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Research Paper

AspenPlus-based techno-economic analysis of solar-assisted sorption-enhanced gasification for hydrogen and chemicals recovery from polyethylene terephthalate waste

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ABSTRACT

Although the recycling of polyethylene terephthalate (PET) bottles is well-operating in several countries, less than 10% of PET plastic waste was recycled in a closed loop globally, and the rest was discarded as leakage. A process to recover hydrogen and valuable chemicals through solar-assisted PET sorption-enhanced gasification was analyzed. PET steam gasification with CaO and solar-assisted calcium looping processes were already experimentally studied in our previous work to obtain optimized processing conditions. In this paper, the integrated process with product purification, steam power plant, and LiBr-H₂O absorption chiller was simulated with Aspen Plus based on previous experimental results to investigate the techno-economic performance. Material flows, energy balance, exergy destruction, and economics were analyzed. Day and night mode operations at different seasons were evaluated based on energy balance and the weather conditions of Naples, Italy. The energy and exergy efficiencies of day and night modes varied between 62%–72%. The annual production yields of hydrogen and benzene were 684 t and 6286 t, respectively. Due to the high production of benzene, its higher price (>1092 ℓ /t) would make the project feasible with a larger than 12% internal rate of return value and competitive break-even hydrogen price (less than 4 ℓ /kg). The results show that this integrated process could be technically and economically feasible. It has the potential to be implemented for hydrogen and benzene recovery from PET plastic waste with sustainable solar heat source and zero fossil CO₂ emissions.

1. Introduction

Plastics provide valuable utility and convenience for many sectors of modern society but cause environmental problems. The natural degradation of petroleum-based plastics can take as long as 250 – 300 years [1]. Polyethylene terephthalate (PET) was the 5th most produced plastic type (accounting for 6% European plastic production in 2021), and it was mainly used for bottles (47%) in Europe; the rest included 20% of trays and 33% of fibers [2,3]. PET bottles are easy to sort, and many EU countries have established mature PET recycling systems. Compared to its share of plastic production, PET recycling represented 26% of the total installed plastic capacity in 2021 in EU27+3 countries (EU member states, Norway, Switzerland, and United Kingdom) [4]. Nonetheless, the overall PET recycling rate was 28%, in which PET bottle recycling rate was 50% in 2019 [3]. It means that there is a significant share of PET plastic waste not being recycled due to possible reasons such as

colorfulness, contamination, and final products (fibers and trays).

Gasification could be one option to convert this non-recyclable PET plastic waste to high-value gaseous fuels such as hydrogen and methane, together with liquid chemicals like benzene, regardless of the quality of the feedstock. PET steam gasification products have been analyzed in our previous research [5], where also summarized other related PET gasification experimental work. Co-gasification of PET with biomass or other plastics with steam have been studied with Aspen Plus modelling. However, gasification was usually ideally modelled as a nonconventional feedstock decomposed into elements in a RYield reactor and reacting with gasification agents in a RGibbs reactor, which could make the results distinct from experimental results. For example, Tavares et al. [6] simulated the PET-biomass steam gasification in Aspen Plus. They observed that increasing the share of PET in the mixture enhanced the concentration of hydrogen while reduced CO2. These results differed from the conclusion that CO2 was the dominant gas product in PET steam gasification obtained in previous experimental

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Nomenclature		ex	Molar exergy (kJ/kmol)
		f	Scaling factor for component cost
Abbreviations		h	Molar enthalpy (kJ/kmol)
4E	Energy, exergy, exergoeconomic and environmental	Н	Enthalpy flow (MW)
	assessments	h_0	Molar enthalpy at reference state (kJ/kmol)
CEPCI	Chemical Engineering Plant Cost Index	i _r	Interest rate
COP	Coefficient of performance	I	Income (€)
CSH	Concentrated solar heating	K _{ea}	Equilibrium constant
DC	District cooling	m	Mass (g)
DFB	Dual fluidized bed	n	Life span of the plant
DM	Day mode	'n	Molar flow rate (kmol/s, mol/s)
DNI	Direct Normal Irradiance	Р	Pressure (Pa)
EES	Engineering equation solver	P_{el}	Electrical power (MW)
FIC	Fixed investment cost	Q	Heat rate (MW)
HHV	Higher heating values	r	Reaction rate (unit depending on the equation)
IRR	Internal return rate	R	Universal gas constant $(J/(mol \bullet K))$
KPI	Key performance indicators	r_d	Discount rate
LAM	Land area multiplier of the solar field	r_{tax}	Tax rate
LHV	Lower heating value	S	Molar entropy (kJ/kmol•K)
NM	Night mode	S	Scale of the component
NPV	Net present value	s_0	Molar entropy at reference state (kJ/kmol•K)
PE	Polyethylene	S_P	Steam-to-PET mass ratio
PET	Polyethylene terephthalate	Т	Temperature (°C or K)
PSA	Pressure swing adsorption	t	Time
SEG	Sorption enhanced gasification	W	Work (MW)
TASC	Total as-spent cost multiplier	у	Molar fraction
0 1 1		α	The term in kinetics
Symbols	A (2)	β	Pressure ratio
Α	Area (m^{-})	ΔT	Temperature difference
c	Gas concentration (kmol/m ²)	ε	Exergy efficiency
C	Cost (€)	η	Energy efficiency
C_a	CaO-to-PET mass ratio	ρ	Density (kg/m^3)
CF	Net Cash now (t)	ϕ	Ratio between LHV and chemical exergy
C_p	Heat capacity $(KJ/Kg \bullet K)$		
E_{χ}	Exergy flow (MW)		

research in Li et al. [5] and PET supercritical water gasification studied by Guan et al. [7] The reason could be the higher elemental hydrogen content in PET than biomass. Similar problem was found in the polyethylene (PE) and PET mixture steam gasification modelling by Zallaya et al. [8]. Both models did not consider the major product tars. Thus, PET steam gasification should be modelled in a different method in Aspen Plus.

The problem regarding relatively low product quality of PET steam gasification was solved by adding CaO to improve hydrogen yield and reduce tars in Li et al. [9]. A separate product gas upgrading reactor would be considered to capture CO₂ with CaO and produce more H₂ by water-gas shift reaction at a lower temperature because most CO2 cannot be captured at optimized H₂ production temperature in the gasifier. Then, the CaO regeneration process should also be integrated to circulate the sorbent. This process is called sorption-enhanced gasification (SEG) which integrates the calcium looping process with gasification to capture CO_2 and improve gas product quality [10–12]. Both gasification and calcination require heat supplies, which is usually provided by fuel combustion and then the calciner also functions as a combustor. The carbonation reaction is exothermic, so it can also provide heat for other processes such as steam generation. Large-scale experiments of SEG (> 100 kWth) have been successfully tested such as at the University of Stuttgart and TU Wien [12,13].

Regarding the SEG process simulation, Wei et al. [14] performed the techno-economic analysis of coal SEG integrated with the natural gas synthesis process with Aspen Plus simulation. Compared with the conventional plant without integrating the calcium looping process, the SEG

process improved the coal-to-natural gas efficiency from 58.3% to 64.2% in terms of higher heating values, reduced 40.0% sour water to be purified, and 10.6% less of the capital investment. AlNouss et al. [15] utilized Aspen Plus to conduct the techno-economic-environmental analysis of biomass SEG integrated with bio-methanol production. They claimed that introducing SEG slightly increased the cost but decreased CO_2 emissions significantly in two different biomass waste cases (42.0% for palm kernel shells and 29.0% for empty fruit bunches).

Solar energy can be implemented for the calcium looping process to provide heat for the calcination process, which has been studied by many researchers. For example, Tregambi et al. [16] and Ortiz et al. [17] summarized the research about solar-assisted Ca looping process in their reviews. Inspired by the ideas of sorption-enhanced gasification and solar-assisted calcium looping process, a novel solar-assisted sorptionenhanced gasification was proposed, and so far, the process simulation has not been widely investigated. Khosravi et al. [18] simulated the solar-assisted sorption-enhanced gasification of municipal solid waste for the cogeneration of hydrogen and power by TRNSYS and engineering equation solver (EES). In their system, 0.6 kg/s of hydrogen and 14 MW of electricity could be produced, with 95.0% CO₂ capture efficiency. The energy and exergy analysis results showed that the total annual energy efficiency was 70.7%, and the highest exergy destruction rate was from gasifier (the second largest energy destruction took place in the carbonator, being half of the gasifier value). Osat et al. [19] conducted 4E analysis (energy, exergy, exergoeconomic and environmental assessments) for a solar-assisted biomass chemical looping and Ca looping gasification process in Aspen Plus and compared the performance of two

feedstocks: rice straw and microalgae. In their system, air acted as the heat transfer media for recovering heat from hot syngas products, regeneration of oxygen carrier (Fe₂O₃ in the system) and sorbent, absorbing heat from solar and providing heat for the Rankine cycle to produce electricity. This differs from previous cited research wherein bed materials were the heat transfer media. The energy efficiency of the rice straw system was 4.3%, and the most exergy destructions took place in the Rankine cycle and heat recovery. The CO₂ emissions from both feedstocks were close, 5.2 t/h and 5.3 t/h for rice straw and microalgae, respectively. The exergoeconomic analysis reflected that the microalgae system had more cost-reduction potential than the rice straw.

A novel solar-assisted sorption-enhanced gasification for PET has been proposed, and this research reported here aims to conduct the techno-economic analysis of H_2 and other materials recovery through solar-assisted sorption-enhanced gasification of PET plastic waste process via Aspen Plus modeling. The correlations between gas yields and operating conditions: temperature, steam-to-PET ratio and CaO-to-PET ratio obtained from previous experimental research (Li et al. [9]) were employed to model the PET steam gasification with CaO reaction in this Aspen Plus model. The process investigated by Khosravi et al. [18] would have some similarities to this research, but the energy balance and economic analysis were missing in their work. Moreover, sorptionenhanced gasification of PET plastic waste has not been investigated, and feedstock properties of PET and gasification product compositions are different from biomass. PET contains less moisture and char. According to Ye et al. [20], the activation energy of PET is lower than biomass, meaning that the reaction rate of PET gasification is faster than biomass. Regarding the gasification products, according to our prior research, half of the carbon was converted to tars, which means that tar products are not as negligible as what Khosravi et al. [18] and Osat et al. [19] assumed for biomass gasification. CO₂ was the main gas product (similar concentration as hydrogen with adding CaO). Thus, the process design and results must be different from Khosravi et al. [18]. 3E analysis without environmental impact was conducted for the process, but normal economic analysis would be examined instead of exergoeconomic analysis. This work provides a new approach for PET plastic waste upcycling to recover hydrogen and chemicals sustainably, and to capture fossil CO₂, with investigating the day and night modes and seasonal operations to provide a holistic techno-economic analysis of the new approach.

2. Methods

2.1. Materials

PET plastic waste was fed as the feedstock and specified as a nonconventional component in Aspen Plus, with the ultimate and proximate analysis being the same as the virgin PET used in the experiment of our previous work [9], shown in Table 1. Sand and CaO used in [9] were employed as the bed material and absorbent, respectively. To simplify the model, the purity of CaO was assumed as 100% since it was 96 wt%, and the rest components were all less than 1 wt%. The sand only consisted of 86.53 wt% SiO₂ and 13.47 wt% Al₂O₃.

2.2. Model description

The whole system consists of three main sub-systems: solar-assisted

 Table 1

 Proximate and ultimate analysis of virgin PET (as received basis, wt%)

Proximate analysis		Ultimate a	Ultimate analysis		
Moisture	0.00	С	61.97		
Volatiles	90.54	Н	4.48		
Fix carbon	8.13	0	33.35		
Ash	1.33	Ν	0.20		

PET sorption-enhanced gasification (including PET steam gasification with CaO, syngas upgrading, and solar-assisted calcination) with product separation, heat recovery and utilization for power production by LiBr-H₂O absorption chiller and steam power plant as the schematic diagram of the process shown in Figure 1. PET plastic waste, steam and the circulated CaO and sand from the solar calciner were introduced into the gasifier (high-temperature zone). The gas, tar, CaO, and sand entered the low-temperature zone to upgrade the syngas product, where CO converted to CO2, and CO2 capture took place. The high and low temperature zones of the reactor were simulated as two separate reactors in this model. The gas and solid products were separated. The upgraded syngas product was cooled to remove water and tar by condensation, followed by H₂ purification through a pressure swing adsorption (PSA) unit. The condensation heat was also used for cooling and electrical power production through LiBr-H₂O absorption chiller and steam power plant, respectively. The solid mixture (CaO + CaCO₃ + sand) from the syngas upgrading was introduced into the calciner to regenerate the absorbent. Concentrated CO₂ was stored after heat recovery and compression. The model was solved in Aspen Plus V12.1 with the following general assumptions:

- Steady state and steady flow conditions were considered.
- The property method utilized the Peng-Robinson equation of state with Boston-Mathias modifications [21].
- Ash and N₂ were inert components [21].
- Fluid dynamics of fluidization was not considered in the simulation.
- The storage tank was adiabatic [22].
- Hydrogen compression and storage were not considered in the process because the process is continuous, and hydrogen is directly utilized by other plants.
- The isentropic efficiencies of pumps, turbine, and compressor were 80%, 85%, and 85%, respectively, and the mechanical efficiencies were 95% for all the pressure change devices [23].
- The minimum temperature difference between hot and cold streams was 10 °C in all heat exchangers [23].
- The simulations of oxygen production and CO₂ purification in night mode were not included, but they were considered in economic analysis with the assumptions of purchasing the external service to avoid too extensive process simulation.

The detailed description of each component in the system and the specified assumptions are explained in the following sections.

2.2.1. PET steam Gasification with CaO

PET steam gasification with CaO was simulated in the RYield reactor by implementing gas product yield correlations fitted based on temperature (*T*), steam to PET mass ratio (*S*_P), and CaO to PET mass ratio (*C*_a) (see **Eq (1)** - **Eq (4)** from our previous research [9] with Fortran code. It is worth noticing that these four equations can be applied to the ranges: 700 °C $\leq T \leq 800$ °C, $2 \leq S_P \leq 3$, and $0 \leq C_a \leq 4$. The experimental results of tar and char analysis in [9] showed that benzene was the dominant tar product (80 wt% in detectable tars), and collected char only accounted for 1-2% in carbon from PET. Therefore, benzene was assumed to represent all the tars, and no char was produced. CO₂ captured by CaO was also negligible, and CaO mainly acted as a catalyst. Thus, the carbon in PET was converted to gas products CO, CO₂, CH₄, the tar benzene.

$$H_2 = -4.27 + 0.01093T - 11.19C_a + 1.694S_P - 0.4215C_a^2 + 0.01869TC_a$$

 $CO_2 = -6.58 + 0.01475T + 2.088C_a + 1.36S_P - 0.2666C_a^{2}$ (2)

$$CO = -137.9 + 0.382T - 5.59C_a - 0.000253T^2 + 0.00765TC_a$$
(3)

$$CH_4 = -39.6 + 0.1099T - 7.1 \times 10^{-5}T^2$$
(4)



Figure 1. Schematic diagram of the solar-assisted SEG of PET plastic waste process integrated with a steam power plant and a LiBr-H₂O absorption chiller

As the schematic of the process in Figure 1 depicts, the circulated CaO and sand were not fed into the RYield for two reasons: first, sand and CaO were defined as solid for further separation with gas products, but RYield reactor cannot achieve mass balance when solid materials are involved; second, sand and CaO were from calciner and they provided the required heat for gasification process, so it was easy to investigate and regulate the heat transfer between CaO + sand and the gasification reaction. The feeding rates of PET, steam, and CaO were 1.0 kg/s, 2.5 kg/s, and 2.0 kg/s, respectively. The mass flow rates of steam and CaO were determined by the optimized product steam to PET mass ratio and CaO to PET mass ratio studied in [9]. The gasifier temperature was set between 750 °C and 800 °C to guarantee a relatively high hydrogen yield. The flow rate of sand would be determined by the required heat of gasification and the solar calciner temperature, which would be compared and optimized later.

2.2.2. Syngas upgrading with solar Ca-looping

The gas product, steam, tar, CaO, and sand entered the upper zone of the reactor for gas product upgrading at the lower temperature of 650 °C. Four chemical reactions were defined in the gas product upgrading: CO water gas shift reaction to convert CO₂, CO₂ captured by CaO, and steam reforming reaction of benzene and methane. It was simulated by the RPlug reactor, and chemical reaction kinetics are shown in Table 2.

The kinetics of water gas shift reaction under CaO catalysis. The calcination reactor was simulated by the RGibbs reactor with minimizing the Gibbs energy for the reaction, and the temperature was at 850 $^{\circ}$ C according to our previous research about optimized conditions for the solar-assisted calcium looping process. There was 5% of the syngas product introduced to the RGibbs reactor to initiate the calcination reaction.

In the kinetics equation in Table 2, *r* is the reaction rate; *R* is the Universal gas constant 8.314 J/(mol•K); *P* and *c* are the partial pressure and concentration of each component in the gas mixture, respectively; ρ_{cat} is the density of the catalyst, and m_{CaO} is the mass of CaO.

2.2.3. Heliostat field

This plant would be located in the region of Naples, Italy. Based on the monthly average direct normal irradiance (DNI) and mean daily daylight hours in Figure 2 (A), it can be calculated that the annual average DNI is 1615.70 kWh/m², and the annual mean daily daylight hour is 12.16 h. Thus, the annual hourly average DNI is 364.03 Wh/m² (see the dashed line in Figure 2 (B)). The overall efficiency of the solar heating system was estimated as 0.6, including the heliostat and receiver efficiencies [22]. The single heliostat surface area was assumed to be 176 m² [22].

Table 2

Reaction kinetics implemented in the gas product upgrading reactor.

Reactions	Kinetics	References
$CO + H_2O \Leftrightarrow CO_2 + H_2$	$r = 1.1 \exp\left(-\frac{62100}{RT}\right) \bullet P_{CO}^{0.38} P_{H_2O}^{-0.1} \left(P_{CO_2} P_{H_2}\right)^{0.082} (1-\alpha) \rho_{cat} \alpha = \frac{1}{K_{eq}} \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} K_{eq} = \exp(5693T_s^{-1} + 1.077 \ln(T_s) + 1.077 \ln(T_s))^{-1} + 1.077 \ln(T_s) + 1.077 \ln(T_s$	[24]
	$5.44 \cdot 10^{-4}T_s - 1.125 \cdot 10^{-7}T_s^2 - 49170T_s^{-2} - 13.418(T_s \text{ is the gas upgrading temperature in K)}$ The kinetics of water gas shift reaction	
	catalyzed by CaO.	
$CH_4 + H_2O \Leftrightarrow CO + 3H_2$	$r = 3.1005 \exp\left(-\frac{15000}{T}\right) \left[c_{CH_4} c_{H_2 O} - \frac{c_{CO} c_{H_2}^2}{0.0265(\frac{32900}{T})}\right]$	[25]
$\begin{array}{c} C_6H_6 + H_2O \Leftrightarrow 3C + CO + \\ 2CH_4 \end{array}$	$r = 4 imes 10^{16} ext{exp} igg(-rac{443000}{RT} igg) c_{C_6 H_6}^{1.3} c_{H_2}^{-0.4} c_{H_2 O}^{0.2}$	[26]
$CaO + CO_2 \Leftrightarrow CaCO_3$	$r = 5.007 imes 10^{-3} \mathrm{exp} igg(- rac{20300}{RT} igg) (P_{CO_2} - P_{CO_2,eq}) m_{CaO}$	[27]



Figure 2. (A) Monthly and (B) hourly averaged DNI throughout the year in Naples, Italy (Data source [28])

2.2.4. Heat recovery

The generated heat in the syngas upgrading reactor and the heat in the high-temperature product and flue gases were utilized for a steam power Rankine cycle to produce electricity and LiBr-H₂O absorption chiller to produce district cooling (DC). In the steam power Rankine cycle, 1 kg/s pressurized water (40 bar) was heated by part of the heat released from the syngas upgrading step, and then hot product gas from the solar calciner, at 850 °C, to the superheated vapor at 442 °C. Then, the superheated vapor was expanded to 0.06 bar in the turbine, producing electricity in the generator. The expanded steam was condensed in the condenser and pressurized to 40 bars in the pump for the next cycle. Most of the operating condition data of the LiBr-H₂O absorption chiller were obtained from the simulation of the single-stage LiBr-H₂O absorption chiller through Aspen Plus in Somers et al.[29] work where more details can be found. The heat source for desorption was from the condensed heat in the excess steam to be removed from the syngas product. Thus, the desorption temperature would be adjusted according to the saturated water temperature, and the flow rate of LiBr-H₂O would be determined by the condensed heat in the gas product. The water for gasification was split into two streams and heated by the rest of the heat released from syngas upgrading and product gas before condensing for the desorption chiller, respectively.

2.2.5. Product separation

Most of the CO was converted to CO2, which was captured by CaO in the syngas upgrading reactor. Then, the gas product mainly consisted of steam, H₂, CH₄, and benzene. As previously mentioned, the water in the syngas was separated by cooling and condensation, where the heat was employed for heating the water stream and the desorption of the LiBr-H₂O absorption chiller. Considering the minimum temperature difference between the desorption (59 °C) and condensation with subcooling, the product gas was subcooled to 70 °C. The separation of benzene would require a much lower temperature due to its lower partial pressure (boiling point 78 °C at 1 atm). Thus, part of the cooling produced from the LiBr-H2O absorption chiller was introduced to cool the waterfree gas product to 10 °C. Then, the H2-rich gas product (60 vol%-75 vol %) can be purified through the pressure swing adsorption (PSA) technology, where H_2 content can be enhanced to over 99 vol% [30,31]. The gas was pressurized to 25 bars in the compressor before entering the PSA system. PSA is a complex system, and it is out of the scope of this research to simulate the whole system in detail. It was simulated by a separator with 99.9% efficiency for H₂ purification.

2.3. Energy analysis

Energy analysis was conducted based on the results from Aspen Plus. In Aspen Plus, higher heating values (HHV) were calculated for energy balance calculation. Thus, all the enthalpy flows and efficiencies were computed based on HHV. The enthalpy flow results in Aspen Plus were calculated based on a different reference state, so the actual enthalpy flows were estimated as the sum of the HHV and sensible heat in **Eq** (5), where HHV and heat capacity C_p were obtained in Aspen Plus and the reference temperature was 15 °C.

$$H = \dot{m} (HHV_{15^{\circ}C} + C_p \Delta T)$$
(5)

The efficiency of the Rankine cycle was calculated as the net power out (P_{el}) divided by the heat input of the Rankine cycle $(\dot{Q}_{in,Rankine})$ in **Eq (6)**. Part of the electrical power produced by the steam turbine (W_{turb}) was utilized to power the pump (W_{pump}) and the compressor (W_{compr}) before the PSA unit.

$$\eta_R = \frac{W_{turb} - W_{pump} - W_{compr}}{\dot{Q}_{in,Rankine}} = \frac{P_{el}}{\dot{Q}_{in,Rankine}}$$
(6)

The coefficient of performance (COP) of the LiBr-H₂O absorption chiller was computed as net district cooling \dot{Q}_{DC} divided by the heat provided for the desorption step ($\dot{Q}_{in,desorber}$)in Eq (7). Similarly, a small part of cooling ($\dot{Q}_{chiller}$)was employed for benzene condensation ($\dot{Q}_{benzenecooling}$).

$$COP_{LiBr-H_2O} = \frac{\dot{Q}_{chiller} - \dot{Q}_{benzenecooling}}{\dot{Q}_{in,desorber}} = \frac{\dot{Q}_{DC}}{\dot{Q}_{in,desorber}}$$
(7)

The overall efficiencies of the whole system with day mode (η_{DM}) and night mode are shown in **Eq (8)** and **Eq (9)**, respectively. The steam was heated by the internal reaction heat and product gas. Thus, it is not included in the denominator.

$$Daymode(DM)\eta_{DM} = \frac{HHV_{H_2} + HHV_{Benzene} + HHV_{ResidualGas} + P_{el} + Q_{DC}}{HHV_{PET} + \dot{Q}_{Sun}}$$
(8)

where \dot{Q}_{Sun} is calculated by the heat requirement of the solar calciner divided by the overall efficiency of the solar heating system 0.6.

$$Nightmode(NM)\eta_{NM} = \frac{HHV_{H_2} + HHV_{Benzene} + P_{el} + Q_{DC} + HHV_{ResidualGas,NM}}{HHV_{PET} + HHV_{ResidualGas,DM} + HHV_{ResidualGas,NM}}$$
(9)

In night mode, the residual gas produced in the day mode $HHV_{ResidualGas,DM}$, and night mode $HHV_{ResidualGas,NM}$ was burnt to provide the heat for the calcination and solid heat-up. Part of gas combustion could also be replaced by the heat stored by sand during day mode according to the season. This would not be considered in the efficiency calculation but discussed in the operation of the system.

2.4. Exergy analysis

Exergy analysis is an essential tool to analyze the irreversibility that cannot be avoided in a component/process [32]. The exergy of the solar radiation received by the receiver is calculated as [33]

$$E_{x,solar} = \dot{\mathbf{Q}}_{solar} \left(1 + \frac{1}{3} \left(\frac{T_0}{T_{sun}} \right)^4 - \frac{4}{3} \left(\frac{T_0}{T_{sun}} \right) \right)$$
(10)

where \dot{Q}_{solar} is the heat absorbed by the receiver, T_0 is the temperature of the reference state, 298 K, and the pressure is 1 bar, T_{sun} is the sun's outer surface temperature, assumed as 5600 K in this research [33].

Exergy of constant heat source (E_x^T) equals the transferred heat (\dot{Q}) multiplied by the Carnot factor:

$$\boldsymbol{E}_{x}^{T} = \dot{\boldsymbol{Q}} \left(1 - \frac{\boldsymbol{T}_{0}}{\boldsymbol{T}} \right) \tag{11}$$

For each flow, the total exergy is the sum of the physical exergy $(E_{x,ph})$, chemical exergy $(E_{x,ch})$, kinetics exergy, and potential exergy, where kinetics exergy and potential exergy are negligible. Therefore, the total exergy is [33]:

$$E_x \approx E_{x,ph} + E_{x,ch} \tag{12}$$

where the physical exergy is computed as [33]:

$$\boldsymbol{E}_{\boldsymbol{x},\boldsymbol{p}\boldsymbol{h}} = \dot{\boldsymbol{n}}[(\boldsymbol{h} - \boldsymbol{h}_0) - \boldsymbol{T}_0(\boldsymbol{s} - \boldsymbol{s}_0)]$$
(13)

and the chemical exergy of the gas mixture [33]:

$$E_{x,ch,gas} = \dot{n} \left(\sum y_i e_{x,ch,i} + RT_0 \sum y_i ln y_i \right)$$
(14)

in which, h and s are the enthalpy and entropy at the examined state, respectively, and h_0 and s_0 are the reference state. $e_{x,ch,i}$ is the standard chemical exergy of each component, and y_i is the molar fraction of each component in the mixture.

The physical exergy rate can be obtained from Aspen Plus. However, the physical exergy of LiBr-H₂O absorption chiller calculated in Aspen Plus was not correct due to the electrolytes process simulation; Therefore, the exergy calculation of the LiBr-H₂O absorption chiller followed the procedure provided by Palacios-Bereche et al. [34].

For non-conventional solid fuel PET, the chemical exergy is calculated based on the lower heating value (LHV) of the feedstock [35]:

$$E_{x,PET} = \dot{m}_{PET} \bullet LHV \bullet \phi \tag{15}$$

where ϕ is the ratio based on the ultimate analysis of the fuel in Table 1:

$$\boldsymbol{\phi} = 1.0437 + 0.1882 \bullet \left(\frac{H}{C}\right) + 0.0610 \bullet \left(\frac{O}{C}\right) + 0.0404 \bullet \left(\frac{N}{C}\right) \tag{16}$$

Exergy destruction ($E_{x.des}$) in each unit:

$$E_{x,des} = \sum E_{x,in} - \sum E_{x,out} \tag{17}$$

 $E_{x,in}$ and $E_{x,out}$ include all input and output exergy, respectively, for

example, the streams, heat/work supply, and production. The exergy efficiency (ε) of the system

Daymode
$$\varepsilon_{DM} = \frac{E_{x,H_2} + E_{x,Benzene} + E_{x,ResidualGas} + P_{el} + E_{x,DC}}{E_{x,PET} + E_{x,sun}}$$
 (18)

Nightmode
$$\varepsilon_{NM} = \frac{E_{x,H_2} + E_{x,Benzene} + E_{x,ResidualGas,out} + P_{el} + E_{x,DC}}{E_{x,PET} + E_{x,ResidualGas,in}}$$
 (19)

2.5. Economic analysis

The fixed investment cost (FIC), net present value (NPV), internal rate of return (IRR), and break-even H_2 price were employed to evaluate the economic performance of the system. The fixed investment cost was calculated as **Eq (20)** [36].

$$FIC = i_{TASC} \bullet (1 + i_{labor} + i_{project}) \bullet \sum C_{component}$$
(20)

where i_{TASC} , i_{labor} and $i_{project}$ are the total as-spent cost multiplier (TASC), the indicators of labor cost and project cost, assuming as 1.13, 0.35, and 0.50, respectively [36]. The calculation equations of each component are listed in Table 3.

LAM: Land area multiplier of the solar field, which is 5.9; $A_{heliostats}$: the total area of heliostats; \dot{Q}_{Carb} and \dot{Q}_{Calc} are the heat production from the carbonator and heat requirement for the calciner, respectively; η_{is} is the isentropic efficiency; A_{HX} is the required heat transfer area for the heat exchanger; β is the pressure ratio (>1); $\dot{n}_{gas,inPSA}$ is the inlet gas flow rate (in kmol/h) of the PSA system.

There are no specific equations for absorption chiller, benzene condenser, sand storage, and CO_2 purification cost calculation. They were computed based on the reference cost and scale from Ogidiama et al. [40], Bayon et al. [41], Shemfe et al. [42] and Abbas et al. [43] according to Eq (21)[37].

$$C_{component,i} = C_{ref,i} \bullet \left(\frac{S_i}{S_{ref,i}}\right)^f \bullet \frac{CEPCI_{2023}}{CEPCI_{ref,i}}$$
(21)

where $S_{ref,i}$ and $C_{ref,i}$ are the scale and the corresponding cost of the component in the reference, and *f* is the scaling factor, and it is assumed as 0.7 in all components. Since the costs vary in different years, the Chemical Engineering Plant Cost Index (CEPCI) of this year and the reference year were considered [44].

The net present value (NPV) is the sum of the net cash flow throughout the life span (*n*) of the plant, determined as **Eq (22)** [36]. Internal rate of return (IRR) is usually employed to evaluate the feasibility of the project, and it is the r_d value when NPV is 0 in **Eq (22)**[45]. The break-even H₂ price is the price of H₂ when NPV equals 0 with fixing other terms.

$$NPV = \sum_{t=1}^{n} \frac{CF_{t}}{(1+r_{d})^{t}}$$
(22)

in which the net cash flow (CF_t) is computed by subtracting FIC, the tax cost (C_{tax}) , operation and maintenance cost $(C_{O\&M})$, and materials cost $(C_{Materials})$ from the income of all products and the salvage value (I_{SA}) [36]

$$CF_{t} = \left[\sum I_{product\,i} + I_{SA} - C_{Materials} - C_{O\&M} - C_{tax} - FIC - loan\right]_{t}$$
(23)

and the formula for tax cost [36]

$$C_{tax} = \left(\sum I_{product,i} - C_{Materials} - C_{0\&M}\right) \cdot r_{tax}$$
(24)

The prices of materials and products, as well as important basic parameters are shown in Table 4.

- T	ab.	ıe	3	

Unit	Calculation Equation (\mathfrak{E})	References
Heliostats	$84.43 ullet (A_{heliostats}[m^2])$	[37]
Receiver	$36.05 \bullet (\dot{Q}_{Calc}[kW])$	[37]
Land cost	$8.443 \bullet (A_{heliostats}[m^2]) \bullet LAM$	[37]
Gasifier	$1516.8 \bullet (\dot{m}_{PET}[kg/h])^{0.67}$	[38]
Syngas upgrading $+$ boiler	$16591 \bullet (\dot{Q}_{Carb}[kW])^{0.67}$	[36]
Calciner	$13140 \bullet (\dot{Q}_{Calc}[kW])^{0.67}$	[36]
Pumps	$668.8 \bullet (W_{Pump}[kW])^{0.71} \bullet \left[1 + \frac{0.2}{1 - \eta_{is,Pump}}\right]$	[37]
Heat exchangers	$2541.59 \bullet (A_{HX}[m^2])^{0.59}$	[37]
Steam turbine	$\frac{454.67 \bullet \dot{m}_{steam,in}[kg/s] \bullet ln\beta \bullet \left[1 + \exp(0.036T_{steam,in}[K] - 54.4)\right]}{0.92 - \eta_{is,turbine}}$	[37]
Generator	$24.83 \bullet (W_{net}[kW])^{0.95}$	[37]
Compressor	$\frac{67.44 \bullet \dot{m}_{gas,in}[kg/s] \bullet \beta \bullet ln\beta}{0.92 - \eta_{is, compressor}}$	[37]
PSA	$27.96 imes 10^6 \left(rac{\dot{n}_{gas.inPSA}}{17069} ight)^{0.6}$	[39]

Table 4

Prices of 1	materials	and proc	iucts, i	important	basic p	parameters	tor N	۱٩V	calculation	ł
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	Items	Amount/ Price	References
Important basic	Construction	3 years	-
parameters	time		
	Life span	30 years	-
	Capacity factor	85%	-
	Discount rate	6%	[36]
	(r_d)		
	Loan rate	5.6%	[46]
	Loan share	80%	[36]
	Company tax	24%	[47]
	rate		
	Salvage value	20% of FIC	[36]
	O&M	4% of FIC	[37]
Material prices	PET waste	150 €/t	Medium market
			price
	Water	0.01 €/t	[48]
	LiBr	6160 €/t	[40]
	CaO	50 €/t	Medium market
			price
	Oxygen	70 €/t	[49]
Product prices	Electricity	161.08	[50]
		€/MWh	
	District cooling	55 €/MWh	[51]
	Benzene	910.67 €/t	[52]
	CO ₂	100 €/t	[49]
	H ₂	4000 €/t	[53]

3. Results and discussion

3.1. Model validation and molar flow results

The PET steam gasification with CaO was simulated based on the correlations fitted by experimental data, and the correlations were already validated in the research paper with acceptable differences [9]. The results show that the conversion rate of CO was around 98% in the syngas upgrading step in this research. According to the CaO enhancing water gas shift reaction research conducted by Li et al. [54], the equilibrium CO conversion was 95% at 650 °C and steam/CO molar ratio 3.0, and the conversion rate was 77% in the experiment at the same condition. The steam/CO ratio was much higher than 3.0, which improved the CO conversion and the equilibrium conversion rate.

Although the kinetics equation implemented for water gas shift reaction was obtained between 270–510 $^{\circ}$ C with a steam/CO ratio of 0.7–1.7 [24], which were both lower than the temperature and steam/CO ratio in this research, the error of total hydrogen yield should be less than 10%. Therefore, these should reflect that the gas upgrading kinetics models gave low errors compared with experimental data, and the model can be further investigated.

The molar flows of different streams are shown in Figure 3. Stream (7) is the product of PET steam gasification with CaO calculated based on the correlations obtained from experimental data fitting. Although the excess steam accounted for 77 vol% of the gas product composition (127.5 mol/s of steam in the total molar flow rate of 165.3 mol/s), the partial pressure provided by the excess steam must be enough for the water gas shift reaction according to the chemical kinetics calculation. Therefore, a steam to PET mass ratio larger than 2.0 is necessary even though the heat requirement of steam production is significant, and a steam to PET mass ratio of 2.5 is a compromise between hydrogen yield and heat requirement. Stream (10) is the gas product after upgrading under CaO, which acted as a catalyst for water gas shift reaction and absorbent for CO₂ capture. Hydrogen yield was improved by 54 vol%



Figure 3. Gas yields of different streams

material or stored permanently.

3.2. Energy analysis

92 vol% CO₂ was captured, including the CO₂ produced from PET gasification with CaO and water gas shift reaction. Lower reaction temperatures favored the water gas shift and carbonation reactions since they are both exothermic reactions. However, CH₄ and benzene yields did not change in the gas product grading but increased in the solar calciner at around 850 °C by steam reforming reactions. Thus, CO and H₂ appeared in Stream (14), the gas product of CaCO₃ solar calcination, where 5 vol% of Stream (10) was introduced to initiate the calcination reaction.

after upgrading, increasing from 12.1 mol/s to 18.6 mol/s, and around

After cooling the gas to 70 °C (Stream (25)) and 10 °C (Stream (28)), 91.0 wt% and 99.8 wt% water was removed, respectively, while only nearly 70 wt% benzene was collected after cooling to 10 °C. The hydrogen volumetric concentration in the dry gas products increased from 32.0 vol% in the gasifier to 66.0 vol% after gas upgrading, then 75.0 vol% after water and benzene removal, and the final purity of the hydrogen product was 99.8 vol% after PSA. Other gases, including benzene, CH₄, and CO₂ (Stream (36)), were separated from hydrogen in PSA. Stream (14) and Stream (36) would be mixed and stored temporarily, called residual gas, and they can be burnt with pure oxygen to supply heat for the process during the night. Then, all combustible carbon-based gaseous fuel in the residual gas from day mode operation was then converted to high concentration CO₂, which can be separated from water after cooling and compression for further use as a raw The energy balance Sankey diagrams of the system in day mode and night mode were illustrated in Figure 4 (A) and (B), respectively. The night mode was designed to run with half of the day mode capacity to reduce the energy storage requirement. There was \pm 0.1 MW error in the energy balance due to the rounding. As the Sankey diagram of the day mode depicts, the mixture of sand and CaO provided 4.06 MW heat for PET steam gasification with CaO and steam to reach desired temperature. The circulation rate of the mixed sand and CaO from the solar calciner was 26.2 kg/s to provide the required heat for PET gasification with CaO in the gasifier [26].

The gasification products, the circulated sand, and CaO entered the syngas upgrading zone at a lower temperature, where the water gas shift reaction, carbonation reaction, and high-temperature inlet mixture can deliver all heat, 7.57 MW. It was employed to heat up the water/steam for gasification (5.01 MW) and the Rankine cycle (2.46 MW). Then, the water and steam in Rankine cycle were heated by the gas after calcination and expanded in the turbine to produce the power. The net electrical power was 0.62 MW. The condensed heat of 4.46 MW during the separation of water from the product gas was utilized to run the LiBrH₂O absorption chiller to produce 3.52 MW of cooling in which 0.69



Figure 4. Sankey diagrams of the system with (A) Day mode and (B) Night mode (Unit: MW)

MW was used to condense benzene and water, and the rest was sold out as district cooling. The evaporation temperature of the steam was $\sim 1^{\circ}$ C, indicating that it can provide high-quality cooling for different purposes. The overall efficiency of the day mode was 69.4%. As for the night mode, the energy consumption and product flow during gasification and syngas upgrading were almost half of the day mode due to the reduction of feedstock feeding. The heat source for calcination would be the oxyfuel combustion of the gas and/or the heat in the sand stored in the day mode, and heat requirement was 6.94 MW when the heat was entirely provided by gas combustion at 850 °C. The rest of the heat in flue gases would be utilized for power production. The net electricity production was higher than the day mode due to a larger flow rate of flue gas and heat content. The temperature of the flue gas after providing heat for the Rankine cycle was 260 °C, which can be utilized for other processes, for example, drying biomass before condensation and separation. The flue gas was not employed to heat the combustion gas because a higher gas temperature would require less combustible gas flow to reach the fixed calcination temperature of 850°C. This would reduce the flow rate of flue gas and directly decrease electrical power production. The overall efficiency of the night mode system was 71.7%.

Based on the heat requirement of 11.15 MW for the calcination process and weather conditions provided in section 2.2.3, the number of heliostats was estimated as 290. The corresponding land area requirement was 30.11 hectare. March, June, September, and December were selected as representatives to analyze operations in different seasons. According to the daylight time throughout the year in Figure 2 (B), the operation between 7:00 and 17:00 would be the day mode, and the rest would be the night mode. The excess produced solar heat (the part that DNI is higher than the annual daily average) would be stored in the sand in the short or long term. Since it is much more costly to store energy in gas than sand (more tanks and compressors), the gas stored from day mode and produced from night would firstly be burnt to provide the required heat and then the hot sand. Then, the exceeded hot sand can be for seasonal storage [22]. Figure 5 illustrates the required heat of the night mode and the heat provided by the gas combustion and hot sand in different seasons. It shows that gas combustion was enough for the night operation in summer, and the hot sand can be used in other seasons, when the sum of the heat from hot sand and gas combustion is much less than the requirement. However, it still needed an additional heat source. Therefore, the winter day mode was operated as 80% of the other seasons, and the night mode was still operated at half the original capacity. A small amount of hot sand would remain for backup in this operation. The energy can be well self-balanced in September. Part of the sand stored in summer can be used in autumn, and the newly stored sand can



be introduced in spring to avoid too much heat loss due to very longterm storage. With this operation, the volume of the sand storage should be 708 m³ for at least 3-month storage. In the night mode, when the calcination required heat was only produced by sand, the electricity production was half of the night mode because there was only CO₂ flow from calcination. This integrated process can recycle 19 kt PET plastic waste and capture 20 kt fossil CO₂ each year. The annual production of hydrogen, benzene, electrical power, and district cooling are shown in Table 5.

3.3. Exergy analysis

The exergy efficiencies of day and night mode operations were 62.6% and 69.2%, respectively. Exergy is mainly destroyed due to heat transfer and chemical reactions. Figure 6 illustrates the exergy destruction pie charts for the day (A) and night (B) modes. It shows that solar radiation represented more than half of the total 15.51 MW exergy destruction in day mode. This result was similar as the exergy analyses of solar assisted calcium looping process studied by Karasavvas et al. [33] and solar biomass gasification reported by Bai et al.[55]. Zare and Hasanzadeh [56] observed that in a solar assisted Brayton system, the exergy losses in heliostat fields and central receiver accounted for about 60% and 30% of the total exergy loss, respectively. The reason is the massive heat loss between the high-temperature solar radiation (5600 K in this research) to a lower temperature (about 1273 K) on the central receiver. This exergy destruction could be reduced by improving the performance of the solar collection system, including the heliostats and central receiver system. For example, if the overall efficiency of the solar collection system increases from the current setting of 0.6 to 0.7, the exergy destruction would decrease to 5.38 MW and 41% of the total exergy destruction. This could be achieved by the optimized design of heliostat (including the optical properties of a single heliostat and the layout of heliostat field) and aperture size of the central receiver to reduce the radiative and convective losses [57,58].

The second most exergy destruction was from the sum of all heat exchangers, in which water evaporation and condensation were dominant. The most considerable exergy destruction appeared in the condensation in the steam power plant, which is not avoidable due to the low condensation temperature and pressure. The exergy destroyed in chemical reactors was as follows: gasifier (7.9%), syngas upgrading (11.2%), and solar calciner (9.7%). The exergy destructions in these reactors also included heat transfer. For example, steam in the gasifier and solid in the calciner were heated to the target temperature by the hot solid and the concentrated solar irradiation, respectively. Moreover, the exergy destruction of heating water to steam with the heat produced in the syngas upgrading process was also included since it is considered as

Main technical	key performance	indicators (KP	I) of the system
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Items		Value	Items	Value	Unit
Overall system efficiency	Day mode	69.4%	H ₂ yield	684	t/yr
	Night mode	71.7%	Benzene yield	6826	t/yr
Electrical efficiency of the	Day mode	19.2%	Net Electricity	4378	MWh∕ yr
Rankine cycle	Night mode	23.3%	District cooling	19814	MWh∕ yr
LiBr-H ₂ O COP (net)	Day mode	0.63	Number of heliostats	290	-
	Night mode	0.67	Required land area for the heliostat field	30.11	hectare
Exergy efficiency	Day mode	62.6%	The volume of the sand storage tank	708	m ³
	Night mode	69.2%	PET recycled	19.00	kt/yr
			Captured CO ₂	20.21	kt/vr



Figure 6. Exergy destruction distribution for (A) Day and (B) Night modes

a reactor with a boiler. Exergy destruction in the absorption chiller accounted for 4.4%, and the rest was from other units, for example, PSA and steam turbine. The exergy destruction in night mode was similar to the day mode in most components due to the half-running capacity, except for the calciner because the heat source was wholly or partially the combustion of the residual gas from the day mode operation. When the calciner heat source was fully provided by gas combustion, the exergy destruction in calciner stood for 40.7% of total exergy destruction, and it was almost double the second-highest exergy destruction in syngas upgrading and steam heaters.

3.4. Economic analysis

The result of the fixed investment cost breakdown is illustrated in Figure 7. It shows that the sorption-enhanced gasifier which includes gasification, syngas upgrading, and calcination accounted for more than 60% of the fixed investment cost, followed by concentrated solar heat production (22.4%). The dual fluidized bed or calcium looping reactor is usually the highest investment [17,59]. For example, when there was no solar heating, Schweitzer et al.[11] observed that around 70% of capital expenditure cost was from the sorption-enhanced gasifier and Michalski et al.[36] obtained a similar number for the calcium looping process. Due to the size of the plant, the cost of concentrated solar heating (CSH) system was not the dominant investment. This conclusion is similar to

the same flow rate solar-assisted coal gasification integrated with methanol production studied by Xin et al. [37], where the investment cost of the gasifier was 10.75 M\$, and the sum of the concentrated solar heating system was 3.53 M\$. If the gasification temperature is increased to 800 °C to maximize the hydrogen yield, the circulation rate of solid should be more than double the current rate 26.2 kg/s when the calciner temperature is kept at 850 °C to reduce CaO deactivation. Although according to Wilk and Hofbauer[60], the temperature difference between the combustor and gasifier can be 40 °C–60 °C, the heat required for heating the solid in the calciner (from 650 °C to 850 °C) would double. This means the cost of the calciner and CSH system would be significantly increased. Therefore, the gasification temperature should be kept at 750 °C when the calcination temperature is 850 °C. The sand storage and CO₂ purity with storage accounted for 6.30% of the total investment cost. The daily storage of residual gases (the mixture of stream (14) and stream (36)) was not considered since the day production would be combusted during the night operation. The cost of PSA and absorption chiller were close (around 3.6%). The heat exchangers, pumps, turbine, and compressor costs represented less than 1% because of the small size of the plant and electricity production.

The sensitivity analysis of NPV with varying selected parameters $\pm 20\%$ was investigated, and the results are shown in Figure 8. Among 9 selected parameters, NPV was the most sensitive to benzene price: the $\pm 20\%$ change in benzene price would cause $\pm 73\%$ NPV variation. This



Figure 7. Fixed investment cost breakdown of the plant

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Figure 8. Sensitivity analysis of NPV with selected parameters

is because of the vast production of benzene from the plant compared with other products. NPV was significantly affected by the loan rate and inflation rate of this plant (around 40%). In many studies, the NPV variations with loan rate and inflation rate cases were less than 10% with a larger scale [11,36,61]. NPV was also altered by CO₂ price by 23% and it was assumed to sell CO2 with the highest price to highincome EU or EEA countries in Palone et al. [49]. However, CO₂ price is determined by many factors such as location, markets, policies, etc. [62]. Thus, CO₂ price uncertainties would be more critical than 20% and affect NPV more essentially. The CO₂ price aims to be higher for the wide implementation of renewable energy, from which this integrated process would benefit. The feedstock PET price was also one of the critical factors for NPV. The gasification process is flexible with PET flake's color, so the sorting based on color is unnecessary, which could further reduce the cost of PET feedstock. H2 price has a decreasing trend with the development of technology, which would negatively affect on the NPV of this process. The deduction or exemption of tax on renewable energy production would be favorable. Due to their low production, electricity, and district cooling prices did not play important roles in NPV. Therefore, the fluctuation of electricity prices in the market would slightly affect the NPV of this plant. All previous sensitivity analysis results reflect that this small-scale plant was significantly influenced by the economic situation and policies, and the resistance to financial risk

was low. A higher capacity plant should be built.

The variation of the internal rate of return (IRR) and H_2 break-even price with CO_2 and benzene prices are illustrated in Figure 9. IRR is a parameter to evaluate the economic feasibility of the project, and the threshold is 12% [63]. IRR higher than 12% indicates that it is economically feasible. Similar to the sensitivity analysis on NPV, benzene price affected more than CO_2 price on IRR. IRR increased 1% and 3% when increasing 20% of CO_2 and benzene prices, respectively. IRR was only higher than 12% when the benzene price was 1092 \notin /t. It means that this project is economically feasible if the benzene price increase around 20% of the current price. However, it would also be feasible at a lower benzene price when the CO_2 price is higher than 120 \notin /t since IRR value at a CO_2 price of 120 \notin /t, benzene price of 911 \notin /t was slightly lower than 12% (11.9%).

The break-even hydrogen prices at low benzene and CO_2 prices were also lower than the initial hydrogen price setting of $4 \notin \text{kg}$. Moreover, H_2 break-even prices were zero when the CO_2 and benzene prices were at higher levels, meaning that the NPV is positive even when the hydrogen price is $0 \notin \text{kg}$. The reason is that hydrogen is not the dominant product in this plant. The project is profitable with a clear decreasing trend of hydrogen prices in the future and competitive with hydrogen produced from other renewable technologies at certain benzene and CO_2 prices. For example, the highest break-even hydrogen price varied between 5.38 \notin /kg and 6.90 \notin /kg when hydrogen was produced from wind-powered water electrolysis with electricity storage [64]. However, as previously discussed, the relatively low hydrogen production could not meet the massive demand of the hydrogen market.

4. Conclusion

This work simulated solar-assisted sorption-enhanced gasification of PET plastic waste integrated with a steam power plant and a LiBr-H₂O absorption chiller in Aspen Plus. It demonstrated that the process is technically and economically feasible. Syngas upgrading was simulated using carbonation and water-gas shift reaction kinetics, and the results showed that hydrogen yields were improved by more than 50% and that 92% CO₂ was captured compared with the PET steam gasification with CaO step. Based on the energy balance analysis and the weather conditions of selected location Naples, Italy, day and night mode operations at different seasons were proposed to solve the intermittency of solar energy during the day and throughout the year. The energy and exergy efficiencies of day mode and night modes were 69.6%, 62.6%, 71.7%, and 69.2%, respectively. Due to the high production and price of benzene (6826 t/year, 911 \in /t), the NPV of the whole plant was very



Figure 9. IRR (A) and H₂ break-even price (B) varied with CO₂ and benzene prices

sensitive with benzene price; $\pm 20\%$ benzene variation would cause $\pm 73\%$ of NPV change. A higher benzene price would also make this project feasible in terms of IRR and lower H₂ break-even price to compete with hydrogen prices from other processes. This research would contribute to PET waste upcycling and achieve zero plastic waste and carbon neutral goals. This model should be improved by adding fluidization regimes and dynamics study in the future to include the effect of recirculation time and deactivation of CaO in the simulation. Sand storage tank should be studied in detailed to evaluate the heat loss during the long-term storage, and new operating strategies could be proposed. Moreover, the assumption of pure benzene production from tar should be improved by adding other tar species, such as toluene, to ensure the process is closer to the actual process.

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CRediT authorship contribution statement

Shouzhuang Li: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. Timo Laukkanen: Writing – review & editing, Validation, Methodology, Investigation, Formal analysis. Dingyi Jiang: Writing – review & editing, Visualization, Methodology, Investigation, Formal analysis. Ville Vuorinen: Writing – review & editing, Visualization. Mika Järvinen: Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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