Intensified and Electrified Monophasic and Biphasic Plasma Microreactors for the Production of Chemicals

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Highlights

- Two concepts are introduced to increase the selectivity and yield of plasma reactors: (1) biphasic gas/liquid flows and (2) single-step chemistry to chemicals.
- We demonstrate the first concept for producing hydrogen peroxide, the selective oxidation of ethane to alcohols, and the selective oxidation of paraffins obtained from the hydrogenolysis of polyethylene.
- We demonstrate the second concept to produce HCN.

1. Introduction

Sustainable and decentralized manufacturing of chemicals is essential for the sustainability and decarbonization of the chemical industry. Plasma is an electrification method that can activate chemical bonds at low temperatures. However, it is typically unselective, resulting in many products requiring extensive separations, and produces low concentrations and yields due to being indiscriminate of molecules by dissociating the product via the same electron impact mechanism. Further plasma processes attempt to replace existing processes by doing the chemistry like conventional processes. For example, HCN synthesis is done from methane and ammonia; the latter is a multistep process of a reformer, two water gas shift reactors, and ammonia synthesis. There is an opportunity to alter the chemical paths and reduce the number of chemical steps, increasing atom efficiency.

In this work, we present two strategies for intensifying plasma reactors. The first is the concept of a biphasic gas/liquid reactor where the liquid can serve as an absorber or evaporator and absorber, and the gas is where the plasma is ignited. The liquid temperature controls the concentration of radicals. We demonstrate the concept for hydrogen peroxide (H_2O_2) production, the selective oxidation of ethane to methanol and ethanol, and the oxidation of long alkanes to upgrade plastics catalytic recycling alkanes produced in our lab via hydrogenolysis of polyethylene. The second strategy demonstrates a single-step production of HCN. Below, we show representative results to demonstrate the concepts.

2. Methods

Our plasma microreactor consists of a coaxial dielectric barrier discharge (DBD) configuration as a modular, adaptable, and scalable intensified unit with a spiral tubular reactor through which liquid slugs flow in a continuous gas stream (Figure 1). The electrodes and tube lengths were adjusted to tune the residence time in the plasma. A gas mixture for a monophasic system and a gas/liquid H_2O steam is coded, and the plasma is ignited and sustained by a sinusoidal power supply. Gas chromatography was employed to analyze the liquid and gas phase composition.

3. Results and discussion

We first demonstrate the production of H_2O_2 to replace the energy and waste-intensive anthraquinone process. We investigated the H_2O_2 formation pathways using DMSO as ·OH radical scavenger, and found that H_2O_2 forms by dissolution of gaseous H_2O_2 at low interfacial areas and is enhanced probably due to the interfacial recombination of ·OH radicals at large gas-liquid interfacial area. The reactor temperature can also be externally controlled to intensify the production rate and energy yield of H_2O_2. Concentrations of up to 33 mM can be attained with a small-footprint reactor with a maximum energy yield of 4 g kWh^{-1}.

Next we demonstrate the selective upgrade of ethane (C_2H_6) to liquid ethanol (C_2H_5OH), methanol (CH_3OH), and acetic acid (CH_3COOH) in a catalyst-free, continuous, biphasic argon plasma microreactor. The liquid water (H_2O) evaporates and dissociates via plasma into $OH^{\cdot}$ radicals that perform the oxidation. The oxygenates are protected from the plasma discharge by directly absorbing into H_2O, which serves the dual role of an oxidizer and an absorber (Figure 2). The biphasic system is the first demonstration of reactive separation in plasma systems. We find a plasma-assisted path reminiscent of the low-temperature thermocatalytic ethane steam reforming, which leads to significant H_2 co-production. The gaseous stream also comprises CO_2 and C_2H_4. Up to 1.3 and 1 μmol min^{-1} of liquid C_2H_5OH and CH_3OH are attained, while carbon selectivity can be tuned from >70% liquid oxygenates to 60% C_2H_4. The desired overall reaction is R1. C_2H_6 dissociation followed by oxidation leads to the overall reaction R2.

$$\text{Plasma} - \text{induced ethane partial oxidation overall reactions:}$$

$$C_2H_6 + H_2O \rightarrow C_2H_5OH + H_2 \qquad (R1)$$

$$C_2H_6 + 2H_2O \rightarrow 2CH_3OH + H_2 \qquad (R2)$$

The products, CH_3OH and C_2H_5OH, can absorb into the aqueous phase and become protected from dissociation by the plasma, allowing their concentration to increase with residence time. The microreactor operates as a reactive absorption unit where the H_2O is the oxidizer and the absorber. This scheme can also yield significant fractions of gaseous H_2 stored or used for power generation and upgrading fuels, biomass, and plastics.

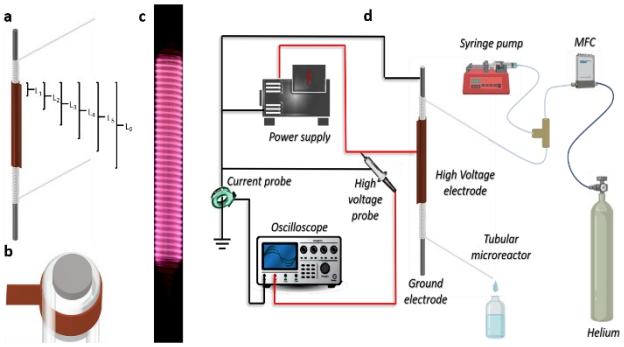

Figure 1. (a) Side and (b) top view of coaxial dielectric barrier discharge (DBD) microreactor assembly.

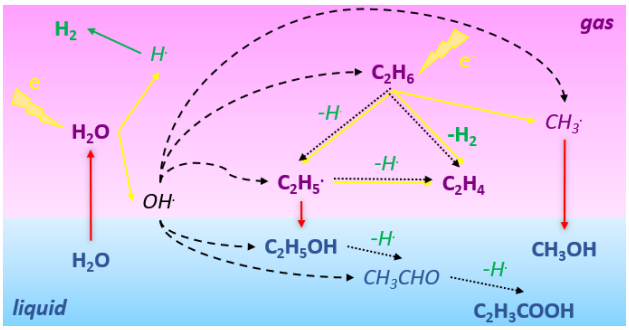

Figure 1. Simplified reaction scheme for the H_2O-assisted plasma-activation of C_2H_6. The yellow and black arrows represent electron impact and oxidation reactions, respectively. The red arrows indicate mass transfer between phases. The green arrows are related to radical recombination. Bold font is used for stable measured species, italic font indicates intermediate species.

4. Conclusions

We introduced two general concepts to increase the selectivity and yield of chemicals made by plasma. We demonstrated these concepts with three gas/liquid systems (H_2O_2 production from water, alcohol production from ethane and water, and oxygenates from paraffins and O_2) and the single step production of HCN. The plasma microreactor could epitomize a powerful process intensification tool for sustainable and distributed chemical manufacturing. The low footprint, electrified, modular set-up could pave the way for the valorization of underutilized shale gas resources in remote areas. We will compare energy efficiency and global warming potential for these processes compared to their conventional counterparts.

Keywords
Plasma, process intensification, process electrification, microreactors, novel reactors.