Plasma-Based CH₄ Conversion into Higher Hydrocarbons and H₂: Modeling to Reveal the Reaction Mechanisms of Different Plasma Sources

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ABSTRACT: Plasma is gaining interest for CH₄ conversion into higher hydrocarbons and H₂. However, the performance in terms of conversion and selectivity toward different hydrocarbons is different for different plasma types, and the underlying mechanisms are not yet fully understood. Therefore, we study here these mechanisms in different plasma sources, by means of a chemical kinetics model. The model is first validated by comparing the calculated conversions and hydrocarbon/H₂ selectivities with experimental results in these different plasma types and over a wide range of specific energy input (SEI) values. Our model predicts that vibrational–translational nonequilibrium is negligible in all CH₄ plasmas investigated, and instead, thermal conversion is important. Higher gas temperatures also lead to a more selective production of unsaturated hydrocarbons (mainly C₂H₂) due to neutral dissociation of CH₄ and subsequent dehydrogenation processes, while three-body recombination reactions into saturated hydrocarbons (mainly C₂H₆, but also higher hydrocarbons) are dominant in low temperature plasmas.

1. INTRODUCTION

The conversion of methane (CH₄) into higher hydrocarbons and H₂ is gaining interest as an alternative to steam reforming of crude-oil derivatives to form light olefins.¹ These olefins are the main building blocks in the chemical industry for fibers, synthetic rubbers, and other organic compounds.²,³ Usually, CH₄ conversion is performed thermally, using high energy input and temperatures to activate the molecule.⁴ Catalysts can make the process more efficient and/or selective, but catalyst instability due to carbon deposition is a major drawback.⁵

Plasma technology is gaining increasing interest for the nonoxidative conversion of CH₄, overcoming most of the drawbacks of thermal processes.⁶ Plasma is created by applying electric energy to a gas. It is an ionized gas, consisting of various chemically active species (i.e., various types of radicals, ions, excited atoms and molecules, and electrons), besides the neutral gas molecules. The electrons in the plasma gain most of the applied electric energy, because of their small mass, and they activate the molecules by excitation, ionization, and dissociation, creating the above-mentioned reactive species, which can further react to form new molecules. This allows chemical conversions to occur at lower temperatures (even up to room temperature) than in thermal conditions.⁷ Plasma is also very flexible and can easily be switched on/off, so it can use intermittent green electricity, which cannot be stored on the grid.⁸

Various types of plasma configurations have been applied already for CH₄ conversion, as summarized by Scapinello et al.⁹ The most commonly used plasma types are dielectric barrier discharges (DBDs), microwave (MW), and gliding arc (GA) plasmas. DBDs are created by applying an electric potential difference between two electrodes, of which at least one is covered by a dielectric barrier. They typically operate at (or slightly above) room temperature, and conversions were reported in the range between 1%⁷ and 47%,⁸ for a specific energy input (SEI, i.e., ratio of plasma power over gas flow rate) ranging between 0.1 and 300 kJ L⁻¹. Ethane (C₂H₆) is one of the main products formed, with selectivities ranging between 20%⁸ and ca. 60%,⁹ followed by the other C₂ hydrocarbons (i.e., ethylene (C₂H₄) and acetylene (C₂H₂)), C₃–C₅ compounds and soot. According to Scapinello et al.⁹ the best overall result in a DBD, in terms of energy efficiency, conversion and product formation, was obtained by Xu and Tu,¹⁰ with a CH₄ conversion of 11%, C₂H₆ selectivity of 34%, a selectivity of 19% for the other C₂ hydrocarbons, and the remainder being C₃–C₅ hydrocarbons and soot. These results were obtained at an SEI of 9 kJ L⁻¹ (or 2.1 eV molec⁻¹), yielding a rather high energy cost for CH₄ conversion of 20 eV molec⁻¹ and a low energy efficiency of 3.4%.

MW and GA plasmas operate at higher temperatures (typically 1000–3000 K), and are therefore called “warm plasmas.”⁶,¹¹ They produce more unsaturated compounds, such
as C$_2$H$_4$. The conversions in MW plasmas range from 5% until above 90%,\textsuperscript{12} at SEI values varying between 6.8 and 360 kJ L$^{-1}$\textsuperscript{12,13}.\textsuperscript{12} The corresponding C$_2$H$_4$ selectivities vary from below 10% until approximately 90%,\textsuperscript{12,13} depending on the input power and gas pressure used, with higher pressures and/or powers producing more C$_2$H$_4$. The best result was obtained by Heintze and Magureanu\textsuperscript{10} at low pressure (30 mbar) and an SEI of 28 kJ L$^{-1}$\textsuperscript{10}, yielding a CH$_4$ conversion of 94%, an C$_2$H$_4$ selectivity of 65%, followed mainly by C$_2$H$_2$ (10%) and C$_2$H$_6$ (2%), and an energy cost of 6.9 eV molec$^{-1}$ or energy efficiency of 23%.

Likewise, for GA plasmas, CH$_4$ conversions were reported from 0.2%\textsuperscript{15} until 92%,\textsuperscript{11} for SEI values between 2 and 42 kJ L$^{-1}$\textsuperscript{11,16} and with C$_2$H$_4$ selectivities between 5%\textsuperscript{17} and nearly 100%.\textsuperscript{15} The best result was obtained by Polak,\textsuperscript{18} reporting a CH$_4$ conversion of 86% and an C$_2$H$_4$ selectivity of 88%, followed by C$_2$H$_2$ (3%), at an SEI of 14 kJ L$^{-1}$\textsuperscript{18} (or 3.2 eV molec$^{-1}$). This resulted in a quite high energy efficiency of 49% and a low energy cost of 3.7 eV molec$^{-1}$.

Although the above plasma types show potential for CH$_4$ conversion into light olefins, only high power thermal arc discharges are up to now able to approach thermodynamic equilibrium conversions.\textsuperscript{18} Therefore, more research is needed to improve the performance of the above plasma reactors. Specifically, we need to gain more knowledge on the most important reaction pathways in these kind of plasmas, to optimize the formation of higher hydrocarbons. Indeed, it is clear from the above that different plasma reactors yield very different hydrocarbon selectivities and CH$_4$ conversions, but the underlying reasons have not yet been studied in detail. A broad picture of possible pathways was presented by Scapinello et al.,\textsuperscript{15} but to our knowledge, the importance of the different pathways in different reactors has not yet been clarified.

Therefore, in the present paper, we study the different reaction pathways of CH$_4$ conversion and (mainly) C$_2$ hydrocarbon and H$_2$ formation, using 0D chemical kinetics modeling, in the three most important plasma reactors discussed above.

A 0D chemical kinetics model is the most appropriate choice for describing a detailed plasma chemistry. In literature, some models have been presented already for CH$_4$ conversion in a DBD,\textsuperscript{19–22} MW,\textsuperscript{23} and GA plasma.\textsuperscript{24} Also, CH$_4$/H$_2$ mixtures were modeled in moderate pressure MW plasmas, albeit for another application, i.e., plasma-assisted diamond deposition.\textsuperscript{25,26} However, electron impact excitation of the internal degrees of freedom, such as vibrational and rotational excitation of CH$_4$, which might be important in warm plasmas (MW and GA plasmas) have not yet been taken into account into these plasma models. Moreover, a detailed comparison between the mechanisms in DBD, GA, and MW plasmas, based on such models, has not been performed yet. Hence, this will be the focus of the present paper.

### 2. MODEL DESCRIPTION

First, we will give a short outline of the 0D model and the chemistry used to describe CH$_4$ conversion, followed by explaining the assumptions made in the 0D approach to describe the different plasma reactors.

#### 2.1. 0D Model Equations and Chemistry

The conservation eq 1 in a 0D model is solved for all species (see below):

\[
\frac{dn_i}{dt} = \sum_{j=1}^{l} ((a^R_{ij} - a^L_{ij})R) \tag{1}
\]

where $n_i$ is the density of species $i$ (in cm$^{-3}$), $j$ the total number of reactions in which that particular species is produced or consumed, $a^R_{ij}$ and $a^L_{ij}$ the stoichiometric coefficients at the left-hand side and right-hand side of a particular reaction equation, and $R_i$ the rate of that reaction (in cm$^{-3}$ s$^{-1}$), given by

\[
R_i = k_i \prod_s n_s^{a^R_{is}} \tag{2}
\]

where $k_i$ is the rate constant (in cm$^{3}$ s$^{-1}$ or cm$^6$ s$^{-1}$ for two-body or three-body reactions, respectively) and $a_{is}$ was defined above.

The chemical set applied in this study is based on the pure CH$_4$ chemistry part of the models developed by Snoeckx et al.\textsuperscript{27} and Cleiren et al.,\textsuperscript{28} extended with excitation and relaxation of the lowest vibrational and rotational levels. The set contains 57 different species (see Table 1), i.e., eight ground state molecules, 12 radicals, 16 ions, the electrons, six excited species of CH$_4$, and 14 of H$_2$. These species interact with each other through various chemical reactions. In total, 2174 reactions are included in our model, of which 378 are electron impact reaction, 380 are ionic reactions, 196 are vibration-vibration (VV) relaxation reactions for CH$_4$ and H$_2$.

We solve this 0D model with the ZDPlaskin code.\textsuperscript{29} The rate coefficients of the electron impact reactions are calculated from the corresponding energy-dependent cross sections and the electron energy distribution function, using the built-in Boltzmann solver BOLSIG+.\textsuperscript{30} The rate coefficients of the other (i.e., heavy particle) reactions are adopted from literature. They are often a function of the gas temperature. Details of the CH$_4$ and H$_2$ vibrational levels and their reactions are given in the Supporting Information (SI, Table S.1). In addition, the full list of all the reactions and their corresponding rate coefficients, as well as the references of the cross sections used, are presented in Tables S.2–S.5 of the SI.

#### 2.2. Modeling the Different Plasma Reactors with a 0D Approach

##### 2.2.1. General Aspects

In all simulations, we made some general approximations, independent of the plasma reactor used:

1. Gas expansion can occur upon conversion of CH$_4$, e.g., when two new species are formed out of one, so we calculate the gas pressure and mass flow rate at every time step from the actual species densities, gas temperature, and velocity. To conserve the gas pressure and mass flow rate, the species densities (as calculated with the above conservation equations; see eq 1) and velocities are then corrected to account for this effect, following the method of Kozak and Bogaerts.\textsuperscript{31}
2. The gas temperature is calculated self-consistently for the MW plasma in the same manner as done by Kozak and Bogaerts, and a detailed description is given in the SI. For the DBD and the GA plasma, we adopt a temperature profile, as explained below.

3. A 0D model calculates the species densities as a function of time only, and neglects spatial variations. However, the time evolution can be translated into a spatial evolution (i.e., as a function of position in the plasma reactor) by means of the gas flow rate. In this way, local variations in the applied plasma power can be implemented in the model, as power pulses as a function of time (see details below).

4. The conversion of CH₄ is calculated as

\[
X_{\text{CH}_4}(\%) = 100\% \frac{n_{\text{CH}_4,i}(\text{cm}^{-3})v_{i}(\text{cm} \text{s}^{-1}) - n_{\text{CH}_4,f}(\text{cm}^{-3})v_{f}(\text{cm} \text{s}^{-1})}{n_{\text{CH}_4,i}(\text{cm}^{-3})v_{i}(\text{cm} \text{s}^{-1}) - n_{\text{CH}_4,f}(\text{cm}^{-3})v_{f}(\text{cm} \text{s}^{-1})}
\]

where \(n_{\text{CH}_4,i}\) and \(n_{\text{CH}_4,f}\) are the densities of CH₄ at the end and the beginning of the simulation, respectively, and \(v_{i}\) and \(v_{f}\) are the corresponding velocities.

5. The selectivities of the different hydrocarbons are calculated as

\[
S_{\text{C}_x\text{H}_y}(\%) = 100\% \frac{xn_{\text{C}_x\text{H}_y}(\text{cm}^{-3})v_{y}(\text{cm} \text{s}^{-1})}{n_{\text{C}_x\text{H}_y}(\text{cm}^{-3})v_{y}(\text{cm} \text{s}^{-1}) - n_{\text{CH}_4}(\text{cm}^{-3})v_{f}(\text{cm} \text{s}^{-1})}
\]

with \(n_{\text{C}_x\text{H}_y}\) the density of the hydrocarbon. Note that these selectivities are C-based. We also define the H₂ selectivity, which is H-based:

\[
S_{\text{H}_2}(\%) = 100\% \frac{0.5nx_{\text{H}_2}(\text{cm}^{-3})v_{i}(\text{cm} \text{s}^{-1})}{n_{\text{H}_2}(\text{cm}^{-3})v_{i}(\text{cm} \text{s}^{-1}) - n_{\text{CH}_4}(\text{cm}^{-3})v_{f}(\text{cm} \text{s}^{-1})}
\]

6. The specific energy input SEI deposited on the initial CH₄ flow is calculated as

\[
\text{SEI}(\text{kJ L}^{-1}) = \frac{P(\text{W})60(\text{s min}^{-1})}{\Phi(\text{sccm})}
\]

\(P\) is the deposited power in the plasma and \(\Phi\) the flow rate. This SEI value can be converted into eV molec⁻¹ as follows:

\[
\text{SEI}(\text{eV molec}^{-1}) = \frac{\text{SEI}(\text{kJ L}^{-1})16.24 \times 10^{-10}(\text{eV} \text{ mL}^{-1})24.5(\text{L} \text{ mol}^{-1})\Phi(101325 \text{ Pa})}{6.022 \times 10^{23}(\text{molec mol}^{-1})p(\text{Pa})}
\]

with \(p_0\) and \(p\) the atmospheric pressure and pressure inside the reactor, respectively. This allows us to calculate the energy cost for CH₄ conversion (either in kJ L⁻¹ or eV molec⁻¹, depending on the unit of SEI):

\[
\text{EC} = \frac{\text{SEI} \times 100\%}{X_{\text{CH}_4}(\%)}
\]

where \(\Phi\) is the fraction of CH₄ present in the feed gas.

2.2.2. Dielectric Barrier Discharge (DBD). As mentioned in the Introduction, a DBD is created by applying an electric potential difference between two electrodes, of which at least one is covered by a dielectric barrier. A DBD in CH₄ exhibits filamentary behavior, i.e., microdischarges between these electrodes. Hence, the CH₄ molecules will pass through several microdischarge filaments on their way throughout the reactor, which we mimic in the model as microdischarge power pulses as a function of time (cf. previous section). We applied our model to the DBD reactor of Xu and Tu, and to the micro-DBD reactor of Wang et al., in order to first verify our modeling results with their experiments, as a validation of our model. Indeed, these results are a good representation of other DBD reactor studies on CH₄ conversion, as reviewed by Scapinello et al. Figure 1 illustrates a schematic picture of the cylindrical DBD reactor of Xu and Tu, which has a length of 9 cm and a discharge gap of 0.3 cm, resulting in a discharge volume of 13.6 cm³. The micro-DBD reactor of Wang et al. looks similar, but with a discharge gap of 0.09 cm, a length of 20 cm, and a discharge volume of 1.4 cm³.

We assume that the plasma power is uniformly deposited in pulses (or microdischarges) with lifetimes of 11 ns for 15 W and 14 ns for 55 W, based on linear interpolation of the micro-discharge lifetime as a function of power, adopted from Ozkan et al. During one AC period in a DBD reactor, these authors measured approximately 400 microdischarges at 50 W and 500 microdischarges at 100 W, with an almost linear increase of the number of discharges as a function of power. The local power deposition per pulse \(P_{\text{pulse}}\) (in W) is defined as

\[
P_{\text{pulse}} = \frac{P_{\text{total}}}{N_{\text{pulse}}\Phi_{\text{AC}}}\]

Figure 1. Schematic illustration of a typical cylindrical DBD reactor, based on the design of Xu and Tu (a), representation of the filaments in this reactor (b), and the corresponding power density profile as a function of time in this DBD reactor, for three pulses, at an input power of 15 and 55 W and a frequency of the applied power of 20 kHz (c).
where $P_{\text{total}}$ (in W) is the global power input, which is varied between 15 and 55 W, based on the experiments of Xu and Tu, and between 10 and 30 W for the experiments of Wang et al. $N_{\text{pulse}}$ is the number of pulses per AC cycle, $f_{\text{AC}}$ (in Hz) the frequency of the applied power, which is 20 kHz in our simulations, again based on Xu and Tu and Wang et al., and $t_{\text{pulse}}$ (in s) is the lifetime of the microdischarges (see above). Each of these microdischarges can be represented as a cylinder with a typical radius of ~0.13 mm and a length equal to the discharge gap. Following Snoeckx et al., we assume that every molecule passes such a microdischarge every 100 half cycles, irrespective of power deposited. Detailed information on how the microdischarges are treated in the model, including the number of pulses per AC cycle and the temperature, is given in the SI.

2.2.3. Microwave (MW) Plasma. According to Scapinello et al., the majority of results for CH$_4$ conversion in MW plasmas were obtained by Heintze and Magureanu at reduced pressure, and by Shen et al. at atmospheric pressure. Both reactors are so-called surface wave MW plasmas, where microwave power is applied from the side, through a waveguide, to a cylindrical tube through which the gas flows (see schematic diagram in Figure 2).

Hence, we applied our model to the wide range of conditions in both studies, to validate our model. Details of both reactor configurations and discharge conditions, and the assumptions made in our model on power deposition and corresponding temperature in the plasma, are given in the SI.

2.2.4. Gliding Arc (GA) Plasma. The results on GA performance, as reviewed by Scapinello et al., are quite scattered. A classical GA is formed between two flat converging electrodes, between which an electric potential difference is applied, creating an arc discharge, that glides along the electrodes under influence of the gas flow, toward rising interelectrode distance, until it extinguishes and a new arc is formed at the shortest interelectrode distance. However, the residence time of the gas inside the arc plasma is quite limited in classical GA discharges. For this reason, a cylindrical GA discharge, also called gliding arc plasmotron (GAP), was developed by Nunnally et al., and showed promising results for CO$_2$ splitting and dry reforming of CH$_4$. Therefore, we performed experiments in this GAP for pure CH$_4$ conversion to validate our model. A schematic picture of this GAP configuration is given in Figure 3.

It consists of a cylindrical reactor body (at cathode potential) and a reactor outlet (at anode potential). The gas flows in through six tangential inlets, creating a vortex flow. When the anode (= outlet) diameter is smaller than the cathode (= reactor body) diameter, the incoming gas will not immediately escape the reactor through the outlet at the bottom of the reactor, as it follows a vortex flow with larger diameter, so it will be forced upward in the cathodic part of the reactor, in a so-called forward vortex flow (FVF) pattern. When the spiraling gas arrives at the top of the reactor, the rotational speed will be reduced due to friction and inertia, and it will start to move downward in a smaller vortex, toward the outlet at the bottom, i.e., in a reverse vortex flow (RVF). The latter stabilizes the arc in the center of the reactor and it minimizes heat losses toward the walls. In this way, the residence time inside the arc is longer than in classical GA discharges, with a larger plasma volume. Therefore, the performance in terms of gas conversion is generally better than in classical GA discharges.

The arc plasma in a GAP is confined within the inner vortex and is more or less uniform, allowing a straightforward description of this GA configuration with our 0D model. Moreover, the arc dimensions change little with electric current, as investigated by Trenchev et al. We assume that the arc has a diameter of 4 mm, as in our earlier simulations. This corresponds to an arc volume of 383 mm$^3$. Right next to the arc, there is still a warm zone until the edge of the inner vortex, where the temperature is still above 1000 K, and thus where thermal CH$_4$ conversion can still take place.
In both the experiments and simulations, we did not use pure CH$_4$, as the latter did not allow plasma ignition in our GAP reactor. Therefore, we added between 80% and 50% N$_2$, and consequently, we expanded the chemistry in our model with N$_2$ and CH$_4^{-}$N$_2$ chemistry, as explained in the SI. The power deposited inside the plasma was 224 W and the flow rate was 10 L min$^{-1}$. Based on earlier 3D fluid dynamics calculations by Trenchev et al.$^{44}$ this corresponds to a velocity of 196 cm s$^{-1}$ and a residence time of 15 ms. The SEI value is 1.3 kJ L$^{-1}$.

3. RESULTS AND DISCUSSION

In the following sections, we will always first compare the calculated CH$_4$ conversion and energy cost with experimental data, as well as the selectivities of the most important hydrocarbons (and H$_2$ when available), for a wide range of conditions, to verify whether the model predicts the right chemistry in each of the plasma sources. Subsequently, we can use the model to elucidate the underlying reaction pathways for CH$_4$ conversion into higher hydrocarbons and H$_2$, in DBD, MW, and GA plasmas. It should be noted that only C atom formation, but no solid carbon formation is included in our model, because we only describe the gas phase chemistry. Furthermore, it was stated in the experimental papers to be always below 10% in the DBD and MW plasma at atmospheric pressure,$^{10,14,32}$ while in the MW plasma at reduced pressure, it was also stated to be negligible in the pulsed mode.$^{12}$ In the MW plasma at reduced pressure in continuous mode and in our own GAP experiments, however, significant solid carbon formation was observed, so in the future, we should improve our model to account for it, by adding surface processes.

3.1. DBD Plasma. 3.1.1. Comparison of Calculated and Measured CH$_4$ Conversion, Energy Cost, and Product Selectivities. The calculated and experimental results for CH$_4$ conversion, energy cost, and selectivities of the most important hydrocarbons and H$_2$ in the DBD reactor of Xu and Tu$^{10}$ are plotted as a function of flow rate and plasma power in Figures 4 and 5, respectively. The experimental and calculated data follow (more or less) the same trend with increasing flow rate. The largest discrepancies are seen for the selectivities of C$_2$H$_6$ and C$_2$H$_2$ (or C$_2$H$_4$) with maximum relative discrepancies of 62% for C$_2$H$_6$ at 50 mL min$^{-1}$ and 53% for C$_2$H$_2$ (or C$_2$H$_4$) at 300 mL min$^{-1}$ (see Figure 4). Also the trends as a function of plasma power are in reasonable agreement, except for the C$_2$H$_6$ selectivity, which decreases in our model, whereas the experiments indicate a small rise. The largest discrepancy for the C$_2$H$_6$ selectivity is however still only 31% (see Figure 5). The average discrepancy between the calculated and experimental results is 25%, which is satisfactory, in view of the complex chemistry and the assumptions made in the 0D model. Hence, we believe the model is able to elucidate the most important mechanisms in this DBD discharge.

The calculated and experimental conversions, energy costs and product selectivities for the DBD reactor of Wang et al.$^{32}$ are plotted in Figures 6 and 7, as a function of flow rate and plasma power, respectively. The H$_2$ selectivity was not measured as a function of flow rate, and therefore, only the calculated H$_2$ selectivities are shown in Figure 6. Again, the conversion, energy cost, and selectivities generally follow the same trends. Note that the energy cost is rather constant in the model, while the experimental values slightly drop as a function of flow rate (see Figure 6), but this is because the measured conversion drops more slowly than the calculated values at rising flow rate (and thus lower SEI). Indeed, when the flow rate rises by a factor 3 and thus, the SEI drops by a factor 3, at constant power, the calculated conversion drops by a factor 3 as well (thus explaining the constant energy cost), while the measured conversion only drops by a factor 2 (thus explaining why the energy cost slightly

![Figure 4. Calculated (dashed lines) and experimental (solid lines) CH$_4$ conversions and energy costs (a), as well as selectivities of the most important hydrocarbons and H$_2$ formed (b), as a function of flow rate, at a plasma power of 45 W in an atmospheric pressure DBD reactor. The experimental results are adopted from Xu and Tu.$^{10}$](https://dx.doi.org/10.1021/acs.jpcc.0c00082)

![Figure 5. Calculated (dashed lines) and experimental (solid lines) CH$_4$ conversions and energy costs (a), as well as selectivities of the most important hydrocarbons and H$_2$ formed (b), as a function of plasma power, at a flow rate of 100 mL min$^{-1}$ in an atmospheric pressure DBD reactor. The experimental results are adopted from Xu and Tu.$^{10}$](https://dx.doi.org/10.1021/acs.jpcc.0c00082)
drops). In addition, also the C2H2/C2H4 selectivities show some discrepancy, because the experimental data slightly drop and the calculation results slightly rise upon increasing plasma power (see Figure 7). However, the maximum relative difference is about 50%, which is still reasonable, in view of the assumptions made in the 0D model. Also the absolute values of the calculated and experimental results are in satisfactory agreement, except for the C3H8/C3H6 selectivities, which exhibit a maximum discrepancy of 72% at a plasma power of 15 W and a flow rate of 20.2 mL min\(^{-1}\) (see Figure 7). The average discrepancy between the calculated and experimental results is 37%, which we believe is good enough for explaining the underlying chemistry in a DBD reactor.

In both reactors, the conversions vary between 7% and 21%, decreasing with rising flow rate and increasing with power. Based on the conditions used, this corresponds to energy costs varying between 82 kJ L\(^{-1}\) (or 19 eV molec\(^{-1}\)) at a plasma power of 15 W and a flow rate of 100 mL min\(^{-1}\) (i.e., SEI = 9 kJ L\(^{-1}\), for the conditions of Xu and Tu\(^{10}\) Figure 5), up to 509 kJ L\(^{-1}\) (or 118 eV molec\(^{-1}\)) at a plasma power of 30 W and a flow rate of 20.2 mL min\(^{-1}\) (i.e., SEI = 89 kJ L\(^{-1}\), for the conditions of Wang et al.\(^{32}\) see Figure 7). The average energy cost for CH4 conversion for all conditions studied is 259 kJ L\(^{-1}\) (or 60 eV molec\(^{-1}\)), which is very high. Both in the model and experiments, C2H6 is by far the most important hydrocarbon, followed by C2H2 and C2H4, C4H10, and finally C3H8. Other (unsaturated or higher) hydrocarbons were not reported in both papers, but according to our model, C5H12 can also be formed, and further polymerization toward C6 and higher hydrocarbons is also possible. In addition, H2 is formed in large amounts, both in the experiments and our model.

3.1.2. Underlying Reaction Pathways. The most important reactions in the DBD plasma are visualized in Figure 8. The thickness of the arrow lines is a measure for the importance of the reactions, determined by the reaction rates, as calculated in the model. These calculated rates are listed in the SI (Table S.6).

Figure 6. Calculated (dashed lines) and experimental (solid lines) CH4 conversions and energy costs (a), as well as selectivities of the most important hydrocarbons and H2 formed (b), as a function of flow rate, at a plasma power of 25 W in an atmospheric pressure DBD reactor. The experimental results are adopted from Wang et al.\(^{12}\)

Figure 7. Calculated (dashed lines) and experimental (solid lines) CH4 conversions and energy costs (a), as well as selectivities of the most important hydrocarbons and H2 formed (b), as a function of plasma power, at a flow rate of 20.24 mL min\(^{-1}\) in an atmospheric pressure DBD reactor. The experimental results are adopted from Wang et al.\(^{32}\)

Figure 8. Most important net reaction pathways in a DBD at atmospheric pressure. Blue, pink, yellow, green, and orange arrow lines represent electron impact reactions, three-body reactions, two-body reactions with H atoms, reactions with hydrocarbon molecules or radicals, and two-body reactions with H2, respectively. The thickness of the arrow lines is proportional to the reaction rate, while the size of the boxes is proportional to the species density, as calculated in the model. The black boxes represent stable molecules and the white boxes intermediates (radicals or ions).

Figure 8. Most important net reaction pathways in a DBD at atmospheric pressure. Blue, pink, yellow, green, and orange arrow lines represent electron impact reactions, three-body reactions, two-body reactions with H atoms, reactions with hydrocarbon molecules or radicals, and two-body reactions with H2, respectively. The thickness of the arrow lines is proportional to the reaction rate, while the size of the boxes is proportional to the species density, as calculated in the model. The black boxes represent stable molecules and the white boxes intermediates (radicals or ions).
CH4 is mainly converted by electron impact dissociation into CH radicals (e− + CH4 → e− + CH3 + H), as well as into CH2 and CH radicals (e− + CH4 → e− + CH3 + H2 and e− + CH4 → e− + CH + H + H). The dissociation into CH2 and H2 (e− + CH4 → e− + CH3 + H2) is one of the most important H2 formation processes (together with e− + C3H6 → e− + C2H4 + H2; see below).

In addition, CH4 undergoes electron impact ionization and dissociative ionization (e− + CH4 → e− + CH3 + e and e− + CH4 → e− + e− + CH3 + H). The CH3+ and CH4+ ions formed in this way are not indicated as separate species in Figure 8, as they quickly react with CH4 forming C2H5+ (CH3+ + CH4 → C2H5+ + H2) or CH4+ (CH3+ + CH2 + CH3). The CH3 radicals partially recombine with H (CH3 + H + M → CH4 + M) forming again CH4, but they also recombine with another CH3 radical (CH3 + CH3 + M → C2H4 + M) to form C2H4, which is the most important production mechanism of C2H4, and it occurs mainly in the microdischarge pulses of the DBD, where the CH3 radicals as necessary building blocks are formed.

C2H6 is partially converted into C2H2 by electron impact dissociation (e− + C2H6 → e− + C2H4 + H2), which is the main population mechanism of C2H2, and one of the main population mechanisms of H2 (cf. above). In addition, C2H2 is also formed upon (radical) recombination reactions (CH4 + CH2 → C2H2 + H) and CH3 + CH → C2H2 + H).

C2H6 partially recombines with H into C2H4 (C2H2 + H + M → C2H2 + M), and C2H4 recombines further with C2H6 into C2H10 (C2H4 + C2H2 + M → C2H10 + M), as well as with H (C2H2 + H + M → C2H2 + H2) forming again two CH2 radicals, and with CH3 (C2H4 + C2H2 + M → C2H4 + M) forming C2H4. The latter reaction is however less important than the other two reactions, explaining why C2H10 was formed in larger amounts than C2H6/C2H4 in the experiments of Xu and Tu (see Figures 4 and 5). Moreover, C2H2 also undergoes electron impact dissociation (e− + C2H2 → e− + C2H2 + H2 and e− + C2H2 → e− + C2H2 + H2).

In addition, C2H2 and C2H4 react with CH3+ ions, forming C2H5+ (CH3+ + C2H2 → C2H5+ + H2 + CH4 and CH2+ + C2H2 → C2H3+ + CH3). C2H5+ is an important intermediate for the formation of C2H4 and C2H6 by dissociative recombination with electrons (e− + C2H5+ → C2H4 + H + H, e− + C2H5+ → C2H6 + H2 + H and e− + C2H5+ → C2H2 + H + H + H). The C2H radicals mainly recombine with C2H radicals into C2H4 (C2H3+ + C2H4 + M → C2H4 + M), as well as with H (C2H3+ + H → C2H2 + H2) forming C2H2.

C4H10 undergoes electron impact dissociation into C2H2 (e− + C4H10 → e− + C2H4 + CH2), but it mainly recombines with H, forming C2H4 (C2H4 + H + M → C2H4 + M). The latter radical quickly forms C2H4 upon reaction with H2 (C2H4 + H2 → C2H4 + H), as well as by three-body recombination with H (C2H4 + H + M → C2H4 + M).

C5H12 undergoes electron impact dissociation (e− + C5H12 → e− + C2H4 + C3H6 + H2) or it recombines with CH4 into C2H10 (C2H4 + C3H6 + M → C2H10 + M). Finally, C2H10 recombines with CH2 radicals into C2H12 (C2H10 + CH2 + M → C2H12 + M), which will further react into the formation of higher hydrocarbons by the same type of recombination reaction.

Hence it is clear that in a DBD electron impact dissociation processes are predominant. They create radicals, which mainly recombine with other radicals or H atoms, due to the lower temperatures, forming especially the saturated hydrocarbons, such as C2H6, C3H8, and C4H10.

### 3.2. MW Plasma

#### 3.2.1. Comparison of Calculated and Measured CH4 Conversion, Energy Cost, and Product Selectivities

The experimental and calculated CH4 conversions, energy costs, and selectivities of the most important hydrocarbons are plotted as a function of SEI in Figures 9 and 10, for a MW discharge at reduced pressure, i.e., 30 mbar, for a continuous and a pulsed discharge, respectively. Again, no H2 selectivities were reported in the experiments, so only the calculated values are given. In the pulsed regime, we also compare the calculated and measured gas temperature in Figure 10. Figures 11 and 12 show the experimental and calculated CH4 conversions, energy costs, and most important product selectivities in a MW discharge at atmospheric pressure, as a function of power and flow rate, respectively. Note that these experiments were performed in a CH4/H2 mixture, so the H2 selectivities could not be determined, since H2 is also a reactant.

In general, the difference between the calculated and experimental results is higher for lower powers and reduced pressure than for higher pressures and higher powers. The C2H2 selectivities in the reduced pressure MW plasma in continuous mode show the largest discrepancies, even up to almost a factor of 5 (i.e., calculated C2H2 selectivity of 5% versus 23%, for an SEI value of 12 kJ L−1). The reason is probably the underestimation of the gas temperature and the assumption that the power is evenly distributed over the whole radial distance of the reactor tube. In the atmospheric pressure MW plasma the largest discrepancies are found for the C2H4 selectivities, i.e., up to a factor of 6 (calculated C2H4 selectivity of 3% versus 18%, at 400 W and 500 mL min−1; see Figure 11). Nevertheless, in both the reduced pressure and atmospheric pressure MW plasma the...
Experimental and calculated results show the same trend and on average the discrepancy between calculated and experimental results is 40% for the reduced pressure MW plasma and 44% for the atmospheric pressure plasma. In addition, the difference between calculated and measured gas temperature in the pulsed reduced pressure MW plasma is less than 12%, so we believe that a qualitative description of the reaction mechanisms in MW plasmas operating in different pressure regimes is feasible with our model and will be presented in the next section.

It is clear that the CH₄ conversion in the MW plasma, both at reduced and atmospheric pressure, can reach values above 80%, for high power and low flow rate or high SEI values. The energy costs range from about 50 to above 100 kJ L⁻¹ at reduced pressure, which is lower than in a DBD. In the atmospheric pressure MW plasma, the energy costs vary from 200 to above 1000 kJ L⁻¹, which is of the same order or even higher than in the DBD. However, it should be mentioned that the gas flow in this case was diluted with H₂ (CH₄/H₂ ratio of 1/4), which reacts to a large extent with the dissociation products of CH₄ forming again CH₄. This means that not all of the power is efficiently used for CH₄ conversion, explaining the higher energy cost.

For lower power and pressure, the main products formed are C₂H₆ (with selectivities ranging between 5% and 75%), C₂H₄ (with selectivities ranging from 8% to 20%), and C₂H₂ (with selectivities ranging from 8% to 80%). Higher hydrocarbons, such as created in the DBD, were not observed in our model, and also not reported experimentally. This is attributed to the high temperatures in the MW plasma (above 1000 K), which will cause dissociation of these higher hydrocarbons back in smaller compounds. Furthermore, the higher the SEI value, the larger the shift toward C₂H₂ and C₂H₄, instead of C₂H₆. At atmospheric pressure, CH₄ is mainly converted into C₂H₂.
with a selectivity of \( \sim 85\% \), and to \( \text{C}_2\text{H}_4 \) with a selectivity of \( \sim 15\% \). Although different conditions give different product selectivities, especially at reduced pressure, we can draw an overall picture of the most important mechanisms at reduced pressure vs atmospheric pressure, as outlined in next section.

3.2.2. Underlying Reaction Pathways. It is clear from above that the different pressure regimes in a MW plasma show different product distributions, which are attributed to different mechanisms, as can be seen in Figures 13 and 14. Again, the

\[
\begin{align*}
\text{H}_2 & \rightarrow \text{CH}_4 & \\
& & + \text{CH}_2 + \text{M} \\
& & + \text{CH}_3 + \text{M} \\
& & + \text{C}_2\text{H}_4 + \text{H}_2 \\
& & + \text{C}_3\text{H}_8 + \text{M} \\
& & + \text{C}_4\text{H}_{10} + \text{M} \\
\end{align*}
\]

Figure 13. Most important net reaction pathways in a MW plasma at reduced pressure. Blue, pink, yellow, green, and orange arrow lines represent electron impact reactions, reactions involving a neutral species M in three-body reactions or neutral dissociation, two-body reactions with H atoms, two-body reactions with hydrocarbon molecules or radicals, and with \( \text{H}_2 \) molecules, respectively. The thickness of the arrow lines and the size of the boxes are proportional to the reaction rate and species density, respectively, as calculated in the model. The black boxes represent stable molecules and the white boxes intermediates (radicals).

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& & + \text{CH}_3 + \text{M} \\
& & + \text{C}_2\text{H}_4 + \text{H}_2 \\
& & + \text{C}_3\text{H}_8 + \text{M} \\
& & + \text{C}_4\text{H}_{10} + \text{M} \\
\end{align*}
\]

Figure 14. Most important net reaction pathways in a MW plasma at atmospheric pressure. Pink, yellow, green, and orange arrow lines represent reactions involving dissociation with a neutral species M, two-body reactions with H atoms, two-body reactions with hydrocarbon molecules or radicals, and with \( \text{H}_2 \) molecules, respectively. The thickness of the arrow lines and the size of the boxes are proportional to the reaction rate and species density, respectively, as calculated in the model. The black boxes represent stable molecules and the white boxes intermediates (radicals).

\[
\begin{align*}
\text{C}_2\text{H}_2 & \rightarrow \text{CH}_4 (\text{C}_2\text{H}_4 + \text{M} \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4 + \text{M}), \text{which becomes more important at high SEI values, explaining why high SEI values give lower \( \text{C}_2\text{H}_2 \) selectivities (see Figures 9 and 10). In addition, it also undergoes electron impact dissociation toward \( \text{C}_2\text{H}_4 (e^- + \text{C}_2\text{H}_4 \rightarrow e^- + \text{C}_2\text{H}_4 + \text{H}_2) \), and it reacts with \( \text{CH}_3 \) or \( \text{H} \) radicals into \( \text{C}_2\text{H}_5 (\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_5 + \text{H} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2) \).

\text{C}_2\text{H}_4 \), which is mainly formed by dissociation of \( \text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_4 \), reacts mostly further with \( \text{CH}_3 \) radicals into \( \text{C}_2\text{H}_5 (\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5) \), but a small fraction is also subject to electron impact dissociation, creating \( \text{C}_2\text{H}_5 (e^- + \text{C}_2\text{H}_4 \rightarrow e^- + \text{C}_2\text{H}_5 + \text{H}_2) \), or it reacts with \( \text{H}_2 \), creating again \( \text{C}_2\text{H}_5 (\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_5 + \text{H}) \).

\text{C}_2\text{H}_5 \) radicals react with \( \text{CH}_3 \) radicals into either \( \text{C}_2\text{H}_4 \) or \( \text{H}_2 \) at almost equal rates (\( \text{CH}_3 + \text{C}_2\text{H}_4 + \text{M} \rightarrow \text{CH}_3 + \text{C}_2\text{H}_4 + \text{M} \), and \( \text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5 \)). This is the main formation process of \( \text{C}_2\text{H}_5 \) at high SEI values, while at low SEI values, \( \text{C}_2\text{H}_6 \) is mainly formed by electron impact dissociation of \( \text{C}_2\text{H}_6 (e^- + \text{C}_2\text{H}_6 \rightarrow e^- + \text{C}_2\text{H}_5 + \text{H}_2) \).

At low SEI values, \( \text{C}_2\text{H}_6 \) dissociates mainly into \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_5 \) by electron impact dissociation (\( e^- \rightarrow e^- + \text{C}_2\text{H}_4 \) and \( e^- \rightarrow \text{C}_2\text{H}_5 + \text{H}_2) \) and it forms \( \text{C}_2\text{H}_5 \) upon recombination with H atoms (\( \text{C}_2\text{H}_5 + \text{H} + \text{M} \rightarrow \text{C}_2\text{H}_5 + \text{M} \)). At high SEI values, \( \text{C}_2\text{H}_6 \) mainly forms \( \text{C}_2\text{H}_5 \) upon reaction with H or any other neutral molecule (\( \text{C}_2\text{H}_6 + \text{H} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2 \) and \( \text{C}_2\text{H}_6 + \text{M} \rightarrow \text{C}_2\text{H}_5 + \text{H} + \text{M} \)). \( \text{C}_2\text{H}_6 \) immediately dissociates further into \( \text{C}_2\text{H}_5 (\text{C}_2\text{H}_5 + \text{M} \rightarrow \text{C}_2\text{H}_5 + \text{CH}_3 + \text{M}) \).

\text{C}_2\text{H}_5 \) undergoes electron impact dissociation toward \( \text{C}_2\text{H}_6 \) as mentioned above, but also toward \( \text{C}_2\text{H}_4 (e^- + \text{C}_2\text{H}_5 \rightarrow e^- + \text{C}_2\text{H}_4 + \text{CH}_4) \), and to a smaller extent it reacts with H into \( \text{C}_2\text{H}_4 (\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2) \). \( \text{C}_2\text{H}_3 \) is formed by dissociation of \( \text{C}_2\text{H}_5 \) and recombination of \( \text{C}_2\text{H}_6 \) as mentioned above, but it is also (and even predominantly) formed by dissociation of \( \text{C}_2\text{H}_{10} (\text{C}_2\text{H}_{10} + \text{M} \rightarrow \text{C}_2\text{H}_3 + \text{M}) \). Vice versa, it dissociates into \( \text{C}_2\text{H}_4 (\text{C}_2\text{H}_4 + \text{M} \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3 + \text{M}) \), thus closing the \( \text{C}_2 \) and \( \text{C}_4 \) loop back toward the \( \text{C}_2 \) hydrocarbons, and explaining why the latter are predominantly formed in MW plasmas.
Finally, C₂H₂, which is the main product at high SEI values, is formed by various electron impact dissociation, neutral dissociation and two-body reactions with several C₂ and C₃ compounds, mainly C₂H₆, C₂H₅, C₃H₄ and C₄H₈, while a small portion reacts further with H₂ toward C₂H₃ (C₂H₂ + H₂ → C₂H₃ + H₂), which in turn creates again C₂ compounds, as described above, thus closing the whole cycle.

The chemistry in the atmospheric pressure MW plasma is much less complex, as can be seen in Figure 14. This is attributed to the higher temperature (i.e., >3000 K vs ~2000 K at 30 mbar), causing the dehydrogenation processes to be much more prominent. Like in the reduced pressure case, CH₄ is converted into CH₃ by a combination of electron impact dissociation (e⁻ + CH₄ → e⁻ + CH₃ + H) and reaction with H atoms (CH₃ + H → CH₃ + H₂). These radicals partially recombine back into CH₄ upon reaction with C₂H₂ (CH₃ + C₂H₂ → CH₄ + C₂H₂). In addition, they react with CH₄ to produce C₂H₆ (CH₄ + CH₂ → C₂H₆ + H₂), which however immediately dissociates back into CH₄ (C₂H₆ + H → CH₃ + CH₃ + M) or reacts with CH₄ into the formation of C₂H₅ (CH₃ + C₂H₅ → CH₄ + C₂H₅). Furthermore, two CH₃ radicals also recombine to produce C₂H₅ (CH₃ + CH₃ → C₂H₅), which immediately dissociates into C₂H₄ (C₂H₅ + M → C₂H₄ + H + M).

C₂H₄ in turn reacts with CH₃ and H atoms, forming C₃H₃ (CH₃ + C₂H₄ → CH₄ + C₂H₂ and C₂H₄ + H → C₂H₃ + H₂), which directly reacts further with H into C₂H₂ (C₂H₃ + H → C₂H₂ + H₂). Due to the high temperature, C₂H₂ dissociates into C₂H (C₂H₂ + M → C₂H + H + M), which returns immediately back into C₂H₂ (C₂H + H₂ → C₂H₂ + H). Finally, a small portion of C₂H also recombines with H₂ into the formation of C₂H₃ (C₂H₃ + H₂ + M → C₂H₃ + M), closing the loop. Although H₂ is a reactant, it is immediately formed again by the dehydrogenation processes, forming ultimately C₂H₂.

The reaction pathways in Figures 13 and 14 mainly exhibit thermal reactions, with some contribution of electron impact dissociation at reduced pressure (Figure 13). This is of course due to the high temperature, enabling these thermal reactions, in contrast with the DBD, where electron impact dissociation and also ionization were much more predominant (Figure 8). Lower pressures and lower powers furthermore favor recombination processes, resulting in the formation of C₂ compounds. Higher pressures and higher powers induce dehydrogenation reactions, resulting in more unsaturated hydrocarbons, and thus explaining the high C₂H₂ selectivity in Figures 10–12.

In addition, we investigated the role of vibrational-induced dissociation of CH₄ in the MW plasma, as this process is important in the case of CO₂ splitting and N₂ fixation. Especially in low pressure MW plasmas, where there is a pronounced vibrational—translational nonequilibrium. For this purpose, we calculated the vibrational temperature, from the four vibrational levels included in our model:

\[ T_v = \frac{1}{4} \sum_{i=1}^{4} \frac{E_i}{g_i n_i} \log \left( \frac{n_i}{n} \right) \]  

with \( E_i \) the energy of the first level of vibrational mode \( v_i \) of CH₄ (in K), \( g_i \) its degeneracy and \( n_i \) its density (in cm⁻³). \( n \) is the density of ground state CH₄.

We found that, for the MW plasma conditions in this study, the vibrational temperature of CH₄ is almost equal to the gas temperature, indicating that the vibration-translational nonequilibrium in CH₄ MW plasma is negligible, even at reduced pressure (see Figures S.7 and S.8 in the Supporting Information). This finding is supported by measurements of Butterworth et al.50

3.3. GAP. 3.3.1. Comparison of Calculated and Measured CH₄ Conversion, Energy Costs, and Product Selectivities. The experimental and calculated CH₄ conversions, energy costs and selectivities of the most important hydrocarbons and H₂ are plotted in Figure 15 as a function of CH₄ fraction in the CH₄/N₂ mixture, at a flow rate of 224 W and a flow rate of 10 L min⁻¹.

![Figure 15](https://dx.doi.org/10.1021/acs.jpcc.0c00082)

**Figure 15.** Calculated (dashed lines) and experimental (solid lines) CH₄ conversions and energy costs (a), as well as selectivities of the most important hydrocarbons and H₂ formed (b), in the GAP, as a function of CH₄ fraction in the CH₄/N₂ mixture, for an input power of 224 W and a flow rate of 10 L min⁻¹.
C\textsubscript{3}H\textsubscript{4} (with selectivities between 24\% and 36\%) and finally C\textsubscript{2}H\textsubscript{6} (with selectivities between 9\% and 15\%).

### 3.3.2. Underlying Reaction Pathways

The underlying reaction mechanisms in the GAP are presented in Figure 16.

![Figure 16](image)

**Figure 16.** Most important net reaction pathways in the GAP at atmospheric pressure. Pink, yellow, green, and orange arrow lines represent reactions involving a neutral species M in three-body reactions or neutral dissociation, two-body reactions with H atoms, two-body reactions with hydrocarbon molecules or radicals, and with \( \text{H}_2 \) molecules, respectively. The thickness of the arrow lines and the size of the boxes are proportional to the reaction rate and species density, respectively, as calculated by the model. The black boxes represent stable molecules and the white boxes intermediates (radicals).

They are similar as in the MW plasma at atmospheric pressure, which is logical, because both plasma types operate at similar temperatures and powers, as mentioned above. The calculated rates of the reactions in this figure are listed in the SI (Table S.9).

Just as in the MW plasma at atmospheric pressure, CH\textsubscript{4} is converted into CH\textsubscript{3} radicals upon both neutral dissociation (CH\textsubscript{4} + M → CH\textsubscript{3} + H + M) and reaction with H atoms (CH\textsubscript{4} + H → CH\textsubscript{3} + H\textsubscript{2}). The CH\textsubscript{3} radicals partially react with C\textsubscript{2}H\textsubscript{4} to form CH\textsubscript{2}H\textsubscript{2} again (CH\textsubscript{3} + C\textsubscript{2}H\textsubscript{4} → CH\textsubscript{2}H\textsubscript{2} + C\textsubscript{2}H\textsubscript{5}) but also with N\textsubscript{2}H (CH\textsubscript{3} + N\textsubscript{2}H → CH\textsubscript{2}H\textsubscript{2} + N\textsubscript{2}). Similarly, CH\textsubscript{3} reacting with H atoms (N\textsubscript{2} + H + M → N\textsubscript{2}H + M). Finally, some CH\textsubscript{3} radicals also form C\textsubscript{2}H\textsubscript{4} (CH\textsubscript{3} + CH\textsubscript{2}H\textsubscript{2} → C\textsubscript{2}H\textsubscript{4} + H), which however immediately dissociates back into CH\textsubscript{3} (C\textsubscript{2}H\textsubscript{4} + M → CH\textsubscript{3} + CH\textsubscript{3} + M) or reacts with CH\textsubscript{3} into the formation of C\textsubscript{2}H\textsubscript{5} (CH\textsubscript{3} + C\textsubscript{2}H\textsubscript{5} → CH\textsubscript{4} + C\textsubscript{2}H\textsubscript{5}).

The rest of the pathways is identical to the atmospheric MW plasma, with the exception that C\textsubscript{2}H\textsubscript{4} partially reacts back to C\textsubscript{2}H\textsubscript{6} (CH\textsubscript{3} + C\textsubscript{2}H\textsubscript{4} → C\textsubscript{2}H\textsubscript{6} + CH\textsubscript{2}, and CH\textsubscript{3} + C\textsubscript{2}H\textsubscript{4} → CH\textsubscript{3} + C\textsubscript{2}H\textsubscript{5}) and C\textsubscript{2}H\textsubscript{4} also dissociates in C\textsubscript{2}H\textsubscript{6} using neutral dissociation (C\textsubscript{2}H\textsubscript{4} + M → C\textsubscript{2}H\textsubscript{3} + H + M) due to the higher temperatures in the GAP, especially in the beginning of the arc discharge near the cathode spot.

Thus, dehydrogenation and neutral dissociation reactions of the produced hydrocarbons are the most important processes in the GAP, resulting especially in the formation of C\textsubscript{2}H\textsubscript{2}.

The fact that the majority of CH\textsubscript{4} dissociates in the GAP, even at the high flow rate of 10 L min\textsuperscript{-1} (which is at least a factor 10 higher than in the MW plasma at atmospheric pressure, cf. Figure 12; and even up to 3 orders of magnitude higher than in the DBD; cf. Figures 4–7), point toward the high efficiency of the GAP for CH\textsubscript{4} conversion, compared to the MW and DBD plasmas. This is attributed to the high temperature of the GAP, favoring thermal CH\textsubscript{3} dissociation.

It is clear from previous sections that the higher temperature of MW and GA plasma leads to higher conversion and more selective production of unsaturated hydrocarbons. To investigate whether the conversion in these plasmas is purely thermal or due to (additional) plasma effects, we make a distinction between the plasma effects and the thermal effects for the same range of conditions as investigated in sections 3.2 and 3.3.

**Figure 17** shows the CH\textsubscript{4} conversions for the MW plasma at reduced pressure (30 mbar), obtained in the plasma and by pure thermal conversion at the same temperature (i.e., without electron impact reactions, which are specific plasma-based reactions), as a function of SEI, for the continuous (a) and pulsed (b) regime. The corresponding gas temperature is...
plotted in blue color (right y-axis). Both the maximum temperature and averaged temperature (obtained by averaging over the whole residence time) are plotted. At this reduced pressure, almost all conversion is due to plasma effects. Indeed, despite the fact that the maximum temperatures obtained in both the continuous and pulsed mode can reach 1500 K and more, which is in principle sufficient to induce significant thermal conversion, this temperature is only reached for a short time, even in the continuous mode, due to the triangular power profile, as explained in section 1.7 in the SI (∼30 μs in the pulsed mode and ∼100 μs in the continuous mode), causing the average temperature in the MW plasma to be too low for thermal conversion. During the short plasma time, however, enough reactive species are created, which, due to the higher local temperatures, react further in neutral reactions. These reactive species are mainly CH₂ and H₂ as can be seen in Figure 13, and are mainly created by electron impact dissociation of CH₄ or neutral dissociation of higher hydrocarbons, as illustrated in Figures S.12 and S.13 in the SI.

However, in the atmospheric pressure MW plasma and in the GAP discharge, the conversions obtained with and without electron impact reactions are virtually the same, as is clear from Figures 18 and 19, indicating that the conversion is purely thermal at the high temperatures of 3000–3500 K. However, plasmas can still be beneficial above classical thermal conversion, as high temperatures (3000–3500 K) can be reached by applying electric power (of interest for electrification of chemical reactions) and without damaging the reactor. Indeed, the arc in the GAP can be easily contained in the reactor center due to the reverse vortex flow, which isolates the hot plasma from the reactor walls, and in MW plasmas at atmospheric pressure, gas contraction takes place, also focusing the plasma in the center, and thus also protecting the reactor walls. Finally, plasmas can be switched on and off quite fast, with ignition times equal to several 100 ms in plasma torches, making them compatible with fluctuating renewable electricity.

Besides the gas temperature, also the electron density is completely different in the three different plasma types. In the DBD plasma the electron densities are calculated to be between 5 × 10¹³ cm⁻³ and 2 × 10¹⁴ cm⁻³. In the MW plasma at reduced pressure, the electron densities range between 1.6 × 10¹² and 2.4 × 10¹³ cm⁻³, while in the MW plasma at atmospheric pressure, the electron densities vary between 6.0 × 10¹¹ and 1.4 × 10¹² cm⁻³. Finally, in the GAP the electron density is calculated to be ∼6.0 × 10¹¹ cm⁻³. Thus, the calculated electron density is the highest in the DBD, more specifically inside the filaments. Combined with the low gas temperature (<500 K), it is logical that electron impact reactions, next to three-body recombinations, are dominant. Since a 0D model cannot capture spatial nonuniformities, such as plasma contraction, local higher power densities may be underestimated, which might result in lower electron densities. Nevertheless, since the gas temperatures are around 3000 K or higher in the (atmospheric pressure) MW plasma and the GAP, CH₄ dissociates very fast at these temperatures, so we are confident that our conclusion about the importance of thermal conversion is valid, even if the electron densities would be somewhat underestimated.

To assess whether temperature controls the overall chemical behavior, we plot in Figure 20a,b the CH₄ conversion and product selectivities for a generic type of plasma, at 400 W and a flow rate of 500 mL min⁻¹, as a function of gas temperature. It is clear that the temperature indeed plays a determining role in steering the conversion and the product selectivities. Gas temperatures below 1000 K favor radical recombination processes, resulting in more saturated hydrocarbons (C₂H₆ and higher C₃−C₅ hydrocarbons), as demonstrated in section 3.1.2 for DBD plasmas. Higher temperatures favor neutral dissociation and dehydrogenation, explaining why C₂H₄ and especially C₂H₂ are the dominant products in the MW plasma and the GAP.
Figure 20. Calculated conversion (a) and most important hydrocarbon selectivities (b) inside a generic plasma type at atmospheric pressure, a power of 400 W and a flow rate of 500 mL min⁻¹ for pure CH₄ as a function of gas temperature. In (a) both the plasma conversion and thermal equilibrium conversion are plotted, indicating a clear difference up to 2000 K.

In Figure 20a we also compare the plasma conversion and conversion at thermal equilibrium, demonstrating that up to a temperature of 2000 K, there is still a significant difference. Hence, the plasma effect can still be important in warm plasmas at atmospheric pressure, when the temperature would be below 2000 K. However, for the atmospheric pressure MW plasma and GAP studied in sections 3.2 and 3.3 above, the gas temperature is around 3000 K or above, and the conversion occurs by thermal processes.

4. CONCLUSIONS

CH₄ conversion into higher hydrocarbons and H₂ by plasma technology is gaining increasing interest as more sustainable alternative to conventional steam reforming. However, different plasma types yield a different performance in terms of conversion, energy cost and selectivity toward different hydrocarbons, and the underlying mechanisms are not yet fully understood. Therefore, we developed a chemical kinetics model to elucidate the main conversion mechanisms of CH₄ into the most important hydrocarbons, especially C₂H₂, C₂H₄ and C₃H₆ as well as into H₂, in the three most commonly used plasma reactors, i.e., a DBD, MW, and GAP reactor. We first compared the calculated conversions, energy costs and product selectivities with experimental results in different reactor configurations and in a wide range of operating conditions. The calculation results are in satisfactory agreement with the experiments, which indicates that our model can provide a realistic picture of the underlying chemistry in CH₄ plasmas and even CH₄–H₂–N₂ mixtures, and can be used to elucidate the underlying mechanisms of CH₄ conversion into various hydrocarbons and H₂ in the different plasma reactors.

The CH₄ conversion is around 20% in the DBD, as well as in the MW plasma at reduced pressure, but it rises to values above 80% in the pulsed MW plasma, as well as at atmospheric pressure, both upon rising SEI. In the GAP, conversions around 50% were obtained, even at high flow rates of 10 L min⁻¹. Because of this high flow rate, the GAP operates at much lower SEI than the other plasma sources, i.e., around 1.3 kJ L⁻¹, vs 9–54 kJ L⁻¹ for the DBD, 7–37 kJ L⁻¹ for the reduced pressure MW plasma, and 24–240 kJ L⁻¹ for the atmospheric pressure MW plasma. Therefore, the corresponding energy cost is by far the lowest for the GAP (between 5 and 15 kJ/L, decreasing upon higher CH₄ fraction in the mixture), while it is around 40–140 kJ L⁻¹ in the reduced pressure MW plasma, from 200 until above 1000 kJ L⁻¹ in the atmospheric pressure MW plasma, and around 125–510 kJ L⁻¹ in the DBD. As the GAP operates at the highest temperatures, this illustrates that thermal CH₄ conversion is important, and most efficient. Indeed, our model predicts that vibrational–translational nonequilibrium is negligible in all these CH₄ plasmas.

We can conclude that higher temperatures, especially in the GAP but also in atmospheric pressure MW plasmas, result in more CH₄ conversion, and in neutral dissociation and dehydrogenation processes of the hydrocarbons created, forming especially C₂H₂ and H₂, and (some) C₂H₄. Low temperature plasmas, such as DBD and reduced pressure MW plasmas, result in more electron impact dissociation and three-body recombination processes, creating more saturated compounds, i.e., mainly C₃H₆ but also higher hydrocarbons, such as C₄H₆ and C₅H₁₀.

Thus, high temperature plasmas, and especially the GAP, which operates at high flow rates, are clearly beneficial, for both higher and more energy-efficient CH₄ conversion, as well as more selective production of C₂H₂ and (to a lower extent) C₂H₄. It would even be better if C₂H₄ would be the major product. To realize this, it is possible to add a catalyst after the plasma reactor, to convert C₂H₂ into C₂H₄ as demonstrated by Delikonstantis et al. for a nanosecond pulsed plasma. This will be the subject of our future work.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c00082.

Full description of the 0D model, including the vibrational and rotational kinetics of CH₄ and the vibrational kinetics of H₂, and a list of all reactions included in the model for the CH₄ and CH₄–N₂ chemistry. In addition, details are given on the assumptions made to describe the DBD, MW plasma and GAP, as well as about the experiments performed in these plasma sources. We also present additional calculation results, i.e., the vibrational and gas temperature at high temperatures, these plasma sources, to demonstrate that the various CH₄ plasmas investigated are close to vibrational–translational equilibrium. Finally, we present the calculated rates of the most important reactions in the various plasma sources, to identify the reaction pathways plotted in Figures 8, 13, 14 and 16 and the net contribution of the most important formation mechanisms of H and CH₃ in the reduced pressure MW plasma.
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Notes

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