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Total Heat Integration in the Biobutanol Separation Process

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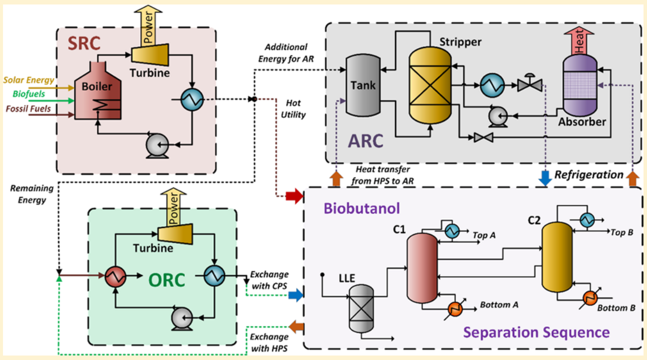
Supporting Information

ABSTRACT: The global warming and climate change problems have become more serious because of the high consumption of fossil fuels during the past century. Recently, biofuels have attracted interest as an option to reduce the extensive use of fossil fuels; particularly, biobutanol appears as an option to replace the petroleum-based fuels. However, the separation process to produce biobutanol requires a lot of energy and yields lots of waste heat at low temperature. Therefore, there is a need to propose options to reduce the required energy in the biobutanol separation process. Consequently, this paper presents an optimization approach for designing energy integrated biobutanol separation processes. The optimization incorporates attractive separation options such as ABE fermentation using different solvents as well as incorporating several options for waste heat recovery involving integrated heat exchanger networks, stream Rankine cycles, organic Rankine cycles, and absorption refrigeration cycles. The results show significant economic and environmental benefits for the simultaneous consideration of the optimization of the separation process with the waste heat recovery for the biobutanol separation process.



1. INTRODUCTION

The huge energy consumption from fossil fuels over the past century has lead to a significant increment in greenhouse gas emissions (GHGEs) promoting global warming and climate change. Furthermore, the high variability in the cost of fossil fuels together with the decrement in oil reserves have promoted research into alternative energy forms.[1,2] This way, biofuels (i.e., fuels from biomass) appear as attractive options for replacing fossil fuels and, at the same time, to attack the global warming problem, decreasing the net carbon dioxide in the atmosphere.[3,4] Recent studies have been focused on synthesizing biogasoline (i.e., bioethanol) and biodiesel; and less attention has been incorporated to the biobutanol.[2,5] It should be noted that biobutanol can be produced from agricultural crops, molasses, and whey permeate; unlike bioethanol, biobutanol can be produced mainly from second generation biosources (e.g., agriculture and forest wastes), which do not compete with food feedstock.[6,7] Biobutanol is currently used as an extractant in the food, pharmaceutical, and flavor industries and as a solvent in cosmetics, hydraulic fluids, detergents, drugs, antibiotics, hormones, vitamins, and also for the synthesis of butyl acrylate and methacrylate.[8] Biobutanol has a higher energy value (27.8 MJ/L) than bioethanol (21.1 MJ/L), closer to the low heating value of gasoline (32.3 MJ/L). Biobutanol can be used as a gasoline replacement and can be blended in any proportion without any car engine modifications or equipment distribution and storage; also it is very hydrophobic with a water solubility of 7.7 g/100 mL at 20 °C. It has a higher boiling point (117.7 °C) and flash point (29 °C) making it less hazardous than other lower alcohols.[7,9] One important problem associated with biobutanol production is the separation process, because there is involved an azeotrope in the mixture acetone−butanol−ethanol obtained from the fermentation process (ABE fermentation). The main strategies identified for the separation of this mixture are adsorption, pervaporation, gas striping, membrane distillation, and liquid−liquid extraction (LLE).[6,10,11] It should be noted that adsorption has lower energy requirements but it is subjected to fouling, and its recovery and selectivity is low. On the other hand, pervaporation offers a selective separation of organics from water; however, more development is needed in the membranes to improve the recovery ratio. Gas striping does not suffer from clogging or fouling by biomass, nevertheless this process leads insufficient recovery of solvents.[12] Membrane distillation shows high selectivity for solvents, but also its membrane suffers from clogging and fouling which reduces the recovery rate.[10,12] Nowadays, biobutanol production is facing some engineering challenges in terms of energy due to its low concentration at the end of the fermentation. This low concentration is because butanol is toxic to microorganisms that rarely tolerate more than

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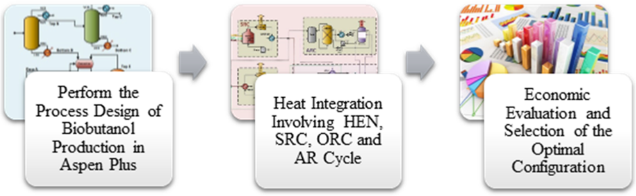

Figure 1. Schematic representation of the optimization methodology.

2% butanol.[13,14] Liquid−liquid extraction (LLE) has high selectivity and great potential in separation of biobutanol from ABE fermentation due to the facts that biobutanol is more hydrophobic than other biofuels and the concentration is lower.[11,15] However, the main concern in the biobutanol separation through LLE is the energy requirement.[3,16] In the LLE of biobutanol process, there are identified several hot streams that require cooling and cold streams that require heating.[17,18] In this context, heat integration emerges as an attractive solution to reduce the costs in the LLE biobutanol separation. Many strategies have been proposed to make the process economically acceptable in terms of energy, and it has attracted a lot of interest in chemical processes.[19]

In this context, Kiran et al.[20] proposed an internally heat integrated distillation column with a vapor recompression column for bioethanol separation, the results showed that the internal heat integration yields better performance in terms of both energy consumption and cost. Zhu et al.[21] presented different heat integration modes for separating an azeotropic mixture of toluene and ethanol using pressure swing distillation (PSD), the results showed that PSD with heat integration is cheaper than conventional PSD. Fornell and Berntsson[22] discussed the heat integration potential based on advanced composite curves in a lignocellulosic ethanol production plant. Fu et al.[23] presented a mixed-integer nonlinear programming (MINLP) model to integrate the air compression train in a cryogenic air separation unit with the regenerative stream cycle in an oxy-combustion coal-based power plant. Hipólito-Valencia et al.[24] proposed a mathematical model for the heat integration in the bioethanol separation process involving an organic Rankine cycle (ORC). Lira-Barragan et al.[25] proposed a mathematical model for synthesizing heat exchange networks (HENs) involving organic Rankine cycles (ORCs), adsorption refrigeration cycles (ARCs), and steam Rankine cycles (SRCs) for power generation and waste heat recovery; these results showed several advantages among economic, environmental, and social objectives.

For the specific case of energy integration in the biobutanol separation process. Aneke and Görgens[26] presented a thermodynamic comparison between three different ABE configurations for biobutanol separation, they applied the first and second laws of thermodynamics, where the results showed that both gas stripping and LLE give better separation efficiency than pure distillation. It should be noted that all previous works have not considered a proper energy integration and waste heat recovery for the biobutanol separation process. Therefore, this paper presents an optimization method for energy integration and waste heat recovery in the biobutanol separation process from ABE fermentation (see Figure 1). The proposed method is based on a new superstructure (see Figure 2) that involves the waste heat recovery through an integrated HEN using SRC, ORC, and ARC.

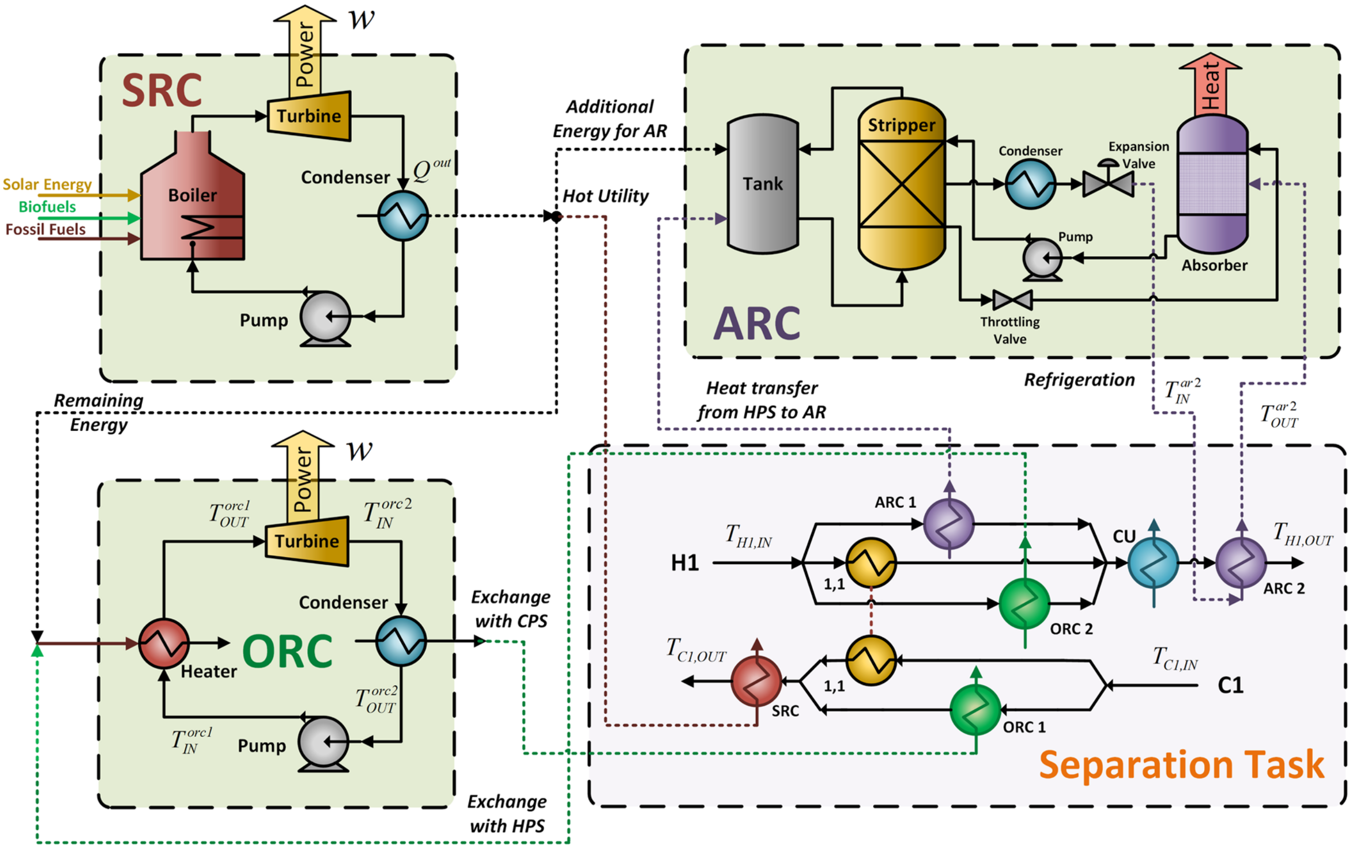

Figure 2. Schematic representation of the heat integration procedure.

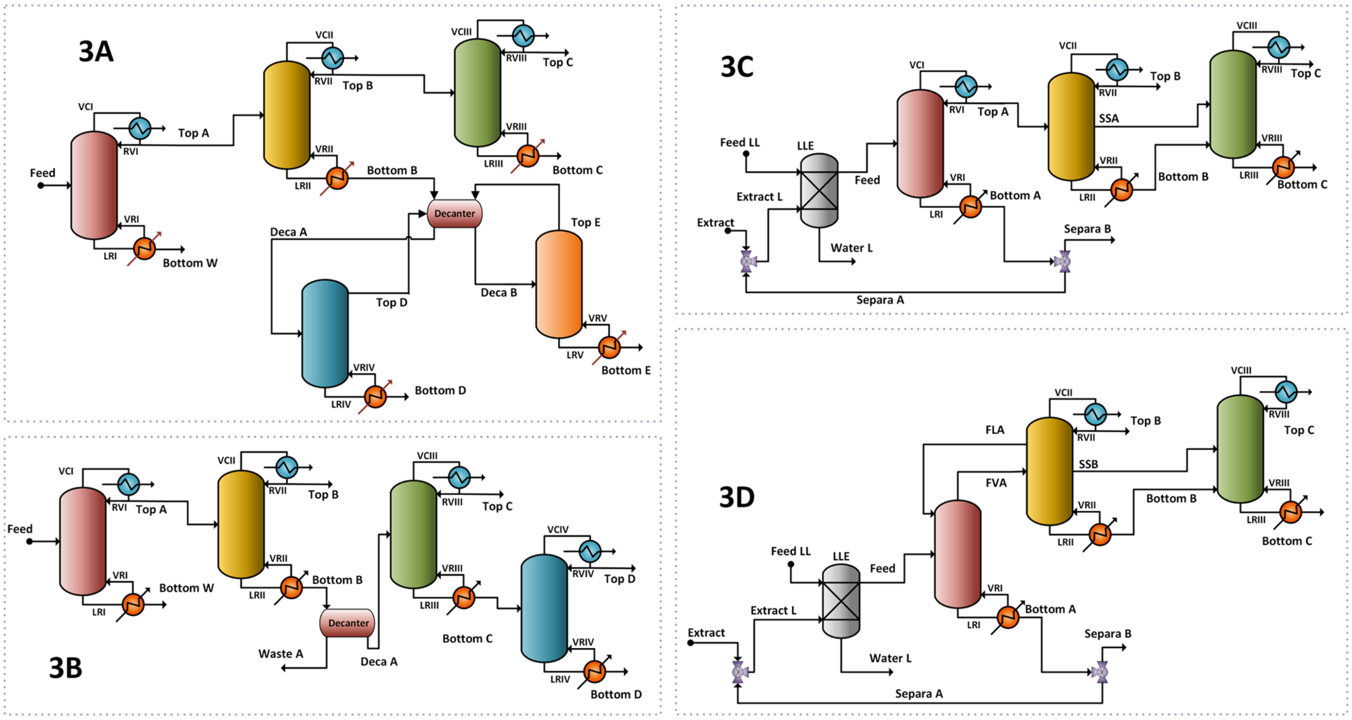

Figure 3. Considered schemes for biobutanol purification: 3A, 3B, 3C, and 3D.

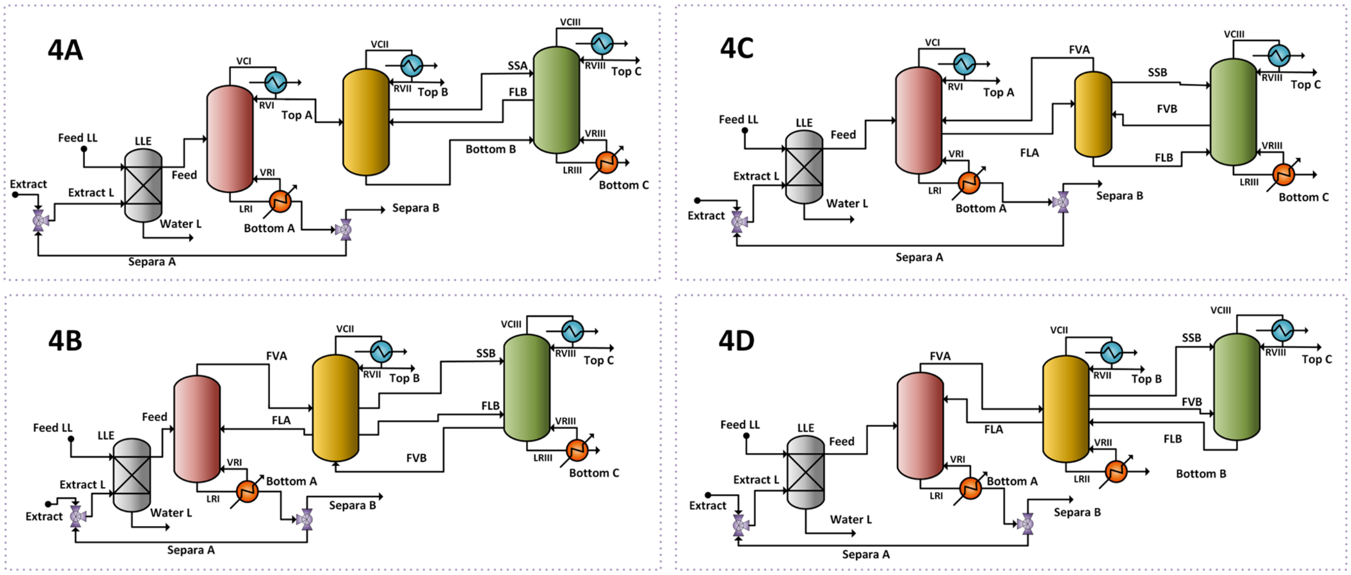

Figure 4. Considered schemes for biobutanol purification: 4A, 4B, 4C, and 4D.

2. OPTIMIZATION PROCEDURE

The implemented methodology can be stated as follows (see Figure 1). First a set of separation sequences for biobutanol from ABE fermentation are identified and designed in the Aspen Plus software; all of those configurations are shown in Figures 3–5. In order to improve their economic and environmental indexes, these configurations are solved simultaneously using stochastic optimization applying both the differential evolution method and the tabu list algorithm. This optimization process has as objective function the total annual cost and the Eco-indicator 99. Then, for each case there are identified hot and cold process streams in the designed separation scheme. In this case, hot process streams are usually at low temperature, then there is a need to incorporate strategies for waste heat recovery as OR and AR cycles,[25] after the hot and cold streams are set up from the identified separation sequences. In this paper there is proposed a superstructure that incorporates an energy integration through a HEN using integrated SR, OR, and AR cycles (see Figure 2). In the integrated approach, hot and cold utilities can be provided by the power and adsorption refrigeration cycles. The residual energy from hot streams and the ORC can be reused to run the ARC, which provides cooling requirements. On the other hand, the heating requirements can be satisfied by the SRC and ORC, using either fossil fuels, biofuels, or solar energy, in order to reduce the external hot utilities (for modeling details see the work of Lira-Barragán et al.[25]).

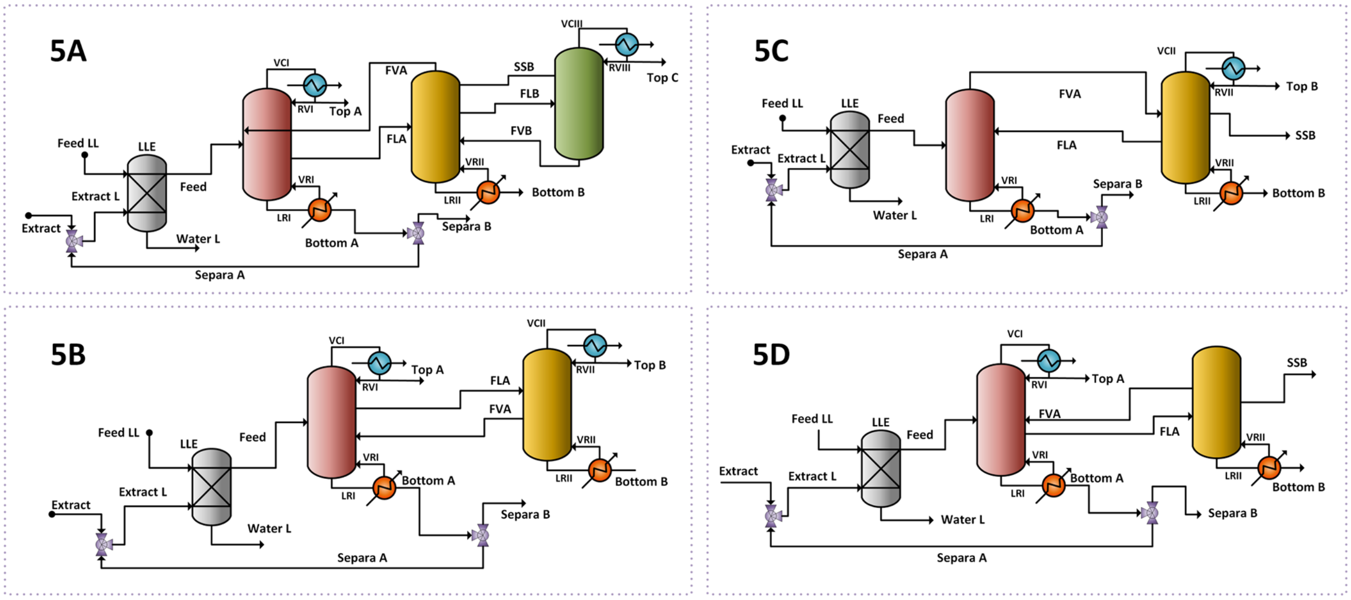

Figure 5. Considered schemes for biobutanol purification: 5A, 5B, 5C, and 5D.

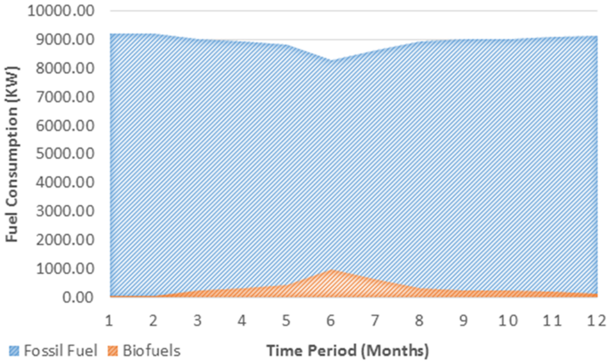

Figure 6. Fuel consumption for case 3A.

3. CASE STUDY

A set of configurations were selected for the biobutanol separation task from ABE fermentation; these configurations are given in Figures 3−5. The broth composition used to model all the separation alternatives was chosen according to the report by Wu et al.[27] The feed physical parameters and the composition are reported in Table 1 (available in the Supporting Information). According to the work of Sánchez-Ramírez et al.,[17] the NRTL-HOC model was selected as the thermodynamic model for all the simulations and hexyl-acetate was chosen as the extractant in the liquid−liquid extraction column. For the optimization process, the minimum purity targets were 99.5 wt % for butanol, 99.5 wt % for acetone, and 95.0 wt % for the ethanol. Only when stand-alone distillation is considered as the separation method, the maximum purity achievable for the ethanol was slightly below the fixed threshold. The selected configurations are then described as follows.

3.1. Separation Flowsheet Based Only on Distillation. When a separation unit is needed, distillation is almost always the first option to be considered. Although some alternatives have been proposed to reduce the energy requirements, distillation continues being the industrial favored unit operation.[28] In this context, Marlatt and Datta[29] presented an ABE separation design reported in Figure 3 (3A). This design, which is based only on distillation, is made-up by three distillation columns and two strippers. The fermentation broth is fed to the first column, where butanol, acetone, and near 95% of the ethanol are recovered in the distillate. This stream is fed to the second distillation column, the distillate flows to the third distillation column for the acetone−ethanol separation. The bottom stream of second column is sent to a decanter, both aqueous and butanol rich phases are stripped, and the vapor is recycled back to the decanter. Water and butanol are obtained from the strippers.

3.2. Hybrid Extraction−Distillation Processes. Several studies have concluded that combining liquid−liquid extraction and distillation are considered quite promising separation alternatives for the ABE purification.[17,30−33] The extraction column is commonly located after the fermenter; the extractant is fed from the bottom, and the fermentation broth from the top. The extract phase obtained from the extractor is fed to the distillation section, where acetone, butanol, and ethanol can be recovered following different arrangements employing simple and/or complex columns. The use of extractant may eliminate the presence of both homogeneous and heterogeneous azeotropes.

3.3. Synthesis of Alternative Separation Configurations. The synthesis of the considered alternatives involves the application of the graph-theoretic method based on P-graphs, which is based on both graph theory and combinatorial techniques; besides, it concentrates on structures of the process system and strictly examines such structures from the mathematical point of view.[34] Recently, few works have been focused on the synthesis of alternative schemes for the ABE separation; however, the work by Liu et al.[35] represents an exception because it explores different process alternatives based on distillation and liquid−liquid extraction applying the P-graph methodology. Moreover, to design and synthesize complex schemes, such as the ones involved in the ABE separation process, there are other methodologies that have been studied and applied in several works.[36,37] However, in this work the P-graph method was considered because it is a heuristic-oriented approach. Furthermore, the hybrid schemes that consider the application of liquid−liquid columns are competitive in terms of

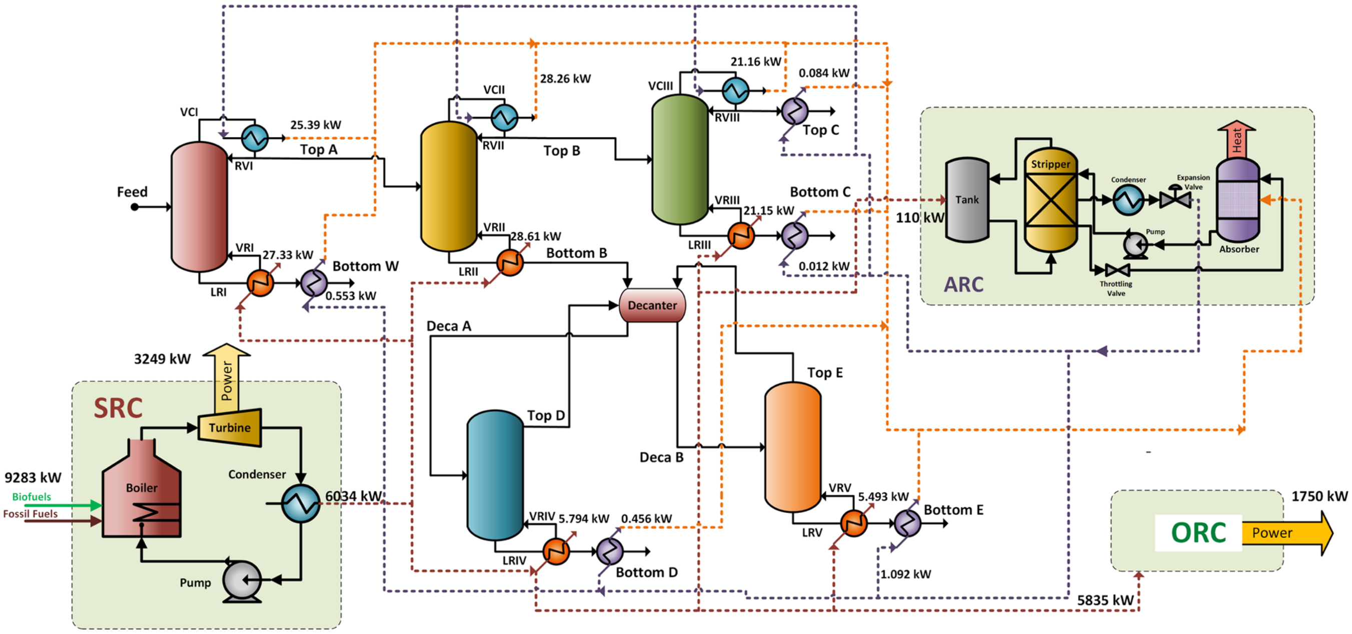

Figure 7. Optimal solution for case 3A.

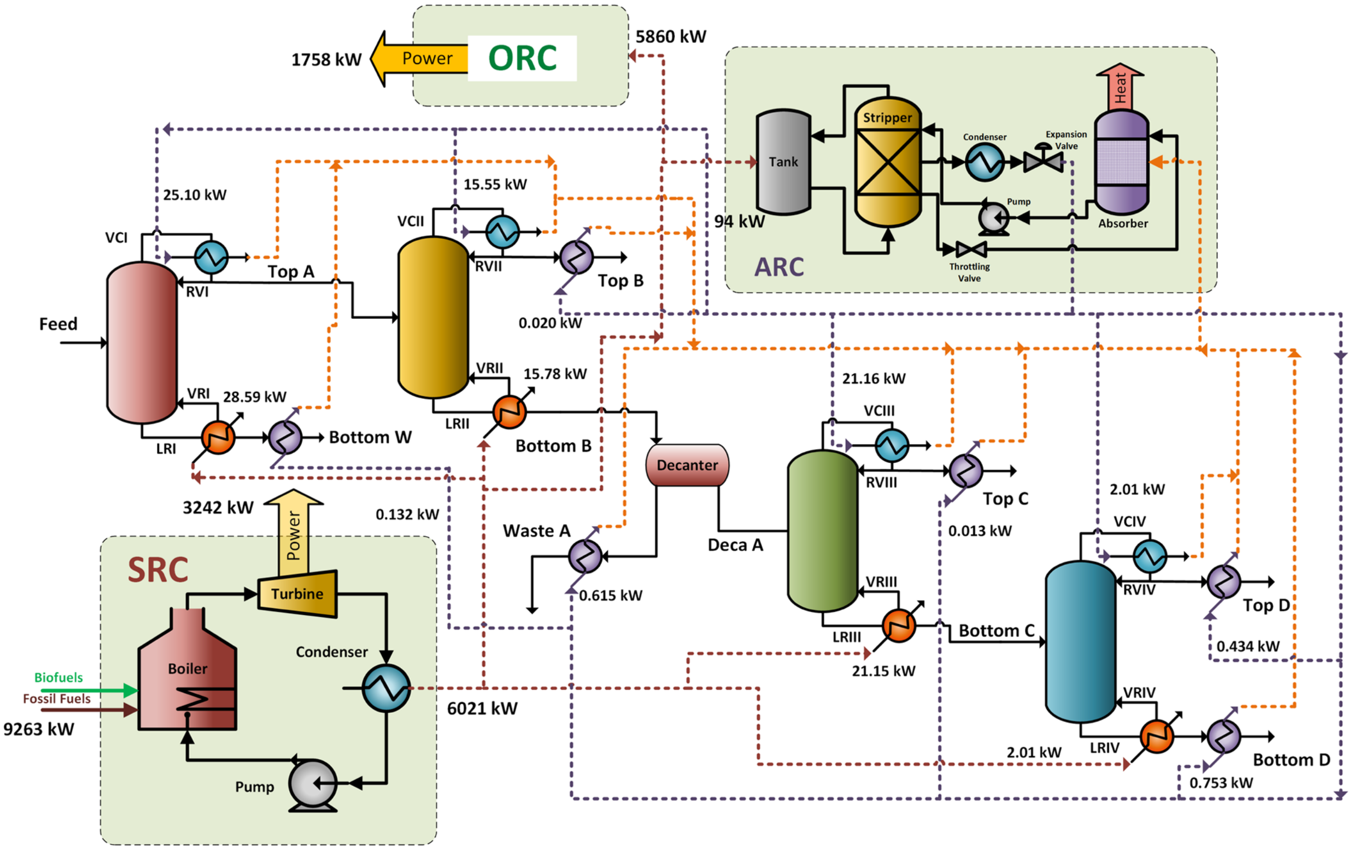

Figure 8. Optimal solution for case 3B.

the total annual cost.[17,30−33] A configuration of this separation scheme is reported in Figure 3 (3C). The flowsheet is composed by a liquid−liquid extraction column followed by three distillation columns, the first one performs the solvent recovery and the last two are for the product purification. In addition, the configuration 3C of Figure 3 was selected as reference to produce the thermally coupled, thermodynamic equivalents, and intensified alternatives. The considered methodology consists of the introduction of thermal couplings, column section transposition, and process intensification.[38,39]

3. 3.1. *Alternative Thermally Coupled Configurations.*

Starting from the reference configuration of Figure 3 (3C), it is possible to obtain the three thermally coupled sequences reported in Figures 3 (3D) and 4 (4A, 4B). One or more thermal

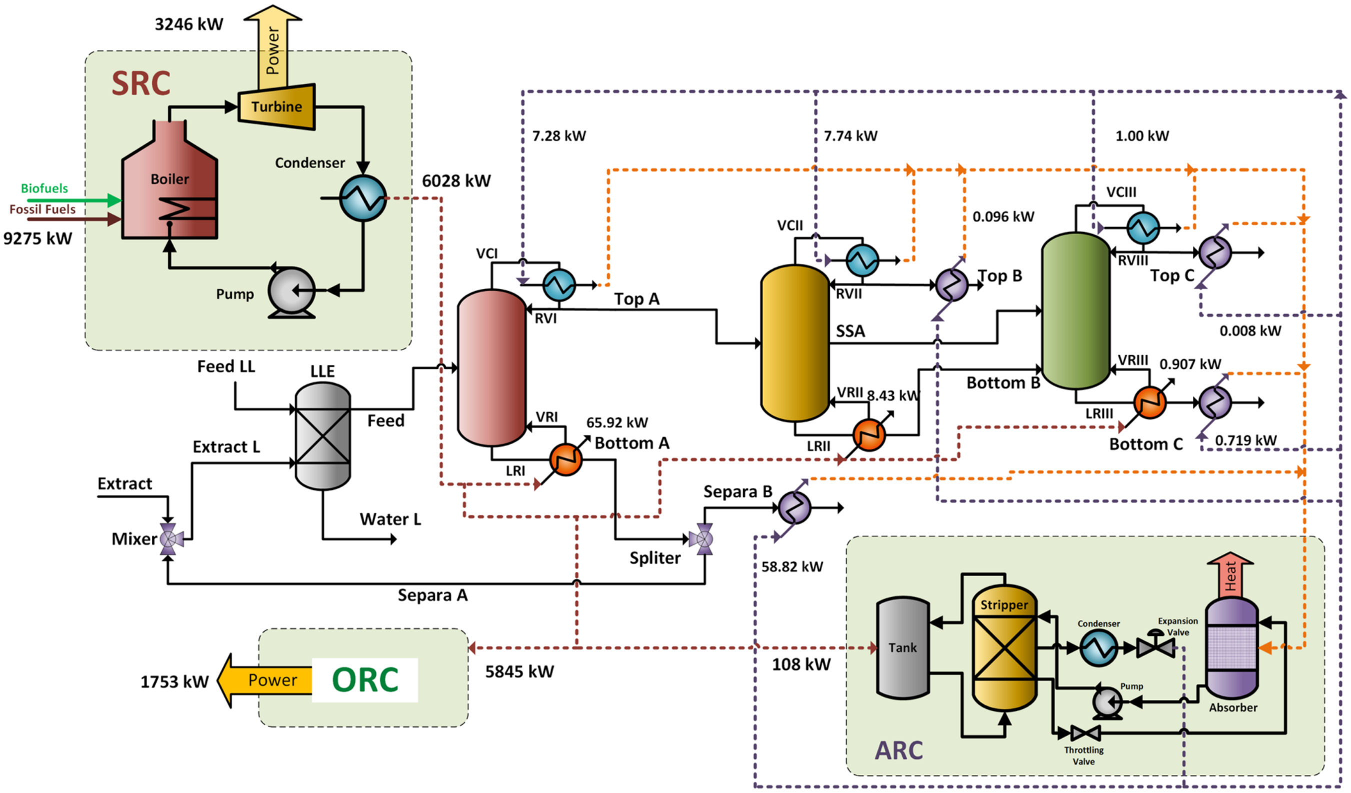

Figure 9. Optimal solution for case 3C.

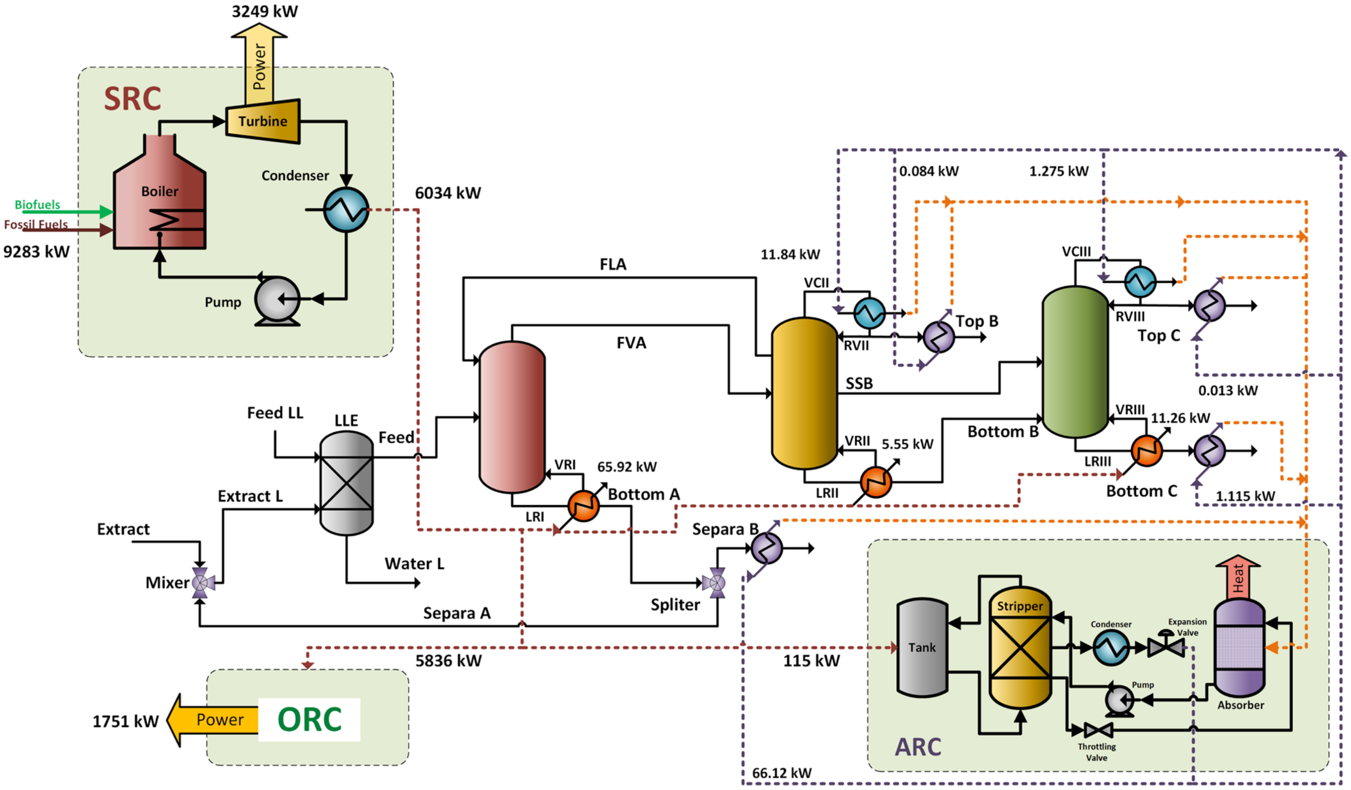

Figure 10. Optimal solution for case 3D.

couplings have been introduced in correspondence to condensers and/or reboilers associated with nonproduct streams. In this way, the configuration of Figure 3 (3D) was obtained by substitution of the solvent recovery column condenser with a thermal coupling. In Figure 4 (4A) the reboiler of the second distillation column was substituted with a thermal coupling and in Figure 4 (4B) both the condenser and reboiler have been removed from the first and second columns, respectively.

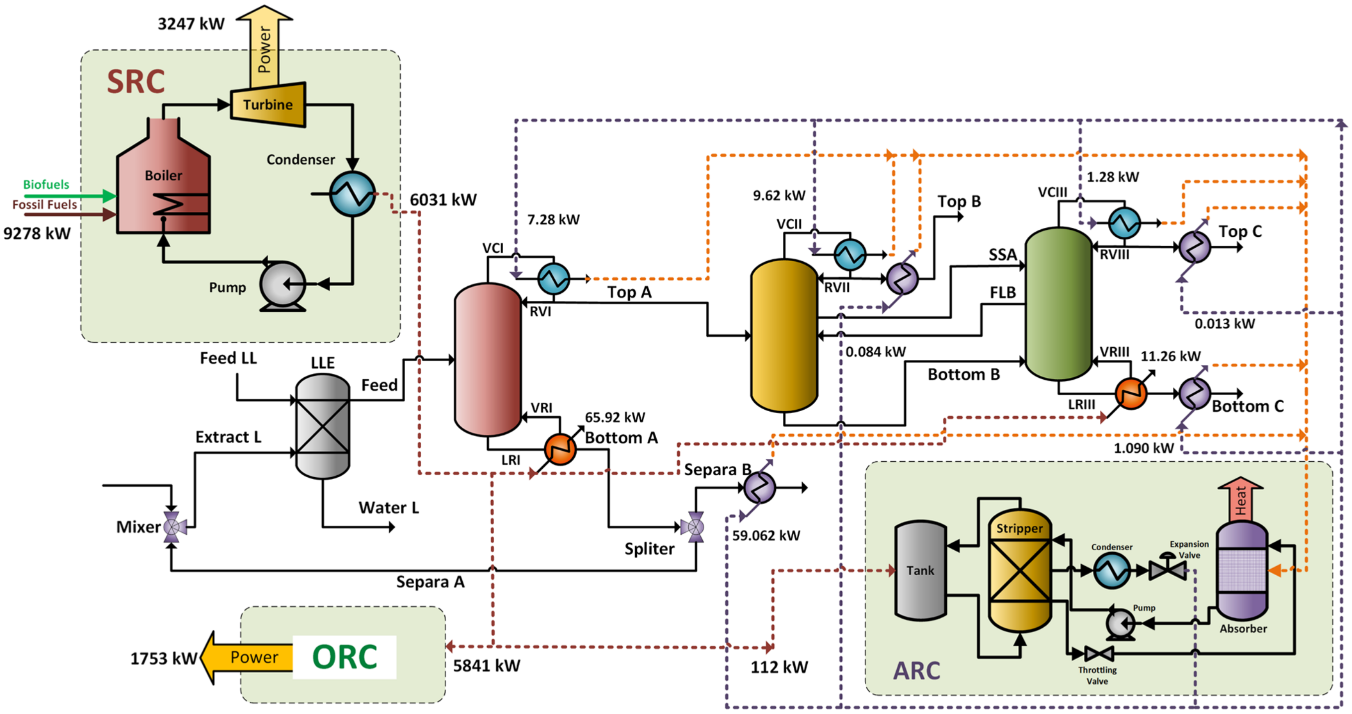

Figure 11. Optimal solution for case 4A.

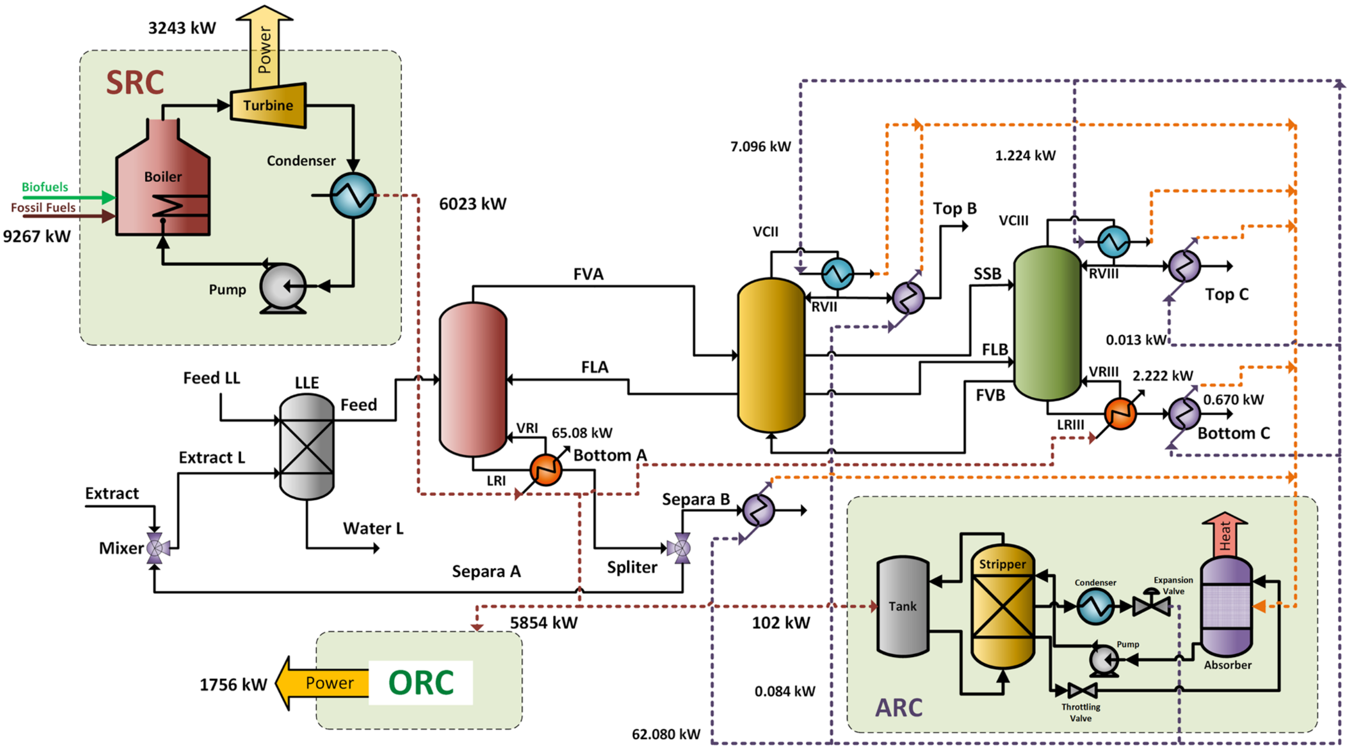

Figure 12. Optimal solution for case 4B.

3.3.2. Thermodynamically Equivalent Alternative Configurations. Every time that a thermal coupling is introduced, there is a column section where the condenser and/or the reboiler provide a common reflux ratio and/or a common vapor boil-up between two consecutive columns. Moving this column section it is possible to generate the thermodynamically equivalent alternatives reported in Figures 4 and 5. Using the double thermally coupled sequence presented in Figure 4 (4B) it is possible to obtain three configurations coming from this double thermally coupled sequence (see Figures 4 (4c, 4D) and 5 (5A)).

3. *3.3. Intensified Alternative Configurations.* The procedure to generate the intensified sequences starts from the thermodynamically equivalent configurations by the elimination of the single column sections defined as transport sections.[38,39] For instance, the configuration shown in Figure 5 (5B) was obtained from the corresponding sequence of Figure 4 (4C) by

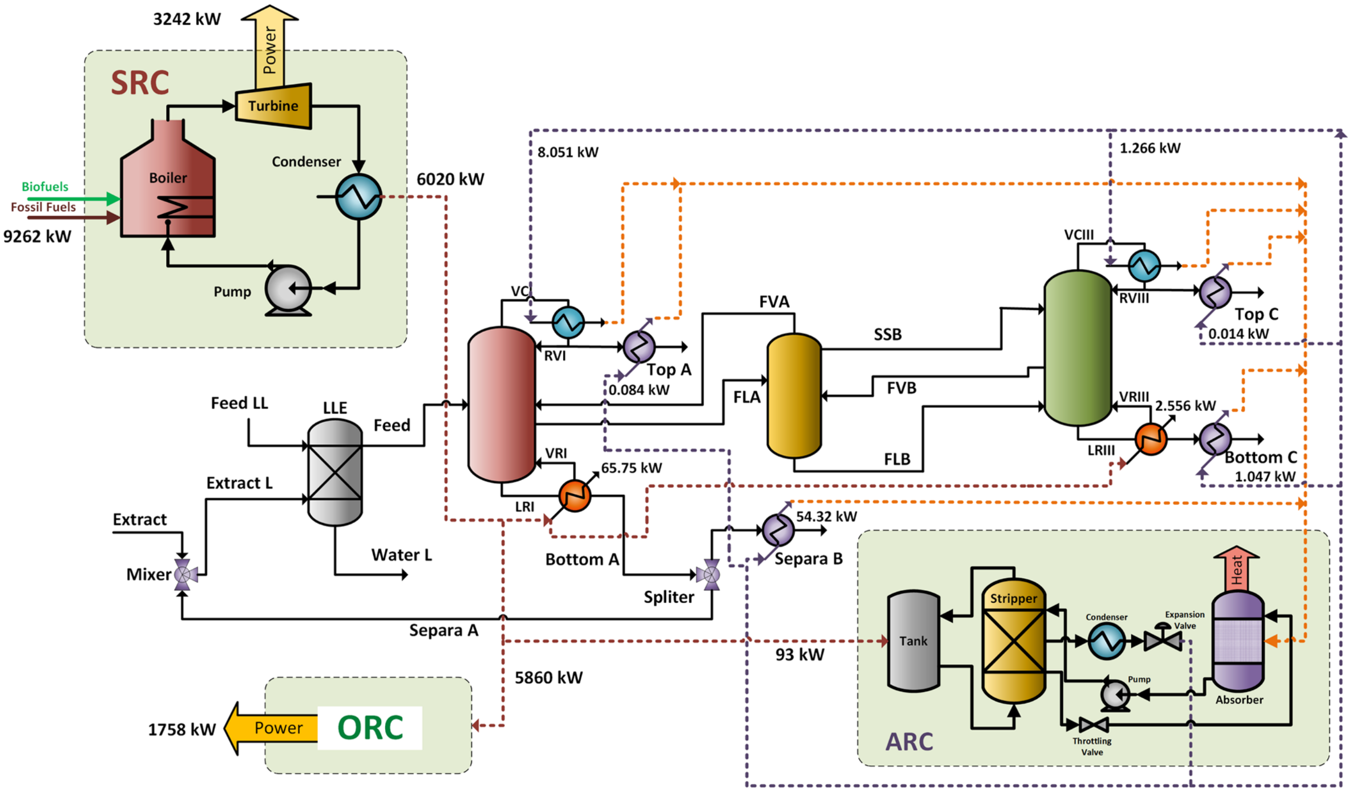

Figure 13. Optimal solution for case 4C.

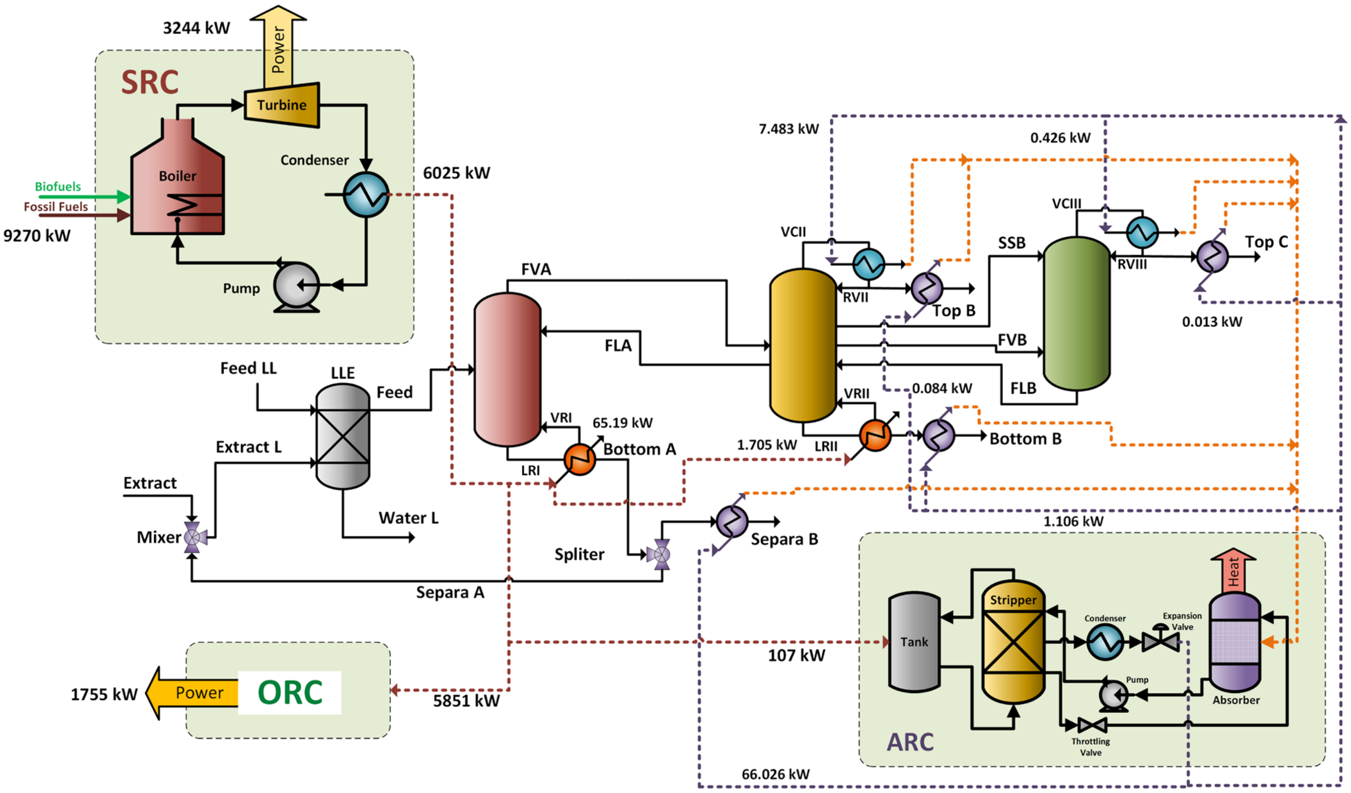

Figure 14. Optimal solution for case 4D.

eliminating sections 4 and 5 and connecting the solvent recovery column to the ethanol/butanol separation column. The same principle has been used for the sequences 5C and 5D of Figure 5.

4. RESULTS AND DISCUSSION

In this section there are presented the results for the heat integration of the separation process of the fermentation mixture

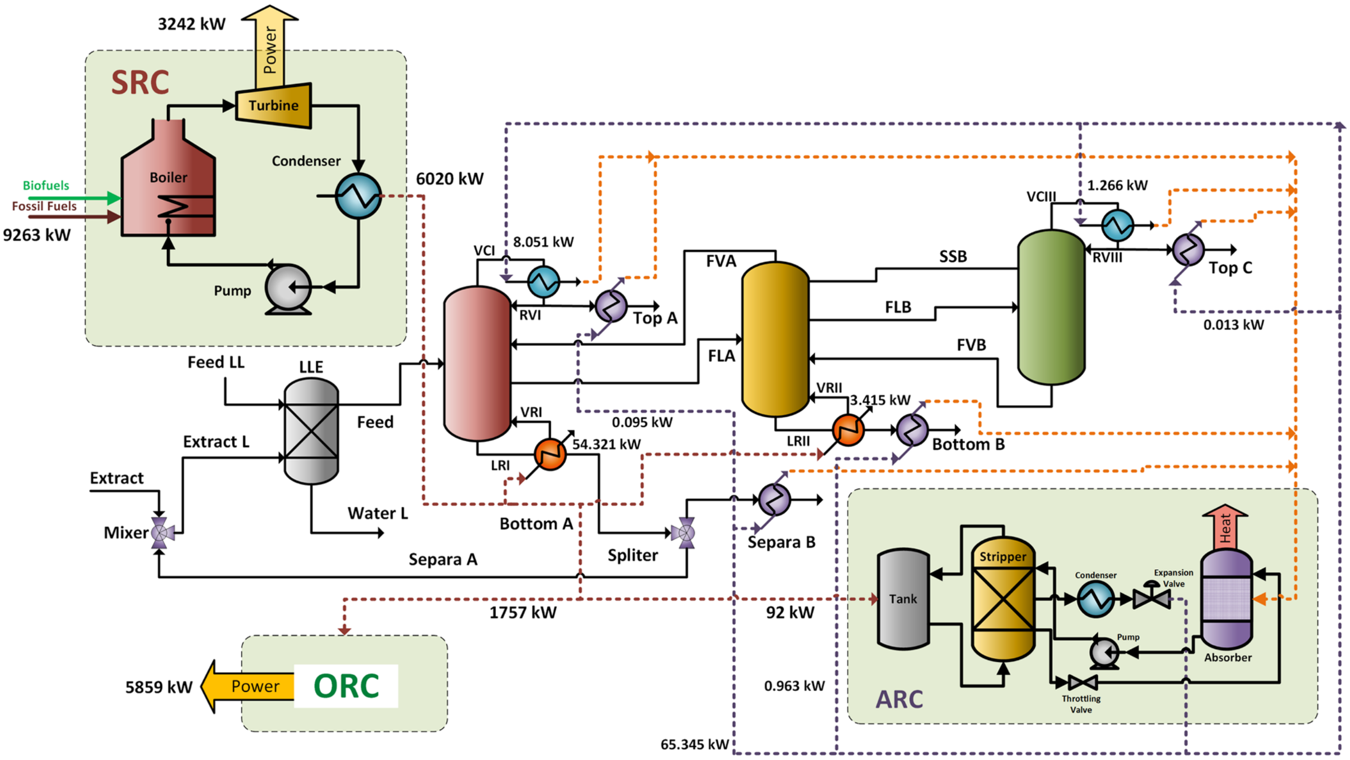

Figure 15. Optimal solution for case 5A.

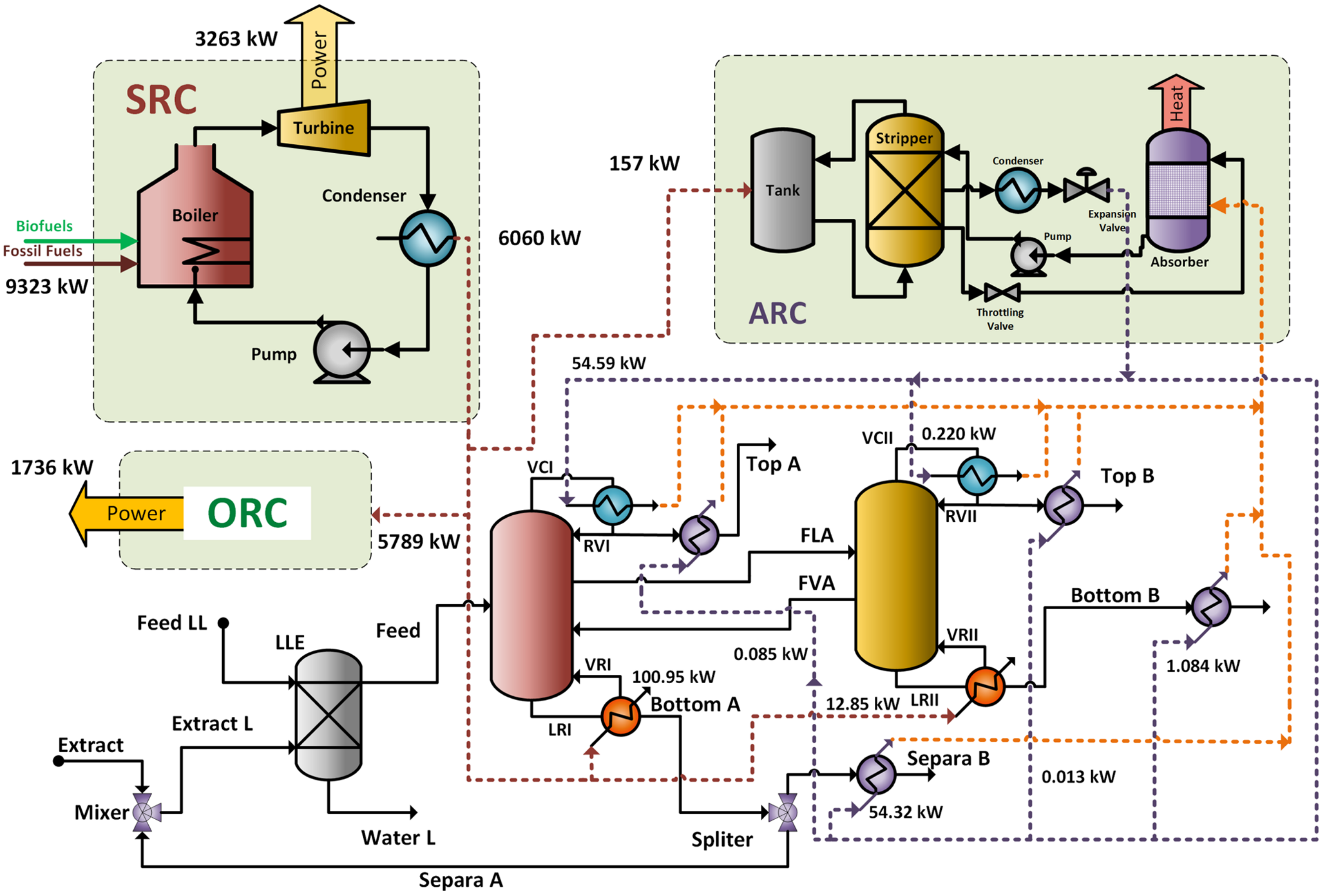

Figure 16. Optimal solution for case 5B.

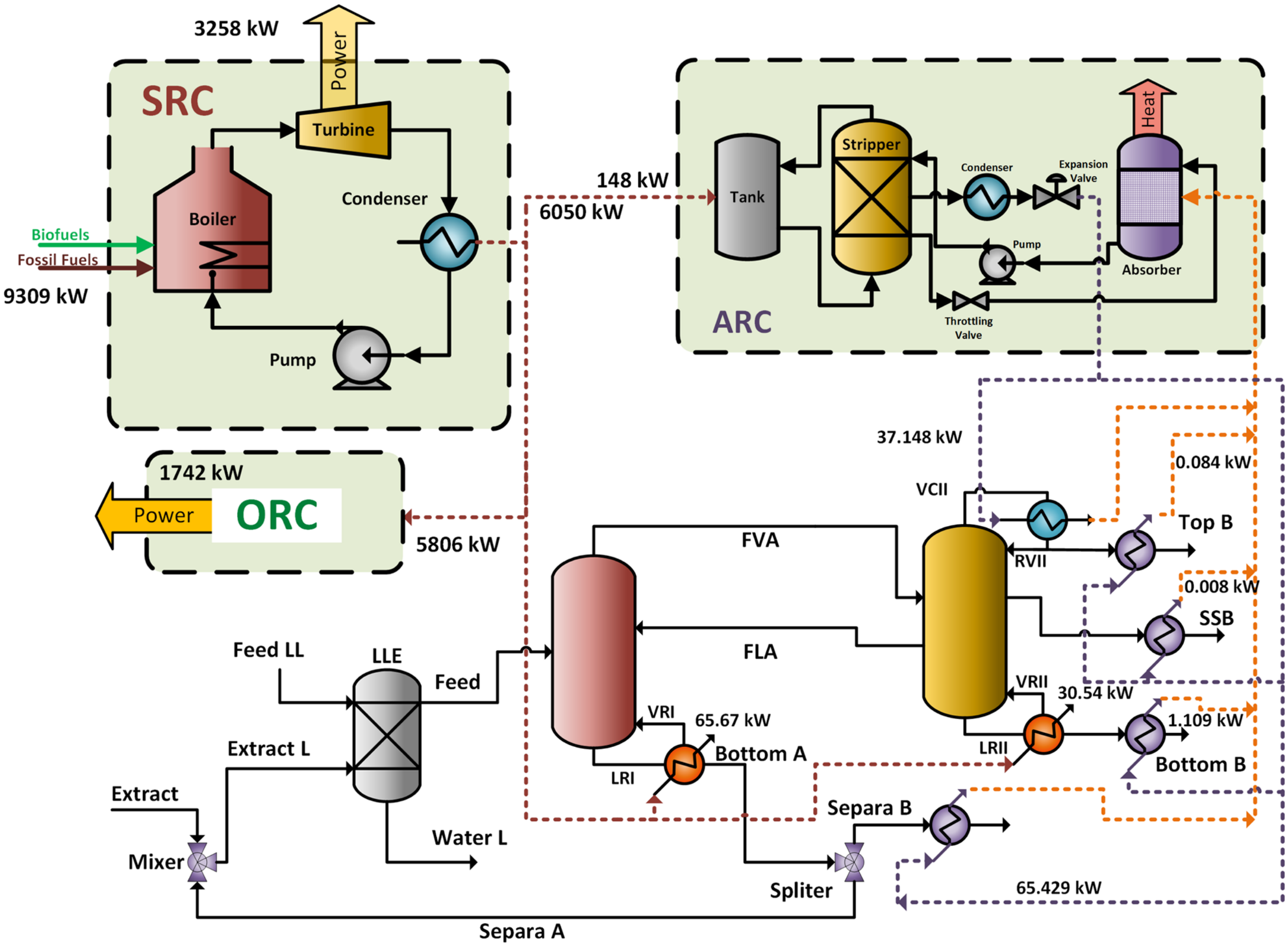

Figure 17. Optimal solution for case 5C.

of butanol−ethanol−acetone−water−hexyl, a set of configurations has been analyzed in order to find the optimal configuration in terms of an economic evaluation. Once the optimization process is done, the results show that the hybrid LL configuration is quite better in economic and environmental indexes in comparison with designs based only on conventional distillation columns. Further, when thermal couplings are included, a reduction in the energy requirement is observed, which is normal and well reported behavior by Triantafyllou et al.[40]

With respect to the thermally coupled designs, the configuration shown in Figure 4 (4B) exhibits a reduction in the TAC of 24.5% and in the Eco-indicator by 11.8%, compared with the base design reported in Figure 3 (3C). When some column sections (rectifying and stripping zones) were removed, no improvement in the TAC and Eco-indicator values are observed. However, when the intensified design was studied, 15% of savings in the TAC with 25% of penalty in the Eco-indicator are observed; this is in comparison with the thermally coupled design of Figure 4 (4B). The reduction in the TAC values for the intensified designs are normal since those designs carry out the same purification process with only two distillation columns instead of three columns as the thermally coupled design does. Moreover, the increment in the Eco-indicator 99 value is because of the slight increment in the energy requirements, which directly impacts Eco-indicator 99. A detailed description of the most promising cases is presented in Tables 2−4 (available in the Supporting Information).

Once those optimization results were obtained, a waste heat recovery methodology was implemented; the proposed model considers that the heating utilities can be satisfied by the energy produced in the SRC and ORC, where the SRC can be fed by either fossil fuels, biofuels, or solar energy. On the other side, cooling utilities can be satisfied by cooling water (CU), the ORC, and by the integration of an AR cycle. Table 5 (available in the Supporting Information) presents the input data for each configuration. Notice that in all the cases, residual streams must be cooled up to 30 °C in order to recover waste heat in these streams. The proposed configurations present similar optimal solutions, there are slight differences in costs based on the heat integration, which can be used to select the optimal solution since the energetic point of view. In all the cases, an annual tax credit reduction of \$10,330/y is observed and around 705 number of jobs are generated. The SRC is fed using fossil fuels and biofuels as shown in Figure 6, this behavior is similar in each of the proposed configurations. The use of fossil fuels or biofuels is mainly linked to the availability of biofuels, whose availability varies drastically through the year. Much of the success of these configurations is associated with the benefit obtained mainly in the OR and AR cycles, which in addition to satisfing the requirements of heating and cooling of the proposed scheme, a revenue is obtained due to the sales of the power generated and the obtained biobutanol. Table 6 (available in the Supporting Information) summarizes the economic results for each case.

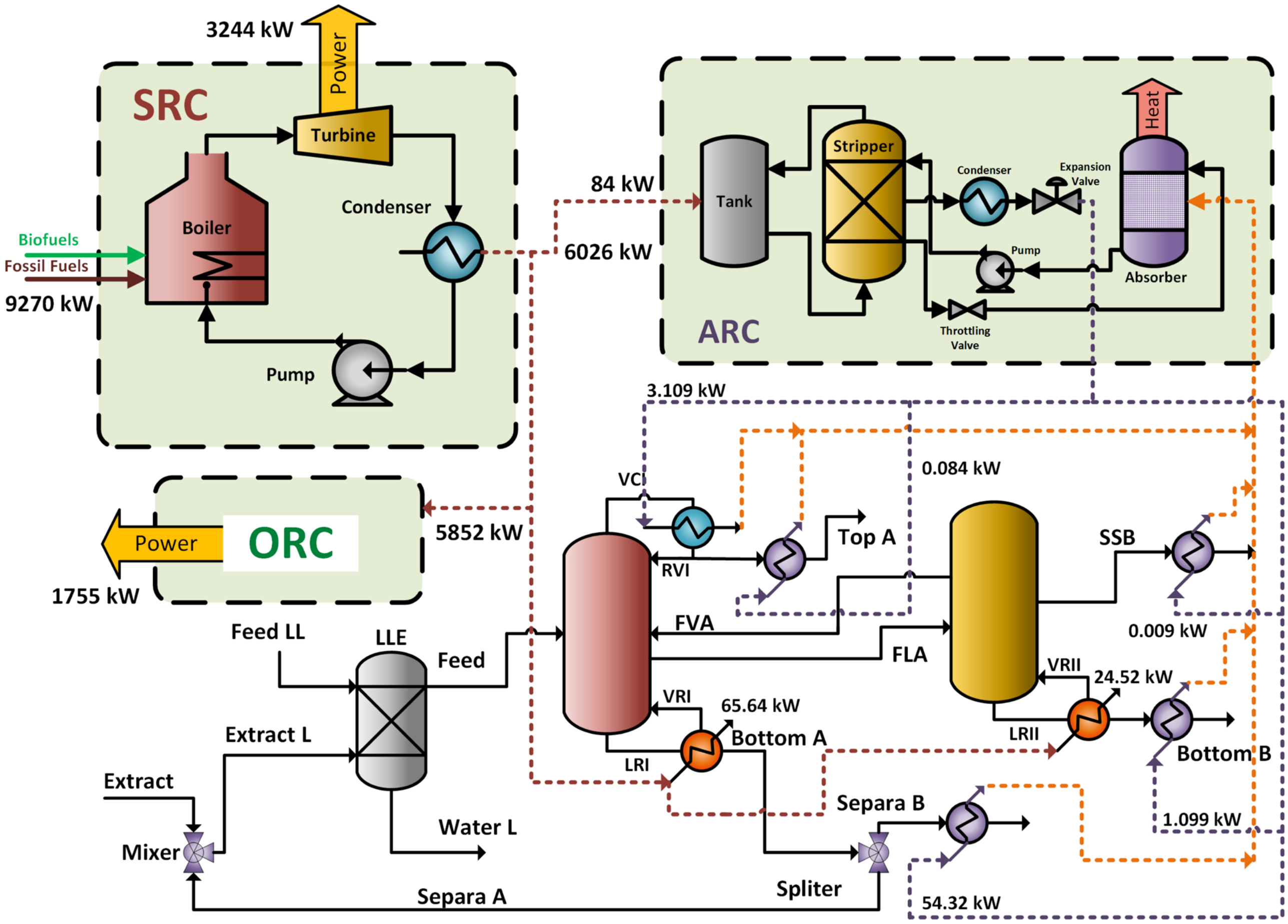

Figure 18. Optimal solution for case 5D.

The optimal solution for case 3A is shown in Figure 7, in which the heating utilities are satisfied by the energy from the SRC while the cooling is performed by the ARC. In this case, the total power sales reach $1,521,949/y, where the total annual cost is $957,434/y mainly for energy sources and the capital cost of the separation sequence, yielding a total annual profit of $734,623/y. For this case, the overall greenhouse gas emissions are 62 739 ton CO_2 equiv/y. Figure 8 shows the optimal solution for case 3B, the fourth column configuration has a total power sales of $1,521,010/y, and the butanol sales are $159,778/y; the key costs include the capital cost ($642/y), fixed cost ($58,604/y), operating costs ($41,017/y), separation sequence cost ($471,446/y), and the cost for energy sources ($459,493/y), yielding a total annual profit of $661,008/y. The overall greenhouse gas emissions for case 3B are 62 597 ton CO_2 equiv/y. Figure 9 shows the optimal configuration for case 3C, in this case the total annual cost is $638,036/y, which yields a total annual profit by $1,055,989/y, and the total greenhouse gas emissions are 62 681 CO_2 equiv/y. Figures 10 and 11 show the optimal configurations for cases 3D and 4A; these configurations yield similar total annual profits by $1,070,554/y and $1,077,750/y respectively; however, there are slight differences in the capital cost and the total power sales. The cases 4B (Figure 12), 4C (Figure 13), 4D (Figure 14), 5A (Figure 15), and 5B (Figure 16) have similar annual profits of around $1,080,000/y; despite their differences in configuration, there is a relationship in terms of energy consumption. Also, the greenhouse gas emissions are similar. Figure 17 shows the optimal solution for case 5C, where the total power sales are $1,523,120/y. In this case, a total annual profit of $1,114,015/y is obtained, the total annual cost is $586,589/y, and 62,916 CO_2 equiv/y of greenhouse gas emissions are generated. Finally, Figure 18 shows the optimal configuration for case 5D; in this configuration, a total annual profit of $1,112,232/y is obtained, the total annual cost is $588,277/y, and the overall greenhouse gas emissions are 62,645 CO_2 equiv/y.

5. CONCLUSIONS

This paper has presented several designs for biobutanol separation from ABE fermentation involving energy integration. The proposed designs were obtained from several separation sequences using a differential evolution method together with the tabu list, and then a HEN for waste heat recovery was implemented for energy integration using organic and steam Rankine cycles as well as an absorption refrigeration cycle. Based on the obtained results, case 5C represents the best economic solution; in this case, the sales of energy and biobutanol as well as the low separation sequence cost yields the best net annual profit. Case 5D is an alternative configuration, where the obtained results are similar to the ones of case 5C; however, there is a slight difference in the configuration, which yields a lower net annual profit. Although in cases 3C, 3D, 4A, 4B, 4C, 4D, 5A, and 5B the results are similar, the results are mainly affected by the separation sequence cost, as shown in cases 3A and 3B, where the costs increase substantially because of the number of columns. The generated configurations are able to take advantage of the lower levels of energy by the incorporation of ARC, ORC, and SRC. The presented configurations permit to identify the optimal heat exchange network, the fuel consumption profile, energy and mass flow rates. Since bioethanol production requires high amount of energy from fossil fuels, the obtained results allow determining attractive solutions from the energetic, economic, and environmental points of view.

It should be noted that large scale biobutanol production is still in development, but the research on biobutanol fermentation and separation stages has been intensified during the last decades and important advances have been achieved. Therefore, biobutanol has emerged as an option for replacing gasoline or as a fuel additive.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b03168.

Detailed information for the identified designs (PDF)

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Notes

The authors declare no competing financial interest.

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