Elimination of Redwater Formation from TNT Manufacture

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14. ABSTRACT

The US Department of Defense requires an environmentally benign synthesis route for the manufacture of military grade trinitrotoluene (TNT) which eliminates the production of redwater arising from the sulfiting process for removing unsymmetrical trinitrotoluene isomers. QinetiQ has found that by using a novel nitrating system, N2O5 in dichloromethane, the proportion of meta-substituted nitrotoluenes can be reduced to 1.3-1.5%, instead of the 4-5% levels in current processes. Additional improvements have been made to the following di- and tri-nitration steps by using alternatives to traditional mixed (sulfuric-nitric) acid systems, namely 100% nitric acid and N2O5–sulfuric acid respectively, resulting in reduced emissions of pollutants (NOx off-gas and tetranitromethane). As a result, TNT with a set point within 0.3 deg. C of the Mil. Spec. (80.2 deg. C) can be made by the QinetiQ process, without the need for sulfite washing; one recrystallization raises this figure to 80.6 deg. C. A study of the process economics has shown that the cost (at 4.5 million lb per annum scale) is not disproportionately greater than current processes.

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List of Acronyms

ARC	accelerated reaction calorimetry
ca.	*circa* (i.e. approximately)
DCM	dichloromethane
DNT	dinitrotoluene (isomer mixture)
d.p.	decimal place
FID	flame ionization detector
GAC	granular activated carbon
GC	gas chromatography
HPLC	high performance liquid chromatography
IPR	In-Progress Review
L	liter
LEL	lower explosive limit
LEV	local exhaust ventilation
LTEL	long-term exposure limit
MNT	mononitrotoluene (isomer mixture)
NMR	nuclear magnetic resonance
NOx	mixture of nitrogen oxides (NO, NO_2 etc.)
m-NT	*meta*-nitrotoluene (3-nitrotoluene or 3-NT)
p-NT	*para*-nitrotoluene (4-nitrotoluene or 4-NT)
OEL	occupational exposure limit
PEL	permitted exposure limit
QPR	Quarterly Progress Report
ROM	rough order of magnitude
SON	Statement of Need
STEL	short-term exposure limit
TA	triacetin (GC reference)
TLC	thin-layer chromatography
TLV	threshold limit value
TNM	tetranitromethane
TNT	trinitrotoluene
UEL	upper explosive limit

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Executive Summary

The US Department of Defense requires an environmentally benign synthesis route for the manufacture of military grade trinitrotoluene (TNT) which eliminates the shortcomings of present methods, namely the production of redwater (arising from the sulfiting process for removing unsymmetrical trinitrotoluene isomers) and other hazardous and noxious by-products such as nitrogen oxides (NO_x) and tetranitromethane. In collaboration with SERDP, the DoD therefore issued SON Number: PPSON-04-05, dated Nov. 23rd 2002, with the goal of eliminating redwater from TNT manufacture.

QinetiQ, a U.K.-based defense R&D organization which also operates in the U.S. as QinetiQ Inc., responded to this SON and was awarded by SERDP a three year research contract, commencing June 2004, to find solutions to this problem based on changes to the fundamental chemistry. The first six months of the contract constituted a proof of concept phase, upon which the remainder of the contract was predicated.

QinetiQ is investigating ways to increase the regioselectivity in the nitration of toluene to suppress formation of *meta*-substituted nitrotoluenes, especially in the step producing mononitrotoluenes. These *meta*-substituted isomers give rise, when fully nitrated, to the unsymmetrical isomers of trinitrotoluene mentioned above and which must not be present in appreciable quantity in the final product. Therefore QinetiQ has carried out research aimed at reducing the proportion of *meta*-substituted nitrotoluenes to around 1.3%, instead of the 4-5% levels in current processes. Such *meta*-nitrotoluene levels will permit manufacture of TNT to Type I military specification without the need for Sellite (bisulfite) treatment. Additional objectives include reduction of hazardous and noxious by-products.

QinetiQ's research has achieved the first objective (to reduce the proportion of *meta*-substituted nitrotoluenes) by using low temperature batch and flow nitration systems, operated at sub-ambient temperature, for the first stage nitration in conjunction with dinitrogen pentoxide (N_2O_5) as a mild nitrating agent. QinetiQ has reduced the proportion of such *meta*-substituted nitrotoluenes to levels of 1.3-1.5%, instead of the 4-5% levels in current processes, by using dinitrogen pentoxide solution in dichloromethane (DCM) as nitrating agent instead of nitric-sulfuric acid mixture. These lower levels of *meta*-isomers will minimize the formation of unsymmetrical TNT isomer in the final product (TNT). Furthermore, use of a flow reactor has added advantages of precise temperature control and reduction of inventory.

Investigation of the second nitration step (mononitrotoluenes [MNTs] → dinitrotoluenes [DNTs]) has indicated that mixed acid is likewise unnecessary here, with the preferred reagent being 100% nitric acid. This step has been successfully carried out in a flow reactor. The removal of the need for sulfuric acid mixtures and harsh conditions has added advantages in recyclability of solvents/reagents and lower corrosion of plant construction materials.

The third nitration step (DNTs → TNT) is advantageously carried out using dinitrogen pentoxide-sulfuric acid mixture at a temperature not exceeding 80°C in a batch reactor. This little-used nitration system is less harsh than the oleum mixtures currently used, and has environmental dividends in the reduction of pollutant emissions (NO_x off-gas and tetranitromethane).

Overall, experimental work has indicated that TNT with a set point within 0.3°C of the Mil. Spec. (80.2°C) can be made by the QinetiQ process, without the need for sulfite washing. One

recrystallization raises this figure to 80.6^{o}C. Other established manufacturing processes to meet the Mil. Spec. either: a) start from toluene and rely on sulfiting or b) use pre-formed 2-nitrotoluene as a feedstock (which raises supply problems for large quantities of this chemical).

Environmental impact aspects of the chemistry of the proposed processes have been addressed and it was found that none of the chemicals proposed for use in the new process would be a "show stopper". Preliminary discussions with a North American explosives manufacturer indicated that the process would, subject to availability of funding, be capable of exploitation particularly if economies of scale came into play regarding the production of N_2O_5. A possible exploitation pathway could involve N_2O_5 as a nitrating agent for a range of products, from nitroaromatics through nitramines to nitrate ester plasticizers, thus achieving the desired economies of scale with enhanced atom efficiency and cleanliness of the respective processes.

1. Objective

This work is aimed at developing a methodology to eliminate the production of redwater during TNT manufacture, as outlined in BAA Announcement, November 23rd, 2002, US Army Corps of Engineers, Humphreys Engineering Center Support Activity, SON Number: PPSON-04-05. The project was funded under the Weapons Systems and Platforms program (ref. WP1408) for 36 months, from June 2004.

The objective of this project was to develop a process for the manufacture of military grade TNT that eliminates the generation of redwater by removing the need for bisulfite ('Sellite') treatment. QinetiQ planned to achieve this by increasing regioselectivity in the nitration of toluene so that the formation of *meta*-substituted nitrotoluenes, especially in the step producing mononitrotoluenes, is suppressed. Such isomers give rise, when fully nitrated, to the unsymmetrical isomers of trinitrotoluene which, if present in TNT for military use, would depress the melting point and render the product unsuitable. The program also focussed on ways to carry out the nitration of dinitrotoluenes (2,4-/2,6-isomer mixture) to TNT more cleanly in order to reduce the production of the pollutants, NO_x and TNM (see "Background").

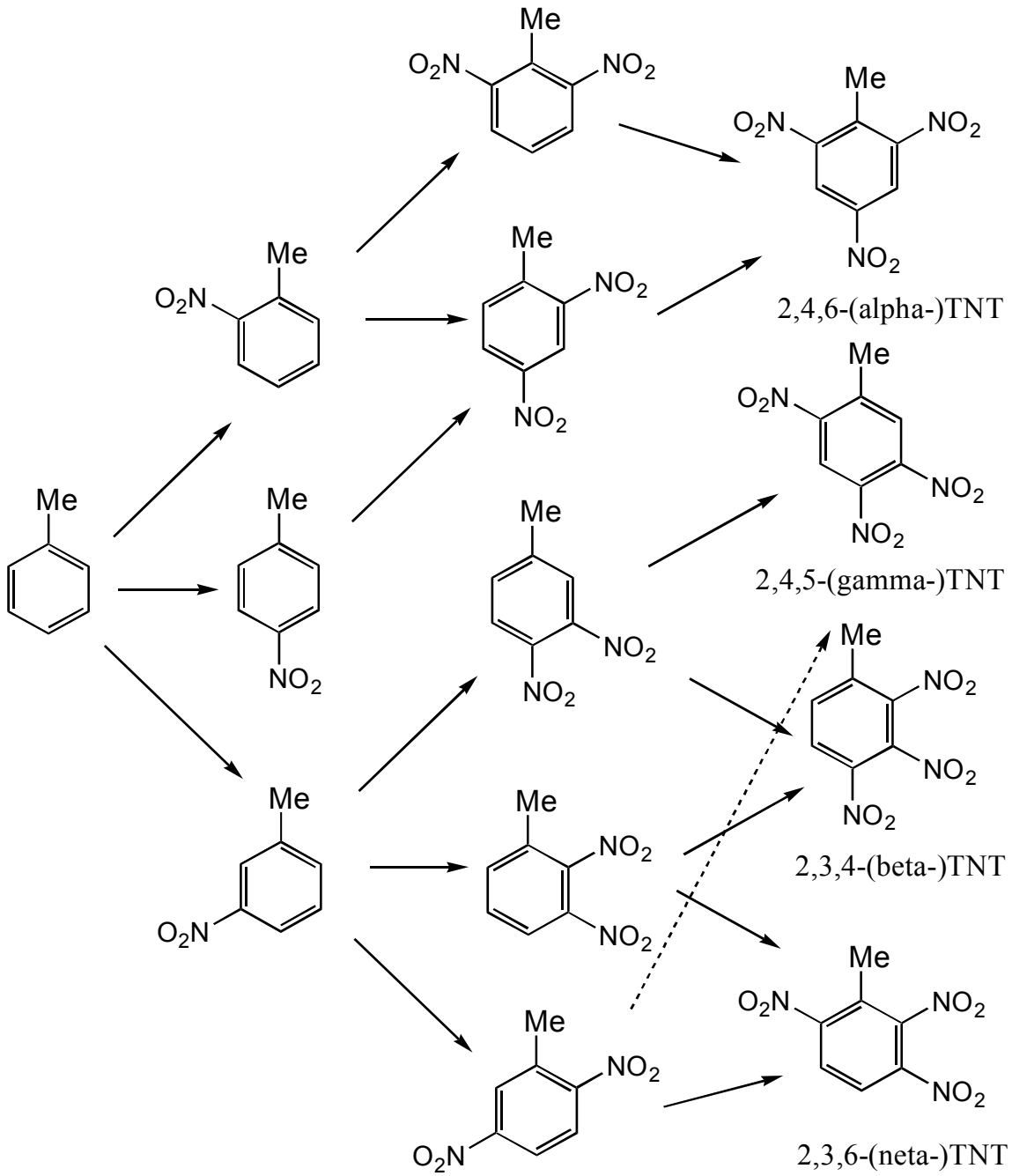
The primary beneficial outcome of this research is to make available to SERDP and DoD information on a manufacturing route to TNT which will avoid the production of redwater, without incurring additional environmental penalties. A subsidiary outcome will be cleaner production of TNT using nitration methodologies which reduce the formation of pollutants such as nitrogen oxide off-gases and tetranitromethane. The routes are aimed at being directly applicable to a manufacturing scale operation.

2. Background

2.1 TNT Manufacture

2,4,6-Trinitrotoluene (TNT), an important military explosive, is produced commercially by the nitration of toluene, initially using mixtures of concentrated nitric and sulfuric acids to give an isomeric mixture of dinitrotoluenes (2,4- & 2,6-DNT), and ultimately with mixtures of nitric acid and oleum (sulfuric acid containing up to 44% free sulfur trioxide) to convert the DNT mixture to TNT. A major shortcoming in the overall process is the production of unsymmetrical TNT isomers (2,4,5-, 2,3,4-, 2,3,6-, 2,3,5- and 3,4,5-trinitrotoluenes) which are generated through nitration in the 3- or *meta*- (*m*-) position of the toluene ring (see Fig. 1). The presence of these compounds in the final product results in TNT which has too low a melting (solidification) point for military use, and so the unsymmetrical isomers must be removed.

The unsymmetrical TNT isomers, in common with other nitroaromatics which possess nitro groups in adjacent ring positions (i.e. *ortho* to each other), are labile to attack by nucleophiles which will displace a nitro group, in the case of treatment with aqueous sodium hydrogen sulfite (sodium bisulfite or 'sellite') giving arylsulfonic acids. These acids are water-soluble and are washed out of the product to give purified TNT with a much increased solidification temperature. The process has problems in that, in addition to the sulfonic acids which must be



Minor TNT isomers - 2,3,5-(epsilon) and 3,4,5-(delta-) are not shown here for clarity.

Proportions in crude TNT (according to ref. 11):
gamma: 2.5%; beta: 1.75%; neta: 0.5%; epsilon: 0.05%; delta: 0.006%.

Figure 1: Nitrotoluene Isomers Produced in the Nitration of Toluene

disposed of, additional side-reactions occur which result in: a) losses of 2,4,6-trinitrotoluene of a few % owing to nitro group displacement (sulfonic acid formation), and b) further losses of 2,4,6-trinitrotoluene by coupling reactions owing to the basic nature of sodium bisulfite - these coupled products or 'nitrobodies' give rise to the red color of the washings, termed 'redwater'. Losses of TNT can amount to 5% or more and, in addition to the cost of disposal of the redwater, it is therefore desirable to remove the need for sulfite treatment altogether.

Further drawbacks of current methods for the production of TNT are the production of substantial amounts of pollutants such as nitrogen oxides (NO_x) and tetranitromethane (TNM), which require removal to prevent damage to the environment. For instance, using conventional methods of manufacturing, *ca.* 0.5 lb of TNM is produced for every 100 lb of TNT produced.

2.2 Toluene Nitration – Initial Stages

The nitration of toluene using mixed acids has been much studied and results up to around 1980 are summarized in various texts [1-4], with some further studies summarized more recently [5]. In addition, accounts of aspects of the industrial nitration of toluene are also available [6-8] although many of these focus on the commercially important formation of 2,4-DNT, which is a precursor for tolylene-2,4-di-isocyanate, an important chemical in the synthetic polymer industry. In the latter case the elimination of *meta*-isomers is not as critical as in the explosives industry and therefore in these studies less attention has been paid to such contaminants.

Before proceeding further, it should be made clear that there is good evidence [1] that in the formation of the undesired trinitrotoluene isomers containing *meta* nitro substitution (i.e. 2,4,5-, 2,3,4-, 2,3,6-, 2,3,5- and 3,4,5-trinitrotoluenes), the *meta* nitro group is introduced in the first stage of the preparation, i.e. nitration of toluene, and not in subsequent transformations, e.g. mono- to dinitrotoluenes or DNT to TNT. This is demonstrated by the fact that when TNT is made using pure *para*-nitrotoluene as a feedstock, instead of the isomeric mixture from a conventional nitration (typically 58:4:38 *o*-:*m*-:*p*- [9]), very pure TNT with a solidification point of 80.78^{o}C is obtained [10]. Clearly then the first stage of the nitration is the stage where improvement is necessary. It should be pointed out that starting from pure *para*- (or *ortho*-) nitrotoluene is not an option for a plant-scale operation such as that proposed here, as the process requires toluene to be used as the feedstock for reasons of economy; in other words, buying in *para*- (or *ortho*-) nitrotoluene as a feedstock (or obtaining it by purifying - by distillation - the isomer mixture from conventional nitration of toluene) would be prohibitively expensive, even without taking into consideration the hazards (distillation of the crude product from the first stage, as has been done in the past [1,11], is well known to give rise to explosions). A further consideration is the output of TNT required from the plant - *ca.* 2 million lb/year, which would require a reliable supply of the *para*- (or *ortho*-) nitrotoluene of similar order of magnitude. This alternative approach will be commented upon further (see Conclusions).

In many studies of toluene nitration carried out before *ca*. 1980, the effects of varying reaction conditions - proportions of acids, temperature, mode of addition, effects of additives etc. - were investigated but the lowest proportion of *m*-nitrotoluene attainable was around 2% [1,4,5].

Without clean-up (i.e. sulfiting) this would give TNT with a solidification point of around 79.9°C [10] which does not meet the military specification, variously described as 80.2°C (for US Type I TNT) or 80.4°C for Type II [11]. Further studies made after 1980 where novel reagents and modified techniques were employed are now summarized - these were compiled from an online search of the Beilstein database and include some references not cited in the most recent text available [5].

The N-nitroheteroaryl salts, N-nitropyridinium hexafluorophosphate [12], N-nitropyrazole/boron trifluoride diethyletherate [13] and N-nitrocollidinium tetrafluoroborate [14], gave *meta* contents in excess of 3% so these systems, which also suffer from the disadvantage of expensive and complex reagents, do not merit further consideration. Other systems which gave >=3% *meta*-nitrotoluene include: nitronium tetrafluoroborate in sulfolane [15], N_2O_5/tetraethylammonium tetrafluoroborate in acetonitrile under anodic conditions [16], N_2O_4/tetraethylammonium tetrafluoroborate in acetonitrile under electrolytic conditions [17], tetra-n-butylammonium nitrate/trifluoroacetic anhydride in nitromethane [18], calcium nitrate in nitric acid [19], nitric acid/acetic anhydride in the presence of zeolite-beta and a solvent [20], and anhydrous vanadium nitrate in dichloromethane [21]. In the following cases the proportion of *meta* isomer was not reported (thus presumed not to be notably low): ceric ammonium nitrate/trifluoroacetic acid (3 day reaction) [22], methyl nitrate under radiolysis [23], nitryl chloride in aqueous trifluoroacetic acid [24], N_2O_4-oxygen in 1,2-dichloroethane in the presence of zeolite beta [25] and ammonium nitrate/trifluoroacetic anhydride in the ionic liquid emim trifluoroacetate [26]. More recently (post-2002) work has been reported using either ceric ammonium nitrate-acetic anhydride [27], nitric acid-lanthanide complexes [28], potassium nitrate-BF_3 complexes [29] or nitric acid mixtures in ionic liquids [30-32], but all of these systems gave *meta* contents in excess of 3%. None of these systems is therefore considered further.

Systems which offer *meta*-nitrotoluene content lower than 3% include (in descending order of *meta* content): aqueous nitric acid in various solvents (2.6%) [33], N_2O_5 in sulfur dioxide (1%, though formation of other by-products is reported) [34], anhydrous copper(II) nitrate on K10 montmorillonite clay in acetic anhydride-carbon tetrachloride [35], and n-propyl nitrate on a zeolite (ZSM-5)[36], subsequently elaborated to include N_2O_5 on this zeolite [37]. More recently (post-2002) work has been reported using scarce or otherwise unsatisfactory reagents either homogeneously (eg. TFAA [38], zinc nitrate- N_2O_4 [39] or ionic liquids [40]) or heterogeneously (ammonium nitrate-perchloric acid on montmorillonite clay [41], nitric acid-P_2O_5 on silica gel [42] or tetramethylammonium nitrate-sulfuric acid on silica gel [43]) or required the used of microreactors [44]. Unfortunately, none of these systems is well suited to scale-up. Nitration with aqueous nitric acid systems is generally to be avoided owing to oxidative side reactions, with benzoic acid derivatives tending to be formed [45]. The heterogeneous systems, based on clays or zeolites, pose particular problems regarding reactor configuration (e.g. fixed *vs*. fluidized bed) and catalyst renewal. Also, certain of these catalysts have been shown to be ineffective in the dinitration step [46], where in any case selectivity enhancements are not required because the nitro group already in the molecule directs the incoming nitro group to the required position, namely *meta* to the nitro group already there [47]. Thus a process utilizing the advantages of these systems to best effect would require three discrete reactors - a heterogeneous (fixed/fluidized bed) reactor to introduce the first nitro group,

and two separate stirred vessel reactors for each of the subsequent steps, the first with mixed acid (to dinitrate) and the second with nitric acid-oleum mixture (to trinitrate). In the present work, QinetiQ has demonstrated that a more streamlined process with only two reactors - a flow nitrator of suitable configuration for the first and second nitration steps and a stirred vessel reactor for the third step - is technically feasible (see Materials and Methods, below). The alternative approach of using zeolites to effect regioselectivity in the nitration of toluene will be commented upon further (see Conclusions).

There have been reports, in conference proceedings in the 1970s, of studies to reduce the *meta*-nitrotoluene content [48,49]. In essence, these authors found that, when mixed acids (nitric-sulfuric acid mixtures) are used to nitrate toluene to DNT, the lower limit of *meta* isomer content was established as 1.4% when reaction was carried out at -35°C, but when a nitronium salt, nitronium trifluoromethanesulfonate (nitronium triflate), was used in a range of solvents and at low temperatures (down to -110°C) the *meta* isomer content could be depressed to as little as 0.23%. Clearly such low temperatures are impractical for plant operation, but at -30°C *meta* isomer content of around 1% is quoted for these systems, a substantial improvement on all of the systems quoted earlier (i.e. in the Beilstein survey). To put the matter into perspective, to reach a solidification point of 80.4°C the *meta* isomer content should be around 0.85% (based on the *meta*-nitrotoluene content in mononitrotoluene), according to the equation [10]:

Solidification pt. (in °C) = 80.80 - 0.465c where c is the percentage of *m*-nitrotoluene.

This is shown graphically in Fig. 2, below:

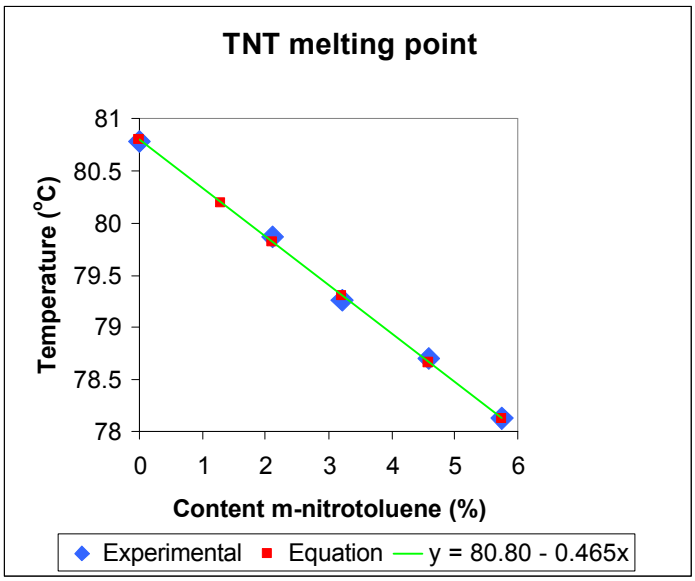


Figure 2: Effect of *m*-NT content (from 1st nitration stage) on melting point of TNT

Alternatively, a solidification point of 80.2°C, adequate for some specifications, would result from a *meta* isomer content of around 1.3%.

Therefore, in **summary**, no system apparently exists which can be conveniently scaled up and which produces less than 1.3% of *meta*-nitrotoluene in the first stage of toluene nitration. Ways

of suppressing *meta* contents to 1.3% or below are considered below (see Section 3, "Materials and Methods").

2.3 Toluene Nitration – Later Stages

Here, particular problems associated with the conversion of the DNT isomer mixture, obtained from initial nitration of toluene, to TNT as final product are considered (referred to as "3rd stage nitration"). This relates to the possible reduction in air emissions from nitration plant, referred to in the SON, which result principally from the recycling of the spent acids from the nitration reaction. Ways to improve the nitration chemistry by eliminating, or at least reducing the dependence on oleum mixtures are also considered here.

3rd stage nitration methods nowadays rely on the use of oleum with up to 60% free SO_3 content [2,50], and in some plant designs the 'spent' acid from the 3rd stage is used to nitrate the incoming toluene stream [51]. However, handling of such highly corrosive acid streams is troublesome and their recycling requires great expertise to minimize pollution [52]; hence it would be better, if an alternative nitrating system of equivalent power were available, to dispense with oleum as a reagent. If less severe conditions were practicable with these alternative reagents, then the build-up of undesired by-products such as tetranitromethane [53,54] could be reduced. A final consideration is the possibility of reducing the large excess of sulfuric acid which is present in the nitrating systems; if such amounts could be reduced to nearer stoichiometric levels (which is all that the chemistry really requires) then the recycling and disposal problems would be greatly diminished.

There appears to have been very little work to find alternative nitration systems for the 3rd stage nitration, most developments concentrating on improvements in plant design rather than altering the fundamental chemistry. It appears, however, that alternative dehydrating systems to oleum-nitric acid should be capable of effecting the nitration to high conversion; also, ways of reducing sulfuric acid content in TNT nitrations have been reported by the proposers [55]. Moreover, the use of N_2O_5 in to produce trinitrated benzene derivates has only received scant attention in the literature [56,57]. These issues will be considered in more detail below (see "Materials and Methods").

3. Materials and Methods

3.1 Reduction of *meta*-nitrotoluene content to <1.3%

In this project QinetiQ has investigated the use of novel nitrating agents, in particular dinitrogen pentoxide (N_2O_5), in conjunction with low temperature flow nitration technology to achieve the desired regioselectivity in the first stage nitration of toluene. N_2O_5, which has been extensively investigated as a clean nitrating agent [58-61], is not as powerful a nitrating agent as nitronium salts such as nitronium triflate [58], and indeed there is evidence that nitrations performed using this reagent in media of low polarity (especially halogenated hydrocarbon solvents) occur with molecular N_2O_5 as the nitrating species [62]. In other words, these nitrations, particularly where the substrate molecule is also of low polarity (e.g. a hydrocarbon such as toluene), do not take place via nitronium ion mechanisms, and so the distribution of isomers in the products changes to give a higher proportion of those products where attack has taken place at the more reactive positions. In the case of toluene, these are the *ortho*- and *para*-positions; such behavior is in accord with the Hammond postulate [63] which states that "less reactive electrophiles are more selective (and *vice versa*), so that these electrophiles should show greater *meta* to *para* differentiation". A similar effect is believed to operate with nitric acid-acetic anhydride mixtures (which contain acetyl nitrate), where high regioselectivity in toluene nitration is observed and meta-nitrotoluene content as low as 1.4% has been observed [64]. (Earlier reports [47] that no *meta* isomer is formed at all, have not been substantiated.) Unfortunately acetyl nitrate systems of certain compositions are detonable [65] and hence are considered to be unsafe for a potential commercial process.

The second factor which should enhance the regioselectivity of the nitration is the proposed adoption of continuous flow reactor technology. This has already been demonstrated to benefit the nitration of compounds possessing labile functional groups, for instance strained rings; within QinetiQ the technology has been demonstrated to be efficacious in the nitration of epoxides and oxetanes bearing hydroxyalkyl side-chains [66,67]. In these instances N_2O_5 selectively attacked the more reactive position on bifunctional molecules such as glycidol, 3,4-epoxybutanol and 3-(hydroxymethyl)-3-methyloxetane in dichloromethane medium in a flow reactor, and in each case the mononitrate ester was isolated with the strained-ring functionality unattacked. It is believed that in such cases the flow nitration methodology assists rapid removal of nitric acid, formed as a by-product, from the reaction zone - if the acid were allowed to build up in concentration it would induce side-reactions, in these cases polymerizations involving the strained ring, and thus give rise to a contaminated product. These problems are encountered in batch reactors where N_2O_5 nitrations of strained-ring substrates such as glycidol, even when carried out at low temperatures (-25°C) are contaminated with oligomeric by-products [68]. In other studies of heterocyclic nitrations using flow reactors improved regioselectivity has also been observed [69] which is ascribed to similar effects.

In the case of flow nitration of toluene at low temperature using N_2O_5, it is anticipated that selectivity may also be promoted, here as regioselectivity in position of attack on the aromatic ring rather than selectivity between different functional groups. However the theme of dispersal of nitric acid by-product, as noted above, is also pertinent, and it is believed that by reducing the concentration of this by-product to a minimum in the reaction zone, the nitrating species will

still be N_2O_5 and in this way, in conjunction with the use of low temperatures, the formation of *m*-nitrotoluene will be minimized.

The type of flow reactor advocated is a co-current (plug flow) reactor (see Fig. 3), rather than the other type common in the chemical industry, namely the constant flow stirred tank reactor. The former has the advantage of reduced inventory of potentially hazardous materials within the reactor, and also there is a greater degree of control of the reaction since the rate of addition of the reactants can be precisely regulated. In combination with the small reaction zone, this means that exothermic nitrations can be more easily controlled leading to an intrinsically safer design. Flow reactors are ideally suited to reactions such as nitrations where the main reaction is rapid and any side-reactions are slow, and they also permit a high throughput suitable for production scale operations [70]. In the case of the present study, it is envisaged that two flow reactors run in tandem would be appropriate owing to the different reactivities of the respective starting materials (toluene and mononitrotoluenes). This area is further discussed under "Production of dinitrotoluenes", below.

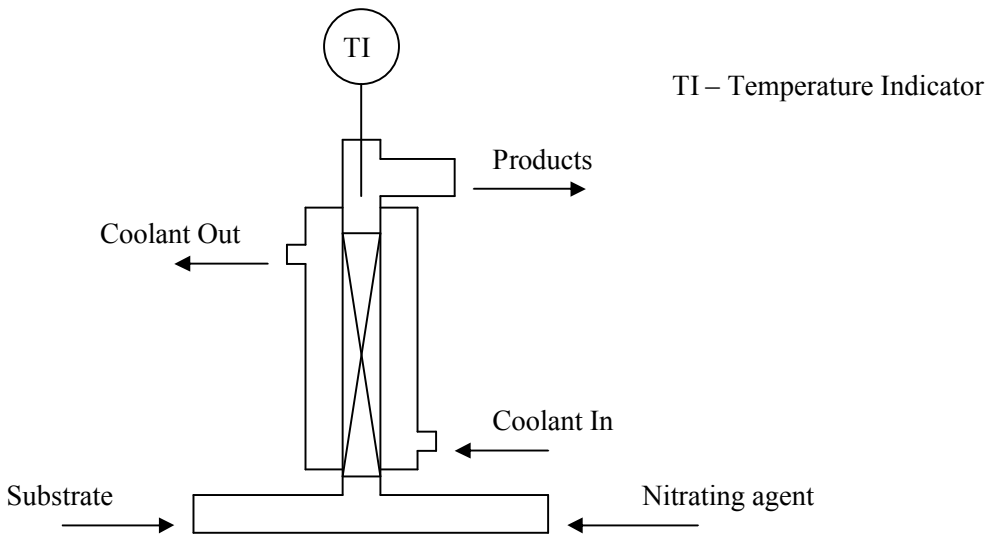


Figure 3: Flow Reactor (schematic)

Although N_2O_5 has been known since the 19th century, it is only recently that methods have been developed for its large-scale synthesis. QinetiQ has been at the forefront of this activity, and holds patents on routes for the scaled-up preparation of this compound, based on the oxidation of N_2O_4 using ozone [71-73], or electrolytic methods [74-76]. QinetiQ has also addressed aspects of the economics of production of N_2O_5 [77,78].

3.2 Production of dinitrotoluenes

Although the nitration of the mononitrotoluene mixture to dinitrotoluenes may be conveniently carried out in a flow reactor, it is believed from earlier studies [79] that N_2O_5 in an organic solvent such as dichloromethane may be insufficiently potent to fully convert the mononitrotoluenes to dinitrotoluenes. Raising the temperature would increase the reactivity but a limitation, of course, is the low boiling point of dichloromethane (b.pt. 40°C); hence it is

anticipated that an alternative way to enhance the potency of the nitrating agent will have to be sought. A simple expedient would be to introduce a stream of pure nitric acid into the flow reactor - the resulting N_2O_5-nitric acid (or "enriched nitric acid"; ENA) medium is well known to be capable of effecting such nitrations [80]. It is also known that nitration of toluene or nitrotoluenes to dinitrotoluenes can be effected by nitric acid alone [81]. Clearly, optimization of parameters such as reagent/residence time/flow rate is necessary to ensure that this reaction goes to completion. Further aspects are considered below (see "Results and Accomplishments").

3.3 Cleaner methods for 3rd stage nitration

QinetiQ has investigated cleaner synthetic routes for the conversion of the dinitrotoluene (DNT) isomer mixture, produced from the flow nitrator studies mentioned above, to TNT, specifically avoiding the use of oleum for the reasons given above. In particular, the possibility of using novel nitration systems based on N_2O_5 was investigated. It is now known that the alternative system based on dissolving N_2O_5 in pure nitric acid (to make "enriched nitric acid" or ENA) which was reported in 1987 [57] does not give sufficiently high yields of TNT to be practicable for its manufacture [82]. These results have been borne out in studies on the related system, 2,4,6-trinitroethylbenzene [79]. However, apart from some studies on the effects of Lewis acids such as boron trifluoride [83] - which do not give systems readily amenable to scale-up owing to the highly corrosive reagents involved, there have been few other studies on systems to enhance the reactivity of N_2O_5. In fact, although it is well known from spectroscopic studies [84] that the nitronium ion concentration is increased dramatically when N_2O_5 is dissolved in sulfuric acid, only one study of syntheses using this medium appears to have been carried out, in 1924 [85], where the nitration of *m*-xylenedisulfonic acid was carried out.

One system for study in the TNT 3rd stage nitration is therefore N_2O_5-sulfuric acid. This mixture is, of course, a dehydrating system with N_2O_5 (the anhydride of nitric acid) taking the place of SO_3 (the anhydride of sulfuric acid) in the conventional system. An alternative way* of activating N_2O_5 is treatment with a strong Bronsted acid (or its anhydride) - an acid of this type which has been shown to be useful is trifluoromethanesulfonic acid (triflic acid) [5,86]. Clearly if such an acid were used its recycling would be a necessary pre-requisite on grounds of expense.

A final possibility for study would be the strategy, already briefly investigated [55], of using inert perfluorocarbon solvents as 'bulking agents' to reduce the amount of sulfuric acid required in the 3rd stage nitration. These studies have indicated that the amount of sulfuric acid can be reduced to around 1/5th that used in conventional systems, and furthermore that oleum is not required, with TNT yields of 85% being obtained. Clearly an advantage would be the minimization of the amount of sulfuric acid that would need to be recycled, resulting in proportionately less pollution. Naturally the robustness of this method, were it to be selected*, towards scale-up would need to be investigated.

*In the event, neither of these alternative nitration methods was employed as N_2O_5-sulfuric acid was found to work very well (see Results and Accomplishments).

3.4 Overall Nitration Process

3.4.1 Reaction Scheme

The chemical steps in the proposed overall nitration process are shown below (Fig. 4):

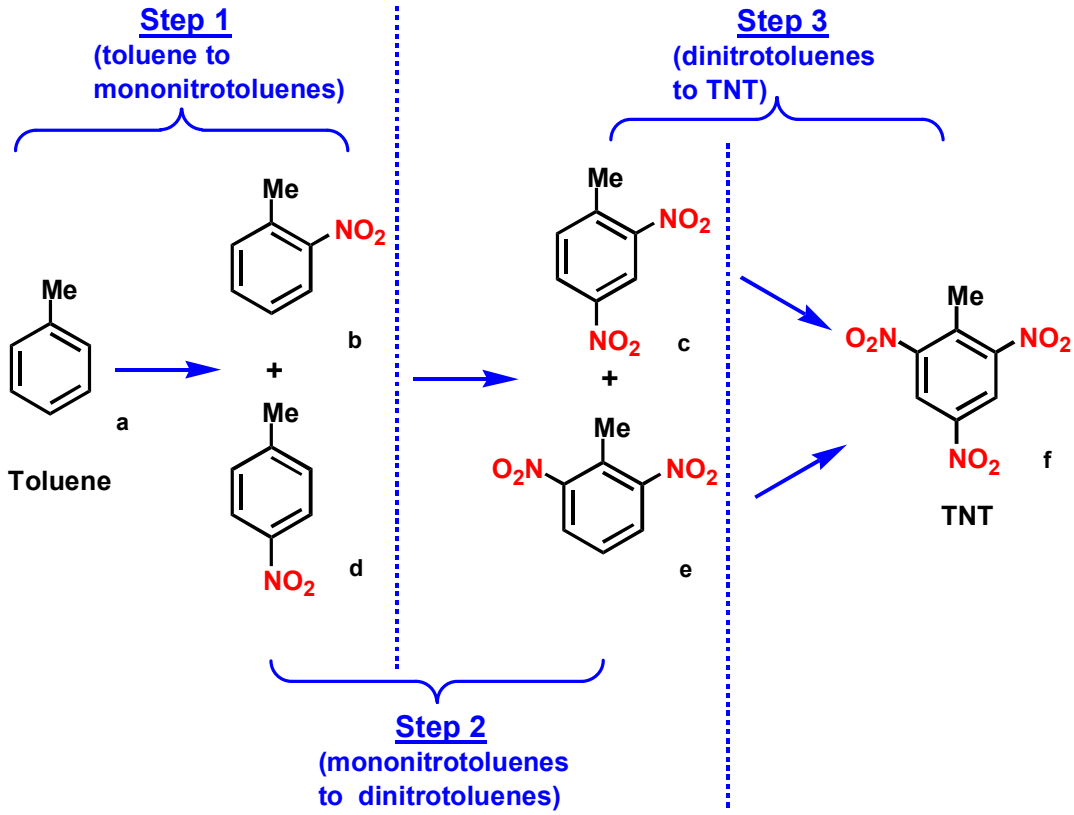


Figure 4: Toluene nitration stages in new route proposed for TNT manufacture

This contrasts with TNT production by conventional nitration (as shown in Scheme 1, above) in that, ideally, as no *meta*-nitrotoluene isomer is produced in the first step – the only products under these circumstances are *ortho*- and *para*-nitrotoluenes (**b** and **d** respectively) – the sole products from the dinitration reaction (step 2) would be only 2,4- and 2,6-dinitrotoluenes (**c** and **e** respectively). This means that, in turn, the only possible product from the third nitration step would be 2,4,6-trinitrotoluene (TNT, **f**), and hence no clean-up by sulfiting would be required.

3.4.2 Process Concept

A conceptual way in which the three nitration stages, using the nitration systems outlined above, may be combined into a single process is shown in Fig. 5 below. As discussed earlier, two flow reactors run in tandem would be appropriate owing to the different reactivities of the respective

starting materials (toluene and mononitrotoluenes). The third stage nitration to produce TNT would be run in batch mode owing to the unsuitability of the reagents/products for use in flow systems – notably the viscosity of the acid mixtures and the possibility of precipitation of solid product during the course of the reaction.

In particular, it is believed that lower *meta* values may be attainable under continuous operating conditions where, in the type of tandem flow reactor proposed (Fig. 5) for a technical demonstrator system, the residence time of the nitration product mixture from the first stage is effectively reduced by direct feed of the product stream (with added nitric acid) into the second flow reactor. This is in contrast to the reactor used in the preliminary reaction where the product stream is currently quenched (see Results and Accomplishments).

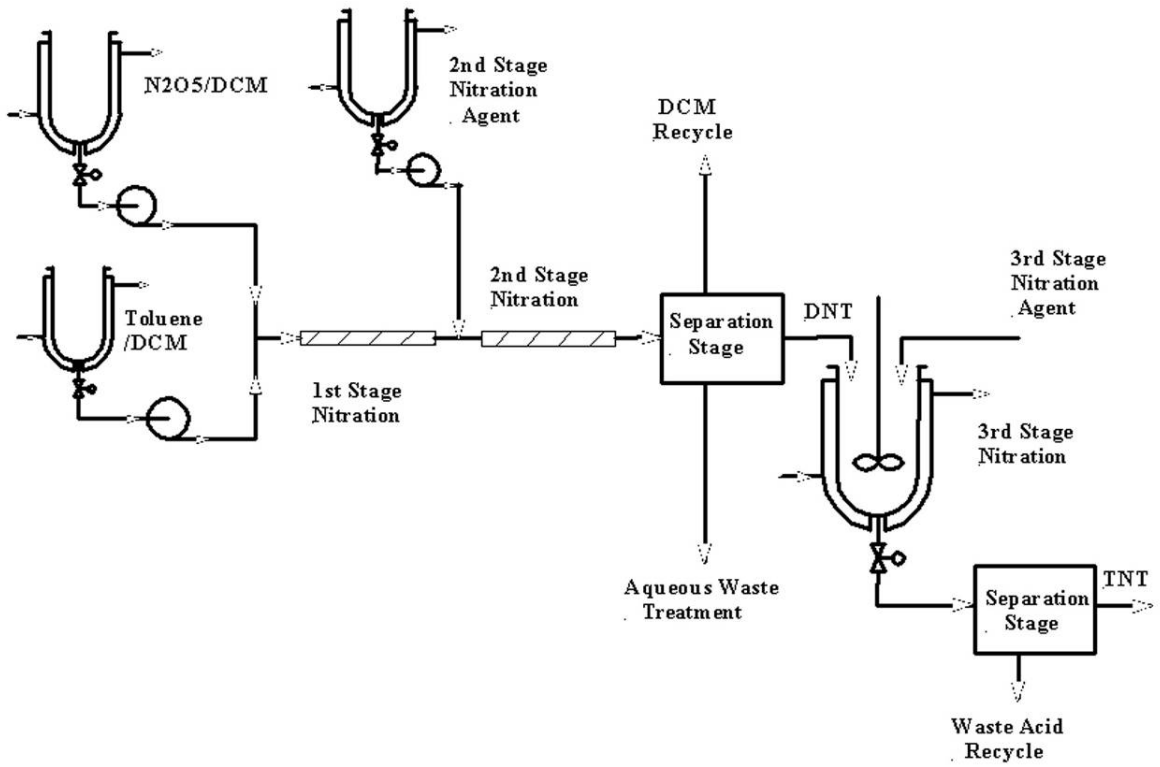


Figure 5: Overall Nitration Process (Schematic)

3.5 Environmental Impact Assessment (Summary)

Full details are given in Appendix C1; a summary of the conclusions is as follows:-

The chemicals involved in the proposed new synthesis routes – nitration reagents, co-reagent for nitrations, solvents and expected by-products – were evaluated on a toxicological/ecological basis using information available from the respective material safety data sheets (MSDSs). It was concluded that, in general, none of the alternative chemicals proposed for the new TNT

manufacturing process will impose environmental burdens greater than the chemicals already in use, although caveats were attached to two compounds:

i) dinitrogen tetroxide (reagent for electrolysis/extractive process for generation of N_2O_5) would require total containment;

ii) dichloromethane (solvent for N_2O_5 reactions in stages 1 & 2) would require total containment;

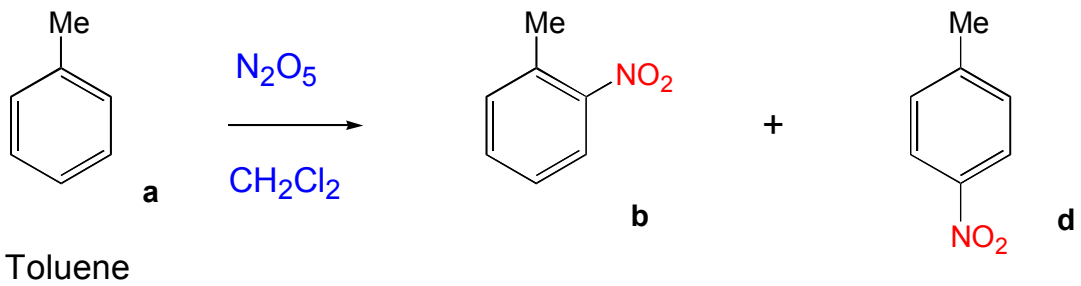
None of these requirements is regarded as a “show-stopper”.

4. Results and Accomplishments

4.1 Nitration of Toluene (1st Stage of TNT Process)

4.1.1 General

The equation for the reaction under study is as follows:-



Stage 1 (toluene to mononitrotoluenes)

An apparatus for the preparation of N_2O_5 on laboratory scale was set up and commissioned. The apparatus and its method of operation are described in Appendix A, Section A.1.

A method using GC analysis was devised for the analysis of mononitration products of toluene. Details are given in Appendix A Section A.2.

The nitration of toluene by N_2O_5 in DCM was studied initially in batch apparatus; two types of experiments were carried out (Experimental details are given in Appendix A, Section A.3):-

a) "Synthesis" runs, where N_2O_5 solution in DCM was added to a solution of toluene in the same solvent under conditions of controlled rate of addition and controlled temperature;

b) Dewar experiment runs, where smaller amounts of the N_2O_5 and toluene solutions were mixed at low temperature and the temperature profile was recorded under adiabatic conditions.

The purpose of the first series of experiments was to carry out the mononitration under conditions replicating those which would prevail in a semi-batch reactor (stirred-tank type), in order to establish what the isomer ratio of the products would be under such conditions.

The purpose of the second series of experiments was to establish the rapidity of the reaction, by analysis of temperature *vs*. time plots, and thus verify its suitability for adaptation to flow conditions. Furthermore, the data should give an indication of the residence time required for complete reaction within the flow reactor tube. The data can also be used to give an indication of the heat of reaction, to aid the safe design and cooling capacity of the continuous reactor.

The results of the batch apparatus reactions are presented below (Section 4.1.2).

The flow reactor for carrying out the nitration of toluene using dinitrogen pentoxide (N_2O_5) in dichloromethane (DCM) is described fully in Appendix A Section A.4, where the method for its operation is also explained. A schematic diagram of the apparatus is shown below at Fig. 6.

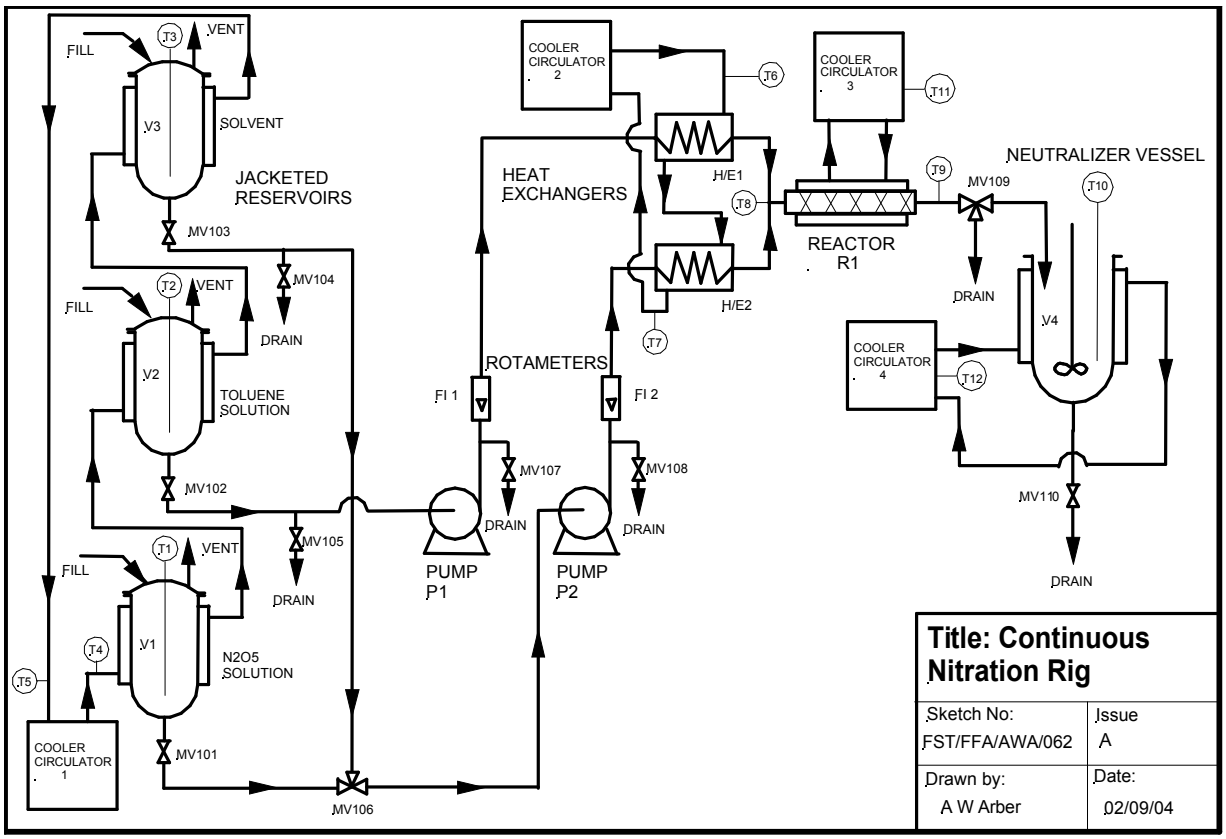


Figure 6: Schematic of Flow Reactor for 1st Stage Nitration

The results of experiments using the flow reactor are presented below (Section 4.1.3).

4.1.2 Results of the Batch Apparatus Reactions (1st Stage Nitration)

A) <u>Synthesis Runs</u>

The experimental details of these runs are reported separately (see Appendix A, Section A.3).

The results are as shown below (see Table 1).

Table 1: Toluene- N_2O_5 Synthesis Runs

Toluene Concentration % w/w	N_2O_5 Concentration % w/w	Toluene: N_2O_5 Ratio	Reaction Temperature °C	Addition time min.	Ortho %	Meta* %	Para %
8.7	10	1:1	0 to 3	60	52.3	2.0	45.7
8.7	10	1:1	0 to 3	60	52.5	2.0	45.5
8.6	10	1:1	-13 to -18	80	53.5	1.9	44.6
8.6	10	1:1	-15 to -18	60	54.0	1.7	44.3
10.2	10	1.2:1	-10 to -20	110	53.4	1.8	44.8
10.2	10	1.2:1	-15 to -20	25	53.6	1.8	44.6
8.6	10	1:1	-15 to -20	16	54.0	1.7	44.3

*See note on robustness of GC analyses, Appendix A, Section A.2
GC data normalized to nitrotoluene isomers only.
All runs gave high (>90%) yields of mononitrotoluenes.

The proportion of *meta*-nitrotoluene, the component of interest, varies from a maximum of 2.0% to a minimum of around 1.7%, with the lowest values obtained at low temperature (*ca.* -20°C). Neither the reaction time nor the ratio of N_2O_5 to toluene appears to materially affect the *meta*-isomer content, with temperature being the most important factor. The *meta*-isomer content is markedly lower than results reported for mixed acid mononitration of toluene (typical values [4]: *ortho* - 61%, *meta* - 4%, *para* - 35%), and are much more akin to those obtained by Norman [64] for nitric acid-acetic anhydride mixtures (*ortho* - 63%, *meta* - 1.5%, *para* - 35.5%), where acetyl nitrate is believed to be the active nitrating species. Whereas *ca.* 2% *meta*-isomer is the lowest value achieved (at impracticably low temperatures) for mixed acid systems [5], where nitronium ion is established as the active species, it is believed that less powerful electrophiles are responsible for the activity of alternate systems used by Norman and ourselves, and greater regioselectivity can be obtained in accord with the Hammond postulate (which, as discussed in Section 3.1, states that less reactive electrophiles are more selective (and *vice-versa*) [63]). Moreover, there is evidence from mechanistic studies that where nitrations are carried out with N_2O_5 in media of low polarity the molecular species is the active nitrating agent [62].

It is anticipated that the figure of 1.7% *meta*-isomer can be lowered through the more precise control of reaction conditions and temperatures achievable using a flow nitrator, so that the goal of 1.3% *meta* or lower may be attained (see also discussion in B below).

B. Dewar experiments

Small scale adiabatic reactions carried out in a Dewar vessel give useful information on the kinetics of a chemical reaction that can be utilized in the design of pilot plant and as a screening technique for suitability of continuous processing.

The initial experiment was carried out with solutions having typical concentrations used in previous N_2O_5 continuous nitrating processes for oxetanes and oxiranes, i.e. around 10% by weight. With toluene under these conditions the boiling point of the solution was exceeded and heat loss occurred through evaporation making the heat of reaction difficult to calculate.

Subsequent experiments were carried out at a lower concentration (5%) at -25 and +5°C. From the temperature profiles it may be deduced that the reaction takes place very quickly, in fact the response of the thermocouple is probably slower than the reaction itself. This makes the reaction ideal for continuous processing where reaction times of a few seconds are preferred especially on a small laboratory scale.

From the thermal characteristics of the Dewar flask and the temperature profiles a figure for the heat of reaction was calculated as 207 $kJmol^{-1}$ for the three experiments at 5% concentration. This figure is of a similar magnitude to previously investigated nitration reactions.

Another Dewar experiment was carried out to compare a fast reaction time (seconds compared to min.) below -15°C, for semi-batch processing as an approximation to continuous processing (see Table 2 below).

Table 2: Toluene-N_2O_5 Dewar Experiments

Toluene Concentration % w/w	N_2O_5 Concentration % w/w	N_2O_5:Toluene Ratio	Start Temperature °C	Addition time s	Ortho %	Meta* %	Para %
4.3	5.0	1:1	-60	15	55.7	1.4	42.9
4.3	5.0	1:1	-60	15	55.5	1.5	43.0

*See note on robustness of GC analyses, Appendix A, Section A.2

The resultant *meta*-nitrotoluene concentration was 1.4 and 1.5% for the two experiments. A final Dewar experiment (see Appendix A Section A.3) was carried out under similar conditions but at lower temperatures (toluene solution <-70°C, N_2O_5 solution -30°C) with rapid addition (15 s.) and short reaction time (15 s.). The ratios of isomers obtained under these conditions were as follows:- *ortho*: 58.2%; *meta*: 1.2%; *para*: 40.6%.

Though the temperatures employed here (starting temperature -60°C) are impractical for large-scale work, the conditions are believed to mimic those prevailing in continuous processing and *meta*-isomer contents of these levels and below should be achievable in a flow nitrator.

Conclusions - semi-batch reactions

Results from the semi-batch reactions indicate a definite trend of lower *meta* concentration as the temperature and reaction time decrease. Indeed under conditions of extremely low temperature and short reaction time, levels of *m*-NT below 1.2% are obtained. Though such conditions are impractical for operation of a manufacturing plant, this trend nevertheless supports the prediction that continuous nitration of toluene with N_2O_5 will successfully produce less than 1.3% of *meta* isomer due to reaction times of the order of seconds and minimization of isotherms by high heat transfer and intense mixing.

The heat of reaction is similar to that experienced in other continuous nitration processes using N_2O_5 and should not pose any significant problem in processing utilizing the laboratory apparatus at QinetiQ.

4.1.3 Results of Flow Reactor Experiments (1st Stage Nitration)

The process description and mode of operation of the flow reactor (schematic shown in Fig. 6 above) are given in Appendix A, Section A.4.

Details of the reaction conditions are shown in Table 3. Two reaction runs (3-2 & 3-3) were performed in which no mechanical problems were encountered. In each case around 1.5 kg of product solution was collected and neutralized. In the first run, concentrated solutions were used with flow of 38 g/min. of solution and reactor outlet temperature of -9°C; in the second run solutions of the same strength but at a higher flow rate (68 g/min. of solution) were used and a reactor outlet temperature of -2°C. In each case the product solution was found to contain 1.7-1.8% *m*-NT.

Further experimental runs were completed, where the cooling circulators were modified to reduce the temperature of the feed streams and the temperature of the reactor.

Two reactions (3-4 & 3-5) were run using a toluene concentration of 2.1% by weight in DCM and 2.5% N_2O_5 by weight also in DCM: a reduced concentration was used to minimize the temperature rise due to the exotherm. The flow rate of each stream was around 11 g/min. making a combined flow of *ca.* 22 g/min. A total of 2 kg was collected over a period of 90 min. The reactor inlet temperature remained fairly constant during the first run at around -16°C and the outlet temperature was –20°C. Reaction time before neutralization was estimated to be 16 s. The product was treated using a sodium bicarbonate wash and then a water wash. Bulk solvent was removed by evaporation and then the remaining material was dried in a vacuum oven. Analysis by GC gave a *meta*-nitrotoluene content of 1.5% and a toluene content of 0.9%, the yield was estimated to be 90%.

The second reaction used the same feed concentrations and feed rates over the same time period. Reactor temperatures were reduced to –23°C for the inlet and –30°C for the outlet. The product was treated in the same manner as before and analysis by GC gave a *meta*-nitrotoluene content of 1.4% and a toluene content of 0.4%, the yield was estimated to be 92%. In a final run (3-6) where the reactor inlet temperature was lowered to -27.5^{o}C the *meta*-nitrotoluene content was also 1.4% (with slightly higher *ortho*-nitrotoluene and slightly lower *para*-nitrotoluene).

It is believed that lower *meta* values may be attainable under continuous operating conditions where, in the type of tandem flow reactor proposed (Fig. 5) for a technical demonstrator system, the residence time of the nitration product mixture from the first stage is effectively reduced by direct feed of the product stream (with added nitric acid) into the second flow reactor. This is in contrast to the reactor used in the preliminary reaction where the product stream is currently quenched.

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Table 3: Summary of continuous nitration experimental results (reaction of toluene to mononitrotoluenes)

Run No.	Toluene Feed Concn. (wt%)	N_2O_5 Feed Concn. (wt%)	Feed rate (g/min.)	Residence time (s.)	Duration of experiment (min.)	Reactor inlet temp. ^oC	Reactor outlet temp. ^oC	2-nitrotoluene *[ortho-]* (wt%)	3-nitrotoluene *[meta-]** (wt%)	4-nitrotoluene *[para-]* (wt%)
3-1	4.3	5.0	38.5	10	**					
3-2	4.3	5.0	38.5	10	40	#	-9.3	53.4	1.8	44.8
3-3	4.3	5.0	68.0	6	20	-7.5	-2.1	53.6	1.7	44.7
3-4	2.1	2.5	22.5	16	90	-16.0	-20	55.2	1.5	43.3
3-5	2.1	2.5	22.6	16	90	-24	-30	56.0	1.4	42.6
3-6	2.1	2.5	23.2	16	90	-27.5	-31.5	57.0	1.4	41.6

* See note on robustness of GC analyses, Appendix A, Section A.2
** Run aborted due to problem with feed pump.
# Thermocouple not functioning.

GO/NO-GO Decision

After the first 6 months' work a GO/NO-GO decision point was invoked based on the following criterion:-
An assessment of the viability of 1st stage nitration was to be made, based on of low (=<1.3%) *meta*-nitrotoluene content being attainable. Although flow nitration studies at this stage had shown that 1.4% *m*-NT was obtainable, Dewar experiments had shown that 1.2% *m*-NT could be attained (figure subsequently adjusted to 1.3% - see Appendix A, Section A.2). Furthermore, it was believed that lower % meta figures from the flow nitration could be attainable. For these reasons the GO criterion was deemed to be satisfied and further work on the project continued.

Optimization studies of 1st stage flow nitration of toluene

Continuous flow nitration of toluene using N_2O_5 in dichloromethane (DCM) has been shown to be effective, giving low *meta*-nitrotoluene (*m*-NT) isomer content at low temperatures. The laboratory flow reactor mentioned above, consisting of concentric tube heat exchangers feeding a jacketed static mixer tube reactor, has been able to perform low temperature nitrations giving yields of greater than 90%.

Initial experiments conducted at reactor temperatures of around -30°C gave *m*-NT values of 1.45 wt.%. These were very encouraging and near to QinetiQ's goal of 1.3%. These experiments were run at the cooling limit of the apparatus hence modifications were required including a lower temperature cooling circulator to reach the 1.3% target. New heat exchangers were constructed and introduced into both feed lines to the reactor, the heat exchanger capacity was doubled and the new cooler could operate at a temperature of -65°C.

On commissioning of the modified apparatus, a serious static discharge problem was evident with audible and visible static discharges occurring when operating the apparatus. Detailed investigation highlighted the poor conductivity of the newly applied insulation to the cooling lines. A more conductive insulation was obtained and fitted but did not eradicate the problem. Copper conducting tape was then applied to the inner tubing and the outer insulation and further earth bonding was applied to bridge any possible breaks in the earthing circuit. High static fields were still measured around the apparatus. Finally the cooling circuit fluid was changed, thus solving the problem. It was concluded that static build-up was caused by the combination of the plastic tubing, the silicone oil and a fine film of ice forming between the tube and the insulation at the extremely low operating temperature.

During this time it was found that the *m*-NT standard used for the analysis of the early experiments was not as pure as stated by the supplier which meant the *m*-NT content was not as close to the target value of 1.3% as at first thought. A new standard was purchased and its purity validated (see note on robustness of GC analyses, Appendix A, Section A.2).

Several experiments have been performed under similar conditions (Runs 4-1 to 4-5; see Table 4), where 2.5 wt.% N_2O_5 in DCM was contacted with a stoichiometric solution of toluene in DCM (2.14 wt.%). The nitrating stream was cooled to around -20°C (at lower

temperatures the N_2O_5 would start to crystallize out) and the toluene solution to -45°C. At the point where the two streams mix and react the temperature was recorded as -32°C and the reactor exit temperature was around -50°C. Under these conditions the *m*-NT content of the product was between 1.47 and 1.60 wt.% as analysed with the new standard.

Increasing the N_2O_5 concentration to 5% and 7.5% increased the mixing temperature to -28°C and -25°C respectively with an associated increase in *m*-NT to 1.66 and 1.92% (Runs 4-6 & 4-7).

Table 4: Summary of further continuous nitration experimental results (reaction of toluene to mononitrotoluenes)

Run	N_2O_5 wt.%	Mixing Temp °C	Reactor Exit Temp °C	Total Flow Rate g/min.	*m*-NT %	Comment
4-1	2.5	-31	-47	44	1.52	
4-2	2.5	-29	-41	60	1.60	Higher flow rate
4-3	2.5	-30	-45	44	1.60	
4-4	2.5	-28	-47	45	1.52	
4-5	2.5	-31	-48	44	1.47	
4-6	5.0	-28	-43	45	1.66	
4-7	7.5	-26	-39	40	1.92	
4-8	2.5	-28	-51	33.5	1.48	Sequential nitration
4-9	2.5	-32	-49	47	1.42	Sequential nitration
4-10	2.5	-29	-46	45	1.56	Extended run

Further experiments were carried out to determine the effect of sequential nitration (Runs 4-8 & 4-9). As before a dilute solution (2.5 wt.% N_2O_5) was used but only half of the required amount was contacted with the toluene. This partially nitrated solution was neutralized in the usual way and washed with water, the organic layer was separated and dried overnight, and analysis from this first stage gave a *m*-NT content of 1.48%. A second nitration was performed on this solution with a resulting *m*-NT content overall of 1.42% and around 9% unreacted toluene.

Batch Dewar vessel experiments performed with a toluene solution temperature of -60°C and a N_2O_5 solution of -30°C and a 10 sec. residence time produced *m*-NT values of 1.22%.

From these results it appears that the mixing temperature is critical in determining the *m*-NT content. The mixing temperature is determined by the concentration of the toluene and N_2O_5 and the heat of reaction as well as relative flow rates and temperatures of the feed streams. A reduction from -30°C to -50°C in the reactor exit temperature did not seem to affect the *m*-NT content leading to the conclusion that the reaction rate is so fast that all of the toluene is reacted at the point of mixing even at these low temperatures and further cooling of the reactor section is for practical purposes pointless, and even having a reactor section post-mixing may not be necessary.

To achieve the conditions of the batch Dewar vessel experiment is beyond the present equipment capability. A cooler circulator operating at -85°C would be required for the toluene feed. This would be a considerable financial outlay and is outside of the planned equipment spend of this project. It was therefore decided to produce a large batch of MNT using the present conditions for further nitration through to TNT and obtaining a melting point determination to assess the criticality of the *m*-NT content on this specification.

Using dilute solutions, a continuous run over 3.5 hr. produced 140 g of MNT with a *m*-NT content of 1.56%; the recovery of MNT was calculated as 92.8% (Run 4-10). The product was worked up in the usual way and most of the DCM evaporated off to leave a 50% solution for the second stage nitration.

The flow nitrator constitutes the "front end" of the integrated process diagram (Fig. 5) which was discussed earlier (Section 3.4.2).

Final optimization studies of 1st stage reaction

From results reported earlier (Section 4.1.3) it appears that the mixing temperature is critical in determining the *m*-NT content. The mixing temperature is determined by the concentration of the toluene and N_2O_5 and the heat of reaction as well as relative flow rates and temperatures of the feed streams. A reduction from -30°C to -50°C in the reactor exit temperature did not seem to affect the *m*-NT content leading to the conclusion that the reaction rate is so fast that all of the toluene is reacted at the point of mixing. A typical run reported earlier, using dilute solutions, over 3.5 hr. produced 140 g of MNT with a *m*-NT content of 1.56%; the recovery of MNT was calculated as 92.8%.

In the 1st stage nitration reaction, with the present continuous nitration reactor (which is of relatively simple construction with concentric tube heat exchangers and a static mixer tube) a mixing temperature of -40°C and reactor exit temperature of -50°C has been achieved. This results in a *meta*-NT content of around 1.4-1.5%, slightly short of the target value (1.3%), and it appears that, as noted above, the mixing temperature is the main critical parameter determining the *meta*-NT content.

Table 5: Results of 1st stage flow nitration.

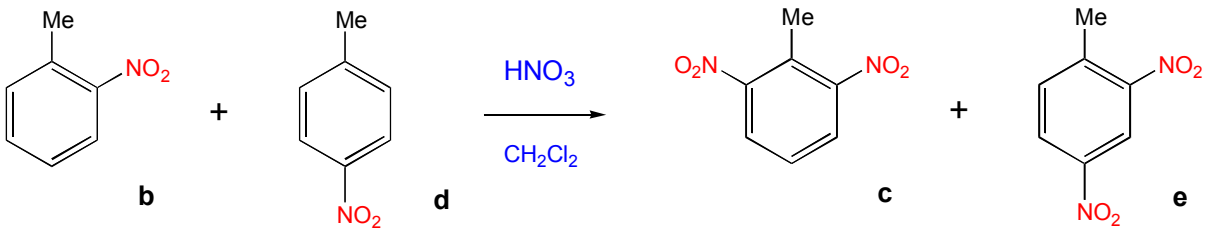
Run No.	Toluene Feed Conc. (wt%)	N2O5 Feed Concn. (wt%)	Feed rate (g/min)	Residence time (s)	Reactor inlet temp. (°C)	2-nitrotol-uene *[ortho-]* (wt%)	3-nitrotol-uene *[meta-]* (wt%)	4-Nitrotoluene *[para-]* (wt%)
5-1	4.3	5.0	38.5	12	-15	53.4	1.8	44.8
5.2	2.1	2.5	23.2	16	-35	57.0	1.4	41.6
5.3	2.1	2.5	44.5	10	-35	61.3	1.5	37.2
5-4	4.3	5.0	44.7	10	-35	61.9	1.7	36.4
5-5	6.5	7.5	40.0	11	-35	62.5	1.9	35.6
5-6	2.1	2.5	60.4	6	-35	62.3	1.6	36.2
5-7	2.1	2.5	44.2	10	-40	61.3	1.5	37.2

Table 5 shows the summarized results for the 1st stage flow nitration, in which feed concentration, feed temperature and feed rate were varied. The reactor inlet temperature is the point at which the two feed streams mix, at this point the reaction takes place and is virtually completed. Further reduction in the *meta*-NT content would seem possible by further dilution of the feed streams but the incurred processing costs of increased energy usage and equipment size would substantially increase the final price of the final TNT product.

For conclusions regarding the 1st stage flow nitration work see Conclusions (Section 5.2).

4.2 Nitration of Nitrotoluene Mixture (2nd Stage of TNT Process)

The equation for the reaction under study is as follows:-



Stage 2 (mononitrotoluenes to dinitrotoluenes)

4.2.1 Preliminary studies of 2nd stage nitration (MNTs to DNTs) – lab. scale

The experimental details of these runs are reported separately (see Appendix A, Sections A.2 (analysis) and A.5 (syntheses)).

Several nitration reactions using the isomer mixture (2-/4-nitrotoluenes with a trace of 3-nitrotoluene) from the 1st stage were attempted using N_2O_5 in DCM (5%, -10°C) to determine if dinitration was possible.

Thus nitration of the isomer mixture from the 1st stage was attempted using 1.1 mol of N_2O_5 in DCM with rapid addition of the N_2O_5 solution to the isomer mix at -20°C. The mixture warmed up to -5°C and was left to stir for several minutes before workup and isolation. TLC of the product showed only starting material. Although longer reaction times and higher N_2O_5 concentrations would be expected to give dinitrotoluenes, use of stronger nitrating media – particularly N_2O_5 in nitric acid – is preferred and attention has been focused on these systems.

Nitration was therefore investigated using N_2O_5 in nitric acid (enriched nitric acid), a system which has been found to be successful in the nitration of ethylbenzenes [79], as follows:

An initial run utilizing an 11.4% wt./wt. solution of N_2O_5 in 100% nitric acid with the mononitrotoluene mixture used above (55.8% 2-NT, 1.4% 3-NT and 42.4% 4-NT) was carried out at -2 to 2°C and then left for a further 5 min. at 5 to 10°C. This gave a 41% yield of dinitrotoluenes after purification and isolation. Increasing the concentration of N_2O_5 to 23% and conducting the reaction at 25°C increased the yield to 88%.

Further optimization reactions are being carried out to decrease reaction times so that a flow nitration setup can also be utilized for the 2nd nitration step.

Dinitration of the isomer mixture was also investigated using N_2O_5 in H_2SO_4 (13% wt./wt. – see 3rd stage nitration, Section 4.3) at -5°C, and the reaction went smoothly to give the dinitro compounds within 15 min. as evidenced by TLC. No starting material was observable. The

dinitro compounds separated out as light yellow solids from the reaction mixture at these temperatures due to their low solubility in the reaction medium. This system may be considered as an alternative to the N_2O_5 in nitric acid system described above, although the use of sulfuric acid would mean that it could not be employed in a flow system.

A separate series of experiments was undertaken as an initial proof of concept exercise to determine how the actual mixture of dinitrotoluenes would affect the purity of the TNT produced in the 3rd stage of the process. The mixture from the first stage nitration run (containing 55.8% 2-NT, 1.4% 3-NT and 42.4% 4-NT) was nitrated using standard mixed acid conditions. The nitration of the mononitrotoluene mixture was achieved by addition of the mixture at 45°C to a mixed acid solution followed by further heating of the mixture to 70°C for 45 min. Workup gave an 89% yield of a mixture of dinitrotoluenes and TNT. GC analysis indicated the mixture contained approximately 76% of 2,4-DNT, 12% 2,6-DNT, 0.4% 2,3-DNT and 9% TNT along with a further 2.5% of unknown material (most likely other DNT isomers). Estimation by ^{1}H NMR was found to give similar results (TNT 8%, 2,6-DNT 75.4%, 2,4-DNT 15.3%, 3,4 and 2,3 DNT 1.3%). This material (Sample X) was nitrated to TNT (see Section 4.3). Experimental details of these syntheses may be found in Appendix A, Section A.5 and the spectral traces in Appendix A, Section A.7.

4.2.2 Optimization studies of 2nd stage nitration (lab. scale)

As reported above (Section 4.2.1), the second stage nitration of mononitrotoluenes (MNTs) was easily accomplished using either N_2O_5-HNO_3 or N_2O_5-H_2SO_4 systems. Since the nitration to dinitrotoluenes (DNTs) was found to occur under relatively mild conditions it was envisaged that maybe milder nitrating agents could be used to simplify the process.

Nitrations

Further nitration studies were undertaken investigating mixed acid and nitric acid for the second stage nitration. It was found that in both cases the reactions gave DNTs in excellent yield (90%). Since nitric acid alone is sufficient for the nitration, the benefits of using a single reagent would simplify the process and reduce the cost during any scale-up process. The nitration with nitric acid was investigated further and results are shown in Table 6.

Table 6: Nitrations of Mononitrotoluenes by Nitric Acid

Run	Wt. of HNO_3 g (mol)	Temp[a] (^oC)	Reaction Time (min.)	Wt. of MNT g (mol)	DCM added to MNT (g)	Wt. of DNT (g)	%Yield
6-1	15 (0.24)	10-25	60	2 (0.012)	0	2.25	85
6-2	15 (0.24)	9-37	10	2 (0.012)	0	2.15	81
6-3	15 (0.24)	8-20	120	2 (0.012)	18	1.95	73
6-4	15 (0.24)	6-30	15	2 (0.012)[c]	2	1.98	74
6-5	15 (0.24)	8-30	40	2 (0.012)	2	2.23[b]	84
6-6	30 (0.48)	8-30	50	4 (0.024)	4	4.81[b]	90
6-7	30 (0.48)	6-30	5	4 (0.024)	4	5.02[b]	94

Notes to Table 6

a. Starting reaction temperature to final temperature during addition.
b. Total weight of product obtained by minimum addition of water to allow phase separation of mixture followed by extraction of acid layer with DCM.
c. Pure samples of 2- and 4-MNT used in 55:45 ratio.

Initial runs (6-1 & 6-2) were carried out by addition of pure MNT to pre-cooled 100% nitric acid (16 mol excess). Since the reaction was exothermic the rate of addition was controlled so that the temperature did not exceed 40°C. Run 6-1 was sampled by TLC (80/20 n-pentane/ethyl acetate) after 1 hr. by which time no starting material could be detected.

Run 6-2 was a repeat of 6-1 but the reaction temperature reached 37°C due to a shorter addition time (1 min.). This reaction was sampled after an additional minute and found to have gone to completion.

As the large exotherm may present problems on scale-up it was decided to dilute the MNT with dichloromethane (DCM) before addition to the nitric acid. This would serve two purposes: firstly to act as a heat sink for removal of heat, and secondly to slow down the reaction and therefore control the exotherm.

Since the MNT produced from the 1st stage nitration was initially in DCM prior to isolation for the 2nd stage nitration this process would allow direct nitration of the MNT without removal of all the solvent from the 1st stage. This would increase process economics and simplify the isolation step.

Initially a 10% MNT solution was chosen but the reaction was found to be too slow (run 6-3), but 50% wt./wt. was found to decrease the time to approx. 5 min. Although the yields for both 6-3 and 6-4 were much lower (73 and 74% respectively) this was thought to be attributed to the scale of the reaction and product losses.

Extraction of DNT

The normal work-up procedure for this process involved addition of the nitration mixture to ice followed by separation of the organic layer, filtration of the solid DNT from the aqueous layer and then removal of the solvent from the organic layer to give the total amount of product. Since the ratio of volumes of organic solvent to aqueous phase was low the isolation of the organic layer was very difficult. Secondly, large amounts of dilute nitric acid from the quenching of the mixture created additional problems which would be undesirable on a large scale.

An alternative approach (runs 6-5 & 6-6) examined an extraction route which would circumvent the aqueous workup. Since DCM and nitric acid are miscible, a homogeneous solution is formed in the reaction. Addition of small amounts of water to this solution led to the phase separation of the nitric acid and DCM. Work-up of both of these solutions gave over 85% DNT recovery. With slight optimization, reaction times of less than 7 min. were achievable. Initially work-up of the nitric acid layer still required quenching onto ice and filtering the solid, however this would present more waste streams of dilute acid and would not be suitable for scale-up.

Further experiments were performed where, after phase separation, the acid layer was extracted with DCM (runs 6-6 & 6-7) giving higher product yields while still retaining the acid concentration around 60%. This would make re-concentration of the acid to a lower strength product feasible and reduce the environmental impact from acid waste streams.

Extraction experiments were then undertaken by using a DNT/nitric acid mix produced from a large scale reaction (approx. 65 g of DNT in 250 ml of 100% nitric acid using 50 wt.% MNT/DCM.

Aliquots of this were taken and a measured amount of DCM followed by water was added to induce phase separation. The layers were separated and the DNT isolated from each layer. The results from the various extraction procedures are given in Table 7.

In run 7-5, the nitration mixture was simply quenched directly onto ice and the precipitated solid was isolated. This gave approximately 4.4 g of DNT which was in agreement with the expected yield from the amount of DNT mixture used.

Runs 7-1 and 7-2 indicate that if an additional 25 ml of DCM is added to the mixture before phase separation, the amount of DNT remaining in the acid layer is reduced. Furthermore as

Table 7: Extraction of Dinitrotoluenes

Run	Volume of DNT added (ml)[a]	Volume of DCM added (ml)[b]	Volume of water added (ml)[c]	Wt. of DNT[d] (g)		
				Aqueous Layer	Solvent layer	Total Wt.
7-1	25	0		4.37[e]		4.37
7-2	25	0		2.7[e]		2.7
7-3	25	25	4	1.51	1.92	3.43
7-4	25	25	8	0.9	2.69	3.59
7-5	25	50	6	0.18	3.98	4.16
7-6	25	50	8	0.14	4.27	4.41
7-7	25	100	8	0.11	4.25	4.36

Notes

a. DNT/nitric acid reaction mixture from large scale run.
b. Amount of additional DCM added to reaction mixture before addition of water.
c. Amount of water required to cause phase separation of the mixture.
d. Weight of DNT isolated after drying at 50°C overnight.
e. Reactions quenched onto ice without addition of DCM.

more water is added (run 7-2) this is reduced further to give an almost 82% extraction efficiency. Addition of larger amounts of DCM (runs 7-3, 7-4 and 7-7) shows that an almost quantitative amount of DNT can be removed from the acid layer without the need to quench the reaction mixture into water.

Dewar Vessel Experiments

Synthesis studies have shown that concentrated nitric acid will nitrate nitrotoluenes (NTs) in good yield and under moderate conditions; these experiments were carried out in batch mode (NT refers to the isomer mixture prepared using the flow reactor – see Section 4.1 "Final Optimization Studies"). For continuous nitration reaction, an understanding of the kinetics is required. A number of Dewar vessel reactions were performed under varying conditions: concentrated nitric acid (90%+) was cooled and placed in the Dewar vessel, and NT or NT diluted with DCM was added rapidly to the acid with stirring. The reaction mixture temperature was plotted against time and these plots are shown in Figs. 7–9.

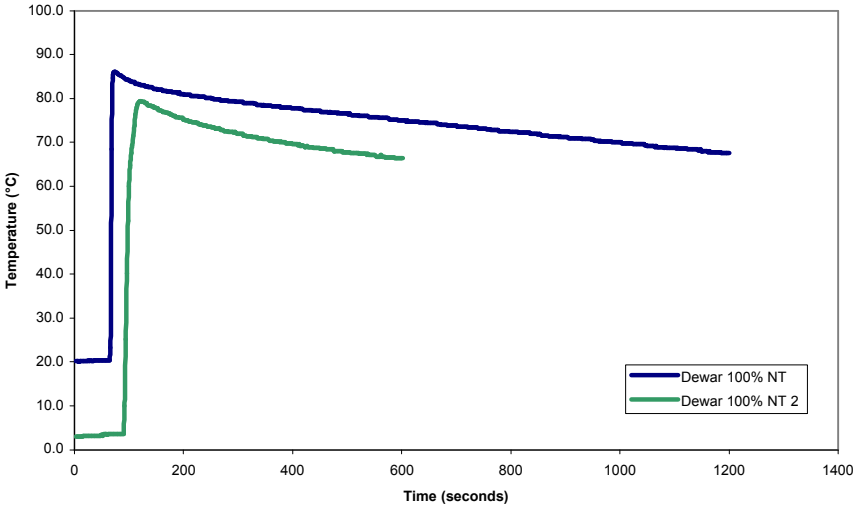


Figure 7: Addition of 100% nitrotoluene to concentrated HNO_3

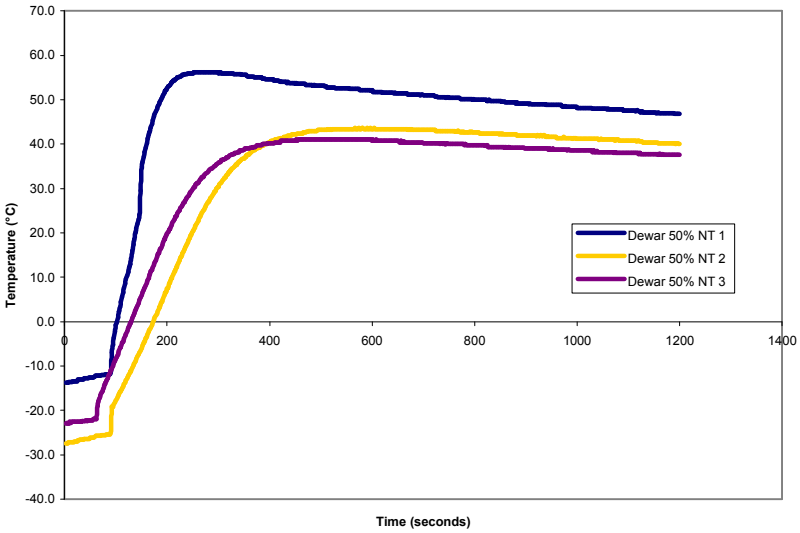


Figure 8: Addition of 50% wt./wt. nitrotoluene in DCM to concentrated HNO_3

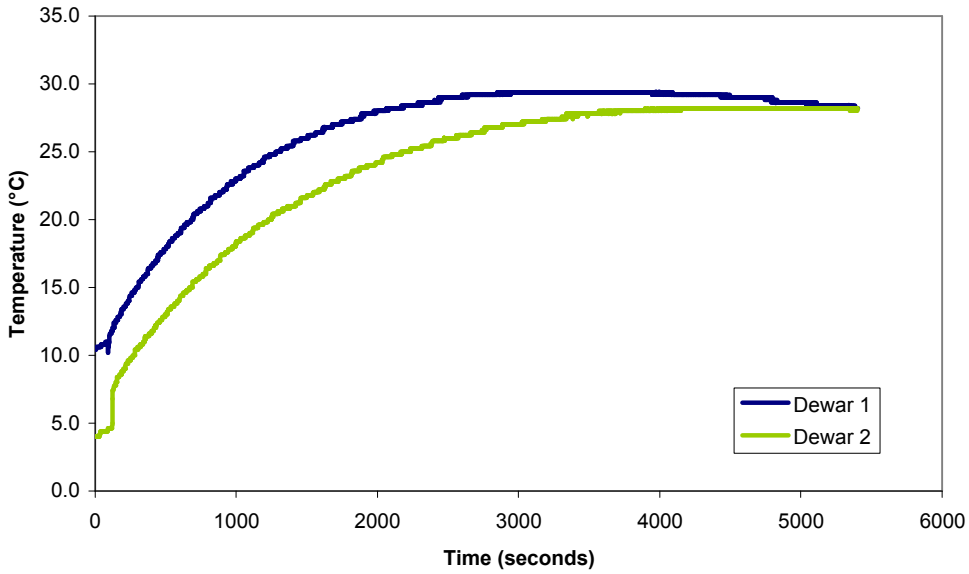


Figure 9: Addition of 10% wt./wt. nitrotoluene to concentrated HNO_3

From the figures it can be seen that the reaction time may be varied from less than a minute to over an hour depending on dilution and starting temperature. The heat of reaction calculated from literature for the NT isomer ratios was 107 $kJmol^{-1}$, and from the Dewar vessel reactions the heat of reaction was estimated as 107, 112 and 91 $kJmol^{-1}$ from 100%, 50% and 10% concentrations respectively. Although the heat of reaction is not as great as for the first stage nitration (200 $kJmol^{-1}$) it is still significant and will need to be controlled. For small scale studies, a reaction time/residence time in the flow reactor should be no more than a few minutes. Longer residence times lead to excessive tube lengths and inventory. To allow a degree of control and a workable residence time it was decided to design the second stage continuous reactor to have a residence time of no more than 5 min. and to use a 50% NT dilution factor. Four coiled tubular reactors have been fabricated with internal diameters of 4, 5.6 and 7 mm and a path length of 2.5 or 5 m. At a mass flow rate of 50 $gsec^{-1}$ these reactors will enable reaction times of between 1 and 5 min. to be studied. Further variation may be achieved by increasing or decreasing the flow rate.

ARC Experiments

Due to the larger inventory of the coiled reactors, up to 200 ml, a hazard study was conducted by ARC (Accelerated Reaction Calorimetry) to assess the likelihood of a runaway reaction. Firstly an experiment was carried out with concentrated nitric acid alone to assess any reaction between the acid and the titanium calorimetry bomb. No reaction was detected therefore no correction factor was applied to the 50% NT/acid reaction mixture. Experimental conditions were:

- starting temperature: 30°C,
- end temperature: 305°C,
- self-heat detection threshold: 0.02°Cmin^{-1},
- step: 5°C,
- wait time: 10 min.,
- bomb: 7.01 g light titanium 2.54 cm dia. - sealed with stainless steel swagelok nut, ferrule and cap (20.28 g),
- sample mass: 1.36 g,
- thermal inertia (ϕ) factor: 7.31.

The resulting plots are shown in Figs. 10 and 11.

No exothermic behavior was detected below 106°C, at which point an accelerating reaction was seen. The reaction(s) continued until a temperature of over 300°C was reached, at which point the bomb ruptured violently. Inspection of the self heat rate *vs* temperature plot (Fig. 11) shows that this occurs by at least two separate reactions, the first of these from 106°C to about 160°C. The implied temperature of no return (runaway) for a small metal tubular reactor with a time constant of 10 min. would be 143°C. From this prediction, the 2nd stage nitration reaction could be operated up to a temperature of 70°C with minimal risk.

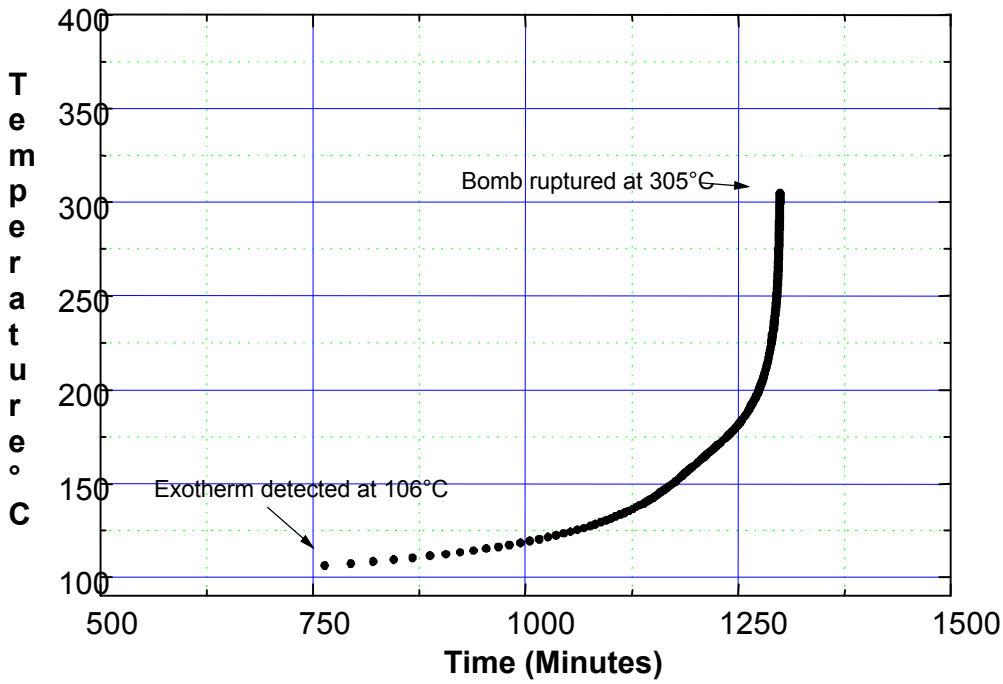


Figure 10: Temperature *vs* Time Plot for MNT-Nitric Acid Reaction

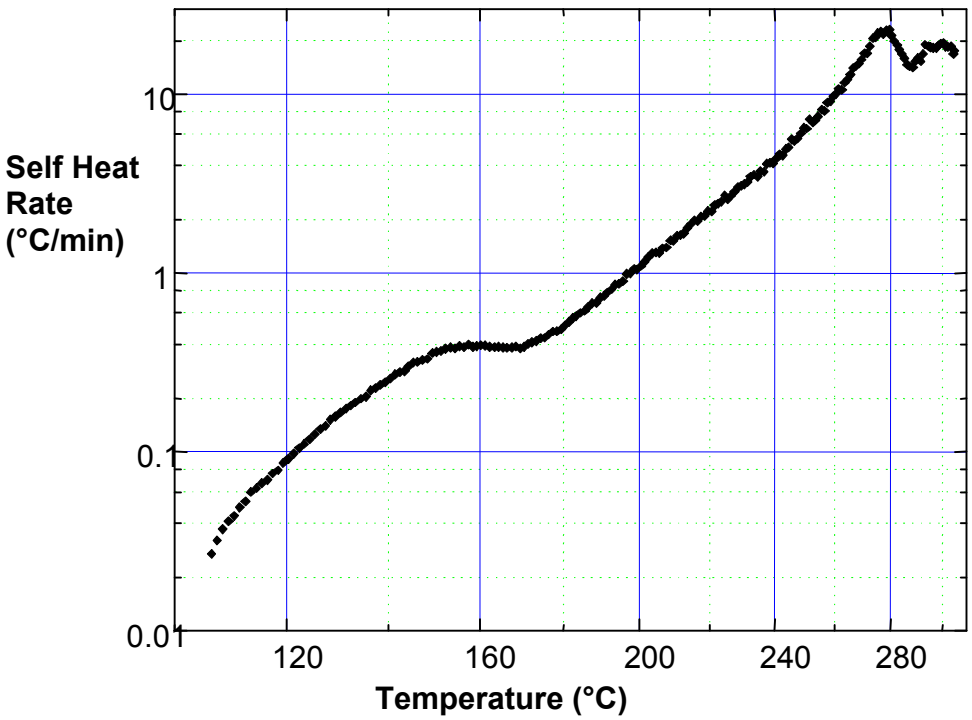


Figure 11: Self-Heat Rate *vs* Temperature Plot for MNT-Nitric Acid Reaction

Final optimization studies of 2nd stage reaction

As reported earlier (Section 4.2.2, above), the second stage nitration of mononitrotoluenes (MNTs) to give DNT mixtures (2,4- and 2,6-DNTs) was easily accomplished with a variety of reagents – either N_2O_5-HNO_3 or N_2O_5-H_2SO_4 systems gave satisfactory results, but the system chosen for the TNT manufacturing process in the present project involved the use of pure nitric acid as the reagent of choice. The reasons for this are discussed in full above (Section 4.2.2), but are, briefly, as follows:

- 100% (anhyd.) nitric acid is effective when used in excess;
- The system is suitable for a flow nitrator;
- The system tolerates the presence of DCM (carried through from the 1st stage);
- Product separation facilitated (add DCM, then water & separate).

In scaled-up runs using 50-150 g of MNTs (see Table 8), DNT mixtures were obtained in 92-97% yield (these runs generated material for the proof-of-concept study, described in Section 14 below). Interestingly. the product mixture from a reaction using a "synthesized" mixture

of MNTs (i.e. generated by mixing commercial samples of the three MNT isomers, making allowance for quoted impurities in each) showed, by analysis by NMR, that as well as the expected products (2,4-DNT, 83.1% and 2,6-DNT, 16.9%) a small amount of the minor isomers – 2,3-DNT (0.6%) and 3,4-DNT (0.9%) – was also present. These results are entirely as expected owing to the presence of 3-NT (1.4%) in the starting mixture (neither of these minor isomers were observed when the starting material consisted solely of 2- and 4-NT).

Table 8: Batch Nitrations of Mononitrotoluenes by Nitric Acid

Run	Wt. of HNO_3 g (mol)	Temp. (^oC)	Addition Time (min.)	Reaction Time (min.)	Wt. of MNT* g (mol)	Wt. of MNT/DCM soln. (wt./wt.)	%Yield
8-1	250 (5.95)	5-30	7.5	17	50 (0.365)	100 g of 50%	92
8-2	750 (17.85)	8-20	8	3	75 (0.547)	150 g of 50%	97
8-3	750 (17.85)	8-22	13	3	150 (1.135)	300 g of 50%	94

*Runs 8-1 & 8-2: 2-NT (55%) & 4-NT (45%); Run 8-3: 2-NT (57.2%), 3-NT (1.4%) 4-NT (41.4%).

The experimental method for these runs is given in Appendix A, Section A.5.

Further aspects of the 2nd stage nitration are discussed in the proof-of-concept study, described in Section 4.4.2 below.

In the 2nd stage nitration using excess 100% nitric acid, further analysis of Accelerated Reaction Calorimetry (ARC) results (see Section 4.2.2, above) has shown that the implied temperature of no return (runaway) for a small metal tubular reactor with a time constant of 10 min. would be 143°C. From this prediction, the 2nd stage nitration could be operated up to a temperature of 70°C with minimal risk.

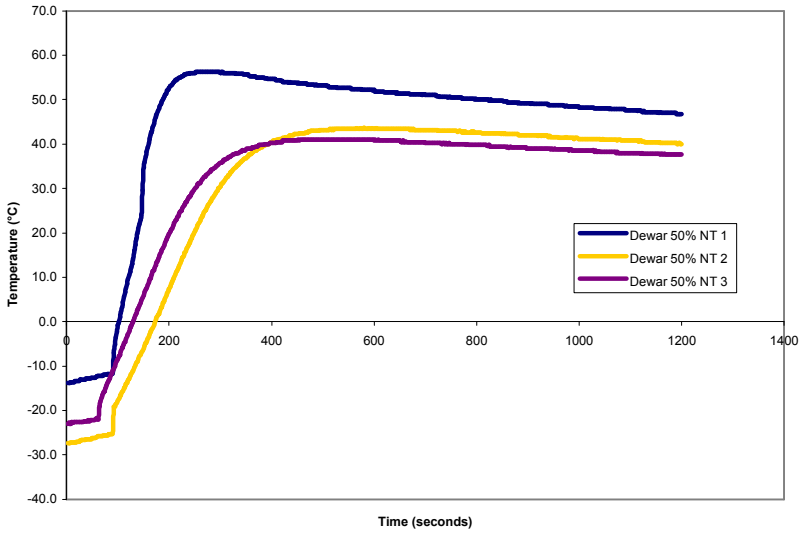


Figure 12: Addition of 50% wt./wt. nitrotoluene in DCM to concentrated HNO_3

Previously reported Dewar experiments in Fig. 12 above show that, at 50% concentration, the reaction takes place over several minutes. This would allow for removal of heat of reaction as it evolves and a practical reactor residence time of several minutes. A higher concentration would necessitate excessive cooling of the feed streams as in stage 1, and more dilute would require a higher temperature and higher residence times, so 50% was a practical starting point for process development purposes. A new reactor was specified for the continuous flow reactor rig used for the 1st stage reaction. A coiled concentric tube heat exchanger with a path length of 5 m and a hold up of 200 ml was used to give a residence time of around 9 min. at a typical combined flow rate of 30 g/minute. Initial results are shown in Table 9.

Table 9: Continuous Nitration of Mononitrotoluenes by Nitric Acid.

Run	Feed Temp (°C)	Reactor Inlet Temp (°C)	Reactor Outlet Temp (°C)	Acid:MNT Molar ratio	Residence Time (min)	Conversion (%)	Yield (%)
9-1	-15	-14	14	9.6:1	9.75	54	44
9-2	2	3	12	11.2:1	8.7	54	50
9-3	13	19	19	7.2:1	11	56	55
9-4	21	25	25	6.4:1	11.3	81	74

The starting MNT isomer ratio was similar to Run 8-3 for the batch reactions (Table 8), and the molar excess of nitric acid was decreased to 10 as the continuous reactor should be more efficient. As a precaution the first runs were performed at low temperatures both on the feed pre-coolers and the reactor jacket to minimize any peak temperatures due to the heat of reaction.

A stirred quench vessel containing DCM and water was used to collect the product stream. The purpose of this was twofold - the water was used to dilute the acid to a point where phase separation would occur and the DCM to extract the product and any unreacted MNT. At the end of the run the aqueous phase was found to contain around 70% of the remaining acid and upon extraction with DCM, 5% of the organic matter.

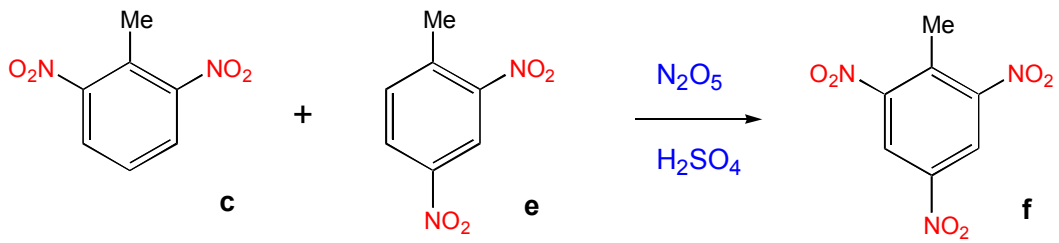
Washing the organic phase twice with water removed virtually all the remaining acid, and extraction of the first water wash yielded only 0.6% additional organic material. Washing the initial organic phase with sodium bicarbonate made no difference to the quantity of recovered material or its composition, therefore water only washes will be used in future to simplify the process.

Phase separation occurred quickly and cleanly indicating that transfer to a continuous process should not pose any major problems. Increasing the reaction temperature and residence time has increased the conversion and yield of DNT obtained thus far. At present the process conditions are giving lower yields than the batch results. Further optimization by manipulation of process variables such as increasing reactor residence time/temperature and/or acid to MNT molar ratio should produce yields much closer to those obtained from batch processing.

For conclusions regarding the 2nd stage nitration work see General Conclusions (Section 5).

4.3 Nitration of Dinitrotoluene Mixture (3rd Stage of TNT Process)

The equation for the reaction under study is as follows:-



Stage 3 (dinitrotoluenes to TNT)

4.3.1. Preliminary investigation of reactivity of reagents for 3rd stage nitration

The initial approach adopted was to utilize nitronium sulfate, prepared by reaction of N_2O_5 with sulfuric acid, for the nitration of a mixture of 2,4- and 2,6-DNTs (ratio 70:30). Such a system has been reported to successfully nitrate *m*-dinitrobenzene to 1,3,5-trinitrobenzene at elevated temperatures [80], and as shown below the conversion of the DNT mixture to TNT has been successfully accomplished by this means.

A mixture of 2,4- and 2,6-dinitro toluenes (70:30) was nitrated using N_2O_5 dissolved in concentrated H_2SO_4 (approx. 15% wt./wt.) at 50-55°C for 24 hrs. The reaction mixture on cooling turned into a solid mass and had to be slightly warmed in order to add the mixture to ice/water. The precipitated white solid which was filtered off, washed with water and dried was found to be pure TNT (>90% yield) as confirmed by NMR and had a melting point of 81.2°C (peak) by DSC (see Appendix A, Section A.8).

In further development of this novel TNT synthesis, the material obtained by the nitration method described above had an acidic odor and, to remove the acidic contaminants, it was taken up into either chloroform or ethyl acetate, washed with aqueous bicarbonate solution and isolated from the organic layer by evaporation. This sample also gave an identical NMR and DSC to the previous sample.

The synthesis of TNT by this novel process has not, apparently, been reported before. The optimization of the reaction, particularly to shorten the reaction time from the present duration of 24 hr. (which may not permit economic application on chemical plant) is described below (Section 4.3.2).

The material (Sample X) from the initial proof of concept experiment (Section 4.4.1, below) was nitrated in the 3rd stage nitration using a 16% wt./wt. N_2O_5-sulfuric acid mixture under the same conditions reported above to give an 88% yield of TNT. GC analysis showed that

this product was 98% pure and contained some unidentified peaks (most likely unsymmetrical TNT isomers originating from previous nitration steps). This result is promising and further samples of the material are being synthesized for evaluation of the physical properties, especially its solidification temperature (see Section 4.4.2).

4.3.2 Optimization studies of 3rd stage nitration

It was reported above (Section 4.3.1) that TNT could be produced in good yield under mild conditions by the use of N_2O_5-H_2SO_4 mixtures. The initial reaction used an approximately 23% wt./wt. solution of N_2O_5-H_2SO_4 at 55^oC for 24 hr. to achieve full conversion of DNTs to TNT. Since scale up of such a process would be impractical due to the extended reaction times further investigations into optimization of the reaction parameters were undertaken. Simple experiments with variation in temperature and N_2O_5 concentration were conducted and are summarized in Table 10.

The general tend shows that by increasing either the N_2O_5 concentration or the temperature, the reaction time can be decreased. The exceptions to this are only if a large excess of N_2O_5 (run 10-5) or less than 1:1 mol equivalent is used.

All the reactions were found to give high yields and excellent product purity as confirmed by GC and/or NMR. Although some of the runs show the GC purity of the product to be less than 99% (runs 10-4 to 10-12) no other peaks were observed. A possible explanation for this discrepancy was non-volatile occluded acid impurities in the samples during the quenching of the mixture. This was borne out by an acid smell from many of the samples. The acid impurities were found to be easily removed by dissolution of the material in DCM followed by washing with dilute sodium bicarbonate solution and water before separation and isolation from the organic layer.

Notes to Table 10 (below)

a. Dissolved in 98% sulfuric acid
b. Mixture of 2,4 and 2,6 DNT in DCM
c. Isolated after drying in vacuum oven at 50^oC overnight.
d. 80:20 n-Pentane/EtOAc.

Table 10: Nitration of DNTs by N_2O_5-Sulfuric Acid

Run	%N_2O_5 wt./wt.[a]	N_2O_5:DNT	DNT Used (g)[b]	Temp °C	Time (hr.)	Yield[c]	GC Analysis (TNT/2,4-DNT/2,6 DNT)	Conversion TLC[d]
10-1	16	3.05	3	55	5.5	85	91.12/7.00	Some DNT
10-2	31	5.75	3	55	5.5	87	95.95/1.15	Some DNT
10-3	16	3.05	3	55	7	85	92.03/5.69	Some DNT
10-4	16	3.05	3	70	3	88	97.63	No DNT
10-5	36	6.87	1.5	55	7	80	97.50	No DNT
10-6	20	3.60	1.5	70	4	85	95.82	No DNT
10-7	20	3.60	1.5	70	4	86	96.24	No DNT
10-8	10	1.80	1.5	70	4	83	95.88	No DNT
10-9	10	1.80	1.5	70-75	4	90	96.20	No DNT
10-10	10	1.80	1.5	80	3	86	98.01	No DNT
10-11	20	3.60	1.5	80	2.5	87	97.33	No DNT
10-12	20	3.60	1.5	80	2.5	89	97.97	No DNT
10-13	2.5	0.45	1.5	80	6	76	65.26/33.05	Some DNT
10-14	2.5	0.45	1.5	80	6	76	61.89/0.81/35.99	Some DNT
10-15	10	0.90	3	80	6.5	89	96.32/1.69	Some DNT
10-16	10	0.90	3	80	6.5	88	93.81/4.01	Some DNT
10-17	10	0.60	4.5	80	6.5	87	72.89/23.73	Some DNT
10-18	10	0.60	4.5	80	6.5	89	81.57/13.43	Some DNT

4.3.3. Final optimization studies of 3rd stage nitration (lab. scale)

It was reported earlier (Section 4.3.2) that TNT could be produced in good yield under mild conditions by the use of N_2O_5-H_2SO_4 mixtures. In general, by increasing either the N_2O_5 concentration or the temperature, the reaction time can be decreased. All the reactions were found to give high yields and excellent product purity as confirmed by GC and/or NMR.

Results of further runs are shown in Table 11. The reaction was scaled-up to a one liter reactor. (As with the batch MNT nitration runs described above, these runs generated material for the proof-of-concept study, described in Section 4.2.2 below).

Thus, as with the 1st and 2nd stage nitrations, QinetiQ has shown that the 3rd scale nitration has been achieved successfully in over 85% yield and the product was found to be consistent with that obtained on the small scale.

An ARC study (Figs. 13 & 14) was carried out on this reaction, and an initial sample (0.79 g) showed no exothermic behavior below 142°C. At this point a small exotherm was seen, but this was barely above the detection threshold and petered out by 149°C. The main exotherm showed a typical accelerating profile between 177 and 274°C, and was assumed to be due to decomposition of the organics and possibly also the acid. These results implied a critical temperature of 150°C for a 25 L vessel and an activation energy of 127 $kJmol^{-1}$. Further investigation of the initial exotherm using a larger sample size (3.5 g) revealed a weak exotherm at 50°C, too small to analyse, and a continuous accelerating reaction from 106°C (Figs. 15 & 16). The activation energy for this reaction was 30 $kJmol^{-1}$ and a critical temperature for a 25 L reactor of 99°C giving a safety margin of around 20°C.

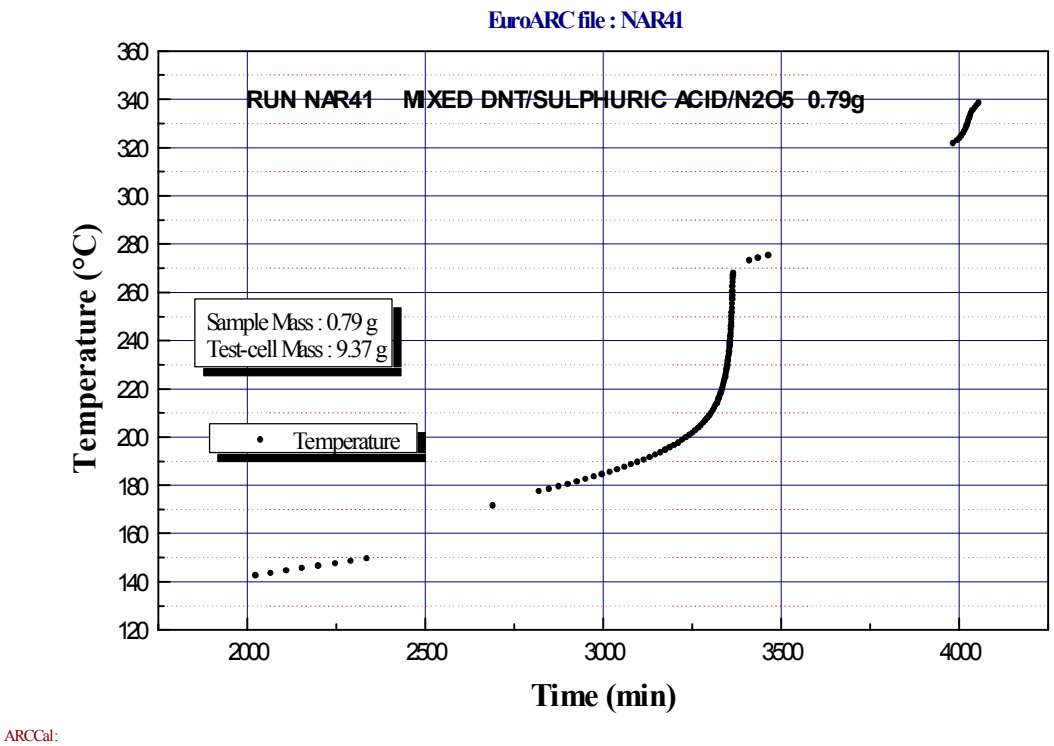


Fig. 13 – Temperature *vs* Time Plot for Mixed DNT-Sulfuric Acid-N_2O_5

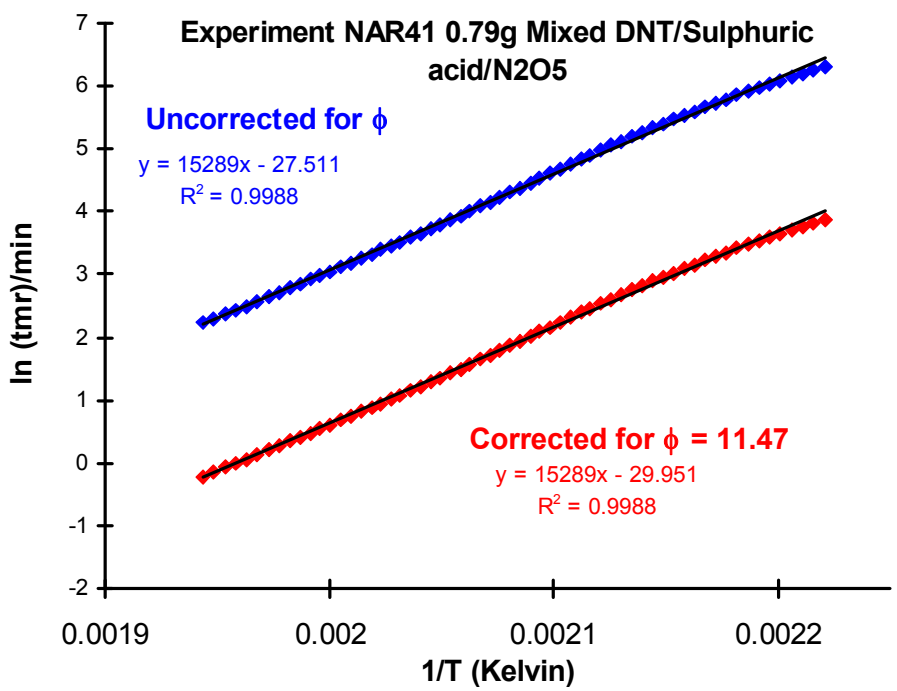


Fig. 14 Time to Maximum Rate Plot for Mixed DNT-Sulfuric Acid-N_2O_5 (using main exotherm data)

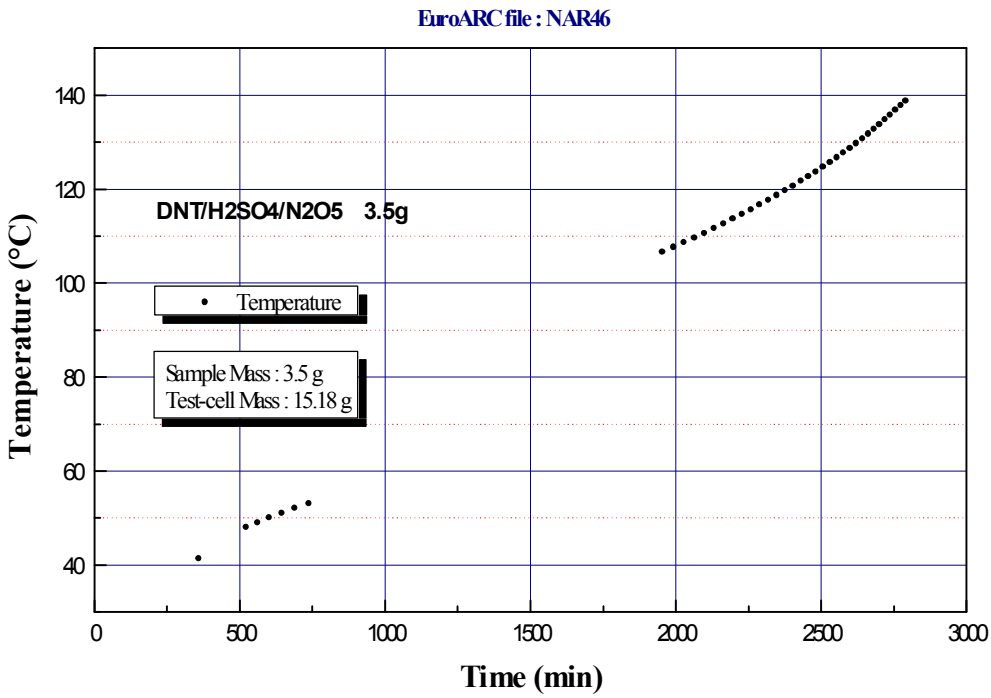


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Fig. 15 – Larger sample - Temperature *vs* Time Plot for Mixed DNT-Sulfuric Acid-N_2O_5

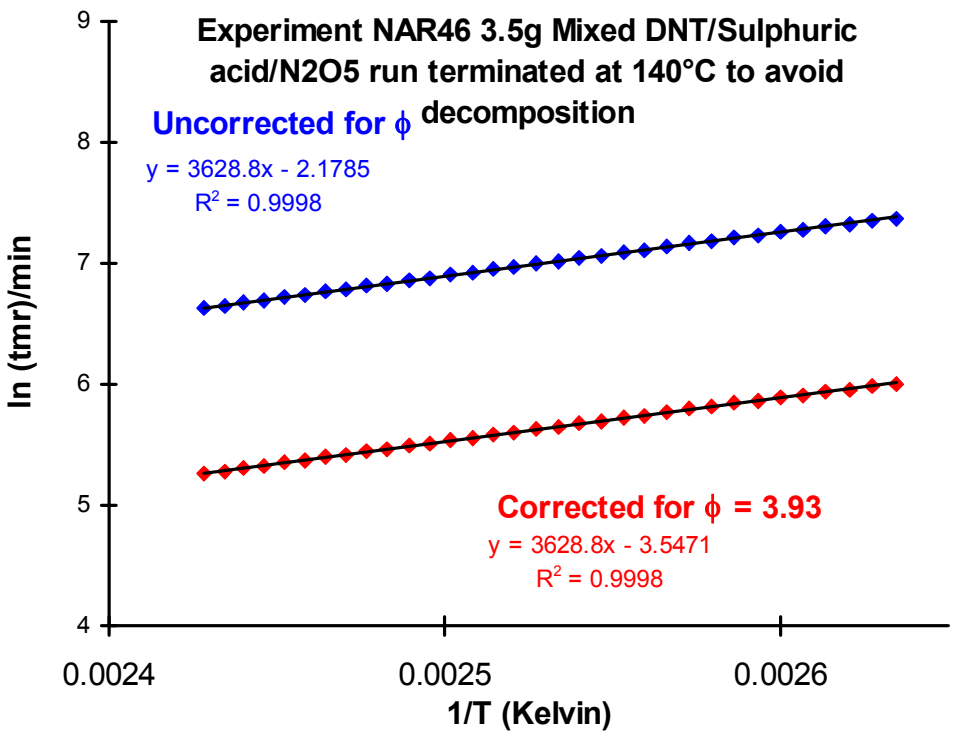


Fig. 16 Larger sample - Time to Max. Rate Plot for Mixed DNT-Sulfuric Acid-N_2O_5 (main exotherm data)

Table 11: Nitration of DNTs by N_2O_5-Sulfuric Acid – Large-Scale Runs

Expt.	% N_2O_5 wt./wt.	Mol N_2O_5:DNT	DNT Used/g	Temp.	Time hr.	Yield (isolated)	GC Analysis (%) (TNT/2,4,5-TNT/2,3,4 TNT)	NMR analysis (%) (TNT/2,4,5-TNT/2,3,4-TNT)
11-1	10	1.71	22.2	75	6.5	90	98.51/0.96/0.53	-
11-2	15	2.18	46	75	4.5	89	98.11/1.09/0.59 (0.21% 2,3,6)	-
11-3	15	1.84	3	75	4	90	99.83/0.12/n.r./trace 2,3,6-TNT	99.79/0.12/n.r./ 0.06 2,3,6-TNT
11-4	12	2.32	46	77	4.5	93	98.71/0.79/0.50	98.56/0.81/0.53
11-5	11	2.31	46	77	4.5	86	98.87/0.77/0.36	99.07/0.56/0.27
11-6	*	*	*	*	*	80	99.90/0.07/0.03	99.84/0.09/0.02

*Recrystallization sample (samples 5-4 & 5-5 combined prior to recrystallization)

n.r. = not recorded

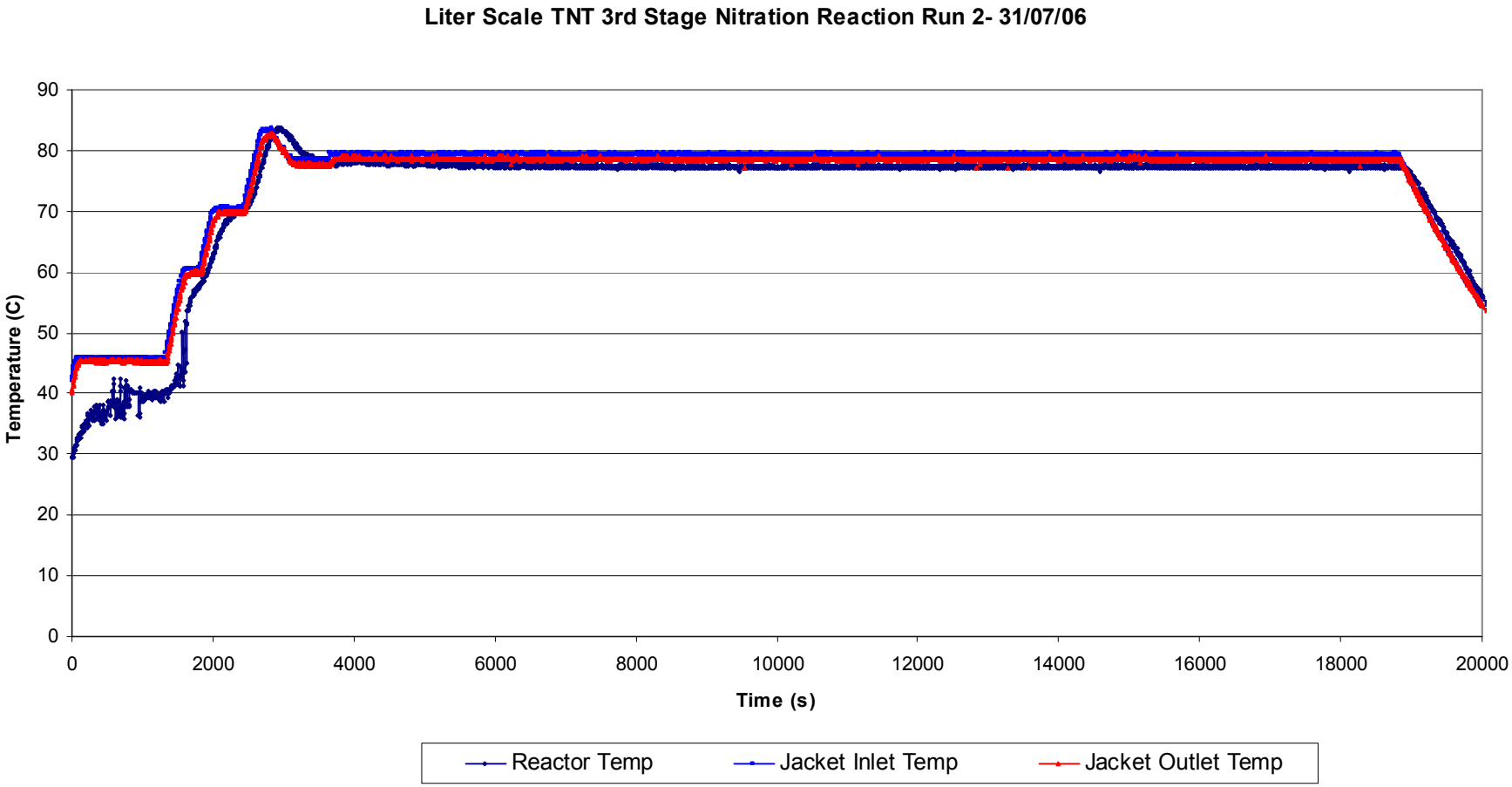


Fig. 17: Reaction temperature profile for liter scale nitration of DNT

Fig. 17 shows the temperature profile for experiment 5-5, and reactor internal temperatures as well as reactor jacket inlet/outlet temperatures are shown. The profile is constant during the reaction, and all three temperatures are similar with the jacket slightly higher than the internal temperature. During the reaction, very little heat transfer is occurring as there is only a small difference between the reactor and jacket fluids. In fact the reaction mixture is being heated to maintain its temperature above ambient.

Preliminary conclusions

The 1st and 2nd scale nitrations have been achieved successfully in over 85% yield and the products were found to be consistent with those obtained on the small scale. A large amount (80-100 g of TNT) was required for the Proof-of-Concept study, and scale-up considerations are addressed presently for that activity (see Section 4.4, below). Likewise, the scale-up conditions for the 3rd stage nitration for the Proof-of-Concept study are also addressed later (see Section 4.4, below).

For final conclusions regarding the 3rd stage nitration work see General Conclusions (Section 5.4).

4.4 Proof-of-concept Studies

4.4.1 Initial study (using mixed acid in Stage 2)

A separate series of experiments was undertaken as an initial proof of concept exercise to determine how the actual mixture of dinitrotoluenes would affect the purity of the TNT produced in the 3rd stage of the process. The mixture from the first stage nitration run (containing 55.8% 2-NT, 1.4% 3-NT and 42.4% 4-NT) was nitrated using standard mixed acid conditions. The nitration of the mononitrotoluene mixture was achieved by addition of the mixture at 45°C to a mixed acid solution followed by further heating of the mixture to 70°C for 45 min. Workup gave an 89% yield of a mixture of dinitrotoluenes and TNT. GC analysis indicated the mixture contained approximately 76% of 2,4-DNT, 12% 2,6-DNT, 0.4% 2,3-DNT and 9% TNT along with a further 2.5% of unknown material (most likely other DNT isomers). Estimation by ^{1}H NMR was found to give similar results (TNT 8%, 2,6-DNT 75.4%, 2,4-DNT 15.3%, 3,4 and 2,3 DNT 1.3%). Experimental details of these syntheses may be found in Appendix A, Section A.5, and the spectral traces in Appendix A, Section A.7.

The material (Sample X) from the above experiment was nitrated in the 3rd stage nitration using a 16% wt./wt. N_2O_5-sulfuric acid mixture under the same conditions reported in Section 4.3.1 to give an 88% yield of TNT. GC analysis showed that this product was 98% pure and contained some unidentified peaks (most likely unsymmetrical TNT isomers originating from previous nitration steps). This result was promising and further samples of the material were therefore synthesized for a fuller evaluation of the physical properties, especially the solidification temperature (see Section 4.4.2, below).

4.4.2 Large-scale Proof-of-concept Study

N_2O_5 has been used to reduce the *meta* content during the 1st stage nitration but to prove whether this amount of undesired isomer would be sufficient for military specification TNT requires a solidification point measurement. Carrying out such measurements would require a minimum of 80 g of TNT produced using this current three stage process. This requires approximately 100 g of MNT from the 1st stage which could then be nitrated to DNT in the 2nd stage and finally to TNT.

Also note that this study differs from the earlier initial proof-of-concept study (Section 4.4.1, above) in that the DNTs were synthesized using nitric acid, not mixed acid, and the product should therefore more closely replicate that obtained on scale-up.

As a large amount (80-100 g of TNT) was required for the Proof-of-Concept study (but due to the explosive license limit in the synthesis laboratories it was not possible to carry out a batch reaction yielding 80 g of TNT), it was decided that an initial scale-up of the 3rd stage nitration (approx. 8 times that which been previously used) would be undertaken which would result in approx. 24 g of TNT. This would then be doubled and the batches combined to give the overall amount required for the Proof-of-Concept study.

From the optimization reactions which had been carried out earlier (see Section 4.3) it was decided that, for the 3rd stage nitration, 10% N_2O_5-H_2SO_4 at 70-75°C would be the optimum conditions to use for the scale-up. However when the reaction was attempted it was found that an extended reaction time was required for completion of the reaction (6.5 hr. instead of 4 hr.). The TNT produced from this run was however found to be pure by GC analysis (99%).

A sample of approx. 100 g of TNT for solidification point determination was thus prepared in batches of 30-50 g by batch nitration of the DNT mixture (as mentioned above, using MNTs from a single 1st stage extended run nitration with a *meta*-NT content of 1.55%). Characterization by chromatography (GC) showed that the material was around 98% pure (with slight batch-to-batch variability), the principal contaminants being 2,4,5-TNT (~1%) and 2,3,4-TNT (~0.5%) [cf. conventional mixed acid nitration: 2,4,5-TNT (2.5%) and 2,3,4-TNT (1.75%)]. DSC showed a trace (see Appendix A, Section A.8) of similar form to samples prepared earlier (described in Section 4.3) – i.e. no untoward instability is anticipated.

Because the solidification point determination could not be carried out by an independent laboratory as had originally been intended (the reason given being a change in the health & safety rules at the laboratory), a suitable apparatus was constructed in-house, modelled on the apparatus at the independent laboratory, and measurements were carried out according to O.B. Specification M202/94 (equivalent to MIL-DTL-248D; method given in Appendix A, Section A.6) on the sample prepared in-house and, for comparison, a sample of commercial TNT (Bridgwater, Type I). According to these measurements, the commercial sample met the Type II specification (set point around 80.4°C over two determinations) whereas the in-house sample was around 79.9°C – i.e. 0.3°C below the minimum figure for Type I TNT (3 determinations). This result is not unexpected since the mononitrotoluene feedstock used for the synthesis contained 1.55% *meta*-NT, instead of the target figure of 1.3%, and confirms the sensitivity of physical properties of TNT to unsymmetrical isomer content.

Further tests were carried out:-

i) clean-up of the in-house sample to ensure that the depression of the solidification point was not due to extraneous impurities, and
ii) recrystallization of another sample to verify that TNT conforming to MIL STD can be prepared by this means.

The results of these tests are reported below.

i) The in-house sample cleaned up by sulfite washing – this satisfied the set point criterion for Type I TNT (i.e. >80.2°C). This indicates that the depression in the set point is caused by unsymmetrical TNT isomers and not extraneous impurities.
ii) A new in-house sample was prepared from purchased MNTs containing 1.4% meta-NT – this also gave a set point figure of 79.9°C. When the sample was recrystallized from a mixture of ethyl acetate and ethanol (1:5 vol./vol.), by the procedure shown in Appendix A, Section A.5, the set point rose to 80.6°C (which exceeds the spec. for Type II TNT). Approx. 88% of the crude weight of TNT was recoverable in this way.

Clearly, recrystallization yields a very pure product but the acceptability of this procedure as an additional step, particularly on plant scale, may be open to question. Also, the potential hazard of

using flammable solvents in an environment where explosives are being processed on large scale would have to be addressed.

Finally, some tests were carried out during a 50 g TNT synthesis run to establish if appreciable amounts of tetranitromethane or NOx were being formed (details in Appendix A, Section A.5). Neither by-product could be detected in the headspace of the reactor vessel, and it is therefore concluded that these compounds are not being formed in appreciable amounts.

4.5 Scale-up and Process Economics

4.5.1 Overall Process

As this project progressed, the information gained has enabled the production of an outline process flow sheet (see Fig. 18) which has made considerable improvements on the earlier proposed clean nitration route. Details of reaction temperatures, flow rates, residence times, yields and quantitative measures all add valuable information to the process that has eventually allowed the construction of a preliminary process flow sheet including mass and energy flows. These figures are vital in calculating ROM (Rough Order of Magnitude) cost estimates for commercial scale industrial manufacture.

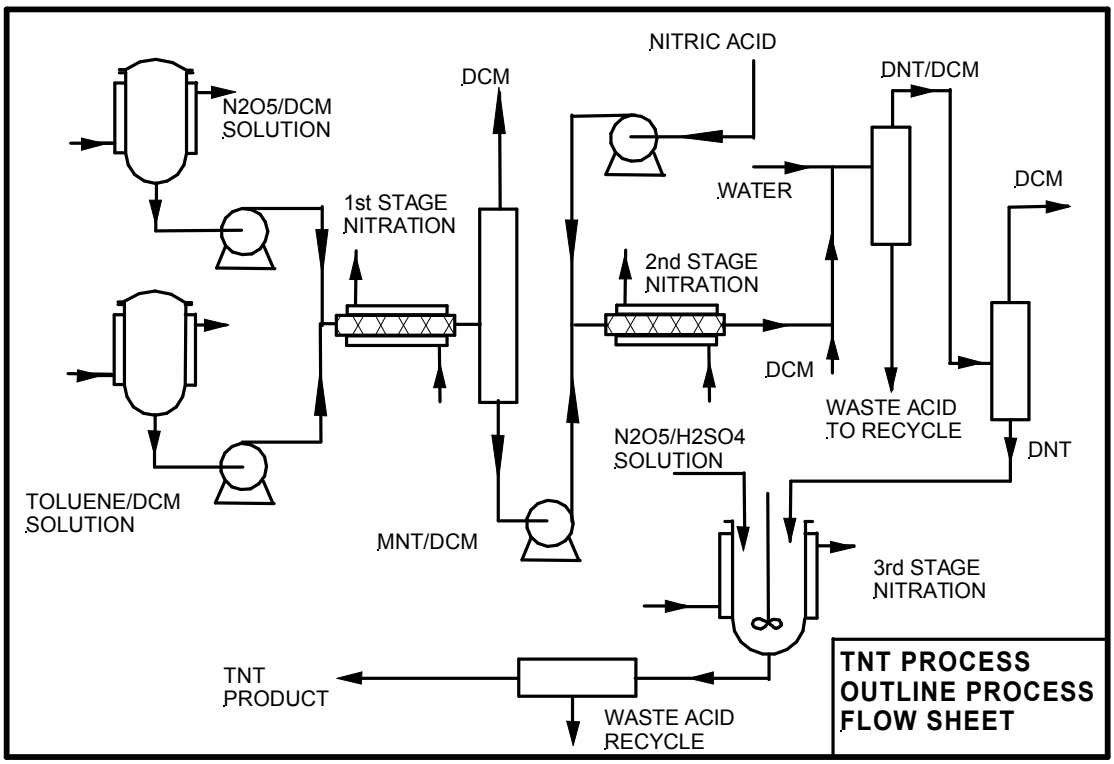


Fig. 18: Schematic for complete nitration process (simplified)

Studies of the 1st stage nitration reaction have shown that to achieve the target of 1.3% *m*-NT stated in the project proposal would require a reaction temperature of -60°C, and that the reaction is almost instantaneous. Attainment of low temperatures and high intensity mixing is difficult to achieve on a laboratory scale. In particular, the present continuous nitration reactor is of relatively simple construction with concentric tube heat exchangers and a static mixer tube for the reactor section. With this arrangement, a mixing temperature of -30°C and reactor exit temperature of -50°C have been achieved resulting in a *m*-NT content of around 1.5%, slightly short of the target. For pilot-scale development a more efficient heat exchanger unit would be

used such as a plate and frame, spiral or miniature shell and tube configuration and a bespoke reactor designed. This should reduce the *meta* content further.

After the 1st stage nitration, the product is neutralized with aqueous sodium bicarbonate (the neutralization step may be dispensed with on scale-up) and the organic layer recovered from the two phase system which separates easily. In the laboratory scale studies this has been done batch-wise but it is proposed to carry out this process continuously on the larger scale.

Furthermore it is proposed that the resultant wet NT/DCM solution will be continuously concentrated using a wiped wall evaporator. From the evaporator, the 50% NT/DCM solution will flow via a cooling unit directly into the 2nd stage nitrator where concentrated nitric acid (>98%) is used as the nitrating agent. Any small amount of water and/or nitric acid remaining in the DCM from the first stage should not affect the reaction but studies should be carried out at pilot-scale to confirm this.

Extraction of the DNT from the 2nd stage nitration has also been studied batch-wise in the laboratory and it has been shown that with the addition of further DCM and water a two phase system can be produced with the top layer containing the organic DNT/DCM stream, representing 97% product recovery. It is proposed that this unit operation will also be carried out continuously possibly by a counter-current solvent extraction type device. Isolation of the DNT is achieved by evaporation of the DCM which could be carried out continuously as well.

The 3rd stage nitration to TNT has been carried out in the laboratory with a nitrating medium of N_2O_5 in sulfuric acid. The kinetics of this reaction are relatively slow and here we would depart from continuous processing to that of a batch reactor. Laboratory studies up to a liter scale have returned good yields and no hazardous exotherms. The final recovery of the TNT is accomplished by extraction with DCM, neutralization of the organic layer and removal of the solvent. Additional product may be recovered from the acid layer by dilution and further extraction.

Although a completely integrated technical demonstrator plant was outside the scope of this project, the individual operations have been tested successfully and the data obtained gives sufficient confidence for an integrated pilot-scale development to proceed where process optimization can be carried out.

4.5.1a GO/NO-GO Decision point based on commercial viability

This decision point was based on information supplied in response to an Action Item in the Spring 2006 IPR (see Appendix C.2).

The point at issue concerned the status of the first stage reactor design, and whether QinetiQ had been able to achieve reasonable throughput with acceptable levels of *meta*-NT.

After taking a number of factors into account, particularly reactant concentrations, flow rates and reaction temperatures, it was concluded that the practical limit for the *meta* content from the first stage nitration was around 1.5%. Further efforts to decrease this figure would be met with a disproportionate increase in production costs. TNT produced from such a feedstock would be

predicted to have a set point of around 80.0°C (cf. Type I specification: 80.2°C). On this basis the SERDP Program Manager indicated that he was content for the project to run for the full duration.

4.5.2 Appraisal of First Stage Nitration

The first stage nitration from toluene to mononitrotoluene in dichloromethane (DCM) using N_2O_5 has reduced the *meta* isomer content significantly. Traditional mixed acid nitration produces around 4% and even at very low temperatures gives a *meta* content of 2.7%, whereas N_2O_5 chemistry has been able to reduce this figure to 1.3%.

Studies into the reaction dynamics of the first stage nitration with N_2O_5 have shown that the reaction is far more exothermic than with mixed acid (165 c.f. 120 $kJmol^{-1}$) and also exceedingly rapid even at very low concentration (2% wt./wt.) and very low temperatures (-60°C). Small scale batch nitration (20 ml) at around 2% substrate concentration and a reaction temperature of -70°C yielded a *meta* content of 1.3%. It was noted that at this low temperature the toluene crystallized out of the DCM and this could have detrimental effects with flow reactors especially if the flow path is small.

Experiments on a flow reactor at concentrations between 2% and 7 % wt./wt., at three different flow rates and a reaction temperature range of -15°C and -40°C have been carried out (Section **4.1**). All experiments produced a *meta* content below 2%. The lower the temperature, flow and concentration then the lower the *meta* content. At best, a *meta* content of around 1.5% was obtained using a 2% wt./wt. toluene feed cooled to -60°C and a N_2O_5 in DCM stream cooled to -30°C. These conditions gave a reaction temperature of -40°C. Further cooling or dilution would reduce the *meta* content further to 1.4% or even lower but risk the formation of solid toluene and N_2O_5 in the heat exchangers and on the cooling surfaces that would cause blockages. Further dilution would significantly increase the cost of production.

As stated before, the reaction is almost instantaneous even at these very low temperatures and dilution factors. Consequently pre-cooling of the reactant streams to counter the reaction exotherm is the only practical method of reducing the reaction temperature in a continuous flow reactor. Cooling process streams below -60°C is approaching the limit of two stage mechanical refrigeration equipment. The use of LN (Liquid Nitrogen) should be considered for cooling duties. The economics of mechanical refrigeration versus LN depends greatly on quantity of LN used, location of the nearest LN supply and utilization of the resultant nitrogen gas on the plant or elsewhere on site. Recovery and recycle of large volumes of DCM produced in all three stages could be carried out by cryogenic condensation processes; these also utilize LN supporting the argument for LN usage. The volumes involved are thought to be too large for GAC systems (Granular Activated Carbon) but GAC systems may be used as a final treatment for exit gases and environmental extracts.

Although N_2O_5 is more expensive than nitric acid as a nitrating medium there is no doubt that it can significantly reduce the *meta* content in the first stage reaction, and in addition this reaction is atom efficient using virtually stoichiometric proportions rather than a large excess which is normally required for nitration reactions with nitric acid. Also, although DCM is also relatively

expensive it is recovered and recycled within the process. Loss of DCM on a commercial scale would be minimized by appropriate plant design and operating procedures.

For rapid exothermic reactions, on a large scale, continuous reactions are usually carried out in small diameter reactor tubes arranged in a parallel configuration. In this way the heat transfer area to volume ratio is maximized and the velocity in the tube is high enough to promote good mixing. For this reaction it has been calculated that at 2% wt./wt. feed concentration based on a tube velocity of 0.1 m/s and internal diameter of 12 mm, a 200 tube reactor would be needed for a commercial size plant (1,000 tonnes/year). Alternatively multiples of smaller bundles of tubes in a modular type construction may be more practical. Since the control of the reaction exotherm relies heavily on pre-cooling the feed streams it may not be necessary to maximize the heat transfer area of the reactor and consequently the reactor tube diameter may be increased leading to fewer tubes in number and a simpler reactor design. Optimization of reactor design would be carried out during pilot-scale studies.

In the laboratory, batch neutralization of the product stream was carried out – this was to allow work up and isolation of the product for analysis of isomer ratio, conversion and yield calculations as well as storage for future use as a feed stream for the second stage reaction. Upon scale-up this would be unnecessary as the product stream from the first nitration reaction could be concentrated by a wiped wall evaporator, a commercially available item of process plant equipment, and fed directly into the next stage. Any minor amounts of unreacted toluene, and the nitric acid formed should not affect the second stage reaction. The molar ratio of acid to MNT is very low and although a small amount of DNT may be formed it is unlikely to present a hazard although pilot-scale trials would be required to confirm this.

4.5.3 Appraisal of Second Stage Nitration

Laboratory studies of the second stage nitration showed that there were a number of nitrating agents available that would perform this reaction successfully (Section 4.2). It was concluded that concentrated nitric acid (>98%) was the best option due to its low cost and it would simplify the process, with no added sulfuric acid or N_2O_5 being required. Batch experiments confirmed the moderate temperatures and reaction times measured in minutes making it ideal for transfer to continuous nitration. Dilution of the MNT feed with DCM had a significant effect on the reaction time.

Furthermore bulk extraction of the DNT product by aqueous dilution of the acid and addition of DCM worked well. Phase separation of the organic and acid layers was clean and quick, facilitating easy integration into a continuous process. Similar to the first stage, the removal of DCM solvent to isolate the DNT would be carried out by standard unit operations. Pilot-scale trials would determine if trace amounts of DCM, MNT and acid in the solid DNT product could have a detrimental effect on the final stage, but it is thought unlikely.

Transfer of the reaction to continuous mode was successful, and good yields were obtained with a residence time of around 10 min. (cf. 10 sec. for 1st stage). It was found that control of the nitration exotherm could be carried out in the reactor alone and pre-cooling was unnecessary.

Further optimization by increasing reactor temperature, acid to MNT ratio or residence time should give higher yields similar to those seen in the batch experiments (>95%).

The large excess of acid in this reaction adds material costs but nitric acid is inexpensive and the first aqueous phase contained around 70% of the unused acid and was >50% in concentration. Recovery, recycle and possible re-concentration of this stream for reuse is a possibility to reduce costs. Recovery of DCM could utilize cryogenic condensation as in the first stage, further building the case for LN use.

Scale-up of the 2nd stage reaction to commercial scale production should not present any significant problems; pilot-scale trials would confirm the practicality of continuous extraction and product isolation and their integration with the nitration stage. Further coupling of stage one and two to produce a seamless process would produce invaluable data for full scale plant design and operational procedures.

4.5.4 Appraisal of Third Stage Nitration

The final nitration stage was accomplished by using nitronium sulfate produced from adding N_2O_5 to sulfuric acid. This system negates the use of oleum and its inherent problems. Initial small gram scale batch reactions indicated reactions times in excess of a day but experimentation and optimization reduced this time to a few hours (Section 4.3), still too long for continuous processing hence it was decided to use bulk reaction mode upon scale-up.

Liter scale reactions were performed with yields similar to those of the small scale experiments. No significant exotherms were detected indicating that the reaction was slow. Once the reaction mixture had reached 80°C, the jacket inlet temperature was higher than the reaction temperature indicating that no cooling was taking place, in fact heat was being applied to the reaction to maintain the temperature. Mixed acid nitration gives a heat of reaction of around 70 $kJmol^{-1}$, lower than the first two stages but still significant. If the heat of reaction was similar for nitronium sulfate, cooling of the reactor would be required even taking into account the extended reaction time, but this was not necessary. This fact leads to the conclusion that nitration by nitronium sulfate is significantly different and apparently less hazardous.

The initial work-up procedure involved drowning the reaction in a water/ice mixture but this produced TNT with acid occlusions. Further work has shown that simple addition of DCM will extract most of the TNT from the acid. Two layers are formed with around 75% of the TNT in the organic layer. Dilution with water and addition of DCM to the acid layer recovered the majority of the remaining TNT. The purity of the TNT product was 99.8%.

Isolation of the solid TNT by removal of the solvent DCM would be carried out by standard unit operations and the DCM recovered by cryogenic condensation.

Utilization of N_2O_5 in both 1st and 3rd stage reaction increases the overall requirement for N_2O_5 production and consequently reduces its unit cost. Although this reaction is not as atom efficient as the 1st stage, 2:1 molar ratio, the sulfuric acid should be recyclable as is the DCM leading to some cost savings.

At this stage the TNT does not meet the required minimum set point temperature (as previously stated), however a simple recrystallization step using ethanol and ethyl acetate produces a product purity of >99.9% thus giving a set point temperature of 80.6°C, greater than both type I and II specifications.

Pilot-scale studies will have to be performed to optimize the operating parameters for all these nitration steps, work-up procedures and final recrystallization.

4.5.5 Process Economics

An industrial scale energy and mass flow sheet has been constructed as Excel spreadsheets for each of the nitration stages from the basic information gained by laboratory scale experiments. The basis of this flow sheet is the production of 2,000 tonnes (*ca.* 4.5 Million lbs) of TNT from a plant operating 24 hours a day, 48 weeks per year (8,000 hrs). Input data may be changed in the spreadsheets to see the effect of process variables on the energy usage and materials cost. The mass and energy balances are by no means complete, and items such as mixing and pumping costs are not included. In fact only the major contributors to production costs are considered at this stage to provide a rough order of magnitude (ROM) cost, and the accuracy of the ROM cost at this stage is similar to a Class IV or V (+40%/-25%) estimate. Further trials at pilot-scale would optimize the process and may make significant changes to the flow sheets hence a more accurate estimate would only be practical after further work.

Considering the nitration stages in turn:

i) 1st stage (flow) nitration: A production scale mass and energy flow sheet has been developed for the first stage nitration reaction (see Figure 19, below). The purpose of this activity is to estimate the magnitude of heating and cooling required for an industrial scale plant along with the volumetric/mass flows. A 2.5% solution of toluene in DCM is fed at a rate of 125 kg/hr of toluene into a continuous reactor where it is nitrated. The stream exiting the reactor is fed into a continuous wiped wall evaporator where most of the DCM is removed, and DCM vapor is condensed and recycled. The product is a 50/50 solution of MNT/DCM with the nitric acid formed from the reaction. This first stage reaction is simple but requires a large amount of heating and cooling energy due to the large fluid volumes, although much of the energy may be recovered by incorporating further heat exchangers for instance by routing of the reactor exit stream to partially cool the inlet streams.

ii) 2nd stage nitration: A production scale mass and energy balance flow sheet has also been developed for the second stage nitration reaction (see Figure 20, below). This has necessitated further laboratory experiments to measure the magnitude of exotherms and endotherms associated with the mixing of process streams particularly in the DNT product isolation stage. Continuous flow nitration experiments have been carried out to enable refinement of the flow sheet. A molar ratio of 6:1, acid to MNT has been used and it is assumed that by extending the reaction time, a full conversion to DNT is attained in the continuous process.

The heat of reaction is removed in the continuous reactor and the exit temperature is at ambient. DCM is added at a 2:1 volume ratio, DCM to reaction stream, to extract the DNT. A drop in

process stream temperature occurs as the mixing is endothermic. Further cooling may be introduced at this stage if necessary to counter the heat of solution of adding water in the next step, but if the acid ratio is low then it should not be necessary. Dilution of the stream with water produces phase separation where approximately 75% of the acid is removed in the lower phase and 96% of the DNT in the upper phase. A second water wash of the organic stream removes most of the remaining acid, 98%, and 99% of the DNT remains in the lower phase. (It is possible that this DNT recovery stage may be simplified by having only one water wash and carrying a small amount of nitric acid through to the 3rd stage nitration.) Finally, the DCM is removed by continuous evaporation to give a solid DNT product, overall yield 94%. Another possible diversion from this route would be to leave a small amount of DCM/nitric acid with the DNT to keep it fluid and suitable for pumping into the third nitration reactor. The effect of the presence of DCM and possibly nitric acid in the 3rd stage nitrator at the start of the reaction is unknown and would have to be studied to ensure there are no detrimental effects.

iii) 3rd stage nitration: A third production scale mass and energy balance flow sheet has been developed for the final stage nitration reaction (see Figure 21, below). The basis for this flow sheet is a batch reaction of one tonne of DNT being nitrated by nitronium sulfate in a batch cycle time of 8 hrs. This may be accomplished in a single reactor but more likely a series of smaller reactors for safety and redundancy/maintenance issues. DCM is added to the reacted mixture to extract the TNT and two phases are formed; the acid phase is diluted with water and further DCM is added to extract the remaining TNT. The two organic phases are combined and neutralized and DCM is removed leaving a solid product. This extraction process post-reactor could be carried out continuously provided a buffer tank was installed to provide a constant source of feed. At the end of the third stage the TNT produced in the laboratory does not meet the required set point temperature and requires further processing by recrystallization.

iv) Recrystallization: A simple process of dissolving the TNT in a mixture of ethanol and ethyl acetate at elevated temperature and then cooling to give TNT with a set point of 80.6 ^{o}C, so that the majority of the unsymmetrical isomers remain with the solvent. Figure 22 shows a simple mass and energy flow sheet. It is assumed that the solvents will be recyclable and that process design will be able to control the hazards associated with using flammable solvents. An overall yield for the four stages is around 80%, most of the losses being in this last stage.

v) Overall process: Figure 23 shows a spreadsheet where material costs and total energy usage is calculated from the previous mass and energy flow sheets. The capital cost is estimated from a step counting method [87] multiplied by CEPCI (Chemical Engineering Plant Cost Index (USA)) to bring the cost up to date and given a hefty 100% uplift to take into account compliance with explosives processing regulations and the premium paid for an explosives processing facility. The outcome of the calculation was $80 million which was given a simple straight line depreciation over 10 years. Plant maintenance costs were taken as 3% of capital.

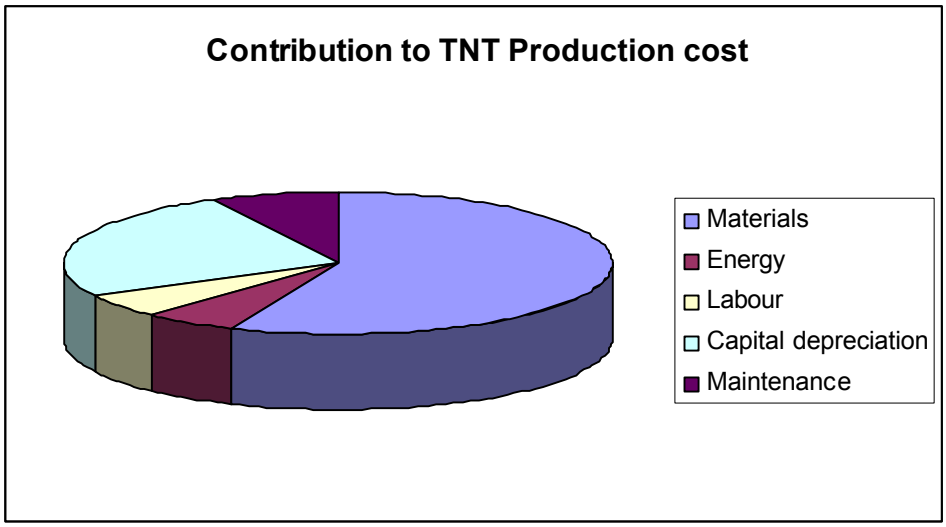
Material costs were sourced from typical bulk chemical prices and the cost of DNPO was estimated from previous work carried out by QinetiQ and updated. It was assumed that DCM losses would be minimized and all the recovered DCM recycled. DCM losses from the recovery process and the environment would be trapped by GAC (Granular Activated Carbon), the remainder being lost in the waste aqueous stream. Waste solvent from the recrystallization step would also be recycled, and in order to avoid a build up of TNT a 10% bleed has been allowed for. After further studies, improvements may be possible to the recrystallization stage giving

improved yield and economics. Incineration has been assumed as the treatment for this stream whereas the aqueous waste is destined for biological treatment.

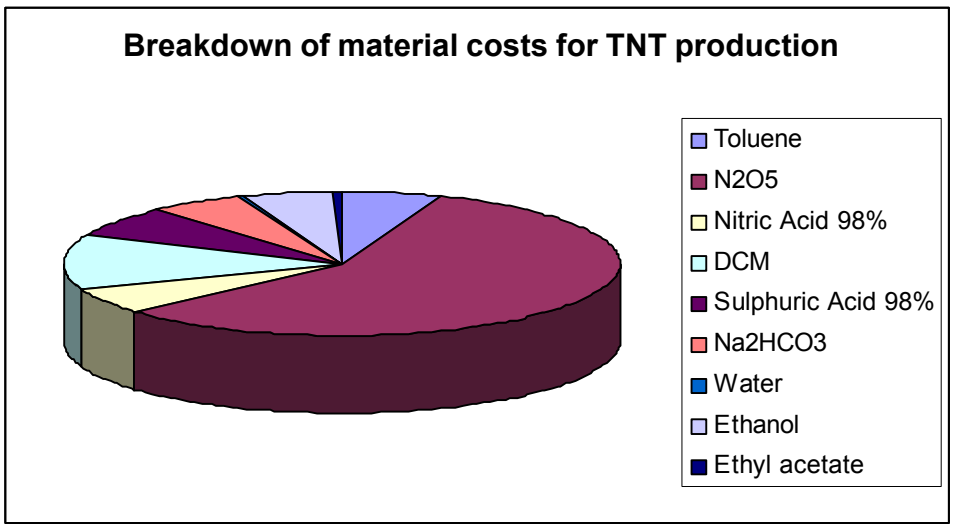
The major energy requirement is in the first stage due to the low reaction temperature and large volumes necessary to provide the very low concentration, but there is much scope for energy recovery by process design.

Labor costs are significant, and an all-in cost of $100k/man-year has been assumed, including supervisory and overhead costs.

A total production cost of $7.34/lb was calculated, and the proportion of the main contributors is shown in the chart below.



From the chart it is plain that the majority of the costs are materials and as shown in the second chart below around half of this cost is DNPO.



Optimization of the process variables at pilot-scale especially in the area of materials minimization and particularly DNPO usage would reap benefits in the overall cost of production as would the cost of DNPO manufacture itself. Another area that would reduce costs considerably is to improve the recrystallization yield, and with that the balance between minimization of the *meta* content in the 1st stage nitration and the need for such a large dilution factor with the practicality of removing the unsymmetrical isomers in the recrystallization stage. Furthermore the extension of the capital amortization period would also produce dividends. For instance, if it were possible to reduce the cost of DNPO to $2/kg, improve the yield from the recrystallization stage from 90 to 95%, recover 30% of the energy and assume a plant life of 20 years a production cost estimate of $5.25/lb is realized.

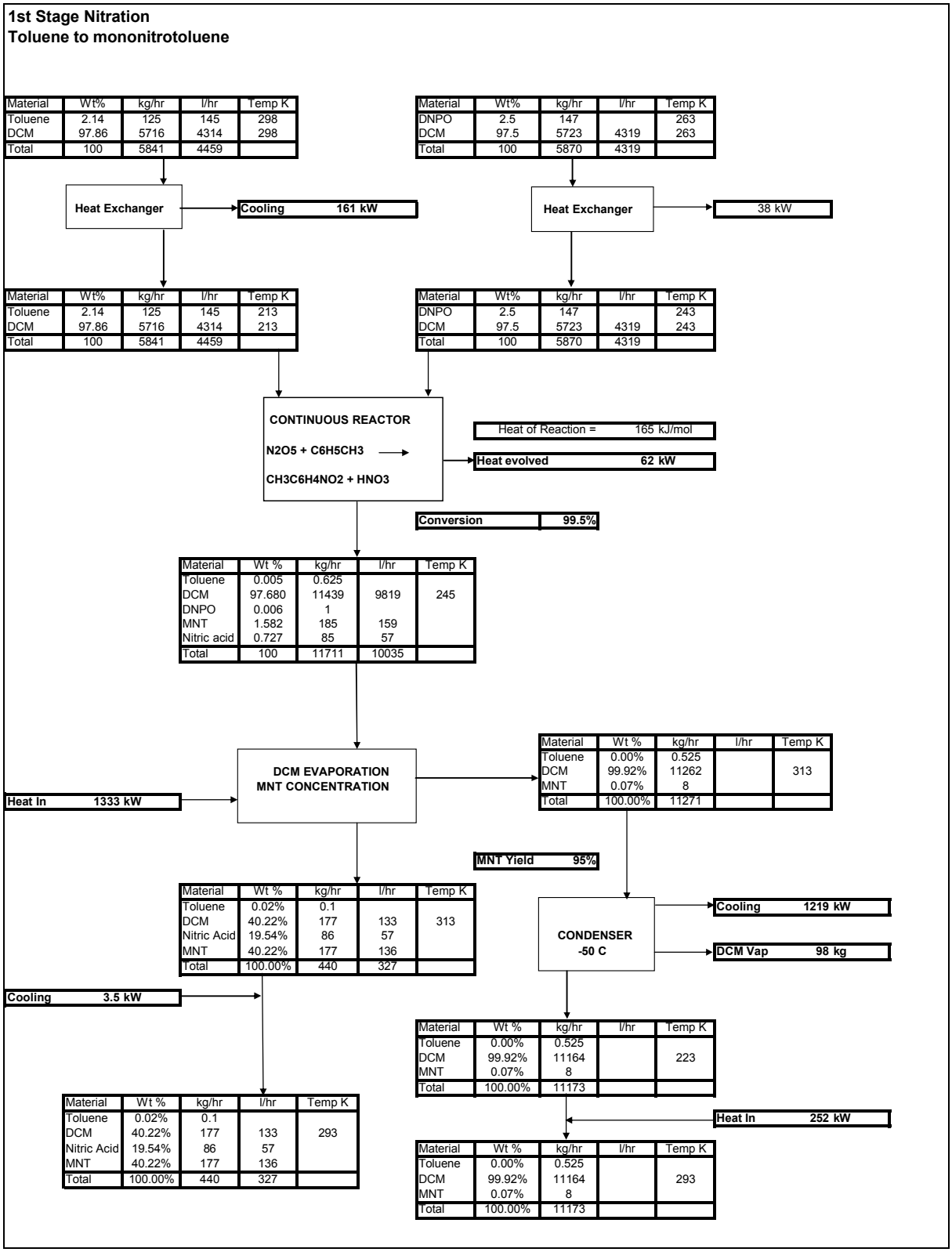


Fig. 19: Production scale mass and energy flow sheet for the first stage nitration reaction

2nd Stage Nitration
MNT to DNT

Material	Wt %	kg/hr	l/hr	Temp K
DCM	40.23%	177	133	293
MNT	40.23%	177	136	
HNO3	19.54%	86	57	
Total	100.00%	440	327	

Material	Wt %	kg/hr	l/hr	Temp K
HNO3	100.00%	402	268	293
Total	100.00%	402	268	

Molar ratio 6 :1

Cooling

CONTINUOUS NITRATION

Heat of Reaction = 110 kJ/mol
Heat of Reaction = 803 kJ/kg
Heat Output = 141984 kJ/hr
Cooling required = 39.4 kW

Conversion 100.0%

Material	Wt%	kg/hr	l/hr	Temp K
HNO3	48.31%	407	271	293
DCM	21.01%	177	133	
MNT	0.00%	0	0	
DNT	27.91%	235	174	
Water	2.76%	23	23	
Total	100.00%	842	602	

Heat of solution = 16 kJ/kg DCM

Material	Wt%	kg/hr	l/hr	Temp K
DCM	100.00%	1576	1190	293
Total	100.00%	1576	1190	

Material	Wt%	kg/hr	l/hr	Temp K
HNO3	16.82%	407	271	
DCM	72.51%	1753	1323	285
MNT	0.00%	0	0	
DNT	9.72%	235	174	
Water	0.96%	23	23	
Total	100.00%	2418	1791	

Cooling = 0 kW

Material	Wt%	kg/hr	l/hr	Temp K
HNO3	16.82%	407	271	
DCM	72.51%	1753	1323	285
MNT	0.00%	0		
DNT	9.72%	235	174	
Water	0.96%	23	23	
Total	100.00%	2418	1791	

Heat of solution = 250 kJ/kg Acid

Acid dilution = 75% wt/wt

Material	Wt%	kg/hr	l/hr	Temp K
Water	100.00%	136	136	288
Total	100.00%	136	136	

Material	Wt%	kg/hr	l/hr	Temp K
HNO3	15.92%	407	271	
DCM	68.66%	1753	1323	301
MNT	0.00%	0		
DNT	9.20%	235	174	
Water	6.22%	159	159	
Total	100.00%	2553	1927	

Fig. 20: Production scale mass and energy flow sheet for the second stage nitration reaction

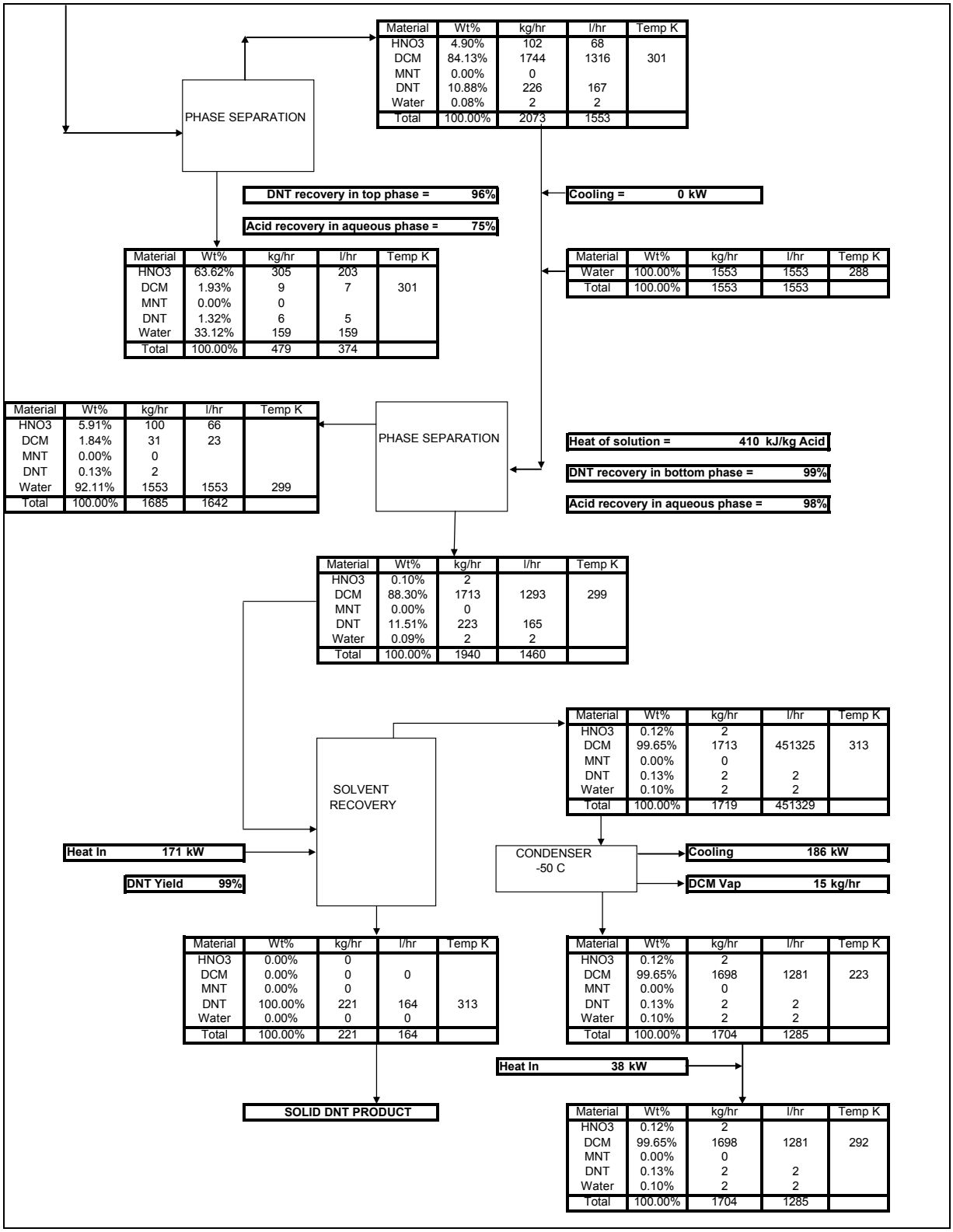


Fig. 20 (continued):

3rd Stage Nitration
DNT to TNT

Material	Wt %	kg	l	Temp K
N2O5	100.00%	2099		253
Total	100.00%	2099		

Material	Wt %	kg	l	Temp K
H2SO4	100.00%	18887	10265	293
Total	100.00%	18887	10265	

Heat of Solution = 320 kJ/kg

Material	Wt %	kg	l	Temp K
N2O5	10.00%	2099		
H2SO4	90.00%	18887	10265	314
Total	100.00%	20986	10265	

Material	Wt %	kg	l	Temp K
DNT	100.00%	1768	1310	293
Total	100.00%	1768	1310	

Load	**0.5 hrs**
Heat	**1 hrs**
Reaction	**3 hrs**
Cool	**1 hrs**
Discharge	**1.5 hrs**
Clean	**1 hrs**
Total	**8 hrs**

Batch Nitration
Reactor
Temp 77 C

Temp = 77 C

Nitration Molar excess = 2

N2O5 concentration (wt/wt) = 10.0%

Conversion = 99.0%

Heating Required = 308 kW/Batch
Cooling Required = 513 kW/Batch

Material	Wt%	kg	l	Temp K
N2O5	4.66%	1060		
HNO3	2.66%	606	404	
DNT	0.08%	18		
TNT	9.60%	2183	1365	
H2SO4	83.01%	18887	10265	293
Total	100.00%	22754	12034	

Wt Ratio DCM:TNT = 10 :1

Material	Wt %	kg	l	Temp K
DCM	100.00%	21834	16479	293
Total	100.00%	21834	16479	

Material	Wt%	kg	l	Temp K
DCM	48.97%	21834	16479	293
N2O5	2.38%	1060		
HNO3	1.36%	606	404	
DNT	0.04%	18	13	
TNT	4.90%	2183	1365	
H2SO4	42.36%	18887	10265	
Total	97.62%	44589	28525	

Fig. 21: Production scale mass and energy flow sheet for the third stage nitration reaction

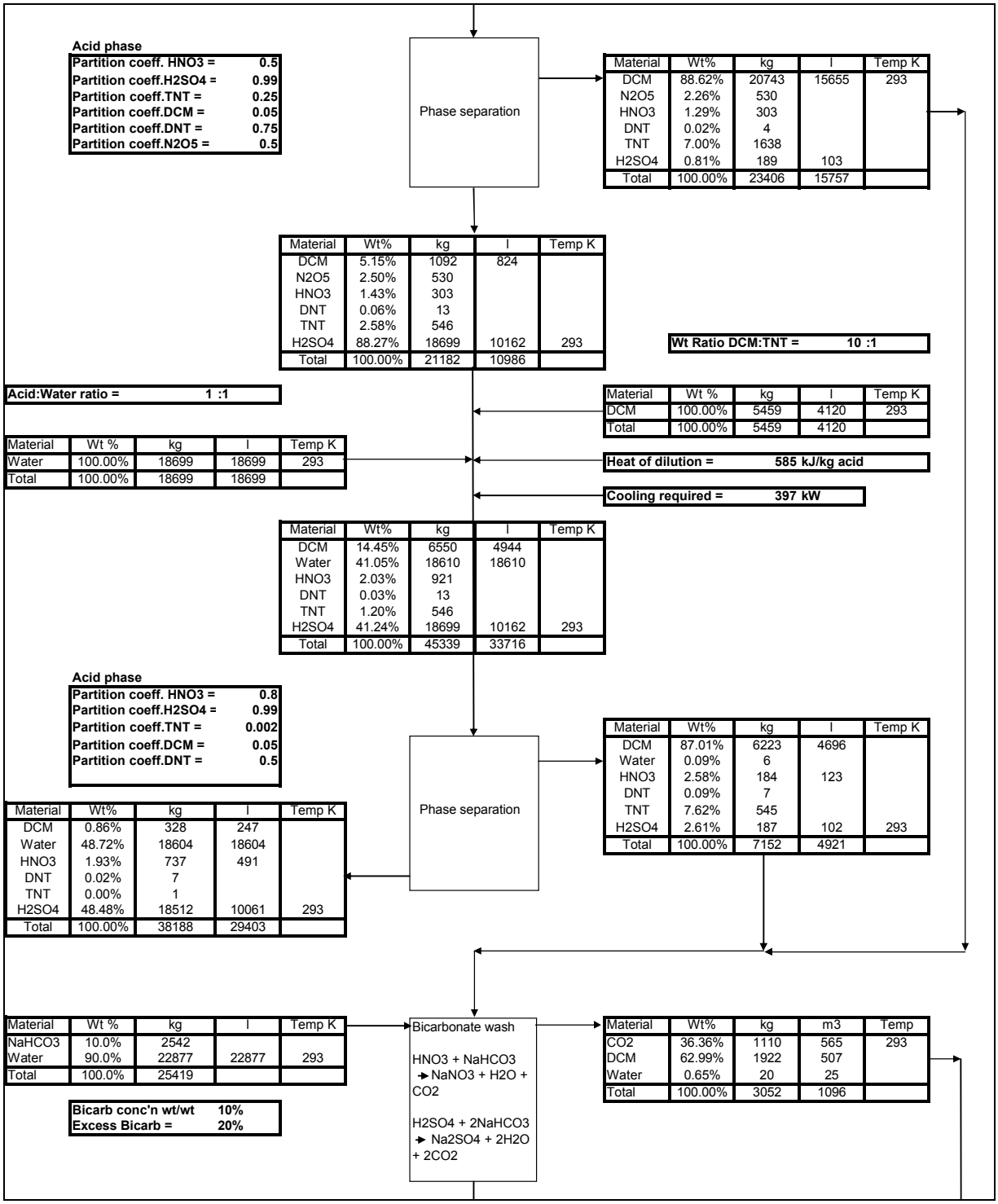


Fig. 21 (continued)

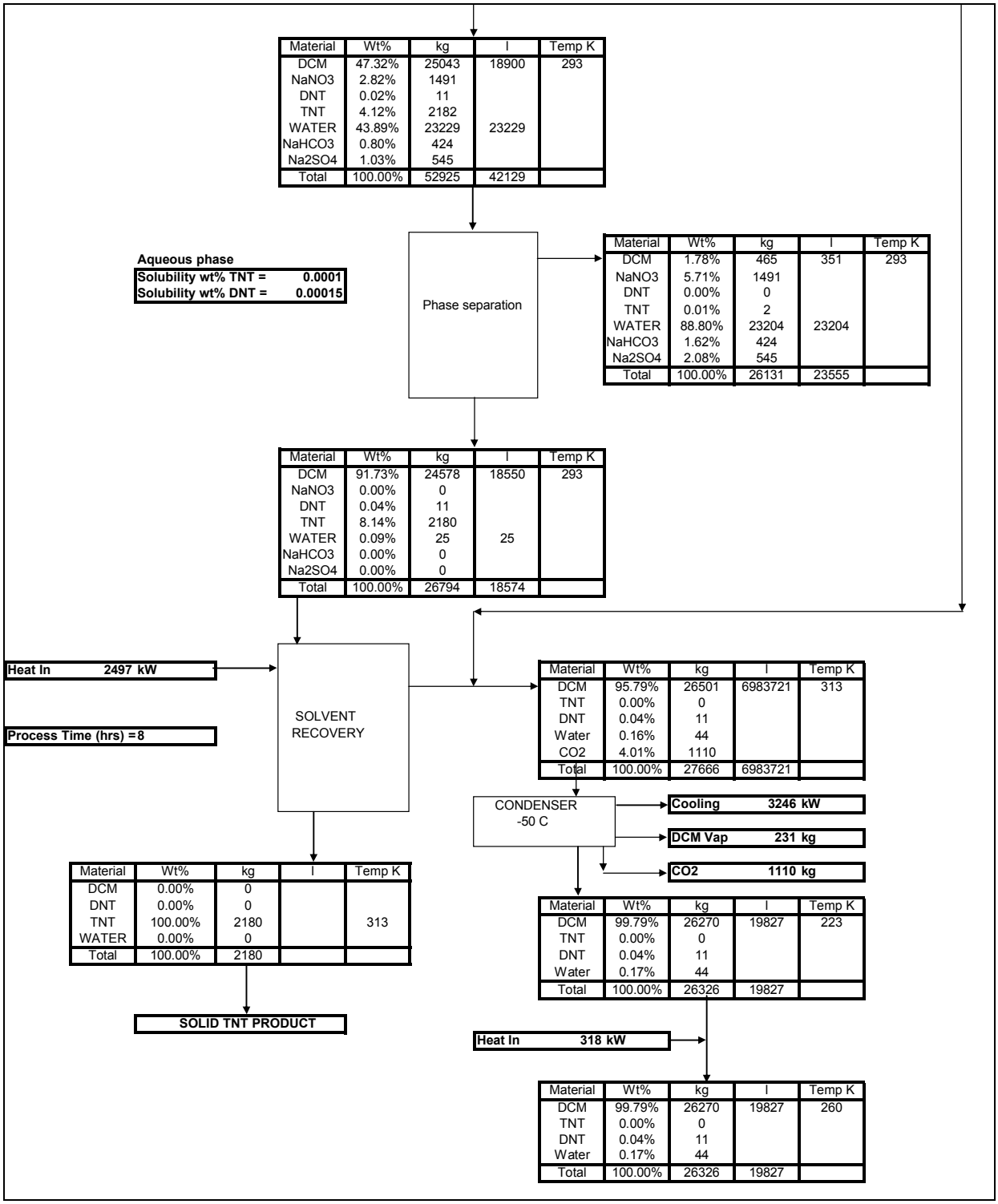


Fig. 21 (continued)

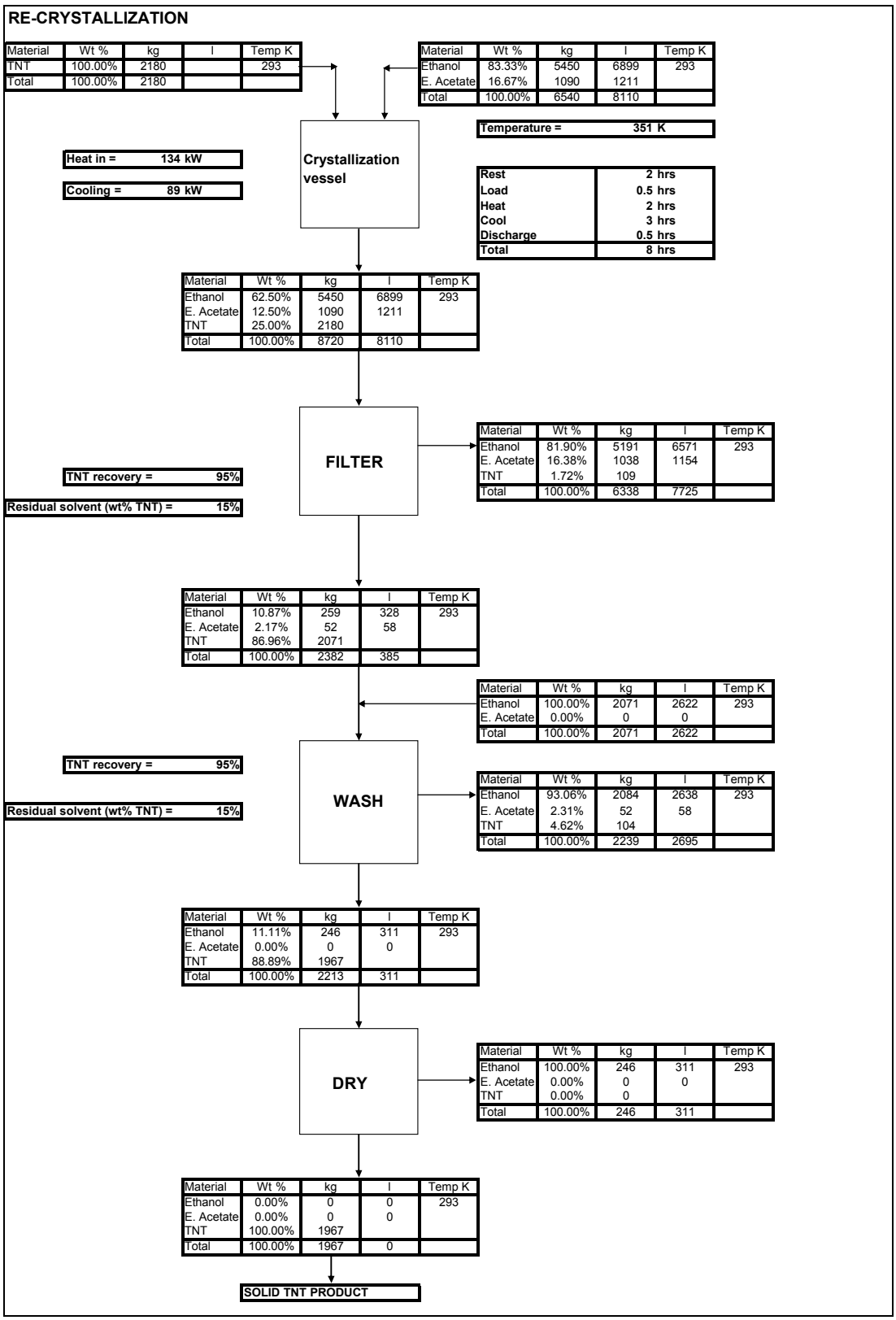


Fig. 22: Production scale mass and energy flow sheet for the recrystallization process.

Toluene to TNT
Basis 2,000 tonnes/year TNT manufacture
Basis 48 weeks/year continuous manufacture.

8,000 hours

Mass Balance

Input

Material	Quantity Tonnes	Cost $/tonne	Cost k$	Comment
Toluene	1000	1000	1000	
N2O5	3273	3000	9818	
Nitric Acid 98%	3216	300	965	
DCM	2120	1000	2120	Make up for losses
Sulphuric Acid 98%	18887	60	1133	
Na2HCO3	2118	460	974	
Water	50964	0.5	25	
Ethanol	752	1200	903	Assumes 10% make up
Ethyl acetate	109	1000	109	Assumes 10% make up
Total	82440		17048	

Output

Material	Quantity Tonnes	Cost $/tonnes	Cost k$	Comment
TNT	1968			
Water Waste	77331	10	773	Tertiary treatment
CO2	1110			
DCM	1135			
Ethanol/Et Acetate/TNT	1074	50	54	Incinerate?
Total	82618		827	

Material Cost TNT= 9.08 $/kg

Energy Balance

Heating MWh	17762			MWh
			Energy Stage 1	24044
Cooling MWh	17517		Energy Stage 2	3494
			Energy Stage 3	7295
Total energy GWh	35		Energy Re-crystallization	535
			Total	35368
Energy cost =	0.05	$/kWh		

Total cost without recovery = 0.90 $/kg TNT

Labour Cost

No of shifts/day	3	
No of men/shift	4	
Utilisation	70%	
Total man power	17	
Cost/man year $	100000	Includes overheads and supervision
Total Labour cost k$	1714	

Labour cost = 0.87 $/kg TNT

Capital Cost

Capital Installed	80	M$
Lifetime of plant	10	years
Simple depreciation	8	M$/year

Fixed Cost 4.07 $/kg TNT

Maintenance 1.22 $/kg TNT 3% of capital

TOTAL PRODUCTION COST = 16.14 $/kg TNT
7.34 $/lb TNT

Fig. 23: Material costs and total energy usage

5. Conclusions

5.1 General Comments

In conclusion, QinetiQ believes that the mononitrotoluene isomeric mixture made by the N_2O_5 nitration process reported here will be suitable to produce TNT with a specification approaching that of military grade TNT (to Type I specification) without any requirement for sulfite treatment, on account of the low content of *meta*-isomers. The improvements which QinetiQ has developed to the reagents used and conditions required for the 2nd and 3rd stage nitrations will give rise to cleaner products, enhanced recyclability of reaction media and reduction in off-gases as well as reduced tetranitromethane (TNM) formation, owing to the lower proportion of isomers bearing *meta*-nitro groups in the feedstock (As noted in the literature [88], formation of TNM has been shown to arise through decomposition of these isomers in the 3rd stage nitration). Conclusions resulting from further scaled-up studies of these aspects, which have been carried out by QinetiQ, are presented below.

Before proceeding further, however, the authors wish to point out that two other current approaches to solving the TNT redwater problem by modification of synthesis routes/conditions have become known to QinetiQ during the course of the project:-

1) The approach starting from *ortho*-nitrotoluene, advocated by ATK Thiokol [89], which involves modification to subsequent nitration steps, and is being implemented at the Radford AAP; and
2) The use of zeolite catalyzed nitration in the first stage (nitration of toluene) to improve the regioselectivity of the reaction and suppress *m*-NT formation to around 1% level; currently under investigation at ARDEC, Picatinny Arsenal (SERDP project WP1409 [90]).

The first approach does not really solve the problem as it is dependent on a source of the *ortho*-nitrotoluene from the chemical industry which may not be reliable in times of crisis – and may be subject to economic vagaries and also accidental destruction of plant (separation of MNT isomers on plant scale relies on distillation, which is an inherently hazardous process with these compounds). QinetiQ therefore believes that, while this approach is meeting an immediate DoD need, it may not meet all of DoD's requirements in respect of the dependability of the process.

The second approach involving zeolite chemistry may indeed meet the DoD's aims of a dependable process starting from toluene, but the availability of zeolites with appropriate reactivity characteristics as well as scale-up of the process to multi-thousand lb operation are challenges, and evidence that the problems encountered in these processes can be solved is still required. The proposed manufacturing route would also employ the traditional methods for second and third stage nitrations with the environmental disadvantages inherent in these processes.

In QinetiQ's approach to the first stage nitration, the regioselective nitration reagent dinitrogen pentoxide (N_2O_5) is used in a reaction medium of low polarity – dichloromethane is ideal regarding inertness toward N_2O_5 (although environmental drawbacks are recognized) – and reaction with toluene at sub-ambient temperature under either batch or flow reactor conditions

has been shown to give a product mixture with much lower amounts of *m*-NT than traditional methods. Detailed analyses of this and subsequent reaction stages follow.

5.2 First Stage Nitration

The first stage nitration from toluene to mononitrotoluene in dichloromethane (DCM) using N_2O_5 has reduced the *meta* isomer content significantly. Traditional mixed acid nitration even at very low temperatures gives a *meta* content of 2.7%, whereas N_2O_5 chemistry has been able to reduce this figure to 1.3%.

Studies into the reaction dynamics of the first stage nitration with N_2O_5 have shown that the reaction is far more exothermic than with mixed acid and also exceedingly rapid even at very low concentration (2% wt./wt.) and very low temperatures (-60°C). Small scale batch nitration (20 ml) at around 2% substrate concentration and a reaction temperature of -70°C yielded a *meta* content of 1.3%. It was noted that at this low temperature the toluene crystallized out of the DCM, this could have detrimental effects with flow reactors especially if the flow path is small.

Experiments on a flow reactor at various concentrations, flow rates and reaction temperatures have been carried out (for further details see Section 4.5.2). All experiments produced a *meta* content below 2%. The lower the temperature, flow and concentration then the lower the *meta* content. At best a *meta* content of around 1.5% was obtained using a 2% toluene feed cooled to -60°C and a N_2O_5 in DCM stream cooled to -30°C. These conditions gave a reaction temperature of -40°C. Further cooling or dilution would reduce the *meta* content further probably to a figure of the order of 1.4%. Consequently pre-cooling of the reactant streams to counter the reaction exotherm is the only practical method of reducing the reaction temperature in a continuous flow reactor.

For rapid exothermic reactions, on a large scale, continuous reactions are usually carried out in small diameter reactor tubes arranged in a parallel configuration. In this way the heat transfer area to volume ratio is maximized and the velocity in the tube is high enough to promote good mixing. For this reaction it has been calculated that at 2% feed concentration and a tube internal diameter of 12 mm, a 200 tube reactor would be needed or multiples of smaller bundles of tubes which would be more practical.

5.3 Second Stage Nitration

Laboratory studies of the second stage nitration showed that there were a number of nitrating agents available that would perform this reaction successfully (Section 4.2). It was concluded that concentrated nitric acid (>98%) was the best option due to its low cost and it would simplify the process, with no added sulfuric acid or N_2O_5 being required. Batch experiments confirmed the moderate temperatures and reaction times measured in minutes, and factors affecting the transfer to continuous nitration were considered (for further details see Section 4.5.3), with no "show-stoppers" being found.

Transfer of the reaction to continuous mode was successful, and good yields were obtained with residence time of around 10 min. (cf. 10 sec. for 1st stage). It was found that control of the nitration exotherm could be carried out in the reactor alone and pre-cooling was unnecessary. Further optimization by increasing reactor temperature, acid to MNT ratio or residence time should give higher yields similar to those seen in the batch experiments (>95%). Other aspects were considered earlier (Section 4.5.3).

Scale-up of the 2nd stage reaction to commercial scale production should not present any significant problems; pilot-scale trials would confirm the practicality of continuous extraction and product isolation and their integration with the nitration stage. Further coupling of stage one and two to produce a seamless process would produce invaluable data for full scale plant design and operational procedures.

5.4 Third Stage Nitration

The final nitration stage was accomplished by using nitronium sulfate produced from adding N_2O_5 to sulfuric acid. This system negates the use of oleum and its inherent problems. Initial small gram scale batch reactions indicated that reaction times in excess of a day were necessary, but experimentation and optimization reduced this time to a few hours (Section 4.3). However, this was still too long for continuous processing hence it was decided to use bulk reaction mode for scaled-up syntheses.

Liter scale reactions were performed with yields similar to those of the small scale experiments. No significant exotherms were detected indicating that the reaction was slow, and in fact heat had to be applied to the reaction to maintain the temperature (for further details see Section 4.5.4). A method for working up the reaction mixture using DCM was developed, which avoided the use of water/ice and gave a TNT product of 99.8% purity (by GC). This material however required recrystallization to meet the MIL STD (i.e. it had a solidification point below 80.2°C).

A simple recrystallization step using ethanol and ethyl acetate produced a product purity of >99.9%, giving a set point temperature of 80.6°C, greater than both type I and II specifications. Pilot-scale studies will have to be performed to optimize the operating parameters for all these nitration steps, work-up procedures and final recrystallization.

5.5 Process Economics

Industrial-scale energy and mass flow sheets were constructed for each of the nitration stages and the recrystallization stage, based on the production of 2,000 tonnes (*ca.* 4,400,000 lb) of TNT per annum for a plant operating 24 hr per day, 48 weeks per year (further details of assumptions used in the calculations may be found in Section 4.5.5). Although small amounts of DCM could be lost in the first, second and recrystallization stages, direct escape to the surroundings would be prevented by trapping using granulated activated carbon. Likewise, QinetiQ has shown that N_2O_5 can be produced in DCM solution on large scale without harm to the environment [71,72], and the data from these earlier studies have been updated and incorporated in the calculations.

Recycle of other waste streams is believed to be feasible, with residual waste being either incinerated or subjected to biological treatment.

The major energy requirement is in the first stage due to the low reaction temperature and large volumes necessary to provide the very low concentration, but there is much scope for energy recovery by process design. After further studies, improvements may be possible to the recrystallization stage giving improved yield and economics. Furthermore, labor costs are significant, and plant amortization issues have also been taken into account.

An initial production cost for TNT of $7.34/lb was calculated, and the breakdown was shown in the pie charts in Section 4.5.5. The major part of the costs was that of materials, with labor the next largest cost – surprisingly, energy costs were third largest, despite the need for refrigeration equipment to be used. Of the materials costs, N_2O_5 was the most expensive accounting for more than half of these costs. If further optimization of the processes were possible – especially reduction in the cost of the N_2O_5, improvement in the recovery of the TNT from the recrystallization, higher energy recovery and extension of the plant life – then the cost of the TNT could be reduced to $5.25/lb.

Clearly the cost quoted above on the initial estimate is *ca.* $5/lb higher than costs using existing plant and processes (*ca.* $2/lb), but of course in such facilities the amortization factor (for the nitration plant) is zero and the costs of cleaning up the redwater waste stream are not fully taken into account – for instance if the aqueous outflow were to be incinerated it would certainly more than double the cost of TNT manufacture by these processes. Sulfuric acid recovery on the larger scale required by these processes is also an issue and could also raise the cost significantly, as new plant build is believed to be required.

In conclusion, QinetiQ has demonstrated that reduction of the proportion of *meta*-substituted nitrotoluenes to around 1.3-1.5%, instead of the 4-5% levels in current processes, is feasible using N_2O_5 in dichloromethane to nitrate toluene. Such *meta*-nitrotoluene levels will permit manufacture of TNT to Type I military specification without the need for Sellite (bisulfite) treatment. Reduction in the amounts of hazardous and noxious by-products was also demonstrated. Thus, the process described in this report should be given serious consideration as a means of producing TNT from toluene with reduced impact on the environment. Indeed, preliminary discussions with a North American explosives manufacturer indicated that the process would, subject to availability of funding, be capable of exploitation particularly if economies of scale came into play regarding the production of N_2O_5 (which was identified earlier as a major contributor to process costs). A possible exploitation pathway could involve N_2O_5 as a nitrating agent for a range of products, from nitroaromatics such as TNT and 2,4-/2,6-dinitroanisole (DNAN) through nitramines such as HMX and CL-20 to nitrate ester plasticizers, thus achieving the desired economies of scale with enhanced atom efficiency and cleanliness of the respective processes.

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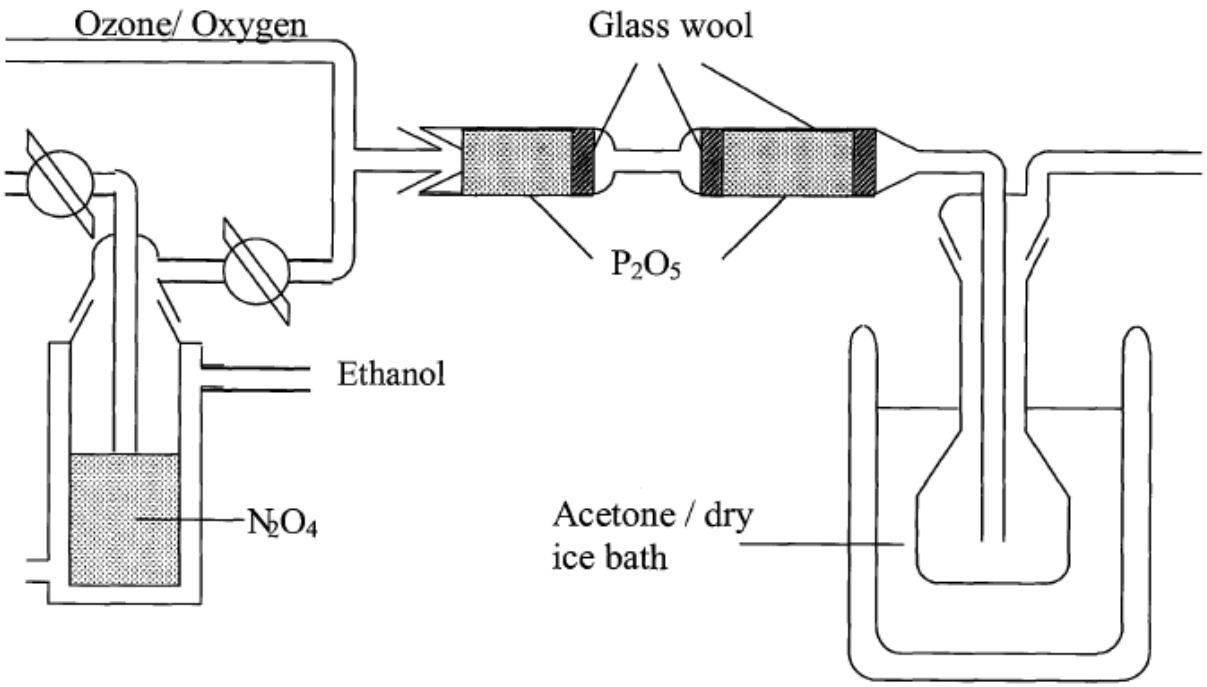
Appendix A: Experimental Section (Supporting Data)

A.1 N_2O_5 Preparation

Apparatus for the preparation of N_2O_5 on laboratory scale has been set up and commissioned. The method involves gas phase oxidation of N_2O_4 by ozone as described in the literature [91,92]. A schematic of the apparatus is shown below, where N_2O_4, in a stream of oxygen, is mixed with a stream of ozone (*ca.* 10% w/w) in oxygen and the product, N_2O_5, is trapped out as a solid in a chilled receptacle (the P_2O_5 desiccant tubes are optional, and for larger scale synthesis are not found to be necessary). Also, trapping efficiency may be improved by adding extra traps.

The N_2O_5 so prepared is stored in weighed tubes or flasks at -60°C before use. Amounts of N_2O_5 in excess of 100 g/day may be prepared using this apparatus.

Schematic of N_2O_5 Apparatus:



A.2 Gas Chromatographic Method for Estimation of Nitrotoluenes

Mononitrotoluenes (MNTs)

The following method was devised for the analysis of mononitration products of toluene:-

Sample Preparation

Approximately 100 mg sample was weighed accurately into a 100 cm^3 conical flask. A solution of triacetin (TA) in dichloromethane was made and 5.0 cm^3 added to the conical flask as an internal standard. The flask was made up to 50 cm^3 with dichloromethane.

The following standards were used (supplier: Aldrich Chem. Co., purity 99.5%):
2-nitrotoluene
3-nitrotoluene
4-nitrotoluene
toluene

Standard Preparation

Approximately 500 mg 2-nitrotoluene and 4-nitrotoluene were weighed accurately (to 2 d.p.) and transferred to a 100 cm^3 volumetric flask. Approximately 30 mg 3-nitrotoluene was weighed (to 3 d.p.) and added to the flask. Due to rapid evaporation, 15 mg of toluene could only be weighed to 1 d.p. and even this could not be considered exact, the toluene was also added to the flask and the flask made up to the mark with dichloromethane.

By means of pipettes, 1.0 cm^3, 5.0 cm^3, 10.0 cm^3 and 20.0 cm^3 of standard solution were transferred to four 50 cm^3 volumetric flasks. Also using a pipette, 5.0 cm^3 internal standard solution was added to the flasks, the flasks were made up to the mark with dichloromethane.

The sample solutions were analyzed by gas chromatography using the following conditions:

GC system – HP6890 series

Oven:
Temp 110ºC
Initial time 5.50 min.
Rate 1 120ºC/min.
Final temp 150ºC
Final time 2.0 min.

Injector:
Splitless
Temp 220ºC
Press. 12.0 psig
Purge flow 25.0 cm^3/min.

FID detector:
Temp. 220ºC
H_2 30.0 cm³/min.
Air 350 cm³/min.

Mode col + mkup = const
Combined flow = 30 cm³/min.

Signal range = 1
Attn. = 3
Column ZB1 30 m x 0.53 mm x 1.5 µm (S/N 047155) capillary column; dimethylpolysiloxane liquid phase (100%)
Injection volume 1 µl
Carrier gas helium

Quantitations were calculated on the basis of relative peak areas against the internal standard (TA) by the algorithms incorporated in the software package. All nitro-toluene isomer peaks were completely resolved (see specimen trace in Section A.3).

The results are quoted to first decimal place accuracy, normalized so that the sum of the three isomer percentages is 100%.

An investigation of the robustness of the analysis method for the first stage nitration products has revealed that a minor re-calibration of the *para*-nitrotoluene (*p*-NT) content is necessary (resulting from the use of an impure standard material in earlier work). This re-calibration means that the values for *m*-NT content reported in Section 4.1.2 were lower than the actual values by around 0.1% (i.e. a reported value of 1.3% would actually be 1.4%). All values reported after Section 4.1.3, Table 3, were obtained using re-calibrated analyses so that the error has been eliminated (those tables affected by the mis-calibration show a footnote to that effect).

Di- and Trinitrotoluenes (DNTs and TNT)

Sample Preparation

Approximately 2-4 mg sample was weighed accurately into a 25 cm³ volumetric flask. A solution of triacetin in dichloromethane was made and 5.0 cm³ added to the flask as an internal standard. The flask was made up to the mark with dichloromethane.

The following standards were used:

2-nitrotoluene
3-nitrotoluene
4-nitrotoluene
Toluene
2,3-dinitrotoluene
2,4-dinitrotoluene

2,6-dinitrotoluene
Trinitrotoluene

Standard Preparation

All the standards apart from toluene were weighed (to 3 d.p.) and added to a 100 cm^3 volumetric flask. Due to rapid evaporation, the toluene could only be weighed to 1 d.p. and even this was could not be considered exact, the toluene was also added to the flask and the flask made up to the mark with dichloromethane.

By means of pipettes, 1.0 cm^3, 5.0 cm^3 and 10.0 cm^3 of standard solution were transferred to three 50 cm^3 volumetric flasks. Also using a pipette, 5.0 cm^3 internal standard solution was added to the flasks, the flasks were made up to the mark with dichloromethane.

Analysis

The sample solutions were analyzed by gas chromatography using the following conditions:

GC system – HP6890 series

Oven:
Temp 110ºC
Initial time 5.50 min.
Rate 1 5ºC/min.
Final temp 180ºC
Final time 1.0 min.

Injector:
Splitless
Temp. 220ºC
Press. 12.0 psig
Purge flow 25.0 cm^3/min.

FID detector:
Temp. 220ºC
H_2 30.0 cm^3/min.
Air 350 cm^3/min.

Mode col + mkup = const
Combined flow = 30cm^3/min

Signal range = 1
Attn = 3
Column ZB1 30 m x 0.53 mm x 1.5 µm (S/N 047155)
Injection volume 1 µl

Quantitations were calculated on the basis of relative peak areas against the internal standard (triacetin) by the algorithms incorporated in the software package. All nitrotoluene isomer peaks were completely resolved.

Authentic samples of unsymmetrical trinitrotoluene isomers

Authentic samples of unsymmetrical trinitrotoluene isomers were synthesized as follows:

2,3,4- and 2,4,5-TNT: by nitration of 2,3- and 2,5-DNTs respectively as described by Dennis *et al*. [93];

2,3,6-TNT was made from a mixture of 2-methyl-3,4-dinitro- and 2-methyl-3,6-dinitroanilines (prepared according to [93]) which was treated with Caro's acid followed by nitric acid according to the method of Brady [94] to give the trinitro compound.

A.3 "Synthesis" and Dewar Runs

See body text, Section 4.1.2 for discussion of results.

Materials

Dichloromethane: Aldrich Chemical Co. 99+% distilled under nitrogen atmosphere over calcium hydride;
Toluene: Aldrich chemical Co. 99% used as supplied;
Dinitrogen Pentoxide: produced in-house;
Sodium hydrogen carbonate: Merck-VWR reagent grade;
Water: distilled in-house.

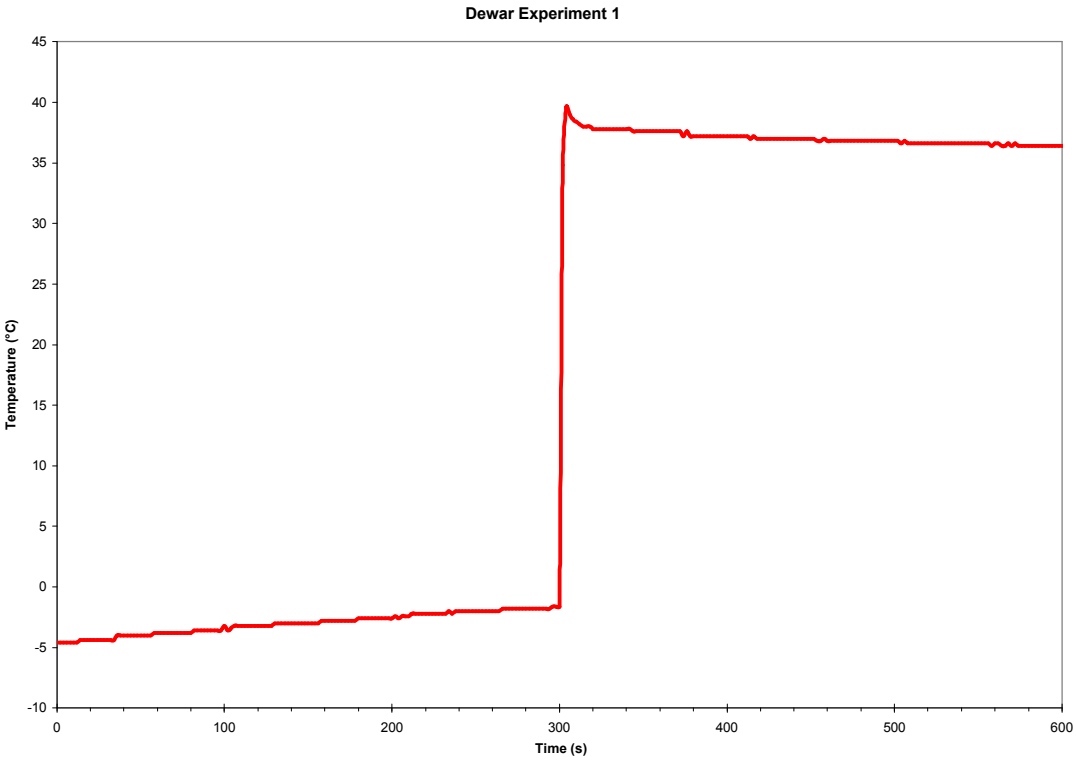
Dewar Experiments

Experimental

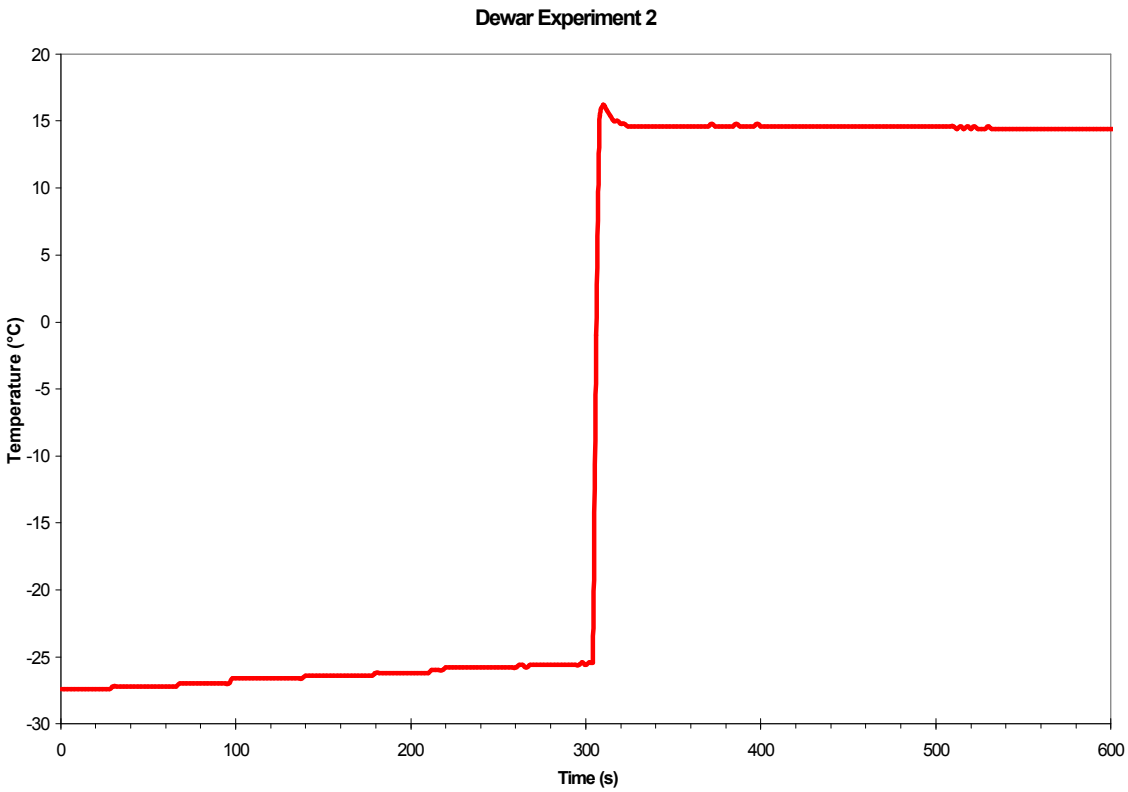
Solutions were prepared such that an equal mass of each would give a 1:1 molar ratio of reactants. Dinitrogen pentoxide was dissolved in dichloromethane which had been cooled to <0°C and the solution stored at <-10°C. Toluene was dissolved in dichloromethane and stored at <-10°C. The toluene solution was added to a Dewar flask fitted with a temperature probe connected to a data logger. Once the temperature had settled the N_2O_5 solution was added rapidly and the temperature rise recorded.

Results

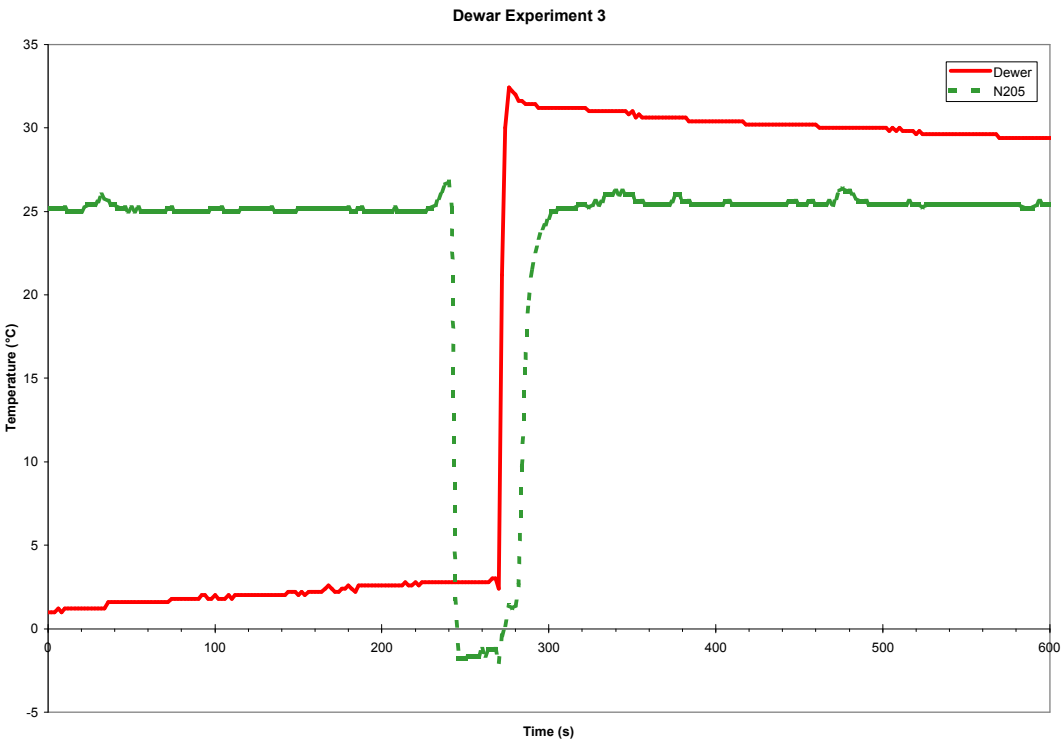
35 ml 10% w/w N_2O_5 solution.
35 ml 8.6% w/w toluene solution.
Reaction temperature reached boiling point of DCM.

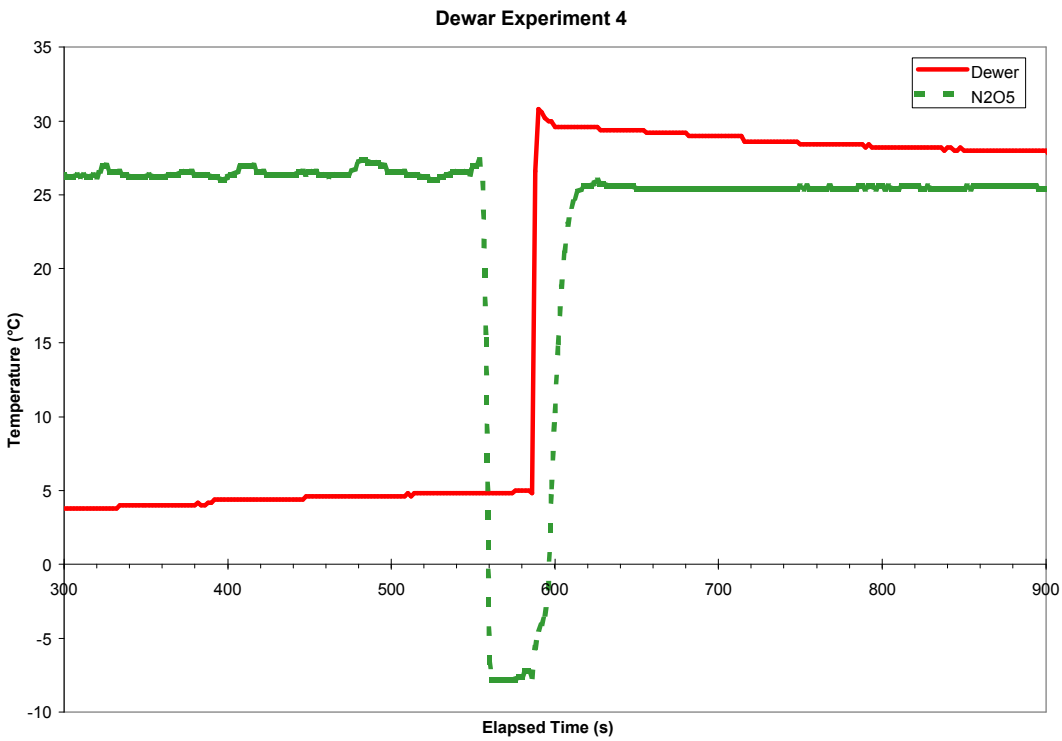


80 ml 5.3% w/w N_2O_5 solution.
80 ml 4.5% w/w toluene solution.



50 ml 5.0% w/w N_2O_5 solution.
50 ml 4.3% w/w toluene solution.
Temperature of N_2O_5 solution measured before & during addition.





Batch Experiments.

Experimental

Solutions were prepared such that an equal mass of each would give the desired molar ratio of reactants. Dinitrogen pentoxide was dissolved in dichloromethane which had been cooled to <0°C and the solution was stored at <-10°C. Toluene was dissolved in dichloromethane and stored at <-10°C. The toluene solution was placed into a jacketed reaction vessel fitted with a thermometer and under flowing nitrogen, and cooled to the desired temperature. The N_2O_5 solution was transferred to a jacketed vessel maintained at 0°C. The N_2O_5 solution was transferred to the reaction vessel by pressure padding with nitrogen at suitable rate to maintain the reaction temperature. After complete addition the reaction was stirred for a further 10 min., except for the reactions where the addition took <20 min. which were stirred for a further 4 min. Saturated aqueous $NaHCO_3$ (50 ml) was added and the reaction mixture poured into flask containing saturated $NaHCO_3$ (100 ml) and stirred for 30 min. The phases were separated and the DCM layer was washed with saturated $NaHCO_3$ (5 x 100 ml) followed by distilled water (2 x 100 ml), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The ratio of nitrotoluene isomers was measured by gas chromatography.

Results

The results from these runs are shown in Table 1 (Section 4.1.2).

Short Reaction Period Batch Experiments.

Reactions were conducted using the same method as for the Dewar experiments. The N_2O_5 solution was added over 15 s. and the reaction quenched with saturated sodium hydrogen carbonate solution (75 ml) after a further 45 s. and stirred for 4 min. The organic phase was washed with sodium hydrogen carbonate solution (5 x 75 ml) followed by distilled water (2 x 75 ml), dried over magnesium sulfate and the solvent removed under reduced pressure. The ratio of nitrotoluene isomers was determined by gas chromatography.

Results

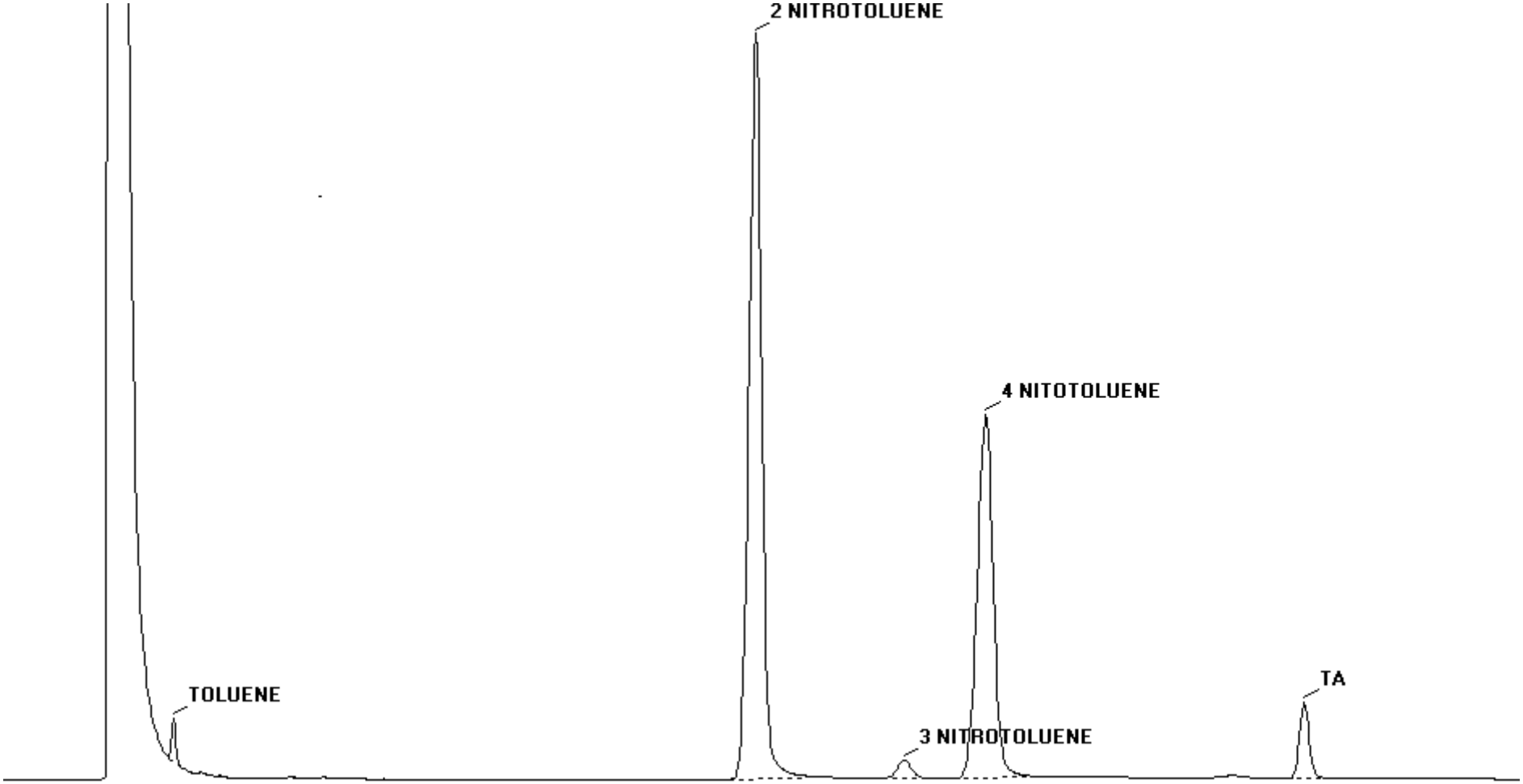
Toluene Concentration % w/w	N_2O_5 Concentration % w/w	N_2O_5:Toluene Ratio	Start Temperature °C	Addition time s	Ortho %	Meta* %	Para %
4.3	5.0	1:1	-60	15	55.7	1.4	42.9
4.3	5.0	1:1	-60	15	55.5	1.5	43.0
2.1	2.5	1:1	-60	5*	58.0	1.2	40.8
2.1	2.5	1:1	-70	15	58.2	1.2	40.6

* See note on robustness of GC analyses, Appendix A, Section A.2
**Reaction quenched after 10 s

2. GC Specimen Chromatogram

SAMPLE: RE/TNTRW/B10

GC CHROMATOGRAM



A.4 Flow Nitrator Operation

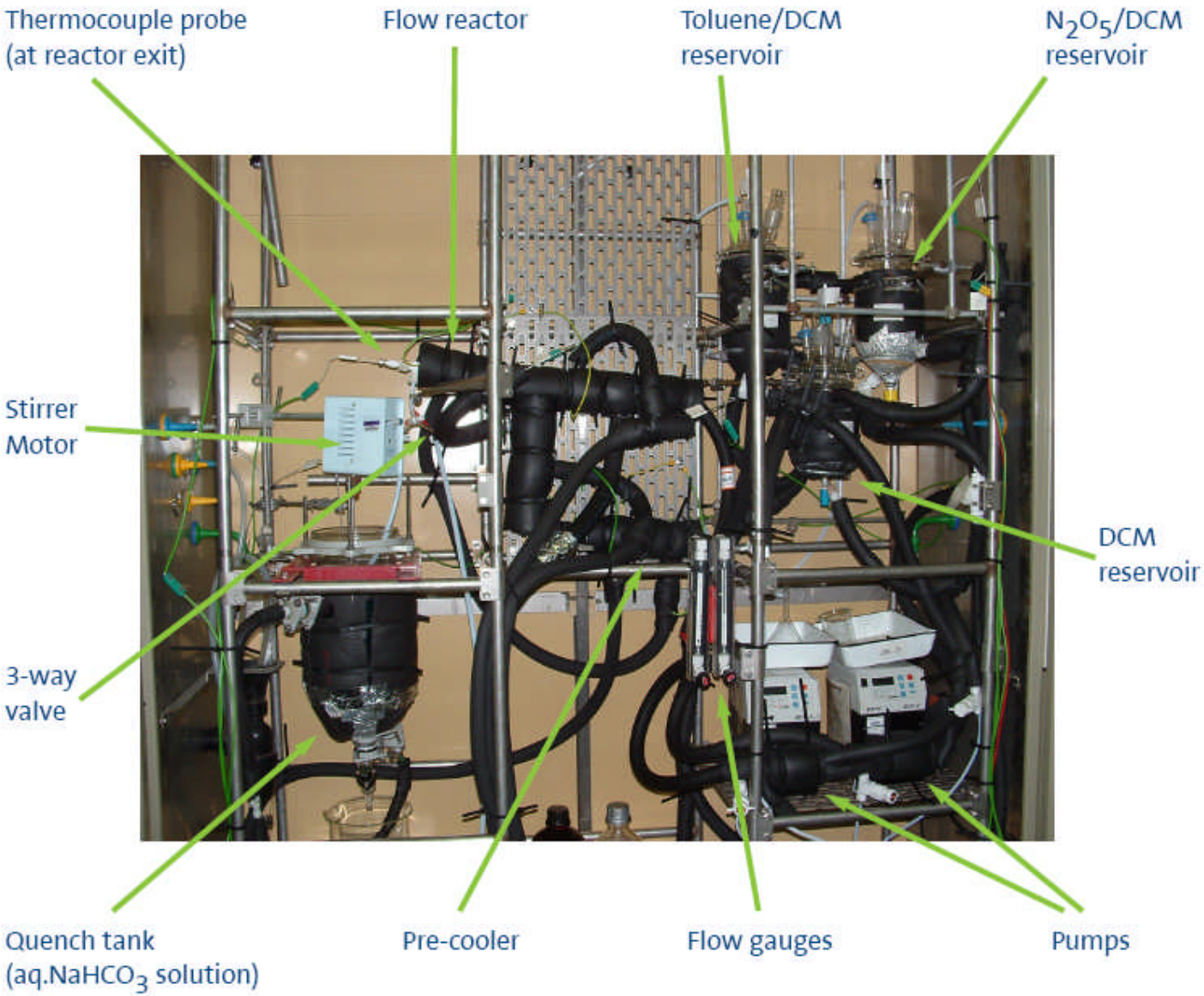
Process description

The Process Flow Diagram (PFD) is detailed in Fig. 6. A photograph of the experimental set-up is shown below.

Three glass jacketed vessels of 1 liter capacity act as feed reservoirs, these are cooled by a circulator feeding each reservoir in series; V1, V2 and V3. V1 contains the nitrating agent N_2O_5 in solvent (dichloromethane, DCM), V2 contains the substrate in solvent (DCM) and V3 contains DCM solvent only. The reservoirs feed two gear pumps that have rotor speed control to enable the flow rate to be varied followed by rotameters to monitor the flow. Both feeds streams are cooled further by passing through heat exchangers fed by a second circulator. The two fluids then mix and pass through the center of a jacketed reactor, the reactor is a static mixer tube imparting high intensity mixing and good heat transfer, cooling is provided by a third independent circulator. After passing through the reactor, the mixture may either be dumped or transferred to a neutralizing vessel, V4, a 5 liter glass jacketed stirred vessel cooled by a fourth circulator. Thermocouples monitor the temperature of the fluids at various points through the process. Materials of construction for parts in contact with reacting chemicals are glass, PTFE and stainless steel. In order to reduce heat gain from the atmosphere and the surrounding structures, all vessels and pipe work are insulated.

Mode of operation

The three reservoirs are filled manually and cooled, then after cooling, the pumps and liquid lines are primed respectively with solvent and substrate solution. V4 is filled with an alkaline solution to neutralize the reactant and the stirrer operated. Both pumps are started and rotor speed is set to give the required flow rate as indicated by the rotameters FI 1 and FI 2. The fluid is further cooled by the heat exchangers and then passed through the reactor. At this point no reaction is taking place so the liquid exiting the reactor is passed to drain where it is collected for recycling of the substrate. Once the system has stabilized in temperature and flow rate, solvent feed from V3 is switched to nitrating solution from V1 and the reacted mixture is fed to the neutralizing vessel V4. Temperatures and flow rates are monitored throughout the run. Before the substrate solution has been completely used, the feed from V1 is switched back to V3 to clear the lines of nitrating agent. After completion the pumps are stopped, the contents of V4 are drained and taken away for workup and the rig is drained of remaining fluid and then rinsed through with clean solvent.


Thermocouple probe
(at reactor exit)
Flow reactor
Toluene/DCM
reservoir
N_2O_5/DCM
reservoir
Stirrer
Motor
DCM
reservoir
3-way
valve
Quench tank
(aq.$NaHCO_3$ solution)
Pre-cooler
Flow gauges
Pumps

A.5 Syntheses of Dinitrotoluenes and TNT

Materials

Dichloromethane: Aldrich Chemical Co. 99+% distilled under nitrogen atmosphere over calcium hydride;
Toluene: Aldrich Chemical Co. 99% used as supplied;
Dinitrogen pentoxide: produced in-house (see Section A.1);
Sodium hydrogen carbonate: Merck-VWR reagent grade;
Water: distilled in-house.

Analyses

GC analyses were carried out as described above (Section A.2). NMR spectra were recorded on a Bruker Avance 400 spectrometer, generally using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. DSC traces were measured on a Mettler Toledo DSC/30 differential scanning calorimeter.

Methods

Synthesis of TNT from a pure 2,4- and 2,6-dinitrotoluene (DNT) mixture (70:30) using N_2O_5/H_2SO_4

Sulfuric acid (18 ml, 98%) was added to a test tube containing solid N_2O_5 (6.2 g, 57.4 mmol) at -45°C. No exotherm was observed during the addition. Dissolution of the N_2O_5 was achieved by gentle agitation of the mixture as it was warmed to 0°C. The solution was transferred to a two neck round bottom flask (50 ml) fitted with a magnetic stirrer and thermometer.

A mixture of 2,4- and 2,6-DNT (3 g, 70:30, 16.5 mmol) was added portionwise with stirring at 0-5°C over 10 min. (no observable exotherm during addition). The flask was then warmed to 50-55°C by which time all suspended solid had dissolved to give a light yellow solution. The solution was left to stir for 24 hr. and then allowed to cool to room temperature during which time a white solid had crystallized out. The mixture at this stage became too viscous to pour and was warmed to 40°C until all material had dissolved. The solution was then added dropwise to a conical flask (500 ml) containing ice (250 g) with stirring. The precipitated off-white solid was filtered through a Buchner funnel and washed with water (2 x 100 ml) and allowed to dry under suction for 2 hr. The solid was then transferred to a vacuum oven and dried overnight at 25°C under vacuum to give 3.52 g of TNT (94%). The sample had a slight acidic odor and was redissolved in chloroform* (100 ml) and washed with 10% wt./vol. $NaHCO_3$ solution (2 x 50 ml) followed by water (1 x 50 ml). The organic layer was separated, dried with $MgSO_4$, filtered and solvent removed under vacuum to give TNT (3.5 g).

Both materials were found to be >99% pure by GC and NMR analysis. The DSC traces for both gave similar melting peaks around 80°C.

*Ethyl acetate may be used with equal efficacy.

Nitration of Mononitrotoluenes (MNTs) Using Mixed Acid

A sample of the MNTs [10 g, 72.9 mmol (from the 1st stage flow nitration, containing toluene 0.4%, 2-NT 55.8%, 3-NT 1.4% and 4-NT 42.4%)] was added dropwise to a nitrating mixture consisting of nitric acid (6 g, 100%, 95.2 mmol) and sulfuric acid (40 g, 98%, 0.41 mol) at 45-50°C with cooling over 20 min. The temperature was then raised to 70°C (oil bath) and the solution left to stir for a further 45 min.

The solution was then cooled to room temperature and added to ice/water (300 g) with stirring. The solid was filtered on a Buchner funnel and washed with water (2 x 100 ml) and allowed to dry under suction for 2 hr. before being transferred to a vacuum oven for further drying overnight at 25°C to give 12.22 g of an off-white solid (92%) containing 2,4-DNT 76%, 2,4-DNT 12%, 2,3-DNT 0.4%, TNT 9.1% and 2.5% of unidentified isomers The relative amounts were also confirmed by ^{1}H NMR which also identified 0.8% of a possible 3,4 isomer.

Preparation of TNT from DNTs Prepared by Mixed acid Nitration of MNTs (shown above)

The above mixture of DNTs (3 g, 16.47 mmol) was added to a mixture of sulfuric acid (18 ml, 98%), containing N_2O_5 (6.22 g, 57.8 mmol) in a round bottom flask fitted with thermometer and magnetic stirrer at 10-15°C over 2 min. The suspension was then heated to 50-55°C for 24 hr. before cooling to 40°C and then added dropwise to ice/water (300 g) with stirring. The solid was filtered and washed with water (2 x 100 ml) and dried under suction for 2 hr. and then transferred to a vacuum oven for further drying overnight at room temperature to give 3.32 g of an off-white solid (89%) which was identified as TNT. GC analysis indicated a purity of 98%.

Preparation of DNTs from nitration of MNTs using N_2O_5/Nitric acid

A sample (3 g, 21.9 mmol) of MNTs was added to a solution of N_2O_5 (3.5 g, 32.4 mmol) in nitric acid (27 g, 100%) at -2 to 2°C over 15 min. and then left to stir for a further 5 min. at 5 to 10°C. the solution was then added dropwise to ice/water (300 g) with stirring. The precipitated white solid was filtered under suction, washed with water (2 x 100 ml) before being allowed to dry overnight at room temperature in a vacuum oven to give 1.65 g (41%) of a mixture of DNTs.

Preparation of DNTs from nitration of MNTs using N_2O_5/Nitric acid Revised Method

A sample (3 g, 21.9 mmol) of MNTs was added to a solution of N_2O_5 (6.59 g, 32.4 mmol) in nitric acid (15 ml, 100%) at 0°C. The temperature was allowed to rise during the addition (3-5 min.) to 25°C and then the solution allowed to stir for a further 5 min. at this temperature before adding the mixture slowly to ice/water (300 g) with stirring. The precipitated solid

was filtered under suction and washed with water (2 x 100 ml) before being allowed to dry overnight at room temperature in a vacuum oven to give 3.52 g (88%) of a mixture of DNTs.

Preparation of DNT from MNT using Nitric acid

100% Nitric acid (10 ml, 15 g, 0.24 mol) was added to a two neck round bottom flask (50 ml) fitted with a magnetic stirrer and thermometer. The solution was cooled to 10°C using an ice bath. A reaction mix of MNTs from the 1st stage nitration (2 g, 14.6 mmol) was added dropwise to the acid with stirring over 3 min. during which time the temperature rose to 25°C. The cooling bath was removed and the reaction was stirred for a further hour at room temperature. A TLC of the reaction mixture (after quenching and extraction into DCM) using 80:20 n-pentane/ethyl acetate indicated no presence of MNTs.

The reaction mixture was worked up by quenching onto ice and filtration of the precipitated solid. Washing and drying in a vacuum oven gave 2.25 g (85%) of a very light yellow solid which was identified primarily as a mixture of 2,4- and 2,6-DNTs (Run 3-1).

A second reaction carried out under similar conditions (Run 3-2) but only left for 10 min. gave an 81% yield of DNTs.

Preparation of DNTs using 10% wt./wt. MNT and DCM

The method used was as above with the exception that the addition time was decreased to 1.5 min. The temperature in this instance was only found to rise from 8-20°C and the isolated yield of product after 2 hr. was found to be 73% (Run 3-3).

Preparation of DNTs using 50% wt./wt. MNT and DCM

The method used was as above with the exception that the addition time was decreased even further to 30 sec. The temperature in this instance was found to rise from 6-30°C and the isolated yield of product after 40 min. was found to be 74% (Run 3-4).

A second run using almost identical conditions gave a 94% yield of DNTs.

Large Scale Preparation of DNT

A solution of MNTs (300 g, 0.55 mol, 25% wt./wt. in DCM) was added dropwise to a cooled solution of 100% nitric acid (750 ml) at 8°C in a two neck round bottom flask (2 L) fitted with a magnetic stirrer and cooled using a cardice/acetone bath. After the addition (approx. 8 min.) the temperature had risen to 20°C. The solution was stirred for a further 3 min. and then poured with stirring (electric) onto ice/water (2.5 kg).

The mixture was then extracted with DCM (3 x 300 ml) and the organic layer washed with 10% sodium bicarbonate solution (2 x 500 ml) and then water (3 x 500 ml) before separation, drying and removal of solvent to give a light yellow solid. Drying at 50°C *in vacuo* gave 97.5 g of DNT (96% yield).

Large scale Preparation of TNT Using N_2O_5/Sulfuric Acid

DNT (22.4 g, 0.12 mol) was added to a solution of N_2O_5/H_2SO_4 (135 ml, 10% wt./wt.) in a 250 ml jacketed vessel at 30°C with stirring (air driven) over 7 min. No exotherm was noted throughout the addition.

The mixture was then gradually heated to 40°C (5 min.) to dissolve the DNT. The temperature was then raised further to 75°C (10 min.) and left for 6.5 hr. After 4 hr. a TLC of the reaction mixture (after workup with water) still showed small amounts of DNT.

The mixture was then cooled to 45°C and poured into ice/water (3 L) with stirring and the mixture extracted with ethyl acetate (3 x 200 ml) before washing with 10% sodium bicarbonate (3 x 100 ml) before drying the organic layer and removing solvent. Drying in a vacuum oven at 50°C overnight afforded 24.5 g TNT as a yellow/white solid (88%). GC analysis confirmed a purity of 99%.

Synthesis of dinitrotoluenes (DNT) from mononitrotoluenes (MNT)

A dropping funnel was charged with a mixture of MNT (150 g, 1.1 mol, 57.5% *o*-, 1.4% *m*- and 41.1% *p*-) in dichloromethane (150g). Fuming nitric acid (750 ml, 17.9 mol) was added to a conical flask (2 L) fitted with magnetic stirrer and thermometer. The flask was cooled using a cardice/acetone bath to 8°C and the addition of the MNT solution started over a period of 8 min. during which time the temperature of the reaction mixture was not allowed to rise above 20°C.

After the addition, the reaction solution was stirred for a further 3 min. before being worked up by pouring onto ice (2.5 kg). The precipitated DNT (isomer mixture) was taken up into dichloromethane (DCM) (300 ml) and the aqueous solution extracted further with DCM (2 x 300 ml). The combined extracts were washed with a solution of 10% sodium hydrogen carbonate (2 x 300 ml) and water (2 x 300 ml) before drying over magnesium sulfate.

Filtration and removal of the solvent under vacuum gave an off-white solid which was dried overnight at 50°C under vacuum to give 187 g (94%) of product.

GC - 16.8% of 2,6-DNT and 82.2% of 2,4-DNT.

NMR ($CDCl_3$) - 16.9% of 2,6-DNT, 81.5% of 2,4-DNT, 0.6% 2,3-DNT, 0.9% 3,4-DNT.

Synthesis of 2,4,6-TNT from DNT

A cooled solution (5-10°C) of 98% sulfuric acid (477 g, 4.87 mol) was added quickly with stirring to a flask containing solid N_2O_5 (63 g, 0.58 mol) at -60°C. Since the reaction was exothermic the flask had to be swirled vigorously to dissipate the heat during the addition. Once all the N_2O_5 had dissolved the mixture was transferred to a closed top jacketed vessel (1 L) fitted with an air driven stirrer and thermocouple. A mixture of DNT (46 g, 0.25 mol) prepared from the above reaction was added over 10-15 min. using a glass funnel with stirring at room temperature. The circulator temperature was then increased to 70°C and after

10 min. the internal reactor temperature had reached 55°C (all DNT had dissolved at this stage). The temperature was increased further to 78°C and the reaction mixture left to stir for 4.5 hr (internal reactor temperature 77°C).

After approximately 4.5 hr the reaction was found to be complete as indicated by TLC (80/20 n-pentane:ethyl acetate) at which point the reactor temperature was reduced to 45-50°C and the warm yellow solution slowly run into ice (2.5 L) with stirring. The precipitated TNT was filtered and washed with water (3 x 150 ml) before dissolution into DCM (250 ml). The organic layer was washed with 10% sodium hydrogen carbonate (3 x 150 ml) and water (3 x 150 ml) before drying over magnesium sulfate and removal of solvent under vacuum to give 49.35 g (86%) of TNT as a white crystalline powder.

GC - 98.87% of 2,4,6-TNT, 0.77% of 2,4,5-TNT and 0.36% of 2,3,4-TNT.

NMR ($CDCl_3$) – 99.07% of 2,4,6-TNT, 0.56% of 2,4,5-TNT and 0.27% of 2,3,4-TNT.

Recrystallization of TNT

100 g of TNT (made from a MNT mixture comprising approx. 1.4% *m*-NT, 57.5% *o*-NT & 41.1% *p*-NT) was dissolved in boiling ethanol - ethyl acetate mixture (5:1 vol./vol., *ca*. 300 ml) and the mixture was allowed to cool. The precipitated TNT was filtered off and washed with cold ethanol (*ca*. 80 ml) then dried under vacuum at 50°C overnight, giving approx. 80 g of purified TNT (with solidification point as indicated in Section A.6).

A further 8 g of material could be obtained by concentrating the filtrate (approx. ¼ of the solvent removed) and collecting the material as indicated above.

Estimation of TNM and NOx in reactor headspace

A large scale prep of TNT (~52 g) using N_2O_5/H_2SO_4 was undertaken and attempts to quantify the amount of NOx and TNM attempted.

Since NOx is highly visible as a brown vapor above the reaction mixture from previous runs quantitation involved introduction of a gentle stream of argon or nitrogen through the reaction vessel followed by a cardice/acetone cold trap to condense the NOx.

After several hours of purging the reaction vessel, approximately 6 g of an acidic light yellow liquid was collected. On warming this liquid to room temperature no brown gaseous vapors were observed (cf. NO_2 bpt. 21°C). The liquid was identified as nitric acid. This could be easily explained by the fact that nitric acid produced during the reaction was actually being carried in the gas stream into the cold trap as the reaction temperature (77-80°C) was close to the boiling point of nitric acid (83°C).

The TNM estimation was carried out on another TNT reaction using the procedure reported by Holahan [88]. This involved sparging the trinitration mixture with nitrogen and passing the gas through an alcoholic solution of potassium hydroxide. The reaction of TNM with potassium hydroxide forms potassium trinitromethide which can be isolated as a yellow precipitate as is a quantitative method for estimation of TNM.

Under the conditions of the reaction even after several hours of sparging no visible precipitate of potassium trinitromethide was isolated.

A.6 TNT Solidification (Set Point) Measurements

Method

Measurements were carried out according to U.K. Ordnance Board Laboratory Method M202/94 [95], which is equivalent to US MIL-DTL-248D.

In brief, the apparatus consists of a 150 x 25 mm test tube located in a 200 x 38 mm boiling tube, both suspended in a glass jar which is screened from direct light. The test tube has an aluminum agitator, and a short-range short stem thermometer, complying with BS 1365, is placed centrally in it.

The apparatus described above is pre-heated to 70-75°C and the TNT sample (80-100 g), melted in a steam kettle, is poured into the test tube to within a few mm of the brim. The sample is agitated until the onset of solidification, at which point the temperature starts to rise; the lowest temperature attained in this step is noted. The sample is then left for a short period while the temperature is observed, and the maximum temperature attained is recorded as the setting point. The necessary corrections* are then made to this value to give the figure tabulated.

*Stem immersion correction, thermometer temperature correction. The ambient temperature should be in the range 20-25°C.

Results

Key to samples:

1) Commercial TNT Ex Bridgwater (1st run ignored due to operator error)
2) In-house TNT – sample from 3-stage nitration of toluene
3) Sample 2, cleaned by sulfiting
4) In-house TNT – sample from MNT mixture containing 1.4% *meta*-NT
5) Sample 4, recrystallized (from ethanol-ethyl acetate)

1) Commercial TNT Ex Bridgwater

Final set point temperature (t0)	81.25
Minimum recorded temperature	80.3
Ambient temp	19.0
Thermometer immersion from stem	76
Thermometer immersion figure (n)	5.25
Stem immersion correction (t)	0.047

Commercial TNT Ex Bridgwater

Final set point temperature (t0)	80.45
Minimum recorded temperature	79.9
Ambient temp	20.0
Thermometer immersion from stem	76
Thermometer immersion figure (n)	4.45
Stem immersion correction (t)	0.038

Thermometer temp correction	0.00
Corrected set point	81.30

Thermometer temp correction	-0.01
Corrected set point	80.48

Commercial TNT Ex Bridgwater

Final set point temperature (t0)	80.36
Minimum recorded temperature	79.6
Ambient temp	20.5
Thermometer immersion from stem	76
Thermometer immersion figure (n)	4.36
Stem immersion correction (t)	0.037
Thermometer temp correction	-0.01
Corrected set point	80.39

2) In-house TNT fresh

Final set point temperature (t0)	79.9
Minimum recorded temperature	78.9
Ambient temp	21.0
Thermometer immersion from stem	75
Thermometer immersion figure (n)	4.9
Stem immersion correction (t)	0.041
Thermometer temp correction	-0.02
Corrected set point	79.92

In-house TNT after 2 hrs

Final set point temperature (t0)	79.9
Minimum recorded temperature	79.2
Ambient temp	21.0
Thermometer immersion from stem	77
Thermometer immersion figure (n)	2.9
Stem immersion correction (t)	0.024
Thermometer temp correction	-0.02
Corrected set point	79.90

In-house TNT after 2 hrs

Final set point temperature (t0)	79.86
Minimum recorded temperature	79.0
Ambient temp	20.0
Thermometer immersion from stem	77
Thermometer immersion figure (n)	2.86
Stem immersion correction (t)	0.024
Thermometer temp correction	-0.02
Corrected set point	79.86

3) In-house TNT (synthesized from Toluene) and cleaned by sulfiting

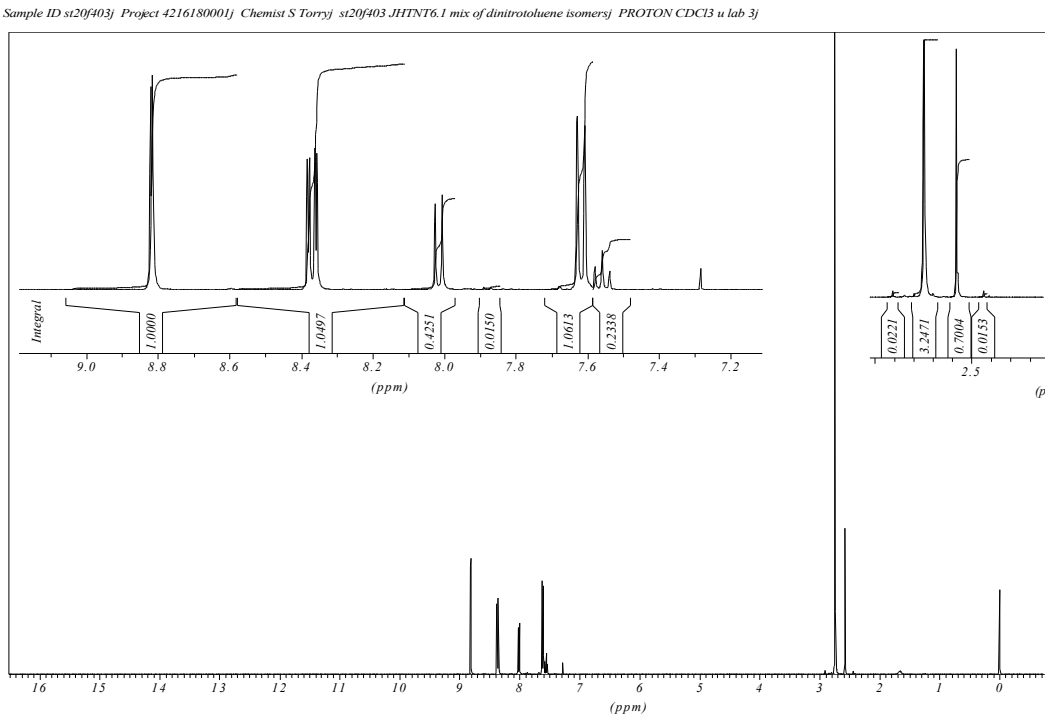
Final set point temperature (t0)	80.2
Minimum recorded temperature	79.6
Ambient temp	21.5
Thermometer immersion from stem	75
Thermometer immersion figure (n)	5.2
Stem immersion correction (t)	0.044
Thermometer temp correction	-0.04
Corrected set point	80.20

A.7 NMR Spectra

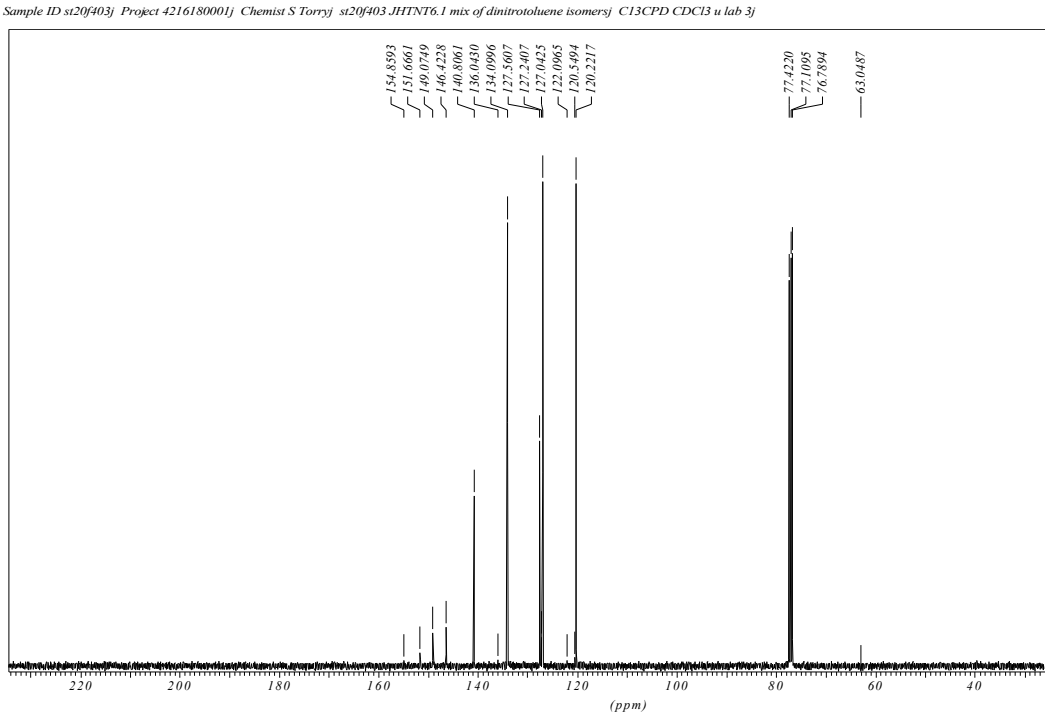
^{1}H & ^{13}CNMR Data – Dinitrotoluenes (from Initial Proof-of-concept Study, Section 4.4)

NMR ($CDCl_3$) Analysis of a sample of dinitrotoluenes (from N_2O_5/H_2SO_4 nitration of 1st stage reaction mixture [comprising 55.8% 2-NT, 1.45% 3-NT and 42.4% 4-NT] to dinitrotoluenes in 89% yield) gave the following results :-

~83% 2,4-DNT and 17% 2,6-DNT, although NMR analysis did show minor amounts of 2,3-DNT but this was not quantified (^{1}H and ^{13}C NMR given below).



^{1}H NMR of Dinitrotoluene Sample

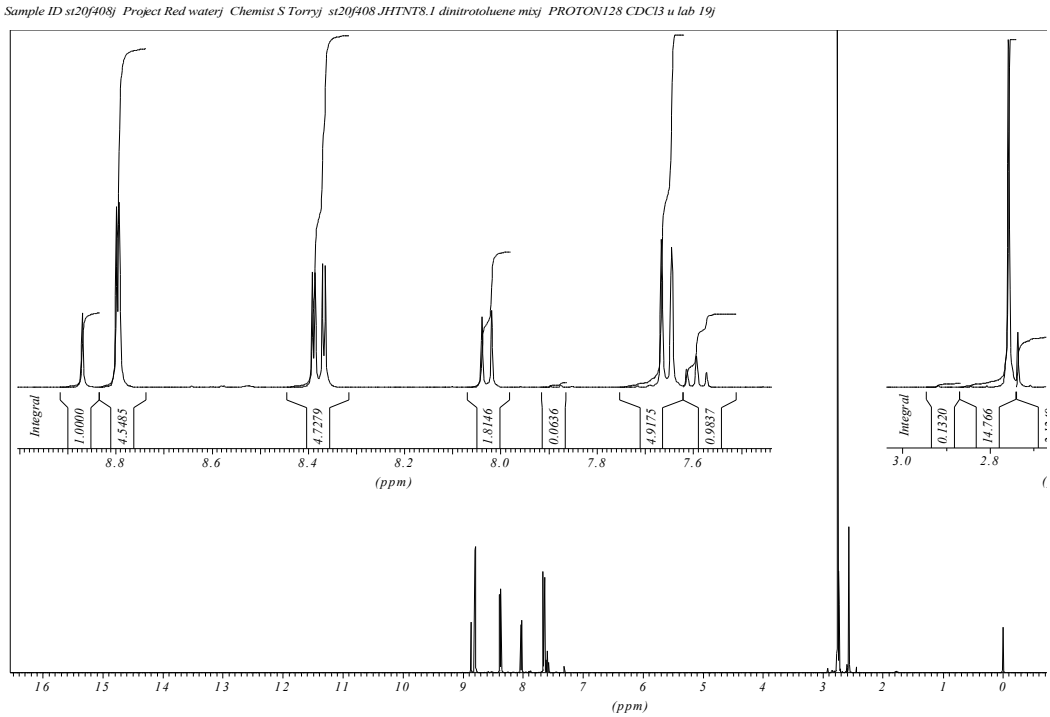


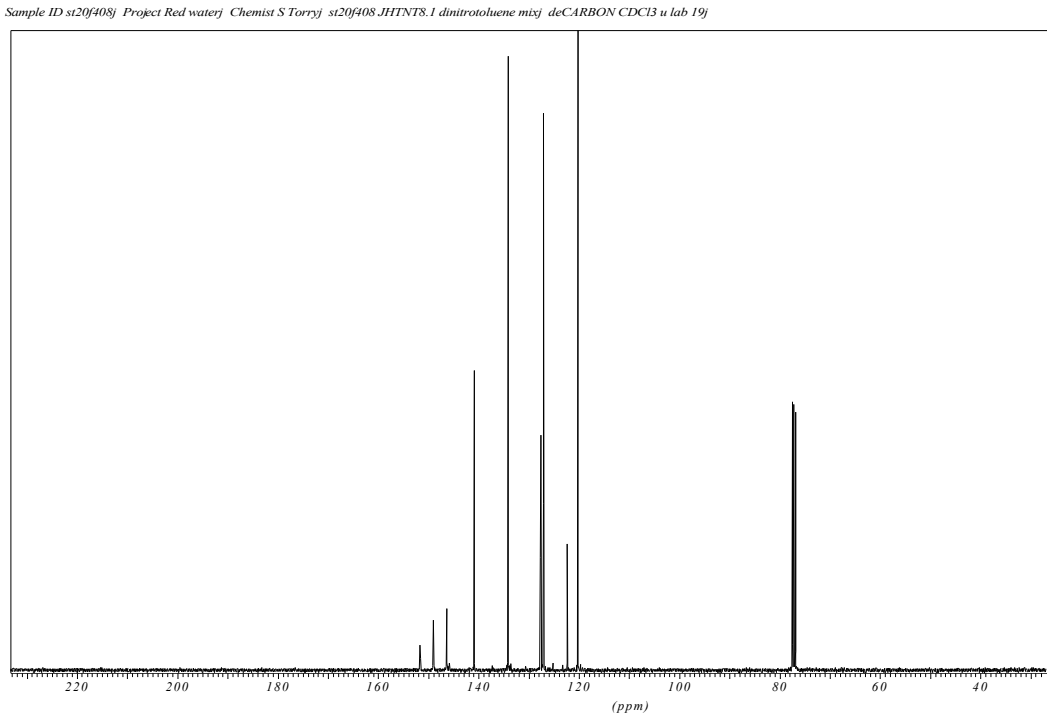
^{13}C NMR of Dinitrotoluene Sample

A sample of DNTs prepared by traditional mixed acid nitration of 1st stage reaction mixture [comprising 52.26% 2-NT, 1.38% 3-NT, and 41.85% 4-NT] to dinitrotoluenes in 92% yield gave the following results from NMR:-

15.3% 2,4-DNT, 75.4% 2,6-DNT, 8% TNT, 1.3% of 2,3- and 3,4-DNTs.

Enlargement of peaks in previous sample:

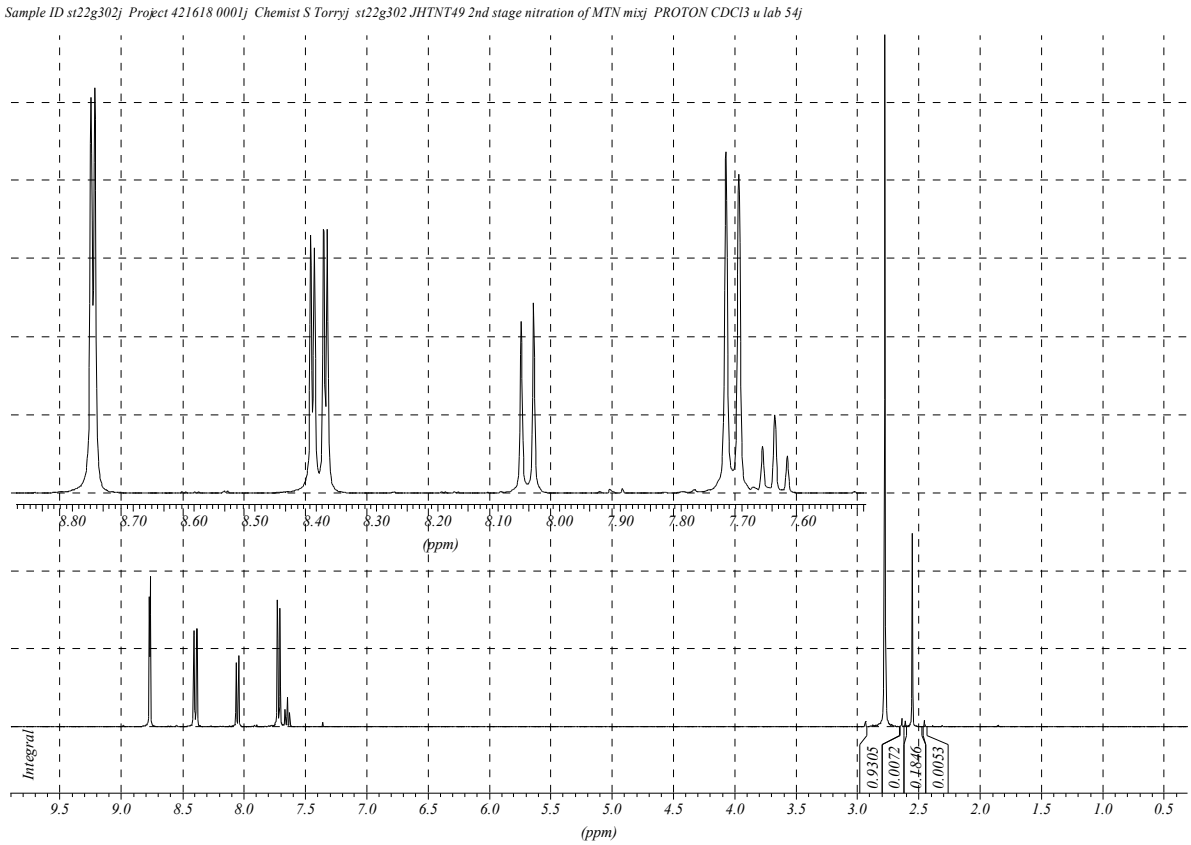




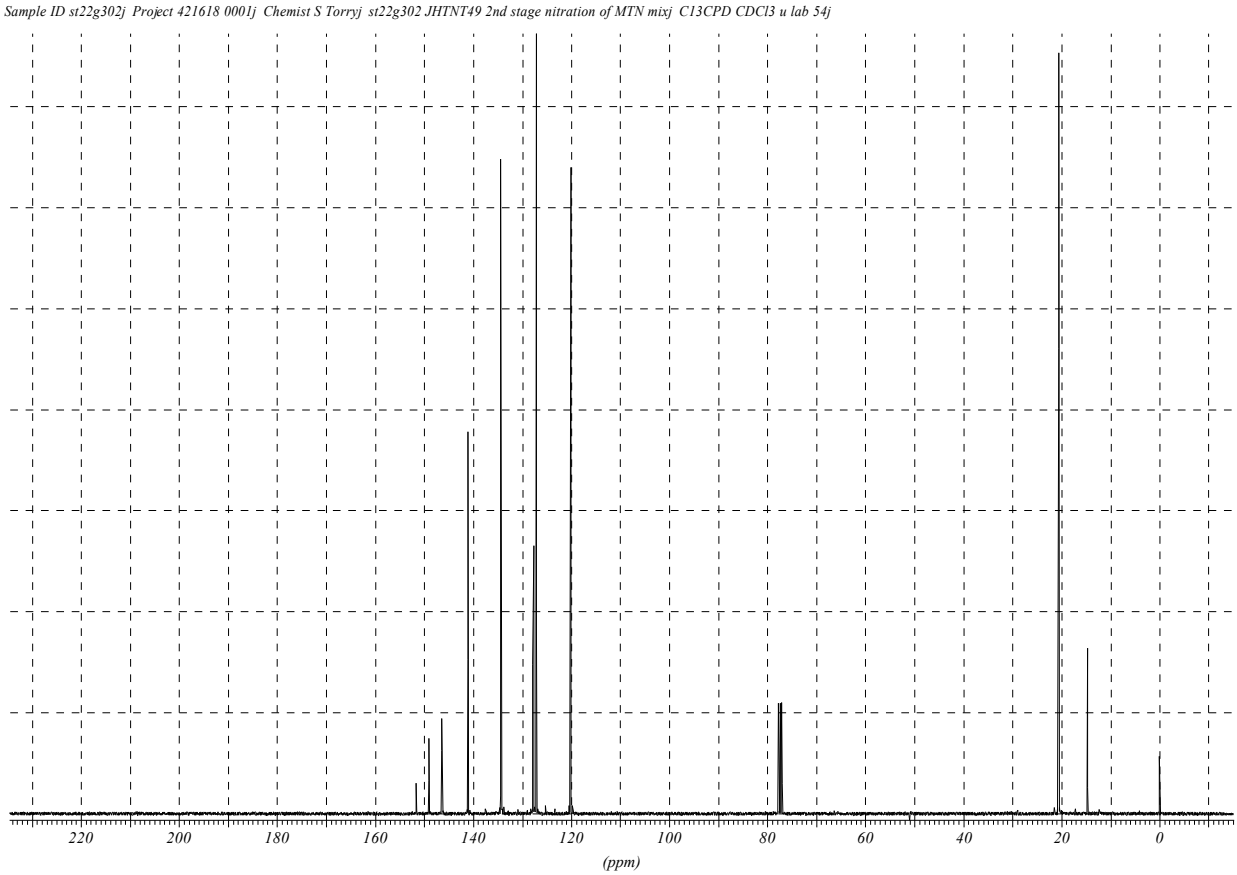
^{1}H & ^{13}CNMR Data – Di- and Trinitrotoluenes (from nitric acid nitration of MNT mixture [Section 4.2] and N_2O_5-sulfuric acid nitration DNTs [Section 4.3])

1) NMR ($CDCl_3$) Analysis of a sample of dinitrotoluenes (from HNO_3 nitration of 1st stage reaction mixture [comprising 57.5% 2-NT, 1.4% 3-NT and 41.1% 4-NT] to dinitrotoluenes in 94% yield) gave the following results :-

81.9% 2,4-DNT, 16.9% 2,6-DNT, 0.6% 2,3-DNT, 0.9% 3,4-DNT (^{1}H and ^{13}C NMR given below)



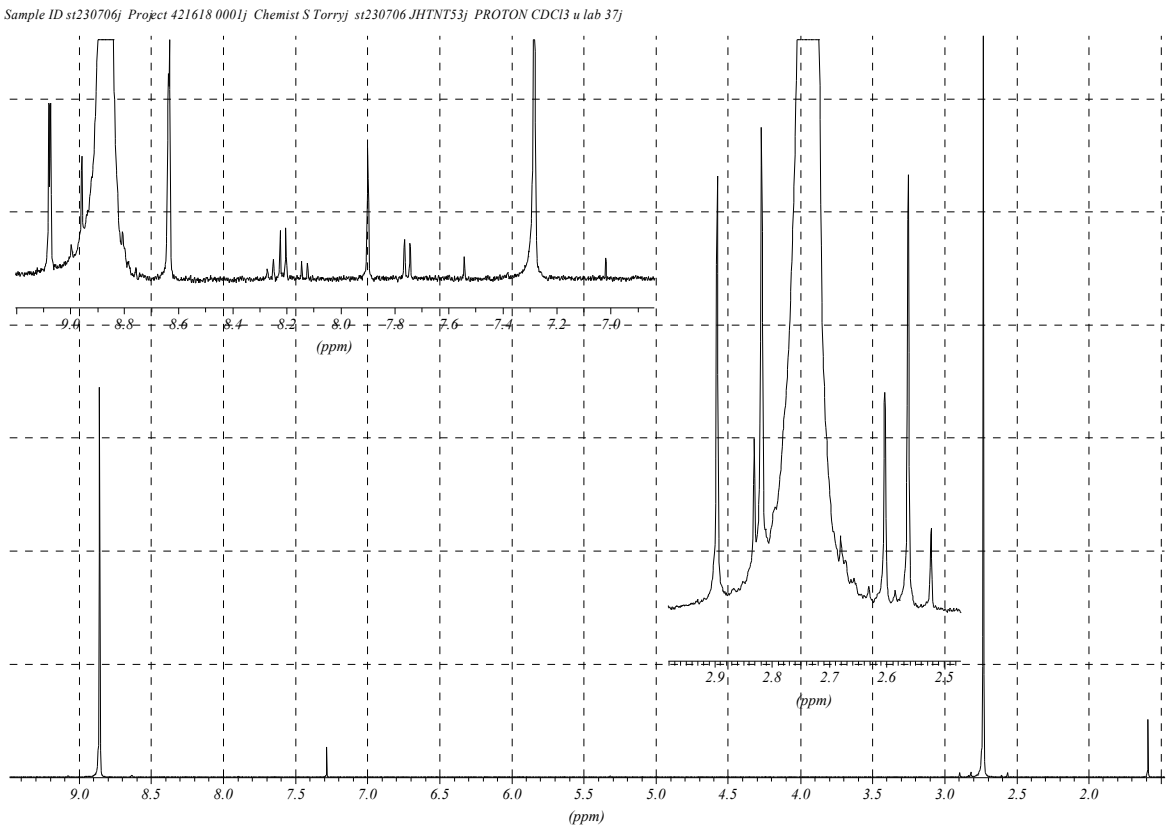
^{1}H NMR of Dinitrotoluene Sample



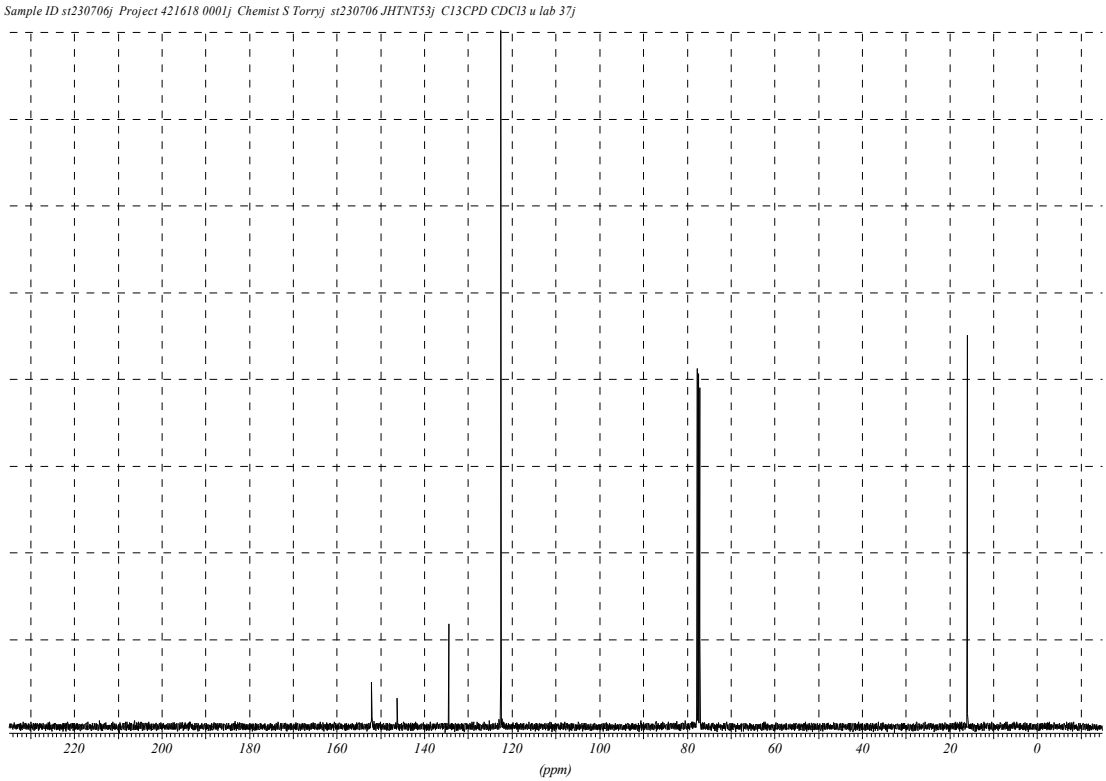
^{13}C NMR of Dinitrotoluene Sample

2) A TNT sample prepared on large scale by N_2O_5-sulfuric acid nitration of the above DNT mixture in 86% yield gave the following results from NMR:-

99.07% 2,4,6-TNT, 0.56% 2,4,5-TNT, 0.27% 2,3,4-TNT, 0.10% 2,3,6-TNT.



^{1}H NMR of Trinitrotoluene Sample



^{13}C NMR of Trinitrotoluene Sample

A.8 DSC Data

Analysis of TNT samples

Conditions were:

Initial temperature	0°C
Final temperature	500°C
Heating rate	10°C/min
Purge gas	Nitrogen

40µl aluminum pan covered with an aluminum lid. In some cases the lid was perforated with a single pinhole and in others the pan was unperforated and sealed with a pressure weld.

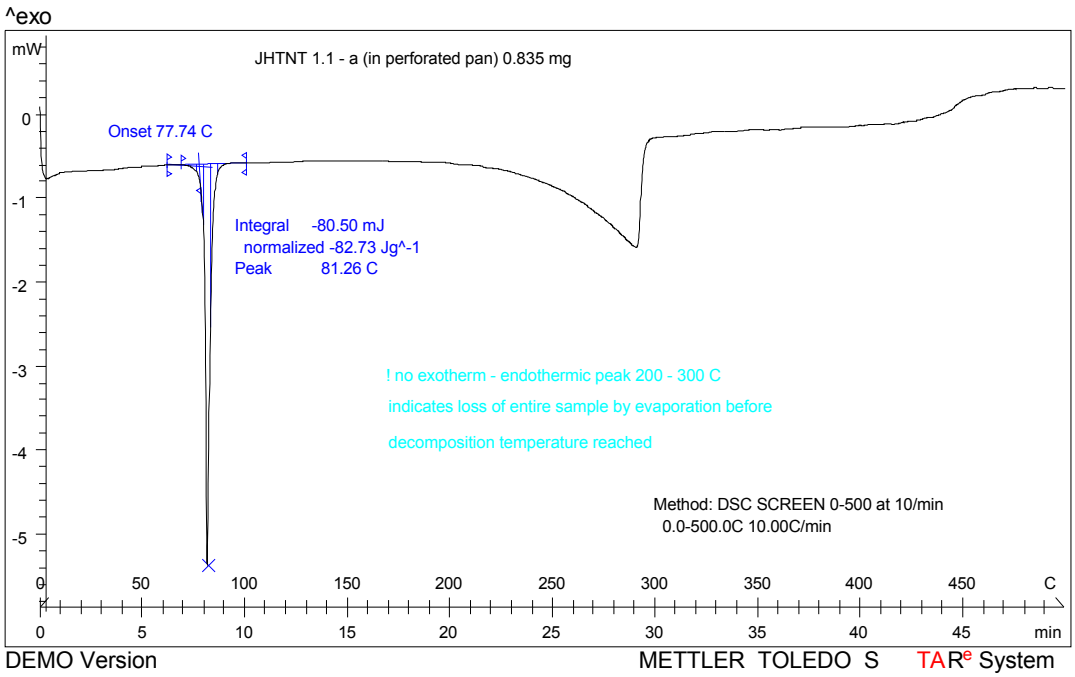


FIG A8.1

Comments: Sample volatilized before any decomposition was seen.

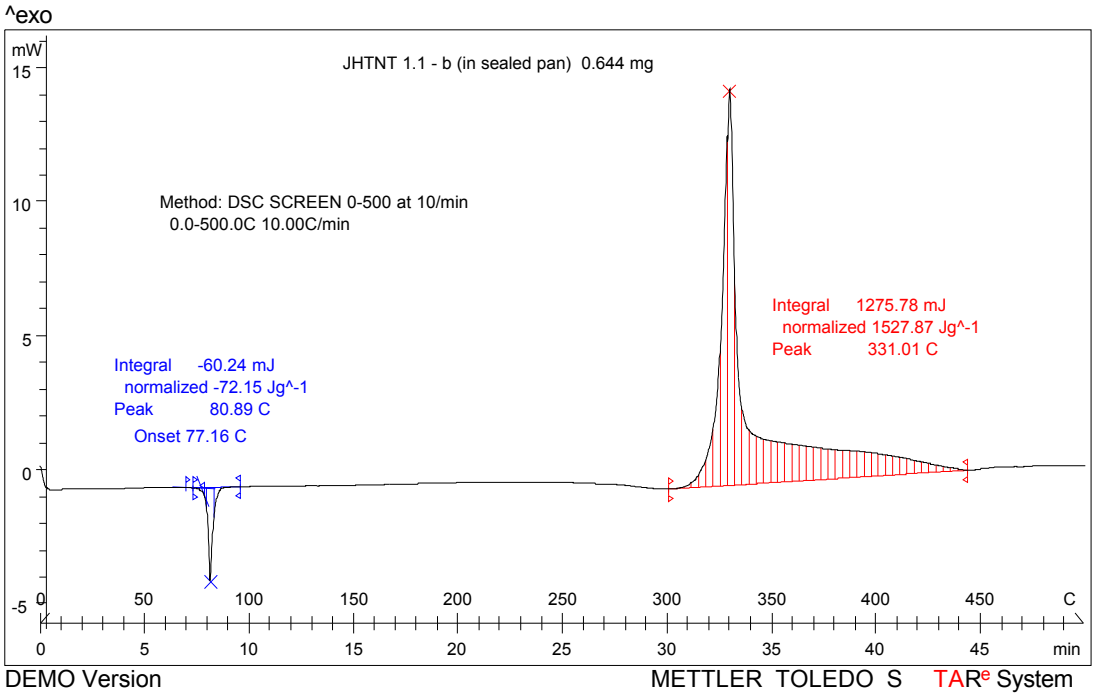


FIG A8.2

Comments: Entire decomposition peak (max. 331°C) recorded (sealed pan used).

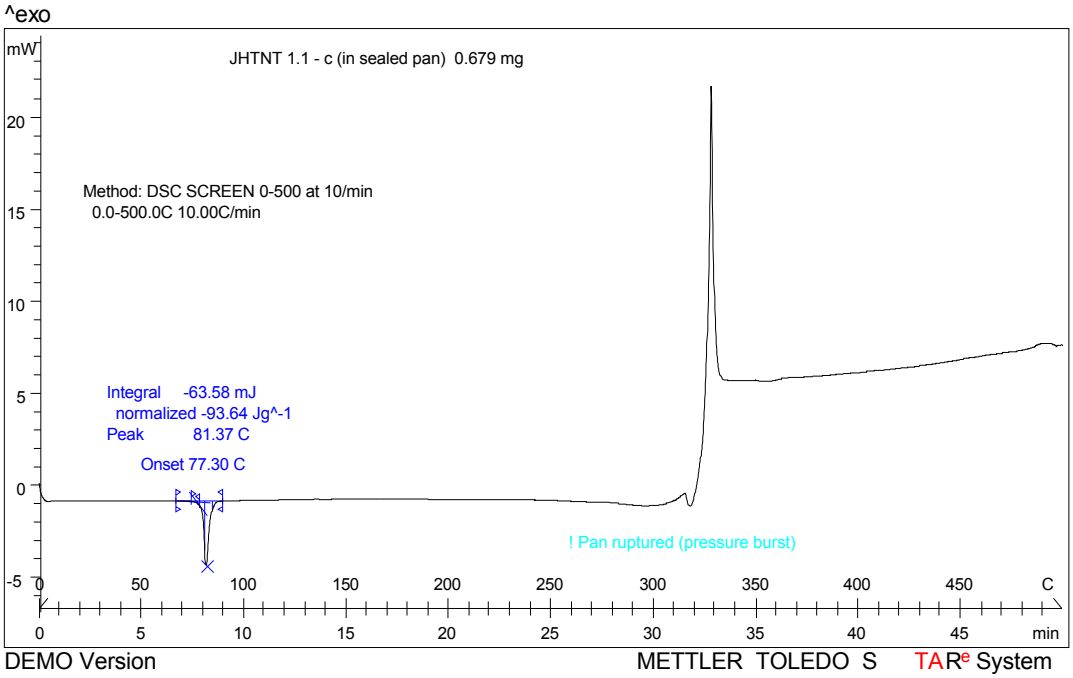


FIG A8.3

Comments: Pan ruptured during the run.

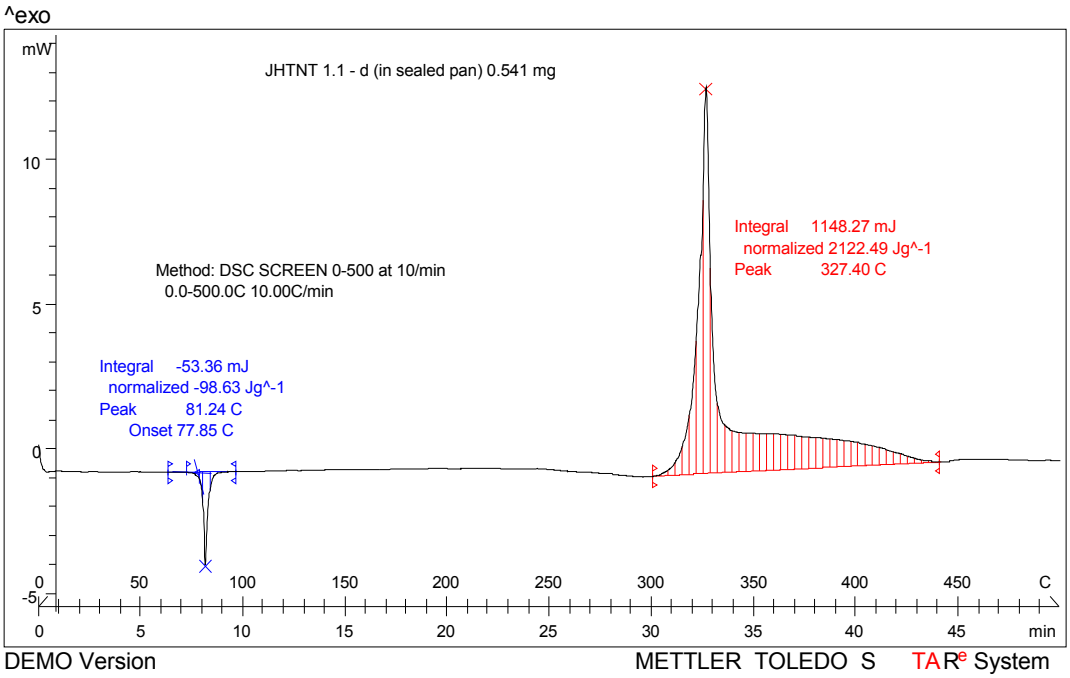


FIG A8.4

Comments: Reduced sample weight; duplicated run in Fig. A2 reasonably well.

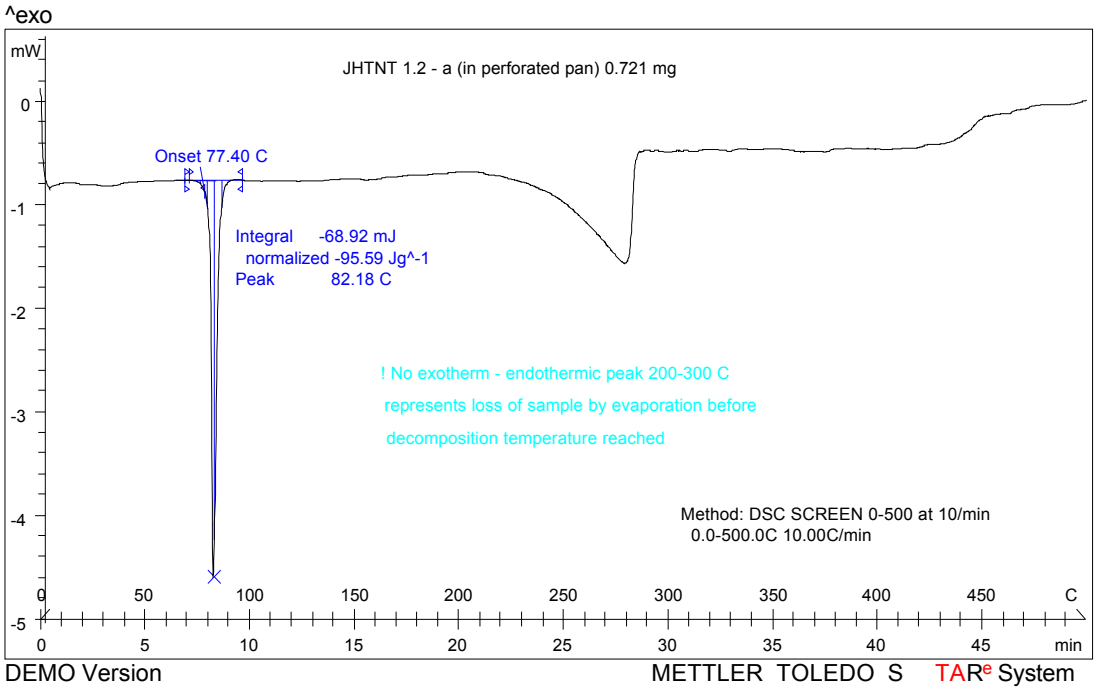


FIG A8.5
Comments: (2nd TNT sample) – sample volatilized before decomposition.

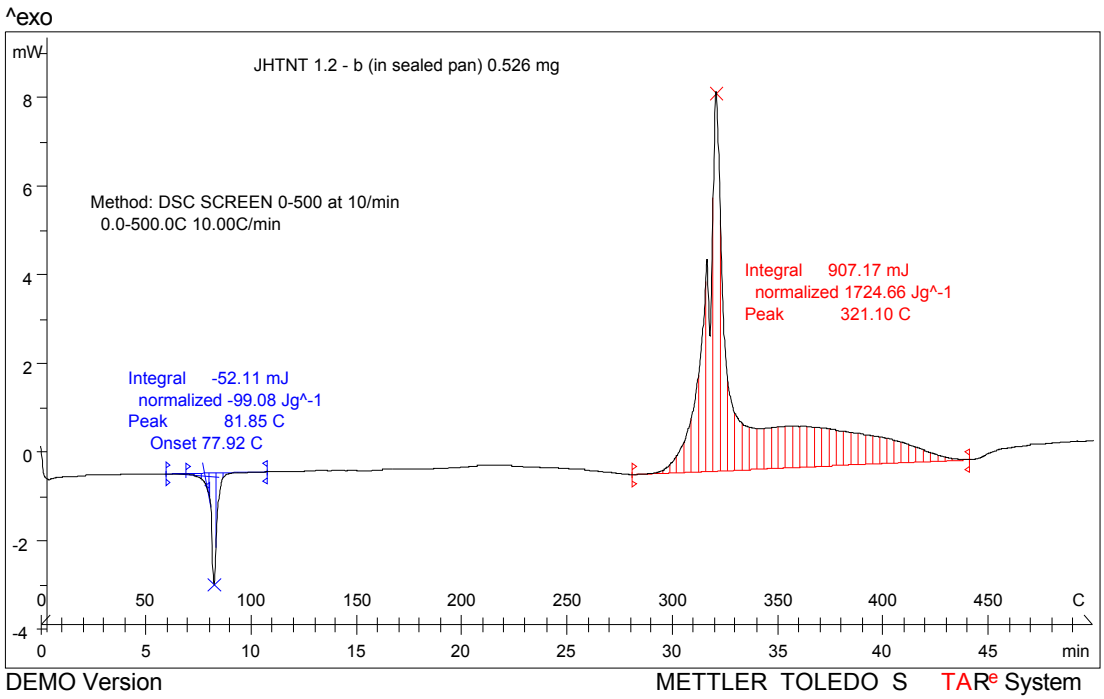


FIG A8.6 Comments: (2nd run of 2nd TNT sample) – decomposition peak evident, with slightly different profile from 1st TNT sample.

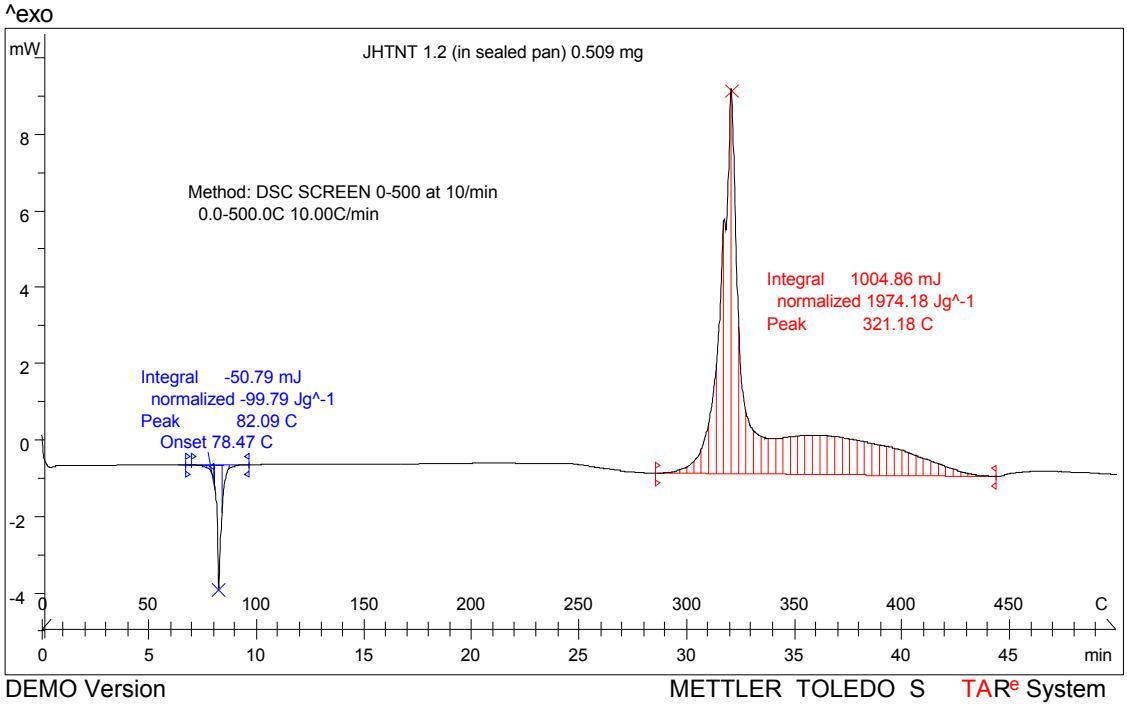
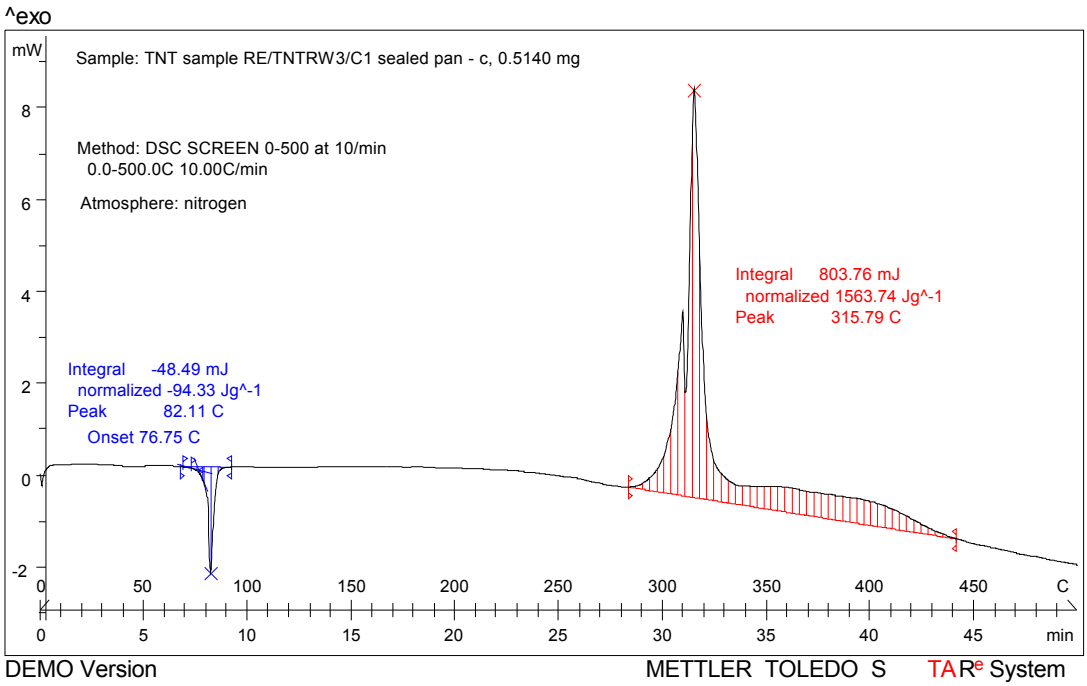


FIG A8.7

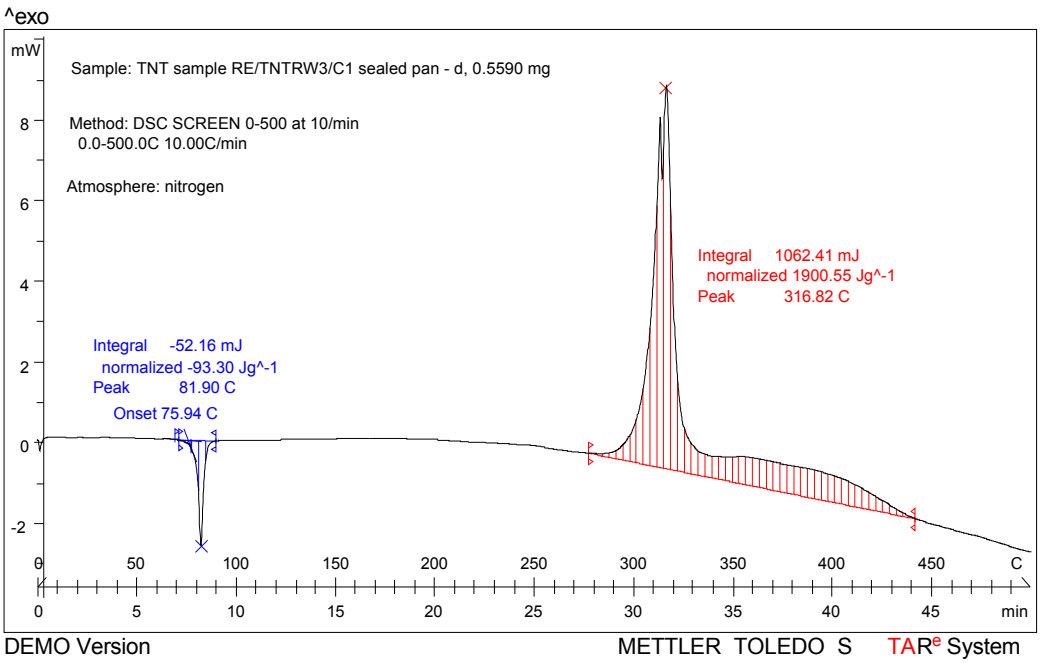
Comments: As for Fig. A6.

Analysis of TNT sample prepared in 50 g run

1st analysis:



2nd analysis:



Appendix B: List of Technical Publications

1. Articles in Peer-Reviewed Journals

Article in preparation (SCI Journal)

2. Technical Reports

None (apart from SERDP annual reports).

3. Conference/Symposium Proceedings

None.

4. Published Technical Abstracts

1. Elimination of Redwater Formation from TNT Manufacture, Ross W. Millar, A. W. Arber, J. Hamid & R. Endsor, poster presented at 2004 SERDP "Partners" Symposium, Washington DC, 30 Nov. – 02 Dec. 2004; poster abstract.

2. Elimination of Redwater Formation from TNT Manufacture, Ross W. Millar, A. W. Arber, J. Hamid & R. Endsor, poster presented at 2005 SERDP "Partners" Symposium, Washington DC, 29 Nov. – 01 Dec. 2005; poster abstract.

3. Improved Regioselectivity in the Nitration of Toluene – The Key to Cleaner Manufacture of TNT, A. W. Arber, R. W. Millar, J. Hamid & R. Endsor, 10th A.C.S. Annual Green Chemistry & Engineering Conference, Washington DC, 26-30 June 2006; abstract of oral presentation.

4. Elimination of Redwater Formation from TNT Manufacture, Ross W. Millar, A. W. Arber, J. Hamid & R. Endsor, poster presented at 2006 SERDP "Partners" Symposium, Washington DC, 29-31 Nov. 2006; poster abstract (#499); poster number 100-W, available at: http://www.serdp.org/Symposium/upload/Wednesday%20Poster%20Abstractsafter%20Symposium.pdf.

5. Published Text Books or Book Chapters

None.

Appendix C1: Environmental Impact Assessment

C1.1 Introduction

This environmental impact assessment focusses on the chemicals proposed for use in the synthesis of TNT by the alternate methodology, which is aimed at reducing, to insignificant level, the by-products (i.e. *meta*-nitro isomers) which would otherwise contaminate TNT produced conventionally where they are currently removed by sulfiting (thus producing redwater). These chemicals are listed below under four categories:-

- Nitration reagents
- Co-reagents for nitrations
- Solvents
- By-products

(The nitroaromatic intermediates and products - mono-, di- and trinitrotoluenes - are excluded from this survey as clearly their use is not in question in TNT manufacture. It is worth noting in passing, though, that all nitroaromatic compounds are toxic to a greater or lesser extent - 2,4-dinitrotoluene is singled out for particularly rigorous control over release into the environment (see Bibliography, ref. 3, page 9) - and all appropriate precautions should be taken to prevent the discharge of these compounds in effluent streams.)

It is the aim of this assessment to ensure that none of these alternate chemicals introduces environmental burdens greater than the chemicals already in use, or produces by-products more environmentally disadvantageous than those already produced - indeed it is anticipated that the alternate methodology will offer distinct advantages over the conventional processes.

It is recognized that in TNT production, as well as the undesired *meta*-isomers mentioned above, other undesired by products are formed - spent acids, tetranitromethane, off-gases containing NO_x, etc. - and the prevention of discharge of these substances to the environment constitutes an important aim of the project. This aim may be achieved through change of the chemical processes involved in the synthesis of TNT and its intermediates, such that formation of the undesired substances is reduced through change of reaction medium (e.g. by carrying out the first and second stage nitrations in alternate nitration/solvent systems such as dinitrogen pentoxide/dichloromethane - thus eliminating the generation of spent acid in these stages), or by change of nitration agent (e.g. use of nitronium sulfate in the third stage nitration, which is anticipated to reduce the amount of tetranitromethane, and possibly also off-gases, generated in this stage).

The compounds involved are now examined in more detail from an environmental and hazard point of view; the use of the compounds is put into context in Section C1.2, their specific hazards are described in Section C1.3, and their potential impact is discussed in the conclusions (Section C1.4).

C1.2 Compounds

Nitration reagents

For preliminary proof-of-concept studies of the respective nitration steps up to and including technical demonstrator scale, it is proposed to use dinitrogen pentoxide generated by the ozonation of N_2O_4. This may be either: a) on lab. scale, using a small scale contact reactor with chilling out of the N_2O_5 as a solid [91], or b) on pre-pilot scale using the solvent ozonation reactor producing a ready-made solution of N_2O_5 in dichloromethane (DCM) [72,92]. In either case, the hazardous chemicals concerned are the same - N_2O_4, ozone, N_2O_5 and DCM. It is not intended that either of these processes would form part of the industrial scale process for TNT manufacture - instead the electrolysis/extraction process, described below, would be used for the manufacturing plant.

The method used to generate N_2O_5 for large scale manufacture would be the electrolysis method, where pure nitric acid/ N_2O_4 mixture is electrolyzed in a specially designed cell [74], where the output stream of enriched nitric acid (i.e. anhydrous nitric acid containing dissolved N_2O_5) is further treated with N_2O_4 as described elsewhere [76, 96] to generate solid N_2O_5 and a waste stream of azeotrope strength (67-70%) nitric acid. In such a combined system the N_2O_4 is totally enclosed and hence significant emissions of this deleterious chemical are not anticipated during the generation of N_2O_5 by this means. The waste stream of aqueous nitric acid could be used for downstream activities such as production of ammonium nitrate or potassium nitrate for fertilizer use. (Nitric acid production and usage in the US is around 7 m tonnes p. a. [97], and the amounts involved in TNT production - 20-30,000 tonnes p. a.* - are dwarfed by this amount.)

Co-reagents for nitrations

Pure nitric acid is anticipated to be a co-reagent for the second stage nitration (mononitrotoluenes to DNTs), and the same considerations apply as above (see Nitration reagents, above). Other co-reagents are sulfuric acid and trifluoromethane sulfonic acid or its anhydride, and these are considered in turn.

The use of sulfuric acid is anticipated to be necessary in the third stage nitration (DNTs to TNT), as a solvent/reactivity enhancer for N_2O_5 (in which the active species would be nitronium sulfate), and this may be in the presence of inert diluents such as perfluorocarbons (see "Solvents", below). The amounts of sulfuric acid used would be much lower - nearer stoichiometric levels - than those typically used in industrial nitrations, where the sulfuric acid is used in excess as a solvent, resulting in troublesome and costly clean-up procedures to enable re-use of the acid. (Sulfuric acid production and usage in the US is around 36 m tonnes p. a. [98], and the amounts involved in TNT production by the process proposed here - of the order of 50,000 tonnes p. a.* - would be dwarfed by this amount.)

*Based on manufacture of *ca.* 5,000 tonnes (11 million lb) of TNT p. a.

Solvents

Dichloromethane (DCM) occupies a unique position in nitration chemistry as being the only volatile organic solvent known (apart from some freons, which are now banned under the Montreal Protocol) which is compatible with dinitrogen pentoxide. Therefore its use is essential to this project. DCM is used extensively as an industrial cleaning agent and solvent for various chemical processes, and in consumer products such as paint stripper. The amount of DCM produced in the US is around 220,000 tonnes p. a. [99]. DCM was targeted, along with 16 other chemicals, by the EPA as a high volume industrial chemical which poses environmental and health concerns [100], and a program for voluntary reduction in the use of this chemical was put in place in 1992.

By-Products

Tetranitromethane (TNM) is a common by-product resulting from the nitration of organic compounds [101,102]. It is toxic and acts as an oxidizer when mixed with combustible organic materials. TNM is known to be formed in the mixed acid nitration of toluene to produce TNT [88], and its presence is believed to have been the cause of explosions in TNT manufacturing facilities. Such explosions may have been caused by the detonation of mixtures of TNM and toluene, condensed in off-gas lines, and which have been found to be as sensitive as nitroglycerine [103]. Therefore it is desirable that formation of TNM during nitrations is minimized for safety and health reasons - indeed there is evidence that a reduction in the *meta*-isomer content of lower nitrated toluenes (MNTs and DNTs) will be effective in reducing TNM formation, as it is believed, from tracer studies [104], that over 80% of all the TNM formed in the production of TNT is derived from such *meta*-isomers.

C1.3 Hazards

Nitration reagents

Pure nitric acid (nom. 100%, typical spec. 99.5%) is a corrosive liquid which fumes in air and is unstable on storage at ambient temperature or on exposure to bright light, decomposing to give oxides of nitrogen (principally NO_2) and water. It is an oxidizing agent, particularly at elevated temperatures, and contact of the neat liquid with combustible material may cause fire. It reacts with numerous materials, including bases, reducing agents, alcohols, many metals and various other substances (the MSDS should be consulted for fuller details). It is highly toxic by inhalation, contact with skin and if swallowed and causes burns. Users must wear acid-resistant protective clothing (including safety goggles, faceshield, heavy rubber gloves, rubber apron) and use an NIOSH/MSHA-approved respirator (latter not required if LEV in operation to keep level below LTEL); STEL (UK) 4 ppm, LTEL 2 ppm. Small amounts may be disposed of by dilution into a large excess of water followed by adjustment of the pH to neutral, separation of any insoluble solids (to be packaged for hazardous waste disposal) and disposal of residual aqueous solution down the drain with plenty of water. No ecological test data are available.

N_2O_5 is considered to have same hazards as nitric acid, except that the compound reacts vigorously with water (releasing nitric acid); N_2O_5 also decomposes slowly (to N_2O_4/NO_2) if it is stored at too high a temperature, although this is not considered a significant hazard under normal plant operating conditions, as the N_2O_5 will be consumed almost as soon as it is formed.

N_2O_4, which is a liquefied gas, is classified as an oxidant which strongly supports combustion - hence it must not be allowed to come into contact with oxidizable material. It is corrosive to the eyes, respiratory system and skin, and is very toxic by inhalation. Users must wear chemically resistant protective clothing (protecting eyes, face and skin), work in a well ventilated area and keep self-contained breathing apparatus available for emergency use. The STEL for the UK is 5 ppm, LTEL 3 ppm; delayed pulmonary edema is possible which may be fatal - the LC50(1h) is 115 ppm. As well as oxidizable materials, the chemical may react violently with reducing agents and alkalis, and forms corrosive acids (which may corrode metals) on reaction with water. Discharge of the gas to the atmosphere should be avoided, particularly into any area where accumulation could be dangerous, esp. below ground level (the gas is heavier than air). N_2O_4 may cause pH changes in aqueous ecological systems.

Co-reagents for nitrations

Sulfuric acid (98%) is a corrosive, involatile viscous liquid which is stable indefinitely at ambient temperature (though hygroscopic). It is a strong dehydrating agent which may explode on contact with water. It reacts vigorously with finely divided materials, especially many metals (liberating hydrogen), and with bases, halides and many organic and inorganic materials (for further details see MSDS). It is classified as highly toxic (USA) and toxic (EU) and is a potential carcinogen (through inhalation). Users must wear suitable protective clothing, including gloves and eye/face protection, and must not breathe the vapor (use of an NIOSH/MSHA-approved respirator is recommended). In the event of spillage, the spilt chemical should be covered with dry lime, sand or soda ash and, once any reaction has subsided, collected and kept in a covered container awaiting disposal; the spill site should be washed after material pickup is complete. The OEL is 1 mgm^{-3} (UK and USA-ACGIH); STEL TLV 3 mgm^{-3} (USA-ACGIH). The chemical may be fatal if inhaled as a mist (owing to destruction of the mucous membranes of the respiratory system), and is harmful if swallowed or absorbed through the skin, causing severe burns. The LDLO for humans is 135 mg/kg. Ecological data are not currently available.

Solvents

Dichloromethane (DCM) is a volatile liquid (b.pt. 40°C) which, although stable under ambient conditions, is incompatible with certain metals (alkali metals and aluminum). It is non-flammable (no flash point) but may form explosive mixtures with air over a narrow range of compositions (LEL 14%; UEL *ca.* 22%). Its autoignition temperature is 660°C. On decomposition or combustion it forms the following hazardous products: carbon monoxide, hydrogen chloride, phosgene. DCM is a possible carcinogen, and an irritant to the eyes, respiratory system and skin, through which it is readily absorbed. The OEL-TWA is 100 ppm (UK), STEL 250 ppm (UK); ACGIH TLV-TWA = 50 ppm; OSHA PEL (8 h TWA) = 25 ppm, STEL = 125 ppm. Users must wear suitable protective clothing, including gloves and eye/face

protection (in order to prevent contact with the skin and eyes), and must not breathe the vapor. Use of self-contained breathing apparatus is recommended. In the event of accidental release the area should be evacuated and the liquid adsorbed on sand or vermiculite and placed in closed containers for disposal. No ecological data are at present available.

By-Products

Tetranitromethane (TNM) is a relatively involatile liquid (b.pt. 126°C, vapor pressure 8.4 mm at 20°C) which may explode when heated and is a) unstable or b) shock sensitive when mixed with a variety of materials. Such materials include: a) copper, brass, iron, zinc and rubber, and b) aromatic or acetylenic compounds and nitriles (very shock sensitive), and aliphatic compounds (esp. short and branched-chain), alkyl nitrates, ethers and alcohols (less shock sensitive mixtures). TNM is also incompatible with strong oxidizing agents, strong reducing agents, strong bases, finely divided metals and organic materials. TNM is classified as highly toxic (USA) and very toxic (EU), with routes of entry to the human system by inhalation (very toxic), ingestion (toxic) and through the respiratory system, eyes and skin (irritant). It is a suspected carcinogen (Calif. Prop. 65) and exposure may cause irreversible effects. The OEL-TWA is 1 ppm (EU countries, Switz. & Australia), OSHA PEL (8 h TWA) = 1 ppm. Users must wear suitable protective clothing, gloves and eye/face protection, and the vapor must not be breathed. Prolonged or repeated exposure should be avoided. In the event of accidental release the area should be evacuated and self-contained breathing apparatus and suitable protective clothing worn during clean-up. The liquid should be adsorbed on sand or vermiculite and placed in closed containers for disposal, and the spillage area kept well ventilated and washed down once material pickup is complete. Animal toxicity tests indicate the following: inhalation - LC50(rat) 18 ppm/4 h; LC50(mouse) 54 ppm/4 h; LC50(cat) 110 ppm/20 min.; oral administration - LD50(rat) 130 mg/kg; LD50(mouse) 375 mg/kg. The chemical should be disposed of by combustion in a chemical incinerator equipped with an afterburner and scrubber. No ecological data are at present available.

C1.4 Conclusions

In general, none of the alternate chemicals suggested for the new TNT manufacturing process will impose environmental burdens greater than the chemicals already in use, though caveats are attached to two compounds:

- i) Dinitrogen tetroxide (N_2O_4)
- ii) Dichloromethane

Each introduces risks, of varying magnitude, not present in the conventional process and which will require mitigation measures detailed further below.

i) Dinitrogen tetroxide - a toxic, lachrymatory gas - must be kept in totally enclosed systems for the protection of personnel. As noted in Section C1.2 (Nitration reagents) it is used, though not consumed, in the generation of N_2O_5 by electrolysis, and again in the extractive process for purification of the N_2O_5. In both these processes it is believed that total containment can be achieved.

ii) Dichloromethane, the only solvent considered suitable for the early nitration stages, will need to be used under total containment as far as possible on account of its health concerns and effect on the environment (atmosphere - ozone depletion). Nevertheless, it is an industrial chemical presently employed in a wide range of applications, and although legislation in some states of the U.S.A. (e.g. California) restricts its use, it is however recognized that a total ban would be quite impracticable. The most recent figure for US production (220 kt p. a.) indicates what a difficult proposition such a ban would be.

Turning to environmental impact as regards reducing the formation of polluting compounds, naturally the removal of the need to use a sulfiting process in the new TNT manufacturing process is the biggest plus point. There is also good evidence that TNM formation will be reduced, on account of the factors mentioned above (see Section C1.2, By-products), with reduction to 20% of current levels being an attainable goal (in conventional TNT manufacture, levels of 0.5 lb of TNM per 100 lb of TNT are encountered). The effect of the new methodologies on the formation of NO_x off-gas is less easily quantified, but as less harsh conditions are anticipated to be necessary it is expected that benefits will be reaped here too.

Finally, a surprising finding of this survey is the paucity of readily available data on the ecotoxicity of the various compounds, based on information available from the respective MSDSs. It is hoped that further information may become available to evaluate the effect of the various chemicals on ecosystems.

C1.5 Supplement to Environmental Impact Assessment

C1.5.1 Sources of MSDSs

Dinitrogen tetroxide: Messer Griesheim GmbH, Krefeld, Germany; MSDS No.: 090/en (01/04/2000).

Remaining chemicals: Sigma-Aldrich Co. Ltd., Gillingham, Dorset, U.K. Dates of issue:-
Nitric acid - 10/1998
Sulfuric acid - 10/1998
Dichloromethane - 10/1998
Tetranitromethane - 10/1998.

C1.5.2 Bibliography

1. *Environmental Impact of Chemicals: Assessment and Control*, Quint, M. D., Taylor, D. & Purchase, R. (Eds.), Roy. Soc. Chem. Spec. Publ. No. 176, Roy. Soc. Chem. Cambridge, 1996 (ISBN 0-85404-795-6). [Proc. Symp. on "Acquiring Environmental Data for Legislative Needs", 17 Oct. 1994, and Proc. Symp. on "Toxicology and Quantitative Risk Assessment, 9 Nov. 1994.]

2. *Waste Minimisation: A Chemist's Approach*, Martin, K. & Bastock, T. W. (Eds.), Roy. Soc. Chem. Spec. Publ. No. 140, Roy. Soc. Chem. Cambridge, 1994 (ISBN 0-85186-585-2). [Proc. Symp. on "The Chemist's Contribution to Waste Minimisation", University of Lancaster, 30 June - 1 July 1993.]

3. *Pollution: Causes, Effects & Control, 4th Edit.*, Harrison, R. M. (Ed.), Roy. Soc. Chem. Cambridge, 2001 (ISBN 0-85404-621-6).

4. *Clean Technology for the Manufacture of Speciality Chemicals*, Hoyle, W. & Lancaster, M. (Eds.), Roy. Soc. Chem. Spec. Publ. No. 260, Roy. Soc. Chem. Cambridge, 2001 (ISBN 0-85404-885-5). [Proc. Symp. on "Clean Technology for the Manufacture of Speciality Chemicals", New Century House, Manchester, UK, 26-27 Sept. 2000.]

Appendix C2: White Paper for Spring 2006 IPR (Action Item)

Query: Request provision of a short white paper on the status of QinetiQ's first stage reactor design. Has QinetiQ been able to achieve reasonable throughput with acceptable levels of *meta*-NT?

Response:

Project Background

Production of TNT from toluene by conventional means (i.e. using mixed acids) suffers from contamination of the product by unsymmetrical (*meta*- or *m*-) isomers, which reduce the melting point of the TNT and may, under adverse conditions, exude from compositions. The formation of these isomers arises from the low regiospecificity in the position of attack on the aromatic ring, especially in the first stage of the nitration process (i.e. toluene to mono-nitrotoluenes [MNTs]). The *meta*-substituted products are carried through subsequent steps of the nitration process and, in conventional treatment, are removed, together with a significant amount of TNT, by reaction with a sulfite salt (commonly sodium sulfite) to form water-soluble products and other products from polynitrotoluene-base reactions, the mixture being known as 'red water'. Red water is difficult and expensive to dispose of.

As hinted above, the key to solving this problem while, of course, still utilizing toluene as the starting material (for reasons of economy and availability) is to eliminate as far as possible the production of *m*-nitrotoluene in the first stage. QinetiQ believes that reduction in the level of *m*-nitrotoluene in the initial product mixture to less than 1.5% – preferably 1.3% – (compared to around 4% in conventional nitrations) would provide a product, after subsequent nitration stages, with a much higher melting point – at least 80.2^{o}C or in other words within *ca.* 0.5^{o}C of that of pure TNT - without the need for sulfite treatment. The subsequent nitration stages could be carried out either by existing methodologies (mixed acid and nitric-oleum) or could, advantageously, be switched either partly or completely to other methodologies which QinetiQ is also investigating under project WP-1408.

Two other current approaches to solving the TNT redwater problem by modification of synthesis routes/conditions are known to QinetiQ:-

3) The approach starting from *ortho*-nitrotoluene, advocated by ATK Thiokol, which involves modification to subsequent nitration steps, and is being implemented at the Radford AAP; and
4) The use of zeolite catalyzed nitration in the first stage (nitration of toluene) to improve the regioselectivity of the reaction and suppress *m*-NT formation to around 1% level; currently under investigation at ARDEC, Picatinny Arsenal (SERDP project WP1409).

The first approach does not really solve the problem as it is dependent on a source of the *ortho*-nitrotoluene from the chemical industry which may not be reliable in times of crisis – and may be subject to economic vagaries and also accidental destruction of plant (separation of MNT isomers on plant scale relies on distillation, which is an inherently hazardous process with these compounds). QinetiQ therefore believes that this approach will not meet all of DOD's requirements in respect of the dependability of the process.

The second approach involving zeolite chemistry may indeed meet the DOD's aims of a dependable process starting from toluene, but the availability of zeolites with appropriate reactivity characteristics as well as scale-up of the process to multi-thousand lb operation are challenges, and evidence that the problems encountered in these processes can be solved is still required. The proposed manufacturing route would also employ the traditional methods for second and third stage nitrations with the environmental disadvantages inherent in these processes.

QinetiQ's Approach and Appraisal of Results on First Stage

In the first stage nitration the regioselective nitration reagent dinitrogen pentoxide (N_2O_5) is used in a reaction medium of low polarity – dichloromethane is ideal regarding inertness toward N_2O_5 (although environmental drawbacks are recognized) – and reaction with toluene at sub-ambient temperature under either batch or flow reactor conditions has been shown to give a product mixture with much lower amounts of *m*-NT than traditional methods. A detailed analysis of this reaction stage follows.

The first stage nitration from toluene to mononitrotoluene in dichloromethane (DCM) using N_2O_5 has reduced the *meta* isomer content significantly. Traditional mixed acid nitration even at very low temperatures gives a *meta* content of 2.7%, whereas N_2O_5 chemistry has been able to reduce this figure to 1.3%.

Studies into the reaction dynamics of the first stage nitration with N_2O_5 have shown that the reaction is far more exothermic than with mixed acid and also exceedingly rapid even at very low concentration (2% wt./wt.) and very low temperatures (-60°C). Small scale batch nitration (20 ml) at around 2% substrate concentration and a reaction temperature of -70°C yielded a *meta* content of 1.3%. It was noted that at this low temperature the toluene crystallized out of the DCM, this could have detrimental effects with flow reactors especially if the flow path is small.

Experiments on a flow reactor at concentrations between 2% and 7 % wt./wt., at three different flow rates and a reaction temperature range of -15°C and -40°C have been carried out. All experiments produced a *meta* content below 2%. The lower the temperature, flow and concentration then the lower the *meta* content. At best a *meta* content of around 1.5% was obtained using a 2% toluene feed cooled to -60°C and a N_2O_5 in DCM stream cooled to -30°C. These conditions gave a reaction temperature of -40°C. Further cooling or dilution would reduce the *meta* content further probably to a figure of the order of 1.4%. Consequently pre-cooling of the reactant streams to counter the reaction exotherm is the only practical method of reducing the reaction temperature in a continuous flow reactor.

For rapid exothermic reactions, on a large scale, continuous reactions are usually carried out in small diameter reactor tubes arranged in a parallel configuration. In this way the heat transfer area to volume ratio is maximized and the velocity in the tube is high enough to promote good mixing. For this reaction it has been calculated that at 2% feed concentration and a tube internal diameter of 12 mm, a 200 tube reactor would be needed or multiples of smaller bundles of tubes which would be more practical.

An order of magnitude cost estimation has been carried out for a large scale (1,000 tons/year) TNT plant based on 1.5% *meta* product from the first stage nitration. The cooling cost contribution to the overall production cost was only around 7% of the total, the major costs being the raw materials (55%) and capital depreciation (31%) resulting in a production cost of around $6/lb (excluding profit). Further dilution and cooling would decrease the *meta* content and increase the set point temperature, but it would also increase cooling costs and plant size resulting in an increase in production cost of TNT. The first two nitration reactions are carried out in a continuous mode, and since continuous plant tends to be modular in construction, halving the concentration to say 1% would double the volume throughput and hence the number of modules and would also have a similar effect on the capital cost. Energy requirements for cooling and solvent recovery would also increase by a similar factor for the first stage where the major cost lies. It has been assumed that no increase in labor would be necessary as this type of plant would have a high degree of automatic control. When these increases are factored into the cost calculation an increase in production cost from $6 to $8.5/lb is predicted.

In summary, the practical limit for the *meta* content from the first stage nitration is around 1.5%. Further efforts to decrease this figure would be met with a disproportionate increase in production costs. TNT produced from such a feedstock would be predicted to have a set point of around 80.0°C (cf. Type I specification: 80.2°C).

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