Packed Distillation Column Process for the Separation of Bio-Ethanol Fuel: Efficiencies and Interaction Coefficients Prediction

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Abstract: Globally, the world attention has drifted toward environmental sustainable development of their countries. This has called for several measures to reduce the emissions generated into the atmosphere. One of such is the blending of ethanol and gasoline for the use of motor vehicles. The blend of both mixtures is known to improve the octane index. However, the problem of recovery of ethanol from the fermentation broth involves distillation of the dilute aqueous alcohol to its azeotrope. This is the basis for the study in addition to generating parameter of interaction coefficients. Through multiple regression for use in physical property prediction models at various temperatures. The study also investigated the process packed distillation column by comparing the efficiency results of conventional packing system (the high and low voidage packing) and the modification of the column to accommodate multiple packing (combinations of both low and high voidage packing). The results showed that efficiencies of the combinations are better than that of the conventional high voidage packing but slightly lower compared to the conventional low-voidage packing. We conclude by suggesting that firm processes involving the use of distillation techniques can be modified to accommodate combination of multiple packing for optimum efficiency. This invariably makes the firm that use this approach more efficient and profitable.

I. INTRODUCTION

During the production of ethanol, large quantities of water are produced with the ethanol. The fermented effluent typically has an ethanol concentration of approximately 10 percent by weight (Tracy and Clifford, 2005). Anhydrous ethanol is widely used in chemical industry as powerful solvent and as raw material or intermediate in chemical synthesis of esters, organic and cyclic compound chains, detergents, paints, cosmetics, aerosols, perfumes, medicine and food, among others (Rejl et al., 2006). Besides, ethanol and gasoline mixtures can be used as fuels, reducing environmental contamination and improving octane index (Meirelles et al., 1992). Several processes for ethanol dehydration include heterogeneous azeotropic distillation, which uses different solvents such as benzene, pentane and cyclohexane; extractive distillation with solvents and salts as separating agents (Fu, 2004a,b); adsorption with molecular sieves and processes that include the use of pervaporation membranes (Ulrich and Pavel, 1988; Pinto et al., 2000). All these processes have had industrial application but some are no longer in use due to the high operating costs, operative problems and high energy consumption.

Meanwhile, distillation process is the most widely applied separation technology. Likewise, it is an important process for the foreseeable future because there is simply no industrially viable alternative around (Olujic et al., 2003). Despite many challenges from other technologies distillation improves and from time to time breakthroughs are made which move this technology to a higher level of sophistication. Distillation is a column-type separation process involving the partial condensation of vapour mixture, carried out to effect the separation of the more volatile component from the less volatile component in the initial mixture. Because of this simultaneous vapourization and condensation, distillation requires large quantities of energy (Rueda et al., 2006) accounting for more than 95% of the energy consumed by separation processes in the chemical process industry (Humphrey and Seibert, 1992). Even though alternative separation techniques are still developed, they cannot replace the distillation process completely, which makes its future use indisputable. Attention hence should be paid to distillation, as a small improvement in its design or performance has a large financial impact. Distillation can be carried out in multistage and continuous contact equipment. These are plate and packed columns for the contacting of liquid and vapour to produce effective mass transfer in the system (Salimi and Depeyre, 1998). In distillation operations, the demand on designers is not only to achieve the desired product quality at minimum cost, but also to provide constant purity of product even though there may be some variation in feed composition (Coulson and Richardson, 2002).

The packed column is favoured over the plate column due to its inherent low pressure drop across the packed section and its economic advantage (Taiwo, 2001). Packed column is an arrangement, which provides the necessary large interfacial area for diffusion, which the cylindrical shell of the column is filled with some form of packing firmly supported on a support plate. It is equipped with a gas inlet and distributing space at the
bottom, a liquid inlet and distributor at the top. The gas and liquid outlets at the top and bottom respectively and a supported mass of inert solid shapes called column packing (see Fig. 1). The column packing support is typically a screen, corrugated to give it strength, with a large open area so that flooding does not occur at the support. The quality and arrangement of packing in the column explain the rate of mass transfer which in turn determines the separation efficiency of the column. The separation performance had been found to vary markedly with a number of parameters, among which are effective interfacial area, components concentrations, system properties, column design and operating condition parameters (Fasesan et al., 1993). Taiwo (2001) demonstrated that liquid viscosity has significant influence on the effective interfacial area even larger than that of the liquid flowrate. Nevertheless, from the point of view of the physical properties for the system, the effective interfacial area will depend mainly on the surface tension, liquid density and packing material. Nonetheless, the effect of liquid viscosity and solute diffusivity is significant on liquid side mass transfer coefficient.

In the chemical and petroleum industries, viscosity of pure components and mixtures is an important property in hydraulics calculations for surface facilities; pipeline systems; and flow through porous media, such as in packed distillation column (Monnery et al., 1995). With the increased popularity of process and reservoir simulators as well as increased need to measure, this property for all mixtures at conditions of interest makes the need for correlations between the property and compositions, as well as temperature inevitable. The need for this correlation cannot be overemphasized in the packed distillation column process as the mixture vapour temperatures at the inlet and outlet are above the experimental viscosity measurement temperature of 60°C. This temperature limit cannot be exceeded without a significant loss of solute by vaporization into the surrounding atmosphere. Therefore, there is a need for a consistent, reliable and accurate analytical predictive method for viscosity calculations.

This paper concentrates on effectiveness of a locally fabricated packing material, including its combination with other conventional packing (Fig. 2) for separation in a packed distillation column; and secondly, to compare two viscosity models reported in the literature with the experimental data in order to adopting the model with the higher degree of confidence for the prediction of viscosity data.

II. PACKED COLUMN PERFORMANCE

Certainly, the distillation is the most widely applied separation technology and will continue as an important process for the foreseeable future because there is simply no industrially viable alternative around (Olujic et al., 2003). Despite the classification of distillation as a mature technology, improvements in the design of contacting devices, especially packings, continue to be made. The development of structure and random packing is an ongoing effort that consumes significant financial resources each year (Schmit et al., 2000). As the development of new devices has taken place, significant advances in modeling of the vapor-liquid mass-transfer process have occurred. The effort in mass-transfer model development have utilized commercial- and pilot-scale mass-transfer and pressure drop data, supplemented to some degree with bench-scale experiments. While this approach has produced reasonable models, a more detailed understanding of the mass transfer and hydraulics is needed to yield truly predictive models and to accelerate further advances in column internals design. Many models for predicting packed-column mass transfer efficiencies and hydraulic characteristics have been proposed. With few exceptions, these models incorporate variables derived from macroscopic properties of the entire column (composition profiles, exit stream concentrations, pressure drop, gross liquid holdup, height equivalent to a theoretical plate (HETP), temperature profiles, etc.). Values of HETP and pressure drop are currently predicted using models that are semi-empirical and do not rigorously represent the underlying momentum, heat, and mass-transfer processes. Typical models for determining hydraulic characteristics include those of Stichlmair et al. (1989) for random packing and Rocha et al. (1993) for structured packing. Models to predict mass-transfer performance (HETP) include those of Wagner et al. (1997) for random packing and Rocha et al. (1996) for structured packing as reported by Schmit et al. (2000). Although series of reports are available on the estimation of column performance, there is still more to understand concerning the interphase mass transfer model for the calculation of distillation efficiency.

III. TRANSFER UNIT APPROACH (NTU AND HTU)

Taiwo (1993, 2001) reported a steady state mass balance over the differential section ‘dz’ (Figure 2.1) in a packed column and that the rate at which component changes within a phase must equal the transfer rate of component to the phase. Holand (1981) put forward the following expression;

\[ dV_m = dL_m \]  \hspace{1cm} (1)

and the component balance is given as

\[ d(V_m y) = d(L_m x) \]  \hspace{1cm} (2)

where \( V_m \) and \( L_m \) is molar vapour and liquid flow rate respectively and \( y, x \) are the mole fractions of components in vapour, and liquid phases respectively.
d(V_m,y) = k_y(y_1 - y)dA = K_y(y^* - y)dA \quad (3)

dA is the interfacial transfer area associated with the differential height dz. This transfer area is highly difficult to measure in packed column hence it is more conveniently represented as 
\[ dA = aSdz \quad (4) \]

where ‘a’ is the interfacial area per unit volume of packing and ‘S’ is the empty column cross-sectional area. Since ‘a’ is usually unknown in a packed column, it is combined with surface coefficient to give composite coefficient (k,a). Thus equation (3) becomes 
\[ d(V_m,y) = k_ya(y_1 - y)Sdz = K_ya(y^* - y)Sdz \quad (5) \]

Qureshi and Smith (1958) solved equation (2.54) using two stagnant film theory and assuming constant fluid flow. Therate equation obtained for the two components mixture 1 and 2 for vapour phases is
\[
\int_{y_{12}}^{y_{11}} \frac{dy_{1b}}{y_{1b} - y_{1b}} = \frac{K_{y1}aS}{V_m} = NTU_{y1} \quad (6)
\]
\[
\int_{y_{21}}^{y_{22}} \frac{dy_{2b}}{y_{2b} - y_{2b}} = \frac{K_{y2}aS}{V_m} = NTU_{y2} \quad (7)
\]

Similarly, for liquid phase
\[
\int_{x_{11}}^{x_{12}} \frac{dx_{1b}}{x_{1b} - x_{1b}} = \frac{K_{x1}aS}{L_m} = NTU_{x1} \quad (8)
\]
\[
\int_{x_{21}}^{x_{22}} \frac{dx_{2b}}{x_{2b} - x_{2b}} = \frac{K_{x2}aS}{L_m} = NTU_{x2} \quad (9)
\]

The quantity \( V_m/k_a, L_m/k_a \) in equations (6 to 9) had been defined as height of transfer units. It is given as 
\[ z = (HTU)/(NTU) \quad (10) \]

where \( z \) is the height of packed section.

IV. LIQUID VISCOSITY CORRELATION

Viscosity data are important properties widely used in numerous chemical engineering correlations regarding the fluid flow, mass and heat transfer calculations. It is also useful for pure substance(s) characterizations (Kijevcanin et al., 2008). Such data are of interest also in the development of theories of liquid state (Teja and Rice, 1981a). It can be regarded as a measure of the internal fluid friction, which tends to oppose any dynamic change in the fluid motion (Reid et al., 1987). Viscosity differs in one important respect from other fluid properties, in that, it is a dynamic non-equilibrium, or transport property, which is a function of the state of fluid e.g. temperature, pressure, and volume, and maybe used to define the states of Newtonian fluid.

Several correlations are available in the literature for prediction of liquid viscosity (McAllister, 1960; Ely and Hanley, 1981; Dizechi and Marschall, 1982; Soliman and Marschall, 1990). The viscosity of mixtures can be estimated by either predictive or correlative models. Kijevcanin et al. (2008) reported that the significance of the predictive approach utilization is that the mixture viscosity is calculated based on pure component data and the relating functional groups parameters. The requirement of the very precise determination of universal group parameters sometimes could be a disadvantage of the applied approach. On the other hand, correlative models usually lead to better results, but for the determination of the interaction parameters, some optimization technique will be involved.

4.1 McAllister Model

One of the popular liquid theories is the reaction rate theory of Eyring and his coworkers (Deepak et al., 2007). It states that the volume in a gas is only sparsely populated by molecules whereas the volume of a liquid is densely populated by molecules with a few “holes”. These holes give a liquid a new degree of translation by permitting the relative motion of molecules near the holes. Viscous flow was considered a “reaction” in which a molecule sometimes acquires the activation energy necessary to slip over a potential energy barrier and move to the next equilibrium position.

Typically, either the application has been via the correlation method of McAllister (1960) or by describing the free energy of activation for flow in terms of thermodynamic excess Gibbs free energy models (Martins et al., 2000).

McAllister (1960) applied Eyring’s equation in terms of kinematic viscosity to binary mixtures:
\[ \nu = \eta/\rho = (hN/M)\exp(AG^*/RT) \quad (11) \]

The main assumption is that the free energy of activation of flow was additive and that the probability of the interactions were proportional to mole fractions. With these assumptions, a three – and four – body interaction for binary mixture was put forward. This was extended to ternary mixture. Dizechi and Marschall (1982) to accommodate polar substances proposed a modification to McAllister 3-body
interation model. Soliman and Marschall (1990) also modified the McAllister (1960) model was well as that of Dizechi and Marschall (1982). These models were reported satisfactory except that one requires more physical constant than the other does.

For 3-body interaction, McAllister presented the theory of viscosity of liquid mixtures as:

\[
\ln \nu = x_1^3 \ln v_1 + 3x_1^2 x_2 \ln v_{12} + 3x_1 x_2^2 \ln v_{21} + x_2^3 \ln v_2 - \ln \left( x_1 + \frac{x_2 M_2}{M_1} \right) + 3x_1 x_2^2 \ln \left( \frac{1 + \frac{M_2}{M_1}}{3} \right) + x_2^3 \ln \left( \frac{M_2}{M_1} \right)
\]

(Detailed derivation of the correlation is available in literature (McAllister, 1960; Monnery et al., 1995). The model contains two undetermined constants \( V_{12} \) and \( V_{21} \) which are assumed independent of composition but varies with temperature as

\[
v_{12} = h N/M_2 \exp \Delta G_{12}/RT
\]

\[
v_{21} = h N/M_2 \exp \Delta G_{21}/RT
\]

These constants can be evaluated from experimental viscosity data for binary mixtures by the multiple regression method. Once these constants are established for a given binary, viscosities at other temperature and composition may be determined.

The four-body model approaches more nearly three-dimensional treatment. The interactions considered include six interactions in which two molecules of each component are involved, eight interactions involving three molecules of each component and one each corresponding to pure component (McAllister 1960).

\[
\ln \nu_m = x_1^3 \ln v_1 + 4x_1^2 x_2 \ln v_{1112} + 6x_1 x_2^2 \ln v_{1112} + 4x_1 x_2^2 \ln v_{2221} + x_2^3 \ln v_2 - \ln \left( x_1 + x_2 M_2/M_1 \right) + 4x_1^3 x_2 \ln \left( \frac{M_2}{M_1} \right) + 6x_1^2 x_2^2 \ln \left( \frac{1 + \frac{M_2}{M_1}}{4} \right) + 4x_1^3 x_2^2 \ln \left( \frac{1 + \frac{M_2}{M_1}}{4} \right) + x_2^3 \ln \frac{M_2}{M_1}
\]

The equation contains three constants, which should be experimentally determined using the least squares method.

4.2 Letsou-Stiel (LS) model

This is the model employed by HYSYS software in predicting the liquid viscosities. This method is based on corresponding states principles. Monnery et al. (1995) and Manojlovic et al. (2001) reported the model of Letsou-Stiel correlation as:

\[
\eta = \left( \frac{\eta^*(\xi)}{\eta^*(\xi)} \right)^{2/3} = 0.0015174 - 0.02135 T_r + 0.0075 T_r^2
\]

\[
(16)
\]

\[
(\eta^*)^2 = 0.042552 - 0.07674 T_r + 0.0340 T_r^2
\]

\[
(17)
\]

\[
\eta^*(\xi) = 21.734 T_r^{1/6} \left( \frac{M_1^{1/2} P_2^{1/3}}{\rho_c} \right)
\]

\[
(18)
\]

Where, \( \xi_r \), \( T_r \), \( \omega \), M, Tc and Pc are viscosity, Thodos and co-workers viscosity reduction temperature,acentric factor, molar mass, critical temperature and critical pressure, respectively. For chemical systems, the modified NBS model of Ely and Hanley (1983) is used for predicting vapour phase viscosities, whereas a modified form of the Letsou-Stiel model is used for predicting the liquid viscosities.

V. MATERIALS AND METHODS

A quickfit visible flow packed distillation column (Corning Process Plant Engineering, Staffordshire, England) was employed for determination of column efficiency. The unit occupies a ground area of approximately 1.7m² with overall height of 5.70m. The column inside diameter was 0.1m and was packed separately with a borosilicate raschig rings (A), wire gauze rings (B) and their combinations (C, D and E) of equal sizes as shown in Table 1, 8mm nominal diameter, to a height of 1.3m. The raschig ring was supplied by ETA Ltd., Staffordshire, England while the wire gauze ring packing was fabricated at the Department of Chemical Engineering, Obafehi Awolowo University, Ile-Ife. The reboiler system consisted of a boiler type heat exchanger fitted externally to a spherical vessel of nominal capacity of about 20 litres a thermo-siphon loop. The region above the packed height, which was below the reflux divider and the region below the packed height but above the reboilerwere chosen for accurate temperature measurement and sample collection. The feed composition range experimented were selected based on the concentration ranges of the product of fermentative production of ethanol which fall between 6 to 12 percent by weight. Figure 1 is a diagrammatic representation of the experimental set up. The analysis of the vapour and liquid samples collected from the column for their compositions are reported elsewhere (Adelopoju, 2011). All the data were collected under the total reflux condition of the distillation column.
The method employed for the viscosity measurement of liquid samples was according to the standard of the Institute of Petroleum which covers the determination of the kinematic viscosity of liquid petroleum products, both transparent and opaque, by measuring the time (in seconds). The viscometers were charged with test samples as dictated by the design of the instrument, which was in conformity with that employed when the instrument was calibrated. The arms were corked to reduce evaporation and lose. The charged viscometers were mounted in the constant temperature bath with the aid of viscometer holder and alignment thereby keeping it in vertical position for about 30 minutes to reach the test temperature. The detailed procedure is given elsewhere (Adepoju, 2011).

VI. RESULT AND DISCUSSION

6.1 Binary System

The distillation column efficiencies for the various packing experimented is presented in figures 3 with most volatile component (MVC) concentrations in the feed mixtures for the ethanol-water binary system as a factor. The distillation column performances were found to decrease monotonously with increase in the more volatile component in the feed. The results showed that at a particular feed concentration of MVC, decrease in the height of a raschig packing in the column by a factor of 25%, and the remainder being wire-gauze ring, the performance of the column increases in that same direction. This assertion corresponds to the direction of decrease in the column pressure drop (see Tab. 1). The results showed that packing B demonstrated the least pressure drop range from 0.25 to 1.90 cm H2O while packing A indicated highest range of 1.10 to 8.50 cm H2O. It shows that as the void fraction increases the pressure drop reduces across the column. The reduction in pressure drop enhances the performance of the packed distillation column, hence the trend of the results obtained. For the system of 0.0127 mole fraction of the MVC in the feed, the performances increased from 2.1554 to 2.9314 with packing E having slight advantage over B and others, C>D>A. However, when the feed concentration was increased to 0.1061 mole fraction of MVC, the column performance dropped to between 1.4629-1.9556 which is about 20% decrease with the best result from packing B. The difference in the performances of these packings can be based on the direct relationship between the rate of mass transfer depicted as overall number of transfer units and the product of effective interfacial area and the liquid mass transfer coefficient. Furthermore, when the feed concentration of ethanol-water system increases from 0.0127 to 0.1061, the overall liquid phase number of transfer units for packing A decreases from 2.1554 to 1.4629, packing B dropped from 2.8818 to 1.9556, packing C reduces from 2.3920 to 1.5977, packing D decreases from 2.2073 to 1.5587 while packing E dropped down from 2.9314 to 1.6379. The results showed the order of packing performance as B>E>C>D>A. The distillation performance was found to decrease with increase in the more volatile component in the feed. This assertion had been previously observed and reported by other workers (Fasesan et al. 1988; Taiwo, 1993; Fasesan et al., 1993). The feed composition has a tendency to contribute significantly to the wetting characteristics of the liquid phase especially when there is added complications introduced by surface tension gradient (King, 1980). Thus, when the more volatile component has the lower surface tension (positive system i.e. ethanol-water) in the distillation of a binary mixture, the froth is more substantial and more stable than when the MVC has the higher surface tension (negative system such as in water-ethylene glycol system). The explanation for this phenomenon is that the liquid in froth becomes more depleted in the MVC during distillation in local regions where the liquid film is thin. Therefore, for a positive system, this greater depletion means that the liquid surface tension is higher in the thin-film regions than at surrounding points. The resultant surface-tension gradient along the surface sets up a surface-energy driving force, causing liquid flow from the low-surface-tension region to the high-surface-tension region. As a result of this flow, thin regions which would otherwise break are made thicker and reinforced, thus, promoting froth stability and as result made liquid to spread more readily over the solid surface and provides more interfacial area (hence greater efficiency) for positivesystems.

6.2 Viscosity

Two models, three-body McAllister model and the LS model in HYSYS package were tested and their results compared. The accuracy of the models was judged based on their absolute deviation (AD) and the average absolute deviation (AAD). The AAD significantly reflected the proximity of the models viscosities to the experimentally determined ones. Fig. 4 to Fig. 7 for ethanol-water systems depicted a maximum value of 0.4 ethanol mole fraction for McAllister model. This corroborated the result of Taiwo (1993) on aqueous alcohol mixtures. The Andrade equation was found to adequately correlate both the variation of pure viscosity and mixtures viscosity interaction coefficients with temperatures. This is an indication that the enthalpies and entropies of activation for viscosity of ethanol-water system are independent of temperature. This assertion gave credence to the work of Taiwo (1993). The LS model showed no minima or maxima values as against that of McAllister model.
Table 2 showed the variation of AAD for LS and McAllister models with temperatures. It revealed an increasing trend of AAD with temperature. The wide deviations in the kinematic viscosities could be because of the thermodynamic property used by the software. This is presented in the review of Rowley (1982) and Monnery et al. (1995) which stated the limitation of the method for predicting viscosity data. The major limitation originated from the development of the model, which required effective treatment of the liquid structure, which is neither completely random nor totally structured. Likewise, the constraint of pure component viscosity data and some thermodynamic binary information, which in practice are obtained through equilibrium data that are neither readily available nor consistent, may also be responsible for the outcome of the predictive model.

The model of McAllister requires adjustable parameters of the mixtures determined experimentally (shown in Tab. 3). These interaction parameters have influenced the quality of the obtained results. This is also evident in the work of Baskaran and Kubendran (2007) and Kijevcanin et al. (2008) that the viscosity is related to the molecular interaction between the components of the mixtures, as well as to the size and shape of molecules.

VII. CONCLUSION

The locally fabricated wire gauze packing offered higher performances for the binary system when juxtaposed with the results of the conventional raschig ring packing. Their combinations also showed greater improvement to the conventional packing especially when the packed column height of wire gauze tripled that of the raschig ring.

The results have also demonstrated that the correlative model (McAllister) predicts experimental viscosity data for the ethanol-water binary system more accurately than does the predictive model (Letsou-Stiel model). The resultant values of the intermolecular interactions obtained were also presented.

REFERENCES

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Figure 1: Schematic Diagram of Packed Distillation Column Source: Taiwo and Adepoju (2010)

Figure 2: Packing dimensions
Figure 3: Variation of Binary Efficiency with Mole Fraction of MVC in the Feed (Ethanol- Water system)

Figure 4: Kinematic Viscosity – Composition Variation of Ethanol(1)–Water(2) at 30°C

Figure 5: Kinematic Viscosity – Composition Variation of Ethanol(1)–Water(2) at 40°C
Figure 6: Kinematic Viscosity – Composition Variation of Ethanol(1)-Water(2) at 50°C

Figure 7: Kinematic Viscosity – Composition Variation of Ethanol(1)-Water(2) at 60°C

Table 1: Packing Column Modification and Characteristics

<table>
<thead>
<tr>
<th>Packing</th>
<th>Column Modification</th>
<th>Void Fraction (%)</th>
<th>Press. Drop (cm. H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100% Raschig ring</td>
<td>70.5</td>
<td>1.10-8.50</td>
</tr>
<tr>
<td>B</td>
<td>100% Wire gauze</td>
<td>93.1</td>
<td>0.25-1.90</td>
</tr>
<tr>
<td>C</td>
<td>0.5A + 0.5B</td>
<td>81.8</td>
<td>0.20-6.80</td>
</tr>
<tr>
<td>D</td>
<td>0.75A + 0.25B</td>
<td>75.6</td>
<td>0.70-7.50</td>
</tr>
<tr>
<td>E</td>
<td>0.25A + 0.75B</td>
<td>86.0</td>
<td>0.20-2.80</td>
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Table 2: LS and McAllister Models Kinematic Liquid Viscosity Average Absolute Deviation Results with Temperatures

<table>
<thead>
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<th>System</th>
<th>Model</th>
<th>Temperature °C</th>
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<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>LS</td>
<td></td>
<td>0.5343</td>
</tr>
<tr>
<td>ET-WA</td>
<td>McAllister (x10^4)</td>
<td>1.0079</td>
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Table 3: McAllister Constants for the viscosity of ethanol-water

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>A</th>
<th>McAllister Constants</th>
<th>B</th>
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<tr>
<td>30</td>
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<td>60</td>
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