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Title: Organic Reactions in Plasma-Liquid Systems for Environmental Applications

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Abstract

Plasma-liquid systems are best recognised in biomedicine, where the generation of plasma-treated water and complex organic-containing solutions affords biological effects. However, plasma interactions with liquids are more diverse. In this review, we look from the chemical point of view at the three fields of plasma-liquid interaction in which plasma is used to convert organic substrates.

In wastewater treatment, plasma decomposes organic substances: the selectivity towards specific products is less crucial than process energy costs. In the conversion of organic liquids for sustainable energy purposes, the carbon and hydrogen selectivity to syngas are important, but these are still destructive reactions yielding small molecules. Finally, we provide a comprehensive plasma application list for synthetic organic chemistry, and discuss their mechanisms and limitations.

Keywords: non-thermal plasma; organic chemistry; plasma-liquid systems; synthetic chemistry; selectivity

Abbreviations: **AOP**, advanced oxidation process; **DBD**, dielectric barrier discharge; **GA**, gliding arc; **MW**, microwave; **PFAS**, perfluoroalkyl and polyfluoroalkyl substances; **PFOS**, perfluorooctanesulfonic acid and derivatives; **ROS**, reactive oxygen species; **RONS**, reactive oxygen and nitrogen species; **RNS**, reactive nitrogen species; **μP**, micropollutant.

1. Introduction: Plasma-liquid systems

Advances in the field of electrical discharges and the associated extensive research of atmospheric pressure low-temperature plasma systems led to shifting the paradigm of plasma usage and technology. The restricted applications of plasma in conditions compatible with low-pressure and/or high-temperature expanded towards more benign processes.¹ Many of the modern-day applications of plasma-liquid systems at atmospheric pressure² span from biomedical (e.g., plasma treatment of aqueous media to induce specific biological effects³) and nitrogen fixation⁴ to polymer synthesis/modification^{5, 6} and preparation of nanomaterials,⁷ with numerous reviews – both field-specific⁸ and generalised.⁹

Plasma-liquid systems can be distinguished by several parameters, e.g., the type of used plasma, the type of plasma-liquid contact, etc. Two plasma categories commonly used are warm plasmas (slightly non-equilibrium, the electron temperature is much higher than the gas temperature, which is still in the order of 1000 °C) and cold plasmas (highly non-equilibrium, gas temperature in the range of 10-100 °C).^{1, 2} Examples of warm plasmas include microwave (MW) plasma, (rotating) gliding arcs (GA) and spark discharges, while dielectric barrier discharges (DBD) are the most common example of cold plasmas. In turn, the contact with the liquid can be realised via (i) direct contact with the gaseous plasma (plasma positioned above the liquid, impinging on it); (ii) bubbling gaseous plasma through the liquid; (iii) igniting plasma inside the liquid, with the initial evaporation of the liquid near the electrodes and subsequent plasma initiation inside the saturated vapour phase. Some of these concepts are illustrated in Figure 1.

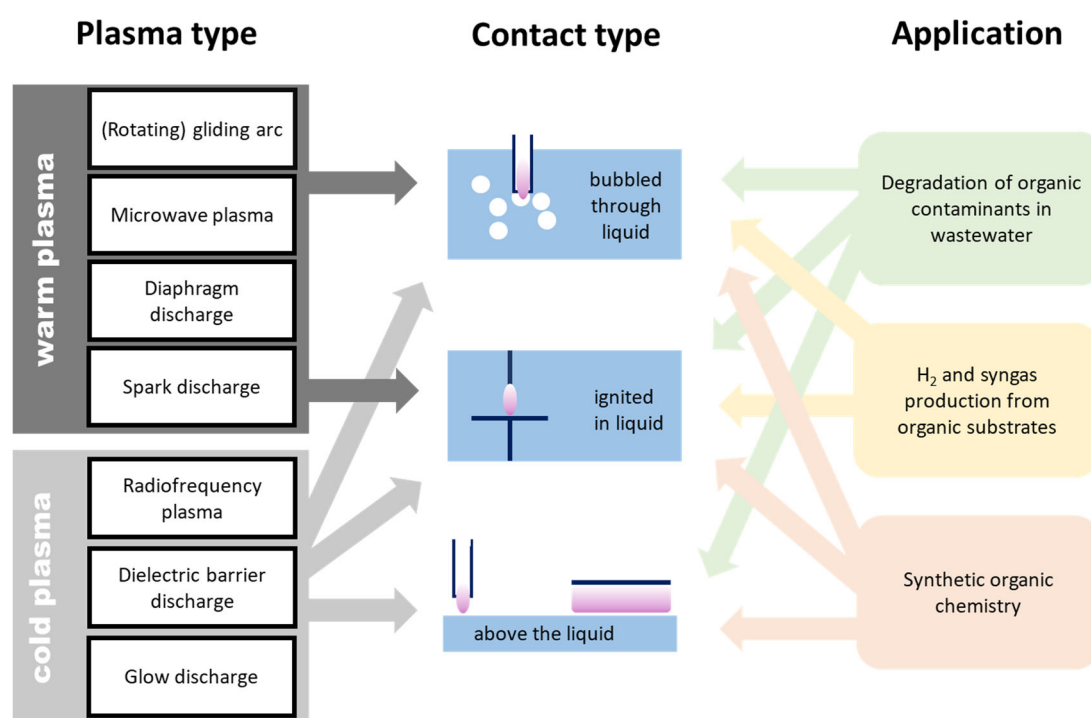


Figure 1. Plasma-liquid interactions for the conversion of organic chemicals discussed in this work: plasma types, types of plasma-liquid contact and applications.

Plasma treatment of wastewater is an environmentally benign way to remove organic contaminants and various “forever” chemicals from water.¹⁰ The interest in the use of plasma for water treatment started growing in the early 1970s, beginning with the generation of H₂O₂ and other active species by glow discharges above liquids.¹¹ The primary interest in the use of plasma in contact with liquids is defined by the possibility of generating a large variety of highly reactive species, including radicals, solvated electrons, and atoms which can oxidise almost any organic contaminant.^{12, 13} The main limiting factor of the water treatment process is the transfer of reactive species generated in the gas phase by non-thermal plasmas towards the liquid phase.^{14, 15} The unique chemical and physical processes taking place at the boundary between plasma and liquid, often referred to as a plasma/liquid interface,¹⁵ can be implemented to effectively decompose dyes,¹⁶ micropollutants,¹⁷ and other chemicals.¹⁸

Similarly, the conversion of bio-derived liquids and organic chemicals (e.g. bio-alcohols and oils) into syngas¹⁹ or H₂²⁰ is an attractive route for the transformation of renewable and waste organic feedstock into H₂ and building blocks. Plasma was introduced into the field as an extension of the Huels process,²¹ but soon expanded to the reforming of gasoline and diesel,²² waste oils,²³ glycerol,²⁴ methanol,²⁵ and ethanol.²² Generally promising results in syngas production using compact reactors, largely without the use of catalysts, make such processes a good fit for coupling with renewable resources and energy.

Atmospheric pressure plasmas are also a very interesting tool for synthetic organic chemistry. Historically, most plasma research was in the gas phase, hence the first applications involved gas-phase reactions. These ranged from the degradation of volatile organics to cyanation of unsaturated hydrocarbons to yield e.g. acrylonitrile (an important commercial precursor for polymers), as summarised in reviews from the 1980s.^{26, 27} Later studies report transformations of benzene, including hydroxylation,^{28, 29} dimerisation,³⁰ reduction,³¹ amination,³² and even substitution of one of the C atoms for N.³³ Despite the promising prospects of using the reactive pathways offered by plasma in the transformation of organic chemicals, the applications were restricted to volatile compounds. In contrast, the interaction with liquids extends the applicability of plasma reactive systems far beyond gaseous compounds.

With this review, we aim to demonstrate the three conceptually similar, yet different ways of plasma application for the conversion of organic molecules, as shown in Figure 1. First, we discuss wastewater treatment by plasma, including the fundamental concepts of plasma-liquid interaction, such as the source of reactive species induced by plasma. Second, we show examples of organics conversion into syngas or H₂. Because of the multiple existing review works in this field, both for wastewater treatment^{10, 34-39} and syngas production,⁴⁰⁻⁴³ we do not intend to give a complete and detailed list of various reactor types and specific organics removal from water by plasma, or all possible liquid substrates converted into CO/H₂. Instead, we demonstrate the concept of non-selective plasma conversion of organics using selected examples.

In contrast, despite active investigation of using plasma as an environmentally friendly agent for organic chemical synthesis, to the best of our knowledge, there are no literature reviews on this topic to date. We aim to give a near-exhaustive list of plasma uses for synthetic organic purposes in liquids. We believe that this is an important application of the reactive chemistry of plasmas, which opens routes for performing organic reactions in a more benign way than used traditionally.

2. Plasma-liquid interaction for wastewater treatment

Due to the very large difference in the energy of electrons and heavy particles achieved in non-thermal plasmas, very unique chemistry can take place in such conditions at relatively low gas temperatures.⁴⁴ Because of the efficient activation of various reactions, such systems are often viewed as chemical reactors where selectivity and performance can be tuned to specific demands by changing the operational parameters.

One of the first applications of non-thermal plasma at atmospheric pressure as a chemically active medium was the generation of O₃ in the gas phase for disinfection, almost one and a half century ago.⁴⁵ In the early 1980s and 90s, the first attempts were made to couple high-pressure electrical discharges with liquids, primarily pulsed streamer discharges, for wastewater treatment.^{46, 47} It was found that various oxidative species, including H₂O₂, ·OH

radicals, singlet oxygen $^1\text{O}_2$ and others, can be effectively generated in the gas phase and transferred to a liquid.

Non-thermal plasmas, colloquially called “cold plasmas” because of the near-ambient gas temperature, can be a very attractive alternative to other methods of water treatment due to their properties such as: (i) facile generation of various reactive oxygen (ROS) and nitrogen species (RNS); (ii) no additional chemicals are required to initiate the degradation of pollutants; (iii) the plasma-initiated processes are characterised by a low affinity for a specific substrate and hence can be applied to remove almost any pollutants from water. Despite the green nature of the plasma-assisted water treatment, the main drawback yet to be solved is the high energy cost of pollutant decomposition, which is typically 3-10 times higher compared to the state-of-the-art advanced oxidation processes (AOPs).

2.1. Reactive species generation and phase transfer

Plasma treatment induces multiple types of reactive oxygen and nitrogen species (RONS) in liquid water, the nature of which depends on the specific design of the plasma-liquid system. In-water (i.e., plasma in liquids) systems mainly generate $\cdot\text{OH}$ and $\cdot\text{OOH}/\text{O}_2\cdot^-$ radicals, H atoms, and H_2O_2 .⁴⁸ Over-water (e.g., plasma jets impinging onto the surface of liquids) systems add to this list the RONS produced by the interaction of the discharge with the gas located between the plasma source and the treated liquid. In ambient air, these are RNS, such as $\cdot\text{NO}$ and $\cdot\text{NO}_2$ radicals, HNO_2 , HNO_3 , HO_2NO , O_3 , O atoms, $^1\text{O}_2$,^{2, 49} whereas in inert gases, any additional RONS may be created only from the evaporated H_2O ,⁵⁰ thus chemically making such system similar to in-liquid plasmas.

Moreover, besides the aforementioned RONS, plasma can be seen as an electron bombardment source aimed at the plasma-liquid interface.^{51, 52} Although the depth of the electron penetration into the bulk liquid water exposed to plasma is reported to be between 2 and 15 nm,^{51, 53} this can be enough to ensure the reactivity if the mass transfer in the solution is sufficiently high. Likewise, the UV irradiation of many plasma sources can be responsible e.g. for homolytic splitting of H_2O molecules, although the typical UV flux generated by non-thermal plasmas operating in air is relatively low.⁵⁴ It can be significantly enhanced by the pulsed mode of operation of the discharge above or inside the liquid and is an important factor in water bio-decontamination.⁵⁵

However, despite the extensive research in the field of pollutant removal from water by plasma, the source of the reactive species which are responsible for the in-liquid chemistry is still perplexing. In the case of plasma jets interacting with liquid water, the contradictory findings by various research groups indicate that some of them may or may not originate from the direct interaction of plasma with the molecules of liquid water. While the gas phase plasma is unambiguously a direct source of solvated electrons, the origin of e.g. $\cdot\text{OH}$ radicals was proposed to be either through the direct interaction of gaseous plasma with molecules of liquid H_2O ,⁵⁶ or through interaction with the evaporated liquid only.^{50, 57, 58} In a similar manner, the formation of NH_x and NO_x species in nitrogen fixation by N_2 plasma over liquid water was shown to occur (i) in the gas phase from the evaporated water,⁵⁹⁻⁶¹ and (ii) through direct interaction of plasma species with the top layer molecules of liquid H_2O .^{62, 63} Furthermore, the O atoms detected in liquids are usually considered to originate from the oxygen content in the gas phase plasma,^{64, 65} and yet computational studies also suggested that it can originate from $\cdot\text{OH}$, which was initially formed from H_2O exposed to plasma.⁶⁶

Clearly, the origin of RONS is not constant but rather depends on the specific system, such as the properties of the gaseous discharge, the geometry of the plasma-liquid interaction, etc.

Correspondingly, the primary direction of research in the field of plasma-assisted water treatment is to optimize the generation of active species and their transport to the liquid, where they can be utilized for pollutant removal. In order to enhance the energy efficiency of the treatment and enable efficient scaling up of the process, the enlargement of the plasma/liquid interface was identified as a primary point of concern. At the current stage, research studies are mainly dedicated to reactor optimisation and improvement of energy costs of the treatment because of the industrial demands for the uptake.

2.2. Plasma removal of pollutants from water

Wastewater treatment is the most studied and developed application of plasma-liquid systems of the three applications discussed in this review paper, with the largest number of dedicated reviews. Below, we discuss the two pathways of organic reactions – oxidation and reduction – caused by different plasma-generated RONS and applicable to different pollutants.

Oxidation pathway

Plasma treatment of water is often considered as a new type of AOP in which various oxidative species are generated by an electrical discharge above or in contact with the liquid. The decomposition of chemical pollutants, both conceptually and with regard to the process efficiency, was tested on numerous compounds.^{10, 34, 35, 37} Commonly, a chemical of high reactivity and a rather simple chemical structure is employed as a reference pollutant. Among different compounds, phenol was treated as a reference for understanding various AOPs because the intermediate products of its oxidation are well known. The oxidation is initiated primarily by $\cdot\text{OH}$ attacks, resulting in the formation of various intermediates, including hydroquinone and catechol.⁶⁷ The intermediate products are easily oxidised further under the action of the ROS: radicals and atomic O. The opening of the aromatic ring leads to the formation of low molecular weight compounds, mainly organic acids. Dissolved O_3 , also typically present in plasma-treated water,^{2, 36} yields muconic acid as another stable intermediate.⁶⁸ Importantly, the exact composition of the mixture of various oxidation products is strongly dependent on the type of electrical discharge and concentration of RONS generated and/or transferred to the liquid medium. With the aim of wastewater treatment, the formed by-products should preferably be completely decomposed and mineralised. In general, plasma AOP results in low selectivity toward specific oxidation products. In this context, additional effort is required in analysing the oxidation pathways as some intermediates can possess high toxicity. Despite numerous studies, complete mineralisation towards CO_2 and H_2O was rarely achieved in plasma processing of wastewater, or required high energy inputs.^{36, 39}

Many configurations of plasma-liquid reactors were studied to enhance the extent of mineralisation, including reactors with falling water film,⁶⁹ droplets and aerosols,^{70, 71} with underwater plasma in bubbles⁷², and many others, as discussed in recent reviews.^{6, 36, 38} In all these cases, cold plasmas generate a large set of oxidative species providing a non-selective oxidation chemistry, which can be applied to remove many pollutants, including the ones difficult to decompose by other means. One such important example is the class of micropollutants (μPs) comprising various types of highly toxic organic compounds, pharmaceuticals and personal care products, pesticides, and industrial compounds. Most of

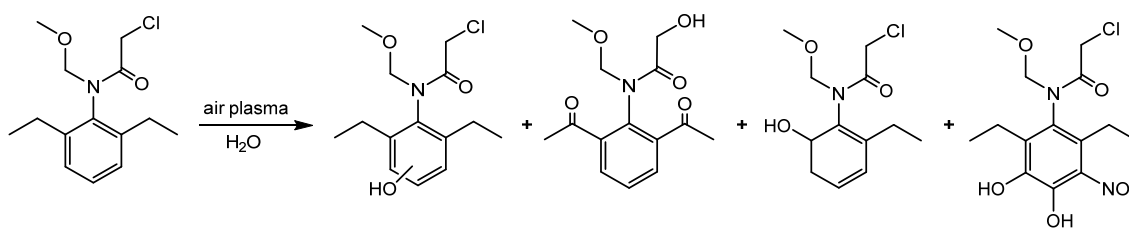
them are very stable in aqueous media with a lifetime exceeding six months. Unfortunately, it has been shown that municipal wastewater treatment plants, which are responsible for the treatment of domestic wastewater, act as the major source for the distribution of μPs in the aquatic environment. In plasma conditions, destruction of μPs can take place with reasonable energy costs varying in the range of 2-20 kWh/m³, depending on operational conditions, type of plasma reactor, and stability of the pollutant.^{73, 74}

To get insight not only into the pathways of oxidation but also into the energy costs of the treatment, various dyes are typically used due to the simplicity of detection (optical methods, without detailed pathway analysis) and their importance for textile chemistry. It has to be noted that the change of the dye concentration observed in treatment is often incorrectly referred to as decomposition, although only decolourisation (due to the partial decomposition of the chromophore group of the dye) is measured experimentally.⁷⁵

The key species responsible for plasma oxidation are expected to be $\cdot\text{OH}$ radicals reacting with most organic compounds at nearly diffusion-controlled regime with reaction rates in the range $k_{\cdot\text{OH}} = 10^8 - 10^{10} \text{ 1/(M}\cdot\text{s)}$.⁷⁶⁻⁷⁸ Overall, three main reaction mechanisms between $\cdot\text{OH}$ and organic compounds have been established: (1) the abstraction of a hydrogen atom, (2) the electrophilic addition of $\cdot\text{OH}$ to multiple bonds, especially C=C, C=N and S=O bonds, and (3) electron transfer reactions.⁷⁹ In the presence of other RONS, multiple other pathways were also investigated, confirming non-selective oxidation, which is a key point of wastewater treatment, where complete mineralisation is desirable and oxidation pathways are less important. The overall degradation kinetics of μPs can be rather complex and strongly depend on both gas and liquid phase composition, and plasma type.

To study the oxidation mechanisms, the herbicide alachlor C₁₄H₂₀ClNO₂ often was used as a reference μP .⁸⁰ The studies revealed five types of degradation steps: (i) hydroxylation, (ii) oxidation (O addition), (iii) dealkylation, (iv) reduction with the loss of aromaticity, and (v) dechlorination, as shown in Scheme 2.1. The latter mechanism, if initiated selectively, can play an important role in water treatment: the formed dechlorinated intermediates are less stable and less toxic than the parent compound and can be completely oxidised by other (complementary) AOPs. Unfortunately, such selectivity of plasma processes is difficult to achieve due to the generally non-selective nature of radical reactions.

In both Ar and O₂ discharge, various products of alachlor oxidation were formed through reactions with ROS,⁸⁰ whereas in air plasma also nitrosylation (and possibly nitration)⁸¹ occurs (see Scheme 2.1), clearly indicating that the more complex is the plasma feed gas composition (and hence the plasma RONS "cocktail"), the more complex is the chemistry of these RONS interacting with the organic substrate. The exact contribution of various RONS in oxidation is still under debate. Similar complexity of decomposition with the formation of multiple intermediates was detected for diuron, isoproturon and other μPs .⁸¹ As RONS produced by plasma react with any organic substrate, the efficiency of treatment is strongly dependent on the composition of the treated liquid and the content of organic matter in it.^{17, 82} Naturally, a higher total organic content (matrix) results in lower energy efficiency of the micropollutants removal, due to scavenging of the active species by the matrix components via competition between oxidation of emergency pollutants and other organics. The reduced efficiency of real matrix treatment and low selectivity of the oxidation have been tackled in various works by coupling plasma oxidation with other AOPs, nanofiltration, and biological steps, suggesting possible future improvements.⁸³⁻⁸⁵

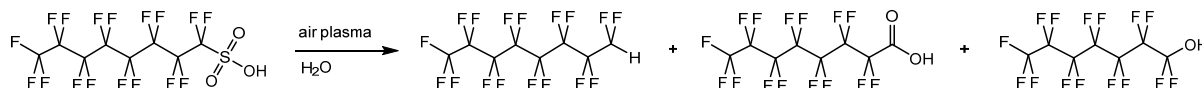


Scheme 2.1. Some of the most abundant initial products of alachlor degradation induced by air plasma during wastewater treatment.

Reduction pathway

As mentioned above, plasma-liquid interactions result in both the generation and solvation of various reactive species. Besides atomic, radical, and molecular RONS, the in-liquid induction of solvated electrons e_{aq} was shown to be important. Efficient generation of e_{aq} at the average local concentration of ca. 1 mM at the plasma/liquid interface has been measured for the cases of plasma impinging onto liquid water.⁵³ In contrast to most RONS having a strong oxidative effect, e_{aq} can enable redox reactions that open the possibility of removing pollutants, which are otherwise very hard to destroy. Other species, such as H atoms (or Ar_2^+ ions in Ar plasmas), can also participate in reduction reactions, albeit with low contribution to the overall pollutant removal due to their short lifetimes and rapid recombination at atmospheric pressure, which significantly reduces their presence at the plasma/liquid interface.^{2, 36}

Reduction chemistry induced by electrical discharges in liquid was used to treat perfluoroalkyl and polyfluoroalkyl substances (PFAS) and perfluorooctane sulfonic acid, its salts, and derivatives (PFOS).⁸⁶⁻⁸⁹ Both pollutants are man-made “forever chemicals” that pose a significant environmental threat due to their toxicity and high chemical stability (i.e., they are difficult to oxidise). Solvated electrons can initiate the breakage of a C-F bond, leading to the formation of short-chain products and, ultimately, to complete mineralisation. Unfortunately, as in the case of the oxidation processes induced by RONS, the e_{aq} chemistry also lacks selectivity towards the C-F bond. The reduction chemistry of PFAS can be activated by e_{aq} through H/F exchange, decarboxylation-hydroxylation-elimination-hydrolysis,⁹⁰ C-F bond dissociation in the α -CF₂ at the carboxyl group⁹¹, and desulfonation in case of PFOS.^{89, 92} The C-chain shortening, the key chemical process in wastewater treatment, can take place by either e_{aq} attachment on the middle -CF₂ group⁹³ or by the formation of the perfluoroalkane anion, which further can dissociate into a shorter chain compound and an alkene due to the reductive cleavage of the C-C bond.⁸⁹ In practice, all indicated reactions take place in parallel, yielding a large variety of fluorinated compounds.⁸⁷ Some of the products of desulfonation, defluorination and chain reduction during PFOS degradation in water are shown in scheme 2.2.



Scheme 2.2. Some of the initial products of PFOS degradation by air plasma during wastewater treatment.

Interestingly, in contrast to the plasma AOP described above, the effect of the organic matrix on the removal of PFAS/PFOS is less critical, and was even suggested to be beneficial in some

studies. The reason is mainly linked to the surfactant properties of fluorinated long-chain organic molecules, which results in their accumulation at the liquid surface (i.e., plasma/liquid interface), where they react with e_{aq} .⁸⁶

Thus, the combination of oxidative chemistry (due to RONS at the surface and in the bulk) with reduction chemistry (mainly due to e_{aq} at the surface) for removal of PFAS/PFOS from wastewater represents an industrially feasible method for perfluorinated pollutants removal at reasonable energy costs. Currently achieved energy metrics on a lab scale are in the range of 20 -200 kWh/m³ for the plasma water film reactor⁹⁴ or gliding arc⁸⁸ whereas energy demands of other alternative methods based on sonochemistry (460-600 kWh/m³), microwave-induced thermal degradation (4800-7300 kWh/m³) or photocatalysis (13000-49500 kWh/m³) are a lot more energy demanding and thus not feasible.⁹⁴

The discussed mechanisms highlight the complexity of plasma-initiated chemical processes, emphasizing their low selectivity with the formation of multiple oxidation/reduction products. Despite the challenges in achieving complete mineralisation, these processes can still be effectively implemented to remove specific classes of pollutants that are otherwise difficult to destroy (e.g., PFAS/PFOS).

3. Conversion of liquid chemicals for energy and into chemical building blocks

Plasma provides an interesting way for the processing of renewable feedstock, such as waste oils and bio-alcohols.⁹⁵ Waste oils are considered a valuable source of energy in the form of H₂ produced from them, and also as a source of syngas used for the synthesis of value-added chemicals. Bio-alcohols (e.g. bioethanol) are already used as renewable fuels in combustion engines, but H₂/syngas production from them greatly expands their range of applications. In addition, plasma offers a potentially cleaner alternative to the oil refining process. Such conversion is done in solvent-free conditions, such that the plasma interacts directly with the organic substrate molecules.

In the 1970s, simultaneously with the first attempts of wastewater treatment by plasma, the studies of plasma-based conversion of liquid hydrocarbons, such as heavy and residual oils, were started commercially to enhance the Huels process and expand the possible feedstock for acetylene production.²¹ The first published works on this topic employed powerful (30–70 kW) plasma reactors based on DC arc discharges used for the Huels process, with hydrogen as the plasma feed gas.^{96, 97}

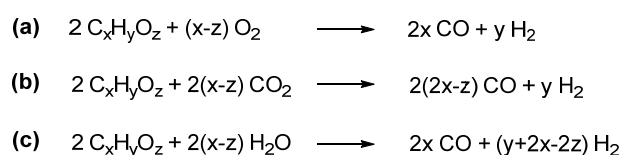
Plasma in these experiments was essentially a heat source for two purposes: (i) evaporation of the liquid hydrocarbons and (ii) pyrolytic decomposition of hydrocarbon vapour.⁹⁷ Thus, although the interaction of plasma with liquid did technically occur, the organic substrates underwent transformations almost exclusively in the gas phase. In comparison, in wastewater treatment (section 2 above) and in organic reactions in liquids (section 4 below), while some evaporation of solvent or substrate is inherently present, at least a portion of the reactions occurs with/in the liquid phase, with the diffusion of the species from the gas phase into the liquid (see section 2.1). Gas-phase reactions are beyond the scope of this review, and hence, a short discussion on them will suffice.

Products of decomposition included H₂, a range of gaseous hydrocarbons, such as CH₄, C₂H₂, and C₂H₄, and soot, but no light liquid hydrocarbons were observed. Higher conversions were observed for non-aromatic hydrocarbons (cyclohexane) compared to partially aromatic

substances (coal and crude oil, ethylbenzene, tetralin, toluene). Using steam as plasma gas was considered an alternative to hydrogen and resulted in higher liquid-to-gas conversion with reduced energy cost and soot formation.⁹⁶ With the addition of steam, a significant amount of CO appeared in the reaction products, leading to the production of syngas alongside light hydrocarbons.

In light of increased concerns regarding growing environmental pollution and greenhouse gas emissions, the 1990s and 2000s saw a renewed interest in plasma-based hydrocarbon decomposition or reforming with additional agents (O₂, CO₂, H₂O) as a source of H₂ for use in transportation vehicles (either as fuel or an additive to other fuels) or as a precursor for syngas production.⁹⁸ This shifted the research focus to converting hydrocarbons into H₂ or syngas, and expanded the field to include oxygen-containing bio-derived alcohols.

A major complicating factor in assessing plasma-based hydrocarbon and alcohol reforming processes lies in various plasma reactor configurations and reactant combinations used in the existing studies. Several pathways for plasma-based hydrocarbon reforming can be highlighted depending on the reactants used: pyrolysis, partial oxidation, steam reforming, and dry reforming (Scheme 3.1). These were sometimes combined to adjust the composition of the products. An assortment of hydrocarbons and alcohols was studied: heavy oils, diesel, gasoline, light liquid hydrocarbons, waste and bio-oils, toluene, glycerol, ethanol, and methanol. Plasma reactors include plasma torches, GA discharges, MW discharges, DBDs, and many others.



Scheme 3.1. Main pathways for plasma-based hydrocarbons and alcohols reforming for syngas production: **(a)** partial oxidation, **(b)** dry reforming, **(c)** steam reforming.

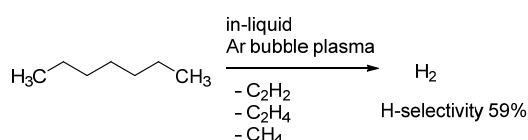
3.1. Conversion of liquid hydrocarbons into syngas and H₂

Initially, plasma use for converting fossil fuels and oils, such as gasoline, diesel, fuel oils and bio-oils, was limited to steam reforming^{22, 99} and partial oxidation⁹⁹ in thermal plasma sources designed around electric arcs. In those cases, plasma was mainly responsible for maintaining high reaction temperatures (over 2000 K¹⁰⁰), providing energy for reforming. Plasma-liquid interaction in such systems was limited to quick evaporation of the liquid feed and pyrolysis of gasified components.

While capable of high conversion, thermal plasmas were highly energy-consuming, which led to the development of non-thermal plasma reactors for the cracking of liquid hydrocarbons based on GA,¹⁰¹⁻¹⁰⁷ corona discharge,¹⁰⁸ and DBDs.¹⁰⁹⁻¹¹⁵ In most cases, liquid reactants were introduced into plasma as aerosols with a flow of air, N₂ or Ar, with or without steam. In these setups, the main role of plasma was considered not as a heat source (although at least partial evaporation of the aerosol still occurred), but as a source of high-energy electrons enhancing the cracking process via electron impact reactions.^{116, 117} Syngas production was the main goal of plasma-based reforming. However, research showed that it was hard to completely shift the selectivity of the process to syngas. Besides H₂ and CO, the rest of the experimental cracking products are mainly composed of a mix of CO₂ and CH₄, with small quantities of C₂H₂,

C₂H₄, C₂H₆, and heavier hydrocarbons, depending on the initial reactants. Different plasma gases impacted the H₂/CO ratio in the reforming products, ranging from approximately 0.8 for air plasma (partial oxidation) to 2 for steam plasma (steam reforming).

Another approach for the cracking of fuel oils or their surrogates involved the use of in-liquid plasma. These systems included pin-to-plate,¹¹⁸⁻¹²³ pin-to-pin,¹²⁴⁻¹²⁶ MW¹²⁷⁻¹³⁰ and spark¹³¹ discharges, ignited inside the gas bubbles in the liquid hydrocarbon, with Ar, N₂ or CH₄ as plasma gases. Unlike the introduction of droplets (including aerosols) in the feed gas and its vaporisation by plasma, these cases are more directly related to the plasma-liquid interaction phenomena – although evaporation of the liquid organics still occurred when in contact with the plasma bubbles, or with the feed gas-free in-liquid plasma discharge. The product composition of such processes contained mainly H₂, C₂H₂, C₂H₄, and CH₄, with the addition of higher hydrocarbons depending on the length of the reactant carbon chains. While the H-selectivity to H₂ reaches 59% (Scheme 3.2),¹²⁷ the main by-product is C₂H₂, from approximately 20% in MW plasma reactors¹²⁷⁻¹³⁰ and up to 50% in a pulsed pin-to-pin reactor.¹²⁵ CO was present in the conversion products in cases when CO₂ was used as the plasma feed gas,¹³⁰ or when alcohols were added to the reactants.^{122, 123} The lack of selectivity and control over conversion products was illustrated by the cracking of *n*-hexadecane with the addition of methanol, which featured both decomposition and hydrogenation of *n*-hexadecane and the production of ethanol due to the dimerisation of methanol molecules.¹²² The same work estimates that the main free radicals during discharge in liquid are generated by the electron impact reactions and include H, ·OH, and ·CH₃. Additional observations show that compounds with higher aromatic content appear to be more resistant to plasma cracking, which results in lower energy efficiency of their decomposition.¹³¹ There are mixed reports regarding the soot or carbon formation during the cracking, reflecting the dependence of the process on specific operating conditions.



Scheme 3.2. Production of H₂ via *n*-heptane decomposition by Ar plasma bubbles.

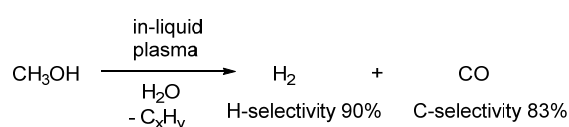
3.2. Conversion of liquid alcohols into syngas and H₂

Aside from hydrocarbons, another group of compounds has been studied as potential reactants in plasma-based cracking for H₂ and syngas production – alcohols. Three alcohols became the research focus: ethanol (EtOH), methanol (MeOH), and glycerol. The reason for this is their availability: EtOH and MeOH are easily produced from renewable feedstock, such as plant biomass, while crude glycerol is generated in significant amounts as a waste from biodiesel production.¹³²

Some of the first reports describe MeOH decomposition investigated using DBD²⁵ or corona plasma.¹³³ Although MeOH is often supplied into such plasma reactors as aerosol, it evaporates at reported temperatures of 100–300 °C, essentially making plasma an energy (heat) source for the vaporisation of the liquid organic substrate, similar to the case of liquid hydrocarbons (see section 3.1). Reported conversion values were between 80% (in non-catalytic DBD) and 90% (with Cu-Mn,¹³⁴ Cu/ZnO,^{135, 136} Ni¹³⁷ catalysts). The H-selectivity to H₂ was <40%, while the C-selectivity of the CO production also suffered from the formation of

large amounts of the overoxidised by-product CO₂.^{138, 139} Computational investigation showed that a wide range of electron energies generated in plasma leads to all possible decomposition reaction channels, indicating the possibility of coupling reactions to form C₃+ hydrocarbons and alcohols in addition to syngas.¹⁴⁰ Besides cold plasma, warm plasma setups derived from GA^{141, 142} or MW^{143, 144} were used, which improved the H-selectivity towards H₂ production.

In-liquid plasma was also employed for MeOH reforming. Various plasma configurations (pin-to-plate,¹⁴⁵⁻¹⁴⁷ spark,^{148, 149} etc.) were used in pure MeOH or MeOH/H₂O mixtures. Franclemont et al. demonstrated pulsed in-liquid plasma for MeOH decomposition in aqueous solutions.¹⁴⁶ Around 50% selectivity to CO and H₂ was achieved regardless of the H₂O fraction in the solution, while by-products comprised various C₂+ alcohols (EtOH, propanol), acetic acid, various esters, and gaseous CH₄, C₂H₄, C₂H₂. Another example of the pulsed in-liquid plasma is the work of Xin et al.,¹⁴⁷ in which a 3:1 mixture of MeOH and H₂O yielded one of the highest reported syngas selectivities (Scheme 3.3).



Scheme 3.3. Syngas production from a 3:1 MeOH-H₂O mixture by an in-liquid AC pin-to-plate discharge plasma.

EtOH is another important precursor for H₂ and syngas production due to the ease of generating it from renewable feedstock. As with MeOH, EtOH is introduced into plasma as a vapour, an aerosol, or in the form of in-liquid plasma ignition. The first examples of EtOH cracking using plasma were done with the EtOH vapour injected into the plasma.¹⁵⁰⁻¹⁵² Studies into the kinetics of plasma-based EtOH cracking posit that high-energy electrons in plasma initiate the process via electron impact dissociation, similar to the MeOH decomposition mentioned above.^{153, 154} The dehydrogenation of EtOH molecules caused by electron collisions is the main source of H atoms, which combine to form H₂. Dehydrogenated species, after a series of transformations, yield CO, CO₂, C₂H₄, C₂H₆, CH₄, and HCHO.¹⁵⁵

EtOH processing using in-liquid plasma was simultaneously researched for the synthesis of carbon nanoparticles^{156, 157} and H₂ production.^{158, 159} In general, H₂ production was the main goal regardless of the second desired product – CO or C particulates. These works used pin-to-pin discharges submerged in liquid EtOH for plasma generation. It was found that when the mixture of EtOH and H₂O is used for the reforming, the ratio between them plays a role in the product composition, with the highest H₂ selectivity achieved in the presence of H₂O (up to ca. 75), with the by-products being CH₄, C₂H₂, and C₂H₄.¹⁵⁹ Interestingly, it was suggested that part of the H₂ originates from the water gas shift reaction, in which some of the initially formed CO reacts with H₂O to yield H₂ and CO₂. Another study involving an in-liquid pin-to-pin discharge demonstrated that the increase of plasma power shifts the composition of reforming products towards higher quantities of H₂ and CO, reducing the amount of C₁-C₄ hydrocarbons in the products.²⁰

An interesting approach is to utilise plasma together with a photocatalyst (TiO₂), which would make use of the UV radiation produced by a spark plasma in liquid EtOH.¹⁶⁰ The addition of the photocatalyst, which was proposed to generate additional ·OH radicals and thus enhance the EtOH decomposition via initial abstraction of labile H from the α-CH₂, helped achieve one of the lowest energy costs for H₂ production from EtOH: 0.5 kWh/m³ H₂, with the typical values

in other works ranging from 1 to 19 kWh/m³.¹⁶⁰ An attempt was made to improve EtOH conversion using Co/ZrO₂ catalyst rings positioned on one of the reactor electrodes during in-plasma reforming.¹⁶¹ Conversion products contained the same components (H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆) with and without the catalyst; however, the use of the catalyst increased the H₂ and CO₂ concentrations in the products and decreased the CO, C₂H₄, and C₂H₆ concentrations.

Other popular plasma reactors for EtOH reforming included GAs,¹⁶² rotating GAs,^{163, 164} and MW torches.^{165, 166} Plasma was brought into contact with the liquid EtOH by, e.g. bubbling the gaseous plasma through it, which interestingly could contain oxygen (e.g., in the air) without compromising the H₂ production.⁴¹ In all these cases, product composition contained similar components (H₂, CO, CO₂, C1-C4), with light hydrocarbon concentrations depending on the presence of liquid EtOH near the plasma.

Plasma-based cracking of glycerol received less attention than the other alcohols, with only a small number of works covering the topic. Different reforming processes were investigated: steam reforming,²⁴ partial oxidation,¹⁶⁷ reforming with the addition of CO₂,¹⁶⁸ and pyrolysis.¹⁶⁹ The process was studied using both warm plasmas (pin-to-plate discharge,²⁴ rotating GA discharge with a liquid electrode,¹⁶⁸ and MW plasma¹⁶⁷) and cold plasma (DBD reactor with and without catalyst¹⁶⁹). Glycerol decomposition using plasma mainly produces H₂, CH₄, C₂H₂, and O-containing products (CO and CO₂). Computational studies showed that the rate-limiting step is the same as with MeOH and EtOH in H₂O-free conditions: abstraction of H from any of the hydroxyl groups or from the CH₂ group, or even a functional group cleavage with a release of ·OH or ·CH₂OH under direct electron impact reactions.¹⁷⁰ Carbon deposition occurred during the glycerol decomposition, forming soot in a warm plasma system²⁴ and poisoning catalysts in cold plasma.¹⁶⁹ The addition of H₂O as a reactant was experimentally^{24, 168} shown to prevent carbon formation via steam reforming, which was later confirmed computationally.¹⁷⁰

Thus, the focus in plasma conversion of hydrocarbons and alcohols into H₂/syngas is put on the process metrics rather than specific pathways of organic reactions, as long as the ultimate products are H₂ (and CO). Net H- and C-selectivity towards them defines the process metrics.

4. Organic synthesis enabled by plasma chemistry

As discussed in previous sections, plasma systems are often used for the degradation of organic pollutants in water or the conversion of organic and inorganic molecules into syngas or H₂. These reactions generally don't require high selectivity as long as the desired processes occur: the degradation of pollutants or the generation of syngas. In the latter, the C-selectivity towards CO and H-selectivity towards H₂ are obviously important: their ratio (and their yield) directly affects the energy costs of the process. However, the energy efficiency of the process is usually the main focus, often at the expense of the desired CO/H₂ ratio.

A whole different field of plasma-liquid applications is the conversion of organic substrates in liquid media with the purpose of selective generation of specific chemical products. The main difference with the other two applications is that here the conversion is non-destructive.

In this section, we discuss the recent advances made in the field of plasma-liquid interactions for synthetic organic purposes. To allow the reader to draw a comparison between the concept of plasma wastewater treatment and organic synthesis in water enabled by plasma,

we divided the section into two parts: aqueous systems (which resembles the removal of pollutants from water, as in section 2), and organic liquids (resembling solvent-free conversion of organic molecules, as in section 3).

Of all three topics discussed in this review, this is the least developed one. Moreover, to date, there is no review that would collect various examples of organic synthetic chemistry in plasma-liquid systems. We attempted to provide a near-exhaustive list of works which contain reports on the topics. We note that some of the works reviewed in this section do not provide the necessary information allowing us to calculate the yield and/or selectivity values, hence the absence of such data in the text. Moreover, some of the reactions are performed as a batch process, while others are done in single- or multi-pass reactors with flowing liquid, making a direct comparison of yields difficult. It is also worth mentioning that in many examined works the reaction conditions remained unoptimised, hence, the yields mentioned are merely illustrative. Likewise, the energy costs are almost never assessed in the discussed works. Hence, we instead put a specific focus on the selectivity towards desired products.

Being the first review on this topic, the following section provides a higher level of detail of the listed processes than the previous ones. Besides addressing basic mechanisms leading to specific product generation, we also briefly discuss the limitations of each of the listed examples.

4.1. Plasma-driven organic reactions in aqueous media

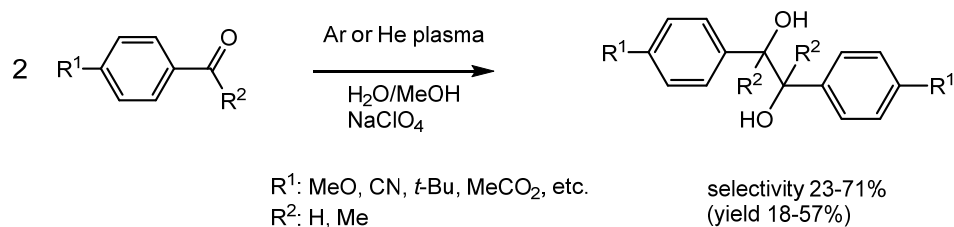
Water is the most environmentally benign reaction medium and/or a reagent (e.g. a source of $\cdot\text{OH}$ radicals), and adding plasma to the reactive system helps avoid toxic reagents and enables waste-free chemical processes. In this subsection, we present a list of examples of using plasma-liquid interaction to perform organic chemical synthesis reported to date.

Pinacol coupling

Solvated electrons are the simplest reactive species which can enable organic redox coupling reactions. In a recent study, the pinacol coupling reaction, i.e. essentially an electron transfer reaction, was realised in a plasma-electrochemical system. This demonstrates that reductive C-C bond formation reactions can be performed in a benign manner using solvated electrons from plasma, instead of the waste-generating catalytic pathways with toxic organometallic compounds.

Conceptually, the plasma setup consisted of a plasma jet impinging onto a solution of the organic substrate.¹⁷¹ An inert gas (Ar or He) plasma jet, comprised of a hollow quartz tube and a needle, was powered by a DC power supply. The substrate was dissolved in a mixture of MeOH and water, and exposed to the plasma jet, with a Pt/Ti mesh ground electrode submerged in the liquid with added sodium perchlorate as an electrolyte. The study showed the possibility of performing the pinacol coupling reaction with a variety of para-substituted organic carbonyl-containing compounds (ketones and aldehydes; Scheme 4.1). By varying the MeOH content in H_2O , it was found that the proton originating from H_2O is the one participating in the reactive mechanism: higher H_2O content afforded higher yields and faradaic efficiency. In general, the substrate conversion reached values up to 80%, with the yield of respective *vic*-diols ranging between 18 and 57%, with isomer selectivity shifted towards meso compounds. However, the method of using plasma-generated solvated electrons for stoichiometric synthetic reactions remains in its infancy, with further studies and

optimisations (i.e., product selectivity, conversion, and faradaic efficiency) required to make this route feasible. Besides, using a noble gas for plasma ignition increases the costs dramatically, and thus decreases the possibility of upscaling, while using ubiquitous gas such as air (N_2+O_2) inevitably result in oxidation and nitration/nitrosylation, as shown below (see Scheme 4.2b and the related discussion).



Scheme 4.1. Pinacol coupling of *p*-substituted aromatic ketones and aldehydes driven by plasma-generated solvated electrons.

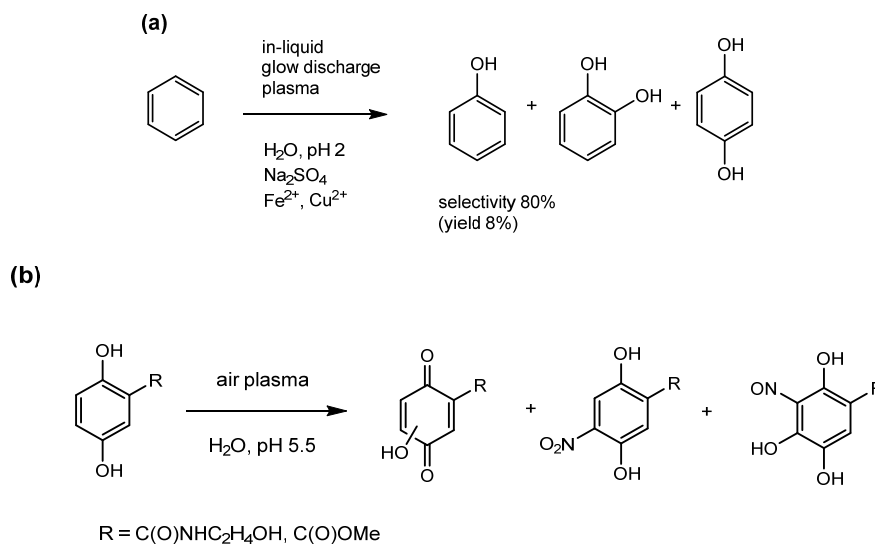
Hydroxylation and oxidation of arenes and alkanes

Transformation of benzene into phenol is one of the largest reactions in industrial organic chemistry, with the annual phenol production reaching several Mt. It is done via the Hock process, where benzene is first converted to cumene via Friedel-Crafts alkylation of benzene (at 30 atm and 250 °C), then oxidised to a peroxide radical in air with radical initiators, and finally transforms in the presence of water into phenol, releasing acetone as a by-product.¹⁷² This multi-step process is not only energy-intensive (due to the first step), non-environmentally benign and waste-generating, but also affords final phenol yields of around 5%. An interesting approach to phenol production via in-liquid ignition of a DC glow discharge plasma in a suspension of benzene in an aqueous sodium sulfate solution was suggested by Liu et al.¹⁷³ The plasma system consisted of a Pt wire anode and a Cu sheet cathode submerged in the suspension. The evaporation of benzene due to the plasma heating of the mixture was suppressed via temperature control (water bath) and mitigated by a condenser.

Water was both a reaction medium (and a solvent for the products) and a reagent: it was the source of $\cdot\text{OH}$ radicals, which enabled the direct phenol hydroxylation. Because some of the $\cdot\text{OH}$ is inevitably lost due to recombination into H_2O_2 , the addition of Fe^{2+} and/or Cu^{2+} ions helped increase the yield and the selectivity of phenol generation via the Fenton (with Fe^{2+}) and the Fenton-like (with Cu^{2+}) reactions producing $\cdot\text{OH}$ from H_2O_2 . Decreasing pH to 2 afforded the highest yield of phenol of 8%, with ca. 80% selectivity, while the by-products were double *ortho*- and *para*-hydroxylated benzenes: catechol and hydroquinone (Scheme 4.2a). Despite this being a one-step reaction that can be carried out at ambient conditions, it still requires the addition of Fenton catalysts, pH adjustment, and temperature control, and suffers from low selectivity, which introduces inevitable costs for product separation.

In the reaction shown in Scheme 4.2a, the plasma was ignited in the liquid water, and thus the main reactive species was the hydroxyl radical. However, when liquid water is exposed to plasma either operated in air, or the plasma feed gas contains oxygen molecules, the formation of other species, specifically O atoms, can occur.^{174, 175} It was suggested that O atoms have very similar reactivity to that of $\cdot\text{OH}$, yielding hydroxylated phenols in a similar way to hydroxylation.^{64, 176} This creates a potential to perform liquid-phase reactions with O atoms – a species that is not easily attainable in liquids by conventional chemical means.⁶⁵ However, we must note that according to the current state-of-the-art, the ability of O atoms

to penetrate into the bulk liquid is debated, with the most recent studies showing that reactions involving O occur mostly near the interface layer of a liquid, separating it from gaseous plasma.⁶⁸ In any case, O₂-containing plasmas can also yield hydroxylation products. The associated limitations of such a synthetic approach are, again, the limited selectivity of the reaction due to the unavoidable formation of dual and triple-hydroxylated compounds: catechol, hydroquinone, resorcinol, pyrogallol, etc.⁶⁸, similarly to the products observed during phenol plasma AOP described in Section 2.2.



Scheme 4.2. Hydroxylation of arenes by plasma in aqueous media: **(a)** transformation of benzene into phenol and benzenediols by glow discharge plasma-generated ·OH radicals; **(b)** hydroxylation, oxidation, nitration and nitrosylation of hydroquinone by air plasma.

Regardless of the nature of reactive species responsible for the transformation of arenes, simultaneous hydroxylation and oxidation of substituted arene diols to quinones can be performed by air plasmas (Scheme 4.2b) as demonstrated by Hahn et al. using an AC pin-to-liquid plasma.¹⁷⁷ Hydroxyl moiety was introduced in the substrate hydroquinone in *para*- or *ortho*-positions to the initial substitute group, depending on its chemical structure. Interestingly, it was also shown that using plasma-treated water can yield different products than a ‘mock’ solution prepared by dissolving nitrite, nitrate, and hydrogen peroxide in pH-adjusted H₂O, suggesting the presence of other RONS besides those above. The reactions can be carried out in the absence of catalysts, under ambient conditions. However, since the work is conceptual (e.g. without quantitatively reported yields or optimised selectivity), this method is still nascent, and its applicability is dramatically limited by the selectivity due to the formation of products of nitration and nitrosation reactions (with the RNS formed in air plasmas), and dimerisation reactions.¹⁷⁷

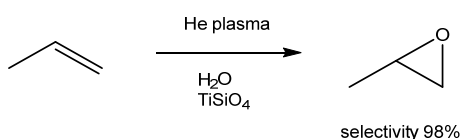
Furthermore, the oxidation of *n*-hexane and cyclohexane was also investigated in a so-called water film plasma reactor.^{178, 179} Functionalisation of higher saturated hydrocarbons is usually performed at elevated temperatures and harsh oxidising conditions, which often lead to C-C bond cleavage and thus overoxidation to formic acid or even CO₂. Hence, oxidation of long-chain alkanes at mild conditions is very sought-after.¹⁸⁰ In short, the reactive system comprised Ar feed gas which contained vaporised alkane or cycloalkane, and a DBD-type pulsed DC discharge occurring over a liquid H₂O surface. Although the substrate here was technically a gas, the presence of liquid H₂O enabled its conversion via C-H bond activation by the ·OH

radicals originating from water, and subsequent transformations of the formed alkyl radicals. The product distribution between alcohols, aldehydes, ketones, and acids depended on various studied conditions. Interestingly, the main products of the *n*-hexane and cyclohexane oxidation were an alcohol (3-hexanol; selectivity 26%) and a ketone (cyclohexanone; selectivity 47%), respectively. In general, the suboptimal selectivity is typical for radical reactions, as was also shown by further computational studies.¹⁷⁸ Overall, this is a non-energy intensive, catalyst-free, environmentally benign method of oxidative transformations of alkanes on the C-H bond. However, the fact that the alkanes had to be gaseous under the studied conditions limits the range of possible substrates to shorter C-chains. Besides, the suboptimal selectivity (due to the multiple routes leading to different oxidation products) and conversion, as well as the necessity to use inert gasses (to avoid plasma RNS which could introduce nitro and nitroso groups into the products) limit the applicability of the process.

Propylene epoxidation

A similar way of oxidative transformation of non-water soluble organics was proposed by Lee et al. to produce propylene oxide, a chemical precursor in the production of polyurethane plastics.¹⁸¹ Epoxidation of propylene with H₂O₂ has been actively investigated to find a benign alternative to industrial processes which employ dangerous intermediates, but H₂O₂ itself is produced industrially with the use of carcinogenic reactants.¹⁸²

Gaseous propylene was bubbled through liquid water with dispersed titanium silicate, which acted as a catalyst. DC He plasma was ignited inside a tube submerged in the liquid, with a Pt rod as an HV electrode and Al wire as a ground. The epoxidation of propylene to propylene oxide with 98% selectivity was driven by the plasma-generated H₂O₂ in combination with the catalyst (Scheme 4.3).¹⁸¹ The reaction proceeded only in the presence of the catalyst, with the rate-limiting factor being the initial H₂O₂ generation from H₂O by plasma. In brief, it was proposed that H₂O is initially split into H and ·OH, the latter further combining into H₂O₂. This H₂O₂ epoxidises propylene on a TiSiO₄ catalyst via the formation of the secondary ·OH radicals.



Scheme 4.3. Plasma-catalytic epoxidation of propylene in water.

Such a concept of in-situ H₂O₂ production and immediate utilisation is an interesting substitute for commercial H₂O₂. However, non-plasma based systems, e.g. comprised of an electrocatalyst to produce H₂O₂ in water and a heterogeneous catalyst to epoxidise propylene,¹⁸³ or even a single-catalyst electrocatalytic system,¹⁸⁴ are cheaper electricity-based alternatives because they do not use noble gas (He) which adds costs to the process.

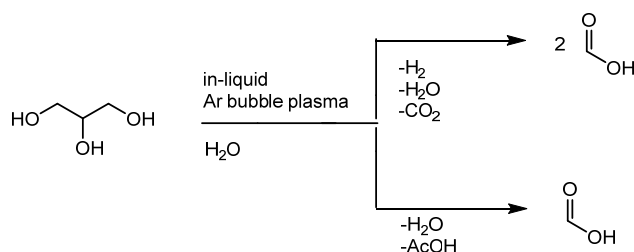
Transformation of glycerol into formic acid

A shift from fossil to more sustainable forms of energy involves the employment of biomass-derived diesel, as discussed in section 3.2. However, glycerol can be valorised not only by converting it into syngas, but also by transforming it into value-added chemicals.¹³² Specifically, an efficient transformation of glycerol into formic acid (a potential H₂ carrier) is a sought-after process. Although such C-C cleaving oxidative conversion was reported in the presence of H₂O₂ as the oxidant at elevated temperatures and in the presence of various

catalysts, Bang et al. recently published the first study dedicated to plasma-based formic acid production from glycerol.¹⁸⁵ A nanosecond DC pulse discharge was used to ignite plasma in Ar bubbles, created by passing Ar gas through an aqueous solution of glycerol. Plasma was ignited in the bubbles between the high voltage electrode which also served as the inlet for the gas, and a metal ground electrode also submerged in the liquid.

Two reaction pathways towards formic acid were proposed (Scheme 4.4). By varying the fraction of glycerol in the aqueous mixture, it was found that the energy cost of formic acid production was the lowest when the glycerol content was 10 vol%. Substrate concentration below 10 vol% expectedly lowered the reaction rate, but with the increased concentration (above 10 vol%) the rate-limiting factor was the generation and propagation of $\cdot\text{OH}$. Similarly to the synthetic routes discussed for other reactions above, water here was an essential component of the reaction because it acts as a source of $\cdot\text{OH}$, the latter being responsible for the H abstraction from glycerol, and (i) the subsequent formation of intermediates which undergo carbon bond cleavage to yield formic acid, or (ii) enolisation with multiple further oxidation steps leading to formic acid. Likewise, adding H_2O vapour to the Ar feed gas increased the product yield via the generation of additional $\cdot\text{OH}$.¹⁸⁵ Adding H_2O_2 helped improve the yield even further. Hypothetically, this may mean that plasma pre-treatment of H_2O to produce H_2O_2 before this $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solution is mixed with glycerol can enhance the process metrics.

Although due to the oxidative shortening of the C-C chain, this reaction resembles the degradation of organic components in water like in the plasma wastewater treatment processes, we discriminate it from them because the aim of this route is the selective production of formic acid rather than simply decomposition of contaminants.



Scheme 4.4. Oxidative cleavage of C-C bond by the plasma-generated $\cdot\text{OH}$ to convert glycerol into formic acid.

Because this process has little preparative interest but rather aims at the energy sector (with HCOOH as a hydrogen carrier), the drawbacks should also be viewed from the industrial perspective. As such, the method suffers from a suboptimal carbon economy, i.e. only 67% (top route in Scheme 4.4) and 33% (bottom route in Scheme 4.4) of the carbon atoms remain in the formic acid; generation of CO_2 as the by-product; and the product separation costs (e.g. acetic and formic acid). Moreover, changing the feed gas from Ar to e.g. air to make the process more feasible economically could suppress the desired mechanism altogether, and/or yield multiple undesired by-products, due to the in-liquid chemistry of the plasma-produced RNS.

Production of oxalic acid from CO_2

One of the most burgeoning fields of plasma application is CO_2 conversion and utilisation.¹⁸⁶ The most direct method is CO_2 plasmolysis into CO and O_2 , but it is often limited by the

recombination of CO and O.¹⁸⁷ An alternative way of CO₂ conversion was recently proposed by Zhang et al., where plasma with CO₂ as the feed gas was bubbled through water, and CO₂ is converted into C₂O₄²⁻.¹⁸⁸ In such a system the chemistry is driven by an AC pulsed spark plasma ignited in a perforated quartz tube containing the HV electrode and submerged in water, and the ground electrode is also positioned in water at a distance from the plasma tube. Both electrodes were produced from W to ensure chemical stability over extended periods of time.

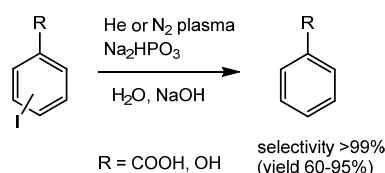
By comparing bubbling CO₂ plasma through water with bubbling Ar plasmas through CO₂-saturated water, it was found that the former case afforded higher selectivity towards oxalic acid. In turn, the lowest CO₂ flow rate afforded the highest total selectivity towards liquid products (as opposed to the formation of gaseous CO). The overall process is essentially a C-C coupling (see also the pinacol coupling described above). Mechanistically, the proposed pathway is electron attachment to CO₂ forming CO₂⁻, which yields HCO₂⁻ in aqueous environment. The coupling of two HCO₂⁻ results in C₂O₄⁻ and emitted H₂. Thus, the reaction proceeds catalyst-free, and without additional sacrificial hydrogen donors.

Oxalic acid finds its use as an anti-rust agent and was recently proposed as a C2 building block for plastics and pharmaceuticals.¹⁸⁹ Multiple literature sources describe electrocatalytic production of oxalate from CO₂ in various media, from ionic liquids to aqueous solutions, but they have higher energy costs and lower production rates than in the case of using CO₂ plasma in liquid, and in the latter H₂O is also partially converted into the value-added H₂O₂, making the process even more appealing.¹⁸⁸ However, we must note that the high selectivity towards oxalic acid was achieved only at low throughput values (e.g. CO₂ feed gas flow rate of 5 mL/min). Besides, the separation from by-products, i.e. other carboxylic acids (formic, acetic), puts restrictions on direct applications of the process.

Deiodination of arenes

The chemical reactions of organic molecules described above utilise plasma-produced species (hydrated electrons, H₂O₂, ·OH, H) in a stoichiometric manner. In some cases, this general approach is hindered by several factors: (i) a fairly low amount of the desired RONS per volume of the used gas which implies impractical volumes of gas and plasma treatment time, (ii) the need to use noble gasses because the production of RONS may create undesired by-products; (iii) low selectivity due to the radical nature of reactions. In contrast, using plasma to initiate chain radical reactions requires limited exposure of substrates to plasma: akin to a conventional radical initiator, plasma here is used to “kickstart” a chain reaction in the presence of a chain transfer agent.¹⁹⁰ Conceptually, this process resembles plasma polymerisation when a liquid monomer substrate is exposed to gaseous plasma.¹⁹¹

Plasma as a radical initiator was used for the dehalogenation of *ortho* and *para* iodo-substituted benzoates and phenolates (Scheme 4.5).¹⁹⁰ A solution containing the substrate arene and sodium dibasic hypophosphite was circulated through a planar DBD reactor with a nanosecond pulsed DC plasma (with both live and ground Cu electrodes embedded in PEEK plates), with He or N₂ as the feed gas. Na₂HPO₃ acted as both the chain transfer agent and the H donor in the deiodination reaction. NaOH was added to an aqueous solution to allow solubilisation of the substrates.



Scheme 4.5. Deiodination of substituted 2- and 4-iodoarenes initiated by plasma in the presence of the chain transfer agent.

The proposed pathway was the abstraction of hydrogen atom from HPO_3^{2-} by $\cdot\text{OH}$, forming a P-centred radical anion, which in turn may abstract the halogen from the arene. The resulting C-centred radical abstracts H from another HPO_3^{2-} anion, thus continuing the chain reaction. When the feed gas was switched to air, the reaction did not proceed because the presence of oxygen terminated the chain propagation. He as the plasma feed gas afforded the highest reaction rate, albeit making the process costly due to the use of noble gas. N_2 as the feed gas still allowed near-quantitative yields but made the process a lot more practical than with He. Interestingly, the deiodinated product was produced exclusively, despite the likely presence of NH and NO and other radicals from the reaction of N_2 plasma with H_2O .⁴

Dehalogenation of arenes is often done with homogeneous organic solvents. Overall, the process uses the radicals produced by plasma from H_2O to initiate the radical reaction. This waste-free process is a sustainable alternative to conventional methods which employ noble metal catalysts,¹⁹² organic solvents,¹⁹³ or toxic radical initiators.¹⁹⁴ However, the method did not work for other halogens such as Cl,¹⁹⁰ and for I required a complex system with the solution continuously circulating through the plasma discharge zone. Besides, the plasma discharge had to be completely oxygen-free, to avoid chain termination.

4.2. Direct plasma treatment of organic liquids

Besides the syngas production as discussed in section 3, plasma treatment of organic liquids is often used for polymerisation (e.g. for biomedical applications¹⁹⁵), where liquid monomer precursors are treated by plasma to create polymer structures without the need for environmentally unfriendly chemical radical initiators.¹⁹⁶ Among other examples are: plasma treatment of organic polymer solutions to enhance properties of nanofibers electrospun from these solutions;¹⁹⁷⁻¹⁹⁹ upgradation of bio-oils via hydrodeoxygenation;²⁰⁰ preparation of metal-organic frameworks;⁵ etc. These applications of plasma are generally well-known, and described in several dedicated reviews.^{6, 123, 196, 200} However, such processes, arguably, cannot be considered preparative from the chemical point of view because they focus either on macromolecular properties, or non-selective cracking for energy purposes. Instead, in this subsection we focus on synthetic organic chemistry reactions enabled by plasma treatment of organic liquids, which are represented either by solutions of organic substrates in other organic solvent, or a direct solvent-free plasma exposure.

Oxidation of alkanes

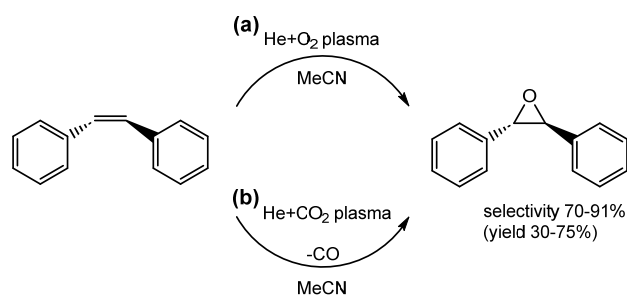
The oxidation of alkanes in water (see section 4.1) was further developed into a completely solvent-free transformation route of *n*-octadecane into a variety of alcohols, diols, ketones and carboxylic acids, as demonstrated by Nguyen et al.²⁰¹ Oxygen atoms formed in a pulsed DC DBD plasma operated in He or Ar with 1 vol% O_2 admixture were used to abstract H from the substrate, yielding alkyl and $\cdot\text{OH}$ radicals. The alkyl radicals could further react with $\cdot\text{OH}$ yielding mono- or double-hydroxylated products, or with O_2 to proceed via peroxy radicals

into aldehydes, ketones, and carboxylic acids. Like other long alkanes, *n*-octane is solid at room temperature, but the heat generated by plasma was sufficient to melt it, thus enabling the plasma treatment of a liquid substrate. Interestingly, the plasma in Ar gave the same conversion but lower selectivity towards specific products. Although such a solvent-free method shows an interesting concept for mild oxidation of alkanes, the limitations are the same as in the conversion of alkanes in the presence of liquid water:¹⁷⁹ noble gas-related costs and suboptimal selectivity.

A microfluidic plasma device has been investigated to increase the selectivity of the oxidation. In general, microfluidic plasma devices allow conducting the exposure of liquid to plasma with a higher degree of control, and enable multi-pass treatment to increase conversion and/or selectivity of plasma-driven oxidation.²⁰² Direct oxidation of cyclohexane was done in a microfluidic chip with a DBD-like plasma discharge in the microchannels with a mixture of Ar and O₂ as the feed gas.²⁰³ A high conversion of cyclohexane (> 35%) was achieved in a single-pass reaction mode with a residence time of the liquid substrate of only ca. 100 s, with a total selectivity towards cyclohexanol and cyclohexanone of 80%, thus revealing the potential of microfluidic devices for synthetic chemistry.

Epoxidation of alkenes with O₂- and CO₂-containing plasmas

Conceptually similar to the epoxidation of propylene by the H₂O-originated ·OH described above, the epoxidation of alkene bonds by plasma-formed O atoms was discovered by Xu et al.²⁰⁴ Propylene can be epoxidised by H₂O₂ with a catalyst, whereas more complex alkenes often require peracids (which are highly corrosive and explosive) to drive epoxidation. Avoiding these agents altogether, an AC cross-field radiofrequency plasma jet consisting of two parallel steel electrodes¹⁷⁴ and operated in He with up to 1 vol% O₂ was used to epoxidise *trans*-stilbene (Scheme 4.6a). A solution of *trans*-stilbene in acetonitrile was exposed to the effluent of the plasma jet. Although this plasma jet operated under the listed conditions can yield various ROS (e.g. O, O₃, and ¹O₂),^{65, 174} it was shown that specifically O atoms are responsible for the production of *trans*-stilbene oxide, while reaction with singlet delta oxygen ¹O₂ yields *cis*-stilbene oxide. The optimisation of reaction conditions by varying the applied voltage, oxygen content, and the time of liquid exposure to plasma, resulted in a 70% product yield with a 64% selectivity, with the only by-product being benzaldehyde produced via interaction of stilbene with formed O₃.²⁰⁴



Scheme 4.6. Epoxidation of *trans*-stilbene with O atoms originating from (a) O₂ and (b) CO₂ in the plasma feed gas.

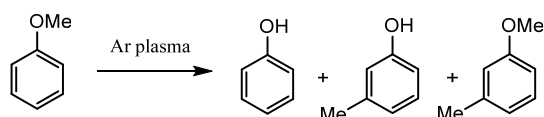
A microfluidic device²⁰⁵ was also tested for stilbene epoxidation. The liquid reaction mixture exiting the AC DBD plasma microreactor was fed back in for additional passes, allowing either a manual multi-pass, or a continuous recirculation process. In the latter, by varying the liquid

flow (solution of *trans*-stilbene in acetonitrile) and the gas flow (He with O₂ admixtures) individually, it was found that a short contact time of the liquid substrate and the gas bubble of 2 s increased the selectivity of the epoxidation reaction, albeit at a cost of decreased substrate conversion.²⁰⁶

The epoxidation of *cis*- and *trans*-stilbenes and other alkenes was also done by O atoms generated by the same plasma jet ignited in He with CO₂ admixtures (Scheme 4.6b).²⁰⁷ Interestingly, the formation of two stereoisomers, *trans*- and *cis*-stilbene oxides, was observed when *trans*-stilbene was exposed to plasma. This was explained by the different reactivity of the two states of atomic oxygen – O(¹D) and O(³P), both of which could be present in the plasma. The reaction with O(¹D) is stereoselective, where O(³D) epoxidises *trans*-stilbene into both *cis*-stilbene oxide (main product) and *trans*-stilbene oxide (minor product), respectively. The substrate range was also expanded and included styrene, β-pinene, etc., all of which yielded the desired epoxides with good selectivity.²⁰⁷ As mentioned previously, the efficacy of CO₂ conversion by plasma is often limited by the re-oxidation of the formed CO by O (or O₂ molecules to which they recombine), and improving it requires scavenging of the formed O species.²⁰⁸ The unsaturated bond of stilbene here is effectively a scavenger for atomic O, i.e. such a process can serve two purposes simultaneously: improve the CO₂ splitting and enable the alkene epoxidation. However, regardless of the source of O atoms, the efficiency of epoxide formation remains an open question in its current state, e.g. because of the potential scavenging of O atoms by the organic solvent.

Transformation of anisole into substituted phenols

A lot of effort is put into converting biomass into polymers, specifically via phenolic compounds which are important polymer building blocks. Plasma here is a benign alternative to high-temperature, high-pressure, and high-maintenance thermal catalytic processes.²⁰⁹ Anisole, a model for lignin-derived chemicals, was converted into phenol and various methylated products by an Ar plasma discharge in an AC DBD reactor with flowing liquid anisole.²¹⁰ The reaction was proposed to proceed via vibrational excitation of the C₆H₅OCH₃ molecule with subsequent loss of H or ·CH₃, which further reacted with the formed C₆H₅O· to yield C₆H₅OH and cresols (methylphenols) (Scheme 4.7). The side-products were methylanisoles formed in reactions of ·C₆H₄OCH₃ and the remaining anisole with ·CH₃, or via bimolecular trans-alkylation reactions. Varying the plasma-deposited energy, it was found that the maximal conversion of ca. 90% was achieved at higher plasma power, together with a good selectivity towards phenol (>50%). In contrast, lower plasma power resulted in 87% total selectivity towards methylated products (cresols/methylanisoles 1:1).²¹⁰ However, the potential of this process is drastically restricted by the noble gas plasma: its cost limits possible upscaling. At the same time, cheaper plasma feed gas (e.g. air) will likely result in undesirable (in this case) oxidation and nitration reactions.

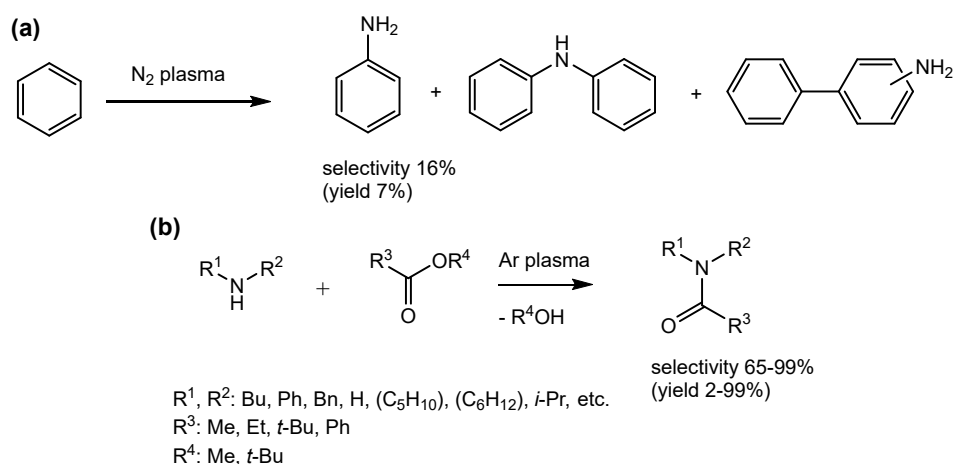


Scheme 4.7. Transformation of anisole into phenolics by plasma.

Amination and N-acylation

Aniline, another important precursor for plastics, can be produced via direct amination of benzene by N-containing plasmas. This is a greener alternative to the currently used methods, which involve first nitration, and then the reduction of the produced nitrobenzene with transition metal catalysts, with both steps done in the presence of highly corrosive acids (HNO₃ and HCl). Xu et al. used a planar DBD plasma reactor, fed with a mixture of N₂ and He.²¹¹ Liquid benzene positioned over a SiO₂ plate, or over oxide (SiO₂, MgO, Al₂O₃) beads, was exposed to plasma, allowing direct plasma-liquid interaction. The initial interaction was proposed to occur in the gas phase with the benzene vapour, where it was driven either by N₂* excited state or by charged species (N₂⁺ or electrons). Expectedly, the by-products of this gaseous phase reaction mixture were di- and triphenylamine, together with aminobiphenyl. Optimisation of reaction conditions (He admixture to N₂, oxide support, voltage, gas flow rate, etc.) gave the total yield of amination products of ca. 45%, but the main products were isomers of aminobiphenyl (Scheme 4.8a), while aniline yield was ca. 7%. Interestingly, this was achieved with the addition of small amounts of aniline to MgO beads over which benzene was distributed during plasma exposure.²¹¹

Unlike the reaction with N₂ plasma, where the formation of diarenes and diarene amines is inevitable because the substrate arene acts as a source of H for the amino group, direct amination of benzene with NH₃ plasma can avoid such by-products. Conceptually, the process resembled a combination of NH₃ plasma amination of ethylene,³² and the use of microfluidic devices for (ep)oxidation of arenes.^{203, 206} An AC plasma discharge in NH₃ was in contact with flowing liquid benzene in a microfluidic chip. Amination was proposed to proceed via the initial H abstraction from C₆H₆ by the H atom formed from NH₃ decomposition (into NH_x and H) in plasma. The resulting phenyl radical interacts with NH₃ or NH_x to yield aniline, while the main by-products are formed via dimerisation, and reduction with the loss of aromaticity. The yield of total amination products was 4% (with a total selectivity of 49%), half of which was aniline, whereas other saturated and unsaturated substrates (cyclohexane, cyclohexene, dodecene, etc.) gave much lower selectivity to aminated products.²¹²



Scheme 4.8. Plasma-driven C-N bond formation: **(a)** amination of benzene by N₂, and **(b)** N-acylation of amines by esters.

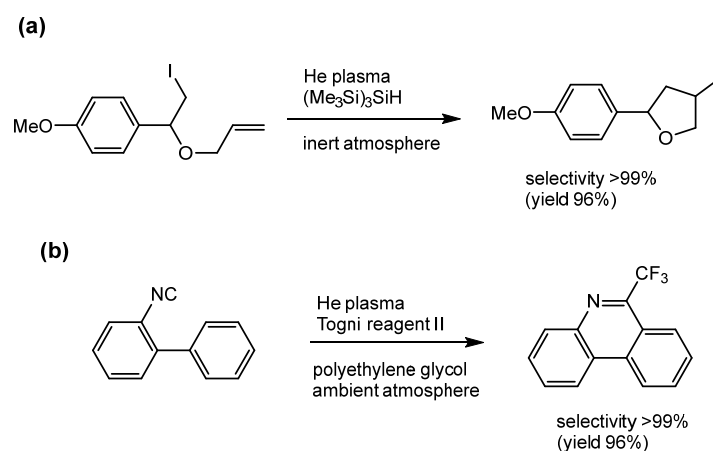
A similar process was proposed for N-acylation of primary and secondary amines.²¹³ A microfluidic device consisted of a flowing liquid mixture of an ester (acylating agent) and an amine substrate, in contact with an AC DBD discharge in Ar. One of the proposed mechanisms was the plasma cleavage of an ester into an acyl and an alkoxy radical. The latter abstracted H

from the amine, and the formed N-centred radical reacted with the acyl radical to yield an N-acylated product. The versatility of the reaction was demonstrated on a large variety of substrates, including secondary aliphatic/cyclic, and primary aliphatic/aromatic amines (Scheme 4.8b), with up to fully quantitative yields. This is an extremely appealing pathway for acylation of amines, in a solvent-free system without using highly unbenign agents (toxic metal complexes and solvents, cyanides, intense UV radiation).²¹³ However, the process is limited to using noble gases to avoid other by-products.

Cyclisation

The synthesis of macrocyclic imines (materials which exhibit properties relevant for industrial separation) suffers from non-selectivity of the imine bond formation: polymers and oligomers are the undesired by-products of the target cyclic compounds, and overcoming this requires a multi-step, multi-solvent synthetic process²¹⁴. In contrast, a single-step, one-pot synthesis was done in CH₂Cl₂ solutions containing cyclohexane-1,2-diamine and a range of aromatic *meta*- or *para*-dialdehyde, and exposed to an Ar AC plasma jet²¹⁵. Optimised conditions afforded high yields (e.g. 95% with benzene-1,4-dicarbaldehyde to yield a 3+3 imine macrocycle) after only 20 min of plasma exposure – in contrast to conventional synthesis which can take up to 24 h. Although the reaction was carried out with a noble gas and still with the use of a toxic solvent (which is very volatile and hence must play a role in the plasma-induced chemistry), this conceptually demonstrates that plasma can be used for synthetic cyclisation reactions with high selectivity.

Another example is C-C radical cyclisation. In section 4.1, we discussed plasma initiating radical reactions in water, with the ·OH radical starting the chain reaction. However, non-aqueous media, or solvent-free conditions, can also be used. An AC parallel-field He plasma jet consisting of a quartz tube with two Cu ring electrodes positioned on its outer surface⁵⁰ was used to initiate a reaction of deiodination of a substituted vinyl iodoxyethane (Scheme 4.9a). Screening of various conditions showed that the optimal chain transfer agent and H donor was tris(trimethylsilyl)silane, which also allowed running the reaction solvent-free. The presence of oxygen terminated the chain propagation, but the plasma exposure of a liquid mixture (consisting of the chain transfer agent and the substrate) under an inert atmosphere afforded quantitative yields of the product. The exact species initiating the chain process were not studied, but it may have proceeded via the initial abstraction of H from the H donor.¹⁹⁰



Scheme 4.9. Two C-C cyclisation reactions initiated by plasma: **(a)** solvent-free deiodination in the presence of chain transfer agent/H donor, and **(b)** trifluoromethylation in polyethylene glycol.

Another example is the use of Togni-II reagent for the radical trifluoromethylation with cyclisation (Scheme 4.9b).¹⁹⁰ Here, solvent-free conditions did not result in high yields. The use of non-volatile solvents was advocated, which afforded a selective 95% conversion of the substrate isocyanobiphenyl. Interestingly, exposing the solution of the substrate and the Togni-II reagent in polyethylene glycol to a He plasma jet in ambient air did not impede the reaction, possibly because O species were scavenged by the solvent, or their diffusion into the solvent was limited. The reaction was hypothesised to be initiated by the plasma-produced solvated electrons, and later this was also further confirmed under plasma-free electrochemical conditions.²¹⁶

Generally, plasma-initiated radical reactions are highly selective, unlike the oxidation or reduction reactions in wastewater where plasma RONS are stoichiometric reagents, but further optimisation studies are required to remove the restrictions on the choice of solvents, plasma feed gasses, etc.

5. Summary and outlook

In this review, we discussed organic reactions in liquids driven by their interaction with plasma in three applications: (i) wastewater treatment for degradation of pollutants, (ii) conversion of fossil- and bio-derived organics into H₂ or syngas, and (iii) preparative synthetic chemistry, as summarised in Figure 2.

Among these three fields, plasma-liquid systems with probably the highest TRL are those used in wastewater treatment. Plasma interacting with water generates a large variety of reactive species (radicals, ions, atoms, electrons, molecules, metastables), whose exact nature and quantity depend on the plasma reactor type, discharge gas, method of plasma-liquid contact, etc. In almost all scenarios, plasma causes partial evaporation of liquid, regardless of whether the plasma impinges onto the liquid surface, or plasma bubbles interact with the bulk liquid, or plasma is ignited within the liquid (in which case initially the liquid component/solvent is first heated up and then the plasma is ignited in the saturated vapour phase). This means that the transport of RONS into the liquid phase plays an important role in the process efficiency.

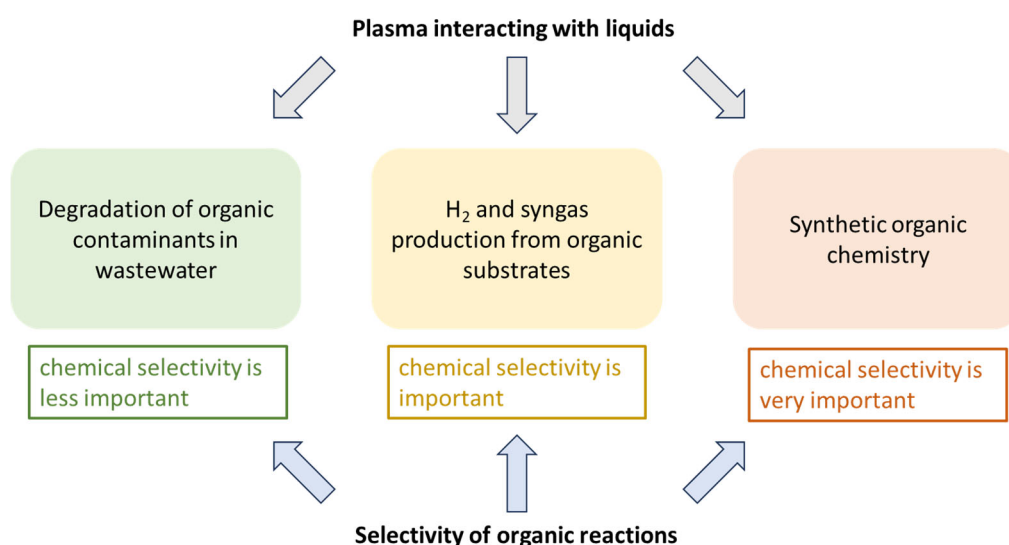


Figure 2. Conceptual diagram of selectivity of organic reactions in the three fields of application discussed in this work.

The RONS “cocktail” drives the degradation of organic pollutants in water in two generalised directions: oxidative pathway (by $\cdot\text{OH}$, O , $\cdot\text{OOH}/\text{O}_2\cdot^-$, H_2O_2 , O_3 , etc.) and reductive pathway (primarily by solvated electrons). While the former pathway meets a lot of competition from traditional, non-plasma pollutant removal methods, the latter is very efficient for removal of polyfluorinated compounds. In general, both pathways can occur in the plasma-liquid systems at the same time, leading to largely non-selective transformation. However, in the case of pollutant degradation, the selectivity of products of organic reactions is usually not the main focus: deep mineralisation is often desired, and the exact reactions leading to it are of lower importance.

Conversion of liquid organic compounds (higher hydrocarbons, alcohols) into H_2 or syngas is another application of plasma-liquid systems. Here, in-liquid plasmas or plasmas bubbled through the liquid (i.e., directly related to plasma-liquid milieu) are relatively scarce compared to gas phase conversion, where the organic substrate is introduced into the plasma in an aerosol form but is vaporised due to the heat of the plasma. In such processes, the selectivity is usually defined as a net H and C selectivity, with the focus on H_2 and CO . Obviously, the selectivity here defines the metrics of the process (e.g. energy cost per mol H_2 produced).

The final application is synthetic organic chemistry in liquids driven by plasma. This represents a shift in the paradigm of plasma-liquid reactivity: in preparative chemistry, not only the conversion of the substrate is non-destructive, but the selectivity towards specific products (achieved via specific pathways) is paramount. Two liquid milieus are distinguished: aqueous (conceptually resembling wastewater treatment) and organic (resembling the conversion of liquid organics for H_2 /syngas). Various reactions are performed with the help of plasma, forming various types of bonds (C-C, C-O, C-N) for different products. In aqueous media, the selectivity of reactions is low, the same as in the case of wastewater treatment when a substrate undergoes e.g. hydroxylation at multiple sites. When RONS generated by plasma are used as stoichiometric reagents, the selectivity is generally lower than when plasma is used as a radical initiator. In non-aqueous media, solvent-free conditions afford good selectivity and yield (as is the case for e.g. N-acylation).

However, despite the clear rising interest for synthetic organic chemistry in liquids, most of the methods listed here are nascent, and require much further studies and optimisation. One of the main factors hindering applicability of the synthetic processes is the restrictions on the plasma feed gas. In the aforementioned N-acylation and most other cases, the gas needs to be inert to avoid generation of RONS which can interact with the substrates and yield undesired by-products via reactions of hydroxylation, oxidation, nitration, nitrosylation, etc. This is the exact opposite of wastewater treatment, where oxygen or air are often used as feed gases.

Plasma offers an electrification-compliant green alternative to many conventional synthetic procedures, which often require toxic solvents, initiators, catalysts, or harsh conditions such as high temperatures or pressures. Future research aimed at feed gas-free plasmas generated directly in liquid, or with more ubiquitous gases (N_2 , O_2 , air) is required to realise the appealing potential of plasma for preparative organic chemistry.

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Conflict of interest

The authors declare that they do not have a competing financial or personal interest which could have influenced their opinions expressed in this manuscript.

Data availability statement

No experimental data were used in the preparation of this manuscript.

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Graphical abstract:

The unique processes at the plasma/liquid interface generate much interest for environmental applications involving the conversion of organic substrates: degradation of organic contaminants in wastewater, H₂/syngas production from organic substrates, and synthetic organic chemistry. In this review paper, these applications are discussed through the lens of non-selective or selective plasma conversion of organics. Special attention is paid to mechanisms and limitations of plasma applications for synthetic organic chemistry as they open new, more environmentally friendly pathways for organic reactions.

