Catalyst-enhanced plasma oxidation of \( n \)-butane over \( \alpha \)-MnO\(_2\) in a temperature-controlled twin surface dielectric barrier discharge reactor

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Abstract

A twin surface dielectric barrier discharge is used for the catalyst-enhanced plasma oxidation of 300 ppm \( n \)-butane in synthetic air. Plasma-only operation results in the conversion of \( n \)-butane into CO and CO\(_2\). Conversion is improved by increasing the temperature of the feed gas, but selectivity shifts to undesired CO. \( \alpha \)-MnO\(_2\) is used as a catalyst deposited on the electrodes by spray coating with a distance of 1.5 mm between the uncoated grid lines and the square catalyst patches to prevent the inhibition of plasma ignition. The catalyst strongly influences selectivity, reaching 40% conversion and 73% selectivity to CO\(_2\) at a specific energy density of 390 J·L\(^{-1}\) and 140°C, which is far below the onset temperature of thermocatalytic \( n \)-butane conversion.

KEYWORDS
catalysis, coatings, dielectric barrier discharges, manganese dioxide, volatile organic compounds

1 | INTRODUCTION

Volatile organic compounds (VOCs) in ambient air of large cities as well as in exhaust gases from industrial plants, car paint shops, or canteen kitchens are detrimental to human health and the environment.\(^{[1-5]}\) The purification of contaminated air is regulated and tightened by federal offices and the European Union.\(^{[6,7]}\) Conventional methods for the abatement of VOCs have several disadvantages. Thermal oxidation has high energy requirements (900°C–1000°C) and is only economically favorable for high VOC concentrations.\(^{[8,9]}\) Thermocatalytic oxidation is prone
to catalyst poisoning by compounds such as SO\textsubscript{x}, NO\textsubscript{x}, or CO\textsubscript{y}.\textsuperscript{[9,10]} In addition, both require a ramp-up time to reach the high operating temperatures.

Nonthermal plasmas (NTPs) offer higher energy efficiency, scalability, and flexibility for the abatement of VOCs.\textsuperscript{[11,12]} They can be operated at atmospheric pressure and ambient temperature. Furthermore, plasma reactors can easily be mounted in parallel and series for upscaling, and there is a ramp-up time of just a few seconds to achieve a steady state.

Among the different NTP concepts, dielectric barrier discharges (DBDs) are frequently chosen for the removal of VOCs.\textsuperscript{[13-17]} The uniform plasma volume, the simple design, and the low energy consumption, compared with other plasma techniques, are promising characteristics for future applications.\textsuperscript{[12,15]} The discharge is formed by applying a voltage on one electrode and grounding the other electrode of the DBD. To prevent the formation of an electric arc, the name-giving dielectric separates both electrodes.\textsuperscript{[18]} DBDs have typical gap distances in the range of one to only a few millimeters and are driven by high voltages in the low kilovolt range and pulses in the kilohertz range. The different possible configurations of DBDs can be divided into two groups: volume DBDs (VDBDs) or surface DBDs (SDBDs).\textsuperscript{[19]} VDBDs have one or more gaps between dielectrics and electrodes, leading to ignitions of plasma in the gaps. In contrast, the electrodes of a SDBD are both in contact with the dielectric and produce an ignition on the surface of the dielectric. The SDBD is more useful for the treatment of gas streams due to the simple application of a heterogeneous catalyst near the plasma ignition volume combined with the relative low pressure drop.\textsuperscript{[20]}

In this study, both electrodes and the dielectric are combined into a single plate, which in the following is referred to as twin SDBD electrode with a driven metal grid on one side and a grounded one on the opposite side. The twin SDBD was characterized by Offerhaus et al.\textsuperscript{[21]} and Kogelheide et al.\textsuperscript{[19]} with respect to the plasma parameters, power densities, and scalability. Schücke et al.\textsuperscript{[22]} performed studies on the dissipated power as a function of the applied voltage, pulse repetition frequency, and VOC mole fraction, and on the formation of byproducts from different VOCs. This study aims at determining the influence of a deposited catalyst on VOC conversion, selectivity, and carbon balance using an identical electrode configuration. \textit{n}-Butane was chosen as a model VOC, as alkanes are easy to handle and rather stable, rendering its full conversion to CO\textsubscript{2} and H\textsubscript{2}O difficult.\textsuperscript{[23-26]}

Heterogeneous catalysts are widely used in industry and academic research for thermocatalytic applications.\textsuperscript{[27]} For the oxidation of VOCs, several noble metal and transition metal oxide catalysts are well known.\textsuperscript{[28]} Among these catalysts, MnO\textsubscript{2} has distinct advantages.\textsuperscript{[10]} As an abundant transition metal oxide, it is relatively inexpensive and easily accessible, furthermore, low toxicity is beneficial. From all modifications of MnO\textsubscript{2}, α-MnO\textsubscript{2} shows the highest activity for the oxidation of alkanes.\textsuperscript{[29]} MnO\textsubscript{2} has already been applied for the oxidation of VOCs by plasma-assisted catalysis.\textsuperscript{[30]} The catalytic activity combined with the potential conversion and production of reactive oxygen species (ROS) such as ozone (O\textsubscript{3}) renders it a promising candidate for further studies.\textsuperscript{[26,30,31]}

### 2 EXPERIMENTAL SECTION

#### 2.1 Catalyst preparation and characterization

The MnO\textsubscript{2} catalyst was prepared by precipitation utilizing the comproportionation of KMnO\textsubscript{4} and Mn(NO\textsubscript{3})\textsubscript{2}, as shown by our group before.\textsuperscript{[32]} The precipitate was calcined at 460°C for 4 h in synthetic air (80% N\textsubscript{2} and 20% O\textsubscript{2}) to produce phase-pure α-MnO\textsubscript{2}. The X-ray diffraction (XRD) pattern was recorded using a Discover D8 (Bruker) diffractometer with a theta–theta geometry. The powder was investigated with Cu K\textsubscript{α} radiation (λ = 0.15406 nm, 40 kV, 40 mA) in a range of 5°–80° 2θ with an increment of 0.02°. The pattern was examined using Diffrac Eva Software with access to the International Centre for Diffraction Data (ICDD) database.

N\textsubscript{2} physisorption was measured using a BELSORP-mini instrument (BEL Japan Inc.) at 77 K. The catalyst powder was pretreated for 2 h at 250°C in vacuum to remove adsorbed water. The specific surface area was derived by the Brunauer–Emmett–Teller (BET) method and the pore volume by the Barrett–Joyner–Halenda (BJH) method.\textsuperscript{[32]}

#### 2.2 Coating

For the coating of the targets, a custom-made spray coater was used (Figure 1). In the following, the procedure for a loading of 3 mg·cm\textsuperscript{-2} is described exemplarily. A suspension of 4 mg·ml\textsuperscript{-1} α-MnO\textsubscript{2} in a 1:1 mixture of isopropanol and water was prepared and treated for 40 min in an ultrasonic bath. This suspension was pumped in 30 µl amounts into a nozzle. There, the suspension was atomized with compressed air and sprayed on the targets. The target surface was heated to 200°C to evaporate the isopropanol–water mixture immediately. After each coating step, the nozzle was moved in 2 mm steps over the length of the target. This procedure was repeated over the whole width of the target with 2 mm
wide rows. The spray steps and the movement of the robotic arm were fully computer-controlled. When the metal grid was fully covered, the ignition was strongly inhibited. Therefore, a mask made of stainless steel was used to prevent the coating of the quadratic metal grids used as electrodes. The mask covered an additional area with a width of 1.5 mm on each side of the grid lines, preventing the inhibition of plasma ignition next to the metallic grid. The distribution and the height of the coating were examined by a laser scanning microscope (LSM; VK9710; Keyence).

2.3 | Applied figures of merit

For all measurements, the degrees of conversion, the selectivities, and the carbon balance were derived. Conversion (Equation 1) is a measure of the converted amount of \( n \)-butane relative to the molar amount in the feed:

\[
X = \frac{n_{\text{butane, initial}} - n_{\text{butane}}}{n_{\text{butane, initial}}}.
\] (1)

Selectivity (Equation 2) is the ratio of the amount of a certain reaction product to the amount of converted reactant. CO and CO\(_2\) were the only measured products, and the factor of 4 is based on the stoichiometry of the reaction \( \text{C}_4\text{H}_{10} + 6.5\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O} \):

\[
S_{\text{CO/CO}_2} = \frac{n_{\text{CO/CO}_2}}{4 \times (n_{\text{butane, initial}} - n_{\text{butane}})}.
\] (2)

The carbon balance (Equation 3) compares the amount of carbon in the feed with its amount in the effluent. When the carbon balance is smaller than 100%, it is an indication of the formation of organic byproducts, which were deposited in the reactor as soot or carbonaceous deposits. Carbon balances over 100% could indicate conversion of carbon that had been deposited on the exposed surfaces beforehand. The carbon balance is derived from the amounts of \( n \)-butane, CO, and CO\(_2\):

\[
\text{carbon balance} = \frac{n_{\text{CO}} + n_{\text{CO}_2} + 4 \times n_{\text{butane}}}{4 \times n_{\text{butane, initial}}}.
\] (3)

The power dissipated in the system can be derived directly from voltage and current (Equation 4), because the phase shift between both waveforms is 90°. \(^{[21]}\) Therefore, voltage and current can be multiplied and integrated over the duration of a single pulse. The obtained energy of a single pulse is multiplied with the pulse repetition frequency (\( f_{\text{pul}} \)) to obtain the power dissipated in the system, which also includes ohmic and dielectric losses in addition to the plasma power:

\[
P = f_{\text{pul}} \int_{T_{\text{pul}}} u \times i \, dt.
\] (4)

The specific energy density (SED) is the ratio of dissipated power \( P \) and volumetric flow rate \( V \):

\[
\text{SED} = \frac{P}{V}.
\] (5)

Furthermore, the energy efficiency is derived as the mass of converted VOC per energy input:

\[
\text{EE} = \frac{\dot{m}_{\text{butane, initial}} - \dot{m}_{\text{butane}}}{P}.
\] (6)

2.4 | Thermocatalytic \( n \)-butane oxidation

Thermocatalytic \( n \)-butane and CO oxidation was performed in a flow setup with a heated plate reactor,
as described in detail by Emmerich et al.\textsuperscript{[33]} The reactor temperature was controlled in a range from 40°C to 450°C using a heating rate of 5 K·min\textsuperscript{−1}. This heating rate was sufficiently slow to achieve a quasi-steady state. The setup was equipped with four gas lines (N\textsubscript{2} 5.0; O\textsubscript{2} 4.8; 1000 ppm C\textsubscript{4}H\textsubscript{10} 2.5 in N\textsubscript{2} 5.0; 4% CO 4.7 in N\textsubscript{2} 5.0; Air Liquide). These gases were mixed to obtain a gas stream of 78.5% N\textsubscript{2}, 20.5% O\textsubscript{2}, 1% CO, and 300 ppm \( n \)-butane with a volumetric flow rate of 80 ml·min\textsuperscript{−1}, which led to the same residence time of 2.3 s as for the plasma-driven measurement series. The catalyst-coated plates were made of aluminum oxide and had dimensions of 50 × 100 × 0.635 mm. The gas composition was analyzed by an online multichannel analyzer (MCA; CO; 0%–1%; ABB) with a non-dispersive IR detector for CO and a quadrupole mass spectrometer (QMS; InProcess Instruments GAM 400) calibrated for \( n \)-butane and CO\textsubscript{2}.

2.5 (Twin) SDBD

The twin SDBD electrode configuration consisted of an Al\textsubscript{2}O\textsubscript{3} plate (190 × 88 × 0.635 mm) with Ni-coated metal grids screen-printed on either side. The grid lines had a width of 0.45 mm and a square size of 1 cm\textsuperscript{2}. On each side, 5 × 15 squares were printed. The secondary side inductance of the high-voltage transformer and the capacitance of the twin SDBD electrode configuration form a series resonant circuit, which was excited by high-voltage pulses (0–300 V) provided by the high-voltage pulse generator (G2000; Redline Technologies). The high-voltage pulses were supplied at a pulse repetition frequency of 4000 Hz and they excited the resonance circuit, forming a damped sine wave with an eigenfrequency of 86 kHz in the kilovolt range. A high-voltage probe (P6015A; Tektronix) and a current probe (bandwidth up to 300 MHz; Model 6585; Pearson Electronics) were connected to a digital oscilloscope (DPO5204B; Tektronix) to monitor the applied voltage and current. These components were also used to determine the power dissipated into the system in real time.

2.6 Plasma-driven \( n \)-butane oxidation

The plasma-driven experiments were performed in a flow setup with a custom-made reactor (Figure 2). The reactor had outer dimensions of 540 × 170 × 51 mm and was made from aluminum. The connection with the flow setup was achieved by KF flanges. The KF flange with a diameter of 25 mm expanded into a rectangular cross-section with 105 × 19 mm side length. In this rectangular area, the twin SDBD electrode was placed insulated from the grounded reactor walls using polyether ether ketone mountings. The twin SDBD electrode was centered vertically, horizontally, and laterally in the reactor. The reactor was thermally insulated and heated by a custom-tailored heating plate. In addition, the feed gas was pre-heated to 15°C above the set temperature by using a resistively heated heat exchanger. The overheating was necessary due to insulation losses. Two thermocouples were installed in the reactor 85 mm before the twin SDBD electrode (upstream) and 85 mm after the twin SDBD electrode (downstream) to monitor the bulk gas temperature. For measurements at higher temperatures, the set temperature of the heating plate was chosen as measurement temperature, neglecting the slight heating by the plasma.

The setup (Figure 3) had a gas supply with three gas lines (N\textsubscript{2} 5.0; O\textsubscript{2} 4.8; C\textsubscript{4}H\textsubscript{10} 2.5; Air Liquide). With these gases, a mixture of 79.5% N\textsubscript{2}, 20.5% O\textsubscript{2}, and 300 ppm \( n \)-butane was supplied for all plasma-driven measurements. The gas flow was always 10 L·min\textsuperscript{−1}. The gas composition was monitored by an online MCA (Emerson X-stream XEGP). The MCA had three nondispersive IR detectors for \( n \)-butane (0–500 ppm), CO (0–10,000 ppm), and CO\textsubscript{2} (0–10,000 ppm), and a paramagnetic detector for O\textsubscript{2} (0%–25%).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{(a) Scheme of the custom-made plasma reactor with windows for monitoring of the plasma and high-voltage connectors insulated by polyether ether ketone. (b) Photograph of the same plasma reactor on the heating plate with thermal insulation.}
\end{figure}
3 | RESULTS AND DISCUSSION

3.1 | Characterization of MnO₂ and the coating

The synthesis and characterization of the catalyst were described by Ollegott et al.\cite{32} for thermocatalytic CO oxidation. Only N₂ physisorption and XRD were repeated after reproducing the synthesis. N₂ physisorption measurements provided a specific surface area of the used MnO₂ of 37 m²·g⁻¹ and an average pore diameter of 20 nm. The XRD pattern shows the presence of phase-pure α-MnO₂ (Figure 4a). The results indicate a successful reproduction of the synthesis of the α-MnO₂ catalyst. In Figure 4b, LSM images of coated twin SDBD electrodes are provided. On the left side, the light microscope views are shown, and on the right side, the corresponding height profiles are shown. The images of 0.75 mg·cm⁻² MnO₂ on the twin SDBD electrode show a well-distributed island-like coating on the surface with heights up to 10.7 µm. The 3 mg·cm⁻² coating is denser and fewer gaps can be seen. Heights up to 10.4 µm were detected. A higher loading led to a denser coating instead of a larger height of the coating on the target.

3.2 | Thermocatalytic removal of n-butane over α-MnO₂

The thermocatalytic measurement was performed using a plate coated with 3 mg·cm⁻² of α-MnO₂. To test the performance of the catalyst for the oxidation of CO and n-butane, both gases were added to the feed stream simultaneously. CO was added to simulate produced CO during plasma operation. Therefore, only one resulting CO₂ mole fraction was measured. Figure 5 shows the mole fractions for the thermocatalytic measurement. For CO, there was a conversion of 5% at a temperature of 86°C, 50% at 140°C, and 95% at 175°C. Furthermore, for n-butane degrees of conversion of 5% at 180°C, 50% at 255°C, and 95% at 319°C were reached. As the CO mole fraction remained at 0 ppm above 180°C, n-butane was totally oxidized to CO₂ with no further CO being formed. The carbon balance was higher than 95%, indicating total oxidation to CO₂ above 320°C. These results demonstrate...
a high activity of the catalyst for the oxidation of CO and n-butane under thermocatalytic conditions. The higher activity for CO conversion than for n-butane conversion should be beneficial for the CO2 selectivity of the plasma-assisted catalysis due to the tendency of CO production by plasma-only VOC oxidation shown later.

### 3.3 Plasma-driven removal of n-butane

#### 3.3.1 Effect of applied voltage

The following measurement series was performed in the plasma reactor without catalyst, as shown in Figure 6. The mole fractions of n-butane, CO, and CO2 as well as the gas temperature before and after the SDBD were monitored and the applied voltage was controlled manually. As no ignition was observed below voltages of 7.5 kV, all measurements started at a voltage of 8 kV. The voltage was increased up to 11 kV in steps of 1 kV, and the pulse repetition frequency was always set to 4000 Hz. At the beginning of each step, the voltage had to be manually readjusted to achieve a stable value before waiting for the n-butane mole fraction to reach a steady state. Then, the next voltage step was performed. Due to the applied high voltage, the gas temperature increased during each measurement, depending on the starting temperature. In the measurement series shown in Figure 6, the downstream temperature after the twin SDBD electrode increased by 12°C and the upstream temperature before the twin SDBD electrode by 5°C. The increase of the downstream temperature was directly correlated with the energy input of the plasma, which can be seen by the sudden increase at each voltage step, whereas the increase in upstream temperature originated from the gradual warming of the reactor.

Setting the discharge to a specific applied voltage allows comparisons within a series of measurements with a fixed electrode configuration and gas composition, but not the comparison of different plasma setups. Therefore, SED is used in the following.

The plasma treatment without catalyst at room temperature led to a decrease of the n-butane mole fraction (Figure 7). The conversion of n-butane started with 5% at 90 J·L⁻¹ and then rose to 26% at 330 J·L⁻¹. CO₂ was the main product with increasing selectivity from 31% to 40% for higher SEDs. However, CO as an undesired second main product had an increasing selectivity of 23%–31% at higher SEDs. The differences in selectivity remained almost the same for all voltages. As both selectivities were
increasing, but still never added up to 100%, the relative amount of undetected organic byproducts had to be decreasing. Although this would suggest an increase in the carbon balance, the opposite is observed, which can be explained by the decreasing amount of unreacted \( n \)-butane at higher SEDs, thereby lowering the carbon balance.

The conversion of \( n \)-butane increased at higher SEDs, but the amount of undetected organic byproducts and of CO increased as well. Nevertheless, higher voltages were increasing the selectivity to \( \text{CO}_2 \) as the desired product, demonstrating the production of ROS such as \( \text{O}_3 \), \( \text{OH} \), or atomic O, which were able to convert a fraction of the VOC into \( \text{CO}_2 \).

### 3.3.2 Influence of the feed gas temperature

The influence of the feed gas temperature on the plasma-only abatement of \( n \)-butane was investigated in the range from 100°C to 160°C in steps at 20°C as a function of the SED. Figure 8 shows the achieved degrees of conversion. For the measurements with heating, significantly higher degrees of conversion for all SEDs were reached. At 90 J·L\(^{-1}\), a temperature increase from room temperature (RT) to 160°C improved conversion from 4% to 11%. At an SED of 330 J·L\(^{-1}\), the difference was even higher, increasing from 24% to 38%. The energy efficiency was the highest at 150 J·L\(^{-1}\) and decreased when more power was dissipated into the system. If the energy necessary to heat the gas stream is not incorporated into the calculation of the removal efficiency, the highest conversion was obtained at 160°C, significantly higher than RT. If a corrected value is used, for which the theoretical power necessary to heat the gas stream is incorporated into the SED, the energy efficiency at 160°C is comparable to the measurement at RT. Thus, it can be concluded that conversion is largely independent of the path by which energy is supplied to the system. The selectivity to CO steadily increased at higher SEDs and temperatures. In contrast, the \( \text{CO}_2 \) selectivity remained largely independent of the SED, but slightly increased with temperature. This observation suggests that the amount of undetected organic byproducts decreases with increasing SEDs. This trend can also be observed in the trend of the carbon balance. At low SEDs, the carbon balance is high due to the high amount of unreacted \( n \)-butane; however, the CO and \( \text{CO}_2 \) selectivities suggest the formation of organic byproducts. At SEDs between 210 and 330 J·L\(^{-1}\), the carbon balance is lower, because less unreacted \( n \)-butane is present, which would increase the carbon balance. Yet, there are still undetected organic byproducts produced, whose formation is lowest at the highest SEDs, thereby increasing the carbon balance again.

In summary, higher SEDs and higher temperatures led to higher degrees of conversion but also favored CO formation. The increased conversion for higher temperatures may be induced by the more rapid decomposition of produced ozone (\( \text{O}_3 \)), releasing highly reactive atomic oxygen,[34] and by changes of the discharge, as shown by Wang et al.[35] Furthermore, the last RT measurement had a slightly lower degree of conversion than the first RT measurement, pointing to an ongoing aging of the twin SDBD electrode over time under highly oxidizing conditions at higher temperatures during the induction period.

### 3.4 Catalyst-enhanced plasma removal of \( n \)-butane over \( \alpha \)-MnO\(_2\)

#### 3.4.1 Influence of the feed gas temperature in the presence of \( \alpha \)-MnO\(_2\)

To enhance the conversion of \( n \)-butane to \( \text{CO}_2 \), \( \alpha \)-MnO\(_2\) was applied on both sides of the electrode configuration by spray coating. Before this study, different coating geometries were investigated, where the one with 1.5 mm gap between metal grid and catalyst proved to be the most suitable. This gap width ensured little disturbance of the discharge by the catalyst, while the catalyst was in close proximity. The coated and uncoated electrode configurations are shown in Figure 9.

The beneficial effect on conversion by heating the reactor and the beneficial effect of the catalyst on the selectivities were combined in the following. For a clear distinction of thermocatalytic and plasma effects on the conversion of \( n \)-butane, the measurements were carried out below the thermocatalytic onset temperature for \( n \)-butane oxidation of 180°C. Figure 10 shows the results of the measurement series performed at RT, 120°C, and 140°C without catalyst and the corresponding measurements with 3 mg·cm\(^{-2}\) catalyst. Heating the reactor led to an increase in conversion independent of the presence of the catalyst (Figure 10a). At 90 J·L\(^{-1}\), the degree of conversion was increased by approximately 5%. This improvement was even higher at higher SEDs, resulting in an improvement of up to 12% in conversion at 390 J·L\(^{-1}\). The highest conversion measured was 40% for the coated electrode geometry at 140°C and 390 J·L\(^{-1}\), whereas 39% conversion were obtained with the uncoated electrode geometry.

The highest impact of the catalyst was found to be on the selectivities. Introducing the catalyst into the plasma
system led to CO selectivities that are independent of the SED. Moreover, the CO selectivities can be decreased by increasing the temperature. For the uncoated electrode geometries, an increase in CO selectivity is observed for both higher SEDs and higher temperatures. The highest difference is found for the coated electrode configuration at 390 J·L$^{-1}$ and 140°C and the uncoated electrode configuration under the same conditions: the CO selectivity can be decreased from 45% to 24% by applying the catalyst. The CO$_2$ selectivity increases as a function of temperature more strongly for the coated than for the uncoated geometries. At 390 J·L$^{-1}$, a CO$_2$ selectivity of

**FIGURE 8** Influence of the temperature on (a) $n$-butane conversion, (b) energy efficiency, (c) CO selectivity, (d) CO$_2$ selectivity, and (e) carbon balance. The energy input in (b) was corrected by assuming a heat capacity of $c_P = 1.005 \text{kJ·kg}^{-1}·\text{K}^{-1}$
oxidation of the plasma-produced CO over the α-MnO₂-coated square-shaped patches between the grid lines.

The energy efficiency for the measurement series is shown in Figure 10e. The measurements without heating show a lower efficiency compared with the ones at elevated temperatures. However, the power needed to heat the gas stream was not taken into consideration. Another observation is that the efficiency is approximately the same for the coated and uncoated electrode configurations except for the measurement at 120°C with catalyst applied. The highest efficiency is derived at 150 J·L⁻¹, which decreases with higher SEDs, because the additional energy cannot be completely utilized to drive the reaction. At 90 J·L⁻¹, a lower efficiency is observed, because the plasma discharge is not strong enough to lead to reactions.

For comparison, Gandhi et al. [25] reached a degree of butane conversion of 65%–90% in 5% O₂ with a dissipated power of 40 W–100 W and a gas flow of 1 L·min⁻¹ resulting in a SED of up to 6000 J·L⁻¹. Aubry et al. [36] report degrees of propane conversion up to 100% with a SED of 750 J·L⁻¹ in air at 300 K. Hill et al. [37] achieved a degree of propane conversion of 63% in air with a SED of 625 J·L⁻¹ leading to an energy efficiency of approx. 6 × 10⁻⁴ mg·J⁻¹. All these studies applied a VDBD or packed-bed reactor, and depending on the applied temperatures, similar degrees of conversion at comparable or lower SEDs were achieved in the present study.

In future studies, the coating geometry will be improved to find the optimal gap distance between the metal grid and the deposited catalyst. Furthermore, the applied pulse shapes will be improved to enhance the energy efficiency for optimal conversion. Optical emission spectroscopy measurements are planned to investigate the influence of catalyst and temperature on electron density and reduced electric field, similar to measurements performed by Offerhaus et al. [21] at ambient temperature, and O₃ densities and those of other ROS will be determined spectroscopically.

4 | CONCLUSION

A twin SDBD was used for the abatement of n-butane as a model VOC in synthetic air. The plasma-only treatment of the gas stream decreased the n-butane mole fraction, and the carbon balances reached about 93%–100%; however, the selectivity for undesired CO was rather high. Heating of the reactor in the range from 100°C to 160°C led to an increase in conversion and carbon balance. However, the selectivity to CO increased further at high SEDs up to 45%. The comparison of the thermocatalytic measurement using a plate coated with
3 mg·cm$^{-2}$ of $\alpha$-MnO$_2$ with the heated plasma-assisted measurements revealed catalyst-enhanced plasma activity at temperatures too low for thermocatalytic $n$-butane oxidation. The application of $\alpha$-MnO$_2$ deposition by spray coating showed that high conversion and CO$_2$ selectivity were reached for the electrodes using the mask during coating with a distance of 1.5 mm between the uncoated Ni grid lines and the square patches of 3 mg·cm$^{-2}$ of $\alpha$-MnO$_2$. Selectivity was strongly shifted to the desired product CO$_2$ in the presence of the catalyst and at higher temperatures. The application of $\alpha$-MnO$_2$ in the plasma-driven abatement of $n$-butane in synthetic air resulted in

FIGURE 10 Comparison of the measured (a) conversion, (b) carbon balance, (c) CO selectivity, (d) CO$_2$ selectivity, and (e) energy efficiency. Measurements at room temperature, 120°C, and 140°C without coating and with mask-coated catalyst as a function of the specific energy density.
the same achieved degrees of conversion, whereas the selectivities and the carbon balance were influenced in a favorable way, indicating a consecutive catalytic oxidation of plasma-produced CO.

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DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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