R & D NOTES

Ethanol Dehydration Column Efficiencies Using UNIFAC

I. A. FURZER

Department of Chemical Engineering
University of Sydney
NSW 2006, Australia

The use of the alcohols, notably methanol, ethanol, and higher saturated alcohols including tertiary butyl alcohol, for blending with gasoline has been the subject of numerous recent articles. For example, methanol has been the subject of direct blending, or blending with a cosolvent tertiary butyl alcohol or conversion to ethers or use with the Mobil-M-Gasoline Process to produce a synthetic fuel.

The use of alcohol-gasoline blends as an automotive fuel supply has been summarized by Greene (1982) under the headings of: 1) volatility and drivability, 2) hydrocarbon solubility, 3) water tolerance, and 4) heat of combustion. The water tolerance of pure methanol is remarkably low, being less than 0.2% wt. before the blend breaks into two liquid phases. The addition of C_2–C_4 alcohols can increase the water tolerance to 1.0% wt. If two liquid phases appear in the fuel system, serious problems can exist with engine stalling. It has been suggested that a stable emulsion can be made by adding an emulsifying agent.

Pure alcohols as an automotive fuel have been discussed by McCallum et al. (1982): 1) exhaust and evaporative emission, 2) power output and fuel consumption, 3) materials compatibility, and 4) environmental considerations. The presence of dissolved water can significantly alter the chemical aggressiveness of alcohol fuels toward metallic materials in the fuel system. To avoid these difficulties with water in the fuel blend, it is necessary to dehydrate the alcohols before they enter the blending stocks. Methanol can be dehydrated by distillation to extremely low water contents, as the vapor-liquid equilibria are simple.

With ethanol, however, the appearance of an azeotrope of 89 mol % ethanol limits the ethanol purity to this maximum composition and mixtures near this composition are marketed as power alcohols. The feed to these simple ethanol stills is often from fermentation units; both batch and continuous plants have been developed to handle a wide range of feedstocks with different yeasts and bacteria. The maximum ethanol content that can be obtained by fermentation is only 4.5 mol %, so a large quantity of water must be removed even to bring the compositions near the azeotropic composition of 89 mol % ethanol. Modern efficient batch plants for farm use producing 100 L/h have been described by Berglund and Richardson (1982).

Black (1980) has reviewed the methods for increasing the ethanol content beyond the azeotropic limit to produce a product with a water content that is suitable for blending with gasoline. The addition of a third component of a hydrocarbon type can have a remarkable effect on the volatilities of ethanol and water. It is possible for ethanol to become the least volatile and to be removed in a high state of purity from the bottom of a second column, known as the final dehydration or azeotropic distillation column. The flowsheet for this two-column arrangement plus third component recycle has been given by Black (1980).

Prokopakis and Seider (1983) have simulated this azeotropic distillation column using the UNIQUAC method with benzene as the third component. They have found that the vapor overhead composition must lie in a narrow window for two liquid phases to form in the overhead condenser. While benzene and diethyl ether have been used in the past, other components have also been investigated, notably pentane, ethylene glycol and a gasoline fraction. The design of these dehydration columns is difficult due to the nonideal liquid behavior leading to large values of the liquid-phase activity coefficients. In addition, the deviations from ideal behavior can become so severe that two liquid phases form on a tray. The final stages of this process design procedure require the use of an overall column efficiency to obtain the actual number of plates and there is an absence of information in the literature on this important point.

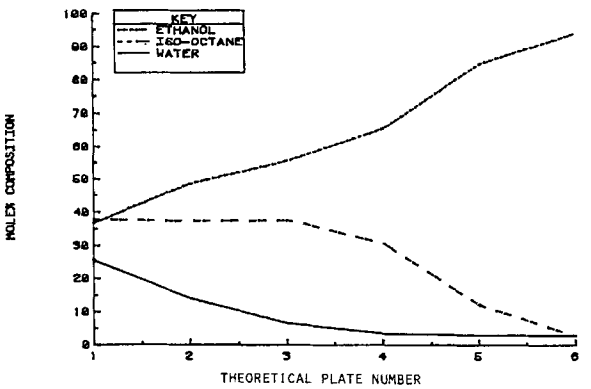

Figure 1. UNIFAC simulated composition profiles.

TABLE 1.
EXPERIMENTAL

Plate	Liquid Composition, mol % Ethanol	Isooctane	Water
1	46.2	36.1	17.6
2	46.2	41.0	12.8
3	44.0	39.5	16.5
4	53.2	36.3	10.5
5	59.5	33.7	6.8
6	70.5	24.2	5.3
7	77.5	18.8	3.6
8	90.0	6.3	3.7
9	94.1	2.0	3.8
Reboiler	96.0	0.2	3.8

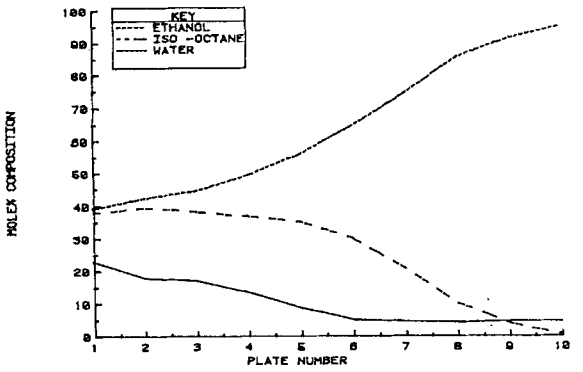

Figure 2. Experimental composition profiles.

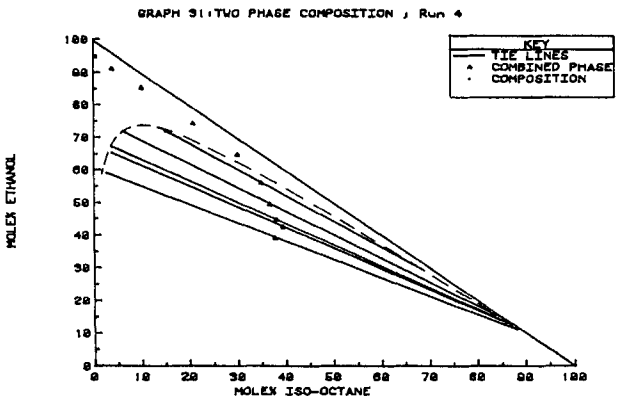

Figure 3. Tie-lines in the two liquid phase region.

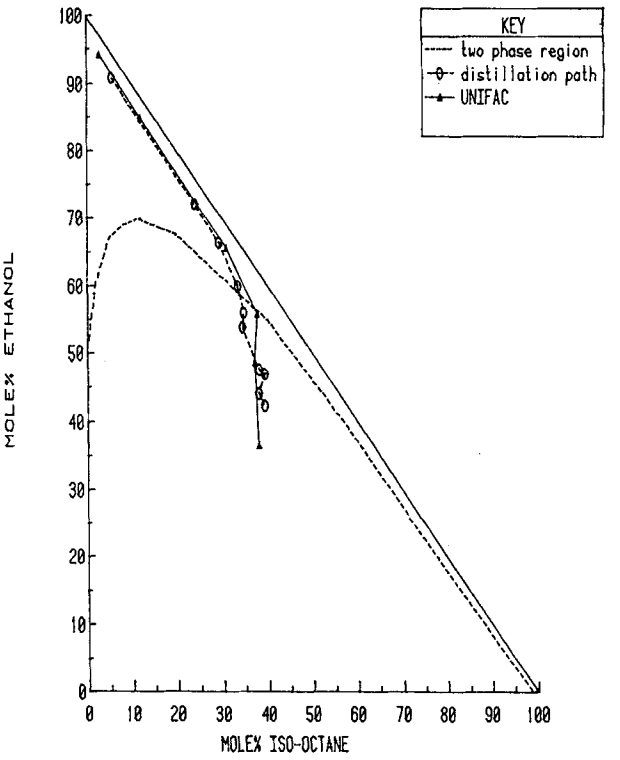

Figure 4. Simulated and experimental composition paths $F = 0.64$.

UNIFAC SIMULATION

The vapor-liquid equilibria in the ethanol dehydration column have been estimated by the UNIFAC group contribution method. One component of gasoline which has a research octane number of 100, is isooctane, (224 trimethylpentane) and a simulation and experimental study has been made of the system ethanol-water-224 trimethylpentane. The simulation program, following Magnussen (1979), uses component and equilibrium relationships for each component on each tray. The K values for each component are obtained from the vapor pressures using Antoine coefficients and the liquid-phase activity coefficients using the UNIFAC method.

Figure 1 shows the simulated composition profiles along a column containing six theoretical plates at total reflux. A feature of the simulation is the rapidly rising ethanol content in the reboiler to beyond 94 mol % and a decreasing water content. Higher ethanol contents could be obtained in columns with more theoretical plates.

TABLE 2.
EXPERIMENTAL

Plate	Liquid Composition, mol % Top Phase Etoh	Top Phase Isooctane	Top Phase H_2O	Bottom Phase Etoh	Bottom Phase Isooctane	Bottom Phase H_2O	Phase Mole Fraction Top Phase	Phase Mole Fraction Bottom Phase
1	10.4	88.8	0.8	68.5	3.5	28.1	0.383	0.617
2	10.5	88.2	1.3	74.5	3.7	21.8	0.441	0.559
3	13.0	85.7	1.3	67.1	5.1	27.8	0.427	0.573
4	17.6	80.7	1.7	74.0	10.3	15.7	0.370	0.630

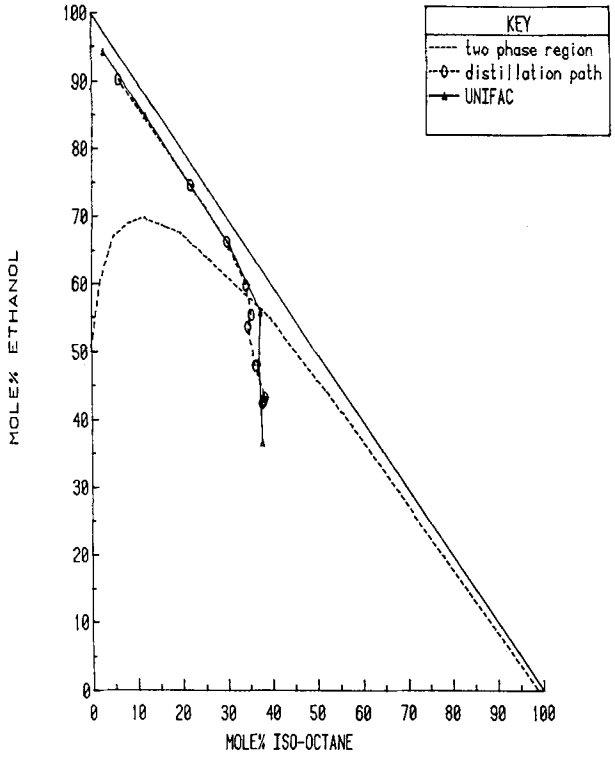

Figure 5. Simulated and experimental composition paths $F = 0.78$.

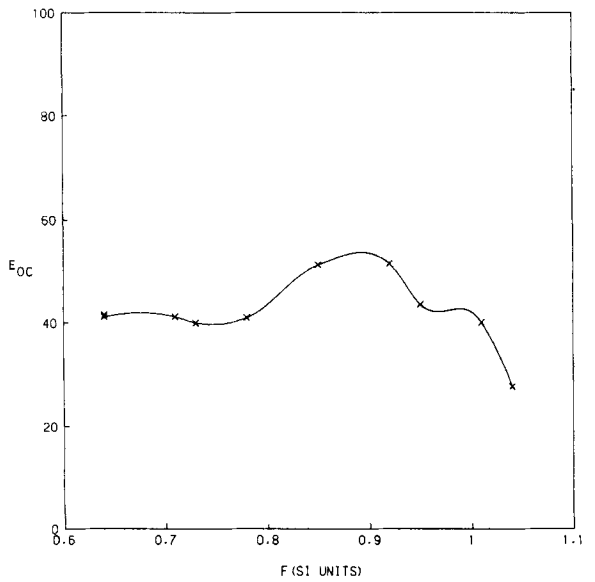

Figure 6. UNIFAC overall column efficiency.

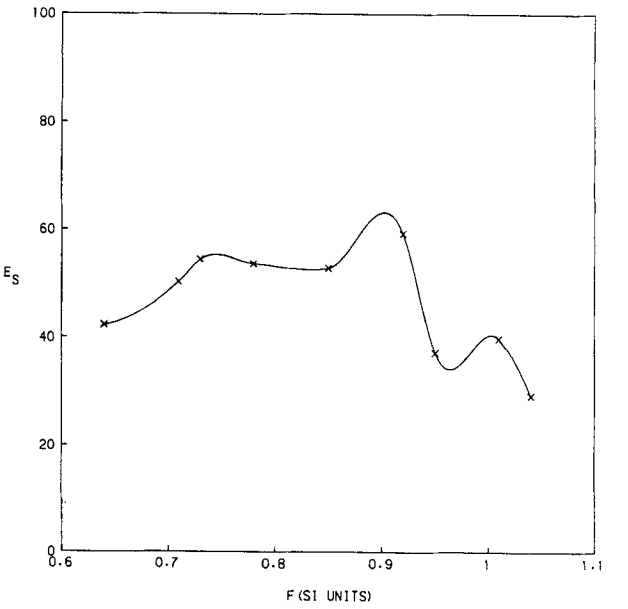

Figure 7. UNIFAC single liquid phase region column efficiency.

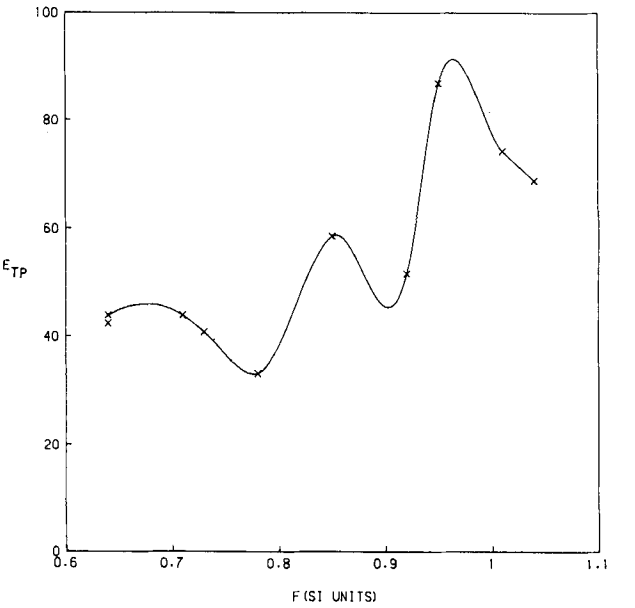

Figure 8. UNIFAC two liquid phase region column efficiency.

DISTILLATION COLUMN

A glass distillation column, 150 mm dia., was fitted with nine dual flow trays with 8 mm dia. holes of 20%-free area on a 300 m spacing. The column was operated at total reflux and samples withdrawn from all plates and the reboiler. The samples were analyzed using a Hewlett-Packard Model 5710A chromatograph fitted with a flame ionization detector. The water contents were independently measured by a Mitsubishi moisture meter, CA-02 using coulometry with the Karl-Fischer titration method.

All liquid samples were slowly withdrawn by syringe and some plates contained an emulsion of the two liquid phases. The composition of each phase and the molal phase ratio were obtained for these samples. The mean composition of this two-phase mixture was also calculated. The experimental results for a run are given in Tables 1 and 2. The experimental composition profile using actual tray number is shown on Figure 2. There is obviously a good agreement between the UNIFAC simulation and the experimental results. These are the first experimental composition profiles with two liquid phases on a tray, reported in the literature.

The experimental results are also shown on a ternary diagram for the system in Figure 3. The composition of the two liquid-phase

samples are shown by tie-lines in the-two phase region of the diagram. These tie-lines and the two-phase envelope were independently determined at the boiling point of the mixture in a separate equilibrium experiment. The results for this run show the deep penetration into the two phase liquid region. This particular run is at an F number ($v\sqrt{\rho_G}$) of 0.85 (SI units). Altogether, a total of ten different runs were completed at F numbers ranging from 0.64 to 1.04. For example in Figure 4 are the UNIFAC simulated flow paths and the experimental flow paths at an F number of 0.64. There is an excellent agreement between the simulation and the experimental results. Figure 5 shows a similarly good agreement at an F number of 0.78.

DEHYDRATION COLUMN EFFICIENCIES

The overall column efficiency (E_{oc}) is expressed as the number of theoretical plates in the column calculated by the UNIFAC simulation compared to the actual number of trays. Values of E_{oc} will depend on the method used to calculate the equilibria and these efficiencies might be called the UNIFAC overall column efficiencies. Values of E_{oc} will depend on the component under consideration and ethanol has been selected as this component. The variation in E_{oc} with F number, with a maximum of 55% at F = 0.9 is shown on Figure 6. An attempt has been made to split the overall column efficiency into values for the single liquid phase region and another for the two liquid phase region. The results are shown on Figures 7 and 8, respectively. The UNIFAC column efficiency in the two-phase region E_{TP} shows a maximum near F = 1.0, while the value E_{sp} for the single-phase region shows a decline at higher F values.

These curves show similar characteristics to published curves for dual flow trays and these early results indicate normal column efficiencies in both the single and two liquid phase regions with the equilibria determined by the UNIFAC method.

These column efficiencies should be of considerable interest to designers of ethanol dehydration columns for use in gasohol production.

ACKNOWLEDGMENTS

Many thanks to Aage Fredenslund and all the UNIFAC team at DTH, Denmark for assistance and to John Faulks who collected the experimental data.

LITERATURE CITED

Berglund, G. R., and J. G. Richardson, "Design of a Small-Scale Fuel Alcohol Plant," *Chem. Eng. Prog.*, **78**(8), 60 (1982).

Black, C., "Distillation Modelling of Ethanol Recovery and Dehydration Processes for Ethanol and Gasohol," *Chem. Eng. Prog.*, **76**(9), 78 (1980).

Greene, M. I., "Alcohol-Based Fuels from Syngas," *Chem. Eng. Prog.*, **78**(8), 46 (1982).

Magnussen, T., M. L. Michelsen and Aa. Fredenslund, "Azeotropic Distillation using UNIFAC," Inst. Chem. Eng. Symp. Soc. No. 56, Third Int. Symp. on Distillation (1979).

McCallum, P. W., et al., "Alcohol Fuels for Highway Vehicles," *Chem. Eng. Prog.*, **78**(8), 52 (1982).

Prokopakis, G. J., and W. D. Seider, "Feasible Specifications in Azeotropic Distillation," *AIChE J.*, **29**, 49 (1983).

Manuscript received June 9, 1983; revision received November 23, and accepted December 6, 1983.