Sub-Atmospheric Distillation for Water (1)
+ Dimethyl Amino Ethyl Azide (2) Mixture

Ghanbari Pakdehi, Shahram*+; Rouhandeh, Hossein

Faculty of Chemistry and Chemical Engineering, Malek Ashtar University of Technology, Tehran, I.R. IRAN

ABSTRACT: *Dimethyl amino ethyl azide (DMAZ) is a good replacement for hydrazine group in space programs. This chemical was purified from water (1) + DMAZ (2) mixture in sub-atmospheric distillation column due to thermal sensitivity of DMAZ. For designing of the column, it is necessary to have vapor-liquid equilibrium data. In this article, T-x,y and y-x diagrams were obtained under 40 mbar pressure. Results showed that there exists an azeotrope in the mixture of water (1) + DMAZ (2). Experiments were conducted at different vapor flow rates in the batch distillation column to determine the time necessary for purification of DMAZ. Comparing the experimental results for the distillation time with the theoretical results presented an error time of about 2.6%.*

INTRODUCTION

Hydrazine derivatives such as monomethyl hydrazine (MMH), un-symmetrical dimethyl hydrazine (UDMH) and Aerozine-50 (a mixed fuel of hydrazine and UDMH) have been used since 1949 in space programs. Despite their good performance, they are carcinogen [1-3]. Therefore, it is pursued to replace them with a non-carcinogen fuel. During an extensive research program, the National Aeronautics and Space Administration (NASA) introduced dimethyl amino ethyl azide (DMAZ) as a novel liquid fuel in space industries [4]. DMAZ is synthesized from the reaction between dimethyl amino ethyl halide and sodium azide. The produced DMAZ contains up to 3 wt% of water [5,6]. For storage and using of DMAZ in satellite carrier rocket, it must be purified so that the final water should be less than 0.3 wt% [1]. Several methods may be used for purification of DMAZ. However, high consumption of DMAZ

for a rocket dictates to provide an industrial method. Distillation is suggested for this purpose. Azide group (-N$_3$) in DMAZ is generally thermal sensitive [7]. So the distillation should be carried out at sub-atmospheric pressure. Preliminary experimental tests showed that pressure of 40 mbar was appropriate in sub-atmospheric batch distillation [8].

In chemical technology, Vapor-Liquid Equilibrium (VLE) data is necessary for design of distillation column [9-12]. Two points should be considered in design of a batch distillation column: (i) the boiling diagram for the components, which serves as the basis for equilibrium diagram, appropriate for process calculation; and (ii) establishment of the necessary data for batch distillation [13]. Batch distillation column can be run in three different modes: with constant reflux ratio, constant overhead composition and as time optimal batch distillation.

The operation with constant overhead composition is closer to the optimal than to constant reflux technique and also easier to control than the optimal batch distillation. To maintain constant overhead composition, the reflux ratio should be increased continuously. When variable reflux control is to be used and determined in advance, the shortest time operation can be achieved [14-18].

VLE data for water-DMAZ system have not been published yet. The aim of this technologic or engineering work is therefore to determine the boiling diagram for water (1) + DMAZ (2) system. Also by conducting the batch distillation, the time necessary for purification of DMAZ at different vapor flow rates will be determined.

EXPERIMENTAL SECTION
Chemicals
DMAZ was synthesized from the reaction between dimethyl amino ethyl chloride and sodium azide [5] with purity >99.9wt%. The water used was re-distilled.

Apparatus
Karl Fischer titration is more expensive than refractometry. On the other hand, the refractive indexes of pure water and pure DMAZ are 1.333 and 1.448, respectively [19,20]. So it seems that the refractory would be a useful method for determination of water content in the mixture for drawing VLE diagram. Refractometry method has been used in a similar work by *Stefanic et al.* [21]. For this purpose, the refractive index was measured using a thermostatically controlled refractometer (OPTECH, Germany) equipped with a digital thermometer, with an uncertainty of ± 0.01 °C.

The vapor-liquid equilibrium data was obtained using of modified dynamic phase equilibrium apparatus (model VLE 602/50, i-Fischer Engineering, Germany). The temperature range of the operation was up to 50°C and the pressure range was from 40 mbar to 1 bar. The amount of mixture loaded in the cell was 100 cm^3. The temperature was detected with a digital precision platinum resistance thermometer (Hart Scientific, Model 1506), calibrated according to the MIL-STD-45662-A standard with the accuracy of ± 0.05°C. A pressure transducer VKH 300, calibrated against an MKS Baratron type 170 M system, was employed to measure the pressure. The pressure was maintained at its set point with an electric pressure controller within ± 1 mbar.
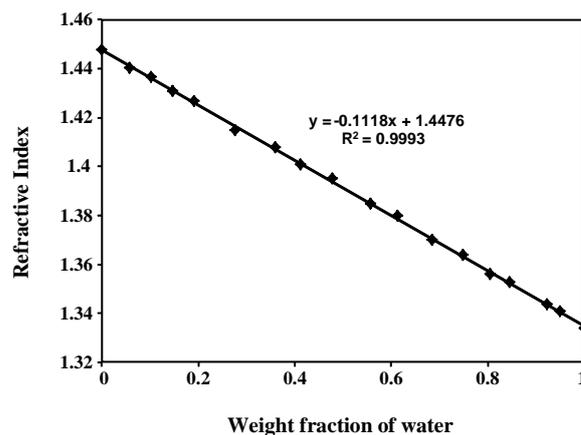

Fig. 1: Calibration line for measuring of water in water (1)-DMAZ (2) mixture

After determining VLE data for DMAZ-water, purification of DMAZ was carried out in a sieve tray distillation column in batch state. The diameter of the column and number of tray were 5 cm and 5, respectively. All parts of the column were made from glass. The column was insulated by glass wool.

Procedure
The refractometer was frequently calibrated using of double-distilled water. Water was circulated into the instrument through a thermostatically controlled bath maintained at the constant temperature with accuracy of ± 0.01 °C. At least, three analyses were made for each sample. The refractive index data was obtained for binary mixture of water (1) + DMAZ (2) at 20°C. The composition of the mixture is expressed by mole fraction *x* of the more volatile component, water in this case.

RESULTS AND DISCUSSION
VLE diagram
Dependency of refractive index on water content in water (1) + DMAZ (2) mixture is illustrated in Fig. 1. As it is shown, there is a good linear relationship between refractive index and the water content.

On the basis of the calibration curve (Fig.1), the vapor-liquid equilibrium measurements were performed over the entire concentration range at 40 mbar pressure.

Fig. 2 demonstrates boiling point of the mixture versus the composition of water. It is considerable that the dew-point (T-y) curve lies above the bubble-point (T-x) curve.
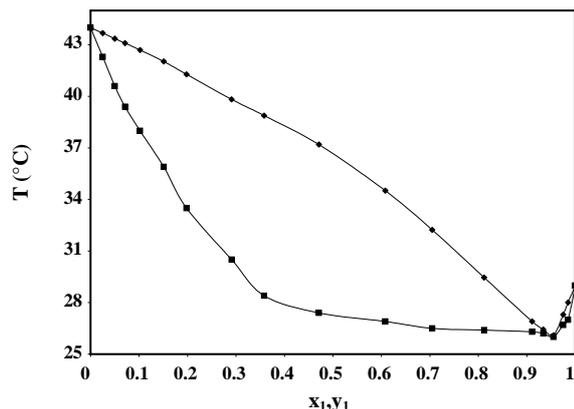
Fig. 2: T-x-y diagram for water (1) + DMAZ (2) at 4 kPa: -■- experimental liquid-phase mole fractions, x_1; -♦- experimental vapor-phase mole fractions, y_1.

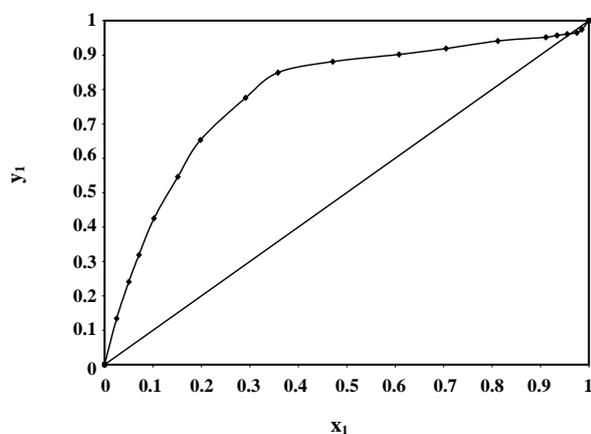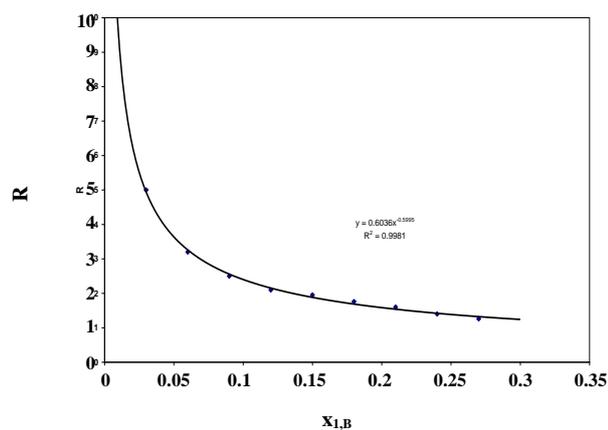*Fig. 3: Equilibrium y-x diagram of water (1) + DMAZ (2) mixture at a constant pressure of 40 mbar.*

Fig. 4: Reflux ratio (R) as a function of water concentration in bottom composition ($x_{1,B}$) to reach an azeotrope concentration ($x_{1,D} = 0.96$).

The mixture has a minimum temperature azeotrope. It may be that nitrogen atom in DMAZ forms hydrogen bonds with water. Also *y-x* diagram of the mixture is given in Fig. 3 at 40 mbar pressure. As it is seen, the mixture shows an azeotrope at x_1 about 0.96.

Dependence of reflux ratio on liquid composition

The dependency of reflux ratio R on bottom composition $x_{1,B}$ can be found by graphical method for the construction of operating lines at different reflux ratios in the equilibrium diagram (Fig.4), taking into account the values: the initial molar bottom composition $x_{1,B0} = 0.03$, the required molar bottom composition $x_{1,Bf} = 0.003$, the distillated composition $x_{1,D} = 0.96$ and 5 trays or stages as an acceptable starting technical solution.

Evaluation of distillation time for a given purification

For the mixture under consideration $R = mx_{1,B}^{n}$ is a useful expression for the solution of Bogart's integral, which describes the time dependency on bottom composition [22]:

$$t = \frac{B_o \cdot (x_{1,D} - x_{1,Bo})}{V} \times \int_{x_{1,Bf}}^{x_{1,Bo}} \frac{(R(x_{1,B}) + 1)dx_{1,B}}{(x_{1,D} - x_{1,B})^2} \tag{1}$$

Where B_0 is the initial total mole of the mixture in the feed vessel and V is vapor flow rate.

Using data from Fig.4, coefficients *m* and *n* were calculated and the relationship between reflux ratio *R* and bottom composition $x_{1,B}$ is obtained:

$$R = 0.6036x_{1,B}^{-0.5995} \tag{2}$$

Equation (2) enables the analytical solution of Bogart's integral (Eq.(1)), taking into account specific technical data like heat flux and vapor flow rate.

For a batch vacuum distillation column with 5 sieve trays, 17.5 mole of the feed (containing 0.525 mole water) and totally condensing, the required time for separation of water was calculated at various flow rates of vapor. The results are given in Table 1. Also the measured times for this purpose are given in this table. In these experiments, receiver is a calibrated cylindrical vessel, so the volume flow rate of distillate (V) is measured in no reflux state. As it is shown in Table 1, the average percent of absolute relative deviation of time between the calculated time of distillation (from Bogart's integral)

Table 1: The time for separation of water from water (1) + DMAZ (2) mixture (B_o = 17.5, $x_{1,D}$= 0.96, $x_{1,Bo}$= 0.03, $x_{1,Bf}$ = 0.003).

Experiment No.	V(mol/min)	Calculated t from eq.(1) (min)	Measured t (min)	Percent of absolute relative deviation of time
1	0.27	16.83	16.95	0.7
2	0.34	13.36	13.86	3.6
3	0.43	10.57	10.94	3.4
4	0.55	8.26	8.52	3.0
5	0.62	7.33	7.51	2.4
6	0.74	6.14	6.28	2.3

and the experimental time is about 2.6%. In measuring the time, it was tried to insulate the column. Also, in each case heat source (mantle) was adjusted to obtain the certain V value.

CNONCLUSIONS

Dimethyl amino ethyl azide (DMAZ), as a novel liquid fuel in space programs, was purified from a mixture of water (1) + DMAZ (2) in a batch sub-atmospheric (40 mbar) distillation column due to thermal sensitivity of azide group in the DMAZ molecule. For this purpose, vapor-liquid equilibrium data (T-x-y and y-x diagrams) were experimentally obtained for this mixture. It was observed the mixture had an azeotrope at x_{water}= 0.96. Also, reflux ratio versus the bottom concentration of water (as a volatile component) was obtained. Using of Bogart's integral, separation time of water from the mixture up to azeotrope concentration was determined both theoretically and experimentally. This study represents a useful basis for technological development of a purification unit as a part of the liquid fuel production equipment.

NOMENCLATURES

B_0 Initial amount of the mixture in the feed vessel, mole

DMAZ   Dimethyl amino ethyl azide ($(CH_3)_2$-N-CH_2-CH_2-N_3)

n_D^{20} Index of refraction of water in mixture

R   Reflux ratio

T   Temperature, ºC

t   Time needed for separation of water from mixture, min

V   Vapor flow rate, mol/min

x_1 Mole fraction of water in liquid phase

$x_{1,B}$ Mole fraction of water in distillation column at any time

$x_{1,B0}$ Mole fraction of water in distillation column at initial time (t=0)

$x_{1,Bf}$ Mole fraction of water in distillation column at final time

$x_{1,D}$ Mole fraction of water at the top of column or in distillate

y_1 Mole fraction of water in vapor phase

REFERENCES

[1] Schmidt E. W., "Hydrazine and Its Derivatives", John Wiley and Sons, New York (2001).

[2] Agrawal J. P., "High Energy Materials: Propellants, Explosives and Pyrotechnics", Wiley-VCH, Weinheim (2010).

[3] Reddy G., Song J., Mecchi M. S., Johnson M. S., Genotoxicity Assessment of Two Hypergolic Energetic Propellant Compounds, *Mutat. Res.-Gen. Tox. En.*, **700**(1-2): 26-31 (2010).

[4] Thompson D., Tertiary Amine Azides in Hypergolic Liquid or Gel Fuels Propellant System, *US Patent 6013143* (2000).

[5] Schiemenz P., Engelhard H., Trimethoxyphenyl Derivatives. I. Synthesis of Amines via Mixed Anhydrides, *Chem. Ber.*, **92**: 857-862 (1959).

[6] Jafarikhah K., "Study on Effective Parameters in Production of DMAZ in Bench Scale and Optimizing Them", MSc Thesis, Malek Ashtar University of Technology, Tehran, Iran (2011).

[7] Darvich M.R., Olyai A., Shabanikia A., Farkhani D., Reaction of Sodium Azide with 1,1'–Dicyclohexenyl–Diepoxides, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **22**(2):49-53 (2003).

[8] Rouhandeh H., Study on Effective Parameters on Purification of DMAZ in a Proper Method and Design of the Unit in Pilot Plant", MSc Thesis, Malek Ashtar University of Technology, Tehran, Iran (2011).

[9] Aucejo A., Loras S., Martinez-Soria V., Becht N., Rio G.D., Isobaric Vapor−Liquid Equilibria for the Binary Mixtures of Styrene with Ethylbenzene, o-Xylene, m-Xylene, and p-Xylene, *J. Chem. Eng. Data*, **51**(3): 1051–1055 (2006).

[10] Lotfollahi M.N., Modarress H., Khodakarami B., VLE Predictions of Strongly Non-Ideal Binary Mixtures by Modifying Van Der Waals and Orbey-Sandler Mixing Rules, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **26**(3):73-80 (2007).

[11] Pahlevanzadeh H., Ahooei A.M., Estimation of UNIQUAC-NRF Model Parameters for NH_3-CO_2-H_2O System, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **24**(1): 21-26 (2005).

[12] Asadi S., Multicomponent Distillation Modeling of an Essential Oil by the SRK and PSRK State Equations, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **33**(3):77-82 (2014).

[13] Ehsani M.R., Prediction of the Operating Conditions in a Batch Distillation Column Using A Shortcut Method, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **21**(2):118-125 (2002).

[14] Narvaez-Garcia A., del Carmen Zavala-Loria J., Enrique Vilchis-Bravo L., Antonio Rocha-Uribe J., Design of Batch Distillation Columns Using Short-Cut Method at Constant Reflux, *J. Eng.*, **14**: 2013-2027 (2013).

[15] Diwekar U.M., "Batch Distillation, Simulation, Optimal Design and Control", CRC Press, New York (2012).

[16] Jain S., Kim J.K., Smith R., Operational Optimization of Batch Distillation Systems, *Ind. Eng. Chem. Res.*, **51**(16): 5749–5761(2012).

[17] Barrera R., Villa A. L., Montes de Correa C., Ricardez-Sandoval L., Elkamel A., Dynamic Modeling and Optimization of A Batch Reactor for Limonene Epoxidation, *Ind. Eng. Chem. Res.*, **49**(18): 8369-8378 (2010).

[18] Fanaei Shykholeslami M.A., Dehghani H., Nadi S., Comparing and Controlling of Three Batch Distillation Column Configurations for Separating Tertiary Azeotropic Mixtures, *Scientia Iranica*, **19**(6): 1672-1681 (2012).

[19] Meyers C.J., Kosowski B.M., Dimethylamino Ethylazide: A Replacement of Hydrazine Derivatives in Hypergolic Fuel Applications, "International Annual Conference of ICT", Fraunhofer, Germany, pp:1-4 (2003).

[20] Perry R. H., Green D., "Perry᾽s Chemical Engineers᾽ Handbook", 7th ed., McGraw-Hill Inc., New York (1997).

[21] Petek S.A., Bradesko L., Zilnik L.F., Zupancic S., Distillation of Water-N-Methylimidazole System, *Acta Chim. Slov.*, **48**: 515-520 (2001).

[21] Coward I., The time-optimal problem in binary batch distillation, *Chem. Eng. Sci.*, **22**(4): 503-516 (1967).