Hybrid Separation Scheme for Azeotropic Mixtures – Sustainable Design Methodology

Ramsagar Vooradi[a,*], Venkata S. Patnaikuni[a], Anjan K. Tula[b], Sarath B. Anne[a], Mario R. Eden[b], Rafiqul Gani[b,c]

[a]Department of Chemical Engineering, National Institute of Technology Warangal, Telangana – 506004, India
[b]PSE for SPEED, 294/65 RK Office Park, Bangkok, Thailand 10520
[c]PSE for SPEED, Skyttemosen 6, DK 3450 Allerod, Denmark
ramsagar@nitw.ac.in

Distillation has been the first choice among the numerous separation techniques employed by chemical industries, primarily because of its inherent advantages. About 80% of industrial separations involving vapour – liquid phases are performed by distillation, in spite of its low thermal efficiency and highly energy intensive nature. More than 50 % of the total energy consumed in distillation, is spent for enriching the product purity from 80-90% to close to 100 %. However, a conventional distillation process operating at normal conditions is ineffective for separating azeotropic mixtures. In this work, a methodology has been proposed to explore the possibility of integrating distillation with membrane separation technique to separate azeotropic mixtures. These units will be operated at their maximum driving force for separation in the proposed hybrid schemes. The designed optimal hybrid schemes result in energy efficient separations compared to conventional distillation processes. The effectiveness of the proposed methodology is demonstrated with the help of two case studies. In the first case study, a well-known example of benzene - cyclohexane separation is presented, while production of 99.9 mole % pure acetonitrile from an ethanol ammoxidation process is discussed in the second case study. Both these systems form azeotropes at atmospheric pressure.

1. Introduction

It is hard to imagine a chemical industry without separation processes as the products are required to be recovered at specified purity level. These processes are in general energy intensive. In chemical and related process industries, distillation is usually the primary option as a separation process because of the following advantages: mature technology, low capital investments, ability to handle bulk volumes, low operational risk, recovery of components relatively in pure form and no requirement of downstream processing. About 95% of all separations in chemical industries are handled using distillation (Jana, 2014). Energy is used as a separating agent in distillation operation and consequently, distillation consumes about 40% of energy used by a chemical plant. In United States, chemical separations alone account for about 10-15 % of national total energy consumption and about half of the total energy utilized by industries. Figure 1 shows the percentage share of industrial energy consumption by different chemical separation techniques (Sholl and Lively, 2016). The main reason for this huge energy consumption in distillation is its low thermodynamic efficiency of less than 10 percent (Eldridge et al., 2005). Therefore, in order to make this separation method more energy efficient, it is important to look for intensification of distillation process or couple it with other advanced processes to form an efficient hybrid distillation scheme. The recent developments in this direction include multi-effect distillation (Gao et al., 2015), heat pump distillation (Jana, 2014), heat-integrated distillation column (Bruinsma et al., 2012), dividing-wall columns (Dejanovic et al., 2010), membrane distillation (Politano et al., 2017) and hybrid schemes with membrane modules (Tula et al., 2017). These are reported to be more energy efficient compared to the conventional distillation process.
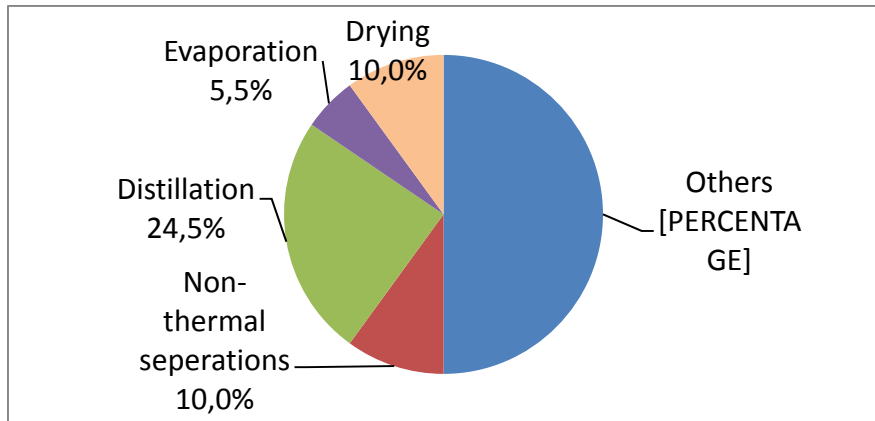
Figure 1: Energy usage by U.S. Industry

Among the above advanced distillation schemes, the hybrid scheme considered in this work, viz., distillation coupled with membrane separation, is easy to implement in the industry as it requires installation of only additional membrane module without changing the existing distillation setup. This makes retrofitting easy and amenable. Most of the existing literature on hybrid schemes highlighted the operational advantages (Fahmy et al., 2001), performance of different membranes (Fontalvo et al., 2005) and application to different systems (Huang et al., 2010). Recently, Tula et al., 2017 proposed a methodology which systematically analyzes the feasibility of hybrid scheme by considering characteristics of separation problem, difficulties in conventional separation, optimal hybrid scheme and expected product purity. However, a systematic methodology is not available for the separation of azeotropic mixtures using hybrid schemes.

In this paper, the methodology proposed by Tula et al., (2017) has been extended for synthesis-design of hybrid distillation-membrane based separation schemes for separating azeotropic mixtures, taking into account the potential for energy savings without compromising on the product specifications, the capital and operating costs.

2. Separation of azeotropic mixture by distillation

A conventional distillation column is mainly divided into two sections: absorption and stripping. In absorption section, which is above the feed tray, the less volatile compounds from gas phase are absorbed in liquid phase as gas rises from bottom to top. In stripping section, which is near to reboiler, high volatile compounds are stripped off from the liquid phase during its contact with high temperature vapour entering from reboiler. For any distillation column with optimal equipment parameters, the operational cost is directly proportional to the reboiler energy requirement. The energy requirement in the reboiler is inversely proportional to the driving force for separation. Therefore, it is strongly advisable to design any process at the maximum possible driving force. In distillation, the driving force (DF_{ij}) is measured as the difference between concentration (mole fraction) of component i in the coexisting phases of vapour (y_i) and liquid (x_i) for a property j as shown in Eq(1) (Bek-Pedersen and Gani, 2004).

$$DF_{ij} = y_i - x_i \tag{1}$$

Binary mixtures with close boiling components and/or a few non-ideal mixtures are likely to form azeotropes. If the azeotrope is pressure insensitive, it will not disappear if the pressure is changed. At azeotropric concentration, the driving force will be zero and separation is not possible by distillation. For the binary mixture of benzene – cyclohexane, which forms a pressure insensitive azeotrope, the driving force diagram at 1 atm pressure is shown in Figure 2. Conventional distillation is not economical to process the feed mixture even at non-azeotropic compositions, if the driving force is very small as shown in Figure 2a. However, addition of an entrainer (furfural) alters the boiling points and makes the separation possible by increasing the driving force and eliminating the azeotrope as shown in Figure 2b. Figure 2b also shows the effect of 'entrainer to feed' ratio on the driving force. Figure 3 shows the variation in reboiler duty with product purity, for the case of separation of benzene – cyclohexane mixture using extractive distillation at a driving force of 17.3. It can be seen that the reboiler duty increases steadily up to a certain degree of separation and then increases exponentially.
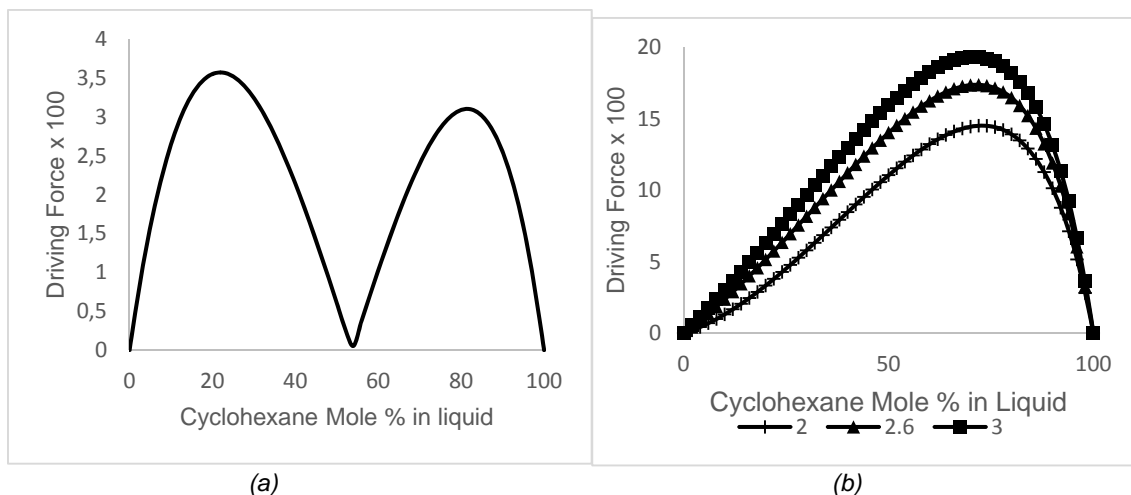
(a)   *(b)*

Figure 2: Driving force diagram for benzene and cyclohexane mixture at 1 atm. a) without entrainer. b) in the presence of furfural as entrainer at different entrainer to feed ratios

If the azeotrope is pressure sensitive, the driving force for separation changes with pressure. For the binary mixture of acetonitrile and water, which forms a pressure sensitive azeotrope, the driving force diagram is shown in Figure 4. As can be observed from Figure 4, the azeotrope disappears at 0.01 atm pressure, vacuum distillation can be used to separate the mixture. However, operation of conventional distillation at non-atmospheric pressure conditions (vacuum or high pressure) requires sophisticated auxiliary equipment and involves high cost.
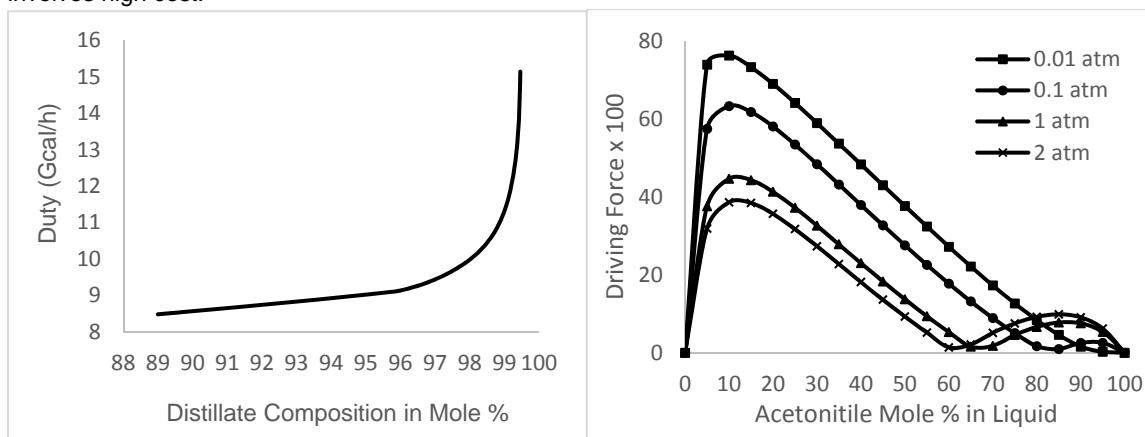

Figure 3: Variation of Reboiler duty with distillate purity at entrainer to feed ratio of 2.6 (driving force of 17.3)   *Figure 4: Driving force diagram for Acetonitrile and water mixture at different pressures*

In order to obtain high purity products from the above two cases, conventional distillation requires higher operational costs due to high reboiler duty and/or maintenance of non-atmpospheric pressure conditions. In these scenarios, hybrid separation scheme involving distillation coupled with membrane module will be a potential option as the products from distillation need not be of high purity. The purpose of using the membrane unit is to remove the selected components in small amounts so as to (i) get the desired purity of the end products and/or (ii) cross the azeotropic composition to facilitate the distillation operation on both sides of the azeotrope. For instance, a suitable membrane can be used to enrich the final product purity from 0.85 to 0.99 by permeating non-key component.

3. Design methodology

The proposed methodology for separation of azeotropic mixtures is presented in two sections: (i) viability of hybrid separation scheme involving distillation and membrane modules based on driving force analysis and (ii) step-by-step procedure for design of hybrid separation scheme.

3.1 Viability of hybrid separation scheme

Calculation of driving force for a given feed mixture using the Eq (1) is the starting step of the procedure. Based on the value of the driving force, suitable separation scheme can be identified using the steps presented in the flow chart shown in Figure 5.
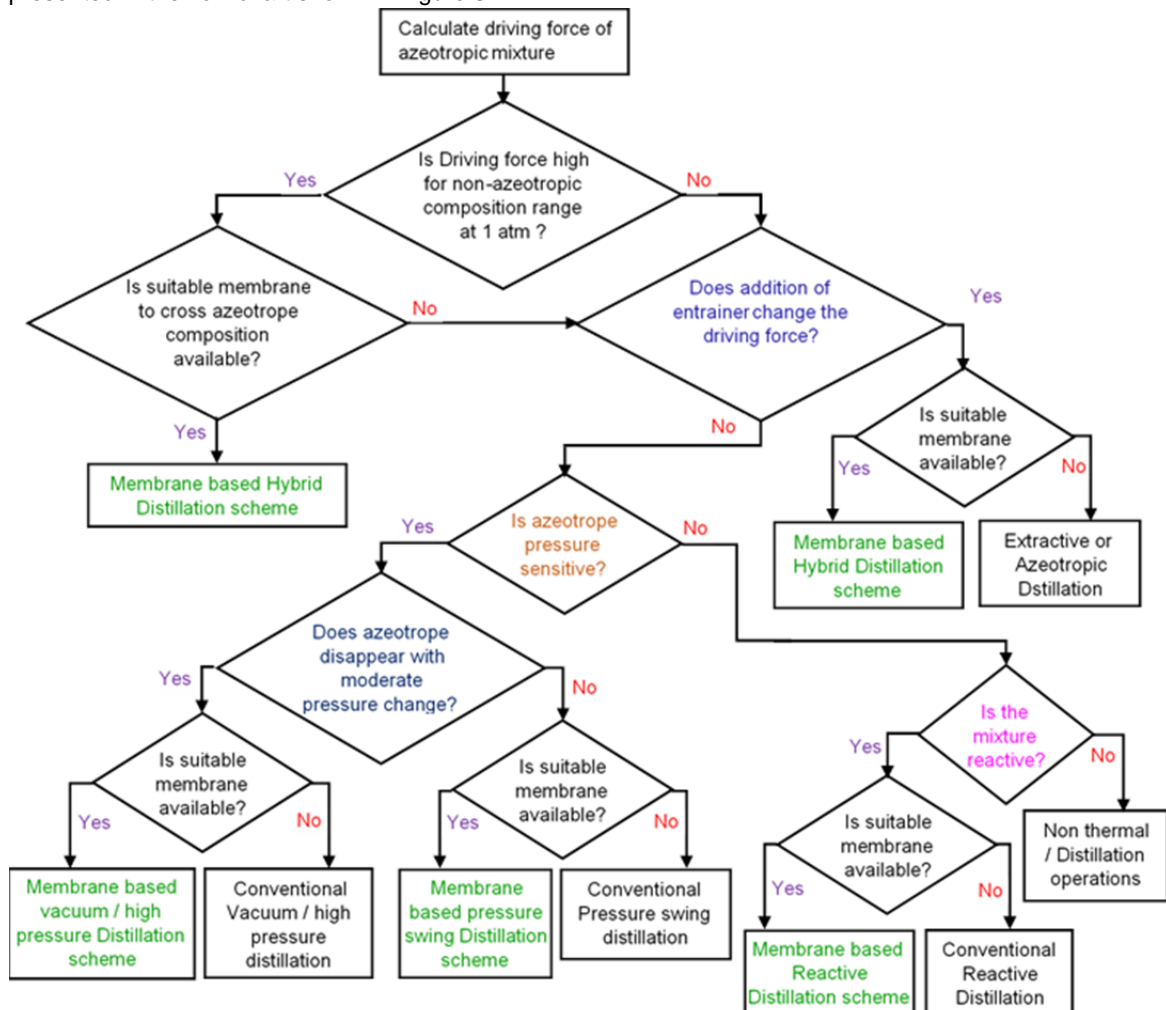

Figure 5: Flowsheet to select the suitable separation technique for azeotropic mixtures

If hybrid separation scheme is the selected option, a suitable combination of distillation and membrane processes needs to be designed.

3.2 Step by step algorithm for design of hybrid scheme

Step 1: Calculate the driving force diagram for separation by distillation and membrane for a given binary azeotropic mixture.

Step 2: Use the calculated driving force and identify the hybrid scheme layout by ensuring the operation of distillation and membrane units at their maximum driving force regions.

Step 3: Perform design of distillation column(s) in the identified layout.

Step 4: Calculate reboiler & condenser duties as a function of purity to find out the potential energy savings.

Step 5: Calculate the membrane area required and capital cost associated with membrane operation.

Step 6: Calculate the overall economics of the layout.

This design would be economical and sustainable compared to stand alone distillation or membrane process as it significantly reduces the reboiler duty and operates with minimum membrane area.

4. Application examples

The proposed methodology is tested on two well-known case studies from the literature. The hybrid scheme simulation results are compared against the separation by conventional distillation. The comparison is made with respect to reboiler energy savings only. The overall process economics with membrane side calculations is not included in this study. The detailed simulation results along with the membrane calculations will be presented in another follow-up publication.

4.1 Application example 1

A feed mixture of 750 kmol/h of benzene and 250 kmol/h cyclohexane with a target purity level of 99.5 % for both benzene and cyclohexane is considered. This mixture forms an azeotrope at 55 % (vol) benzene at 1 atm pressure and the driving force for separation is not high (< 0.035) even at non-azeotropic composition. Furfural is used as the entrainer as it increases the driving force by altering the boiling points. As benzene selective membranes are available, a hybrid separation scheme involving extractive distillation coupled with membrane module is designed by following the steps discussed in the methodology section. The proposed scheme is compared with the conventional extractive distillation at a given entrainer to feed ratio of 2.6. Both the cases are simulated using ASPEN PLUS v9 and the designs along with the simulation results are shown in Figure 6. The total reboiler duty required for separation using conventional extractive distillation is 43.5 Gcal/h, while that required for hybrid shceme is 25 Gcal/h. Hence, for the same degree of separation, hybrid separation scheme designed based on the proposed methodology results in 42.5 % reboiler duty savings and 34.83 % reduction in entrainer running in the loop.
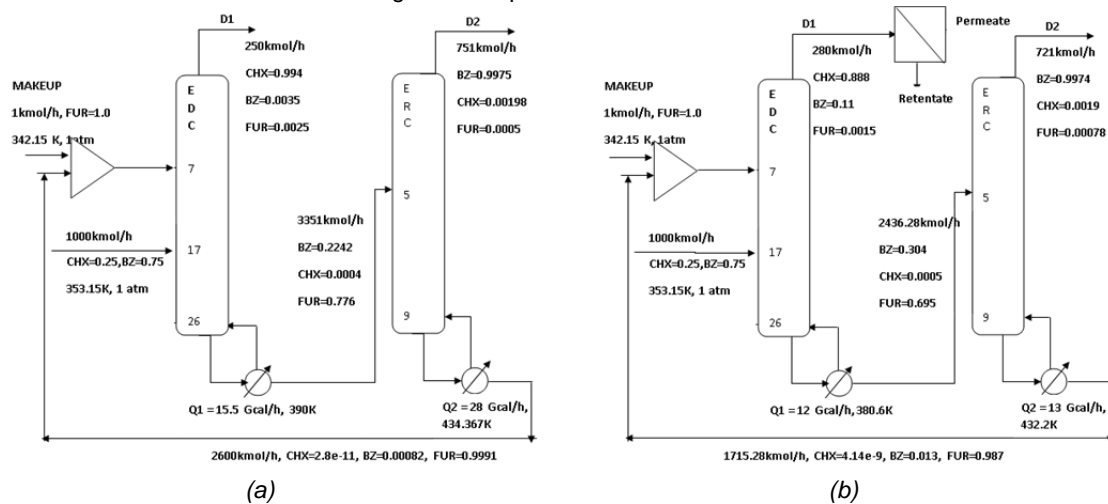

Figure 6: Simulation results for Benzene-Cyclohexane separation task using (a) Conventional Extractive distillation and (b) Hybrid separation scheme with extractive distillation coupled with membrane

4.2 Application example 2

Ethanol ammoxidation process is widely used for producing acetonitrile. The process product stream contains water, acetonitrile along with minute quantities of gases such as CO_2, HCN and unconverted NH_3. Water and acetonitrile form an azeotrope at 67 mole% of acetonitrile at 1 atm pressure. Following the step-by-step methodology presented in section 3, a hybrid separation scheme with distillation and membrane is designed as an alternative to pressure swing distillation scheme of two distillation columns operating at 1 bar and 7 bar studied by Tripodi et al., (2017). Both the schemes are simulated to achieve a target purity of 99.99% acetonitrile with a recovery of 99.9% acetonitrile from gas free water and acetonitrile feed mixture containing 21 % (mole) acetonitrile at 1 bar pressure and 77.21 ^{0}C. In the hybrid scheme, water selective membrane is used to cross the azeotrope composition. This scheme contains two distillation columns operating at 1 bar pressure to handle the separations at the compositions above and below the azeotropic concentration, that is, on either side of the membrane separation. The proposed hybrid scheme along with the simulation results is shown in Figure 7. The results show that the total reboiler duty in the hybrid scheme operating at 1 bar pressure is 32.32 kW whereas that for pressure swing distillation method is 52.6 kW. This shows a 38.55 % savings in the reboiler duty with the hybrid separation scheme.
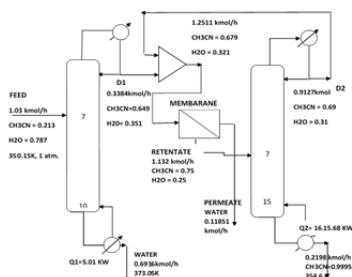
Figure 7: Simulation results for Acetonitrile-Water separation using hybrid separation scheme

5. Conclusions

In this work, a novel methodology is proposed for the separation of any binary azeotropic mixture. This methodology first explores the viability of hybrid separation scheme to realise the energy savings by integration of membrane and distillation modules rather than using standalone membrane process or other distillation processes. The hybrid separation scheme will be energy efficient as the individual separation tasks are handled at their maximum driving forces. The main limitation of the proposed methodology is the availability of suitable membranes for the systems under investigation. The results of the study indicate the vast potential for development of suitable membranes for industrial use in conjunction with distillation. The proposed methodology is tested on well-known example of separation of benzene-cyclohexane mixture. The viability of new hybrid separation scheme designed using proposed methodology is investigated to replace the conventional extractive distillation process. The hybrid scheme, is highly energy efficient, with 42.5% reboiler energy savings and 34.83% savings in the solvent requirement as compared to conventional extractive distillation. In the second case study, a hybrid separation scheme is proposed for production of 99.9 mole % pure acetonitrile from an ethanol ammoxidation process. The proposed hybrid separation scheme containing two distillation columns operating on either side of the membrane module results in 30% energy savings in reboiler duty compared to pressure swing distillation.

References

Bek-Pedersen E., Gani R., 2004, Design and synthesis of distillation systems using a driving-force-based approach. Chem. Eng. Process. Process Intensif., 43,251–262.

Bruinsma O.S.L., Krikken T., Cot J., Saric M., Tromp S.A., Olujic Z., Stankiewicz A.I., 2012, The structured heat integrated distillation column, Chemical Engineering Research and Design, *90*(4), 458-470.

Dejanovic I., Matijasevic L., Olujic Z., 2010, Dividing wall column—a breakthrough towards sustainable distilling, *Chemical Engineering and Processing: Process Intensification*, *49*(6), 559-580.

Eldridge R.B., Seibert A.F., Robinson S., Rogers J., 2005, Hybrid separations/distillation technology. Research opportunities for energy and emissions reduction, Univ. of Texas, Austin, TX (United States).

Fahmy A., Mewes D., Ebert K., 2001, Design methodology for the optimization of membrane separation properties for hybrid vapor permeation-distillation processes, Separation science and technology, *36*(15), 3287-3304.

Fontalvo J., Cuellar P., Timmer J.M.K., Vorstman M.A.G., Wijers J.G., Keurentje J.T.F., 2005, Comparing pervaporation and vapour permeation hybrid distillation processes, Industrial & engineering chemistry research, *44*(14), 5259-5266.

Gao X., Chen J., Tan J., Wang Y., Ma Z., Yang L., 2015, Application of mechanical vapour recompression heat pump to double-effect distillation for separating N-Dimethylacetamide/water mixture, Industrial & Engineering Chemistry Research, *54*(12), 3200-3204.

Huang Y., Baker R.W., Vane L.M., 2010, Low-energy distillation-membrane separation process. Industrial & Engineering Chemistry Research, *49*(8), 3760-3768.

Jana A.K., 2014, Advances in heat pump assisted distillation column: A review. Energy Conversion and Management, *77*, 287-297.

Politano A., Di Profio G., Sanna V., Curcio E., 2017, Thermoplasmonic membrane distillation, Chemical Engineering Transactions, 60, 301-306.

Sholl D.S., Lively R.P., 2016, Seven chemical separations to change the world, *Nature*, 532, 435-437.

Tripodi A., Compagnoni M., Ramis G., 2017, Pressure-swing or extraction-distillation for the recovery of pure acetonitrile from ethanol ammoxidation process: A comparison of efficiency and cost, Chem. Eng. Research and Design, 127, 92-102,

Tula A.K., Befort B., Garg N., Camarda K.V.,Gani R., 2017, Sustainable process design & analysis of hybrid separations, Computers & Chemical Engineering, 105, 96-104.