Forward and reverse vortex compared in microwave plasma for methane coupling

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> **Abstract:** We study CH_4 pyrolysis to achieve ethylene selectivity with plasma, which offers the potential to electrify high-temperature processes using renewable energy. The chemical kinetics of CH_4 coupling and C_2H_x dehydrogenation suggest that sub-millisecond residence times at high temperature favor C_2H_4 selectivity. We compare forward and reverse vortex to test the effects of residence time. The improved C_2H_4 yield in reverse vortex is in line with the expectation of shorter residence time and/or lower gas temperature in the plasma-core.

Keywords: Methane, pyrolysis, microwave, reverse vortex, residence time.

1. Motivation

Methane is a plentiful raw material and important in view of closing carbon cycles. For example, it can be obtained from different sources, such as biogas, plastic recycling and electric naphtha crackers (e-crackers). A long-standing challenge of the chemical industry is a robust means of direct methane coupling to ethylene. Ethylene is the largest volume synthetic commodity chemical, as it is used as a building block for plastics, textiles, and chemicals, with a demand of 150 million tons/year in 2018. It is currently produced via steam cracking of ethane and naphtha, and is one of the most energy and emissions intensive processes in the chemical industry, with an emission of 1-1.5 ton of CO_2 per ton of olefin produced [1].

We foresee two probable transformations in the chemical industry that will result in large volumes of methane as a feedstock. Firstly, pyrolysis oil from plastics recycling will become a "drop-in" to naphtha crackers. The naphtha / pyrolysis-oil cracking process for olefins production creates large volumes of methane as a by-product. Secondly, this methane by-product is combusted in the cracker to drive the strongly endothermic cracking process. These conventional fossil crackers will soon be replaced by "e-crackers", which use industrial heat pumps powered by renewable electricity. Due to this decarbonisation of crackers, huge volumes of excess methane will become available and burning it would result in CO₂ emissions. We envisage that plasma technology could be used to directly convert methane to ethylene. Thus, we can create a closed carbon-loop for the polyolefin and plastic industry, moving towards a CO₂ neutral C₂H₄ production.

There have been many attempts to couple CH_4 to C_2H_4 in conventional thermal catalytical and non-catalytical processes. However, the reaction conditions needed to activate the strong C-H bond tend to overoxidize the products, leading to carbon deposition (i.e. coking). The mechanism of plasma based methane cracking is similar to thermal non-catalytic processes, however, plasma process enables extremely high temperatures and fast heating rates required to steer the selection of products (e.g. carbon, acetylene or ethylene) by varying the residence time distribution and the temperature of the discharge gas.

2. Introduction

Methane pyrolysis in plasma is currently being scaled up by various companies (Monolith, Hiiroc, Meridian, Baryon, Aurora) for carbon and turquoise hydrogen (H_2) production. The demand for hydrogen with a low carbon footprint speeds up these developments, however, in the long run, the high value carbon market is too limited. Complete conversion of methane to hydrogen and carbon is favoured by long residence times in the hot region, on the order of tens of milliseconds. Carbon formation can be avoided by using shorter residence times.



Fig. 1. Simplified methane thermodynamics equilibrium composition as a function of temperature.

Fig.1. shows the thermal equilibrium composition of methane heated to 3000 K calculated by Gibbs free energy minimisation, and with C_s omitted. Dissociation of CH₄ starts at 700K and is completed at 1500K. There is a window where ethylene is a minor product, but the main formed products are acetylene and hydrogen.

The Hüls process, operated on industrial scale since the 1940s, has applied arc discharges to convert natural gas into acetylene (C_2H_2) and H_2 . This process achieves a high acetylene selectivity and avoids carbon formation by using millisecond residence times. The acetylene produced could be catalytically hydrogenated to ethylene, but it results in a significant energy loss. This is illustrated by considering the reaction enthalpies of methane pyrolysis to C_2H_2 and C_2H_4 - it is more energy-efficient to directly produce C_2H_4 , due to its reaction enthalpy being almost half:

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \quad \Delta H = 378 \frac{\text{kJ}}{\text{mol}(C_2H_2)}$$
$$2CH_4 \rightarrow C_2H_4 + 2H_2 \quad \Delta H = 202 \frac{\text{kJ}}{\text{mol}(C_2H_4)}$$

With that in mind, in this project, we investigated CH_4 pyrolysis using a microwave (MW) plasma discharge, where we aim to test the hypothesis that sub-millisecond residence times will favour C_2H_4 selectivity.

3. Vortex configuration

In a tubular flow microwave plasma reactor, a vortex flow is essential to provide gas-dynamic stabilization of the discharge axis in the centre of the tube to prevent wall damage. There are two commonly investigated vortex flow geometries, the so-called "forward-vortex" (FV) and "reverse-vortex" (RV) flows. In both arrangements, gas is injected tangentially into the reactor. In the FV configuration, the inlet and outlet sit at opposite ends of the reactor (Fig 2b). In the RV configuration (Fig 2a), the inlet and outlet are at the same end of the reactor, and a flow restriction at the outlet is used to force gas through the plasma.



Fig. 2. a) Reverse vortex (RV) and b) Forward vortex (FV) configuration in the MW plasma setup [3]

Computational fluid dynamics (CFD) flow simulations in Fig. 3 reveal the typical flow structures of the FV-flow without a plasma heat source. Intense vortex flows cause recirculation (blue zone in Fig.3.), resulting in a local flow reversal in the centre, close to the injection point. This recirculation is believed to cause longer gas residence time distributions.



Fig. 3. - 3D visualization of the vortex flow stream simulation (left) and a cross-section of the axial flow velocity component (center) [3].

Conversely, with RV configuration (Fig 2.a.), we expect to minimize flow recirculation, leading to shorter residence time distribution in the hot region for the same input flow rate. Moreover, with this configuration, we anticipate that plasma-gas contacting will be improved by forcing the gas flow close to the hot plasma core.

4. Description of experiment

A continuous-wave microwave discharge is generated in a tubular quartz reactor (26 mm ID) inserted in a WR340 waveguide. A solidstate microwave generator (pinkRF) supplies up to 3 kW continuous power at 2.45 GHz operating frequency. A 3-stub auto tuner is used for impedance matching of the microwave with the plasma to maximise the absorbed power. Pressure in the reactor is held constant by using a pressure-regulating valve (pressure control solutions) and two parallel 46 m³/h ATEX scroll pumps (Edwards). Methane flowrates up to 20 SLM are tested, with 1 SLM argon injected downstream of the plasma used as an internal standard.

The RV and FV configurations have a tangential gas injection (3 mm diameter) to stabilize the plasma discharge in the center of the tube. The RV also has a nozzle of 10mm in the outlet. For the FV, in addition to the tangential injection, there are swirl inlets (16 inlets of 2 mm inner diameter) that helps stabilizing the plasma discharge. The outlet of the reactor is connected to a GC-TCD (Agilent 990). Methane conversion (X_{CH4}) and hydrocarbon selectivity are defined as:

$$X_{\rm CH_4} (\%) = \left(1 - \frac{n_{\rm CH_4}^{out}}{n_{\rm CH_4}^{in}}\right) \times 100$$
$$S_{\rm C_xH_y} (\%) = \frac{n_{\rm C_xH_y}}{\sum n_{\rm C_xH_y}} \times 100$$

Where n_i the number of mols of species *i* in the outlet.

5. Forward vortex configuration

5.1. Results

The data for experiments in the FV configurations, showing methane conversion as a function of a specific energy input (SEI) is plotted in Fig 5. We can identify three key trends from the plot:



Fig. 5. - Conversion of CH_4 as a function of specific energy input - SEI (eV/molecule) at different flow rates of CH_4 (5, 7.5, 10, 12.5, 15 and 20 slm) in FV configuration.

- 1. For a given specific energy input within this parameter space, CH₄ conversion increases with increasing power.
- 2. A two-fold increase in pressure approximately doubles CH_4 conversion (i.e. at 20 slm and 0.70 eV/molecule, we have 20% CH_4 conversion at 25 mbar and a 41% CH_4 conversion at 50 mbar and).
- 3. By increasing methane flowrate, the methane conversion increases, especially at higher pressure (50 mbar).

Selectivity of the different hydrocarbon products is plotted in Fig 6, as a function of flowrate and pressure at an SEI of 0.56 eV/molecule (CH₄):



Fig. 6. - Hydrocarbon selectivity as a function of CH₄ flowrates in FV configuration at an SEI of 0.56 eV/molecule CH₄.

Increasing pressure shifts selectivity from ethylene to acetylene (i.e. at 20 SLM, there is a 5.5% C_2H_4 selectivity at 50 mbar, whereas at 25 mbar, you have a 34.0 % C_2H_4 selectivity). Doubling pressure in this range leads to a six times decrease in C_2H_4 selectivity. Also, we see that increasing flow rate, decreases C_2H_4 selectivity for both pressures (Fig.6.), particularly at 50 mbar.



Fig. 7. - Plasma photoemission at 25 mbar, different power input and different flowrates of CH₄ in FV configuration. The red dashed figures have nearly same SEI.

From the plasma photoemission (Fig.7.), we observe that at nearly equal SEI, the plasma presents qualitatively very different characteristics. For instance, you see more black body radiation [4] in the plasma core with higher flow rates and nearly same SEI.

5.2. Discussion

We link the observations on conversion and selectivity with input variables as follows:

1 – Increase in conversion with increasing input power

There are two potential reasons that increasing input power increases methane conversion. Firstly, it can be that increasing input power increases power density, and therefore temperature. Secondly, the plasma can become larger with increasing input power, which would increase gas-plasma contact. We do not present the effect of input power on selectivity here, but we note that the effect of pressure and flowrate are stronger.

2 - Increase in conversion with increasing pressure, and shift towards higher C₂H₂ selectivity

As pressure increases from 25 to 50 mbar, we can observe a doubling of CH₄ conversion, which can likely be explained by plasma contraction. Simultaneously, with increasing pressure the selectivity shifts towards less saturated hydrocarbons, i.e. more acetylene. As pressure is increased in microwave discharges, the plasma-volume is generally observed to decrease, a phenomenon known as contraction. Due to the contraction of the discharge and increase in power density, there is an associated increase in peak gas temperature (T_g), electron number density (n_e) and ionization fraction [5]. This increase in power density, and therefore temperature, may explain the higher conversion with increasing pressure.

Other potential contributing factors that will change conversion and selectivity are the increase in mean residence time, and the modification of chemical kinetics (i.e. 3-body reactions) by pressure. Specifically, at elevated pressures, gas volumetric flowrates decrease and therefore flow velocities follow. This may lead to increased methane conversion and higher acetylene selectivity. In contrast, higher pressure should increase the rate of 3-body reactions, which would favour selectivity of more saturated hydrocarbons. This kinetic effect is therefore relatively weak compared to the other effects in this scenario.

3 – Increasing gas flowrate increase methane conversion at a given SEI

The result here is counter-intuitive in consideration of our hypothesis. We hypothesise that short residence time will favour ethylene formation, thus higher flow rates should also favour this. However, what we observe is that increasing gas flow shifts selectivity to acetylene. This can be qualitatively explained, as higher flow rates will lead to a higher gas velocity at the inlet, increasing swirl number and leading to swirl breakdown and gas recirculation. This will have the undesired effect of extending residence time distributions.

Likewise, we must also consider that to maintain constant SEI as we increase gas flowrate, we must also increase the input power. This will affect the plasma properties themselves in a non-trivial way. This is illustrated by Fig 7, which shows that at high flowrates for a fixed SEI there is a strong change in plasma emission. Specifically, there is increasingly strong emission in the plasma core from black body radiation at higher flowrates, indicative of soot formation [4]. This shift might come from either increased power density, or strong gas recirculation in the FV configuration, enabling both higher temperatures and longer residence times.

6. Reverse vortex configuration

6.1. Results

There is compelling evidence that high gas velocities and short residence times may be practically obtained with the RV configuration [2,3,4]. In order to avoid the strong flow recirculation in plasma from the FV configuration, while achieving high gas velocities, we performed experiments with 20 SLM CH_4 in the RV configuration (Fig.8.).



Fig. 8. - Selectivity of C_2H_4 as a function of CH_4 exhaust concentration (20 slm CH_4) in FV and RV configuration.

We observe that decrease in pressure also leads to a higher C_2H_4 selectivity in the RV configuration (Fig.8.). Moreover, at a similar conversion rate of CH₄, there is a higher selectivity of C_2H_4 for RV configuration when compared to FV. For 75 mbar at RV, the yield of C_2H_4 is higher than for 50 mbar at FV. Thus, the RV shows a better performance for C_2H_4 yield.

We also see different plasma characteristics in RV and FV: for the same SEI and pressure there is a stronger emission of black body radiation in the plasma core [4] at FV configuration (Fig.9.).



Fig. 9. - Plasma photoemission at 25 mbar, 20 slm of CH₄ in RV and FV configuration respectively.

6.2. Discussion

We see three factors that may have improvement the selectivity of C_2H_4 in RV:

- 1. The residence time distribution in the RV configuration is shorter due to convective driven gas velocities [3], thus, preventing further cracking to lower hydrocarbons and carbon.
- 2. Lower gas temperatures in the core would change product composition, this is consistent with measurements in CO_2 plasma [3].
- 3. Inlet gas can quench the product output [2], which also favors shorter residence time and higher C_2H_4 selectivity.

On top of this shift in selectivity to higher hydrocarbons in RV configuration, there is a decrease (almost null) in black body radiation emission (Fig.7.), which is in line with recent finding [4]. We also observed no soot on the quartz tube wall with the RV configuration, which might enable a stable and coke-free operation at higher power input. The residence time distribution is still long enough for the dissociation of products, but in RV configuration the mean residence time in the plasma zone is lower, leading to less precursors of the undesired carbon particles. Whereas for the FV configuration, there is significant carbon deposition on the reactor quartz tube, which might be explained by the possible longer residence time of the gas in the core. Additionally, in opposition to the RV, in the FV carbon particles and its precursors are possibly not able to react with the cold inlet gas, and eventually stick to the reactor walls [4].

7. Conclusion

The observed shift to higher C_2H_4 selectivity in the RV configuration, in line with its expected shorter residence time distribution, supports an opportunity for further selectivity improvements by reactor flow optimization. The according improvement in economic viability would define a unique role for plasma pyrolysis as game changing technology to aid the energy transition in the chemical industry.

8. References

[1] Minea, Teofil, et al 2018 *Plasma processes and polymers* **15** (11): 1800087.

[2] Bongers, Waldo, et al., 2017, *Plasma processes and polymers* **14.6**: 1600126.

[3] Van de Steeg, Alex W., Insights into CO₂ dissociation dynamics in microwave plasma using laser scattering (2022)

[4] Biondo, O. et al, 2023, Reverse vortex gas flow as a way to prevent coke deposition in plasma-based dry reforming of methane – *ACS Energy Letters* (under revision)

[5] Van de Steeg, Alex W. et al., 2021 ACS Energy Letters 6, 2876.