Simulation and optimization of ethanol amine production plant

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Abstract−An industrial Ethanol Amine (EA) production plant was simulated and optimized. Due to lack of accurate reaction rate information, the first step involved obtaining reliable kinetic data from the SRI (Stanford Research Institute) industrial database and calculation using error minimization method. In the next step, by implementing the obtained reaction kinetics the whole plant was simulated using Hysys software. Simulation results were compared with the SRI data and showed that there is acceptable agreement between simulation and the measured industrial data. In the next step of study by applying the gradient search (GS) optimization technique the plant was optimized using: feeding ammonia to ethylene oxide (EO) molar ratio, water flow rate in the feed stream, and reactor temperature as optimization variables. Employing process profit as objective function the optimal operating conditions were found to be: ammonia to EO ratio of 5 (mol/mol), water flow rate of 52.59 kg mol/hr and reactor temperature of 85 °C.

Key words: Simulation, Optimization, Ethanol Amine Production, Ethylene Oxide, Ammonia

INTRODUCTION

Regarding the broad application of Ethanol Amine (EA), its production is of great interest to the petrochemical industry. The industrial production of EA was accomplished in 1930 followed by the large-scale production in 1945, when alkoxylation with ethylene oxide (EO) and propylene oxide was replaced by chlorohydrins [1,2]. The commercial importance of EA increased from 1970, when industrial production of EO began. The modern industrial production of EA is operated exclusively by reaction of EO and excess amount of ammonia in presence of water [3]. It has been proved that a small amount of water is necessary to promote reaction. When there is not any water in the system, EO does not react with ammonia. In fact, water plays a catalytic role in the corresponding reactions [2,4]. Based on operational conditions monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) are produced through three parallel-consecutive competitive reactions [1].

EAs react with a large number of compounds such as ammonia, carbon dioxide, sulfuric acid, sodium hydroxide, carbon disulfide, thionyl chloride and also with acids and aromatic aldehydes [4-6]. In general, they are very desirable as H_2S and CO_2 absorbents for natural gas treatment [7]. Because of alcoholic characteristics, MEA and DEA have broader industrial applications. On the other hand, DEA and TEA are used in making detergents, textiles, pharmaceuticals, emulsifiers in drilling and excavation of oil wells, corrosion inhibitors as well as additives to cement [2].

EAs are hygroscopic, colorless and viscous liquids at room temperature. TEA boils at 27 °C, whereas the other two EAs have higher boiling points. Their densities are slightly greater than water den-

sity and have ammonia-like odor. The EA freezing point is considerably decreased by adding water. MEA and DEA are soluble, with any proportion, in water and alcohol but considerably less in ether. All amines form white crystalline solids when freeze [7].

Very few quantitative studies have been conducted for EA synthesis. One source is the study conducted by Japanese researchers [8], yet the lack of confirmed data renders it unsuitable to construct further modeling and simulation based on a few kinetic data.

In Iran, EA is produced at Arak Petrochemical Complex (APC). In this plant EA is produced from a direct reaction of EO and aqueous ammonia solution in liquid phase (without addition of catalyst) in a tubular fixed bed reactor. EO is also produced in the plant, whereas the required ammonia is provided by the domestic petrochemical industry. The annual APC production capacity of EA is 30,000 tons consisting of 10,000 tons MEA, 8,000 tons TEA and the rest is DEA. Purity of the produced MEA and DEA is 99%, while TEA is produced in 99% and 85% purities [6]. This paper aims to simulate and investigate optimal operating condition of the MEA plant. Based on our literature review no work has been done in this case regardless of the importance of MEA.

EA PROCESS DESCRIPTION

The commonly utilized process of EA production is the SRI process, which has been typically designed for producing 45,000 ton/year EA from ammonia and EO, the production capacity that most of the USA, Western Europe, and Japanese factories fall in. The operational conditions of SRI process have been regulated to prohibit formation of any by-product. This designing concept, however, is not employed in the industry, and the industrial applications differ from the SRI process in that the equipment and plant structure are different, but the reaction is identical [1].

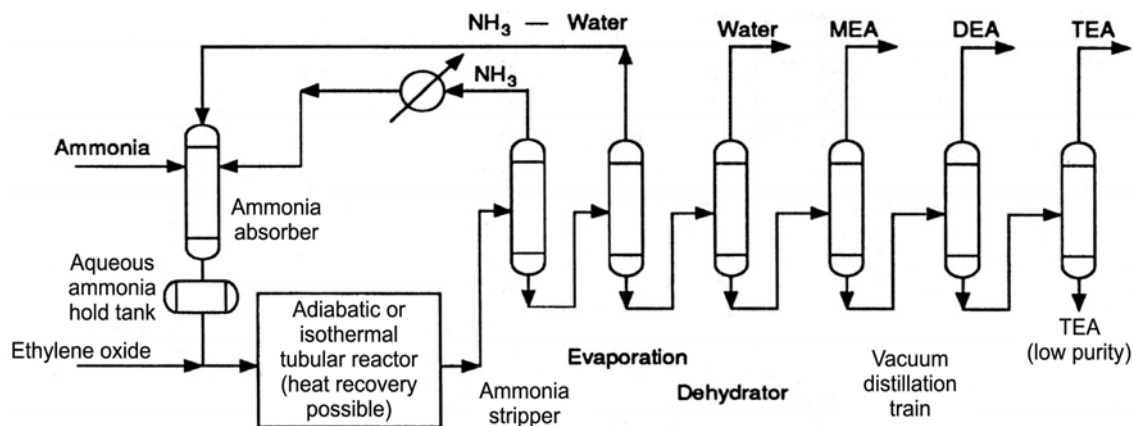†To whom correspondence should be addressed.
E-mail: grzahedi@razi.ac.ir

Fig. 1. Simplified flow diagram of ethanol amine production plant (Adapted from [1]).

Fig. 1 depicts a simplified flow diagram of an EA-producing plant. The flow diagram has two major sections: the reactor and the product separation. EO is added to the concentrated ammonia solution and sent to the reactor section. In general, this section consists of four series of reactors that are adiabatically controlled by an inner coolant. The reactors each are 3 m in length and 0.47 m in diameter. In the reactor section, the 99 wt% ammonia solution reacts with the EO. Almost all of the EO is converted in this section. EO must be added to ammonia solution; otherwise, an explosive polymeric reaction occurs. The output of the reactor enters the ammonia stripper for un-reacted ammonia to be separated as vapor phase and to be sent, after cooling, to an ammonia absorption tower as the make-up ammonia. In the absorber, ammonia is separated and recycled to the feed. The bottom of the ammonia stripper is fed into a vaporizing system to separate water and send it to the absorber. The concentrated dried EAs from the bottom of vaporizer enter into the successive vacuum distillation columns. In the distillation towers MEA (with purity of 99 wt%), DEA (98.5 wt% purity), "commercial" TEA (85 wt% TEA and 15 wt% DEA) and TEA (with purity of 99 wt%) are produced [1,2,4].

An EA production plant is very flexible in order to adapt to market trends and to produce the demanded EA [3]; i.e., many operational parameters may be adjusted to optimize the system to produce desirable product.

One important operational variable affecting product quality is temperature [3]. Higher than required temperature in the ammonia stripper changes color of the product (EAs) and lowers its quaility. Other targeted optimization variables include water content of ammonia solution, and ammonia/EO feedstock ratio. The higher the water feed to the system, the lower the operational pressure and temperature would be, which in turn results in a higher product quality. However, the water addition has to be limitted to decrease utility consumption. Also, a significant amount of water content interferes with the reactions of interest in favor of a side reaction of water with EO to produce ethylene glycol.

The ammonia/EO ratio determines the proportion of final product of EA type [8]. Although this ratio is important, we did not find a systematically optimized value among the literature for this ratio. A non peer-reviewed estimation was identified [10] in which this ratio was enveloped between 10 (when only MEA is virtually pro-

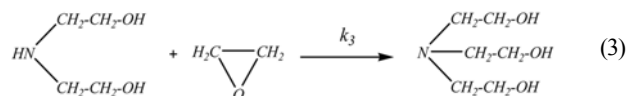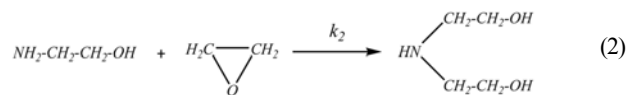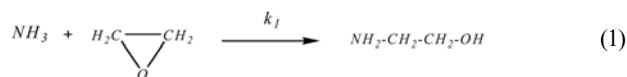duced) to 3 (more even distribution of the three products).

Optimization of other equipment within the plant has been also suggested. For example, the distillation columns can be optimized; however, optimization of the EAs distillation columns is beyond the scope of this work and may be found in other sources (for example, [11] and references therein).

EVALUATION OF REACTION RATE CONSTANTS

There are some industrial processes for the EAs production, including:
- BASF Process
- Dow Process
- Union Carbide Process
- Euteco SPA Process
- Nippon Shokubai Process
- Oxiten Process

All of the above processes exploit reaction of ammonia with EO but are different in the operational conditions (such as residence time, operational temperature and pressure, ammonia concentration and other feed specifications) and equipment (such as adiabatic or isothermal reactors and the number of reactors). Three reactions have mainly been recognized in the ethyl amine production [3,8]:

$$NH_3 + H_2C\underset{O}{\overset{}{\diagdown}}CH_2 \xrightarrow{k_1} NH_2\text{-}CH_2\text{-}CH_2\text{-}OH \tag{1}$$

$$NH_2\text{-}CH_2\text{-}CH_2\text{-}OH + H_2C\underset{O}{\overset{}{\diagdown}}CH_2 \xrightarrow{k_2} HN\underset{CH_2\text{-}CH_2\text{-}OH}{\overset{CH_2\text{-}CH_2\text{-}OH}{}} \tag{2}$$

$$HN\underset{CH_2\text{-}CH_2\text{-}OH}{\overset{CH_2\text{-}CH_2\text{-}OH}{}} + H_2C\underset{O}{\overset{}{\diagdown}}CH_2 \xrightarrow{k_3} N\underset{CH_2\text{-}CH_2\text{-}OH}{\overset{CH_2\text{-}CH_2\text{-}OH}{-CH_2\text{-}CH_2\text{-}OH}} \tag{3}$$

All of the above reactions occur simultaneously in parallel and in series. The ratio of each EA in the final product is controlled by controlling ammonia to EO ratio [8].

Kinetic information pertaining to the reaction of EO with ammonia is not conclusive. Reference [1] reports the effect of different input aqueous ammonia solution on the produced EA characteris-

tics. The reaction of EO with dilute aqueous ammonia solution (less than 3 wt% of NH_3) at 15 °C and variable molar ratio of 0.5/1 to 20/1 of ammonia to EO were studied. The data were explained by an Arrhenius-type relationship (Eq. (4)) with activation energy, and pre-exponential constants for the specific rate of the reactions are given in Table 1.

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (4)$$

where E is activation energy and k_0 is a pre-exponential constant.

Table 1. Arrhenius parameters for Eq. (4) [1]

Reaction	E	k_0
$EO+NH_3$	14.6	4.11×10^8
EO+MEA	15.7	1.13×10^{10}
EO+DEA	15.1	2.94×10^9
EO+TEA	12.7	4.23×10^6

Other relations were presented for the specific rate of contributing reactions as Eqs. (5) to (7) [8]:

$$k_1 = (41 + 4[H_2O]^2) \times 10^2 \exp\left(\frac{-11000}{RT}\right) \quad (5)$$

$$k_2 = (7.2 - 0.042[H_2O]) \times k_1 \quad (6)$$

$$k_3 = (16 - 0.22[H_2O]) \times k_2 \quad (7)$$

Assuming a first order conversion of EO in the temperature range of 20 °C to 125 °C and ammonia solution of 50 to 100 wt%, the general equation has been proposed [12]:

$$k = 1.3 \times 10^7 \left(\frac{C}{100}\right)^{-7.6} \exp\left(\frac{-14500}{RT}\right) \quad (8)$$

where C is the ammonia mass composition in the feeding solution.

Due to the uncertainty in the kinetics data, in this study the data from reference [1] were used to optimize k-values (k_o corresponding to each specific rate) for the reactions.

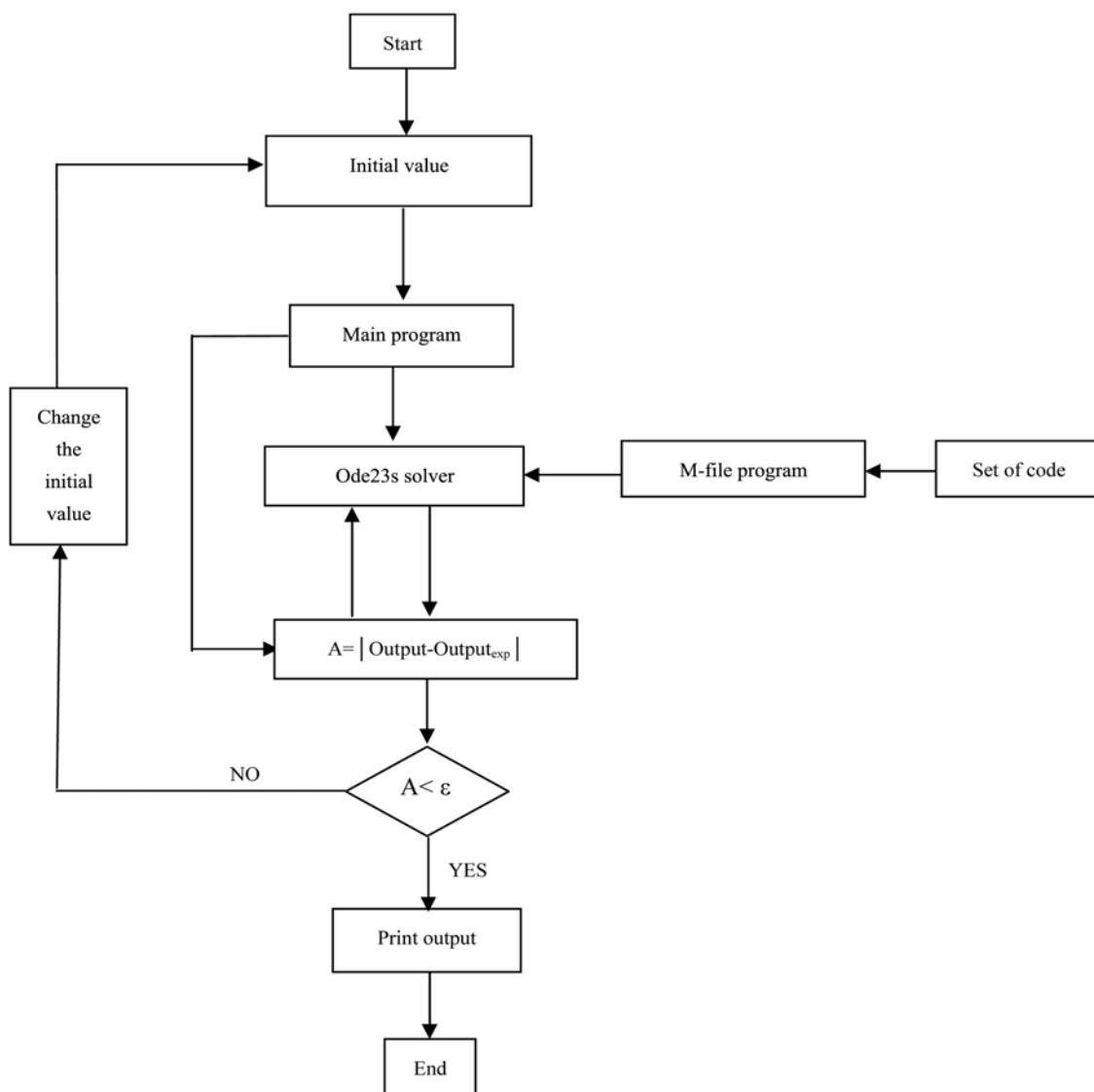Considering the reaction Eqs. of (1), (2) and (3), each compo-

Fig. 2. Optimization algorithm for EA kinetic parameter estimation.

nent reaction rate can be described as follows [13]:

$$\frac{d[NH_3]}{dt} = -k_1[NH_3][EO] \tag{9}$$

$$\frac{d[EO]}{dt} = -k_1[NH_3][EO] - k_2[MEA][EO] - k_3[DEA][EO] \tag{10}$$

$$\frac{d[MEA]}{dt} = k_1[NH_3][EO] - k_2[MEA][EO] \tag{11}$$

$$\frac{d[DEA]}{dt} = k_2[MEA][EO] - k_3[DEA][EO] \tag{12}$$

$$\frac{d[TEA]}{dt} = k_3[DEA][EO] \tag{13}$$

For the optimization, Matlab 7.6 with solver ODE23s [14] was used to solve the series of above ordinary differential equations (ODEs). Fig. 2 illustrates the proposed algorithm for obtaining kinetic constants. The algorithm first estimates the parameters (k_1, k_2, and k_3), followed by solving the ODEs and checking the error between results and the experimental data. The process continues until convergence to the experimental data is reached.

Results of the optimization of reaction rate constants are presented in Table 2.

PROCESS MODELING

The objective of mathematical modeling and simulation is to in-

Table 2. Results of optimization algorithm for kinetic parameters estimation

Reaction	E	k_0
EO+NH$_3$	19660	1.581×10^7
EO+MEA	19660	4.92×10^8
EO+DEA	19660	5.2×10^8

vestigate the effects of different parameters on the process and subsequent optimization of process operation. For the process modeling in this study Hysys 3.2 was used. Fig. 3 illustrates the process flowchart made in Hysys, with the four reactors are labeled as R101A to R101D.

Appropriate equations were selected in order to estimate the physical properties of all components in the system. The results of simulation are strongly influenced by the selected Hysys thermodynamic model, i.e., selection of an inappropriate thermodynamic model will result in error in model predictions. The thermodynamic models in the Hysys environment are classified into three main groups: 1- equations of state such as SRK; 2- equations of activity coefficient such as NRTL; 3- special thermodynamic models such as the amine model prepared for a system consisting of amines, acidic gas and water [15].

SIMULATION RESULTS

To build the process flow diagram in the Hysys environment, the composition of materials, equation of state and reactions were specified. The reactor feed specifications are presented in Table 3.

Table 4 provides a comparison between the simulation and process (SRI) data. For comparison, the errors in the simulation are also given. Maximum error appears to be less than 4%, validating the simulation approach.

For different towers Tables 5, 6 and 7 present the estimated pro-

Table 3. Characteristics of feed to the reactor

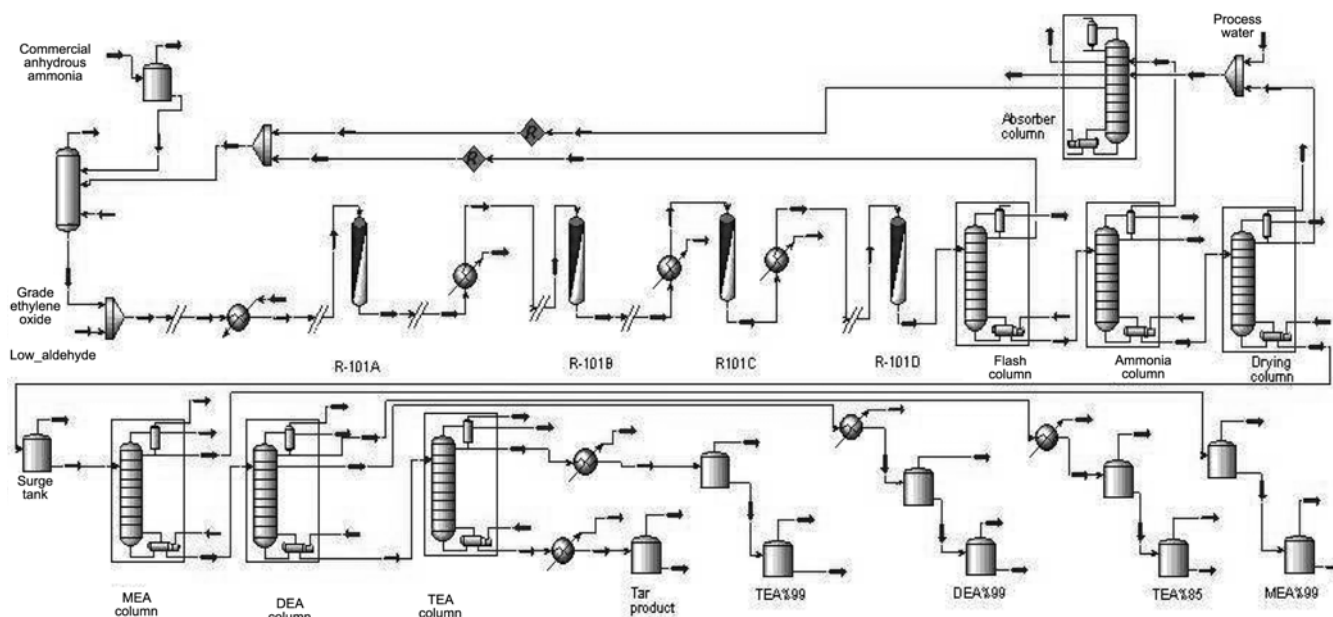|	
Temperature (°C)	85
Pressure (KPa)	1.02×10^4
Total molar flow (kg mol/hr)	687.83
Molar flow of ammonia (kg mol/hr)	529.09
Molar flow of EO (kg mol/hr)	105.82
Molar flow water (kg mol/hr)	52.92

Fig. 3. Hysys process flowchart of the EA production plant.

Table 4. The characteristics of the reactor's effluent stream (mole ratio of ammonia to EO equals 5/1)

Compound	SRI result (kg/hr)	Hysys result (kg/hr)	Percent of relative error
Ammonia	7842	7864	0.28
EO	-	-	-
Water	935	935	0.00
MEA	2456	2365	3.69
DEA	2037	1966	3.47
TEA	1338	1388	3.72

duction of different compounds including EAs and compare them with SRI unseen data. Some significant differences between calculated and SRI data are observed. The main reason may be the limitation of the software, particularly in the thermodynamic models available in Hysys. Again, the differences between the simulated and SRI data are mostly less than 10%, which seems acceptable.

PROCESS OPTIMIZATION

Optimization problems are made up of three basic ingredients:

• An objective function that is to be minimized or maximized. For instance, in a manufacturing process, the objective is to maximize profit or minimize cost.

• A set of unknowns or variables that control the objective function value. In the manufacturing problem, the variables might include the amounts of different resources used or the time spent on each activity.

• A set of constraints that allow the unknowns to take on certain values but exclude others. For the manufacturing problem, it is meaningless to spend a negative amount of time on any activity, so all the "time" variables are constrained to non-negative values [12].

Generally, in optimization of processes, many parameters like temperature, pressure, raw materials flow rate, operational equipment size and the process economy can be considered. To maximize production rate, the optimum values of these parameters should be obtained. For the EA production process in this case, as the sizes of apparatus were already designed, this parameter is considered constant. The operational pressure was also assumed to be constant. Temperature, raw materials flow rate (feed) such as ammonia, EO and water were considered as optimization variables, and the process simulation was carried out for different rates. EA production and cost objective function can be set as the objective func-

Table 5. Comparison between simulation and SRI data (kg/hr)

Component	Bottom product of flash tower		Bottom product of ammonia tower		Bottom product of drying tower	
	SRI data	Hysys result	SRI result	Hysys result	SRI result	Hysys result
Ammonia	470	491.60	24.53	24.49	-	-
EO	-	-	-	-	-	-
Water	934	934	934.21	933.90	6.35	6.03
MEA	2456.60	2366.33	2454.34	2366.33	2444.36	2354.10
DEA	2037.12	1966.43	2037.12	1966.43	2036.67	1966.43
TEA	1338.73	1479.61	1338.73	1479.61	1338.73	1388.91

Table 6. Comparison between simulation and SRI data (kg/hr)

Component	Overhead product of MEA tower		Bottom product of MEA tower		Bottom product of DEA tower	
	SRI result	Hysys result	SRI result	Hysys result	SRI result	Hysys result
Ammonia	-	-	-	-	-	-
EO	-	-	-	-	-	-
Water	-	-	-	-	-	-
MEA	2426.22	2329.03	18.14	18.66	-	-
DEA	16.32	15.29	2020.34	1966.42	1.36	0.96
TEA	0.45	0.51	1338.28	1479.56	468.50	615.80

Table 7. Comparison between simulation and SRI data (kg/hr)

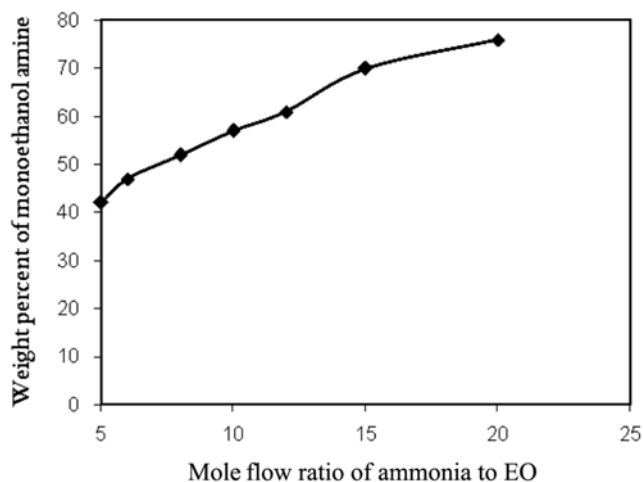| Component	Overhead product of DEA tower		The side product DEA tower		Overhead product of TEA tower	
	SRI result	Hysys result	SRI result	Hysys result	SRI result	Hysys result
Ammonia	-	-	-	-	-	-
EO	-	-	-	-	-	-
Water	-	-	-	-	-	-
MEA	18.14	15.17	-	-	-	-
DEA	1867.96	1541.75	150.56	145.94	1.36	0.52
TEA	6.35	5.74	410.86	410.86	421.75	423.12

Fig. 4. Variation of objective function with molar ratio of ammonia to EO.
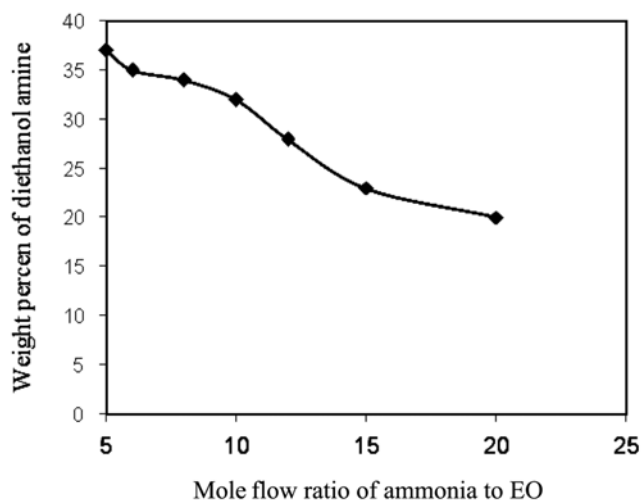

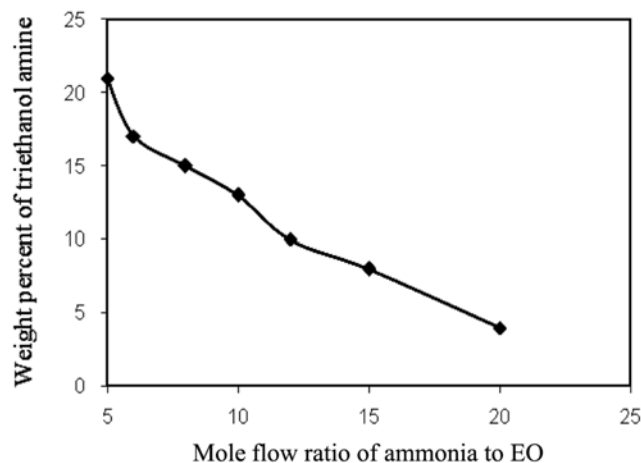**Fig. 5. Effect of ammonia to EO molar ratio on DEA production rate.**

Fig. 6. Effect of ammonia to EO molar ratio on TEA production rate.

Table 8. Price of the raw materials and products [18]

Compound	Price ($/tonne)
Ammonia	25.25
EO	155.26
Water	18.00
MEA	177.40
DEA	193.95
TEA (%99)	190.92
TEA (%85)	187.19

tion in this part of study. As there was not any idea about a suitable practical objective function, both of the objective functions were examined. The GS method was first applied to optimize the molar production of MEA as the objective function as follows:

$$\text{Objective function (J)} = \text{Mole}_{MEA} \qquad (14)$$

Figs. 4 to 6 depict effect of feed specification (ammonia molar flow/ EO molar flow) on the content of three EA types as final products.

Increasing ammonia content in the feed increases the production of MEA and decreases the DEA and TEA in the product: no optimal point appeared in the above figures. As a result, the objective function was changed to the profit function as a realistic approach defined below [13]:

$$\text{Objective function (J)} = [\text{products price}] - [\text{raw materials price}] \qquad (15)$$

$$\begin{aligned} J = & [kg_{MEA} \times price_{MEA} + kg_{DEA} \times price_{DEA} + kg_{TEA(\%85)} \times price_{TEA(\%85)} \\ & + kg_{TEA(\%99)} \times price_{TEA(\%99)}] - [kg_{NH_3} \times price_{NH_3} + kg_{EO} \times price_{EO} \\ & + kg_{H_2O} \times price_{H_2O}]. \end{aligned} \qquad (16)$$

Table 8 presents price of the raw materials and products [18].

The constraints exposed to the optimization process were selected based on operationally practical conditions [3,7,10] and included the ammonia to EO molar flow of 5 to 20, and temperature range of 85 °C to 120 °C. Temperatures beyond this range results mainly in occurrence of side reactions.

OPTIMIZATION RESULTS

Figs. 7, 8 and 9 exhibit the variations of profit function (Eq. (16)) with changes in three selected controlling factors. At the maximum profit, the optimum values of the variables were found to be: ammonia to EO molar ratio 5/1; water molar flow 52.92 kg mol/hr and reaction temperature 85 °C. As observed in Fig. 7, the ratio ammonia/EO=5/1 generates maximum profit which overlaps the maximum profit observed in Figs. 8 and 9.

CONCLUSION AND REMARKS

An EA production plant was simulated by using Hysys software. The results of simulation revealed that the simulated data have a good agreement with the SRI data. There are, however, some errors in the predicted data, mainly because of the software's weakness in this study, and particularly due to the available Hysys thermodynamic models.

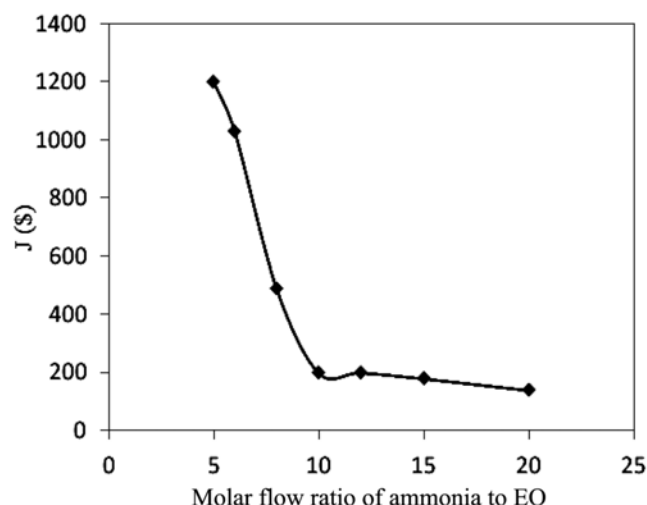The simulation also necessitates using accurate reaction rates.

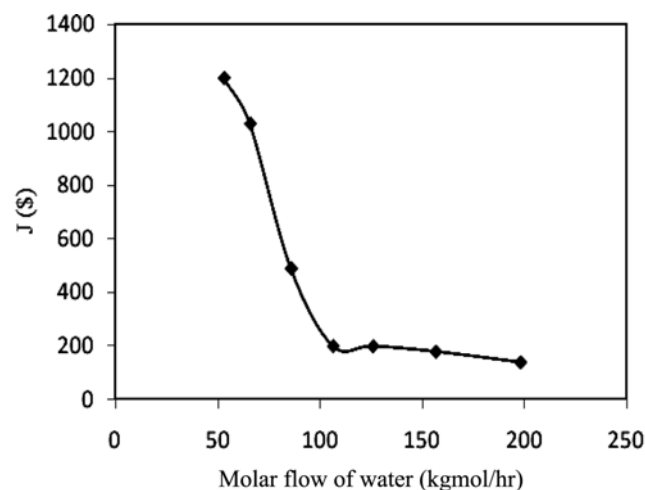**Fig. 7. Economical profit (objective function) in terms of feeding molar ratio of Ammonia to EO.**

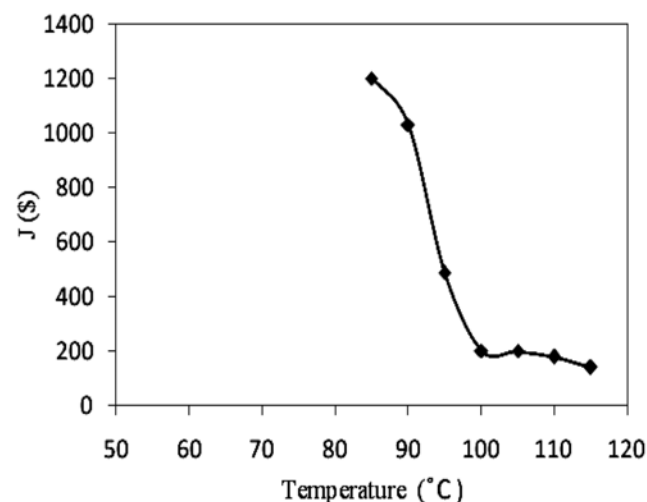**Fig. 8. Variation of objective function with change of water molar inflow.**

Fig. 9. Effect of reactor temperature on the process profit.

Since there are not convincing studies on the EA's production in the literature, a simple kinetics optimization was carried out and results were confirmed by comparison with the available experimental data.

Next step involved optimization of the process to evaluate the effects of feed flow rates and input reactor temperature, while the pressure and equipment size were deemed constant. The MEA yield appeared as an improper objective function having monotonic trends with the selected controlling variables; therefore, no feasible results were found. Consequently, the process profit was set as the objective function. Results of optimization showed that the optimal operation points are the ammonia to EO molar ratio of 5, reaction temperature of 85 °C and water flow rate of 52.92 kg mol/hr.

NOMENCLATURE

C   : concentration [%wt]
E   : activation energy [kcal mole^{-1}]
J   : objective function
k_0 : frequency factor [L mol^{-1} min^{-1}]
k_1, k_2, k_3 : kinetics constants [L mol^{-1} min^{-1}]
ODE : ordinary differential equation
R   : gas constant [kcal mol^{-1} K^{-1}]
T   : temperature [K], or otherwise stated
t   : time [min]

Greek Letter

ε : error

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