Energy Demand of Biofuel Production Applying Distillation and/or Pervaporation

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The energy used for distillation can reach the 40 % of the total energy demand in bioethanol production. The pervaporation is an important alternative membrane separation process to distillation that can be applied as a hybrid process or even as a single process to produce high quality of biofuel. It will be shown how the energy demand, MJ/kg$_{Ethanol}$ energy, can be saved applying pervaporation process with different separation factors and operating modes. It is stated that relatively high separation factor is needed to lower the energy demand below that of a simple distillation column.

1. Introduction

Bioethanol is regarded as one of the main biofuels for application in the transport sector. In this paper the energy demand of the fuel-grade bioethanol production followed by the fermentation will be discussed. The energy used for distillation reaches the 40 % of the total energy demand in bioethanol production (Huang et al., 2008). Similarly, the distillation needs high energy portion in case of lignocellulosic bioethanol production (Porzio et al., 2011) The main question to be answered is that the application of the membrane separation process, namely the pervaporation, offers a real alternative method to the traditional distillation and whether its single application or its combined application with distillation can really decrease the energy demand of the biofuel production (Nagy, 2012)..The ethanol concentration obtained after fermentation is relative low, it can change between 3-12 % depending on the raw materials namely it can be corn starch or lignocellulose. Its concentration up to the biofuel-grad one, it is about 99.4 to 99.9 %, is mostly carried out by distillation in the industry. Nowadays the application of the so called hybrid process, namely combination the distillation with pervaporation could come to the front due to the relative high permeation rate and selectivity of the pervaporation (We et al., 2008).

Downstream from the fermentor is usually dilute aqueous solution containing 3-12 wt% ethanol, especially low can be the ethanol concentration of the fermentation broth if one applies lignocellulosic raw material. Separation of ethanol from the fermentation broth is an energy-intensive process (Nagy et al., 2012). In general, for the solution containing 10-85 wt% ethanol, distillation is generally effective, while for the mixture containing more than 85 wt% ethanol, distillation becomes expensive. The pervaporation process is considered as one of the most effective and energy-saving process for separation of azeotropic mixtures (Vane, 2005).

The main task of this study is to predict the energy demand of pervaporation under different concentrations and separation factor and to show under what conditions can be the pervaporation an alternative process to distillation producing ethanol of the same quality by means of both processes. It will be analyzed how the inlet concentration affects the permeate concentration and the energy demand, depending on the separation factor during the pervaporation process.

2. Theory

2.1 2.1 Energy demand for distillation, activity model

In this approach, an equation of state is used for predicting the vapour fugacity coefficients (normally ideal gas assumption or the Redlich Kwong, Peng-Robinson or SRK equations of state, although a Virial equation of state is available for specific applications) and an activity coefficient model is used for the liquid phase. Although there is considerable research being conducted to extend equation of state applications into the chemical arena (e.g., the PRSV equation), the state of the art of property predictions for chemical systems is still governed mainly by Activity Models. The phase separation or equilibrium ratio K_i for component i, defined in terms of the vapour phase fugacity coefficient and the liquid phase activity coefficient is calculated from the following expression:

$$K_i = \frac{\gamma_i}{x_i} = \frac{\gamma_i f_i^O}{P\phi_i} \tag{1}$$

Although for ideal solutions the activity coefficient is unity, for most chemical (non-ideal) systems this approximation is incorrect. Dissimilar chemicals normally exhibit not only large deviations from an ideal solution, but the deviation is also found to be a strong function of the composition. To account for this non-ideality, activity models were developed to predict the activity coefficients of the components in the liquid phase. The derived correlations were based on the excess Gibbs energy function, which is defined as the observed Gibbs energy of a mixture in excess of what it would be if the solution behaved ideally, at the same temperature and pressure. For a multi-component mixture consisting of ni moles of component i, the total excess Gibbs free energy is represented by the following expression:

$$G^E = RT\sum\left(n_i \, ln\gamma_i\right) \tag{2}$$

The individual activity coefficients for any system can be obtained from a derived expression for excess Gibbs energy function coupled with the Gibbs-Duhem equation.

The UNIQUAC model has been used for calculation the energy demand applying the statistical mechanics and the quasi-chemical theory of Guggenheim to represent the liquid structure.

2.2 2.2 Energy demand for pervaporation

The prediction of the energy demand of pervaporation with different membrane selectivity (ξ) and module configuration will be shown here. The energy required to evaporate will be taken into account, the heat for condensation and its recovery during the process will not considered here. Accordingly, the necessary energy, given in MJ/kg_{Et} involves the evaporation heat, only. The energy required to evaporate permeate in a pervaporation process, normalized per unit of ethanol permeated (Q) is calculated as follows (Vane, 2005):

$$Q = \frac{H_w J_w + H_{Et} J_{Et}}{J_{Et}} \equiv H_w \frac{J_w}{J_{Et}} + H_{Et} \tag{3}$$

where H_i is the heat of evaporation of species i (=water, ethanol). According to Eq. (3), the ratio of the mass transfer rates, namely J_w/J_{et} should be known in order to be able to calculate the energy demand for the pervaporation process. This ratio can be obtained by means of the separation factor (ξ). Its value can be defined as (Baker, 2004):

$$\xi = \frac{[C_w / C_{Et}]^G}{[C_w / C_{Et}]^L} \tag{4}$$

Considering that the permeate concentration ratio of the component is equal to their mass transfer rates' ratio, namely $J_{Et} / J_w = [C_{Et} / C_w]^G$, Eq. (4) can be rewritten as:

$$\frac{J_w}{J_{Et}} = \frac{[C_w]^L}{\xi[C_{Et}]^L} \tag{5}$$

Accordingly, in the knowledge of the ξ value, the energy demand for evaporation can be estimated, during pervaporation. Knowing the ratio of the permeation rates, the concentration of the liquid permeate can easily be predicted, namely e.g.:

$$[C_{Et}]^G = \frac{J_{Et}}{J_{Et} + J_w} \equiv \frac{1}{1 + J_w / J_{Et}} \tag{6}$$

Note that during our calculation the average value of the mass transfer rates can be applied. The differential mass balance equation on species i over a differential area of membrane module can be given as:

$$FdC_i = J_i dA \equiv P\Delta C dA \qquad (7)$$

After solution one can get as:

$$ln\frac{\Delta C_{out}}{\Delta C_{in}} = \frac{P}{F}A \qquad (8)$$

According to Eq. (8), during our calculation the log-mean ethanol feed concentration was used to represent the concentration change in the feed phase during pervaporation. The amount of the permeate rate, $J=J_w+J_{Et}$, was calculated as:

$$JC_{Et}^{G} + (F-J)C_{Et}^{L} = FC_{Et}^{Lin} \qquad (9)$$

The necessary energy needed for the evaporation is calculated as:

$$E = Q_{Et}^{ev} + Q_{w}^{ev}\frac{J_w}{J_{Et}} \qquad (10)$$

where E gives the energy related to the mass of the permeated ethanol (MJ/kg$_{Et}$), Q_{Et}^{ev} =0.838 MJ/kg, $Q_{w}^{ev} = 2.258MJ/kg$.

3. Results and discussion

The energy demand of a single distillation, applying the expressions presented is shown in Figure 1 as a function of the inlet ethanol concentration.
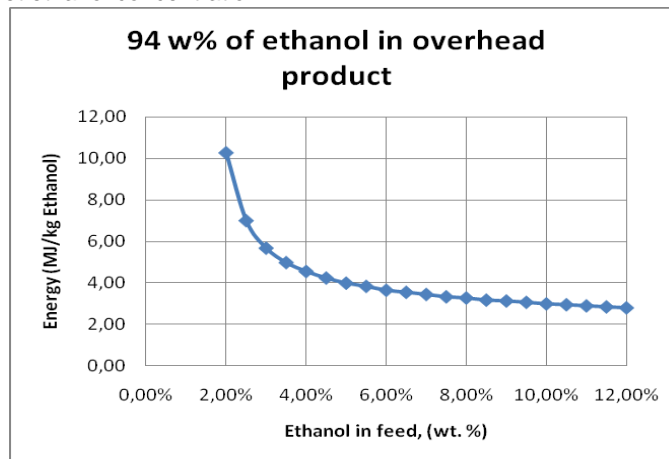

Figure 1: Energy demand of a single distillation applying the UNIQUAC model

These results are similar to that published by Zacchi and Axelsson (1989). As can be seen the energy demand strongly depends on the inlet ethanol concentration. Note that practically the whole amount of the inlet ethanol was removed as product (The outlet concentration of the ethanol in the feed phase was 0.02 w%).

In the next sections the energy demand of the pervaporation well be shown as a function of the inlet ethanol concentration by a few typical figures. The main question is how the separation can be carried out by a single stage pervaporation equipment applying membranes with different separation factor. Figure 2 illustrates the effect of the separation factor on the ethanol concentration of the permeate, in a single stage pervaporation apparatus. As it can be seen the outlet ethanol concentration strongly depends both on its feed concentration and the separation factor. Note that the outlet ethanol concentration of the feed phase is 0.0002 kg/kg, i.e. 99.8 % of the feed amount of ethanol is removed into the permeate phase. On the other hand the amount of water transferred with the ethanol can also be relatively high. If one want to reach the biofuel quality of the ethanol, i.e. more than 99 w% ethanol in the permeate phase, he needs membrane with high separation factor. (Note that for concentration of ethanol from the fermentation broth one needs hydrophobic membrane). Let us look at an example from Figure 1. Assuming that we have a fermentation broth with 12 w% ethanol content, the outlet ethanol concentration is about 67 w% with

membrane of ξ=100 and 95.3 w% with membrane of ξ = 1,000. That means that the biofuel quality cannot be reached even membranes with very high separation factors. Applying lower inlet ethanol concentration the permeate ethanol concentration will be even lower. Nowadays the separation factor of the commercial available silicon membranes has ξ= about 10 in the case of water/ethanol mixtures. This quality is too week for its real industrial application. This figures enables the reader to predict how many stages is needed for solution of a given separation applying a membrane with a given separation factor. It can approximately be read the outlet concentration after every stages from Figure 2.
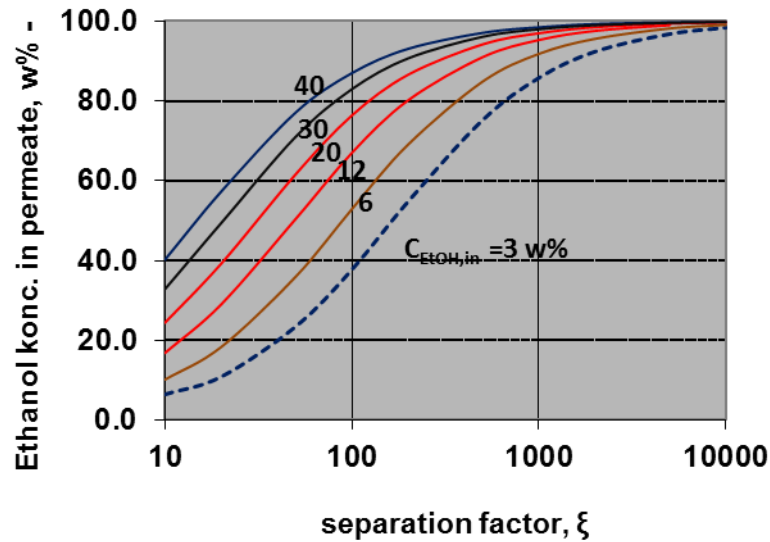

Figure 2: Ethanol concentration in the permeate as a function of the separation factor of the membrane at different values of the feed ethanol concentration
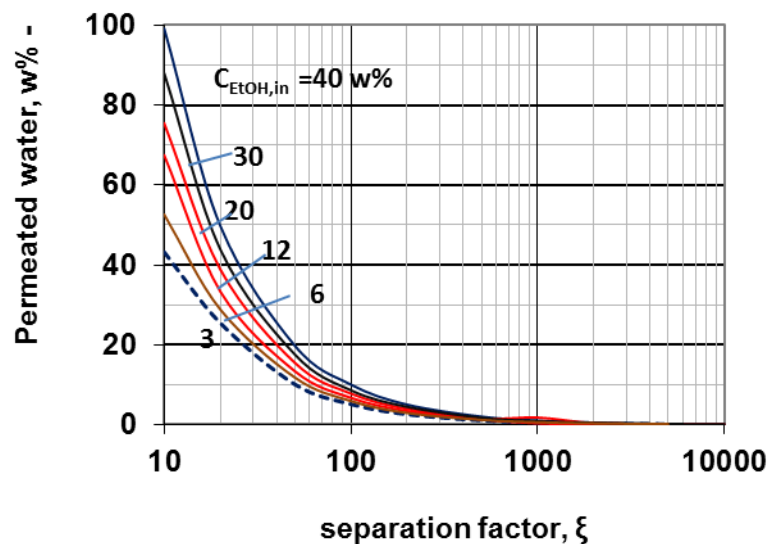

Figure 3: The permeated water related to that of the feed water ($100J_w/F_w$) as a function of the separation factor at different values of the inlet ethanol concentrations

Look at how the permeate water concentration changes as a function of the separation factor (Figure 3). Amount of water permeated through the membrane is rather high with separation factor below 100. Above this value the water concentration is rather low, its amount related to the inlet one is lower than10 %. On the other hand, the amount of water permeated strongly increases with the increase of the inlet ethanol concentration. That means that the removal of larger portion of ethanol needs more water to be permeated

from its lesser amount in the feed mixture. Obviously, the evaporation of this larger amount demands more energy. How the energy demand changes is illustrated by Figure 4. The strong increase of the energy
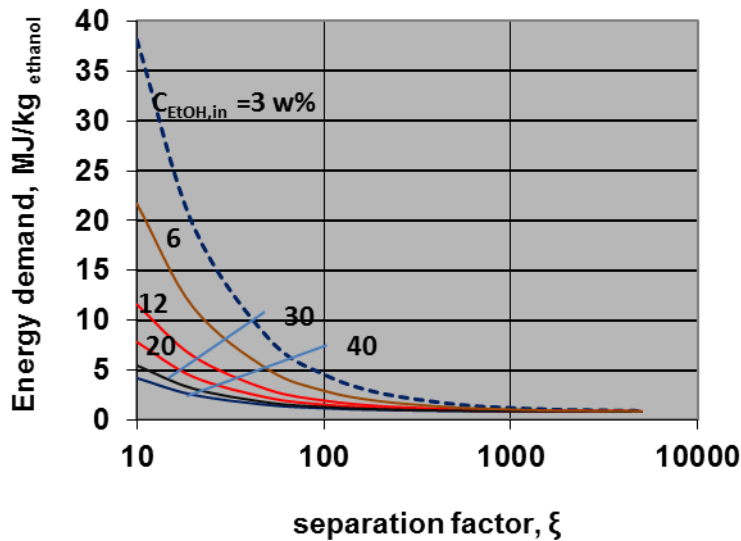

Figure 4: The energy demand as a function of the separation factor, at different inlet concentration during the separation by means of pervaporation

demand is a consequence of the larger amount of water present in the permeate phase at lower values of the separation factor. The energy demand tends close to that of the evaporation heat of the ethanol ($Q_{Et}^{ev} = 0.838 MJ/kg_{Et}$) if ξ will be larger than a few hundred. This figure also well illustrates the importance of the high value of the separation factor. If its value less than 50, its economic application is a difficult task. It can be used for breaking the azeotrope concentration. On the other hand, larger molecules can be separated by much higher separation factor than the case of ethanol/water. The hydrophilic membranes with low separation factor can be recommended first to concentration of azeotropic mixture of water/ethanol in order to reach the fuel grade quality.

During our lecture the application of the pervaporation will be analyzed in details applying one-stage or multi-stage pervaporation apparatus.. From the above figures it can become clear the importance of the membrane quality.

4. Conclusions

It has been shown, how strongly the outlet concentration and the energy demand of the pervaporation process depend on the separation factor of pervaporation the membrane. The application of the pervaporation needs membrane of very high separation coefficient in order to reach the fuel-grade ethanol concentration, directly from the fermentation broth, in a one-stage process. Generally it can be stated that multi-stage pervaporation process is needed to reach the fuel-grade quality of the bioethanol.

5. Nomenclature

A   membrane area, m^2
C   concentration, mol/m^3, w%
f_i^O standard state fugacity of component i
F   inlet liquid flow rate, m^3/s
H   heat of evaporation, KJ/kg
J   permeation rate, $mol/m^2 s$, $kg/m^2 s$
P   permeability coefficient, m/s
P   system pressure, Pa
Q   energy demand for unit oh ethanol permeated, KJ/mol, KJ/kg

Greek letters

γ_i liquid phase activity coefficient of component i

ϕ_i vapour phase fugacity coefficient of component i

ξ separation factor (Eq. 5)

θ ($\theta = J_w / J_{Et}$)

Subscripts

Et   ethanol

w   water

Superscript

L   feed (out phase)

Lin   inlet phase

G   condensed liquid permeate (out phase)

References

Baker R.W., 2004, Membrane Technology and Applications, 2nd Ed., Wiley & Sons, Chichester, UK

Huang, H.J., Ramaswamy, S., Tschirner, U.W. Ramarao, B.V. 2008, A review of separation technologies in current and future biorefineries, Sep. Purif. Technol., 62, 1-21.

Nagy, E., Hajba, L., Hancsók, J., 2012, Energy saving processes of biofuel production from fermentation broth, Chemical Engineering Transaction, 29, 289-294

Nagy, E., 2012, Basic equation of mass transport through a membrane layer, Elsevier, New York, USA.

Vane, L.M. 2005, A review of pervaporation for product recovery from biomass fermentation processes processes, J. Chem. Technol. Biotechnol 80, 603-629

Porzio, G.F., Chiaramonti, D., 2011, Process analysis and modelling for 2th generation lignocellulosic bioethanol production, Chemical Engineering. Transaction, 25, 869-874.

Zacchi, G., Axelsson, 1989 Economic evaluation of preconcentration in production of ethanol from dilute sugar solutions, Biotechn. Bioeng., 34, 223-233.

Wee, S.L., Tye, C.-T., Bhatia, S., 2008, Membrane separation process-Pervaporation through zeolite membrane, Sep. Purif. Technol., 63, 500-516