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Industrial processes for manufacturing amines

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Abstract

Commercial processes for manufacturing methylamines, C_2–C_5 alkylamines, cyclohexylamines, and DABCO are reviewed with emphasis on technology developments that have occurred during the last fifteen years. New technologies which have been explored include zeolite-catalyzed methylamines processes, direct amination of isobutylene to produce *t*-butylamine, and catalytic distillation for production of butylamines and cyclohexylamine. Opportunities for further process improvements are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Amination; Reductive alkylation; Methylamines; Alkylamines; Cyclohexylamine; DABCO; Hydrogenation

1. Introduction

Amines are an important class of compounds which find uses as intermediates in a variety of applications including pharmaceuticals, agricultural chemicals, rubber chemicals, water treatment chemicals, and solvents. In 1995, global demand for C_1–C_6 amines was approximately 500,000 mt per year with growth rates of 4–5% projected for the US and 1–3% for western Europe and Japan [1]. Methods for commercial manufacture of amines vary depending on the specific amine to be produced and on the raw materials employed. Often, there are multiple commercial processes used for manufacturing a particular amine or family of amines. Most processes result in the synthesis of an equilibrium distribution of primary, secondary, and tertiary amines, which is different for every family of alkylamines. The challenge for amines manufacturers is to match production volumes of the respective amines with their market requirements.

In the following paragraphs, industrial processes used for manufacturing methylamines, lower alkylamines (C_2–C_5), and cycloaliphatic amines will be described. In addition, recent technology developments related to amines manufacture will be summarized, and challenges for the future will be discussed.

2. Methylamines

Global capacity for production of methylamines exceeds 800,000 mt per year [2]. Dimethylamine, which is in highest demand, is used as an intermediate for solvents (dimethylformamide, dimethylacetamide), agricultural chemicals (2,4-D), surfactants (fatty amine oxides), and water treatment chemicals (acrylates, Mannich polymers, etc.). Monomethylamine also is used for manufacture of solvents (*N*-methylpyrrolidone), carbamate insecticides (via methylisocyanate), and surfactants, while trimethylamine is used in animal feed supplements (choline chloride), cationic starches, and ion exchange resins. Historically, methylamines have been manufactured via vapor phase amination of methanol with ammonia using variations of the Leonard process [3]. A typical process flow diagram is shown in Fig. 1. The reaction is conducted in an adiabatic, fixed bed reactor

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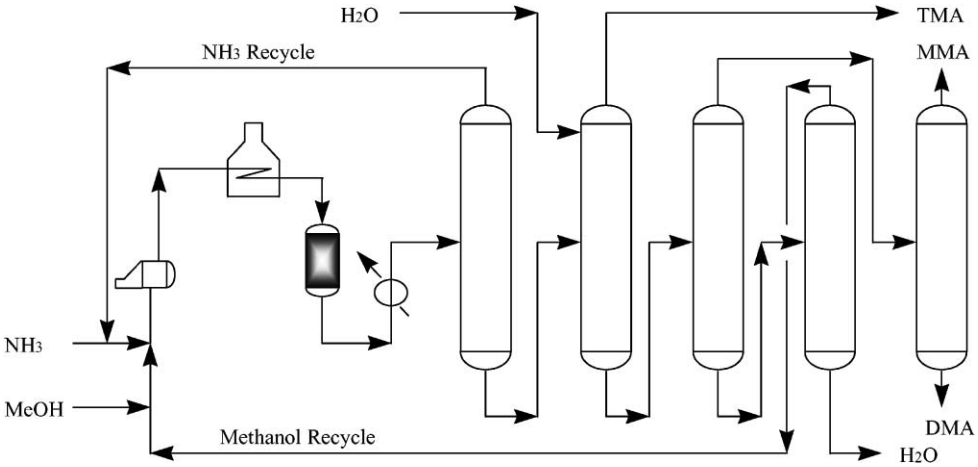


Fig. 1. Methylamines reactor and separation train.

over an amorphous silica-alumina catalyst at temperatures of 400–420 °C and superatmospheric pressure to produce an equilibrium mixture of mono- (MMA), di- (DMA), and tri- (TMA) methylamines (TMA). Although the product composition varies with ammonia to methanol ratio, the selectivity to DMA is the lowest of the three products and is relatively invariant with process conditions. Commercial reactors typically operate at ammonia:methanol (N/C) molar ratios of 1–4, depending on the relative requirements for MMA and TMA. The conventional process offers some flexibility in production volumes of the three products as any undesired product can be recycled over the catalyst and converted to the equilibrium mixture of methylamines.

In response to the high demand for DMA, use of alternate catalyst technologies has been explored in an effort to identify catalysts which give higher selectivity to DMA. A review of these efforts, which largely have been focused on shape-selective catalysts, has recently been published [2]. Several zeolite catalysts have been shown to exhibit high DMA selectivity including Na^+- and Na^+/K^+-modified mordenite [4,5], RHO [6], H-ZK-5 [7], and chabazite [8]. Reduction in TMA selectivity to <10 wt.% has been achieved by surface treatment of the zeolites [8,9]. The methylamines catalyst studies resulted in commercialization of a shape-selective process for production of methylamines by Nitto (now Mitsubishi Rayon) during the early 1990s [10].

The Mitsubishi Rayon methylamines process employs two reactors [11]: one containing an equilibrium catalyst to disproportionate TMA, and the second containing a shape-selective zeolite catalyst [12]. The disproportion reactor is required as TMA does not react over the shape-selective catalyst due to the pore size limitations which are responsible for the shape-selectivity. The effluent from the first reactor is fed to the second reactor along with additional methanol and ammonia to produce a non-equilibrium distribution of methylamines containing a relatively high level of DMA and a low level of TMA. The zeolite catalyst used in the second reactor is a synthetic or natural mordenite catalyst which is modified with Na^+ and possibly K^+ and/or Li^+ at specified levels. For example, when ammonia and methanol are reacted over a mordenite catalyst containing 2.0 wt.% Na^+, 2.2 wt.% K^+, 1.7 wt.% Ca^{2+}, and 0.3 wt.% Mg^{2+} at an N/C ratio of 1.9, 340 °C, 17.6 bar, and 1500 h^{-1} space velocity, a mixture of methylamines containing 36 wt.% MMA, 52 wt.% DMA, and 12 wt.% TMA is produced at 90% methanol conversion. For comparison, methylamines selectivities from an amorphous catalyst are 25.6 wt.% MMA, 22.1 wt.% DMA, and 52.3 wt.% TMA at 91.2% methanol conversion, 1.9 N/C, 360 °C, 17.6 bar, and 1000 h^{-1} GHSV [12]. In the Mitsubishi Rayon process, the crude reaction product, along with the excess ammonia and water of reaction may be separated in a conventional continuous distillation train, as shown in Fig. 1. Alternatively, only DMA

may be recovered as a salable product, with ammonia, MMA, and TMA recovered for recycle to the disproportionation reactor. This latter scheme requires only three distillation columns as compared to the four columns needed for recovery of all three products.

Catalyst deactivation typically is a concern in zeolite-catalyzed reactions. Mitsubishi Rayon investigated potential causes of catalyst deactivation and discovered that formaldehyde, a by-product of the process which is produced in low concentrations, is a precursor to coke formation on the zeolite [13]. Their studies showed that the quantity of formaldehyde contained in the feed to the zeolite must be limited to $\leq$0.15 kg/h kg-cat. They also determined that another means of extending catalyst life is to limit the temperature rise in the reactor containing the zeolite catalyst [14] by using multiple reactor beds and inter-bed cooling. Exposure of the zeolite to high temperatures ($\geq$350 °C) results in rapid catalyst deactivation as evidenced by decreased methanol conversion.

In 1997, a second shape-selective methylamines process was commercialized by Mitsui Chemical (formerly Mitsui Toatsu) in an 8000 mt per year plant in Hikoshima, Japan [15]. In the Mitsui Chemical process, TMA is not recovered from the process in a separate distillation column but is recycled as an azeotropic mixture with ammonia to a disproportionation reactor containing a non-selective H^+-mordenite catalyst [16,17]. The effluent from the disproportionation reactor is combined with fresh methanol and fed to a reactor containing a shape-selective catalyst. Production of TMA during methanol amination is limited by use of a silylated mordenite catalyst which is prepared by liquid phase silylation of H^+-mordenite with tetraethoxysilane [18]. Methylamines selectivities (wt.%) from this catalyst are reported to be 33.3% MMA, 63% DMA, and 3.7% TMA at 90% methanol conversion, 1.9 N/C, 310 °C, 18.6 bar, and 590 h^{-1} GHSV. One of the main advantages of the Mitsui process is elimination of the capital cost required for installation of a distillation column to recover TMA.

In addition to the work on selective catalysts for DMA production, use of feedstocks other than methanol, such as carbon monoxide [19,20], carbon dioxide [21–23] and methane [24,25] has also been explored. Published results to date indicate that yields of methylamines obtained from these feeds are significantly lower than the yields obtained from methanol, and therefore, development of a new process based on an alternate feed will require future technological inventions.

3. Lower alkylamines

The lower alkylamines are comprised of the primary, secondary, and tertiary amines derived from feedstocks containing C_2–C_5 carbon chains. Worldwide capacity for the lower alkyl amines is greater than 400,000 mt per year [1]. These amines are used in pharmaceutical, agricultural, rubber chemical, and catalysis applications. The main processes used to produce the lower alkyl amines on a commercial scale are described in Table 1. Note that the majority of these products can be made by reductive amination and therefore, the same process equipment may be used to manufacture multiple product families. While in most cases, all three amines are produced from reaction of alcohol with ammonia, limitations in separations capability may restrict some manufacturers from recovering all three products. In these situations, the product having the lowest demand is recycled to the reactor. A typical production scheme is shown in Fig. 2.

Although many of the lower alkylamines may be produced via acid-catalyzed alcohol amination similar to the methylamines process, this technology finds limited commercial application. A major drawback to this approach is the production of alkene by-product.

Table 1
Processes for manufacturing lower alkylamines

Product	Feedstock	Process
Ethylamines	Ethanol	Reductive amination
	Acetaldehyde	Reductive amination
n-Propylamines	*n*-Propanol	Reductive amination
Di-*n*-propylamine	Propionitrile	Hydrogenation
Isopropylamines	Isopropanol	Reductive amination
	Acetone	Reductive amination
n-Butylamines	*n*-Butanol	Reductive amination
Isobutylamines	Isobutanol	Reductive amination
t-Butylamine	Isobutylene	Alkene amination
	Isobutylene	Ritter reaction
Amylamines	Amyl alcohol	Reductive amination

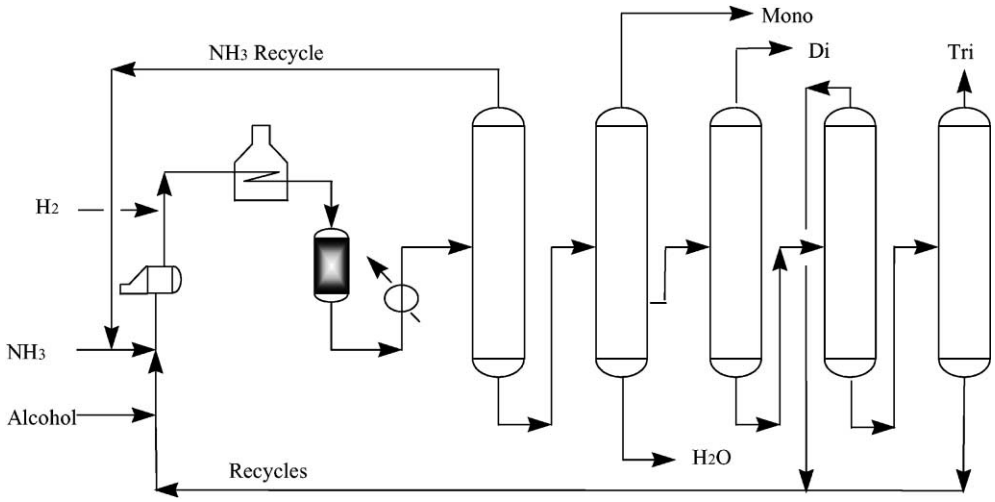


Fig. 2. Generic alkylamines reactor and separation train.

Recently, Lercher has studied the amination of ethanol over zeolite catalysts and has shown that alkene is produced via three routes: alcohol dehydration, ether decomposition, and Hoffmann elimination [26]. He suggests that selectivity to alkene can be reduced by conducting the amination reaction at low temperature (<300 °C), using high partial pressures of ammonia, and choosing the proper catalyst.

3.1. Reductive amination

Reductive amination processes involve reaction of alcohol with ammonia over a supported metal catalyst, typically nickel or cobalt on silica or alumina [27,28] at temperatures ranging from 150 to 210 °C and pressures of 18 to 200 bar. The reaction is conducted in the presence of hydrogen to maintain catalyst activity [29]. Some manufacturers use aldehydes or ketones, such as acetaldehyde or acetone, as feedstocks for reasons of availability and cost relative to the alcohol. When these unsaturated feedstocks are used, the hydrogen requirement exceeds stoichiometric based on the alkyl feed. Continuous, fixed bed vapor phase or liquid phase/trickle bed reactors may be used for alcohol or aldehyde/ketone amination. The heat of reaction is significantly higher for amination of aldehydes/ketones relative to alcohols, and some means of controlling the reactor temperature generally is required. In addition to fixed bed reactors, liquid phase stirred tank reactors also are used commercially, particularly for amination of carbonyl feedstocks. The reactions are usually run under conditions selected to achieve high conversion of the alkyl feedstock, and the product selectivities are controlled by equilibrium as the amination catalysts also catalyze disproportionation.

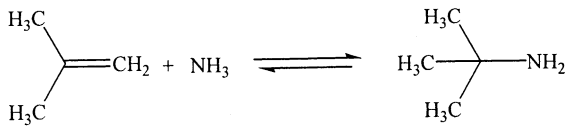
Recent studies on reductive amination have focused on development of improved catalysts for this reaction. Comparison of supported nickel and cobalt catalysts has shown that cobalt catalysts exhibit higher activity relative to nickel catalysts [27,28,30], and the activity of supported cobalt catalysts is related to the quantity of reduced cobalt available for reaction [31]. Patents disclosing catalyst formulations for alcohol amination have described the need for active catalysts which maintain their activity for long periods of time and give reduced levels of by-products. A catalyst comprising 50 wt.% NiO, 17 wt.% CuO, 1.5 wt.% MoO_3, and 31. 5 wt.% ZrO_2 was developed by Reif et al. [32] of BASF to address these issues. Alcohols having both short and long alkyl chains have been aminated using this catalyst. Other bimetallic catalysts also have been shown to exhibit high activity for alcohol amination [33]. These catalysts consist of 15–20% nickel or cobalt and 0.5–3% palladium on an alumina, silica, or titania support. Comparison of the bimetallic catalysts with standard catalysts containing higher levels

of nickel or cobalt shows that the bimetallic catalysts have higher activity and are activated (reduced) at significantly lower temperatures (200 °C versus 400 °C).

Methods to obtain non-equilibrium product selectivities using selective catalysts as well as alternate processing schemes have been explored. Cobalt exchanged Y-zeolite catalysts have been developed to enhance formation of primary and secondary amines relative to tertiary amines [34]. Amination of ethanol over a Co–Y zeolite reduced triethylamine selectivity by 75% relative to a Co/SiO_2 catalyst. Selective preparation of tertiary amines via alcohol amination over a copper catalyst in a liquid phase, fixed bed reactor also has been described [35]. Reaction of ethanol with ammonia at a molar ratio of 1:0.1 in the presence of 50% NaOH solution gave triethylamine in 95.8% selectivity at 24% ethanol conversion. A process method to enhance tertiary amine production involves the use of two reactors containing conventional catalysts, operating in series. The equilibrium mixture of amines is obtained from the first reactor, the primary, secondary, and tertiary amines are separated, and the recovered secondary amine along with alcohol are fed to the second reactor to produce additional tertiary amine [36]. Another process-related technique for selectively producing amines is catalytic distillation [37]. A distillation column containing a Ni/Al_2O_3 structured catalyst is used for the reaction of ammonia and alcohol and also for recovery and recycle of products. Selective production of tri-*n*-butylamine has been demonstrated using this technology.

3.2. Alkene amination

Amines containing tertiary alkyl groups, such as *t*-butylamine, historically have been manufactured via the Ritter process. This method involves reaction of an alkene with hydrogen cyanide in the presence of sulfuric acid to produce the desired amine, and formate and sulfate salt co-products. However, in 1994, a new process for manufacturing *t*-butylamine involving direct amination of isobutylene with ammonia was commercialized. Technology for producing amines from alkenes was first patented in 1945 [38]. Supported metals, particularly cobalt, were used to catalyze the reaction. A key technological development occurred in the early 1980s when the use of acid catalysts, such as naturally-occurring or synthetic crystalline aluminosilicates, was disclosed [39,40]. Amination of ethylene, propylene, and isobutylene over zeolitic catalysts such as mordenite, X-zeolite, and various ion-exchanged forms of Y-zeolite was demonstrated. The reaction, as shown below for isobutylene, is equilibrium-limited, and the yield of amine is favored at higher reaction pressures and also at lower reaction temperatures.



Although many companies have investigated this technology, BASF is the only company to commercialize a process based on alkene amination. They first constructed a pilot plant and then a commercial scale plant in Antwerp, Belgium to produce *t*-butylamine via amination of isobutylene under supercritical conditions. The commercial plant has an announced capacity of 8000 mt per year [41]. The initial BASF patents describe primarily aluminosilicate and borosilicate catalysts having pentasil structures [42,43]. Process conditions described in the patent examples are 1.5:1 (molar) ammonia:isobutylene, 300 °C, and 300 bar. Isobutylene conversions range from 9 to 17% with selectivities to *t*-butylamine >95%. Several patents assigned to BASF have issued in recent years which describe other catalysts for alkene amination [44–53].

Although manufacture of other amines via alkene amination has been investigated, these processes have not been commercialized, due to the low alkene conversions which typically are achieved. Because the reaction proceeds through a carbonium ion intermediate, isobutylene amination is the most facile due to formation of a tertiary carbonium ion. Alkenes such as ethylene and propylene form less stable primary and secondary carbonium ions, leading to lower yields of amine products.

4. Cyclohexylamines

The family of cyclohexylamines includes both the unsubstituted cyclohexylamine itself, as well as N- and C-substituted cyclohexylamines, and dicyclohexylamine. A list of some of these products and

Table 2
Processes for manufacturing cyclohexylamines

Product	Feedstock	Process
Cyclohexylamine	Aniline	Hydrogenation
	Cyclohexanol	Reductive amination
	Phenol	Hydrogenation/reductive amination
Dicyclohexylamine	Aniline	Hydrogenation
	Cyclohexanol	Reductive amination
	Cyclohexylamine + cyclohexanone	Reductive alkylation
	Phenol + Aniline	Hydrogenation/reductive alkylation
	Cyclohexanone + aniline	Hydrogenation/reductive alkylation
2-Methylcyclohexylamine	*o*-Toluidine	Hydrogenation
N,*N*-Dimethylcyclohexylamine	Cyclohexanone + dimethylamine	Reductive alkylation
N-Ethylcyclohexylamine	Cyclohexanone + monoethylamine	Reductive alkylation
N,*N*-Diethylcyclohexylamine	Cyclohexanone + diethylamine	Reductive alkylation

methods for their preparation is given in Table 2. Cyclohexylamine is the most important product from a commercial standpoint as the market is several 1000 mt per year. Cyclohexylamine is used primarily in boiler water treatment and rubber chemical applications.

Cyclohexylamine may be manufactured via either of two processes: reductive amination of cyclohexanol or phenol or by hydrogenation of aniline. The route used depends on the relative costs of the feedstocks and the process equipment available. Cyclohexanol can be reductively aminated via the same method used for manufacture of alkylamines described above, and the process may be operated in the same equipment. An equilibrium mixture of cyclohexylamine and dicyclohexylamine is produced in the reactor, and the products are recovered from the process in accordance with sales requirements. Amination of cyclohexanol in a liquid phase batch reactor over a Ru/Al_2O_3 catalyst has been reported to give cyclohexylamine in high selectivity [54,55]. Continuous amination of phenol with either ammonia or aniline in a fixed bed reactor containing Pd on niobic acid/carbon at 180 °C and 270 bar is claimed to give cyclohexylamine or dicyclohexylamine as the primary product [56]. A similar gas phase process over supported nickel catalyst also has been described [57].

Hydrogenation of aniline to cyclohexylamine typically is conducted in a liquid phase batch or continuous reactor at temperatures of 100–250 °C and pressures of 1–350 bar. Supported ruthenium catalysts are often used, and several patents have issued describing specific catalyst formulations [58–63], many of which contain mixtures of ruthenium and palladium on an alumina support. Conversions of aniline generally are >99% and selectivities to cyclohexylamine are reported to be >90%. A continuous process for hydrogenating aniline to cyclohexylamine over a nickel catalyst also has been described in which cyclohexylamine is recovered in 99.9% yield, and dicyclohexylamine selectivity is minimized by feeding ammonia to the reactor [64]. Continuous hydrogenation of aniline in a catalytic distillation reactor has been shown to produce cyclohexylamine in 65–75% selectivity along with phenylcyclohexylamine and dicyclohexylamine co-products [65].

Dicyclohexylamine may be produced from a variety of feedstocks via reductive alkylation or as a co-product of aniline hydrogenation. Selectivity to dicyclohexylamine during aniline hydrogenation appears to be influenced by choice of catalyst and reaction conditions [66,67]. Hydrogenation of aniline over an alumina-supported Ru-Pd catalyst containing NaOH has been reported to give dicyclohexylamine in 80% selectivity (60). High yields (>90%) of dicyclohexylamine also may be achieved from reductive alkylation processes involving reaction of cyclohexanone with cyclohexylamine or aniline [68]. These reactions typically are catalyzed by supported palladium catalysts.

As shown in Table 2, the N-substituted cyclohexylamines are manufactured by reductive alkylation of cyclohexanone with the appropriate primary or secondary amine. The reactions generally are conducted in a batch reactor using supported platinum or palladium catalysts (Pd/C or Pd/Al_2O_3) at temperatures of 50–150 °C and pressures of 5–35 bar. As the markets for these amines are relatively small and the processes to manufacture them have been optimized, there is little incentive to identify new process schemes or to develop improved catalysts.

5. DABCO (TEDA)

1,4-Diazabicyclo[2.2.2]octane or DABCO (also known as triethylenediamine or TEDA) is one of the principal catalysts used for production of polyurethanes from polyisocyanates and polyols. DABCO is manufactured by acid-catalyzed condensation of polyethyleneamine-based feedstocks. Early routes to DABCO involved cyclization of substituted piperazines, such as aminoethylpiperazine, *N*-(2-hydroxyethyl)piperazine, or *N*,*N*′-di(2-hydroxyethyl)piperazine, in the vapor phase over alumina [69,70] or in the liquid phase in the presence of an aromatic carboxylic acid catalyst [71]. Yields of DABCO were reported to be in the 50–70% range. In the mid-1980s, a strontium hydrogen phosphate catalyst was developed which produced DABCO from *N*-(2-hydroxyethyl)piperazine in 93% yield [72]. Zeolite catalysts, particularly those having the pentasil structure, have also been shown to be active for these cyclization reactions, although DABCO selectivities equivalent to that obtained from the β-$SrHPO_4$ catalyst have not been achieved [73–75]. Recent efforts to identify process improvements have focused on the reaction of other polyethyleneamine feedstocks, such as monoethanolamine, ethylenediamine, and diethylenetriamine, over modified ZSM-5 zeolites [76–81].

6. Future directions

Most of the amines described in this article are commodity chemicals. Consequently, reducing production costs is the primary objective of the manufacturers of these products. The major cost components which can be influenced by technology improvements are raw materials, capital (equipment) costs, and energy costs. Reduction in raw material costs potentially can be achieved by using feedstocks which are raw materials for the current feedstocks, e.g. syngas instead of methanol for making methylamines, alkenes instead of alcohols for making alkylamines, etc. A recent article describes the synthesis of amines from alkenes via hydroaminomethylation [82], i.e. reaction of alkene with ammonia and CO/H_2 in the presence of a homogeneous catalyst.

Equipment costs can be decreased by eliminating processing steps, such as distillation, as a result of improved yields of the desired products through the use of more selective catalysts. Another method of reducing equipment costs may involve conducting multiple operations in the same equipment. Manufacture of butylamines via catalytic distillation has demonstrated that reaction and distillation may be performed within a single distillation column [40]. Separations generally are responsible for the major portion of the energy costs. Use of alternate means of separating products, by-products, and raw materials may offer potential for cost reductions. Membranes represent an example of one alternate technology which, in the future, may find applications in amines manufacturing processes. Although the applicability of polymeric membranes is limited due to solubility issues, inorganic membranes may be a viable alternative if high selectivity with high flux can be demonstrated.

In summary, while the technologies used to manufacture amines may seem mature, there are opportunities to improve these processes. Although the challenges are significant, they represent exciting areas for future research.

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References

[1] CEH Marketing Research Report 611.5030E, Alkylamines (C1–C6), 1997.

[2] D.R. Corbin, S. Schwarz, G.C. Sonnichsen, Catal. Today 37 (1997) 71.
[3] The Leonard Process Co. Inc., Hydrocarbon Process 58 (1979) 194.
[4] F.J. Weigert, J. Catal. 103 (1987) 20.
[5] Y. Ashina, T. Fujita, M. Fukatsu, J. Yagi, US Patent 4,578,516 (1986).
[6] H.E. Bergna, M. Keane Jr., D.H. Ralston, G.C. Sonnichsen, L. Abrams, R.D. Shannon, J. Catal. 115 (1989) 148.
[7] R.D. Shannon, M. Keane Jr., L. Abrams, R.H. Staley, T.E. Gier, G.C. Sonnichsen, J. Catal. 115 (1989) 79.
[8] F.C. Wilhelm, G.E. Parris, B.A. Aufdembrink, T.R. Gaffney, US Patent 5,399,769 (1995).
[9] K. Segawa, H. Tachibana, Stud. Surf. Sci. Catal. 75 (1993) 1273.
[10] Japan Chemical Week (1992) 2.
[11] Y. Ashina, M. Fukatsu, US Patent 4,485,261 (1984).
[12] Y. Ashina, T. Fujita, M. Fukatsu, J. Yagi, US Patent 4,578,516 (1986).
[13] Y. Ashina, T. Fujita, K. Niwa, T. Inagaki, Y. Nikaido, US Patent 5,068,442 (1991).
[14] T. Fujita, K. Niwa, K. Ogura, M. Fukatsu, US Patent 5,688,854 (1997).
[15] Japan Chemical Week 38 (1997) 2.
[16] T. Yasautake, N. Iwanaga, Japan Patent 8-169,864 (1996).
[17] T. Anbu, T. Iwanaga, Japan Patent 8-311,000 (1996).
[18] T. Kiyoura, K. Terada, US Patent 5,382,696 (1995).
[19] K. Klier, R.G. Herman, G.A. Vedage, US Patent 4,642,381 (1987).
[20] M. Subrahmanyam, S.J. Kulkarni, A.V. Rama Rao, J. Chem. Soc., Chem. Commun. (1992) 607.
[21] S.V. Gredig, R.A. Koeppel, A. Baiker, J. Chem. Soc., Chem. Commun. (1995) 73.
[22] S.V. Gredig, R.A. Koeppel, A. Baiker, Catal. Today (1996) 339.
[23] S.V. Gredig, R.A. Koeppel, A. Baiker, Catal. Lett. 46 (1997) 49.
[24] K. Ogura, C.T. Migita, T. Yamada, Chem. Lett. (1988) 1563.
[25] K. Ogura, C.T. Migita, M. Nakayama, J. Chem. Soc., Faraday Trans. 86 (1990) 2265.
[26] V.A. Veefkind, J.A. Lercher, J. Catal. 180 (1998) 258.
[27] D.A. Gardner, R.T. Clark, US Patent 4,255,357 (1981) to Pennwalt Corporation.
[28] J.V. Martinez de Pinillos, R.L. Fowlkes, US Patent 4,314,084 (1982) to Air Products and Chemicals Inc.
[29] A. Baiker, J. Kijenski, Cat. Rev. Sci. Eng. 27 (1985) 653.
[30] G. Sewell, C. O'Connor, E. van Steen, Appl. Catal. A 125 (1995) 99.
[31] G.S. Sewell, C.T. O'Connor, E. van Steen, J. Catal. 167 (1997) 513.
[32] W. Reif, L. Franz, P. Stops, V. Menger, R. Becker, R. Kummer, S. Winderl, US Patent 5,530,127 (1996) to BASF AG.
[33] G.A. Vedage, K.S. Hayes, M. Leeaphon, J.N. Armor, US Patent 5,932,769 (1999) to Air Products and Chemicals Inc.
[34] M. Deeba, US Patent 4,913,234 (1990) to Air Products and Chemicals Inc.
[35] R. Fischer, H. Mueller, US Patent 4,851,578 (1989) to BASF AG.
[36] B.K. Heft, C.A. Cooper, R.L. Fowlkes, European Patent 379,939 (1990) to Air Products and Chemicals Inc.
[37] S.P. Nemphos, D. Hearn, US Patent 5,679,862 (1997) to Chemical Research and Licensing Company.
[38] J.W. Teter, US Patent 2,381,470 (1945) to Sinclair Refining Company.
[39] J.O.H. Peterson, H.S. Fales, US Patent 4,307,250 (1981) to Air Products and Chemicals Inc.
[40] J.O.H. Peterson, H.S. Fales, US Patent 4,375,002 (1983) to Air Products and Chemicals Inc.
[41] Chemical Week (1994) 23.
[42] V. Taglieber, W. Hoelderich, R. Kummer, W.D. Mross, G. Saladin, US Patent 4,929,758 (1990) to BASF AG.
[43] V. Taglieber, W. Hoelderich, R. Kummer, W.D. Mross, G. Saladin, US Patent 4,929,759 (1990) to BASF AG.
[44] M. Hesse, W. Steck, H. Lermer, R. Fischer, M. Schwarzmann, European Patent 431,451 (1991) to BASF AG.
[45] U. Dingerdissen, K. Eller, European Patent 752,411 (1997) to BASF AG.
[46] K. Eller, R. Kummer, P. Stops, US Patent 5,739,405 (1998) to BASF AG.
[47] K. Eller, R. Kummer, P. Stops, US Patent 5,886,226 (1999) to BASF AG.
[48] K. Eller, R. Kummer, P. Stops, US Patent 5,786,510 (1998) to BASF AG.
[49] K. Eller, R. Kummer, E. Gehrer, US Patent 5,773,660 (1998) to BASF AG.
[50] K. Eller, R. Kummer, M. Hesse, US Patent 5,780,681 (1998) to BASF AG.
[51] K. Eller, R. Kummer, M. Dernbach, European Patent 822,179 (1998) to BASF AG.
[52] K. Eller, R. Kummer, US Patent 5,840,988 (1998) to BASF AG.
[53] K. Eller, R. Kummer, US Patent 5,877,352 (1999) to BASF AG.
[54] K. Uehara, Japan Patent 5,148,191 (1993) to Idemitsu Petrochemical Co.
[55] K. Uehara, Japan Patent 601,758 (1994) to Idemitsu Petrochemical Co.
[56] O. Immel, H.J. Buysch, G. Darsow, DE Patent 4,133,675 (1993) to Bayer AG.
[57] H. Matsumoto, K. Hirasaka, M. Hashiguchi, H. Arimatsu, Japan Patent 60,239,444 (1985) to Honshu Chemical Industry Co.
[58] O. Immel, H.H. Schwarz, R. Thiel, DE Patent 3,801,755 (1989) to Bayer AG.
[59] M. Irgang, L. Wambach, DE Patent 4,207,314 (1993) to BASF AG.
[60] G. Darsow, O. Immel, G. Petruck, H. Waldmann, G.M. Petruch, European Patent 501,265 (1992) to Bayer AG.
[61] H. Ruetter, T. Ruehl, B. Breitscheidel, J. Henkelmann, A. Henne, T. Wettling, DE Patent 19,533,718 (1997) to BASF AG.
[62] H.J. Buysch, G. Darsow, O. Immel, R. Langer, WO Patent 9,815,351 (1998) to Bayer AG.
[63] G. Darsow, R. Langer, DE Patent 19,754,571 (1999) to Bayer AG.

[64] I. Naramoto, T. Kiyuma, US Patent 4,914,239 (1990) to New Japan Chemical Co. Ltd.
[65] D. Hearn, S.P. Nemphos, US Patent 5,599,997 (1997) to Chemical Research and Licensing Company.
[66] O. Immel, H.H. Schwarz, R. Thiel, DE Patent 3,824,822 (1990) to Bayer AG.
[67] O. Immel, H.H. Schwarz, European Patent 324,984 (1989) to Bayer AG.
[68] M. Pies, F. Helmut, European Patent 513,640 (1992) to Bayer AG.
[69] H.G. Bosche, K. Baer, K. Schneider, DE Patent 2,442,929 (1976) to BASF AG.
[70] I. Hudea, M. Biemel Werner, R. Czifra, RO Patent 85,563 (1984) to Institutul de Cercetari Produse Auxiliare Organice.
[71] G. Engemann, G. Spielberger, US Patent 3,080,371 (1963) to Bayer AG.
[72] J.E. Wells, US Patent 4,514,567 (1985) to Air Products and Chemicals Inc.
[73] T. Ogawa, N. Mizui, S. Tate, S. Kumoi, Japan Patent 5,017,460 (1993) to Tosoh Corp.
[74] T. Ogawa, N. Mizui, S. Tate, S. Kumoi, Japan Patent 5,017,461 (1993) to Tosoh Corp.
[75] T. Ogawa, N. Mizui, S. Tate, S. Kumoi, Japan Patent 5,017,462 (1993) to Tosoh Corp.
[76] H.J. Buysch, A. Botta, L. Puppe, DE Patent 3,934,459 (1991) to Bayer AG.
[77] W.T. Reichle, J. Catal. 144 (1993) 556.
[78] H.-X. Li, J.G. Santiesteban, J.N. Armor, US Patent 5,731,449 (1998) to Air Products and Chemicals Inc.
[79] J.G. Santiesteban, H.-X. Li, J.N. Armor, US Patent 5,741,906 (1998) to Air Products and Chemicals Inc.
[80] J.N. Armor, J.G. Santiesteban, H.-X. Li, US Patent 5,756,741 (1998) to Air Products and Chemicals Inc.
[81] H.-X. Li, J.G. Santiesteban, L.A. Emig, J.N. Armor, European Patent 952,152 (1999) to Air Products and Chemicals Inc.
[82] B. Zimmerman, J. Herwig, M. Beller, Angew. Chem. Int. Ed. 39 (1999) 2372.