TOLUENEDIAMINE

1. Introduction

Toluenediamine (diaminotoluene, *m*-TDA) is an important industrial chemical intermediate; it is produced in the largest volume of any arylamine and is the lowest priced diamine (1). Worldwide production in 2004 was estimated at 1.4×10^{-6} metric tons ; the United States accounts for $\sim 40\%$ of the volume. The TDA producers in the United States include Air Products and Chemicals (merchant only), Bayer-AG, BASF AG, Lyondell Corporation, and Rubicon Corporation. The principal use for TDA is in the manufacture of toluenediisocyanate (TDI), the predominent diisocyanate in the flexible foams and elastomers industries. Reaction with phosgene converts TDA to TDI, which undergoes reaction with a polyol to give the corresponding polyurethane. The isomer *o*-toluenediamine is also produced in commercial quantities in the United States and is supplied for producing tolytriazoles and polyols. Available volume of *o*-TDA is limited by the isomer distribution of the precursor nitration reaction.

2. Physical Properties

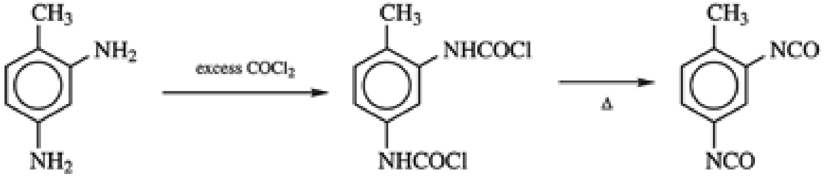
Although all six possible toluenediamine isomers are made in the commercial synthesis, only two products are available commercially. The properties of the individual isomers are summarized in Table 1. Specifications for the commercial products, named by the relative position of the predominant groups, along with some physical properties, are shown in Table 2.

3. Reactions

The aromatic toluenediamines undergo typical amine reactions. The general chemistry is similar to that of the phenylenediamines or the cyclohexanediamines except that the aromatic diamine is a weaker base than its cycloaliphatic counterpart. Only reactions of industrial importance particular to commercial toluenediamines are discussed below.

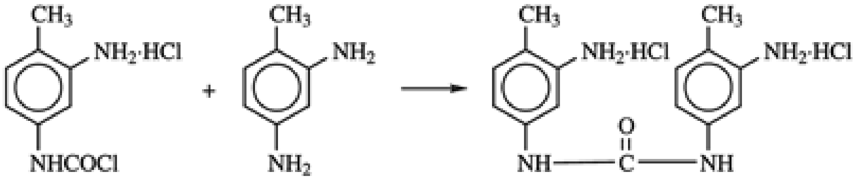
3.1. Phosgenation.

The most important reaction of *m*-toluenediamine is with phosgene [75-44-5] to give toluene diisocyanate TDI (see ISOCYANATES, ORGANIC).



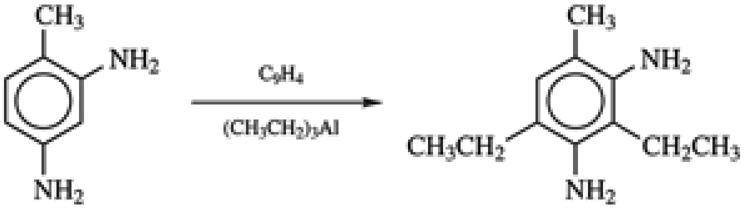
m-TDA dicarbonyl chloride *m*-TDI

To avoid partially phosgenated intermediates and coupling reactions, such as

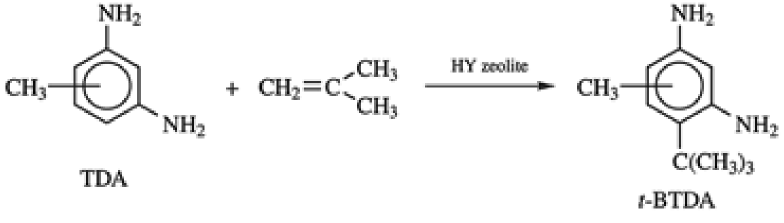


the procedure for making TDI from TDA involves a cold phosgenation in an inert solvent with excess phosgene, followed by heating with excess phosgene. By products are substituted ureas and benzimidazolone formed from ortho-substituted diamines and phosgene. The by-products are tarry dark materials that are difficult to remove and may lead to environmental problems. Therefore, the presence of ortho diamine results in lower yield in the manufacture of TDI and a very objectionable impurity in the final product.

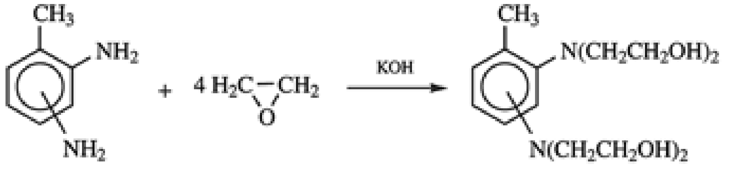
3.2. Ring Alkylation. Ortho alkylation of TDA has taken on increasing commercial importance. Ortho ethylation, the first commercial process, is carried out (5-9) using an alkyl aluminum halide or an aluminum anilide. The alkylation rate decreases for higher alkenes (1).



Acid catalysis using strong acid catalysts, especially zeolites that enhance selectivity because of pore size restrictions, has been used for a variety of alkenes and dienes (10-13).

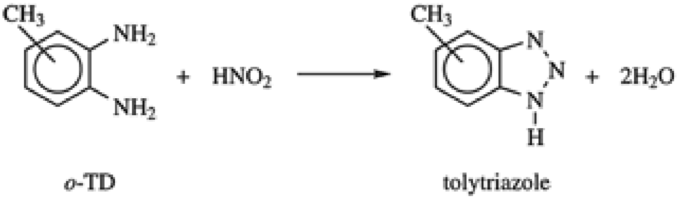


3.3. Alkoxylation. Ethoxylation of toluenediamines proceeds easily. Typical conditions are 90−120°C at pressures up to 500 kPa (72.5 psi) using a basic catalyst, eg, potassium hydroxide (14).



Many specific reaction conditions using other alkylene oxides (15) or combinations of alkylene oxides (16) may be found in the patent literature.

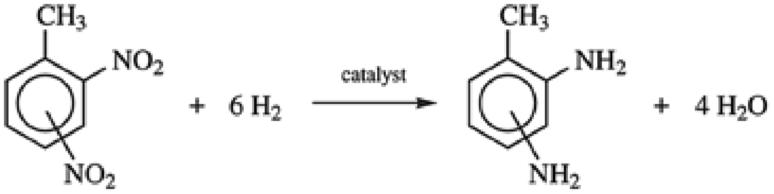
3.4. Diazotization. The general reactions of *o*-diamines with an alkali nitrite and an acid with subsequent ring closure are well known.



Several process improvements using aqueous solution at elevated temperatures (350°C) and pressure (17) or using an organic solvent and an acid at milder temperatures (<80°C) have been described for *o*-TD (18).

4. Manufacture

Dinitrotoluenes can be catalytically hydrogenated to toluenediamines under a wide variety of temperatures, pressures, and solvents; the catalyst can be supported noble metal, eg, Pd/ C or nickel, either supported or Raney type. The reduction requires 6 mol of hydrogen per mole of DNT and produces 4 mol of H_2O.



Since nitroarenes are reported to be catalyst poisons (19), the concentration of DNT in the reaction medium is kept as low as is practical with regard to production goals and catalyst usage. The mechanism for catalytic hydrogenation of nitro compounds has been the subject of many investigations and there is much evidence that this reaction proceeds through several intermediate species. The most widely accepted mechanism for the hydrogenation of nitro compounds was proposed by Haber in 1898 (20). Haber based this mechanism on the electrochemical reduction of nitrobenzene, but it has since been used by many researchers to explain the results of hydrogenation studies.

Recent studies of the hydrogenation of 2,4-dinitrotoluene over both Ni (21) and Pd (22) catalysts, built on the research of Neri (23-25) and Janssen (26,27), have borne out the proposed mechanism. In all of the abovementioned work, Langmuir-Hinshelwood type rate expressions were used to model the reaction, which resulted in excellent fit of the data presented. The latest analysis of the kinetics assume competitive adsorption of both the organic species and hydrogen as the rate-limiting step. It is suggested that a dual site mechanism is appropriate for Pd catalysts, while a single site approach is satisfactory for Ni catalysts. Similar results were found by Kurschner et al. (28), who were able to monitor the progress of the hydrogenation while feeding dinitrotoluene controlled by the electrochemical potential of the catalyst, thereby keeping constant the surface concentration of hydrogen at the catalyst surface.

4.1. Processes. Toluene is nitrated in two stages. Mononitration occurs in mixed acid, 30% HNO_3 and 55% H_2SO_4, at 30–70°C in a series of continuous stirred-tank reactors. Heat is liberated and must be removed. The isomer distribution is ∼ 58% *o*-nitrotoluene, 38% *p*-nitrotoluene, and 4% *m*-nitrotoluene (Fig. 1).

The mononitrotoluenes ($C_7H_7NO_2$) are then nitrated in a second set of continuous reactors with a stronger mixed acid (30% HNO_3 and 63% H_2SO_4) to give dinitrotoluenes ($C_7H_6N_2O_4$): 75.8% 2,4-DNT, 19.5% 2,6-DNT, 0.7% 2,5-DNT, 1.5% 2,3-DNT, and 2.5% 3,4-DNT; the 3,5 isomer is undetectable. In Fig. 1, the ortho isomers, 2,3-DNT and 3,4-DNT, are derived from nitration of *m*-nitrotoluene ; these eventually become undesired by-products in the manufacture of TDI. (see also NITROBENZENE AND NITROTOLUENES) Patents for the catalytic hydrogenation of DNT differ in catalyst, temperature pressure, solvent, and type of reactor. Examples of the main variations in the technology are described in the following.

Hydrogenation with a noble metal catalyst and external filter is described in a series of patents assigned to the Du Pont Company (29-32). The DNT is introduced into a continuous stirred tank reactor with Pd/C catalyst and hydrogen at 550–690 kPa (80–100 psi) at 70–80°C. The DNT content must be kept low (∼ 0.5%) to keep yields high (99%). One part of the product stream is recycled to the reactor to act as the reaction solvent; the remainder is filtered to remove catalyst and then purified. The use of a precious metal catalyst allows mild operating conditions and provides high reaction yield. The high cost of the catalyst requires near perfect catalyst recovery. Energy recovery at the low operating temperatures is difficult.

A process based on a nickel catalyst, either supported or Raney type, is described in Olin Mathieson patents (33,34). The reduction is carried out in a continuous stirred tank reactor with a concentric filter element built into the reactor so that the catalyst remains in the reaction zone. Methanol is used as a solvent. Reaction conditions are 2.4–3.5 MPa (350–500 psi), 120–140°C. Keeping the catalyst inside the reactor increases catalyst lifetime by maintaining a hydrogen atmosphere on its surface at all times and minimizes handling losses. Periodic cleaning of the filter element is required.

Yield for the process at low catalyst loading is 95%. *N*-Methyltoluenediamine, one of the reaction by-products, represents not only a reduction in yield, but also a highly objectionable impurity in the manufacture of toluene diisocyanate. Low concentrations of CO (0.3–6% volume) control this side reaction.

Another nickel catalyzed process is described in a Tolochimie patent (35). Reaction conditions claimed are 1–2.4 MPa (150–350 psi) at 100°C minimum. The combination continuous stirred reactor and gravity decanter uses density-driven circulation between the two vessels to recirculate the catalyst to the reaction zone without the use of filters or pumps. Yield and catalyst usage can be controlled by varying the feed rates.

Bayer AG holds a number of patents (36-39) covering the use of a bubble-tube reactor for carrying out the reduction. DNT along with recycled reactor mixture, solvent, catalyst, and hydrogen are fed upward through a column. A wide variety of catalysts are claimed as suitable, both supported precious metal and Raney metals. Catalyst must be in a finely divided form and is held in suspension by excess hydrogen flow. Reaction pressure is given as between 4 and 20 MPa (600 and 3000 psi) at a temperature of 140–250°C. Several interesting process modifications are claimed in these patents including generation of steam from reactor cooling, and high pressure cross-flow catalyst filtration.

The use of fixed-bed catalysts is described in several patents (40-44). Methods of operation include upflow, trickle bed, and even vapor phase. Typically, a large volume of solvent is used to moderate the temperature rise associated with the high heat of reaction for nitro group reduction. Subsequent separation of this solvent imposes substantial capital and operating cost penalties. A Bayer AG patent (44) claims use of a solvent in which DNT is soluble, but in which the TDA is practically insoluble. This allows separation and recycle of the solvent to the reactor without any distillation process.

Recently, improvements in slurry reactors for the production of toluenediamine were described in patents. Bayer AG patented both a loop type reactor (45) and an improvement heat transfer in a conventional continuous stirred tank reactor (46). BASF AG has patented a loop-type reactor (47) in which the heat transfer and gas–liquid mixing occur internal to the main reaction chamber, unlike a conventional loop type reactor.

There have also been attempts to develop fixed-bed reactors for toluenediamine production. Air Products and Chemicals, Inc. patented the use of a structured bed or monolith (48) for a catalyst support. Rhodia Chemie patented the use of two conventional fixed beds (49), while Bayer AG patented one fixed-bed or trickle-bed reactor (50). None of these reactors are believed to be commercial at the time of this publication.

Work continues to be done to try to improve Ni catalysts used for production of toluenediamine. The preferred catalyst is typically based on Ni due to the expense of using precious metal catalysts. Improvements have been made to allow these catalysts at the higher temperatures needed to generate steam to remove the heat of reaction. Bayer AG patented a Raney catalyst modified with metals such as Fe, Mo, Ta, Cr, or Cu (51). The same company patented a similar Raney-type catalyst allowed to solidify rapidly, which is claimed to have increased life (52). BASF patented the use of Ni supported on SiO_2 or $Zr)_2$, optionally doped with a metal from transition group I, V, VI, and VIII (53). Rhodia Chemie patented the use of a Raney-type catalyst with a reduced Al content, to reduce fouling of reactor surfaces (54).

Purification after catalyst removal requires separation of the TDA from the water of reaction and tars, and, depending on the procedure used in preparing TDI, from the ortho-substituted diamines. The general scheme for the purification shown in Fig. 2 is based on Allied Chemical patents (55,56). The first column is an atmospheric column that removes water of reaction and any toluidine formed. Then the crude *m*-toluenediamine (*m*-TDA) is distilled under reduced pressure, 1.3–2.6 kPa (10–20 mm Hg) recovering the *o*-toluenediamine (*o*-TD) overhead. The TDA is taken from the bottom of the first vacuum column and redistilled to remove the heavy products. This process gives more than a 99% TDA yield. A recent modification of this process involves recycling a portion of the *o*-TD to a heavies stripper to minimize losses of *m*-TDA to the heavies stream (57). Although vacuum distillation would appear to be the most economical purification of TDA, several other methods for removing the *o*-TDA have been described (58-62). Most of these are based on formation of cyclic products [eg, methylbenzimidazolinones and Ni(II) complex salts], which can be easily separated from the TDA. Cost of reactants and the need for further purification limits the usefulness of these methods.

Recently, the use of melt crystallization to isolate pure 2,4-TDA was developed (63).

Efforts have been made to simplify the transport of *m*-TDA. One technique patented was the conversion to flowable particles of solid TDA (64). Two other patents involve either leaving water in the distilled *m*-TDA (65) or adding water back to the anhydrous product of the distillation process (66). The water content acts to lower the melting point to allow long-term storage or shipment in large containers.

5. Toxicity

Toluenediamine is classed as toxic. The oral LD_{50} for animals is between 270 and 350-mg/kg body weight (67). TDA is readily absorbed through the skin and this is the major route of human exposure. Several studies have shown the 2,4 isomer of TDA to be carcinogenic for rats and mice, but tests on the 2,5 and 2,6 isomers were not positive. All three of the isomers have been shown to be mutagenic (67). Results of limited studies on the reproductive hazards for male workers are equivocal, but animal experiments have shown TDA to cause adverse reproductive effects (67).

6. Uses

Only a few commercial uses for TDA per se have been found. In epoxy curing applications, 2,4-TDA has been used as a component of a eutectic mixture with short-chain aliphatic glycidal ether resins (68) as well as by itself (68,69); TDA (68) and single isomers (69) are also used as amine curatives. TDA can be used as a chain extender in polyurethanes (70,71). The TDA is cited as a monomer in making aromatic polymers with unique properties, eg, amorphous polyamides (72), powdered polyamides (73), and low melting, wholly aromatic polyamides (74). Amorphous polyamide having a high heat distortion temperature can be syntheized from TDA (75).

Almost all TDA use is as a chemical intermediate, mostly in polyurethanes. Toluenediamine derivatives are found as all three components of urethanes: isocyanates, chain extenders, and polyols (see ISOCYANATES, ORGANIC; URETHANE POLYMERS).

Almost all TDA derived chain extenders are made through ortho-alkylation. Diethyltoluenediamine (DETDA) ($C_{11}H_{18}N_2$) (76), with a market of $\sim$ 33,000 t, is the most common. Many uses for *t*-BTDA have been cited (1,12). Both DETDA and *t*-BTDA are especially useful in RIM applications (71,76-78). Di(methylthio)-TDA, made by dithioalkylation of TDA, is used in cast urethanes and with other TDI prepolymers (79). Styrenic alkylation products of TDA are said to be useful, eg, as in the formation of novel polyurethane–polyurea polymers (80,81). Alkenylated toluendiamines can be used as antioxidants for organic materials (82). Progress in understanding aromatic diamine structure–activity relationships for polyurethane chain extenders should allow progress in developing new materials (83). Chlorinated TDA is used in polyurethane–polyurea polymers of low hysteresis (70) and in reinforced polyurethane tires (84). The chloro-TDA is made by hydrolysis of chloro-TDI, derived from TDA (85).

TDA-derived polyols are made by alkoxylation. Polypropylene oxide adducts of TDA (14) and TDA-initiated polyether polyols (13,15) are used in rigid polyurethane foams and continue to be included in new formulations (86) as well as older applications.

Alkylated and alkenated toluenediamines are used as antioxidants (qv) in oils and elastomers (10,76,87-89), as chemical intermediates for polyamides, polyimides, and polyesterimides (76) and as epoxy curatives (76,81,90)(see EPOXY RESINS). Recently, the use of 2,4-TDA as a cross-linker in the synthesis of epoxy liquid crystalline monomers was reported (91). *N*-Cyanoethylated toluenediamines have also been reported as latent curing agents for epoxy resins (92). Both *m*-TDA and *o*-TD can be hydrogenated to their corresponding methylcyclohexane diamines, which can be used as epoxy intermediates (93,94).

The most significant commercial use of *o*-TDA is in the manufacture of tolytriazoles. Tolytriazoles are used as corrosion inhibitors, chemical intermediates, photographic chemicals, and catalysts (16). Other uses for *o*-TDA include polyols (13,77) and antioxidants (77).

Toluenediamine derivatives are used as dyes (95,96) (see also DYES, AZO, AMINES, AROMATIC, PHENYLENEDIAMINES). A variety of other hard-to-classify uses are found. Improved fatigue resistance and dyeability are claimed for a fiber prepared from toluene-2,4-diamine and various diacids (97). An anhydride reacts with a formaldehyde–toluenediamine copolymer to give an impact-resistant resin (98). A fluorinated polyamide elastomer containing TDA has been described (99). The synthesis of benzimidazolethiols, useful as antioxidants, from the byproduct *o*-TDA obtained during TDI manufacture, has been described (100). Treatment of polyester fibers with toluenediamines improves the adhesion of elastomers (101,102). Uses as specific stabilizers for fungicides have been patented (103,104). Hydraulic fluids have been synthesized from toluene-2,4-diamine and alkylene oxides, preferably glycidol (105). Diamines can be used as sensitizers for explosive compositions (106,107). Aromatic bis(dialkly) ureas can be prepared from 2,4-TDA (108).

Recently, *o*-TD was used as a starting material, by conversion to quinoxaline, for a multistep synthesis to obtain a pharmaceutical intermediate (109).

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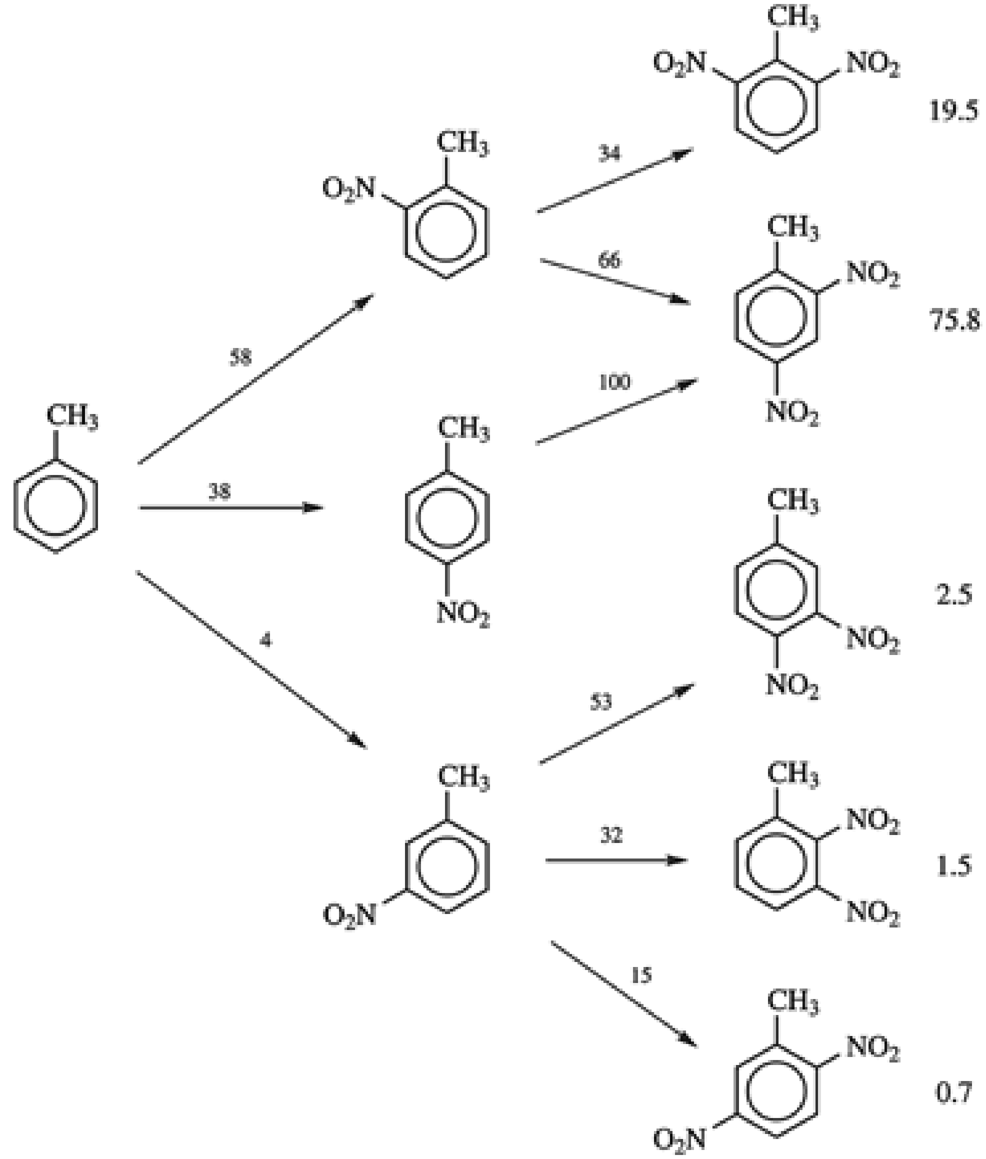

Fig. 1. Nitration of toluene, percent distribution.

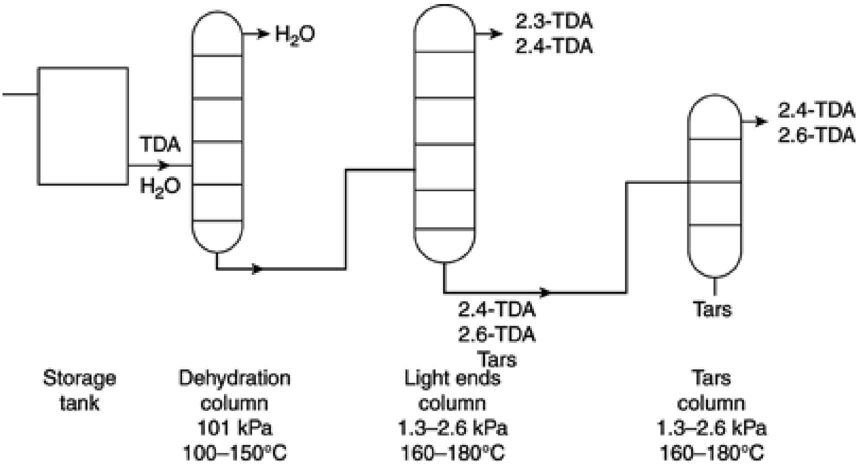

Fig. 2. Purification scheme for crude (TDA).

Table 1. **Physical Properties of the Toluendiamine Isomers**[a]

Diaminotoluene isomers	CAS Registry Number	Melting point, °C	Boiling point, °C	Vapor pressure, kPa (at °C)
2,3	[2687-25-4]	63–64	255	1.20 (150) 1.87 (160) 2.67 (180)
2,4	[95-80-7]	99	292	1.47 (150) 2.27 (160) 4.80 (180)
2,5	[95-70-5]	64	273–274	
2,6	[823-40-5]	106		2.13 (150) 3.33 (160) 7.60 (180)
3,4	[496-72-0]	89–90	265 (subl)	
3,5	[108-71-4]	<0	283–285	

[a] Ref. 2.

Table 2. **Specifications and Physical Properties of Commercial Toluenediamines**

	Specifications, wt %	
Property	*m*-TDA[a]	*o*-TDA[b]
m-TDA, purity normalized isomer ratio	99.2 min	
2,4 [95-80-7]	79–81	
2,6 [823-40-5]	19–21	
o-TDA, (2,3 [2687-25-4] and 3,4 [496-72-0]	0.3 max	99.5 min
para isomers (2,5 and 3,5)	0.8 max	
meta- plus para isomer content		0.3 max
nitrobodies as DNT	0.03 max	
moisture	0.05 max	0.5 max
toluidines	0.05 max	0.3 max
molecular formula	$C_7H_{10}N_2$	$C_7H_{10}N_2$
molecular weight	122.17	122.17
physical appearance	light yellow to tan solid[c]	light gray to purple solid[a]
boiling point at 101.3 kPa, °C	283	265 (3,4 TDA) 255 (2,3 TDA)
viscosity at 100°C, mPa·s (=cP)	5	5
density, g/mL	1.041 (105°C)	1.045 (100°C)
melting range, °C	88–96	61–92
flashpoint, closed cup, °C	140	157
heat of varporization, kJ/mol	61.3 (2,4 TDA)	68.0
heat of fusion, kJ/mol	19.9 (2,4 TDA)	19.8
specific heat at 150°C, kJ/(kg·K)	2.53	2.53
vapor pressure at 100°C, kPa	<133	266

[a] Ref. 3.

[b] Ref. 4.

[c] Tends to darken on storage and exposure to air.