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ORIGINAL PAPER

Multiplicities in dividing wall distillation columns in the purification of bioethanol: energy considerations

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Abstract In this paper, we present results about the energy requirements in the reboilers of an extractive dividing wall distillation column and a thermally coupled distillation sequence with a side rectifier for bioethanol dehydration using glycerol as entrainer, and the study generates the appearance of multiple steady states. During the energy optimization of the dividing wall distillation column, using glycerol as entrainer, the recycle streams were varied until the energy consumption in the reboiler was obtained and the multiple steady states can present a difference of up to 400%. This finding is important since we are interested in detecting the optimal energy consumption in order to reduce the environmental impact caused by the usage and production of energy from petroleum. This information is being used in a current pilot plant in order to detect the optimal operation conditions to dehydrate bioethanol.

Keywords Dividing wall column · Petlyuk column · Bioethanol · Multiple solutions

Introduction

Distillation is the most used separation technique in industrial practice despite its high energy demand and low thermodynamic efficiency (Agrawal and Fidkowski 1998; Flores et al. 2003). The high energy demand can be explained by the fact that although the total energy is supplied in the reboiler at the highest temperature, which is used in the trays to achieve separation, most of the energy is rejected to the cooling fluid in the condenser at the lowest temperature in the distillation column. Therefore, important studies have been conducted regarding energy savings in distillation columns and increasing the thermodynamic efficiency; for instance, the use of complex distillation columns such as thermally coupled distillation columns is a good choice. Among the thermally coupled distillation columns, the Petlyuk distillation column is considered the most important option because it can be implemented using a single shell divided by a wall (Kaibel 1987). The Petlyuk distillation column consists of a prefractionator (C-1 column) fully coupled to the main distillation column (C-2 column), as indicated in Fig. 1a. In this complex distillation sequence, a ternary mixture (ABC), component A being the lightest and component C the heaviest, is separated into three nearly pure components; component A is obtained as a distillate, component B as the side-stream product and component C as the bottoms (Triantafyllou and Smith 1992).

The key concept in the Petlyuk distillation column is the replacement of the reboiler and condenser of the prefractionator (C-1 column) by two recycle streams with the main distillation column (C-2 column), i.e., thermal couplings. It is important to mention that in industrial practice, the Petlyuk distillation column is implemented in a single shell divided by a wall in the middle section. This industrial implementation is called a dividing wall distillation column (DWDC, Fig. 1b) and is thermodynamically equivalent to the Petlyuk distillation column when no heat transfer occurs through the wall (Lestak et al. 1994).

In 1949, Wright (1949) patented the first DWDC, reporting important savings in energy consumption in contrast to the conventional distillation trains. However, the first industrial implementation was not achieved until 1987 by Kaibel

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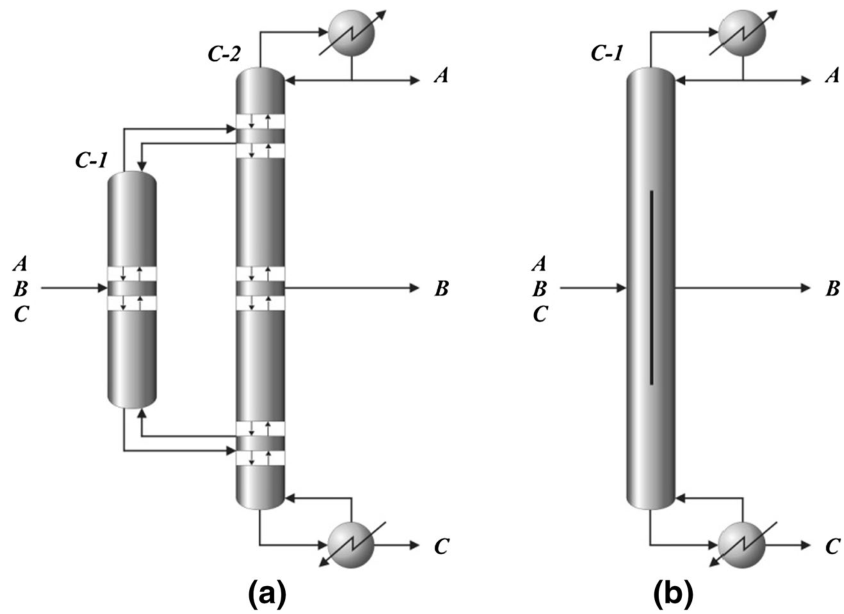


Fig. 1 Thermally coupled distillation columns: **a** Petlyuk column and **b** dividing wall distillation column

in BASF, reporting savings of around 30% in both energy and capital costs. After the implementation of the DWDC in BASF industries, several studies have been conducted on the application of this complex distillation column; for instance, Kiss (2011) and Kiss et al. (2012) have reported applications of DWDC for the production of biodiesel via reactive distillation and the purification of bioethanol.

In the context of dehydration of bioethanol, Kiss and Ignat (2012), Kiss (2013) and Vázquez-Ojeda et al. (2013) have investigated the optimization of the separation of bioethanol using an extractive dividing wall distillation, and they have found that the energy required can be reduced in the range between 20 and 60% by using the dividing wall distillation technology.

Most of these studies have been conducted using process simulators, reporting significant reductions in the energy required in the reboilers. In the same context, Cossío-Vargas et al. (2011), Delgado-Delgado et al. (2012) and López-Ramírez et al. (2016) have reported simulation and experimental studies about the esterification of oleic acid and methanol using an experimental DWDC.

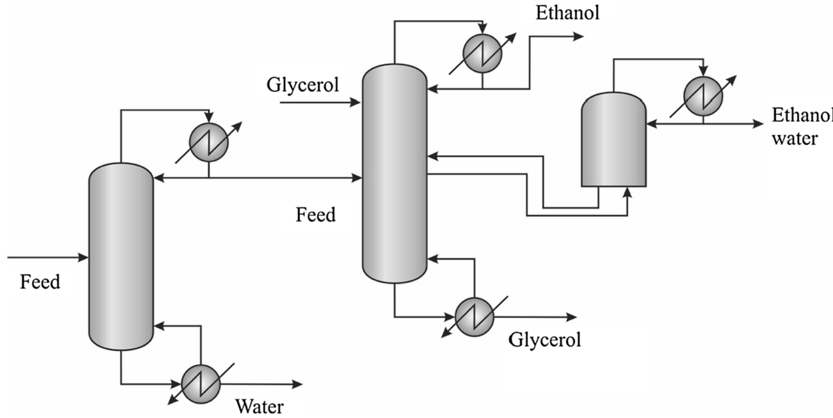
Another important application of the DWDC has occurred in the production of bioethanol because, despite the route used, the product of the fermentation process is a dilute solution of bioethanol (7–12 wt% bioethanol). From that stream process, the bioethanol must be purified up to 99.5 wt% in order to be mixed with gasoline in combustion engines, and usually, this purity is achieved using two distillation columns. In the context of purification, Singh and Rangaiah (2017) have reported that this stage has considered energy integration and complex distillation schemes in order to reduce the energy requirements, but other important techniques like hybrid options, including distillation and membranes, can be more efficient than distillation alone, and the cost of membranes can be reduced in the near future due to significant advances in this field.

As it can be read in the literature, research and development need to be carried out in both design and control of complex distillation options to dehydrate bioethanol. For instance, Tututi-Avila et al. (2017) reported how to design energy-efficient side-stream extractive distillation process and, in the case of bioethanol dehydration, the thermally coupled distillation sequence with a side rectifier was transformed into a distillation sequence with a side stream reducing the energy demand of the process.

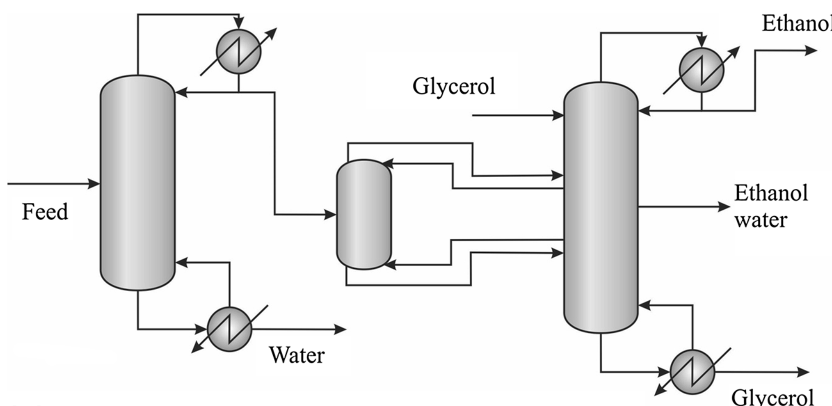
Regarding the control of extractive distillation processes for bioethanol dehydration, Arslan and Kaymak (2017) have studied several distillation configurations and have found that the two-column distillation option can adjust the bioethanol composition close to the design specification in the presence of disturbances. Also, Zheng et al. (2017) have reported that integrated extractive distillation process can be controllable by using control loops of temperature. Finally, Patrascu et al. (2017) have reported that a heat-pump-assisted extractive dividing distillation option can be controllable and operable. This point is important since it can be concluded that energy savings can be achieved without introducing control problems.

The first distillation column, as indicated in Fig. 2a, b, removes most of the water as bottom product, and the distillate is a stream product rich in bioethanol whose composition is below the azeotropic point (95.6 wt% bioethanol). In the second part of the process (dehydration using glycerol), extractive distillation can be used to obtain high-purity bioethanol as reported by Hernández (2008). In that work, Hernández showed that the DWDC can be used to

Fig. 2 Process flowsheet for the purification of bioethanol using conventional distillation and extractive distillation



(a) Distillation sequence with a side rectifier.



(b) Distillation sequence using a Petlyuk distillation column.

obtain high-purity bioethanol as distillate using ethylene glycol as entrainer; the side stream is a mixture of ethanol and water, and the bottoms product is ethylene glycol. The author showed that the DWDC can exhibit two solutions in the heat duty required in the reboiler for the same values of the interconnecting liquid and vapor streams.

To complement that study, in this work we use glycerol as entrainer in the dehydration of bioethanol, since ethylene glycol may be forbidden in the near future, due to toxicity, and its high availability for being a low-cost side product, obtained during biodiesel production (Ravagnani et al. 2010; Bauer and Hulteberg 2013). Also, we have conducted experimental studies about dehydration of ethanol using ethylene–glycol, glycerol and ionic liquids, and the highest compositions in the produced ethanol were achieved by using glycerol (Navarrete-Contreras et al. 2014). Moreover, new results about multiplicities in DWDC are found: up to three values of the heat duty required in the reboiler can be obtained for a set of values assigned to the interconnecting streams. As a result, it is important to detect the minimum energy consumption in order to reduce costs in the complete process of bioethanol production.

Case study

The tray structures (total number of stages and interconnecting stages, see Table 1) for the distillation sequences shown in Fig. 2 were taken from the previous work by Hernández (2008), considering a feed flow of 45.4 kg-mol/h of a mixture of ethanol and water with a mole fraction of ethanol of 10%, as saturated liquid at 1 atm. It is important to mention that ethylene glycol was replaced by glycerol (as saturated liquid at 1 atm) in order to use a non-toxic entrainer (Ravagnani et al. 2010). The first option considers a thermally coupled distillation sequence with a side rectifier (Fig. 2a), and the second option includes a DWDC (Fig. 2b).

It is important to mention that the preliminary designs of the thermally coupled distillation sequences of Fig. 2 were obtained by using the short-cut design method reported in Hernández and Jiménez (1999) based on the Fenske–Underwood–Gilliland method.

The simulation studies were conducted using a rigorous model of the distillation columns, using the RadFrac module of Aspen Plus, and the NRTL model was used for representing the vapor–liquid equilibrium. As reported by Hernández (2008), the energy required in thermally coupled distillation

Table 1 Important design variables for the distillation sequences

Conventional distillation column	Total stages = 30[a] Feed stage = 26	
Distillation column with a side rectifier	Main distillation column: Total stages = 20 Glycerol feed stage = 3 Feed stage = 10 Side-stream stage = 15	Side rectifier: Total stages = 10
Petlyuk distillation column	Main distillation column: Total stages = 20 Glycerol feed stage = 3 Vapor feed stage = 6 Liquid feed stage = 16 Side-stream stage = 10	Prefractionator: Total stages = 10 Feed stage = 5

[a]Stages are numbered from top to bottom

columns depends strongly on the values assigned to the interconnecting flows. For that reason, in order to detect the minimum energy consumption for a given tray structure, a complete search on the interconnecting flows is required. In the case of the Petlyuk distillation column or its equivalent in the form of the DWDC, it is necessary a search in the liquid and vapor interconnecting streams.

The energy optimization of the DWDC was conducted in the following manner: A value for the interconnecting vapor flow was set, and a complete search in the interconnecting liquid stream was carried out so that the local minimum energy required in the reboiler was obtained. It is important to highlight that usually the search is conducted from low to high values of the interconnecting liquid flow, but in order to detect multiple solutions, the search must be repeated in the opposite direction starting from high to low values of the search variable. The optimization procedure is repeated for several values of the interconnecting vapor stream until the global minimum of energy is detected. It is important to mention that our study is focused on the energy optimization because, according to Doukas and Luyben (1978), even for complex distillation sequences, the utility costs represent up to 80% of the total annual costs.

Results

As indicated in the case study section, the first distillation option involves the use of a thermally coupled distillation with a side rectifier where a reboiler is replaced by a vapor stream (Fig. 2a). The variation of this stream is depicted in Fig. 3, considering several flows of glycerol, where the feed stage can be either 3 or 5. It is important to mention that the entrainer must be supplied near to the top of the distillation column since the ethanol–water forms a minimum boiling point azeotrope. According to Fig. 3, the energy consumption is increased with the flow of glycerol due to its high boiling point, and the minimum amount of glycerol required

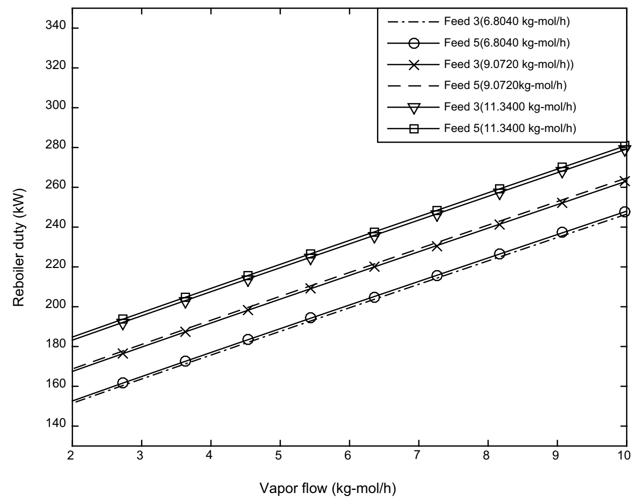


Fig. 3 Energy optimization of the thermally coupled distillation sequence

to achieve the purity of ethanol is 6.8040 kg-mol/h. Also, it is noted that energy consumption is very similar when the glycerol is fed in either stage 3 or 5. Finally, for the first option, Fig. 4 indicates the composition profile of the main distillation column and the mass fraction of ethanol of 0.995 is reached in the top of the distillation column, representing a mole recovery of ethanol of 98%. Also, an advantage of this complex distillation sequence is that glycerol is recovered at high purity in the bottoms.

The energy optimization for the DWDC is complex since two recycle streams need to be varied to detect the optimal requirement of energy in the reboiler. Since no important changes were observed in the optimization of the thermally coupled distillation column with a side rectifier for feed tray of glycerol at either 3 or 5, we fixed tray stay as suitable for the feed of glycerol. Several values of glycerol were considered; for instance, in Fig. 5 we can see that for some values of the interconnecting flow of

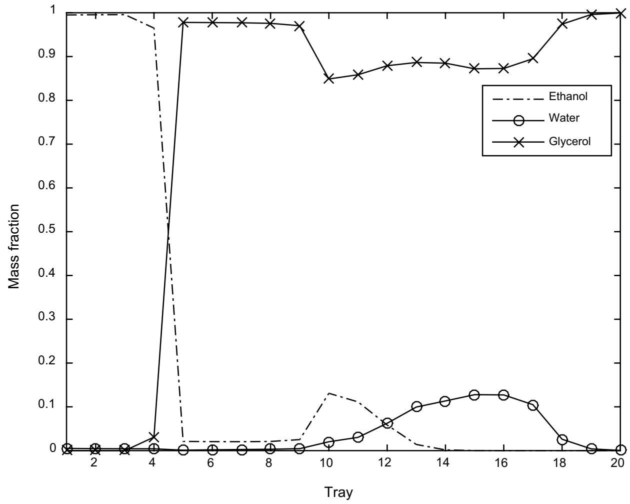


Fig. 4 Liquid composition profiles in the main distillation column of the thermally coupled distillation sequence with a side rectifier

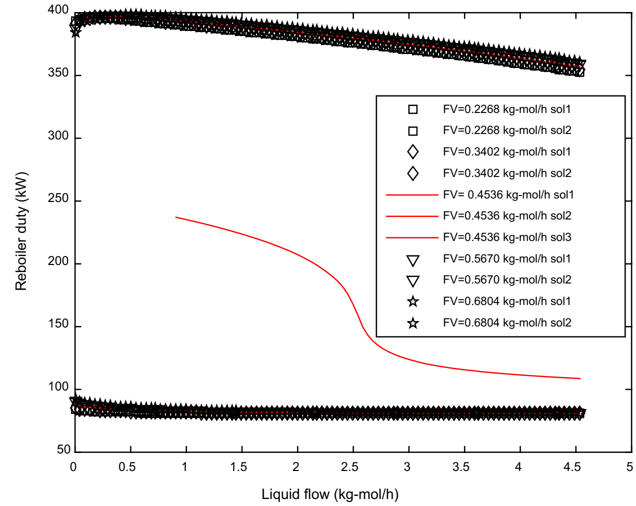


Fig. 6 Search for the energy required in the DWDC for low values of liquid interconnecting flow

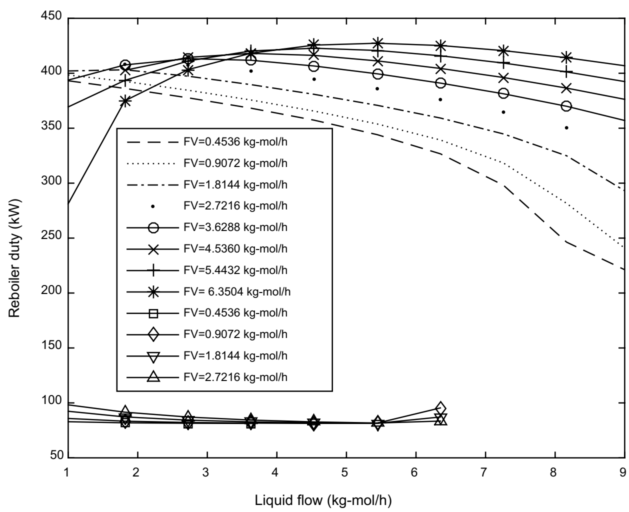


Fig. 5 Energy optimization of the DWDC for given flow of glycerol of 6.81 kg-mol/h

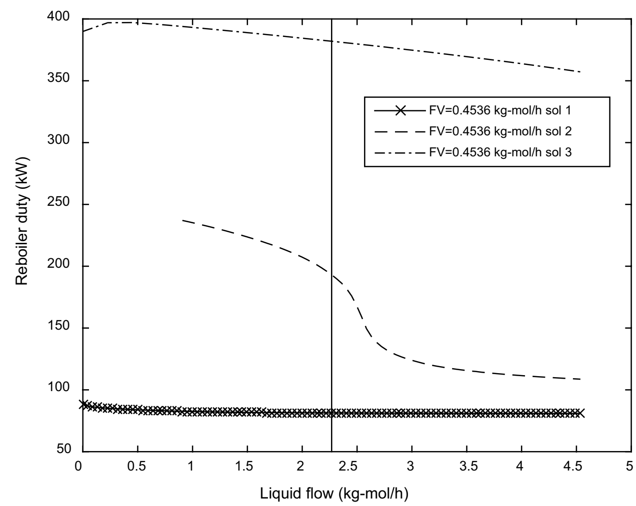


Fig. 7 Multiplicities in the DWDC in the bioethanol dehydration

vapor, two values of heat in the reboiler are obtained. It can be observed that both steady states differ significantly; as a result, it is important to detect the minimum energy consumption, since differences of up to 400% can be presented. This finding has several implications; for instance, the differences in the green house gases emissions and cooling water requirements are of the same order of magnitude and the huge energy usage in the upper case can lead to a very important reduction in the net energy gain in the bioethanol production. This implies that reductions in the energy consumption are translated into reductions in greenhouse gases emissions, because most of the energy used in distillation is obtained from fossil fuel. Also, the reduction in the energy required in the reboiler diminishes the cooling water required in the condenser.

We detected a new curve for the energy required in the reboiler when the interconnecting vapor flow is 0.4536 kg-mol/h by conducting a search for low values of the interconnecting liquid flow and considering several search starting points. As a result, for a given value of the interconnecting liquid flow, three solutions can be found (Fig. 6), but according to the shape of the curves, the middle curve represents unstable solutions (Fig. 7). This result is very similar to that obtained in the operation of chemical reactors that can present similar multiple solutions (Fogler 1999). It is important to mention that Kano et al. (2011) have found multiple steady states in binary distillation, and these multiplicities depend on the physical properties of the mixture, and the study is inspired in the occurrence of multiplicities in a non-isothermal continuous stirred tank reactor. Also, using the same base, Purohit et al. (2013) have concluded that the interaction between reaction and distillation can conduct multiple steady states in reactive distillation. Finally, for the BTX separation process, Wang (2015) and Gupta and Kaistha (2015) have reported the presence of multiple steady states that must be considered in the operation and control.

Another important point to take into account in the use of ethylene glycol or glycerol as entrainer in the bioethanol dehydration process is associated with the normal boiling points of the entrainers. The normal boiling points are 197.08 and 287.71 °C for the ethylene glycol and glycerol, respectively. It is important to highlight that in the case of the use of glycerol, the pressure of the heating vapor is higher than in the case of ethylene glycol, conducting to the use of a more expensive heating medium.

Our future research will be focused on finding multiple steady states in experimental tests and the corresponding controllability study in order to detect the best design in terms of energy and control (García-Ventura et al. 2016); for that reason, we have implemented an experimental dividing wall distillation column which consists of three packed sections of 2.5 m of total height and 0.17 m of inner diameter. The column is filled with Teflon Raschig rings and is instrumented with six thermocouples. Our preliminary tests indicate that it is possible to obtain high-purity bioethanol using the dividing wall distillation column and glycerol as entrainer; for example, Fig. 8 presents the composition of the distillate during the time and the composition of ethanol is around 99 wt%. Other important variables that we have registered are the temperatures; in Fig. 9, Tb represents the temperature in the reboiler of the distillation column, and as expected, it is higher than the temperature in the distillate (T5) during the complete operation of the experimental DWDC. The temperature obtained in the reboiler is important since it is associated with the cost of the heating medium.

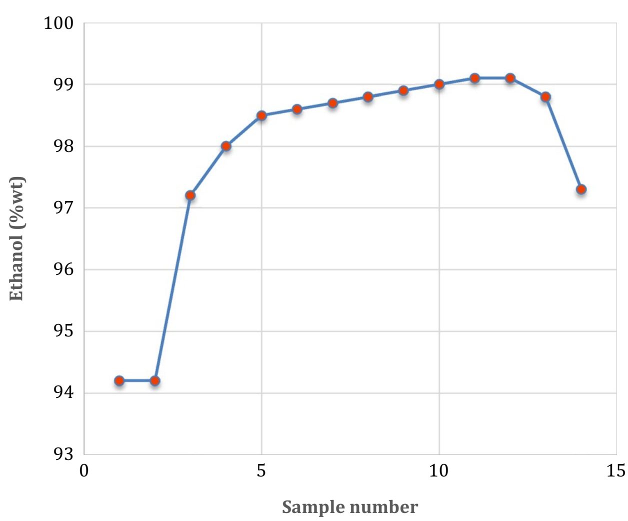


Fig. 8 Composition of ethanol in the distillate of the experimental DWDC

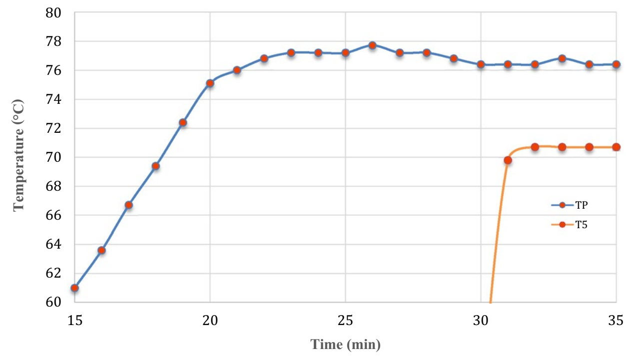


Fig. 9 Temperatures of the bottoms (TP) and distillate (T5) of the experimental DWDC

Conclusions

The energy optimization of thermally coupled distillation sequences for the purification of bioethanol using glycerol as entrainer was revisited. The energy optimization revealed a region where three solutions for the heat duty supplied to the reboiler can be found. As reported in the open literature, these multiplicities are found in binary distillation and complex reactive distillation columns. These multiplicities can be attributed to nonlinearities in the model, physical properties and interactions between the reaction and the separation.

Two of them are stable solutions with a very significant difference; as a result, the detection of the solution with the minimum energy consumption is essential. The third solution is a curve with a sigmoid shape with unstable solutions. This result has not been reported previously in the open literature according to the review and knowledge of the theme in our research group. Also, it is important to detect the dehydration process with the minimum energy consumption since it is well known that this step is very energy intensive. Furthermore, the reductions in energy consumption are translated into reductions in gas emissions and cooling water used in the condenser. Finally, we can conclude that glycerol can break the ethanol–water azeotrope, but the temperature in the bottom part of the distillation column is increased.

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