Computer-Aided Design of Intensified Separation Sequences for a Complex Mixture of Renewable Hydrocarbons

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Abstract

In this work, four intensified distillation schemes are presented for the separation of Sustainable Aviation Fuel (SAF) and other biofuels. The intensified schemes include a Petlyuk sequence (PTK) and a double-wall sequence for the separation of three pseudo-components (DDWC-3), as well as a dividing wall sequence (DWC-4) and a double dividing wall column (DDWC-4) for the separation of four pseudo-components. It is important to note that the number of components in the hydrocarbon mixture to be separated is 49, obtained from two ASTM-certified production processes for the production of SAF. These complex designs have been evaluated from its energy requirements, realizing a deep sensitivity analysis in Aspen Plus V.11.0. According to results, 4.85 %, 4.83 %, 7.39 % and 4.08 % of energy savings are obtained from PTK, DWC-3, DWC-4, and DDWC-4, respectively, regarding to direct conventional sequence. The intensified schemes, when compared to the conventional one, demonstrate energy savings in each scenario. However, the DWC-4 scheme stands out by eliminating the need for two reboilers and two condensers, resulting in greater energy savings than other intensified sequences. These proposals are good alternatives for enhance the energetic performance of renewable processes for biofuels production.

**Keywords**: Complex renewable hydrocarbons mixture, process intensification, simulation, sustainable aviation fuel.

* 1. Introduction

Since 2020, due to the pandemic caused by virus SARS-CoV2, the aviation sector has aimed to reduce its environmental impact and achieved sustainable economic recovery (IEA, 2022); including 50 % reduction in CO2 emissions by 2050, necessitating fuels with a lower carbon footprint. In this context, the development of Sustainable Aviation Fuel (SAF) has been actively promoted as a resilient and promising medium to long-term strategy. In this sense, various efforts have focused on reducing the production cost of SAF, primarily linked to the high energy demand in product separation processes.

Gutiérrez-Antonio et al. (2015) pioneered an intensified hydroprocessing method for SAF separation through thermally coupled sequences involving 20 renewable hydrocarbons. This approach yielded a 21 % reduction in energy consumption for the thermally coupled direct sequence compared to the original process developed by UOP Honeywell (McCall et al., 2009). In 2018, a SAF production process using microalgae biomass was proposed, employing a directly thermally coupled sequence for renewable fuel purification. This method achieved a 34 % reduction in CO2 emissions compared to the conventional direct sequence (Gutiérrez-Antonio et al., 2018). Subsequently, Moreno-Gómez et al. (2021) presented modeling, simulation, and intensification of chicken fat hydroprocessing to produce SAF using 30 renewable hydrocarbons for separation. Results indicated that intensified schemes constituted the most favorable scenario concerning environmental and economic indicators. In the same year, energy intensification and integration were performed in the separation zone for the ATJ-SPK process, resulting in up to a 34.75% reduction in energy requirements (Romero-Izquierdo et al., 2021). Following this, Carrasco-Suárez et al. (2022) applied process intensification in the separation zone of a biorefinery scheme for SAF production derived from used cooking oil as raw material, this led to a 3.07% reduction in CO2 emissions and a 66.95% energy savings in the intensified scheme compared to the conventional one. It is evident that intensification proposals for SAF production have yielded energy savings. However, the mixing of renewable hydrocarbons before separation is limited to a specific number of compounds. Therefore, it's essential to consider blends that more accurately represent the real complexity of the issue. This work proposes the intensification of the SAF separation zone using the effluent from two processes: hydroprocessing (HP) and the alcohol to jet (ATJ). This effluent comprises a complex mixture of 49 components (Romero-Izquierdo, 2020), divided into four pseudo-components: light gases, naphtha, sustainable aviation fuel, and green diesel. The proposed separation schemes include four intensified sequences with multiple dividing walls for SAF production.

* 1. Modelling and simulation

According with Romero-Izquierdo (2020), the renewable hydrocarbon mixture to be separated is divided by four pseudo-components: light gases (A), naphtha (B), sustainable aviation fuel (C), and green diesel (D), as shown in Table 1, with their respective distributions and mass flows. The methodology towards intensification begins with the design of the Direct Conventional Sequence (DCS), followed by two thermally coupled distillation sequences: the Petlyuk sequence (PTK) and the three pseudo-component double-wall dividing sequence (DDWC-3). Next, for four pseudo-components: one dividing wall (DWC-4) and double-wall dividing sequence (DDWC-4) were designed, employing BK10 as the thermodynamic model in all cases. For each sequence, rigorous modeling was conducted, accompanied by sensitivity analysis to reduce the energy requirements of reboilers and condensers, achieving 99 % recovery for all key pseudo-components and carried out an average of 300 iterations per sequence. It's important to highlight that reboiler duty minimization was primarily accomplished through interconnection flows for PTK, DDWC-3 and DDWC-4. For the DWC-4 sequence was considered the feed stage as an additional variable apart from the interconnection flows. Also, in order to ensure the comparison of energy requirements, the reflux ratio was established as the main variable that maintained the product compositions in each sequence. Finally, it is worth to mention that the (A) product requires a partial-vapor condenser for the light gases separation, thus, for all designs, this component is obtained as the lighter cut, restricting the indirect distillation designs (Romero-Izquierdo, 2020).

**Table 1.** Renewable hydrocarbons mixture to separate.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Pseudo-compounds** | **Compound** | **Formula** | **Mass Flow (kg/h)** | **Pseudo-compounds** | **Compound** | **Formula** | **Mass Flow (kg/h)** |
|  Light gases (A) | Methane | CH4 | 800.6508 |  | N-Decane | C10H22 | 32232.1754 |
| Ethane | C2H6 | 13677.7170 | N-Undecane | C11H24 | 14911.0443 |
| Propane | C3H8 | 2759.4941 | 2-Methylundecane | C12H26 | 10621.5727 |
| 1-Butene | C4H8 | 483.0010 | 1-Decene | C10H20 | 64.5164 |
| N-Butane | C4H10 | 49719.4538 | 1-Dodecene | C12H24 | 64.5164 |
| Naphtha (B) | 2-Methylbutane | C5H12 | 0.1598 | N-Dodecane | C12H26 | 25452.3104 |
| 1-Pentene | C5H10 | 2.2834 | Cycloundecane | C11H22 | 12.9029 |
| N-Pentane | C5H12 | 42308.8520 | 1-Undecene | C11H22 | 2.2834 |
| 2-Methylpentane | C6H14 | 0.0013 | 1-Tetradecene | C14H24 | 64.5163 |
| N-Hexane | C6H14 | 40390.0284 | N-Tridecane | C13H28 | 5739.7902 |
| 1-Hexene | C6H12 | 357.1645 | 2,2,4,4,6,8,8-Heptamethylnonane | C16H34 | 16864.8346 |
| 2-Methylhexane | C7H16 | 1457.1671 | N-Tetradecane | C14H30 | 42065.2966 |
| 1-Heptene | C7H14 | 2.2834 | N-Pentadecane | C15H32 | 22157.0094 |
| N-Heptane | C7H16 | 10764.8198 | 1-Hexadecene | C16H32 | 64.5165 |
| SAF (C) | 2-Methylheptane | C8H18 | 18984.7220 | 1-Pentadecene | C15H30 | 2.2834 |
| 1-Octene | C8H16 | 273.1774 | N-Hexadecane | C16H34 | 11075.5625 |
| N-Octane | C8H18 | 57652.1169 | Green diesel (D) | N-Heptadecane | C17H36 | 4623.5472 |
| Ethylbenzene | C8H10 | 6.1259 | 1-Octadecene | C18H36 | 64.5164 |
| 3-Methyloctane | C9H20 | 9551.4866 | N-Octadecane | C18H38 | 32503.4317 |
| 1-Nonene | C9H18 | 2.2834 | N-Nonadecane | C19H40 | 4456.0915 |
| N-Nonane | C9H20 | 2725.1832 | N-Eicosane | C20H42 | 6536.7617 |
| Isopropylbenzene | C9H12 | 29.1798 | N-Heneicosane | C21H44 | 29985.1641 |
| 1-Heptadecene | C17H34 | 2.2834 | 1-Nonadecene | C19H38 | 2.2834 |
| N-Propylbenzene | C9H12 | 3.6869 | 1-Eicosene | C20H40 | 64.5164 |
| 3-Methylnonane | C10H22 | 5265.9133 |  |

The design procedure for each sequence is described below. Starting with the Direct Conventional Sequence (DCS) illustrated in Figure 1, each distillation column in the train is designed using shortcut methods (DSTWU module), and then is rigorously simulated using the RadFrac module. From the rigorous modelling of DCS, two thermally coupled sequences are obtained following the methodology of Rong and Errico (2012).

**Figure 1.** Direct Conventional Sequence (DCS).

The design for the Petlyuk column (PTK) is shown in Figure 2, considering the recommendations from Caballero, (2009) and Petlyuk (1965). Initially, a conventional sequence is generated following the methodology presented by Rong and Errico (2012), using the minimum energy requirements for each sequence as the criteria selection. Then, two thermal couplings were performed to form the pre-fractionator, which, through interconnection flows and the movement of sections, generates the main column. The variables considered for the sensitivity analysis are the interconnection flows L1 and V2, in order to reduce the thermal load of the reboilers of C1 and C3.





**Figure 2.** Petlyuk sequence (PTK).

Next, the three pseudo-component double-wall sequence (DDWC-3) was developed for separation. This sequence is designed based on the design parameters of the thermally coupled sequences, involving modifications in the number of stages and interconnection flows, along with the addition of the post-fractionator (C3). The variables included for sensitivity analysis were the interconnection flows: L1, V2, L3, and V4. The DDWC-3 is depicted in Figure 3.



**Figure 3.** Three pseudo-component double-wall sequence (DDWC-3).

The design of the four pseudo-component dividing wall sequence (DWC-4) is shown in Figure 4, derived from thermally coupled distillation sequences, with alterations in the feed stage and the number of stages in both post-fractionators generated through interconnection flows (L1, V2, L3, and V4) and analyzed to reduce the heat duty of C1.



**Figure 4.** Four pseudo-component dividing wall sequence (DWC-4)

The DDWC-4 scheme presented in Figure 5 has been designed based on the chosen parameters obtained from the Petlyuk and quaternary dividing wall sequences (DWC-4). A preliminary design is obtained by adopting the number of stages from the columns, interconnection flow feed stage, and reflux ratio of the base sequences. Subsequent modifications involve adjustments in the feed stage of all interconnection streams and the removal of unnecessary stages from each column. Sensitivity analysis is then conducted to reduce the reboiler duty using interconnection flows (L1, V2, L3, V4, L5, and V6).



**Figure 5.** Four pseudo-component double-wall sequence (DDWC-4).

* 1. Results

Table 2 illustrates the comparison of number of stages, the stage feed, the interconnexion flows and the energy savings obtained regarding to the conventional scheme, for each designed sequence. In the case of DCS the number of stages is 149, this count is lower than the intensified sequences due to additional stages required for separation in those sequences. In most intensified sequences, the feed stage remains constant, except for DWC-4. In DWC-4, the mixture is fed from the stripping section instead of following the norm in other sequences. Moreover, the installation of posfractionators alongside multiple divided wall columns adjacent to corresponding principal column stages is crucial for ensuring efficient operation and maintaining proper flow within the system. In assessing energy savings achieved, each intensified sequence displays varying levels of energy savings in comparison with the conventional sequence. Based on the obtained savings, the DDWC-3 sequence yields the lowest savings of 3.14 % for the condenser and 4.83 % for the reboiler. In contrast, DWC-4 sequence demonstrates the most significant savings, reaching up to 11.06 % and 7.39 % for the condenser and reboiler, respectively. Meanwhile, the DDWC-4 sequence achieves savings of 6.94 % and 4.09 % for the condenser and reboiler, respectively. It is worth to note that the intensified schemes, when compared to the conventional one, demonstrate energy savings in each scenario. Notably, DWC-4 distinguishes itself by eliminating the need for two reboilers and condensers, resulting in the highest energy savings compared to other intensified sequences; its thermodynamic advantages are evident, exhibiting minimal thermodynamic losses in the flow mixture. Finally, it is mentioned that the control and optimization of these sequences are necessary to verify their operability and enhance their efficiency. Undoubtedly, this critical aspect of control and optimization will be the focus of future work, seeking to validate the feasibility and performance enhancements of these sequences in real-world operational environments.

**Table *2*.** Comparison of main results of conventional and intensified sequences.

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| --- | --- |
| **Parameters** | **Sequences** |
| DCS | PTK | DDWC-3 | DWC-4 | DDWC-4 |
| Number of stages | 149 | 171 | 216 | 207 | 255 |
| Condenser duty (MW) | - 71,77 | - 64.64 | - 69.52 | - 63.83 | - 66.79 |
| Energy savings (%) | - | 9.94 % | 3.14 % | 11.06 % | 6.94 % |
| Reboiler duty (MW) | 102.01 | 97.05 | 97.01 | 94.46 | 97.83 |
| Energy savings (%) | - | 4.85 % | 4.83 % | 7.39 % | 4.08 % |

* 1. Conclusion

In this work has been presented four intensified proposals for separating SAF from a complex mixture of 49 renewable hydrocarbons. The intensified schemes, when compared with the conventional scheme, demonstrate the technical feasibility and energy savings in each case. Among these, the double-wall sequence (DWC-4) sequence stands out by avoiding the use of two reboilers and two condensers, resulting in greater energy savings compared to the other intensified sequences. DWC-4 could be utilized as a promising sequence for separating SAF due to the energy savings of 11.06 % and 7.39 % in condenser and reboiler, respectively, resulting in the highest energy savings compared to other intensified sequences. The successful implementation of these intensified sequences relies on robust control mechanisms and optimized configurations to ensure operability and maximize efficiency. Further exploration and refinement in the control and optimization of these sequences are essential steps toward realizing their potential in practical applications.

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