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VAPOR PHASE NITRATION OF BUTANE IN A
FUSED SALT REACTOR.

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VAPOR PHASE NITRATION OF BUTANE
IN A FUSED SALT REACTOR

by

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ABSTRACT

In this work butane was successfully nitrated continuously in the vapor phase in a fused salt reactor. The reactor, constructed of cast iron and mild steel, had built into it an arrangement for preheating both reactants and vaporizing the acid along with a simple, but effective, contacting and mixing section.

Nitroparaffin yields per pass based on hydrocarbon fed ranged from 3.4 to 6.5%, while yields per pass based on hydrocarbon consumed ranged from 60.2 to 82.0%. Nitroparaffin conversion per pass based on nitric acid fed ranged from 20 to 39%.

Flexibility of the reactor as an experimental tool was demonstrated by obtaining the stated yields and conversions while controlling certain operating variables. The mole ratio of hydrocarbon to acid was varied from 3.1 to 7.2; acid normality from 8 to 15; fused salt temperature from 745°F to 805°F; moles of butane fed per hour from 6.8 to 12.0; and the space velocity from 29.9 to 40.9 ft.³ of reactants per second per ft.³ of reactor zone space. The mole % distribution of the nitroparaffins produced ranged as follows: nitromethane, 8-14; nitroethane, 20-26; 2-nitropropane, 0.04-0.29; 2-methyl-2-nitropropane, 0-0.34; 1-nitropropane, 5-9; 2-nitrobutane, 36-51; 2-methyl-1-nitropropane, 0-0.04; 1-nitrobutane, 14-20.

Material balances were able to account for 89.6% (average) of the carbon fed and 96% (average) of the nitrogen fed.

A successful gas-liquid partition chromatographic method for the

quantitative analysis of the products resulting from the vapor phase nitration of commercial butane in a fused salt reactor has been developed.

DEDICATION

To Janet

INTRODUCTION

The earliest research concerning vapor phase nitration of saturated hydrocarbons of less than five carbon atoms appeared in 1936 (36). Several economic considerations lead logically to a chemical engineering investigation of this unit process. They are, 1. the abundance and low cost of high purity, low molecular weight alkanes, 2. low cost tonnage nitric acid, and 3. relatively valuable nitration products.

In support of the first consideration, Table 1 shows the annual U.S. sales of liquified petroleum (IP) gases. Of the sales of IP gases in 1959, 27.6% of the total was reported (12) to have gone to chemical manufacturers. The average price paid to producers in cents per gallon for IP gases was 5.09 in 1956, 3.96 in 1957, 4.37 in 1958, 4.40 in 1959, and was estimated to be about the same level in 1960 and 1961 (89, p. 333).

Production and capacity figures given in Table 2 show that quantities of nitric acid are available. The current market price (78) of 68% nitric acid is \$3.90 per 100 pounds (100% basis).

There is only one U.S. producer of nitroparaffins using the vapor phase route. Propane and azeotropic (67%) nitric acid are the feed stocks. The rated capacity of the plant is 10,000,000 pounds of nitroparaffins per year (22). The approximate distribution of the products produced from propane (11) and their current market prices (78, p. 14) are shown in Table 3.

A brief cost estimate of the raw materials needed to produce one pound of nitroparaffin will show the economic attractiveness of this process. Several simplifying assumptions have been made. The most

Table 1. Sales of liquified petroleum gases in the United States, 1954-1959^a

Year	C ₃	n-C ₄	iso-C ₄	C ₃ -C ₄	Other mixtures	Total
(millions of gallons per year)						
1954 ^b	-	-	-	-	-	5,125
1955 ^b	3,261	724	-	1,428	709	6,122
1956	3,626	888	36	1,160	924	6,635
1957	4,009	1,117	26	934	851	6,939
1958	4,274	1,119	25	1,050	1,019	7,462
1959	5,132	1,298	11	1,143	550	8,919

^aAdapted from Minerals Yearbook 1959 (89, p. 327).

^bBasis of reporting changed in 1956.

Table 2. United States capacity and production of nitric acid^a

Year	Capacity ^b	Production
(millions of short tons per year)		
1951	1.7	1.5
1956	3.1	2.6
1957	3.8	2.8

^aData obtained from (86, p. 1).

^bDoes not include about 2.3 million tons of governmental capacity.

Table 3. Typical nitroparaffin distribution from propane and current price

Nitroparaffin (NP)	Distribution, ^a weight %	Current price, ^b cents per lb. in car load lots	Current price, ^b cents per lb. in smaller lots
Nitromethane (NM)	25	24	27.5
Nitroethane (NE)	10	26	30
1-Nitropropane (1-NP)	25	26	30
2-Nitropropane (2-NP)	40	16	20

^aApproximate, typical, obtained from (11).

^bAs of July 1, 1961 (78, p. 14).

important of these is that all reactants undergo complete transformation into nitroparaffins without decomposition or side reactions, or a 100% yield. Another is that only the lowest priced nitroparaffin, 2-NP, is produced. The calculations are summarized below:

Reaction	HNO_3	+	C_3H_8	\longrightarrow	$\text{C}_3\text{H}_7\text{NO}_2$	+	H_2O
moles	1		1		1		1
lbs.	63		44		89		18
lbs./lb. NP	1.026		0.494		1		0.206
cost/lb. NP	\$0.040 ¹		\$0.00583 ²				
selling price/lb. NP					\$0.16		\$0.0

¹Calculated as current cost, \$3.90/100 lbs. acid (78).

²Calculated as current cost, \$0.05/gal. (77) using 4.2 lbs./gal. (23, p. 46).

This shows a maximum margin, without conversion cost, of \$0.114 per pound of NP produced. The raw material costs are thus indicated to be about 28% of the value of the nitrated product. Production of any of the higher valued nitroparaffins will help offset the manufacturing costs and losses which have not been included in this rudimentary cost estimate.

Aside from the economic considerations just shown, the nitroparaffins warrant interest because of their excellent solvent powers and, in particular, their possibilities as unique chemical intermediates. Some of the classes of chemicals that may be easily produced are hydroxylammonium salts, amines, nitroolefins, nitroalcohols and aminoalcohols.

In the vapor phase nitration of the lower alkanes, many combinations of reactants, nitrating agents and reactors are possible. The choice of the particular system investigated in this research was influenced by several factors.

Among the various nitrating agents which have been used by previous investigators are nitrogen dioxide (8, 32), nitric oxide (31) and nitric acid. Some difficulty has been experienced with corrosion of equipment used to vaporize nitric acid (52, 64). If the acid were to be vaporized in the reaction zone, its heat of vaporization could be used to help control the reaction temperature. The presence of water adds to the analytical difficulties (84, 99). Since water is one of the reaction products, any additional water introduced with the nitrating agent only increases the degree, not type, of analysis problem. However, conversion (based on nitrating agent) and yield (based on alkane) are, in general,

higher when the latter nitrating agent is employed. This information coupled 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 the research.

Butane was selected for use as the alkane. An economically interesting possibility would be the use of a mixed propane-butane feed stock as this is the cheapest IP mixture available in large quantities. Propane has been extensively studied, however, so an investigation of butane alone would have more fundamental value. Another advantage of butane is that the same nitroparaffins are obtained as may be gotten from propane plus four additional nitroparaffins. These additional products are: 1-nitrobutane (1-NB), 2-nitrobutane (2-NB), 2-methyl-2-nitropropane (2-M-2-NP), and 2-methyl-1-nitropropane (2-M-1-NP). Two studies of butane in tubular reactors have been made by Hass, Hodge, and Vanderbilt (36) in 1936 and by Bachman, Hass, and Addison (7) in 1952. These provide data for comparison purposes.

Perhaps one of the reasons butane has not been as fully investigated as propane is because of the analytical difficulties involved. 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 products. In this work one of the newer analytical techniques, gas-liquid partition chromatography (GLPC), has been heavily relied upon to provide a large measure of the quantitative data presented. A considerable portion of this research effort has been devoted to developing

techniques and methods of analysis (16, 17, 18, 19).

The majority of the vapor phase nitration studies have utilized pyrex tubular reactors of one sort or another. Corrosion and a gradual poisoning effect (2, 3) have been observed in nitration vessels constructed of ordinary materials. Since this type of nitration has been postulated to proceed through a free radical mechanism (5, 29, 36), these effects are of some importance. To avoid these effects, pyrex, gold-lined, platinum-clad, and silica apparatus have been used but these are expensive for large scale vessels. Introduction of alkali and alkaline earth metal compounds into the reaction vessel have successfully prevented reaction inhibiting characteristics from developing (45, 46, 63). It has been necessary to introduce reactants either at multiple points (79) or in stages (22) to maintain temperature control. To avoid catalytic effects and maintain better temperature control, some work has been done substituting a molten salt filled pyrex pot for the tubular reactor (2, 21, 42).

A fused salt reactor, constructed of ordinary cast iron and mild steel, has been designed, built, and operated in this study. Separate preheaters and acid vaporizers normally have been used in previous research. In this work the functions of both have been incorporated into the reactor itself, along with a simple, but effective, contacting and mixing section. The reactor and the associated pilot plant have operated successfully.

REVIEW OF LITERATURE

Historical

The history of the nitroparaffins has been traced back in some of the literature (85, p. 429) to 1844 when 1,1-dinitro alkanes were apparently prepared from nitric acid and ketones, although the actual structure was not determined until much later. Chloropicrin, or trichloronitromethane, was prepared by Stenhouse (87) in 1848 by chlorination of picric acid. Bromopicrin was synthesized via a similar method in 1854 (88). The first successful nitration of an aliphatic compound was that of Mills (74) in 1871 of chloropicrin from chloroform and nitric acid.

The work generally recognized as the start of nitroparaffin research was that of Victor Meyer and Stüber (71, 72, 73) in 1872, when metathesis of silver nitrite and alkylhalides produced nitroalkanes. Up to this time, only the preparation of nitroparaffins by chemical synthesis had been described in the literature. However, eight years later, in 1880, the first direct nitration of a paraffin was accomplished by Beilstein and Kurbatov (13, 14). 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.

At this point several investigators began studying the nitration of the alkanes since considerable progress had been made with nitration of the aromatic hydrocarbons in the aniline dye industry. During this time many of the cycloparaffins, aliphatic paraffins ranging from isopentane to dodecane, and high-boiling petroleum distillate fractions were

nitrated, almost exclusively in the liquid phase.

An excellent review of the work accomplished in this period is given in Hass and Riley (38, pp. 376-378), so no detailed discussion will be given here. However, two of the many researchers established important points. Konwalow (54, 55) working with hexane in a sealed tube showed that increasing the temperature increased the yield. Markownikoff, working in a different direction, compared the effect of mixed sulfuric-nitric acid to that of nitric acid alone. His work (61, 62) indicated that the mixed acid approach customarily used for the nitration of aromatic hydrocarbons caused considerable degradation of the nitro-paraffins. 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: polynitroparaffins are predominant; hydrogen atoms are reactive in the order, tertiary, secondary, primary; there is severe oxidation; and reaction is slow.

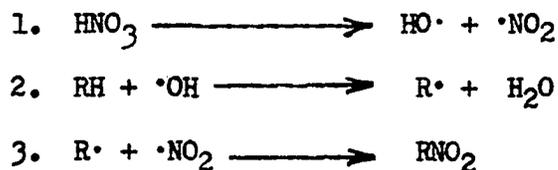
Much of this work was succinctly summarized in 1928 by Gruse (27, p. 60) who stated: "The nitration of petroleum fractions has been studied to some extent but no results of either scientific or technical importance have been obtained because of the mixed nature of the fractions and the complexity of the reaction." Attempts at commercialization were being made however. Hopkins and Buc (48) in 1928 patented the use of nitrated mixtures as cellulose ester solvents.

In the 1930's with the advent of large quantities of the lower molecular weight paraffins from the developing petroleum industry and

cheap nitric acid from the ammonia oxidation process, Dr. H. B. Hass (22, p. 9) at Purdue University started investigation of vapor phase nitration of the lower alkanes. The initial projects by Vanderbilt and Hodge working with isobutane showed the practicality of vapor phase nitration (35). These projects showed that with a vapor phase reaction all eight possible nitroparaffins were obtained from butane (36), which was contrary to the liquid phase results. This development, and others which will be discussed later, introduced some question as to the mechanism by which the reaction proceeds that has yet to be satisfactorily answered. From this beginning, vapor phase nitration has been taken under study by many persons who have investigated various alkanes, nitrating agents, and additives among other things. These are further discussed under the appropriate headings in the remainder of this section.

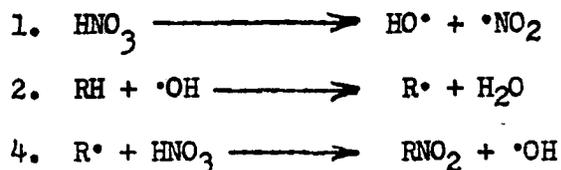
Mechanism

Vapor phase nitration has been postulated to occur by means of free radical mechanisms (5, 6, 29, 68). The exact mechanism is uncertain. Several of those proposed are presented here. One presented by Bachman *et al.* (5) consists of the following three reactions:



There is some question as to whether the rate of decomposition of the nitric acid is sufficient to supply the $\cdot\text{NO}_2$ radical consumed in reaction 3 at the rate indicated by the nitroparaffin formation.

An alternate mechanism preferred by Albright *et al.* (2, 3), Alexander (4, 31), and McCleary and Degering (68) consists of a chain reaction between 2 and 4 as follows:



It can be seen that equations 2 and 4 allow the formation rate of nitroparaffin to exceed that of the thermal decomposition rate of nitric acid.

Alkyl radicals smaller than those obtained directly from the original hydrocarbon by loss of a hydrogen atom are presumed (6) in the case of propane to be formed by degradation of propyl, propoxy, or peroxy (81) radicals.

Conversion and Yield

The results of most of the vapor phase nitration research are reported in terms of conversion and yield. These terms can be misleading in that both may be based on either reactant. It has not been made clear, in some cases, whether the reactants have been considered to be the input quantities or only the amount of material undergoing reaction. Usually the term conversion implies the molar ratio of RNO_2 obtained/ NO_2 charged as such or as HNO_3 . This usage is followed in this work. This is contrary to the usual engineering practice of using conversion when referring to single pass and yield when referring to the complete process.

The percentage conversion has been found (39) to increase with

increased mole ratio of paraffin to nitrating agent. Working with methane and nitric acid, for example, it has been found (35) that a mole ratio of seven produces a conversion of 14%, while a mole ratio of 13 produces a conversion of 26%. There is a limit, however, because extrapolation to infinite ratio does not result in 100% conversion. Conversion based on the hydrocarbon introduced is very rarely presented since a large excess of the hydrocarbon (10 or 20 to 1) is used to increase the conversion as previously defined. This becomes quite important when estimating the potential of an industrial process because a prodigious amount of material must be recycled to obtain high ultimate conversions.

The term yield also has an unusual connotation in previously published vapor phase nitration research. Usually yield has implied the molar ratio of RNO_2 obtained/RH consumed. For example, many of the yields reported to have been 30-50% based on hydrocarbon consumed correspond to yields of less than 1% when based on hydrocarbon fed to the unit. The precaution about recycle quantities is applicable here, also. However, for comparative purposes, the same basis of RH consumed will be used for yield in this research, as well as the true yield based on the hydrocarbon introduced to the reactor.

Paraffins Nitrated in Vapor Phase

Methane

While difficulty in nitrating methane had been experienced in the Purdue laboratories (1), Landon in 1939 disclosed in two patents (56, 57)

successful nitration of methane in either ferrous or non-ferrous tubular reactors. He employed a high temperature-short contact time process typical of successful vapor phase nitration. As the maximum reported yield was low, only 8.8%, Boyd and Hass (20) then investigated methane nitration. They were able to increase the yield slightly, to about 14%. At a later date Hass et al. (40) obtained a maximum yield of 26%. Methane was further studied by Alexander (4, 31) although his emphasis was on effect of additives. None of the preceding investigators found the dinitroparaffins reported earlier by Urbański and Sloń (92, 93) in 1936. The latter used a low temperature process and had difficulty with methane as evidenced by poor yields and explosions (92).

Ethane

Ethane was the object of a study by Hibshman et al. (41). The nitrated product was found to be 27% nitromethane, the balance being nitroethane. This immediately aroused interest because in the originally proposed mechanism (68) there was no provision for a single carbon radical since one cannot come from the ethyl radical (38, p. 380). Ethane was also briefly touched upon by Hass et al. (35) as previously mentioned, and the subject of a patent (33).

Propane

When Urbański and Sloń extended their researches to propane (90) they obtained higher yields (up to 80%) but also found some dinitropropanes. Upon investigating pentane through nonane (91) they reported the ratio of mono- to di- nitro compounds usually to be 60:40 (94). Hass

et al. (32) nitrated propane under similar conditions but at a higher temperature several years later. They were unable to find any polynitroparaffins. Propane has been studied perhaps the most extensively of all the alkanes nitrated in the vapor state. Using nitric acid, Bachman et al. (6) and Alexander (4) studied the effect of a single catalyst while Bachman and Pollack (11) and Bachman and Kohn (10) checked combinations of two catalysts. With the same nitrating agent, Bachman et al. (9) investigated multiple (triple) catalytic reactions. Hass and Alexander (31) used nitrogen dioxide as a nitrating agent with and without a catalyst. Nitration of propane using nitrogen dioxide was also reported by Hass et al. (32) and by Bachman et al. (8).

All of these investigators used tubular reactors under varying conditions. More recently propane has been nitrated in fused salt reactors. Coldiron et al. (21) used propane alone while Hill (42) and Albright et al. (2, 3) have added oxygen to the reaction mixture.

Butane

The initial vapor phase experiment (35) in this country was directed toward producing only a mononitroparaffin. In line with the observations of reactivity gained in liquid phase nitration, isobutane was used because it has only a single tertiary hydrogen atom, the other nine being primary. Using sealed glass tubes, 2-M-2-NP was produced as expected in 22% yield (actually conversion as previously defined), based on nitric acid reacting, and was of high purity, 90%. A flow process was then tried on isobutane. At least four mononitroparaffins (30) were produced which was most unexpected.

The importance of the tertiary hydrogen was then tested by nitrating n-butane. This time five mononitroparaffins were isolated showing that the order of attack was quite different from that of the liquid phase reactions. This new process was patented (36) in 1934. Test 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 iso- and n-butane was nitrated by Levy (38, 59, 60) using catalysts. He reported some 2,3-dinitrobutane but Hass and Shechter (39) state that they have several times unsuccessfully attempted to verify these results.

The first work on butane in which any of the oxygenated by-products were ever qualitatively identified was by Addison (1, 7). The major emphasis of this work, however, was on the effect of various additives, so there is still a lack of quantitative data on the nitration of butane.

Pentane

Hass and Patterson (37) nitrated n-pentane in 1938 and a year later isopentane data were published by Seigle and Hass (83). The primary concern of these researchers was qualitative identification of the nitro compounds. In each case seven nitroparaffins were obtained. Several generalizations were noted which distinguished vapor from liquid phase nitration of paraffins. These were:

1. Either any hydrogen or any alkyl group may be replaced by a nitro group.

2. At high temperatures, polynitroparaffins are generally not produced unless higher molecular weight alkanes are used.

Neopentane and neohexane

These two substances were nitrated by Howe and Hass (49). The neohexane (2,2-dimethylbutane) study produced products quite different from those found by Markownikoff (62) who reported 2,2-dimethyl-3-nitrobutane to be the only nitroparaffin found. Two additional previously unreported primary nitroneobutanes and a total of eight nitroparaffins were found in this study. The ratio of fissioned to hydrogen-substituted products was 80:20. In the neopentane (2,2-dimethylpropane) study this ratio was 62:38. The primary emphasis was placed on identification of nitrated products.

Reactors and Auxiliaries

Tubular

By far the majority of vapor phase nitration studies have been carried out in tubular reactors. Most of these reactors have been of glass but stainless steel has been used on occasion (2, 3, 32, 41) with one instance of a gold-lined stainless steel tube (40). Copper and carbon steel reactors each have been tested (2, 3). Conversions rapidly dropped with time of operation to zero in copper while in a mild steel reactor they gradually rose to those obtained in glass. In stainless steel, conversions gradually decreased from those obtained in glass. This phenomenon has been investigated and, while not understood, it can be arrested (45, 46, 63).

The effects of surface to volume ratio have been investigated in glass by Bachman and co-workers (6, 8, 10). Surface to volume ratio from 4 cm.⁻¹ to 300 cm.⁻¹ produced no readily discernible trends in the distribution of nitroparaffin products.

Molten salt

These reactors have been recently developed in an effort to provide better temperature control of the exothermic nitrating and oxidizing reactions. The use of sodium and potassium nitrates was a natural outgrowth of the earlier work by Hodge (45) and Swallen (46). They had found that these salts prevented the gradual increase of oxidation at the expense of nitration occurring in stainless steel nitration vessels.

Hill (42) in 1952 first used the technique of bubbling the reaction mixture through these molten salts. Two additional studies (2, 3, 21) have appeared in the literature in the past two years. Coldiron et al. (21) report that they were able to run at hydrocarbon to acid ratios of one to one in molten salt without explosions previously reported (37) at ratios below two to one in tubular reactors. They attribute this to better temperature control. Albright et al. (2, 3) found tubular reactors gave slightly higher conversions than did molten salt reactors. In none of the published reports of nitration carried out in molten salt reactors were actual product distribution data presented.

Auxiliaries

Many different methods and sequences for getting the alkane and the nitrating agent into the vapor state, mixing them, preheating them, and

getting them into the reactor have been used. The nitrating agent has been vaporized by dripping nitric acid on an external molten salt surface (63), by forcing carbon dioxide or other inert gas through cylinders of nitrogen dioxide (34), by spraying nitric acid into ceramic-packed conical pots (52), by bubbling preheated hydrocarbon through liquid nitric acid (35), by contacting acid and hydrocarbon countercurrently in packed towers (64), and by direct injection of the nitrating agent into either the preheaters or reactor (37, 41, 81, 85). Equally varied acid and alkane preheating techniques have been used (11, 30, 31, 32, 40).

Temperature Effects

All of the research conducted in molten salt reactors indicated that the temperature for optimum conversions was lower than that found in tubular reactors (about 410°C versus 425°C for propane). Work on isobutane by Hass, Hodge, and Vanderbilt (35) showed increasing the temperature from 150°C to 420°C greatly increased the yield of primary nitroparaffins. Propane nitrated between 100°C and 200°C by Urbański and Słoń (90, 91, 92, 93, 94) was reported to yield some dinitro compounds. When the temperature is raised to 400 - 450°C, as has been done in most of the propane nitration studies in this country, not a single evidence of poly-nitroparaffins has been noted. Bachman et al. (6) have shown that as the temperature of propane nitration is raised, the percentage of NE found in the products increases, that of 2-NP decreases, while that of 1-NP and of NM remain the same. Work by Bachman et al. (9) and Bachman and Kohn (10) substantiate the increase of NE and decrease of 2-NP ratios. In general the percentage of carbonyls and nitric oxides tends

to increase with temperature.

From the data which have been published it is possible to draw several general conclusions about the effects of temperature (39). There is an optimum temperature for maximum conversion for each hydrocarbon. If contact time (in tubular reactors) is matched with the temperature, total yields of nitroparaffins will be approximately the same. The temperature coefficients for hydrogen substitution approach equality as the temperature increases. The ratio of fission to substitution reactions increases. Oxidation and decomposition also become important.

Pressure Effects

Very little data exists on this subject. Hass et al. (40) working on methane concluded that moderate pressure (100 psig.) increased conversion based on nitric acid. Optimum temperatures and contact times decreased (i.e., the rate of reaction increases) at both 100 psig. and 1000 psig. and temperature control became more critical at the higher pressure.

Nitrating Agents

In vapor phase research conducted to date nitrogen dioxide and nitric acid have been the most widely used nitrating agents. Hass et al. (32) found that both reagents yield the same nitroparaffins. Longer contact times and lower temperatures were beneficial in the case of nitrogen dioxide work.

When Bachman et al. (8) added a catalyst (oxygen) to nitrogen dioxide the conversion and yield were increased. The yield rose to a

level above that obtained using nitric acid. Conversions are higher with nitric acid, however. It was found that a lesser amount of the nitrating agent was converted to elemental nitrogen (3% versus about 15%) when nitrogen dioxide was used (8). Bachman et al. (9) have stated that more carbon oxides and fewer olefinic and carbonyl compounds are found using nitrogen dioxide. They also note that the use of catalysts decreases the differences observed between the two nitrating agents. Thus it appears the relative future usage of these nitrating agents will be determined by economic considerations.

Catalysts

Heterogeneous

From the materials used in reactors, it may be concluded that pyrex glass, silica, platinum, and gold are essentially non-catalytic with respect to either nitration or oxidation. Hass et al. (35) report that aluminum nitrate has no effect while silica gel and platinum oxide promote oxidation. Bachman et al. (8) have shown that ferric oxide, boric oxide, and 1-propanol do not have a beneficial effect on nitration. Copper has been found to be very detrimental while mild steel exposed to air (presumably oxidized) gives poor nitration conversions that improve with time (3). Stainless steels gradually become catalytic with respect to oxidation (2) unless protected with nitrate salts (45, 46). The relatively noncatalytic character of sodium and potassium nitrates is evidenced by the molten salt reactors (2, 3, 21, 42). Levy (58, 59, 60) has claimed the use of borosilicate glass containing antimony and/or

arsenic catalyzes formation of nitro-paraffins. His work has not yet been duplicated, however (39).

When Bell et al. (15) studied catalytic oxidation of isobutane they noted that a boric acid coating kept their conversions at a high, consistent level. A silica gel coating, however, almost completely inhibited oxidation.

In summary then, the literature examined indicated that no heterogeneous catalysts have been found that accelerate nitration. Those catalysts that show any activity have increased the competing oxidation reaction, usually at the expense of the nitration reaction.

Homogeneous

In this class of catalysts nitric oxide, oxygen, and halogens are among the most important. A great deal of work has been done on the last two mentioned and they will be discussed at some length later in this section.

Nitric oxide decreases conversion (10, 31), presumably by action as a chain stopper. This effect has been nullified by use of halogens and oxygen.

Oxygen added to a butane reaction mixture in a tubular reactor decreases the nitrobutane mole ratio and increases that of the lower nitroparaffins (7). The ultimate yield based on hydrocarbon is greatly decreased but the optimum conversion is increased. There is a marked increase in carbonyls and olefins produced as more oxygen is added. When oxygen is added in a molten salt reactor, nitration conversions are not increased (2, 3).

Table 4. Effects of homogeneous catalysts on vapor phase nitration of propane^a

Catalyst	Yield %	Conversion %	C/NO ₂ ratio	Propylene % yield	Carbonyls % yield
None	27	23	2.63	48 ^b	9.5
O ₂	38	39	2.28	20	30
Br ₂	50	27	lower	20	11
O ₂ and Br ₂	48	46	2.00	3	38
Cl ₂	66	40	higher	-	-
Cl ₂ and O ₂	43	45	2.15	4	45

^aSource: references 9, 10, and 11.

^bThis figure includes ethylene.

Effects of halogens and oxygen upon the nitration of propane have been extensively studied. Some typical results from several investigations (9, 10, 11) are included in Table 4. The maximum yields and conversions have been picked to emphasize the effects attainable and therefore all conditions of the experiments are not identical.

Cyclic Processes

In all of the published research a maximum of about 20-25% conversion of the nitrating agent into nitroparaffins was reported. Yields of up to 80% of the hydrocarbon consumed have been reported. However, in the few cases where sufficient information is given to calculate the

yield on the basis of the hydrocarbon fed to the reactor it appears that between 0.5-1.5% yield has actually been obtained. In order to have an economical process, recovery and recycling are necessary.

The first approach was to condense the products at ambient temperatures, remove nitric acid and oxides of nitrogen, and recycle the hydrocarbon (34, 36, 60). It was found that yields and conversions dropped. Water scrubbing followed by sulfuric acid scrubbing of the recycle hydrocarbon to remove aldehydes and ketones helped (65, 66). Further improvement was obtained by then catalytically hydrogenating the alkane before returning it to the reactor (43, 44). Another alternative was to dilute (up to 80% inerts) the gas in the reactor (79). Since the sulfuric acid scrub destroyed aldehydes and ketones an alternate method of scrubbing with hydroxylamine hydrochloride solution was developed (50) which permits their recovery. Silica gel absorbers to strip traces of nitro-paraffins from the exit gases have been patented (53).

In general, the oxides of nitrogen have been oxidized to NO_2 with air and either returned directly to the reactor (47) or converted to nitric acid and returned (34).

EXPERIMENTAL

Description of Pilot Plant

General

The pilot plant which was built for this study consists of four sections which are: 1. the nitric acid system, 2. the butane system, 3. the reactor, and 4. the product recovery system. These are described in detail under the appropriate headings in this section. Figure 1 presents various views of the pilot plant while the schematic flow diagram is shown in Figure 2.

All systems comprising the pilot plant were designed for continuous operation, limited only by the capacity of the butane cylinder. The plant was sized to produce a maximum of 100 ml. per hour of nitroparaffin product. This was based on the assumption that yields and conversions similar to the optimums previously reported could be obtained.

Brass and copper were used as materials of construction for the butane system. Stainless steel was used for the nitric acid and product recovery systems. The reactor was made of cast iron and mild steel. Glass was used in various places; e.g., rotameters, acid column, and sampling containers.

To reduce the number of variables, the reactor and product recovery system operate at substantially atmospheric pressure. However, provision was made for relatively simple conversion to a variable pressure system.

Because of the somewhat uncertain nature of the reaction and the previous reports of occasional explosions, a blast shield was built.

Figure 1. Photographs of the pilot plant and reactor head plate

Upper left: Control panel
Upper right: Reactor head plate
Bottom: Assembled reactor

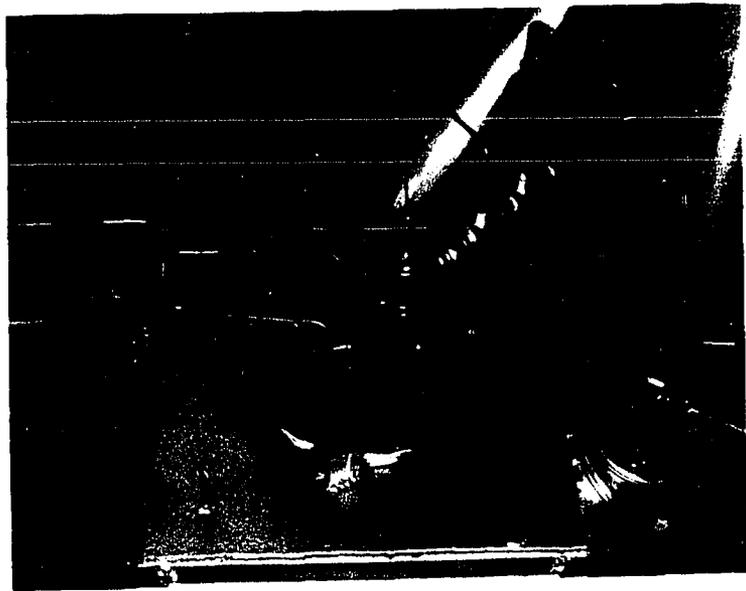
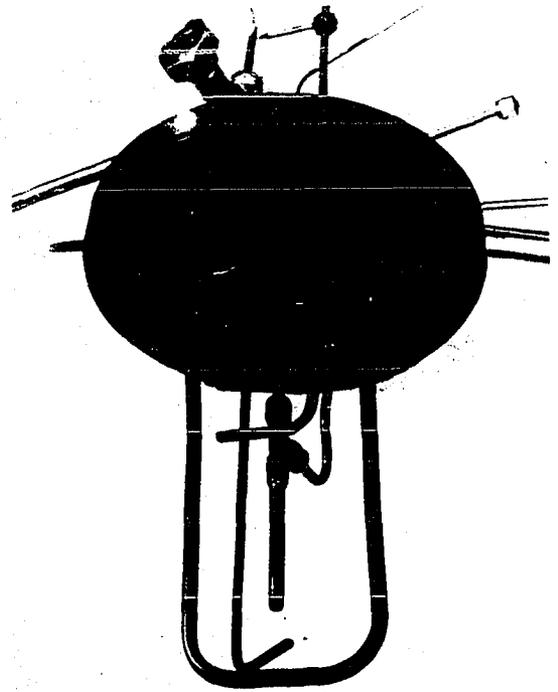
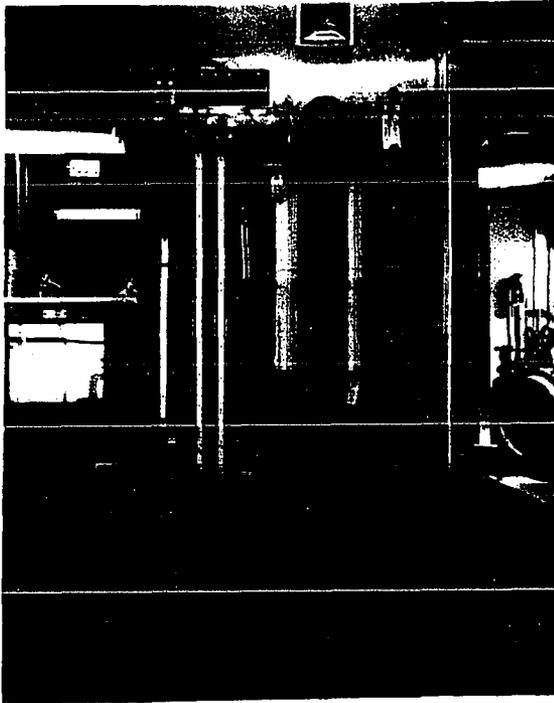
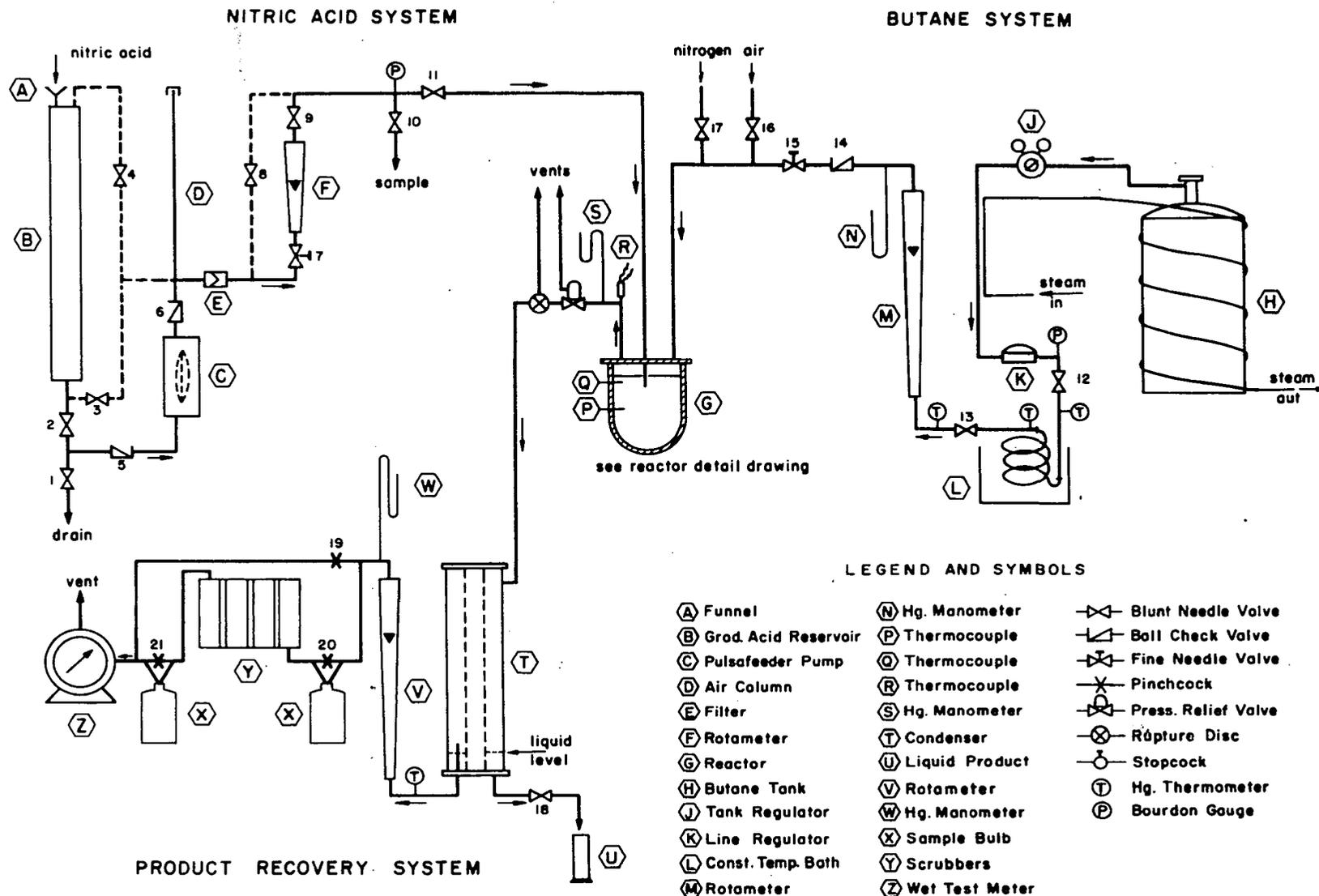


Figure 2. Schematic flow diagram of the vapor phase nitration pilot plant



Only the reactor portion of the pilot plant, shown in Figure 1, lower, is located within the enclosure. One side of the enclosure opens toward a window. This provides illumination and pressure relief if ever needed. The main portions of the shield are made of 1/4 in. steel plate bolted to a frame which is securely anchored to the floor, ceiling, and wall of the laboratory. Plexiglass sections provide observation and aluminum plate encloses the remainder.

Instrumentation and controls were centralized as much as possible either on or near the main steel blast plate. This became the control panel which is shown in Figure 1, top left. The feed and product recovery systems are also located outside the enclosure. This facilitated operation and safety. No one is permitted within the shield while the reactor is operating.

Butane system

The butane system is shown schematically in Figure 2. The tank was steam heated and insulated to maintain a pressure of about 60 psig. in the tank. Gas was supplied by a single stage regulator to a low pressure "pancake" regulator. Butane, at 8 psig., after passing through a constant temperature bath, was metered in a Brooks 600 mm. rotameter where pressure and temperature were measured. A check valve protected the manometer and rotameter from reactor pressure surges. The rate of flow was controlled by a fine needle valve. Both compressed air and nitrogen could be added to the gas feed system without disturbing the butane rate.

The rotameter was calibrated with a Precision wet test meter after taking proper precautions to insure saturation of the meter fluid. The

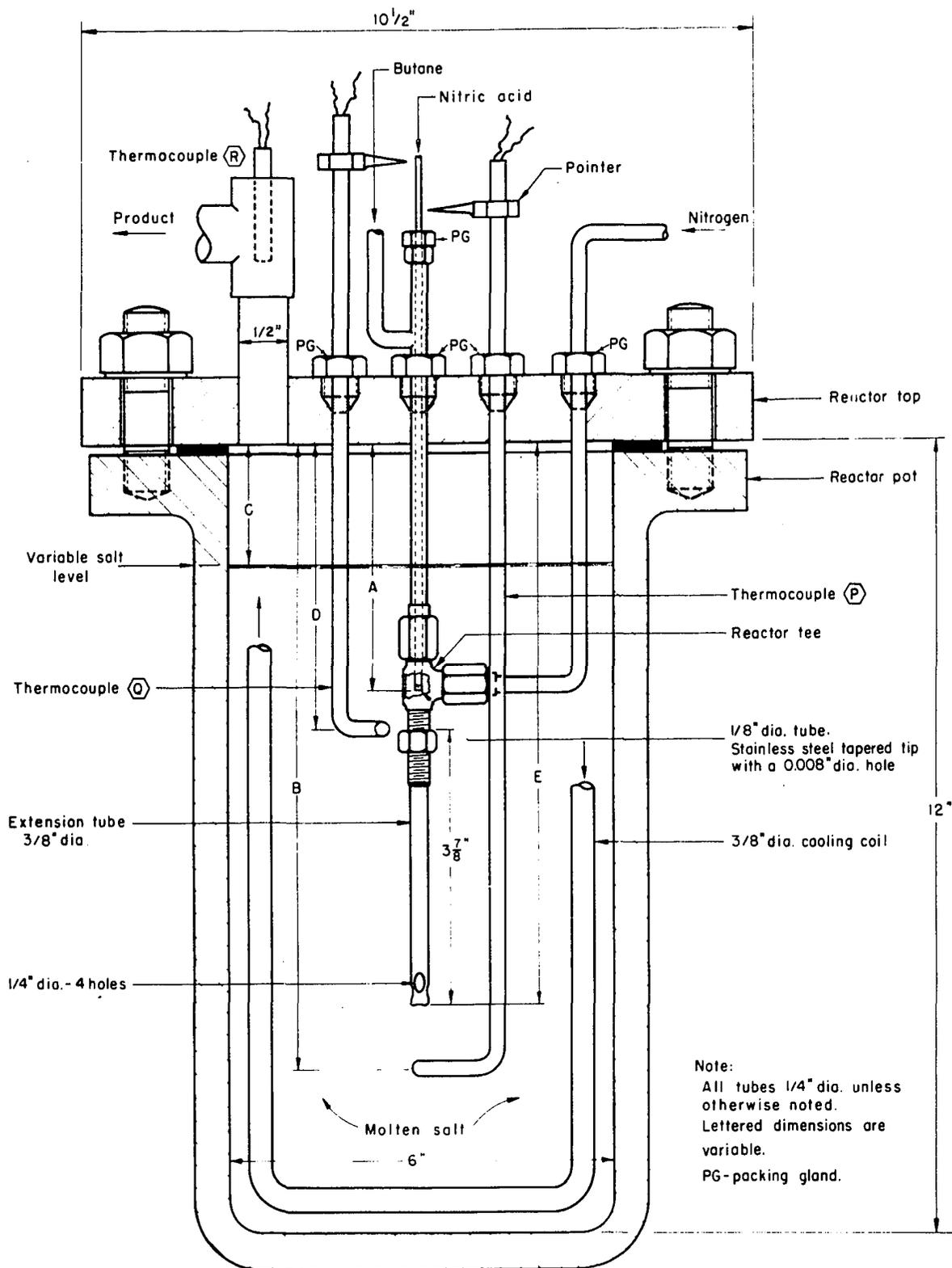
system will measure and deliver butane at rates from 2 to 26 standard cubic feet per hour (2 to 30 gram-moles per hour) which provides considerable flexibility.

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

Nitric acid system

The nitric acid system consists of a reservoir, pump, rotameter, and assorted plumbing as may be seen in Figure 2. The acid reservoir, B, is made of a 5 ft. length of 1 in. glass pipe with Saran end fittings. The pipe, which holds 700 cc., is graduated in mm., calibrated, and serves as a time-integrating rate meter as well as supply source. Acid is withdrawn from the reservoir by a Lapp Pulsafeeder pump, C, and is delivered through a 10 micron sintered stainless steel filter, E, and fine needle control valve, 7, to the rotameter, F. The air column, D, and by-pass valve, 4, back to the acid column serve to dampen pulsations from the pump. From the safety shielded rotameter the acid flows past the sampling point, where system pressure is measured, to the reactor. The acid line is reduced from 1/4 in. to 1/8 in. immediately prior to entering the reactor. Figure 3 shows that the 1/8 in. tubing may be positioned above or below the molten salt level. It is inside a 1/4 in. tube to which it is sealed with a packing gland at the top. Butane flowing in the annular space between the two tubes acts as a coolant and prevents premature vaporization of the nitric acid. Nitrogen can be supplied through a snap-action toggle valve directly from the regulator and may be used to supply diluent immediately if the reaction seems to be

Figure 3. Reactor cross section



No scale

getting out of control. The acid is introduced to the reaction zone through a 0.008 in. diameter hole in a tapered stainless steel plug welded in the end of the 1/8 in. tube.

The rotameter was calibrated and delivers acid at ranges from 20 ml. per hour to 200 ml. per hour. This is equivalent to a range of 0.4 gram moles per hour to 3.3 gram moles per hour using 70% acid.

Reactor

This portion of the pilot plant is made up of two separate parts, the reactor head plate and the reactor pot, which fit together and are supported in a furnace. Figure 3 is a cross section drawing of the assembled reactor, modified slightly by rotation of the cooling coil and main thermocouples to permit all the important components to be shown in one plane. Figure 2, upper right, is a photograph of the reactor head plate while Figure 2, lower, shows the assembled reactor, ready to operate, mounted in the furnace.

The furnace is an 18 in. hollow cube of fire brick interlocked in an angle iron frame with steel bottom and top plates. If the pot should ever rupture, any fragments would have to pass through the fire brick, thus losing considerable energy. A layer of transite, insulated from the furnace top plate with asbestos cement, forms the upper surface of the firebox. The reactor pot extends down into the firebox through a close fitting hole cut in the top layers.

Heat is supplied by a burner inserted in the firewall just above the furnace floor. The electrodes of the ignition system extend into the baffled chamber immediately in front of the burner and are controlled

from the instrument panel. City gas and primary air are metered to the burner through rotameters and drawn out of the furnace by an air eductor located in the end of the exhaust stack. An indication of furnace temperature is provided by a thermocouple located in the exhaust gas stream. Temperatures, as measured in the molten salt, can be varied from 222°C to 600°C with little difficulty. The reactor pot is made of cast iron with 1/2 in. thick walls. The working space within the pot is 6 in. in diameter and 12 in. deep. The pot holds approximately 17 pounds of molten salt when 1-1/2 in. space is left at the top for expansion and disengagement. In this work a eutectic mixture of 54 wt. % KNO_3 and 46 wt. % NaNO_3 has been used which melts at 222°C.

The reactor head plate, to which are attached all of the reactor internals, is sealed to the pot with asbestos gaskets and may be lifted and removed with the aid of an overhead hoist. Butane enters the central tube above the reactor, flows down the annulus, through the top, cooling the nitric acid, until it passes the tip of the nitric acid injector where vaporization and reaction take place. The dimensions of the annulus and the flow rates are such that the gas is in the turbulent flow region. In order to increase contact and mixing time of the nitric acid and butane, a 3/8 in. diameter extension tube is threaded on the lower end of the reaction tee. From the bottom of this tube the gas bubbles up through the molten salt and leaves the reactor in a 1/2 in. pipe. This 1/2 in. line has a safety relief valve, a rupture disc assembly, a pressure tap, and a thermocouple in it between the reactor and the condenser. The hairpin-shaped cooling coil is used to make fine adjustments

in the temperature of the molten salt bath and uses air as the cooling medium. All lines going to or from the reactor head plate have unions in them to facilitate maintenance.

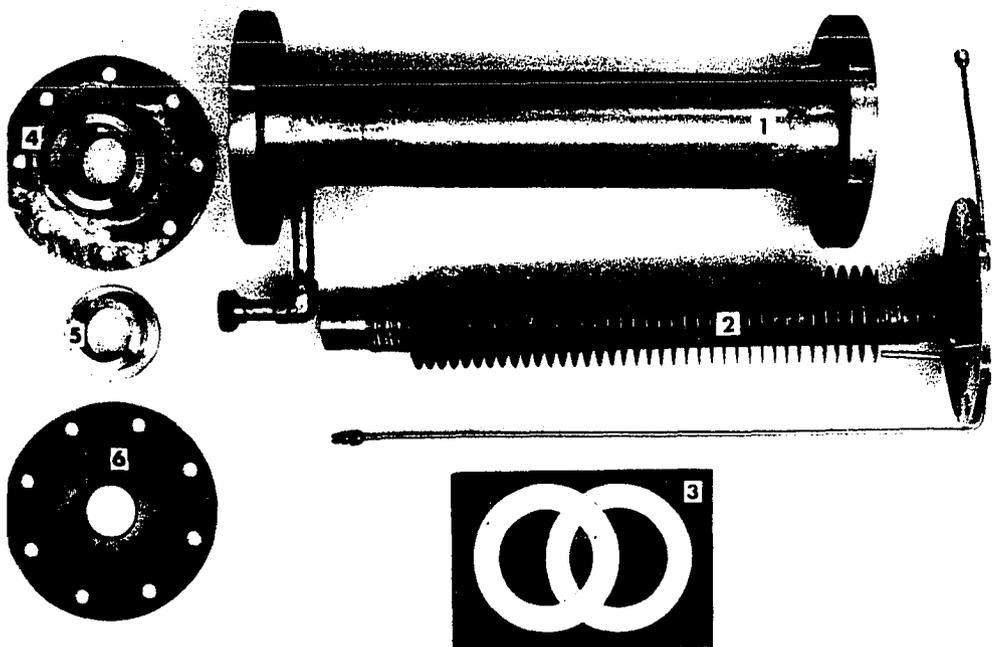
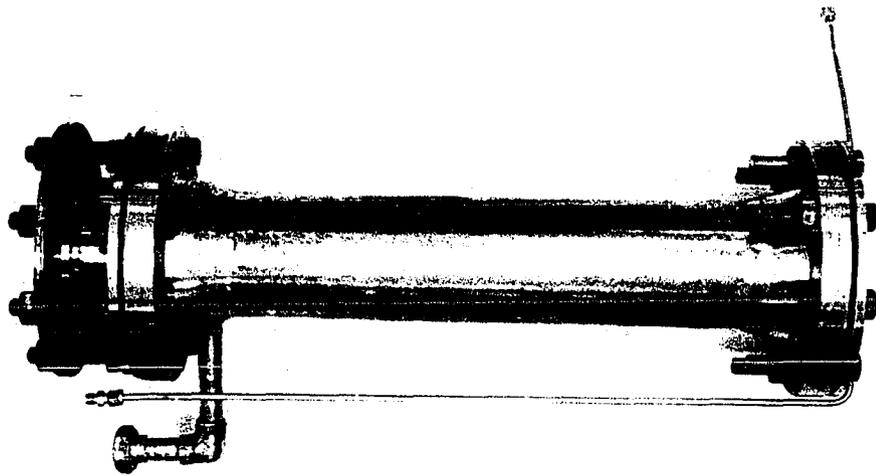
The two main thermocouples may be moved up or down and rotated in their packing glands. They are chromel-alumel couples welded in the tips of 1/4 in. tubes and have a speed of response on the order of 100°C per minute. Pointers on the top of the thermocouples locate the tips with respect to the reactor tee, while scribe marks on the tubing show depth. Temperatures measured by these thermocouples plus the one in the product line and the one in the exhaust stack are recorded on a Brown Elektronik multi-point recorder.

Product recovery system

From the reactor, the product gases pass to the condenser as shown in Figure 2. The assembled condenser is shown in Figure 4, top, while the component parts are shown in Figure 4, bottom. The hot product gases enter the top of the co-current condenser through the 1/2 in. pipe seen in the photographs and pass down the annular space between the inner and outer shells. The fins on the inner pipe fit the shell closely and force the gas to descend in a spiral path. Liquid products condensed from the gas stream are swept toward the bottom and collect in the 3 in. high annular space which has been left free of fins. This space also serves as an entrainment separator since the gas velocity is much lower here than between the fins. A length of 1/4 in. tubing extends up through the liquid seal formed and the uncondensed gases leave the condenser through this tubing. The internal free volume of the condenser is 3 liters.

Figure 4. Photographs of the condenser

Top: Assembled condenser
Bottom: Component parts



The condenser shell (Figure 4, bottom, item 1) is made of 4 in. sch. 40 pipe while the finned inner shell (item 2) is made of 2 in. sch. 40 pipe. The two pieces slip together with teflon gaskets (item 3) on either end of the outer shell. The packing glands (item 4 and 5) are placed over the top or machined end of the finned tube and are sealed by pressure exerted on the graphited asbestos packing rings by the top plate (item 6). All metal parts are of stainless steel.

The unit is submerged in a tank of ice water when in operation. A recirculating pump forces the cold water down the center hole. Liquid product is drained off at intervals through the bottom 1/4 in. tube into a graduated cylinder.

The uncondensed gases pass through a 600 mm. rotameter identical to that used in the butane feed system. Temperature and pressure are measured at the rotameter. The gases are then sampled, if desired, scrubbed to absorb acidic gases, measured in a wet test meter and vented.

Operating Procedure

Start up

The steam heating system is turned on to bring the butane system up to operating pressure. Ice is chipped and placed in the condenser tank which is then filled with water. The furnace is started and, when the salt melts, the reactor head plate is lowered into place, secured, and all piping connections made. The reactor is then purged with nitrogen. The nitrogen diluent line and the relief valve are tested. Leaks are found and repaired. The recorder is turned on and the furnace controls

are manipulated until the salt temperature "lines-out" at the desired value.

In the butane system (Figure 2), the constant temperature bath is turned on and the piping is purged of any air that may have accumulated. Pressures are adjusted and the desired flow rate is set on rotameter M using fine needle valve 15. Valve 13 is then closed shutting off the butane supply but leaving the flow rate setting undisturbed. The reactor is again purged with nitrogen.

The acid reservoir B is then filled. The Pulsafeeder pump C is started with the acid injector pulled out of the head plate. Acid is pumped through valve 11 to purge air bubbles and insure that the injector is not plugged. Valve 11 is then closed. Since the pump is oversize, the column bypass valve 4 is adjusted to return most of the acid and produce a pressure in air column D that gives minimum pulsation at the rotameter.

Since the calibration of the rotameter changes with acid concentration, the rotameter is used to maintain constant delivery rates during a run. The actual quantity of acid fed is determined by the change in levels in the calibrated reservoir. The setting on the rotameter for the desired delivery rate is made by timing the acid flow through valve 10 into a buret.

The product recovery system is prepared for operation next. The condenser is checked to see that it is dry and liquid product valve 18 is closed. Scrubbers are checked to see that they are filled and connected properly. Gas sample bottles are placed in the line and the system

checked for leaks. Additional sample bottles and necessary glassware are prepared.

Operation

The acid injector is inserted to the desired depth. The butane and acid flows are started after noting the time, the wet test meter reading, and height of acid in the reservoir. Flow rates are adjusted to desired conditions and maintained throughout the run. The condenser recirculation pump is started. Pressures, temperatures, volumes, and flow rates are recorded at regular intervals.

Gas samples are taken during the run by manipulating the proper pinchcocks. The sample bottles are sealed by rubber serum caps, through which samples are later withdrawn by microsyringe for analysis.

Liquid product is drained from the condenser at intervals into a graduated cylinder. After the volumes of the aqueous and oil layers are recorded, they are separated and stored for analysis at the termination of the run.

The run is ended by recording the level in the acid reservoir, the wet test meter reading, and the time. Simultaneously, the input of reactants is stopped.

Shut down

The pulsafeeder pump is shut off and bypass valves 3 and 4 opened to relieve pressure in the acid system. The butane flow is shut off by valve 13. The reactor is purged with nitrogen admitted by valve 17. The condenser recirculating pump is shut off. The acid injector is removed

from the packing gland to prevent plugging. The temperature recorder is shut off.

If another run is to be made shortly, all systems are left primed and at operating temperature. If operation is not planned upon for several days, the furnace is shut off and the reactor head plate is removed from the salt bath. This is done to prevent damage from expansion and contraction of the salt as it changes phases. The butane system is bled down and purged.

Nitric Acid Solubility in Molten Salt

If nitric acid is soluble in the molten salt to any appreciable extent, the nitrate radical concentration in the bubbles of reaction gas should be maintained at a high level by diffusion into the bubble. In other words, if a reservoir of the nitrating agent can be maintained in the molten salt this would tend to replace the nitrating agent in the bubble as it is used up in the reactions.

Accordingly, the solubility of nitric acid vapor in the molten salt was investigated. The raw unmelted salt was found to be barely acid. Approximately 0.06 ml. of 0.1 N base neutralized 100 gms. of salt. After melting the salt and bubbling nitric acid vapor through the melt for an hour, samples were trapped in the molten state, dissolved in distilled water and titrated. These tests were run with melt temperatures of 239°C, 301°C, and 320°C. In all cases the results were the same as for the new unmelted salt. It was concluded that nitric acid vapor is not soluble in the molten salt.

Analytical Procedure

General

The primary objectives of the analytical procedures are twofold:

1. to provide a means of determining quantitatively the mononitroparaffins present, and 2. to provide sufficient information so that overall material balances can be made on both the carbon and nitrogen. Gas-liquid partition chromatography (GLPC) has been developed to the point where it can be used with confidence to accomplish these objectives (16, 17, 18).

Replicate samples used in 3 columns give satisfactory quantitative separation of the C₁ to C₄ mononitroparaffins, alcohols, aldehydes, C₁ to C₄ paraffins, and NO, NO₂, CO, CO₂, all in the presence of water.

The nitrator product is obtained as a liquid phase and an off-gas. The liquid product is recovered and immediately separated into two layers: an oil layer, containing approximately 80-90% nitroparaffins, 1-10% water, 2% oxygenated organics, and about 2% dissolved gases; and an aqueous layer containing, in addition to the majority of the water and other oxygenated compounds produced in the reactor, less than 1% nitroparaffins, 1 to 2% dissolved gases (primarily carbon dioxide and nitrogen dioxide), and nitric acid. The off-gas consists primarily of butane. Oxides of nitrogen and carbon, water vapor, and propane are also present.

Equipment and technique

The unit used for this work was the F & M Scientific Corp. Model 500A programmed temperature gas chromatograph, as modified by Bethea and Adams (16, 17). The injection port was maintained at 200°C. Liquid

samples were injected through a self-sealing silicone rubber septum with a 10 μ l. Hamilton microsyringe. The carrier gas used for these analyses was helium (minimum purity, 99.98 mole %, The Matheson Co.) which was dried before use by passing through a 12 in. length of 3/8 in. pipe filled with No. 5A Linde molecular sieves installed in the inlet line to the thermal conductivity cell. The flow rate through the reference side of the cell was maintained constant at 30 ml. of helium per minute, measured at 28°C with a calibrated Brooks "Shorate" 150 rotameter, tube No. 1-15-6, stainless steel float. Gas samples used for calibration were collected in 250 ml. sample bulbs, fitted with 2 stopcocks. After the sample was obtained and the stopcocks closed, a rubber serum cap was fitted to the stub end through which the samples were withdrawn (by opening the cock, inserting the needle, sampling, withdrawing the needle and closing the cock) with a 1 cc. gas-tight syringe (Teflon-tipped nylon plunger, Wilkens Instrument and Research). Liquid samples used were 4 μ l. The gas samples used were 200 μ l. and 20 μ l. 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 analysis of the nitrator products was broken down into 3 segments (Table 5). The oil layer samples were analyzed on the Armeen SD-Apiezon N column for the quantitative separation of the nitroparaffins and the oxygenated compounds. The dissolved gases in the oil layer, which appeared as three small incompletely resolved peaks, were separated by running duplicate oil layer samples through the squalane-Fluoropak column and through the squalane-activated charcoal column. The aqueous

Table 5. Procedure for product analysis by GIPC

Use	Column	Flow rate ^a	Temperature	Compounds separated quantitatively
Oil	A ^b	60	L.T.P. ^c	NP's, H ₂ O, oxygenated aliphatics, ^d C ₂ H ₆ , C ₃ H ₈ , n-C ₄ H ₁₀ , iso-C ₄ H ₁₀ , CO ₂ , CO + NO + NO ₂ + N ₂
Oil	B ^e	66	22°C	CO, HCHO, NO ₂ + N ₂ , N ₂ O ₄ , NO
Oil	C ^f	77	50°C	C ₂ H ₆ , C ₃ H ₆ , n-C ₄ H ₁₀ , iso-C ₄ H ₁₀ , CO ₂ , NO ₂ , NO + CO
Off-gas	B ^e	66	22°C	CO, HCHO, NO ₂ + N ₂ , N ₂ O ₄ , NO
Off-gas	C ^f	27	30°C	CO ₂ , NO ₂ + N ₂ , H ₂ O + C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀
Off-gas	C ^f	77	50°C	H ₂ O + C ₂ H ₆ , oxygenated aliphatics, ^d NM, NE, 2-NP, 2-M-2-NP, 1-NP, NO ₂ , CO ₂
Aqueous	B ^e	66	22°C	CO, HCHO, NO ₂ + N ₂ , N ₂ O ₄ , NO
Aqueous	C ^f	27	30°C	CO ₂ , NO ₂ + N ₂ , H ₂ O + C ₂ H ₆ , C ₃ H ₆ , C ₄ H ₁₀
Aqueous	C ^f	77	50°C	H ₂ O + C ₂ H ₆ , oxygenated aliphatics, ^d NM, NE, 2-NP, 2-M-2-NP, 1-NP, NO ₂ , CO ₂

^aml. helium per minute measured at 28°C, atmospheric pressure.

^bColumn A: a 2:1 weight mixture of Armeen SD and Apiezon N, each 10/100 on C-22, -48 + 65 Tyler standard mesh, 1/4 in. OD x 6 ft.

^cL.T.P.: Linear temperature programming at 2.9°C per minute starting from 40°C.

^dIncludes all C₁ to C₄ RCHO, ROH, ROR', RCOOR', and RR'C=O.

^eColumn B: 2/100, squalane on activated charcoal, -65 + 80 Tyler standard mesh, 1/4 in. OD x 20 ft.

^fColumn C: 10/100, squalane on Fluoropak, -30 + 80 U.S. Standard mesh, 1/4 in. OD x 24 ft. 11 in.

layer samples were analyzed on the squalane-Fluoropak column at the higher temperature and flow rate to pick out the water, oxygenated compounds, and the nitroparaffins. Duplicate water layer samples were then run through the column at the lower temperature and flow rate and initially through the squalane-activated charcoal column for the analysis of the dissolved gases. This analysis showed that the acidity of the aqueous layer was due almost entirely to the presence of nitric acid. In later runs, an immediate titration with standard base provided the same information as Column B. These results can best be summarized by Table 5, which is a diagram of the analytical procedure followed for routine analysis.

The limits of accuracy and reproducibility for any given component in Columns A and C were $\pm 2\%$ of the true value of the component when calibrated against known gravimetric samples containing that component. The GIPC analyses were obtained by measuring the peak areas with a Model K2-1 integrator (Disc Instruments, Inc.). Working with known volumes of pure gases, Column B was found to have similar limits. The purity of the compounds used for calibration was the highest normally available. The nitroparaffin samples used for calibration had a minimum purity of 99.8 mole %.

Analytical Results

The molten salt nitrator was operated with butane flows from approximately 6.8 to 12.0 moles per hour, mole ratios of hydrocarbon to nitric acid from 3.1 to 7.2, with salt temperatures from 745°F to 805°F. The normality of the nitric acid used ranged from 8 to 15. Experimental

conditions, reactor geometry, and weights of products produced are presented in Table 6.

Complete analyses of the three product streams from the pilot plant are presented in Table 7. These analyses were obtained by use of GIPC techniques developed at Iowa State University as part of this work.

The chromatograms of the samples from Run 13 are presented as Figures 5-8. They are typical of those obtained in the course of this investigation. The chromatograms used for quantitative analysis of the oil layer are shown as Figure 5. Similarly, the aqueous layer chromatograms in Figure 6 and gas chromatograms in Figures 7 and 8 are shown.

These analyses permitted calculation of carbon and nitrogen material balances for the reactor. These data, together with the yields and conversions obtained, are summarized in Table 8.

The nitroparaffin distributions obtained from the pilot plant runs are presented in Table 9.

Table 6. Experimental conditions and material produced per hour for runs 8-14

	8	9	10	11	12	13	14
Duration, min.	70	72	70	70	80	80	69
Salt temp., °F	745	805	800	785	805	785	745
Acid normality	15.67	8.265	8.280	8.825	8.632	12.102	12.102
Moles of butane per hour	9.809	12.037	8.031	6.825	7.847	7.810	6.669
Mole ratio, alkane to acid	4.483	7.191	4.637	3.887	4.223	3.616	3.152
Dimension A, ^a inches	-3 3/16	-4 1/2	-4 1/2	-3 3/8	-3/4	-3/4	-1 3/4
Dimension C, ^b inches	1 1/4	1 1/4	1 1/4	1 1/4	1 1/4	1 3/8	1 3/8
Dimension E, ^c inches	6 1/8	9 3/8	9 3/8	6 3/4	9 5/16	9 5/16	9 5/16
Space velocity ^d	32.90	40.90	33.86	37.14	41.62	35.49	29.88
Oil, gms.	41.34	48.28	62.96	40.36	55.56	48.78	40.54
Aqueous, gms.	100.51	155.06	192.74	167.72	196.95	174.28	157.74

^aSee Figure 3. Location of acid injector tip; referenced from lower face of reactor head plate, down is positive.

^bSee Figure 3. Salt depth.

^cSee Figure 3. Depth to holes.

^dSV calculated as ft.³ of reactants per second per ft.³ of tubular reactor space; reactants as gases at salt temperature.

Table 7. Complete analysis of reactor products, gram-moles per hour

	8	9	10	11	12	13	14
011	(Entries valid to 4 significant figures)						
NM ^a	0.05391	0.07507	0.07272	0.04165	0.04520	0.03763	0.03612
NE	0.10072	0.10760	0.17193	0.09409	0.12234	0.10936	0.08268
2-NP	0.00130	0.00022	0.00035	0.00023	0.00083	0.00016	-
2-M-2-NP	-	-	0.00012	0.00031	0.00202	0.00024	0.00106
1-NP	0.02223	0.04579	0.04820	0.02383	0.03482	0.02300	0.01825
2-NB	0.20490	0.19186	0.28091	0.18341	0.26589	0.21623	0.20801
2-M-1-NP	-	0.00019	-	-	-	-	-
1-NB	0.06799	0.10717	0.09641	0.06231	0.11546	0.07469	0.06109
NO	0.00069	-	-	-	trace	-	-
NO ₂	0.00449	0.00682	0.00561	0.00947	0.00799	0.01071	0.01498
CO ₂	0.00160	0.00132	0.00072	0.00147	0.00056	0.00233	0.00175
H ₂ O	0.05132	0.04636	0.04264	0.14270	0.00817	0.26426	0.09023
n-C ₄ H ₁₀	0.00100	0.00133	0.00249	0.00125	-	0.00176	-
HCHO	0.00427	0.00627	0.00901	0.00349	0.00367	0.00520	0.00203
CH ₃ CHO	-	0.00910	0.01129	-	0.00111	-	0.00074
CH ₃ OH	0.00581	0.00422	0.00039	0.00327	0.00038	0.00320	-
C ₂ H ₅ OH	-	0.00084	-	0.00210	0.00106	0.00254	0.00106
(CH ₃) ₂ CHOH	-	0.00064	0.00052	0.00067	0.00041	0.00041	0.00081
C ₂ H ₅ CHOHCH ₃	-	0.00078	0.00501	0.00474	0.00165	0.00434	0.00082

^aIncludes NM from aqueous layer, if any.

Table 7 (Continued)

	8	9	10	11	12	13	14
Aqueous							
NO ₂ ^b	0.24724	0.25086	0.27550	0.26294	0.30196	0.20162	0.29895
CO ₂	0.01119	0.00803	0.02847	0.09983	0.13873	0.05979	0.11133
C ₂ H ₆	0.01070	0.00263	-	-	-	-	-
C ₃ H ₈	-	0.01245	0.01880	0.00456	-	-	-
H ₂ O	5.40948	8.51368	10.41331	8.98033	10.55542	9.49535	8.43902
NM	0.01564	0.02413	-	0.00687	-	trace	-
Off-gas							
NO	0.2473	0.2827	0.7939	0.3981	0.5213	1.2504	1.0459
NO ₂	0.9037	0.9820	0.3137	0.4088	0.1210	0.0824	0.0179
CO ₂	0.2256	0.1592	0.1975	0.1958	0.1417	0.1954	0.2466
C ₃ H ₈	0.0803	0.2050	0.0395	0.1515	0.1322	0.2147	0.0671
n-C ₄ H ₁₀	8.2582	10.2169	6.8836	5.7750	6.5577	6.5163	4.8124

^bBy titration.

Figure 5. Chromatograms of the oil layer

Top: Column C, 50°C, 77 ml.
helium per minute

Bottom: Column A, L.T.P., 60
ml. helium per minute

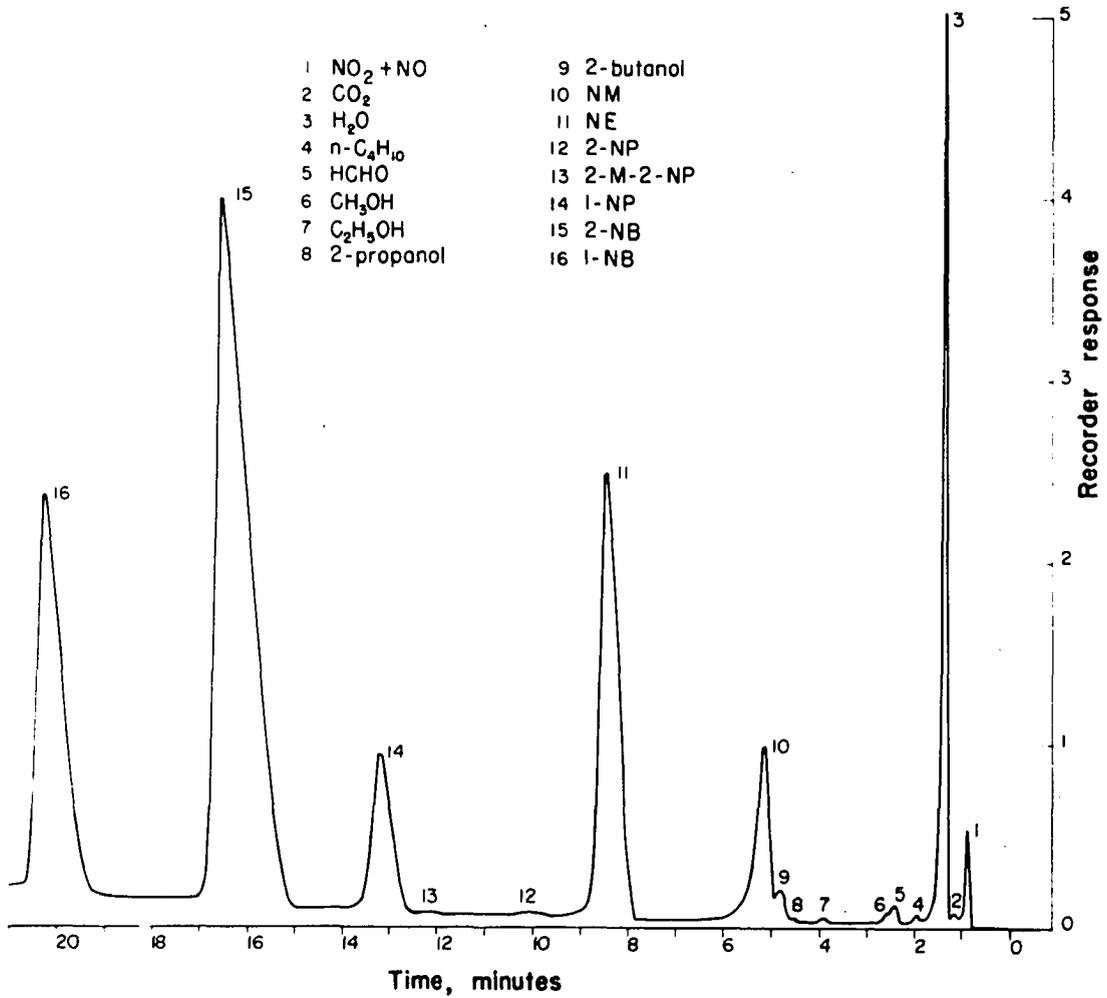
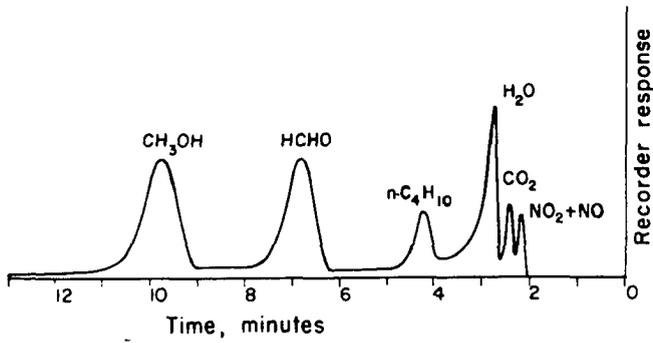


Figure 6. Chromatograms of the aqueous layer

Top: Column C, 50°C, 77 ml.
helium per minute

Bottom: Column C, 30°C, 27 ml.
helium per minute

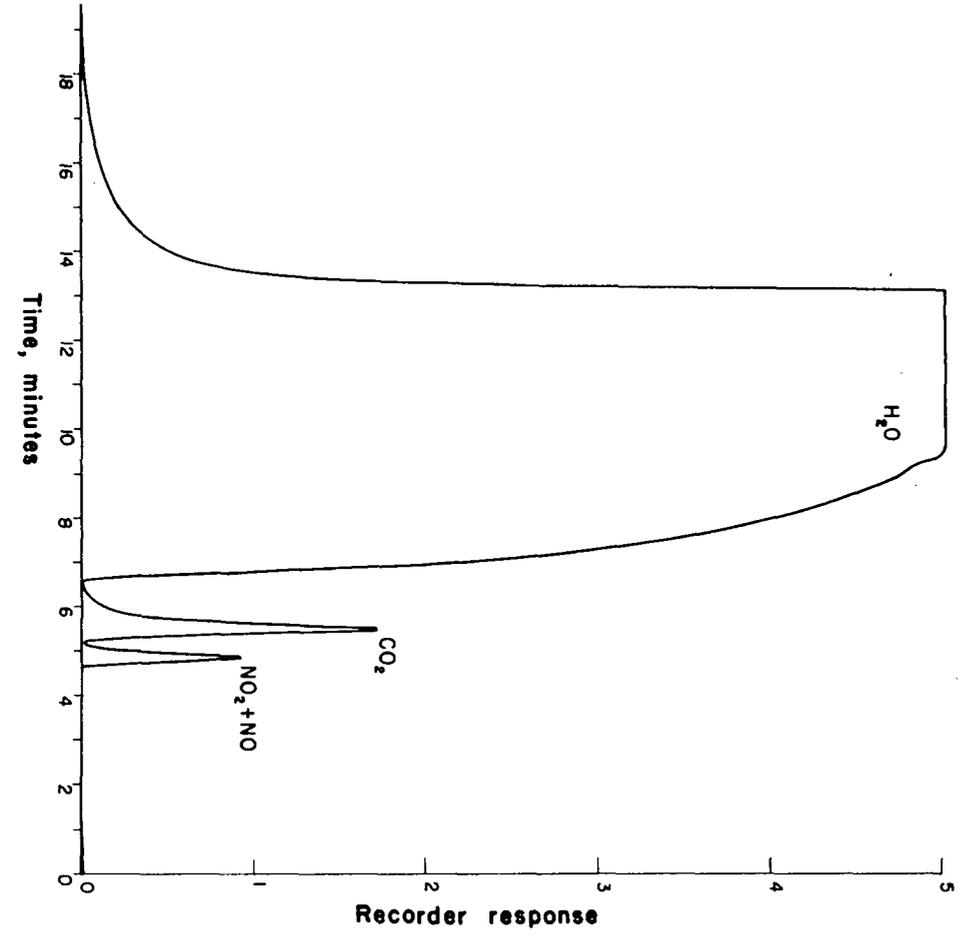
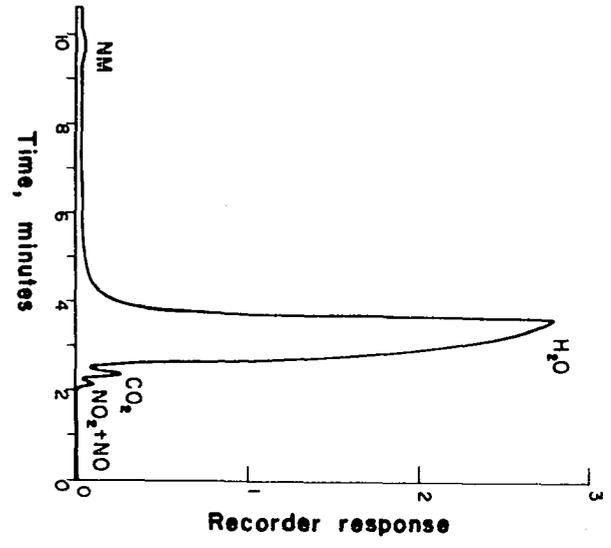


Figure 7. Chromatograms of the off-gas

Top: Column C, 50°C, 77 ml.
helium per minute

Bottom: Column B, 22°C, 66 ml.
helium per minute

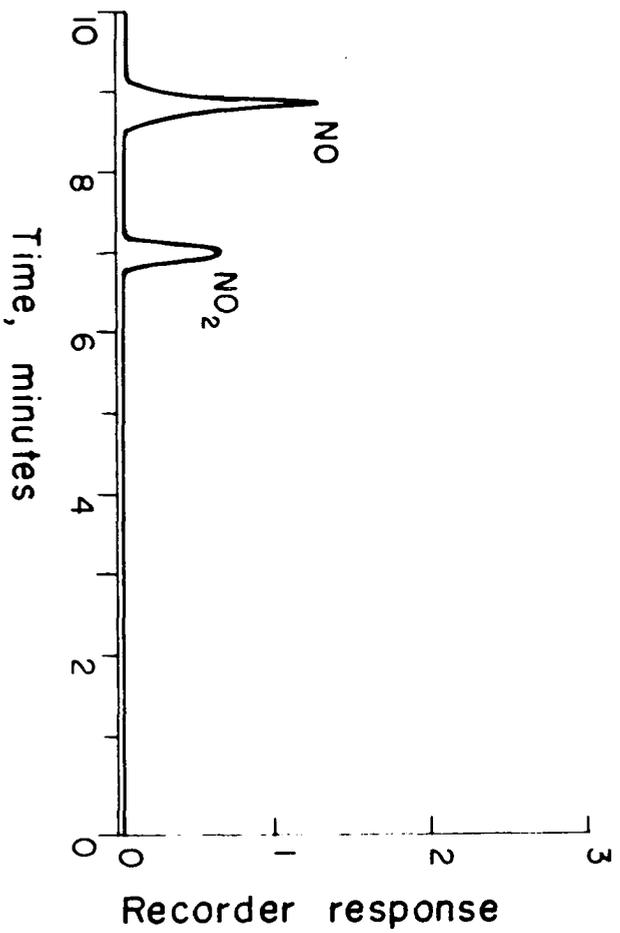
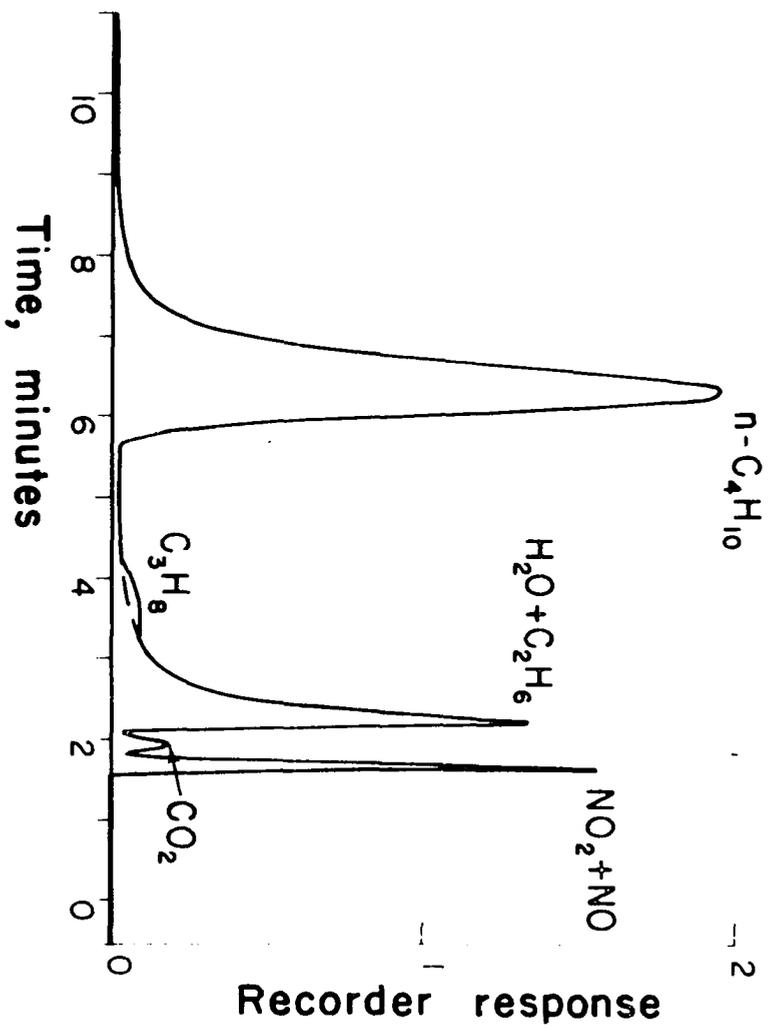


Figure 8. Chromatogram of the off-gas; Column C, 30°C, 27 ml. helium per minute

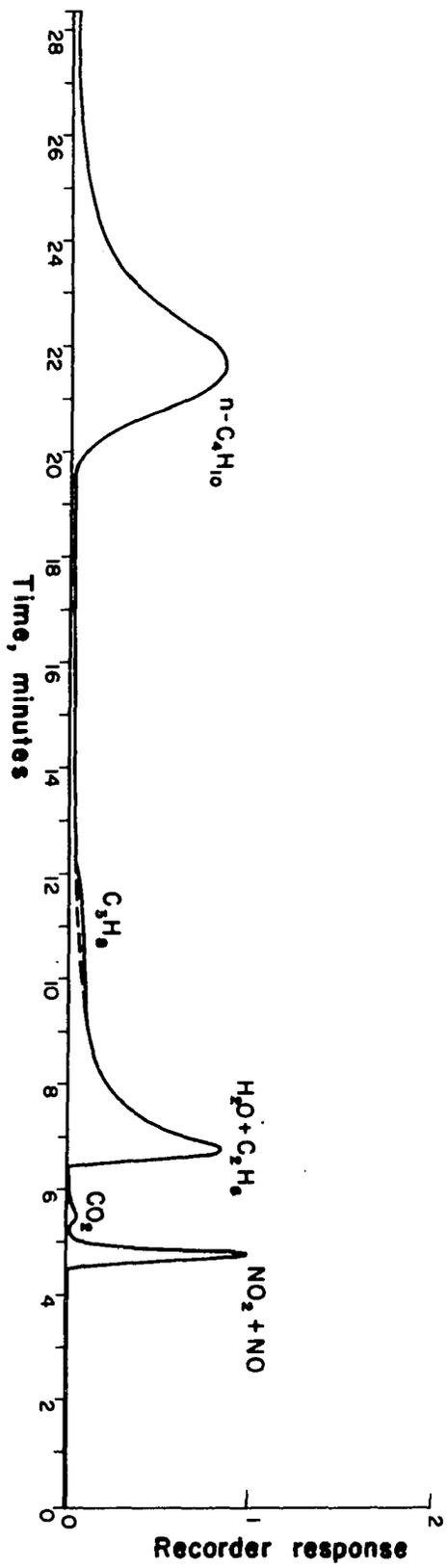


Table 8. C and N material balances for runs 8-14, gram-atoms per hour

	8	9	10	11	12	13	14
C found:							
Oil	1.4331	1.6672	2.1363	1.2445	1.9471	1.5319	1.3499
Aqueous	0.0326	0.1656	0.0849	0.1135	0.1387	0.0598	0.1113
Off-gas	<u>33.4994</u>	<u>41.6418</u>	<u>27.8504</u>	<u>23.7503</u>	<u>26.7692</u>	<u>26.9047</u>	<u>19.6975</u>
	34.9651	43.4746	30.0716	25.1083	28.8550	28.4964	21.1587
C input	39.239	48.148	32.124	27.300	31.388	31.240	26.676
% of input	89.11	90.29	93.61	91.97	91.93	91.22	79.32
% yield ^a	3.61	3.38	6.45	4.42	6.15	4.77	5.01
% yield ^b	73.51	65.22	81.99	60.20	73.56	61.48	70.02
N found:							
Oil	0.4562	0.5347	0.6763	0.4153	0.5946	0.4720	0.4222
Aqueous	0.2472	0.2509	0.2755	0.2629	0.3020	0.2016	0.2989
Off-gas	<u>1.1510</u>	<u>1.2647</u>	<u>1.1076</u>	<u>0.8069</u>	<u>0.6423</u>	<u>1.3328</u>	<u>1.0638</u>
	1.8544	2.0503	2.0594	1.4851	1.5389	2.0062	1.7849
N input	2.188	1.674	1.732	1.756	1.858	2.160	2.116
% of input	84.75	122.48	118.90	84.57	82.83	92.88	84.35
% conv. ^c	20.61	31.94	39.05	23.65	31.57	21.85	19.95

^aRatio of carbon in NP's to carbon fed.

^bRatio of carbon in NP's to carbon reacting.

^cRatio of nitrogen in NP's to nitrogen fed.

Table 9. Nitroparaffin distribution for runs 8-14, mole %

Component	8	9	10	11	12	13	14
NM	11.95	14.22	10.84	10.26	7.71	8.16	8.87
NE	22.33	20.38	25.64	23.18	20.86	23.71	20.30
2-NP	0.29	0.04	0.05	0.06	0.14	0.04	-
2-M-2-NP	-	-	0.02	0.08	0.34	0.05	0.26
1-NP	4.93	8.67	7.19	5.87	5.94	4.98	4.48
2-NB	45.43	36.35	41.89	45.19	45.33	46.87	51.08
2-M-1-NP	-	0.04	-	-	-	-	-
1-NB	15.07	20.30	14.38	15.35	19.68	16.19	15.00

DISCUSSION

Analytical Problem

The value of a pilot plant study of this type is heavily dependent upon the accuracy and precision of the analyses. At the inception of this work, there were no adequate analytical tools available which would provide complete analysis of the expected nitrator products. Most of the previously reported work has relied upon Orsat gas analysis, Kjehldahl or Dumas analyses for total nitrogen, colorimetric procedures for one or two nitroparaffins (82) and other procedures which, even in the aggregate, do not provide complete information. In an effort to provide more detail, two investigators (6, 11) turned to mass spectrometry for nitroparaffin analysis. This method becomes cumbersome because each additional nitroparaffin requires expansion of the spectrographic matrix by one in each dimension. This necessitates solving at least an eight by eight matrix in the case of butane nitration. Orsat analysis is subject to inherent error when butane is the major constituent due to solubility problems (75). In short, it became of prime importance to develop a rapid, relatively simple, reproducible and precise quantitative analytical method.

Gas-liquid partition chromatography (GLPC) appeared to be the only method which showed promise of meeting all of these requirements. Early in this investigation qualitative separation of all eight nitroparaffins was obtained, but quantitative separation was possible only for NM, NE, 2-NP, and 1-NP (19).

GLPC Columns Studied for Oil Layer

A standard sample was made up gravimetrically for eight nitro-paraffins and was used as a test mixture for 14 columns, each 50 in. long by 1/4 in. I.D. These columns were (quantities per 100 gr. of brick): 1-decanol, β, β' -oxydipropionitrile, Ucon LB 500x (Perkin-Elmer R packing), THEED (tetrahydroxyethylethylenediamine), squalane, 30 gr. each; 2,2,4-trimethyl-1,3-pentanediol, 35 gm.; Apiezon M, 10 gr.; Apiezon L, 10 gr.; Armeen SD (a soya amine recommended by Zarembo and Lysyj (99) for the quantitative separation of water and alcohols), 30 gr.; Armeen SD, 15 gr.; a 2 to 1 mixture by weight of Apiezon T and Armeen SD, each containing 30 gr. of substrate; a 1 to 1 mixture by weight of the same packing; a 1 to 1 mixture by weight of Apiezon M, 10 gr., and Armeen SD, also 10 gr.; and a 2 to 1 mixture by weight of Apiezon M, 10 gr., and Armeen SD, 10 gr.

As the last packing in this list provided the best separation, it was further tested in 6 and 12 ft. columns made of 1/4 in. copper tubing. The 12 ft. column required excessive analysis times to obtain sufficient peak separation and showed unacceptable peak shape due to tailing. The 6 ft. column seemed to offer the best chance for obtaining the desired separation.

Mixed Substrates

The columns tested which provided reasonably good separation of the nitroparaffins caused considerable tailing for oxygenated compounds. Those which provided good separation for oxygenated compounds caused leading of the nitroparaffins. The use of mixed substrates eliminated

leading altogether and eliminated tailing except in the methanol and nitromethane peaks. Further studies showed that the substitution of Apiezon N for Apiezon M greatly improved the separation of the nitro-paraffins.

Optimum Conditions

A statistical experiment was designed and carried out to determine the optimum operating conditions for the mixed substrate column (Column A, Table 5). It was found that linear temperature programmed operation (at 2.9°C per minute, starting at 40°C) of the mixed Armeen SD-Apiezon N column was effective in the separation of the nitroparaffins in the oil layer in the presence of small amounts of light hydrocarbon gases, water, and the lower molecular weight alcohols, aldehydes, and ketones. The flow rate used was 60 ml. of helium per minute (measured at 28°C). The very slight tailing of nitromethane, methanol, and water which is typical of this column under all operating conditions, did not affect the precision and accuracy of the analyses.

Problems with Water and Oxygenated Products

It was found that in general substrates which are commonly used for the separation of water (Armeen SD); alcohols (dibutyl sebacate, 1-decanol, dibutyl phthalate, Carbowax 600 and 1500); aldehydes (Carbowax 20 M); and dissolved gases such as CO, CO₂, N₂, O₂, CH₄, C₂H₆, C₃H₈, C₄H₁₀, etc. (squalane, activated carbon, activated alumina, silica gel, and a 1:1 mixture by weight of glutaronitrile and propylene carbonate) lose their effectiveness when used for the separation of samples

containing compounds from the other classes. It was found that the substitution of Fluoropak (Wilkins Instrument and Research) for the Type C-22 firebrick and the Chromosorb P greatly reduces or even eliminates the tailing so often encountered in the analysis of samples containing water by GLPC. However, when this change of support material was tried for the mixed Armeen SD-Apiezon N substrate for the analysis of the nitroparaffins in the oil layer, a decrease in resolving power was observed.

Aqueous Layer Column

A column (Column C, Table 5), 24 ft. 11 in. long x 1/4 in. O.D. copper tubing, filled with a packing consisting of 10 gr. of squalane per 100 gr. of the -30 + 80 U.S. standard screen fraction of Fluoropak, when operated at 50°C at a helium flow of 77 ml. per minute (measured at 28°C) gave excellent separation of the oxygenated constituents of the aqueous layer. Under these conditions, the nitroparaffins were retarded for 20 minutes, allowing the aqueous layer analyses to be made on a nitroparaffin-free basis. The first four nitroparaffins (NM through 1-NP) can be determined quantitatively in the squalane column if sufficient time is allowed. 1-NP has a retention time of 69.5 minutes under these conditions.

Off-gas Columns

A 1:1 mixture by weight of glutaronitrile and propylene carbonate, Carbowaxes 600 and 20M, a 1:1 mixture by weight of Armeen SD and Apiezon N, all in the ratio of 10 gm. substrate per 100 gm. support; 2 wt. %

squalane on activated carbon; 2 wt. % dibutyl sebacate on silica gel; activated carbon; and the squalane column used for the aqueous layer samples were tested for the analysis of the off-gas leaving the reactor. This stream contains primarily n-butane, 9-11 mole % NO and NO₂, 2-3 mole % propane, 1.5-2.5 mole % carbon dioxide, and traces of carbon monoxide, methanol, water, and formaldehyde. The gas stream is water saturated. Of the packings tested for the separation of the gas phase components, Column C gave satisfactory quantitative separation of ethane, propane, n- and iso-butane, carbon dioxide, methanol, acetaldehyde, formaldehyde, and NM through 1-NP when operated at 50°C and a helium flow rate of 77 ml. per minute. Under these conditions, N₂, NO, NO₂, and CO were eluted as a single peak just before CO₂. Operation of Column C at 30°C and 27 ml. helium per minute gave quantitative separation of CO and NO, but N₂ and NO₂ still appeared as a single peak. Under these conditions, however, the separations of water, methanol, formaldehyde, and acetaldehyde were unsuitable for quantitative work. The NO₂ and N₂ were also separated completely by running duplicate samples on a 1/4 in. O.D. column (Column B, Table 5), 20 ft. long filled with the -65 + 80 Tyler standard screen fraction of activated charcoal impregnated with 2 parts by weight of squalane per 100 parts of the activated charcoal. Operating conditions were 22°C and 66 ml. of helium per minute (measured at 28°C).

Absence of Certain Expected Products

The presence of certain compounds (hydrogen, nitrogen, oxygen, methane, alkenes, alkynes) which might be expected in the product streams was ruled out by the use of certain columns which are most satisfactory

for qualitative work. Hydrogen and methane can be qualitatively separated from the other components expected to be present in the oil and off-gas samples in a 1/4 in. O.D. column 4 ft. long filled with a packing consisting of 5 gr. of squalane per 100 gr. of the -65 + 80 Tyler standard screen fraction of reagent grade silica gel. When the oil layer and off-gas samples were analyzed in this column at 0°C and a helium flow rate of 5 ml. per minute (measured at 28°C), no hydrogen or methane was found. The off-gas samples were also analyzed at 30°C in a 1/4 in. O.D. column 10 ft. 5 in. long filled with the -65 + 80 Tyler standard screen fraction of activated carbon using hydrogen at a pressure of 11 psig. and at a flow rate of 84 ml. per minute (measured at 28°C). Neither oxygen nor nitrogen was found. The absence of alkenes and alkynes in the oil and gaseous products was demonstrated when those samples were analyzed at 0°C and a helium flow rate of 20 ml. per minute (measured at 28°C) in a 6 ft. 1/4 in. O.D. column filled with a mixture of equal parts by weight of two separate packings, glutaronitrile and proylene carbonate, each containing 24 gr. of substrate per 100 gr. of the -80 + 100 U.S. standard screen fraction of nonacid-washed, silicone treated Type C-22 Johns-Manville firebrick. Since these compounds were not present in the samples taken from several of the nitrator runs at different conditions, no further attempts were made to develop quantitative separations for them.

Nitroparaffin Distribution

The first 7 runs with the reactor were required to perfect operating procedures, improve mechanical features, and develop satisfactory

analytical methods. Since only partial data were obtained, results from these runs have not been included. With the first completely successful run, run 8, a program was undertaken to survey changes in the nitro-paraffin distribution caused by varying operating conditions. The range of compositions obtained is presented in Table 10 along with those obtained by previous workers.

Conversion and Yield

Since none of the previously reported experimental conditions are identical with those used in this study, it is difficult to make comparisons. In general, the best conversion from this work is 118% of the best previously reported work with comparable experimental conditions used by Addison (1, run 12). Similarly, the poorest yield in this work is 246% higher than that of Addison. Previously used mole ratios of butane to nitric acid were 14 and higher. The runs in this research were made at mole ratios of 3 to 7, thus considerably easing the recycle load for a commercial process. The yields and conversions reported in this work are felt to be significant because the uncorrected average of the per cent accounted for is 89.6 for carbon and 96 for nitrogen (Table 8).

Accountability

Disregarding the carbon accountability of run 14 since it falls outside the 99% confidence interval, the average accountability of the carbon is 91.3. The nitrogen figures for runs 9 and 10 are above 100%. A possible explanation of this may lie in the fact that the gas samples for these runs were collected at 95°F and 97°F, respectively. The sample

Table 10. Product distributions obtained from nitration of butane

	Source			
	This work	McCleary and Degering (68)	Addison ^a (1)	Hass et al. (35)
NM	8-14	2-9	19	6-10
NE	20-26	11-25	32	12-13
2-NP	0.04-0.29	-	-	-
2-M-2-NP	0-0.34	-	-	-
1-NP	5-9	5-7	11	5-8
2-NB	36-51	23-49	21	45-50
2-M-1-NP	0-0.04	-	-	-
1-NB	14-20	27-32	17	24-27
Yield ^b	60-82	^c	17.4	^c
Conversion	20-40	18-20	33	28 ^d

^aRun 12, with oxygen added; 2 moles per mole HNO₃.

^bBased on hydrocarbon consumed.

^cInsufficient data available.

^dBased on HNO₃ consumed, not fed.

bottles had cooled to approximately 65°F by the time the analyses were made, causing a corresponding reduction in sample pressure. As the samples were taken from the bottles by the standard syringe technique, air would have entered the syringe to equalize the pressure. This additional air would have shown up in the GIPC analyses as NO₂ (Table 7) thus raising the reported nitrogen values. Deviations from perfect (100%) material balances may be attributed to product loss during sampling, product deterioration between sampling and analysis, admitted errors in analysis, and certain unavoidable operating losses. However, the fact that the carbon and nitrogen material balances consistently check within $\pm 7\%$ and are both of the same order of magnitude is a strong argument for their validity.

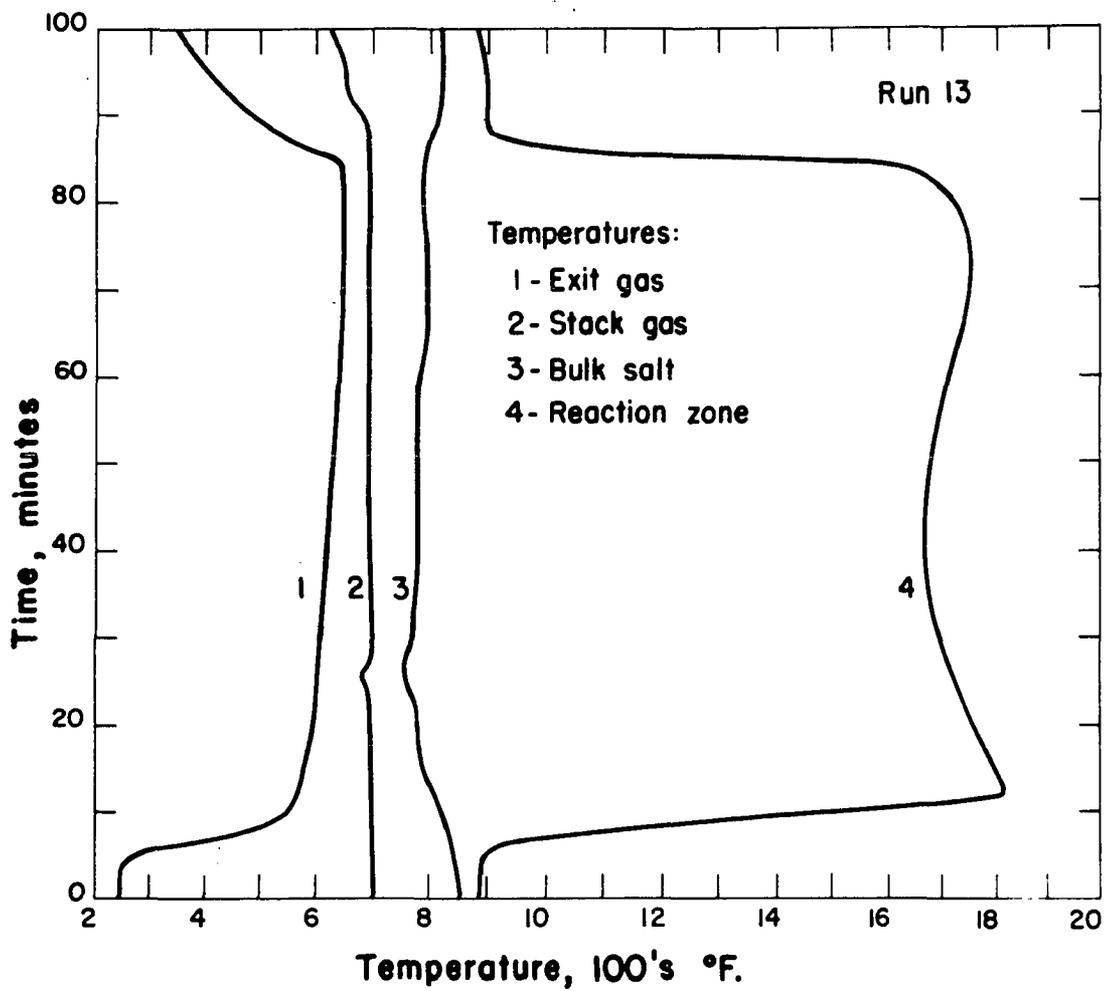
Calculations

In all GIPC analyses used in this investigation, area per cent was equal to weight per cent. Material balance calculations were straightforward and routine, except for those involving the off-gas. The sample taken immediately prior to the scrubber was used to determine the percentage composition of the gas stream. The butane content of the downstream sample, together with the volume indicated by the wet test meter, permitted use of butane as a tie-substance to establish the gas volume at the initial sampling point.

Temperatures

Figure 9 shows the temperature vs. time profiles for run 13. Temperature profiles from the other runs are similar. Trace 1 from

Figure 9. Temperatures vs. time for run 13



thermocouple R (Figure 2) shows the temperature of the product gases immediately after they leave the reactor. Trace 2 is a record of the furnace stack gases and was used to assist in controlling the reactor salt temperature. The molten salt temperature is shown by trace 3, while trace 4 was obtained from a thermocouple placed in the end of the extension tube (Figure 2). Trace 4, as shown, has been smoothed from a band approximately 100°F wide produced as the recorder tried to follow the rapidly fluctuating reaction zone temperatures. The temperatures indicated by this thermocouple were most surprising. Previous investigators had reported the reaction temperature to be that of the molten salt in which their tubular reactors were immersed. This is apparently not the case with this nitrator.

The shape of trace 4 may be explained as follows: the initial peak is caused by initiation of the highly exothermic reactions; then the temperature drops off as the reaction products carry out latent heat; and, finally, the gradual rise occurs as the equilibrium temperature is approached.

The Reynolds number for run 8 was approximately 13,000 and was calculated on the basis of the following assumptions: 1. bulk gas temperature was 300°F; 2. area used in velocity calculation was that of the annulus between the acid injector and butane supply tubes; and 3. pressure was atmospheric. Reynolds numbers for the other runs were found to be greater than 6,000, which implies excellent mixing.

The analyses for runs 8-14 show not more than 0.25% total yield of aldehydes and alcohols. This is in direct contrast with the 5-7% reported

by Addison (1). It is interesting to note that his nitroparaffin yield was only 1/3 that of the carbonyls. Likewise, his olefin yield was three times that of the nitroparaffins. GIPC techniques developed in the course of this work showed that no olefins or ketones were formed.

The deleterious oxidation effects observed by Hass et al. (32) in a stainless steel tubular reactor were not encountered, nor were corrosion problems. Once the reaction was initiated, no problems arose with continuous operation.

CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations derived from this investigation are:

1. Butane has been successfully nitrated continuously in the vapor phase with nitric acid in a fused salt reactor.

2. Nitroparaffin yields per pass based on hydrocarbon fed ranged from 3.4 to 6.5%, while yields per pass based on hydrocarbon consumed ranged from 60.2 to 82.0%.

3. Nitroparaffin conversions per pass based on nitric acid fed ranged from 20 to 39%.

4. A successful GIPC method for the quantitative analysis of the products resulting from vapor phase nitration of butane in a fused salt reactor has been developed.

5. No difficulties have been experienced from excessive oxidation or corrosion.

6. Reaction zone temperatures are considerably higher than those previously reported. It is suggested that further research be initiated to ascertain more precisely the temperatures in the reaction zone.

7. The precise effects of molten salt temperature, changes in reactor geometry, space velocity, acid concentration, mole ratio of hydrocarbon to nitrating agent, and other major variables should be isolated. Perhaps a micro-kinetic study would shed some light on the actual reaction mechanisms and rate constants could then be determined and used to find optimum reaction conditions.

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