Delft University of Technology

Enhanced downstream processing of NGL using intensified fluid separation technologies

Bosman, Danforth Brandon; Li, Qing; Kiss, Anton A.

DOI
10.1016/j.energy.2024.131186

Publication date
2024

Document Version
Final published version

Published in
Energy

Citation (APA)
Bosman, D. B., Li, Q., & Kiss, A. A. (2024). Enhanced downstream processing of NGL using intensified fluid separation technologies. *Energy*, *296*, Article 131186. https://doi.org/10.1016/j.energy.2024.131186

Energy 296 (2024) 131186

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Enhanced downstream processing of NGL using intensified fluid separation technologies

Danforth Brandon Bosman [a,b], Qing Li [a], Anton A. Kiss [a,*]

[a] Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ, Delft, the Netherlands
[b] Baker Hughes, PBF Torrance Refinery, 3700 W 190th St, Torrance, CA, 90504, USA

ARTICLE INFO

Handling editor: Wojciech Stanek

Keywords:
Fluid separation
Process intensification
Dividing-wall column
Heat pumps
Sustainability

ABSTRACT

Downstream processing of natural gas liquids (NGL) provides feedstock needed for plastic production, upgraded fuels and heating, but it is one of the largest high-pressure and energy intensive processes. This original study is the first to integrate novel process intensification options from a holistic viewpoint for the full process covering all sections: 1) NGL recovery, 2) NGL fractionation, and 3) isomerization. Intensified fluid separation technologies (e.g. complex columns, thermal coupling, and heat pumps) are explored and integrated into a full NGL process to improve the energy efficiency and mitigate GHG emissions, and to establish the limits of operation, utility usage, and specific product costs. All NGL processes are rigorously simulated in Aspen Plus, and evaluated based on a fair economic and sustainability analysis.

The enhanced recycle split vapor process for NGL recovery results in a full heat recovery for the reboiler of the demethanizer (2.9 MW energy savings), while the enhanced gas subcooled process results in 17.9% reduction of the refrigerant duty, 20.2% reduction of the electrical duty, and 19.9% reduction of the total utility cost. For the NGL fractionation section, heat pump assisted double dividing wall process improves energy intensity for a fraction of the utility cost although requiring external incentives (e.g., carbon tax) to become commercially viable. The total utility costs as well as GHG emissions are reduced up to 30% and 49%, respectively, while the specific product cost reduces to $23.45/t or $24.38/t with carbon tax. The heat pump assisted recycled isomerization process for the last section increased AKI from 65.3 to 89.6, with 19.1% reduction of utility usage and 42.4% reduction of carbon emission.

1. Introduction

With the existing energy infrastructure as well as the petrochemical foothold on the chemical industry, the transition to a fossil fuel free industry will likely be slow and costly. As of 2019, 84.3% of global energy comes from fossil fuels, a decrease of 1.8% from the year 2000 [1]. Despite providing 22.4% of global energy, the relative percentage of CO_2 emissions is only 21.3% for natural gas, making it the only fossil fuel to emit less of a percentage than energy provided. Prior to natural gas being commercially available for industrial and residential use, raw natural gas must first be refined in one of the most energy-intensive processes. Process intensification of this large-scale high-pressure cryogenic process could help mitigate carbon emissions (and related economic penalties) realized by companies in their transition to greener technologies and practices (e.g. electrification of industry).

Depending on the composition of the natural gas, the heavier hydrocarbons of natural gas called natural gas liquids (NGL) are typically dried from the methane predominant sale gas to meet pipeline and product specifications. Currently, shale gas is being introduced into the market as rich natural gas due to its high composition of NGL. Since NGL consist of ethane, propane, butanes, and natural gasoline (C5+ components), new gas refineries are being set up to extract these inherently higher value products.

In the past, the oil absorption process was commercially used to recover around 75% of butane and 85–90% of pentane and higher. With the increased ethane demand for plastic production, as well as being a

---

* Correspondingauthor.
E-mail addresses: TonyKiss@gmail.com, A.A.Kiss@tudelft.nl (A.A. Kiss).

https://doi.org/10.1016/j.energy.2024.131186
Received 21 August 2023; Received in revised form 2 March 2024; Accepted 1 April 2024

petrochemical feedstock, most industries have switched their NGL recovery section to cryogenic distillation since 95% of ethane can be recovered from the sale gas [2]. For reference, the volumetric throughput of this NGL process section is in the range of 5.95–59.5 million standard cubic meter (SCM) per day [2]. Depending on the feed composition, product specifications, energy costs, and the needed operational flexibility, different types of configurations such as gas subcooled process (GSP) or recycle split vapor (RSV) can be justified. The difference between the GSP and RSV configurations is the partial recycling of pressurized sale gas [3]. Islamm et al. [4] and Usman and Pervaiz [5] compiled together many configurations for the NGL recovery section in order to provide a techno-economical overview. Yet, the focus of these research or reviews is on the demethanizer for NGL recovery only, without considering the following NGL fractionation as well as the isomerization from a holistic viewpoint. Also, there are no reported researches that rigorously simulate the RSV and GSP configurations and study the economic benefit of using the ethane recovery and rejection modes of RSV to GSP.

After recovering the NGL stream at the bottom of the demethanizer, this stream is then fractionated over a series of distillation columns into the desired products (ethane, propane, isobutane, n-butane, and natural gasoline). In recent years, several intensified technologies for fluid separations – e.g. dividing wall column (DWC), heat pump assisted distillation, thermally coupled distillation – have had relative success in reducing utility demands as well as capital expenditure by minimizing unnecessary component mixing or upgrading the stream energy level with a reasonable temperature lift [6]. Long and Lee [7] investigated the use of a DWC for NGL fractionation and reported that a double DWC configuration (to replace the depropanizer, debutanizer, and deisobutanizer) had the most energy savings of 28.74%. In a separate study, they also found out that the implementation of heat pump assisted distillation for the debutanizer and deisobutanizer columns [8] can improve the energy efficiency of distillation columns – which are ineffective heat engines [9] – by upgrading the low quality heat rejected at the condenser and reinserted as high quality heat in the reboiler using heat pumps. Further, applying heat pumps to the intensified DWC process shows promising benefits for the NGL fractionation, yet Long and Lee [7, 8] did not further explore the integration of heat pumps and DWC for the entire NGL fractionation section to enhance the energy efficiency. One other technique that could reduce overall utility use is the external thermal coupling of columns, where elements directly heat each other which minimizes thermal losses across mediums. Becker's group developed a patent for the thermal coupling of the deethanizer to a DWC depropanizer, yet they did not provide an indication of performance [10]. More recently, Li et al. [11] proposed a new method for the process synthesis and optimization of energy integrated advanced distillation sequences, using NGL fractionation as a case study and determining the most energy effective sequences, but the interaction of the previous NGL recovery section or the following octane upgrading are not considered. Qyyum et al. [12] reviews many research studies on the NGL process, and reveals that there are no previous studies that explore the interactions among different sections.

In order to upgrade the octane rating of natural gasoline, isomerization is needed after the NGL fractionation section. One of the most profitable methods of increasing the octane rating of gasoline to prevent uncontrolled combustion from knocking is to convert the linear components into their isomers. In the past, the main method of performing this equilibrium limited reaction was to use a chlorinated alumina catalyst, which required specialized equipment to handle hazardous components and was extremely sensitive to catalytic poisoning. Recently, there has been a shift towards zeolites and sulfated metal oxides that have high activity, resistive to catalytic poisoning, and are regeneratable catalysts [13]. With most of research focused either on the kinetics of reaction or on the improvement of traditional heat recovery of the entire process, there is no available research available that explores any intensified technologies (e.g. heat pumps) in this final section, especially for the deisopentanizer column prior to isomerization.

Therefore, the original contribution of this work is to develop an energy-efficient and cost-effective complete process for the NGL separation from a holistic point of view, considering the interactions between systems components in terms of material and energy recycles – i.e. separate methane (C1) from raw natural gas; separate individual NGL subcomponents (C2, C3, iC4, nC4 and C5+); and C5+ gasoline isomerization – in order to provide a full optimized process, in contrast to conventional methods which focus on the smaller sub-systems only. To achieve a more energy efficient process, and to reduce capital expenditures, operating expenses and carbon footprint, several intensified fluid separation technologies (such as thermal coupling, complex columns, and heat pumps) are evaluated and integrated as part of a large process flowsheet with energy/mass recycles for the three sub-sections of the NGL process. Additionally, this paper aims to systematically provide a fair comparison on the same basis for all intensified techniques on the NGL separation process in terms of economic indicators (e.g. total capital investment and operating cost) and sustainability metrics (e.g. material/energy intensity, GHG emissions).

2. Design and simulation approach

A typical plant processing capacity of 3016 ktpy (377 t/h = 15,000 kmol/h) is considered in this work. Since the feed comes after the pretreatment of natural gas (desulfurization and dehydration) it will be pressurized at 50 bar and have a temperature of 15 °C. As a large percentage of natural gas sources will be sourced from shale gas in the future, a rich composition of NGL was considered in the feed, namely: 75.5 mol% C1, 11.1 mol% C2, 7.0 mol% C3, 1.9 mol% iC4, 1.2 mol% nC4, 3.2 mol% C5+, 0.1 mol% H_2S, similar to literature reports [14]. All the product pressures and temperatures were determined considering a 3.5 bar overpressure above the respective vapor pressure to keep the product liquid near atmospheric temperature. The following generic product stream purities were considered (in line with literature data): ethane 95 mol%, propane 98 mol%, isobutane 97 mol%, normal butane 95 mol%, and natural gasoline 99 mol% [12].

The full process was rigorously simulated using Aspen Plus V12. As suitable property model, the Peng-Robinson equation of state was used, being highly reliable for gas-processing applications. Initial data from DSTWU shortcut models (e.g. number of stages, feed location, and reflux rate) were used as input data for the RadFrac units used for rigorous simulations. A generic pressure drop of 0.1 psi or 6.9 mbar per stage was used [15]. The optimization of simple columns was performed using NQ plots (number of stages versus reboiler duty). This Aspen Plus feature utilizes a defined energy cost set between the utilities used in the condenser and reboiler to minimize the total objective utility cost while varying the number of stages and feed stage location. The maximum number of stages was set at 92 stages due to construction logistics and operational feasibility. Each distillation column was rigorously simulated and optimized to fit the smart design principle where columns are slightly oversized to provide operational flexibility and utility savings [16]. For the modelling of DWCs, multiple RadFrac units were arranged in a Petlyuk configuration, which is thermodynamically equivalent to a DWC, to generate temperature and composition profiles to initialize the MultiFrac unit [17]. The final rigorous simulations were based in MultiFrac due to its robust ability to provide continuous profiles of temperatures, compositions, and flowrates in a distillation column while maintaining design specifications via the control of process variables (product flowrates, condenser duty, reboiler duty).

Mechanical vapor recompression (MVR) heat pump was selected and rigorously modeled as it is the most commercially viable heat pump for this scale of production that does not introduce water into the system and has a higher heat recovery efficiency as compared to traditional vapor compression [16,18,19]. To avoid unnecessary vapor recompression, a bypass valve was implemented to redirect unused vapor while maintaining an exit vapor fraction of 0.05 for the column's reboiler. To quantify the effectiveness of each heat pump, the coefficient of performance (COP) was evaluated as the heat recovered divided by the work input [20]. To find the optimal pressure ratio for the compressor (and thus the COP), the log mean temperature difference (LMTD) between the heat sinks and the heat sources was determined based on the trade-off between equipment expenditure (e.g. cost of heat transfer surface area) versus energy savings [21].

The two essential sections of heat recovery in the initial NGL recovery section that makes cryogenic distillation profitable are the Coldbox and the Coolbox. The Coldbox is a series of heat exchangers inside a refrigerated container that pre-cool the feed using refrigerants and internal slipstreams [22]. The Coolbox is the overhead Coldbox that uses the demethanizer overhead to sub cool the reflux stream prior to re-entry to the column. The MHeatX (multiple heat exchanger) model was used since it can build stream/heat profiles via the use of multiple pinch analyses for optimal heat exchange. The number of zones decided for the Coldbox was 5 and for the Coolbox was 1 since this allowed for a sufficient cost-effective LMTD used for sizing the heat exchangers.

For the isomerization of natural gasoline, the Aspen Plus yield reactor was used (see details in the *Supplementary Information* file). Considering a 75 mol% n-Pentane and 25 mol% n-Hexane feed into the reactor, the product distribution reported by Rabo's group was followed considering a 37 s contact time and weight hourly space velocity of 2 kg of reactant flow per kg of catalyst per hour [23]. The reaction occurs at 350 °C and 31 bar in a fixed bed reactor. Prior to entering the reactor, the reactor feed is saturated with a 3:1 M ratio of hydrogen gas to feed to prevent coking of the catalyst. The catalyst in use is Catalyst MB 5390, which is a zeolite type catalyst with a density of 720 kg/m^3. Anti-Knock-Index (AKI) values per component were taken from the literature [24].

The following utility energy costs were considered based on literature recommendations [15]: refrigerant(-34 °C) = \$13.17/GJ, refrigerant(-12 °C) = \$6.47/GJ, cooling water = \$1.29/GJ, Low Pressure Steam (LPS) = \$6.22/GJ, medium pressure steam (MPS) = \$7.67/GJ, natural gas = \$5.22/GJ, and electricity = \$19.44/GJ.

3. Results and discussion

3.1. Process design and simulation

This part covers the main results related to the three sections of the process, namely the NGL recovery (1), NGL fractionation (2), and natural gasoline isomerization (3) – each of them including various process configurations, as illustrated in Fig. 1 and described hereafter. The detailed mass and energy balances, along with the heat duties, Aspen Plus flowsheets, equipment sizing and costing are provided in the *Supplementary Information* file.

3.1.1. Section 1: NGL recovery

The base case of the NGL recovery process is taken from the process set-up and parameters of the RSV configuration with propane refrigerant configuration from Jiang et al. [14], as shown in Fig. 2. The major contrast in operation is that the compressed sale gas (Stream 16) was rerouted to the demethanizer reboiler for internal heating, thus the duty of the reboiler of demethanizer has been saved (2.9 MW in LPS cost). The second large change in operation is the exit temperature of Stream 14 since it has to be increased to above freezing conditions to prevent external condensation on the compressor, resulting in equipment damage over time. Due to the internal refrigeration streams (Streams 24 to 29), only 8 MW of propane refrigerant is needed in the refrigeration cycle for the pre-cooling of gas feed and 12.9 MW of electrical duty to recompress the sale gas to a suitable pressure and temperature to begin the liquefication process needed for liquefied natural gas (LNG). The annual utility cost is estimated to be \$10.3 million. The bottom of the demethanizer is then transferred to the NGL fractionation section for the full separation of NGL products.

Using the same equipment as in the RSV configuration, the GSP configuration for the ethane rejection mode was accomplished by closing Stream 20 and rerouting Stream 10 to the reflux tray of the demethanizer. Since there is no traditional reflux being re-entered into the demethanizer, none of the sale gas is redirected back in the system which lowers the overall flowrate in the system, reducing the electrical duty of the compressor as well as the needed refrigerant for pre-cooling. At 79 mol% recovery of ethane in the NGL bottom stream, the recovery of propane began to exponentially decrease. At that point, 99.5 mol% of propane recovery was achieved in the NGL stream, reducing overall refrigerant duty by 1.43 MW (17.9%), the electrical duty by 2.6 MW (20.2%), and total utility cost by \$2.05 mln (19.9%).

3.1.2. Section 2: NGL fractionation

The base case model (Configuration 2.1) is a direct sequence of simple distillation columns (Long, 2011; [11]) until the debutanizer

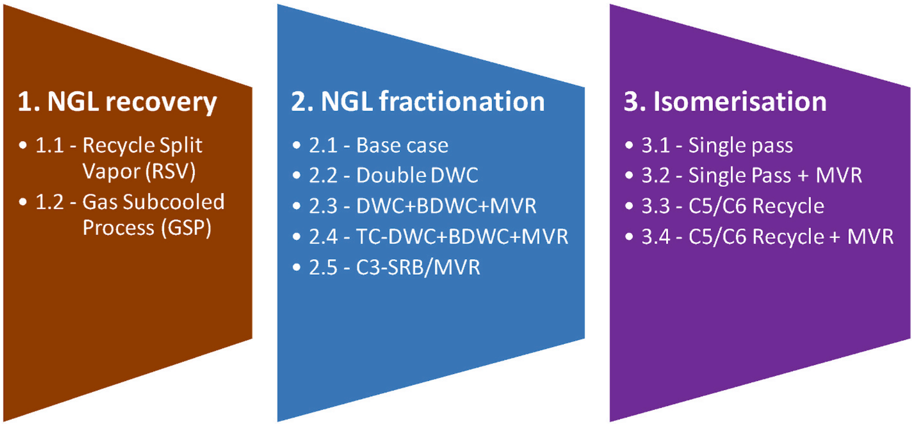


Fig. 1. Overview of the NGL process sections and configurations.

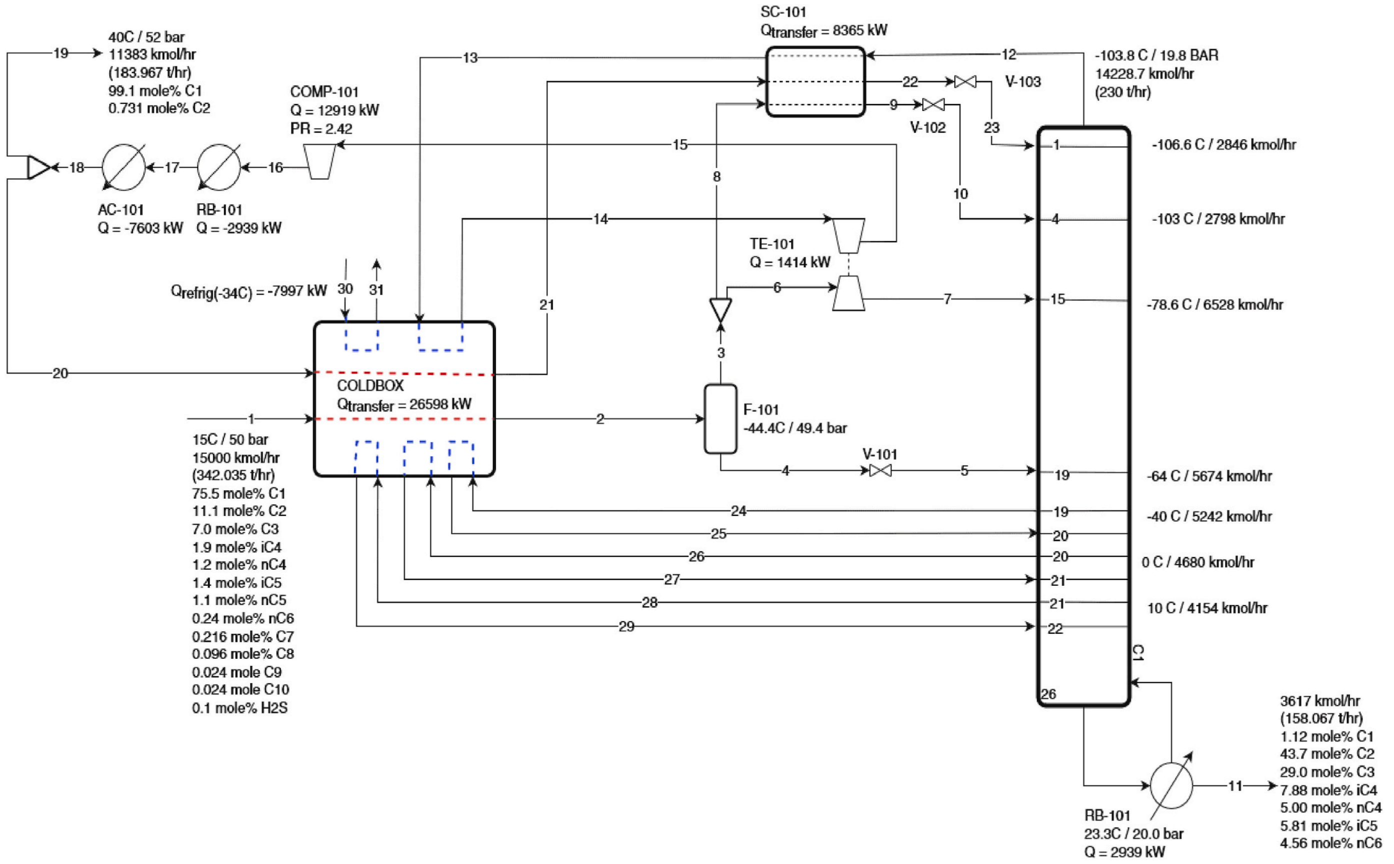


Fig. 2. PFD of proposed NGL recovery section using a Recycle Split Vapor (RSV) Configuration (Configuration 1.1).

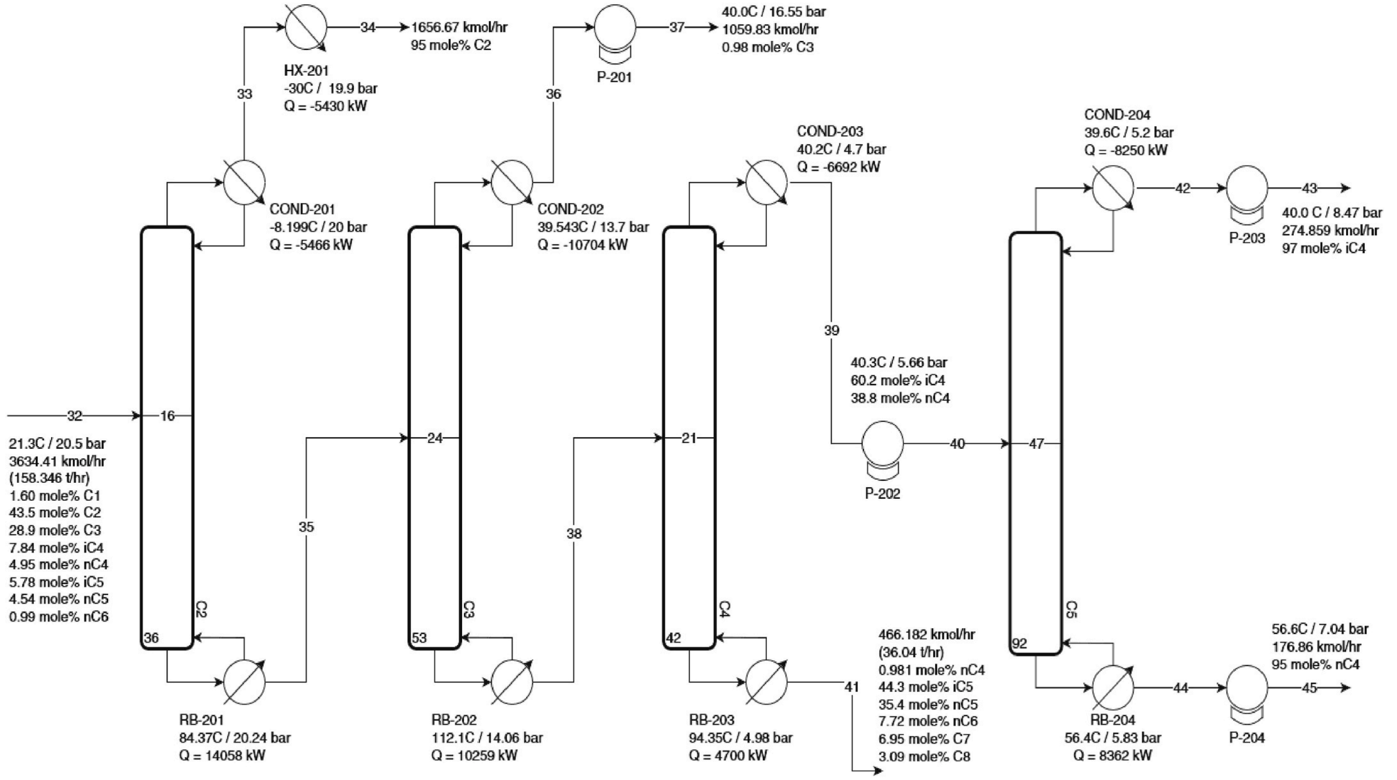


Fig. 3. NGL fractionation PFD of the base case (Configuration 2.1).

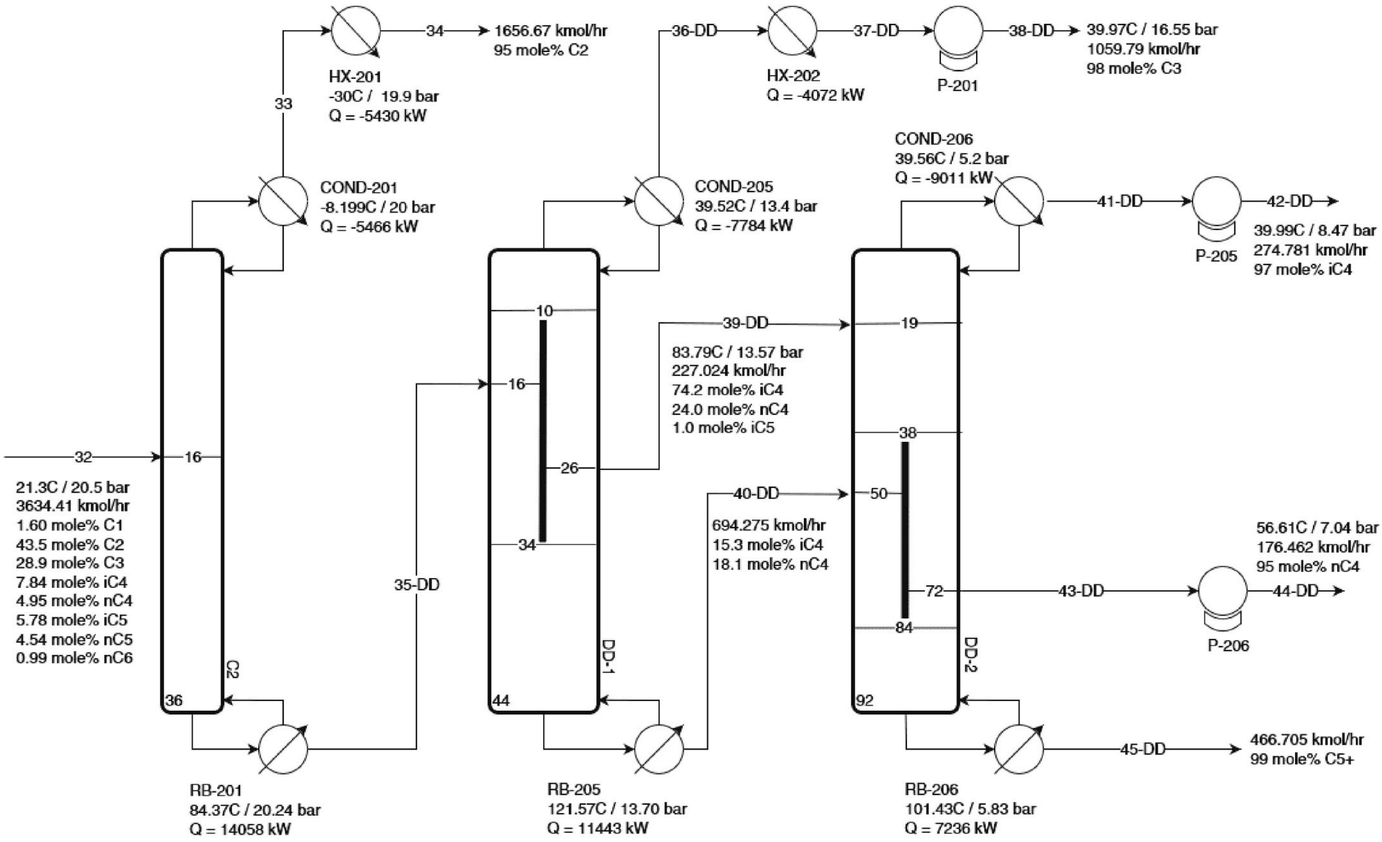


Fig. 4. NGL fractionation PFD of DDWCs (Configuration 2.2).

(C4), where the distillate is fed into a deisobutanizer (C5), as shown in Fig. 3. All columns were set to operate at the lowest pressure that allowed cooling water to be used, except for the deethanizer. The deethanizer was operated at 20 bar to accommodate the cheapest refrigerant available. For a total of 37.4 MW of LPS, −5.43 MW of Ref (−34 °C), −5.47 MW of Ref (−12 °C), and −25.6 MW of Cooling Water, the base case utility cost was estimated to be $10.7 million per year.

Several other intensified process alternatives were proposed and

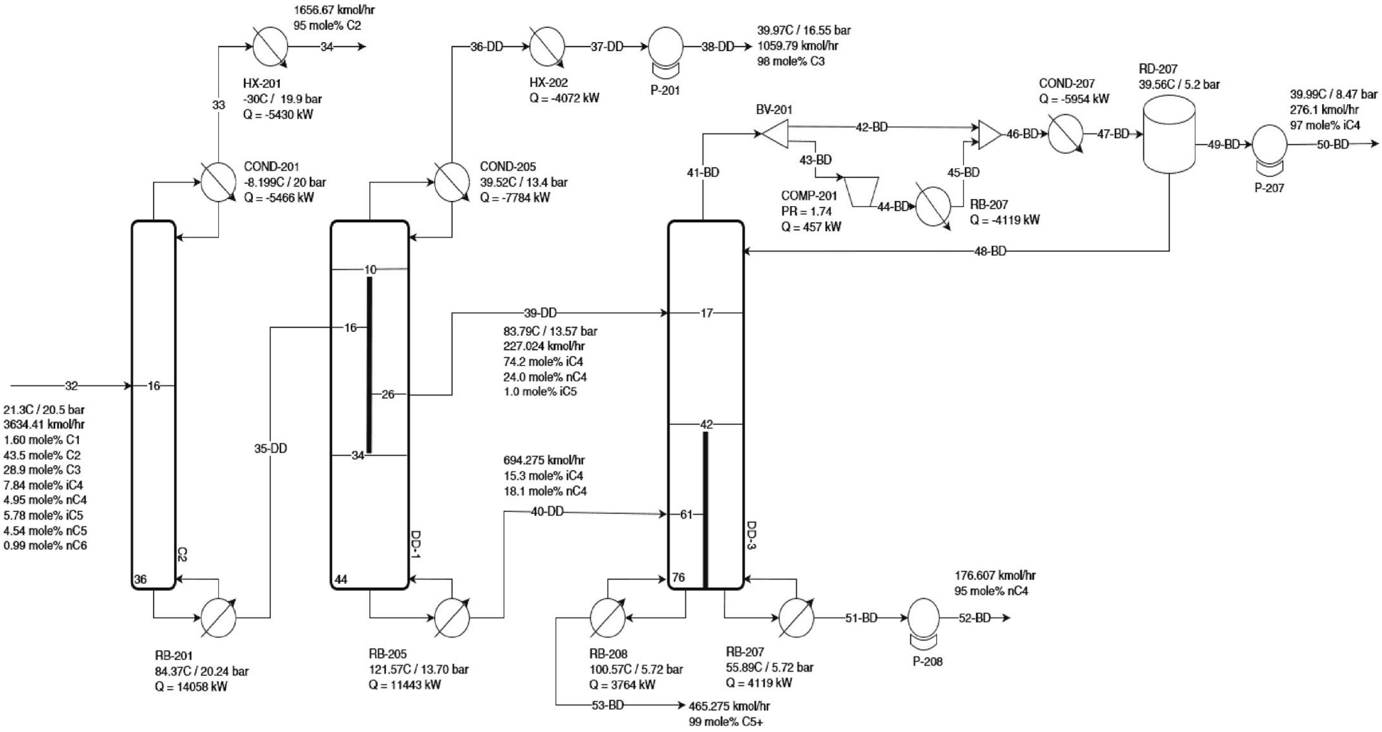


Fig. 5. NGL Fractionation PFD of DWC and BDWC with an MVR heat pump (Configuration 2.3).

evaluated for this section.

- Double DWC (Configuration 2.2), as shown in Fig. 4, by letting the first DWC act as a prefractionator for the second DWC, there is less overall intermixing of components. Based on the units replaced, LPS duty decreases by 4.6 MW (19.7%), cooling water duty decreases by 4.7 MW (18.4%), and utility cost decreases by $1.01 million/yr (19.6%).
- Mechanical Vapor Recompression (MVR) heat pump assisted Bottom Dividing Wall Column (BDWC) – which replaces the second DWC of Configuration 2.2 – as shown in Fig. 5 (Configuration 2.3). With a coefficient of performance (COP) of 9.01, heating and cooling duty is reduced by 8.1 MW (34.8%) and 7.8 MW (30.5%), respectively. This configuration performed the best in terms of annual utility cost, reducing the utility cost by $1.51 million/yr (29.5%). Due to the high temperature difference (50 °C) across the wall of the BDWC, the dividing wall needs to be insulated via a vacuum separated wall.
- Thermal coupling of the deethanizer to the first DWC of Configuration 2.3, as shown in Fig. 6 (Configuration 2.4). This configuration places the reboiler duty of the deethanizer onto the reboiler of the depropanizer, bypassing heat transfer inefficiencies of using another reboiler. Due to the high pressure required in the deethanizer, a compressor is needed to recompress the vapor drawn from the lower pressure depropanizer. If the pressure of depropanizer were increased so a compressor is not needed, the energy requirement is greater than the savings had. In the base case, only the deethanizer needed to be rated to handle the hydrogen sulfide concentration. With thermal coupling, the diameter size of the DWC was increased (4.5 m→7.1 m) and in combination with having to use stainless steel as well as a compressor, the equipment cost significantly increases. With no significant change in refrigerant duties, the effective COP of Comp-202 is 2.06, increasing the utility cost by $210K as compared to the non-thermally coupled version.

3.1.3. *Section 3: isomerization*

For this section, a single pass process (Configuration 3.1) and a pentane/hexane recycled isomerization process (Configuration 3.3) were set up similarly to the one described by SIE Neftehim [13,25]. Further, the single pass process is integrated with a deisopentanizer MVR (Configuration 3.2), while the C5/C6 recycled isomerization is also enhanced with a deisopentanizer MVR (Configuration 3.4). The natural gasoline feed into this section has an AKI of 65.3. For single pass isomerization, the highest achievable COP for an MVR heat pump on the deisopentanizer was found to be 5.58, saving $877k (24.9%) in utility. The isomerate product stream had its AKI raised to 84.2 with a total section utility cost of $3.52 million, as shown in Fig. 7. When n-pentane and n-hexane are recycled back into the isomerization reactor, the resulting isomerate AKI was found to be 89.6 at a total utility cost of $7.07 million, as shown in Fig. 8. This includes a COP of 4.92 for the MVR heat pump on the deisopentanizer, saving $1.23 million (19.1%) in utility cost.

3.2. *Economic analysis*

To perform the economic analysis used to justify the introduction of complex columns and heat pumps, a variety of purchase cost metrics were used to estimate the total capital investment (TCI) and the operating cost. Following the purchase cost correlations from the literature, the TCI for the construction of the plant was determined via the Lang Method, which gives an accuracy of ±35% [15]. Using the *Chemical Engineering Plant Cost Index* (CEPCI) of 607.5 in 2019, the estimated purchase price can be comparable to pre-COVID work [26]. To calculate the total operating cost, direct cost, indirect cost, plant overhead, and various general expenses for administration and financing had to be accounted for, as described in the *Plant Design and Economics for Chemical Engineers* [27]. Considering 8000 operating hours per annum, the base operating cost was calculated considering 10% depreciation on equipment. After dividing the total operating cost by the total product amount, the Specific Product Cost (SPC) was calculated as the final metric to provide a standardized overall cost of production (e.g. $ per tonne throughput). Table 1 and Fig. 9 provide an overview of the annual utility cost, total capital investment (TCI), annual operating cost, and SPC per each section of the NGL process. For the detailed equipment breakdown (sizing and costing), please refer to the *Supplementary*

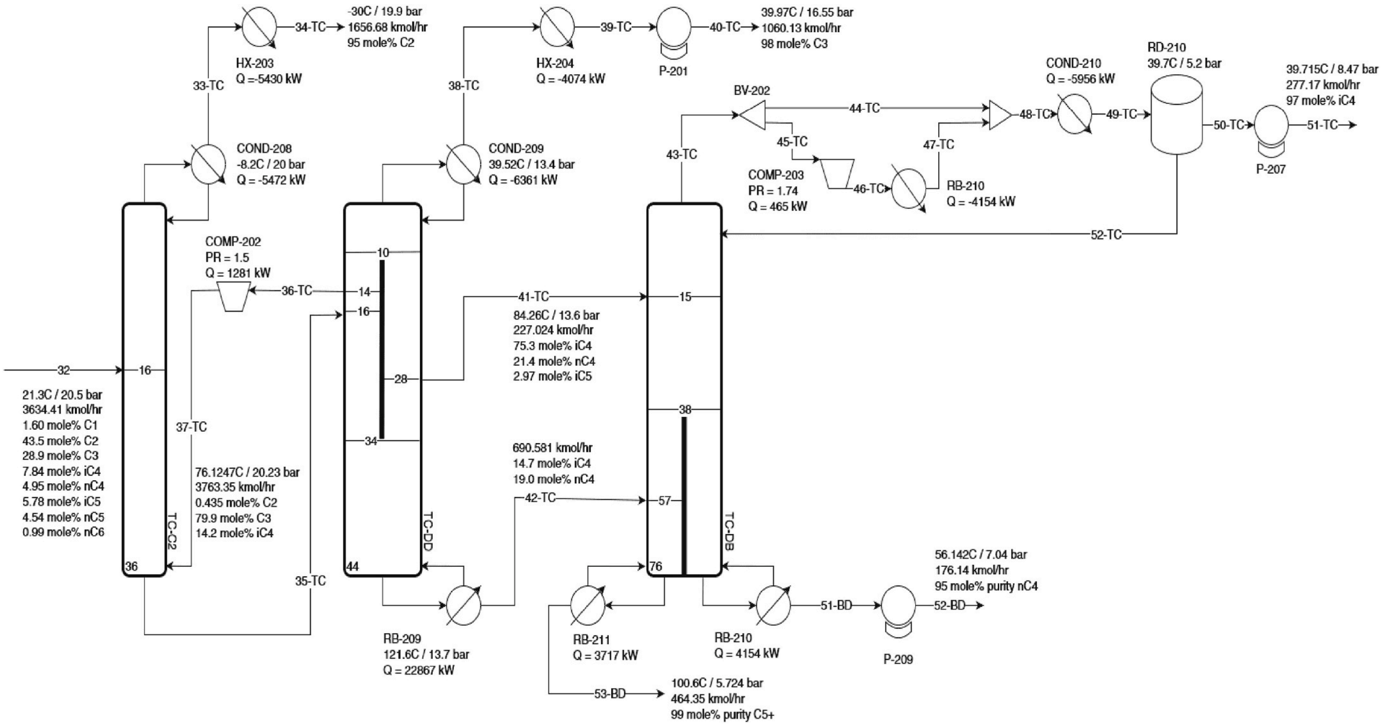


Fig. 6. PFD of thermal coupling deethanizer to DWC and BDWC with an MVR heat pump (Configuration 2.4).

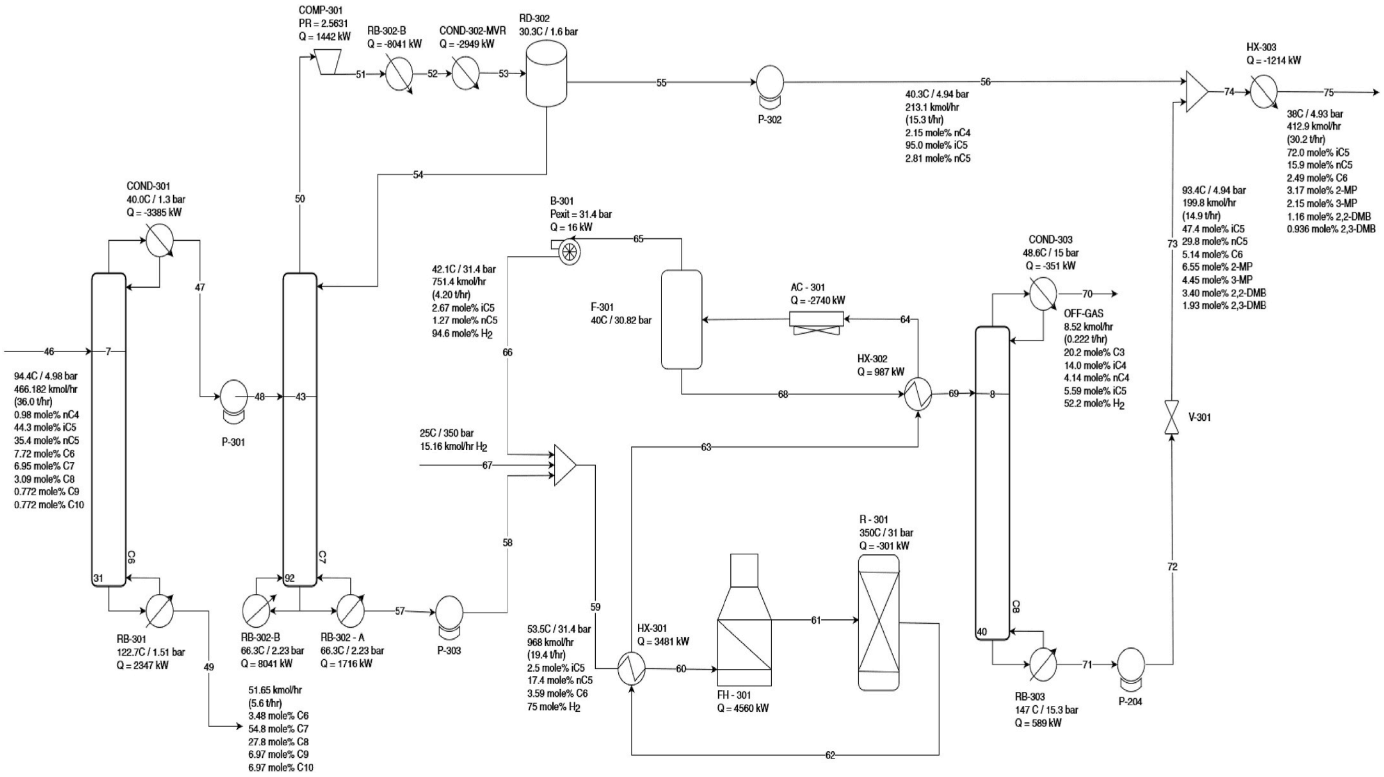


Fig. 7. PFD of natural gasoline isomerization single pass with an MVR heat pump placed on the deisopentanizer (Configuration 3.2).

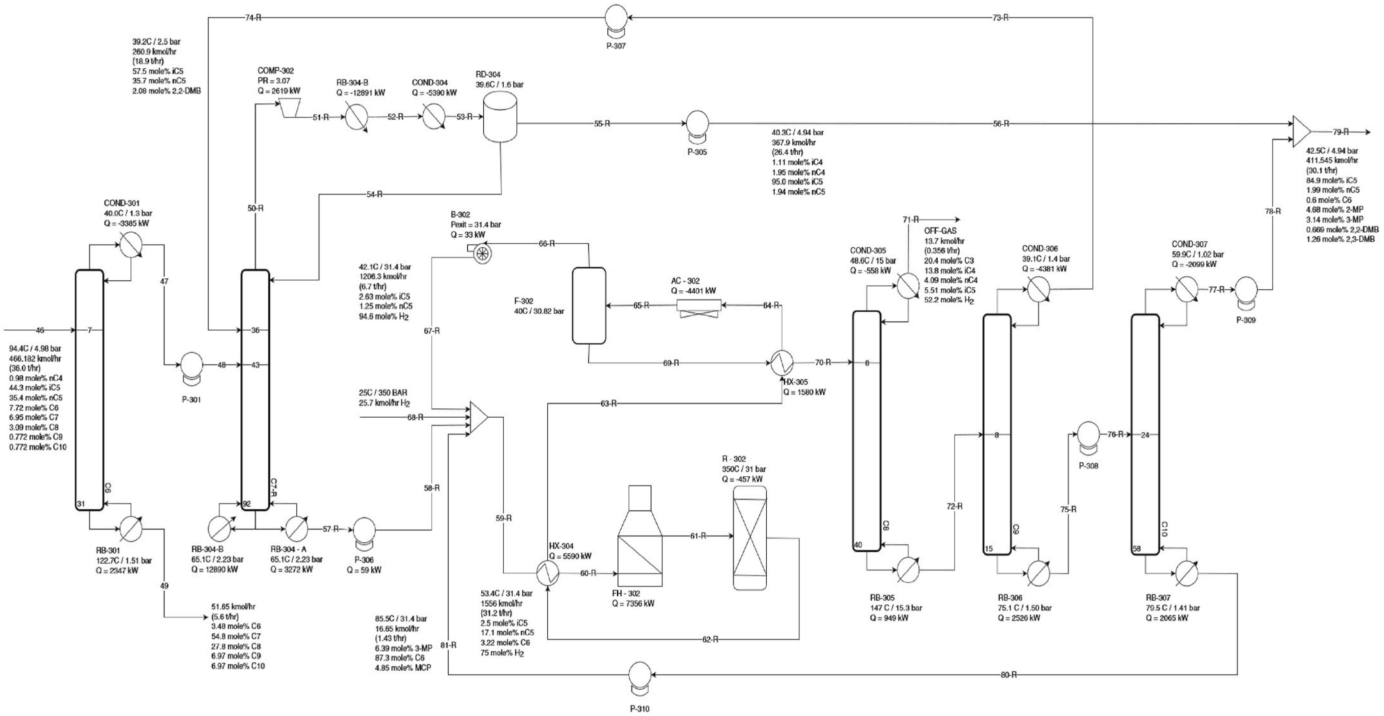


Fig. 8. PFD of natural gasoline isomerization with recycle stream and an MVR heat pump on the deisopentanizer (Configuration 3.4).

Information file.

For the NGL recovery section, the base TCI was estimated to be $142 million. With the RSV process parameters set to recovery 95 mol% of ethane in the NGL bottom stream, the SPC is $16.56 per tonne throughput. When switched to the GSP process parameters, this SPC drops to $15.74 per tonne throughput. However, for the switch in configuration to be worth the utility savings, the price of ethane must be within 4.94% of the price of sale natural gas.

For the NGL fractionation section, the base case (configuration 2.1) has a TCI of $26.6 million at an SPC of $15.93/t. For the double DWC (configuration 2.2), the TCI drops to $26.0 million with an SPC of $14.59/t, making this the least costly overall process alternative. The

Table 1
Annual utility cost, total capital investment (TCI), annual operating cost, and specific product cost (SPC) per each section of the NGL process.

Sections & Configurations	Annual cost of utilities (M$/yr)	TCI (M$)	Annual operating cost (MS/yr)	SPC without carbon tax ($/t)	SPC with carbon tax ($/t)
(1.1) NGL Recovery: RSV	10.3	142.0	45.3	16.56	16.56
(1.2) NGL Recovery: GSP	8.3	142.0	43.1	15.74	15.74
(2.1) NGL-Fractionation: Base	10.7	26.6	20.2	15.93	18.50
(2.2) NGL-Fractionation: DDWC	9.7	26.0	18.5	14.59	16.88
(2.3) NGL-Fractionation: DWC + BDWC + MVR	9.2	29.1	18.9	14.89	16.90
(2.4) NGL-Fractionation: TC-DWC + BDWC + MVR	9.4	62.8	26.7	21.08	22.83
(2.5) NGL-Fractionation: C3-SRB/MVR	10.6	29.7	21.0	16.60	18.99
(3.1) Isomerization: Single Pass	3.5	39.4	16.7	58.31	63.35
(3.2) Isomerization: Single Pass with deisopentanizer MVR	2.6	45.4	17.3	60.33	62.93
(3.3) Isomerization: C5/C6 Recycle	6.4	62.6	26.6	92.64	101.88
(3.4) Isomerization C5/C6 Recycle with deisopentanizer MVR	5.2	66.1	26.2	91.70	97.03

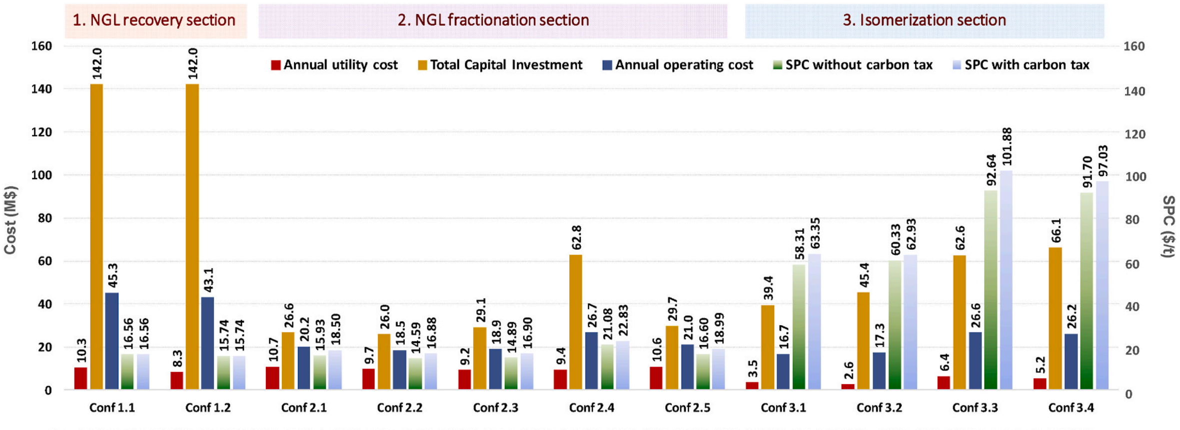
Note: (1.1) NGL Recovery - RSV (1.2) NGL Recovery - GSP (2.1) NGL Fractionation – base case; (2.2) NGL Fractionation - DDWC (2.3) NGL Fractionation - DWC + BDWC + MVR (2.4) NGL Fractionation - TCDWC + BDWC + MVR (2.5) NGL Fractionation - C3-SRB/MVR (3.1) Isomerization - Single Pass (3.2) Isomerization - Single Pass with deisopentanizer MVR (3.3) Isomerization - C5/C6 Recycle (3.4) Isomerization - C5/C6 Recycle with deisopentanizer MVR.
Utility Energy Cost: Refrigerant(-34 °C) = $13.17/GJ, Refrigerant(-12 °C) = $6.47/GJ, Cooling Water = $1.29/GJ, Low Pressure Steam = $6.22/GJ, Medium Pressure Steam = $7.67/GJ, Natural Gas = $5.22/GJ, Electricity = $19.44/GJ.

second-best alternative based on cost is the heat pump assisted one (configuration 2.3). With a more expensive TCI of $29.1 million, the SPC of operating is $14.89/t. Since this configuration cost more than the base case but realizes larger savings, the savings payback time to the base case is only 1.83 years. The proposed option (configuration 2.4) for this section is the thermal coupled deethanizer of the previous configuration, requiring a significant TCI of $62.8 million. Notably, the hydrogen sulphide concentrations require more equipment to be made of stainless steel versus the cheaper alternative of carbon steel. With the increased column diameter from 3.3 m to 7.1 m for the depropanizer to account for increased vapor flow, the SPC of this configuration is raised to $21.08/t to account for equipment write off. For configuration 2.2 and 2.3 to have the same operating cost, the energy cost of LPS must be raised to $9.59/GJ, an increase of 48.3%. This is roughly equivalent of decreasing the electricity to thermal energy (low pressure steam) cost ratio from 3.1 to 2.1. With this increase in steam costs, the new SPC for these configurations is raised to $18.79/t (+20.0%), $17.38/t (+19.1%), $17.38/t (+16.7%), and $23.35/t (+10.8%). Notably, the carbon tax is expected to increase dramatically over the next few decades, as demand will continue to grow but will be limited by the fixed production cap. When combining all sections together (without isomerization or increases in steam cost and considering the RSV configuration), the total SPC of each configuration in sequential order is $23.93/t, $23.33/t, $23.45/t, $25.46/t.

For single pass isomerization, the TCI for the entire section without MVR is $39.4 million and would operate with an SPC of $58.31/t throughput. By adding an MVR heat pump to the deisopentanizer, as shown in Fig. 7, all other costs except for direct cost are increased, resulting in a TCI of $45.4 million and an SPC of $60.33/t. For the heat pump to be viable, the energy cost of LPS and MPS would have to be increased by 36.3%, resulting with an SPC of $62.50/t. This is equivalent to decreasing the electricity to LPS cost ratio from 3.1 to 2.3.

To increase the AKI further, the recycling of n-pentane and n-hexane is required. For the base case scenario without heat pumps, the TCI is estimated to be around $62.6 million with an SPC of $92.64/t feed. When installing the MVR heat pump to the deisopentanizer, as shown in Fig. 8, the TCI is increased to $66.1 million with an SPC of $91.70/t feed. In contrast to the single pass isomerization, the addition of the MVR heat pump to the recycled process is cost effective without external incentives.

Overall, when combining Configurations 1.1 (RSV) and 2.2 (DDWC) with Configuration 3.1 (single pass isomerization), the total SPC would amount to $29.64/t throughput. If a higher AKI product is desired (Configuration 3.4), the total SPC would be increased to $32.89/t. If Configuration 2.3 (heat pump assisted BDWC) is preferred over Configuration 2.2, the total SPC is increased to $29.77/t (AKI = 84.2)



Note: (1.1) NGL RECOV: RSV; (1.2) NGL RECOV: GSP; (2.1) NGL-FRAC: BASE; (2.2) NGL-FRAC: DDWC; (2.3) NGL-FRAC: DWC+BDWC+MVR; (2.4) NGL-FRAC: TC-DWC+BDWC+MVR; (2.5) NGL-FRAC: C3-SRB/MVR; (3.1) ISOMERIZATION: Single Pass; (3.2) ISOMERIZATION: Single Pass with deisopentanizer MVR; (3.3) ISOMERIZATION: C5/C6 Recycle; (3.4) ISOMERIZATION: C5/C6 Recycle with deisopentanizer MVR
Utility Energy Cost: Refrigerant (-34°C) = $13.17/GJ, Refrigerant (-12°C) = $6.47/GJ, Cooling Water = $1.29/GJ, Low Pressure Steam = $6.22/GJ, Medium Pressure Steam = $7.67/GJ, Natural Gas = $5.22/GJ, Electricity = $19.44/GJ

Fig. 9. Overview of the economic analysis for the NGP process including all sections.

and \$33.03/t (AKI = 89.6), respectively.

3.3. Sustainability metrics

The sustainability of the process can be evaluated using several metrics proposed by industrial experts: material and energy intensity, water consumption, toxic and pollutant emissions, greenhouse gas (GHG) emissions. Lower values means of these metrics represent a better performance in terms of sustainability [28,29]. An overview of the sustainability metrics for each configuration is provided in Table 2.

- *Material intensity (MI)* expresses the mass of wasted materials (not converted to desirable product) per unit of output. In the NGL process, the only section to have generated waste is the isomerization section when stabilizing the isomerate after reaction. This waste is expected to be flared at 7.37 $kg_{waste}/tonne_{isomerate}$ for the single pass isomerization and at 11.8 $kg_{waste}/tonne_{isomerate}$ for the recycled configuration.
- *Energy intensity (EI)* represents the primary energy consumed per unit of output. Only the electricity (used also for heat pumps and refrigeration), reboiler and additional heater duties were accounted for energy intensity. The NGL recovery section requires 136 kJ/kg for the RSV configuration and 108 kJ/kg for the GSP configuration, making the first section actually the least energy intensive section. For the NGL fractionation section, the EI in sequential order is 850 kJ/kg (Configuration 2.1), 744 kJ/kg (Configuration 2.2), 676 kJ/kg (Configuration 2.3), and 643 kJ/kg (Configuration 2.4). As expected, the addition of heat pumps lowers overall energy input by upgrading otherwise lost low-quality heat into useable heat. The same trend can be seen in the isomerization section, where EI drops from 1.73 to 1.07 MJ/kg in the single pass configuration, and from 3.15 to 2.13 MJ/kg for the recycling of pentane and hexane configuration.
- *Water consumption* expresses the amount of water used per unit of output. It is considered that 7% of water is lost to natural evaporation in cooling towers [28], and the steam condensate has a recovery rate of 70% to account for potential steam leaks, condensate losses, steam trap failures, and other possible inefficiencies in the steam generation and usage process [30]. Thus, the water consumption found for NGL fractionation is as follows sequentially: 2.07 m^3/t, 1.69 m^3/t, 1.45 m^3/t, 1.33 m^3/t, 1.93 m^3/t. Using heat pumps reduces the water consumption since the heat required for operations is delivered from the upgrading the heat rejected at the condenser [31]. Through the minimization of external utility demands, less water will be subjected to losses, allowing for a more sustainable closed loop system. The same can be seen in the isomerization section where water consumption drops from 5.03 to 2.72 m^3/t in single pass and from 9.14 to 5.47 m^3/t in the recycled configuration.
- *Greenhouse gas (GHG) emissions* expresses the total GHG emitted per unit of output. Arguably the most important sustainability metric, GHG emissions based on steam production was accounted for using an efficiency factor of 0.85 and a CO_2 emission factor of 5.589×10^{-8} kg CO_2/J from natural gas [32]. For NGL fractionation, the GHG emissions are estimated to be as followed in sequential order: 55.9 kg/t, 48.9 kg/t, 43.7 kg/t, 39.7 kg/t. For isomerization, MVR reduces the GHG emissions from 109.4 kg/t to 56.3 kg/t for single pass and 200.1 kg/t to 115.3 kg/t for the recycled configuration. Considering a carbon tax of \$46.15/t, the new SPC for the fractionation section in sequential order is \$18.50/t (+16.2%), \$16.88/t (+15.7%), \$16.90/t (13.5%), and \$22.83 (+8.28%) [33]. For the isomerization section, the addition of an MVR heat pump to both configurations decreases the SPC from \$63.35/t to \$62.93/t for single pass and \$101.88/t to \$97.03/t for the recycling of pentane and hexane configuration.

Table 2
Sustainability metrics (material intensity, energy intensity, water consumption, greenhouse gases emissions) for each section of the NGL process.

Sections & Configurations	Material intensity ($kg_{waste}/t_{isomerate}$)	Energy intensity (kJ/kg)	Water consumption (m^3/t)	GHG emissions (kg_{CO2}/t)
(1.1) NGL Recovery: RSV	–	136	–	–
(1.2) NGL Recovery: GSP	–	108	–	–
(2.1) NGL-Fractionation: Base	–	850	2.07	55.9
(2.2) NGL-Fractionation: DDWC	–	744	1.69	48.9
(2.3) NGL-Fractionation: DWC + BDWC + MVR	–	676	1.45	43.7
(2.4) NGL-Fractionation: TC-DWC + BDWC + MVR	–	643	1.33	39.7
(2.5) NGL-Fractionation: C3-SRB/MVR	–	812	1.93	52.6
(3.1) Isomerization: Single Pass	7.37	1730	5.03	109.4
(3.2) Isomerization: Single Pass with deisopentanizer MVR	7.37	1070	2.72	56.3
(3.3) Isomerization: C5/C6 Recycle	11.8	3150	9.14	200.1
(3.4) Isomerization: C5/C6 Recycle with deisopentanizer MVR	11.8	2130	5.47	115.3

4. Conclusions

The main sections of natural gas refinement (recovery and fractionation) and a third section for upgrading natural gasoline are successfully and rigorously designed, simulated, optimized, economically and sustainably assessed. New intensified technologies as part of a large process flowsheet with energy/mass recycles for all sub-sections of the NGL process were explored and integrated from a holistic viewpoint, and a fair comparison was made on the same basis in terms of key economic and sustainability metrics. Overall, for the different NGL process configurations proposed based on intensified fluid separation technologies, using internal thermal coupling and heat pumps have systematically improved all the sustainability metrics.

- For the NGL recovery section (section 1), the enhanced RSV configuration is the most economically profitable. It results in full heat recovery of the reboiler duty of the demethanizer (2.9 MW energy savings), requiring only 8 MW of power for refrigeration and 12.9 MW for gas compressor power. The enhanced gas subcooled process (GSP) results in 17.9% reduction of refrigerant duty, 20.2% reduction of electrical duty, and 19.9% reduction of total utility cost (ethane recovery reduces to 79.9 mol%). The bounds of efficient ethane recovery in the NGL recovery section are between 95 and 79.9 mol% recovery, operating between a \$16.56–15.74/t SPC. For the GSP configuration to be profitable, the price of ethane must be within a 4.94% price margin of the sale gas.
- For the NGL fractionation section (section 2), Configuration 2.2 (standard double DWC) is the most economical process. However, Configuration 2.3 (DWC followed by heat pump assisted BDWC) is found to be more sustainable due to its lower overall utilities as well as less sensitive to carbon taxation with a similar specific product

cost of ~\$16.90/t (including carbon tax). Overall, 29.5% total utility cost saving, 8.65% total operating cost saving, and 21.8% reduction of total GHG emissions are achieved. In addition, Configuration 2.4 (thermal coupled deethanizer to Configuration 2.3) is proved to be the most eco-friendly but the CAPEX is too high for it to be profitable. Therefore, the resulting enhanced process (without isomerization) is the combination of Configuration 1.1 (RSV Configuration) with Configuration 2.3 (DWC followed by heat pump assisted BDWC), leading to a total SPC of \$23.45/t (or \$24.38/t with carbon tax).

- For the natural gasoline isomerization section (section 3), the addition of an MVR heat pump to the deisopentanizer is not economical for single pass isomerization (unless steam cost is higher by 36.3%) due to external factors, such as carbon taxation. In contrast, the addition of MVR to the C5/C6 recycled configuration can dramatically reduce utility use (by 19.1%) and GHG emissions (by 42.4%).

CRediT authorship contribution statement

Danforth Brandon Bosman: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Qing Li:** Visualization, Validation, Software, Investigation, Conceptualization, Writing – review & editing. **Anton A. Kiss:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Conceptualization, Formal analysis, Investigation, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.energy.2024.131186.

References

[1] Ritchie H, Roser M, Rosado P. Our World in Data (OurWorldinData.org/energy); 2022. https://ourworldindata.org/energy-overview. [Accessed 21 April 2023].
[2] Speight JG. Production of hydrocarbons from natural gas. In: Handbook of industrial hydrocarbon processes. Laramie: Gulf Professional Publishing; 2019. p. 143–92.
[3] Yoon S, Binns M, Park S, Kim J-K. Development of energy-efficient processes for natural gas liquids. Energy 2017;128:768–75.
[4] Islam M, Al-Sobhi SA, Naquash A, Qyyum MA, Lee M. Optimal process selection for natural gas liquids recovery: energy, exergy, economic, and environmental perspectives. Energy 2024;289:129757.
[5] Usman M, Pervaiz E. An inclusive review on the assessment of different techniques for natural gas liquid recovery. Chem Eng Technol 2023;46:1397–410.
[6] Mantingh J, Kiss AA. Enhanced process for energy efficient extraction of 1,3-butadiene from a crude C4 cut. Separ Purif Technol 2021;267:118656.
[7] Long NVD, Lee M. Improvement of natural gas liquid recovery energy efficiency through thermally coupled distillation arrangements. Asia Pac J Chem Eng 2012;7/S1:S71–7.
[8] Long NVD, Lee M. Design and optimization of heat integrated dividing wall columns for improved debutanizing and deisobutanizing fractionation of NGL. Kor J Chem Eng 2013;30:286–94.
[9] Blahusiak M, Kiss AA, Kersten SRA, Schuur B. Quick assessment of binary distillation efficiency using a heat engine perspective. Energy 2016;116:20–31.
[10] Becker A, Hemphill C, Niemeyer C, McCoy E. Process for separating hydrocarbons in a liquid feed utilizing an externally heated reboiler connected to a dividing wall column as the primary source of heat energy. Kansas City, MO (USA). Patent no: US 28 December 2021;11:207–611.
[11] Li Q, Finn AJ, Doyle SJ, Smith R, Kiss AA. Synthesis and optimization of energy integrated advanced distillation sequences. Separ Purif Technol 2023;315:123717.
[12] Qyyum MA, Naquash A, Haider J, Al-Sibhi SA, Lee M. State-of-the-art assessment of natural gas liquids recovery processes: techno-economic evaluation, policy implications, open issues, and the way forward. Energy 2022;238:121684.
[13] SIE Neftehim LLC. Pentane-hexane isomerization process and catalysts 2015. URL: https://nefthim.com/manual/Isomerization-process/. [Accessed 21 April 2023].
[14] Jiang H, Zhang S, Jing J, Zhu C. Thermodynamic and economic analysis of ethane recovery processes based on rich gas. Appl Therm Eng 2019;148:105–19.
[15] Seider WD, Lewin DR, Seader JD, Widagdo S, Gani R, Ng KM. Product and process design principles: synthesis, analysis and evaluation. New York: John Wiley & Sons, Inc.; 2017.
[16] Kiss AA. Distillation technology – still young and full of breakthrough opportunities. J Chem Technol Biotechnol 2014;89:479–98.
[17] Waltermann T, Skiborowski M. Conceptual design of highly integrated processes – optimization of dividing wall columns. Chem Ing Tech 2017;89/5:562–81.
[18] van de Bor DM, Infante Ferreira CA, Kiss AA. Low grade waste heat recovery using heat pumps and power cycles. Energy 2015;89:864–73.
[19] Tiong C, Nandong J. Retrofitting options for Natural Gas Liquid (NGL) fractionation trains using the concept of single column development. Procedia Eng 2016:923–31.
[20] K. Mehra, Heat pump in distillation column, ChemEnggHelp, URL: https://www.chemengghelp.com/heat-pump-distillation/[Accessed 24-June-2023].
[21] Luo H, Bildea CS, Kiss AA. Novel heat-pump-assisted extractive distillation for bioethanol purification. Ind Eng Chem Res 2015;54:2208–13.
[22] Wang X, Economides M. Liquefied natural gas (LNG). Advanced Natural Gas Engineering 2009:209–41.
[23] Rabo JA, Pickert PE, Mays RL. Pentane and hexane isomerization. Ind Eng Chem 1961;53:733–6.
[24] Demirbas A, Ahmad W, Balubaid MA. Octance rating of gasoline and octane booster additives. Petrol Sci Technol 2015;33:1190–7.
[25] DWC Innovations, Light Naphtha (C5-C6) Isomerization Units, URL: https://www.dwcinnovations.com/light-naphtha-isomerization/[Accessed 21-May-2023].
[26] Jenkins S. 2019 chemical engineering plant cost Index annual average. Chemical Engineerin Business & Economics 2020. https://www.chemengonline.com/2019-chemical-engineering-plant-cost-index-annual-average/.
[27] Peters MS, Timmerhaus KD, West RE. Plant design and economics for chemical engineers. McGraw Hill; 2003. 5th Edition.
[28] Schwarz J, Beloff B, Beaver E. Use sustainability metrics to guide decision-making. Chem Eng Prog 2002;98:58–63.
[29] Dicks AP, Hent A. Green chemistry metrics, A guide to determining and evaluating process greenness. Jiapur: Springer; 2015.
[30] Lieberman NP, Lieberman ET. Steam generation. In: A working guide to process equipment. fifth ed. McGrawHill; 2022. p. 261–76.
[31] Kiss AA, Infante Ferreira CA. Heat pumps in chemical process industry. CRC-Press (Taylor & Francis Group); 2016.
[32] AlNouss A, Ibrahim M, Al-Sobhi SA. Potential energy savings and greenhouse gases (GHGs) emissions reduction strategy for natural gas liquid (NGL) recovery: Process simulation and economic evaluation. Journal of cleaner production 2018;194:525–39.
[33] EU Emissions Trading System (EU ETS), URL: https://climate.ec.europa.eu/eu-action/eu-emissions-trading-system-eu-ets_en [Accessed 12-July-2023].