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Hybrid Prediction-Driven High-Throughput Sustainability Screening for Advancing Waste-to-Dimethyl Ether Valorization

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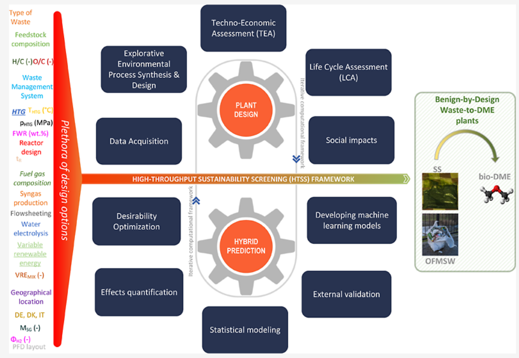
ABSTRACT: Assessing the prospective climate preservation potential of novel, innovative, but immature chemical production techniques is limited by the high number of process synthesis options and the lack of reliable, high-throughput quantitative sustainability pre-screening methods. This study presents the sequential use of data-driven hybrid prediction (ANN−RSM−DOM) to streamline waste-to-dimethyl ether (DME) upcycling using a set of sustainability criteria. Artificial neural networks (ANNs) are developed to generate *in silico* waste valorization experimental results and *ex-ante* model the operating space of biorefineries applying the organic fraction of municipal solid waste (OFMSW) and sewage sludge (SS). Aspen Plus process flowsheeting and ANN simulations are postprocessed using the response surface methodology (RSM) and desirability optimization method (DOM) to improve the in-depth mechanistic understanding of environmental systems and identify the most benign configurations. The hybrid prediction highlights the importance of targeted waste selection based on elemental composition and the need to design waste-specific DME synthesis to improve techno-economic and environmental performances. The developed framework reveals plant configurations with concurrent climate benefits (−1.241 and −2.128 kg CO_2-eq (kg DME)$^{-1}$) and low DME production costs (0.382 and 0.492 € (kg DME)$^{-1}$) using OFMSW and SS feedstocks. Overall, the multi-scale explorative hybrid prediction facilitates early stage process synthesis, assists in the design of block units with nonlinear characteristics, resolves the simultaneous analysis of qualitative and quantitative variables, and enables the high-throughput sustainability screening of low technological readiness level processes.



KEYWORDS: *sustainable-by-design, hybrid machine learning, explorative decarbonization, waste-to-chemicals, hydrothermal gasification, artificial neural network, process synthesis, optimization*

1. INTRODUCTION

Developing innovative waste valorization processes is vital to evolving modern societies toward climate neutrality.[1] Biological wastes are generated in large quantities in various industries (e.g., wood and forestry, food manufacturing, municipal waste and wastewater, and paper and animal processing[2]), offering ideal low-carbon feedstocks for producing synthetic platform materials. Dimethyl ether (DME)—an environmentally benign substitute for fossil-based chemicals—has gained high attention as it can be applied as large-scale hydrogen storage medium,[3] fuel for long-distance marine shipping,[4] and feedstock for chemical processes (e.g., olefin production[5]). One of the major challenges of DME synthesis is to supply synthesis gas using renewable resources that, compared to the steam reforming or oxy-combustion of natural gas,[6] do not suffer from high environmental impacts (1.14 kg emitted CO_2 (kg syngas)$^{-1}$[7]), and highly volatile prices due to geopolitical instabilities.[8] The environmental and supply issues necessitate a shift toward a new stage of syngas production based on upgrading abundantly and locally available raw resources (e.g., biomass and wastes). For this reason, the conversion of bio-wastes to platform molecules (e.g., synthesis gas, a mixture of H_2, CO, and CO_2) is becoming a particularly attractive valorization pathway that opens the possibility of producing value-added bulk chemicals without using conventional fossil-based petrochemical refining.

The effective neutralization and upcycling of high-moisture-containing biogenic waste resources are complex multilayer tasks limited by strict environmental and technological boundary requirements. On the one hand, the uncontrolled decomposition of bio-wastes and conventional waste management techniques (e.g., landfilling, incineration, or composting) are characterized by high greenhouse gas emissions. On the other hand, using well-established thermochemical waste

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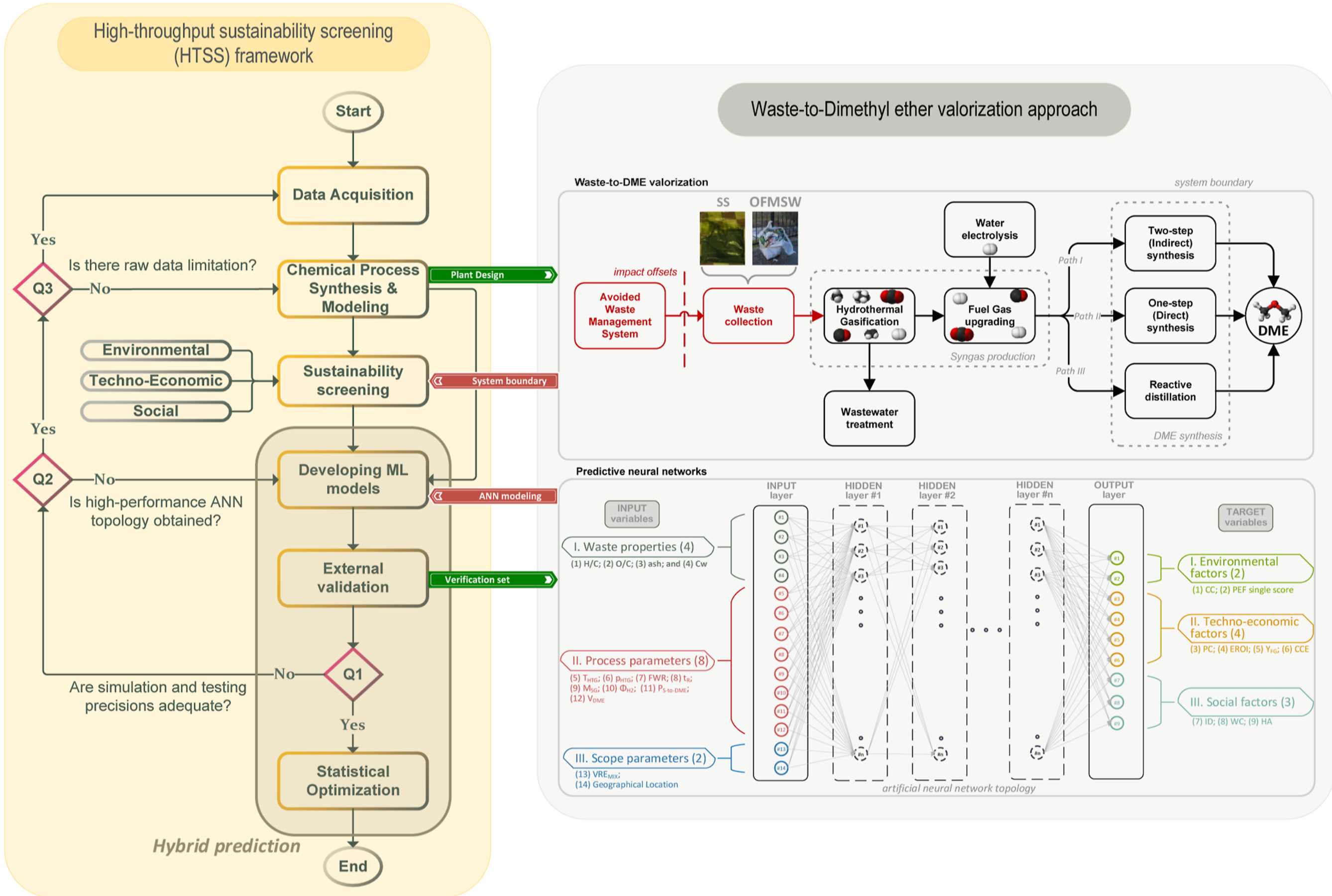

Figure 1. Flowchart of the HTSS framework applied for explorative waste-to-DME valorization.

valorization processes (e.g., atmospheric pyrolysis, gasification, and torrefaction) requires pretreated and dried secondary fuels. As a bypass solution, the excess moisture content of waste resources can be employed as a green solvent in sub- or supercritical water decomposition technologies (also known as hydrothermal conversion), phasing out the necessity for an energy-intensive waste pretreatment step.[9] However, despite strong research efforts from the past two decades (i.e., adopting various high-pressure reactor designs (plug flow tubular,[10] fluidized bed,[11] and autoclave reactors[12]), homogeneous,[13] and heterogeneous[14] catalysis), the hydrothermal processing of waste is still an immature technology at a low technological readiness level (TRL).[15] Large-scale commercialization requires advancements in different areas, such as (i) maintaining robust operation by reducing the negative effects of reactor plugging and corrosion,[16] (ii) mapping process integration and intensification possibilities to lower energy requirements,[17] and (iii) gathering critical know-how on fuel gas valorization strategies yielding high-value products.

The demand for intensified renewable resource utilization and the implementation of innovative high-risk and high-gain technologies necessitate conducting early stage process synthesis to guide the transformation toward a more sustainable and reliable chemical industry. Single- or multi-scaled mechanistic kinetic and transport models were proposed to advance low-TRL catalyst-driven CO_2 reduction involving computational fluid dynamics,[18] kinetic Monte Carlo,[19] and density functional theory[20] simulations. System-level process synthesis and intensification of novel circular biorefineries are highly sophisticated tasks involving the selection of suitable feedstocks, processing technologies,[21] scope parameters (e.g., geographical location), and determining the most favorable plant configurations among a large number of alternatives that comply with a set of performance criteria[22] (e.g., energy and exergy efficiencies,[23] safety considerations,[24] and product and solvent recovery[25]). The high number of processing alternatives and configurations, the difficulty of defining adequate initial superstructures without omitting several potentially feasible process flowsheets,[26] and the lack of available sustainable-by-design screening algorithms hinder the reliable advancement of novel and potentially disruptive biochemical technologies.

Machine learning (ML) and its sub-disciplines (e.g., artificial neural networks (ANNs),[27] random forests,[28] and regression trees[29]) are gaining increasing attention in the fields of chemical and environmental sciences. The application of ML tools is already demonstrated in the fields of energy, environmental, and process engineering, e.g., biochar production,[30] co-pyrolysis of sewage sludge (SS) and peanut shell,[31] anaerobic digestion,[32] glycolic acid manufacturing,[33] evaluating refinery concepts,[34] and modeling of complex biochemical unit operations and reaction kinetics.[35] The toolsets of ML were found to be useful in combination with environmental assessments to predict the greenhouse gas emissions for automotive lightweights,[36] evaluate urban metabolism assessments,[37] and facilitate the screening and cleaning of datasets.[38] The ability to handle big data and solve complex nonlinear problems makes ML methods particularly suitable to address the challenges that arise with early stage sustainable process syntheses; however, the black-box

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nature of ML models limits the in-depth description and fundamental understanding of engineered environmental systems. Hybrid ML (HML) models combine the benefits of distinct standalone models and provide more robust preprocessing,[39] postprocessing,[40] and/or improved classifier performance.[41] HML algorithms were typically applied to improve reliability, capability, prediction accuracy (e.g., as shown in modeling biogas[42] and photovoltaic power production[43]), and optimize operating conditions by implementing data expansion on reaction kinetics to overcome data scarcity.[33] The benefits of engineering-based sustainability assessment are the high level of transparency and the possibility of gaining insights into mechanistic relationships. The toolsets of data science can open new applications and perspectives in the field of environmental science, especially if they are combined with engineering applications; however, such methodological pairings must demonstrate the potential to improve the in-depth understanding of engineered environmental systems. The main obstacle before higher credibility and use of the sustainability performance prediction results is the issue of interpreting the results and linking them to the process factors. The present study proposes a hybrid sequential prediction algorithm to overcome the black-box nature of neural networks and provide mechanistic insights into causal relationships.

Designing reliable biogenic waste-to-energy and waste-to-chemical systems, such as waste-to-DME valorization, requires adapting a multi-perspective, economically, environmentally, and socially benign-by-design process synthesis concept. The presented work combines single computational tools, i.e., ML and statistical modeling, early stage flowsheeting and process simulations, techno-economic and life cycle assessments (LCAs), and social modeling into a hybrid prediction algorithm enabling high-throughput system-level quantitative sustainability screening to evaluate and guide the development of innovative, low-TRL bioconversion processes.

2. METHODS

2.1. High-Throughput Sustainability Screening Framework. The high-throughput sustainability screening (HTSS) framework developed for explorative waste-to-DME process design is presented in Figure 1. The HTSS algorithm consists of four major steps, as detailed below:

1. First, data acquisition was performed to supply initial values for superstructure models that formulate mixed-integer nonlinear programming (MINLP) problems containing discrete and continuous variables with constraints. Experimental data on waste hydrothermal gasification (HTG) (i.e., type of feedstock, ultimate and proximate compositions of wastes, design of HTG reactor (tubular, fluidized bed, and autoclave), reaction temperature, pressure, feedstock-to-water ratio (FWR), residence time, and fuel gas component yields) were collected from the literature using peer-reviewed scientific papers (as is summarized in Table S1).
2. In the second step, explorative process synthesis and simulation of waste-to-DME plant configurations were carried out by accumulating a broad range of records on plant data, operating conditions, and techno-economic performance (such as production cost of DME, carbon conversion efficiency (CCE), energy return on investment, and fuel gas yield). The obtained input-target relations were used to (i) perform data-driven hybrid predictions and (ii) set up a detailed life cycle inventory for environmental sustainability assessment.
3. In the next step, *ex-ante* environmental and social LCAs were conducted with selected indicators. The created database in step 2 was expanded with scope parameters (geographical location and electricity mix composition) and sustainability indicators (i.e., climate change impact, product environmental footprint (PEF), working capacity, intellectual disability, and housing availability).
4. Data-driven hybrid prediction (ANN−RSM−DOM) of sustainability indicators was sequentially performed by developing ANNs, generating polynomial response surfaces, and solving multiresponse problems with desirability optimization, as summarized below:
   (a) ANNs were trained using the formerly compiled input-target dataset containing 500 waste-to-DME plant configuration entries. The developed ML models were applied to (i) simulate the thermochemical decomposition of waste resources considering feedstock composition and operating and design parameters, (ii) examine complex system-level relationships, and (iii) supply *in silico* experimental results for full factorial design of experiments (DOEs). The target variables were techno-economic (fuel gas yield, CCE, and energy return on investment), environmental (carbon and aggregated environmental footprints (EFs)), and social (working capacity, intellectual disability, and housing availability) impact indicators. The developed ANNs were validated externally using an independent validation set with a size of 5% of the training set.
   (b) The outputs of neural networks were post-processed to evaluate the effects and possible interactions of input factors. Full factorial mixed-level DOE was generated for each type of waste (the organic fraction of municipal solid waste (OFMSW) and SS) to set out a statistical modeling space where second-order polynomial functions were fitted to the *in silico* experimental data. Response surface methodology (RSM) and analysis of variance (ANOVA) were used to identify hot−spot parameters, i.e., variables that influence the performance of waste valorization significantly and to quantify the effects of factors.
   (c) Finally, desirability optimization methodology (DOM) is used for multi-factorial optimization in sequences based on the number of qualitative variables that correspond to the integer variables in MINLP problems to determine ideal waste-to-DME plant configurations.

The HTSS algorithm is an iterative computational framework. If simulation and testing precisions of ML models are inadequate and high-performance ANN topologies are not obtained, then neural networks are re-trained using changing topologies (number of hidden layers and neurons) or training methods. If high-performance neural networks are obtained but the accuracy of ML models is low, then potential raw data limitations are examined. If data limitations are not detected, the process synthesis and flowsheeting phases are improved by adopting novel superstructures of plants and/or refining the modeling of process block units. If data availability limitations

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Table 1. Properties of Input Variables Used for Hybrid Prediction

input group	independent factor	type of variable	description	training interval/levels
waste properties	(1) waste category (C_W, —)	qualitative	the factor determines the applied AWMS	SS, OFMSW
	(2) H/C (—)	quantitative	ratio of elemental hydrogen (weight percent (atomic weight)$^{-1}$) and carbon (weight percent (atomic weight)$^{-1}$)	1.068−1.824
	(3) O/C (—)	quantitative	ratio of elemental oxygen (weight percent (atomic weight)$^{-1}$) and carbon (weight percent (atomic weight)$^{-1}$)	0.466−0.793
	(4) ash (wt %)	quantitative	inert composition of waste	1.36−28.96
W-t-DME process parameters	(5) T_{HTG} (°C)	quantitative	applied temperature during the HTG of waste feedstocks	480−850
	(6) p_{HTG} (MPa)	quantitative	applied pressure during the HTG of waste feedstocks	24.00−28.25
	(7) FWR (wt %)	quantitative	applied FWR during the HTG of waste feedstocks	2.0−15.0
	(8) type of reactor (t_R)	qualitative	the applied reactor design during the thermochemical conversion of wastes	tubular, fluidized bed, and autoclave
	(9) M_{SG} (—)	quantitative	synthesis gas modular, composition, and quality of synthesis gas	−0.38 to 3.01
	(10) ϕ_{H_2} (—)	quantitative	hydrogen modular	0.20−0.68
	(11) $P_{S\text{-}t\text{-}DME}$	qualitative	applied flowsheets for DME production	two-step, one-step, and reactive distillation
	(12) V_{DME} (t DME (a)$^{-1}$)	quantitative	annual production volume of dimethyl ether	3,003−25,466
scope parameters	(13) geographical location	qualitative	the variable was defined to track the effects of different AWMSs and energy mix compositions	DE; DK; IT
	(14) VREmix (—)	quantitative	the variable was defined to evaluate the effects of variable renewable energy utilisation	0−1

are spotted, the data acquisition stage is revised by expanding the number of experimental or simulation entries.

2.2. Explorative Plant Design and Sustainability Assessment. The process flowsheeting of waste-to-DME refineries was carried out using the Aspen Plus V11 simulator.[44] The Predictive Soave−Redlich−Kwong (PSRK) property method was applied to modeling mixtures of non-polar and polar compounds in combination with light gases up to high temperature (<850 °C) and pressure (<28.3 MPa) conditions. Biological waste feedstocks (i.e., the OFMSW and SS) were defined as non-conventional solid materials using elemental (C, H, N, O, S, and Cl) and proximate (volatile matter, fixed carbon, ash, and moisture) compositions (as is shown in Table S1).

The process flow diagram of waste-to-synthesis gas conversion is illustrated in Figure S1. High moisture-containing biowastes were converted into fuel gas (a mixture of H_2, CO_2, CO, CH_4, and light hydrocarbons) via HTG. The fuel gas was upgraded using pre-and tri-reformings (a combination of dry reforming, partial oxidation, and steam reforming reactions) to produce high-quality synthesis gas. Additional hydrogen was supplied to the system by applying water electrolysis, assuming that the required electricity for water splitting was supplied by employing variable renewable energy sources (i.e., wind turbines and photovoltaic panels). The syngas-to-DME conversion was evaluated by investigating three different process alternatives: (a) two-step/indirect DME synthesis, (b) one-step/direct DME synthesis, and (c) DME synthesis via reactive distillation. The experimental settings, backgrounds for reaction kinetics, fuel gas yield, and product composition applied for the simulation of supercritical water gasification (SCWG), and the fuel gas-to-DME valorization alternatives are detailed in Section S1 in the Supporting Information.

The sustainability assessment of prospective plant designs was based on techno-economic, social, and environmental life cycle analyses. Process flowsheeting and design results are specified and available in the open research data repository file (1). The economic assessment of DME production scenarios was carried out using the chemical engineering plant cost index (CEPCI) with cost curves[45] and Aspen Process Economic Analyzer V11 software[46] to determine purchased and installed equipment costs. The techno-economic assessment of plant scenarios is detailed in Section S2 in the Supporting Information. Techno-economic indicators were selected to test the financial viability of refinery configurations (PC), the effectiveness of hydrothermal fuel gas production using various supercritical reaction conditions and reactor designs (YFG), energy conversion efficiency (EROI), and the goodness of waste-to-DME upcycling (CCE).

The environmental assessment of waste-to-DME plant scenarios was carried out using a LCA conducted in accordance with the requirements of the ISO 14040:2006[47] and ISO 14044:2006[48] standards and the guidelines of the EU Commission's ILCD Handbook.[49] The scenario development followed an explorative nature to assess how future technological development could influence environmental impacts. The explorative assessment implied cornerstone scenarios at the edge of solution space to improve technology mapping potentials. The life cycle systems were modeled using the SimaPro V9.2.0.1 software.[50] The PEF was assessed by applying the EF 3.0 V1.01 method proposed by the European Commission to model climate change and aggregated environmental impacts.[51] The functional unit (FU) was 1 kg of bio-DME (with a mass fraction (w_{DME}/w) ≥ 0.98) produced via the thermochemical valorization of OFMSW and SS and the upgrading of reformed HTG synthesis gas. The applied cradle-to-gate system boundary is illustrated in Figure S2. The avoided (replaced) incumbent waste management system (AWMS) is detailed in Table S4 and Section S2 in the Supporting Information. Environmental performance indicators (climate change impact, CC; PEF) were selected to gain insights into the

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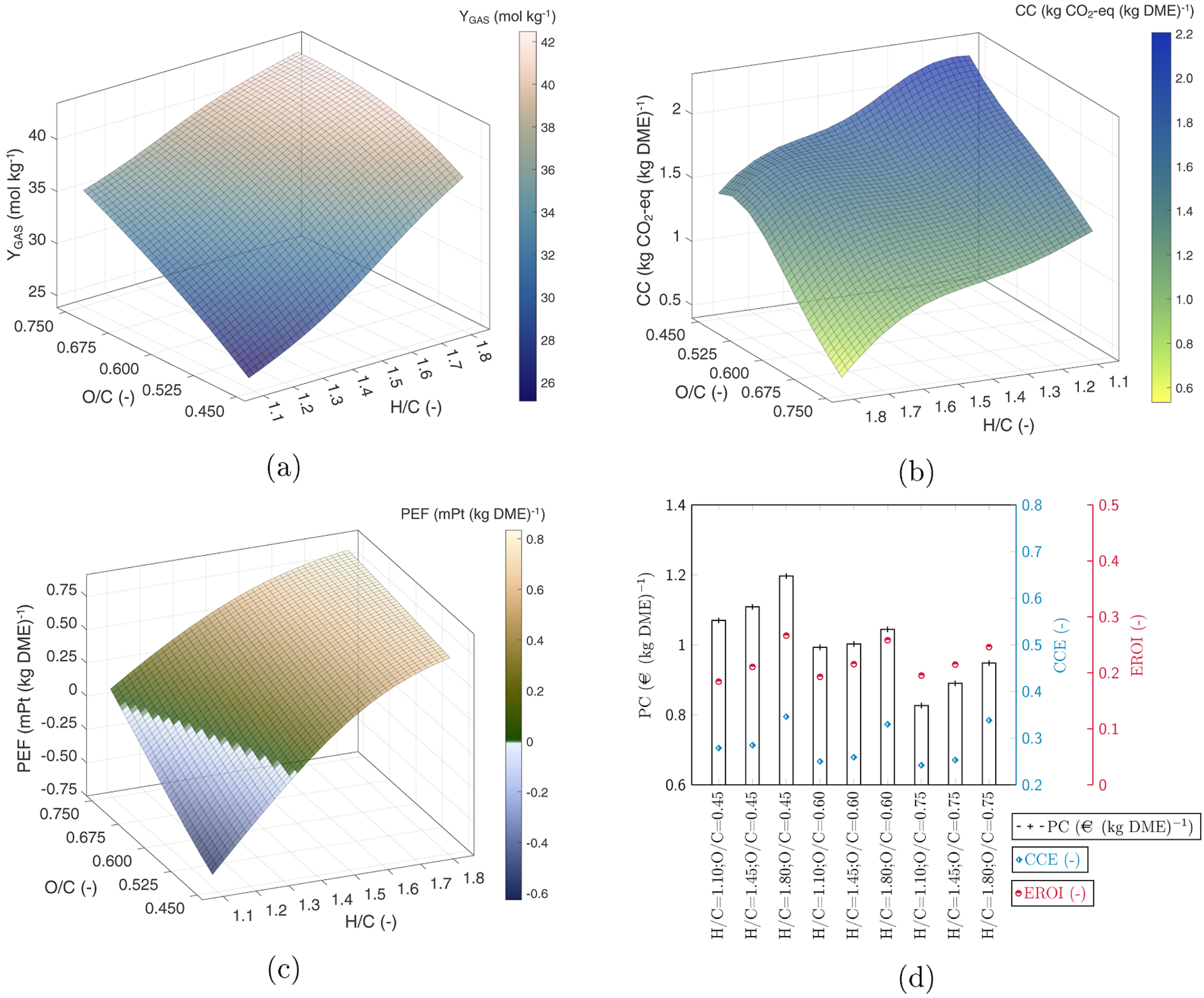

Figure 2. Impacts of waste composition on (a) fuel gas yield (OFMSW), (b) climate change (OFMSW), (c) PEF (SS), and (d) techno-economic parameters (OFMSW). Applied independent factor levels: ash = 9.3 wt %; T_{HTG} = 650 °C; p_{HTG} = 25 MPa; FWR = 9.0 wt %; t_R = autoclave HTG reactor; M_{SG} = 1.7; ϕ_{H_2} = 0.40; syngas-to-DME process = indirect; VRE_{MIX} = 0.70; geographical location = DK; and annual production = 12,500 t DME (a)$^{-1}$. PC: production cost (€ (kg DME)$^{-1}$), CCE: carbon conversion efficiency (—), and EROI: energy return on investment (—).

carbon emission and aggregated environmental damage profile of waste-to-DME conversion.

Social impact assessment is an unresolved analysis that lacks standardization and can easily overlap with weighted environmental factors such as impacts on human health.[52] Mattioda et al.[53] highlighted social and socioeconomic subcategories (e.g., secure living conditions, access to material and immaterial resources, work hours, forced labor, and opportunities/discrimination) that could be suitably considered to evaluate and indicate the social impacts of biochemical processes. Based on the latter recommendation, three impact categories were selected for evaluating social aspects: (i) housing availability (HA, m^2); (ii) working capacity (WC, PersonYr); and (iii) intellectual disability (ID, PersonYr). The social aspects of waste-to-DME plant scenarios were quantified using the EPS (Environmental Priority Strategies) 2015dx V1.00 impact assessment methodology.[54]

2.3. Hybrid ML and Statistical Modeling. The results of process flowsheeting and sustainability assessment were organized into an input-target dataset that was used to train ANNs. The training set is specified in the open research data repository file (2). The hybrid prediction aimed to (i) simulate the operation space of prospective waste-to-DME valorization plants, (ii) reveal the effects and interacting relationships between independent variables, and (iii) ease the *ex-ante* sustainability screening of bioprocessing technologies characterized by medium to high data dimensionality. Multilayer perceptrons were developed using MATLAB R2021a software.[55] Broyden, Fletcher, Goldfarb, and Shanno (BFGS) quasi-Newton backpropagation and resilient backpropagation algorithms were used for the training phases. The properties of input variables are summarized in Table 1. The ANN training set was allocated randomly to training (80%), testing (10%), and internal validation (10%) phases. Moreover, an external validation set was used to extend the ANN model verification. The external validation set was not part of the initial ANN training set, hence providing a higher level of model verification. The size of the independent external dataset was 5% of the

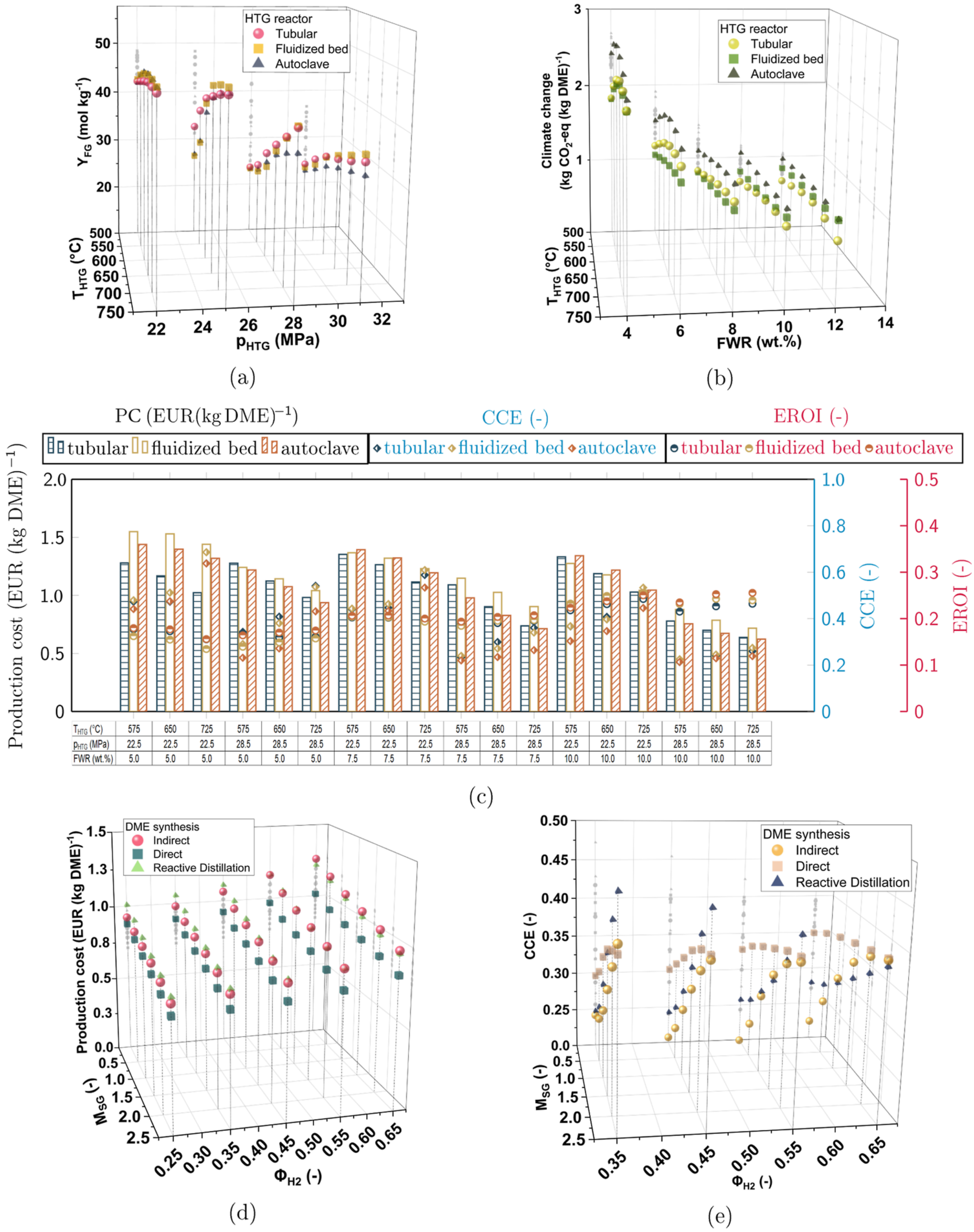

Figure 3. Effects of HTG process parameters on fuel gas and DME production. (a) Effect of HTG temperature and pressure on the fuel gas yield (FWR = 7.5 wt %). (b) Effect of HTG temperature and FWR on climate change (p_{HTG} = 25 MPa). (c) Effect of HTG temperature, pressure, and FWR on techno-economic indicators of DME production. Applied settings: type of waste: OFMSW; H/C = 1.6; O/C = 0.739; ash = 9.300 wt %; M_{SG} = 1.7; ϕ_{H_2} = 0.4; indirect DME synthesis; VRE_{MIX} = 0.7; geographical location: DK; and production volume = 12,500 t DME (a)$^{-1}$. Effects of syngas and hydrogen supply modulars on (d) the production cost and (e) CCE (T_{HTG} = 650 °C and p_{HTG} = 25 MPa. FWR = 10.0 wt %).

training set. The plant scenarios used for the external validation are given in Table S7. Detailed data on the training dataset, data preprocessing, model testing, and validation are provided in Section S3 in the Supporting Information.

The "black box" nature of the ML approach enables predictions of a wide range of process perturbations but makes it challenging to provide insights into the effects of independent variables on sustainability indicators and better understand environmental system behaviors. To bypass these limitations, ANNs were applied to provide *in silico* experimental results for mixed-level full factorial DOE. Statistical model regressions were performed based on quadratic polynomial functions using the RSM. The adequacy of statistical models was tested by the ANOVA. The desirability function approach[56] was used to determine the combined extremum of selected sustainability indicators (i.e., in the present case, the combined minimum of climate change impact and DME production cost). Additional information on the modeling background is provided in Section S3 in the Supporting Information.

3. RESULTS

3.1. Impact of Waste Quality on Valorization Performance. The model analysis and hybrid prediction performance are detailed in Section S3 in the Supporting Information. ML models enable the explorative simulation of waste decomposition cases that are not available in the literature due to data limitations (e.g., not existing or inaccessible). The techno-economic and environmental impacts of waste composition on HTG fuel gas formation and DME production are illustrated in Figure 2. Figure 2a shows that the elemental composition of waste sources influences the fuel gas evolution during supercritical water decomposition. Processing wastes with higher H/C and O/C ratios elevates the total gas yield. The simulation results indicate that the formation of HTG fuel gas can be increased from 24.75 mol (kg waste)$^{-1}$ (H/C = 1.10 and O/C = 0.45) to 42.54 mol (kg waste)$^{-1}$ (H/C = 1.80 and O/C = 0.75) by applying the same thermochemical reaction conditions (T_{HTG} = 650 °C; p_{HTG} = 25 MPa; FWR = 9.0 wt %; and autoclave reactor design).

The simulations demonstrate that waste selection is key in achieving low carbon emission DME production due to its influence on the effectiveness of fuel gas production, biogenic CO_2 fixation, and the composition of the AWMS. It is obtained that climate change impacts can be reduced by converting OFMSW streams with higher H/C and O/C factor levels. Figure 2b shows that an interacting effect can be expected between the two factors that results in elevated climate impact reduction. Greenhouse gas emissions can be reduced by a factor of 4.6 to 0.48 kg CO_2-eq (kg DME)$^{-1}$ by adopting waste resources with higher H/C (1.80) and O/C (0.75) characteristics. The effects of waste elemental composition on the PEF single score are illustrated in Figure 2c. Applying waste feedstocks with higher H/C and O/C ratios elevates the fuel gas yield, which is found to be beneficial to decreasing the carbon footprint; however, the aggregated environmental impacts indicate an inverse tendency for damage mitigation. Feedstocks that are characterized by lower H/C and O/C levels reduce the PEF score of DME synthesis significantly. The explorative simulations indicate that there is an interaction between H/C and O/C factor levels, and multiple waste composition combinations have the potential to yield environmentally benign negative PEF scenarios. These results call attention to case specificity and targeted waste selection to minimize overall environmental impacts.

The effects of waste composition on conversion efficiency and economic parameters are illustrated in Figure 2d. It is found that processing waste resources with lower H/C and higher O/C ratios decreases the production cost of DME. Dissimilar effects are observed in the cases of energy return on investment and CCE. OFMSW feedstocks characterized by higher H/C values contribute to achieving more efficient DME synthesis with higher EROI and CCE values. The results show that the elemental composition of waste affects the upcycling process, and changes in waste quality significantly influence the techno-economic and environmental performance of DME synthesis. These findings stress the importance of waste pre-selection and composition monitoring to maintain high-performing DME production.

3.2. Sustainability Implications of Process Design and Scope Parameters. The effects of process design and operating conditions on HTG fuel gas and DME production are illustrated in Figure 3. Figure 3a shows that higher HTG reaction temperatures and lower pressure levels increase the total fuel gas yield. The HTG fuel gas formation can be raised up to 48.47 mol (kg OFMSW)$^{-1}$ by employing a fluidized bed HTG reactor design at 750 °C and 22 MPa. The neural network-based modeling demonstrates that the applied high-pressure reactor design affects attainable gas yields. The results show that tubular reactors provide a higher fuel gas yield at 28 MPa applying less than 700 °C SCWG reaction temperature. The batch autoclave reactor prevails at low pressure (22 MPa) regimes and when low gasification temperature (550 °C < T_{HTG} < 650 °C) is combined with low pressure (<22 MPa) settings.

The climate change impact is illustrated as a function of HTG reaction temperature, FWR, and type of reactor in Figure 3b. Applying reduced water solvent concentrations during the supercritical conversion (up to 12.0 wt % total solids) results in lower greenhouse gas emissions. The autoclave reactor offers significant climate advantages compared to other HTG reactor designs. Fluidized bed gasifiers lag behind the other two reactor options at low feedstock concentrations (FWR < 10 wt %).

The effects of thermochemical parameters on techno-economic indicators are illustrated in Figure 3c. It is observed that higher FWR (10 wt %), pressure (28.5 MPa), and elevated temperature levels contribute to reducing the production cost of DME. A factorial interaction is detected between the applied high-pressure reactor design and HTG reaction conditions. Tubular reactor configurations operate more cost-effectively using dilute feedstocks (≤7.5 wt %) under low pressure (22.5 MPa) settings. At higher factor levels (725 °C, 28.5 MPa, and 10 wt %), the autoclave reactors offer the lowest DME production cost. The lowest PCs are reached at 725 °C, 28.5 MPa and 10 wt % FWR for each design alternative.

The simulation results show that the FWR highly affects process efficiency indicators. Lower FWR factor levels (5.0 wt % of total solids) are favored to increase the CCE. In comparison, higher FWR levels (10.0 wt % of total solids) are found to be more beneficial in boosting the EROI. Lower FWR levels equal higher supercritical water solvent concentrations that elevate the decomposition of macromolecules and specific carbon-rich fuel gas component yields. Higher FWR levels reduce the amount of water that must be heated up to high reaction temperatures, which results in energy savings.

The presented ML simulations demonstrate that interactions can be expected between HTG reactor design and operating parameter factors. These results suggest a strong case sensitivity where the reachable fuel gas yield or climate change impact with a given high-pressure reactor type is influenced by the applied levels of operating parameters and type of waste. The identified strong case sensitivity does not stop within the battery limit of waste thermochemical conversion. The synthesis gas-to-DME conversion pathways are influenced by the (i) type of waste, (ii) synthesis gas (M_{SG}), and (iii) hydrogen supply (ϕ_{H_2}) modulars. Figure 3d presents that the production cost of DME can be

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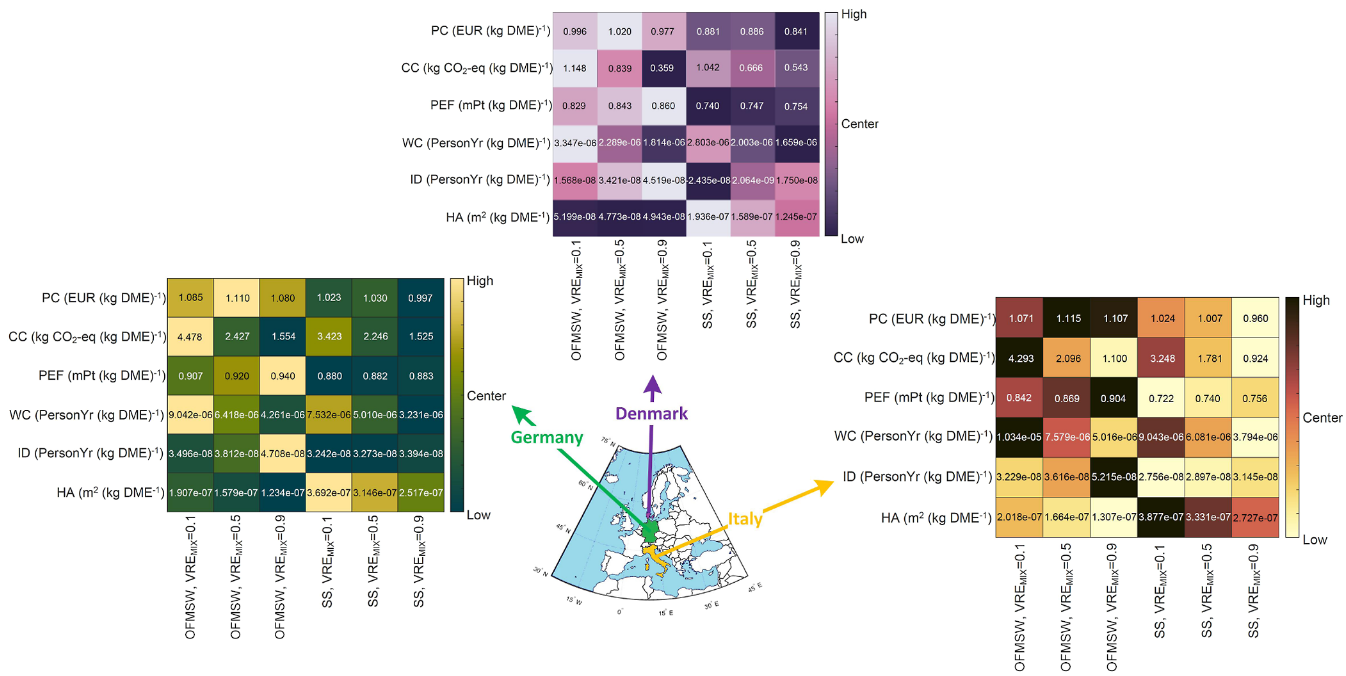

Figure 4. Effects of geographical locations, type of waste, and variable renewable electricity mix on sustainability indicators. HTG reactor design: tubular, T_{HTG} = 650 °C; p_{HTG} = 25 MPa; FWR = 7.5 wt %; M_{SG} = 1.7; ϕ_{H_2} = 0.4; indirect DME synthesis; and production volume = 12,500 t DME (a)$^{-1}$. PC: production cost (€(kg DME)$^{-1}$), CC: climate change (kg CO_2-eq (kg DME)$^{-1}$), PEF: product environmental footprint (mPt (kg DME)$^{-1}$), WC: working capacity (PersonYr (kg DME)$^{-1}$), ID: intellectual disability (PersonYr (kg DME)$^{-1}$), and HA: housing availability (m^2 (kg DME)$^{-1}$).

reduced by applying M_{SG} values between 2.0 and 2.5 combined with reduced ϕ_{H_2} (0.25) levels for each synthesis configuration. The results indicate that the lowest PC can be attained via direct one-step DME synthesis followed by indirect two-step conversion. The reactive distillation method could outperform the two-step DME production at elevated hydrogen modular levels (ϕ_{H_2}> 0.65), but it cannot compete with the one-step syngas conversion.

The characteristic curve of CCE displays that lower ϕ_{H_2} (0.35) and higher M_{SG} (2.0) values are preferred to maintain a high carbon conversion ratio, as is illustrated in Figure 3e. The results show that the achievable CCE in the indirect and reactive distillation methods depends highly on the applied level of syngas modular. The highest CCE (CCE = 0.482) is attained by the reactive distillation method.

The effects of scope parameters, i.e., the geographical location and the share of variable renewable energy sources within the national electricity grid mixes, are illustrated in Figure 4. Increasing the share of fluctuating renewables (VRE_{MIX}, eq S16) from 0.5 to 0.9 contributes to a decrease in GHG emissions between 0.480 and 0.996 kg CO_2-eq (kg DME)$^{-1}$ and 0.123–0.857 kg CO_2-eq (kg DME)$^{-1}$ using OFMSW and SS feedstocks, respectively. The differences in GHG emission mitigation potentials can be explained by the country-specific AWMSs. The highest emission reduction potentials are identified in Italian cases, where the share of landfilling in the AWMS is considerably higher compared to the other locations. The results show that applying a higher share of renewables in the electricity mix reduces impacts on working capacity and housing availability, irrespective of geographical locations.

3.3. Effects of Quantification and Desirability Optimization. Understanding the root causes of deviations and irregularities in ML-assisted chemical processes and sustainability modeling is inhibited by the black-box nature of the ANN models. The hybrid prediction enables the quantification of standardized factor effects, providing deeper insights into governing parameters. The quantified production cost and climate change impact effect sizes are shown in Figure 5a,b, and the ANOVA results are detailed in Tables S10 and S11.

The results show that the predicted PC is significantly influenced by the FWR (F = 48,010.8; $p < 1 \times 10^{-6}$), the production volume (F = 4,278.21; $p < 1 \times 10^{-6}$), and the interaction between the two factors (F = 3,487.93; $p < 1 \times 10^{-6}$). Syngas-to-DME processing parameters (i.e., M_{SG} and ϕ_{H_2}) also have high effects on the production cost, displaying the importance of water electrolysis, hydrogen evolution rate in the hydrothermal process, and the optimized use of hydrogen in synthesis gas valorization. The positive standardized effect of the hydrogen modular factor reveals that elevated factor levels increase the production cost and carbon footprint of DME synthesis and thus stress the importance of boosting the hydrogen yield during the hydrothermal conversion to decrease the value of ϕ_{H_2}. Figure 5a presents that the FWR, production volume, and the share of variable renewable energy in the electricity mix have negative linear effects on the production cost. Optimizing the level of these factors contributes to attaining better refinery margins. The measure of the magnitude of statistical effects indicates the high importance of the thermochemical conversion of waste resources in the waste-to-DME valorization chain. The FWR factor has a negative standardized effect estimate, meaning that higher factor levels are preferred to reduce the production cost and carbon footprint. The high-pressure and high-temperature HTG is a highly energy-intensive process. Applying increased water solvent concentration contributes to decomposing waste

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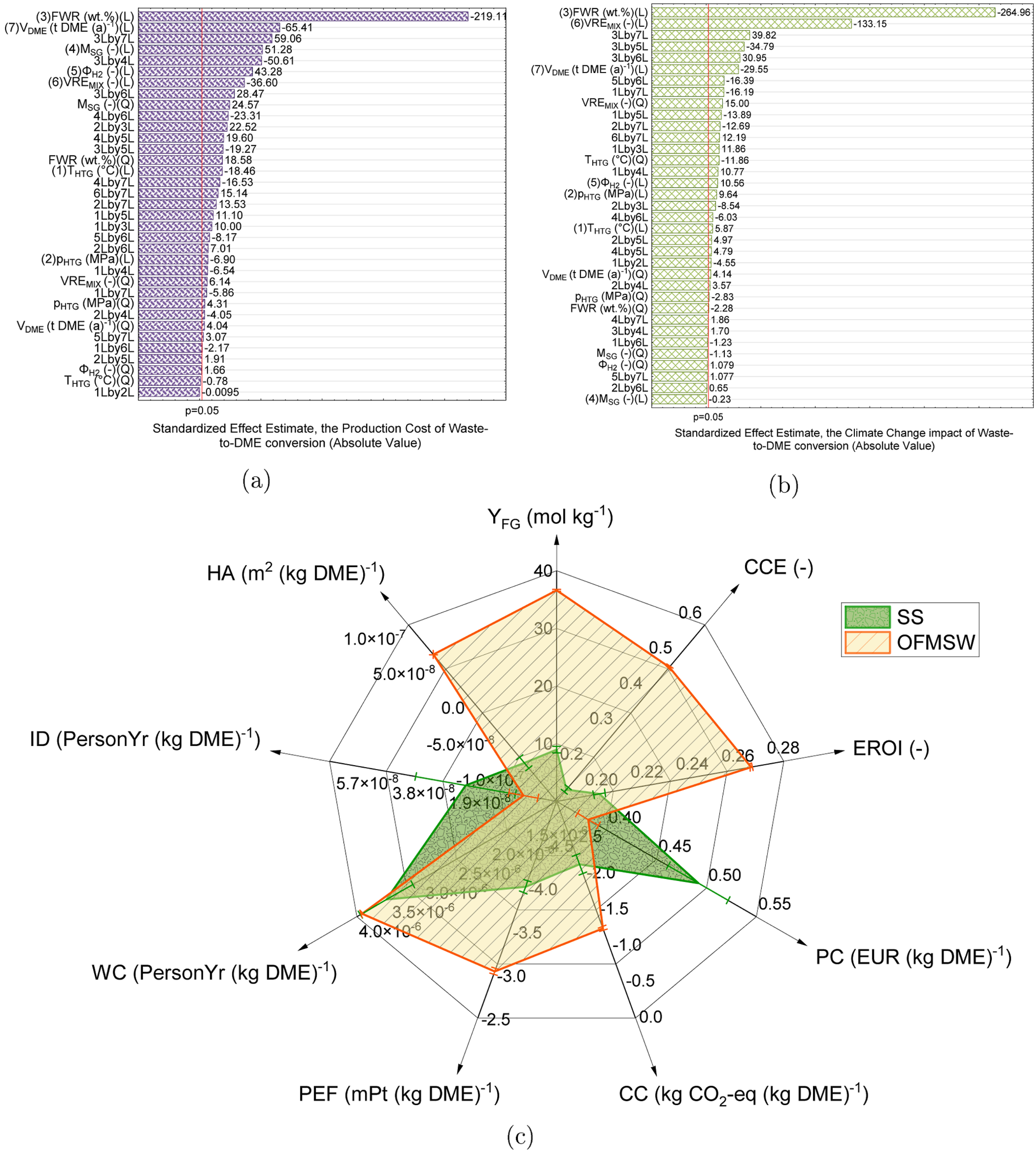

Figure 5. Comparing the results of the HTSS algorithm for SS and OFMSW feedstocks. (a) Standardized effect estimates for the production cost of DME. (b) Standardized effect estimates for the climate change impact of waste-to-DME valorization. L = linear and Q = quadratic effect. (c) Illustrating the results of desirability optimization on a radial graph. Error bars indicate ± 95% confidence intervals. Y_{FG}: fuel gas yield (mol kg^{-1}); CCE: carbon conversion efficiency (—); EROI: energy return on investment (—); PC: production cost (€ (kg DME)$^{-1}$); CC: climate change (kg CO_2-eq (kg DME)$^{-1}$); PEF: product environmental footprint (mPt (kg DME)$^{-1}$); WC: working capacity (PersonYr (kg DME)$^{-1}$), ID: intellectual disability (PersonYr (kg DME)$^{-1}$), and HA: housing availability (m^2 (kg DME)$^{-1}$).

materials more effectively (as is illustrated in Figure 3b,c); however, heating up a large amount of water relative to the mass of waste feedstock increases the energy requirement of the thermochemical conversion that can be translated into higher costs and climate impacts. The results show that energy input reduction (by using elevated FWR levels) is favored over in situ fuel gas yield enhancement. The second most influential factor is the production volume. Scaling up DME production is beneficial to reduce specific unit costs. This effect is also observed and

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described by experience curves that specify the relationship between unit cost and cumulative production capacities.[57]

The ANOVA of the climate change impact shows that the Fischer's variance ratio (F) is high with low probability in the case of the linear FWR (F = 70,203.49; $p < 1 \times 10^{-6}$) and VRE_{MIX} (F = 17,728.52; $p < 1 \times 10^{-6}$) factors. The effects estimate shows that both factors negatively impact GHG emissions (Figure 5b). Higher FWR factor levels equal lower energy requirements that decrease the climate change impact of DME production.

Plant configurations that are characterized by the lowest combined production cost and climate change impact are determined by involving all qualitative input factors (i.e., the type of waste, geographical location, design of the HTG reactor, and DME synthesis process) at all nominal levels, resulting in a total of 54 optimization sequences as detailed in Tables S12 and S13. The optimized OFMSW- and SS-to-DME biorefinery configurations are compared in Figure 5c. Figures S14 and S15 illustrate the profiles for predicted optimized values and desirability. Both plant setups offer climate and EF benefits. The SS-based DME production offers better carbon emission removal (−2.13 kg CO_2-eq (kg DME)$^{-1}$); however, applying OFMSW feedstock results in superior techno-economic performance, i.e., higher fuel gas yield, CCE, energy return on investment, and 22.4% lower production cost (0.382 € (kg DME)$^{-1}$). Housing availability and working capacity social factors are influenced more positively in the case of the SS-based alternative, while the intellectual disability impact is found to be lower for the OFMSW plant setup. These findings can be explained by the different composition of alternative resources and waste management systems. According to the ecoinvent database, the trace heavy metals content of SS sources is lower than the OFMSW feedstock. Avoided heavy metal's related emissions to the air are obtained to be higher in the case of the OFMSW feedstock in Germany can be translated into lower damages on intellectual disability impact category.

Rendering optimal biorefinery configuration by simultaneously minimizing production cost and climate change impact results in different preferred process flowsheets for OFMSW and SS cases. The differences in HTG reactor design and DME synthesis procedure suggest that waste feedstock substitution could be limited after installation and highlight the importance of waste pre-screening.

4. DISCUSSION

Conventional sustainability assessments are suitably used to quantify and compare the techno-economic, environmental, and social performance of distinctive chemical plant configurations. However, guiding the research and development of potentially disruptive but still immature technologies requires testing a wide range of process alternatives and configuration settings, resulting in a lengthy and time-consuming modeling procedure. The explorative hybrid prediction-driven screening follows a different methodological approach than traditional sustainability assessments. It does not only evaluate specific chemical plant configurations but also maps the prospective refinery development space, creating an efficient prediction toolset for uncovering the most beneficial configurations and development pathways. The hybrid prediction-driven algorithm combines the benefits of single computational methods and facilitates the evaluation of novel low TRL processes by (i) enabling the use of complex medium- to high-dimensional datasets containing nonlinearities, (ii) providing causal backgrounds for ML-assisted analyses via determining main effects and interactions between independent variables, and (iii) identifying benign-by-design process scenarios based on a set of sustainability criteria. The proposed hybrid ML algorithm (ANN-RSM-DOM) does not only determine the best process configurations but also provides valuable information on the governing parameters of environmental systems. It provides not only optimal values but also mechanistic insights into causal relationships, that is, know-how on how those optimal values could be reached. Understanding the main driving effects of engineered environmental systems is essential to guiding the development of early stage, potentially disruptive technologies. The HTSS algorithm is a generic framework that could be applied to other areas of chemical, biochemical, environmental, and process engineering. The framework is well suited to the evaluation of early stage and/or complex technologies where additional critical know-how needs to be acquired on sustainability determinants before the technology reaches a large commercial scale. The applicability could be limited in cases where high performance and accurate ML models are not obtained, and data limitation is detected in the training dataset. The HTSS methodology is designed to be an iterative computational framework to bypass these limitations. Chemical process synthesis and modeling can be challenging in certain situations, e.g., in the case of missing reaction kinetics. In such a case, additional data acquisition is needed to gather experimental data that could be used to develop flowsheeting models and then capture the reaction characteristics using the hybrid prediction algorithm, as is demonstrated in the present waste-to-DME case study.

The targeted selection of waste resources has a vital role in achieving high hydrothermal fuel gas yield, climate and PEF benefits, and techno-economic advantages (as is detailed in Figure 2). Götze et al.[58] collected physicochemical waste characterization data on a global scope and concluded that the C, H, and O content of the OFMSW range in a wide interval between 4.4 and 73.0 wt %; 1.5−15.5 wt %; and 5.3−55.8 wt %. The uncertain and fluctuating nature of waste material composition poses challenges in assessing the goodness of prospective sustainability analyses. Feedstock suitability is also influenced by scope parameters. Figure 4 illustrates that the climate change impact of identical technological configurations can vary in function of geographical characteristics (waste availability and technology-specific suitability). The environmental benefits of waste upcycling are linked to the impact offsets of country-specific AWMSs. The composition of AWMS and national-level energy mixes are determinant factors in reducing the carbon emission footprints of waste-to-chemicals technologies. Extracting the effects of waste type, composition, and geographical characteristics (e.g., avoided climate change impacts and electricity mix composition) on sustainability performance aids *ex-ante* plant design, improves the robustness of assessments, and enables performing waste suitability projections for scaled-up industrial applications.

Process configuration screening of emerging technologies is a data-sensitive task. Performing conventional LCA is a robust way to obtain accurate process performance estimations; however, it requires a high amount of data at an established commercial scale and is thus better suited to assist in the precise monitoring of mature processes. Applying the toolsets of data science for early stage process screening can bypass the limitations of missing data in foreground and background inventories, increasing screening efficiency. Zhu et al.[59] developed a deep neural network-based screening framework

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to predict life cycle impacts using molecular descriptors that could reflect the physicochemical properties of chemical products. Kleinekorte et al.[60] applied neural networks-assisted process screening using molecular and process descriptors with automatized flowsheeting to evaluate the impacts of emerging chemical processes. Karka et al.[34] proposed a modular framework to estimate the climate change impact of chemical technologies using decision trees and ANN models, highlighting the importance of data collection to perform optimization in foreground systems. The HTSS framework directly integrates explorative chemical process design and modeling into the algorithm, providing time-efficient feedback on lucrative plant configurations, research, and development trajectories, expanding the evaluation space to system-level scope parameters, and providing a more insightful view on the governing parameters of "black-box" models by determining statistically significant technological and scope variables, their effect size, interactions between parameters, response surfaces that simplify complex relationships to second-degree polynomials, and optimal chemical plant configurations.

Conducting sustainability assessments driven by ML modeling is a powerful tool, but simulations and *in silico* experiments are limited in several aspects. The compiled database ultimately influences the capabilities of neural networks. Experimental results on the HTG of wastes were available mainly on laboratory scales. Data from scaled-up thermochemical waste conversions could impact yields and fuel gas composition and improve the goodness of simulations on a commercial scale. Catalytic HTG conversions were not addressed in the current study due to data availability limitations. Developing cost-effective catalysts with high turnover numbers and frequencies, resistance to catalyst poisoning, and deactivation at high temperatures could provide new process development aspects. The developed ML-driven sustainability framework demonstrates the feasibility of including social sustainability assessment, but according to the current state-of-the-art, the results for the environmental and techno-economic indicators are to be taken as the basis for an evaluation of the configurations. The availability of a standardized social assessment method could influence the interpretation of social impacts; however, the developed HTSS algorithm can be suitably extended to incorporate any additional sustainability indicators. Additionally, aggregation of LCA results into a single score (e.g., PEF) does not have a scientific basis; thus, optimization of refinery configurations is limited to indicators that are not subject to value judgment. There is a trade-off to be expected between time-effective high-throughput process screening and accurate conventional data-intensive LCA. Early stage process screening could be characterized by high uncertainties derived from the pioneering nature of technology development, LCI or LCIA making it important to consider external verification and conduct additional conventional LCA to further test the exact process configurations obtained by the high-throughput pre-screening algorithm.

Baena-Moreno et al.[61] investigated the profitability of bioeconomy paths and concluded that the selling price of DME should be increased almost six times compared to the current market values (that is, 363 € $(\text{t DME})^{-1}$) to reach profitability. Do et al.[62] proposed green DME synthesis via gas-to-liquid conversion and reported an eco-friendly 0.781 \$ $(\text{kg DME})^{-1}$ production cost using renewable utilities in the chain. Michailos et al.[63] conducted a techno-economic analysis on DME synthesis via the hydrogenation of captured CO_2 and determined a minimum selling price in a range of € 1,828−2,322 $(\text{t DME})^{-1}$. The determined OFMSW- and SS-to-DME production costs offer competitive alternatives (0.382 ± 0.010 € $(\text{kg DME})^{-1} \leq \text{PC} \leq 0.492 \pm 0.030$ € $(\text{kg DME})^{-1}$) compared to formerly reported DME synthesis routes with combined environmental benefits. The economic viability of immature biochemical technologies is highly influenced by the EU Emission Trading System (EU ETS). The EU carbon emissions permits have increased significantly in the past few years from € 6 $(\text{t } CO_2)^{-1}$ (2017) to around € 90 $(\text{t } CO_2)^{-1}$ in early 2023.[64] The climate benefits of optimized biorefineries, coupled with an expected increase in carbon emissions tax,[65] could positively influence the profitability of waste-to-DME alternatives.

The waste-to-DME approach provides multiple benefits over conventional waste management methods. The utilization of hydrothermal conversion enables the decomposition of various high-moisture containing organic waste materials without the need for applying energy intensive pre-drying steps or complex and expensive secondary fuel production stages (e.g., refused derived fuel or solid recovered fuel). The production chain offers decarbonization potential for those niche applications that are difficult to turn into carbon neutral (e.g., marine fuel for long distance transportation,[4] power generation,[66] fuel blend with ammonia,[67] feedstock in olefins production,[5] aerosol and propellant,[68] and solvent in extraction[69]). Moreover, the valorization chain has the potential to integrate the power-to-X energy storage approach and balance the fluctuating nature of variable renewable energy sources. Former studies investigated the environmental impacts of DME production using various scopes and system boundaries. Christensen et al.[70] discussed that climate impact reduction could be achieved by producing DME in the carbon emissions capture and utilization framework ($-1{,}927$ kg CO_2-eq $(\text{t of MSW})^{-1}$) if a non-fossil-based energy system is applied. Tomatis et al.[71] showed that bio-DME is a 3.5-times cleaner automotive fuel compared to diesel, with a carbon emissions footprint of 584 kg CO_2-eq $(\text{t of bio-DME})^{-1}$. Domingos et al.[72] investigated the environmental performance of an integrated chemical plant that produced DME from paper pulp and reported a net CO_2 emission balance of −0.57 t of CO_2 $(\text{t of pulp})^{-1}$. The present study confirms that using alternative resources to synthesize DME offers climate benefits (-2.128 ± 0.129 kg CO_2-eq $(\text{kg DME})^{-1} \leq \text{CC} \leq -1.241 \pm 0.025$ kg CO_2-eq $(\text{kg DME})^{-1}$) within the bioenergy with carbon capture and utilization (BECCU) scheme. The climate benefits are obtained largely due to the substitution effects (i.e., avoided emissions), future technological developments, and the use of fluctuating renewable electricity in the conversion chain.

The initial waste-to-DME valorization training set contains cost-effective OFMSW plant configurations that are environmentally less appealing (e.g., 0.499 $(\text{€ kg DME})^{-1}$ production cost combined with 1.000 kg CO_2-eq $(\text{kg DME})^{-1}$ carbon footprint) and SS upgrading alternatives that offer climate benefits only at high production costs (e.g., −2.007 kg CO_2-eq $(\text{kg DME})^{-1}$ and 0.629 $(\text{€ kg DME})^{-1}$). Applying the developed HTSS framework provides a robust way of identifying technological and environmental hotspots, designing environmentally benign systems, and guiding the development of technologies at low TRL. The hybrid prediction enables mapping the operating space of complex biochemical plants and provides a mechanistic understanding of driving factors that affect the sustainability and performance of processes. The hybrid prediction of waste-to-DME biorefineries shows that

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carbon emission profiles can be further mitigated compared to recently reported values by using targeted waste resource selection, advancing thermochemical decomposition of waste materials and fuel gas upgrading, and involving system-level scope parameters in the optimization process. The HTSS framework provides a generic and adaptable tool to (i) accelerate the development of novel chemical technologies via the use of hybrid prediction, (ii) prospectively evaluate the techno-economic and social performance of immature processes using medium- to high-dimensional data entries, and (iii) improve the sustainability characteristics of biochemical processes to meet the needs of future generations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.3c01892.

Chemical process modeling of synthesis gas to DME conversion pathways, techno-economic, and environmental assessments of waste-to-DME process alternatives and developing and analyzing ML and statistical models (PDF)

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Notes

The authors declare no competing financial interest.

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Open repositories: File (1): waste-to-DME plant configurations, Aspen Plus simulation results, and stream compositions.xlsx (DOI: 10.11583/DTU.21946106). File (2): Input-target database on waste-to-DME conversion and ML modeling.xlsx (DOI: 10.11583/DTU.22178171).

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