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Plasma Based Liquefaction Of Methane: The Road From Hydrogen Production To Direct Methane Liquefaction

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For the energy industry, a process that is able to transform methane—being the prime component of natural gas—efficiently into a liquid product would be equivalent to a goose with golden eggs. As such it is no surprise that research efforts in this field already date back to the nineteen hundreds. Plasma technology can be considered to be a novel player in this field, but

nevertheless one with great potential. Over the past decades this technology has evolved from sole hydrogen production, over indirect methane liquefaction to eventually direct plasma-assisted methane liquefaction processes. An overview of this evolution and these processes is presented, from which it becomes clear that the near future probably lies with the direct two phase plasma-assisted methane liquefaction and the far future with the direct oxidative methane liquefaction.

1   Introduction

1.1   Methane Liquefaction

Interest for transforming methane into more valuable liquid products dates back as far as the beginning of the 20th century. At present, several promising methane sources are available, such as the regular natural gas, biogas, landfill gas, methanated CO_2 and shale gas, all coming with their own advantages and drawbacks depending on the viewpoint one takes. Although some sources may be debatable, one cannot neglect the fact that to date methane is one of the cheapest sources of energy available in the world.[1] As such it is not surprising that a very large fraction is used for heating and electrical power generation, for which methane in many respects is an attractive fuel—besides its current price point. Nevertheless, it can be considered to be one of the most underutilized feedstocks with regard to the production of value-added chemicals and liquid fuels, the main obstacle being its physical condition, the—industrially undesirable— gaseous state. As such, one can imagine that a lot of research effort has already been performed for the development of efficient natural gas conversion technologies. The most well-developed are the indirect synthesis routes, which first convert methane into the intermediate syngas, a mixture of CO and H_2, with the main processes being steam methane reforming (SMR), dry reforming of methane (DRM) and partial oxidation of methane (POX). The syngas is then

further processed by Methanol or Fischer-Tropsch synthesis to obtain the desired liquid products.[2] Although, successful from a technical perspective, these methods are marked by low overall yields and high energy inputs.[3] Their direct (thermo-catalytic) synthesis counterparts circumvent the expensive and energy intensive syngas step, but are technologically still very challenging and costly, while achieving no better results concerning product yields.[2]

1.2 Plasma Technology

Unsurprisingly, interest for alternative (non-conventional) reforming processes took a spike and one of the alternatives considered to have great potential in this area is plasma technology.[4,5] The advantage of (non-thermal) plasmas is that the gas can be "activated" by electron impact excitation, ionization and dissociation reactions, instead of the need for heating the entire reactor. Several types of plasmas have already been used for the conversion of methane,[6–9] including dielectric barrier discharges (DBD),[7–39] microwave discharges,[7–9,25,40–44] glow discharges,[7,9,25,45–48] coronas,[7–9,25,46,49–51] sparks,[9,22,25,38,52,53] gliding arcs,[6–9,22,25,54–61] radio frequency (RF) plasmas[9,25,62,63] and thermal plasmas.[5,7,9,64–68]

Figure 1 gives an overview of the different directions that are being investigated regarding plasma-based methane liquefaction approaches. The 'direct gas phase plasma methane liquefaction', is the conversion of pure methane into hydrogen gas and liquid hydrocarbon chains originating from the remaining CH_2 blocks. The 'oxidative plasma liquefaction' methods, can be subdivided in an indirect and a direct approach. The indirect approach converts methane into syngas together with an oxidant, such as O_2, CO_2 or H_2O, known as partial oxidation of methane (POX), dry reforming of methane (DRM) and steam methane reforming (SMR), respectively. The syngas is then further processed into liquids using Fischer-Tropsch or methanol synthesis. The direct approach, on the other hand, tries to convert methane with the same oxidants into oxygenated liquid products, such as alcohols and aldehydes, in one step. Finally, recently a new approach 'direct two phase plasma-assisted liquefaction' has emerged,

which—as its name suggests—aspires the direct liquefaction of methane, through its incorporation into a second phase, namely existing liquid hydrocarbons.
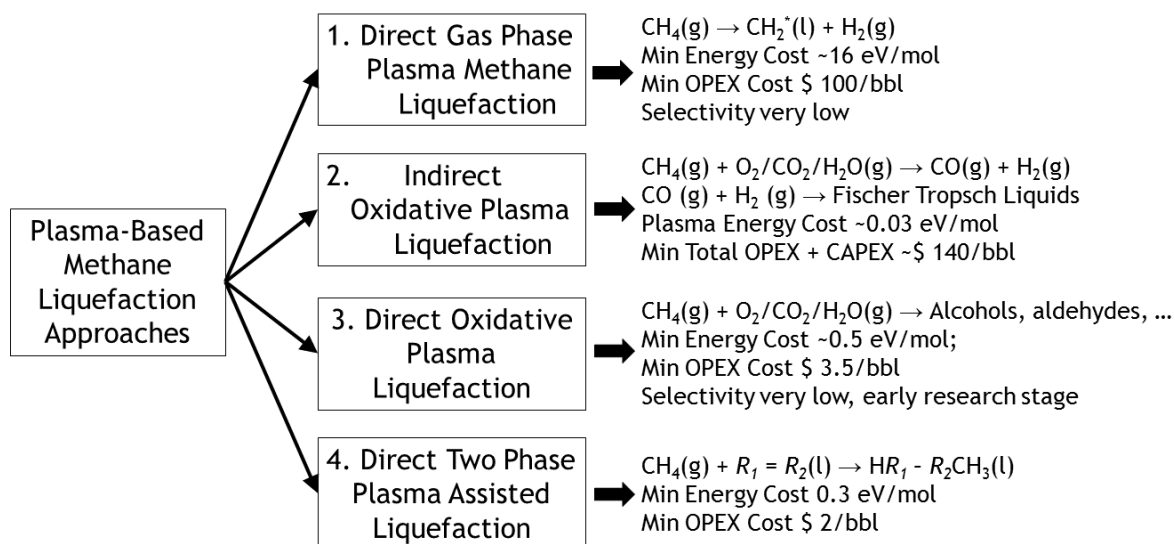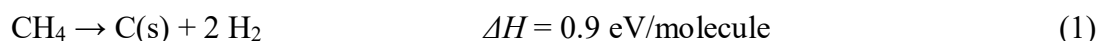

Figure 1. Overview of the different plasma-based methane liquefaction approaches.

This review will give an overview of the efforts made to date in the field of plasma-based liquefaction of methane. Looking at the minimal energy cost in eV/molecule—and subsequently the resultant operational expenditure (OPEX) cost—for these different approaches in Figure 1, it already becomes clear that to date the two most promising techniques are the 'direct oxidative plasma liquefaction' and the 'direct two phase plasma-assisted liquefaction'. The former still needs a lot of research and development regarding an increase of the selectivity, before it can be successfully applied on an industrial scale, and thus becomes important in the long run, while the latter, if successfully up scaled, can already be implemented on a short term.
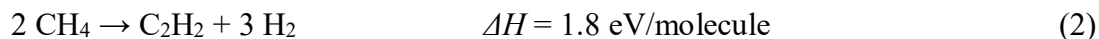
2   Direct Gas Phase Plasma Methane Liquefaction

The direct conversion of methane in the absence of oxidants such as O_2, CO_2 and H_2O, better known as 'the pyrolysis of methane' is a technique which can be used to synthesize higher hydrocarbons.[25]

Total pyrolysis:

$$CH_4 \rightarrow C(s) + 2\ H_2 \qquad\qquad \Delta H = 0.9\ \text{eV/molecule} \qquad\qquad (1)$$

Partial pyrolysis:

$$2\ CH_4 \rightarrow C_2H_2 + 3\ H_2 \qquad\qquad \Delta H = 1.8\ \text{eV/molecule} \qquad\qquad (2)$$

Under equilibrium conditions (i.e. thermal plasma arc discharge) the synthesis of H_2 and C_2H_2 (acetylene) is already being successfully applied on an industrial scale. It reaches a conversion of 95–98 % and an acetylene selectivity of 90–95 %, with an energy consumption of 2.5–3 eV/molecule (see also table 1).[69] The same process for atmospheric pressure non-thermal plasma discharges, on the other hand, has a much higher energy consumption, varying from 14–25 eV/molecule in a pulsed spark discharge, 17–21 eV/molecule for a streamer discharge, 38–57 eV/molecule in a pulsed DC DBD and a staggering 116–175 eV/molecule for an AC DBD.[38] **Table 1** gives an overview of the results for these different plasma discharges.

One might ask why there is still such a big interest for these non-thermal approaches. The answer is: not only do they have the advantage of operating at room temperature, in comparison to the thermal process which yields acetylene and H_2, but they can also yield a wide variety of products with a higher commercial value, including: ethane, propane, butane, ethylene, acetylene, isobutene and hydrogen.[21,22] Furthermore, it has been shown that the plasma characteristics, i.e. electron energy and the degree of 'warmness', greatly affects the product selectivity. Plasma sources that have strong non-thermal characteristics show higher C_2H_6 selectivity, while, upon increasing degree of warmness, the selectivity of H_2 and C_2H_2 increases. As such the proper selection of a plasma source can be used as a tool to control the reaction pathway.[22]

Nevertheless, looking at Figure 1 and Table 1 it becomes clear that non-thermal plasma discharges are inefficient for the (partial) pyrolysis of methane, because of the high activation energy required by electron impact processes.[24] The combination of a catalyst together with the reactive plasma species might be the key to enhancing the selectivity, and therefore the

energy efficiency to targeted products. Indeed, numerical simulations show that vibrationally excited methane species are the abundant long-lived excited species. Due to the fact that these species are highly reactive on transition metal catalysts, a synergistic effect between DBD and Ni-catalysts can be achieved.[24] These vibrationally excited methane states will also be important for the last technique described in this review, i.e., 'the direct two phase plasma-assisted liquefaction'.

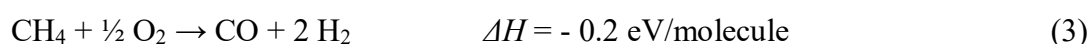*Table 1.* **Overview of methane pyrolysis results.**

Discharge type	Conversion (%)	Energy Consumption (eV/molecule)	Ref.
Gliding arc	34	0.82	[70]
Arc DC (thermal)	95	3.0	[69]
Hollow cathode	26	1.19	[22]
Rotating arc	42	1.56	[22]
Spark AC	83	2.21	[22]
Spark	70	6.1	[25]
Corona	25	52	[25]
DBD AC	15	82.9	[22]
DBD AC	5–8	116–175	[38]
Pulsed microwave	90–100	1.0	[71]
Pulsed double pointed	23.5	3.8	[25]
Pulsed spark	49	6.94	[22]
Pulsed spark	18–69	14–25	[38]
Pulsed electron beam	5–7	18	[25]
Pulsed streamer	19–41	17–21	[38]

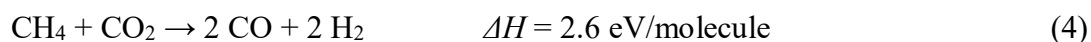|			
Pulsed DBD	9	19	[22]
Pulsed DBD DC	6–13	38–57	[38]
Gliding arc + catalyst (Al$_2$O$_3$)	18	2.4–7.3	[25]
Spark + catalyst (Fe, Co, Ni on HZSM-5)	40	19	[72]
DBD + catalyst (SiO$_2$)	45	52	[25]

3   Oxidative Plasma Liquefaction

Although plasma technology is based on a different principle than the conventional thermal methods, pure methane reforming can have the same drawback of carbon deposition due to total pyrolysis (reaction 1). In other applications this might be beneficial like for the pure production of hydrogen, carbon nanotubes and carbon black.[5,73,74] However, in the present case every carbon molecule deposited as soot is a loss of building blocks and eventually energy. Furthermore, the deposited carbon tends to be very conductive, which, depending on the process, can influence the plasma discharge(s).[75] As such, in analogy with their conventional counter parts, an oxidizing agent was added to minimize this carbon formation and deposition,[76] the candidates being again O$_2$, CO$_2$, and H$_2$O yielding partial oxidation (reaction 3), dry reforming of methane (reaction 4) and steam methane reforming (reaction 5), respectively. These processes yield mainly the syngas components CO and H$_2$, which can be further processed into Fischer-Tropsch liquids or methanol. An additional reason for adding an oxidizing agent is the aspiration for the direct formation of value-added oxygenated products such as formaldehyde, methanol, ethanol, dimethyl ether, formic acid, etc. These two options are therefore called the 'indirect and direct oxidative plasma liquefaction' approaches, respectively. In both areas a lot of research effort is also directed to the combination of a plasma system with a catalyst, which falls outside the scope of the current review and for which we refer to the work of Neyts et al.[73]
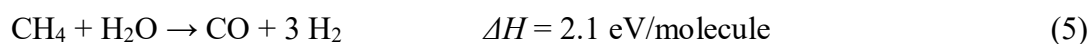
Partial oxidation of methane:

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow CO + 2\,H_2 \qquad \Delta H = -0.2 \text{ eV/molecule} \qquad (3)$$

Dry reforming of methane:

$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2 \qquad \Delta H = 2.6 \text{ eV/molecule} \qquad (4)$$

Steam methane reforming:

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \qquad \Delta H = 2.1 \text{ eV/molecule} \qquad (5)$$

3.1 Indirect Oxidative Plasma Liquefaction

The 'indirect oxidative plasma liquefaction' approach consists of producing liquid products from methane in two stages. The first stage entails the successful production of the syngas components CO and H_2, by plasma-based partial oxidation, dry reforming of methane or steam methane reforming. Subsequently, this syngas is then further processed into liquid chemicals and fuels using the traditional catalytic Fischer-Tropsch processes or methanol synthesis. Although industrially possible, this two-step process has a high capital cost, since in its essence we are oxidizing the carbon atoms present in the first step, only to reduce them again afterwards in the second step. This also explains the high—combined OPEX and APEX—cost as presented in Figure 1, despite its extremely low energy cost (in the case of partial oxidation of methane, see below).

3.1.1 Partial Oxidation Of Methane

The reaction enthalpy shows that partial oxidation of methane is a slightly exothermic process. Taking this into account, the process can be realized with a very low energy input, by selective generation of radicals, charged and excited species, stimulating the low temperature long chain reactions.[9] (Near-)atmospheric pressure non-equilibrium discharges have proven to be effective for this purpose. The different plasma systems include pulsed corona discharges,[9,50] microwave discharges,[8,9,25,41,44] dielectric barrier discharges,[8,9,13,25–29] and gliding arc discharges.[8,9,25,58,59] For lower pressure non-equilibrium discharges, results have been obtained

for radio frequency,[9,63] and pulsed discharges.[9] In general, the non-thermal discharges can obtain high energy efficiencies, but fail when it comes to the industrially requested high production (flow) rates of the syngas. One of the exceptions are the gliding arc discharges, which can generate a strongly non-equilibrium, mainly non-thermal plasma, even at relatively high power levels.[77] To date the best results regarding a combination of yield and energy efficiency have been achieved with a reverse vortex flow gliding arc discharge,[9] as shown in **Table 2**.

Table 2. **Overview of oxidative plasma liquefaction for partial oxidation of methane.**

Discharge type	Conversion (%)	Energy Consumption (eV/molecule)	Ref.
Microwave (thermal)	100	0.5	[25]
Arc DC (thermal)	100	1	[78]
Vortex rotating arc	30	1.4–5.0	[79]
Rotating arc	78–99	1.6–2.2	[80]
DBD 75 kHz	14–27	5–13	[25]
DBD 30 kHz	24	13	[26]
DBD micro reactor	45	17	[81]
DBD + catalyst (Yt + Zr)	50	88	[25]
DBD + catalyst (CZA)	29–45	89–159	[82]

3.1.2 Dry Reforming Of Methane

Dry reforming of methane has the advantage of using carbon dioxide as oxidizing agent, thus allowing the utilization of the main greenhouse gas as a feedstock and leading to a 'greener' reforming of methane, especially when the syngas is intended for further conversion.[1] However, the thermodynamics for dry reforming of methane (DRM) are not as feasible as for

the partial oxidation of methane (POX). As a result the thermodynamic barrier makes processes relying on heat unfavorable. As such it is no surprise that plasma technology is amongst the most popular of the unconventional approaches reported in literature.[1] Plasmas allow for a high conversion of methane and many of them show positive results regarding the energy balance.[1] Just like for the partial oxidation, several kinds of non-thermal plasmas have been applied for DRM, such as corona discharge,[7,8,25,51] dielectric barrier discharge (DBD),[7,11–14,17–20,25,30–37] microwave discharge,[7,40] atmospheric pressure glow discharge (APGD),[7,46] spark discharge[53] and gliding arc discharge.[7,8,25,55,60,61] In general, the application of non-equilibrium plasma allows for dry reforming of methane at a relatively low temperature without using any conventional catalyst. Although, depending on the plasma source, the energy efficiency can exceed 40 %, the total consumption of electric energy can be relatively high in the process.[9] The type of plasma which is currently most often used for investigating DRM (and gas conversion in general) is the dielectric barrier discharge (DBD).[12,76] However, when evaluating the existing non-thermal technologies, it appears that arcs, together with microwave and glow discharges, show the best performances because of their high energetic densities and their ability to create a large reactive volume.[5,8,9]

In an extensive review by Tao et al.[7] regarding dry reforming of methane by different plasmas, it was concluded that three key factors need to be taken into account for achieving high conversions and energy efficiency, i.e., the electron density, plasma temperature and reactor configuration. As such, the treatment capacity for corona discharge and DBD are restricted due to their non-uniformity, low electron density and limited reaction volume, while microwave discharges, gliding arc discharges and APGDs possess high electron energy and electron density, as well as the proper plasma temperature. **Table 3** shows an overview of the obtained results in the field of 'indirect oxidative plasma liquefaction' research for dry reforming of methane.

Table 3. **Overview of oxidative plasma liquefaction for dry reforming of methane.**

Discharge type	Conversion (%)	Energy Consumption (eV/molecule)	Ref.
Pulsed corona	16	0.7	[25]
Glow	54	0.89	[45]
Arc DC (thermal)	~8	1	[65]
Cold plasma jet	38.7	2.09	[83]
Microwave	70	3.18	[84]
Glow	50.5	3.24	[85]
Gliding arc	9.8	3.44	[60]
Radio frequency	61.9	4.44	[86]
Gliding Arc	35.5	6.30	[55]
Corona DC	83.3	11.8	[87]
Corona	55.1	18.6	[46]
Gliding arc AC	8	20	[25]
DBD (0.4 - 2 kHz)	9.8–22.8	38–70	[25]
DBD (2 - 40 kHz)	25–65	73–100	[25]
DBD (30 kHz)	35–75	52–85	[25]
DBD	61.3	84.2	[88]
DBD	58.6	75.6	[37]
Cold plasma jet + catalyst ($NiAl_2O_3$)	48.2	1.39	[83]
DBD + catalyst (starch)	48	16	[25]
Corona + catalyst (Zeolite)	39.6	41.7	[89]
DBD + catalyst ($NiAl_2O_3$)	44.6	107.6	[90]

3.1.3 Steam Methane Reforming

A third option to be considered as oxidizing agent is H_2O, leading to the so-called steam methane reforming (SMR). A lot of research is still ongoing in this area. In general, the same kind of non-thermal plasmas can be, and have been, used for SMR as for DRM,[25,91–95] and the same principles hold due to the endothermic nature of both processes. The main difference is that SMR can generate a maximum hydrogen yield and/or high syngas ratio, since both CH_4 and H_2O are converted into H_2, while the presence of O from H_2O prevents soot formation. The use of H_2O compared to O_2 or CO_2 as oxidizing agent allows several options to deliver the H_2O in the plasma, e.g. as liquid, vapor or steam. Depending on this (energetic) state of the H_2O, the electrical characteristics, plasma chemistry, conversions and energy efficiency vary widely even within the same discharge type. A detailed analysis of the latter is outside the scope of this review paper, but a brief summary of results obtained in literature for plasma-assisted steam methane reforming is shown in **Table 4**.

Table 4. **Overview of oxidative plasma liquefaction for steam methane reforming.**

Discharge type	Conversion (%)	Energy Consumption (eV/molecule)	Ref.
Gliding arc	48–71	1.08–1.26	[91]
Spark	55	5.3	[25]
MW	91.6	28	[92]
Corona AC	28–80	33–105	[93]
DBD	17	53	[94]
DBD	50	54	[95]
Gliding arc + catalyst (Ni/Al$_2$O$_3$)	73–82	0.90–1.33	[91]
Spark + catalyst (Ni)	70	1.6	[25]

DBD + catalyst (Ni/SiO$_2$)	66–86	3.8–18.4	[95]

3.2 Direct Oxidative Plasma Liquefaction

In contrast to the indirect approach, the 'direct oxidative plasma liquefaction' approach tries to synthesize oxygenated liquid products in one step. The main product categories that can be defined are: alcohols (e.g., methanol, ethanol), aldehydes (e.g., formaldehyde), ethers (e.g., dimethyl ether) and acids (e.g., formic acid, oxalic acid). To achieve this, in general the same techniques and setups are used as for the indirect approach, but the operating conditions are tuned in order to try to produce these more valuable products in higher amounts compared to the aforementioned syngas. In general, DRM favors the formation of H$_2$, CH$_2$O, CH$_3$CHO, and CH$_2$CO, while POX yields higher concentrations of H$_2$O$_2$, CH$_3$OH, C$_2$H$_5$OH, CH$_3$OOH, and C$_2$H$_5$OOH, as revealed by computer simulations.[13] In both processes CO is formed and during POX significant amounts of undesired CO$_2$ can be formed. An explanation for this difference in product formation is proposed and is attributed to the crucial role played by the CH$_3$ radicals.[13] During DRM these radicals primarily recombine to hydrocarbons, while during POX the formation of CH$_3$O$_2$ radicals is favored. The production of these CH$_3$O$_2$ radicals lead to the formation of methanol, and subsequently formaldehyde.[13] Two other computational studies using a zero-dimensional chemical kinetics model obtained the same findings for DRM and also illustrated the tradeoff between conversion and energy efficiency.[11,12] As a result it was posed that classical DBDs would probably not be competitive, and that it would be more interesting from a combined economic and ecological point of view to focus on more efficient discharges, such as microwave discharges, gliding arcs and packed bed DBDs.[12] Furthermore, notwithstanding all the research in this area, the main products formed currently remain the syngas components CO and H$_2$ and the gaseous C$_2$ hydrocarbons, ethane, ethylene and acetylene, with few studies reporting the production of significant amounts of liquid hydrocarbons.[1,7,11,76] Recent efforts are therefore, among others, focused on the synergism

between plasma and catalysis for this process, in which the underlying idea is for the plasma to activate the inert gas molecules and to have the catalyst to react and/or recombine these reactive species in a selective way towards the desired (liquid) products.[73,74] From these findings it becomes clear that although the 'direct oxidative liquefaction of methane' is one of the most promising in theory, a lot of research is still needed to improve the yield of the desired (oxygenated) liquid products.

4   Direct Two Phase Plasma-Assisted Liquefaction

Reports show that the API gravity of extracted crude oil has been decreasing,[96] this means that the most useful and valuable part, i.e., the light crude, is decreasing. Combined with the limited supplies of fossil hydrocarbons, attention is being focused on new technologies to process the cheaper heavy crude fractions. The aim is to convert these heavier crudes into more economic valuable products by reforming, cracking or upgrading.[97–100] The most common methods used in refineries are thermal and catalytic cracking. All these traditional methods are carried out at relatively high temperatures and moderate pressures, which often results in the production of high amounts of coke as unwanted byproduct. In this field as well, plasma technology can be used as a way to convert a wide variety of hydrocarbons. In such a plasma cracking process, the overall reactions are the same as for conventional cracking. However, energy and free radicals provided by the plasma are used for the cracking – instead of heat – allowing the plasma cracking process to operate at ambient temperature and atmospheric pressure unlike the traditional non-catalytic cracking processes.[100]

Several promising results have already been achieved for the cracking of heavier crudes using plasma technology, including pure liquid plasma reformers and combinations with active gases such as methane and ethane mixtures with N_2, He and Ar.[96,98–100] In this cracking process the long chain hydrocarbons are split into shorter chain hydrocarbons, which then react with the radicals in the gas phase to form a termination product. Although promising, a lot of energy is

still being put in the endothermic process of the hydrocarbon bond cleavage and radical production. An energetic more favorable approach would therefore be preferred.

This knowledge of plasma based hydrocarbon cracking, in combination with the mixed results obtained when trying to achieve the liquefaction of methane through the above mentioned reforming paths (mainly just resulting in the production of syngas), led to another novel approach. This new approach can be seen as a combination of the above mentioned plasma based reforming and cracking processes, namely, the direct liquefaction of methane by its incorporation in existing liquid hydrocarbons. Two possible pathways for the successful incorporation are suggested:[101,102]

Saturation of double bonds:

$$CH_4 + R_1 = R_2 \rightarrow HR_1 - R_2CH_3 \qquad\qquad \Delta H = - 0.5 \text{ eV/molecule} \qquad\qquad (6)$$

Polymerization:

$$CH_4 + R_1 - R_2H \rightarrow R_1 - R_2CH_3 + H_2 \qquad\qquad \Delta H = 0.6 \text{ eV/molecule} \qquad\qquad (7)$$

The saturation of double bonds (reaction 6) is the preferred process, since it is exothermic with an eventual plasma energy cost of only 0.3 eV per molecule of CH_4, due to its exothermicity, while all the other hydrocarbon reactions in non-thermal plasmas, such as polymerization (reaction 7) and dissociation, require much higher energy inputs, mainly due to their endothermic character, making them ineffective for the energy efficient direct liquefaction of CH_4. To promote the saturation process (and hence its energy efficiency), local heating needs to be avoided, by working in the non-equilibrium discharge region.

The key to this approach lies in the selective vibrational excitation of CH_4, which allows for an exothermic plasma catalytic incorporation with extremely low energy cost.[102] Theoretically, this allows the energy cost to remain beneath 0.3 eV/molecule, which would be a significant improvement over conventional gas-to-liquid Fischer-Tropsch synthesis.[102] The only plasma systems known to be able to provide the necessary vibrational-translational non-equilibrium at atmospheric pressure are high gas flow gliding arc, microwave and atmospheric pressure glow

discharges, which have a vibrational temperature of 2000–4000 K. Another requirement for the effective incorporation at low energy cost (0.3–0.5 eV/molecule) is a gas temperature below 700–900 K in the reactor.[102]

For two plasma systems the successful incorporation of CH_4 into liquid hydrocarbons at this low energy cost has already been achieved: an atmospheric pressure nanosecond pulsed DBD and an atmospheric pressure glow discharge. Both discharges were ignited inside gaseous bubbles fed through liquid hydrocarbons; this bubbling is used in order to increase the reaction surface area as well as the mixing.[101–103] In the DBD system a continuous flow of 0.2 SLPM was applied and gas samples were taken after the reactor. While for the APGD system a fixed volume of gas (i.e. 2.97 L) was continuously recycled and a gas sample was taken after 5 min. **Table 5**, shows the gas composition before and after plasma treatment. In both cases the decrease in CH_4 volume could not be explained by the formation of its dissociation products C_2H_6, C_2H_2 and H_2. Leaving the CH_4 incorporation into liquid as the only reasonable explanation. This thesis was supported by NMR and FTIR analysis of the treated liquid samples combined with the GC analysis of the gas phase, which showed the effective fixation of methane in the liquid fuel, a corresponding decrease of the methane concentration in the gas phase, as well as structural changes to the liquid hydrocarbons (i.e. double bond saturation and aromatic ring opening).[101] **Figure 2** shows the FTIR spectra of the liquid sample before and after plasma treatment and its difference, significant changes can be seen for C-H bond absorption at 2850–3100 cm^{-1} and phenyl functional groups at 700–800 cm^{-1}. The increase of saturated C-H bond and decrease in phenyl functional groups and unsaturated C-H bonds suggests that phenyl rings are opened, and the activated methane saturates the carbon double bonds. Although this proves that the concept is feasible with non-thermal plasmas, further research is targeted toward a better understanding of the chemical processes taking place and increasing the conversion rates.

Table 5. **Gas composition before and after DBD and APGD treatment of a CH$_4$/N$_2$ mixture in diesel.**[101]

|	DBD Treatment		APGD Treatment	
	Without discharge	Treatment (continuous)	Without discharge	Treatment (batch-recycle)
N$_2$ (L)	0.106	0.106	0.27	0.27
CH$_4$ (L)	0.094	0.093	2.7	2.313
C$_2$H$_6$ (L)	3×10^{-5}	17×10^{-5}	19×10^{-5}	21×10^{-5}
C$_2$H$_2$ (L)	Not detectable	3×10^{-5}	Not detectable	8×10^{-5}
C$_2$H$_4$ (L)	Not detectable	Not detectable	Not detectable	Not detectable
H$_2$ (L)	Not detectable	4×10^{-4}	Not detectable	54×10^{-5}
***Total** (L)*	*0.200*	*0.199*	*2.97*	*2.583*
Difference (L)	0.001 L		0.387 L	
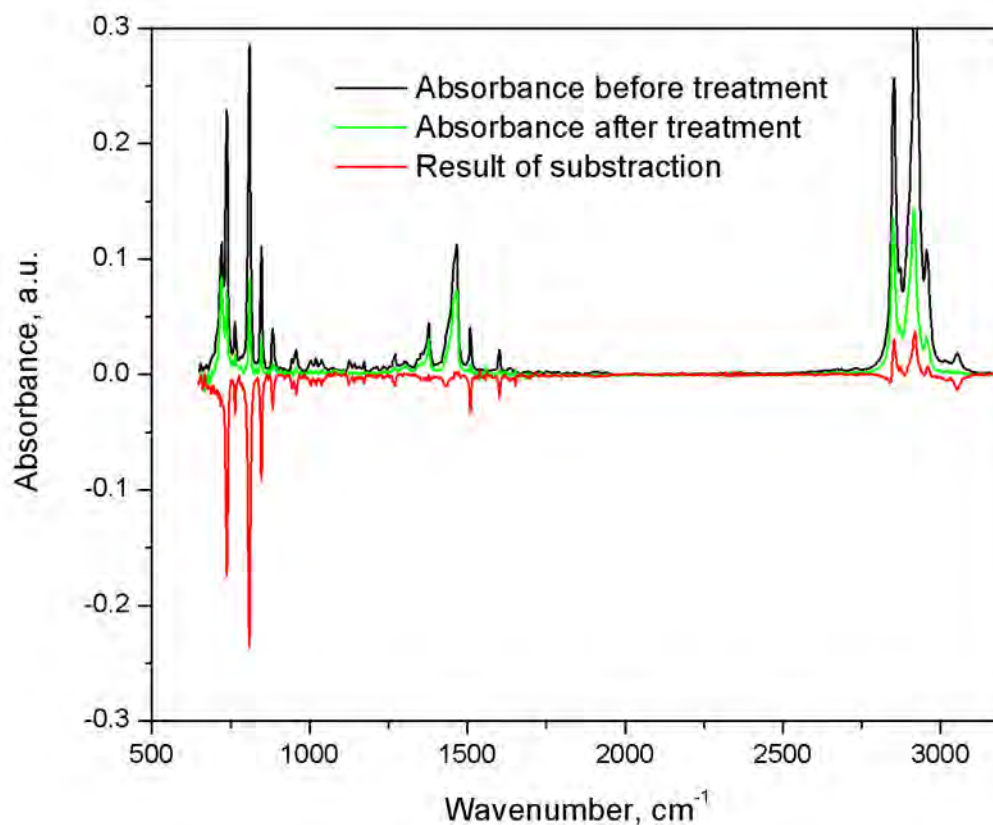
Figure 2. FTIR spectrum of the liquid sample before and after plasma treatment with methane.[101]

5 Conclusion

An overview of the progress in the field on plasma based liquefaction of methane has been given. From all the available literature, ranging from experiments, to model predictions and physicochemical insights, we can draw the following conclusions. It becomes clear that plasma technology can definitely play an important role in this field and it is not beyond our grasp to think about the eventual industrial implementation of this technology. Nevertheless, as always only a few candidates seem suitable for the specific task at hand. To be more precise, we can

identify two candidates, each for a more specific task and with a different timeline on the implementation horizon.

In the long run it seems evident that the 'direct oxidative liquefaction' has the highest potential for the efficient production of value-added liquid chemicals, such as alcohols, aldehydes, esters and acids. Furthermore, from both experimental and computational results it appears that partial oxidation of methane is more suited than dry reforming of methane, although the use of CO_2 presents a more ecologically attractive oxidant. For now, however, a lot of research in this area is still needed to increase the selectivity towards these valuable bulk chemicals over the currently produced syngas, possible by combinations with catalysts. Regarding the treatment capacity and hence the industrial applicability, corona discharges and DBDs seem restricted, while microwave, gliding arc and atmospheric pressure glow discharges possess the necessary properties, i.e. high electron energy and electron density, as well as proper plasma temperature. In the shorter run the 'direct two phase plasma-assisted liquefaction' could already deliver on the basic promise of liquefying methane. The latter is achievable not by its complete transformation into value-added products, such as is the case for the 'direct oxidative liquefaction', but rather by increasing the value of to date unusable—and hence invaluable—crudes by its successful incorporation, based on double bond saturation and polymerization reactions with vibrationally excited methane.

From the current analysis it becomes evident that the later solution can reach industrial implementation at a faster pace. Nevertheless, the former path should not be abandoned, since—when successful—it offers us the possibility of producing a wide variety of value-added chemicals and fuels starting from the same building block and allowing the flexibility to tune the output depending on the market's needs.

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Graphical Abstract

An overview of the efforts made to date in the field of plasma-based liquefaction of methane is given. Interest for transforming methane into more valuable liquid products dates back as far as the beginning of the 20th century, and it becomes clear that plasma technology can definitely play an important role in this field leading to a potential industrial implementation.

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Plasma Based Liquefaction Of Methane: The Road From Hydrogen Production To Direct Methane Liquefaction