Supplementary Information for

Assessing technological pathways for a circular PET management in Switzerland integrating MFA, LCA and TEA

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Aim of this document

This document presents the modeling of the PET treatment and recycling technologies, particularly recycling processes such as depolymerisation, with utility systems and heat integration.

1. Mechanical recycling unit modeling

1.1. Process steps

Mechanical recycling begins with a shredding step, during which the incoming plastic is reduced to pieces approximately 10 cm in size, providing a homogeneous particle size suitable for subsequent processing stages (Figure 1). Next, the plastic is washed with water to remove small impurities, such as dust. The plastic pieces are milled into three- to four-centimeter flakes to facilitate the float-sink separation. It will separate the last impurities that have passed through the sorting process. The weight of the particles helps separate them, which requires a homogeneous flake size for shredding. Then, a mechanical dryer (centrifuge) and a thermal dryer reduce the water content of the stream. Finally, impurities and other plastic streams from the float-sink separation are incinerated. The plastic is then milled a second time to obtain flakes of less than 1 cm in size, to be sent to the extruder. It heats the plastic, decontaminating it to meet food contact standards and turning it into homogeneous granules of recycled plastic. Obtained pellets have properties similar to those of virgin plastics, but with slightly less resistance. Indeed, the shredding process has broken down certain structures and partially altered the strength of the plastic [16], [5], [22]. Finally, the wastewater from washing and flotation separation is treated to be either reused in the process or discarded.

1.2. Main parameters of the model

The recycling rate of PET in this facility is set at 80%, a conservative value derived from various sources, including laboratory analyzes of PET recycling processes [36, 43], industrial-scale operations (such as the German recycling system reported by [9] and the broader European context discussed by [1]), and modeling studies [28]). After three to four recycling cycles, PET loses its initial properties and becomes unsuitable for food consumption due to shorter chains and loss of viscosity [5], [22]. It can then be downgraded and used in other sectors, such as textiles. The downcycling cascade is specified in SI1 M1.3 and is derived from the work of [19], [20].

The electricity requirement is assumed to be 560 kWh t^{-1} of PET treated, a conservative value derived from the mechanical recycling of LDPE, PP, and PS [23]. For comparison, [28] reports an electricity demand of 500 kWh t^{-1} for PET, while [9] indicates a range of 200–350 kWh t^{-1}.

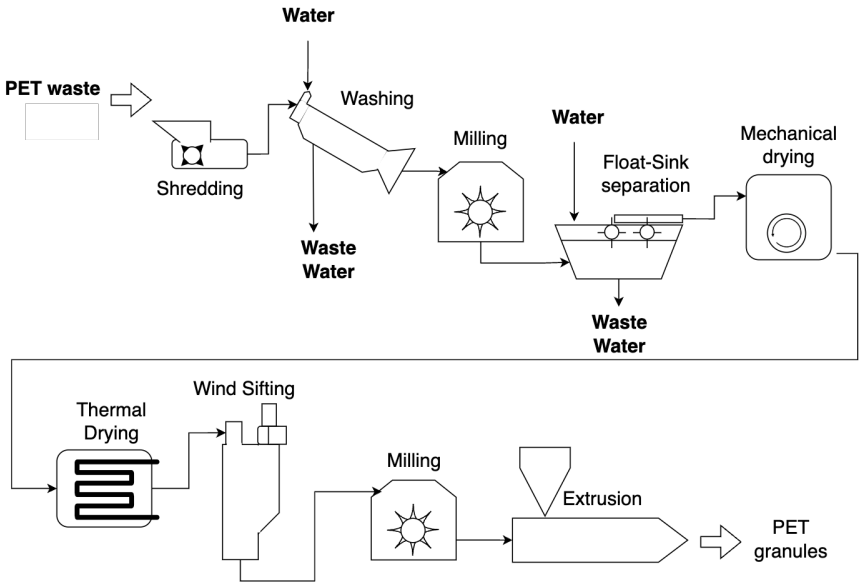

Fig. 1. Detailed PFD of the mechanical recycling unit.

Finally, water consumption is estimated at 3 t. t_{PET}^{-1}, based on [28], who report 2 t. t^{-1}, and [9], who indicate a range of 0.7–4.5 t. t^{-1}. The remaining PET and impurities are sent for incineration. The heat generated by the incinerator is recovered and integrated into the system, supplying the mechanical recycling unit and thereby avoiding the need for a dedicated boiler.

2. Enzymatic depolymerisation modeling

2.1. PET characterization

PET is modeled as a non-conventional solid. The proxanal, ultanal, and sulfanal compositions used are shown in Table 1 [34].

Table 1. Nonconventional solid input for proxanal and ultanal composition of PET NC solid input.

Proxanal		**Ultanal**	
Moisture	0.00	Ash	0.31
Volatile matter	5.60	Carbon	62.25
Fixed carbon	94.09	Hydrogen	4.06
Ash	0.31	Oxygen	33.38

2.2. PET pre-treatment

Before PET can be hydrolyzed, the PET balls recovered from the recycling units need to be pre-treated into PET flakes small enough for hydrolysis.

The pre-treatment is done in two steps, as illustrated in Figure 2. Firstly, the PET flakes, having a size of 10mm, are fed into an extruder after being heated to 265°C by a heat exchanger (HX1). The extruder works by heating the plastic slightly above its melting temperature of 250°C to melt it and shape it into a smaller size. It is modeled with a crusher (C1) at 265°C and by defining the desired exit particle size distribution (PSD) of the PET particles. This step is mostly required to reduce the crystallinity of the PET, which leads to more efficient depolymerization [39]. The exit PSD uses a normal distribution function with a d50 = 4mm and a standard deviation of 2mm [12, 24, 38]. The extruder used for this process is a twin-screw extruder with a residence time of five minutes. This results in an extruder volume of $0.377m^3$. Assuming a length to diameter ratio of 40, the diameter is 0.23m and the length 9.16m.

After the extrusion, the PET flakes need to be reduced further to a diameter below 1mm to have enough surface area for the hydrolysis to take place effectively. This is done by using a cryo-grinder at 5°C and 1 bar to prevent any degradation of the PET. This is modeled with a crusher with a specified PSD. Before being fed to the crusher (C2) the PET flakes are cooled with a heat exchanger (HX2). The final PSD of the PET flakes is d50 = 0.5mm and a standard deviation of 10^9m [4]. To reach such a particle size distribution, the plastic cryo-grinder requires a residence time of ten minutes [18]. From this residence time, it has been determined that the length of the cryo-grinder is $0.755m^3$.

2.2.1. NaOH dissolution

Sodium hydroxide (NaOH) is required in the process to maintain a pH range in which the cutinase enzyme remains active. Since the hydrolysis reaction is carried out in an aqueous medium, the addition of solid NaOH to the process results in its spontaneous dissolution. To simulate this

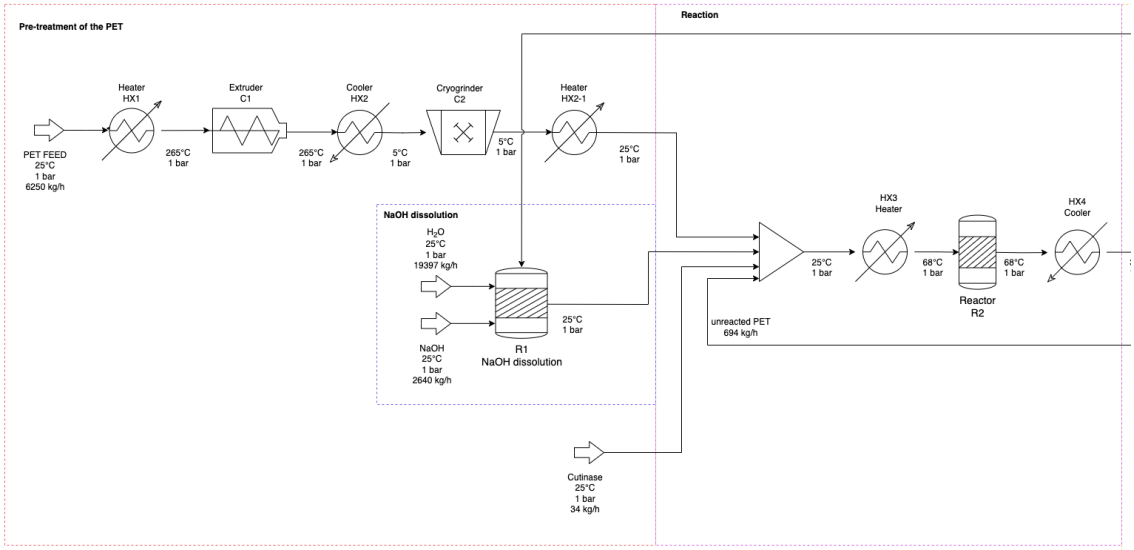

Fig. 2. Detailed PFD of PET pre-treatment, NaOH dissolution, and enzymatic depolymerisation reaction step.

behavior, an `RSTOICH` reactor (R1) operated at 25 °C and 1 bar is included in the Aspen simulation, where Reaction (1) takes place with 100% conversion:

$$\mathrm{NaOH\ (s) \rightarrow Na^{+}\ (aq) + OH^{-}\ (aq)} \tag{1}$$

The NaOH fed to the reactor is in solid form and is dissolved using recycled process water as well as fresh make-up water.

The amount of NaOH introduced into the process is adjusted using a design specification block to match the quantity of terephthalic acid (TPA) produced by the hydrolysis reaction that must be neutralized to form the terephthalate dianion (TPA^{2-}). This ensures that the system does not become excessively acidified due to the production of terephthalic acid. The neutralization reaction is described by Reaction 2:

$$\mathrm{TPA\ (s) + 2\,OH^{-}\ (aq) \rightarrow TPA^{2-}\ (aq) + 2\,H_2O\ (aq)} \tag{2}$$

Before neutralization, the TPA produced is solid as it has a low solubility in water ; however, the charged TPA^{2-} salt is soluble.

2.2.2. Enzymatic hydrolysis reaction

The core of the process is the hydrolysis reaction used to depolymerize the pretreated PET flakes. The overall reaction is as follows:

$$\mathrm{PET\ (s) + 2\,H_2O\ (l) \xrightarrow{cutinase} TPA\ (s) + EG\ (aq) + PET\ (s)} \tag{3}$$

This reaction (R3) is catalyzed by cutinase. To achieve a PET conversion of 90%, approximately 5 mg of cutinase are required per gram of PET processed [39]. The inlet flow of enzyme is controlled using a design specification block to maintain this ratio.

The reactor that models the hydrolysis step is an `RYield` reactor (R2). It operates at a temperature of 68 °C and a pressure of 1 bar, respectively, to ensure optimal enzyme activity and sufficient accessibility of the ester bonds [4]. The remaining inputs correspond to the expected yields of each component participating in the reaction.

Sodium ions (Na^+) and cutinase are not consumed during the reaction and are defined as non-reactive species, resulting in identical inlet and outlet flow rates. Since the amount of sodium hydroxide present in the system is specifically adjusted to neutralize all solid TPA produced, hydroxide ions (OH^-) react completely, and their yield is set to zero.

Table 2. Yields of each component for the PET depolymerization reaction.

Component	Yield
PET	0.0152
H_2O	0.825245
TPAIONS	0.116344
EG	0.0432108
OH^-	0

The yields of the remaining components are based on a target PET conversion of $\approx$ 90%. For a basis of 100 kg of PET fed to the reactor, the reaction results in $\approx$ 10 kg of unreacted PET, $\approx$ 66 kg of terephthalate dianion (TPA^{2-}, accounting for the neutralization step), and $\approx$ 24 kg of ethylene glycol (EG). Based on this reference basis, the expected mass flow rates of the products are calculated and normalized by the total mass of reacting species. The resulting mass-based yields are summarized in Table 2. Inert components are NA^+, cutinase, and other impurities.

This reactor is used to model the depolymerization, which is done as a batch process with an assumed residence time of 96 hours [39]. In order to process the volume flow simulated, it would require a reactor of 4927 m^3, which is split into five 1000 m^3 reactors in series.

Operating in series helps control the feed flow. Indeed, precise control is required due to the presence of solid PET and the possible inhibition of the enzyme due to byproduct build-up or pH. This reaction require a long residence time, ensuring that the PET continues to get progressively more broken down. The stirring also needs to be controlled and remain between 200 and500 rpm, due to the enzyme, which might become damaged if it is too strong. It remains important to ensure good contact between the reactants and the catalyst. A stirring of would be appropriate [13].

pH control is key in this process, where a cutinase enzymatic catalyst is used to ensure it remains active. The pH should remain around 9, which is the case in the stream exiting the reaction. Finally, the temperature is controlled to maintain isothermal conditions in the reactor. Maintaining the temperature at 68°C is required, as it corresponds to an optimum between the enzyme activity

and the availability of ester bonds in PET as it approaches its glass transition temperature and becomes more flexible [21, 35].

2.2.3. Purification of unreacted components

Following the reaction, unreacted components are separated into the stream containing TPA and EG, as illustrated in Figure 3.

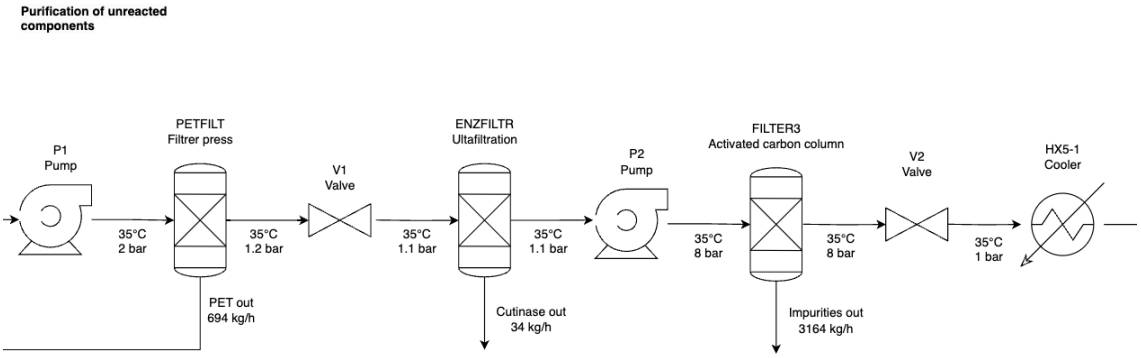

Fig. 3. Detailed PFD of the purification of unreacted components (PET, cutinase, and other impurities) following the depolymerisation reaction.

PET filtration

After the reaction, the temperature is reduced to 35°C using a heat exchanger (HX4), and the pressure is increased with a pump (P1) to 2 bar. The first step of the purification process is to filter out the unreacted PET. This is done by a filter press and by recycling the PET flakes back into the mixer preceding the reactor. The inlet of PET is adjusted using a design specification calculator, ensuring that the total PET entering the process remains at 6250 kg.h^1. The filter press works by applying pressure to pump the slurry through the filter plates. The pressure drop through this unit is 0.8 bar, and the final pressure of the streams exiting it is 1.20 bar.

This unit is modeled using a separator block and setting split fractions. Here, all of the PET is assumed to be recovered into the out stream, and every other component in solution is assumed to continue through the process. The necessary capacity of the filter press is calculated using the flow rate that needs to be passed through per cycle, as well as the solid fraction of 1.59% in the slurry. Assuming that the press operates for 8-hour days and goes through three cycles each day, the capacity is 4 m^2, which corresponds to a filtration area of 60 m^2.

Enzyme filtration

The enzyme used to catalyze the reaction is filtered out next, after the pressure is decreased from 1.20 bar to 1.10 bar using a valve (V1). This separation is done using ultrafiltration. Since cutinase has an average molecular weight of 30 kDa, the molecular weight cut-off of the membrane necessary for this separation is 30 kDa [29]. The ultrafiltration is performed at moderate pressures,

typically between 1 and 3 bars, to preserve enzymatic activity and due to the cutinase volume fraction, which is very low compared to the total volume flux.

For the ultrafiltration sizing, the flow to treat is a mass flow rate of $\approx$ 50'000 L.h^1. It is therefore advisable to choose a high specific flow of 50 L.h^2.m^{-1}, and to separate the flow to be treated into five lines of 10,000 L.h^1. The surface area for each of these lines would then be 200 m^2, and each could be treated with several ultrafiltration modules. This is modelled with a separator block (ENZFILTR), where the split fraction of cutinase is 1 into the ENZOUT stream.

Activated carbon column

In this process, there are no impurities such as ash and glue considered; however, in reality, these would need to be removed as well. It could be done using an activated carbon column operating at 35°C and 8 bar. This column is modeled using a separator block (FILTER3) based on split fractions from [39] to remove some water and EG. The pressure is increased to 8 bar using a pump (P2) and then decreased back to 1 bar with a valve (V2).

2.2.4. TPA purification

TPA is separated from the other components in the process by means of crystallization, following the steps presented in Figure 4. At this stage of the process, TPA is present in the form of terephthalate dianions (TPA^{2-}), which are highly soluble in water and therefore remain in the aqueous phase. These ions are subsequently neutralized using sulfuric acid.

As was previously done with sodium hydroxide, sulfuric acid (H_2SO_4) is introduced into the process in solid form and mixed with water in an `RStoic` reactor (R3) operated at 25 °C and 1 bar. This setup is used to simulate the spontaneous dissociation reaction that occurs when sulfuric acid is dissolved in water. The reaction, which is assumed to proceed with 100% conversion, is described by Equation 4:

$$H_2SO_4\ (s) \rightarrow 2\,H^+\ (aq) + SO_4^{2-}\ (aq) \tag{4}$$

Crystallization of TPA

To separate TPA from the remaining components, it is crystallized in a crystallizer unit (`TPACRYST`). Since uncharged TPA exhibits very low solubility in water, crystallization can be carried out at 20 °C and 1 bar. At 25 °C, the solubility of TPA in water is reported to be 0.018 g L^{-1} [11, 31].

The reaction taking place corresponds to the neutralization of the terephthalate dianion (TPA^{2-}) by the protons released during the dissociation of sulfuric acid, as shown in Reaction 5:

$$TPA^{2-}\ (aq) + 2\,H^+\ (aq) \rightarrow TPA\ (s) \tag{5}$$

The crystallizer unit also requires specification of the PSD of the crystallized product. This distribution is defined as a normal distribution with a median particle diameter (d_{50}) of 80 µm and a standard deviation of 25 µm [25].

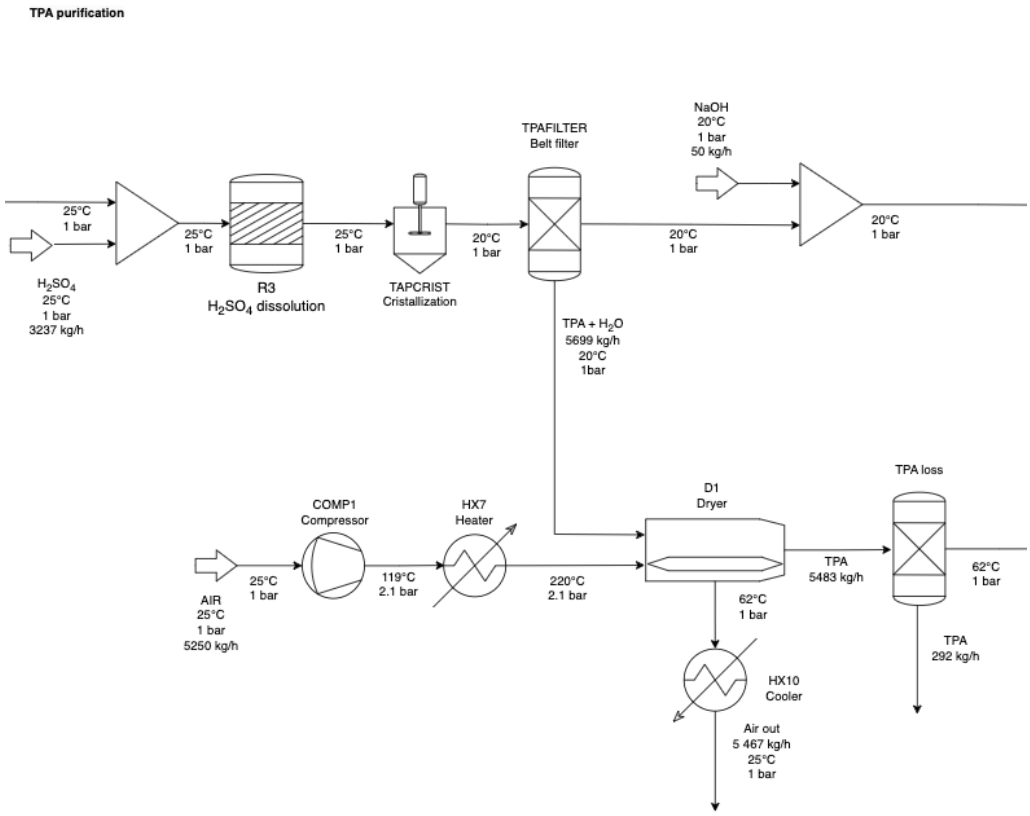

Fig. 4. Detailed PFD of the TPA purification, cristallization and drying steps.

The required size of the crystallizer can be estimated based on the inlet mass flow rate of TPA and the targeted crystal size. The crystal growth velocity is approximated as 2 µg min^{-1}. Based on this value, the residence time required for crystal growth is calculated to be 40 min. Given a volumetric flow rate of 0.014 m^3 h^{-1}, the resulting crystallizer volume is estimated to be 32 m^3. Assuming a minimum crystallizer length of 7m and a cylindrical geometry, this corresponds to an internal diameter of approximately 2.4m [44].

TPA filtration

Once solid TPA has been crystallized, it is separated from the liquid phase using a belt filter. This separation is modeled using a separator block (`TPAFILTR`), in which all solid TPA along with a fraction of the process water are directed to the drying unit (S29). The remaining water, EG, and all dissolved ionic species are sent to downstream purification steps (S20).

The use of a belt filter is well suited for this application, as it is capable of handling large volumetric flow rates and separating particles with sizes typically ranging from 1 to 100 µm, even when significant variations in solids content are present in the feed stream. In the present case, the average particle size of TPA crystals is characterized by a d_{50} of 80 µm, with a total mass flow rate

of approximately 43'000 kg h^{-1} and a solids content of 13%. These operating conditions fall well within the typical operating range of belt filtration systems [7].

Drying

After crystallization, the remaining water is separated from the solid TPA using a direct rotary dryer, which uses hot air to evaporate the water from the crystal surface. The wet TPA flows under gravity, due to the incline of the dryer, in direct contact with the hot air, so the remaining moisture can be evaporated through heat transfer [40]. Air is first compressed to 2.10 bar using a compressor (COMP1). This operation also raises the temperature to 123°C. The final operation is to raise the temperature of the hot air to 220°C using a heat exchanger (HX7). The dryer unit (D1) is designed using the shortcut design of the Aspen unit. It requires the specification of the final temperature and pressure. The exit temperature is calculated with a design specification linked to the dryer block, which sets the correct value based on the heat balance. As the drying process relies on the exchange of heat between the compound to be dried and the hot air, the following balance is established (Equations 6 and 7).

$$Q_{\text{air}} = Q_{\text{drying}} \tag{6}$$

$$\begin{aligned} \dot{m}_{\text{air}} C_{p,\text{air}} \left(T_{\text{in,air}} - T_{\text{out}}\right) = {} & \dot{m}_{\text{H}_2\text{O}} C_{p,\text{H}_2\text{O}} \left(T_{\text{vap}} - T_{\text{in,TPA}}\right) \\ & + \dot{m}_{\text{H}_2\text{O}} \Delta H_{\text{vap}} \\ & + \dot{m}_{\text{H}_2\text{O}} C_{p,\text{H}_2\text{O}} \left(T_{\text{out}} - T_{\text{vap}}\right) \\ & + \dot{m}_{\text{TPA}} C_{p,\text{TPA}} \left(T_{\text{out}} - T_{\text{in,TPA}}\right) \end{aligned} \tag{7}$$

where $\dot{m}$ denotes the mass flow rate of the respective components in kg h^{-1}, and C_p represents the specific heat capacity of each component in kJ kg^{-1} K^{-1}. ΔH_{vap} is the enthalpy of vaporization of water, equal to 2,257 kJ kg^{-1}.

$T_{\text{in,air}}$ is the inlet temperature of the hot air, which is set to 220 °C. $T_{\text{in,TPA}}$ corresponds to the inlet temperature of both water and TPA entering the dryer and is equal to 20 °C. T_{vap} is the vaporization temperature of water, which is 100 °C at ambient pressure. T_{out} represents the outlet temperature of all components and is the value calculated from the energy balance. Based on this energy balance, the calculated outlet temperature is found to be 61.64 °C.

In the simulation, the outlet stream containing solid TPA (`TPA`) does not contain any residual water, as all the moisture is assumed to be fully evaporated. The evaporated water exits the system together with the drying air (`AIRTOENV`) after being cooled back to ambient temperature using a heat exchanger (`HX10`). The direct-heated rotary dryer operates at atmospheric pressure and is typically of cylindrical geometry [10]. Based on the required processing conditions, the dryer volume is estimated to be 8.5 m^3, corresponding to a length of 6.5 m and a diameter of 1.3 m.

2.2.5. Sodium sulfate purification

From the TPA filter, the remaining ions present from the various neutralization reactions need to be removed, following Figure 5. This is done by crystallizing out sodium sulfate salt (Na_2SO_4).

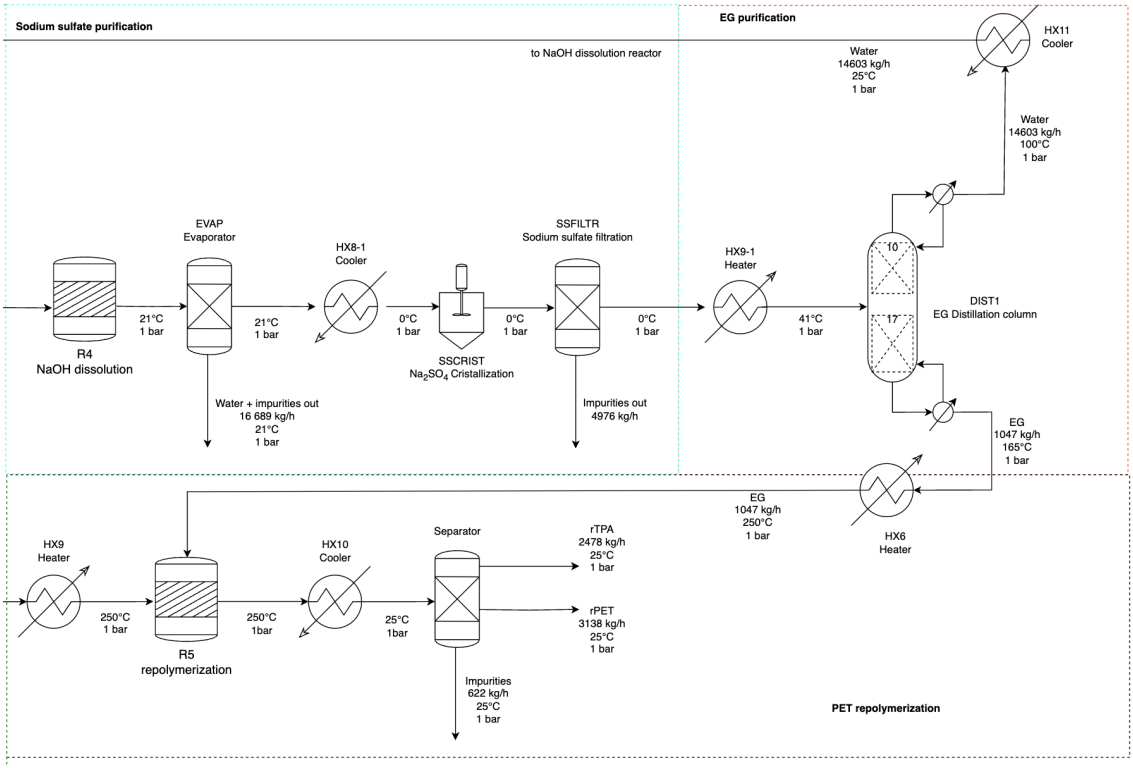

Fig. 5. Detailed PFD of sodium sulfate purification, EG distillation, and PET repolymerisation steps.

To do so, NaOH is added to the system to adjust the pH. Its dissolution is modeled the same way as previously in reactor R1.

Evaporation

The first step is to remove some water to facilitate the subsequent crystallization of Na_2SO_4 by decreasing its solubility in this system. According to the quantity of flow to be treated, an MVR evaporator (mechanical vapor recompression) is used. This type of evaporator offers high efficiency and relatively low operating costs. In fact, the steam produced during evaporation is reused to continue feeding the evaporator [10]. It can handle flows from 10 to 200 t/h [2], which is within the volumes of this process (37 t/h). It removes a approximately half of the water, with losses of ethylene glycol.

Crystallization of sodium sulfate

The crystallization of sodium sulfate occurs according to the reaction shown in Reaction 8 and must be carried out at 0 °C due to the high solubility of this salt in water at elevated temperatures. The flow is cooled before entering the crystallizer using a cooler (HX8). The solubility of sodium sulfate is reported to be 4.97 g L^{-1} at 32.4 °C and decreases to 0.7 g L^{-1} at 0 °C. Under these

conditions, the salt that precipitates is Glauber's salt, sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$) [6].

$$2\,Na^+\,(aq) + SO_4^{2-}\,(aq) \rightarrow Na_2SO_4\,(s) \tag{8}$$

The particle size distribution (PSD) specified for this crystallization step is defined as a normal distribution with a median particle diameter (d_{50}) of 350 µm and a standard deviation of 120 µm [15].

The sizing of the sodium sulfate crystallizer (`SSCRYST`) is determined using the same methodology as that applied for the TPA crystallizer. This results in an estimated crystallizer volume of 8 m^3, corresponding to a diameter of 1.2 m and a length of 7.4 m [42].

Sodium sulfate filtration

The crystallized sodium sulfate, together with the remaining dissolved ionic species, is separated in the `SSFILTR` unit, which is modeled using a separator block. For this separation step, a pusher centrifuge is selected, as this type of equipment is capable of handling a solid throughput of up to 150 t h^{-1} and is well suited for the filtration of sodium sulfate [3].

Based on the supplier's operating data [3] and considering a solid throughput of approximately 4,500 kg h^{-1} in the present process, the required filtration area A can be estimated. Assuming a conservative solids flux of 1,500 kg m^{-2} h^{-1}, the filtration area is calculated as:

$$A = \frac{\dot{m}_{\text{solid}}}{R} = \frac{4{,}500\ \text{kg h}^{-1}}{1{,}500\ \text{kg m}^{-2}\ \text{h}^{-1}} = 3\ \text{m}^2 \tag{9}$$

Where R is the capacity of the filter, and $\dot{m}_{\text{solid}}$ is the solid mass flow rate . This filtration area is consistent with the capacities of commercially available pusher centrifuges.

2.2.6. EG purification via distillation

To perform the re-polymerization of PET using TPA and EG, EG needs to be purified and separated from the remaining water. This is done via a distillation column.

Prior to distillation, the process stream is heated to 41 °C using a heat exchanger in order to provide suitable thermal conditions for phase separation. The heated stream is then directed to a distillation column designed to separate water from EG.

Due to the significant difference in boiling points between water (100 °C) and EG (197.3 °C), water is recovered as the light component while EG is collected as the heavy component. The column operating conditions are selected to achieve a near-complete recovery of water in the distillate, while minimizing EG losses. A high water recovery is targeted to enable its reuse elsewhere in the process, whereas only trace amounts of EG are allowed to exit with the overhead stream.

To ensure an appropriate balance between energy consumption and separation efficiency, the reflux ratio is 0.15. Under these conditions, the column requires 13 theoretical stages, including the condenser and the reboiler, with the feed introduced at stage 9.

The condenser operates as a total condenser, as non-condensable gases are present in the system. The overhead stream exits the condenser at approximately 100 °C, while the bottom stream leaves the reboiler at around 165 °C. The corresponding condenser and reboiler duties are approximately 9.6 MW and 10.1 MW, respectively.

Following distillation, the bottom product reaches an ethylene glycol purity of 96.8 wt%, which is considered sufficient for its subsequent use in PET repolymerization, particularly since the esterification reaction inherently produces water. The overhead water stream is cooled to 25 °C and recycled back to the depolymerization step. The required make-up water is adjusted to maintain a total water flow rate of 37,000 kg h^{-1} for the hydrolysis reaction, accounting for the amount recovered through distillation. Only trace quantities of EG remain in the recycled water stream.

The distillation column is sized based on standard design practices. It consists of 13 stages with a tray spacing of 0.6 m and a tray thickness of 3 mm. These specifications result in an internal column diameter of 3 m and a total column height of 6.7 m. The wall thickness is 20 mm and the column is constructed using stainless steel 304. The resulting total shell volume is estimated at 46.11 m^3, corresponding to a total steel mass of approximately 9.2 t.

2.2.7. PET repolymerization

Following the purification of EG and TPA, they can react with one another to form recycled PET. When combining TPA and EG, PET is produced by direct esterification. The reaction happens in several steps and at various conditions; however, the average temperature of this process is 250 °C, and the average pressure is 1 bar. There is first an esterification reaction that yields BHET, which is prepolymerized until it reaches a degree of polymerization of around 30. PET is then formed by polycondensation, which forms higher molecular weight polymers.

The esterification step proceeds according to the reaction shown in Equation 10. This reaction is typically carried out at temperatures ranging from 220 to 260 °C and at moderate pressures (between 3 and 6 bar) [33].

$$2\,\mathrm{EG} + \mathrm{TPA} \rightarrow \mathrm{BHET} + 2\,\mathrm{H_2O} \tag{10}$$

Once bis(2-hydroxyethyl) terephthalate (BHET) molecules are formed, they undergo a prepolymerization step in which the monomer units are linked together. This step is conducted at similar temperatures but under reduced pressure in order to continuously remove the water formed during the reaction. Water is additionally removed from the system through distillation to shift the equilibrium toward polymer formation.

In the final stage, the PET oligomers produced during prepolymerization are further extended through melt polycondensation. This reaction takes place at temperatures typically between 260 and 280 °C under high vacuum conditions, which promote the removal of ethylene glycol and water and enable the formation of high-molecular-weight polymer chains.
These polymerization steps are generally carried out in a series of continuously stirred reactors to ensure effective mixing and heat transfer. The overall polymerization reaction can be expressed

by Reaction 11, where the degree of polymerization of the resulting polyethylene terephthalate (PET) is directly related to the initial amounts of ethylene glycol and terephthalic acid [33]:

$$n\,EG + n\,TPA \rightarrow [PET]_n + 2\,n\,H_2O \tag{11}$$

The polymerisation process (Reaction 11) is modeled using a stoechiometric reactor at 250°C, followed by a separator at ambient temperature giving the recycling PET, the remaining TPA, and impurities.

2.3. Heat integration

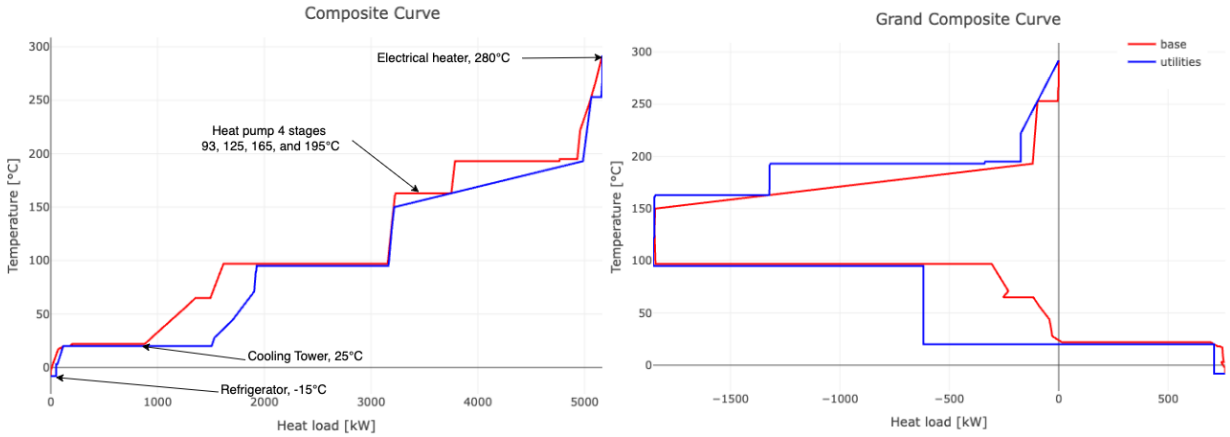

Fig. 6. Composite (right) and Integrated Composite Curve (left), including utilities of the process, with heat integration and complete power recovery. Results are presented in kWh/1t of PET depolymerised.

3. Methanolysis depolymerisation modeling

3.1. Property method

In the vapor-phase methanolysis process, the reacting system contains a mixture of polar and nonpolar species, including methanol, water, ethylene glycol (EG), dimethyl terephthalate (DMT), mono hydroxy-ethyl terephthalate (MHET), and PET. Due to the presence of highly polar and size-asymmetric molecules, the system exhibits significant non-ideal behavior in the liquid phase. To represent these non-idealities, the UNIQUAC activity coefficient model is employed for this phase. UNIQUAC provides a robust framework for modeling non-ideal mixtures by accounting for both combinatorial effects (arising from molecular size and shape differences) and residual interactions (due to polarity and hydrogen bonding). In this study, the binary interaction parameters for DMT-methanol and DMT-water (Table 3 were regressed from literature data [47,48], while the DMT-EG interaction was estimated using the UNIFAC group contribution method.

For the vapor phase, the Ideal Gas equation of state is used. Given the moderate pressures (1–3 bar) and elevated temperature (260 °C) involved in the process, the main vapor-phase components (methanol and water) exhibit near-ideal gas behavior, making the ideal gas law an appropriate and computationally efficient choice for accurate vapor-phase property predictions.

Table 3. UNIQUAC binary interaction parameters used to simulate DMT interactions

i	j	b_{ij}	b_{ji}	a_{ij}	a_{ji}
DMT	Water	−184.6	−252.1	0	0
DMT	Methanol	−1000.0	91.40	0	0
DMT	EG	82.40	−197.7	0	0

3.2. PET molecule Simulation

The PET molecule is defined as a polymer composed of distinct molecular segments that reflect its chemical structure. Specifically, PET was modeled using three structural segments: EG-E, EG-R, both representing ethylene glycol as end group; and T-R, representing the terephthalate aromatic repeating group as shown in Table 4.

Table 4. Segment Definition of PET Used in the methanolysis process.

Segment	**Type**	**Molecular Formula**	**Number per Polymer Chain**
EG-E	End group	$C_2H_5O_2$-E	2
EG-R	End group	$C_2H_4O_2$-R	79
T-R	Repeating unit	$C_8H_4O_2$	80

This segmented approach allows for a flexible polymer representation while preserving the essential structural features that influence the PET reactivity during depolymerization. The polymer was assembled using these segments repeatedly, with EG-E and EG-R serving as the diol-based terminal and internal units, and TR representing the aromatic acid component. To match the behavior of real PET as used in industrial applications, the degree of polymerization was selected to achieve a final number-average molecular weight of approximately M_n = 16 000g/mol.

3.3. PET pre-treatment

Before PET can be methanolysed, the PET balls recovered from the recycling units need to be pre-treated into PET flakes small enough for methanolysis. The process is similar to the PET pre-treatment for the enzymatic hydrolysis pathway, using an extruder and a cryogrinder.

3.4. Reaction Unit

The vapor-phase methanolysis of PET operates in a continuous stirred-tank reactor (CSTR) at a temperature of 260°C and pressure of 3 bar, with an excess of methanol. Figure 7 presents the proposed configuration of the reaction unit. Methanol enters the process at Tamb (25°C) and is first compressed to 3 bar and vaporized at approximately 96°C. It is then combined with compressed recycled methanol and PET feed. The combined stream is heated to the reaction temperature of 260°C, and additional recycled PET is introduced before entering the reactor. Following the reactor, a flash separator is used to separate vapor-phase products from the liquid-phase components, mimicking the industrial approach of shifting reaction equilibrium by continuously removing volatile products.

To prevent accumulation of heavy byproducts in the reactor, a purge stream equal to approximately 0.5% of the reactor volume is implemented. This value is selected based on a sensitivity analysis with respect to mass balance convergence tolerance. A design calculator is developed to ensure

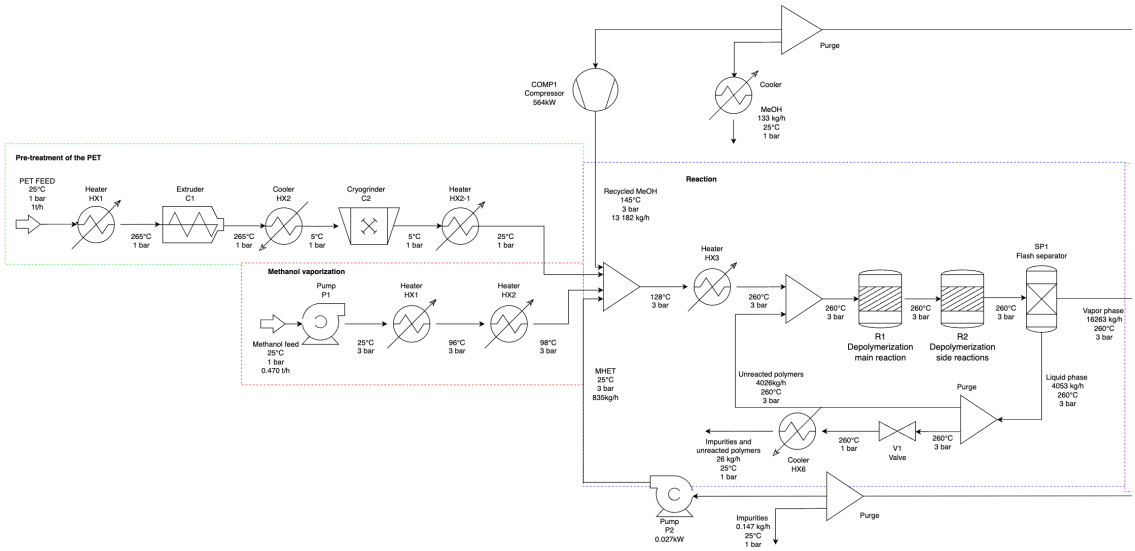

Fig. 7. Detailed PFD of the reaction unit with methanol vaporization and reaction steps.

that the methanol-to-PET mass ratio of 4:1 is maintained by adjusting fresh and recycled methanol and PET flow rates accordingly. The liquid residence time ranges between 4.2 and 9 hours, corresponding to a reactor volume of approximately 1 m^3 [17].

In this study, the reactor is modeled in Aspen Plus using an `R-STOIC` block, due to the absence of detailed kinetic and thermodynamic data for PET methanolysis in the open literature. Although `R-STOIC` does not account for reaction rates, it allows for stoichiometric conversions to be applied directly, making it suitable for yield-based process modeling. To capture the vapor-phase nature of the process, the `R-STOIC` reactor is followed by a flash separator. The main reaction is assumed to proceed via random scission, with the primary (R12 and R13) and side reactions (R14 and R15) defined as follows:

$$(C_{10}H_8O_4)_n + 80CH_3OH \longrightarrow 80C_{10}H_{10}O_5 + C_2H_6O_2 \tag{12}$$

$$C_{10}H_{10}O_5 + CH_3OH \longrightarrow C_{10}H_{10}O_4 + C_2H_6O_2 \tag{13}$$

$$2C_2H_6O_2 \longrightarrow C_4H_{10}O_3 + H_2O \tag{14}$$

$$C_2H_6O_2 \longrightarrow CH_3CHO + H_2O \tag{15}$$

Stoichiometric conversions are defined based on values reported by McNeeley et al. [27]: 0.28 for PET, 0.60 for MHET, and 0.01 for each EG side reaction.

3.5. Purification and recovery of the components

After the reaction, monomers in the form of vapor are sent to purification units to recover MHET, EG; DMT, and MeOH, as illustrated in Figure 8.

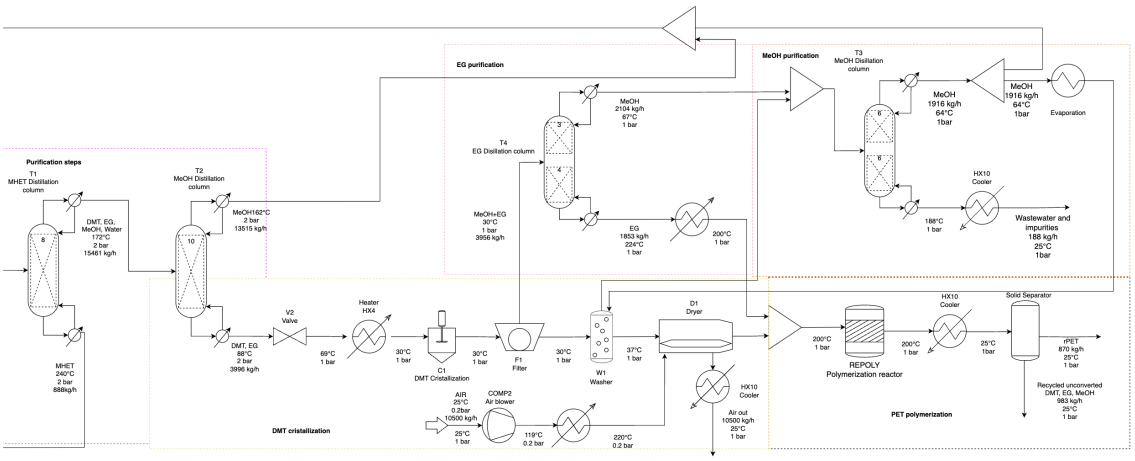

Fig. 8. Detailed PFD of the purification steps of the PET methanolysis components.

3.5.1. MHET recovery column

The first column, T1, separates MHET in the heavy key from the other components to recycle it in the reactor. The recovery of EG in the light key is set at 99.99% using a design specification calculator. The column is specified with 8 theoretical stages and a reflux ratio of 0.06. It operates at 2 bar. The feed is optimally introduced at stage 8.

3.5.2. Methanol recovery column

The T2 column is designed to recover methanol from the T1 distillate and to separate it from heavier reaction products, namely DMT and EG. The top product, rich in methanol, is compressed to 3 bars and recycled to the reactors, while the bottom stream containing mainly EG and DMT is sent to a crystallizer for further DMT recovery. A purge, representing the inefficiencies of the methanol recycling steps, with a separation of 85%, is added before the reactors.

The light key of T2 is specified as water, with a target recovery of 90% in the distillate, while the heavy key (EG) is targeted for just 0.1% recovery in the distillate. A total of 10 theoretical stages are specified. The feed is introduced at the bottom stage. Two design specifications are implemented: 99.8% methanol recovery in the distillate and 99.9% EG recovery in the bottoms with varying reflux ratios. To improve energy efficiency, the column is optimized by eliminating the reboiler and using a partial condenser. The reflux ratio is 0.4.

3.5.3. DMT recovery

After separation in T2, the DMT is recovered in solid form through controlled crystallization. The crystallized DMT is then separated from the remaining liquid phase, which primarily contains EG

and methanol. The crystallization time ranges from 40 to 60 min [32]. To improve product purity, the solid DMT is washed with methanol to remove impurities and residual organics. Finally, the washed crystals are dried to obtain the final purified DMT product in solid form.

The DMT and EG flow exiting the column is firstly depressurized and cooled to 1 bar, 30°C before entering the crystallizer. Solubility data of DMT in methanol are recovered from the literature [48]. The solubility curve is presented in Figure 9. In these conditions, 99.92% of the DMT is solidified.

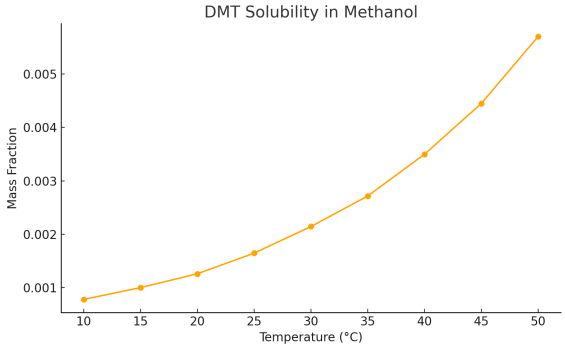

Fig. 9. DMT solubility in MeOH [48]

Then, the flow enters the filter (F1), used to separate the solidified DMT from the other liquids. The filter is set as a solid separator, separating 99% of the liquid fraction to the liquid outlet and 100% of the solid to the solid outlet. It operates at atmospheric pressure and 30°C. The solid flow exiting is sent to a washer and dryer, whereas the liquids are sent to a column for further separation of EG and MeOH.
The solid DMT is then washed to reduce impurities. Recovered MeOH is used as a washing liquid in a 0.8:10 ratio with the solid feed. The washed DMT is then transferred to a dryer where MeOH is evaporated. For the heat duty of the washer, the value is taken from literature, giving a heat duty of 223 kW/kg of PET for the indirect contact dryer used in this modeling [26].

3.5.4. Ethylene Glycol purification column

The liquid from the crystallizer, which is filtered, is composed mainly of EG, with 20% (molfrac) of methanol. This filtrate is sent to the distillation column T4. The distillate is the separated methanol, which is circled back to T3, while its bottom product is 99.5% EG, which represents a purity level suited for the market.

The column is optimized to 7 stages, and the feedstock enters in the third stage. It operates at 1 bar and is equipped with a partial condenser and a kettle reboiler, respectively kept at 67 °C and 224 °C. The ethylene glycol is then cooled down to 200 °C before repolymerisation.

3.5.5. Methanol purification column

The column T3 is designed to purify the recovered methanol streams. The distillate is composed of 99.25% (molfrac) of methanol, while the bottom product of the column is a flow of waste water

and impurities that will be cooled to ambient temperatures and disposed of.

T3 operates at 1 bar and is equipped of a partial condenser kept at 64°C and of a kettle reboiler, which is maintained at 188 °C. The design specification of the column targets a methanol mass recovery of 99%, obtained by having the distillate to feed ratio of 0.9. The reflux ratio is 0.8.

3.6. PET repolymerisation

Following the purification of EG and DMT, they can react with one another to form recycled PET via transetherification. The reaction happens in several steps, with an average temperature of 200°C and pressure of 1 bar [41]. Following the transetherification, BHET is formed, which transforms into PET by polycondensation. The transesterification step proceeds according to the reaction shown in Equation 16.

$$2\,\mathrm{EG} + \mathrm{DMT} \rightarrow \mathrm{BHET} + 2\,\mathrm{MeOH} \tag{16}$$

Finally, the polycondensation of BHET into PET follows the steps explained in the formation of PET from TPA and EG section. The polymerisation process is modeled using a stoichiometric reactor at 200°C, followed by a separator at ambient temperature, giving the recycled PET, the remaining MeOH, and impurities. MeOH is recycled back into the MeOH distillation column T3.

3.7. Heat integration

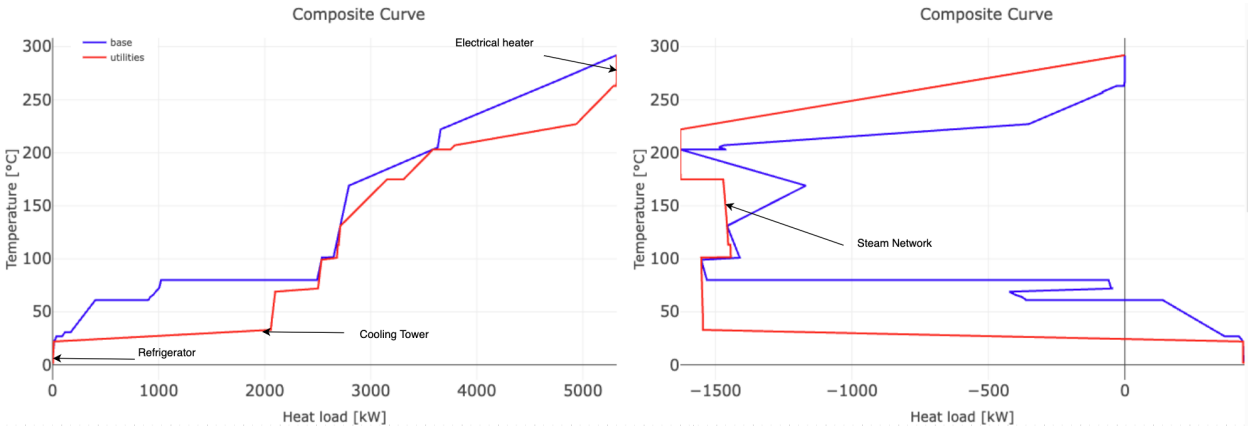

Fig. 10. Composite (right) and Integrated Composite Curve (left), including utilities of the process, with heat integration and complete power recovery. Results are presented in kWh/t(PET depolymerised).

4. Glycolysis depolymerisation modeling

4.0.1. Property method and PET characterization

As in the methanolysis depolymerisation process, the UNIQUAC thermodynamic model is employed to describe the non-ideal behavior of the liquid phase, resulting from the presence of highly polar and size-asymmetric molecules. PET is treated as a non-conventional solid, with its composition specified according to Table 1.

4.0.2. PET pre-treatment

Before PET can be glycolysed, the PET balls recovered from the recycling units need to be pre-treated into PET flakes small enough for the reaction to occur. The process is similar to the PET pre-treatment for hydrolysis, using an extruder and a cryogrinder.

4.0.3. Reaction Unit

PET (PET-FEED) and ethylene glycol (EG-FEED) are fed into a mixer (M100) upstream of the reactors in order to remove entrained air from the mixture prior to reaction. EG is preheated to 150 °C (H100) to facilitate mixing, after which the stream is compressed to 2 bar (P102) and heated to approximately 220 °C (H102) before entering the reactor. The reactor is modeled using an RYIELD block. This reactor type accounts for the desired outlet mass or molar composition. In order to reduce reaction time, minimize reactor volume, and achieve a satisfactory conversion of PET to BHET, the process employs three reactors in series (R101A, R101B, and R101C). With the same objective of reaction time optimization, a 1,3-dimethylurea/$Zn(OAc)_2$ catalyst can be used under these operating conditions (220 °C, 2 bar, EG/PET molar ratio of 4/1) [26, 45].

Since the catalyst can be reused up to five times without significant loss of activity, 20% of the catalyst is removed at the outlet of the third reactor, and 20% is added at the inlet in order to satisfy the overall mass balance. Sensitivity analyses were conducted to select temperatures around 220°C for the reactions, allowing the generation of a sufficient amount of EG vapor (approximately 0.33 t_{vap} / t_{PET}). The vapor stream is treated (PR1010) and redistributed evenly to the reactors at similar flow rates (PR1013, PR1014, and PR1015). BHET and other species exit the reaction section and are processed in a flash separator (PR1008).
Among the remaining recycle streams, PR3004 constitutes the main source of EG (4.05 t_{EG} / t_{PET}), while PR2353 enables the recycling of PET polymers that were not converted to BHET. A schematic overview of the process is provided in Figure 11.

4.0.4. EG and acetaldehyde columns

The vapor streams exiting the reactors (PR1010) are treated in two distillation columns (T110 and T310) to separate ethylene glycol (EG), water, and acetaldehyde. Water, recovered as the heavy phase (PR3101), is used for BHET solid crystallization and washing, while acetaldehyde, recovered as the light phase (PR3100), is sent to a downstream treatment step. For the separation of EG from impurities, a column with 11 theoretical stages and a feed introduced at the 10th stage is employed. The reflux ratio is set to 1.5 (molar basis), and the distillate-to-feed ratio is fixed at 0.11 (molar basis). In order to reduce energy consumption and heat duty requirements, the separation is carried out at 170 °C and 0.7 bar. These operating conditions allow the column to remain below the process pinch point, thereby reducing the overall energy demand of the process. At the

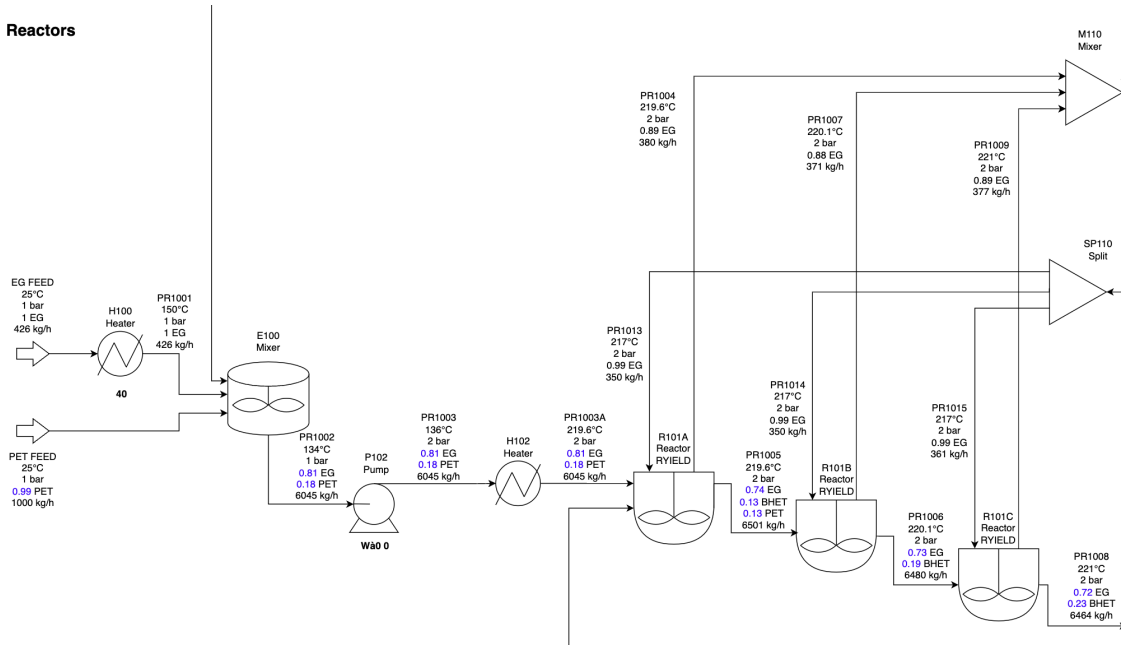

Fig. 11. Detailed PFD of PET glycolysis depolymerisation reaction steps.

outlet of the column bottom stream, a pump (P111) is installed to re-inject EG into the reactors at a pressure of 2 bar. The valve (V110) located at the column inlet is used to model a steam-ejector system, enabling the pressure to be reduced below 1 bar. A schematic overview is provided in Figure 12.

The light phase exiting column T110 contains water and acetaldehyde, which are separated in column T310. The stream is pressurized using a pump in order to return it to atmospheric pressure. Subsequently, two heat exchangers are used to heat the column feed stream. The first heat exchanger (H310) heats the liquid up to its dew point temperature, while the second heat exchanger (H311) partially vaporizes the stream to reach the target temperature of 66 °C. The column consists of 9 theoretical stages, with the feed introduced at the 4th stage. The reflux ratio is set to 1.66 (molar basis), and the distillate-to-feed ratio is 0.32 (molar basis). The water stream, which still contains a fraction of EG and BHET, is sent to the water treatment column, while acetaldehyde is incinerated together with other impurities, contributing to the process heating requirements.

4.0.5. Water column

After the separation of water and acetaldehyde, the aqueous stream is recovered to remove the remaining traces of EG. Once purified, the water (light phase) is used for BHET crystallization and subsequent washing. After these steps, a portion of the water is recycled to the column inlet. The EG-rich stream (heavy phase) is sent back to the flash separators. This separation is carried out using a distillation column, as displayed in Figure 13. The column temperature is set to 165 °C in order to remain below the process pinch temperature. Three heat exchangers are used to preheat

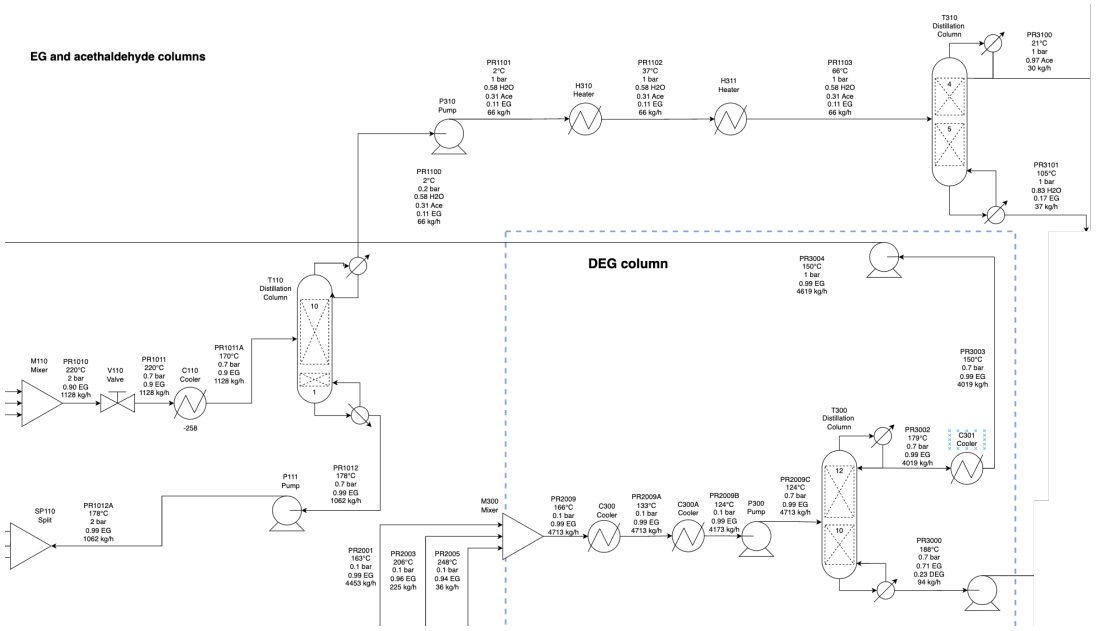

Fig. 12. Detailed PFD of the EG, water, and acetaldehyde purification steps.

the inlet stream and to induce the phase change (H320–H322). By adjusting the reflux ratio and lowering the feed stage, the selected column configuration consists of 27 theoretical stages, with the feed introduced at the 14th stage, a reflux ratio of 0.97, and a distillate-to-feed molar ratio of 0.96. At the column outlet, a first heat exchanger is used to condense the remaining vapor, allowing the pressure of the liquid stream (heavy phase, composed mainly of EG) to be reduced using steam ejectors modeled by a pump. Finally, two heat exchangers are used to heat the fluid before it enters the second flash separator (E202).

4.0.6. Flash separators

After leaving the reactors (PR1008), BHET and EG must be separated. Given the large difference in boiling temperatures between the two species (197 °C for EG and 317 °C for BHET), flash separation is employed. To enhance separation efficiency, a series of three flash separators is implemented. The EG recovered from the flash units is subsequently sent to the DEG column (PR2001, PR2003, PR2005, as shown in Figure 12) and then recycled back to the reactors, while BHET undergoes several purification steps prior to crystallization and washing. The two main operating parameters governing these separation steps are temperature and pressure. The monitored variables are the BHET mass flow rate and purity at the outlet of the final separation stage. An increase in operating pressure leads to a decrease in BHET purity at the outlet. Consequently, in order to achieve a BHET purity above 98 % without inducing a significant increase in operating costs, the separation steps are carried out at 0.1 bar [26]. The temperature of each flash separator is selected to maximize the BHET mass flow rate at the outlet. Accordingly, the first flash operates at 163 °C, the second at 206 °C, and the third at 248 °C, while also ensuring that the minimum purity threshold is achieved. For stream conditioning, a pump is used to simulate steam ejectors (P201),

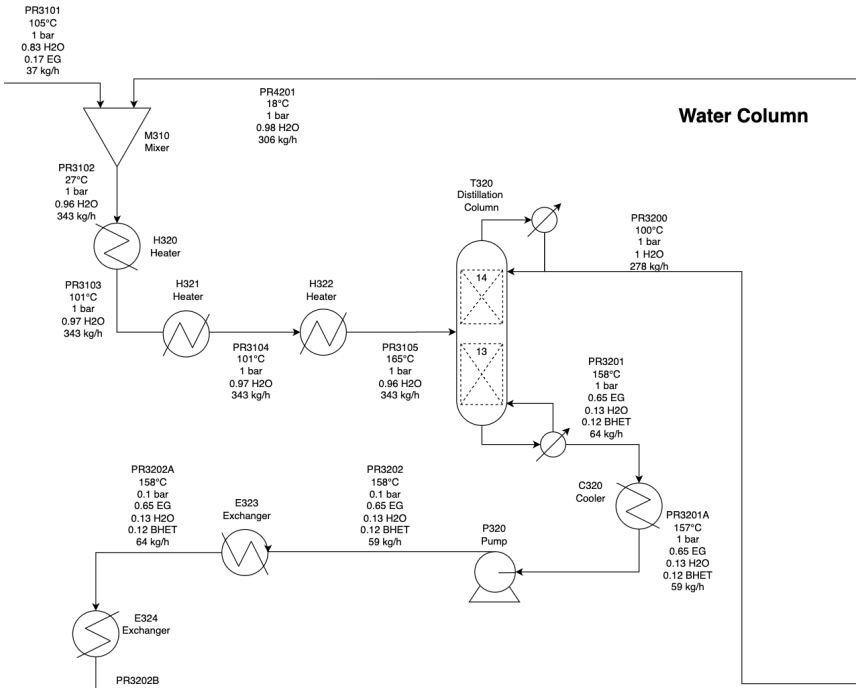

Fig. 13. Detailed PFD of the water purification unit.

and two heat exchangers are considered upstream of each flash separator, thereby simulating phase change and temperature increase.

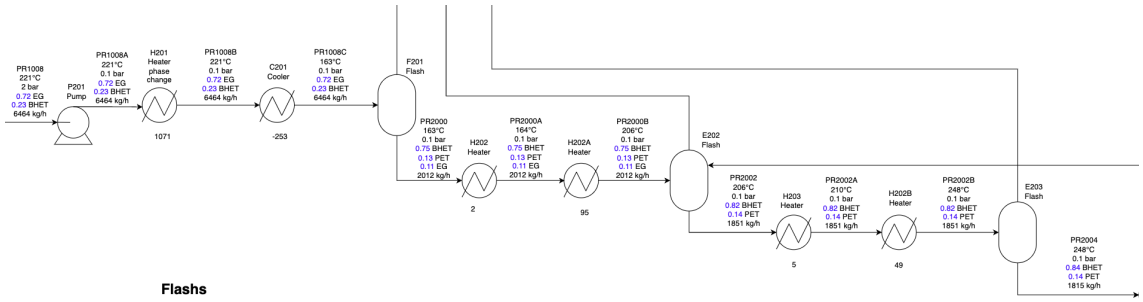

Fig. 14. Detailed PFD of the flash separation units' steps.

4.0.7. DEG column

From the outlet of the flashes, DEG vapors (PR2009) are sent to an additional distillation column (T300) in order to separate DEG (heavy phase) from EG (light phase, PR3002), as shown in Figure 12. The column consists of 24 theoretical stages, with the feed introduced at the 10th stage. The column operates at a temperature of 124 °C and a pressure of 0.7 bar. The reflux ratio is set

to 1.16 (molar basis), and the distillate-to-feed ratio is 0.98 (molar basis). After separation, EG is recycled back to the reactors for reuse as a solvent (PR3004), while DEG is sent to downstream treatment (PR3001).

For stream conditioning, two heat exchangers (C300 and C300A) are used to cool and condense the incoming EG-rich vapors (PR2009), allowing the stream to be pressurized using a pump (P300). At the EG outlet (PR3002), a heat exchanger (C301) and a pump (P301) are required to heat and compress the stream prior to its return to the reactors. Regarding the DEG outlet (PR3000), a pump (P303) pressurizes the liquid to 1 bar before incineration of impurities, which contributes to meeting the process heating requirements.

4.0.8. BHET column

BHET is separated from other polymers upstream of the crystallization step using a distillation column (T205, as shown in Figure 18). The PET-rich heavy phase is subsequently recycled to the depolymerization reactors, while the BHET-rich light phase is sent directly to the crystallizer. The column design and operating principle are based on the patent of [8]. It operates at a pressure of 0.1 bar and a temperature of 180 °C. The column consists of eight theoretical stages, with the feed introduced at the fourth stage, a distillate flow rate of 1330 $kg \cdot h^{-1}$, and a molar reflux ratio of 0.1. These operating conditions represent a compromise between the column energy consumption, BHET purity, and BHET mass flow rate.

Upstream of the column, a heat exchanger (C205) is used to reduce the temperature of the incoming stream. A first pump (P203) is required to increase the pressure to 1 bar at the BHET outlet. In parallel, a second pump (P205) and a second heat exchanger (C205) are installed on the PET-rich polymer outlet stream to condition the flow before entering the first depolymerization reactor.

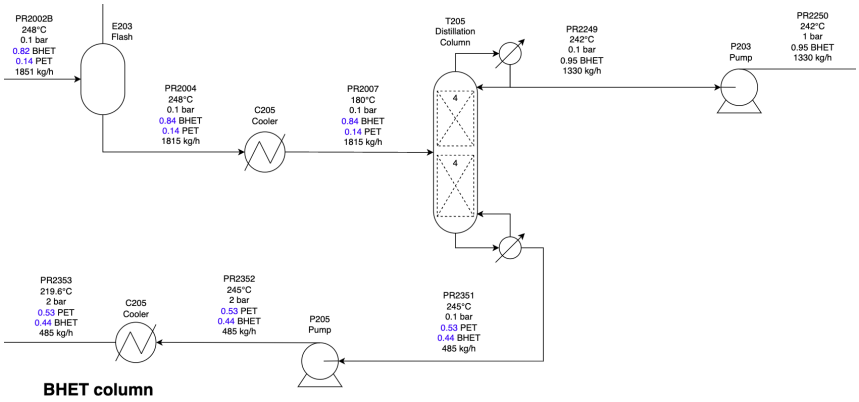

Fig. 15. Detailed PFD of the BHET purification column, including temperature and pressure variations of inlet and outlet streams

4.0.9. Water treatment

After water has been separated from acetaldehyde, it is recovered to remove the remaining traces of ethylene glycol (EG). Once purified, the water (light phase) is used for BHET crystallization

and subsequent washing. After these steps, part of the water stream is recycled to the inlet of the column. The EG-rich stream (heavy phase) is sent back to the flash units. This separation is carried out using a distillation column (T320, as shown in Figure 16).

The selected column consists of 27 theoretical stages, with the feed introduced at the 14^{th} stage, a molar reflux ratio of 0.97, and a distillate-to-feed molar ratio of 0.96. The column operates at a constant pressure of 1 bar and a feed temperature of 165 °C. These parameters were determined based on the number of stages, the molar fraction of EG in the light phase, the reflux ratio, and the condenser and reboiler duties.

For stream conditioning, two heat exchangers are required to cool and condense the fluid (H321, H322). At the bottom of the column, a first heat exchanger is used to condense the remaining vapor, followed by a pressure reduction of the liquid using ejectors modeled as a pump (C320, P320). Finally, two heat exchangers (E323, E324) are employed to heat the stream before it enters the second flash separator.

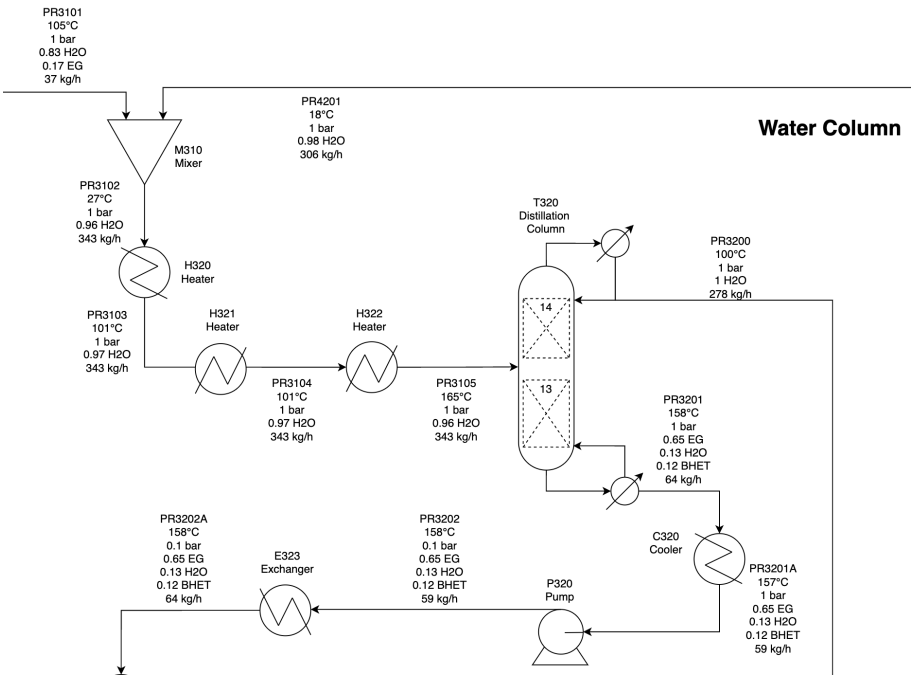

Fig. 16. Detailed PFD of the water purification column, including temperature and pressure variations of inlet and outlet streams.

4.0.10. BHET purification

During this step, BHET is crystallized and subsequently washed. To this end, the BHET stream recovered downstream of the BHET purification column is combined with the water stream from the previous separation step. In addition to this recycled water, make-up water is added to ensure

sufficient availability for both crystallization and washing. Part of the water is sent directly to the washing column, while the remaining fraction is mixed with the BHET stream. After mixing, BHET crystallizes in the crystallizer.
The crystallizer is modelled using the crystallization reaction

$$\mathrm{BHET}_{(aq)} = \mathrm{BHET}_{(s)},$$

together with the temperature-dependent solubility of BHET in water between 10 °C and 45 °C [46]. Crystallization is performed at 1 bar (CR400). The crystallization temperature and water flow rate were selected to maximize the mass flow rate of solid BHET, resulting in operating conditions of 6 °C and 120 $\mathrm{kg \cdot h^{-1}}$ of water.

After crystallization, BHET is filtered and washed in a washing column. The filter (FL400) is modelled by assigning the mass fraction of solids to the solid outlet and the mass fraction of liquid to the liquid outlet, following the approach described in [26], with separation efficiencies of 99% for both phases. The washing column (WA400) is modelled using the SWASH model, which requires specifying the ratio between the liquid and solid mass fractions. This ratio was selected to achieve a high BHET purity at the outlet ($\geq$ 95%). Finally, the purge fraction was set to the minimum value ensuring convergence of the model. The purified BHET is then sent to a dryer. For stream conditioning, a heat exchanger is required to cool the BHET stream upstream of the crystallizer, while a second heat exchanger is used to discharge the purge wastewater at 25 °C.

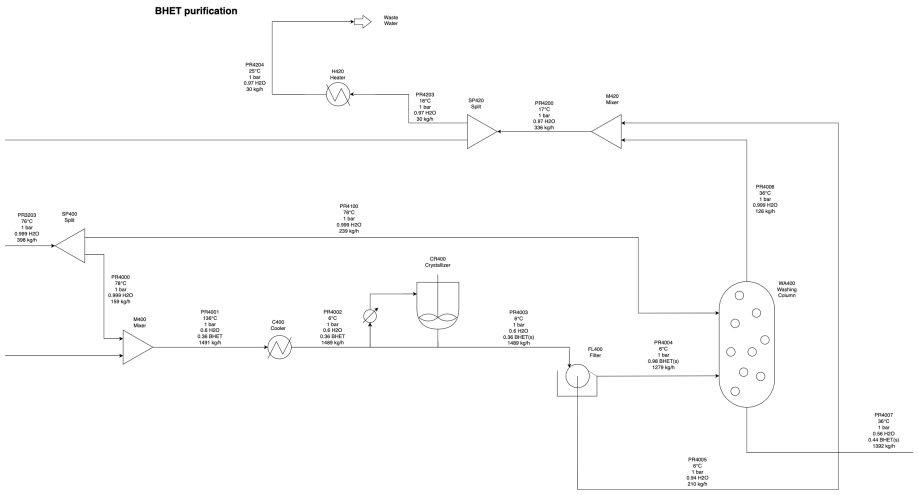

Fig. 17. Detailed PFD of the BHET purification and cristallisation steps, including temperature variations of the inlet and outlet streams.

4.0.11. Dryer

After crystallization, BHET is dried to remove excess water. A direct-contact dryer (DR400) is used for this purpose, with a power demand similar to that reported by [26]. After drying, the BHET stream is cooled to 25 °C using a heat exchanger (C401). The water vapor is also cooled to 25 °C using three heat exchangers, resulting in total condensation (C402, C402A, C403).

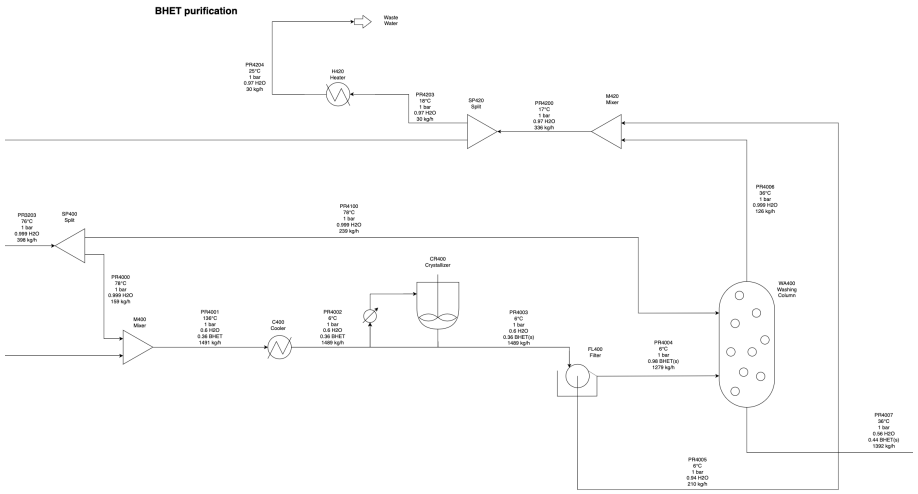

Fig. 18. Detailed PFD of the BHET dryer, including temperature variations outlet streams.

4.0.12. Incineration unit

At this stage, only DEG, residual EG, and acetaldehyde remain to be treated. However, the produced quantities and purities of these compounds are low. As a result, the most suitable option is incineration, with heat recovery to supply the remaining process energy demand, as shown in Figure 19. This step is modelled using an RSTOIC reactor. An air inlet (79% N_2 and 21% O_2) is added. Incineration is modelled assuming complete oxidation of DEG, EG, and acetaldehyde, following standard combustion reactions. The reactions implemented in the RSTOIC reactor are given by Eqs. (17), (18), and (19):

$$C_4H_{10}O_{3(aq)}\ (\text{DEG}) + 5\,O_{2(g)} \rightarrow 4\,CO_{2(g)} + 5\,H_2O_{(g)}, \tag{17}$$

$$2\,C_2H_6O_{2(aq)}\ (\text{EG}) + 5\,O_{2(g)} \rightarrow 4\,CO_{2(g)} + 6\,H_2O_{(g)}, \tag{18}$$

$$2\,C_2H_4O_{(aq)}\ (\text{acetaldehyde}) + 5\,O_{2(g)} \rightarrow 4\,CO_{2(g)} + 4\,H_2O_{(g)}. \tag{19}$$

The inlet air is preheated to 300 °C to facilitate incineration. Finally, a series of three heat exchangers is used downstream of the reactor to recover heat and cool the flue gas to 25 °C.

4.1. PET repolymerisation

The BHET produced can be polymerised by polycondensation, forming PET and EG. The reaction occurs at 283°C [37]. The polymerisation process is modeled using a stoechiometric reactor at 283°C, with conversion of the BHET to PET at 68% [30], [14], [37], followed by a separator at ambient temperature giving the recycled PET, and impurities.

4.2. Heat integration

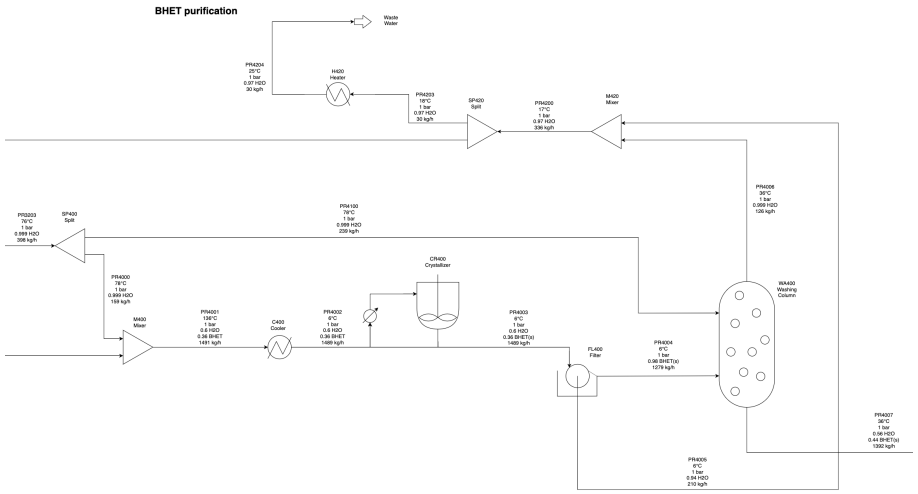

Fig. 19. Detailed PFD of the incineration unit, including heat recovery of the flue gases.

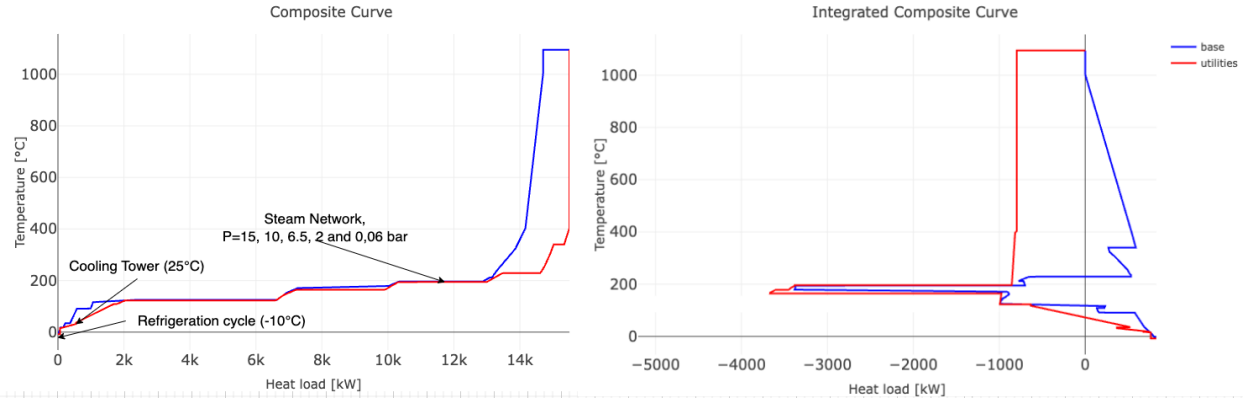

Fig. 20. Composite (right) and Composite Curve (left), including utilities of the process, with heat integration and complete power recovery. Results are presented in kWh/t(PET depolymerised).

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