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PLASMA PROCESSES AND POLYMERS

SCIENTIFIC PERSPECTIVE

Plasma-based conversions with in situ product removal

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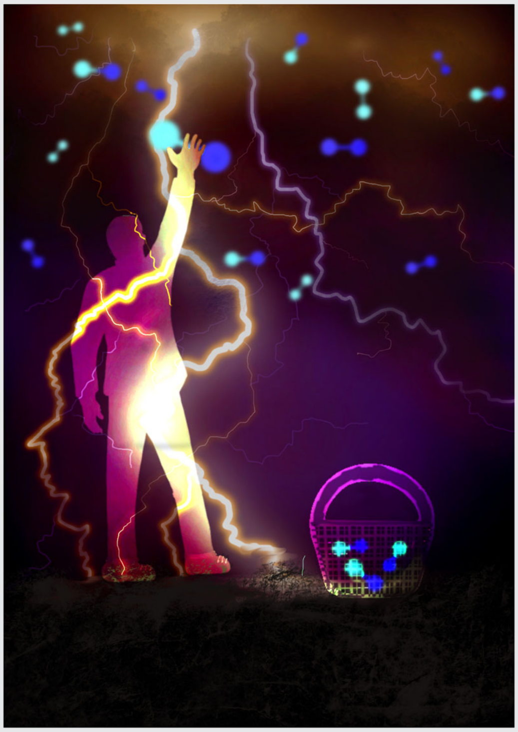
Abstract
This short review focuses on in situ product removal as a method to improve the energy efficiency and product yield of plasma-based conversions. After recapping the advantages of in situ separations in thermal-catalytic processes, different strategies for in situ product removal for plasma-based conversions are discussed. Advantages and challenges are discussed regarding four strategies, that is, absorption and adsorption using solids, use of sacrificial reactants, separation with ceramic dense membranes, and product removal in the liquid phase.



KEYWORDS
adsorption, cold plasma, product separation

1 | INTRODUCTION

Renewable electricity generation from solar and wind has drastically reduced in cost over the past decades.[1] This implies electricity-driven chemical conversions have gained traction. Plasma driven conversions are considered here, as an alternative to electrochemical conversion. A benefit of plasma-driven conversions is that plasmas can be turned on and off fast, for example, to follow fluctuations in solar and wind electricity.[2]

The addition of catalysts to plasma reactors has been shown to improve the conversion of reactants and selectivity to the desired products.[2,3] These results in higher concentrations of products, which in turn leads to an enhancement of a fundamental limitation of plasma reactors: enhancing the reverse reaction by plasma

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activation of products, thereby limiting the energy efficiency of plasma-driven conversions.

One of the strategies proposed is to use pulsed plasmas, which limits the plasma duration, thereby limiting product activation. This has shown significant improvement in the energy efficiency for plasma-driven catalytic ammonia synthesis.[4–6] One limitation of pulsed plasmas is that short plasma duration typically also results in low conversions, making separation of the desired product from the reactants difficult.

This perspective discusses an alternative method to limit plasma activation of products via in situ product removal technologies, based on existing concepts in applied heterogeneous catalysis and chemical reactor engineering. Therefore, we will first briefly summarize the state-of-the-art of integrating conversion technologies and separation technologies for thermal and thermal-catalytic processes, before discussing integration of separation with plasma-based conversion. We present examples without aiming to completely cover results in literature. The aim is to raise awareness of the potential of in situ separation.

1.1 | In situ product removal for thermal-catalytic processes

Integration of thermal-catalytic conversion with separation or mixing can be achieved in multifunctional reactors, for example, catalytic distillation[7,8] and membrane reactors.[9,10] Technologies that are applicable to plasma-driven conversions are discussed hereafter.

A motivation of in situ product removal is to shift the equilibrium of the reaction by removing at least one of the products. The usual technology, with separation downstream of the reactor, makes separation expensive at low concentrations, as well as recycling necessary. Sorption-separation processes have been proposed for CO_2 removal during the water-gas-shift reaction,[11] during reforming reactions.[12,13] Adsorption of ammonia is being studied to shift the equilibrium of ammonia synthesis, enabling operation at mild pressure.[14] Another motivation for in situ product removal is improvement of selectivity, preventing subsequent reactions. An example of this is methane conversion to methanol, suppressing CO_2 formation by adsorbing methanol on a zeolite.[15]

In practice, this type of technology can be implemented with a moving bed concept, where the catalytic sorbent is circulated between a first reactor vessel for adsorption of the targeted product, and a second vessel for desorption of the product. Desorption is achieved by either increasing temperature or decreasing pressure. Alternatively, a switching bed concept can be utilized, operating the catalytic sorbent in multiple fixed beds, operated alternating in reaction-adsorption and regeneration mode, respectively.

An alternative to adsorption of product molecules is reversible reaction of a product with a solid material. An example of this is ethane and propane dehydrogenation to ethylene and propylene, resulting in H_2 as a byproduct. Oxides such as CrO_X and FeO_X can be utilized as oxygen sources for H_2 conversion to H_2O, thereby shifting the dehydrogenation equilibrium via reduction of the oxide catalyst(s).[16,17] The reduced material is regenerated by reoxidation of the oxides, restoring lattice oxygen for the next cycle.

Catalytic membrane reactors allow for conversion of the reactant(s), while removing at least one of the desired products via permeation through the membrane. For that purpose, both porous membranes as dense membranes are being used.[18] Dense Pd membranes are used for removing H_2, in for example, ammonia cracking, permeating H_2 through the Pd membrane obtaining pure H_2,[19] for example, for a hydrogen fuel cell vehicle demonstration in Australia.[20] Other examples include solid oxide membranes for oxygen removal,[21] and proton-conducting membranes for dehydrogenation reactions operating at high temperatures.[22,23] Deibert et al.[24] recently reviewed the application of ceramic dense membranes, allowing diffusion of O^{2-} ions either via electrochemical pumping, or based on diffusion-driven by a difference in the oxygen partial pressure at both sides of the membrane. In the latter case, electron conductivity of the membrane is required.

The goal of this review is to explain that the potential of integration of conversion and separation is even more significant in the case of plasma-driven conversion in plasma-reactors and plasma-catalytic reactors. For this purpose, the results obtained so far in literature will be summarized.

2 | IN SITU PRODUCT REMOVAL FOR PLASMA-DRIVEN PROCESSES

The motivations for in situ product removal relevant for thermal processes also apply for plasma-driven processes. Removal of at least one of the products allows to shift the equilibrium. This is probably even more relevant for plasma-driven processes, as conversions beyond thermal equilibrium have been reported.[25,26] In presence of a thermally active catalyst, the reverse reaction would also be catalyzed, reducing the overall conversion and energy efficiency, and thus in situ product removal is required.

Second, plasma activates both reactants and products. Plasma-activation increases with concentration. Therefore, in situ product removal is required to suppress activation of products in the plasma zone. Examples of in situ product removal are discussed hereafter.

2.1 | Ammonia synthesis: Preventing product decomposition via in situ ammonia removal

Plasma-driven (catalytic) ammonia synthesis has been widely studied.[27–29] The main drawback is the very low energy efficiency. Pulsed plasmas and addition of catalysts resulted in improvement. Unfortunately, these improvements are too modest, which is partly due to plasma-dissociation of the produced NH_3 molecules.[6,30] Solid sorbents can remove ammonia from the plasma phase. Plasma cannot form in pores smaller than typically 1 μm[31] because of a too short free pathway for electrons to obtain sufficient energy for generating plasma, whereas pores in solid sorbents are typically even much smaller. Furthermore, the lifetime of excited species is typically too short to enable diffusion into porous particles.[32] Therefore, molecules present in the pores are not in contact with any excited plasma species and therefore the product NH_3 is protected against plasma activation. An overview of strategies for improving plasma-based ammonia synthesis is shown in Figure 1.

Peng et al.[5] demonstrated that the metal halide $MgCl_2$ can be used to absorb NH_3 during plasma-driven ammonia synthesis in a DBD (dielectric barrier discharge) reactor, forming $Mg(NH_3)_XCl_2$ ammine complexes. Ammonia can be removed via heating of the sorbent or by reducing the pressure in the absence of plasma. A drawback is the reactivity of $MgCl_2$ with N radicals in the plasma, forming MgN_2, as demonstrated by XRD.[5] This deactivates the sorbent and releases poisonous Cl_2 gas. Thus, the material stability of the sorbent in the plasma environment is a key consideration for sorbent selection.

A more chemically stable alternative was proposed by Rouwenhorst et al.,[34] using a zeolite for in situ adsorption of NH_3 during plasma-driven ammonia synthesis in a DBD reactor. After the zeolite sorbent was saturated with NH_3, the plasma was turned off, and the NH_3 was removed from the zeolite upon heating the sorbent. The zeolite is chemically stable over many cycles.[34] Wang et al.[33] reported similarly improved energy efficiency by using Ni supported on MCM-41 as a bi-functional material, acting both as catalyst and adsorbent.

Remarkably, similar observations on efficiency were reported earlier with several porous materials, including

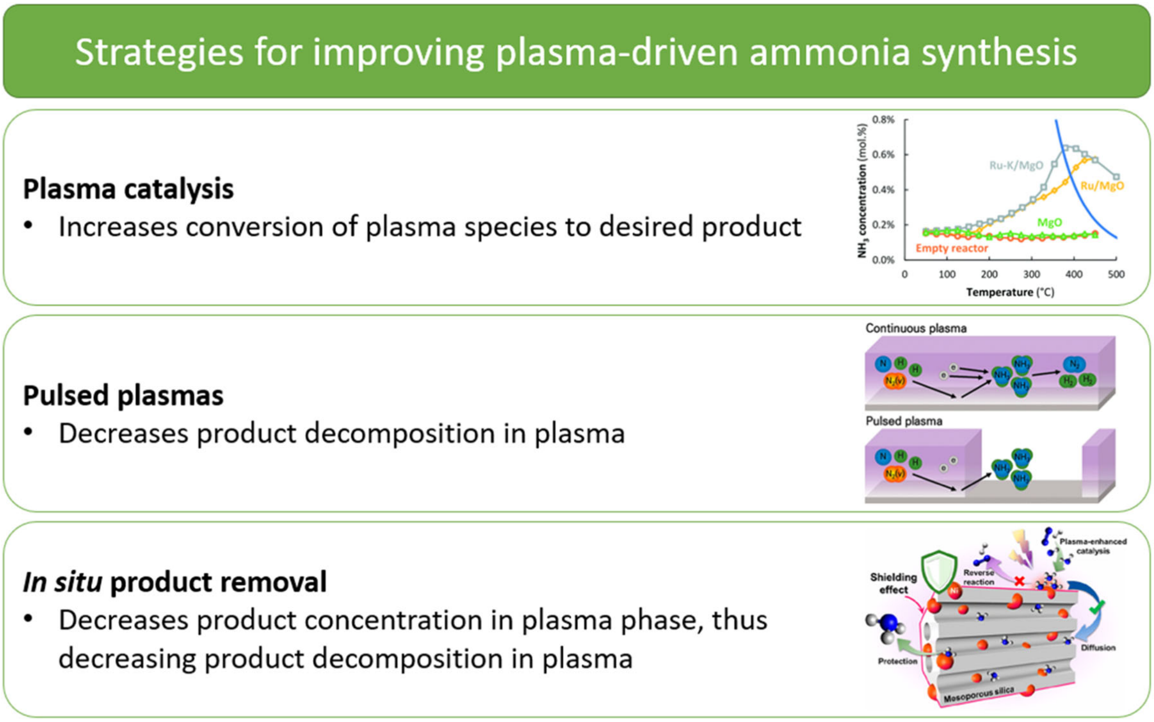


FIGURE 1 Strategies for improving plasma-driven ammonia synthesis. Plasma catalysis figure reproduced from Rouwenhorst et al.[26] Pulsed plasma figure reproduced from Kim et al.[6] In situ product removal figure reproduced from Wang et al.[33]

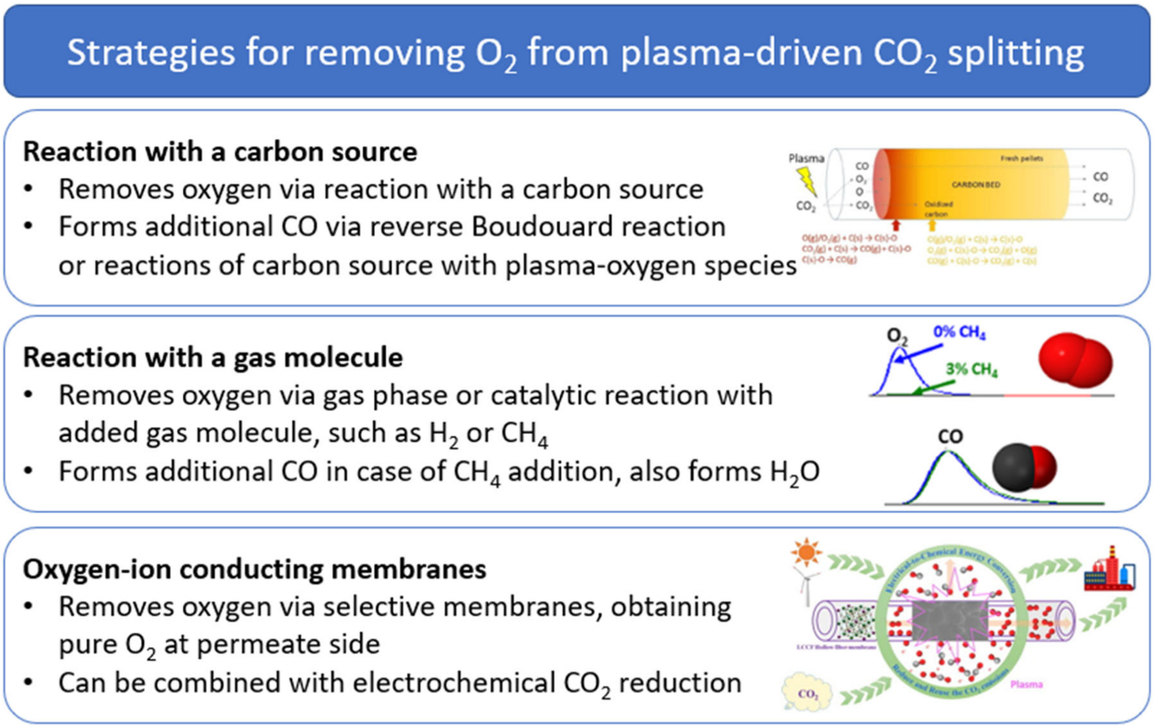
supported catalysts, for example, zeolite 5A,[35] Ru-MCM-41,[30] Ni-MOF-74,[36] Ni/MgO/SBA-15,[37] silica with different porosity,[38] and ZIFs.[39] However, the enhanced ammonia yields were interpreted in terms of differences in catalytic effects, for example, BET surface area, pore size, metal dispersion[37] or the presence of adsorbed ammonia,[36] or interpreted in terms of plasma effects induced by the presence of MOF.[36] Improved energy efficiency due to protective adsorption of ammonia combined with deliberate desorption of ammonia in the absence of plasma was not yet considered. It is not possible to judge to what extent protective ammonia adsorption has contributed, because experiments are usually done in continuous mode, instead of the cyclic operation used by Wang et al.[33] and Rouwenhorst et al.[34] In very recent work, Gorky et al.[40] demonstrated the use of a membrane of CC3, a so-called porous organic cage material, to remove ammonia from a DBD reactor, significantly improving the efficiency of ammonia formation. This was explained in terms of protective adsorption of ammonia in the pores of the CC3, in combination with diffusion of ammonia through the membrane, resulting in a mixture enriched in ammonia, outside the DBD plasma.

It should be noted that desorption of ammonia requires heat, decreasing the energy efficiency. Therefore, materials for adsorption should be developed with a relatively weak interaction with ammonia, just sufficient to drive the adsorption during plasma operation. Therefore, the adsorption should be sufficiently strong to enable adsorption at slightly increased temperatures in the DBD plasma.[34]

2.2 | CO_2 splitting: The case of O_2 removal

CO_2 can be converted to CO and O_2 via vibrational excitation, requiring 5.5 eV (530 kJ mol-CO^{-1}).[41] The presence of the O_2 byproduct also implies that the backward reaction can occur thermal-catalytically, as this is thermodynamically favorable. Plasma-activation of O_2 to excited molecular O_2 or O radicals could even enhance the reaction with the CO to form CO_2 again, reducing the overall energy efficiency of CO formation. Therefore, removal of O_2 is crucial for improving the energy efficiency of plasma-driven CO_2 splitting.[42,43]

Various strategies can be utilized to remove O_2 from the product stream (see Figure 2), along three pathways: (1) reaction with a carbon source, (2) reaction with a gas molecule, (3) using oxygen-conducting membranes.



Strategies for removing O_2 from plasma-driven CO_2 splitting

Reaction with a carbon source

- Removes oxygen via reaction with a carbon source
- Forms additional CO via reverse Boudouard reaction or reactions of carbon source with plasma-oxygen species

Reaction with a gas molecule

- Removes oxygen via gas phase or catalytic reaction with added gas molecule, such as H_2 or CH_4
- Forms additional CO in case of CH_4 addition, also forms H_2O

Oxygen-ion conducting membranes

- Removes oxygen via selective membranes, obtaining pure O_2 at permeate side
- Can be combined with electrochemical CO_2 reduction

FIGURE 2 Strategies for removing O_2 from plasma-driven CO_2 splitting. Reaction with carbon source figure reproduced from Girard-Sahun et al.[44] Reaction with a gas molecule figure reproduced from Aerts et al.[45] Oxygen-ion conducting membranes figure reproduced from Chen et al.[46]

Solid carbon can be utilized as a sacrificial material for O_2 removal, as well as for additional CO_2 conversion to CO via the reverse Boudouard reaction. Girard-Sahun et al.[44] placed in a charcoal bed after a gliding arc plasmatron (GAP) reactor to enhance CO_2 conversion and to promote O and O_2 removal, thereby increasing the CO yield. The CO_2 conversion nearly doubled, while the CO concentration increased by a factor three. Similar results have been reported by Huang et al.[47] and Li et al.[48] In these studies, carbon is positioned close to the plasma, partly in the afterglow. The reactions occurring at local high temperatures likely involve both plasma species like O radicals and molecular O_2 and CO_2. Solid carbon can be produced via methane pyrolysis,[49,50] where CH_4 is converted to H_2 and solid carbon, for example, utilizing plasma. Alternatively, biochar or charcoal can be utilized as a carbon source. The overall economics of solid carbon as a sacrificial material would depend strongly on the cost of solid carbon as a feedstock.

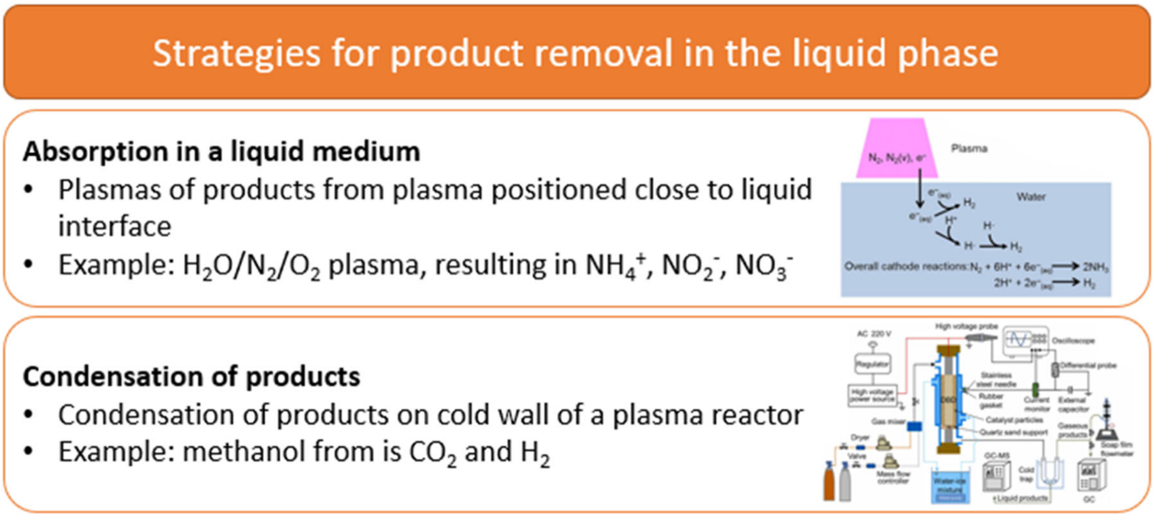
A sacrificial reactant in the gas phase can be added to convert O_2. For example, Aerts et al.[45] added small fractions of CH_4 or H_2 to the CO_2 feed stream in a DBD reactor, showing that 3%–4% addition of CH_4 or H_2 can effectively suppress O_2 concentrations. This is due to the reaction of O_2, forming H_2O in the case of H_2 addition, and forming CO_2 and H_2O in case of CH_4 addition. It should be noted that this approach is less interesting for practical purposes, because overall CO and H_2O is produced from CO_2 and H_2 or CH_4. The overall reactions are therefore the RWGS reaction, in the case of H_2, and dry reforming reaction, in the case of CH_4. As these reactions are much less endothermic than CO_2 splitting, the overall energy efficiency is much lower. Also, thermal-catalytic processes are commercially available for these processes, implying the use of plasma may be unnecessary.

Alternatively, ceramic membranes with sufficient mobility of O^{2-} ions can be used to remove O_2.[24] Chen et al.[46] demonstrated the use of solid oxide hollow fiber membranes in a microwave plasma reactor. The O_2 membrane permeation increased upon plasma illumination, which is attributed to the plasma-induced formation of CO and O_2. Unfortunately, the effect of the membrane operation of CO_2 conversion was not quantified. Pandiyan et al.[51] reported that electrolysis-based CO_2 conversion in a solid oxide electrolyzer can be integrated with a microwave plasma, where the O_2 is removed through the membrane as O^{2-}. Electrochemical CO_2 reduction reaction is only possible at applied potentials of at least 1.0 V, whereas the plasma conversion of CO_2 results in O^{2-} fluxes at lower applied voltages. A key consideration when utilizing a membrane in plasma reactors is the chemical stability of the membrane used, which is reported to be the case for the solid oxide membranes used by Chen et al.[46] and Pandiyan et al.[51]

2.3 | Product removal in the liquid phase

Products can also be removed in the liquid phase, either by (1) absorption in a liquid medium or by (2) condensation of products (see Figure 3).

Examples of product removal by absorption in a liquid medium for nitrogen fixation have been reported



Strategies for product removal in the liquid phase

Absorption in a liquid medium

- Plasmas of products from plasma positioned close to liquid interface
- Example: $H_2O/N_2/O_2$ plasma, resulting in NH_4^+, NO_2^-, NO_3^-

Condensation of products

- Condensation of products on cold wall of a plasma reactor
- Example: methanol from is CO_2 and H_2

FIGURE 3 Strategies for product removal in the liquid phase. Absorption in a liquid medium figure reproduced from Hawtof et al.[52] Condensation of products figure reproduced from Mei et al.[53]

by Gorbanev et al.[54] and Hawtof et al.[52] A plasma jet of nitrogen and steam was contacted with water, thereby producing ammonia and nitrogen oxides, which were subsequently absorbed in the liquid. Absorption in water resulted in the formation of NH_4^+, NO_2^-, and NO_3^- ions, which are stabilized due to solvation with water and consequently less reactive than NH_3 and NO_x molecular species in the plasma. Also, plasma cannot penetrate liquid water, protecting products from plasma activation. The resulting plasma-activated water (PAW) can be utilized for fertilization in, for example, greenhouses.

Wang et al.[55] fed CO_2 and H_2 in a DBD reactor, producing oxygenates upon plasma illumination. Cooling the reactor wall with a water jacket resulted in condensation of methanol and ethanol, thereby limiting product decomposition. The methanol yield was as high as 7.1% while no methanol and ethanol was detected in the absence of reactor cooling.

3 | OUTLOOK

Plasma-based conversions are widely studied to convert highly stable molecules such as CO_2, N_2, CH_4 to useful chemicals and fuels. The addition of a selective catalyst, as well as pulsed plasmas have been identified as methods to improve the energy efficiency of plasma-based conversions. However, energy efficiency remains an issue, primarily due to the presence of products in the gas phase, resulting in plasma enhanced reversed reaction. This is even more compromising energy efficiency when conversion is beyond thermodynamic equilibrium based on reactants and products in ground state, as reversed reactions are highly favorable even without plasma activation of product molecules. An obvious solution would be to operate at low conversion, which would not be very practical because of costs of separation and recycling of unconverted reactants.

In this short review, we have identified how in situ product removal is an effective method to improve plasma-based conversions. First, in situ product removal prevents the reversed reaction, thereby improving the overall energy efficiency. Second, in situ product removal results in a concentrated product stream, simplifying further processing or purification. Thus, in situ product removal is likely key to process design for plasma-based conversions.

Further research is clearly needed to identify the most favorable options for specific cases. All methods discussed can improve energy efficiency of the plasma conversion, at the price of a more complex reactor as well as increased operation costs including energy consumption. For example, desorption of products from adsorbents as well as from a membrane requires energy. It is not clear upfront whether in situ adsorption or membrane separation is preferred. For example, O_2 can be removed via dense membranes as discussed, but also removal via oxidation of a multivalent metal-oxide via a redox cycle could be an option. Furthermore, the choice of which product to adsorb leads to unanswered questions. In the case of CO_2 dissociation, one could aim at the removal of O_2 as discussed, but also removal of CO might be an option. Therefore, research to answer these questions might bring plasma driven conversion closer to practical applications.

DATA AVAILABILITY STATEMENT

Only data are available in open literature.

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REFERENCES

[1] IRENA, *Renewable Power Generation Costs in 2020*, **2021**.
[2] A. Bogaerts, E. C. Neyts, *ACS Energy Lett.* **2018**, *3*(4), 1013. https://doi.org/10.1021/acsenergylett.8b00184
[3] E. C. Neyts, K. K. Ostrikov, M. K. Sunkara, A. Bogaerts, *Chem. Rev.* **2015**, *115*(24), 13408. https://doi.org/10.1021/acs.chemrev.5b00362
[4] H.-H. Kim, Y. Teramoto, A. Ogata, H. Takagi, T. Nanba, *Plasma. Process. Polym.* **2017**, *14*(6), 1. https://doi.org/10.1002/ppap.201600157
[5] P. Peng, P. Chen, M. Addy, Y. Cheng, E. Anderson, N. Zhou, C. Schiappacasse, Y. Zhang, D. Chen, R. Hatzenbeller, Y. Liu, R. Ruan, *ACS Sustain. Chem. Eng.* **2019**, *7*, 100. https://doi.org/10.1021/acssuschemeng.8b03887
[6] M. Kim, S. Biswas, G. Nava, B. M. Wong, L. Mangolini, *ACS Sustain. Chem. Eng.* **2022**, *10*, 15135. https://doi.org/10.1021/acssuschemeng.2c04593
[7] G. J. Harmsen, *Chem. Eng. Process. Process Intens.* **2007**, *46*, 774. https://doi.org/10.1016/j.cep.2007.06.005
[8] A. A. Kiss, M. Jobson, *Chem. Eng. Trans.* **2018**, *69*, 553. https://doi.org/10.3303/CET1869093
[9] J. Shu, B. P. A. Grandjean, A. V. Neste, S. Kaliaguine, *Can. J. Chem. Eng.* **1991**, *69*(5), 1036. https://doi.org/10.1002/cjce.5450690503
[10] F. Gallucci, E. Fernandez, P. Corengia, M. van Sint Annaland, *Chem. Eng. Sci.* **2013**, *92*, 40. https://doi.org/10.1016/j.ces.2013.01.008
[11] E. R. Van Selow, P. D. Cobden, P. A. Verbraeken, J. R. Hufton, R. W. Van Den Brink, *Ind. Eng. Chem. Res.* **2009**, *48*(9), 4184. https://doi.org/10.1021/ie801713a
[12] M. Shokrollahi Yancheshmeh, H. R. Radfarnia, M. C. Iliuta, *Chem. Eng. J.* **2016**, *283*, 420. https://doi.org/10.1016/j.cej.2015.06.060
[13] B. Dou, C. Wang, Y. Song, H. Chen, B. Jiang, M. Yang, Y. Xu, *Renew. Sustain. Energy Rev.* **2016**, *53*, 536. https://doi.org/10.1016/j.rser.2015.08.068
[14] M. J. Kale, D. K. Ojha, S. Biswas, J. I. Militti, A. V. McCormick, J. H. Schott, P. J. Dauenhauer,

E. L. Cussler, *ACS Appl. Energy Mater.* **2020**, *3*, 2576. https://doi.org/10.1021/acsaem.9b02278

[15] M. A. Newton, A. J. Knorpp, V. L. Sushkevich, D. Palagin, J. A. Van Bokhoven, *Chem. Soc. Rev.* **2020**, *49*(5), 1449. https://doi.org/10.1039/c7cs00709d

[16] R. C. Schucker, G. Dimitrakopoulos, K. Derrickson, K. K. Kopeć, F. Alahmadi, J. R. Johnson, L. Shao, A. F. Ghoniem, *Ind. Eng. Chem. Res.* **2019**, *58*(19), 7989. https://doi.org/10.1021/acs.iecr.9b00974

[17] Z. Nawaz, *Rev. Chem. Eng.* **2015**, *31*(5), 413. https://doi.org/10.1515/revce-2015-0012

[18] C. Algieri, G. Coppola, D. Mukherjee, M. I. Shammas, V. Calabro, S. Curcio, S. Chakraborty, *Catalysts* **2021**, *11*(6), 691. https://doi.org/10.3390/catal11060691

[19] J. L. Cerrillo, N. Morlanés, S. R. Kulkarni, N. Realpe, A. Ramírez, S. P. Katikaneni, S. N. Paglieri, K. Lee, A. Harale, B. Solami, A. Jamal, S. Mani Sarathy, P. Castaño, J. Gascon, *Chem. Eng. J.* **2022**, *431*, 134310. https://doi.org/10.1016/j.cej.2021.134310

[20] S. H. Crolius, *Ammonia Energy* **2021**. https://www.ammoniaenergy.org/articles/csiro-demonstrates-ammonia-to-hydrogen-fueling-system/

[21] A. B. Stambouli, E. Traversa, *Renew. Sustain. Energy Rev.* **2002**, *6*(5), 433. https://doi.org/10.1016/S1364-0321(02)00014-X

[22] S. Hossain, A. M. Abdalla, S. N. B. Jamain, J. H. Zaini, A. K. Azad, *Renew. Sustain. Energy Rev.* **2017**, *79*, 750. https://doi.org/10.1016/j.rser.2017.05.147

[23] Y. Feng, J. Luo, K. T. Chuang, *J. Phys. Chem. C* **2008**, *112*(26), 9943. https://doi.org/10.1021/jp710141c

[24] W. Deibert, M. E. Ivanova, S. Baumann, O. Guillon, W. A. Meulenberg, *J. Membr. Sci.* **2017**, *543*, 79. https://doi.org/10.1016/j.memsci.2017.08.016

[25] P. Mehta, P. M. Barboun, Y. Engelmann, D. B. Go, A. Bogaerts, W. F. Schneider, J. C. Hicks, *ACS Catal.* **2020**, *10*(12), 6726. https://doi.org/10.1021/acscatal.0c00684

[26] K. H. R. Rouwenhorst, H. G. B. Burbach, D. W. Vogel, J. Núñez Paulí, B. Geerdink, L. Lefferts, *Catal. Sci. Technol.* **2021**, *11*(9), 2834. https://doi.org/10.1039/D0CY02189J

[27] K. H. R. Rouwenhorst, Y. Engelmann, K. van 't Veer, R. S. Postma, A. Bogaerts, L. Lefferts, *Green Chem.* **2020**, *22*(19), 6258. https://doi.org/10.1039/D0GC02058C

[28] P. Mehta, P. Barboun, D. B. Go, J. C. Hicks, W. F. Schneider, *ACS Energy Lett.* **2019**, *4*(5), 1115. https://doi.org/10.1021/acsenergylett.9b00263

[29] M. L. Carreon, *J. Phys. D Appl. Phys.* **2019**, *52*(48), 483001. https://doi.org/10.1088/1361-6463/ab3b2c

[30] P. Peng, Y. Cheng, R. Hatzenbeller, M. Addy, N. Zhou, C. Schiappacasse, D. Chen, Y. Zhang, E. Anderson, Y. Liu, P. Chen, R. Ruan, *Int. J. Hydrogen Energy* **2017**, *42*(30), 19056. https://doi.org/10.1016/j.ijhydene.2017.06.118

[31] A. Bogaerts, X. Tu, J. C. Whitehead, G. Centi, L. Lefferts, O. Guaitella, F. Azzolina-Jury, H. H. Kim, A. B. Murphy, W. F. Schneider, T. Nozaki, J. C. Hicks, A. Rousseau, F. Thevenet, A. Khacef, M. Carreon, *J. Phys. D Appl. Phys.* **2020**, *53*, 443001. https://doi.org/10.1088/1361-6463/ab9048

[32] H.-H. Kim, Y. Teramoto, N. Negishi, A. Ogata, *Catal. Today* **2015**, *256*(1), 13. https://doi.org/10.1016/j.cattod.2015.04.009

[33] Y. Wang, W. Yang, S. Xu, S. Zhao, G. Chen, A. Weidenkaff, C. Hardacre, X. Fan, J. Huang, X. Tu, *J. Am. Chem. Soc.* **2022**, *144*(27), 12020. https://doi.org/10.1021/jacs.2c01950

[34] K. H. R. Rouwenhorst, S. Mani, L. Lefferts, *ACS Sustain. Chem. Eng.* **2022**, *10*(6), 1994. https://doi.org/10.1021/acssuschemeng.1c08467

[35] J. R. Shah, F. Gorky, J. Lucero, M. A. Carreon, M. L. Carreon, *Ind. Eng. Chem. Res.* **2020**, *10*(1021/ac), 5167. https://doi.org/10.1021/acs.iecr.9b05220

[36] J. Shah, T. Wu, J. Lucero, M. A. Carreon, M. L. Carreon, *ACS Sustain. Chem. Eng.* **2019**, *7*(1), 377. https://doi.org/10.1021/acssuschemeng.8b03705

[37] S. Li, Y. Shao, H. Chen, X. Fan, *Ind. Eng. Chem. Res.* **2022**, *61*(9), 3292. https://doi.org/10.1021/acs.iecr.1c04968

[38] F. Gorky, S. R. Guthrie, C. S. Smoljan, J. M. Crawford, M. A. Carreon, M. L. Carreon, *J. Phys. D Appl. Phys.* **2021**, *54*(26), 264003. https://doi.org/10.1088/1361-6463/abefbc

[39] F. Gorky, J. M. Lucero, J. M. Crawford, B. Blake, M. A. Carreon, M. L. Carreon, *ACS Appl. Mater. Interfaces* **2021**, *13*(18), 21338. https://doi.org/10.1021/acsami.1c03115

[40] F. Gorky, H. M. Nguyen, J. M. Lucero, S. Guthrie, J. M. Crawford, M. A. Carreon, M. L. Carreon, *Chem. Eng. J. Adv.* **2022**, *11*, 100340. https://doi.org/10.1016/j.ceja.2022.100340

[41] R. Snoeckx, A. Bogaerts, *Chem. Soc. Rev.* **2017**, *46*, 5805. https://doi.org/10.1039/C6CS00066E

[42] R. Vertongen, G. Trenchev, R. Van Loenhout, A. Bogaerts, *J. CO2 Util.* **2022**, *66*, 102252. https://doi.org/10.1016/j.jcou.2022.102252

[43] K. H. R. Rouwenhorst, van G. J. Rooij, L. Lefferts, *Engineering Solutions for CO_2 Conversion: A Global Challenge*, Wiley-VCH Verlag GmbH, Weinheim **2022**, p. 429.

[44] F. Girard-Sahun, O. Biondo, G. Trenchev, G. van Rooij, A. Bogaerts, *Chem. Eng. J.* **2022**, *442*(2), 136268. https://doi.org/10.1016/j.cej.2022.136268

[45] R. Aerts, R. Snoeckx, A. Bogaerts, *Plasma Process. Polym.* **2014**, *11*(10), 985. https://doi.org/10.1002/ppap.201400091

[46] G. Chen, F. Buck, I. Kistner, M. Widenmeyer, T. Schiestel, A. Schulz, M. Walker, A. Weidenkaff, *Chem. Eng. J.* **2020**, *392*, 123699. https://doi.org/10.1016/j.cej.2019.123699

[47] J. Huang, H. Zhang, Q. Tan, L. Li, R. Xu, Z. Xu, X. Li, *J. CO_2 Util.* **2021**, *45*(2020), 101429. https://doi.org/10.1016/j.jcou.2020.101429

[48] Z. Li, T. Yang, S. Yuan, Y. Yin, E. J. Devid, Q. Huang, D. Auerbach, A. W. Kleyn, *J. Energy Chem.* **2020**, *45*, 128. https://doi.org/10.1016/j.jechem.2019.10.007

[49] S. Schneider, S. Bajohr, F. Graf, T. Kolb, *ChemBioEng Rev.* **2020**, *7*(5), 150. https://doi.org/10.1002/cben.202000014

[50] N. Sánchez-Bastardo, R. Schlögl, H. Ruland, *Ind. Eng. Chem. Res.* **2021**, *60*(32), 11855. https://doi.org/10.1021/acs.iecr.1c01679

[51] A. Pandiyan, V. Kyriakou, D. Neagu, S. Welzel, A. Goede, M. van de Sanden, M. N. Tsampas, *J. CO2 Util.* **2022**, *57*(2021), 101904. https://doi.org/10.1016/j.jcou.2022.101904

[52] R. Hawtof, S. Ghosh, E. Guarr, C. Xu, R. M. Sankaran, J. N. Renner, *Asian J. Chem.* **2019**, *31*(2), 1. https://doi.org/10.1126/sciadv.aat5778

[53] D. Mei, M. Sun, S. Liu, P. Zhang, Z. Fang, X. Tu, *J. CO2 Util.* **2023**, *67*(2022), 102307. https://doi.org/10.1016/j.jcou.2022.102307

[54] Y. Gorbanev, E. Vervloessem, A. Nikiforov, A. Bogaerts, *ACS Sustain. Chem. Eng.* **2020**, *8*(7), 2996. https://doi.org/10.1021/acssuschemeng.9b07849

[55] L. Wang, Y. Yi, H. Guo, X. Tu, *ACS Catal.* **2018**, *8*(1), 90. https://doi.org/10.1021/acscatal.7b02733

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