Advanced process integration for supercritical production of biodiesel: Residual waste heat recovery *via* organic Rankine cycle (ORC)

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ABSTRACT

Biodiesel production using supercritical methanolysis has received immense interest over the last few years. It has the ability to convert high acid value feedstock into biodiesel using a single-pot reaction. However, the energy intensive process is the main disadvantage of supercritical biodiesel process. Herein, a conceptual design for the integration of supercritical biodiesel process with organic Rankine cycle (ORC) is presented to recover residual hot streams and to generate electric power. This article provides energy and techno-economic comparative study for three developed scenarios as follows: original process with no energy integration (Scenario 1), energy integrated process (Scenario 2) and advanced energy integrated process with ORC (Scenario 3). The developed integrated biodiesel process with ORC resulted in electric power generation that has not only satisfied the process electric requirement but also provided excess power of 257 kW for 8,000 tonnes/annum biodiesel plant. The techno-economic comparative analysis resulted in favouring the third scenario with 36% increase in the process profitability than the second scenario. Sensitivity analysis has shown that biodiesel price variation has significant effect on the process profitability. In summary, integrating supercritical biodiesel production process with ORC appears to be a promising approach for enhancing the process techno-economic profitability and viability.

KEYWORDS

Biodiesel, supercritical methanolysis, organic Rankine cycle, process simulation integration, techno-economic study.

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HIGHLIGHTS

- Residual hot streams in supercritical biodiesel process are valorised into electric energy *via* ORC.
- Supercritical biodiesel process integration with ORC provides self-sufficiency in electric energy.
- Three scenarios for the supercritical biodiesel production process were compared for techno-economic viability.
- The developed integrated biodiesel process with ORC is the optimal techno-economic scenario.

List of abbreviations:

ORC, organic Rankine cycle; BORC, basic organic Rankine cycle; RORC, regenerative organic Rankine cycle; GHG, greenhouse gases; WCO, waste cooking oil; FFA, free fatty acids; RSM, response surface methodology; HEN, heat exchanger network; FPSO, floating production storage and offloading; TCI, total capital investment; APC, annual utilities cost; ATR, annual total revenues; AP, annual profit; PBP, payback period; NPV, net present value; PI, profitability index; PRSV, Peng-Robinson Stryjek-Vera; DME, Dimethyl ether; MMUSD, million US dollars; CO, carbon monoxide; NOx, nitrogen oxides.

1. INTRODUCTION

The global energy consumption has recorded a noticeable increase during the last decades and is expected to continue to rise in the foreseeable future. The demand of fossil fuels, as the main source of energy, has dramatically raised along with the increasing growth of population and metropolitan industrial societies. The world's heavy dependence on fossil fuels has led to environmental impacts including air pollution, global warming, climate change and water contaminations [1]. Fossil fuels combustion exhausts from transportation vehicles and industrial burners/boilers are the main cause of air pollution. It has been reported that the replacement of fossil fuels with biofuels will have a significant impact on air pollution reduction and hence lead to a greener environment [2,3]. A number of researchers have highlighted the importance of public transport in minimising the impact on air pollution. Other researchers have mentioned a significant effect of exhaust gas filtration in improving the air quality [4,5]. Several governments have encouraged people to use bicycles as a transportation means where they have announced several funding schemes i.e. cycling to work scheme in the UK [6].

Recently, the global air pollution has recorded steep reduction where the environment has been allowed to be self-healed. This was a consequence of a novel infectious virus, COVID-19, identified in late December 2019 of which most governments have introduced serious lockdown policies [7]. It has been reported that the emission of nitrogen oxides (NOx), carbon monoxide (CO) and particulate matters reduced by 20-30% [8]. Therefore, the current situation has provided a non-intended reduction in air pollution, which should be continued after releasing the lockdown by decreasing the fossil fuels dependency and moving towards greener renewable fuels.

The search for alternative renewable and greener source of energy has been considered as a vital requirement. Lignocellulosic biomass is a sustainable and renewable feedstock for production of biofuels that are promising replacements for fossil fuels due to the physicochemical similarities. Further, biofuels are superior to fossil fuels as being renewable, non-toxic, biodegradable and producing less greenhouse gases (GHG) emissions. Finally, biomass valorisation into biofuels is projected to play a key role in circular bioeconomy *via* thermo/biochemical conversion technologies [9–12].

Specifically, biodiesel has received a significant interest as it could be fuelled in the diesel engines without modifications [13]. Biodiesel is produced from vegetable oils, animal fats and microalgae by catalytic transesterification reaction of triglycerides and alcohol into fatty acids alkyl esters. Generally, edible vegetable oils have been considered the main feedstock for biodiesel production. However, the food price hikes and shortages due to the increasing competition with food supplies over arable lands, crops and water resources. Accordingly, biofuels research has been oriented to use non-edible and waste cooking oils (WCO) as an alternative non-food competitive feedstock [14]. However, the main problem associated with WCO is the high acidity of the feedstock. Several pre-treatment steps have been developed for free fatty acids (FFA) conversion, i.e. esterification and neutralisation [15,16]. Two-steps reactions process has been developed as an efficient solution where the feedstock is esterified using acidic catalysts to convert FFA into biodiesel, which is followed by transesterification of triglycerides using alkaline catalysts [17].

Recently, non-catalytic supercritical production of biodiesel has provided an ideal strategy for converting high acidity feedstock into biodiesel. It has been observed that supercritical methanol is highly miscible in WCO where simultaneous esterification and transesterification take place without the aid of catalysts. In addition, the process has several advantages over catalytic conventional processes including high yield of biodiesel, elimination of wastewater, reduction of process unit operations, simple product separation and high-quality of biodiesel [18]. Several researchers have studied the supercritical valorisation of high acidity feedstock into biodiesel [19,20]. In our previous study [21], we have successfully valorised high acid value WCO into biodiesel with 98.8% yield and optimised the process parameters using response surface methodology (RSM). We have also observed that supercritical methanolysis using low acid value WCO has yielded lower biodiesel at the same process parameters than high acid value WCO. We have explained that the esterification reaction has higher rate with supercritical methanolysis than transesterification and hence high acidity feedstock is an advantage for supercritical process [21,22].

The harsh reaction conditions and high energy consumption are considered as the main disadvantages of supercritical biodiesel production. Researchers have studied lowering of supercritical process parameters while achieving high yield of biodiesel using co-solvents [23]. Catalytic supercritical approaches have been investigated at milder reaction conditions [18]. On the other hand, researchers have applied energy integration approaches to minimise the process energy requirements. Several process simulation studies have been conducted on supercritical biodiesel production [24,25]. In our previous study [26], we have designed an optimal heat exchanger network (HEN) for supercritical production of biodiesel where it has resulted in lowering about 45% of the process energy requirements.

Ziyai et al. [27] have reported a novel process for integrating biodiesel with hydrogen production unit using glycerol supercritical water reforming. They have reported that the combustion of the produced hydrogen has significantly reduced the process external heating requirements. In addition, they have demonstrated that the produced electric energy by hydrogen combustion has exceeded the process electric requirements and hence considered as process revenue.

Organic Rankine cycle (ORC) has been considered as a promising technology for waste heat valorisation for producing electricity. It has a similar principle for the steam Rankine cycle but using organic solvents with lower boiling temperatures than water, which allows the heat recovery of low temperature resources. It has been reported that the application of ORC for residual heat recovery has resulted in reduction of process operation costs [28,29]. The basic organic Rankin cycle (BORC) consists of 4 main units named as turbine expander, condenser, pump and evaporator. Solvents are vaporised at elevated pressures and fed to turbine for power generation and then condensed to be fed to the pump as a closed loop [30]. In an attempt to increase the process efficiency, researchers have reported a regenerative organic Rankin cycle (RORC) to pre-heat the solvent stream prior to the evaporator with the hot outlet stream of the turbine. This has resulted in decreasing the heating and cooling requirements for the evaporator and condenser, respectively [31].

Camporeale et al. [32] have observed significant loss of ORC efficiency when operating the solvents at their supercritical state. Accordingly, they have recommended to use subcritical conditions for the solvents and preferably close to saturation. ORC has been applied for low grade waste heat recovery [33]. Reis and Gallo [34] have applied ORC for gas turbine exhaust gases in a floating production storage and offloading platform (FPSO). The produced electricity has covered about 21% of the electric energy requirement of the plant. It has also reduced plant fuel consumption and carbon dioxide emissions by 22.5%. To the knowledge of the authors, the integration of supercritical biodiesel production process with ORC has not been reported yet. This article is considered the first study that aims to contribute in empowering the supercritical biodiesel process by valorising the residual waste heat into electric energy.

In this paper, a conceptual advanced process integration for supercritical production of biodiesel has been implemented by recovering residual waste heat using ORC. The process residual heat streams have been defined based on our previously published energy integrated process [26]. An integrated HEN has been developed to exchange the waste heat from the residual streams with organic Rankine solvent. By integrating waste heat with ORC, not only the electrical requirements of the process are met but also additional power is generated. A comprehensive analysis for three biodiesel production scenarios has been conducted to highlight the processes energy requirement and techno-economic feasibility. In addition, the paper includes a complete study of 8 organic Rankin solvents to assess their applicability to maximise power generation. Herein, the considered scenarios are as follows: the original supercritical production of biodiesel without energy integration (Scenario 1), the published energy integrated process (Scenario 2) and the developed advanced integrated process with ORC (Scenario 3). Finally, a sensitivity analysis has been performed to assess the influence of variations in feedstock, biodiesel and electricity prices on the process techno-economic figures.

2. PROCESS SIMULATION

2.1 Process design

The biodiesel supercritical production process was simulated according to our previous published data [26]. In summary, oil and methanol were entered to two pumps to increase their pressure to approximately 200 bar. The reactants were then mixed and heated to 253.5 °C. The conditioned reactant mixture was then fed to a kinetic reactor with 91% conversion of WCO to methyl esters (biodiesel) and glycerol. The product stream was then depressurised and introduced to a flash separator to recover the vaporised unreacted methanol. The liquid mixture stream of methyl esters, glycerol and methanol was then directed to a distillation column to separate methanol. The distillation product stream was cooled and entered a decanter to separate glycerol from methyl esters. The methyl esters stream was fed to a vacuum distillation column to separate the excess triglycerides, so the biodiesel product meets the EN14214 specifications.

The chemical components of the feedstock and the products were defined based on our previous reported process design for supercritical biodiesel production [26]. The same kinetic reactor was defined using the reported kinetic and thermodynamic parameters. The previous reported original process was named as "Scenario 1" where all the heating and cooling energy requirements were supplied using external utilities as shown in Figure 1. Our previous study has also developed a HEN that achieved the Pinch targets for both heating and cooling energy requirements. The reported energy integrated process using optimal HEN was fully simulated in this paper (including all heat-exchangers) and named as "Scenario 2". Further, this paper has developed an advanced process by integrating the residual heat streams with ORC and the process was fully simulated "Scenario 3". The three scenarios were fully modelled and simulated using Aspen-HYSYS® (V11) commercial software (Aspen Technology Inc., USA). All the designed heat exchangers were simulated and operated in the simulation environment. The full simulation of an integrated design eases the process comparison and highlights the differences in external utilities consumption and may provide basis for further future online-optimisation.

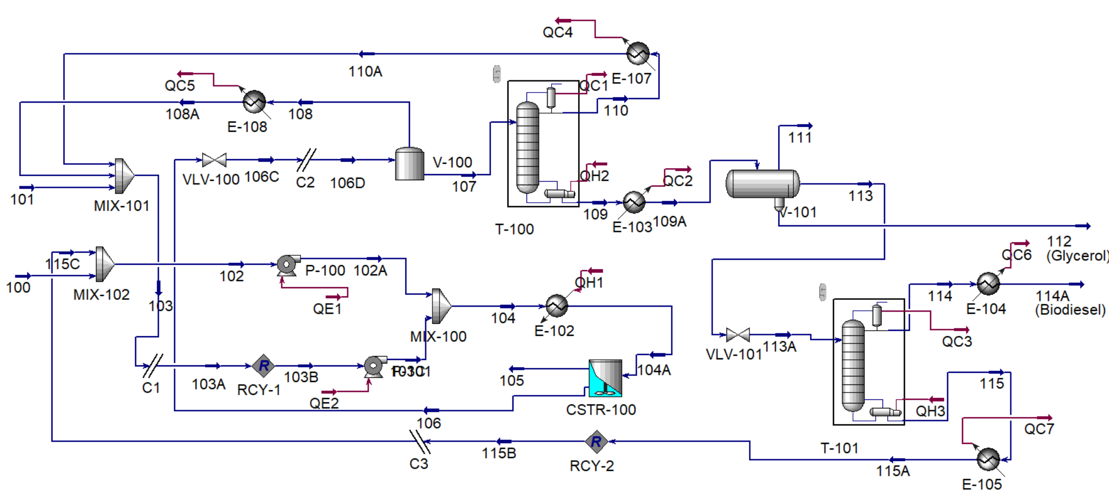


Figure 1. Original supercritical production of biodiesel (Scenario 1)

2.2 Energy and techno-economic analysis

The developed scenarios were compared for the overall electric, heating and cooling energy consumptions. Further, an economic feasibility and profitability studies were performed by calculating several economic indicators for each process including total capital investment (TCI), annual operating cost (APC), annual total revenues (ATR), annual profit (AP), payback period (PBP), net present value (NPV) and profitability index (PI). The detailed equations of the mentioned indicators were comprehensively described in [27]. It is worth mentioning that the products of the process are only methyl esters, glycerol and electrical power (scenario 3).

A techno-economic analysis was performed using Aspen Process Economics Analyser® (V11) commercial software (Aspen Technology Inc., USA). The costs of the feedstock and products including methanol, waste cooking oil (WCO), glycerol and methyl esters (biodiesel) were defined in the software as presented in Table 1. The required utilities for both heating and cooling were defined in the software i.e. cooling water and steam. The cost of the heating, cooling and electric utilities were computed based on cost library information provided by the software. Mass and energy balance for each energy equipment was applied to calculate the value of the required utilities using Aspen-HYSYS software. The detailed economic equations for the TCI and APC are reported elsewhere [27].

Table 1. List of the prices of reactants, products and process utilities

Subject name	Price (USD/kg)	Reference
WCO	0.224	[27]
Methanol	0.268	[27]
Biodiesel	0.99	[27]
Crude glycerol	0.2	[35]
Cooling water	0.013	[27]
Low-pressure steam	12.68	[27]
Medium-pressure steam	13.71	[27]
High-pressure steam	16.64	[27]
Electricity	0.2 (USD/kWh)	[27]

2.3 Definition of residual heat streams

Based on our previous reported optimal HEN for supercritical biodiesel production process, several hot streams were observed to use external cooling facilities where significant heat is lost to cooling water [26]. The residual streams were identified as reported in Table 2 where only streams with significant available heat energy (>250 kW) were considered for utilisation. The selected residual streams for recovery were identified as follows: 109, C2, 108 and 114. The total available energy of the selected residual streams was reported as 4,888.25 kW. As most of the available waste energy were identified by streams C2 and 108, the cold stream maximum temperature constraint was set based on their inlet temperature (89 °C). Accordingly, the maximum achievable temperature for the cold stream (organic Rankine solvent) was set to 79 °C.

Table 2. Potential residual host streams from biodiesel process (scenario 2)

Stream name	T_{inlet} (°C)	T_{outlet} (°C)	Enthalpy rate (kW)
109	134.1	25	765.18
C2	89.4	63.7	479.46
108	89	65	3,565.4
114	80.4	25	252.57
C1	66.5	66.4	205.34
115	134.1	25	76.19
110	66.5	65	0.603

2.4 Organic Rankine cycle (ORC)

The basic organic Rankin cycle (BORC) system is composed of 4 main components including turbine expander, condenser, pump and evaporator (heating source). The schematic of the ORC system is depicted in Figure 2. The evaporator was replaced in this process by exchanging heat with residual streams. The evaporated solvent was then introduced to the turbine expander to generate power. The expanded vapours were then fed to a condenser where the fluid exchanges heat with cooling water. The fluid then entered a pump to increase the pressure and then returned to the evaporator to complete the cycle.

Alternatively, RORC has an additional heat exchanger unit to the 4 units of BORC. The heat exchanger is aimed to recover the available heat of the outlet stream from the turbine (HT-LP) to preheat the pressurised liquid stream (LT-HP). The application of RORC reduce the required heating and cooling energies at the evaporator and condenser. Figure 3 provides a schematic of the RORC units and operation.

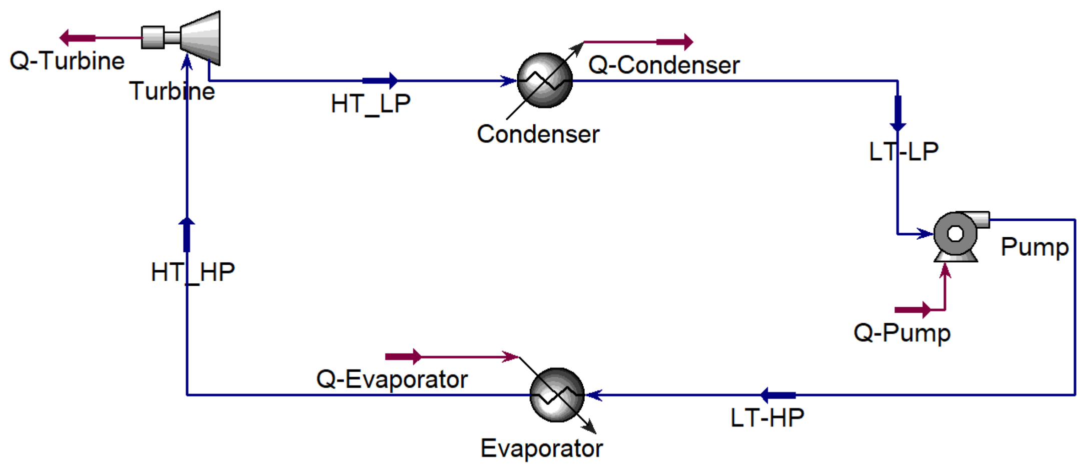


Figure 2. Schematic of the basic organic Rankine cycle (BORC)

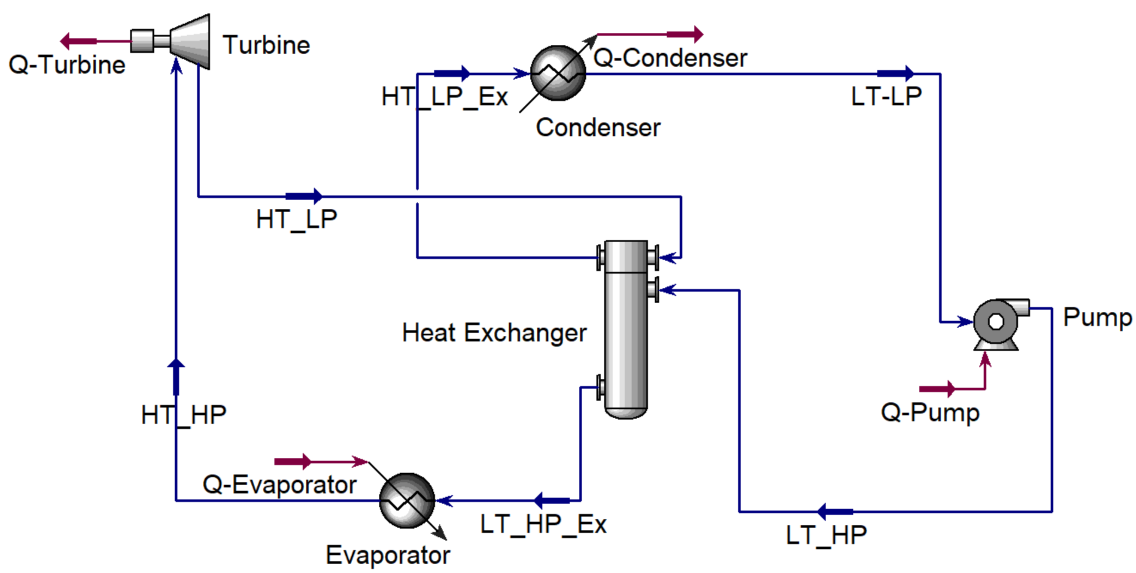


Figure 3. Schematic of the regenerative organic Rankine cycle (RORC)

Based on the available waste heat evaluation study, several constraints were applied for the ORC to match the process requirements. For instance, cooling water was chosen as a cooling utility and hence the outlet temperature of the ORC condenser was set to a minimum temperature of 30 °C. Further, as the main residual hot streams are available at net temperature of 89 °C where hereafter a maximum temperature limitation of 79 °C was set for the evaporator outlet stream. The aforementioned constraints had significantly narrowed the organic solvent selection process. The selected solvent should be in vapour phase at elevated pressure at 79 °C and also should be in liquid phase at reduced pressure at 30 °C.

On the other hand, the available waste heat energy from the selected residual heat streams was reported as 4,888.25 kW. Hence, an independent ORC for each organic Rankin solvent was simulated with an evaporator duty of 4,888 kW to identify the maximum flowrate of the solvent that could achieve the energy target of the evaporator.

The modified cubic equation of state Peng-Robinson Stryjek-Vera (PRSV) was used as a thermodynamic fluid package to calculate the properties of the ORC solvents as per Equations 1-7 [36]. Aspen-HYSYS software was used to analyse the ORC performance. Eight solvents have been selected for the study including Propane, Propene, *iso*-butane, *n*-butane, butene, R22, Ammonia and Dimethyl ether (DME). The properties of the selected solvents are presented in Table 3 [37].

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{1}$$

$$b = 0.0777896\,\frac{RT_c}{P_c} \tag{2}$$

$$a = (\alpha)0.45724\,\frac{R^2 T_r^{0.5}}{P_c} \tag{3}$$

$$\alpha = [1 + k(1 - T_r^{0.5})]^2 \tag{4}$$

$$k = k_1(1 + T_r^{0.5})(0.7 - T_r) + k_o \tag{5}$$

$$k_o = 0.378893 + 1.48915\omega - 0.1713848\,\omega^2 + 0.0196544\,\omega^3 \tag{6}$$

$$T_r = T/T_c \tag{7}$$

Where T_c, P_c and ω represent critical temperature, pressure and acentric factor, respectively.

Table 3. Thermodynamic data of the ORC solvents

Solvent	T_b (°C)	T_c (°C)	P_c (bar)	k_1
Propane	-42.10	96.74	42.56	0.0316
Propene	-47.75	91.85	46.20	0.0332
Iso-butane	-11.73	134.95	36.48	0.0378
n-butane	-0.50	152.05	37.97	0.0395
Butene	-6.25	146.45	40.22	0.0664
R22	-40.75	96.05	49.75	0.0262

Ammonia	-33.45	133.7	112.76	-0.2432
DME	-24.84	126.85	53.20	0.0220

3. RESULTS AND DISCUSSION

3.1 Development of an optimal HEN for residual-ORC

The selected residual streams with significant heat energy i.e. 109, C2, 108 and 114 have been integrated with a cold stream representing the organic Rankine solvent. The organic Rankine solvent was defined with an inlet temperature of 31.9 °C and outlet temperature of 79 °C. The temperatures have been set based on specified constraints as mentioned in section 2. The available energy for the cold stream was defined as 4,844 kW (considering minimum energy losses).

The HEN design has been developed based on Pinch technology where a composite curve has been developed of the hot and cold streams as presented in Figure 4. The Pinch temperatures have been defined between 31.9 and 41.9 °C as per a reasonable assumption of ΔT_{min} of 10 °C. Accordingly, the maximum allowable cooling temperature above the Pinch for the hot streams has been set to 41.9 °C. On the other hand, the maximum heating temperature for cold streams below the Pinch (if any) has been set to 31.9 °C.

The process residual hot streams are represented in a single composite curve (shown in red) while the ORC process cold stream is represented in a different composite curve (shown in blue). The overlap between hot and cold composite curves illustrates the available energy integration between streams. The cold stream (organic Rankine solvent) was defined so it could reach its target without the aid of any external heating utility (to replace the evaporator). However, further external cooling utility (cooling water) will be required for hot streams to reach their targeted temperature. Using the developed composite curves, the energy targets have been calculated as 0 and 217.2 kW for both heating and cooling, respectively. Aspen Energy Analyzer® commercial software (Aspen Technology Inc., USA) has been used to develop the composite curves and to calculate the target (minimum) energy requirement for both heating and cooling.

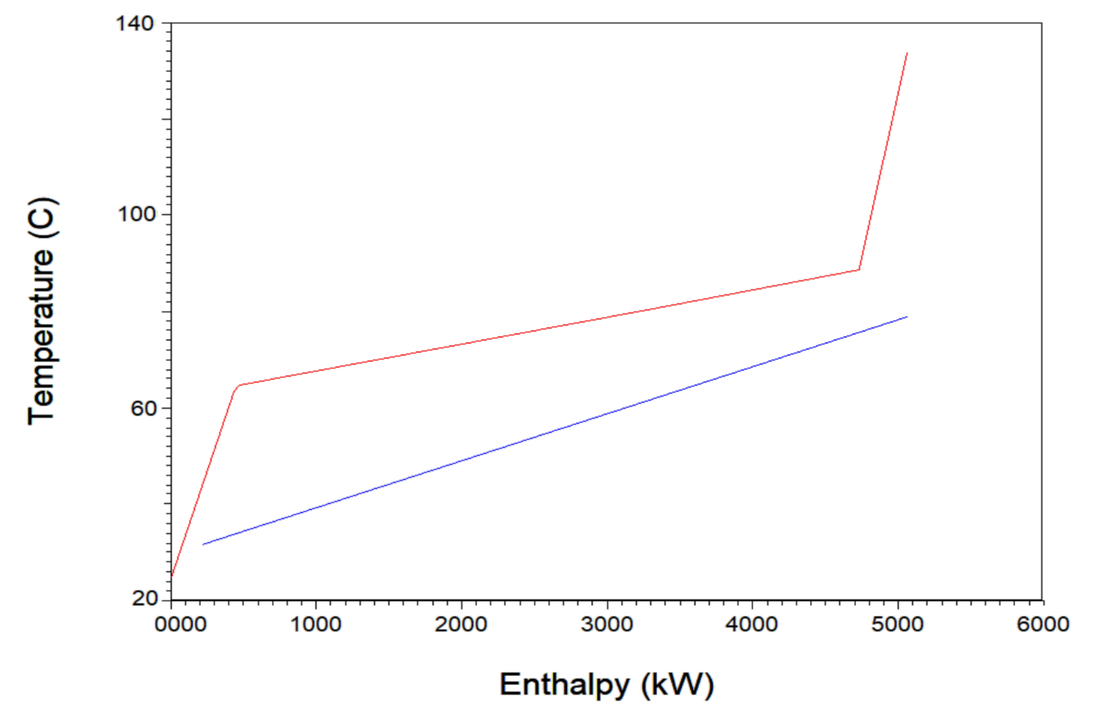


Figure 4. Hot and cold composite curves for selected residual streams and BORC solvent

An optimal HEN has been designed based on graphical Pinch method using 6 heat exchangers as shown in Figure 5. In order to achieve the zero-heating target, the ORC cold stream has been divided into three splits where each split has been heated from 31.9 °C to 79 °C without any external heating utility. The integration starts with developing an exchanger with stream 114 as it has an inlet temperature of 80.4 °C and could not be used to heat a cold stream up to more than 70.4 °C as per the applied ΔT_{min}. Hence, it has been used as a pre-heater for one of the organic Rankine solvent splits. The cooling temperatures for streams 109 and 114 have been achieved using external cooling utility (cooling water) with a combined cooling energy requirement of 256.5 kW. According to the Pinch target of external energies, the designed HEN has achieved 100 and 117.8 % of the target for heating and cooling energies, respectively.

The graphical Pinch method has been used to limit the trial procedures and to assess the validity of the developed exchangers. The graphical Pinch method, as shown in Figure 6, has represented each exchanger as a straight line on T-T diagram. The length of each exchanger line represents the heat transfer within the exchanger. In addition, the slope is function of the ratio of heat capacities and flows [38]. It has been observed from Figure 6 that the designed exchangers are all presented at the optimal area for heat recovery (above the Pinch) as explained previously by Gadalla [39].

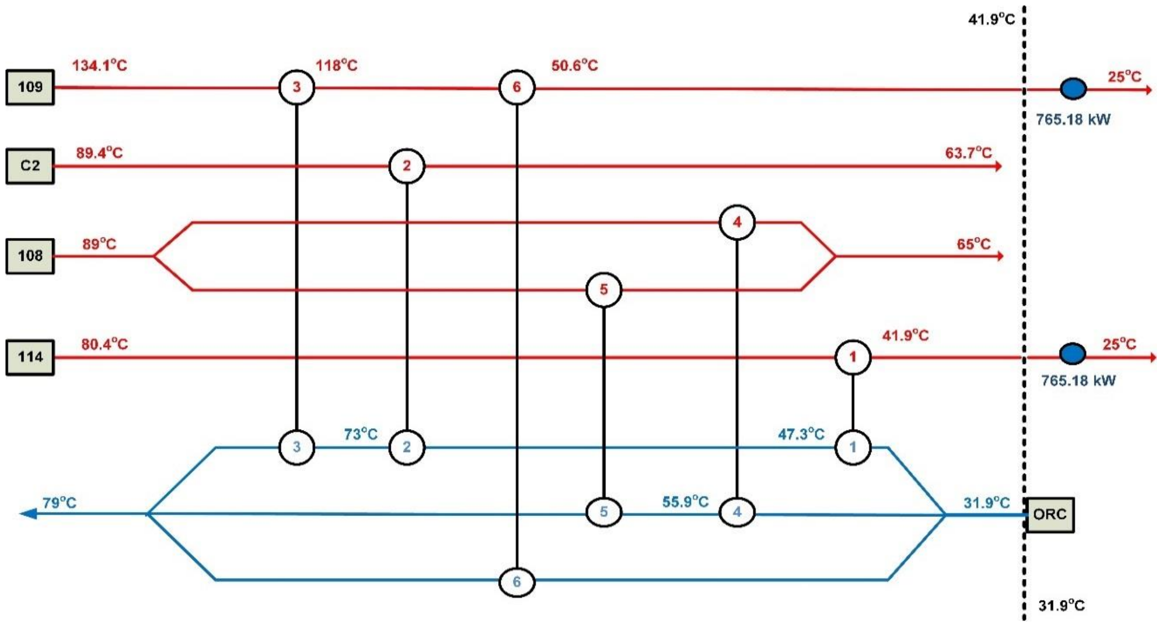


Figure 5. Developed heat exchanger network for residual streams and BORC solvent

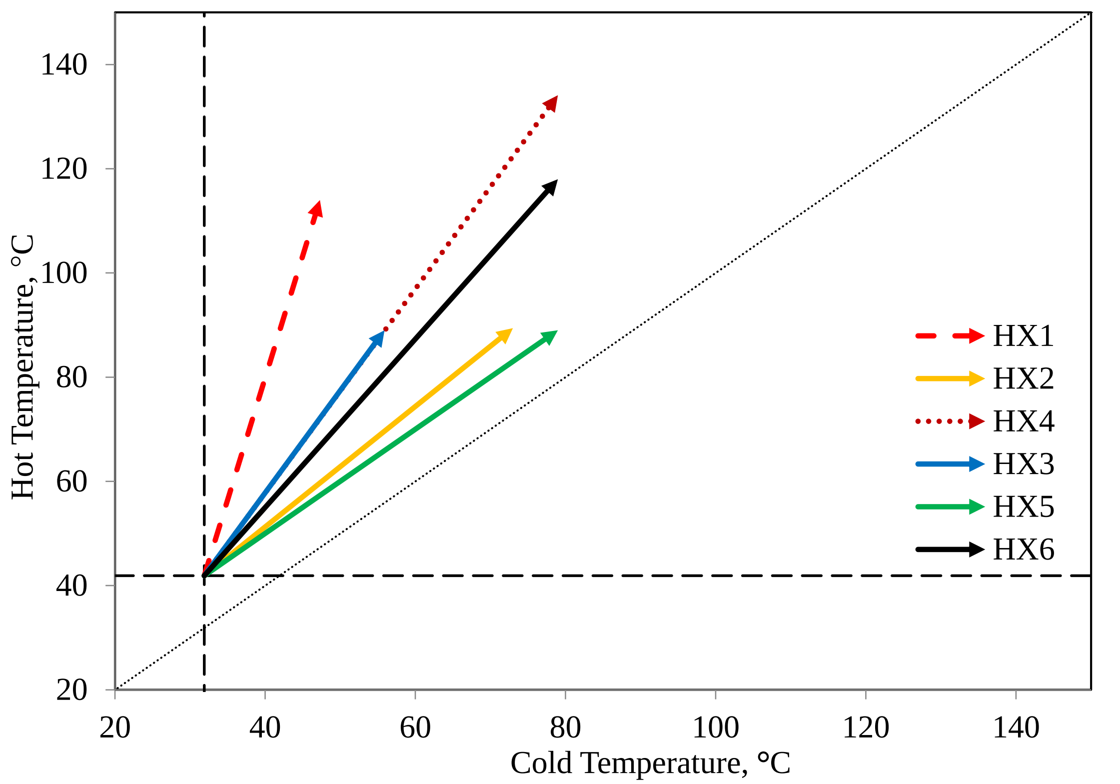


Figure 6. Graphical representation of each heat exchanger (HX) of the designed HEN on T-T diagram

3.2 ORC simulation

The development of ORC process simulation has been commenced using selection of chemical component. Eight organic Rankine solvents (working fluids) have been selected for the simulation environment including propane, propene, *iso*-butane, *n*-butane, butene, R22, ammonia and dimethyl ether (DME). This has been followed by selecting PRSV as a thermodynamic fluid package. The system has been assumed to operate with steady-state conditions. In addition, several assumptions have been defined to simplify the simulation as follows:

- Heat loss from/to the environment has been ignored.
- Kinetic and potential energy changes have been ignored.
- Pressure drop across the pipelines has been ignored.
- Constant efficiency for pump and turbine.

The isentropic efficiency of the turbine and the pump have been set to a constant value of 80% as reported previously [40]. The organic Rankine solvents have been operated at subcritical conditions. The ΔP across the turbine has been determined based on the thermodynamic properties of the organic Rankine solvents. Fixed parameters have been set for the cycle including evaporator duty of 4,844 kW, condenser outlet temperature of 31.9 °C and evaporator maximum temperature of 79 °C. The flowrate of the solvents and ΔP across the turbine have been varied to preserve the constant set parameters. A maximum allowable inlet pressure for the turbine has been set to 28 bar as reported elsewhere [41]. Table 4 represents the turbine inlet and outlet conditions, solvent flowrate and the turbine electric output for each solvent.

Table 4. ORC turbine working parameters with different solvents

Working fluid	Flowrate (kg/h)	Pin (bar)	Pout (bar)	Tin (°C)	Tout (°C)	Power (kW)
n-butane	40,890	9.5	3	79	48	438.5
butene	41,800	11.5	3.6	79	43.1	455
iso-butane	45,570	13	4.2	79	46.1	455
Propane	47,670	28	11	79	36.6	439
Propene	47,000	28	13.5	79	43.2	371.8
R22	89,840	28	12.5	79	33.3	379
DME	39,800	20.5	7	79	32.1	453.6
Ammonia	14,130	28	12.5	79	32.6	319.7

The inlet pressure for each solvent has been defined as the highest pressure that allows the solvent to be in vapour phase at 79 °C. On the other hand, the output pressure has been set based on the minimum pressure that allows the solvent to be condensed at 31.9 °C. It has been observed in Table 4 that *n*-butane, butene and *iso*-butane could meet the process constraints and feed the turbine at relevant low pressure (<13 bar). In addition, *iso*-butane and butene have showed the maximum power output for the process of 455 kW. DME has exhibited an entering turbine pressure of 20.5 bar with a relatively high-power output of

453.6 kW. The rest of the studied solvents including R22, propane, propene and ammonia have displayed an elevated fed turbine pressure of 28 bar (the maximum allowable pressure). Further, they have reported lower turbine power output with a range between 319.7 – 439 kW. Accordingly, butene has been selected as the optimal solvent for the integrated supercritical process study.

3.3 A comparative study between BORC and RORC in this application

The overarching aim of the development of RORC is to increase the efficiency of the ORC process by integrating the available heat of the turbine outlet stream to pre-heat the evaporator inlet stream [31]. This generally results in reduction of the required heating and cooling energy at the evaporator and condenser, respectively. However, the present work is designed to fully replace the evaporator unit with a set of heat exchangers in the process. Accordingly, the pump outlet stream does not require a pre-heat as it is already fully heated by energy integration with other residual process streams.

In particular application of RORC for the present work, a simple comparison in energy reduction between BORC and RORC (presented in Figures 2 and 3) has been conducted. By considering the process constrains discussed in section 2.4, the implementation of RORC has resulted in decreasing the temperature of condenser inlet stream from 43.1 °C (shown in Table 4) to 41 °C. Furthermore, this has increased the temperature of the evaporator inlet stream from 31.7 °C to 33.1 °C. Accordingly, reduction in heating and cooling energy requirement have been observed as 0.82% and 0.93%, respectively. It is worth mentioning that the increase in temperature of pump outlet stream from 31.7 °C to 33.1 °C in RORC will result in decreasing the amount energy that could be recovered/integrated from the biodiesel residual energy streams. This will also lead to a backward increase in the external cooling energy requirement presented in Figure 5 as the hot Pinch temperature will be 43.1 °C instead of 41.7 °C. Hence, streams 109 and 114 will be externally cooled from 43.1 °C to 25 °C.

Hence, for this particular application, both BORC and RORC have been observed to have similar efficiency. In addition, using RORC will result in increase in the capital costs of the process by installing an additional heat exchanger with no reduction in the operational costs. As a result, BORC has been chosen in the present work.

3.4 Process integration with ORC

Our previous developed HEN has been simulated in biodiesel production process by introducing all the developed heat exchangers to the simulation environment and named as Scenario 2 as shown in Figure 7. Five heat exchangers have been simulated where the temperature difference and the heat capacity have been defined based on the published HEN [26]. Both distillation columns in the original case have been disconnected to a separate column, reboiler and condenser. The disconnection was necessary to simulate heat exchangers between streams in the main case with the distillation column internal streams (special simulation environment for the column). The simulation has been used for further energy and techno-economic analysis as described in section 3.4.

The new developed HEN, in the present study, between organic Rankine solvent and residual hot streams of biodiesel process has been also simulated where 6 new heat exchangers have been introduced to the simulation environment. In addition, the ORC described in section 3.2 has been simulated to accompany the supercritical biodiesel process. The ORC evaporator equipment shown in Figure 2 has been replaced with the 6 developed heat exchangers shown in Figure 8. The newly developed process has included 11 heat exchangers as demonstrated in Figure 8. The ORC has been operated using PRSV fluid package as explained in section 2.3.

It is quite noticeable that the implementation of ORC to an existing process is challenging, specifically for a similar case to the present study, where the evaporator has been totally replaced with a set of heat exchangers. However, the conceptual design of the process is promising, where it could be applied to the grassroots designs for new biodiesel production plants. For revamping an existing plant, the topology of the existing equipment and the piping costs of connections should be carefully considered. An optimisation is needed to select the best location of the energy recovery. Additionally, the uncertainties of the actual plants and the heat loss in the pipelines would lead to the construction of an evaporator unit to the ORC to ensure that the solvent is fully in the vapour phase and to avoid any consequences in the turbine.

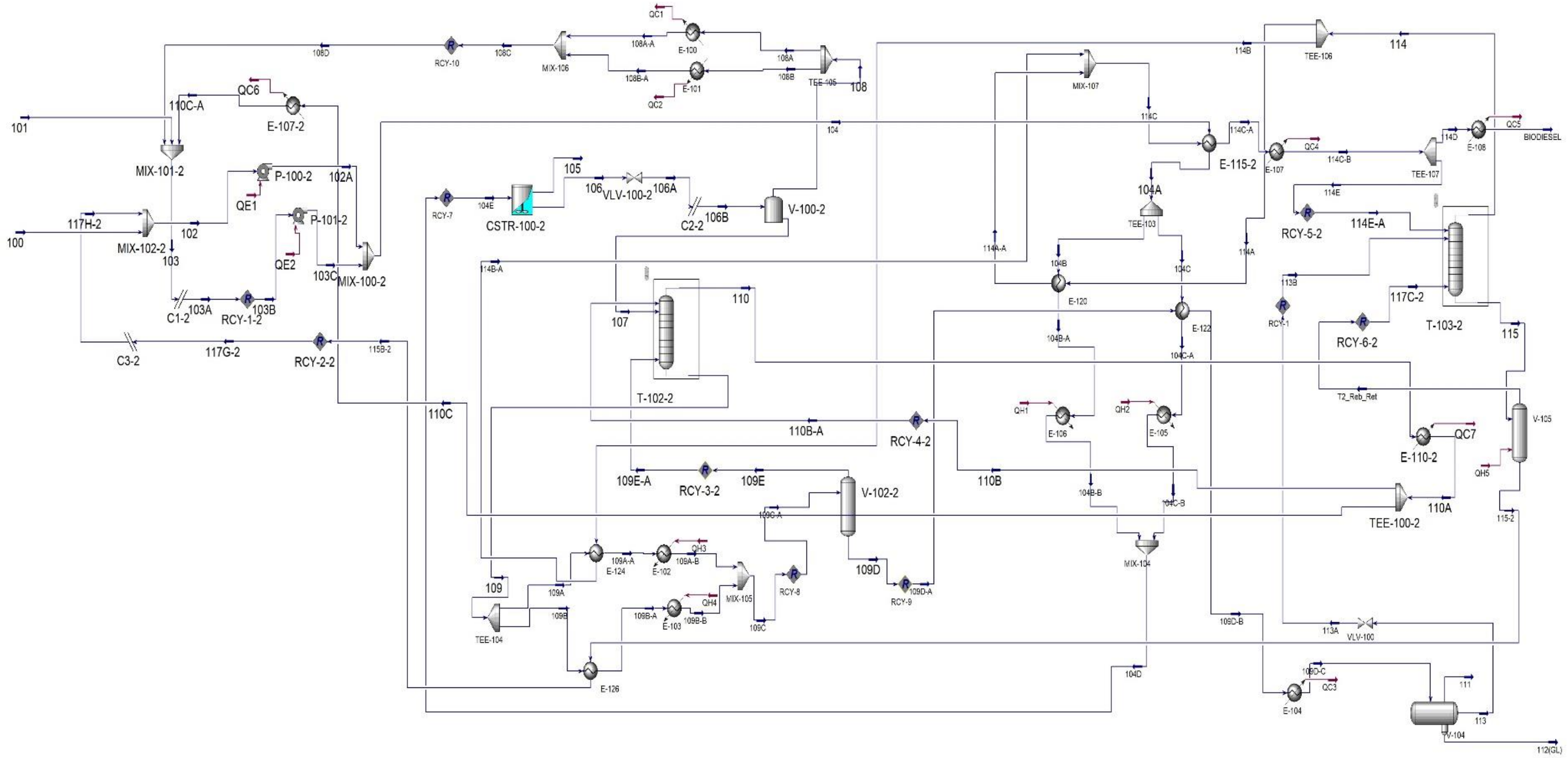


Figure 7. The developed process simulation for the second scenario

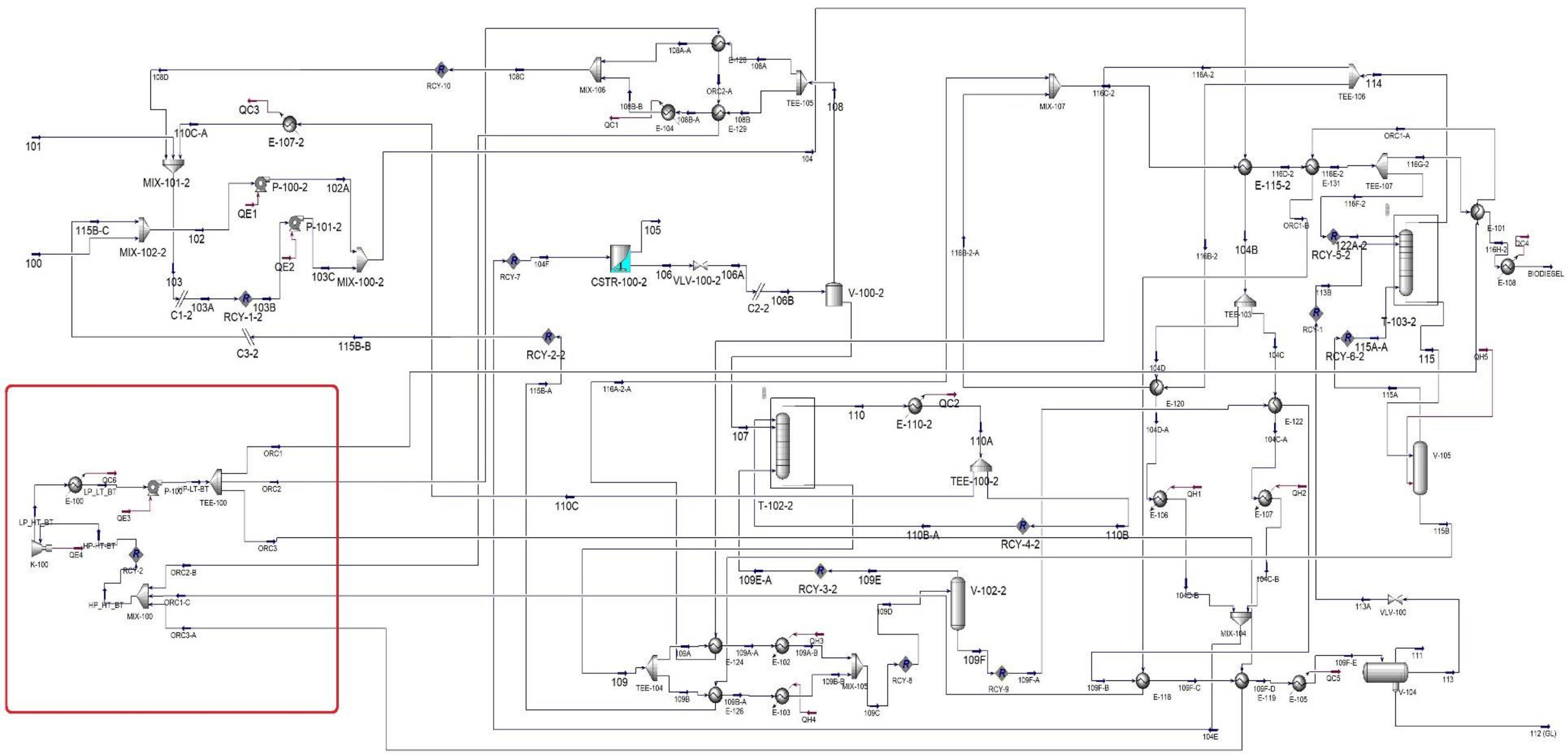


Figure 8. The developed process simulation for the third scenario

3.5 Process energy analysis

The energy balance of the developed scenarios has been tabulated in Tables 5-7. The summation of the electric energy has been calculated by adding the consumed electric power to the generated power (negative value). It has been observed (logically) that the first scenario has the highest energy consumption where no energy integration exists. However, the second scenario showed significant reduction of approximately 44% for both heating and cooling energies as a result of energy integration.

In the third scenario, the residual waste heat integration with ORC has resulted in electric energy generation of 455 kW from the turbine. The net process electric energy has resulted in an excess of 270 kW to be considered as process revenue. In addition, the process cooling energy for the third scenario has been significantly reduced resulting in 472.2 kW with nearly 90% reduction (without considering ORC solvent condensation). However, ORC condenser itself requires approximate of 4,110 kW. Accordingly, the overall process cooling energy is almost the same for both scenarios 2 and 3 as the reduction in the biodiesel process cooling energy is compensated by ORC condenser. Further, the heating energy is almost the same for both scenarios since the developed ORC has only targeted the waste heat. However, the developed ORC integrated process has resulted in generation of 270 kW instead of 165 kW consumption as described in the second scenario.

Conceptually, the integration of supercritical production process with ORC has significantly reduced the process utilities cost. However, the cost of installing the ORC units in addition to 6 heat exchangers should also increase the process capital cost. Hence, a comparative techno-economic analysis for the three scenarios has been developed to provide a complete insight whether ORC integration would increase the profitability of the process or not.

Table 5. Overall process energy balance for the first scenario

Scenario 1			
Stream	Electricity (kW)	Heating Energy (kW)	Cooling Energy (kW)
QE1	49.08		
QE2	116.27		
QH1		2,931.75	
QH2		1,354.47	
QH3		2,964.73	
QC1			257.47
QC2			1,608.49
QC3			2,594.22
QC4			0.62
QC5			3,558.25
QC6			273.5
QC7			154.49
SUM	165.35	7,250.95	8,447.04

Table 6. Overall process energy balance for the second scenario

Scenario 2			
Stream	**Electricity (kW)**	**Heating Energy (kW)**	**Cooling Energy (kW)**
QE1	49.079		
QE2	116.27		
QH1		438.43	
QH2		60.15	
QH3		209.71	
QH4		362.4	
QH5		2,963.63	
QC1			1,778.74
QC2			1,779.42
QC3			677.45
QC4			249.45
QC5			178.8
QC6			0.64
QH7			280.37
SUM	165.349	4,034.32	4,664.5

Table 7. Overall process energy balance for the third scenario

Scenario 3			
Stream	**Electricity (kW)**	**Heating Energy (kW)**	**Cooling Energy (kW)**
QE1	49.08		
QE2	116.27		
QE3	19.81		
QE4	-455		
QH1		438.43	
QH2		60.15	
QH3		201.22	
QH4		369.81	
QH5		2,966	
QC1			4.87
QC2			242.2
QC3			0.473
QC4			80.67
QC5			144.02
QC6			4109
SUM	-269.84	4,035.61	4,581.233

3.6 Techno-economic analysis

The developed scenarios have been all simulated to produce biodiesel with a capacity of 8 tonnes per hour (approximate of 70,080 tonnes per annum) according to our previous study. However, the presented techno-economic evaluation in this study has been applied for a downscaled process for the production of biodiesel with a capacity of 8,000 tonnes per annum so it could be compared with previous techno-economic studies in the literature [42,43] The analysis has followed similar approach for the techno-economic analysis of biodiesel plant published elsewhere [27]. Table 8 represents a summary of the comparative economic analysis for the developed scenarios.

Table 8. Summary of the techno-economic analysis results for the three scenarios

Economic indicator	Unit	Scenario 1	Scenario 2	Scenario 3
TCI	MMUSD	7.73	9.26	10.03
TOC	MMUSD/year	8.23	6.73	6.41
ATR	MMUSD/year	8.08	8.08	8.55
AP	MMUSD/year	- 0.15	1.35	2.14
PBP	Years	-	6.87	5.20
NPV	MMUSD	-	11.2	15.2
PI		-	1.3	1.5

It has been observed from Table 8 that the third scenario has the highest TCI cost of 10.03 MMUSD. This attributes to the installation of 11 heat exchangers for advanced process energy integration in addition to the ORC units i.e. turbine, condenser and pump. In comparison with the second scenario that includes only 5 heat exchangers, the value of TCI is lower. The process simplicity of the first scenario and limited units has resulted of the lowest TCI value of 7.73 MMUSD.

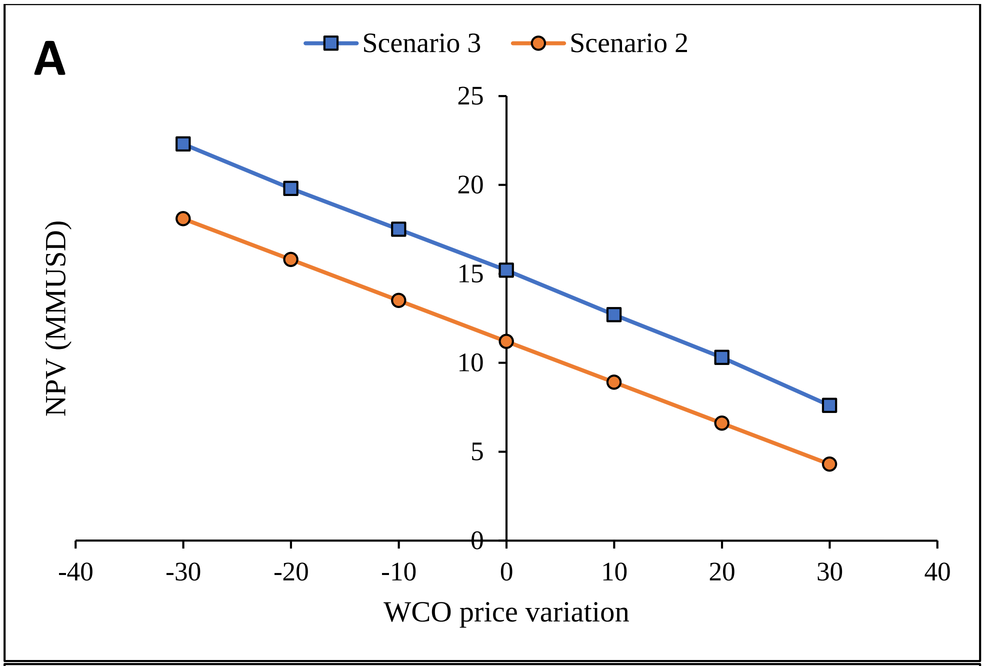
On the other hand, a different costing pattern has been observed for TOC for the three developed scenarios. The TOC is mainly based on the cost of raw materials and the process utilities. For the three scenarios, the raw materials are the same, but the utilities are different as described previously in section 3.4. The first scenario has reported the highest operating cost as it requires more external utilities than the other scenarios. A minor difference of the TOC values of scenarios 2 and 3 referred to the electric energy utility requirements as shown in Tables 6 and 7 (from section 3.4).

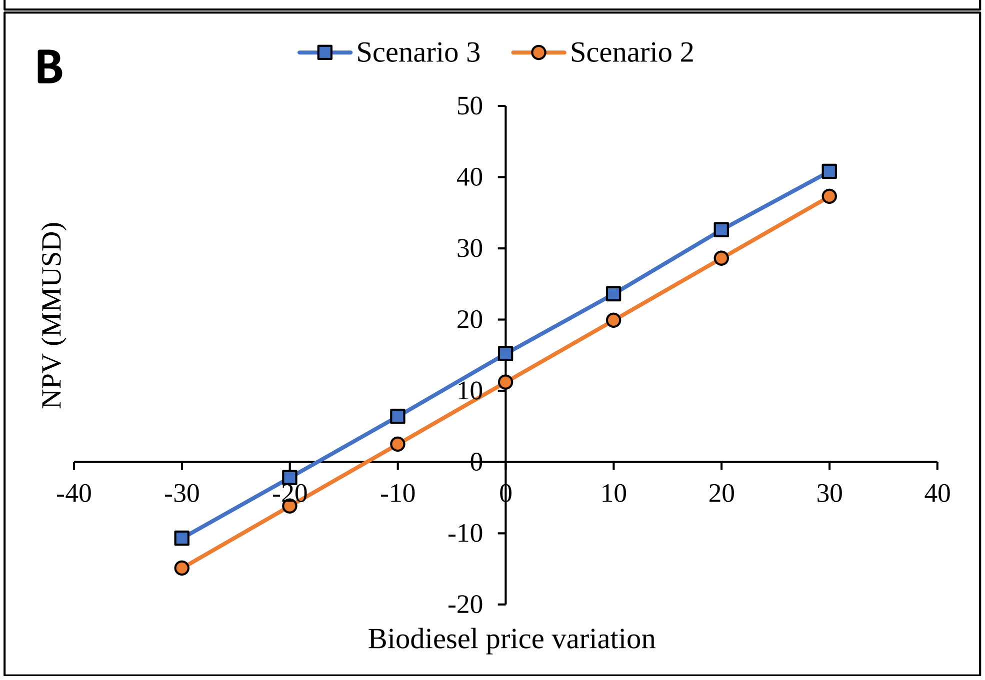
The total production of biodiesel for all scenarios is 8,000 tonnes per annum, approximately 913 kg/h. which represents a revenue of 7.918 MMUSD per annum. In addition, glycerol is produced with 0.16 MMUSD. Accordingly, the total revenue for both first and second scenarios is 8.08 MMUSD per annum as shown in Table 8. The third scenario has an additional revenue of 269.48 kW of electric energy (reported in Table 7), which represents an additional annual revenue of 0.47 MMUSD.

The profitability of the developed scenarios has been checked using the AP value, NPV, PI and PBP. The developed integrated biodiesel process with ORC (scenario 3) has shown the maximum profitability among the other scenarios where it recorded the highest AP, NPV, PI and lowest PBP. The AP value of the first scenario has shown a negative value which means that the process is not profitable. However, both second and third scenarios have shown AP values of 1.35 and 2.14 MMUSD/year, respectively. Thus, the techno-economic analysis has proven that integrating supercritical production of biodiesel with ORC has increased the process profitability.

A sensitivity analysis for the prices variation of the main input and outputs on the NPV of the overall process has been performed. The analysis has varied the prices of WCO, biodiesel and electricity about ± 30%. The results demonstrated in Figure 9A have shown the negative linear effect of increasing the price of WCO on the process NPV. On the other hand, the variation in biodiesel price showed the most significant variable affecting the process NPV where the increase in biodiesel price has an obvious positive effect. Further, the results presented in Figure 9B have shown high sensitivity of the overall process with the variation effect of biodiesel price where the process become non-profitable (NPV equals to zero) with decrease of biodiesel prices by 11.2% and 15.1% for both Scenarios 2 and 3, respectively. Finally, the effect of electricity price variation on the process NPV is illustrated in Figure 9C. The increasing price of electricity has a positive effect on the NPV of Scenario 3 and negative effect on Scenario 2. This observation attributes to the fact that Scenario 3 generates excess of electricity while Scenario 2 rely on external electric supply.

Ziyai et al. [27] have simulated three processes for biodiesel production from WCO using three cases technologies i.e. two-steps acid-alkaline catalysed process (case 1), acidic catalysed process (case 2), acidic catalysed followed by hexane extraction (case 3). They have integrated the three cases with supercritical water reforming for glycerol valorisation into hydrogen. They have reported that their first case has the maximum profitability with NPV of 15.7 MMUSD and AP of 2.3 MMUSD/year. In comparison with the developed ORC integrated process in this study, very similar economic profitability results have obtained for the same biodiesel production capacity. This ensures that integrating biodiesel process with waste valorisation technologies i.e. glycerol conversion to hydrogen and ORC waste heat recovery for electric power generation are the future routes to boost the process profitability.


A
Scenario 3
Scenario 2
NPV (MMUSD)
25
20
15
10
5
0
-40
-30
-20
-10
0
10
20
30
40
WCO price variation


B
Scenario 3
Scenario 2
NPV (MMUSD)
50
40
30
20
10
0
-10
-20
-40
-30
-20
-10
0
10
20
30
40
Biodiesel price variation

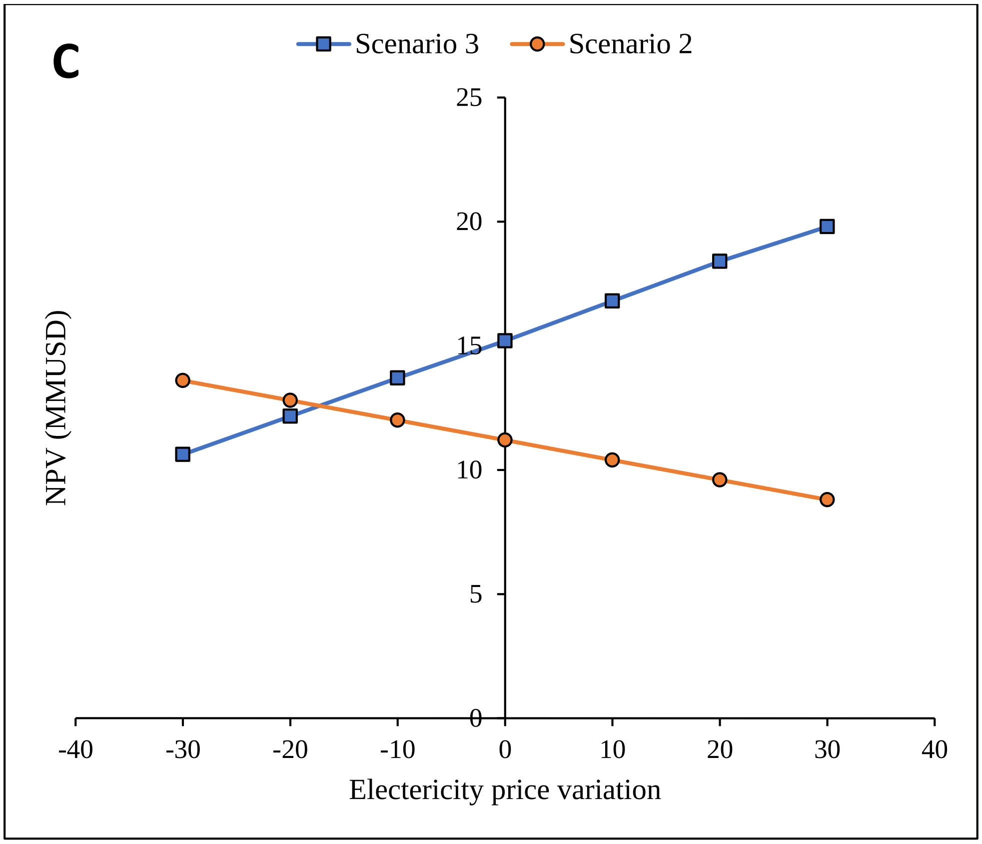


Figure 9. Effects of the price variation of WCO (A), biodiesel (B) and electricity (C) on the process NPV

4. CONCLUSIONS

This article presents a novel integration approach for supercritical biodiesel process with ORC in an attempt to increase the process profitability and valorise the residual process heat. The process has been developed to valorise residual hot streams in a previously published work using ORC. The temperature range of the ORC solvent has been defined between 31 and 79 °C, based on the minimum temperature of the process residual hot streams (89 °C). Eight organic Rankine solvents have been used to operate the developed ORC where butene has been selected as an optimal solvent with the highest power generation of 455 kW at moderate pressure scale. The developed new process (scenario 3) has been economically compared with previously published processes without ORC. The key findings of the techno-economic comparative study are summarised below:

- The TCI of the first scenario has reported the lowest value due to the simplicity of the process followed by second scenario that has 5 heat exchangers.
- The TCI of the third scenario has reported the highest value due the additional cost of ORC and 6 additional heat exchangers than second scenario.
- TOC of the developed scenarios has varied according to consumption of the utilities where the first scenario has recorded the highest value.

- ATR of the first and second scenarios are almost the same as they are only based on the produced biodiesel and glycerol sales unlike the third scenario that has additional electrical power sales.
- The third scenario has resulted in net production of electricity of 257 kW for 8,000 tonnes/annum biodiesel production plant.
- The first scenario has been found to be a non-profitable process.
- The third scenario has provided the best economical approach with the highest NPV, AP and PI.

In summary, the integration of supercritical biodiesel process with ORC has provided a new approach to increase the process profitability. The developed approach has not only provided self-sufficiency in electric energy for the process, but also produced excess electric power as revenue. Future research work will include an exergoeconomic analysis to provide a wider vision for the profitability of the developed approach. Further, retrofit optimisation of the process HEN should be considered for better residual heat recovery.

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