CHEMICAL ENGINEERING TRANSACTIONS

VOL. 35, 2013

A publication of
AIDIC
The Italian Association
of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Varbanov, Jiří Klemeš, Panos Seferlis, Athanasios I. Papadopoulos, Spyros Voutetakis

ISBN 978-88-95608-26-6; **ISSN** 1974-9791

DOI: 10.3303/CET1335213

Breaking Azeotropes by Azeotropic and Extractive Distillation in a Dividing-Wall Column

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This study gives a brief overview about using dividing-wall column (DWC) technology in azeotropic and extractive distillation processes aimed to break azeotropes. The relevant case study considered here is the bioethanol dehydration process that requires significant energy to overcome the azeotropic behaviour of ethanol-water mixture. The results of the rigorous Aspen Plus simulations show that energy savings of 10 – 20 % are possible for the novel process intensification alternative based on DWC, while using less equipment units as compared to the conventional azeotropic and extractive distillation configurations.

1. Introduction

Bioethanol is the most promising biofuel alternative, being readily usable in the existing car engines and conveniently distributed within the current infrastructure. The present industrial scale production relies on few processes, such as: corn-to-bioethanol, sugarcane-to-bioethanol, basic and integrated lignocellulosic biomass to ethanol (Balat et al., 2008). All of them have one common feature, namely the production of diluted bioethanol – in the range of 5-12 %wt bioethanol – that needs to be further concentrated up to 99-99.8 %wt (Figure 1), to match the requirements of current international standards (Kiss and Ignat, 2013).

Due to the presence of the binary azeotrope ethanol-water (95.63 %wt ethanol), several steps are required in order to reach the purity target. Typically, the first step involves the bioethanol pre-concentration from 5-12 % up to 92.4-94 %wt (Vane, 2008), while the second step is the dehydration to higher concentrations – above the composition of the binary azeotrope – by using a mass separating agent (MSA) or solvent (Huang et al., 2008). These steps are typically carried out in a classic sequence of distillation columns – a pre-concentration distillation column (PDC), an azeotropic or extractive distillation column (EDC) and solvent recovery column (SRC) – with energy penalties and large investment costs (Kiss and Ignat, 2013).

A solution to overcome the high energy demands of conventional distillation is using advanced process intensification and integration techniques, such as thermally coupled distillation columns or dividing-wall columns. DWC is a very good example of proven process intensification technology in distillation, with over 120 implementations in the chemical industry (Kiss, 2013). Actually, DWC allows significantly lower investment and operating costs while also reducing the equipment and carbon footprint (Yildirim et al., 2011). Remarkable, the DWC technology is not limited to ternary separations alone, but it can be used also in azeotropic separations (Sun et al., 2011), extractive distillation (Ignat and Kiss, 2012), and even reactive distillation – e.g. for the production of ETBE (Bumbac et al., 2009) or FAME (Kiss et al., 2012)

This work provides a brief overview about the use of DWC for azeotropic (Kiss and Suszwalak, 2012) and extractive distillation (Kiss and Ignat, 2012, 2013) in the bioethanol dehydration process. Rigorous simulations were carried out in Aspen Plus (Aspen Technology, 2011), and all process alternatives were optimized using the sequential quadratic programming (SQP) method (Boggs and Tolle, 1995), in terms of minimum energy requirements and lowest total annual cost, while taking into account the purity constraints. The results show that significant energy savings of 10-20% are possible for the novel process intensification alternatives based on DWC, while using less equipment units as compared to the conventional azeotropic and extractive distillation configurations, and having a reduced plant footprint.

Please cite this article as: Kiss A.A., Suszwalak D.J.P.C., Ignat R.M., 2013, Breaking azeotropes by azeotropic and extractive distillation in a dividing-wall column, Chemical Engineering Transactions, 35, 1279-1284 DOI:10.3303/CET1335213

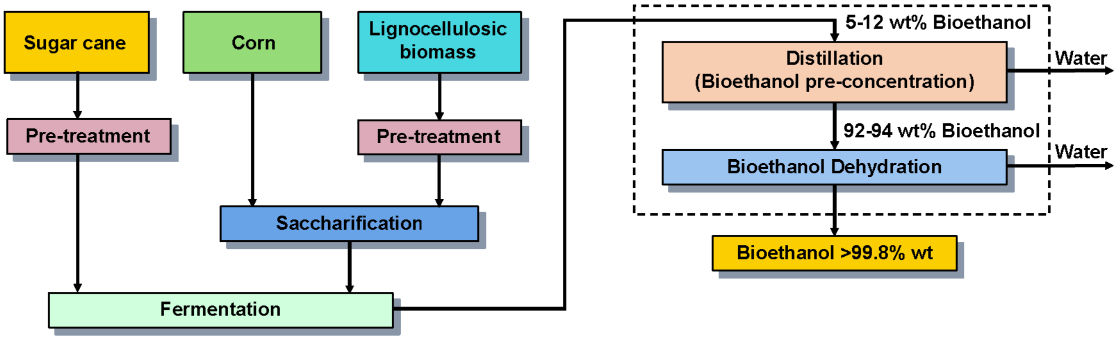

Figure 1: Block flow diagram of bioethanol production from various feedstock

2. Problem statement

For the use as fuel or additive, bioethanol must have a purity of min. 99-99.8 %wt, according to the current international standards (EN 15376, ASTM D 4806). Due to the presence of the binary azeotrope ethanol-water (95.63 %wt ethanol), several steps are required in order to reach the purity target, which implies very high energy penalties and large investment costs. Considering the high demand of bioethanol, novel improved alternatives are needed to reduce the overall costs. To solve this problem, we proposed novel azeotropic and extractive DWC configurations that can break efficiently the ethanol-water azeotrope.

3. Results and discussion

Aspen Plus simulations were performed using the rigorous RADFRAC unit. NRTL and UNIQUAC property methods can be used due to the presence of a non-ideal mixture containing polar components (Kiss and Suszwalak, 2012). The feed stream considered here is the diluted ethanol stream (10 %wt or 4.2 %mol) obtained by fermentation, while the pre-concentrated ethanol stream has a concentration of 93.5 %wt. The production rate is 100 kt/y bioethanol. All process alternatives described hereafter were optimized in terms of minimal energy demand using the SQP method available in Aspen Plus (Bartholomew-Biggs, 2008).

3.1 Azeotropic distillation

Azeotropic distillation (AD) is carried out by adding other chemicals to generate a new, lower-boiling azeotrope that is heterogeneous – thus producing two immiscible liquid phases (typically an organic phase and an aqueous phase) that are conveniently separated in an additional decanter (Kansha et al., 2009).

One of the best entrainers for ethanol dehydration by azeotropic distillation is n-pentane, as it forms a low-boiling ternary azeotrope with ethanol and water. The mixture ethanol-water-pentane presents three binary azeotropes, one ternary heterogeneous azeotrope, and a significant liquid phase split envelope. A head-to-head comparison of the conventional system and the A-DWC system is clearly possible by using the same feed conditions (pre-concentrated ethanol) and the same purity targets and recovery constraints.

Figure 2 shows a schematic representation of the conventional AD and the newly proposed A-DWC configuration. The A-DWC setup consists of a single shell, two reboilers and only one condenser. The azeotropic top stream is fed to a decanter from which the organic phase is recycled back to the feed side (stage 15), while the aqueous phase is returned to the other side of the column (35 stages in total).

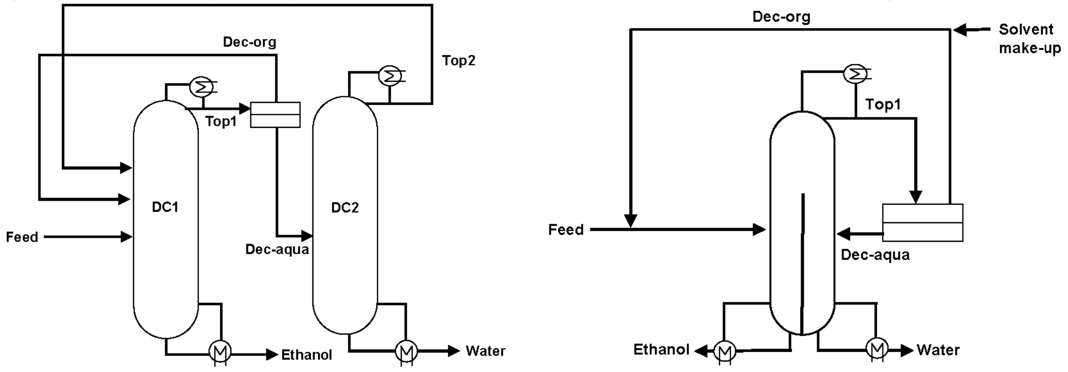

Figure 2. Two-columns azeotropic distillation sequence (left) and A-DWC alternative (right)

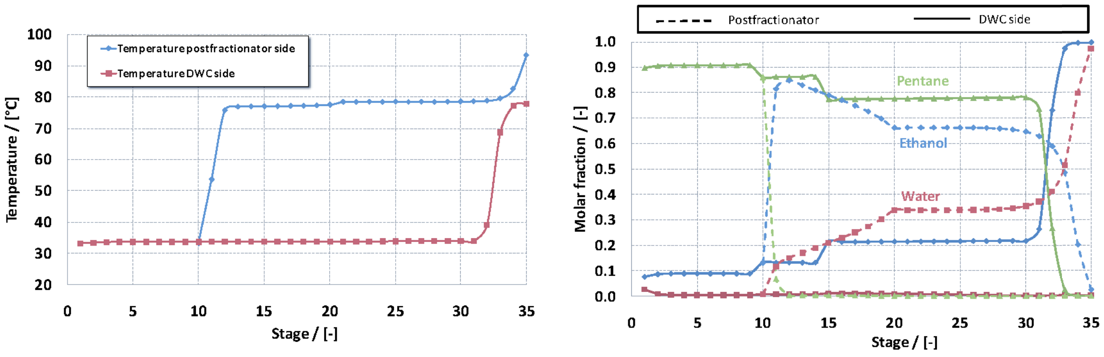

Figure 3: Temperature and composition profiles in the A-DWC (dashed line used for the pre-fractionator side, while continuous line is used for the main DWC side)

Figure 3 shows the temperature and composition profiles along the A-DWC – note the partition wall from stage 10 to 35. Table 1 gives a comparison of the energy requirements for the conventional two-column sequence versus the proposed A-DWC – saturated vapor feed was considered in both cases. The specific energy requirements are 1.78 kW.h/kg for the classic AD and only 1.42 kW.h/kg bioethanol for the A-DWC alternative, respectively. Thus, over 20% energy savings are possible using the A-DWC configuration.

Table 1: Comparison of condenser and reboiler duty for azeotropic distillation

	Direct sequence AD			A-DWC		
	DC1	DC2	Total	DWC	PostFrac	Total
Condenser duty (kW)	-7,165.75	-955.88	-8,121.63	-12,500.0	0.00	-12,500.0
Reboiler duty (kW)	5,948.76	994.02	6,942.78	4,062.9	1,475.20	5,538.1

3.2 Extractive distillation

Extractive distillation (ED) performs the separation in the presence of a miscible, high boiling, relatively non-volatile component that forms no azeotrope with the other components in the mixture. Ethylene glycol (EG) remains the most common entrainer used in the extractive distillation of ethanol-water. Note that the ternary mixture ethanol-water-glycol presents a single binary azeotrope and no liquid phase splitting.

Figure 4 shows the conventional setup and the conceptual design of the proposed E-DWC. In the E-DWC unit the solvent is separated as single bottom product, while two distillate products are collected on each side of the wall – ethanol and water, respectively. Figure 5 plots the temperature and liquid composition profiles in the E-DWC. The prefractionator consists of 16 stages with the bioethanol feed located on stage 13 while the extractive agent ethylene glycol is added on stage 3. The dividing-wall goes down from the top to stage 14, of the 20 stages column. High purity and recovery is obtained for all three products of the extractive DWC: ethanol and water as top distillates, and EG solvent as recovered bottom product.

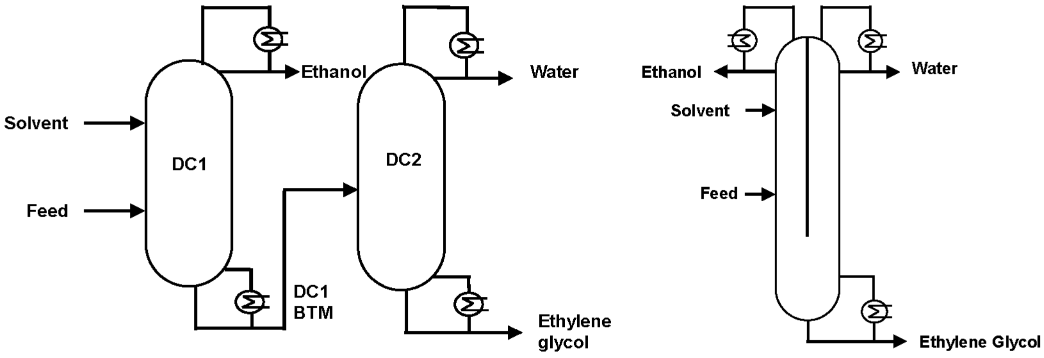

Figure 4: Two-columns extractive distillation sequence (left) and E-DWC alternative (right)

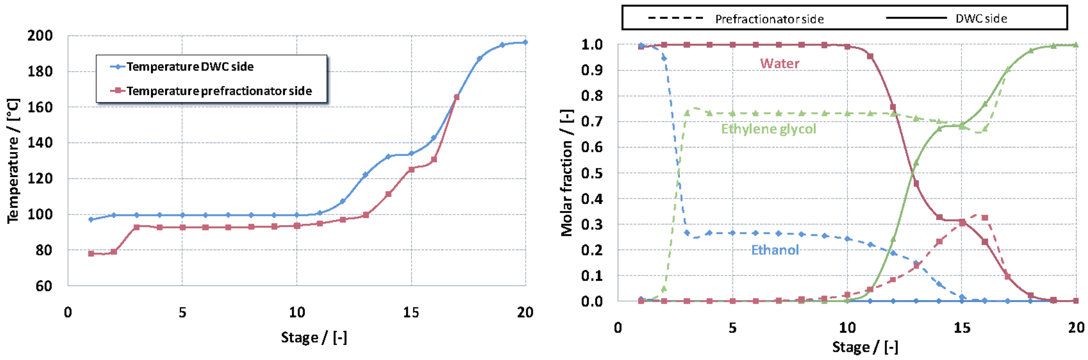

Figure 5: Temperature and composition profiles in the E-DWC (dashed line used for the pre-fractionator side, while continuous line is used for the main DWC side)

Table 2 presents a comparison of the reboiler and condenser duties for the conventional two-column sequence versus the proposed E-DWC. The specific energy requirements are 0.51 kWh/kg for ED and only 0.46 kWh/kg bioethanol for E-DWC, respectively. Hence energy savings of around 10% are possible with the E-DWC, as compared to the optimized conventional ED. Note that the E-DWC approach is very competitive but more convenient than the molecular sieve – Pressure Swing Adsorption (PSA) – approach, a widely used method for bioethanol dehydration a smaller scales, requiring 0.42-0.45 kWh/kg bioethanol.

Table 2. Comparison of condenser and reboiler duty for extractive distillation

	Direct sequence ED			E-DWC		
	DC1	DC2	Total	PreFrac	DWC	Total
Condenser duty (kW)	-1,200.62	-367.29	-1,567.90	-1,175.01	-205.09	-1,380.10
Reboiler duty (kW)	1,402.43	605.39	2,007.82	0.00	1,819.52	1,819.52

3.3 All-in-one extractive DWC

The previous two configurations (A-DWC and E-DWC) considered only the dehydration step, leaving out the pre-concentration step (Figure 6, left), which is in fact the most energy intensive. This section illustrates an innovative distillation setup (Figure 6, right) – based on a novel extractive DWC – that is able to concentrate and dehydrate bioethanol in a single step, by integrating all units of the conventional sequence into only one column (Kiss and Ignat, 2012). In this column, the feed side (prefractionator) acts as the PDC unit of the conventional sequence. Water is removed as liquid side stream, but an additional side reboiler is needed to return the required amount of water vapors to the column. The liquid feed stream is fed on top of the prefractionator side, thus serving as a reflux to the PDC section.

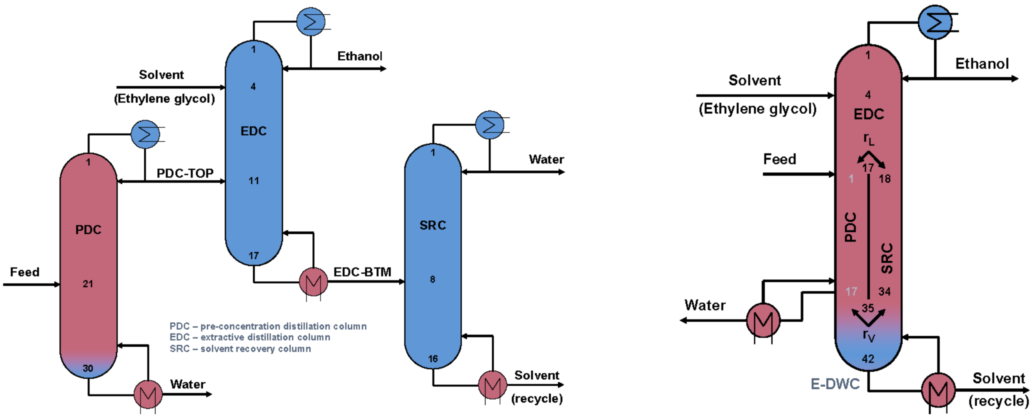

Figure 6: Conventional sequence (left) and the all-in-one E-DWC alternative (right) for the bioethanol pre-concentration and dehydration by extractive distillation

Table 3. Design and process parameters of an optimal all-in-one E-DWC

Design parameters	**Value**	**Unit**
Total number of stages	42	–
Number of stages pre-fractionator side	17	–
Feed stage on pre-fractionator side	1	–
Feed stage of extractive solvent (main column side)	4	–
Side stream withdrawal stage	17	–
Wall position (from - to stage)	18-34	–
Column diameter	3.35	m
Operating pressure	1	bar
Feed stream flowrate (mass)	125,000	kg/h
Solvent flow rate (mass)	20,793	kg/h
Feed composition (mass fraction)		
Ethanol : water	0.1 : 0.9	kg/kg
Feed stream temperature	30	°C
Reflux ratio	3.4	kg / kg
Liquid split ratio (r_L)	0 : 1	kg / kg
Vapor split ratio (r_V)	0.4 : 0.6	kg / kg
Total reboiler duty (side reboiler and bottom reboiler)	25,775	kW
Condenser duty	-12,964	kW
Ethanol recovery	99.81	%
Water recovery	99.99	%
Purity of bioethanol product	99.81/ 99.60	%wt / %mol
Purity of water by-product	99.80/ 99.90	%wt / %mol
Purity of ethylene glycol recycle	99.99/ 99.99	%wt / %mol

The vapor leaving the feed side of the E-DWC has a near azeotropic composition. Solvent is added at the top of the E-DWC, this section acting as the EDC unit of the conventional sequence. Ethanol is separated here as high purity top distillate, and removed as the main product. The liquid flowing down the top section (EDC) is collected and distributed only to the (SRC) side opposite to the feed side (prefractionator) and further down the bottom of the E-DWC. This complete redistribution of the liquid flow is required in order to avoid the presence and loss of solvent on the feed side (PDC section). In the SRC section, the solvent is separated as bottom product and then recycled in the process (Kiss and Ignat, 2012).

It is worth noting that the vapor coming from the bottom of the E-DWC to the bottom of the dividing-wall consists mainly of water. However, this amount is not sufficient for the PDC section, thus the requirement for an additional side reboiler. The key parameters of the optimal design are presented in Table 3. In contrast to a standard DWC configuration, the side stream is collected here from the same (feed) side of the column, not the opposite. Figure 3 plots the temperature as well as the liquid composition profiles in the E-DWC. Remarkable, the temperature difference between the two sides of the wall is very low (less than 20 °C) – such conditions being feasible for practical implementation (Dejanović et al., 2010). It is also worth noting that the diameter of the E-DWC unit is only slightly lower than the diameter of the PDC unit of the conventional sequence, although it does require some additional stages. In practice, this means that the revamping of existing plants is possible by re-using an existing PDC unit (i.e. add more stages by extending the height of the column or by using a more efficient structured packing).

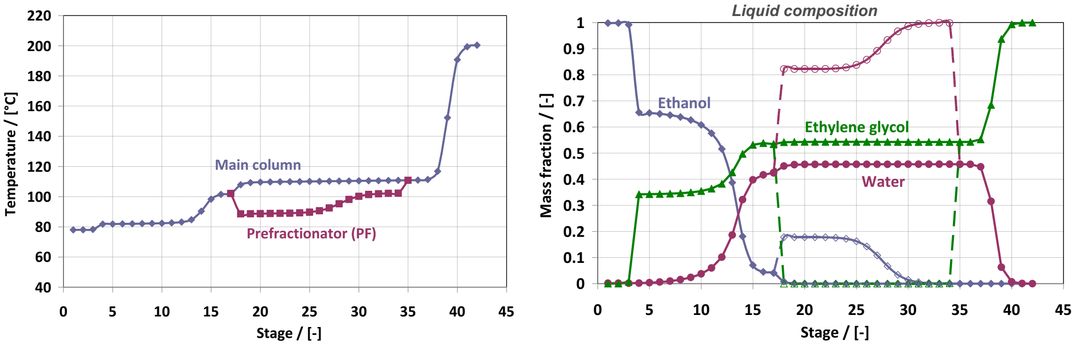

Figure 3: Temperature and composition profiles in the E-DWC (dotted line means the prefractionator side or the feed section of the column)

Table 3: Head-to-head comparison of the conventional sequence of 3 columns vs E-DWC alternative

Key performance indicators	Conventional	E-DWC alternative	Savings
Total investment cost (TIC)	k$ 4,410	k$ 3,626	17.8 %
Total operating costs (TOC)	k$ 6,446	k$ 5,355	16.9 %
Total annual costs (TAC)	k$ 6,887	k$ 5,718	17.0 %
Energy requirements (kW·h/t bioethanol)	2,470	2,070	16.5 %
CO_2 emissions (kg CO_2/t bioethanol)	345.77	288.31	16.6 %

Table 3 provides a head-to-head comparison of the key performance economic indicators. Remarkable, the all-in-one E-DWC alternative is the most efficient in terms of energy requirements allowing energy savings of 17 % while also being the least expensive in terms of capital investment and operating costs.

4. Conclusions

The novel DWC configurations for azeotropic and extractive distillation are not only technically feasible but also very attractive economically, leading to reduced footprint plants, significant overall energy savings of 10-20 % and a similar reduction of the total investment and operating costs.

Acknowledgments

The support given by AkzoNobel to David Suszwalak (ENSCMu, France) during his MSc internship and to Radu Ignat (Politehnica University of Bucharest, Romania) during his PhD internship, as well as the financial support received from the Sector Operational Program Human Resources Development 2007-2013 of the Romanian Ministry of Labor, Family and Social Protection through the Financial Agreement POSDRU/88/1.5/S/61178 are gratefully acknowledged.

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