Process Optimization for the Gas-Liquid Heterogeneous Reactive Crystallization Process Involved in the Preparation of the Insensitive High Explosive TATB

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Abstract: The thermally stable, insensitive, high explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is manufactured by amination of 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) in toluene with NH_3 gas. It is an isothermal, single-feed, semi-batch, gas-liquid heterogeneous, reaction crystallization process. The amination process is discussed by applying the chemical engineering methodology of mass transfer and reactive crystallization processes based on Two-Film Mass-Transfer (TFMT) theory. Kinetic expressions have been developed to define the chemical reactions as well as the physical phenomena (mass transfer) associated with this process. A single expression has been derived to explain the dependence of the ammonia consumption rate on various process parameters. Subsequently, the influence of various process parameters on the product quality (particle size and chloride impurity content) has been studied on the laboratory scale. Finally, the process has been established in the pilot plant, with optimized process conditions, to realize TATB of desired particle size and chloride content. The effects of feeding excess ammonia, and the presence of mercaptans/hydrogen sulphide impurities in poor quality toluene on the formation of certain undesirable by-products in TATB, are also discussed.

Keywords: TATB, TCTNB, amination, reaction crystallization, chloride impurity, particle size

1 Introduction

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) is an aromatic high explosive of special interest because of its insensitivity, thermal stability (>350 ºC) and respectable performance compared with conventional high explosives such as TNT, RDX and HMX [1-3]. Although some alternative routes for TATB synthesis have been reported [4-6], the large-scale production of TATB is still an adaptation of the Benziger route (Scheme 1) starting from 1,3,5-trichlorobenzene (*sym*-TCB) [7-9]. This laboratory has also adopted this route and the process has been scaled up to a pilot plant level [10-14]. TATB preparation by the Benziger route consists of two-steps: *sym*-TCB is first nitrated to 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB), and the product TATB is synthesized in the second step by amination of the intermediate TCTNB in toluene with ammonia gas.
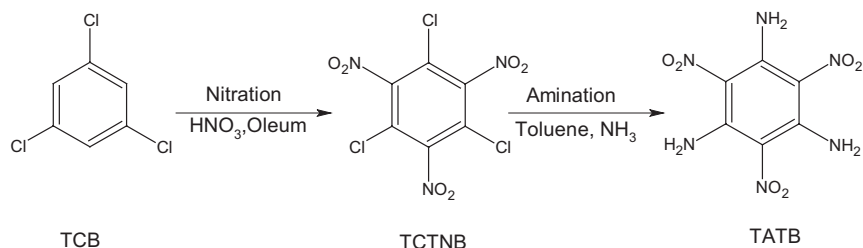
Scheme 1. Benziger Route for synthesis of TATB.

Unlike other military explosives (*e.g.* TNT, RDX, HMX *etc.*), TATB is virtually insoluble in most common solvents [15]. The insolubility of TATB is related to the strong intra- and inter-molecular hydrogen bonds (between nitro and amino groups) present in the molecular packing of the crystal lattice [16]. Thus, conventional crystallization is found to be unsuitable, and also uneconomical for further purification and for realizing TATB of different particle sizes [17]. Earlier, various authors were successful in producing fine TATB (< 5 μm) by a drowning-out crystallization [18-20]. TATB was dissolved in DMSO-NaOH or concentrated H_2SO_4, and precipitated by addition of a suitable anti-solvent. However, as a part of process development research, emphasis was given to the amination process for producing high purity TATB (low chloride impurity content) of reasonably large particle size (> 50 μm) [7-9, 21-24]. TATB of larger particle size gives a higher density, better fluidity, castability and solid loading in high explosive formulations [1-3]. The chloride impurity in TATB causes compatibility problems in certain ammunitions, and hence, is detrimental to the storage life [25].

Amination of TCTNB is an isothermal, single-feed, semi-batch, gas-liquid, heterogeneous, reaction crystallization process. The chemical reaction and crystallization occur simultaneously in this process. The product TATB and the bi-product NH_4Cl are formed at the gas-liquid interface. They are insoluble in toluene and hence, resulting in co-precipitation of crude TATB (TATB-NH_4Cl crystals). Crude TATB is further purified (removal of NH_4Cl by dissolution) by hot water digestion (90 °C).

The earlier process development research was mainly focused on reducing the chloride impurity in the product. In the present paper, the amination process has been studied by applying the chemical engineering methodology of a reactive crystallization process. A model has been conceptualized based on Two-Film Mass-Transfer (TFMT) theory [26-29]. Kinetic equations were developed to define the various chemical reactions and the physical phenomena (mass transfer) associated with this process. The influence of the process parameters on the product quality (particle size and chloride content) has been studied on the laboratory scale. Subsequently, the process has been demonstrated with optimized process conditions on pilot plant scale. The effect of feeding excess ammonia, and the presence of mercaptans in the toluene, on the formation of certain undesirable impurities in the TATB, has also been discussed.
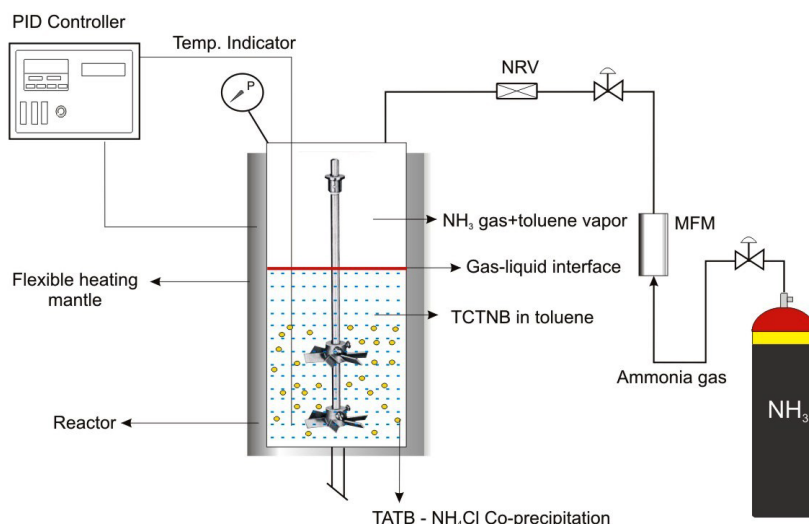
2 Experimental

2.1 Reagents

In-house synthesized, crude TCTNB (purity ~88%, impurities 1,2,3,5-tetrachloro-4,6-dinitrobenzene (T_4, ~9%) and 1,3,5-trichloro-4,6-dinitrobenzene (T_3, ~3%)) was used for this study. It was prepared by nitration of *sym*-TCB in the pilot plant of this laboratory. Toluene (pure and nitration grade, IS-537-1967) and acetone [IS-170-1986 (3rd Revision) reaffirmed 1992] were used for the batch experiments. Anhydrous ammonia gas [IS-662-1980 (1st Revision)] from a cylinder was used.

2.2 Laboratory experiments

Laboratory experiments on the amination process were carried out in a small scale (2 L), Parr pressure reactor (Model 4532M). The reactor was equipped with an agitator, a pressure gauge, electrical heating and a temperature indicator/controller. A schematic diagram of the experimental set up is shown in Figure 1. Ammonia (NH_3) gas was metered through a mass flow meter (MFM) and fed

through the top of the reactor (without sparger).

The internal diameter and depth of the reactor were 101.6 mm and 266.7 mm, respectively. A six blade turbine impeller (d = 63.5 mm) was used for agitation. A discharge valve at the bottom of the reactor was used to drain out the reaction mixture. A non-return valve was fitted at the gas inlet line to prevent back flow of the reaction mixture. The total system represents a realistic single-feed, semi-batch, isothermal reactor to study the gas-liquid heterogeneous, reaction crystallization process involved in the amination of TCTNB in toluene.


Figure 1.   A schematic diagram of the laboratory scale experimental process.

A typical laboratory experiment is described here. Crude TCTNB (100 g) was dissolved in toluene (1200 mL) and the resultant solution was filtered to remove any toluene-insoluble matter ($<0.2\%$). The solution was transferred to the reactor. A measured quantity of water was added (in the case of wet amination). The reactor was sealed and heated to attain the desired reaction temperature. The reactor pressure is released through a relief valve for venting-off non-reacting gases. Ammonia gas was fed into the system from the cylinder ($\sim$4.5 kg/cm^2) at the desired rate until the reaction was complete (indicated by a slow rise in reactor pressure). After completion of the feeding of the desired quantity of ammonia gas, the reactor was cooled and opened. Toluene was decanted from the reaction mixture. Water ($\sim$1 L) was added to the yellow solid (crude TATB)

and the reactor was resealed. The crude TATB was purified by heating in hot water (~90 °C) for 1 h. The solid was filtered off and washed sequentially with hot water and acetone. The cake was dried in a vacuum oven (80 °C) and the final product (TATB) was obtained.

2.3 Pilot plant batches

Experiments at pilot plant scale (~10 kg TATB/batch) were carried out in an in-house designed pilot plant. A schematic diagram of the pilot plant is shown in Figure 2. A typical batch experiment was as follow: TCTNB (15 kg) was dissolved in 180 L toluene in a dissolution vessel. The solution was filtered and transferred into a glass-lined steel reactor (250 L; internal diam. 675 mm). Water (9 L) was also added to the reactor and it was then sealed. The temperature of the reaction mixture was raised to 90 °C by circulating hot thermic fluid in the reactor jacket. The reactor pressure (~0.5 kg/cm²) was released through a relief valve for venting-off non-reacting gases. The temperature was then raised to 110 °C. Dry ammonia gas (5.0 kg) was metered (mass flow meter) from a cylinder and fed into the system at a defined rate from the top of the reactor. The temperature slowly rose to 125 °C due to the mild exothermicity of the amination reaction. The temperature was maintained at ~125 °C for the entire period of ammonia feeding.
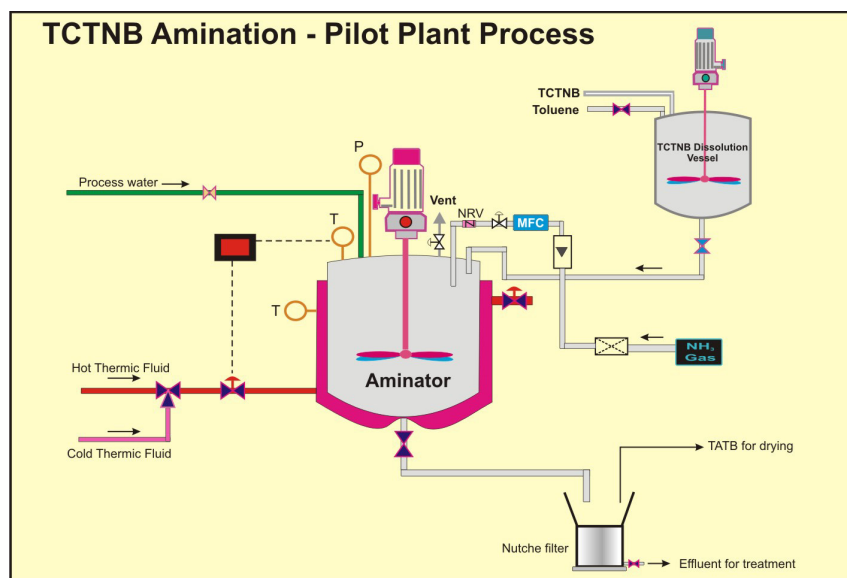
Figure 2.   A schematic diagram of the pilot plant amination process.

After completion of the amination process (indicated by a slow pressure rise and loss of exothermicity), the reaction mixture was cooled to room temperature. The crude TATB slurry in toluene was filtered off. The crude TATB was transferred back into the reactor. Water (200 L) was also added and the reactor was sealed. The crude TATB was purified (removal of NH_4Cl by dissolution) by hot water digestion (90 °C). The slurry was cooled to 50 °C, and was filtered through a Nutsche filter. The filter cake was washed with hot water and finally acetone (5 L). The cake was dried in a vacuum oven (80 °C) to obtain the final product (TATB).

2.4   Analytical techniques

Particle size distribution analysis was carried out using a Malvern particle size analyzer (Model: Mastersizer 2000). An earlier method developed by Nandi *et al*. [19] was adopted for particle size analysis. Distilled water was used as the medium for dispersion of the sample. The stirrer speed was 2150 rpm. The sample was added to water in portions until the obscuration level was 11-15%, as specified by the equipment manufacturer. Stirring was continued with ultrasonication at level 10 for 3 min. The measurement was performed in triplicate and the average reading was recorded. The surface weighted mean diameter (D [3,2]) was considered as the average particle size.

The chloride impurity content in TATB was estimated by potentiometric titration of an acidified digested TATB solution (digested in 10 N NaOH solution) using an Ag/AgCl electrode (DG141) in a Mettler Toledo Autotitrator (Model: DL55) [30].

The TATB purity was determined by the amino group estimation method in a modified Kjeldhal apparatus [31]. Digestion of the TATB with dilute sodium hydroxide solution converts it into 1,3,5-trinitro-2,4,6-trihydroxybenzene (trinitrophloroglucinol) with quantitative evolution of three equivalents of NH_3. The liberated NH_3 was estimated by absorbing it in a known quantity of dilute H_2SO_4 solution.

An environmental SEM (Make: FEI, Netherland; Model: Quanta 200) was used for crystal imaging. Images were taken at room temperature using a tungsten filament as the electron source of 20-30 kV energy. A Large Field Detector (LFD) was used for secondary electron imaging in the pressure range 0.1-1.0 torr.

Differential Scanning Calorimetry (DSC) analysis was performed in a Perkin Elmer DSC instrument (Model: DSC-7). Analysis was carried out with around 1 mg sample at a heating rate of 5 ºC/min in an inert atmosphere of ultrapure N_2 (flow rate: 100 mL/min). Impact sensitivity was determined by the drop hammer method using a 2-kg drop weight, and friction sensitivity was determined utilizing a Julius Peter apparatus using standard methods.

3 Reaction Scheme and Elemental Steps in the Amination Process

TCTNB reacts with dissolved NH_3 in toluene and the product TATB is formed along with the by-product HCl. This HCl is immediately neutralized by ammonia. The reaction proceeds very fast via the aromatic nucleophilic substitution (SN^{Ar}) mechanism (Scheme 2) [32] with NH_3 acting as a nucleophile. Thus, the three chlorine atoms present in TCTNB are replaced by NH_2 in a stepwise fashion (Scheme 3). However, there are five elemental steps involved in the overall amination process. These steps may be written as:
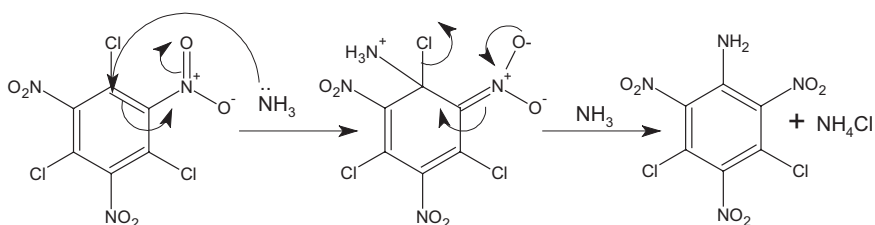
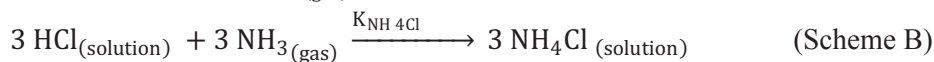**Scheme 2.** Mechanism of nucleophilic aromatic subtitution (SN^{Ar}) involved in amination reaction.
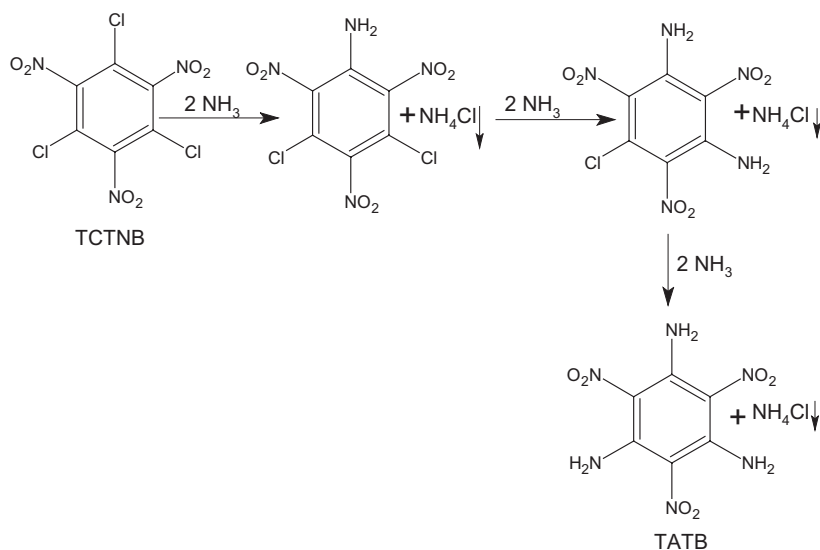
Scheme 3. Consecutive reactions involved in TATB formation.

1. NH_3(gas) $\xrightarrow{\text{Diffusion}}$ NH_3(solution)

2. TCTNB(solution) + NH_3(solution) $\xrightarrow{\text{Chemical reaction}}$ TATB (solution) + HCl (solution)

3. HCl (solution) + NH_3(solution) $\xrightarrow{\text{Neutralization reaction}}$ NH_4Cl (solution)

4. TATB (solution) $\xrightarrow{\text{Crystallization}}$ TATB (crystals)

5. NH_4Cl (solution) $\xrightarrow{\text{Crystallization}}$ NH_4Cl (crystals)

4 Mass Transfer and Chemical Reaction Kinetics

For a reactive crystallization process, the driving force responsible for the crystallization is the generation of supersaturation by the chemical reaction. The process is essentially complex, as it involves the simultaneous occurrence of both the chemical reaction, and the crystallization. As already mentioned, the product TATB and the by-product NH_4Cl are sparingly soluble in toluene, and hence they will crystallize out at different rates depending on their nature (TATB is an organic crystal whereas NH_4Cl is an inorganic crystal). Accordingly, two separate overall reaction schemes viz., (A) amination of TCTNB, and (B) neutralization of hydrochloric acid (HCl) by ammonia may be defined as:

$$TCTNB_{(solution)} + 3\,NH_{3\,(gas)} \xrightarrow{K_{TATB}} TATB_{(solution)} + 3\,HCl_{(solution)} \quad \text{(Scheme A)}$$

$$3\,HCl_{(solution)} + 3\,NH_{3\,(gas)} \xrightarrow{K_{NH\,4Cl}} 3\,NH_4Cl_{\,(solution)} \qquad \text{(Scheme B)}$$

Table 1. Definition of the kinetic/chemical symbols used in Eqs. 1-20

R	Universal Gas constant (J mol^{-1} K^{-1})
H_{NH_3}	Phase distribution coefficient or Henry's Law constant of ammonia (Pa·m^3/mol)
N_{NH_3}	Ammonia Flux (mol·m^{-2}·s^{-1})
p_{NH_3}	Partial pressure of ammonia (Pa)
C_{NH_3}	Concentration of ammonia in bulk liquid (mol·m^{-3})
C_{TATB}	Concentration of TATB in bulk liquid (mol·m^{-3})
C_{TCTNB}	Concentration of TCTNB in bulk liquid (mol·m^{-3})
ΔC_{TATB}	Supersaturation for TATB (mol·m^{-3})
ΔC_{NH4Cl}	Supersaturation for ammonium chloride (mol·m^{-3})
$k_{NH_3}^g$	Mass transfer coefficient for ammonia in the gas film (mol·m^{-2}·Pa^{-1}·s^{-1})
$k_{NH_3}^l$	Mass transfer coefficient for ammonia in the liquid film (m^3 liquid·m^{-2}surface)
k_{TCTNB}^l	Mass transfer coefficient for TCTNB in the liquid film (m^3 liquid·m^{-2}surface)
$p_{NH_3}^i$	Partial pressure of NH$_3$ gas in equilibrium with $C_{NH_3}^i$ in the liquid; $p_{NH_3}^i = H_{NH_3}C_{NH_3}^i$
$\mathfrak{D}_{NH_3}^l$	Molecular diffusion coefficient (m^2·s^{-1}) of ammonia in the liquid phase
$\mathfrak{D}_{TCTNB}^l$	Molecular diffusion coefficient (m^2·s^{-1}) of TCTNB in the liquid phase
r_{NH_3}	Rate of reaction of ammonia (mol·m^{-2}(surface)·s^{-1})
r_{TCTNB}	Rate of reaction of TCTNB (mol·m^{-2}(surface)·s^{-1})
r_{TATB}	Rate of generation of TATB (mol·m^{-2}(surface)·s^{-1})
j_{TATB}	Primary nucleation rate of TATB (no. (kg solvents)$^{-1}$)
J_{TATB}^0	Constant for primary nucleation rate of TATB
n_{TATB}	Exponent for primary nucleation rate of TATB
j_{NH_4Cl}	Primary nucleation rate of ammonium chloride (no. (kg solvents)$^{-1}$)
$J_{NH_4Cl}^0$	Constant for primary nucleation rate of ammonium chloride
n_{NH_4Cl}	Exponent for primary nucleation rate of ammonium chloride
G_{TATB}	Overall linear crystal growth rate of TATB (m·s^{-1})
G_{TATB}^0	Constant for crystal growth rate of TATB
g_{TATB}	Exponent for primary growth rate of TATB
G_{NH_4Cl}	Overall linear crystal growth rate of ammonium chloride (m·s^{-1})
$G_{NH_4Cl}^0$	Constant for crystal growth rate of ammonium chloride
g_{NH_4Cl}	Exponent for primary growth rate of ammonium chloride
$\Delta H_{NH_3}^{avg}$	Averaged enthalpy of vaporization of ammonia for the selected temperature range (J·mol^{-1})

We have derived an equation for the ammonia flux consumed in the amination reaction (A) and the neutralization reaction (B) based on Two-Film Mass-Transfer (TFMT) theory [26-29]. According to the TFMT theory, there exists a stagnant ammonia gas film on one side of the gas-liquid interface and a stagnant liquid film on the other side, as depicted in Figure 3. The interface shown is real, but the two films are imaginary (dashed lines) [26]. In this model, the following two assumptions are made:

(i) It is a steady-state model, *i.e.* the indicated concentration profiles inside the films are established instantaneously, and remain unchanged (for a given agitation rate).

(ii) There is a steady-state transport of ammonia and TCTNB through the

stagnant gas film and liquid film respectively, and they are essentially driven by molecular diffusion and hence, characterized by the molecular diffusivity $\mathfrak{D}_{NH_3}$ and $\mathfrak{D}_{TCTNB}$, respectively.
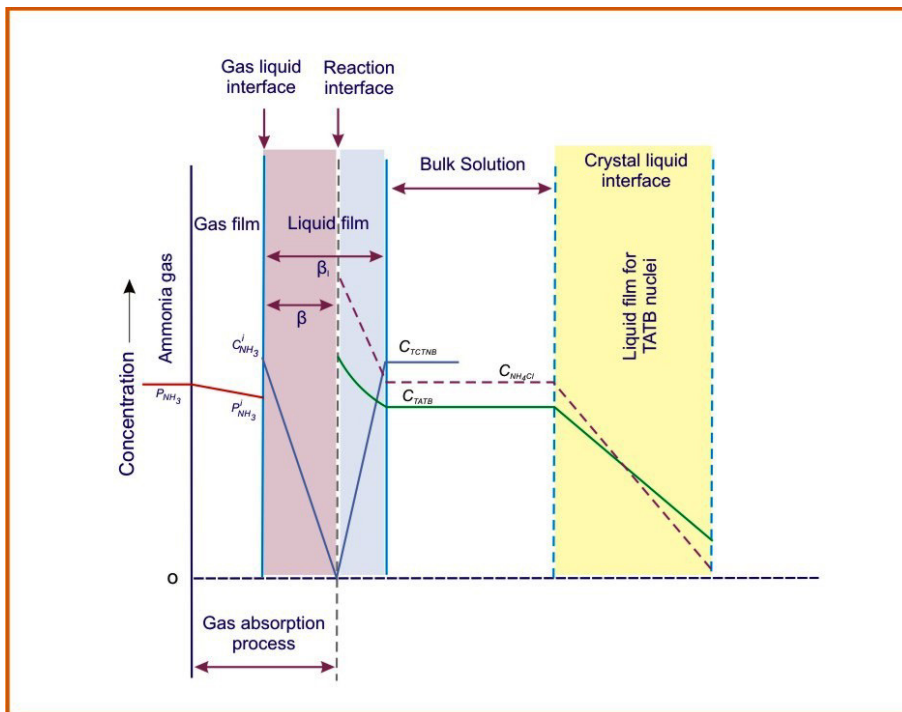
Figure 3.   The conceptual model for the amination reaction based on Two-Film Mass-Transfer (TFMT) theory.

As we can see, there are two resistances in the series for mass transfer, viz., the gas film, and the liquid film. Thus, the mass transfer of ammonia from gas to liquid can be defined by two separate rate expressions, one for the gas film (Eq. 1), and the other for the liquid film (Eq. 2). (Hereafter all symbols used for deriving the kinetic equations are defined in Table 1.).

$$N_{NH_{3\,g}} = k_{NH_3^g}\left(p_{NH_3} - p_{NH_3^i}\right) \qquad (1)$$

$$N_{NH_{3\,l}} = k_{NH_3^l}\left(C_{NH_3^i} - C_{NH_3}\right) \qquad (2)$$

Similarly for TCTNB, we have defined (Eq. 3):

$$N_{TCTNB_l} = k_{TCTNB^l}\left(C_{TCTNB} - C_{TCTNB^i}\right) \tag{3}$$

The reaction between ammonia and TCTNB is instantaneous with respect to mass transfer, and therefore the concentrations of ammonia and TCTNB both become zero at the reaction "plane" (Figure 3) [26-29, 33]. Thus, the entire process becomes mass-transfer controlled. Ammonia gas diffuses to the reaction plane from the bulk gas, first through the gas film and then through the portion of the liquid film of thickness (βl), and TCTNB diffuses from the bulk liquid through the remaining portion of the liquid film of thickness ($\beta l - \beta$). At steady state, the fluxes of NH_3 in the gas and liquid films are equal. At the interface, the relationship between $p_{NH_3^i}$, and $C_{NH_3^i}$ is given by the distribution coefficient, called Henry's Law constant (H_{NH_3}) applicable for dilute gas-liquid systems (Eq. 4):

$$p_{NH_3^i} = H_{NH_3} \cdot C_{NH_3^i} \tag{4}$$

As defined in reaction Scheme A, the consumption rate of ammonia and TCTNB are stoichiometrically related as shown in (Eq. 5), *i.e.* one mole TCTNB consumes 3 mole NH_3.

$$N_{NH_3(A)} = 3N_{TCTNB_l} \tag{5}$$

Thus, we have a rate expression ($r_{NH3}(A)$, Eq. 6) for the reaction between ammonia and TCTNB as shown in Scheme A.

$$r_{NH3(A)} = N_{NH_3(A)} = k_{NH_3^g}\left(p_{NH_3} - p_{NH_3^i}\right) = k_{NH_3^l}\left(C_{NH_3^i} - 0\right)\frac{\beta_l}{\beta}$$

$$= 3k_{TCTNB^l}(C_{TCTNB} - 0)\frac{\beta_l}{\beta_l - \beta} \tag{6}$$

The relation between the liquid-phase diffusivities and the mass-transfer coefficients is defined by Eq. 7:

$$\sqrt{\frac{\mathfrak{D}_{NH_3}}{\mathfrak{D}_{TCTNB}}} = \frac{k_{NH_3^l}}{k_{TCTNB^l}} \tag{7}$$

Solving Eqs. (1) to (7) for ammonia consumption, we obtain Eq. 8:

$$r_{NH_{3(A)}} = N_{NH_{3(A)}} = \cfrac{3\,C_{TCTNB}\sqrt{\cfrac{\mathcal{D}_{NH_3}}{\mathcal{D}_{TCTNB}} + \cfrac{p_{NH_3}}{H_{NH_3}}}}{\cfrac{1}{H_{NH_3}\cdot k_{NH_3}^g} + \cfrac{1}{k_{NH_3}^l}} \tag{8}$$

Ammonia is sparingly soluble in toluene and hence the gas-side mass transfer coefficient will always be much greater than the liquid side mass transfer coefficient. In that case $\dfrac{1}{H_{NH_3}\cdot k_{NH_3}^g} \approx 0$. According to the stoichiometry of reaction Scheme A, 3 moles of ammonia are consumed for the production of one mole of TATB. Thus Eq. 8 reduces to Eq. 9:

$$r_{NH_{3(A)}} = 3\,r_{TATB} = N_{NH_{3(A)}} = k_{NH_3^l}\left(3\,C_{TCTNB}\sqrt{\frac{\mathcal{D}_{NH_3}}{\mathcal{D}_{TCTNB}} + \frac{p_{NH_3}}{H_{NH_3}}}\right) \tag{9}$$

HCl neutralization by ammonia gas (Scheme B) is essentially an instantaneous inorganic reaction, *i.e.* one mole of ammonium chloride is produced as soon as HCl is formed (by reaction of TCTNB with one mole of ammonia).

As $k_{NH_3^l} \ll K_{TATB} \lll K_{NH4Cl}$, we can make the valid assumption (Eq. 10) from the reaction stoichiometry:

$$r_{NH4Cl} = 3.r_{TATB} \tag{10}$$

Also, in reaction (B), ammonia is consumed at the mole ratio of 1:1, and hence:

$$r_{NH_{3(B)}} = r_{NH4Cl} = 3\cdot r_{TATB} \tag{11}$$

Thus we have the net consumption of ammonia by the two reactions as:

$$N_{NH_3} = N_{NH_{3(A)}} + N_{NH_{3(B)}} \tag{12}$$

or

$$r_{NH_3} = N_{NH_3} = r_{NH_{3(A)}} + r_{NH_{3(B)}} \tag{13}$$

Thus:

$$r_{NH_3} = N_{NH_3} = 2 \cdot k_{NH_3^l} \left(3 \cdot C_{TCTNB} \sqrt{\frac{\mathfrak{D}_{NH_3^l}}{\mathfrak{D}_{TCTNB^l}}} + \frac{p_{NH_3}}{H_{NH_3}} \right) \qquad (14)$$

5 Crystallization kinetics

The process of crystal formation involves two important steps, viz. nucleation *i.e.* the formation of tiny crystals, and crystal growth. Generally, secondary nucleation is considered insignificant for a reactive crystallization process [34, 35]. As already mentioned, TATB and NH$_4$Cl have very poor solubility in toluene. Hence the supersaturation level (ΔC) for the precipitation process is very high. Thus, primary nucleation predominates over secondary nucleation. Moreover, this reactive crystallization system is considered to be an isothermal one, and hence the heat effect of the crystallization is normally negligible.

There are various expressions available to mathematically represent the primary nucleation process. However, we have defined a simple empirical relationship which is generally used to express primary nucleation for an industrial crystallization process [34, 35]. The primary nucleation rates for TATB and NH$_4$Cl are shown in Eqs. 15 and 16 respectively, which relate the primary nucleation rate (j) to the supersaturation (ΔC), the primary nucleation rate constant (j^0), and the order of the nucleation process (n).

$$j_{TATB} = j_{TATB}^0 (\Delta C_{TATB})^{n_{TATB}} \qquad (15)$$
$$j_{NH4Cl} = j_{NH4Cl}^0 (\Delta C_{NH4Cl})^{n_{NH4Cl}} \qquad (16)$$

Similarly, the crystal growth rates are also expressed as Eqs. 17 and 18, respectively:

$$G_{TATB} = G_{TATB}^0 (\Delta C_{TATB})^{g_{TATB}} \qquad (17)$$

$$G_{NH4Cl} = G_{NH4Cl}^0 (\Delta C_{NH4Cl})^{g_{NH4Cl}} \qquad (18)$$

6 Results and Discussion

6.1 Effect of temperature
The reaction temperature plays an important role on product quality (particle size and colour). The reaction was found to be feasible even at room temperature, and

fine particles (< 20 μm) were formed. It has been observed experimentally that higher temperatures give coarser particles. A good quality, yellow coloured TATB is obtained up to a reaction temperature of 125 °C. At temperatures > 130 °C, a reddish-yellow coloured TATB was obtained. The DSC profile of reddish-yellow TATB (double decomposition peak) is different from yellow TATB (single decomposition peak in the DSC analysis). This may be due to either degradation of the product or base hydrolysis of TCTNB/TATB, leading to the formation of 1,3,5-trinitro-2,4,6-trihydroxybenzene (trinitrophloroglucinol) [21-24, 30]. Hence, it is necessary to maintain the reaction temperature at ~125 °C. The amination reaction was found to be mildly exothermic, and hence it was found possible to keep the reaction temperature at ~125 °C during amination (with ammonia being fed at a constant rate) without the supply of any external heat.

At a given ammonia flux, an increase in reactor pressure was observed during experiments at higher temperatures (125 °C). This is mainly due to two factors viz. an increase in the vapour pressure of toluene and accumulation of ammonia gas in the reactor head space. As defined in Eq. 14, the consumption rate of ammonia (N_{NH_3}) is related to three mass transfer related factors viz. the mass transfer co-efficient for ammonia ($k_{NH_3}^l$), the Henry's Law constant (H_{NH_3}) and the partial pressure of ammonia in the vapour phase (p_{NH_3}). $k_{NH_3}^l$ and H_{NH_3} are temperature dependent coefficients, whereas p_{NH_3} is decreased at higher temperatures (due to an increase in the vapour pressure of toluene at a given reactor pressure). Generally, the liquid-side mass transfer coefficient varies according to the square root of temperature, *i.e.* $k_{NH_3}^l \propto \sqrt{T}$, and hence temperature has a moderate positive effect on $k_{NH_3}^l$. However, Henry's Law coefficient is strongly dependent on temperature (Eq. 19) [36]:

$$H_{NH_3}^T = H_{NH_3}^{T_0} \exp\left[A\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \tag{19}$$

where T_0 = 293 K

$$A = \frac{\Delta H_{NH_3}^{avg}}{R} \tag{20}$$

Thus, $k_{NH_3}^l$ is affected less than H_{NH_3} when the reaction is carried out at higher temperatures. However, an increase in reaction temperature will have a combined effect on the rate of mass transfer of ammonia (N_{NH_3}) into toluene according to Eq. 14. Considering the temperature dependent factors discussed above, one can logically conclude that N_{NH_3} will be reduced at higher temperatures. Thus,

we found it difficult to perform experiments at elevated temperatures by keeping both the feed rate, *i.e.* ammonia flux (N_{NH_3}), and the reactor pressure (*e.g.* 4 bar, the upper limit of the designed pilot plant reactor) unchanged. This is due to the decrease in mass transfer rate. Hence, we had to adjust the feed rate, *i.e.* ammonia flux (at a lower level), to perform experiments at elevated temperatures under a given reactor pressure (4 bar).

At a lower level of ammonia flux N_{NH_3}, the production rate of TATB is decreased, as is the crystallization rate. Also, at higher temperatures, the solubility of TATB is increased [15]. Thus, at elevated temperatures, the supersaturation level (ΔC_{TATB}) is decreased due to the lower production rate and the higher solubility of TATB in toluene. These two factors will reduce both the nucleation and crystal growth rates. However, the nucleation rate will be more affected than the crystal growth rate (as n > g) [34-38]. A slower nucleation rate favours the formation of coarse grained TATB. Moreover, the higher solubility of TATB at elevated temperatures may broaden the metastable zone (MSZ) width of the TATB crystallization process, resulting in a slower nucleation rate and a higher crystal growth rate.

6.2 Effect of water

TCTNB is prone to undergo a hydrolysis reaction in the presence of base (-OH) [21-24]. Thus, it was envisaged that the presence of water in toluene (NH₄OH will be formed with ammonia) will cause the product purity to deteriorate and thereby the process yield. However, the weak base NH₄OH does not cause any harm to the process under moderate reaction temperatures (< 130 °C). On the contrary, it improves the product quality (particle size and chloride content).

It has been observed experimentally that dry amination gives finer particles (< 20 µm) with a high chloride content (>1.5%). The presence of a small percentage of water in toluene (~5%) improves the particle size (> 50 µm) and also reduces the chloride content (< 0.5%). The SEM photographs of dry aminated and wet aminated TATB are shown in Figure 4. TATB is co-precipitated with by-product NH₄Cl, which is then removed from the crude product during water digestion, leaving a porous structure on the crystal surface. The effect of water on product quality is shown in Figure 5.
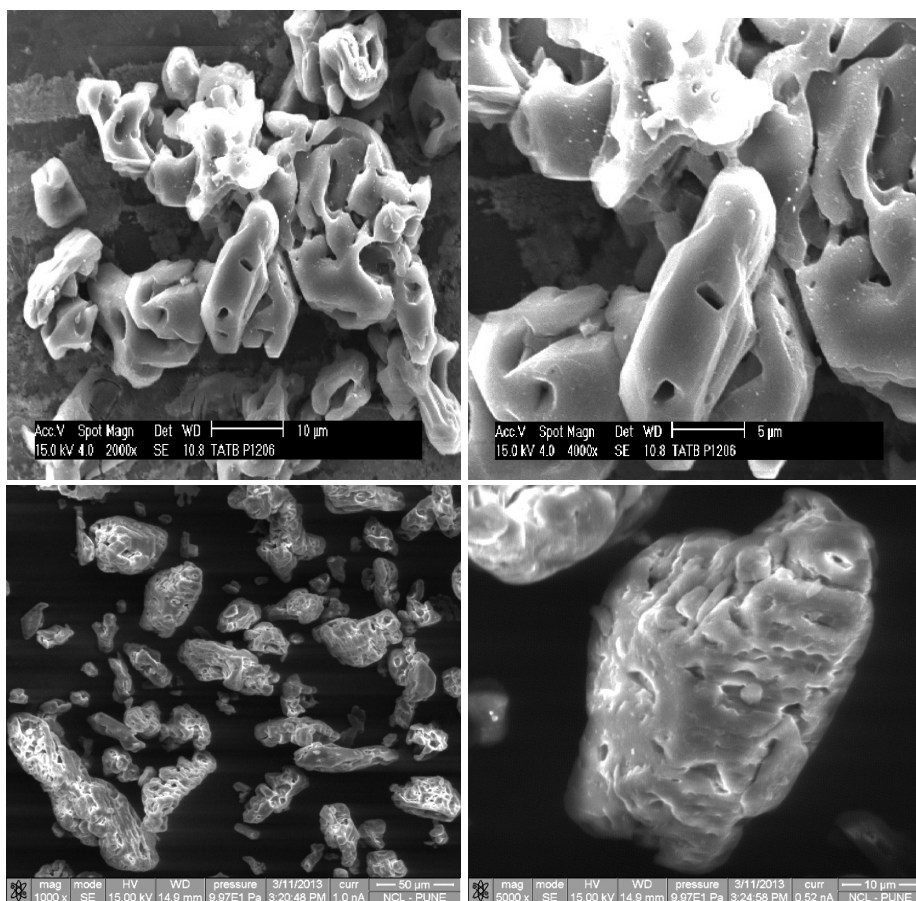
Figure 4.   SEM photographs of (a) dry aminated and (b) wet aminated TATB
              (5% water in toluene).

As already mentioned, the product TATB and the by-product NH_4Cl are
crystallized out (co-precipitated) simultaneously, resulting in the formation of
crude TATB with high chloride content (~24%) [11]. The chloride impurity is
largely removed by digesting the crude product in hot water (due to the very
high solubility of NH_4Cl in water) [7-10, 11]. However, crude TATB contains
a certain percentage of ammonium chloride (< 1%) which is occluded into the
TATB crystal lattice. This occluded chloride does not get removed by digestion
of the crude product in water [30].
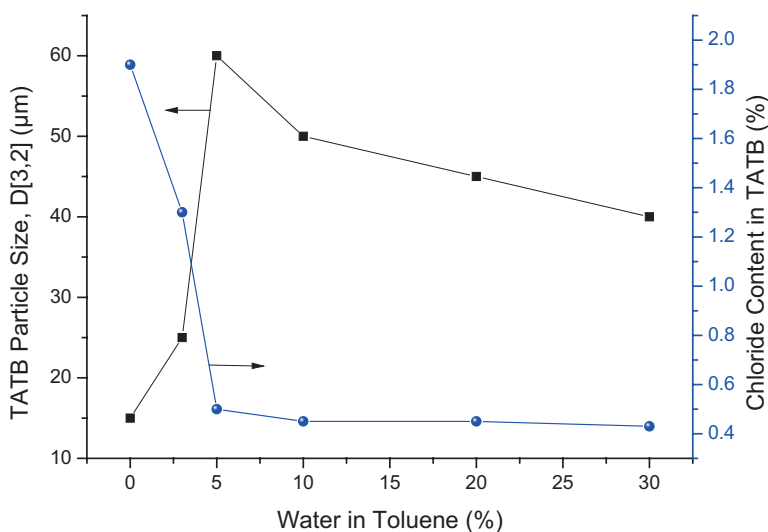
Figure 5. Effect of water on the particle size and chloride content in TATB. *(Other process conditions: TCTNB conc. in toluene: 0.262 mol/L; NH₃ flux: 0.03 mol·m⁻²·s⁻¹; reaction temp. 125 °C; stirrer: 200 rpm).*

TATB is an organic material whereas NH$_4$Cl is an inorganic material. Accordingly, they are expected to crystallize at different rates. The nucleation and crystal growth rates are defined in Eqs. 15-18. J^0_{NH4Cl} and G^0_{NH4Cl} are expected to be much higher than those of TATB due to the inorganic nature of the ammonium chloride crystals. Moreover, 3 molecules of NH$_4$Cl are produced with the formation of a single TATB molecule. Hence, at a given time, there will be a greater number of NH$_4$Cl nuclei (tiny crystals) compared to those of TATB. For an ideal case, the growth will take place on their respective nuclei, *i.e.* NH$_4$Cl and TATB will grow on their own nuclei. However, due to the high population density of NH$_4$Cl nuclei, TATB will grow indiscriminately on both NH$_4$Cl and TATB nuclei. Thus, the effective nucleation rate for TATB will be higher, resulting in the formation of fine particles of TATB having occluded ammonium chloride. The formation of a greater number of NH$_4$Cl occluded TATB crystals generates a higher percentage of chloride content in the product (> 1.5%).

The presence of a small percentage (~ 5%) of water in toluene deliquesces the NH$_4$Cl nuclei (since it is highly soluble in water), and converts it to a semi-solid consistency, which may not be capable of serving as a nucleation centre for TATB crystal growth. Thus, the effective supersaturation level and hence the nucleation rate for NH$_4$Cl will be lower compared to that which occurs in

the absence of water. As a result, TATB will grow on its own nuclei, which will result in a slower nucleation rate, better crystal growth, and the formation of TATB with less occluded NH_4Cl. Thus, the presence of water makes a noticeable improvement in the product quality (Figure 5). However, we do not find a significant effect of water when it is used in more than 5%. In fact, the particle size is marginally diminished at higher water content. As mentioned above, the process is essentially mass transfer controlled which is described by the TFMT theory. As pointed out earlier, ammonia is sparingly soluble in toluene, which results in a higher liquid-side mass transfer resistance. Due to an increase in the percentage of water in toluene, the solubility of ammonia in the liquid will increase (water has a higher affinity for NH_3), and hence, the liquid-side mass transfer resistance will be decreased, resulting into a higher mass transfer rate of ammonia. Thus, the mass transfer controlled regime (as described in the TFMT model) becomes disturbed due to the presence of higher percentages of water (>20%). Under these conditions, NH_3 gas may be initially absorbed by the water, and then the chemical reaction may proceed by mass transfer of NH_3 through the water-toluene interface instead of the gas-liquid interface. Thus, the production rate may be increased resulting in a marginally lower particle size.

After realizing the very positive effect of water on the product quality, we have focused on performing the remaining process development using 5% water in toluene.

6.3 Effect of ammonia flux

As shown in the reactions of Scheme 3, one mole of TCTNB consumes 6 moles of NH_3, and produces one mole of TATB and 3 moles of NH_4Cl. As described above, the reaction is mass transfer controlled, and the reaction rate is controlled by N_{NH_3} *i.e.* NH_3 flux. We have studied the effect of the ammonia flux on the particle size of the product (Figure 6) at a reaction temperature of 125 °C and have observed the formation of higher particle sizes at lower NH_3 fluxes. The NH_3 flux controls the reaction rate (Eq. 14), as both of the chemical reactions (both TCTNB amination and HCl neutralization) are very fast, *i.e.* instantaneous. The higher reaction rate results in a higher degree of supersaturation (ΔC_{TATB}), which in turn leads to a higher nucleation rate compared to growth rate (as $n > p$), and hence it produces finer particles. It may be noted that a lower value of N_{NH_3} increases the batch time, which is one of the undesirable aspects of a chemical process. Hence, we decided to maintain an acceptable ammonia flux (N_{NH_3} ~ 0.03 mol·m^{-2}·s^{-1}) for our pilot plant process.

As it is a single-feed, semi-batch process, at a constant feed rate N_{NH_3}, the bulk concentration of TCTNB in toluene will gradually decrease due to

its consumption. Some authors [39, 40] have suggested a general protocol of feeding, for a reactive crystallization process, by introducing cubic feeding (programmed feeding) to minimize the nucleation rate, and to encourage crystal growth (onto seed crystals formed in the initial reaction period), *i.e.* secondary crystallization. We have also explored this concept in the present case. The required quantity of ammonia gas was fed incrementally at a variable rate, keeping the average NH_3 flux unchanged. However, no significant positive effect was observed on the average particle size. This indicates that secondary crystallizationis less important in this reaction crystallization process. This may be due to the poor solubility of TATB in toluene leading to a high degree of supersaturation as the reaction progresses.
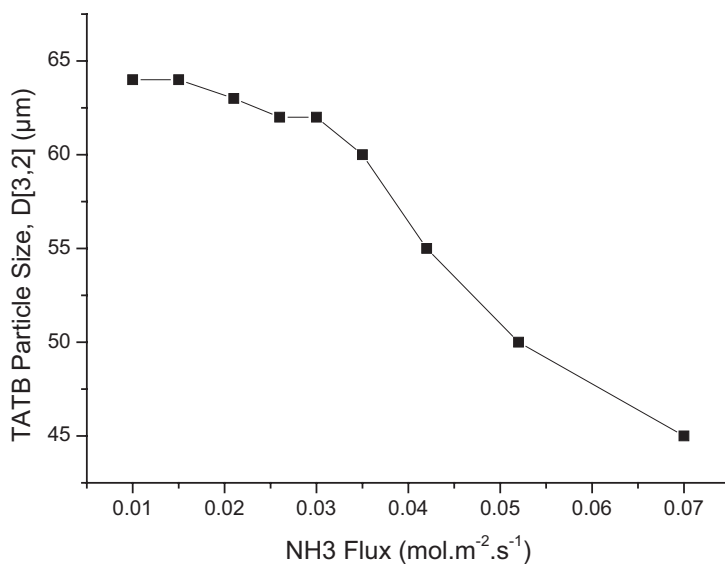
Figure 6. Effect of NH_3 flux on the particle size of TATB. (*Other process conditions: 5% water in toluene; TCTNB conc. in toluene: 0.262 mol/L; reaction temp. 125 °C; stirrer: 200 rpm*).

6.4 Effect of mixing

Mixing plays an important role for any reactive crystallization process [41]. Both macromixing and micromixing will affect the reaction rate and the crystallization rate, and hence they have an influence on the particle size of the product. High rates of agitation (vigorous mixing) will break the crystals resulting in the formation of fine particles of TATB. However, a certain level of agitation is also necessary to keep the crystals in suspension for the necessary crystal growth.

An agitation of 100-300 rpm (tip speed 6-20 m/s) did not show much difference in particle size (55-60 μm). Hence, it was recommended to keep the tip speed between 6-20 m/s in the pilot plant process. A lower or higher tip speed resulted in decreased particle size (minor effect).

6.5 Effect of mercaptan impurities present in toluene

Sometimes mercaptan/H_2S was found to be present in poor quality toluene (confirmed by the Doctor's test) [42]. The use of this poor quality toluene will lead to the formation of grey/coffee coloured TATB (TATB is a yellow coloured, powdery material). TCTNB is susceptible to nucleophilic attack, and hence the mercaptans/H_2S present in the toluene may immediately react with TCTNB, and form a dark brown coloured, soluble product (Scheme 4). This dark brown coloured impurity when mixed with the yellow TATB results in discolouration of the product. The presence of mercaptans/H_2S in toluene may be analyzed by the Doctor's test. However, it may also be tested for by TCTNB itself. The crude TCTNB is dissolved in the toluene sample (obtained from the lot to be used for the amination process) in a test tube, and kept for 0.5 h to observe the change in colour (if any). If the solution becomes brown, the toluene contains free mercaptans/H_2S, and hence it cannot be used for the amination process.
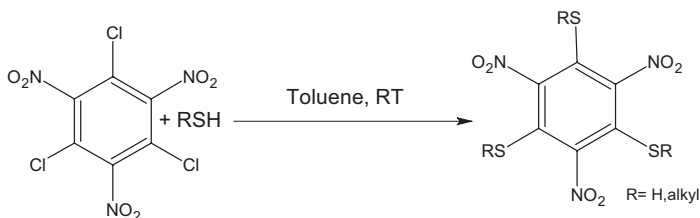

Scheme 4. Reaction of a marcaptan with TCTNB

6.6 Effect of excess ammonia (formation of a sensitive impurity in TATB)

The nitration of *sym*-TCB (starting material) gives an intermediate crude TCTNB which contains two significant impurities, 1,2,3,5-tetrachloro-4,6-dinitrobenzene (T_4, 7-9%) and 1,3,5-trichloro-2,4-dinitrobenzene (T_3, 2-3%). The reaction mechanism which leads to the formation of these two impurities in the nitration process is well reported in the literature [6, 11, 43] and hence is not discussed here. These impurities are not reactive towards the weak nucleophile ammonia (the −R effect of two nitro groups does not activate the aromatic ring sufficiently for nucleophillic attack), and hence the crude precursor can be used in the amination process without further purification. However, if excess ammonia is fed into the system, NH_3 reacts with T_4, and the product 1,3,5-triamino-2-chloro-4,6-

dinitrobenzene (TACDNB) is formed (Scheme 5) and is precipitated out due to its poor solubility in toluene. Only the Cl groups which are in the o- and p- positions with respect to a NO_2 group are replaced as the nitro group directs to the o- and p- positions for nucleophilic attack. The chlorine at the meta position remains unchanged. T_3 also reacts with excess ammonia and forms 1,3,5-triamino-2,4-dinitrobenzene (TADNB). However, TADNB has good solubility in toluene and hence does not precipitate out like TACDNB
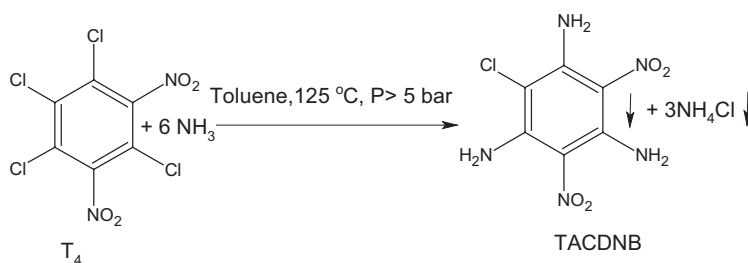
Scheme 5. Formation of the sensitive impurity TACDNB in the TATB process.

TACDNB is an orange-red coloured, visible impurity (larger particles), distinctly different from the yellow coloured TATB. TACDNB affects the product sensitivity towards impact and hence is an undesirable impurity in TATB [13].

6.7 Demonstration of the process in the pilot plant

The optimized process conditions have been established based on the study discussed above (Table 2). These conditions were implemented in the pilot plant (Figure 2). Ammonia gas was fed in at the top of the reactor, and no sparger was used. This feeding arrangement forced the reaction to take place at the gas liquid interface which is available to gaseous ammonia throughout the cross sectional area of the reactor. The results of the pilot plant batches are shown in Table 3. The process yield and the product quality (purity, chloride content and particle size) were found to be consistent and matched the laboratory scale data. The particle size distribution and the DSC profile of a typical production batch sample are shown in Figures 7 and 8, respectively. The height for 50% explosion (by impact with 2.0 kg drop-weight) for a pilot plant batch sample was 155-170 cm, and it was found to be insensitive to friction up to 36 kg.

**Table 2.** Optimised process conditions for the amination process

Process conditions	Parameters
Temperature (°C)	125
Pressure (bar)	4
Water in toluene (%)	5
TCTNB concentration in toluene (moles/L)	0.262
NH$_3$/TCTNB ratio (molar)	6:1
NH$_3$ flux (mol·m^{-2}·s^{-1})	0.03

Table 3. Results of the TCTNB amination process (pilot plant batches)

Batch No.	Yield (%)	Product characteristics			
		Purity (%)	Cl$^-$ Content (%)	DSC (T$_{max}$, °C)	Particle Size (D [3,2], µm)
1	88.2	98.5	0.47	384.5	54.3
2	87.6	98.7	0.48	383.9	55.4
3	87.9	99.0	0.42	382.7	57.1

TCTNB 15 kg; Toluene 180 L; Water 9 L; NH$_3$ 5 kg; Reaction temperature 125 °C; NH$_3$ flux 0.03 mol·m^{-2}·s^{-1}; Crude TCTNB used (purity = 89%); NH$_3$/TCTNB molar ratio 6:1.
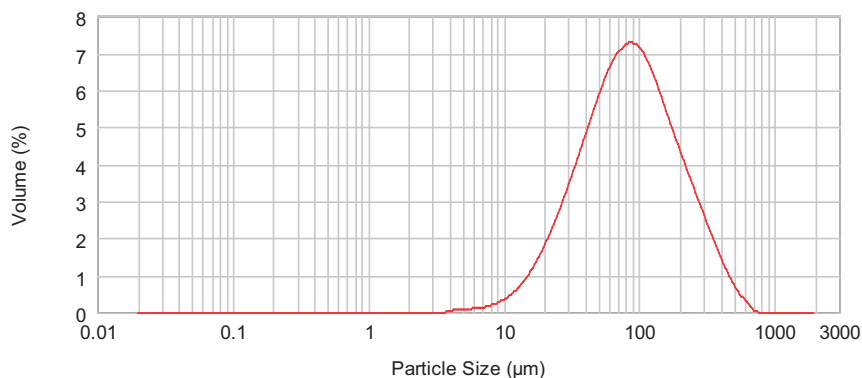
Figure 7. Typical particle size distribution of TATB (pilot plant batch sample).
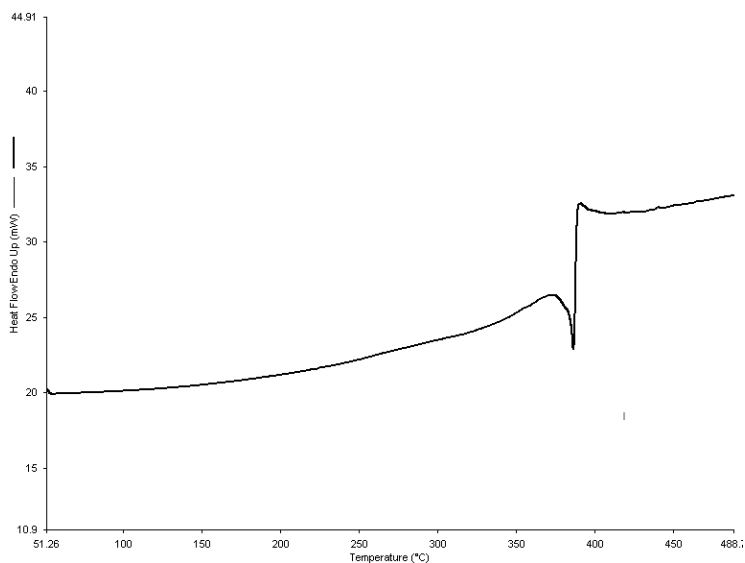
Figure 8. Typical DSC profile of TATB (pilot plant batch sample).

As already discussed, the reactivity of the intermediate TCTNB with ammonia gas is higher than that of T_4 and T_3. Hence, in a competitive environment, TCTNB becomes aminated first. In the pilot plant process, the ammonia gas was fed into the reactor at a constant rate from a cylinder and the reactor pressure was maintained at 4 bar. Towards the completion of the reaction, *i.e.* after the consumption of all TCTNB, a slow rise in reactor pressure (> 4 bar) was observed due to the accumulation of unreacted ammonia gas in the reaction vessel. The formation of TACDNB takes place during this period. Accordingly, in the pilot plant process, the ammonia feed rate was controlled towards the end of the reaction, not allowing the reactor pressure to exceed 5 bar, conditions which would favour the formation of TACDNB.

Table 4. Analysis of TATB samples obtained from the laboratory and pilot plant scale processes

Parameters	Passing standard in the product specification	Laboratory scale sample	Pilot plant sample
Purity (%)	98.0 (min.)	98.5	98.4
Cl⁻ content (%)	1.0 (max.)	0.45	0.47
DSC exotherm ($T_{max.}$/°C)	380 (min.)	382	383
Average particle size (D[3,2] /µm)	50 (min.)	55	62

TATB has been synthesised under optimum process conditions both in the laboratory and at pilot plant scale. The product has been analysed as per the specification [44]. A comparative study has been made on the product quality (Table 4). The pilot plant batches gave a marginally higher particle size and the reproducibility was also better. This may be due to better control of the ammonia flux in the pilot scale reactor. However, there was no difference in the other properties of the product, *e.g.* purity, Cl⁻ content and DSC profile.

7 Conclusions

Amination of TCTNB is an isothermal, single-feed, semi-batch, gas-liquid heterogeneous, reaction crystallization process. The chemical reaction and crystallization occur simultaneously in this process. A conceptualized reaction model based on Two-Film Mass-Transfer (TFMT) theory gave a single kinetic expression which is capable of defining the chemical reactions and physical phenomenon (mass transfer) associated with this process. The influence of the process parameters on the product quality (particle size and chloride content) has been explained by the developed reaction model. The process has been established at the pilot plant scale (10 kg TATB/batch) with optimised process conditions. Consistency in the product quality (particle size ~60 μm and chloride content ~0.5%) was observed.

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