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# OPERATING PARAMETERS EFFECT ON METHANOL–ACETONE SEPARATION BY EXTRACTIVE DISTILLATION

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## ABSTRACT

A relatively complex azeotrope of methanol–acetone with boiling temperature very close to that of the more volatile compound in the system (acetone) was studied using water as an entrainer. The effect of operating parameters such as entrainer feed position and temperature and state of feed (liquid below boiling temperature, at boiling temperature, liquid–vapor mixture and saturated vapor) on the separation process was investigated. Experimental results showed that the position of entrainer has pronounced effect on the separation and quality of top product while its temperature has adverse effect at both low and high temperatures. State of feed did not show any effect on both separation and quality of top product,

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therefore both feed of azeotrope and entrainer may be supplied to the column at ambient temperature and atmospheric pressure. This will make the process more economical compared to similar operations at different temperature and pressure. Computer simulation with HYSYS supported the conclusions for the system under study.

*Key Words*: Extractive distillation; Azeotropes; Methanol–acetone

## INTRODUCTION

The separation of liquid mixtures into their several components is one of the major operations in the chemical and petroleum industries. Throughout the chemical industry, the demand for purer products, coupled with relentless pursuit for greater efficiency, has necessitated continued research into the techniques of distillations. There are many methods of distillation such as simple distillation, partial distillation, flash or equilibrium distillation, rectification, azeotropic distillation, and solvent-extraction distillation.[1,5,15] When the components of a system have low relative volatility ($0.95 < \alpha < 1.05$), separation becomes difficult and expensive because a large number of trays are required and, usually, a high reflux ratio as well. Both equipment and utilities increase markedly and operation can become uneconomic. If the system forms azeotropes, the azeotropic composition limits the separation, and for a better separation, this azeotrope must be bypassed in some ways. For many systems the vapor–liquid equilibrium of the feed mixture can be altered by deliberately adding a new material. In extractive distillation, the entrainer is a higher boiling material (303–323K more than that of the minor compounds of the binary azeotrope) that affects the heavier components in the feed and exits at the bottoms. The choice of the entrainer must affect the vapor–liquid equilibrium relations and the key components (relative volatilities), and it should be easily separable from the components with which it leaves the column. The principle of extractive distillation lies in the addition of a new substance to the mixture so as to increase the relative volatility of the two key components, and thus make the separation relatively easy.[1] The substance added forms an azeotrope with one or more of the components in the mixture, and as a result is present on most of the plates of the column in appreciable concentration. The substance added is relatively nonvolatile compared with the components to be separated, and therefore fed continuously near the top of the column. This entrainer runs down the column as reflux and is present in appreciable concentration on all the plates. The separation of azeotropes is considered a complicated process. The complicity depends on liquid–liquid; vapor–liquid equilibrium of the system under study, in another words depends on the type and nature of azeotropic structure in the system.[1,11]

A number of food and chemical applications benefited from this type of separation processes are: volatile components of fruit,[13] edible oils,[2,4] wine aroma compounds[3] and polycyclic aromatic hydrocarbons, phenols and aromatic amines in particulate phase cigarette smoke.[6]

The relationship of relative volatility for ideal mixtures has the following form:

$$\alpha_{AB} = \frac{p_A^0}{p_B^0} \tag{1}$$

where $p_A^0$, $p_B^0$ is the vapor pressure of pure components A and B.

This relationship for nonideal systems becomes:

$$\alpha_{AB} = \frac{\gamma_A}{\gamma_B}\frac{p_A^0}{p_B^0} \tag{2}$$

where $\gamma_A$ and $\gamma_B$ are the activity coefficients for components A and B.

The solvent added to the mixture (entrainer) in extractive distillation affects the activities of the two components $\gamma_A$, $\gamma_B$, and hence the relative volatility $\alpha_{AB}$.[1]

The entrainer should have the following characteristics: lower volatility than the volatilities of the mixture components, a role in increasing relative volatilities of the mixture, preferably not to form azeotropes with the mixture components, should not be appreciably vaporized in the fractionator, and available and cheap.[1,5] Water has many of the above characteristics, therefore it was used in a number of studies as a entrainer for many systems such as methanol–methyl acetate, methanol–vinyl acetate, methanol–chloroform, methanol–methylene chloride, and methanol–chloroform.[7–9,12]

In this article, we describe an experimental study that concentrates upon the effect of position of extractive agent, effect of temperature of extractive agent, and effect of condition of feed on the separation of methanol–acetone mixture. This mixture is considered to be one of the most complex azeotropes since it is homogeneous and has a boiling temperature very close to that of the acetone. Water was used as entrainer.

## EXPERIMENTAL EQUIPMENT AND PROCEDURES

Extractive distillation was carried out in a packed column of eight practical sections each of 300 mm high and 50 mm diameter with a sampling point. The column is packed with small random glass pieces of 1–2 mm average dimensions. Each section is provided with an electrical coil for initial heating during the start-up and to assist the rising vapor along the column. The coils are connected to a main control of the column. The column is operated at an ambient temperature and atmospheric pressure. Figure 1 shows a schematic diagram of the column.

Methanol and acetone were purchased from Sigma-Aldrich (The Old Brickyard, New Road, Gillingham, Dorset SP8 4XT, U.K.). The feed consisted of 50% mol of methanol and 50% mol acetone with a bubble point of 331.5K, a dew point of 332.3K, density of 787.9 kg/m$^3$, and a viscosity of 0.427 cP was used as a feed in this study. State of the feed was liquid below boiling temperature and introduced into the column at 298K. Water was used as an entrainer throughout the study. The second step was choosing the ratio of water to methanol–acetone ($q$) at which the azeotrope starts shifting, $q = 4$. Operating conditions such as flow rate and position of both the feeds and entrainer and composition of azeotrope are fixed before carrying out each experiment. During the experiments, the flow and temperatures at top and bottom of the column are measured every 15 min. Temperature at the bottom of the column was within the range of 361–364K and in the range of 329–329.2K at the top of the column. Reflux ratio was $R = L/D = 4.5$. Samples were taken from each section and from both top and bottom of the column every 1 hr for analysis. After reaching the steady state condition, the column is kept under strict observation for 3–4 hr with samples

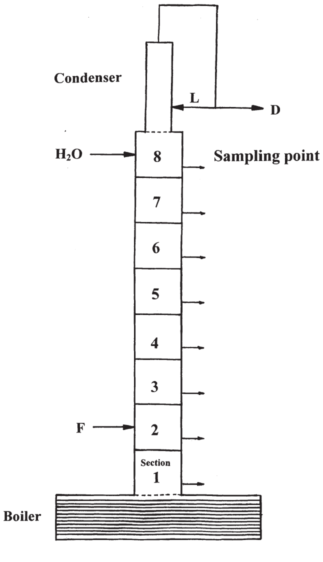

*Figure 1.* Schematic diagram of the column.

taken from all the sections to make sure of the steady state condition and final data analysis were recorded after that. Full details of the equipment, experimental procedure, and analysis are described elsewhere.[12]

## RESULTS AND DISCUSSION

The results reported in this study are for methanol–acetone system using water as an entrainer, therefore the new system is methanol–acetone–water and its structure for phase equilibrium liquid–vapor is shown in Fig. 2 which is constructed according to the physical properties of the system components.[10,14,16]

The feed in all the experiments was chosen to be 50% mol of methanol and 50% mol acetone and was introduced in section 2 of the column.

Water is a liquid capable of forming strong hydrogen bonds. These bonds introduce the deviation from Raoult's law. In extractive distillation, water tends to associate with methanol (the higher boiling component) and increases the relative volatility of the lighter component (acetone). Water is of low volatility, usually added near the top of the column, present throughout the tower, and exits at the bottoms. Later, the entrainer must be separated from the original components by distillation.

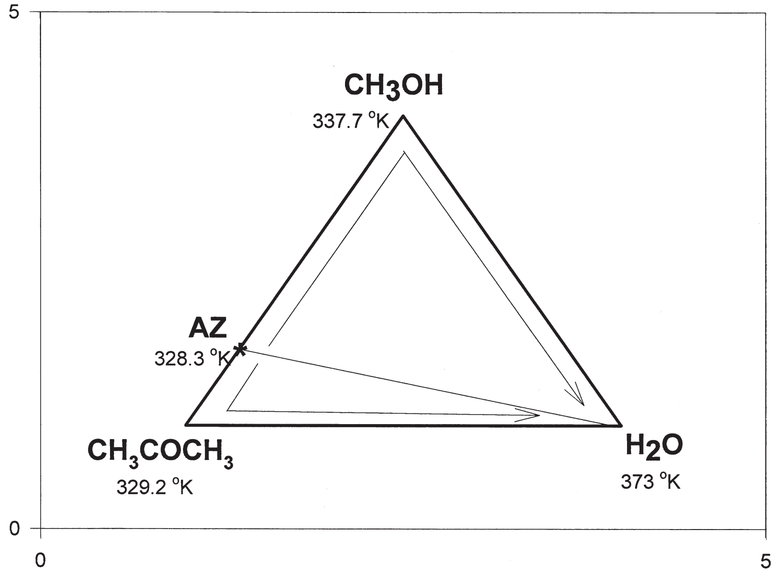

*Figure 2.* Equilateral-triangular phase diagram of methanol–acetone–water system.

## Effect of Position of Entrainer

Water is relatively a nonvolatile component compared with acetone and methanol, and it is therefore usually fed continuously near the top of the column. Both acetone and methanol separately form nonideal liquid solution with water, but the extent of nonideality with acetone is greater than with methanol. When all the three substances are present, acetone and methanol themselves behave as nonideal mixture, and then relative volatilities become higher. It is the custom that the entrainer is added at or near the top of the tower and exits at the bottom. If this agent is not added at the top of the column, the plates from the top down to the entrainer feed plate serve to knock back this agent. This is likely to occur when the entrainer is somewhat volatile. However, water does not satisfy these conditions and therefore there is no reason why the extracting agent should be added or near the top of the column.

To test the effect of entrainer location, the water was introduced into the column at different positions starting from section 3. The experiments were started by increasing the flow rate of the entrainer when it was fed to section 3 until the azeotrope began to shift at the ratio of water feed to methanol–acetone feed of 4 mol/mol. After that, all the parameters were fixed and the position of entrainer was changed from section 3 along the column until section 8. Experimental results are shown in Fig. 3.

Figure 3 shows the strong effect of the distance between the methanol–acetone feed and the feed of entrainer. There was a gradual decrease of methanol in the top product from 17.7% mol when extractive agent was fed at section 3 to 0% mol when that feed was at section 8.

This shows that the entrainer requires a sufficient distance along the column to fully separate methanol from the system. This distance plays an important role on the effect of the entrainer on the activity coefficients ratio $\gamma_A/\gamma_B$ and therefore the relative volatility $\alpha_{AB}$ enabling full shift of the azeotrope under study to obtain the pure final product.

## Effect of Temperature of Entrainer

The entrainer must be added in relatively high concentration in the liquid within each stage. Since the volatility of this agent is low, the overflow of this agent from stage to stage is relatively constant from the entrainer entry at the bottom stage. The agent will tend to increase in temperature owing to the condensation of the nonagent material as agent flows down the column, but since the liquid in each stage is at its bubble point, the stage temperature is controlled by the stage pressure and composition. The entrainer always boils so far above the fresh feed components that the formation of new azeotropes is impossible. In

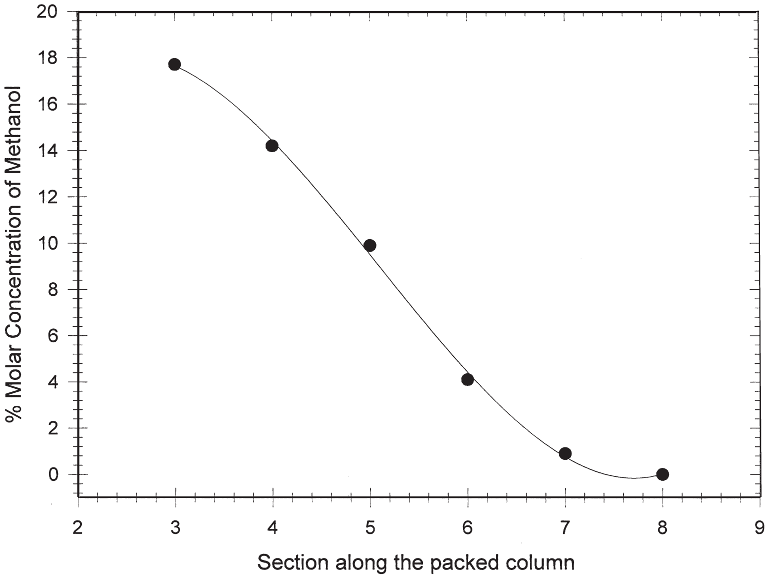

***Figure 3.*** Effect of entrainer's position.

order to maintain high concentration throughout most of the column, the extract must always be introduced above the fresh feed stage.

To study the effect of entrainer temperature on the separation of system, the extractive agent was fed to section 8 since at this location we obtained the best top product of all the sections investigated, see "Effect of Position of Entrainer." The temperature of the entrainer was then changed by 5K increments within the range of 278–333K.

Figure 4 shows that the temperature of the extractive agent has a clear effect on separation of the system. This effect is negative in both high and low range of temperatures. Methanol clearly appears in the top product in the range of temperature between 278 and 288K, while it disappears in the range between 293 and 313K and reappears again in the range between 318 and 333K. The amount of methanol appearing in the top product increases when its boiling temperature is approached.

The appearance of methanol in the low temperature range is most probably due to the high cooling rate of the rising vapors in the top sections of the column. This will lead to the increase in condensation of acetone vapors, which is replaced by methanol vapors, therefore reducing the acetone concentration in this region.

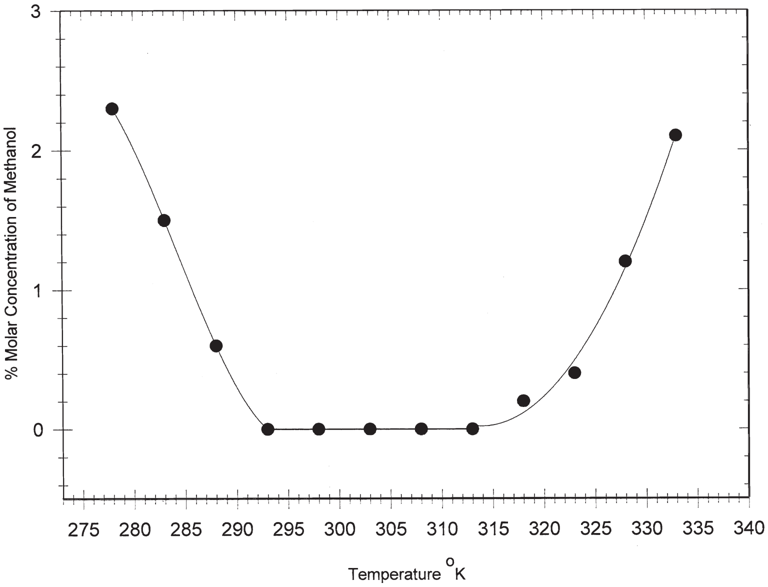

*Figure 4.* Effect of entrainer's temperature.

The reappearance of methanol in the top product at high temperature range and its gradual increase near the boiling temperature is most probably due to the increase of methanol vaporization in the falling liquid near the top of the column.

## Effect of State of Feed

For a feed/extract agent ratio there is usually an optimum reflux rate, which strikes a balance between the inherent benefits of reflux and the effect of solvent concentration on the volatilities. A vapor feed may be more desirable because a liquid fresh feed dilutes the descending entrainer and results in a lower entrainer concentration in the bottom section. Reflux at the top of the column also dilutes the agent, and increased reflux is therefore not always synonymous with increased separation. If the feed is liquid, the agent liquid concentration will change across the feed stage and this could be a disadvantage to the separation.

Methanol–acetone mixture was fed to the column at different conditions, liquid below boiling temperature, at boiling temperature, liquid–vapor mixture and saturated vapor to study the effect of these conditions on solvent-extraction distillation. Extractive agent was fed to section 8 at ambient temperature and atmospheric pressure and methanol–acetone mixture was introduced to section 2 of the column.

Figure 5 shows no effect of the state of feed on final product. Methanol in the top product did not appear at the ratio of water feed to methanol–acetone feed of 4 mol/mol when the conditions of feed changed. Reducing this ratio to a value of 3.8 gave the same percentage of methanol (0.25%) in the top product at all conditions.

## HYSYS SIMULATION

Theoretical study using HYSYS simulation was considered to be very helpful to support the experimental findings in the present work. This will be the subject of a future study along with an overall economic optimization. Some preliminary simulation results are shown here. The simulation was undertaken with the HYSYS model version 2.1 under license from Hyprotech.[17]

The acetone–methanol binary feed with water solvent was studied with the scenario described in Fig. 3. That is a 50% by mol methanol–acetone mixture fed into stage 2 and water fed into section 3 with a $q$ value of 4 for the first simulation. Then the water was fed into section 4 for the next simulation, and so on up to

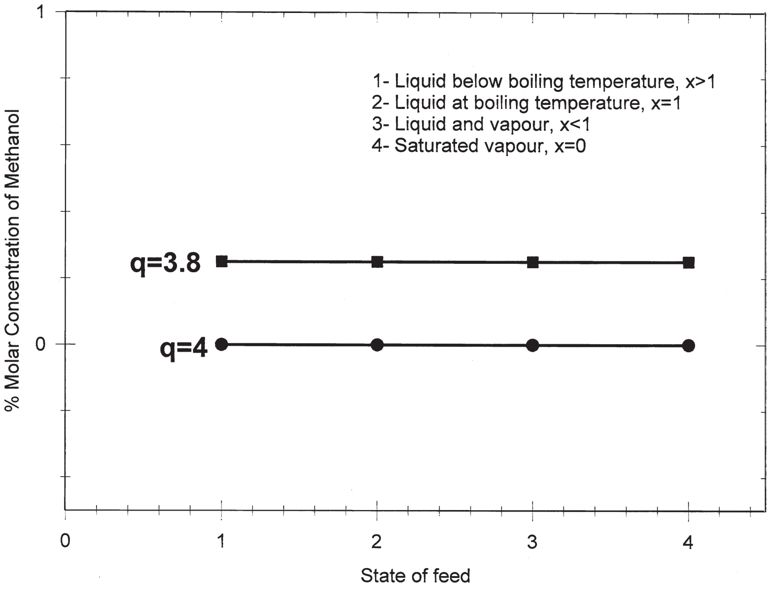

***Figure 5.*** Effect of state of feed.

section 8. The feed streams were at 298K and atmospheric pressure. Various activity models in HYSYS were tried and they all gave similar results. The Van Laar package was used for the results shown here. The rigorous column was used and the main uncertainty was how many ideal trays to use. The experimental column contained packing. From the simulation results obtained, it is clear that this can be represented at the extreme by 8–32 ideal trays. The column solution converged in all cases using a distillate flow (47.8% of binary feed) specification and reflux ratio ($R$) specification. The value of $R$ was not critical for the results. Figure 6 shows the results obtained for 8 ideal tray column and Fig. 7 for 32 ideal tray column. The experimental results in Fig. 3 are reproduced in Figs. 6 and 7 to facilitate comparison with the simulation.

The simulation results for the 8-tray column are in reasonable agreement with the experiment except that when the water enters tray 8 there is a significant amount of methanol remaining in the distillate. This is not so for the 32-tray column simulation, but here there is overall a much bigger difference between the results. It is conjectured that the column is nearer to eight ideal sections, but that the region above the feed for the "8-solvent-entry" case is not adequately represented in the 8-section simulation.

The simulation results also show how the water composition in the distillate changes. Clearly the solvent entry position significantly affects this value and its importance must be evaluated in the future economic study.

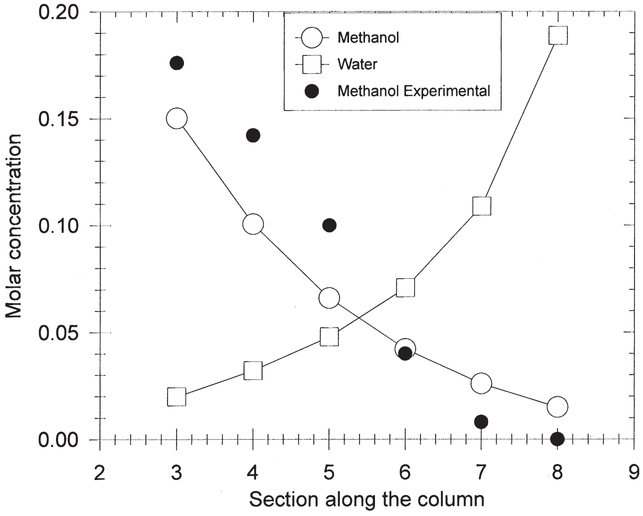

***Figure 6.*** HYSYS simulation effect of entrainer position for 8 ideal tray column.

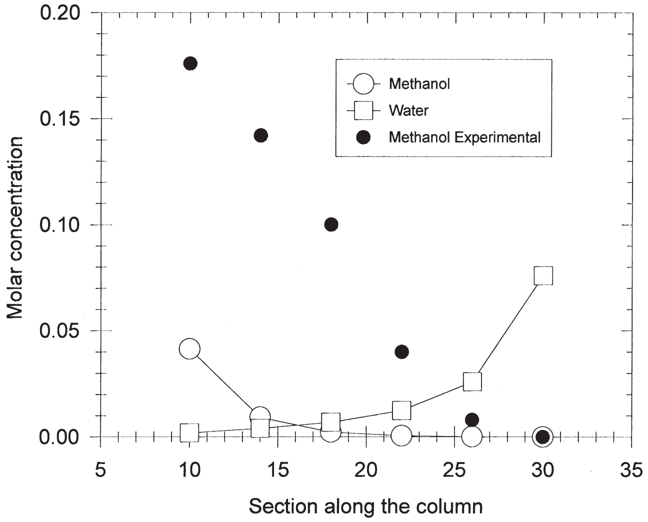

***Figure 7.*** HYSYS simulation effect of entrainer position for 32 ideal tray column.

## CONCLUSIONS

This article shows experimental investigation on extractive distillation of methanol–acetone system using water as a entrainer. It has been shown that the entrainer requires a sufficient distance along the column to fully separate methanol from the system and no practical benefit from changing temperature of both methanol–acetone mixture and entrainer since best results were obtained at ambient temperature. Results also show that there is no effect of state of feed on quality of product. Some preliminary computer simulations have supported the experimental conclusion for the effect of solvent feed location.

## NOMENCLATURE

| | |
|---|---|
| $p^0$ | vapor pressure (kN/m$^2$) |
| $q$ | ratio of entrainer to methanol–acetone feed |
| $\alpha$ | relative volatility |
| $\gamma$ | activity coefficient |

*Subscripts*

| | |
|---|---|
| A, B | pure components A and B |

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