MODELLING OF CARBON CAPTURE THROUGH CALCIUM LOOPING TECHOLOGY FOR THE INTEGRATION OF POWER TO GAS IN A BLAST FURNACE-BASED IRON AND STEEL INDUSTRY

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ABSTRACT

Nowadays, the reduction of CO₂ emissions from the iron and steel works has become a strategic objective for those industries to minimize the emission taxes and, therefore, to ensure competitiveness. The Calcium Looping (CaL) capture technology presents advantages such as lower energy penalty, versatility, adaptability to many large-scale sources of CO₂, and a cheap, non-toxic and available sorbent. Besides, this technology can also be used for desulphurization purposes, as CaCO₃ (direct desulphurization) and CaO (indirect desulphurization) react with SO₂ to form stable CaSO₄. However, properly accounting of the effects of sulphur presence represents an additional challenge for the modelling, which is normally overlooked. In the present work, a CaL plant for CO₂ and SO₂ capture has been modelled in Aspen Plus and validated with experimental and simulation data from the literature. The kinetics of carbonation, calcination, direct and indirect desulphurization has been implemented. Additionally, the mentioned CaL capture system has been integrated with a power-to-gas scheme in an oxy-blast furnace-based iron and steel industry, and analysed from a techno-economic point of view, obtaining a reduction of 28% in CO₂ emissions, an energy penalty of 21.71 MJ/kg_{CO2}, a CO₂ avoidance cost of 425.5 \notin /t_{HM} and a specific implementation cost of 230.1 \notin /t_{HM}.

1 INTRODUCTION

The decarbonization of energy-intensive industries is a key step in order to limit the increase of the world average temperature to 1.5 - 2 °C by the year 2050 (European Commission, 2022). The Iron and Steel (I&S) industry, contributing up to 27% of global manufacturing sector CO₂ emissions, with over 70% attributed to ironmaking blast furnaces (BF), plays a pivotal role (Iron and Steel Technology Roadmap, 2020). Steel production primarily follows two routes: (i) blast furnace-basic oxygen furnace (BF-BOF) accounting for 70% market share and (ii) electric arc furnace (EAFs) holding a 30% market share (EUROFER, 2013).

The BF-BOF route, being the most energy-intensive, consumes approximately 13-14 GJ/t_{HM} with specific emissions reaching 2200 kgCO₂/t_{CS} (Iron and Steel Technology Roadmap, 2020). The EAF route produces steel by melting recycled scrap using electricity. Direct reduced iron (DRI) can also be utilized in instances of scarce scrap availability. The DRI-EAF route presents s significantly lower energy consumption and CO₂ emissions, ranging from 4-10 GJ/t_{HM} and 400-1300 kgCO₂/t_{HM}, respectively (Iron and Steel Technology Roadmap, 2020). However, the BF-BOF route is expected to persist as the dominant force due to factors such as the inability to meet global steel demand solely with recycled scrap and the infrequent phase-out of blast furnaces, which only occurs during relining, occurring every 20-35 years (Scheele, 2021).

A suitable option to substantially reduce the CO₂ emissions associated to the BF-BOF is Power-to-gas (PtG) (Bailera et al., 2021a). In this concept, renewable electricity is utilized to obtain valuable products.

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When a carbon capture stage is included, CO_2 can be combined with H_2 produced by electrolysis to obtain synthetic natural gas (SNG), which can then be recycled, for example substituting a fraction of the coke introduced in the blast furnace (Perpiñán et al., 2021a) (Bailera et al., 2021b). Carbon with amines is a well-established technology used in many industries to reduce greenhouse gas emissions. Although effective, it still faces several concerns, such as the degradation, corrosion and toxicity, which have not yet been solved. Furthermore, the presence of sulphur compounds in the BFG poses an additional challenge for the carbon capture, as heat stable salts (HSS) form when amines react with SO₂. These HSS cannot be reclaimed (Rahimpour et al., 2020).

Post-combustion calcium looping (CaL) systems for carbon capture are increasingly applied in different pilot plants in Europe and elsewhere. The reasons behind the emergence of this technology are many, but the cheapness of its main resource (CaCO₃, which is the second most abundant material on Earth after water) (Domínguez, 2018), its versatility (it can be applied to both renewable and fossil-fuel based power plants as energy storage and CO₂ capture system, respectively (Domínguez, 2018) and its tolerance to the SO₂ concentration in the flue gas make it a good candidate for CO₂ capture systems (Alonso et al., 2014). Because of the great potential of the CaL process, a fast development with a relevant cost reduction is expected (Domínguez, 2018). Besides, this technology can also be used for desulphurization purposes, as CaCO₃ (direct desulphurization, eq. 1) and CaO (indirect desulphurization, eq.2) react with SO₂ to form stable CaSO₄ (Alonso et al., 2014). However, properly accounting of the effects of sulphur presence represents an additional challenge for the modelling, which is normally overlooked.

$CaCO_3 + SO_2 + 0.5 O_2 \rightarrow CaSO_4 + CO_2$	$\Delta H_r = -324 \text{ kJ/mol}$	(1)
$CaO + SO_2 + 0.5 O_2 \rightarrow CaSO_4$	$\Delta H_r = -502 \text{ kJ/mol}$	(2)

In the present work, a CaL plant for CO₂ and SO₂ capture has been modelled in Aspen Plus and validated with experimental and simulation data from the literature. The kinetics of carbonation, calcination, direct and indirect desulphurization has been implemented. Additionally, the mentioned CaL capture system has been integrated with a power-to-gas scheme in a blast furnace-based iron and steel industry. To the best of the author's knowledge, only one study regarding the use of Calcium Looping in a steelmaking plant in Aspen Plus is published (Carbone et al., 2023). However, in this study, CO2 is solely captured and compressed for other uses. This article is the first to implement calcium looping in an advanced steelmaking plant, which includes oxycombustion, top-gas recycling, and power-to-gas. Furthermore, it opens the door for future models which take into account the sulphur compounds present in the blast furnace gas, allowing to design and implement desulphurization strategies in Aspen Plus for the steelmaking plant.

2 METHODS

The process models have been realized in Aspen Plus v11. A description of the kinetics built into the model is discussed in Section 2.1. The CaL model is described in Section 2.2. The low-carbon concept is detailed in Section 2.3. The economic parameters and the key parameter indicators (KPIs) are discussed in Section 2.4 and Section 2.5, respectively.

2.1 Kinetics

Both calciner and carbonator reactors include kinetic models for the main reactions taking place in a CaL cycle with sulfur presence (calcination, carbonation, direct sulfation and indirect sulfation). The reaction rates are calculated in molar base according to the following equation (Myöhänen, 2011):

$$\mathbf{r}^{\prime\prime\prime}_{\text{reac},i} = \mathbf{k}_{\text{reac},i} \ast \mathbf{\epsilon}_{\text{r},i} \ast \mathbf{\rho}_{\text{r}} / \mathbf{M}_{\text{mass},i}$$
(3)

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where r["]_{reac,i} is the reaction rate in molar units, k the reaction rate, ε_{i} the volume fraction and ρ_{r} the density. The suffix "i" makes reference to the reacting species of each reaction "reac".

First-order models are considered, in such a way that CaCO₃ is the first-order reactant for calcination and direct sulfation, and CaO for carbonation and sulfation. The rate constant for each reaction is defined as follows:

$$k_{calc} = 1.22 * a_{calc} * exp(\frac{-4026}{T}) * (P_{cq} - P_{CO2}) * A_{m0,CaCO3} * M_{CaCO3}$$
(4)

$$\kappa_{\rm carb} = 0.0169 * a_{\rm carb} * \exp(\frac{-3488}{T}) * (P_{\rm CO2} - P_{\rm eq}) * A_{\rm m0,CaO} * M_{\rm CaO}$$
(5)

$$P_{eq} = 4.137 * 10^{7} * \exp(\frac{-20474}{T})$$
(6)

$$k_{dir,sulf} = 0.01 * a_{dir,sulf} * \exp(\frac{-3031}{T}) * C_{SO2}^{0.9} * C_{CO2}^{-0.75} * C_{O2}^{0.001} * A_{m0,CaCO3} * M_{CaCO3}$$
(7)

$$k_{\text{indir,sulf}} = 0.001 * a_{\text{indir,sulf}} * \exp(\frac{-2400}{T}) * \exp(-8 * X_{\text{CaSO4}}) * C_{\text{SO2}} * C_{\text{O2}} * A_{\text{m0,CaO}} * M_{\text{CaO}}$$
(8)

$$A_{m,CaCO3} = a_{calc} * A_{m0,CaCO3}$$
⁽⁹⁾

Carbonation and indirect sulfation are expected to occur at carbonator conditions, so they are only introduced in the carbonator model in Aspen Plus, while in the calciner reactor only calcination and direct sulfation are considered.

2.2 Calcium Looping model

1

2.2.1 General scheme: The Aspen Plus model of the CaL system is shown in Figure 1. No solid-solid heat exchanger has been considered. The calciner has been modelled as a mixed chamber CFB (circulating fluidized bed), in which O_2 and NG (fuel stream) enter from the bottom, fluidizing the particles. CO_2 is also recirculated to simulate air-combustion conditions (21% O_2 and 79% CO_2) at the inlet (Haran et al., 2021). The fuel stream is preheated using the hot CO_2 stream leaving the calciner. This CO_2 stream is further treated, encountering a filter, a condenser, and finally being compressed up to 130 bar in a compression train (Arroyave et al., 2020). The clean gas leaving the carbonator is used to pre-heat the flue gas, and later goes through a filter intercepting the remaining particles. Make-up limestone (98%wt CaCO₃ (Ramezani et al., 2017)) is introduced through the carbonator. The main input data is listed in Table 1.



Figure 1: Aspen Plus main model

Table 1: Input data of the CaL system

Variable	Value	Units
CO ₂ capture efficiency	0.9	-
CO_2 exit pressure	130	bar
Cyclone efficiencies (Haran et al., 2021)	0.999	-
Flash temperature	50	°C
CO ₂ at calciner inlet	21	%
F _r /F _o	6	

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F _o /F _{CO2}	0.03	
Calciner		
Temperature	900	°C, uniform
Pressure loss (Žalec et al., 2022)	0.15	bar
Heat losses (Junk et al., 2014)	10	%
Residence time	5	S
Carbonator		
Temperature	650	°C, uniform
Pressure loss (Hanak et al., 2020)	0.15	bar
Heat losses (Junk et al., 2014)	10	%

The residence time of the carbonator is left as a dependant variable to obtain a 90% CO₂ capture efficiency (Ortiz et al., 2017) at reactor outlet. Meanwhile, the calciner residence time is fixed to a 5 s, which is a common, conservative value for a calcination CFB reactor (Sánchez-Biesma et al., 2013)(Kremer et al, 2013), enough for a 100% conversion. F_r/F_o (molar ratio between solids recirculated and make-up) and F_o/F_{CO2} (molar ratio between make-up and CO₂ in the flue gas) are obtained from experimental data from La Pereda (Arias et al., 2013). F_r/F_o is directly correlated with the ratio used there, which is approximately 6. F_o/F_{CO2} is fixed to a value that allows for a CaSO₄ concentration in the solids streams of around 5%wt, a documented value in the La Pereda test run.

There is a lack of data regarding temperature distributions inside the calciner and the carbonator reactors. Ylätalo et al. (Ylätalo et al., 2013) provide a 3D CFD simulation of a calciner reactor. Their results show that the temperature profile inside it varies only from 900 to 940 °C, which can be considered negligible for this model. No data has been obtained for the carbonator, but similar temperature variations are to be expected.

2.2.2. Calciner model: The modelled calciner is seen in Figure 2. As it has been mentioned before, it is built as a mixed chamber CFB, with the blocks trying to mimic the real processes that occur inside it. The NG combustion (CALC-STO block) and the solids inlet (CALC-2 stream) are modelled to occur at the bottom of the reactor. These streams are also mixed with the CO_2 that is recirculated to the reactor (CALC-3). The rest of the reactor, where the reactions take place, is modelled as a single continuously stirred tank reactor (CSTR), since the calcination reactor is an almost instant reaction. Finally, a valve takes account of the pressure drop occurring within the reactor.

NG combustion has been considered as stoichiometric and complete. The heat provided by this reaction covers the endothermic processes naturally occurring there. These are (i) the heating of the solids at the inlet from 650 to 900 °C (CALC-HEX) and (ii) the calcination reaction. 10% heat losses have been considered (Junk et al., 2014).

2.2.3. Carbonator model: The carbonator model is seen in Figure 2. It is divided into two main parts: the inlet and the reactor. CARB-1 simulates the recirculated solids inlet, CARB-3 simulates the makeup limestone, and CARB-4 the gas to be cleaned. A network of heat-exchangers and mixers is used to simulate theoretical heat exchanges between these streams. The recirculated solids are cooled from 900 to 650 °C (CARB-HX2), and part of the released heat is used to heat the make-up and the flue gas to 650 °C (CARB-HX3).

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Figure 2: Aspen plus carbonator model

The reactor is divided into several CSTR reactors to compute the carbonation of the sorbent along the reactor (Atsonios et al., 2015; Yan et al., 2018). In order to determine how many reactors should be included a sensitivity analysis was realized. Different simulations with different residence times and number of reactors have been conducted. The former have been varied from 3 to 12 s, which are expected residence times for CFB reactors (Smolders and Baeyens, 2000), and the latter from 2 to 7 reactors. The objective was to determine the variation in CO_2 capture efficiency between the simulation and the corresponding one with one reactor less:

$$Variation (\%)_{n reactors} = 100 * (E_{CO2, n reactors} - E_{CO2, n-1 reactors}) / E_{CO2, n reactors}$$
(10)

where $E_{CO2,n}$ reactors represents the CO₂ capture efficiency achieved with n reactors. With 7 reactors, a variation of less than 1% is observed for all the different residence times, thus concluding that it is a suitable number of reactors to be included.



Figure 3: Sensitivity analysis regarding number of reactors

Cooling necessities are computed as the sum of the released heat of all the reactors. 10% heat losses have also been included (Junk et al., 2014). The addition of 7 reactors allows for a more gradual approach to the pressure drop in the system. Instead of adding a valve at the end, the inlet pressure of each reactor is decreased to simulate the real pressure drop.

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2.3 Integration of CaL in steel industry

The CaL plant has been integrated in the steel industry, in the context of a PtG integration in an oxyblast furnace. A process flow of the integration is described in Figure 4. A more detailed description of the oxy-blast furnace model can be found in the work of (Perpiñán et al., 2023b). Likewise, a more detailed description and anaylsis of the conventional iron and steel plant is also found in (Perpiñán et al., 2023b). For comparison purposes, the analysis has been performed in specific units (per ton of hot metal obtained as output of the BF, t_{HM}) and afterwards sized to net amounts for a steelmaking plant (320 t_{HM}/h).

The simulated blast furnace is externally calculated through a revisited Rist Diagram (Bailera et al., 2022). The hot blast temperature is 1200 °C, and is enriched with O_2 until a 95 vol% O_2 environment is reached at the inlet. The PEM electrolyzer generates O_2 and H_2 with an assumed energy consumption of 42,3 kWh/kg_{H2} (NEL hydrogen). The methanation plant consists of two isothermal fixed-bed reactors working at 300-350 °C and 5 bar (Izumiya and Shimada, 2021)(Rönsch et al., 2016). The CaL model has been detailed in the previous section. No CO_2 compression train has been included, since the captured CO_2 will be recirculated within the system, not stored.



Iron and steel plant integrated with PtG, carbon capture and oxy-BF

Figure 4: Process flow diagram of an integration with power to gas, carbon capture, and oxy-BF

2.4 Economic parameters

A time horizon of 20 years with an annual interest of 4% is assumed for the economic analysis. The initial CAPital EXpenditure (CAPEX) is composed of the methanation cost, the electrolysis cost, the cost of the CaL plant, and the cost of retrofitting the blast furnace for oxy-combustion operation, as well as other direct and indirect costs. The Operational EXpenditure (OPEX) is composed of the catalyst renovation (15% yearly renovation), the water consumed (1.47 \notin /t), the purchased electricity (60.3 \notin /MWh), the operation and maintenance (3% of total CAPEX), as well as the limestone renovation (10 \notin /t). Incomes are summarized in the excess O₂ by produced in the electrolyzer (80 \notin /t), which is sold, the excess steel gases, which are flared (19.60 \notin /MWh), the CO₂ tax (84 \notin /t_{CO2}) and the coal avoided (149.3 \notin /t). Although the steelmaking industry operates under continuous production, service and maintenance stops are also considered, rendering an equivalent of 8000 h of production per year.

2.5 Key Performance Indicators

16 KPIs are introduced to evaluate the obtained results (Table 2) KPIs 1 to 4 refer to the carbon capture system and the methanation stage. KPIs 1 and 2 allude to the required thermal energy for the CaL system, per mass of CO_2 captured and per mass of hot metal produced, respectively. KPIs 3 relates to the amount of SNG produced in the methanation system, while KPI 4 relates to the size of the methanation reactors. KPIs 5 to 10 allude to the system operation. KPI 5 amounts for the CO_2 emissions in the steelmaking plant. Avoided CO_2 emissions with respect to case 0 (1943 kg/t) are summarized in KPI 6. KPI 7 informs about the electrolyzer size, which is the main responsible for the electrolyzer, after

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subtracting the O_2 needs of different equipments within low-carbon concept scheme. The energy penalty (KPI 10) is defined as the net energy consumed in the industry per kg of CO_2 avoided with the PtG-steelmaking integration (eq. 11).

$$E_{\text{penalty}} = (\Delta E_{\text{cons}} - \Delta E_{\text{coal}} * \eta_{\text{elec}} - \Delta E_{\text{gases}} * \eta_{\text{elec}}) / \Delta \dot{m}_{\text{CO2}} [\text{MJ/kg}_{\text{CO2}}]$$
(11)

where ΔE_{cons} is the electricity consumed in the industry (MJ/t_{HM}), ΔE_{coal} is the coal energy avoided (MJ/t_{HM}), ΔE_{gases} is the excess of gases sold to nearby industries, η_{elec} is the energy conversion factor from coal to electricity (0.33) and $\Delta \dot{m}_{CO2}$ is the amount of CO₂ avoided (kg_{CO2}/t_{HM}).

The economic analysis is summarized in KPIs 11 to 16. KPI11 references the 20-year balance of the case. KPI12 is the CAPEX, KPI13 the incomes and KPI14 the OPEX. KPIs 15 (CO₂ avoidance cost) and KPI16 (specific implementation cost) are calculated by eqs.12 and 13.

$$KPI15 = \left(\frac{KPI14}{n} - KPI15\right) / \Delta \dot{m}_{CO2} \left[M \notin /y\right]$$
(12)

$$KPI16 = \left(\frac{KPI14}{n} - KPI15\right) / \Delta \dot{m}_{HM} \left[M \notin y\right]$$
(13)

where n represents the loan amortization period (in this case, 20 years), $\Delta \dot{m}_{CO2}$ the amount of CO₂ avoided yearly (t_{CO2}/y) and $\Delta \dot{m}_{HM}$ the annual hot metal production (t_{HM}/y).

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3 RESULTS AND DISCUSSION

The technical analysis comparing both cases is discussed in Section 3.1. The economic aspect is discussed in Section 3.2.

3.1 Technical analysis

KPIs are presented in Table 2. Even though the CaL plants requires a high amount of heat, it is to be noted that the calciner has to be heated to 900 °C. Far from being a disadvantage, it presents an opportunity to recycle these heat streams in an easier way as with other carbon capture technologies, such as amine scrubbing. A reduction of a 28% in CO_2 emissions is achieved. This value is slightly hindered by the fact that the calcium looping plant requires the combustion of CH4 to operate. These extra emissions leave with the clean BFG stream, which is recirculated to other units, where eventually it is released, after combusting the BFG. Emissions of every stage of the steelmaking plant are summarized in Figure 5. The 97% of the net electricity consumption can be directly tracked to the electrolyzer consumption, while the remaining 3% represents the work of compressors and ancillary elements.

KPI	Related to	Description	Units	Value
1	CC	Thermal energy required	MJ/kg _{CO2}	3.338
2	CC	Thermal energy required	MJ/t_{HM}	1735
3	PtG	SNG produced	kg_{SNG}/t_{HM}	191.5
4	PtG	Methanator size	$m^{3}_{reactor}/t_{HM}$	673.0
5	Operation	Net CO ₂ emissions	kg_{CO2}/t_{HM}	1402
6	Operation	CO ₂ avoided	kg _{CO2} /t _{HM}	540.9
7	Operation	Electrolyzer size	MWh/t _{HM}	4.031
8	Operation	Net electricity consumption	MWh/t _{HM}	4.142
9	Operation	Excess O ₂	kg_{O2}/t_{HM}	151.3
10	Operation	Energy penalty	MJ/kg _{CO2}	21.71
11	Economics	20-year-VAN	M€	-8838
12	Economics	CAPEX	M€	2597.6
13	Economics	Incomes	M€/y	266.4
14	Economics	OPEX	M€/y	725.7
15	Economics	CO ₂ avoidance cost	€/t _{CO2}	425.5
16	Economics	Specific implementation cost	€/t _{HM}	230.1

Table 2: Comparison of KPIs



Figure 5: Contribution of different stages to net CO₂ emissions

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3.2 Economic analysis

With the current prices the integration is far from being rentable. By this reason, a sensitivity analysis (Figure 6) varying the electricity price and the CO₂ taxes have been conducted. A range of 0 to 100 \notin /MWh for electricity prices is considered, which englobes the standard price for industrial electricity consumption. Similarly, the CO₂ tax range is set from 0 to 600 \notin /t_{co2}, covering scenarios without any tax, the current price tax, and a plausible maximum limit of 600 \notin /t_{co2} for future CO₂ price tax. No rentable scenarios are obtained with no CO₂ tax. When electricity is completely subsidized, a CO₂ tax of 96 \notin /t_{CO2} is required. When the electricity price assumed in this work is considered (60.3 \notin /MWh), 552 \notin /t_{CO2} are required. Considering the electricity price to be equal to the cost of production of solar (51 \notin /MWh) or wind energy (35 \notin /MWh), 504 \notin /t_{CO2} or 384 \notin /t_{CO2} would be required to obtain actual benefits (Strefler et al., 2021) suggest that CO₂ tax prices will rise in the following years, reaching 128 \notin /t_{CO2} by 2050 and between 384 \notin and 907 \notin /t_{CO2} by 2100. With this premise, a completely subsidized electricity production would pay benefits sooner than 2050, while profitability with current prices may be achieved by 2100.





4 CONCLUSION

In the present work, a CaL plant for CO_2 and SO_2 capture has been modelled in Aspen Plus and validated with experimental and simulation data from the literature. The calciner has been modelled as a mixed chamber CFB under oxy-combustion conditions, in which O_2 and NG enter from the bottom, fluidizing the particles. CO_2 is recirculated to approximate to the air-combustion conditions ($O_2:CO_2$ ratio of 21:79) at the inlet. The carbonator, also modelled as a CFB, has been divided into seven sections to properly reproduce the carbonation rate along the reactor. The kinetics of carbonation, calcination, direct and indirect desulphurization has been implemented.

The novel CaL model has been integrated in the context of an oxy-blast furnace with power-to-gas. The high temperature required for the CaL plant allows it to recycle the heat, reducing the energy penalty. A reduction of 28% in CO2 emissions is achieved with an electrolyzer consumption of 4.013 MWh/t_{steel} and an energy penalty of 21.71 MJ/kg_{CO2}.

The integration is not profitable with the current prices. CaL presents a CO_2 avoidance cost of 425.5 \notin/t_{HM} and a specific implementation cost of 230.1 \notin/t_{HM} , respectively. If a complete subsidy of electricity were obtained, the rise in the CO_2 tax prices would make them profitable by 2050. In the more realistic case than electricity price is maintained, or slightly reduced, profitability may be achieved by 2100.

^{37&}lt;sup>th</sup> INTERNATIONAL CONFERENCE ON EFFICIENCY, COST, OPTIMIZATION, SIMULATION AND ENVIRONMENTAL IMPACT OF ENERGY SYSTEMS, 30 JUNE - 4 JULY, 2024, RHODES, GREECE

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