
Thesis summary

Light olefins (i.e. acetylene, ethylene, propylene and butylene) are important building blocks for chemicals, plastics and synthetic fuels production^{1,2}. Light olefins are produced through a well-established industrial process, the naphtha steam cracking. However, the crude oil depletion as well as the significant amounts of CO₂ and NO_x produced in cracking furnaces fueled the search for alternative feedstocks. Methane (CH₄) is a promising substitute due to high capacity and worldwide availability. Recent hydrocarbon(s) exploration activities have discovered an abundance of conventional and unconventional gas reserves rich in methane (i.e. tight gas and shale gas, methane hydrate, coalbed methane) but mostly located in decentralized areas, far away from the market³⁻⁹. Therefore, the capital intensive gas transportation infrastructure and the energy intensive gas liquefaction process are the main reasons why those gas reserves still remain unvalorized¹⁰⁻¹². Moreover, reach-in-methane gas released along with crude oil extraction at remote reserve locations is directly flared. Only in 2012, the total flared gas was estimated at 143 billion cubic meters, representing ~3.5% of the global natural gas “production”¹³. Consequently, a potential raw material is depleted and CO₂ is emitted^{14,15}. Therefore, new technologies capable of decentralized valorization of methane gas streams to added-value products are needed¹⁶.

Various thermally activated methane reforming paths, resulting in different product distribution have been studied so far, namely pyrolysis, partial oxidation, dry/steam methane reforming (DMR and SMR, respectively) and non-oxidative methane coupling. The latter path is currently getting more attention over the others since products of high commercial value are directly formed: two CH₄ molecules are directly coupled to acetylene (C₂H₂) and ethylene (C₂H₄) at high temperatures (>1000°C¹⁷). Acetylene is widely used in metal constructions (i.e. as oxyacetylene flames or acetylene-air flames for welding) and chemical industry, serving as precursor for chemicals formation (i.e. acrylic acid or vinyl monomers), while ethylene is mainly used in polymer industry and other bulk chemicals formation such as acetaldehyde and ethylene oxide. Methane pyrolysis is used for carbon-free hydrogen and carbon^{18,19} whereas synthesis gas (syngas) in different compositions is produced when methane is reformed by oxygen, carbon dioxide or steam. Syngas is further used for synthetic fuels production through the Fischer-Tropsch process²⁰. In order to decrease the energy requirements, methane partial oxidation can be integrated either with DMR²¹⁻²³ or SMR^{24,25}, enabling the so-called auto-thermal methane reforming²⁶⁻²⁸ or even with both, making the so called methane tri-reforming²⁹⁻³³. The heat released from the exothermic oxidation reaction is absorbed by the endothermic DMR and SMR reactions. CH₄, O₂ and steam ratios can vary, leading to different syngas composition^{34,35} and affecting the downstream processing.

As methane is a very stable molecule, owing to the high C-H bond strength (434 kJ/mol³⁶), high energy input and high temperatures are required to activate it³⁷. Moreover, catalysts are usually employed to enhance the formation of the desirable product¹. Collectively, the high-energy demand and catalyst instability due to carbon deposition are the most considerable drawbacks of such thermally driven processes. In addition, the shortcomings of pyrolytic furnaces, such as long start-up/shut-down periods, high volumetric footprint, high capital expenditure and maintenance cost, low energy efficiency in the radiation box, NO_x and CO₂ emissions are also considered significant technological limitations.

Plasma-assisted methane reforming is currently investigated as a promising alternative technology³⁸⁻⁴⁰, overcoming some of the issues the thermal processes face. Methane is activated via electron impact reactions: the high-energy electrons of the plasma zone can effectively generate a huge number of chemically active species, such as radicals, ions and excited species through electron-CH₄ molecule collisions. Those active species can rapidly undergo several recombination reactions³⁸ at atmospheric pressure and mild temperatures (<<1000°C). Furthermore, relatively low reaction volumes are needed due to the fast reactions and high energy density. Finally, CO₂ emissions are

diminished in case the electricity input is drawn from renewable energy sources. On the downside, plasma is not very selective and usually generates wide product distributions.

Types of Plasma

Plasma is considered the fourth fundamental state of matter. It is an electrically conductive but quasi-neutral ionized gas, comprising a cloud of different (active) species (electrons, ions, radicals, excited species and neutral molecules). The high energy densities and high concentrations of chemically active species in several plasma media can be taken advantage of in terms of process intensification. Depending on the average energies of the plasma particles (neutral and active species) and of their degrees of freedom (vibrational, rotational and translational), which determine the plasma temperature, different types of plasma may be ignited.

Thermal plasma

In thermal plasmas, all generated species have the same temperature since they are in thermal equilibrium. The local thermal equilibrium (LTE) is reached when the mean electron temperature (T_{electron}) is equal to the neutral species temperature (T_{neutral}). The absolute temperature value is very high, too (approximately in the order of 10^4 K). Under such conditions, the active species are indistinctly produced by thermal activation or electron collisions. Arc discharges is a characteristic example of thermal plasmas and they are widely used in specific applications, where high temperatures are required (i.e. metallurgy, acetylene synthesis).

Non-thermal plasma

In non-thermal plasmas, the temperature of the different plasma species varies substantially. The energy is preferentially channeled into the electrons, which subsequently transfer it to the heavier species through electron-molecule collisions. The temperature sequence of the plasma species in non-thermal plasmas is: $T_{\text{electron}} \gg T_{\text{ions}} > T_{\text{neutral}}$. Dielectric Barrier Discharges (DBD), corona (DC, AC and pulsed) and nanosecond pulsed discharges are typical examples of non-thermal or cold plasmas. It has been observed, however, that some arcs do not reach the LTE even though the temperature is rather high. Moreover, in some non-thermal plasmas the neutral species have relatively high temperature (T_{neutral} in the order of 10^3 K). In the aforementioned cases, the discharges show an intermediate behavior. Only recently, those discharges have been grouped in a third category known as “warm plasmas”⁴¹. Microwave (MW), radio frequency (RF), glow and spark discharges belong to this group.

Plasma-assisted technologies for methane coupling

Numerous plasma-assisted technologies have been investigated for direct CH_4 reforming to added value products as depicted in **Error! Reference source not found.** C_2 compounds (C_2H_6 , C_2H_4 and C_2H_2), C and H_2 are the main products obtained. Considering the reported experimental results, there are three possible cases: i) C_2H_2 is formed as main product in high-energy discharges (GA, MW and spark); ii) C is obtained as main product under specific conditions in the discharge and iii) C_2H_6 is obtained as main product (in the case of DBD). In the first and second cases, the calculated carbon amount also includes the amount of C_3 or higher hydrocarbons (generally unsaturated). Consequently, the calculated values of reaction enthalpy and efficiency, based on the equations above, may be slightly underestimated. In the third scenario, the calculated carbon amount contains mainly saturated C_3 or higher hydrocarbons and the calculated values may be slightly overestimated.

Table 1. Highest performance of different plasma-assisted technologies for methane coupling. Specific energy input (SEI), specific energy requirement (SER), efficiency (η) and energy cost (EC) are calculated to facilitate a fair comparison. At atmospheric pressure, arc thermal plasma^{42,43} and non-thermal pulsed discharge⁴⁴ attain the highest performance in terms of efficiency and energy requirement (kJ/mol_{C₂H₂}) whereas, when operating under vacuum, MW plasma attains the highest performance⁴⁵.

Plasma Technology	SEI (kJ/mol)	Conversion (%)	Carbon selectivity (%)			SER (kJ/mol)	$\eta_{\text{calculated}}$ (%) (η_{reported} , %)	EC C ₂ H _x (kJ/mol _{C₂H_x})	Ref.
			C ₂ H ₆	C ₂ H ₄	C ₂ H ₂				
<i>Arc (Hüels®)</i>	275.4	70.5	-	4.5 ⁴²	72.9	391	40.5	1080	42
<i>Arc</i>	310.9	86.0	-	3.2	88.4	362	48.7 (46)	818.3	43
DBD	201.7	10.5	34.0	19 (C ₂ H ₂ + C ₂ H ₄)		1921	3.4	-	46
DBD + catalyst	60.5	6.2	28.0	36.0	29.0	976	10.8	6731	47
Corona	194.0	8.5	-	-	76.5	2278	7.1	5957	48
Corona + catalyst	145.0	4.5	6.6	6.4	58.5	3228	4.4	11034	49
<i>PD (Spark)</i>	86.0	23.5	1.9	5.4	85.0	365	46.9	860	44
MW	1076.0	50.7	-	11.5	61.4	2122	6.9	6920	50
MW (30 mbar)	617.0	93.7	1.8	9.8	65.3	659	22.9	2018	51
<i>MW (107 mbar)</i>	256.6	-	-	-	85 (Yield)	-	(61)	604	45
GA (from NG)	118.0	21.0	-	6.4	63.0	562	17.6	1780	52
GA (from CH ₄)	115.3	15.0	2.9	8.7	75.0	769	20.9	2050	53
GA + catalyst	57.8	7.0	-	-	84.0	826	20.6	1966	54

Thermal arc plasma is the only technology which has industrially been launched for CH₄ coupling (Hüels process⁴²). In thermal arc, all plasma species (ions, electron and molecules) are in thermal equilibrium, thus, it is considered a conventional thermal process. It has especially been developed for acetylene and carbon production. The Hüels process comprises a 1.2 m long arc, with power of 8 MW and flow rate of 2344 Nm³ h⁻¹. The products are mainly acetylene (yield ~50%), hydrogen, ethylene and carbon. Right after plasma cracking, quenching takes place to maximize the acetylene/ethylene production and reduce carbon formation. Carbon formation is not totally avoidable, and it generally decreases the efficiency and increases the energy cost for acetylene production. Carbon synthesis is favored at longer reaction times (ethylene 10⁻⁶–10⁻⁵ s, acetylene 10⁻⁴–10⁻³ s and carbon 10⁻³ s) so, a quenching rate of 5·10⁶ K/s is required for carbon suppression. Water or hydrocarbons are used as quenching media. At the aforementioned conditions, the efficiency reaches 40% and the energy cost for acetylene production is ~1080 kJ/mol. Further modifications, such as use of a magnetic rotating arc (DuPont process®) and a conical shape arc, co-feeding of H₂ and higher hydrocarbons to facilitate the quenching were adopted to increase the energy efficiency. The use of H₂ as carrier gas at high concentration (up to 80%) facilitates the conversion of thermal to chemical energy and prevents diacetylene formation, which is a precursor of carbon. Consequently, a higher amount of acetylene is produced (up to 76%) while carbon is minimized. To improve the energy efficiency of the process (up to 46%) a preheating step of the feeding gas with the exhaust gas is introduced. Preheated gas at 500°C increases the acetylene yield and decreases the energy cost by 25%. Thus, the electric cost for acetylene formation decreases to 818 kJ/mol. However, thermal plasma converters are still energy demanding units due to the high thermal losses in the form of sensible heat of products (36%) and hardware (18% in cooling the plasmatron).

On the other hand, non-thermal discharges work at lower temperature, at which thermal losses are lower than in thermal discharges. In principle, DBD yields the lowest efficiencies as seen in **Error! Reference source not found.**^(46,47). Nozaki et al.³⁶ analyzed the reasons of the low efficiency through kinetic modeling: at low electric field strengths, CH₃ is the main radical with a density 10 times higher than the electron density and vibrational channel excitation has a significantly lower energetic threshold (0.2-0.4 eV) as compared to CH₄ dissociation reaction to CH₃ (9 eV); therefore, excited methane species have a density of 150 times higher than the electron density, which is typically low (10¹⁴ cm⁻³)³⁶. Due to the large cross-section, 36% of the electric energy input is channeled to vibrational excitation and lost through molecular collisions³⁶. In addition, heat is dissipated to dielectric material and gas heating. Eventually, the energy efficiency of C₂ production drops to ~1%.

An effective way to increase the efficiency as proposed by Nozaki et al.⁵⁵ is to apply **nanosecond pulsed** voltage (<10–100 ns) to suppress the undesired energy losses caused by ion current generation (resulting in gas heating). Ravasio and Cavallotti et al.⁵⁶ indicated that the voltage repetition in the same plasma volume is useful in terms of energy efficiency because at high frequencies (>10 kHz) the memory effect facilitates the breakdown event and the energy required to initiate the microfilament decreases. However, the most effective solution is the **plasma-catalyst integration**; a part of thermal losses is efficiently utilized in catalytic reactions, thus increasing the efficiency. Vibrationally excited CH₄ molecules and gas temperature (expected to be higher than the catalyst bed temperature) can promote catalytic CH₄ coupling, increasing the overall conversion. However, this synergetic effect of plasma-assisted catalysis has not been adequately explained yet and still remains debatable. Therefore, many authors have focused their research on understanding this effect; some works confirm the improvement of performance when catalyst is present; in other works, the presence of catalyst decreases the overall conversion. These works have been gathered in a few review papers in the last two years^{57,58}.

Plasma-assisted methane coupling outlook

Non-oxidative methane coupling is one of the most attractive methane valorization routes leading to commodity chemicals with high commercial value especially for the polymer and chemical industry. Non-equilibrium electrical discharges, channeling the electric energy directly into molecular dissociation may be a promising alternative, for methane coupling, to conventional thermal processing, which is characterized by low equilibrium conversion and requires catalyst and high operating temperatures necessitating bulky and costly gas-fired furnaces. Major advantages of non-thermal plasma techniques are the low operating temperature, the low thermal inertia and the fast response to fluctuating

or intermittent operating conditions. However, attaining high-energy efficiency is the biggest challenge towards industrialization of the plasma-driven process. High energy efficiency may be attained through plasma performance optimization and integration of plasma and catalysis.

As regards the first aspect, on-going technological developments may permit to overcome current process limitations and open new operating windows leading to plasma performance optimization. However, these technological developments (i.e. nanosecond pulsed generators and related pulsed discharges) must be accompanied with a full comprehension of the involved mechanisms and clear view of the strengths and weaknesses of the latest technology use. Models and diagnostics of gas-phase plasma chemistry would considerably contribute towards this direction. Tuning and controlling the parameters that influence the plasma characteristics may also improve plasma performance. For instance, the decomposition rate increases when part of the dissipated energy is channeled into the vibrational excitation mode. Consequently, it is possible for a part of the dissipated thermal energy to be utilized in the radical chemistry, thus enhancing conversion and improving plasma performance. Different ways to channel the dissipated energy into the vibrational excitation modes might be a future research topic in gas-phase plasma chemistry.

Many efforts have been carried out to integrate plasma and catalysis in one step. It has been observed that plasma-catalyst interaction (not only for non-oxidative methane coupling) leads to a synergistic effect; conversion and selectivity, as well as energy efficiency, are affected and different products are formed, as compared to plasma alone or thermal catalytic processing. However, hybrid plasma-catalytic systems still face several challenges, some being of technical nature (i.e. coke formation and deposition resulting in catalyst deactivation and discharge suppression due to short circuits, catalyst instability and decomposition inside the discharge) and some of scientific nature (diffusion and surface chemistry enhancement by the electric field, effect of catalyst presence on the electric field pattern, nature of the reactive species that are produced by plasma and interact with the catalyst surface). Global models taking into account both gas-phase plasma chemistry and catalyst surface chemistry contributions will provide insight into the associated fundamental phenomena and plasma-catalyst interaction.

Finally, regarding technology industrialization, the first challenge is to change the perception of part of the community on plasma technologies and their applications, which are often considered energy-intensive and high-cost technologies and profitable only for specific high-tech products, such as electronics. The second challenge concerns the electric energy cost, which at present is higher compared to thermal energy that drives most chemical processes. In the future, however, the electricity cost is expected to be significantly reduced owing to the high availability of renewable energy sources and concurrent fossil fuel depletion. In this context, research on and development of electricity-based technologies is an essential step towards conversion of renewable electric energy into valuable products (power-to-chemicals concept). When these two challenges are addressed, technical issues related to technology upscaling will become less important than today. On the top of that, an assessment of the plasma technologies socio-economic impact (i.e. carbon footprint and economic potential) is further necessitated, in order to convince the industry that an up-coming transition from the traditional, well-established thermally driven processes to novel electrified process guarantees low environmental burden as well as sufficient economic viability.

Objectives and outline of the thesis

The current doctoral thesis aims at exploring the potential of a novel plasma-based technology, applicable to rich-in-methane gas streams valorization to olefins and specifically to ethylene. To achieve this, a holistic approach is adopted: novel plasma reactor systems are first developed, investigated and optimized at lab scale, followed by techno-economic evaluation and sustainability assessment. Plantwide process models that simulate the whole plasma-assisted process and life cycle assessment are employed to facilitate the evaluation. The evaluation outcome serves, then, as feedback for further reactor improvements and advances towards i) lower ethylene energy cost that allows for positive economic potential and ii) large scale operation, tackling current limitations such as short operating periods, reactor clogging due to carbon formation and very broad operating windows. This holistic approach seeks to:

- ✓ prove that nanosecond pulsed plasmas can be used for methane valorization through non-oxidative methane coupling to ethylene. (applicability)
- ✓ explore new operating windows far from the thermodynamic equilibrium and establish the optimum one within which ethylene yield and conversion of electric into chemical energy are maximized. (optimization)
- ✓ attain ideal thermal and chemical integration between plasma and catalyst zone in order to maximize ethylene yield and minimize energy cost. (optimization)
- ✓ elucidate the impact of active plasma species on catalyst surface properties and subsequently on catalyst performance. (process understanding)
- ✓ reveal reaction paths of non-oxidative methane coupling enabled in nanosecond pulsed plasmas at different operating conditions. (process understanding)
- ✓ evaluate the technical and economic potential of such electrified processes at large scale and identify cost drivers that must be further optimized in order for plasma processes to be competitive. (process upscaling)
- ✓ establish plasma reactor heuristics applicable to a wide range of applied conditions that allow for maximum reactor performance and, propose a reactor design that is robust to carbon formation and enables long operating periods and electrodes decoking. (process upscaling)
- ✓ determine the carbon footprint of the technology and identify the most sustainable process through which ethylene should be produced in the near future. (process upscaling)

The research objectives, which are addressed in the current doctoral dissertation, are summarized in Figure 1.

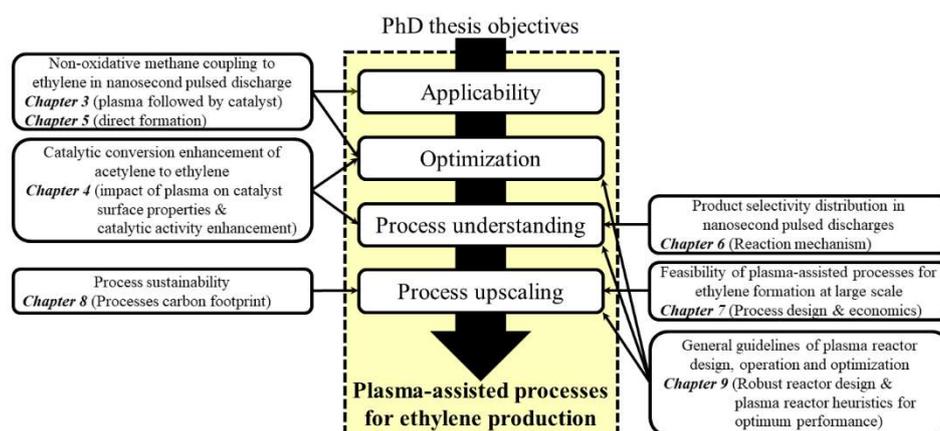


Figure 1. Schematic representation of the research objectives addressed in current doctoral dissertation and its breakdown into the Chapters in which each objective is addressed.

Highlights and conclusions of the thesis

Low energy cost methane conversion to ethylene in a hybrid plasma-catalytic reactor system was first investigated: methane conversion to acetylene by a nanosecond pulsed discharge (NPD) and subsequently, acetylene hydrogenation to ethylene using a Pd-based catalyst placed in the post-plasma zone is possible. Ethylene is formed as major product at 25.7% yield per pass, demanding 1642 kJ/mol_{C₂H₄} in a single reactor, when operating at applied voltage ~17 kV, pulse repetition frequency 3 kHz, discharge gap 2.4 mm and total feed flow rate 200 sccm of H₂:CH₄ = 1:1 and utilizing 0.5 g of catalyst. The hybrid reactor is self-sustained since both heat and H₂ required for the hydrogenation reaction are provided by methane cracking in the plasma zone itself, while operating periods of ~1 h are achieved. Higher ethylene yields and thus lower energy costs can be attained via hydrogenation catalyst activity enhancement using NPD treatment. The impact of treatment energy via pulse voltage, pulse frequency and treatment time individual variation on acetylene-to-ethylene hydrogenation reaction performance was also investigated: up to 11.2% increase in C₂H₂ conversion can be attained after plasma treatment at specific energy input of 5340 J/g_{cat} whereas C₂H₄ selectivity remains constant. The catalyst characterization revealed that C₂H₂ conversion increase is attributed to the higher active metal surface attained after the plasma treatment while no surface distractions (i.e. phase change and active metal

sputtering) occur. Finally, it is concluded that the plasma-treatment impact on catalyst performance is driven by the specific energy input, irrespective of the operating conditions (pulse voltage, pulse frequency and treatment time).

Direct plasma-assisted non-oxidative methane coupling to ethylene is also possible. Ethylene can be formed as major product at ~20 % yield per pass without utilizing any hydrogenation catalyst downstream the plasma zone, demanding 2020 kJ/mol_{C₂H₄}. This was attained by employing an NPD reactor, featuring rapid product quenching rates, (recyclable) hydrogen, co-feeding (CH₄:H₂=1:1) and operating at elevated pressures (5 bar). A study on the reaction pathways involved in non-oxidative methane coupling in NPD reactor via isotopic analysis was further conducted to explain the product selectivity shift. Plasma-assisted reactions with isotopes, serving as tracers, were performed in two ratios (CH₄:D₂=1:1 and CH₄:D₂=1:3) and elevated pressures (up to 5 bar) while acetylene hydrogenation reactions were also performed in a tubular reactor under conventional furnace heating to simulate post-plasma zone conditions. It is concluded that C₂H₂ is mainly formed via CH₃ radicals coupling to ethane followed by stepwise dehydrogenation (C₂H₆ → C₂H₅ → C₂H₄ → C₂H₃ → C₂H₂) when operating at ambient pressure. However, two additional reactions, not important at ambient pressure, are enabled when operating at elevated pressures: i) direct CH₃ radicals coupling to ethylene and ii) acetylene hydrogenation to ethylene catalyzed by the copper-based electrode. The combined effect of the two reactions result in C₂H₄ formation as major product at pressures higher than 3 bar.

Plantwide simulations of the hybrid plasma-catalytic and direct ethylene formation processes were performed. After performing sensitivity analyses on the key process parameters (reflux ratio, operating pressure and column stages) and heat integration, the economically preferable operating window was defined and the economic potential of plasma-assisted processes for ethylene production was evaluated. It is concluded that plasma-assisted processes are not economically viable at present, given that break-even electricity prices of 23 and 35 USD/MWh are calculated for the one-step and two-step process, respectively, while the current electricity prices for some energy intensive industries in certain countries can be as low as 50 USD/MWh. Further, life cycle assessment was conducted to estimate the carbon footprint of the plasma-assisted process and benchmark it against the carbon footprint of other green-considered ethylene production processes. It is concluded that coupling of plasma-assisted process with wind turbines is necessitated to attain significantly low carbon footprint (1.3 kg CO₂-eq./kg_{C₂H₄}).

Finally, the ethylene energy cost that allows for positive economic potential determined in the abovementioned economic evaluation, was set as new targeted performance. To meet the targeted performance, the plasma reactor was redesigned and reoptimized; a plate-to-plate configuration was tested. Discharge characterization was also applied to link the operating parameter (pulse repetition frequency, discharge gap and pressure) values with the discharge regime and CH₄ fragmentation pattern, which drives the plasma chemistry. Acetylene yield of 33.5% using 870 kJ/mol_{C₂H₂} was attained, which allows for positive process economic potential. Moreover, stable performance and long operating periods that are required at large scale operation were achieved and general guidelines (high load-impedance matching) for optimum plasma reactor performance were also established.

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