

Synthesis Process Development of Diethylene Tricarbamide as a Starting Material for Wood Composite Binder

Diethylene Tricarbamide–Formaldehyde Resins

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Abstract

A three-step carbamylation reaction of diethylene triamine (DA) with urea was investigated to find an efficient synthesis procedure for large-scale production of diethylene tricarbamide (D), a monomer of D-formaldehyde resin binders for wood composite boards with very low formaldehyde emission potential. *n*-Butanol, pyridine, and others with minor amounts of polar solvents were investigated as a reaction medium. Urea is added to the solvent in a stirred reactor and heated to the boiling point of the solvent, which is about 110°C to 130°C. This was followed by the gradual addition of DA while allowing evolved ammonia to escape through the condenser. A delicate balance exists between voluminous particles of di-substituted intermediates and the hard fine particles of tri-substituted final product, and an excessive buildup of the former often occurs, resulting in stirring difficulties, reaction stoppage, and low reaction yields, which are minimized by adding some polar solvents and also by programmed addition of DA. Free-flowing microcrystalline particles of D were obtained in yields of 90 to 98 percent based on DA in 6 to 12 hours of reaction by simple filtration, hot washing with solvents, and drying procedures. These organic solvent-based synthesis procedures appear possible to adapt to large-scale production of D. The ammonia that evolves from the reaction needs to be captured, and solvent losses should be minimized. The high current price of DA, the need to reuse ammonia, and the complexity of the reaction indicate that a company that manufactures ammonia, urea, and DA fit to adopt this technology in support of the wood composite board industry.

The annual usage of urea-formaldehyde (UF) resins amounts to 3.3 billion pounds in North America and 15.8 billion pounds worldwide, mostly as binders for interior-grade wood composite boards, such as particleboard, medium-density fiberboard, and hardwood plywood (Innovation Group 2006, Kennedy 2006), but these wood composite boards entail free formaldehyde emission problems, unresolved or only partially resolved until recently (Myers 1990, Go 1991), with the emission values in the recent past ranging from 0.15 to 0.20 ppm when tested by the standard Large-Chamber test method (Graves 1993, Sigvartsen and Dunky 2006). Federal and state formaldehyde emission laws have been drastically tightened in recent legislation (State of California 2007, US Senate Bill 2011). These new laws have also introduced new definitions for “no-formaldehyde-added resin” and “ultralow formaldehyde-emitting resin” classes with a new expectation value of 0.04 ppm to encourage the industry to strive for new resin systems. The European and Japanese governments are also aiming to achieve ultralow formaldehyde-emitting wood composite boards (Sigvartsen and Dunky 2006).

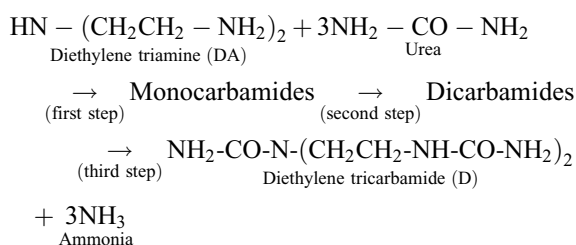
UF resins are manufactured by reacting urea and formaldehyde, where hydroxymethylureas are initially formed and the hydroxymethyl groups are then reacted further to form methylene groups between urea units in the resin as well as during the curing stages to form a high-molecular-weight thermosetting polymer. The formation reaction of the hydroxymethyl groups is slightly reversible, and the small amount of formaldehyde that remains in the resin and that is generated during curing causes formaldehyde emission problems (De Jong and De Jonge 1952a, 1952b, 1953; Myers 1984, 1990). Suppression of the reverse

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reactions of the hydroxymethyl groups is possible only by increasing the content of amide groups in the resin system by adding more urea, that is, lowering the formaldehyde/urea (F/U) mole ratio of resin. This method has been used extensively but is accompanied by longer hot-pressing times and decreased strength values of the boards due to the reduced cross-linking capacity of the resin (Plath 1967, Go 1991, Graves 1993). A recent laboratory report indicates that UF resins with an F/U mole ratio of 1.05 and low levels of melamine may approach current formaldehyde emission regulation levels of about 0.08 ppm (US Senate Bill 2011), but the strength properties are reduced, and longer hot press times are also needed (Mao et al. 2013).

The challenge of raising the amide group content can be resolved through the use of a new monomer, diethylene tricarbamide (D), which has three amide functional groups— $\text{NH}_2\text{CO-N}-(\text{CH}_2\text{CH}_2-\text{NH}-\text{CO}-\text{NH}_2)_2$ —as reported in US patent literature (Kim 2013). This compound is a known material in the literature, synthesized by reacting diethylene triamine (DA) and urea in a three-step reaction using water as reaction medium (Bentoniere and Rowland 1979):



Compound D was found to react readily with formaldehyde to give diethylene tricarbamide–formaldehyde (DF) resins, which showed curing speeds similar to those of UF resins of the same mole ratio, and the formaldehyde emission potential was reduced by about 75 percent in comparison with UF resins, as reported in a sequel article in this issue of *Forest Products Journal* (Kim et al. 2019), indicating that DF resins could be a potential replacement candidate for UF resins.

The high current selling price of DA (\$1.75/lb) compared with urea (~\$0.30/lb) appeared to be the major roadblock to large-scale production of D, but the author concluded that a higher volume production could narrow this price gap since it is manufactured from relatively low cost materials: ethylene and ammonia. On this premise, an efficient synthesis procedure of D from DA and urea was sought, since the reported synthesis procedure using water as a reaction medium gives poor yields of 56 percent with a long reaction time and long work-up procedure (Bentoniere and Rowland 1979). Therefore, we investigated the three-step carbamylation reaction of diethylene triamine (DA) with urea in pyridine, *n*-butanol, and pentanols and also using polar cosolvent additions to find an efficient synthesis procedure of D, aiming at one that can be scaled up for industrial production. The results are reported in this article.

Experimental and Results

Chemical and physical properties of D.—The D obtained in this study and that recrystallized from water was found to be a stable, colorless (white), nonhygroscopic, microcrystalline powder with a melting point of 218°C to 222°C, which was slightly higher than the reported value of 210°C

(Bentoniere and Rowland 1979). It is sparingly soluble in water (~2.0 g/100.0 g) at room temperature, and its solubility increases to about 30 g/100.0 g water at 90°C and is nearly insoluble in methanol and slightly soluble in warm dimethylsulfoxide (DMSO). CHN analysis for $\text{C}_7\text{H}_{16}\text{N}_6\text{O}_3$ (232.24): calculated (%), C 36.20, H 6.95, N 36.19; found (%), C 36.12 percent, H 7.13 percent, N 35.72 percent. ^{13}C NMR (DMSO- d_6 , ppm): 38.53 (2), 47.44 (2), 158.7 (1), 159.26 (2). FTIR (KCl, cm^{-1}): 1,560, 1,660, 2,950, 3,220, 3,370, and 3,420.

Synthesis of D using water as a reaction medium (Bentoniere and Rowland 1979).—We added 1,500.0 g of water, 993.0 g of DA (9.625 moles), and 2,350.0 g of urea (39.167 moles) (U/DA = 4.069) into a 5,000-mL reactor equipped with a heating mantle, stirrer, and a distillation setup of condenser. The reaction mixture was heated to boiling over a period of 1 hour, and a slow boiling rate was maintained at 95°C to 103°C. Ammonia soon began to evolve and escaped through the condenser, and a very slow distillation of water was maintained for 22 hours. During this reaction time, some white precipitates formed on the reactor wall. The reaction mixture was then allowed to cool without stirring to room temperature over several hours, and precipitates that were mostly formed during the cooling period were collected by filtration and washed with cold water briefly to yield 1350.0 g of precipitates: 60.5 percent yield, with a melting point of 216°C to 219°C. For recrystallization, 45.0 g of D were dissolved in a mixture of 150.0 g water and 15.0 g acetic acid, stirred, and heated to 95°C and allowed to cool to room temperature overnight. The precipitates were filtered and dried to yield ~40.0 g of D with a melting point of 220°C to 221°C. The results from duplicate experiments using various U/DA ratios and varying reactant solids levels are shown in Table 1. The results indicate that long reaction times of 16 to 22 hours are necessary due to the slow decomposition rate of urea at 100°C, and yields of only 55 to 61 percent were possible while satisfying the melting point targets. Due to the relatively ample solubility of the final product D in boiling water, the reaction mixture at the end of the reaction needed to be cooled down slowly over several hours to complete the precipitation process of the product. Also, after the first crop was obtained, the filtrate needed further processing to obtain a second crop, which was a long, costly work-up procedure. The final filtrate water was yellowish in color and showed some viscosity to indicate that oligomeric waste products were formed (see Eq. 5). Overall, the reaction in water was considered not promising as a large-scale production method.

Synthesis of D using sodium cyanate in water (Vogel 1972).—We added 103.0 g DA (1.0 mole), 400 mL of water, and 240.0 g of acetic acid to a 2,000-mL stirred reactor equipped with an external ice/water cooling setup, and then the reaction mixture was cooled to room temperature. A slurry made of 300 mL of water and 240 g of sodium cyanate (3.70 moles) was added dropwise to the reactor over a period of 0.5 hours. The reaction mixture reached 51°C at the end of sodium cyanate addition, and after removing the cooling bath, it was allowed to stir for 3.75 hours. Precipitates were filtered, washed with cold water and methanol, and then dried to yield 102.0 g of D (44.0%) with a melting point of 216°C. The reaction is an alternate synthesis method but resulted in a low yield and a large amount of reaction by-product sodium acetate.

Table 1.—Synthesis of diethylene tricarbamide in water as the reaction medium.^a

Exp. no.	DA (g)	U (g)	Water (g)	U/DA ratio	Yield (g/%)	Melting point (°C)	Reaction temp. (°C) /time (h)
4-101	993.0	2,350.0	1,500.0	4.07	1,350/60.5	219	98/22.0
3-23-2	1,089.0	2,350.0	1,500.0	3.70	1,510/61.0	215	98/22.0
3-23-1	1,200.0	2,350.0	1,500.0	3.36	1,410/52.2	216	98/22.0
3-46	206.0	468.0	400.0	3.90	285/61.4	210	98/20.0
3-65	208.0	432.0	300.0	3.57	257/55.5	216	99/16.0
3-67	208.0	432.0	400.0	3.57	244/52.4	216	99/16.0
3-68	208.0	432.0	400.0	3.57	231/57.5	216	99/16.0
Total/avg.	4,112.0	8,814.0		3.68	5,287/57.1		

^a DA = diethylene triamine; U = urea.

Therefore, we turned to reactions with urea using various organic solvents as reaction media.

Synthesis of D in pyridine and with minor amounts of water as cosolvents.—We added 30.0 g of DA, 86.0 g of urea (U/DA = 4.92), 295.0 g of pyridine, and 5.0 g (1.7%) of water to a 500-mL stirred reactor equipped with a condenser. The reaction mixture was heated to and maintained at 112°C to 114°C. At 1.5 hours of reaction time, some turbidity started to arise. The reaction was continued for another hour to reach a stage where the stirring became inefficient due to the precipitates that formed. Then the reaction temperature was lowered to about 80°C, and 30 mL of methanol were added and the mixture was heated back to reflux at 102°C and maintained for 1 hour. The stirring became difficult again, and 20 mL of methanol and reflux were continued at 102°C to 106°C for 4 hours. The reaction mixture was then allowed to cool to room temperature, and precipitates were filtered, washed with methanol, and dried to yield 62.0 g of D (91.8%) with a melting point of 220°C (8.5 h of reaction). The results of similar reactions carried out in this work are reported in Table 2. All reactions were carried out by charging all reactants at once in the beginning, and similar stirring difficulties were observed, but stirring improved when small amounts of methanol or *n*-propanol were added. Yields were generally somewhat low, and melting points were good, except for when the reaction was carried out without water. The reaction with 3.6 percent water went smoothly at a small scale, but when the size of the reaction was increased, the same phase disruption occurred. The reaction at 13.7 percent water went smoothly, but the yield was lower. In all cases when water was added to pyridine, the reaction temperatures were lower, resulting in longer reaction times. The purity of products was good, with high melting points reaching up to 222°C, indicating the positive effect of water

in dissolving out the impurities. Overall, the method of using pyridine as a solvent appears to be improvable with a programmed addition method of DA.

Synthesis of D in pyridine with minor amounts of DMSO as cosolvents.—The mixture was stirred in a 500-mL reactor equipped with a condenser where we sequentially added 30.0 g of DA, 65.0 g of urea (U/DA = 3.70), 250.0 g of pyridine, and 50.0 g (16.7%) of DMSO. The reaction mixture was heated to and maintained at 119°C for 1 hour, at which point some turbidity started to arise. Continuation of the reaction for 1.5 hours led to a stage where the stirring became slightly inefficient, but the reaction soon returned to normal and was ended after 2.5 hours of reaction. The reaction mixture was allowed to cool, and precipitates were filtered, washed with methanol, and dried to yield 54.0 g of D (80.0%) with a melting point of 220°C (5.0-h reaction). Results of similar reactions carried out using various levels of DMSO and various U/DA ratios are shown in Table 3. With DMSO levels between 1.7 and 9.1 percent, the reactions encountered some stirring difficulties in the decreasing order/levels, but all mixtures transitioned back to smooth stirring after about an hour. This stirring issue might be further minimized if a programmed addition method of DA were used. Yields were generally high, up to 96.7 percent. Advantages include short reaction times and relatively good purity of the final products with melting points ranging from 216°C to 219°C. However, the higher costs of solvents are negatives versus *n*-butanol in large-scale industrial production.

Synthesis of D in n-butanol.—The mixture was stirred into a 1,000-mL reactor equipped with a condenser in which we added 450.0 g of (undried) *n*-butanol and 190.0 g of urea; separately, 78.0 g of DA and 100.0 g of *n*-butanol mixture were set up in an addition funnel, and about one-eighth of the DA/*n*-butanol solution was added to the

Table 2.—Synthesis of diethylene tricarbamide in pyridine and with additive water.^a

Exp. no.	DA (g)	U (g)	Pyridine (g)	H ₂ O (g/%)	U/DA ratio	Yield (g/%)	Melting point (°C)	Reaction temp. (°C) /time (h)
3-84	30.0	65.0	300.0	0	3.70	58.0/85.9	212	116/9.50
3-81	30.0	86.0	295.0	5.0/1.7	4.92	62.0/91.8	220	106/8.50
4-85	135.0	310.0	1,350.0	50.0/3.6 ^b	3.94	278.0/92.0	223	107/12.0
4-87	405.0	930.0	3,375.0	125.0/3.6 ^c	3.94	706.0/77.3	222	104/16.0
5-95	206.0	400.0	1,510.0	240.0/13.7	3.33	359.0/77.4	221	102/17.0

^a DA = diethylene triamine; U = urea.

^b No methanol treatment needed during the reaction.

^c The reaction was met with difficulty of stirring and needed to add 200 g H₂O to make it smooth stirring.

Table 3.—Synthesis reactions of diethylene tricarbamide in pyridine with minor amounts of dimethylsulfoxide (DMSO).^a

Exp. no.	DA (g)	U (g)	Pyridine (g)	DMSO (g%)	U/DA ratio	Yield (g%)	Melting point (°C)	Reaction temp. (°C) /time (h)
3-85	30.0	65.0	250.0	50.0/16.7	3.70	54.0/80.0	220	119/5.00
3-87	30.0	65.0	275.0	25.0/8.3	3.70	58.0/85.9	219	118/6.00
3-88	30.0	75.0	275.0	25.0/8.3	3.33	61.0/90.3	219	118/3.50
3-88-2	30.0	75.0	280.0	20.0/6.7	4.50	62.0/91.8	219	118/3.50
3-91	60.0	150.0	588.0	12.0/2.0	4.50	125.0/92.5	220	116/6.00
3-93	61.0	130.0	590.0	10.0/1.7	3.66	128.0/93.2	217	117/6.50
3-97	135.0	285.0	1,350.0	30.0/2.2	3.62	290.0/95.4	216	114/12.0
3-102	135.0	310.0	1,350.0	50.0/3.6	3.80	294.0/96.7	216	116/10.0
3-101	135.0	300.0	1,350.0	135.0/9.1	3.94	291.0/95.1	215	117/12.0

^a DA = diethylene triamine; U = urea.

reactor. The reaction mixture was then heated to and maintained at 110°C. Dropwise addition of DA solution was initiated and completed in 1.6 hours. At about 2.5 hours of reaction time, white voluminous precipitate particles of di-substitution products began to appear, and then hard compact fine particles of final product soon began to appear. Both types of particles increased in amount over time, causing stirring problems, but could be handled by increasing the stirring speed. The latter type of particles soon increased in amount and became the dominant particles in the reaction mixture. After 13.5 hours of total reaction time, the reaction mixture was allowed to cool to about 90°C, and precipitates were filtered hot at 90°C, washed with warm ethanol, and dried to yield 166.0 g of D (94.5%) with a melting point of 213°C to 215°C. Similar reactions were carried out four more times using the filtrates and replenishing amounts of *n*-butanol as a reaction medium, as shown in Table 4. The results indicate that the reaction could be completed in as short as 8.5 hours and as long as 15.5 hours, depending on how well the stirring difficulties were handled. Relatively high yields in the range of 94.5 to 95.7 percent were obtained, but the melting point was about 4°C lower after washing with methanol, possibly indicating the presence of some amounts of intermediate products or urea. The dropwise addition of DA carried out in these experiments helped to alleviate the stirring issue, but there was still a period of time with some stirring difficulty regardless of the stirring speed, and this issue could be significant in a large-scale reactor. It also appeared that minor amounts of intermediate products were so intimately mixed with the final product in this solvent system that they resisted washing, but overall the potential advantages of

using *n*-butanol are shown, with high reaction yields and relatively clean and low-colored filtrates that can be reused in subsequent experiments up to five times while replenishing for the amount of unrecovered solvent by being held up in the filter cake of the product. When dried *n*-butanol was used, the reaction had to be stopped due to stirring difficulties, indicating the positive effect of a minor addition of water as a polar component.

Synthesis of D in n-butanol with minor amounts of pyridine.—The mixture was stirred into a 1,000-mL reactor where 180.0 g of urea, 450.0 g of butanol, and 4.0 g (0.73%) of pyridine were added sequentially. Separately, 78.0 g of DA and 100.0 g of *n*-butanol mixture were set up in an addition funnel, and about one-eighth of the DA/*n*-butanol solution was added to the reactor. The reaction mixture was then heated to and maintained at 110°C. First, dropwise addition of DA solution was commenced and completed in 2 hours, and the reaction was continued for the next 8 hours, during which time some stirring difficulties arose; this was handled by raising the stirring speed. The reaction mixture was cooled briefly to about 90°C, and the precipitates were filtered hot at 90°C, washed with ethanol, and dried to yield 162.0 g of D (93.1%) with a melting point of 215°C. Similar reactions were carried out two more times using 1.46 percent of pyridine addition and lower amounts of urea and using filtrates of previous experiments with replenishing amounts of *n*-butanol and pyridine as reaction media. Also, four more similar reactions with higher amounts of the cosolvent pyridine were carried out, as shown in Table 5. In all experiments, the stirring difficulties were present and handled by adjusting the stirring speed. It is apparent that cleaner products with better melting points were obtained,

Table 4.—Synthesis reactions of diethylene tricarbamide in *n*-butanol (*n*-BuOH) using various ratios of urea (U) to diethylene triamine (DA).

Exp. no.	DA (g)	U (g)	U/DA ratio	<i>n</i> -BuOH (g) ^a	Yield (g%)	Melting point (°C)	Reaction temp. (°C) /time (h)
7-155-1	78.0	190	4.18	550 ^b	166.0/94.5	214	110/13.5
7-155-2	78.0	160	3.52	F + 60 ^b	166.0/94.5	218	111/15.0
7-155-3	78.0	150	3.30	F + 80 ^b	168.0/95.6	216	105/15.5
7-155-4	78.0	150	3.30	F + 100 ^b	168.1/95.7	216	118/8.5
7-155-5	78.0	160	3.52	F + 100 ^b	167.1/95.1	214	115/8.5
Total/avg.	390.0	810	3.56		835.2/95.1		
7-50	104.0	230	3.73	550 ^c			117°C/3.0 ^c

^a F = filtrates obtained in the previous experiments.

^b Used undried *n*-butanol.

^c Use of dried *n*-butanol (by distillation) led to formation of too much ppt, resulting in reaction stoppage.

Table 5.—Synthesis reactions of diethylene tricarbamide in *n*-butanol (*n*-BuOH) with various amounts of pyridine.^a

Exp. no.	DA (g)	U (g)	U/DA ratio	<i>n</i> -BuOH (g)	Pyridine (g/%)	Yield (g/%)	Melting point (°C)	Reaction temp. (°C) /time (h)
7-145-1	78.0	180	3.96	550	4.0/0.73	165.0/94.0	215	110/10.0
7-145-2	78.0	160	3.52	F + 160	8.0/1.46	165.4/94.2	216	115/9.0
7-145-3	78.0	150	3.30	F + 160	8.0/1.46	168.0/95.6	216	118/10.0
Total/avg.	234.0	490	3.60			498.4/94.6		
7-121-1	78.0	170	3.74	500	50/9.10	161.0/91.6	218	120/7.0
7-121-2	78.0	170	3.74	F + 160	60/10.0	166.0/94.5	214	120/7.0

^a DA = diethylene triamine; U = urea; F = filtrate obtained in the previous experiments.

and shorter reaction times were possible, especially at about 10 percent levels of pyridine. The yields are in the 91.6 to 95.6 percent range, and the overall reaction went relatively smoother than runs done in *n*-butanol alone, showing the potential of attaining overall shorter reaction times.

Synthesis of D in n-butanol with various amounts of dimethylformamide (DMF).—The mixture was stirred into a 1,000-mL reactor in which 104.0 g of DA, 180.0 g of urea, 200.0 g of butanol, and 400.0 g of DMF were added all at once, and the reaction mixture was heated to and maintained at 120°C for 8.0 h. The reaction mixture was cooled briefly to about 90°C and the precipitates were filtered hot, washed with ethanol, and dried to yield 167.0 g of D (71.3%) with a melting point of 218°C. Similar reactions were carried out five more times using various decreasing amounts of DMF down to 3.0 percent, and the results are reported in Table 6. The reactions went relatively smoothly and were completed within 8 hours or less, probably due to the refluxing temperature, which was higher by about 5°C than with *n*-butanol alone, as well as the increased polarity of the solvent system. The stirring disruptions were minimal, indicating that the intermediate products stayed dissolved longer in the liquid phase, but lower yields were observed, indicating that the final product D in the liquid phase was delayed in the formation of particles, and this allowed the formation of more side-reaction products per Equation 5. Low levels of DMF, slightly lower reaction temperatures, and programmed addition of D appears necessary to use when investigating large-scale production opportunities in the future.

Synthesis of D in n-butanol with various amounts of ethylene glycol (EG).—The mixture was stirred into a 1,000-mL reactor in which 104.0 g of DA, 230.0 g of urea, 400.0 g of butanol, and 100.0 g of EG were added all at once, and then heating was applied. The reaction mixture reached as high as 120°C, and the reaction was continued at 120°C to 122°C for 4 hours. Stirring difficulties arose and were handled similarly by increasing the stirring speed. The reaction mixture was cooled to about 90°C, and the

precipitates were filtered hot at 90°C, washed with methanol, and dried to yield 195.0 g of D (71.3%) with a melting point of 216°C. Similar reactions were carried out four more times using various decreasing amounts of EG and also decreasing amounts of urea and with repeated use of filtrates in subsequent reactions with replenishing additions of each solvent, as shown in Table 7. As with the DMF cosolvents used above, higher levels of EG resulted in lower yields and cleaner products. At lower EG levels, yields were higher, but the reaction time was longer, indicating that finer adjustments are necessary to make the reaction go smoothly, that is, without the excessive formation of precipitates of intermediate products. Yields are generally higher than reactions carried out with DMF cosolvents, and filtrates appeared cleaner to make seven repeat runs possible with yields ranging higher at up to 98.1 percent, although the melting-point spreads ranged to the lower side more than when using pyridine or DMF as cosolvents. Overall, it appears to be one of the methods to investigate further during scale-up investigation.

Synthesis of D in n-butanol with ammonium acetate.—The mixture was stirred into a 5,000-mL reactor equipped with a condenser and Dean-Stark (DS) trap in which 2,000.0 g of *n*-butanol, 1,022.0 g of urea, and 10.0 g of ammonium acetate were added. Separately, 500.0 g of *n*-butanol and 390.0 g of DA were mixed in a measuring flask that was connected to a liquid pump through a 5-mm-diameter propylene tubing to dropwise add the mixture into the reactor. The reaction mixture was heated to 90°C, and DA was pumped at a rate of about one drop per 4 seconds. At about 0.5 hours of reaction time, the temperature reached 113°C, and about 28 mL of distillates of water-butanol mixture were collected in the D-S trap, which was drawn out. Then the temperature rose to 116°C, which was maintained afterward, and the addition rate of DA was raised to about two drops per second. In 1 hour of reaction time, the addition of DA progressed to one-sixth of the DA mixture. At 2 hours of reaction time, two-sixths of the DA addition was completed, and 28 mL of distillates were

Table 6.—Synthesis reactions of diethylene tricarbamide in *n*-butanol (*n*-BuOH) with minor amounts of dimethylformamide (DMF).

Exp. no.	DA (g)	U (g)	U/DA ratio	<i>n</i> -BuOH (g)	DMF (g/%)	Yield (g/%)	Melting point (°C)	Reaction temp. (°C) /time (h)
7-40	104.0	230.0	3.50	200.0	400/66.7	167.0/71.3	218	122/7.5
7-42	104.0	230.0	3.50	300.0	300/50.0	182.0/78.4	218	122/8.0
7-43	104.0	230.0	3.50	500.0	100/20.0	200.0/85.4	217	122/8.0
7-44	104.0	230.0	3.50	450.0	50/10.0	207.0/88.4	217	122/6.5
7-45	104.0	230.0	3.50	475.0	25/5.0	211.0/90.1	217	122/6.5
7-46	104.0	230.0	3.50	485.0	15/3.0	213.0/90.9	218	122/6.5

Table 7.—Synthesis reactions of diethylene tricarbamide in *n*-butanol (*n*-BuOH) with various amounts of ethylene glycol (EG).^a

Exp. no.	DA (g)	U (g)	U/DA ratio	<i>n</i> -BuOH (g)	EG (g)	Yield (g%)	Melting point (°C)	Reaction temp. (°C) /time (h)
7-53	104.0	230.0	3.50	400.0	100.0	195.0/83.0	216	120/4.0
7-54	104.0	230.0	3.50	450.0	50	210.0/89.6	216	117/6.0
7-55	104.0	230.0	3.50	470.0	30	Difficult to stir		118/3.0
7-136	78.0	170.0	3.74	510.0	40.0	161.0/91.6	216	118/10.0
7-141	78.0	170.0	3.74	530.0	20.0	156.5/89.1	217	118/9.5
7-143	78.0	160.0	#	F + 150.0	2.0	165.4/94.2	215	116/8.0
7-143-2	78.0	150.0	#	F + 150.0	2.0	167.2/95.2	215	111/14.5
7-144	78.0	145.0	#	F + 150.0	4.0	149.0/84.8	216	110/8.0
7-145	78.0	170.0	#	F + 150.0	2.0	167.2/95.2	216	110/11.5
7-149	78.0	155.0	#	F + 150.0	2.0	172.3/98.1	214	110/11.0
7-150	78.0	155.0	#	F + 150.0	2.0	165.0/94.8	214	110/9.0
Total/avg.	546.0	1,150.0	3.48			1,142.6/92.5		

^a DA = diethylene triamine; U = urea; # = U/DA ratio of 3.77 is approximately maintained with lesser amounts of urea due to remaining urea in filtrates from previous runs; F = filtrate obtained in the previous experiments.

collected in the D-S trap, which was drawn out. At about 3 hours of reaction time, the reaction mixture was slightly separated (i.e., some curding of precipitates occurred), resulting in irregular stirring, and therefore the addition of DA was stopped. At 4 hours of reaction time, the stirring became more normal and addition of DA was resumed, and at 4.7 hours of reaction time, it progressed to an addition of three-sixths of the DA mixture. Thereafter, addition of DA was progressed by one-sixth of the DA mixture every hour and completed at 6.7 hours of reaction time. The reaction was continued for 2.5 hours at 115°C with a total reaction time of 8.7 hours. After cooling the reaction mixture briefly to about 90°C, precipitates were filtered hot, washed with methanol, and dried to yield 850.0 g of D (96.8%) with a melting point of 210°C to 212°C. A small sample was washed again with methanol to obtain an increased melting point of 219°C. Similar reactions were carried out five times using filtrates obtained in previous experiments plus replenishing amounts of *n*-butanol of about 800 mL as the reaction media. In these experiments, lower urea loads and shorter reaction times were made possible by programmed addition of DA mixture. The results are reported in Table 8. It should be noted that these reactions were carried out on a scale that is five times larger than the experiments in Table 4 and with programmed addition of DA over a longer period of time (6 h). The stirring difficulties were less severe with this scale-up technique, and yields were improved by about 3 percent, although the melting points showed greater spreads toward the lower side. This new procedure was found useful due to less formation of voluminous precip-

itates of intermediate products. It appeared, above all, that the solvent system needs to be made slightly more polar in the future for cleaner products to be obtained. The pale yellow color of filtrates increased in intensity with repetition. In the final experiment, 220.0 g of urea were precipitated out when the filtrates were allowed to cool and stand for 1 day. After filtration of the urea, evaporation of *n*-butanol of the filtrates on a rotary evaporator gave about 200 g of thick-viscosity material that did not yield any crystalline product on standing, indicating polymer formation through side reactions (Eq. 5).

Synthesis of D in n-butanol with trimethylphenol (TMP).—The mixture was stirred into a 1,000-mL reactor in which 180.0 g of urea, 2.0 g of TMP, and 450.0 g of *n*-butanol were added; separately, 78.0 g of DA and 100.0 g of *n*-butanol mixture were set up in an addition funnel, and about one-eighth of the DA/*n*-butanol solution was added to the reactor. The reaction mixture was heated to and maintained at 118°C, and dropwise addition of the DA mixture was completed in 6 hours, followed by a further reaction at 118°C to 119°C for the next 2 hours, followed by cooling down slightly. Then the precipitates were filtered hot at 90°C, washed with ethanol, and dried to yield 162.0 g of D (93.1%) with a melting point of 216°C to 217°C. Similar reactions were carried out four more times using the filtrates in subsequent reactions with replenishing amounts of *n*-butanol and TMP as reaction media, as shown in Table 9. Yields were in the range of 95 percent with relatively good melting points, and the overall reaction went relatively smoother than previous synthesis methods. All four

Table 8.—Synthesis reactions of diethylene tricarbamide in *n*-butanol (*n*-BuOH) with minor amounts of ammonium acetate (AA).^a

Exp. no.	DA (g)	U (g)	U/DA ratio	<i>n</i> -BuOH (g)	AA (g)	Yield (g%)	Melting point (°C)	Reaction temp. (°C) /time (h)
6-157-1	390.0	1,022.0	4.50	2,500.0	10.0	850.0/96.8	211	115/8.7
6-157-2	390.0	716.0	3.15	F + 800.0	0	862.0/98.2	209	118/11.5
6-157-3	390.0	716.0	3.15	F + 800.0	0	861.0/98.0	209	119/10.0
6-157-4	390.0	716.0	3.15	F + 800.0	0	850.0/96.8	213	117/9.25
6-157-5	390.0	716.0	3.15	F + 800.0	0	850.0/96.8	210	117/8.0
6-157-6	390.0	750.0	3.30	F + 800.0	0	839.5/95.5	210	117/6.0
Total/ave.	2,340.0	4,416.0	3.24 ^b			5,112.5/97.0		

^a DA = diethylene triamine; U = urea; F = filtrates obtained in the previous experiments.

^b Average with recovered urea (220.0 g) at the end of cycle 6 included;

Table 9.—Synthesis reactions of diethylene tricarbamide in *n*-butanol (*n*-BuOH) with trimethylphenol (TMP).^a

Exp. no.	DA (g)	Urea (g)	U/DA ratio	<i>n</i> -BuOH (g)	TMP (g)	Yield (g/%)	Melting point (°C)	Reaction temp. (°C) /time (h)
7-187	78.0	180.0	3.96	550.0	2.0	162.0/92.2	216	118/8.0
7-187-2	78.0	170.0	3.74	F + 160.0	0	170.4/96.8	216	118/8.0
7-189	78.0	160.0	3.52	F + 160.0	1.0	170.5/96.8	217	118/8.0
7-189-2	78.0	150.0	3.30	F + 160.0	1.0	165.7/94.3	216	118/8.0
Total/ave.	312.0	660.0	3.63			668.6/95.1		

^a DA = diethylene triamine; U = urea; F = filtrates obtained in the previous experiments.

reactions were completed within 8 hours, a result of minimal stirring disruption compared with the reactions done in *n*-butanol without TMP or with ammonium acetate. Thus, it appears that TMP, an acid species, can help push the cyanic acid form to isomerize to the isocyanic acid form, as proposed in Equation 6. However, TMP appeared to degrade over the course of the reaction, resulting in filtrates with a stronger yellow color than usual. Also, further improvement of the reaction yields could perhaps be desired.

Synthesis of D in n-pentanol and with various amounts of EG or DMF.—The mixture was stirred into a 1,000-mL reactor in which 230.0 g of urea and 500.0 g of *n*-pentanol were added; separately, 104.0 g of DA and 100 g of *n*-pentanol mixture were set up in an addition funnel, and about one-eighth of the DA/*n*-butanol solution was added to the reactor. The reaction mixture was heated to and maintained at 120°C. Dropwise addition of the DA mixture was completed in 4 hours, followed by further reactions for 4 hours. The reaction mixture was then cooled briefly, and precipitates were filtered at 90°C, washed with methanol, and dried to yield 214.0 g of D (91.3%) with a melting point of 214°C. Similar reactions were carried out two more times with similar results, and more reactions were done with minor amounts of EG or DMF. At the highest amount of EG usage (Experiment 7-70), however, the reaction led to a meltdown of precipitates that did not recover back into fine particles, and this halted the reaction. At lower levels of EG and DMF cosolvents, the reactions were normal. The results are shown in Table 10. Reaction temperatures available for use were 120°C to 130°C, significantly higher than for *n*-butanol. The results showed somewhat less of a stirring problem, but with lower yields in the range of 92 percent. The results showed the potential to use higher temperatures, but it is apparent that finer reaction controls and solvent polarity adjustments are necessary in large-scale reactions.

Synthesis of D in various mixed alcohol solvent media.—The mixture was stirred into a 1,000-mL reactor in which 200.0 g of urea, 280.0 g of *n*-pentanol, and 230.0 g of *n*-butanol were added; separately, 78.0 g of DA were mixed with 50.0 g of *n*-pentanol and 50.0 g of *n*-butanol and set up in an addition funnel, and about one-eighth of the DA mixture was added to the reactor. The reaction mixture was heated to and maintained at 115°C. Dropwise addition of the DA solution was completed in 2 hours, followed by a further reaction for 7 hours. The reaction mixture was cooled briefly, and precipitates were filtered at 90°C, washed with methanol, and dried to yield 167.5 g (96.3%) of D with a melting point of 216°C. Similar reactions were carried out with a mixture of iso-pentanol and *n*-butanol and also with a mixture of *n*-hexanol and cyclohexanol with yields and melting points of D as shown in Table 11. The results are generally similar to those obtained with *n*-butanol to indicate that reaction solvent systems can be one or mixtures of various aliphatic alcohols in boiling point ranges of 110°C to 130°C. In these experiments, it was noticed that raising the temperature to about 120°C or higher leads to some discoloration of reaction medium, perhaps due to undesirable decomposition paths of urea.

Results and Discussion

Carbamylation reaction of DA with urea.—Urea is known to reversibly decompose into cyanic/isocyanic acids and ammonia (Eq. 1) (Werner 1913; Vogel 1972). The decomposition reaction of urea is of the first order and the rate depends on the reaction temperature. In other words, the decomposition rate is relatively slow at room temperature but increases with increasing temperatures. The cyanic/isocyanic acid mixture actually is in an equilibrium (i.e., interconvertible) between the two species, and isocyanic species is the agent of the carbamylation reaction (i.e.,

Table 10.—Synthesis reactions of diethylene tricarbamide in *n*-pentanol (*n*-PeOH) and with various amounts of ethylene glycol (EG) or dimethylformamide (DMF).

Exp. no.	DA (g)	U (g)	U/DA ratio	<i>n</i> -PeOH (g)	EG (g)	DMF (g)	Yield (g/%)	Melting point (°C)	Reaction temp. (°C) /time (h)
7-83	104.0	230.0	3.50	600.0			214.0/91.3	214	120/8.0
7-85	104.0	210.0	3.20	550.0			215.0/92.7	215	121/8.25
7-86	78.0	180.0	3.96	550.0			160.0/92.0	216	120/8.50
7-70	104.0	230.0	3.50	500.0	100.0		Meltdown; stop ^b		130/5.0
7-75	104.0	230.0	3.50	525.0	75.0		216.0/92.2	214	126/7.0
7-73	104.0	230.0	3.50	550.0	50.0		190.0/81.1	214	131/4.5
7-65	104.0	230.0	3.50	450.0		50.0	203.0/87.5	215	130/9.0
7-67	104.0	210.0	3.20	450.0		150.0	197.0/84.1	214	135/4.0

^a DA = diethylene triamine; U = urea.

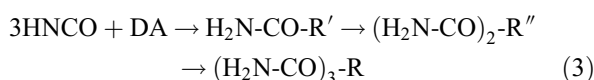
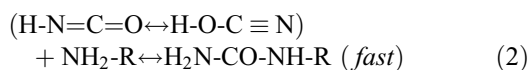
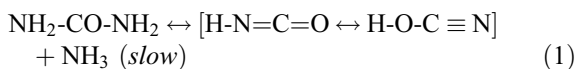
^b The precipitates collapsed into globs of semiliquid that did not return to fine particles.

Table 11.—Synthesis reactions of diethylene tricarbamide in various other solvent systems.^a

Exp. no.	DA (g)	U (g)	U/DA ratio	Solvents (g)	Yield (g/%)	Melting point (°C)	Reaction temp. (°C) /time (h)
7-159	78.0	200.0	4.40	<i>n</i> -Butanol 280.0 <i>n</i> -Pentanol 280.0	167.5/96.3	216	118/9.15
7-48	104.0	230.0	3.80	<i>n</i> -Butanol 200.0 iso-Pentanol 500.0	212.0/90.5	216	117/6.50
7-109	78.0	170.0	3.74	<i>n</i> -Hexanol 170.0	158.0/89.9	215	120/9.0
7-110	78.0	160.0	3.52	Cyclohexanol 160.0	150.0/85.4	216	115/12.0

^a DA = diethylene triamine; U = urea.+

reacts with amines to form carbamides) (Eq. 2) (Belson and Strachan 1982). This decomposition reaction of urea is expedited by eliminating the liberating ammonia from the reaction system, for example, by allowing it to escape selectively through a condenser. However, the overall rate of carbamylation reaction of DA is relatively slow, principally because of the slow decomposition rate of urea even at 110°C to 130°C used in this study. Further, the reaction consists of three stepwise or consecutive reactions that involve formation of two monosubstituted and two di-substituted intermediates before reaching to the final product D (Eq. 3). An ideal solvent system would be one that can dissolve urea and all four reaction intermediates well, at least at near reaction temperatures, but it was not the case in synthesis reactions of D from DA; some reaction intermediates are not adequately soluble in all the solvent systems studied, except the water system where the solubility of final product is so high that it results in low yields due to further transformation into waste products:



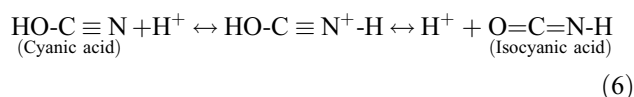
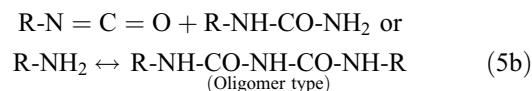
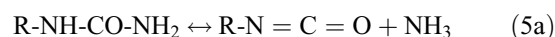
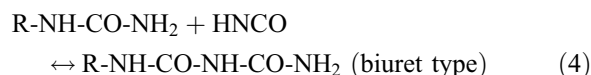
where R' = -NH-CH₂CH₂-NH-CH₂CH₂-NH₂ and -N(CH₂CH₂-NH₂)₂, R'' = -NH-CH₂CH₂-NH-CH₂CH₂-NH- and -N(CH₂CH₂-NH₂)CH₂CH₂-NH-, and R = -N(CH₂CH₂-NH-)₂.

Factors to consider and selection of n-butanol or pyridine as reaction media.—Various factors were considered in selecting organic solvents for the various synthesis procedures of D. Some important factors include high yields with adequate purity of product, high reactor efficiency, short reaction time, simple work-up procedure, low-cost solvents, solvent recovery potential, minimum generation of waste products, and minimal health and safety issues. The properties of reactants, intermediates, and final products observed from the reaction using water as reaction medium led to select organic solvents of intermediate polarities, such as aliphatic alcohols and pyridine. In these solvent systems, starting materials and intermediate reaction products were fully/partially soluble, and the final product was least soluble at boiling temperatures. Also, to attain short reaction times, the solvents need to have boiling points of 110°C or higher to increase the decomposition rate of urea. This consideration led us to select *n*-butanol (117.7°C) and pyridine (115.2°C). When several small-scale reactions in

these solvents were carried out, the yields were relatively high, in the range of 80 to 95 percent, with about 6 to 12 hours of reaction time (i.e., varying reaction times and varying reaction yields).

Causes of irregularity of reactions and addition of polar cosolvents.—This irregularity of reactions observed in *n*-butanol and pyridine as solvents arose more severely when the size of the reaction was increased. The underlying cause was traced back to di-substituted intermediate products that accumulated to form voluminous, partly soluble or swollen precipitates that cause, first of all, the stirring and reaction inefficiency, resulting in longer reaction times. The lower melting points often observed of final products were attributable to the residual intermediate products present in them due to their resistance to the washing with hot solvents (The intermediate products that showed melting points of about 180°C are, in theory, undesirable in DF resin compositions.) Therefore, solvents of higher polarity, such as DMF, DMSO, EG, water, and pyridine (vs. *n*-butanol), were experimented as cosolvents at various levels. With some of these modified solvent systems, the stirring disruption was diminished (i.e., less formation of precipitates of di-substituted intermediates). Also, the purity of final product appears to improve with the use of cosolvents. For larger-scale reactions in the future, finer adjustments of solvent polarity would be necessary at every step of scale-up development.

Increasing the acidity of reaction medium for smoother reaction.—As discussed above, increasing the polarity of the reaction medium was found to have some limitations. It appeared that the final product D became partially soluble in solvents of higher polarity and that its carbamide groups go into the formation of biuret-type (Eq. 4) and oligomer-type side-reaction products (Eq. 5a, 5b):



Therefore, another way to solve the stirring issue and improvement of reaction yields was through the use of acid catalysts. It was considered that an acidic species can intervene in the decomposition process of urea by

expediting the isomerization process of the cyanic acid form into the isocyanic acid form (Eq. 6), which is the active species in carbamylation reactions with DA, possibly resulting in faster overall carbamylation reactions. The reactions carried out with a small amount of ammonium acetate or trimethylphenol turned out to show a mild positive effect for stirring while increasing the yields of reaction. This method appears useful and should be considered for large-scale experiments in the future.

Handling of final stages of reaction.—The final product D was found to advantageously come out from the liquid reaction phase as hard microcrystalline particles that were insoluble and finely dispersed in reaction media, allowing the use of the low-cost filtration method for product isolation. Also, the particles hold low levels of solvents at the end of the hot filtration stage (about 90°C). Another consequence of this characteristic is that in the final stages of reaction, as the voluminous precipitates of di-substituted intermediates particles were being replaced by finely dispersed hard particles of D, the reaction mixture's apparent viscosity became significantly reduced and the stirring more efficient, allowing for some reaction solvents to be distilled out. In large-scale reactions, the distilled-out hot solvents can be used later in the washing of the final product. The reaction end points can also be gauged by visual inspection from these viscosity/stirring changes, allowing appropriate time samples to be taken that can be filtered, washed with methanol, dried, and taken the melting points. The target melting point is 218°C to 220°C, and lower values often obtained in this work indicated the presence of impurities such as urea and di-substituted products, which is a signal that indicates longer reaction times are necessary.

Hot filtration of product.—After the reaction is completed, it is preferable to let the mixture cool to about 90°C to 100°C and filter the precipitates using a preheated filtering funnel and suction; the resultant hot filter cake is washed with hot *n*-butanol or warm methanol or ethanol to remove unreacted urea and other impurities, followed by drying. The product is free-flowing, fine, colorless particles of D. When the filtration was carried out at lower temperatures, it was found that unreacted urea and other side-reaction products also come out of the liquid phase and mixed in with the final product, which needed to be washed again with methanol or other, similar solvents; however, this washing was not always effective. Overall, aside from the relatively high yields of reaction, this relatively straightforward isolation procedure of final product shows the benefits of using organic solvents in comparison to the synthesis method of using water, in which the major portion of the final product stays in solution until the end of the reaction and takes a long time to crystallize out completely. Also, the hot *n*-butanol, partly obtainable by distillation of the reaction mixture toward the end of reaction, could be used for washing of the final product. Using hot *n*-butanol for washing as well as for reaction means that a one-solvent system can be realized, simplifying the solvent recovery process in large-scale manufacturing. However, solvents like warm methanol and ethanol were found to work in most cases for the washing of products at lower temperatures. In some cases, hot washing with hot *n*-butanol or warm washing with methanol or ethanol was found to be ineffective even by repeated washings, indicating that a clean reaction product needs to be obtained in the first place.

Organic solvent reaction media of higher boiling points and other factors for lowering of reaction costs.—Pentanols (boiling point 131°C to 138°C) and hexanols (boiling point 155°C to 161°C) and also their mixtures with *n*-butanol were investigated as reaction media, and it was found that yields and reaction behaviors were similar to those reactions carried out in *n*-butanol to indicate that they can provide a method of reaction at higher temperatures for faster reaction rates. On the other hand, it was observed that temperatures that were higher than about 130°C tended to increase the side-reaction products. Also, isomeric butanols and pentanols could be used as lower-cost alternatives to using pure *n*-butanol. Other major solvent-related factors that can lower costs are minimization of evaporation losses and recovery costs. It is important to note that the amount of solvent held up in the filter cake of the final product was found to be about 25 to 30 percent by weight of the solvents used in the reaction, and this needs to be captured in the drying process of the filter cakes. In addition, the reusability of the filtrates for subsequent reactions without distillation, shown up to six times for several more optimum solvent systems in this study, indicates lower distillation costs in the solvent recovery step and less generation of side-reaction waste products. It would be necessary to optimize the solvent recovery processes in future studies.

Conclusions

1. In the three-step carbamylation reaction of DA with urea investigated in various organic solvent media at near their boiling points, most of urea dissolves slowly but completely in the early part of the reaction to form a transparent, one-phase reaction system. Then, partially insoluble voluminous particles of di-substituted intermediates arise first, and, in time, finely dispersed hard particles of final product start to arise, and the reaction enters into a period where a delicate balance exists between these two types of particles. Stirring difficulties or even halting of the reaction can occur when the former particle types accumulate excessively and precipitate out and do not readily come back into the reaction phase. This problem was found to be ameliorated by selecting the right kind solvent and also by adding effective amounts of polar cosolvents as well as by the programmed addition of DA over several hours rather than all at once in the beginning.
2. Organic solvent systems investigated were *n*-butanol, pyridine, and pentanols at temperatures ranging from 110°C to 130°C that allowed urea to decompose at reasonable rates and carbamylation reactions to be completed in about 6 to 12 hours. Shorter reaction times and higher purity of final product D are realized when phase disruptions are minimized, and optimum polarity of reaction media is attained by using polar cosolvents.
3. The final product D has a very low solubility in most reaction media used in this study, and the particles come out of the liquid reaction phase as hard particles that are so finely dispersed that settling down to the bottom of reactor is prevented when a slow stirring of about 30 ppm is maintained, allowing a relatively smooth reaction to proceed. This property of D also allows (1) some reaction solvents to be distilled out toward the end of reaction without increasing the stirring resistance, (2) a simple hot-filtration and hot-solvent washing process to use in

the product isolation step, (3) a porous filter cake of product containing about 25 percent by weight solvent used in reaction to be obtained that can be washed of impurities with hot solvents on the same filtering funnel and then the held-up solvent to be dried efficiently at elevated temperatures up to about 120°C without much of any major mechanical manipulation needed on the product, and (4) a final product of free-flowing, nonhygroscopic, microcrystalline, stable particles to be obtained.

4. Yields of D obtained in more optimized organic solvent systems were relatively high, up to 90 to 98 percent, in comparison with reactions done in water. However, a few percentages of side-reaction products could be a big burden in disposal, and the reaction yields need to be maximized, possibly by using right reaction solvent systems, programmed addition of DA, optimum reaction temperature, accurate reaction end-point determination, correct washing and drying of the product, and so on, all of which need to be fine-tuned further in the scale-up process development stage.
5. Filtrates obtained in this study were found to be reusable several times without distillation due to minimal amounts of waste products present in them. Also, distilling out the extra solvents toward the end of reactions may provide the hot solvent needed in the hot washing of final product.
6. In spite of various favorable results discussed above, it is recognized that the ammonia evolving continuously from the reaction must be captured to be used at a fair value and that the solvent loss in the filtering and drying steps of the final product needs to be minimized as much as possible to make the overall procedure economically feasible.
7. Considering the high selling price of DA, the necessity of reusing ammonia derived from reaction, and the complexity of this carbamylation reaction, a chemical company that currently manufactures DA, ammonia, and urea might want to consider further developing this technology for commercial production to help wood composite board industries manufacture boards with very low levels of formaldehyde emission potential.

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