

## CONCENTRATION OF NITRIC ACID BY VACUUM DISTILLATION

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### ABSTRACT

Nitric acid was concentrated by atmospheric distillation, stripping of dissolved  $N_2O_4$  gases and vacuum distillation. A packed column was locally constructed to determine the theoretical stages required for concentration of nitric acid. The evaluation of the packed column was achieved by using methanol-water system as a test system. By vacuum distillation, the azeotropic nitric acid (68.5 wt.%  $HNO_3$ ) was concentrated up to 98 wt.%  $HNO_3$  within 6 theoretical stages at total reflux and 150 mmHg.

To submit a packed column design for 1 ton/day of concentrated nitric acid (98 wt.%  $HNO_3$ ), the vapor-liquid equilibrium data of the nitric acid-water system at 150 mmHg was predicted by using Wilson model as a thermodynamic model. The stripping of the dissolved  $N_2O_4$  gases from the azeotropic nitric acid was necessary for the concentration step of nitric acid by vacuum distillation where the reduction of dissolved  $N_2O_4$  gases from 0.85 to 0.02 wt.%  $N_2O_4$  was achieved in a stripping column.

### INTRODUCTION

Nitric acid lies second after sulfuric acid in the world production and consumption list of inorganic acids, and has many important fields of utilization. The chemical industry is the main consumer of the acid itself: nitration of organic compounds supplies the dyestuff, pharmaceutical and explosives.

The growing use of concentrated nitric acid or  $N_2O_4$  in the missile and rocket field could form a promising new outlet too. In addition to important applications in the explosive industry, inorganic nitrates, and mainly ammonium nitrate, have found the most extensive market in fertilizer manufacture where about three-fourths of the nitric acid produced is used in the fertilizer industry. The nitric acid needed in the fertilizer industry is usually dilute nitric acid with a concentration of 50-70 wt.%  $HNO_3$ .

In general, the production of nitric acids via the catalytic oxidation of ammonia involves three main steps: (1) The oxidation of ammonia to nitrogen oxide. (2) The oxidation of nitrogen oxide to nitrogen dioxide. (3) The absorption of the nitrogen dioxide in water to make nitric acid. All three reactions are exothermic.

### Concentrated Nitric Acid Production

There is a substantial need for stronger acid, particularly for acid with a concentration in the range of 90-100 wt.%  $HNO_3$ . Such acid is, for example, used in nitrogen reaction. However,

concentrated nitric acid cannot be directly prepared by distillation of dilute acid of 60 wt.%  $HNO_3$ , because nitric acid and water form an azeotrope at 68.5 wt.%  $HNO_3$  at 1 bar.

Concentrated nitric acid can be produced following either of two main routes: the indirect or the direct method, and for every method there are many proprietary processes. Among these processes, three adopted in Iraq to produce concentrated nitric acid, namely: HOKO, PLINKA, and MAGGIE.

Indirect methods start with dilute nitric acid coming from a normal oxidation-absorption plant and breakdown the azeotropic mixture which would form in the distillation by adding a third component, a dehydrating agent, a technique called extractive distillation. The dehydrating agents, which have found industrial application, are concentrated sulfuric acid and 72 wt.% magnesium nitrate.

In the direct methods, concentrated nitric acid is directly obtained from ammonia without any need for external dehydrating agents. There are two routes, first the classic route was developed where  $N_2O_4$  is produced in liquid form from the gas mixture by absorption in concentrated nitric acid and then lets it react under pressure with pure oxygen and water.

In the last three decades a second possibility was discovered: the superazeotropic acid route. The comparison among these types of concentration methods is illustrated in table (1).

An alternative process was developed by Davy



Mckee AG company in 1960 (Chilton, 1968). This process used vacuum technology for concentration of nitric acid by using a system consisting of only atmospheric and vacuum distillation. In the first column, operating at 760 mmHg, dilute nitric acid (55 wt.% HNO<sub>3</sub>) concentrates to 68.5 wt.% HNO<sub>3</sub> azeotropic mixture with pure water coming off overhead. In the second column, operating at only 150 mmHg, however, the azeotropic composition is only 66 wt.% HNO<sub>3</sub>. This means that the feed stream of 68.5 wt.% HNO<sub>3</sub> is on the nitric acid side of the equilibrium curve so that 98 wt.% HNO<sub>3</sub> distills off while the 66 wt.% HNO<sub>3</sub> bottoms is recycled to the first column.

Table (1) Comparison of Concentration methods for production of concentrated nitric acid

Method	Advantage	Disadvantage
Condensation and direct synthesis	Capability of steam exporting	<ul style="list-style-type: none"> <li>- Pure oxygen demand, high pressure in the autoclave, and high refrigeration load resulting in a higher capital and operating costs.</li> <li>- Higher content of NO<sub>x</sub> in the tail gas (300 ppm)</li> </ul>
Superazeotropic acid	<ul style="list-style-type: none"> <li>- Corrosion problems are essentially eliminated.</li> <li>- Low content of NO<sub>x</sub> in the tail gas (200 ppm).</li> <li>- Low operating cost.</li> </ul>	<ul style="list-style-type: none"> <li>- High capital cost</li> <li>- Detailed data has not been published</li> </ul>
Extractive distillation using sulfuric acid	<ul style="list-style-type: none"> <li>- Simplicity of operation.</li> <li>- Withstand to the corrosion.</li> </ul>	<ul style="list-style-type: none"> <li>- Glass columns cannot withstand high strength.</li> <li>- Sulfate contamination in product concentrated acid.</li> </ul>
Extractive distillation using magnesium nitrate	Lower capital cost	<ul style="list-style-type: none"> <li>- Using special equipment to prevent solidifying the 72 wt.% Mg(NO<sub>3</sub>)<sub>2</sub> solution.</li> <li>- Depends on imports of MgO.</li> </ul>

With reference to Fig. (1) which is constructed from the published experimental vapor-liquid equilibrium data at different pressures for the nitric acid-water system, it is interesting to note that a reduction in pressure results in a small change in the position of azeotropic point, even at lower pressure (50 mmHg). In addition to that, the difficulty arises from the fact that a considerable pressure drop must exist from the bottom to the top of the column and as the pressure is reduced, the pressure drop is increased (Jones, 1967).

## EXPERIMENTAL WORK

For rational design of distillation column, it is necessary to estimate the vapor-liquid equilibrium of the nitric acid-water system at 150 mmHg, since the required experimental data are not available at this pressure.

The equilibrium behavior of the nitric acid-water system may be described by the relation:

$$P y_i = \gamma_i P_i^0 x_i \quad (1)$$

In this work, the Wilson model was chosen for prediction of activity coefficient for the component of this system. Binary interaction of Wilson's parameters ( $\lambda_{12}$ - $\lambda_{11}$ ,  $\lambda_{21}$ - $\lambda_{22}$ ) for large number of binary systems were given by Nagata, (1973), but they are not available for nitric acid-water system.

For the determination of the binary interaction parameters, experimental vapor-liquid equilibrium data at 100 mmHg were correlated to Wilson model. Then, objective function ( $F_{obj}$ ) was chosen as follows:

$$F_{obj} = \sum_{j=1}^s \sum_{i=1}^n (\ln \gamma_{i,exp.} - \ln \gamma_{i,calc.})^2 \quad (2)$$

Now, we have calculated the binary interaction parameters that will minimize  $F_{obj}$ . In equation (2),  $n$  is the number of components and  $s$  is the number of data points used. The resultant binary interaction parameters were then used to generate a series of points of vapor-liquid equilibrium data at 150 mmHg for this system. The work reported here was done using a computer simulation package named *Design II*.

The experiments in the present work were carried out using a 3.8 cm I.D. glass column 130 cm long filled with 5 mm glass rashing rings. The performance of the packed column was examined. The measure of packed column performance used was the height of packing equivalent to a theoretical plate, HETP. The testing method was performed in an atmospheric distillation unit shown in Fig. (2). A methanol-water mixture was employed as a test mixture where a 2 liters of 10 mol% methanol was charged into the still pot and brought to the boil. The technique of testing was by operating under total reflux for long enough time to allow a steady state to be reached.

The preconcentration of nitric acid was carried out by atmospheric distillation unit shown in Fig. (2). Two liters of diluted nitric acid of 47 wt.% HNO<sub>3</sub> was charged into the still pot. Water and



azeotropic nitric acid of 68.5 wt.%  $\text{HNO}_3$  were separated as the distillate and the residue respectively. To maintain a constant purity of water, the reflux ratio was progressively increased (from 2 to total reflux) during the distillation process. The azeotropic nitric acid was collected for use in the next step of stripping.

The stripping of the dissolved  $\text{N}_2\text{O}_4$  from the nitric acid was performed in a stripping unit. Four, liters of nitric acid of 68.5 wt.%  $\text{HNO}_3$  which contained 0.85 wt.% dissolved  $\text{N}_2\text{O}_4$  was charged in an overhead reservoir, then it was fed by gravity to the packed column through a needle valve adjusted to give 61 ml/min. Compressed air at 2 bar with flow rate of 3  $\text{m}^3/\text{hr}$  was fed into the bottom of the packed column. The experimental temperature was collected in a product reservoir and then used for next step of vacuum distillation.

The concentration of nitric acid experiments were conducted using the vacuum distillation unit in Fig. (3). The experiments were carried out with two types of charges: the unstripped azeotropic nitric acid (0.85 wt.%  $\text{N}_2\text{O}_4$ ) and the stripped azeotropic nitric acid (0.02 wt.%  $\text{N}_2\text{O}_4$ ). The experiments were carried out at a pressure of 150 mmHg and the amount of charge was fixed to be 2 liters. The technique of operation was under total reflux for long enough time to allow a steady state to be reached.

## RESULTS AND DISCUSSION

The resultant binary interaction parameters of Wilson model were,  $\lambda_{12} - \lambda_{11} = -5407.78 \text{ kJ/kmol}$  and  $\lambda_{21} - \lambda_{22} = -3494.35 \text{ kJ/kmol}$  (Perry, 1984).

The predicted vapor-liquid equilibrium is shown in Fig. (4), where the azeotropic composition is 35.9 mol%  $\text{HNO}_3$  (66.22 wt.% at 78.6°C). To check this result, with reference to Fig. (3), it is interesting to note that at  $P=150 \text{ mmHg}$ , the azeotropic composition is 66.34 wt.% and the azeotropic boiling point is 79°C. It is clear that the agreement between the values obtained from two routes is excellent.

The evaluation of the packed column was achieved by using methanol-water mixture. The composition of distillate ( $X_D$ ) and still pot ( $X_B$ ) were determined by using the temperature/equilibrium data and by analyzing the samples, which were taken from the reflux divider.

The analysis was based on the measurement of the refractive index. The composition of the

distillate and still pot were:  $X_D = 99 \text{ mol\%}$  methanol and  $X_D = 9.6 \text{ mol\%}$  methanol.

By using the Fenske equation and the McCabe-Thiele method (Coulson, 1983), it was found that this distillation with total reflux correspond to 6 theoretical stages. Thus,

$$\text{HETP} = \frac{\text{Actual column length (m)}}{\text{No. of theoretical stages in the column}} \quad (3)$$

$$\text{HETP} = \frac{1.30}{6} = 0.217\text{m (21.7cm)}$$

The atmospheric distillation of dilute nitric acid of 47 wt.%  $\text{HNO}_3$  represents the preconcentration step where this acid was concentrated up to 68.5 wt.%  $\text{HNO}_3$  by using the unit shown in Fig. (2). The 2.65 wt.%  $\text{HNO}_3$  was taken off overhead as distilled and the azeotropic nitric acid 68.5 wt.%  $\text{HNO}_3$  as residue. Fig. (5) shows the composition of the distillate content as a function of percent volume distilled. It is shown that 38 vol% was taken off as distillate with composition of 99.9 wt.%  $\text{H}_2\text{O}$ . This purity was attained by applying the technique of variable reflux ratio which is progressively increased during the distillation. Volume percent which was taken off as distillate was 40.5 vol% with composition of 97.35 wt.%  $\text{H}_2\text{O}$  (2.65 wt.%  $\text{HNO}_3$ ).

The bleaching of azeotropic nitric acid from the dissolved  $\text{N}_2\text{O}_4$  gases was conducted by stripping unit which gave satisfactory results where the reduction of  $\text{N}_2\text{O}_4$  content from 0.85 to 0.02 wt.%  $\text{N}_2\text{O}_4$  was achieved at the overhead reservoir to white at the product reservoir.

A significant problem associated with vacuum distillation of unstripped azeotropic nitric acid (0.85 wt.%  $\text{N}_2\text{O}_4$ ) was the large volume of  $\text{NO}_x$  reddish gases evolving from the liquid in the still pot passing through the packed column, the reflux divider, the overhead condenser and the vacuum line to the vacuum pump whose efficiency was progressively decreased because of corrosion of internal parts of the pump, thus causing pump failure. The evolution of these gases was the result of using low pressure (150 mmHg) although the boiling point of the charge was not attained.

The evolution of  $\text{NO}_x$  gases problem was eliminated by using a stripped azeotropic nitric acid (0.02 wt.%  $\text{N}_2\text{O}_4$ ) where this acid was concentrated up to 98 wt.%  $\text{HNO}_3$  and the composition of the liquid in the still pot was 66.7 wt.%  $\text{HNO}_3$ .



As stated above, the number of theoretical stages ( $N_m$ ) at total reflux was:  $N_m = 6$  stages and HETP = 21.7 cm. We calculate the number of theoretical stages ( $N$ ) at desired reflux ratio. From Fig. (6), we determine the minimum reflux ratio ( $R_{min}$ ). Since  $X_D = 98$  wt.%  $HNO_3$  (93.3 mol%),

$$y = \frac{X_D}{R_{min} + 1} = \frac{0.933}{R_{min} + 1} = 0.17$$

$$\therefore R_{min} = 4.49$$

Since  $R_{opt.} = 1.2 R_{min}$ . (Walas, 1987), where,  $R_{opt.}$  is the optimum reflux ratio. This gives  $R_{opt.}$  of 5.4. From Erbar-Maddox correlation (Erbar and Maddox, 1961):

$$\frac{R_{min}}{R_{min} + 1} = 0.818 \quad \text{and} \quad \frac{R_{opt}}{R_{opt} + 1} = 0.844$$

$$\frac{N_m}{N} = 0.5 \quad \text{and} \quad N = \frac{6}{0.5} = 12 \text{ stages}$$

12 theoretical stages with HETP=21.7 cm of 5 mm glass rashing rings at 5.4 reflux ratio are required for concentrating nitric acid. For scale up, to produce 1 ton/day of concentrated nitric acid (98 wt%  $HNO_3$ ). Firstly, for vacuum column, the flooding velocity ( $u_f$ ) is calculated by Sawistowski's equation (Pirani, 1961).

$$\ln \left[ \frac{u_f S \rho_G}{g \epsilon^3 \rho_L} \left( \frac{\mu_L}{\mu_W} \right)^{0.2} \right] = -4 \left( \frac{L}{G} \right)^{0.25} \left( \frac{\rho_G}{\rho_L} \right)^{0.125} \quad (4)$$

which  $\frac{3}{4}$  inch (19.05 mm) porcelain rashing rings, and from Backhurst and Harker, 1977:  $S = 242$   $m^2/m^3$  and  $\epsilon = 0.72$ . Therefore,  $u_f = 5$  m/s.

Since the product rate is 1 ton/day and the reflux ratio 5.4, hence the vapor rate is  $(R+1) \times 1 = 6.4$  ton/day (0.0741 kg/s). By taking the velocity ( $u$ ) as 50% of the flooding velocity,  $u_f$  (Pirani, 1961),  $u = 0.5 u_f = 2.5$  m/s. which gives cross section area ( $A$ ) of  $0.0741/u\rho_G = 0.1275$   $m^2$ , which gives column diameter ( $D$ ) of:

$$D = 2 \sqrt{\frac{A}{\pi}} = 2 \sqrt{\frac{0.1275}{\pi}} = 0.403 \text{ m (40.3 cm)}$$

The ratio of column to packing diameter at least 15 (Walas, 1987) is  $40.3 \text{ cm}/1.905 \text{ cm} = 21.15$ . Therefore, the size of the packing unit is acceptable.

For estimating the height of the packing ( $Z$ ), we calculate the HETP from the correlation of Hand and Whitt (Hengstebeck, 1968):

$$HETP = \frac{70}{\left( \frac{L}{d_p \mu_L} \right)^{0.5}} \quad (5)$$

$$\therefore HETP = 70 / 1.672 = 41.86 \text{ cm}$$

Since the required height of packing ( $Z$ ) is given by HETP  $\times$  (No. of theoretical stages required). This gives  $Z = 41.86 \times 12 = 502.32$  cm (5.023 m).

To adjust the use of 150 mmHg pressure operation the following points were considered: although the reduction in operating pressure from (say) 150 mmHg to 50 mmHg reduces the number of stages (for the present case) from 12 to 10 stages. And also, reduces the boiler (bottom) temperature from 83°C to 75°C, resulting in a small reduction in boiler duty. The net result is some saving in capital and operating cost. However, the pressure drop is 3 folds and the column diameter is nearly twice as much as operating pressure goes from 150 to 50 mmHg operation.

As a conclusion from the values discussed above a pressure of 150 mmHg was found to be the best operating pressure for the present case.

## CONCLUSION

The conclusions of the present work are stated as follows:

1. The behavior of vapor-liquid equilibrium was described very well by using Wilson model, which gave an accurate determination of azeotropic point. The binary interaction parameters of Wilson model ( $\lambda_{12}$ - $\lambda_{11}$ ,  $\lambda_{21}$ - $\lambda_{22}$ ) can be estimated very well by using an experimental isobaric vapor-liquid equilibrium data.
2. The experimental approach of using a test mixture appeared as a successful procedure in evaluating packed column performance and should be a useful tool in such cases.
3. Preconcentration of dilute nitric acid can be achieved by using atmospheric distillation which gave an azeotropic nitric acid (68.5 wt.%  $HNO_3$ ) as residue and an overhead stream (2.65 wt.%  $HNO_3$ ) as distillate.



4. It is important to note that there is indeed necessary for adding a stripping step before vacuum distillation to remove the dissolved  $N_2O_4$  gases present in azeotropic nitric acid.
5. Concentration of azeotropic nitric acid to 98 wt.%  $HNO_3$  can be achieved by using vacuum distillation column provided with six theoretical stages at total reflux and 150 mmHg.
6. Production of 1 ton/day of concentrated nitric acid (98 wt.%  $HNO_3$ ) can be achieved by using a 0.403 m I.D. column, 5.03 m long filled with  $\frac{3}{4}$  inch porcelain rashing ring, which provides 12 theoretical stages at 5.4 reflux ratio and 150 mmHg.

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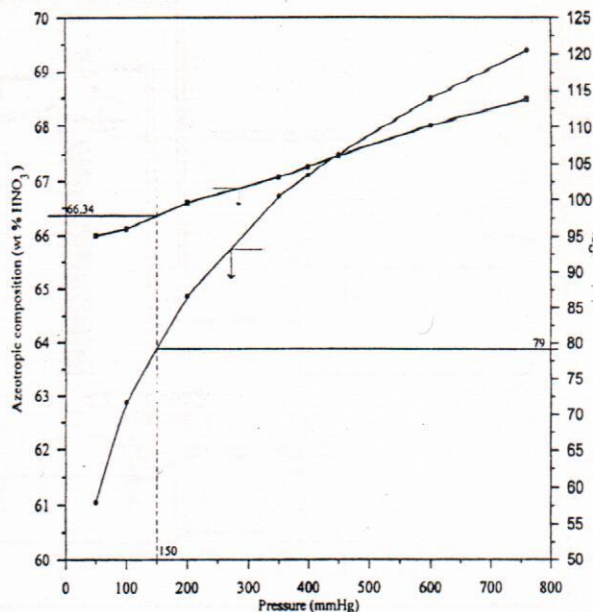


Fig. (1) The azeotropic boiling point and the azeotropic composition as a function of pressure for the nitric acid-water system.

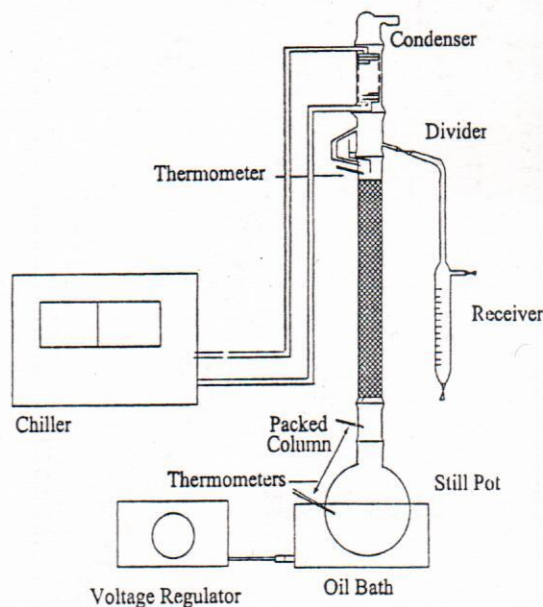


Fig. (2) Atmospheric Distillation Unit



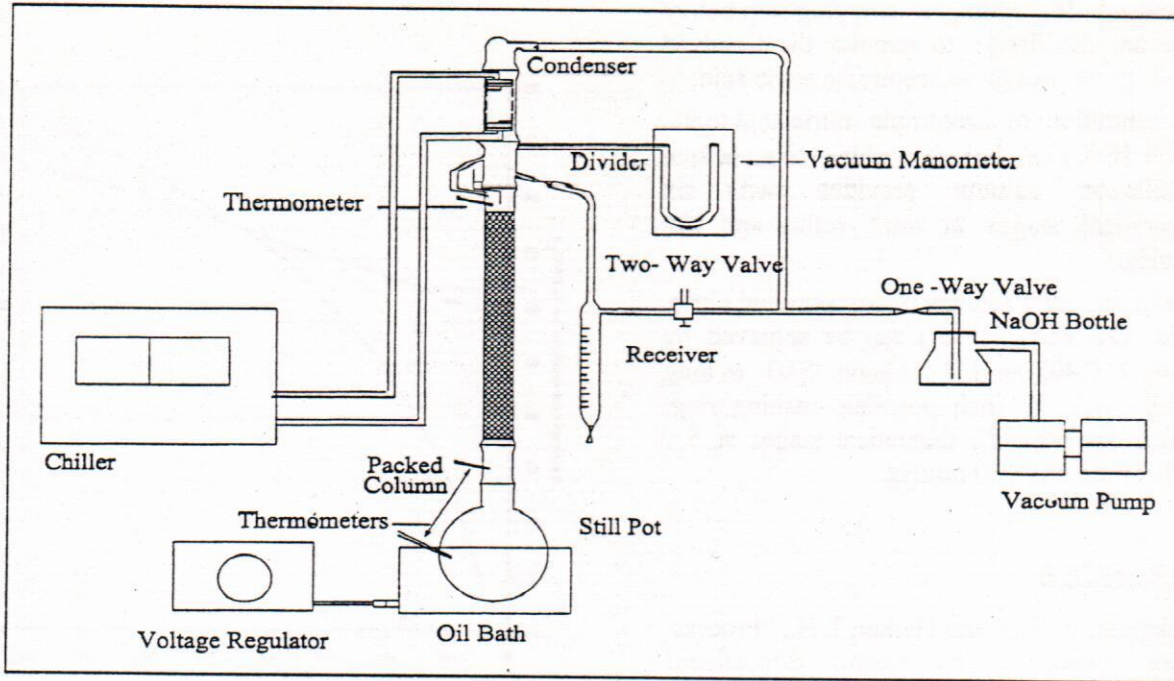


Fig. (3) Vacuum distillation unit

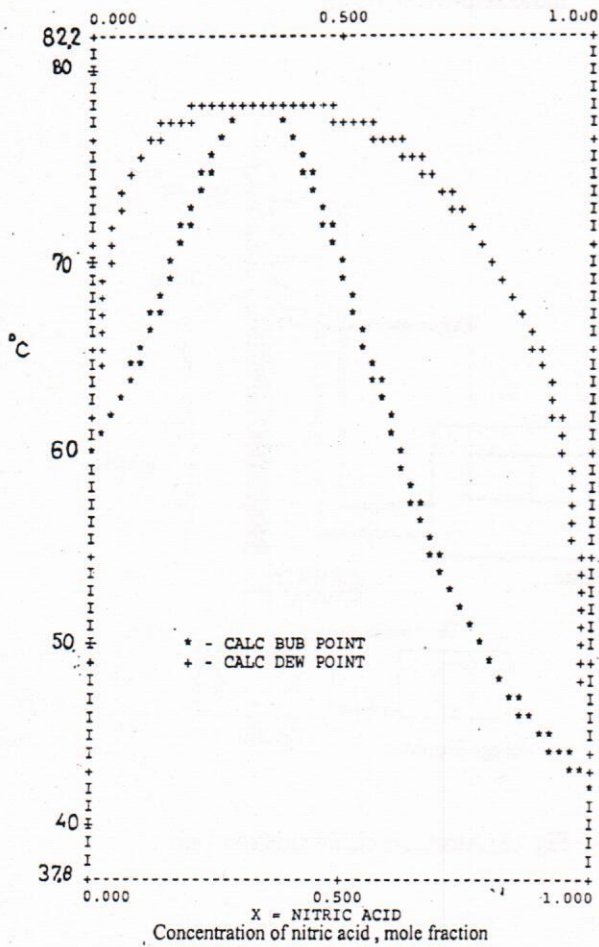


Fig. (4) Temperature-composition diagram for the nitric acid-water system at 150 mmHg

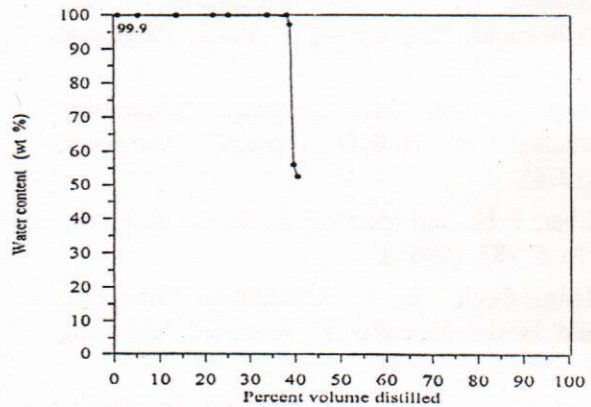


Fig. (5) Composition of the distillate content as a function of the percent volume distilled

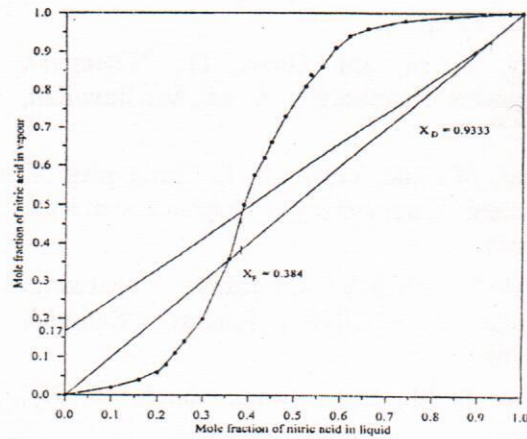


Fig. (6) Vapor-liquid equilibrium diagram for the nitric acid-water system at 150 mmHg

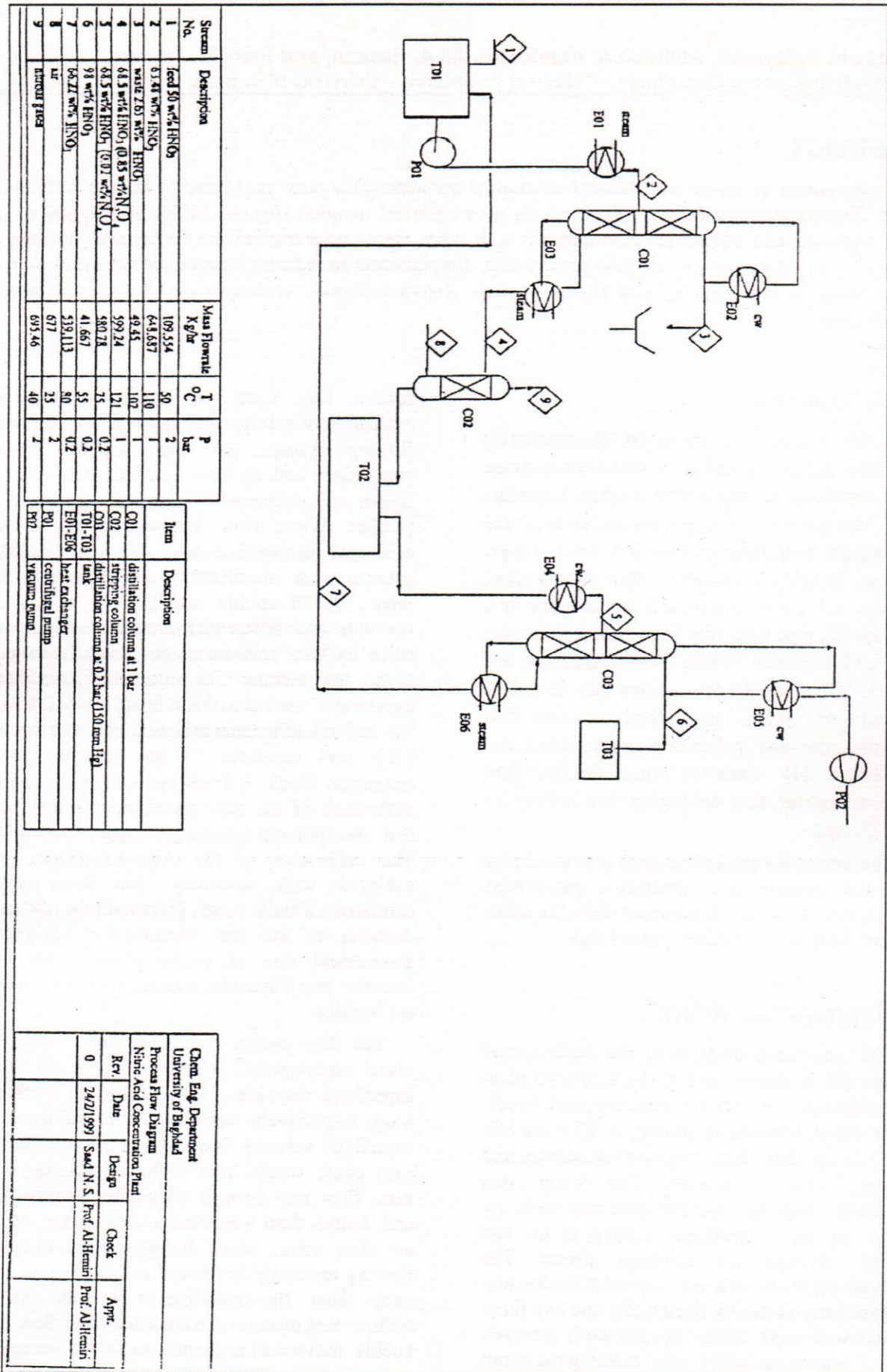


Fig. (7) Suggested process flow diagram