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ORIGINAL PAPER

Some operational aspects and applications of dividing wall columns: energy requirements and carbon dioxide emissions

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Abstract High prices of oil and biofuels as well as tight environmental regulations on gas emissions have promoted theoretical and industrial developments in distillation; in particular, in complex distillation columns. The dividing wall distillation column (DWDC) has been adopted in industrial practice in order to achieve savings in both energy and cooling water requirements, reductions in green house gases emissions, and production and purification of biofuels. Simulation studies and practical implementations in the area of process control have shown that the control properties of DWDC are similar to those of conventional distillation columns. This work provides a discussion about the operational issues and a review of the practical applications of DWDC's.

Keywords Dividing wall column · Energy savings · CO_2 emissions · Biofuels

Introduction

Distillation is the most extensively used separation technique in chemical industry. It is a common practice to compare the performance of any new separation method with that of distillation. Further, distillation is a mature technology with well-known design methods, control strategies, and practical operation policies; however, its main disadvantages are a large demand of energy and a very low thermodynamic efficiency (Flores et al. 2003). Only a small part of the energy supplied at the point with the highest temperature in the column (reboiler) is used for the separation in each equilibrium stage; the remaining energy is extracted by the cooling water at the top stage with the lowest temperature of the column (condenser), causing a thermodynamic efficiency lower than 20 % (Flores et al. 2003; Dejanović et al. 2010).

Energy requirements in the reboiler are obtained usually through the combustion of fossil oil. Therefore, reduction in the energy requirements has many positive implications; for instance, reductions in the use of cooling water and gas emissions. This connection between energy and distillation has favored an extensive research in industry and academia in order to obtain new designs that can achieve lower energy requirements and higher thermodynamic efficiencies (Asprion and Kaibel 2010; Kaibel 1987). In this context, in the area of complex distillation columns, the thermally coupled distillation sequences can present energy savings of around 30 % in comparison to the conventional distillation sequences for the separation of some mixtures (Nguyen and Moonyong 2011; Wang et al. 2011). For instance, the separation of a ternary mixture (A,B,C) can be done using the conventional distillation sequences shown in Fig. 1. These conventional distillation systems are used extensively in industry, and heuristics recommend the use of the conventional direct sequence when the lightest component (A) is the most abundant component in the ternary mixture, and the use of the indirect distillation sequence for a high content of the heaviest component (C). In contrast, when the intermediate component (B) is the

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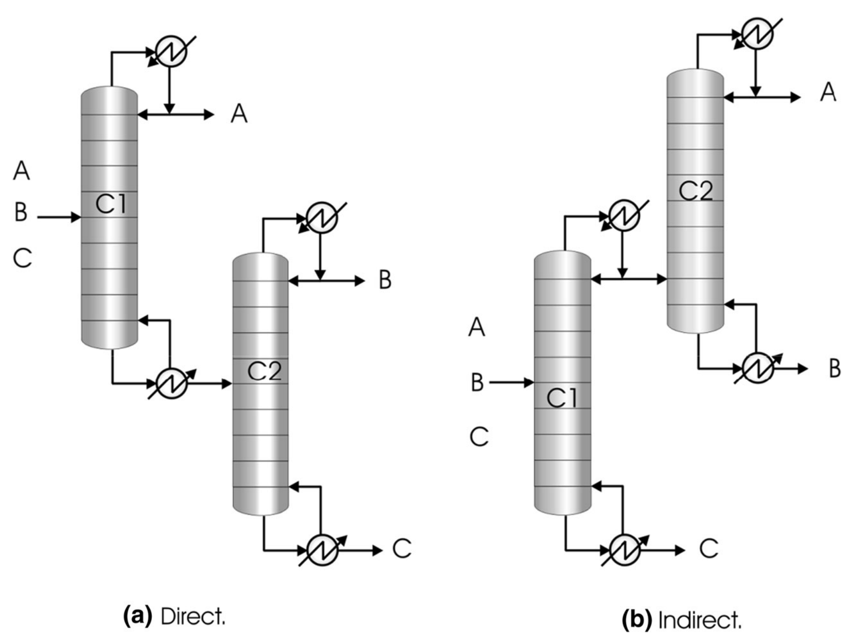


Fig. 1 Conventional distillation sequences

lowest or the highest in the ternary mixture, the use of the thermally coupled distillation schemes indicated in Fig. 2 results in energy savings of around 30 % (Flores et al. 2003).

The study of thermally coupled distillation sequences (TCDS) started with the patent of Wright (1949) of a distillation column with a wall inside which separates the feed and a sidestream. After this work, Petlyuk et al. (1965) presented a complete thermodynamic analysis of the Petlyuk distillation column, explaining the efficiency in the use of energy in terms of the internal composition profiles. Those works were academic studies with no applications in the chemical industry.

During the 1970s, the research on energy-efficient distillation schemes was accelerated by the first crisis in the oil prices as it became critical to save energy in the chemical processes. Then, Tedder and Rudd (1978) presented a complete study about the energy requirements in conventional and complex distillation sequences, reporting energy savings using TCDS options.

The next decade was characterized for several studies about the design of thermally coupled distillation sequences using shortcut methods (Glinos and Malone 1988) but, certainly, the most important contribution was the implementation of a Petlyuk distillation column in BASF (Kaibel 1987) using a single shell divided by a wall. This distillation column was designated as a dividing wall distillation column (DWDC, Fig. 3). The DWDC opened a new research field in distillation, since this configuration allows savings in both energy and capital costs.

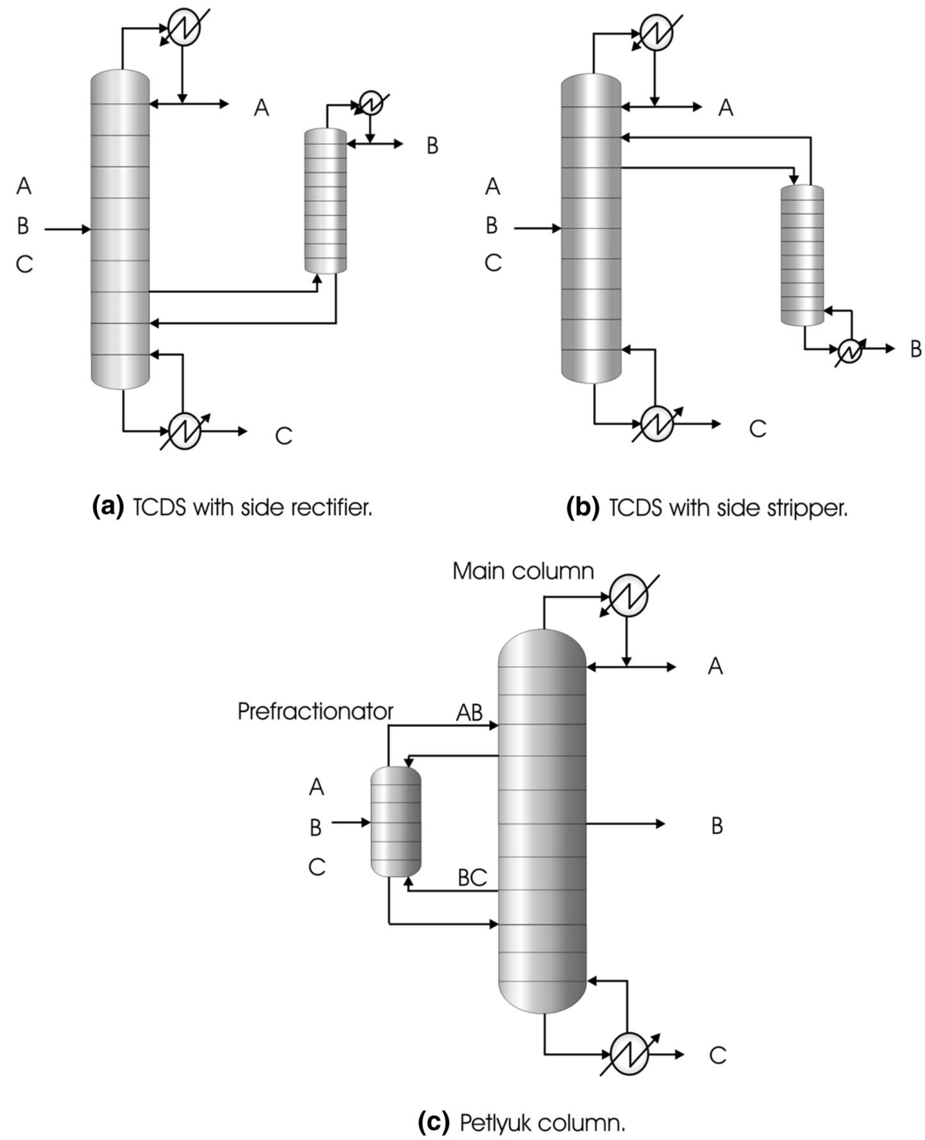
Triantafyllou and Smith (1992) showed that energy savings are obtained in the DWDC because the sidestream is withdrawn from the maximum in the composition profile of the intermediate component. During the 1990s, the research on DWDC's was focused on shortcut and rigorous design methods since it had been demonstrated that energy savings were achieved in industrial practice. Also, the theoretical control properties and the closed-loop dynamic behavior under feedback control were studied for the DWDC because it was thought that control problems might appear due to the presence of recycle streams. Results indicated, however, that energy savings were obtained without additional control problems. In fact, in some cases, the dynamic behavior of the DWDC was better than that of conventional distillation columns.

During the end of 20th century and beginning of the 21st, oil prices reached 100 USD per barrel, and more attention was given to environmental regulations on carbon dioxide emissions. As a result, applications of the DWDC in the field of biofuels were developed. Two of the most important developments are the purification of bioethanol and the production of biodiesel using reactive distillation.

In the case of the production of bioethanol, a DWDC can be used as the final stage of the purification process in order to obtain bioethanol with no more than 0.5 % wt of water, so that the bioethanol can be mixed with gasoline. This application requires the use of an extractive solvent (for instance, ethylene glycol, glycerol, or ionic liquids), but the solvent can also be recovered in the same DWDC (Sun et al. 2011; Kiss and Suszwalak 2012).

Similarly, the production of biodiesel can be carried out using reactive distillation with various benefits, such

Fig. 2 Thermally coupled distillation sequences



as (*i*) in situ heat integration, (*ii*) higher conversions (since products are removed as they are formed), and (*iii*) the recovery of the excess of reactants. In this area, the DWDC can be used to carry out esterification reactions between fatty organic acids and methanol to produce a mixture of esters that can be used as biodiesel; moreover, the excess of methanol is recovered in the same complex distillation column (Kiss 2011; Nguyen and Demirel 2011). This application requires the use of either homogeneous or heterogeneous acids catalysts (Puna et al. 2010).

Further applications have been implemented in DWDCs. For instance, the separation of methanol and glycerol from the biodiesel production has been achieved successfully using this complex distillation column (Kiss and Ignat 2012). Also, some industrial applications have been reduced to a single DWDC, like the dimethyl ether separation (Kiss and Ignat 2013).

Other important aspects related to the operation of complex distillation columns have been reported; for instance, Szabo et al. (2011) have reported how a dividing wall distillation column can be obtained with minimum energy requirements in the reboiler since the production of cold and hot energy causes important environmental loads, i.e., carbon dioxide emissions, dust pollution, and others. In similar context, Tarighaleslami et al. (2012) have used the exergy profiles of distillation columns to identify the option with the maximum energy savings among several retrofit options. Other applications like solar distillation have been improved using exergy analysis in the desalination process, conducting to reductions in carbon dioxide emissions (Ranjan and Kaushik 2014).

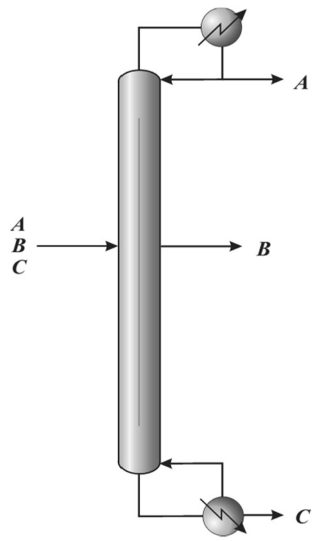


Fig. 3 Dividing wall distillation column

The following sections provide a more complete discussion about some of the most significant applications of a DWDC.

Purification of bioethanol

It is important to mention that the Petlyuk distillation column shown in Fig. 2c is thermodynamically equivalent to the dividing wall distillation column (Fig. 3), when no heat transfer occurs through the wall (Hernandez et al. 2006). The simulation studies were conducted using the process simulator AspenONE Aspen Plus, where a module of the DWDC is not contained; as a consequence, the DWDC was modeled using a Petlyuk distillation column that can be represented by a combination of conventional distillation columns included in the simulator (Hernandez et al. 2006). Each stage can be modeled using MESH equations (mass balances, equilibrium, summation constraints, energy balance) and solved through numerical methods such as the bubble point or the Newton–Raphson with appropriate convergence criteria for each equation (Seader and Henley 2005). Simulation of complex distillation columns has been completed successfully using the radfrac module of AspenONE Aspen Plus (Suphanit et al. 2007; Suphanit 2011).

DWDCs have already been implemented successfully in BASF, Dow chemical, and other industries. Of particular interest in this context is the use of a DWDC to obtain high-purity bioethanol. First, a dilute solution of bioethanol–water (less than 0.1 mol fraction of bioethanol) is introduced into a conventional distillation column in order to remove most of the water as bottoms product; the top product is a mixture of bioethanol–water with a content of bioethanol of approximately 0.85 mol fraction. Such a value of the distillate composition of bioethanol is limited by the homogeneous azeotrope of ethanol–water with a composition of 0.88 mol fraction of ethanol. It can be shown that, as the distillate composition increases, the energy demand also increases; so that, for compositions close to the azeotropic point, the energy requirements in the reboiler and the stages increase dramatically. An extractive DWDC can be used to overcome the azeotropic point. The enriched feed of bioethanol–water is introduced typically next to the reboiler; the ethylene glycol

Fig. 4 Implementation of the Petlyuk distillation column in AspenONE aspen plus for the purification of bioethanol

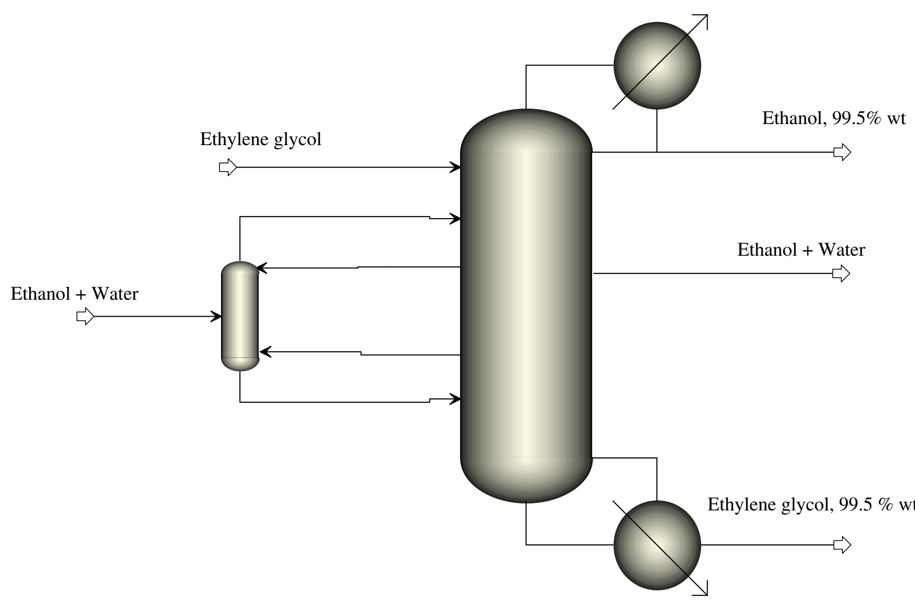
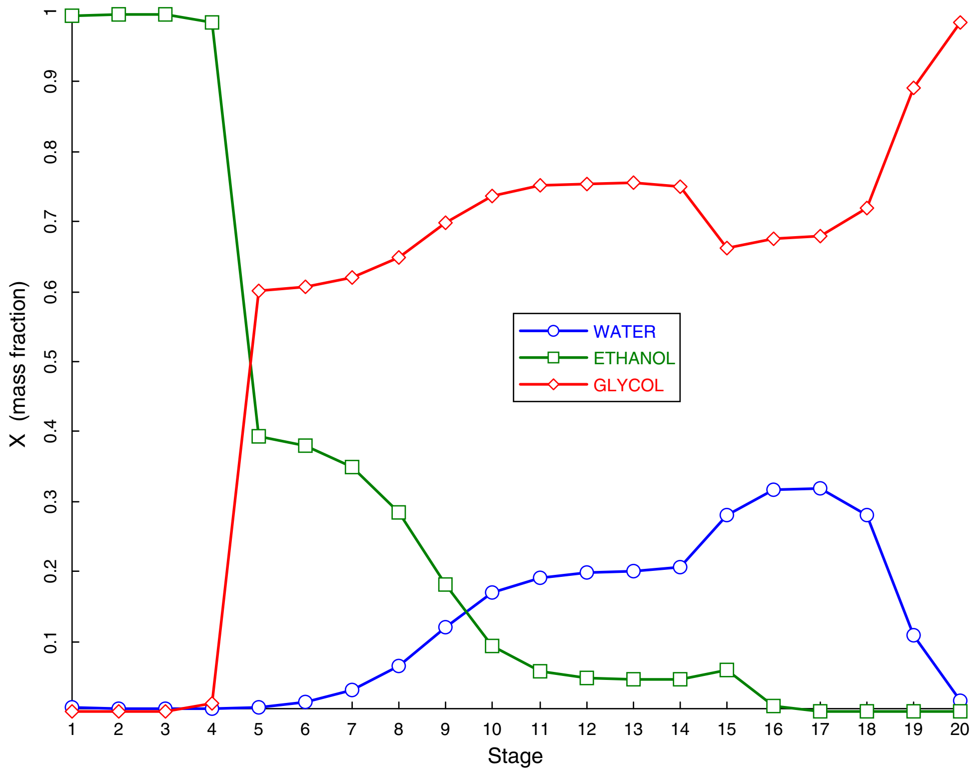


Fig. 5 Composition profiles of the Petlyuk distillation column for the purification of bioethanol



(entrainer) is fed close to the top of the column (Fig. 4). Figure 5 shows the composition profiles for such a process. It can be seen that bioethanol with a high composition of 99.5 % wt (design specification) is obtained as distillate, and the ethylene glycol is recovered in the bottoms product to be recycled. This specific case uses ethylene glycol, but other entrainers like glycerol, tetraethylene glycol, or ionic liquids can be used (Pacheco-Basulto et al. 2012; Navarrete-Contreras et al. 2014). At this point, our experimental research studies indicate that it is possible to propose a complete process to obtain high-purity bioethanol, using a conventional distillation column and an extractive dividing wall distillation column using glycerol as entrainer, resulting in a process with minimum energy consumption and less carbon dioxide emissions in comparison with conventional distillation columns.

Some studies have demonstrated the use of wet ethanol (lower than 80 % ethanol volume fraction) in Homogeneous Charge Compression Ignition [HCCI] engines (Mack et al. 2009) that can be used for transportation and stationary applications. HCCI combustion is a thermal autoignition of a premixed fuel–air mixture, with no flame propagation (as occurs in spark ignition engines) or mixing-controlled combustion (as in diesel engines). It is important to mention that this ethanol composition can be achieved easily in a dividing wall column to obtain wet ethanol as product.

Biodiesel production

Biodiesel is a mixture of fatty organic methyl esters that can be produced through esterification reactions between fatty organic acids and methanol using acid catalysts. Fatty organic acids can be obtained from vegetal oils (Cossío-Vargas et al. 2011), for instance, *Jatropha Curcas*. The *Jatropha Curcas* oil can be modeled as a mixture of oleic, linoleic, and palmitic acids (Cossío-Vargas et al. 2012). The reaction between acids and methanol usually is carried out using 20 % of excess of methanol in order to ensure a complete reaction of the fatty organic acids (Kiss et al. 2012). The use a DWDC in the production of biodiesel is depicted in Fig. 6 where methanol and acids are introduced in one side of the wall. The reaction occurs in all stages of the distillation column. As shown in Fig. 7, a mixture of fatty acid methyl esters is obtained as bottoms product with a combined mass fraction higher than 99 % wt suitable for use as biodiesel. A significant advantage of the use of a DWDC for biodiesel production is that the excess of methanol is recovered as distillate and can be reused. Our simulation results prove that it is possible to intensify the production and separate biodiesel using reactive dividing wall distillation columns with minimum energy requirements in the reboiler.

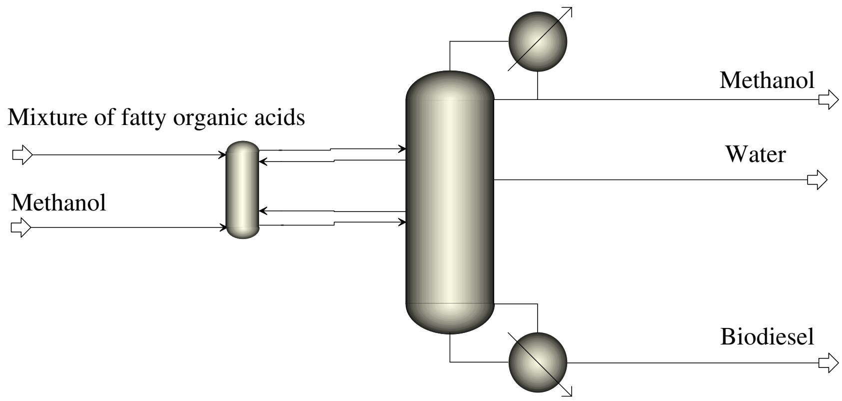


Fig. 6 Implementation of the Petlyuk distillation column in AspenONE aspen plus for the biodiesel production

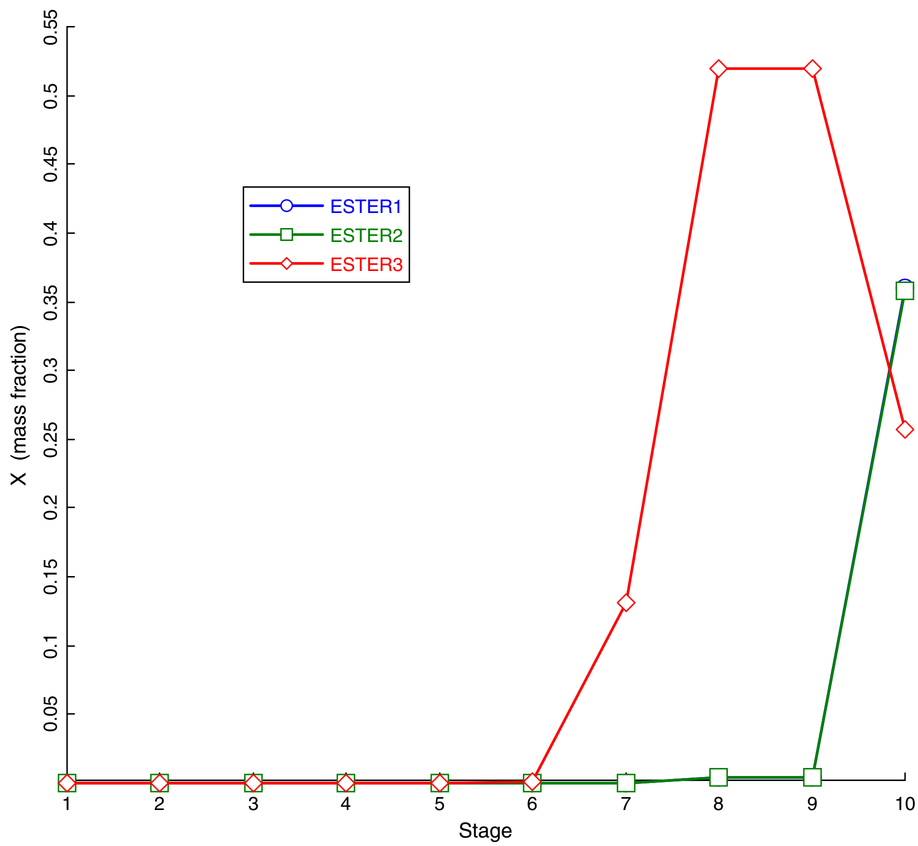


Fig. 7 Composition profiles of the fatty acid methyl esters in the production of biodiesel using the Petlyuk distillation column

Operational aspects of the ethyl acetate production

As reported by Delgado-Delgado et al. (2012), an experimental DWDC was used to carry out the production of ethyl acetate through an esterification reaction between acetic acid and ethanol using sulfuric acid as catalyst. The optimization of the DWDC indicates that the energy required in the reboiler depends strongly on the values assigned to the interconnecting liquid (FL) and vapor (FV) flows. FL is a liquid stream taken from the main distillation column and fed to the top of the prefractionator (Fig. 2c), and FV is vapor stream that leaves the main distillation column and is introduced into the bottoms section of the prefractionator (Fig. 2c). An experimental search for the best values of the interconnecting flows of a DWDC producing ethyl-acetate indicates that, for a given set of values to the interconnecting streams, two different heat duties in the reboiler can be feasible. This implies that two steady states can be present with two different values for the energy requirements in the reboilers (Fig. 8). Therefore, it is critical to set the operation parameters of the DWDC so that the minimum energy requirement in the reboiler is achieved. In order to achieve the steady state with minimum energy requirement in the implemented DWDC, it is possible the manipulation of the interconnecting liquid flows to both sides of the dividing wall, the reflux ratio, and

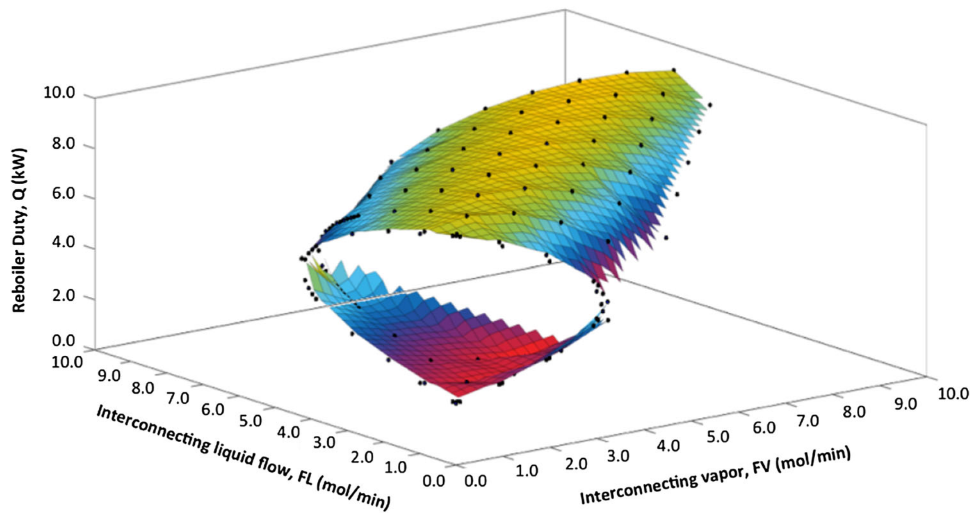


Fig. 8 Search for the minimum energy demand in the reboiler of the DWDC

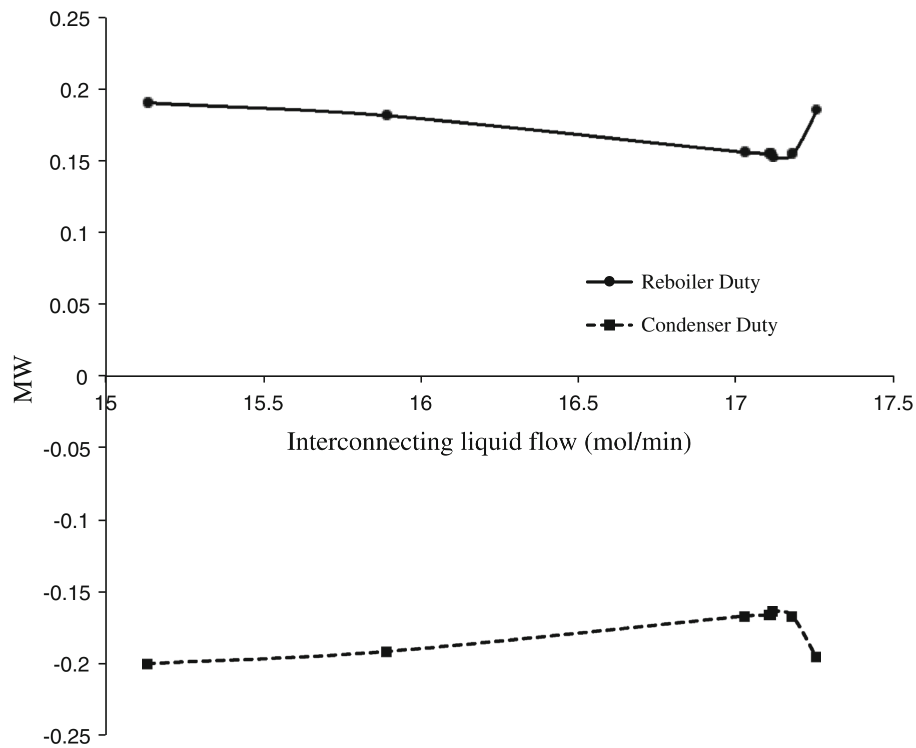


Fig. 9 Energy required in the reboiler and extracted from the condenser in the purification of bioethanol using the Petlyuk distillation column

the heat duty supplied to the reboiler (Delgado-Delgado et al. 2012).

Additional issues related to the operation of a DWDC

The use of the DWDC in the purification of bioethanol or in the production of biodiesel incorporates some additional benefits; for instance, the reductions in the energy requirements in the reboiler are directly linked to reductions in the energy removed in the condenser and, as a consequence, the use of cooling water is also reduced. Considering the purification of bioethanol as an illustrative example, Fig. 9 shows how the energy demand changes with the interconnecting liquid flow (FL) for a fixed value of the vapor stream (FV). It can be seen that the minimum energy required in the reboiler is achieved with an interconnecting liquid flow of around 17.025 mol/min. Also, the minimum energy removed from the condenser is obtained for the same value of the interconnecting liquid stream. As a result, the reduction in the energy demand can be translated to reductions in the

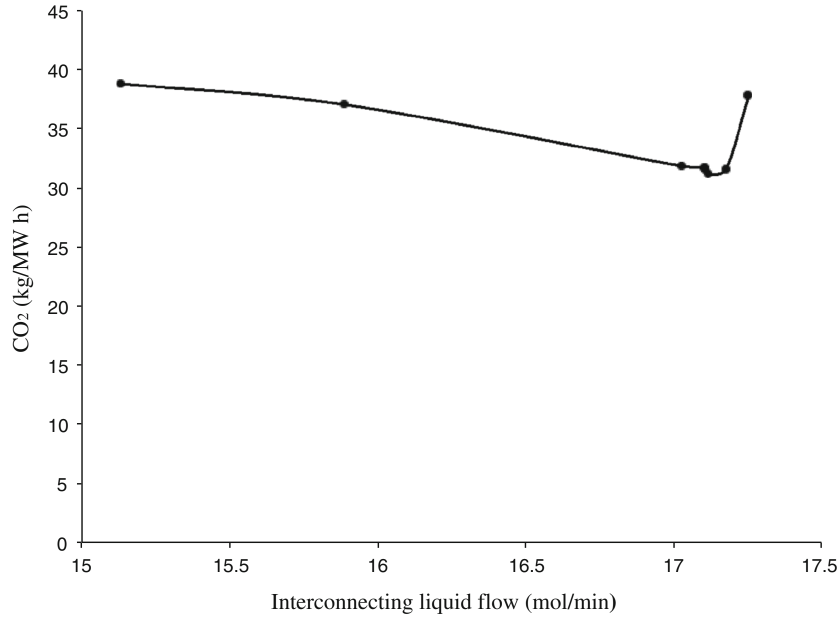


Fig. 10 CO_2 emissions in the purification of bioethanol using the Petlyuk distillation column

energy removed from the condenser, i.e., less cooling water is needed in the condenser. Finally, according to Fig. 10, the carbon dioxide emissions follow the same behavior; increments in the energy required in the reboiler are translated into more emissions of carbon dioxide. In fact, these emissions of carbon dioxide can be calculated by multiplying the heat supplied to the reboiler by a factor (for CO_2 the factor is 204 according to Emtir and Etoumi (2009)).

Conclusions

Recent applications of complex distillation sequences, like dividing wall distillation columns, have been implemented due to increments in the price of the fossil oil and to the need for the use and production of biofuels. Of particular interest are the new applications of DWDC for the purification of bioethanol and the production of biodiesel, achieving important energy savings and reductions in both the use of cooling water and the carbon dioxide emissions.

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