure the temperature of the acid just before it entered the reaction tube. The butane entered the reaction tube from a side connection located just above the nitric acid spray. A coiled tube (not shown in Figure 4) extended down into the molten salt and provided the option of preheating the butane by first passing it through the coil before it entered the reaction tube.

The reaction tube had a 1/4 in. inside diameter. Five 1/8 in. diameter thermocouples measured the temperature profile along the tube and a 1/8 in. diameter side tube was connected to a mercury manometer for pressure measurements. From the bottom of the tube the gas passed through four 1/16 in. diameter holes, bubbled up through the molten salt, and left the
Figure 4. Reactor headplate cross-section
42

1/8" DIA. THERMOCOUPLE

NITRIC ACID

AIR IN

TO Hg MANOMETER

THERMOCOUPLE

AIR OUT

BUTANE

5 THERMOCOUPLES 1/8" DIA.

PRODUCT

1/2" 3 3/4" 6 1/2" 9 1/2" 11"

1/4" DIA. TUBE 4 HOLES OF 0.005" DIA.

REACTION TUBE 1/4" INSIDE DIA.

1/16" DIA. 4-HOLES

NO SCALE
reactor in a 1/2 in. pipe which had a thermocouple and a pressure tap in it. Two 1/4 in. diameter thermocouples measured the molten salt temperature at different depths. All of the thermocouples were chromel-alumel. Temperatures measured by these thermocouples were recorded by a Brown Electronik multipoint recorder.

**Product recovery system**

From the reactor, the product gases flowed into the condenser, R, as shown in Figure 3. The condenser consisted of two double pipe heat exchangers connected in series. The exchangers were 1/2 in. pipe and 3/8 in. tubing. Coolant entered the annulus of the condenser at about -10°C and flowed countercurrently to the product stream. Conditions in the condenser were usually sufficient to liquify some of the butane. This reduced the residence time of the nitroparaffin products in the condenser by increasing the liquid rate and prevented liquid entrainment in the rest of the system by greatly reducing the gas velocity.

The condensed product flowed by gravity into two glass separatory funnels, S, connected in series. This arrangement permitted liquid product to be collected quantitatively over any desired time interval without disturbing the flow of materials in the reactor. The gases flowed to a 3 way stopcock, 12, where they were either vented or passed through a 250 mm. coiled glass condenser, U. In the glass condenser,
butane and nitrogen dioxide were liquified and collected in a pyrex flask, V. The flask was partially submerged in a dry ice-acetone bath to keep the contents from evaporating. The uncondensed gases flowed into a flexible plastic balloon, X, which was inside a large glass bottle, Y, filled with water. A mercury manometer, W, was used to measure the pressure inside the balloon. The water displaced by the gases filling the balloon overflowed into a graduated cylinder, Z.

The refrigeration system

The refrigeration system supplied all of the coolant used in the condensers and heat exchangers. The heart of the system was a Mills 2-cylinder gas compressor driven by a 3 hp. induction motor. A water-cooled gas condenser was mounted on the side of the compressor frame. Freon-22 was used as the refrigerant. Freon gas left the compressor at a pressure of approximately 180 psig, was liquified in the condenser, and flowed into a receiving vessel. From the receiving vessel the liquid refrigerant flowed through an expansion valve into the expansion coil. The expansion coil consisted of a 50 ft. length of 3/8 in. copper tubing located inside 3 ft. lengths of 1/2 in. iron pipe. The iron pipes lined the bottom and sides of a well insulated galvanized iron tank. The tank contained about 50 gallons of a 1:1 mixture by weight of water and ethylene glycol. A small gear pump was used to force the solution through annular space around the expansion coil and
to the other systems where it was used. Under normal operating conditions, the temperature of the solution inside the tank was constant at about -10°C.

Operating Procedure

Start up

The refrigeration system was turned on several hours before a run was to be made to insure that the coolant would be down to operating temperature when the run started. The furnace power was increased and the molten salt level was adjusted if necessary. The reactor headplate was secured to the reactor pot. All piping and thermocouple connections were then made. The temperature controller and temperature recorder were turned on. The controller and furnace power were then adjusted to give the desired operating temperature in the reactor.

In the butane system, the tank regulator was adjusted to give an output pressure of 20 psig. The barometer reading was taken and corrected for temperature. Valves 9 and 10 were then adjusted to give the desired flow rate and absolute pressure in the rotameter, L.

The acid reservoir, B, was then filled through a funnel, A. The centrifugal pump, C, was started with valves 2, 5, 6, and 7 open and all others closed. When air had been cleared from the acid lines, valve 7 was closed and valves 3 and 8 were opened. The flow of acid to the reactor was then adjusted by
fine needle valve 5.

In the product recovery system, the stopcock on the upper separatory funnel, S, was opened to permit the liquid product to flow into the lower funnel. The gases flowed to stopcock 12 and were vented to the outside atmosphere. Stopcock 11 was then closed. The receiving flask, V, was weighed and positioned in place beneath the glass condenser, U. A dry ice-acetone bath was prepared in a wide mouth dewar flask and the receiving flask was submerged in it. The plastic balloon, X, was evacuated of gas by using a water aspirator. The glass bottle, Y, was then filled with water. Receiving vessels for the liquid product were weighed and preparations were complete for the run.

Operation

To begin the run, the stopcock on the upper separatory funnel, S, was closed and stopcock 12 was positioned to route the gases through the glass condenser, U. The level in the acid reservoir was recorded. The lower separatory funnel was emptied and stopcock 11 was opened. The stopcock on the upper funnel was then opened. A mark was made on the temperature recorder chart to indicate where the run began. The acid reservoir level, reaction tube pressure, reaction pot pressure, butane rotameter temperature, and the time were recorded every ten minutes on a data sheet.

To terminate the run, the stopcock on the upper separatory funnel was closed and stopcock 12 was turned to the vent posi-
tion. The level in the acid reservoir and the total time were recorded. Acid flow to the reactor was shut off by closing valve 8 and turning off the centrifugal pump. When the butane had evaporated from the lower separatory funnel, the gas pressure in the plastic balloon and the volume of water displaced were measured and recorded. Stopcocks 11 and 13 were then closed. The liquid product was drained from the lower separatory funnel in two phases, the aqueous phase and the organic phase. Each phase was drained into a tared flask, weighed and stored on dry ice. The receiving flask, V, was removed from the dry ice-acetone bath, wiped dry, weighed, and stored on dry ice. The products were then analyzed.

Shut down

All valves in the nitric acid system and butane system were closed. The temperature controller and temperature recorder were turned off. The furnace power level was reduced to about 500 watts and the refrigeration system was turned off. The reactor headplate was then disengaged from the reactor pot.

Analytical Procedure

General

The primary objective of the analytical procedure was to qualitatively and quantitatively determine the products emerging from the reactor. This permitted overall material balances
to be made on both carbon and nitrogen. A procedure using gas-liquid partition chromatography was developed to accomplish this objective. Replicate samples used in three different columns gave a satisfactory analysis of the C₁ to C₄ mononitroparaffins, alcohols, aldehydes, paraffins, and NO, NO₂, N₂, O₂, H₂, CO, CO₂, and water.

The reactor products were separated into four parts in the product collection system; an organic phase containing mostly nitroparaffins and oxygenated organics, an aqueous phase containing mostly water, a liquified gas containing mostly butane, and an off-gas consisting of butane and oxides of carbon and nitrogen. After the liquified gas was analyzed it was evaporated at room temperature to yield a small amount of liquid residue containing mostly nitroparaffins. This residue was weighed and added to the organic phase which was then analyzed.

**Equipment and techniques**

The units used for this analysis were F and M Scientific Corp. Model 500A and 609 linear programmed temperature gas chromatographs. The injection ports were maintained at 200°C. Liquid samples were injected through a self-sealing silicone rubber septum with a 10 µl. Hamilton microsyringe. Gas samples were injected using a 10 cc. Yale Leur-Lok hypodermic syringe.
Helium (minimum purity, 99.98 mole %, the Matheson Co.) was the carrier gas used for this analysis.

The Model 500A unit used a thermal conductivity cell as the detector. The flow rate through the reference side of the cell was about 30 ml. of helium per minute as measured with a calibrated Brooks Sho-Rate "150" rotameter, tube No. 1-15-6, stainless steel float. The output signal from the thermal conductivity cell was recorded at a chart speed of 30 in. per hour on a Bristol Dynamaster Potentiometer, Model 1PH-570. The potentiometer was equipped with a Model K2-1 integrator (Disc Instruments, Inc.) which automatically measured the peak areas.

The Model 609 unit had a flame ionization detector and used an air-hydrogen flame. The hydrogen flow rate was 50 ml. per minute and the air flow rate was 550 ml. per minute as measured with calibrated Brooks Sho-Rate "150" rotameters, tube Nos. R-2-15-AAA and R-2-15-A for hydrogen and air respectively, sapphire floats. The signal from the detector was recorded at a chart speed of 30 in. per hour on a Brown Electronik high speed recorder Model 143X58. The recorder was equipped with a Model 201 integrator (Disc Instruments, Inc.) which automatically measured the peak areas.

Column A was used with the Model 500 A chromatograph. This column was a 20 ft. length of 1/4 in. O.D. copper tubing filled with a packing containing 30 grams of bis (2-ethyl-
hexyl) adipate per 100 grams of the \(-30 + 60\) U.S. standard screen fraction of Johns-Manville acid-washed Chromosorb W. A forecolumn section consisted of an 8 in. length of 1/4 in. O.D. copper tubing filled with the \(-20 + 60\) U.S. standard screen fraction of calcium carbide. The purpose of the forecolumn was to convert water to acetylene since water did not produce quantitative peaks in the column. The column was originally operated at 25°C and a helium flow rate of 50 ml. per minute as measured at 28°C and atmospheric pressure. The helium supply pressure was 20 psig. The operating temperature was later increased to 40°C as it was found that this substantially reduced the analysis time without seriously affecting the degree of component separation. All four product fractions were analyzed with this system. The liquid samples used were 5 ul. The gas samples used were 3 ml. A sample chromatogram for this system is shown in Figure 5.

Column B was used with the Model 609 chromatograph. This column was a 20 ft. length of 1/8 in. O.D. copper tubing filled with a packing consisting of 30 grams of bis (2-ethyl-hexyl) adipate per 100 grams of the \(-60 + 80\) U.S. standard screen fraction of Johns-Manville acid-washed Chromosorb W. The column was operated at 25°C for 5 minutes. The temperature was then quickly raised to 60°C and increased linearly at a rate of 1.3°C per minute until all components were eluted from the column. The helium flow rate was 6 ml. per minute.
Figure 5. Sample chromatogram using column A with a thermal conductivity detector. Conditions: 25°C and 50 ml. of helium per minute
as measured at a supply pressure of 80 psig and 28°C. All four product fractions were analyzed with this system. The liquid samples used were 5 µl. The gas samples used were 600 µl. A sample chromatogram for this system is shown in Figure 6.

Some of the component separations were made possible by the fact that the oxides of carbon and nitrogen, nitrogen, and water are not detected by the flame ionization unit. Inspection of the chromatogram in Figure 5 shows that nitrogen, nitric oxide, nitrogen dioxide, carbon monoxide and methane all have a retention time of about 3.4 minutes and that carbon dioxide and ethane have a retention time of about 4.3 minutes. When a sample containing these compounds is analyzed on the flame ionization unit, only methane and ethane yield any response. By relating these compounds to a tie substance (usually butane) which is detected by both units, the peak areas for carbon dioxide and the composite of nitrogen, nitric oxide, nitrogen dioxide, and carbon monoxide can be determined by difference. It was assumed that conditions in the product collection system were such that nitrogen dioxide was not present in significant amounts in the off-gas. This was not a critical assumption since any significant quantity of nitrogen dioxide in the off-gas would be indicated by its reddish brown color.

Off-gas samples were also analyzed on column C which con-
Figure 6. Sample chromatogram using column B with a flame ionization detector.
Conditions: 25°C for 5 minutes then 60°C + 1.3°C/minute and 6 ml.
of helium per minute at 80 psig

1 Methane
2 Ethane
3 Propane
4 Isobutane
5 n-Butane
6 Acetaldehyde
7 Methanol
8 Propionaldehyde
9 Ethanol
10 t-Butanol + isobutyraldehyde
11 2-propanol
12 n-Butyraldehyde
13 1-Propanol
14 Nitromethane
15 2-Butanol
16 Isobutanol
17 Nitroethane
18 n-Butanol
19 2-Nitropropane
20 2-Methyl-2-nitropropane
21 1-Nitropropane
22 2-Nitrobutane
23 1-Nitrobutane
sisted of a 7 ft. length of 1/4 in. O.D. stainless steel tubing filled with the -14 + 30 U.S. standard screen fraction of type 13X molecular sieves (The Linde Co., Tonowanda, New York). When this column was operated at 25°C and a helium flow rate of 70 ml. per minute with the Model 500 A unit, it separated hydrogen, oxygen, nitrogen, nitric oxide plus methane, and carbon monoxide in that order. The sample size used was 3 ml. The total information obtained from chromatographs of the off-gas on all three columns was sufficient to provide a complete analysis.

Compounds are usually identified on the completed chromatogram by their retention time. Because the combined effects of high pressure and linear temperature programming using column B caused noticeable variations in retention time, the compounds were identified by their retention times relative to one or more of the nitroparaffin peaks which were easily identified by their characteristic size and shape. The area under each component peak was determined and multiplied by the calibration factor for that component. The adjusted areas were proportional to weight per cent. The calibration factors were determined from chromatograms of mixtures of known composition.
DISCUSSION

Conversion and Yield

Conversion and yields based on both hydrocarbon and nitrating agent are important values in vapor phase nitration investigations because these values are used directly to determine the economic feasibility of the process. To promote accuracy and reliability, an experimental design was used which permitted the use of statistical methods to evaluate the results. This design is presented in Table 2. The experimental conditions and results for all runs are presented in Table 3. The variables studied were temperature, mole ratio of butane to nitric acid, and residence time. Three levels of each variable were used to give a total of 27 combinations. The order in which each combination was run was determined by the code number assigned to it in Table 2. Three runs were made in a day. The first numeral refers to the day and the letter refers to the order of the runs within the day. After all 27 combinations were completed, some of the combinations were run again as a check. The numeral subscript indicates which combinations were run a second time. The use of this particular design was to prevent a linear time trend from affecting comparisons between the different levels of each variable. Such a trend might be caused by a gradual poisoning of the reactor or by a gradual improvement in the techniques of the investigator with practice.
Table 2. Statistical arrangement used for collecting the data

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Table 3. Experimental conditions and results for all runs

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^a Molar ratio of nitrogen in NP's to nitric acid fed.
^b Molar ratio of nitrogen in NP's to nitric acid consumed. The quantity of acid consumed is based on the assumption that both NO and NO₂ can be recovered and converted back to nitric acid.
^c Molar ratio of carbon in NP's to carbon fed.
^d Molar ratio of carbon in NP's to carbon consumed. The amount of carbon consumed is based on the assumption that n-butane is the only hydrocarbon that can be recovered.
^e Molar ratio of carbon in NP's to carbon consumed. The amount of carbon consumed is based on the assumption that propane, isobutane, and n-butane are recoverable hydrocarbons.
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<td>2.82</td>
<td>2.80</td>
<td>3.24</td>
<td>3.27</td>
</tr>
<tr>
<td>conversion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% hydrocarbon</td>
<td>60.14</td>
<td>26.22</td>
<td>26.02</td>
<td>26.73</td>
<td>67.56</td>
<td>73.79</td>
<td>76.62</td>
</tr>
<tr>
<td>yield I</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% hydrocarbon</td>
<td>64.22</td>
<td>34.24</td>
<td>33.21</td>
<td>33.54</td>
<td>73.30</td>
<td>80.82</td>
<td>81.54</td>
</tr>
<tr>
<td>yield II</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The analysis of variance for nitric acid conversion, hydrocarbon yield II, and hydrocarbon conversion is presented in Tables 4, 5, and 6. The results for the first 27 runs were used in partitioning the sum of squares for the various effects. The repeated runs were used to estimate random error. The reader unfamiliar with the use of analysis of variance
The analysis of variance for the techniques is referred to Snedecor (82) for a more detailed explanation.

The results in Table 4 indicate that temperature was the only variable to significantly affect nitric acid conversions. Using the F test for the equality of variance, the ratio temperature mean square/error mean square is 62.98 as compared to a tabular F ratio of 13.27 at the 99% confidence level. The mean squares for the other effects are all smaller than the error mean square which is rather unusual. Although such a result could be due solely to random chance, it is highly unlikely. The error mean square is probably too large because of a time trend in the data. When runs 3a, 3b, and 3c were repeated, the values for nitric acid conversion were always higher by an amount of 2 to 3% which indicates that failure of these values to be exactly the same was not caused solely by random error but also by a time trend. The fact that changes in mole ratio or residence time did not appreciably affect the conversions of nitric acid is in agreement with the results of Coldiron et al. (20). They found that varying the residence time from 0.67 to 1.62 seconds and the mole ratio from 2 to 20 had little effect on conversion.

The analysis of variance for hydrocarbon yield is presented in Table 5. The results are much the same as those obtained for nitric acid conversion with temperature being the
Table 4. Analysis of variance for conversions of nitric acid

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>1</td>
<td>11,903.2203</td>
<td></td>
</tr>
<tr>
<td>Temperature (T)</td>
<td>2</td>
<td>979.5596</td>
<td>489.7798a</td>
</tr>
<tr>
<td>Mole ratio (MR)</td>
<td>2</td>
<td>3.8024</td>
<td>1.9012</td>
</tr>
<tr>
<td>Residence time (RT)</td>
<td>2</td>
<td>3.2092</td>
<td>1.6046</td>
</tr>
<tr>
<td>T x MR</td>
<td>4</td>
<td>13.6358</td>
<td>3.4090</td>
</tr>
<tr>
<td>T x RT</td>
<td>4</td>
<td>.7222</td>
<td>0.1806</td>
</tr>
<tr>
<td>MR x RT</td>
<td>4</td>
<td>15.0270</td>
<td>3.7568</td>
</tr>
<tr>
<td>T x MR x RT</td>
<td>8</td>
<td>35.6962</td>
<td>4.4620</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>27</td>
<td>12,954.8727</td>
<td></td>
</tr>
<tr>
<td><strong>Error</strong></td>
<td>5</td>
<td>38.8816</td>
<td>7.7763</td>
</tr>
</tbody>
</table>

^Significant at the 99% confidence level.

Table 5. Analysis of variance for hydrocarbon yield II

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>1</td>
<td>93,010.1515</td>
<td></td>
</tr>
<tr>
<td>Temperature (T)</td>
<td>2</td>
<td>9517.3951</td>
<td>4758.6976a</td>
</tr>
<tr>
<td>Mole ratio (MR)</td>
<td>2</td>
<td>48.8707</td>
<td>24.4354</td>
</tr>
<tr>
<td>Residence time (RT)</td>
<td>2</td>
<td>4.3124</td>
<td>2.1562</td>
</tr>
<tr>
<td>T x MR</td>
<td>4</td>
<td>81.2521</td>
<td>20.3130</td>
</tr>
<tr>
<td>T x RT</td>
<td>4</td>
<td>88.2155</td>
<td>22.0539</td>
</tr>
<tr>
<td>MR x RT</td>
<td>4</td>
<td>38.3557</td>
<td>9.5889</td>
</tr>
<tr>
<td>T x MR x RT</td>
<td>8</td>
<td>78.7664</td>
<td>9.8458</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>27</td>
<td>102,867.3194</td>
<td></td>
</tr>
<tr>
<td><strong>Error</strong></td>
<td>5</td>
<td>65.5234</td>
<td>13.1047</td>
</tr>
</tbody>
</table>

^Significant at the 99% confidence level.
only significant variable. The error mean square for hydrocarbon yield is almost twice as large as the error mean square for nitric acid conversion. The amount of hydrocarbon consumed in the reactor is found as a small difference of two large numbers and is therefore subject to considerable variation. This value is used directly in calculating the yield which accounts for the larger error mean square.

The analysis of variance for hydrocarbon conversion shows both temperature and mole ratio to be highly significant variables. The F ratios for temperature and mole ratio are 89.12 and 87.66 respectively as compared to a tabular F of 13.27 at the 99% confidence level. The temperature by mole ratio interaction sum of squares is broken down into its four component parts in Table 6. The subscripts L and Q signify linear and quadratic. Although the overall mean square for the temperature by mole ratio interaction appears to be significant, a breakdown is desirable because two of its components, $T_L^{MRQ}$ and $T_Q^{MRQ}$, are confounded with the time trend. The only one of these terms which appears to be significant is $T_Q^{MRQ}$ with an F ratio of 13.78 as compared to a tabular F of 6.61 at the 95% confidence level. The $T_Q^{MRQ}$ interaction term is confounded with time and tends to make the calculated value of F too large but the error is also confounded with time and tends to make the value of F too small. Considering that these
Table 6. Analysis of variance for hydrocarbon conversions

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>1</td>
<td>316.4872</td>
<td></td>
</tr>
<tr>
<td>Temperature (T)</td>
<td>2</td>
<td>32.6913</td>
<td>16.3456(^a)</td>
</tr>
<tr>
<td>Mole ratio (MR)</td>
<td>2</td>
<td>32.1538</td>
<td>16.0769(^a)</td>
</tr>
<tr>
<td>Residence time (RT)</td>
<td>2</td>
<td>0.8998</td>
<td>0.4499</td>
</tr>
<tr>
<td>(T \times MR)</td>
<td>(4)</td>
<td>(3.6505)</td>
<td></td>
</tr>
<tr>
<td>(T_{L \times MR_L})</td>
<td>1</td>
<td>0.4720</td>
<td>0.4720</td>
</tr>
<tr>
<td>(T_{Q \times MR_Q})</td>
<td>1</td>
<td>0.1696</td>
<td>0.1696</td>
</tr>
<tr>
<td>(T_{L \times MR_Q})</td>
<td>1</td>
<td>0.4807</td>
<td>0.4807</td>
</tr>
<tr>
<td>(T_{Q \times MR_L})</td>
<td>1</td>
<td>2.5821</td>
<td>2.5821(^b)</td>
</tr>
<tr>
<td>(T \times RT)</td>
<td>4</td>
<td>0.2649</td>
<td>0.0662</td>
</tr>
<tr>
<td>(MR \times RT)</td>
<td>4</td>
<td>0.2568</td>
<td>0.0642</td>
</tr>
<tr>
<td>(T \times MR \times RT)</td>
<td>8</td>
<td>0.6809</td>
<td>0.0851</td>
</tr>
<tr>
<td>Total</td>
<td>27</td>
<td>387.0852</td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>5</td>
<td>0.9170</td>
<td>0.1834</td>
</tr>
</tbody>
</table>

\(^a\)Significant at the 99% confidence level.
\(^b\)Significant at the 95% confidence level.

tendencies will partially cancel each other, such a large value of \(F\) can be declared significant. This is not surprising because the \(T_{Q \times MR_L}\) term should be significant. In other words, an increase in the mole ratio should cause a decrease
in the degree of quadratic curvature of a hydrocarbon conversion versus temperature curve.

The results of this section are summarized in Figure 7. Average values of nitric acid conversion, nitric acid yield, hydrocarbon yield II, and hydrocarbon conversion are plotted against temperature. The hydrocarbon conversion values are for a mole ratio of 3.4 only. The relative mole% of nitroethane, the highest priced nitroparaffin, is also plotted against temperature. As the temperature increases, the mole% of nitroethane increases while yields of hydrocarbon and nitric acid decrease. Conversions of hydrocarbon and nitric acid increase to a maximum and then decrease. The figure clearly shows the importance and also the difficulty of choosing the most economic operating conditions.

Analytical Results

General

The analytical method developed for this work proved to be entirely satisfactory for the analysis of butane nitration products. Material balances for carbon and nitrogen averaged over 32 runs show a nitrogen accountability of 99.1% and a carbon accountability of 96.5%. The fact that these values are close to 100% and differ by only 2.6% indicates the high degree of accuracy obtainable by this method. Accountabilities for the individual runs are given in Table 3.
Figure 7. Conversion and yield for hydrocarbon and nitric acid and mole percent nitroethane as a function of temperature (Refer to Table 3 for a definition of these quantities)
\[ \text{HNO}_3 \text{ CONV.} \]
\[ \text{HNO}_3 \text{ YIELD} \]
\[ \text{HYDROCARBON CONV.} \]  
AT MOLE RATIO = 3.4
\[ \text{HYDROCARBON YIELD II} \]
\[ \text{MOLE \% NE OF TOTAL NP'S PRODUCED} \]

TEMPERATURE, °C

371 427 482
Column B was particularly high in resolving power. In addition to the compounds listed in Figure 6, 2-butanone and acrolein were also separated on this column. When a flame ionization detector was used in conjunction with column B, compounds which were as little as 0.01% of the total sample were easily detected. Reproducibility for any given component was ±2% of the true value of that component when calibrated against known gravimetric samples provided that duplicate analyses were made and the component was more than 1% of the total sample.

Of the C_1 to C_4 mononitroparaffins, only NM, NE, 1-NP, 2-NB, and 1-NB were found in appreciable quantities. Formaldehyde and acetaldehyde were the major aldehydes found along with much smaller amounts of acrolein, proprionaldehyde, and n-butyraldehyde. No alcohols were found except for occasional traces of 1-propanol and 2-butanol. The only ketone found was 2-butanone. The off-gas contained all of the C_1 to C_4 saturated hydrocarbons, nitrogen, nitric oxide, carbon monoxide, and carbon dioxide. When nitrations were performed at 482°C, traces of hydrogen were found. The quantity of oxidation and decomposition products such as aldehydes, methane, ethane, carbon and nitrogen oxides increased with increases in the nitration temperature. The complete analysis of nitrator products for runs 3a_1 to 3c_2 is given in Table 7.
Table 7. Complete analysis of reactor products for runs 3a$_1$ to 3c$_2$, gram-moles

<table>
<thead>
<tr>
<th></th>
<th>3a$_1$</th>
<th>3a$_2$</th>
<th>3b$_1$</th>
<th>3b$_2$</th>
<th>3c$_1$</th>
<th>3c$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NM</td>
<td>0.04323</td>
<td>0.04514</td>
<td>0.05346</td>
<td>0.03848</td>
<td>0.02608</td>
<td>0.03077</td>
</tr>
<tr>
<td>NE</td>
<td>0.10604</td>
<td>0.10510</td>
<td>0.08682</td>
<td>0.08374</td>
<td>0.06827</td>
<td>0.07067</td>
</tr>
<tr>
<td>2-NP</td>
<td>0.00052</td>
<td>0.00019</td>
<td>0.00036</td>
<td>0.00017</td>
<td>0.00021</td>
<td>0.00020</td>
</tr>
<tr>
<td>2-M-2-NP</td>
<td>0.00082</td>
<td>0.00038</td>
<td>0.00093</td>
<td>0.00052</td>
<td>0.00178</td>
<td>0.00026</td>
</tr>
<tr>
<td>1-NP</td>
<td>0.03512</td>
<td>0.03366</td>
<td>0.02852</td>
<td>0.02482</td>
<td>0.02246</td>
<td>0.02172</td>
</tr>
<tr>
<td>2-NB</td>
<td>0.15039</td>
<td>0.16471</td>
<td>0.12779</td>
<td>0.15126</td>
<td>0.10170</td>
<td>0.11708</td>
</tr>
<tr>
<td>1-NB</td>
<td>0.08977</td>
<td>0.08614</td>
<td>0.07516</td>
<td>0.07988</td>
<td>0.05529</td>
<td>0.05583</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>4.28809</td>
<td>4.46626</td>
<td>3.53045</td>
<td>3.65304</td>
<td>3.00167</td>
<td>3.00586</td>
</tr>
<tr>
<td>CH$_3$CHO</td>
<td>0.06918</td>
<td>0.04091</td>
<td>0.08137</td>
<td>0.05706</td>
<td>0.05823</td>
<td>0.05823</td>
</tr>
<tr>
<td>C$_2$H$_5$CHO</td>
<td>0.00413</td>
<td>0.00348</td>
<td>0.00406</td>
<td>0.00301</td>
<td>0.00248</td>
<td>0.00229</td>
</tr>
<tr>
<td>CH$_2$CHCHO</td>
<td>0.00126</td>
<td>0.00197</td>
<td>0.00142</td>
<td>0.00130</td>
<td>0.00083</td>
<td>0.00111</td>
</tr>
<tr>
<td>C$_3$H$_7$CHO</td>
<td>0.00065</td>
<td>0.00072</td>
<td>0.00049</td>
<td>0.00043</td>
<td>0.00042</td>
<td>0.00029</td>
</tr>
<tr>
<td>CH$_3$COC$_2$H$_5$</td>
<td>0.00372</td>
<td>0.00340</td>
<td>0.00298</td>
<td>0.00327</td>
<td>0.00239</td>
<td>0.00586</td>
</tr>
<tr>
<td>C$_3$H$_7$OH</td>
<td>0.00014 trace</td>
<td>0.00012 trace</td>
<td>0.00023 trace</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_5$CH(OH)CH$_3$</td>
<td>0.00011 trace</td>
<td>0.00010 trace</td>
<td>0.00026 trace</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCHO</td>
<td>0.32383</td>
<td>0.30395</td>
<td>0.27391</td>
<td>0.27419</td>
<td>0.22178</td>
<td>0.15260</td>
</tr>
<tr>
<td>HNO$_3^a$</td>
<td>0.02983</td>
<td>0.03202</td>
<td>0.01988</td>
<td>0.03624</td>
<td>0.01332</td>
<td>0.02246</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.11663</td>
<td>0.10307</td>
<td>0.08456</td>
<td>0.09480</td>
<td>0.07252</td>
<td>0.07598</td>
</tr>
<tr>
<td>NO</td>
<td>0.71053</td>
<td>0.66044</td>
<td>0.65523</td>
<td>0.55538</td>
<td>0.53074</td>
<td>0.44506</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>0.04250</td>
<td>0.05419</td>
<td>0.04529</td>
<td>0.04060</td>
<td>0.03328</td>
<td>0.06839</td>
</tr>
</tbody>
</table>

$^a$Obtained by titration of the aqueous phase.
Table 7. (Continued)

<table>
<thead>
<tr>
<th></th>
<th>$3a_1$</th>
<th>$3a_2$</th>
<th>$3b_1$</th>
<th>$3b_2$</th>
<th>$3c_1$</th>
<th>$3c_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.19878</td>
<td>0.15651</td>
<td>0.16479</td>
<td>0.12851</td>
<td>0.10074</td>
<td>0.09159</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.14970</td>
<td>0.14519</td>
<td>0.13449</td>
<td>0.16478</td>
<td>0.09271</td>
<td>0.09176</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.00884</td>
<td>0.12844</td>
<td>0.00574</td>
<td>trace</td>
<td>0.00279</td>
<td>trace</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.03047</td>
<td>0.03719</td>
<td>0.02450</td>
<td>trace</td>
<td>0.01514</td>
<td>trace</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0.02353</td>
<td>0.01675</td>
<td>0.01799</td>
<td>0.00241</td>
<td>0.006520</td>
<td>0.00187</td>
</tr>
<tr>
<td>i-C$<em>4$H$</em>{10}$</td>
<td>0.02720</td>
<td>0.01987</td>
<td>0.02110</td>
<td>0.00927</td>
<td>0.018855</td>
<td>0.01097</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>3.72034</td>
<td>3.47971</td>
<td>3.13213</td>
<td>3.03114</td>
<td>2.32123</td>
<td>0.25048</td>
</tr>
<tr>
<td>$\Delta$H$_2$O$^b$</td>
<td>1.58144</td>
<td>1.39835</td>
<td>1.17480</td>
<td>1.19260</td>
<td>0.89353</td>
<td>0.86457</td>
</tr>
</tbody>
</table>

$^b$Difference between output and input quantities.

Difficulties and problems encountered

After 3 or 4 aqueous phase samples were analyzed on column A, severe tailing of the water and formaldehyde peaks was encountered. It was concluded that the calcium oxide formed by the reaction of water and calcium carbide in the fore-column section strongly adsorbed these compounds. It was therefore necessary to replace the forecolumn section with a new one containing freshly ground calcium carbide after 3 samples had been analyzed. This was a bothersome and time consuming task. Fortunately, the water free analysis of the aqueous phase using column B$^1$ permitted the amount of water

$^1$Column B was used with a flame ionization detector which does not yield any response for water.
to be determined by difference when the sample volume and density were accurately measured. This method was sufficiently accurate to justify its use for the majority of the aqueous phase analyses.

Nitrogen accountabilities tended to be too low when nitration were carried out at $371^\circ$C. At this temperature much of the nitric acid remained undecomposed as evidenced by the fact that the aqueous phase was about 30 wt. % nitric acid\textsuperscript{1}. The reaction of nitric acid with other compounds caused boiling and evolution of CO$_2$ and NO$_2$. Nitrogen loss from these reactions possibly explains the low accountabilities. The aqueous phase was periodically withdrawn from the product collection vessel and refrigerated in an attempt to prevent these losses.

Nitroparaffin Product Distribution

Nitroparaffin distribution data for all runs are presented in Table 8 and the experimental conditions for each run are given in Table 3. Changes in the residence time or the mole ratio produced no observable changes in the distribution of the nitroparaffins. The effect of temperature is shown graphically in Figure 8 as a plot of the average mole per cent of

\textsuperscript{1}Determined by titration with sodium hydroxide using bromphenol blue as an indicator.
Table 8. Nitroparaffin distribution for all runs, mole%

<table>
<thead>
<tr>
<th>Run no.</th>
<th>NM</th>
<th>NE</th>
<th>2-NP</th>
<th>2-M-2-NP</th>
<th>1-NP</th>
<th>2-NB</th>
<th>2-M-1-NP</th>
<th>1-NB</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>10.12</td>
<td>31.91</td>
<td>0.07</td>
<td>2.98</td>
<td>12.27</td>
<td>9.01</td>
<td>0.08</td>
<td>32.56</td>
</tr>
<tr>
<td>lb</td>
<td>9.35</td>
<td>35.56</td>
<td>0.08</td>
<td>1.74</td>
<td>12.53</td>
<td>9.34</td>
<td>0.55</td>
<td>30.85</td>
</tr>
<tr>
<td>lc</td>
<td>9.28</td>
<td>32.96</td>
<td>0.06</td>
<td>0.52</td>
<td>12.83</td>
<td>10.56</td>
<td>0.47</td>
<td>33.59</td>
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<td>2a1</td>
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<td>0.13</td>
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<tr>
<td>4b</td>
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<td>0.20</td>
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<td>-</td>
<td>12.23</td>
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<tr>
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<tr>
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<td>trace</td>
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<td>12.96</td>
<td>-</td>
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</tr>
<tr>
<td>6b</td>
<td>8.82</td>
<td>34.90</td>
<td>0.08</td>
<td>0.69</td>
<td>12.52</td>
<td>8.52</td>
<td>-</td>
<td>34.47</td>
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Table 8. (Continued)

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<th>Run no.</th>
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<th>NE</th>
<th>2-NP</th>
<th>2-M-2-NP</th>
<th>1-NP</th>
<th>2-NB</th>
<th>2-M-1-NP</th>
<th>1-NB</th>
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<td>6c</td>
<td>5.59</td>
<td>29.79</td>
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<td>0.52</td>
<td>13.43</td>
<td>9.71</td>
<td>-</td>
<td>40.93</td>
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<tr>
<td>7a</td>
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<td>21.88</td>
<td>0.10</td>
<td>0.44</td>
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<td>44.69</td>
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<tr>
<td>7b</td>
<td>6.73</td>
<td>24.00</td>
<td>-</td>
<td>-</td>
<td>6.48</td>
<td>44.36</td>
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<td>18.43</td>
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<tr>
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<td>0.07</td>
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<td>43.35</td>
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<td>36.36</td>
<td>0.09</td>
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<tr>
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<td>0.07</td>
<td>1.27</td>
<td>13.06</td>
<td>6.08</td>
<td>0.16</td>
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<tr>
<td>9a</td>
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<td>19.60</td>
<td>-</td>
<td>0.17</td>
<td>2.82</td>
<td>57.22</td>
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<td>2.79</td>
<td>54.84</td>
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<td>11.16</td>
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<tr>
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<td>22.15</td>
<td>0.03</td>
<td>0.16</td>
<td>2.50</td>
<td>54.00</td>
<td>-</td>
<td>10.37</td>
</tr>
</tbody>
</table>

Each nitroparaffin produced vs. temperature. 2-Nitropropane, 2-methyl-2-nitropropane, and 2-methyl-1-nitropropane are not included in this figure since they usually were less than 1% of the total nitroparaffins formed. The amount of lower nitroparaffins produced increased with temperature. The increase in the amounts of nitromethane and 1-nitropropane was small but the amount of nitroethane increased from an average of 20 mole % at 371°C to an average of 35 mole % at 482°C. The amount of 1-nitrobutane increased from an average of 12 mole %
Figure 8. Nitroparaffin distribution as a function of temperature
at 371°C to an average of 32 mole % at 482°C while the average amount of 2-nitrobutane correspondingly decreased from 56 mole % to 9 mole %. This seems to contradict one of the general conclusions drawn by Hass and Shechter (40) that the rate of substitution of the primary and secondary positions approaches equality as the temperature increases. However, the product distribution data probably does not actually represent the rate of substitution between the primary and secondary positions because other factors such as the decomposition rates of 1-nitrobutane and 2-nitrobutane also affect the results.

Indicated Reaction Mechanisms

The alkyl nitrite decomposition mechanism suggested by Gray (30) and Rice and Rodowskas (74) adequately accounts for the production of lower nitroparaffins in the vapor phase nitration of n-butane. As shown below, the mechanism consists of two steps. The alkyl nitrite first breaks up into a nitric oxide molecule and an alkoxide radical. The alkoxide radical then breaks up into a lower alkyl radical and an aldehyde. The second step is probably much faster than the first so that an overall one step reaction would give a satisfactory representation of the decomposition process.
In these reactions, one mole of nitric oxide is formed for each mole of lower alkyl radicals produced. Assuming that each lower alkyl radical produced reacted to form a nitro-paraffin, 2 moles of nitric acid would be required to produce one mole of lower nitroparaffins. This partially accounts for the reduced conversions of nitric acid at higher temperatures which favor the production of lower nitroparaffins. Inspection of Table 7 shows that the amount of nitric oxide produced exceeds the amount of lower nitroparaffins formed. Other sources of nitric oxide are the decomposition of nitric acid and the decomposition of nitroparaffins.
The molar ratio of methane + nitromethane/proprionaldehyde varied from approximately 100 at 371°C to 20 at 482°C. This is evidence that reaction 20 is not a significant source of methyl radicals. The major source of methyl radicals is probably the mechanism described by reactions 7 and 10.

The molar ratio of ethane + nitroethane/ acetaldehyde varied from 0.9 to 2.0 which is evidence that reaction 19 is a significant source of ethyl radicals. If all of the ethyl radicals were generated via reaction 19, this ratio would be ideally be one. In reality, this ratio tends to be greater than one because acetaldehyde rapidly decomposes under nitration conditions according to reactions 40 through 43 (p. 23, 24) and similar reactions. Acetaldehyde decomposition reactions are also a source of methyl radicals. Reactions 12 and 13 are another source of ethyl radicals.

The production of lower alkyl radicals from the thermal cracking of carbon to carbon bonds was ruled out when butane was passed through the reactor at 482°C. Analysis of the output stream showed only traces of propane, ethane, and methane indicating that no appreciable reaction had occurred.

Reactions 56 and 57 are proposed by the author to account for the amounts of n-butyraldehyde and 2-butanone found in the products. The quantity \( \cdot A \) represents any hydrogen accepting free radical.
The molar ratio of 2-butanone/n-butyraldehyde decreased from about 40 at a nitration temperature of 371°C to 3 at 482°C. Such a result would be expected from the proposed reactions. As the temperature of nitration increases, the formation rates of primary and secondary butyl nitrite approach equality. The formation rates of n-butyraldehyde and 2-butanoic acid which are produced directly from these nitrites also approach equality. The proposed reactions also suggest that the amounts of n-butyraldehyde and 2-butanoic acid produced will be relatively small since they are derived from unstable butyl nitrites whose concentrations are small. This is in accordance with the experimental results.

The amount of nitrogen formed increased with increases in temperature and varied from 10% to 25% of the total nitrogen charged to the reactor. Bachman et al. (9) state that for propane nitration about 20% of the nitric acid is converted to nitrogen in contrast to a 3% conversion to nitrogen when nitrogen dioxide is used. Apparently a number of violent oxidation reactions occur between nitric acid and some of the organic compounds. These would account for the large amounts of nitrogen, carbon dioxide, and water produced.
Temperatures

No difficulty was encountered in maintaining temperatures constant throughout a run. However, individual temperatures did vary with changes in flow rate and molten salt temperature. At the point of injection to the reaction tube, nitric acid temperatures varied from 43 to 65°C which was well below the boiling point. Inlet butane temperatures varied from 140 to 220°C. Gas temperatures at the reactor outlet varied from 220 to 320°C indicating that the gases cooled rapidly after emerging from the molten salt. Temperatures at the reaction tube inlet were 50 to 60°C less than the entering butane temperature. From this point, the temperature rapidly increased and approached the molten salt temperature at the reaction tube exit. The highly exothermic reactions were apparently under control at all times as no temperatures exceeding the molten salt temperature were observed anywhere in the reactor.

Economic Evaluation of Process

Inasmuch as the nitration of propane has achieved commercial success, there is good reason to believe that butane nitration can also be a profitable operation. An economic evaluation for a nitroparaffin plant using butane and nitric acid as the feed materials is presented in Tables 9, 10, and 11 and Figures 9 and 10. The rated capacity of the plant is 14,000,000 lb./yr. Operation is based on a 24 hour day and
330 days a year. The operating conditions were chosen as 427°C and a mole ratio of 3.4. Under these conditions, the experimental values for nitric acid yield and hydrocarbon yield were 61.9% and 63.0% respectively. The plant operations include recovery and re-use of nitric acid and hydrocarbon so the yield values were used to determine the amount of feed materials needed to produce one pound of nitroparaffins.

The nitroparaffin distribution data were obtained from Figure 8. Using the nitroparaffin distribution data in weight per cent, the selling price per pound of product was determined to be 23.4¢/lb. by taking a weighted average of the current selling prices of the nitroparaffins. The average price of the nitrobutanes was estimated to be 21¢/lb. by assuming that their price would be similar to the price of the nitropropanes.

Factors and percentages used to estimate costs were obtained from cost estimation data given by Aries and Newton (5), Chilton (18), and Villbrandt and Dryden (91). Labor and utility requirements were estimated by comparing the vapor phase nitration process to similar chemical processes whose requirements are given by Chilton (18). The fixed capital cost of the plant was estimated by scaling up a cost estimate for the 10,000,000 lb./yr. nitroparaffin plant built by the Commercial Solvents Corporation in 1954. The 14,000,000 lb./
yr. capacity of the proposed plant could be obtained using equipment the same size as in the present plant assuming that some process improvements have been made over the last ten years and considering that the average molecular weight of the products is higher when butane is used instead of propane. Using information obtained from the literature (21, 68), the cost of this plant, as it was built in 1954, was estimated at $4,200,000. This cost was increased by 15% to account for the extra equipment necessary for product purification and separation when butane is used and multiplied by the ratio of the Marshall and Stevens chemical industry index for the second quarter of 1964 (26) to the Marshall and Stevens chemical industry average index for 1954 (22). This gave a fixed capital cost estimate for the proposed plant of $6,240,000.

In the preparation of Tables 9 and 10, it was assumed that the company or corporation building the plant would manufacture its own nitric acid and sell it to the plant at cost. The production cost of nitric acid was taken as 80% of the current market price. In actual practice, a company might sell the nitric acid to its nitroparaffin plant at the standard market price to simplify the bookkeeping. Using this point of view, a true economic evaluation of the nitroparaffin plant would be made by considering its effect on the company as a whole which, of course, cannot be done here.
Table 9. Production cost estimate for a nitroparaffin plant

<table>
<thead>
<tr>
<th>Item</th>
<th>Units/lb</th>
<th>Cost/unit</th>
<th>Cost/lb. product</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Direct costs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw materials</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Nitric acid</td>
<td>1.110 lb.</td>
<td>3.120¢/lb.</td>
<td>3.463¢</td>
</tr>
<tr>
<td>B. Butane</td>
<td>0.8005 lb.</td>
<td>2.984¢/lb.</td>
<td>2.389¢</td>
</tr>
<tr>
<td>Labor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Plant superintendant</td>
<td>0.000214 hr.</td>
<td>$5.00/hr.</td>
<td>0.107¢</td>
</tr>
<tr>
<td>B. Supervisors</td>
<td>0.000566 hr.</td>
<td>$3.20/hr.</td>
<td>0.181¢</td>
</tr>
<tr>
<td>C. Operators</td>
<td>0.001886 hr.</td>
<td>$2.30/hr.</td>
<td>0.434¢</td>
</tr>
<tr>
<td>Services</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Water</td>
<td>30 gal.</td>
<td>0.004¢/gal.</td>
<td>0.120¢</td>
</tr>
<tr>
<td>B. Steam</td>
<td>6 lb.</td>
<td>0.075¢/lb.</td>
<td>0.450¢</td>
</tr>
<tr>
<td>C. Electric power</td>
<td>0.2 kwh</td>
<td>1.0¢/kwh</td>
<td>0.200¢</td>
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<td>Maintenance (5% of total fixed capital investment per year)</td>
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<td></td>
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<tr>
<td><strong>Indirect costs</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Depreciation (10% of total fixed capital investment per year)</td>
<td></td>
<td>4.457¢</td>
<td></td>
</tr>
<tr>
<td>Taxes and insurance (5% of operating labor)</td>
<td>0.036¢</td>
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</tr>
<tr>
<td>Plant overhead (50% of operating labor)</td>
<td>0.361¢</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total production cost</strong></td>
<td>14.426¢</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Calculated as 80% of the current market price of 39¢/lb. of 100% nitric acid (72).

b Calculated at current cost (71) of 14¢/gal. of butane (minimum purity, 95 mole %) using 4.78 lb./gal.
Table 10. Estimate of working capital for a nitroparaffin plant

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material inventory</td>
<td></td>
</tr>
<tr>
<td>A. Nitric acid (15 day supply)</td>
<td>$22,030</td>
</tr>
<tr>
<td>B. Butane (30 day supply)</td>
<td>$30,380</td>
</tr>
<tr>
<td>Product inventory (15 day supply at production cost)</td>
<td>$91,750</td>
</tr>
<tr>
<td>Operating money (30 days at production cost)</td>
<td>$183,500</td>
</tr>
<tr>
<td>Consumer credit (30 days at selling price of 23.4¢/lb)</td>
<td>$297,650</td>
</tr>
<tr>
<td>Total working capital</td>
<td>$625,310</td>
</tr>
</tbody>
</table>

Table 11. Per cent return on investment for a nitroparaffin plant

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual sales (14,000,000 lb at 23.4¢/lb)</td>
<td>$3,276,000</td>
</tr>
<tr>
<td>Annual production cost</td>
<td>-$2,019,640</td>
</tr>
<tr>
<td>Gross profit</td>
<td>$1,256,360</td>
</tr>
<tr>
<td>Administration expenses (selling, advertising, 8% of annual sales)</td>
<td>-$262,080</td>
</tr>
<tr>
<td>Net profit before income tax</td>
<td>$994,280</td>
</tr>
<tr>
<td>Federal income tax (48% of net profit)</td>
<td>-$477,250</td>
</tr>
<tr>
<td>New earnings</td>
<td>$517,030</td>
</tr>
<tr>
<td>Per cent return on investment =</td>
<td></td>
</tr>
<tr>
<td>new earnings</td>
<td></td>
</tr>
<tr>
<td>fixed capital + working capital x 100 = 7.53%</td>
<td></td>
</tr>
</tbody>
</table>
In the preparation of Tables 9 and 10, the cost of butane was taken as the current market price of $14.50/gal. (71). However, the selling price of butane, as quoted by an individual supplier, would vary widely depending on location and season. For this reason, production cost and per cent return on investment estimates are presented as a function of butane cost in Figures 9 and 10. As the cost of butane drops from $14.50/gal. to $5.00/gal., the production cost per pound of product decreases from $14.43 to $12.87 while the return on investment increases from 7.53% to 9.24%.

Although the cost of butane is an important factor, maintenance and depreciation account for approximately 50% of the total production cost. These costs could be reduced by building a much larger plant. Since the size of a plant depends on the demand for the products it produces, the success of a commercial butane nitration process will depend on the demand that can be created for its products.
Figure 9. Estimated production cost as a function of butane cost

Figure 10. Estimated per cent return on investment as a function of butane cost
CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations derived from this investigation are:

1. Yields and conversions were not appreciably affected by changes in mole ratio of butane to nitric acid from 3.4 to 7.8 and of changes in residence time from 0.5 to 0.7 seconds.

2. Yields and conversions were significantly affected by changes in molten salt temperature from 371°C to 482°C. Yields based on both nitric acid and hydrocarbon decreased with increases in temperature. Conversions based on both nitric acid and hydrocarbon increased with increases in temperature to a maximum and then decreased with further increases in temperature.

3. Gas chromatography techniques have been developed which provide an accurate quantitative analysis of the significant products resulting from the vapor phase nitration of butane.

4. Nitroparaffin distributions were not affected by changes in mole ratio or residence time but varied greatly with changes in temperature. The amount of lower nitro-paraffins formed increased with increases in temperature.

5. The alkyl nitrite decomposition mechanism adequately
accounts for the production of lower nitroparaffins in the vapor phase nitration of butane.

6. The effect of pressure on the vapor phase nitration of butane should be investigated.

7. A method of analysis should be developed that will permit the reaction products to be analyzed directly from a single sample of the gases emerging from the reactor. This would eliminate the need for product collection equipment and greatly reduce the time required to perform an experiment.
BIBLIOGRAPHY


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