Overview of hydrogen production by methane pyrolysis process and possible applications of the solid carbon products

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OVERVIEW OF HYDROGEN PRODUCTION BY METHANE PYROLYSIS PROCESS AND POSSIBLE APPLICATIONS OF THE SOLID CARBON PRODUCTS

Master's Thesis

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PREGLED PROIZVODNJE VODIKA POSTUPKOM PIROLIZE METANA I MOGUĆE PRIMJENE ČVRSTOG UGLJIKA

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Rad izrađen: Sveučilište u Zagrebu
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Sažetak

Europska Unija namjerava postići klimatsku neutralnost do 2050. godine, odnosno postati gospodarstvo s nultim neto emisijama stakleničkih plinova. Ovaj cilj je u skladu s Europskim zelenim planom i predanošću Europske Unije globalnoj klimatskoj akciji prema Pariškom sporazumu. Vodik se smatra značajnim dijelom rješenja za postizanje ovoga cilja, ali pozitivan učinak vodika na smanjenje stakleničkih plinova uvelike ovisi o vrsti tehnologije koja se koristi za njegovu proizvodnju. Piroliza metana je toplinsko cijepanje prirodnoga plina na vodik i čvrsti ugljik. Navedeni proces proizvodi vodik bez emisija ugljikovog dioksida koji je poznat i kao tirkizni vodik. Tehnologije pirolize metana se mogu podijeliti u tri kategorije: toplinska, katalitička i plazma piroliza. Izazovi za razvoj tehnologije pirolize metana uključuju visoke energetske zahtjeve i odvajanje čvrstog ugljika u reaktoru. Ovaj rad daje sveobuhvatan pregled tehnologija pirolize metana danas. Trenutno je plazma piroliza metana najnaprednija tehnologija (do danas je jedino kompanija Monolith Materials 2020. stavila u pogon termalno plazma postrojenje industrijskog razmjera). Ostale tehnologije su u razvoju s planovima za pilot projekte. Tijekom plazma pirolize na svaku proizvedenu tonu vodika, kao nusproizvod, proizvedu se i tri tone čvrstog ugljika. Ovisno o vrsti tehnologiji koja se koristi, pirolizom metana moguće je dobiti različite vrste čvrstog ugljika kao što su industrijska čađa, ugljikove nano-cijevi, ugljikova nano-vlakna, grafit, grafen, itd. Ovaj diplomski rad također detaljno opisuje različite vrste čvrstog ugljika koji bi se potencijalno mogli proizvesti pirolizom metana, točnije njihove značajke, najčešće uporabe danas i potencijalne buduće uporabe. Naglasak je stavljen na industrijsku čađu jer je to najveće i najstarije tržište. S obzirom da implementacija pirolize metana na industrijskoj razini ima za posljedicu proizvodnju velikih količina čvrstog ugljika, potrebno je pronaći nova tržišta za te proizvode.

Ključne riječi: piroliza metana, vodik, toplinska piroliza, katalitička piroliza, plazma piroliza, čvrsti ugljik, industrijska čađa

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OVERVIEW OF HYDROGEN PRODUCTION BY METHANE PYROLYSIS PROCESS AND POSSIBLE APPLICATIONS OF THE SOLID CARBON PRODUCTS

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Thesis completed at: University of Zagreb
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Abstract

The European Union aims to be climate-neutral by 2050, i.e., an economy with net-zero greenhouse gas emissions. This goal is compliant with European Green Deal and the European Union's commitment to global climate action under the Paris Agreement. Hydrogen is seen as an important part of the solution to achieve this goal, but the positive impact of hydrogen on the mitigation of greenhouse gas emission relies heavily on the type of technology used to produce it. Methane pyrolysis is the thermal decomposition of natural gas into hydrogen and solid carbon. It produces CO_2-free hydrogen, also known as turquoise hydrogen. Methane pyrolysis technologies fall into three categories: thermal, catalytic, and plasma decomposition. The technical challenges in the development of methane pyrolysis technology include the high energetic requirements and the separation of solid carbon in the reactor. This thesis provides a comprehensive overview of methane pyrolysis technologies currently under development. At the moment, plasma methane pyrolysis is the most advanced technology. Monolith Materials has been operating an industrial scale thermal plasma plant since 2020. The other technologies mentioned are still under development and are intended for pilot projects. For every tonne of hydrogen produced, three tonnes of solid carbon are also produced as a byproduct. Depending on the technology, methane pyrolysis can produce different types of solid carbon products, such as carbon black, carbon nanotubes, carbon nanofibers, graphite, graphene, etc. In this thesis, different types of carbon products that could be produced by methane pyrolysis are described in detail, especially their properties, most common present uses and possible future uses. The focus is on carbon black, as this is the largest and oldest market. However, if methane pyrolysis is carried out on an industrial scale, large amounts of solid carbon will be produced, and new markets for carbon products have to be found.

Keywords: methane pyrolysis, hydrogen, thermal decomposition, catalytic decomposition, plasma decomposition, solid carbon products, carbon black

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TABLE OF CONTENTS

I. LIST OF FIGURES

II. LIST OF TABLES

III. LIST OF ABBREVIATIONS

AC – Alternating Current

AE – Alkaline Electrolyzers

AEA – Ammonia Energy Association

AmC – Amorphous Carbon

ARPA-E – Advanced Research Projects Agency-Energy

ASTM – American Society for Testing and Materials

ASX – Australian Securities Exchange

AUD – Australian Dollar

BAU – Business as Usual

BE – Battery-Electric

BMBF – German Federal Ministry of Education and Research

C – Solid Carbon

CAS – Chemical Abstracts Service

CB&H – Carbon Black and Hydrogen

CCUS – Carbon Capture Utilization and Storage

CDP – Commercial Demonstration Plant

CF – Carbon Filaments

CH_4 – Methane

CHP – Combined Heat and Power

CMK – Ordered Mesoporous Carbons

CNT – Carbon Nanotubes

CO – Carbon Monoxide

Co – Cobalt

CO_2 – Carbon Dioxide

CO_2eq – Carbon Dioxide Equivalent

Cr – Chromium

CSP – Concentrating Solar Power

CuCl – Copper(I) Chloride

DC – Direct Current

DIN – German Institute for Standardization

EC number – European Commission number

EMI/RFI shielding – Electromagnetic Interference and Radio Frequency Interference shielding

ESD – Electrostatic Dissipation

EV – Electric Vehicles

FBR – Fluidized Bed Reactor

Fe – Iron

FID – Final Investment Decision

GC - Graphitic Carbon

GHG – Greenhouse Gas

H_2 – Hydrogen

H_2O – Water

H_2S – Hydrogen Sulfide

HENG – Hydrogen-Enriched Natural Gas

HFC – Hydrogen Fuel Cell

HHV – Higher Heating Value

IASS – Institute for Advanced Sustainability Studies

ICBA – International Carbon Black Association

IEA – International Energy Association

Ir – Iridium

IRENA – International Renewable Energy Agency

ISO – International Organization for Standardization

KIT – Karlsruhe Institute of Technology

KOH – Potassium Hydroxide

LCA – Life Cycle Assessment

LOI – Letter of Intent

$MgCl_2$ – Magnesium Chloride

Mo – Molybdenum

MW – Microwave

MWCR – Multi-Walled Carbon Nanotube

NaBr – Sodium Bromide

NaCl – Sodium Chloride

NaOH – Sodium Hydroxide

Ni – Nickel

NiCl – Nickel(II) Chloride

NPPD – Nebraska Public Power District

OC1 – Olive Creek I

OC2 – Olive Creek II

PAH – Polycyclic Aromatic Hydrocarbon

PAN – Polyacrylonitrile

Pd – Palladium

PEME – Proton Exchange Membrane Electrolyzers

PMP – Pulsed Methane Pyrolysis

PSA – Pressure Swing Adsorption

PSA – Pressure-Swing Adsorption

Pt – Platinum

PV – Photovoltaic

R&D – Research and Development

Re – Rhenium

RED II – Renewable Energy Directive 2018/2001/EU

RES – Renewable Energy Sources

RF – Radiofrequency

Rh – Rhodium

Ru – Ruthenium

SMR – Steam Methane reforming

SOFC – Solid Oxide Fuel Cell

SWCN – Single-Walled Carbon Nanotubes

TC – Turbostratic Carbon

TCD – Thermocatalytic Decomposition

TGC – Total Graphite Content

TNO – The Netherlands Organization for Applied Scientific Research

UNFCCC – United Nations Framework Convention on Climate Change

UOP – Universal Oil Products

U_{rev} – Reversible Voltage

USA – United States of America

USD – United States dollar

UV – Ultraviolet

W – Tungsten

WGS – Water-Gas Shift

WWS – Wind-Water-Solar

WWTP – Wastewater Treatment Plant

$ZnCl_2$ – Zinc Chloride

ΔH° – Heat of Formation of the Molecule

1. INTRODUCTION

Reducing greenhouse gas (GHG) emissions to limit global warming is considered one of the most important challenges of our time. The European Union (EU) has set a goal to become climate-neutral by 2050. This goal is the core of the European Green Deal and is in line with the commitment to global climate action under the Paris Agreement. The Paris Agreement aims to limit global warming to well below 2 °C, preferably to 1.5 °C, compared to pre-industrial levels (United Nations Framework Convention on Climate Change [UNFCCC], 2015). Achieving this goal is a major challenge, given that the average global temperature increase over the past 40 years has been little more than 1 °C, and that the global carbon dioxide (CO_2) concentration has risen rapidly from 340 to 421 ppm over the same period, which is an average increase rate of about 2 ppm/year (NASA Earth Observatory, 2022; Global Monitoring Laboratory, 2022). Currently, the energy sector accounts for about two-thirds of all anthropogenic GHG emissions, so transforming the global energy system is considered one of the most important elements for successful global warming mitigation (International Energy Agency [IEA], 2015). There is general agreement that a transition from a fossil fuel based society to a low-carbon society is needed.

Considering these efforts, hydrogen is seen as an important component for future energy systems worldwide since its use in fuel cells does not lead to CO_2 emissions (Kovač et al., 2021). Hydrogen can be found in chemical compounds such as water, hydrocarbons, fossil fuels, and biomass, making it a highly regarded substitute for fossil fuels. It is the lightest and most abundant element in the universe (CGI, 2022). Moreover, electrochemical combustion of hydrogen produces more energy on a mass basis than conventional fossil fuels (Abbas and Wan Daud, 2010).

Hydrogen as an energy carrier shows a wide range of existing and potential applications. At the moment, hydrogen is used primarily in fertilizer production and oil refining. If hydrogen is to make a significant contribution to clean energy transitions, it must also be implemented in sectors, like transport, buildings, and power generation (IEA, 2019). Hydrogen plays an important role in the use of CO_2 as feedstock to produce methane, synthesis gas, and higher-value chemicals such as methanol. For the latter case, if the goal of using CO_2 is to reduce CO_2 emissions, the production of hydrogen and its utilization to produce aforementioned products must emit less total CO_2 into the atmosphere than the amount of CO_2 that this hydrogen binds (Machhammer et al., 2016).

Even though hydrogen is a zero-emission fuel when used in fuel cells, whether it has a positive impact on reducing of GHG emissions depends heavily on the energy and the process used for its production (Kovač et al., 2019). Hydrogen can be produced by using a large variety of fossil fuel and sustainable energy sources, which means that GHG emissions can be released depending on the type of production process. Currently, about 50% of the total hydrogen production comes from natural gas steam methane reforming (SMR), 30% from naphtha/oil reforming in the chemical industry and 18% from coal gasification (utilized mainly in China) (IEA, 2018). The remainder, about 2%, of hydrogen production is based on electrolysis (IEA, 2019).

In 2021, global hydrogen demand amounted to more than 94 million tonnes, which includes more than 70 million tonnes of hydrogen used as pure hydrogen and more than 20 million tonnes of hydrogen mixed with carbon-containing gases in methanol production and steel manufacturing (IEA, 2022). Almost all hydrogen is derived from fossil fuels: 6% of the world's natural gas and 2% of the word's coal are used for hydrogen production (IEA, 2019). Less than 0.7% of current hydrogen production comes from using renewable energy sources (RES) or from fossil fuel plants equipped with carbon capture utilization and storage (CCUS) (IEA, 2022).

Figure 1-1 shows the timeline for 143 countries responsible for 99.7% of world emissions to transition from conventional fuels, i.e., business as usual (BAU) case, to 100% wind-water-solar (WWS) in all energy sectors. An 80% transition to WWS in all energy sectors is suggested to happen latest by 2030. No later than 2050, 100% of end-use power in the annual average will be delivered by WWS across all energy sectors. The percentages next to each WWS energy source represent the 2050 predicted percent supply of end-use power. The energy sectors transitioned consist of the electricity, transportation, building heating/cooling, industrial, agriculture/forestry/fishing, and military sectors. Figure 1-1 also shows annually averaged end-use power demand reductions, which lead to a 57.1% reduction in total demand:

- the efficiency of using heat pumps for building heat instead of combustion-produced heat,
- the efficiency of using electricity for high-temperature industrial heat over combustion,

- the efficiency of using battery-electric (BE) vehicles and hydrogen fuel cell (HFC) vehicles over combustion vehicles,
- eliminating the energy to mine, transport, and process fossil fuels, biofuels, bioenergy, and uranium,
- improving end-use energy efficiency and reducing energy use compared to the BAU case.

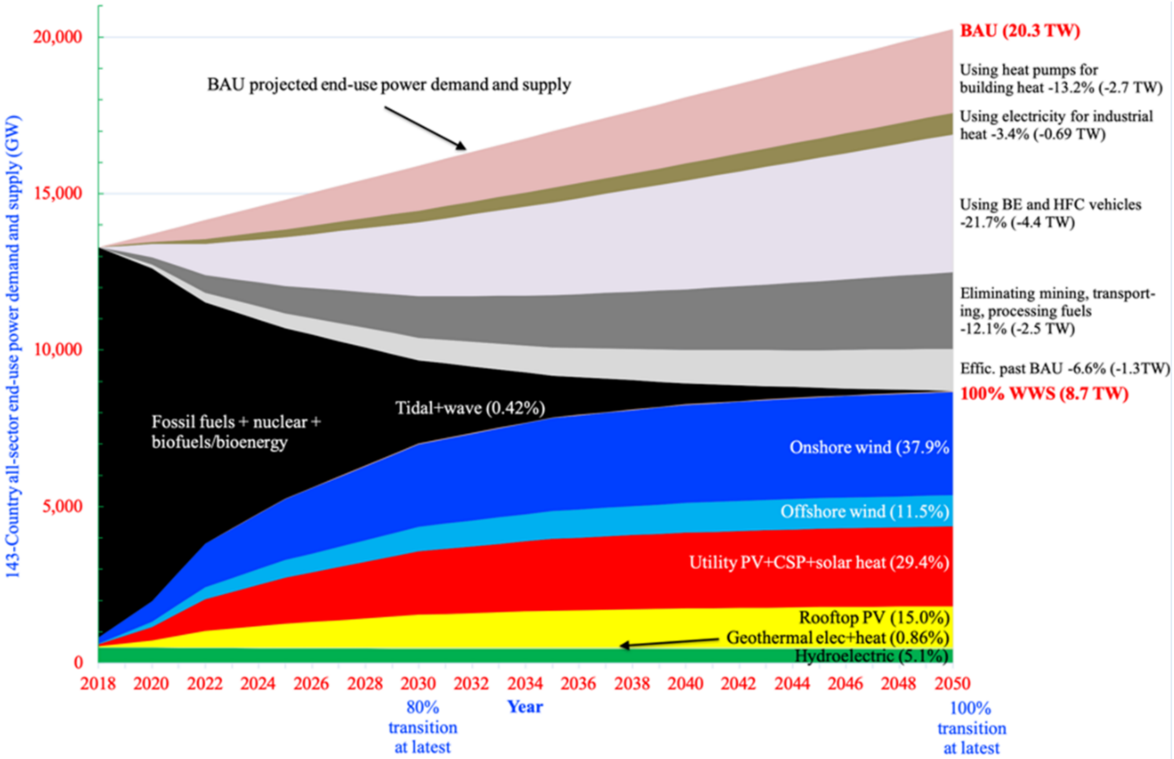


Figure 1-1. Timeline for transition to 100% renewable energy until 2050 (Jacobson, 2020).

Methane pyrolysis, also called thermal decomposition of methane, can be considered a bridging technology between the current carbon intensive energy system and a future RES-based system. In this process methane is directly broken down into its components, hydrogen, and solid carbon. The ultimate advantage of this reaction is that it generates no CO_2 emissions (Abbas and Wan Daud, 2010; Abánades at al., 2013; Weger et al., 2017). When talking about different colors of hydrogen, hydrogen produced by methane pyrolysis is referred to as turquoise hydrogen. The methane pyrolysis processes described in the literature can be divided into three categories: thermal decomposition, catalytic decomposition, and plasma decomposition. Methane pyrolysis is in the early stage of large-scale implementation, with Monolith Materials being the leading company and commissioning their commercial scale plant “Olive Creek I” in 2020.

Another benefit of methane pyrolysis is the production of solid carbon which is considered a value rather than a waste. Depending on the quality and price of the carbon byproduct, its sale can bring additional revenue and improve the economics of the process (Muradov and Veziroğlu, 2008; Abánades at al., 2012; Weger et al., 2017; Parkinson et al., 2018). Reaction conditions and used catalyst determine the characteristics of the produced carbon (Sánchez-Bastardo et al., 2021). There is a wide range of potential carbon products, including carbon black, graphene, carbon fibers, carbon nanotubes, carbon nanofibers, needle coke, etc. Carbon product prices vary widely depending on product properties and purity (Dagle at al., 2017). While early process deployments are expected to find receptive markets for carbon product, large-scale implementation of pyrolysis technologies would result in market oversaturation. Therefore, new applications for solid carbon byproduct must be found (Muradov and Veziroğlu, 2005; Abánades at al., 2012; Dagle at al., 2017; Parkinson et al., 2018).

This thesis presents the fundamentals of methane pyrolysis and briefly compares methane pyrolysis with two relevant hydrogen production technologies: steam methane reforming (SMR), and water electrolysis. Thermodynamic conditions and process requirements for each methane pyrolysis category, i.e., thermal, catalytic and plasma pyrolysis, are described. Some considerations for industrialization of methane pyrolysis are briefly mentioned. Furthermore, a comprehensive overview of methane pyrolysis technologies, both developed in the past and available on the market today, and the status of their commercialization is given. Different types of solid carbon product, including carbon black, graphene, graphite, carbon nanotubes, and carbon fibers, are detailed. Most common uses and potential future uses for these carbon products are stated.

2. FUNDAMENTALS OF METHANE PYROLYSIS

Methane pyrolysis (also referred to in the literature as thermal methane decomposition, methane cracking, or methane splitting) is a process in which methane is decomposed into gaseous hydrogen and solid carbon under high temperatures according to the following endothermic reaction (Muradov, 1993):

$$CH_{4\,(g)} \rightarrow C_{(s)} + 2H_{2\,(g)}, \quad \Delta H° = 75.6\,kJ/mol. \tag{2-1}$$

The energy required to decompose one mole of CH_4 is 75.6 kJ, which is the heat of formation of CH_4 ($\Delta H°$). Since oxygen is not involved in this reaction at all, no CO_2 or CO emissions are produced. The stoichiometry of the pyrolysis reaction (2-1) shows that, theoretically, two moles of hydrogen are formed per mole of methane. In reality, the process will yield less due to the byproducts formed (e.g. aromatics, olefins) (Dagle et al., 2017). Equation (2-1) describes only the main reaction pathway. In addition to the main products hydrogen and carbon, side reactions yield additional saturated and unsaturated hydrocarbons and (poly)cyclic aromatic compounds, which can occur in all three states of aggregation (Guéret et al., 1997; Fau et al., 2013). From a mass balance viewpoint, each mole of CH_4 can produce a maximum of 4 g of hydrogen and 12 g of carbon. This mass ratio of carbon to hydrogen of 3:1 suggests that for every tonne of hydrogen formed, 3 tonnes of carbon are produced. From this perspective, carbon is the main product of the reaction and should therefore be used to improve the economics of the process.

The theoretical energy efficiency of the methane pyrolysis process, shown in Equation 2-2, equals 59%. The remaining energy originally contained in the methane is sequestered in carbon (Timmerberg et al., 2020). To calculate the theoretical efficiency, hydrogen higher heating value (HHV) of 286 kJ/mol, methane HHV of 890 kJ/mol and heat of formation of CH_4 of 75.6 kJ/mol were used (Muradov, 1993; Harrison et al., 2010):

$$\eta_{theo} = \frac{2HHV\,(H_2)}{HHV\,(CH_4) + \Delta H°} = \frac{2 \times 286\,\frac{\mathrm{kJ}}{\mathrm{mol}}}{890\,\frac{\mathrm{kJ}}{\mathrm{mol}} + 75.6\,\frac{kJ}{mol}} = 59\% \tag{2-2}$$

Where:

η_{theo} – theoretical energy efficiency (%)

HHV – higher heating value (kJ/mol)

$\Delta H°$ – heat of formation of CH_4 (kJ)

One of the major challenges in carrying out the methane pyrolysis reaction is the high strength of the carbon-hydrogen bond, so very high temperatures are required to break it. Guéret et al. (1997) state that temperature is the most important parameter in the pyrolysis reaction. The Gibbs energy for methane pyrolysis is zero at 819 K (545 °C), suggesting that the reaction theoretically proceeds spontaneously above this temperature (Villacampa et al., 2003). However, in order to achieve a reasonable yield, a temperature above 1200 °C is required for non-catalytic thermal decomposition. This temperature can be lowered considerably by using a catalyst (Abbas and Wan Daud, 2010).

2.1. Comparison of methane pyrolysis with other relevant hydrogen production technologies

Figure 2-1 summarizes the main features of today's most relevant hydrogen production technologies, giving a separate color code for each technology. The hydrogen color code nomenclature is used to describe different methods of hydrogen production depending on the process and energy source. According to the International Renewable Energy Agency (IRENA) (2021), grey hydrogen refers to hydrogen produced from fossil fuels by either steam methane reforming (SMR) or coal gasification. When CCUS is used in conjunction with SMR or coal gasification, hydrogen produced in this manner is referred to as blue hydrogen. Turquoise hydrogen is produced by methane pyrolysis and green hydrogen is hydrogen produced via water electrolysis using RES.

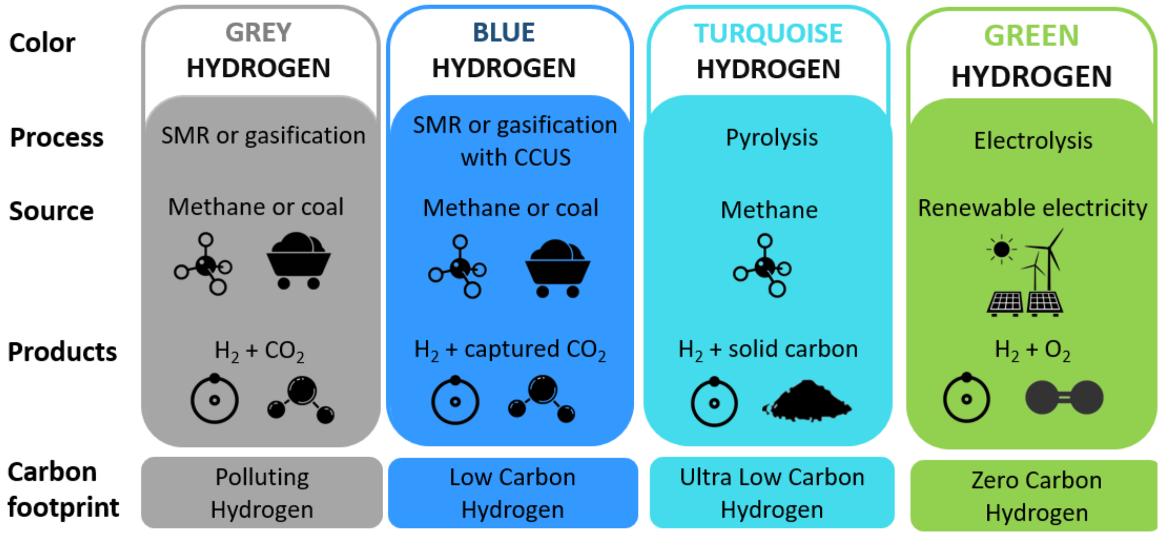


Figure 2-1. Selected colors of hydrogen (after Muradov, 2017; IRENA, 2021).

However, colors should be avoided as it can lead to misunderstandings. Today, renewable hydrogen means following the Renewable Energy Directive 2018/2001/EU (RED

II), which describes it as hydrogen produced using RES with at least 70% CO2eq emissions reduction compared to SMR reference. The system boundary chosen is not a full Life Cycle Assessment (LCA) approach as the assumption is that renewable electricity has no CO2eq emissions. For the European Taxonomy, the threshold has been fixed on 3 kg CO2eq/kg H_2. Thus, if it can be demonstrated, using a full LCA approach, that hydrogen production leads to less than 3 kg CO2eq/kg H_2, then that hydrogen can be considered renewable hydrogen (if using RES) or low carbon hydrogen (if using non-RES, i.e., CCUS and nuclear electricity) (Kovač et al., 2021).

Other than the above mentioned technologies there are several other possible hydrogen production pathways. Biomass gasification is an established process for converting biomass into hydrogen containing gas mixture. Separation and further purification are then needed to produce clean (renewable) hydrogen; therefore, biomass gasification is typically used to produce direct syngas rather than clean (renewable) hydrogen. Thermochemical water splitting process uses high heat, attained from concentrated solar power, and chemical reactions to produce hydrogen and oxygen from water. The most common thermochemical water splitting process includes redox-active metal oxide cycles which require temperatures above 1300 °C. Today, this process is still industrially attainable due to its low efficiency and high production cost (Sánchez-Bastardo et al., 2021). Energy efficiencies of mentioned hydrogen production technologies are shown in Table 2-1.

Table 2-1. Energy efficiencies of different hydrogen production technologies (after Sánchez-Bastardo et al., 2021; Agyekum et al., 2022).

Technology	energy efficiency in transformation (%)	energy efficiency with CCS (%)
Coal gasification	60	43
Steam methane reforming	75	60
Methane pyrolysis	58	58
Water electrolysis	60-80	/
Thermochemical water splitting	20-45	/
Biomass gasification	30-40	/

2.1.1. SMR

SMR is currently the most common hydrogen production pathway, generating about 50% of total hydrogen production worldwide (IEA, 2018). In conventional SMR, CH_4 reacts with high temperature steam (700 °C–1000 °C) using a catalyst to produce CO and hydrogen (Equation 2-3). Then, in the water-gas shift (WGS) reaction, additional hydrogen is obtained by reacting CO with water (Equation 2-4). The combination of the SMR and WGS reactions leads to the main products hydrogen and CO_2 (Equation 2-5). The final step is the pressure-swing adsorption (PSA) process, which removes the CO_2 and any additional impurities, leaving essentially pure hydrogen (Dagle et al., 2017).

$$CH_4 + H_2O_{(g)} \rightleftharpoons 3H_2 + CO, \quad \Delta H^{\circ} = 206\ kJ/mol \qquad \text{SMR (2-3)}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2, \quad \Delta H^{\circ} = -41\ kJ/mol \qquad \text{WGS (2-4)}$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \quad \Delta H^{\circ} = 165\ kJ/mol \qquad \text{Net Reaction (2-5)}$$

Although SMR appears to be more favorable from a material perspective compared to methane pyrolysis as it produces twice as much hydrogen (Equations 2-1 and 2-5), SMR is at a disadvantage from energy demand perspective. The energy demand for methane pyrolysis is 37.8 kJ/mole H_2 produced which is significantly lower than 63.3 kJ/mole H_2 necessary for the SMR process (Kerscher et al., 2021).

The major drawback of SMR is that it generates significant amounts of CO_2. The reaction stoichiometry (Equation 2-5) suggests a production of 5.5 kg CO_2/kg H_2, but in reality, the amount is much higher, ranging from 10.7 to 15.9 kg CO_2eq/kg H_2. When SMR is combined with CCUS, total system emissions decrease and range from 3.1 to 5.9 kg CO_2eq/kg H_2 (Bhandari et al. 2012; Parkinson et al. 2019). Regarding methane pyrolysis, the direct CO_2 emissions associated with methane pyrolysis result largely from the recovery and extraction of natural gas, making the CO_2 footprint of methane pyrolysis much smaller than that of SMR. For instance, the Monolith states that their methane pyrolysis process produces about 0.45 kg CO_2 eq./kg H_2 (Monolith, 2021a).

Even though SMR has a high energy efficiency (75%) the need to reduce the GHG emissions by implementing CCUS reduces the net energy efficiency to 60% and becomes comparable to 58% for methane pyrolysis (Table 2-1) (Steinberg, 1999). Another advantage of methane pyrolysis is that the remaining 42% is in the form of stored energy as carbon particles, whereas for the SMR the remaining 40% is lost as CO_2 (Blok et al., 1997; Timmerberg et al., 2020).

2.1.2. Water Electrolysis

Water Electrolysis is an electrochemical process of decomposing water into hydrogen and oxygen by applying external DC voltage to two electrodes (anode and cathode) that are in contact with the working medium, i.e., electrolyte. For the electrolysis process to occur, the DC voltage must be equal to or greater than the reversible voltage (U_{rev}) of 1.23 V. The overall reaction of water electrolysis is shown in Equations 2-6 to 2-9 (Đukić, 2013):

$$H_2O_{(aq)} + electricity \rightarrow H_{2\,(g)} + 0.5O_{2\,(g)} \tag{2-6}$$

$$1\,mol\,H_2O + energy \rightarrow 1\,mol\,H_2 + 0.5O_2 \tag{2-7}$$

$$18{,}008\,g\,H_2O \rightarrow 2{,}008\,H_2 + 16\,g\,O_2 \tag{2-8}$$

$$(9\,kg\,Water = 1\,kg\,Hydrogen + 8\,kg\,Oxygen) \tag{2-9}$$

A system in which water electrolysis is used to produce hydrogen and oxygen in gaseous phases is called an electrolyzer. In its basic form, the electrolyzer consists of two electrodes (cathode – a negative electrode and anode – a positive electrode) immersed in an electrolyte. Oxidation reactions takes place at the anode, i.e., oxygen is produced, and reduction reaction takes place at the cathode, i.e., hydrogen is produced. The electrodes are separated by a membrane to prevent possible reactions between the electrolysis products. The electrodes are typically made of metals (platinum, nickel, various alloys, and steels) coated with platinum.

Electrolyzer type is determined by the type of electrolyte used in it (Đukić, 2013). The most common electrolyzers today are the proton exchange membrane electrolyzers (PEME) and alkaline electrolyzers (AE). Alkaline electrolyzers are considered good candidates for large-scale hydrogen production from RES, as they are more economical compared to other electrolyzers. Particularly, electrolyte and electrode material are cheaper and more accessible while still maintaining high energy efficiency and high gas purity. Hydrogen produced by alkaline electrolysis has a purity of 99,98%. The solutions of potassium hydroxide (KOH) and sodium hydroxide (NaOH) in water, both alkaline bases, are the most commonly used electrolytes for alkaline electrolysis (Kovač et al., 2019). Figure 2-2 illustrates the operating principle of the alkaline electrolyzer.

Water electrolysis powered by solar energy is currently the only commercial technology for hydrogen production with zero CO_2 emissions (Đukić, 2015).

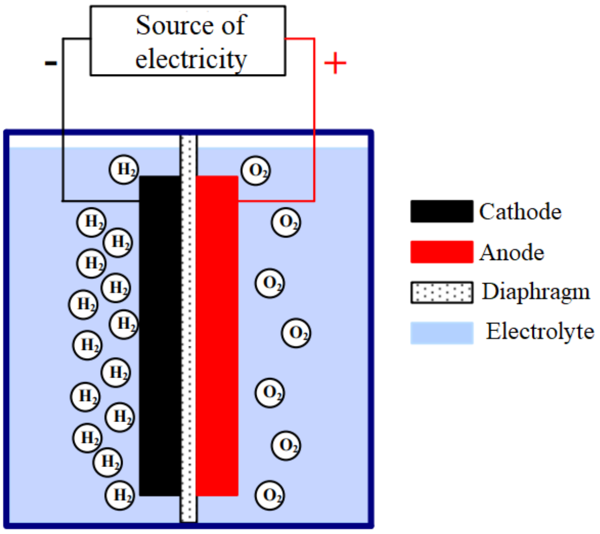


Figure 2-2. Basic operating principle of alkaline electrolyzer (after Đukić, 2013).

3. METHANE PYROLYSIS CATEGORIES

In this chapter, the thermodynamic conditions and process requirements for each methane pyrolysis category are briefly discussed.

Methane pyrolysis technologies described in the literature fall into three distinct categories (Schneider et al., 2020):

1. Thermal (or non-catalytic) decomposition,
2. Catalytic decomposition,
3. Plasma decomposition.

3.1. Thermal decomposition

Thermal or non-catalytic decomposition of methane requires high temperatures of 1200 °C to 1400 °C which is a major drawback of this technique (Muradov, 2017). Abánades et al. (2011) experimented with non-catalytic methane decomposition to evaluate the scientific feasibility and reaction characterization over a wide temperature range, from 875-1700 °C. They found that at temperatures below 1200 °C thermal methane decomposition was incomplete, and the output stream contained many hydrocarbons and additional intermediate products, in addition to hydrogen and carbon powder. At temperatures above 1350 °C, decomposition was virtually complete, and the output gas stream consisted essentially just of hydrogen with almost no traces of hydrocarbon gases, in addition to solid carbon.

Figure 3-1 illustrates the influence of temperature, residence time and pressure on CH_4 conversion and product yield during the thermal decomposition process. Higher temperatures and longer residence times promote the production of hydrogen and carbon while lower temperatures and short contact times in the reactor lead to gaseous products with higher amounts of olefins and aromatics. At low pressure, more olefins tend to be produced while higher CH_4 conversion is achieved. The intermediates, olefins and aromatics are first formed and then further decomposed to carbon and hydrogen. The predominant decomposition mechanism, which is determined by the operating conditions, controls the solid carbon morphology (Dagle et al., 2017).

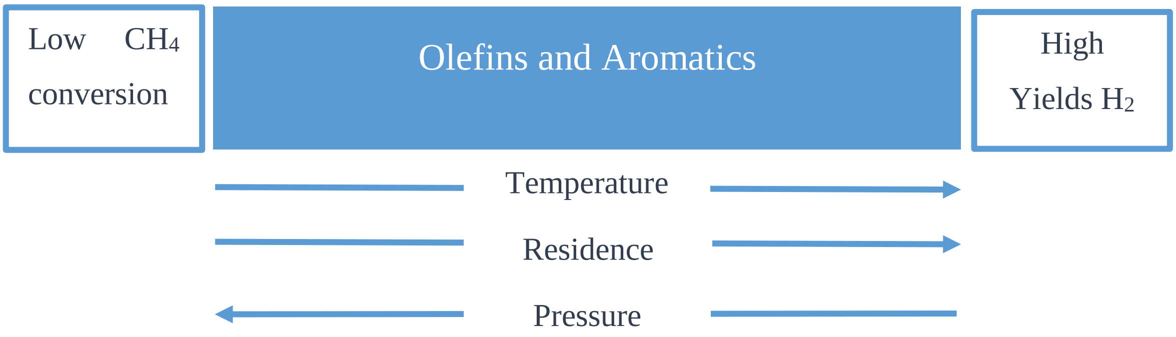


Figure 3-1. Conceptual depiction of the influence of operating conditions on CH_4 conversion and product yields (after Dagle et al., 2017).

3.2. Catalytic decomposition

To lower the high operating temperatures required for thermal decomposition, a variety of catalysts have been extensively researched on a laboratory scale over the years. Catalytic (or thermocatalytic) decomposition of methane generally exhibits reasonable conversion rates at temperatures well below 1000 °C (Schneider et al., 2020; Yousef and Donne, 2022). Two types of catalysts have been widely studied:

1. metal based catalysts and
2. carbon based catalysts.

Muradov and Veziroğlu (2005) summarized most of the published data on several different catalysts, the temperature range in which they operate in and the type of carbon they produce during the catalytic methane pyrolysis process (Figure 3-2). Nickel-based catalysts have been widely studied for their ability to produce filamentous carbon (CF) (which includes carbon nanotubes [CNT]) at moderate temperatures of 500-700 °C. Iron-based catalysts are also capable of forming CNT, but at higher temperatures (700-950 °C). Carbon-based catalysts produce both CF and turbostratic carbon (TC) while operating in the 850-950 °C temperature range. A variety of catalysts, such as Cobalt, (Co), Nickel (Ni), Palladium (Pd**),** Platinum (Pt), Chromium (Cr), Ruthenium (Ru), Molybdenum (Mo) and Tungsten (W) catalysts, operate in the temperature range of 700 to 1000 °C and produce TC and graphitic carbon (GC). At temperatures above 1150 °C, non-catalytic decomposition occurs, leading to formation of amorphous carbon (AmC), e.g. carbon black (CB).

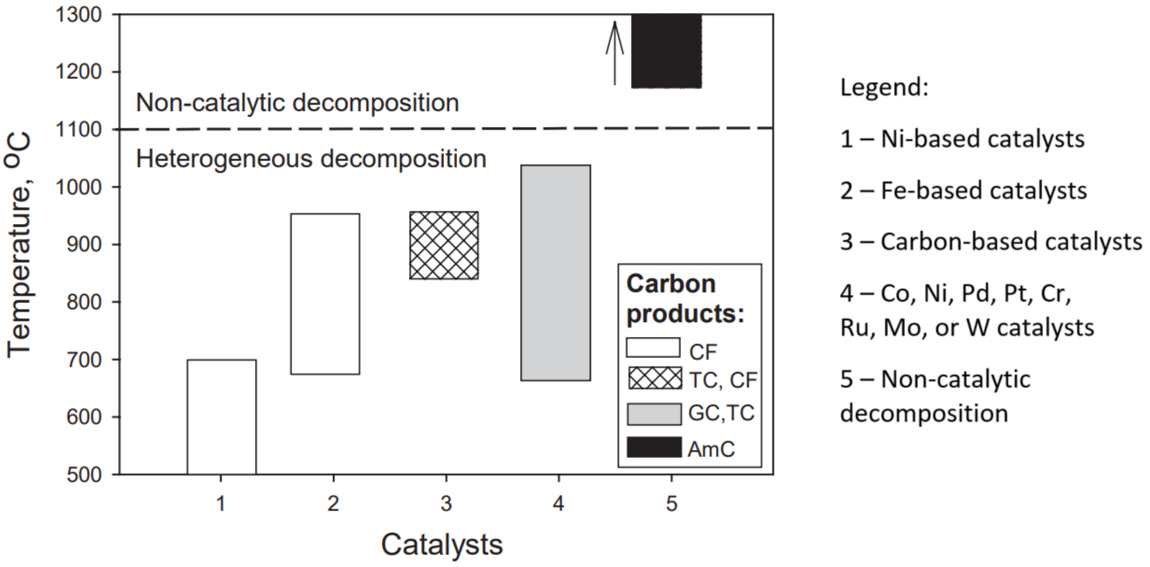


Figure 3-2. Overview of available data on different types of catalysts, temperature ranges and carbon types produced related to catalytic methane pyrolysis (after Muradov and Veziroğlu, 2005).

The effectiveness of a catalyst depends on its activity and lifetime (Dagle et al., 2017). According to Ermakova et al. (2000), highly effective catalysts must be developed for catalytic methane pyrolysis to gain practical importance. Catalyst effectiveness is based upon its activity and its operating lifetime (Dagle et al., 2017).

3.2.1. Metal catalysts

Since the 1960s, it has been well-known that some transition metals, such as Fe, Ni, and Co, show significant catalytic activity for methane pyrolysis reactions (Muradov, 2017). Since then, a wide variety of metal-based catalysts have been investigated as possible catalysts. Abbas and Wan Daud (2010) reported the following order of transition metals in terms of their catalytic activity: Co, Ru, Ni, Rh > Pt, Re, Ir > Pd, Cu, W, Fe, Mo. In other reports, the following order of activity was given: Ni > Co > Fe (Kutteri et al., 2018; Sánchez-Bastardo et al., 2021).

Among all catalysts, the main focus has been on Ni- and Fe-based catalysts because of their availability, activity, low cost, and ability to produce high-value forms of carbon (e.g. CNT) under optimal operational conditions (Muradov and Veziroğlu, 2008; Ashik et al., 2015). Several studies have shown that Ni- and Fe-based catalyst can effectively produce hydrogen and filamentous carbon (CF). They also pointed out that it is practically unattainable to achieve output gas with high hydrogen concentration, high CNT yield per unit of catalyst and long catalyst lifetime, as these aspects seem to be in contradiction. Longer catalyst lifetime and higher CNT yield can be attained at the cost of lower hydrogen concentration in output gas (Li et al., 2000; Ermakova and Ermakov, 2002; Takenaka et al., 2003; Muradov, 2017).

Even through Ni-based catalysts have the highest initial activity, they are rapidly deactivated at temperatures above 600 °C. In fact, one of the key issues of catalytic decomposition process is the rapid deactivation of the catalysts due to the encapsulation of the active metal sites in the carbon formed during the reaction. Higher activity of a catalyst leads to faster encapsulation (Yousef and Donne, 2022). Cobalt catalysts have not been explored in depth due to their lower activity and higher price compared to nickel, as well as problems related to toxicity (Sánchez-Bastardo et al., 2021). Fe-based catalysts are less active than Ni-based catalysts but have higher stability at higher temperatures (700–950 °C). Compared to Co- and Ni-based catalysts, Fe-based catalysts are inexpensive and more environmentally friendly (Ashik et al., 2015). The carbon product resulting from the Fe-based catalyzed reaction is free of harmful metals and therefore has the potential to be used in further applications. For these reasons an Fe-based catalyst is considered the best candidate for industrial use of methane pyrolysis (Sánchez-Bastardo et al., 2020).

3.2.2. Carbon catalysts

Compared to metal-based catalysts, carbon-based ones exhibit lower catalytic activity and require higher operating temperatures (around 800-1000 °C) but at the same time are more stable and exhibit longer catalyst lifetime (Sánchez-Bastardo et al., 2021). They are also less expensive. The carbon formed by the reaction could potentially exhibit catalytic effects and therefore be used as a catalyst precursor (Abbas and Wan Daud, 2010). As will be discussed in more detail in Section 4.1, unlike metal-based catalysts, carbon-based catalysts are not affected by sulfur and other impurities present in natural gas. In this case, carbon product is not contaminated with metal particles. Although carbon-based catalysts have a longer lifetime than metal-based ones, they also become gradually deactivated. The surface area, pore volume, and particle size of carbon are important factors affecting their deactivation (Dagle at al., 2017).

Numerous carbon materials have been evaluated for catalyzing methane pyrolysis reaction: activated carbon, carbon black, glassy carbon, acetylene black, graphite, diamond powder, CNTs, fullerenes $C_{60/70}$, fullerene soot, charcoal and ordered mesoporous carbons

(CMK materials) (Sánchez-Bastardo et al., 2020). Based on their crystallinity, these carbon materials can be classified into (Muradov et al., 2005a):

- highly ordered carbons (graphite and diamond),
- less ordered carbons (turbostratic and pyrolytic, e.g. glassy carbon, fullerene soot, fullerenes $C_{60/70}$, CNTs, and CMK materials),
- disordered carbons (amorphous, e.g. carbon black, activated carbon, charcoal and acetylene black).

The catalytic activity of carbons for methane pyrolysis varies according to the ordered nature of carbon in the following order: amorphous > turbostratic > graphite (Abbas and Wan Daud, 2010). Amongst all carbon materials, most research focused on activated carbon and carbon black because of their high catalytic activity. Although activated carbon initially has higher catalytic activity, carbon black is more stable and has longer catalyst lifetimes (Guil-Lopez et al., 2011).

3.2.3. Catalyst regeneration

The issue that arises from the use of catalysts is that their application requires a regeneration process. Regeneration of the deactivated catalyst involves removing the carbon deposits and restoring its activity. This can be done by burning the carbon with oxygen or air, which in both cases would result in significant CO_2 emissions (Abbas and Wan Daud, 2010; Dagle et al, 2017). Gasification with CO_2 or steam has also been proposed but also results in CO_2 emissions. In addition, all of the above mentioned regeneration options destroy the carbon product (Sánchez-Bastardo et al., 2021). For these reasons, other regeneration techniques must be developed or alternative solutions have to be found (as is the case of the Hazer Process, which uses a sacrificial catalyst, as mentioned in Subection 5.2.2).

3.3. Plasma decomposition

Plasma, often referred to as the fourth state of matter, is an ionized gas state that contains free electrons and ions (Lee, 2015). When a gas is heated to a certain temperature, it can shift to the state of plasma, making the ionized gas particles highly electrically conductive (Plenesys, 2022). Based on the generation method, plasma can have numerous manifestations. Plasma generation methods can be categorized by the type of electric field used and shape and arrangement of the electrodes. Based on the type of electric field, plasma can be categorized as alternating current (AC), direct current (DC), microwave (MW) and radiofrequency (RF) plasma. Based on the electrode shape, plasma can be categorized as corona discharge, dielectric barrier discharge, gliding arc, hollow cathode plasma, spark plasma etc. The electron temperature and density are different for each type of plasma (Lee, 2015).

Plasma methane pyrolysis processes fall into two main categories (Dagle et al., 2017):

- thermal plasma (also known as “hot” plasma or equilibrium plasma) – typically above ~ 700 °C,
- non-thermal plasma (also known as “cold” plasma or non-equilibrium plasma) – below ~ 700 °C.

For a thermal plasma, a high electrical power must be injected into the discharge both the electrons and the neutral species reach the same temperatures of around 5,000-10,000 °C, i.e., they are in thermal equilibrium. Since the temperatures in the reactor are very high, additional energy is needed to cool the electrodes. In non-thermal plasma much lower power input is needed, so only the temperatures of the electrons increase (they can reach temperatures of several 10,000 °C) while temperature of neutral species does not change. Hence, the total gas temperature remains as low as the room temperature (Paulmier and Fulcheri, 2005; Timmerberg et al., 2020).

Figure 3-3 shows an overview of all plasma processes mentioned in the literature that can be used to produce hydrogen via methane pyrolysis. Thermal plasmas use a plasma torch to generate plasma from electricity (Kerscher, 2021). Typical non-thermal plasma sources include MW plasma, corona discharge plasma, dielectric barrier discharge plasma, gliding arc, spark plasma and electron beam plasma (Tsai and Chen, 2009; Dagle et al., 2017; Muradov, 2017; Kerscher et al., 2021; Raza et al., 2022). Discharge volume and discharge power are two important factors in the generation of non-thermal plasma and are controlled by the power supply, gas flow, and reactor design (Raza et al., 2022). Some of the aforementioned non-thermal plasma technologies such as corona discharge, MW plasma, dielectric barrier discharge and gliding arc technology have already been used for the reforming of methane, i.e., the conversion of CH_4 with the addition of O_2, CO_2, or H_2O (Paulmier and Fulcheri, 2005).

To operate under plasma conditions, mainly electrical energy and plasma gas (also called carrier gas or plasma-forming gas) are needed, which can be N_2, H, Ar, H_2, CO, etc. Thermal plasma process operates in temperature range between 700 and 5500 °C. Plasma processes can be operated with or without catalysts. Most processes do not utilize catalysts as they have not been shown to significantly improve methane conversion (Dagle et al., 2017).

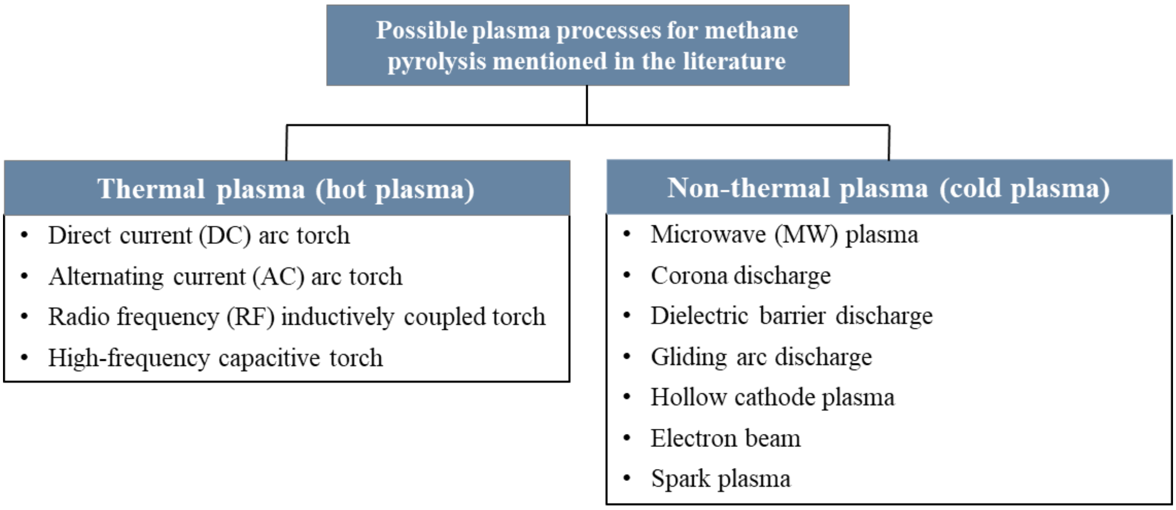


Figure 3-3. Classification of plasma processes that could be used for methane pyrolysis (after Tsai and Chen, 2009; Dagle et al., 2017; Muradov, 2017; Kerscher et al., 2021; Raza et al. 2022).

Compared to non-thermal plasmas, thermal plasmas have been shown to achieve higher methane conversion efficiencies due to being homogenous in discharge space (Dagle et al., 2017). Non-thermal plasmas have inhomogeneous distribution in reactors, resulting in a restricted reaction range, which in turn limits methane conversion (Tao et al., 2011). On the other hand, non-thermal plasmas have higher chemical selectivity in comparison to thermal plasma (Raza et al., 2022). Tsai and Chen (2009) and Mašláni et al. (2021) have shown that thermal plasma can achieve high methane conversion efficiencies (>80%) with hydrogen as the main product. Byproducts could include acetylene, benzene, and ethane (Fincke et al., 2002).

Using plasma decomposition to achieve the high energy levels required for the process has several advantages. Many authors have concluded that the potential advantage of thermal plasma is the ability to produce high quality carbon structures (e.g. carbon black, carbon nanotubes, graphene) by varying operating conditions (Fulcheri et al., 2002; Tsai and Chen, 2009; Zhao et al., 2011). The main advantage of non-thermal plasma is the lower energy consumption due to the lower temperatures required for the process (Paulmier and Fulcher, 2005). Electrode erosion is much lower in non-thermal plasma than in thermal plasma because no cooling of the electrodes is required. Plasma reactors are much smaller compared to conventional reactors (Dagle et al., 2017). Additionally, plasma systems can be powered by a fluctuating RES supply, which means that there are no indirect GHG emissions (Lee, 2015).

4. INDUSTRIALIZATION OF METHANE PYROLYSIS

4.1. Natural gas as feedstock

Theoretical assumptions and laboratory testing are usually preformed with pure methane without consideration of other reaction parameters, while the application of methane pyrolysis on an industrial scale requires the use of natural gas as feed gas. As a result, the issues related to operation with natural gas and the effects of natural gas impurities on the process are not fully addressed. In addition to methane as a main constituent, natural gas can contain several different minor compounds depending on its origin. These impurities include higher hydrocarbons (ethane, propane, butane, etc.), CO_2, H_2S, H_2O, mercaptans etc. All of these compounds react under pyrolysis conditions and can affect the conversion rate and reaction products (Schneider et al, 2020).

Pinilla et al. (2009) studied the effect of minor hydrocarbons present in natural gas by carrying out experiments with natural gas-like mixtures (85% methane, 10% ethane, 5% propane) at 900 °C with carbon catalysts. The results showed complete conversion of ethane and propane, as the resulting gas consisted only of hydrogen and unconverted methane. Due to the higher hydrogen content in ethane and propane, the hydrogen content in the outlet gas increased. More importantly, experiments showed that the carbon byproduct did not deactivate the carbon catalyst and did not negatively affect the process. A recent study on the decomposition of methane and ethane mixtures found that methane was activated with the help of ethane (Ogihara et al., 2020).

Fidalgo et al. (2012) studied the effect of small amounts (0.5-1.0 vol.%) of H_2S in feed gas on methane pyrolysis over carbon and metal-based catalysts. The presence of H_2S did not deactivate the carbon catalyst. Moreover, the experiments with the carbon catalyst showed that the CH_4 conversion was significantly increased, suggesting that H_2S had a positive catalytic effect on the methane decomposition rate. In contrast, the metal catalysts were strongly deactivated in the presence of H_2S. In this case, purification pretreatment of natural gas would be necessary.

Regardless of these reports, the impact of all minor impurities in natural gas on the catalytic activity and stability is still not completely understood and specified and further studies must be conducted.

4.2. Reactor Types

At laboratory scale, fixed-bed reactors are typically preferred as they are easy to use and give a better picture of the effects of different operating conditions and catalyst performance. However, during long-term operation, they fill up with carbon product that eventually block the gas flow. To prevent this, the carbon should be removed frequently. Various types of reactors have been proposed in the literature for large-scale implementation of methane pyrolysis, such as fluidized-bed reactors, moving-bed reactors or liquid bubble column reactors (Dagle et al, 2017; Sánchez-Bastardo et al., 2021).

Fluidized-bed reactors are reported as the most promising option for industrial operation. They allow continual addition of new catalyst as well as the removal of spent catalyst and carbon deposits. This allows long continuous operation, as the pressure drop in the reactor does not increase considerably. Additionally, the temperature in the reactor can be effectively controlled so that hot spots cannot be formed (Dagle et al., 2017; Sánchez-Bastardo et al., 2020). One of the technologies using fluidized bed-reactors is Hazer (further detailed in Subsection 5.2.2).

Regarding the use of moving-bed reactors, technology developed by BASF utilizes moving bed of carbon granules (further detailed in Subsection 5.1.1).

Recently, the use of liquid bubble column reactors has been gaining momentum (examples include technologies developed by TNO and KIT, which are discussed in more detail in Subsections 5.1.3 and 5.1.4, respectively). In this type of reactors, molten metals (Ti, Pb, Sn, Ga), molten metal alloys (Ni−Bi, Cu−Bi) or molten salts (KBr, NaBr, NaCl, NaF, $MnCl_2$, KCl) are used as heat transfer fluids (Sánchez-Bastardo et al., 2021). In addition, they can also act as potential catalysts for reactions (an example is C-Zero technology, which is discussed in more detail in Subsection 5.2.3).

As for the heat needed for the process, the reactor must be heated with electricity to have a process that produces CO_2-free hydrogen. If the entire lifecycle of the process is considered, then electricity needs to come from RES to produce completely CO_2-free hydrogen (as is the case with water electrolysis mentioned in Subsection 2.1.2). If the reactor is heated by burning natural gas or carbon, this leads to significant CO_2 emissions (example is Hypro process from the 1960s, which is explained in more detail in Subsection 5.2.1.1).

5. OVERVIEW OF METHANE PYROLYSIS COMMERCIAL EFFORTS

While Chapter 3 provides an overview of thermodynamic conditions and process requirements for thermal, catalytic and plasma methane pyrolysis, this chapter will attempt to summarize all the methane pyrolysis technologies currently being developed and their status of commercialization. Previous attempts to develop methane pyrolysis will also be mentioned.

5.1. Thermal methane pyrolysis technologies

Table 5-1 provides an overview of the thermal methane pyrolysis technologies currently being developed, further described below.

Table 5-1. Summary of developing thermal methane pyrolysis technologies.

Developer/ Technology	Location	Target Product	Reactor description	Technology development summary and future outlook	Current Status of technology	References
BASF	Germany	H_2	Moving bed of carbon granules	**2013-2017**: Basic R&D: laboratory level **2019-2022**: 2nd R&D: larger test facility **Planned after 2nd R&D**: Pilot Facility **Planned by 2030**: Commercial scale facility	Testing ongoing at experimental plant	Bode, 2019 BASF, 2020 BASF, 2021b BASF, 2022
Ekona	Canada (Vancouver)	H_2	Pulsed methane pyrolysis (PMP) reactor	**2017**: Company founded **2021**: Investment led by Baker Hughes to accelerate technology industrialization **Planned**: Pilot project (no clear date)	N/A	Baker Hughes, 2021 Ekona, 2021 CRIN, 2022
TNO / EMBER	Netherlands	H_2	Molten gallium bubble column	**Until 2019**: Proof of concept **2020 - 2023**: Lab-scale testing **Planned by 2025**: Pilot Plant **Planned by 2030**: Commercial scale demonstration plant	Lab-scale: scale up of continuous operation ongoing	Daliah, 2021 TNO, 2019 Bhardwaj et al., 2021
KIT	Germany	H_2	Liquid tin bubble column	**Since 2013**: Development of methane pyrolysis process **2019**: Partnership with Wintershall Dea to lay foundation for future industrial use	Proof of concept for technology established	KIT, 2018 Wintershall Dea, 2019

The difference between these technologies is the type of reactor used for the process. All the technologies mentioned are still under development in laboratory scale or in the experimental plants. None have yet been tested at pilot scale, but this is planned for the future. It seems unlikely that commercial scale facilities for thermal methane pyrolysis will be deployed before 2030.

5.1.1. BASF's technology

BASF, a German multinational chemical company, has been working on methane pyrolysis since 2010. Since 2013, it has been leading a consortium developing methane pyrolysis as a part of a project funded by the German Federal Ministry of Education and Research (BMBF) (BASF, 2020). Hydrogen is the target product, but the potential commercial use of the carbon product is also being intensively researched. An initial research and development (R&D) project was conducted at the laboratory level from 2013 to 2017. Technical feasibility and reaction kinetics were investigated and a first reactor concept with a moving carbon bed was developed. Samples of solid carbon were also successfully produced, but the reactor was destroyed during sample production (Bode, 2019).

BASF's thermal methane pyrolysis technology uses the electrically heated moving carbon bed reactor. Figure 5-1 shows the schematic of original moving carbon bed reactor developed as part of the first R&D project (Bode, 2019). The cold natural gas entering the bottom of the moving-bed reactor is preheated by the hot carbon granules leaving the reactor. The carbon granules, fed at the top of the reactor flow toward the gas phases. Electrodes directly heat the carbon bed in the reaction zone reaching temperatures up to 1400 °C. The heat is transferred to the natural gas and pyrolysis reaction takes place. It is assumed that the pyrolysis reaction takes place mainly at the at the surface of the granules. The hot product gas leaving the reactor at the top preheats the cold carbon granules entering the reactor (Schneider, 2020).

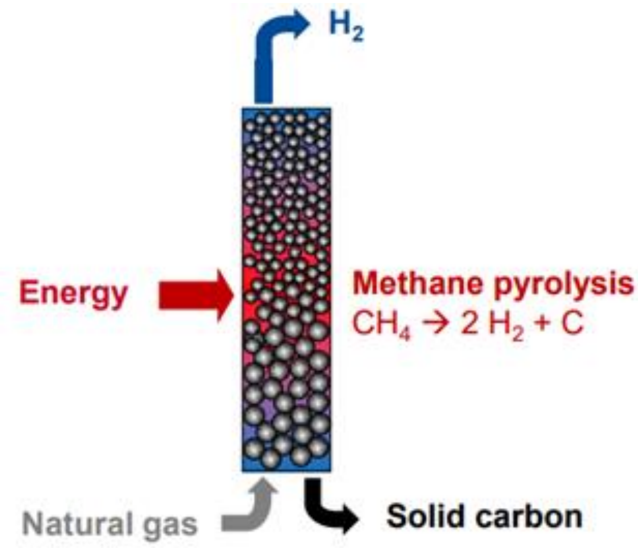


Figure 5-1. First moving carbon bed reactor scheme (Bode, 2019).

The principle of the second R&D project, which has been running since 2019, is to move from the laboratory to a larger test facility (BASF, 2020). The experimental plant in Ludwigshafen was successful commissioned and went into trial operation in 2021 (Figure 5-2) (BASF, 2022). The challenge in this project is to master the processing technology with electrical heating and the use of innovative high-temperature materials in the reactor. The right operating window for the reactor also needs to be determined (BASF, 2021a). The objective is finding out whether the process can also be successful on an industrial scale. Once the test plant is running stably, BASF plans to start building a pilot plant (BASF, 2020).

Figure 5-2. BASF methane pyrolysis test facility in Ludwigshafe, Germany (BASF, 2021c).

There is still a long way to go before the project is commercialized, as the plant for large-scale production should be ready by 2030 at the latest (BASF, 2021b).

5.1.2. EKONA's technology

Ekona Power Inc. is a Vancouver-based start-up founded in 2017 that is working on a patent-pending pulsed methane pyrolysis (PMP) reactor that splits methane based on the principles of pulse-combustion and high-speed gas dynamics. This solution is designed to solve the problem of carbon deposits by using pulsed injection of thermal and mechanical energy in PMP reactor, resulting in the automatic removal of carbon-buildup due to unsteady flow (Ekona, 2021).

In November 2021, Ekona received funding from a group of companies led by Baker Hughes to accelerate the scaling up and industrialization of the technology by identifying suitable pilot plant (Baker Hughes, 2021). Pilot deployment of Ekona’s PMP solution is planned for the future, but no date has been announced so far (CRIN, 2022).

5.1.3. TNO's technology

The Netherlands Organization for Applied Scientific Research (TNO) has been working on the patent-pending EMBER “Molten metal methane pyrolysis” technology. EMBER technology utilizes a molten metal reactor at temperatures above 1,000 °C to produce hydrogen as the main product and separates carbon from the molten metal using a molten salts approach (TNO, 2019; Daliah, 2021).

Figure 5-3 illustrates the molten gallium bubble column reactor. Methane enters at the bottom of the reactor and flows upwards through the molten metal reaction zone. Contact between the rising gas and the molten gallium results in the formation of bubbles. The methane pyrolysis reaction (Equation 2-1) occurs at the gas-liquid interface between the bubble and molten gallium. The bubbles become larger due to the molar expansion caused by the hydrogen formation, resulting in larger gas volume flow. Once the entire interface is covered by the carbon the reaction is complete. The bubbles continue to rise until they reach molten gallium surface, where they open and release both hydrogen and carbon. The main issue of the molten metal bubble reactor is the separation of the solid carbon from the molten metal. TNO has resolved this problem by floating a layer of molten salt on top of the molten metal. Hydrogen and carbon flow through the molten salt layer and, due to density differences, the carbon deposites in layers on the molten salt as hydrogen leaves the reactor (Bhardwaj et al., 2021; Pérez et al., 2021).

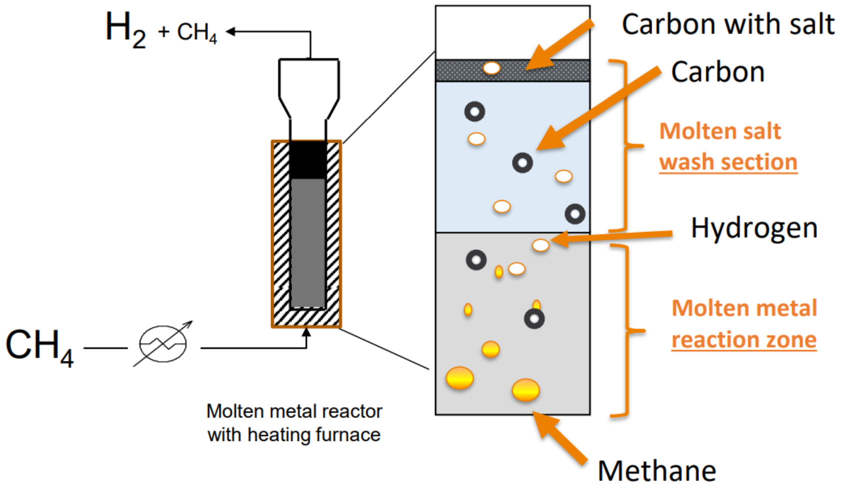


Figure 5-3. EMBER principle: molten gallium bubble column reactor (Bhardwaj et al., 2021).

By 2019, proof of concept for carbon removal was achieved. More than 96% of the carbon was recovered in the salt layer with continuous bubbling of gas. From an initial list of 35 salts, seven salts were experimentally tested. Separation based on flotation and density differences was successfully performed: NaCl, NaBr $ZnCl_2$ were separate carbon by flotation, while NiCl, CuCl, $MgCl_2$ by density. Analysis of the carbon formed shows that it has graphitic properties. At the moment, a lab-scale pilot test is underway, where salt recycle loop has been added for semi-continuous separation of carbon, and continuous process is being scaled up. Pilot plant is scheduled for 2023, and commercial demonstration plant is expected to be ready by 2030 (Bhardwaj et al., 2021).

5.1.4. KIT's technology

The Karlsruhe Institute of Technology (KIT), in collaboration with the Institute for Advanced Sustainability Studies (IASS), is developing a process for methane pyrolysis using a liquid metal bubble column reactor. The experimental reactor is made of quartz glass and stainless steel, filled with liquid tin, and operates at temperature up to 1,200 °C (KIT, 2018). One of the main issues in designing the reactor was to find suitable materials, since liquid tin corrodes severely, at the required high temperatures, almost all conventional materials of construction. Quartz glass has been shown to be chemically resistant to tin corrosion and to provide stable operating conditions up to 1200 °C. Therefore, all parts of the reactor that come into contact with liquid tin are made of quartz glass (Geißler et al., 2015).

Methane enters at the bottom of the reactor and flows through the reactor, forming bubbles as it comes in contact with liquid tin. When the gas in the bubbles reaches the reaction temperatures, methane pyrolysis reaction occurs. Bubbles open at the surface of the liquid tin, releasing hydrogen and carbon. How the carbon is separated from the liquid tin is not known. In laboratory scale methane pyrolysis experiments, a conversion rate of up to 78% was achieved (KIT, 2018).

This research was awarded the Innovation Award of the German gas industry in 2018 (KIT, 2018). In October 2019, KIT partnered with Wintershall Dea for a three-year joint study project with the goal of laying the groundwork for the future industrial use of methane pyrolysis (Wintershall Dea, 2019).

5.2. Catalytic methane pyrolysis technologies

Table 5-2 and Table 5-3 summarize catalytic methane pyrolysis technologies, both past attempt and technologies currently being developed, further described below.

Table 5-2. Summary of terminated catalytic methane pyrolysis technologies.

Developer / Technology	Location	Target Product	Reactor description	Catalyst	Technology development summary and future outlook	Current status of technology	References
Universal Oil Products (UOP) / HYPRO process	McCook, Illinois	H_2	Fluidized bed reactor	Nickel catalyst - regeneration by carbon combustion	**1960s**: laboratory plant with a CH_4 throughput of up to 7 m^3/h **Development was stopped**	**Terminated**	Muradov and Veziroğlu, 2005 Dagle et al., 2017 Schneider et al., 2020
Florida Solar Energy Center	USA	H_2	2-stage fluidized bed	Carbon catalyst	**1999-2005**: Laboratory research **2005:** Last publication	**Terminated**	University of Central Florida, 2004 Muradov et al., 2005b Schneider et al., 2020

The Hypro process is mentioned to show one of the first efforts to develop catalytic methane pyrolysis. The Florida Solar Energy Center investigated carbon catalyzed methane pyrolysis but did not develop it further. Both technologies have been terminated.

Table 5-3. Summary of developing catalytic methane pyrolysis technologies.

Developer / Technology	Location	Target Product	Reactor description	Catalyst	Technology development summary and future outlook	Current status of technology	References
HAZER Group	Australia	H_2 and graphite	Fluidized bed reactor	Powdered iron ore (ground to 200-500 µm) - no regeneration of catalyst	**2007**: Research at University of Western Australia **2010**: Company founded **2015 - 2020**: Bench testing **from 2017**: Pre-pilot plant testing **06/2022**: Commercial Demonstration Plant (CDP) completion of construction **2022**: Burrard Hydrogen Project - partnership to build pilot plant in British Columbia, Canada **Planned for 2023**: - Production of hydrogen and graphite from CDP - FID for Burrard Hydrogen Project	Commercial demonstration plant (CDP) constructed, start of production planned for 2023	Hazer Group, 2017a Hazer Group, 2018 Atchison, 2021 Hazer Group, 2020 AEA, 2021 Hazer Group, 2022a Hazer Group, 2022b
C-Zero	Santa Barbara, California	H_2	Molten salt bubble column	Binary Chloride Salts	**2016**: Research on methane pyrolysis begins at University of California **2018**: Company founded **2020-2022**: ARPA-E projects for reactor design and carbon removal system design **Planned for 2023**: First pilot plant online **Planned for 2025**: First commercial unit online **Planned for 2028**: World scale plant built	Lab-scale: High pressure pyrolysis reactor demonstrated	C-Zero, 2021 Eni Next, 2021 SoCalGas, 2021 C-Zero, 2022 Saadi 2022
Hycamite TCD Technologies	Kokkola, Finland	H_2 and carbon	Fixed-bed and fluidized-bed reactors	N/A	**2020**: Company founded **09/2021**: Test facility opened **Planned for 2022**: Start construction of industrial scale demonstration plant **Planned for 2024**: Start operation of industrial scale demonstration plant	Laboratory- and and pilot-scale operations underway	Hycamite, 2020 Grönqvis, 2021 Hycamite, 2021a Hycamite, 2021b Rahikka, pers. comm. 20th October
Carbotopia	Austria	H_2	Fluidized bed reactor	Metal-based catalyst	**2010 - 2011**: Pilot plant operated for several thousand hours **Today**: Prototype reactor (800 tonnes H_2/year) ready for technical implementation	Prototype reactor ready for implementation	Timmerberg et al., 2020 Murphy, 2021 Mauthner and Malkamäki, 2022

Technologies listed in Table 5-3 are currently being developed at laboratory scale or test facilities. Hazer Group finished construction of its first pilot plant in June 2022 and is expected to begin hydrogen production in the first quarter of 2023. C-Zero plans to test their technology in a pilot plant in 2023. Hycamite is already working at lab- and and pilot-scale and plans to have industrial scale demonstration plant up and running in 2024. Carbotopia has built a prototype reactor that is ready to be implemented. As is the case with thermal pyrolysis technologies, it seems unlikely that commercial scale facilities will be operational before 2030.

5.2.1. Past Efforts

This subchapter describes past attempts at developing catalytic methane pyrolysis.

5.2.1.1. *Universal Oil Products's technology*

The “HYPRO” process, one of pioneering methane pyrolysis processes for hydrogen production, was developed by Universal Oil Products (UOP) company in the 1960s. UOP operated a laboratory plant with a methane throughput of up to 7 m^3/h in McCook, Illinois (Muradov and Veziroğlu, 2005; Dagle et al., 2017; Schneider et al., 2020). This process uses a nickel catalyst in a fluidized bed reactor (FBR), operated at 800–1000 °C to decompose light hydrocarbons (Schneider et al., 2020). As mentioned in Subsection 3.2.1, one of the main challenges of catalytic methane decomposition is the catalyst deactivation problem. In this process, the nickel catalyst is regenerated by combusting the carbon deposited on the catalyst and regenerated catalyst is recycled back into the process. Combusted carbon provides heat for the process, but it also resulted in significant CO_2 emissions (Muradov, 2017). The development of this process did not continue.

5.2.1.2. *Florida Solar Energy Center's technology*

In 2003, Florida Solar Energy Center issued a research report investigating catalytic methane pyrolysis process using carbon particles (University of Central Florida, 2004). This process utilizes two fluidized bed reactors, one in which the pyrolysis reaction takes place and another in which the carbon catalyst is regenerated. The proposed solution for heat supply to the reactor is natural gas combustion, which would result in direct CO_2 emissions (Muradov et al., 2005b). The last publication dates from 2005 and there is no further indication that this development has continued (Schneider et al., 2020).

5.2.2. Hazer Group's technology

The HAZER® process uses iron ore as a catalyst to decompose natural gas or biogas into two highly valuable products (Ammonia Energy Association [AEA], 2021):

- Hydrogen (99.99%+ purity),
- Synthetic graphite (80–95% TGC).

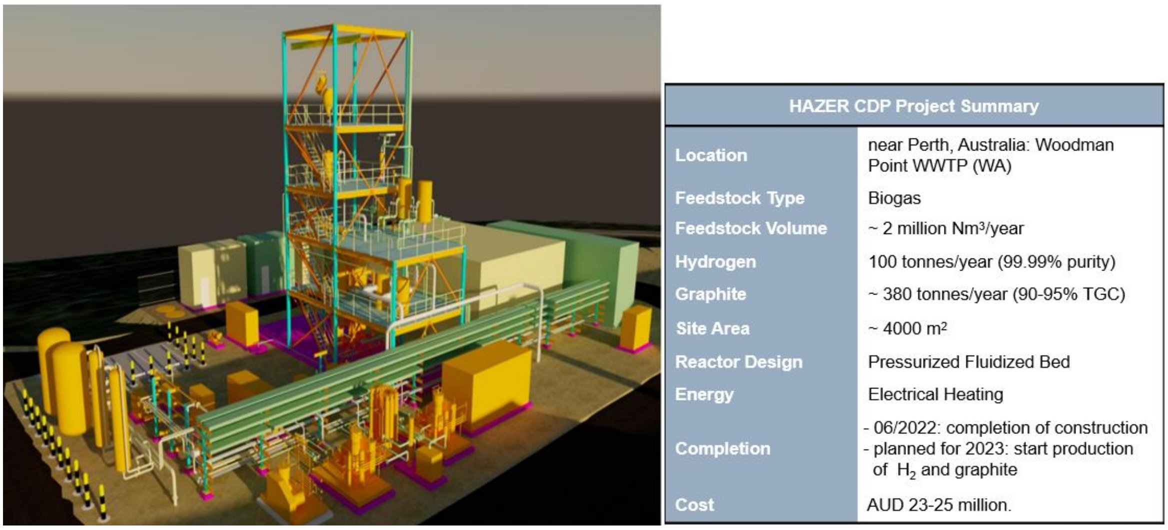
In the past, precious metals were often used as catalysts (e.g. nickel in Hypro process) which had to be constantly regenerated. The Hazer process solved this challenge by using iron ore, a low-cost, locally abundant sacrificial catalyst, to yield a useful product, graphite. The Hazer plant uses a fluidized bed rector (FBR), heated to approximately 900 °C, into which powdered iron ore (ground to 200-500 μm) is added (Hazer Group Limited, 2018; Atchison, 2021). In the reactor, powdered iron ore is additionally fragmented into nano-sized iron fragments, which become the site of methane decomposition. After hydrogen is released, graphite is formed around the iron nano-fragments. The catalyst is spent and the graphite produced must be further refined (Atchison, 2021).

Hazer's original concept was developed at the University of Western Australia. Hazer Group was founded in 2010 to commercialize this technology and was listed on Australian Securities Exchange (ASX) in 2015. From 2015 to 2020 pre-commercial research was conducted in lab-scale reactors in cooperation with the University of Sydney (AEA, 2021). In July 2017, Hazer's Fluidized Bed Reactor (FBR) pre-pilot plant was successfully commissioned, located in St Mary's, Sydney (Figure 5-4) (Hazer Group, 2017a). Pre-pilot testing resulted in successful production of graphite with a crude purity of 87% and with room for improvement as reactor design is further improved. The achieved purity levels are very optimistic, as Hazer has previously demonstrated the production of 99.95% ultra-high purity synthetic graphite from crude graphite with a purity level of 86% (Hazer Group, 2017b). In April 2018, Hazer Group announced that the pre-pilot plant had achieved fully continuous operation a successfully demonstrated on-line injection of iron ore catalyst and continuous graphite removal from the reactor. Later that year, the FBR pre-pilot plant was moved to its new location at Mineral Resource's Site in Kwinana, Western Australia, to demonstrate the commercial viability of synthetic graphite production (Hazer Group, 2018).

Figure 5-4. Hazer's pre-pilot plant in St Mary's, Sydney (Hazer Group, 2017a).

In July 2020, the final investment decision (FID) was announced for the Hazer Commercial Demonstration Plant (CDP), the first fully integrated larger scale demonstration plant of the Hazer Process on a larger scale (Hazer Group, 2020). Construction and commissioning were completed in June 2022, and the first phase of the testing program, i.e., cold operations will be conducted at low temperatures using a temporary carbon steel reactor to test gas processing, solids handling, process control, safety and utilities systems (Hazer Group, 2022a). The second phase, hot commissioning, and full operation of the CDP, was delayed due to setbacks in the delivery of the Hazer reactor and high-temperature heat-exchanger equipment during manufacturing. As a result, production of hydrogen and graphite at the plant is not expected to take place until 2023 (Hazer Group, 2022b).

The CDP is located at the Water Corporation's Woodman Point Wastewater Treatment Plant (WWTP) near Perth, in Western Australia. Biogas generated at the treatment plant, which is currently flared, will be used as feedstock. CDP will have the capacity to produce 100 tonnes of fuel cell grade hydrogen per year and 380 tonnes of synthetic graphite per year (Figure 5-5) (AEA, 2021). CDP project also includes a stationary hydrogen fuel cell power-generation system that will use a portion of the produced hydrogen to generate CDP's own renewable power (Hazer Group, 2020). The final cost of the project is predicted to be at the high end of the previously announced range of AUD 23-25 million (Hazer Group, 2022c).



HAZER CDP Project Summary	
Location	near Perth, Australia: Woodman Point WWTP (WA)
Feedstock Type	Biogas
Feedstock Volume	~ 2 million Nm³/year
Hydrogen	100 tonnes/year (99.99% purity)
Graphite	~ 380 tonnes/year (90-95% TGC)
Site Area	~ 4000 m²
Reactor Design	Pressurized Fluidized Bed
Energy	Electrical Heating
Completion	- 06/2022: completion of construction - planned for 2023: start production of H_2 and graphite
Cost	AUD 23-25 million.

Figure 5-5. Hazer's Commercial Demonstration Plant (CDP) final design (left) and project summary (right) (after AEA, 2021).

In 2022, Hazer Group entered into a collaboration with Suncor Energy Inc. and FortisBC Energy to build a hydrogen plant based on the Hazer Technology in British Columbia, Canada. Natural gas is to be used as the feedstock and the plant is expected to have a capacity of 2,500 tonnes of hydrogen per year and approximately 9,000 tonnes of synthetic graphite by-product. FID for the proposed “Burrard Hydrogen Project” is scheduled for 2023 and commissioning is planned for 2025 (Hazer Group, 2022b).

5.2.3. C-Zero's technology

C-Zero is a start-up company based in Santa Barbara, California, developing innovative thermocatalytic methane pyrolysis technology that uses molten salt bubble column reactor to decarbonize natural gas (Eni Next, 2021; Saadi 2022). C-Zero process is 100% optimized for hydrogen production, assuming in the base case that the carbon product is sequestered. Company was founded in 2018 and is based on technology initially developed by Professor Eric McFarland of the University of California (SoCalGas, 2021). From the beginning, the biggest challenge with the technology was producing a clean carbon product. Metal contamination was a major concern early on, so research shifted to using molten salt catalysts (McFarland, 2019).

In 2020, C-Zero received two grants from U.S. Department of Energy’s Advanced Research Projects Agency-Energy (ARPA-E) to develop a methane pyrolysis reactor and a carbon removal system. Both projects ran from 2020 to 2022. The goal of the first project was to demonstrate in-situ spectroscopic measurements of carbon formation under methane pyrolysis reaction conditions and to design and build a methane pyrolysis reactor with:

- ≥ 70% CH_4 conversion,
- ≥ 90% H_2 selectivity,
- ≥ 5 mol $H_2/\ m^3\ s$,
- high pressure (≥ 5 bar).

The second project aimed to demonstrate a stable, active, binary chloride melting system with hydrogen selectivity greater than 90% and to design and build a carbon removal system capable of:

- high temperature (1000 °C),
- continuous carbon removal (≥ 24 hours),
- high pressure (≥ 10 bar).

C-Zero has succeeded in demonstrating continuous carbon removal from methane pyrolysis by fluidization for more than 24 h (Figure 5-6). In this system, hydrogen and carbon products pass through a 3-phase separation zone designed for minimal fluid carryover and carbon separation is conducted via cyclones connected in series, a conventional gas/solid separation method (Saadi, 2022).

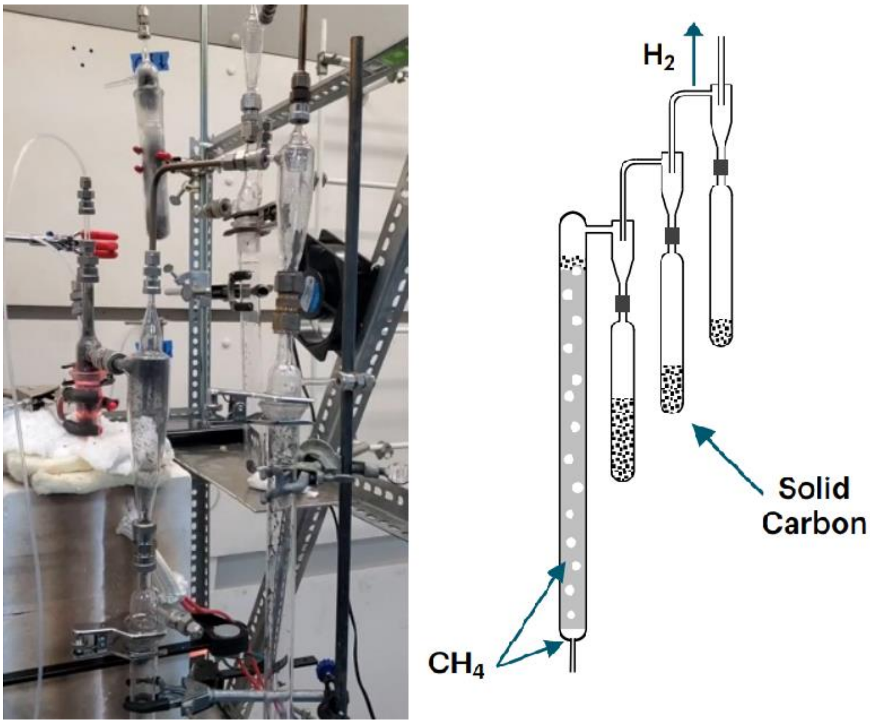


Figure 5-6. Demonstration of continuous carbon removal from methane pyrolysis by fluidization (Saadi, 2022).

High pressure pyrolysis reactor (up to 20 bar) with continuous carbon removal using internally heated reactors was also demonstrated (Figure 5-7). Stainless steel cyclones were fabricated using additive manufacturing. This system was successfully operated continuously for more than 6 hours (Saadi, 2022).

Figure 5-7. High pressure reactor demonstration (Saadi, 2022).

Heat for the process can come from three different sources, making the process very flexible (Atlantic Council, 2021; SoCalGas, 2021):

1. natural gas – base case assumption (process would not be completely emission free, but still 75% less than conventional SMR),
2. hydrogen produced – about 1/3 of hydrogen produced would be needed,
3. electricity.

In 2021, C-Zero received funding co-led by Breakthrough Energy Ventures and Eni Next, with participation from Mitsubishi Heavy Industries and AP Ventures, to accelerate the first commercial-scale deployment of C-Zero’s technology (C-Zero, 2021). In 2022, additional founding round was led by SK Gas, with participation from Engie New Ventures and Trafigura. These funds will be used to build C-Zero’s first pilot plant with a production capacity of 400 kg H_2/day. The location of the pilot plant is not disclosed, but the commissioning is planned for the first quarter of 2023 (C-Zero, 2022). As for the other plans announced to date, the first commercial plant (about 6,000 kg H_2/day) is planned for 2025, and a world scale plant is planned for 2028 (about 270,000 kg H_2/day) (Eni Next, 2021; SoCalGas, 2021).

5.2.4. Hycamite TCD Technologies's technology

Hycamite TCD Technologies, formerly Hydrogenius, markets thermocatalytic decomposition (TCD) technology developed in collaboration with the University of Oulu and the University of Tampere in Finland. The company was founded in 2020 and it is headquartered in Kokkola, Finland (Hycamite, 2020; Hycamite, 2021a). Hycamite uses electrically heated fixed-bed and fluidized-bed reactors alongside sustainable catalysts to produce hydrogen and solid, high-quality carbon from natural gas or biomethane. Hydrogen and unreacted methane exit on the top of the reactor and pass through the carbon filter to remove all carbon residue. They are then separated in a pressure swing adsorption (PSA) unit and the methane is returned to the reactor (Figure 5-8) (Hycamite, 2021b). Depending on the desired allotrope of carbon, temperatures in the reactor range between 600 to 800 °C. Pressure in the reactor is close to atmospheric. Hycamite's process technology innovations include energy savings through heat exchange, product stream differentiation, catalyst regeneration and several other innovations (Grönqvis, 2021). Hycamite is developing its own catalysts but the type of catalyst used is not disclosed.

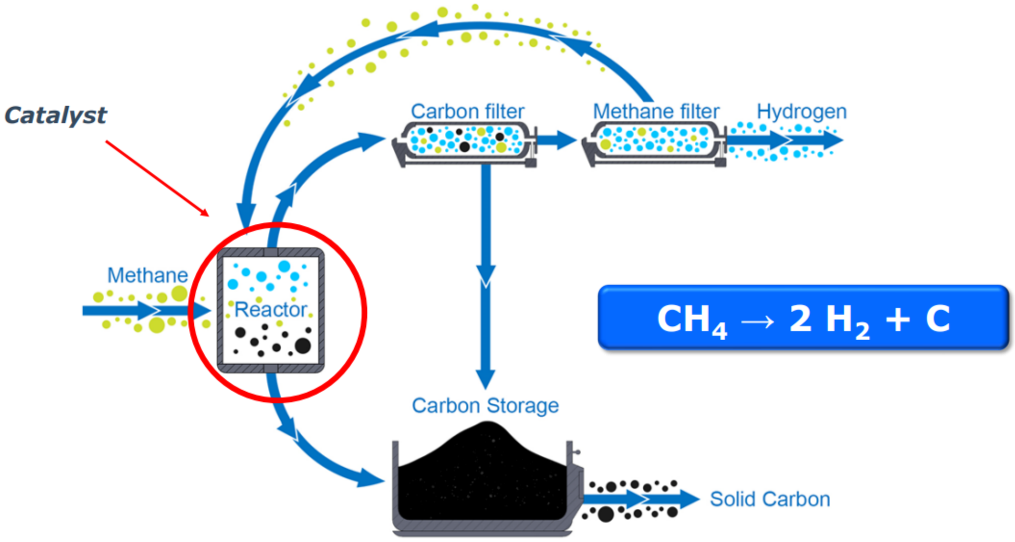


Figure 5-8. Schematic of Hycamite's thermocatalytic decomposition (TCD) technology (Grönqvis, 2021).

In September 2021, a test facility was opened at Kokkola Industrial Park where further research and testing will be conducted and catalysts developed (Hycamite, 2021b). In addition to the laboratory- and pilot-scale operations already underway, Hycamite will begin construction of an industrial scale demonstration plant in 2022. This plant will also be located at Kokkola Industrial Park and is expected to be operational in early 2024 (Rahikka, 2022, pers. comm. 20th October). The industrial-scale demonstration plant will serve two purposes: to produce and demonstrate the technology for producing hydrogen and to deliver carbon samples for high-value carbon customers. This plant will have an annual nominal capacity of 2,000 tons of hydrogen and 6,000 tons of solid carbon, while the power consumption of the site will be around 2.6 MW. Biogas will be used as a feedstock (Mauthner and Malkamäki, 2022).

Hycamite claims that their process can produce different allotropes of carbon (carbon nanotubes, carbon nanofibers, activated carbon or graphite), depending on the customer’s needs. Carbon nanotubes, carbon nanofibers and graphite, for example, can be used in production of electric car batteries or in the electronics industry (Hycamite, 2021a; Grönqvis, 2021). Therefore, Hycamite's production supports the development of electric battery production in Finland in addition to the development of the hydrogen industry (Hycamite, 2021c). In 2022, Hycamite has signed letter of intent with Jervois Finland for the potential supply of hydrogen. Jervois Finland is exploring the possibility of using Hycamite’s hydrogen in its own production for the reduction of cobalt (Hycamite, 2022).

5.2.5. Carbotopia's technology

Carbotopia is a non-profit organization from Austria that has developed a thermocatalytic methane pyrolysis technology that produces hydrogen and solid carbon from natural gas (Murphy, 2021). Carbotopia's technology is based on the use of fluidized bed reactors with metal-based catalysts. Different sources mention different types of carbon produced, Timmerberg et al. (2020) and Mauthner and Malkamäki (2022) mention carbon nanotubes, while Carbotopia (2022) mentions solid activated carbon. As for the efficiency of the process, splitting the methane requires 10% of the converted energy (Carbotopia, 2022). The purity of the hydrogen produced is about 95% vol (Mauthner and Malkamäki 2022).

Pilot plant, producing 4.3 kg of hydrogen and 13 kg of carbon per day, operated for several thousand hours between 2010 and 2011 (Timmerberg et al., 2020). Today, a standard vertical reactor with a capacity of 800 tonnes per year of hydrogen has successfully passed all feasibility tests and is ready for technical implementation. At future sites, these reactors could be assembled in up to fivefold parallel multiple setups to address the demand for on-site hydrogen (Mauthner and Malkamäki, 2022).

5.3. Plasma technologies

Table 5-4 and Table 5-5 summarize both past attempt and current developing plasma methane pyrolysis technologies, further described below. Plasma methane pyrolysis, or more specifically thermal plasma, is the most mature category of methane pyrolysis since it is used on an industrial scale to produce carbon black.

Table 5-4. Summary of terminated plasma methane pyrolysis technologies.

Developer / Technology	Location	Target Product	Plasma Type	Technology development summary and future outlook	Current status of technology	References
Kværner (now Aker Solutions) / Kvaerner CB&H Process	Fornebu, Norway	Carbon Black	Thermal Plasma	**1987**: Thermal plasma research group established at NTNU - SINTEF **1992**: Pilot plant successfully tested in Sweden **1999**: Commercial-scale plant commissioned - Karbomont plant in Canada **2003**: Karbomont plant decommissioned due to insufficient carbon quality	**Terminated**	Jensen, n.d. Bakken et al., 1998 Gautier et al., 2017 Labanca, 2020 Philibert, 2020
Atlantic Hydrogen Inc. / CarbonSaver ™	New Brunswick Canada	begining: H_2-enriched natural gas (HENG) later: H_2	Not clear from available info	**2002**: Company founded **2009**: Pilot plant commissioned in New Brunswick **2015**: During the construction of demonstration pilot plant company went bankrupt	**Terminated**, company went bankrupt	Hamilton, 2009 Samuel and Oliver, 2010 Stanley, 2014 Schneider et al., 2020
GasPlas AS	Norway	-	Non-thermal Plasma	**2008**: Company founded Laboratory scale No information on further activities available today	**Terminated**	Juda et al., 2015 Timmerberg et al., 2020

Kværner's Karbomont plant was the world’s first commercial methane pyrolysis plant. The plant started operation in 1992, but it was shut down in 2002 due to unsatisfactory carbon black quality. Atlantic Hydrogen developed Carbonsaver process and began operating a pilot plant, but the company went bankrupt before construction of the demonstration plant was completed.

Table 5-5. Summary of developing plasma methane pyrolysis technologies.

Developer / Technology	Location	Target Product	Plasma Type	Technology development summary and future outlook	Current status of technology	References
Monolith	USA Lincon, Nebraska	CB	Thermal plasma	**2012**: Company Founded **2014 - 2018**: Seaport pilot plant **2016**: Construction started of commercial scale plant Olive Creek I **2020 - present**: Olive Creek I commissioned (CB capacity: 14 kt/year) **Planned for 2023**: Start construction of Olive Creek II plant (CB capacity:180 kt/year) **Planned for 2025**: Completion of Olive Creek II	Commercial scale plant (OC1) commissioned	Monolith, 2016 Hardman, 2017 Rens and Hanson, 2019 Labanca 2020 Monolith, 2020 Mesrobian, 2022 Monolith, 2022a Monolith, 2022b
Graforce / Methane-Plasmalyzer	Berlin, Germany	H_2	Non-thermal plasma	**2012**: Company founded **2020**: Successful trial of technology at MOA hotel, Berlin	Demo plant in operation in Berlin	Graforce, 2022a Graforce, 2022b Business Wire, 2020
Plenesys / HyPlasma	Valbonne, France	H_2	Thermal plasma	**2018**: Company founded **March, 2022**: collaboration with Pure Hydrogen to build a pilot plant in Brisbane in the next 12 months	Demonstration unit under development	Plenesys, 2021 Plenesys, 2022 Pure Hydrogen, 2022
HiiROC	Hull, England	H_2	Thermal plasma	**2019**: Company founded **08/2021**: Wintershall Dea and VNG AG invest in pilot project **Planned for 2023**: pilot facility to into operation (capacity: 400 kg H_2/day), to be located in Germany	N/A	Carbon Copy, 2021 HiiROC, 2021 Wintershall Dea, 2021
Spark Cleantech	Gif-sur Yvette, France	H_2	Non-thermal plasma	**02/2022**: Company founded **So far**: proven concept on a unit producing 1 Nm^3 H_2/h **Planned for 2023**: installation of demonstration unit **Planned by 2025**: commercialization of technology	Concept proven on a unit producing 1 Nm^3 H_2/h	Cleantech, n.d. SAAT Paris-Saclay, n.d. Université Paris-Saclay, 2021 Le Figaro, 2022 Louis, 2022
Levidian / LOOP	Cambridge UK	Graphite	Non-thermal plasma	**2012:** Company founded **2022:** Trials with UK's National Grid to test LOOP process **05/2022:** First customer agreement with Zero Carbon Ventures to deploy over 500 LOOP50s to the UAE	Trials of LOOP process ongoing	Levidian, n.d. Levidian 2022c Levidian 2022d
Sakowin Green Energy	Aix-en Province, France	H_2	Non-thermal plasma	**2017:** Company founded **So far:** Prototype developed **Planned by 2025:** technology commercialization	Prototype unit developed	Sakowin, 2021a Sakowin, 2021b Gatt, 2022

Monolith Materials developed technology based on Kværner technology and in 2020 began commercial scale operation of Olive Creek I plant with a production capacity of 14 kt/year of carbon black. Monolith also announced the plans to build Olive Creek II plant with a production capacity of 180 kt/year of carbon black, with the construction to begin in 2023. Today, a number of companies are developing plasma methane pyrolysis technology, e.g. Graforce, Plenesys, HiiROC, Spark CleanTech, and are planning pilot plants across Europe.

5.3.1. Past efforts

This subchapter describes past attempts at developing plasma methane pyrolysis.

5.3.1.1. *Kværner's technology*

In 1987, a thermal plasma research group was established at NTNU – SINTEF. The Norwegian company Kværner (now Aker Solutions) in collaboration with SINTEF-NTNU, developed Kværner Carbon Black and Hydrogen (CB&H) Process, a thermal plasma process for decomposing methane and other hydrocarbons into hydrogen and carbon black (Figure 5-10). CB&H Process uses a DC plasma torch reactor with coaxial graphite electrodes (Figure 5-9). The arc discharge can be spatially focused during its generation; therefore, a magnet coil is applied to avoid this. Magnet coil induces rotation of the arc discharge at predetermined speed, which ensures uniform heating of the feedstock and plasma gas. The arc rotation also reduces electrode erosion (Bakken et al., 1998). Hydrogen is used as the plasma gas; therefore, a portion of the hydrogen produced is recirculated into the plasma torch. Before entering the reactor, natural gas and plasma gas are preheated before hydrogen and CB leave the reactor (Figure 5-10) (Jensen, n.d.).

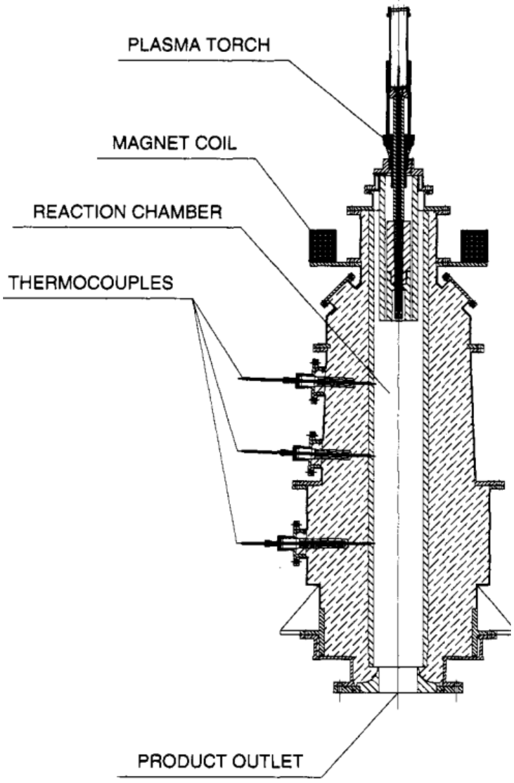


Figure 5-9. Plasma reactor for CB&H process (Bakken et al., 1998).

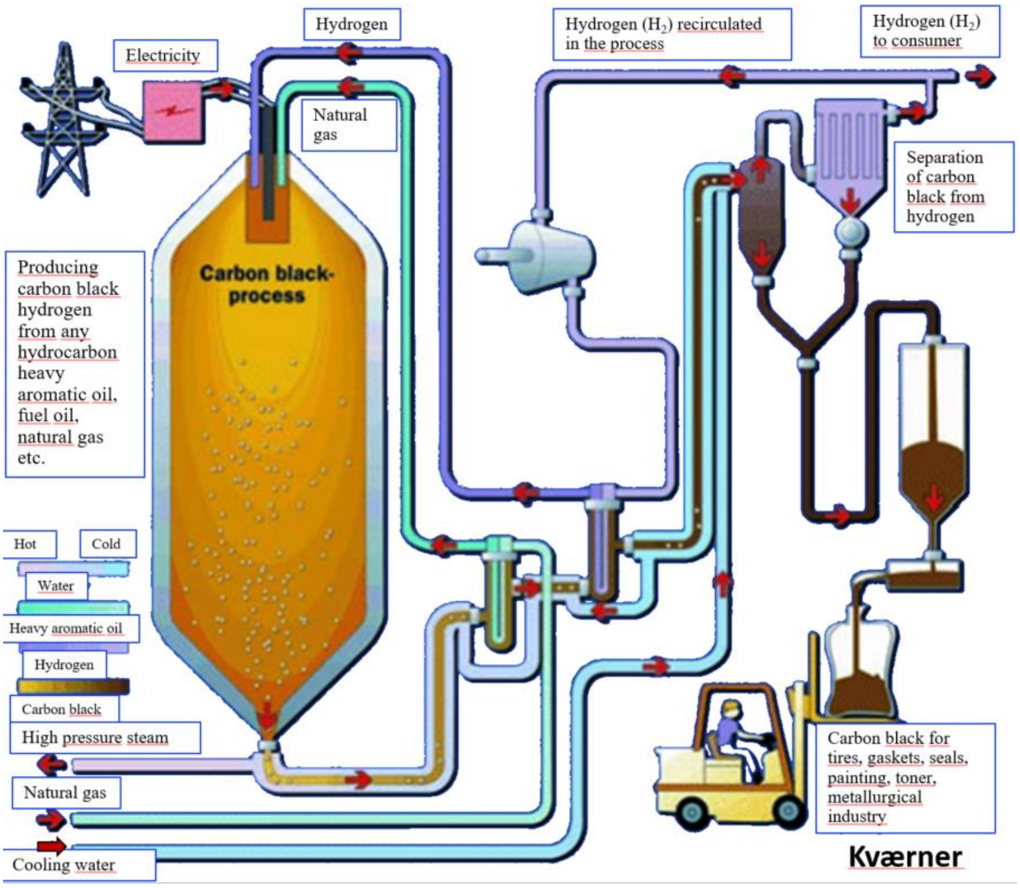


Figure 5-10. Kværner CB&H process (Jensen, n.d.).

In 1992, a full-scale pilot plant with a plasma output of 3 MW was successfully installed and operated in Sweden (Gautier et al., 2017). In 1997, Kværner began construction of a 6 MW commercial-scale “Karbomont” plant near Montreal, Canada. The Karbomont plant was commissioned in 1998 and had the production capacity of 20,000 tons of CB (Gautier et al., 2017; Jensen, n.d.). It proved difficult to produce the expected quality of CB and the carbon was sold at a much lower price than expected, while the nearby refinery bought the hydrogen produced. The plant was closed in 2002 and demolished in 2003 because of insufficient quality of CB product (Labanca, 2020; Philibert, 2020).

5.3.1.2. *Atlantic Hydrogen Inc's technology*

Canadian Company Atlantic Hydrogen Inc. has developed CarbonSaver™ technology, which consists of series of proprietary pulsed plasma torches and additional equipment. The initial goal was to produce hydrogen-enrichen natural gas (HENG), i.e., natural gas with up to up to 20vol% H_2 (Samuel and Oliver, 2010). The CarbonSaver process can be used at a number of points along a pipeline close to end users: compressor stations, underground storage facilities, city gateways that bring gas to homes and businesses, and power plants and industrial sites that receive natural gas (Hamilton, 2009). It operates at near-atmospheric pressure, typically up 1 bar and it can use electricity from off-peak periods (Boutot et al., 2009; Samuel and Oliver, 2010). Regarding the type of plasma used, different sources mention different types. Boutot et al. (2007) filed a patent for a cold arc discharge plasma that allows the reactor to operate at temperatures below 200 °C, while Hamilton (2009) mentions a thermal plasma torch reactor that operates at temperatures of 1,500-2,500 °C. In 2009, a three-year pilot project was commissioned, producing about 25 m^3/h of natural gas with a 10% H_2 mixture (Hamilton, 2009). According to Staley (2014), later on the company changed its course to producing hydrogen suitable for fuel cells using a 100 kW microwave plasma to reach temperatures of 700-900 °C. A field demonstration plant was under construction in New Brunswick and was scheduled to be operational in 2015. That same year, the company filed for bankruptcy and the technology was not further developed (Schneider et al., 2020).

5.3.1.3. *GasPlas's technology*

GasPlas, a Norwegian company, has developed and patented a technology for methane pyrolysis using non-thermal microwave plasma at atmospheric pressures (Timmerberg et al., 2020). The GasPlas reactor is expected to be highly scalable and connect to existing natural gas networks to produce hydrogen on-demand at the point of use. The technology has been tested at laboratory scale on the double vortex plasma reactor with microwave powers ranging from 1.5 to 6 kW. A conversion rate of natural gas to hydrogen of over 90% was achieved and a range of carbon morphologies were obtained: amorphous carbon, nanographite and carbon nanotubes. With increasing plasma power, greater variety but lower selectivity of carbon nanoforms were obtained (Juda et al., 2015). No further information about the company or further activities is currently available.

5.3.2. Monolith Materials's technology

Monolith Materials was founded in 2012 in Palo Alto, California by two Stanford engineering graduates. Monolith's technology is based on Kværner technology, which they licensed from Aker Solutions in 2013, and the work of Laurent Fulcheri’s research team at the Centre for Processes, Renewable Energies and Energy Systems at Mines Paris Tech PSL Research University. The company took these two different, unfinished technologies and, through further engineering and by combining them, developed the Monolith process (Hardman, 2017; Labanca 2020).

Monolith uses its proprietary thermal plasma process to produce carbon black as a primary product and hydrogen tail-gas as a valuable byproduct (Monolith, 2016). Natural gas, along with process gas, is fed into the top of a plasma reactor, where it is heated to 1,500-2,000 °C by electric plasma (Jenkins, 2020). The heat breaks the bond between hydrogen and carbon in the CH_4 molecule. Produced hydrogen and carbon exit separately at the bottom of the reactor (Figure 5-11) (Monolith, 2022a). For operation, Monolith uses 100% renewable electricity, acquired through renewable energy certificates (Monolith, 2021b).

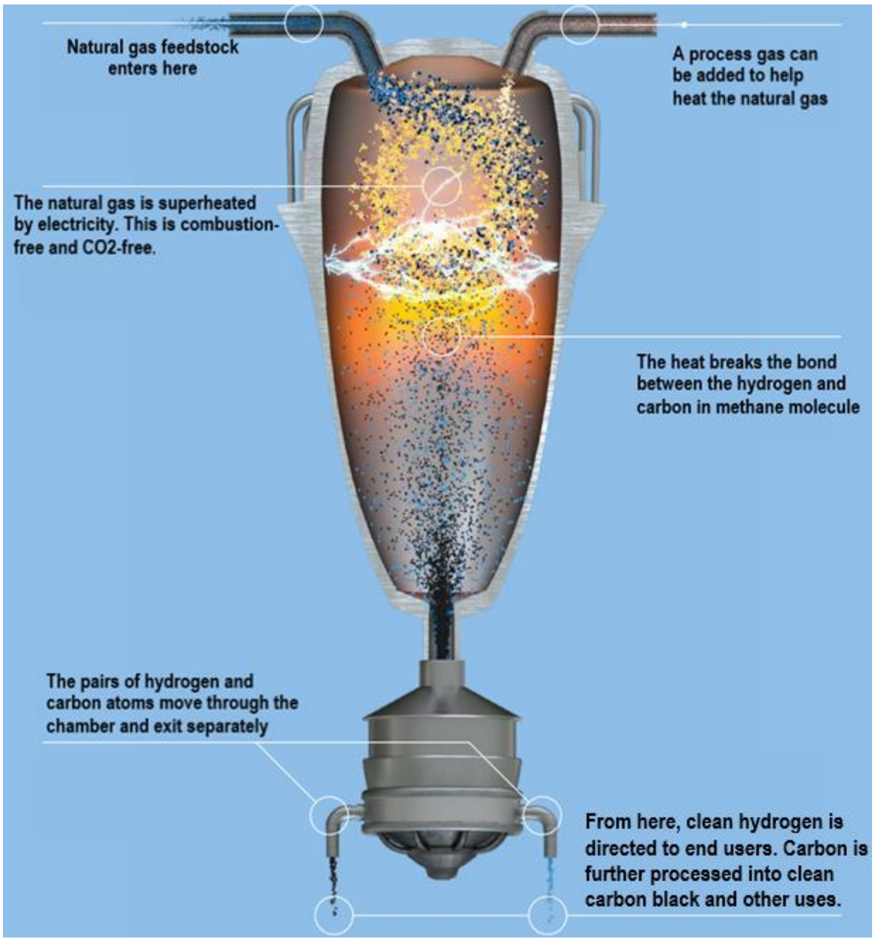


Figure 5-11. The Monolith process (after Monolith, 2022a).

Monolith maintains an active partnership with the Center for Processes, Renewable Energies and Energy Systems at the MINES ParisTech PSL Research University in Paris, where pilot-scale reactor testing have been underway since 2018 (Mesrobian, 2022). The company is also working with Aker Solutions to build on experience gained from Karbomont, a commercial scale plant described in Subsection 5.3.1.1 (Philibert, 2020).

In September 2014, the Seaport I demonstration pilot plant located was completed in Redwood City, California and carbon black production began at the facility in April, 2015. The plant had the production capacity of 700 tonnes of carbon black per year and 200 tonnes of hydrogen per year (Rens and Hanson, 2019). Over the next three years, the plant was operated to establish product range and reliability, demonstrate yield and stockpile samples for further testing. Over 3,700 hours of operation, Monolith demonstrated significantly improved yield, reliability, and carbon product quality control (Figure 5-12). Additionally, carbon fouling, a major reliability issue, was controlled through a combination of design and process conditions (Mesrobian, 2021). Pilot plant was decommissioned in the fall of 2018 after successful demonstration of technology (Rens and Hanson, 2019).

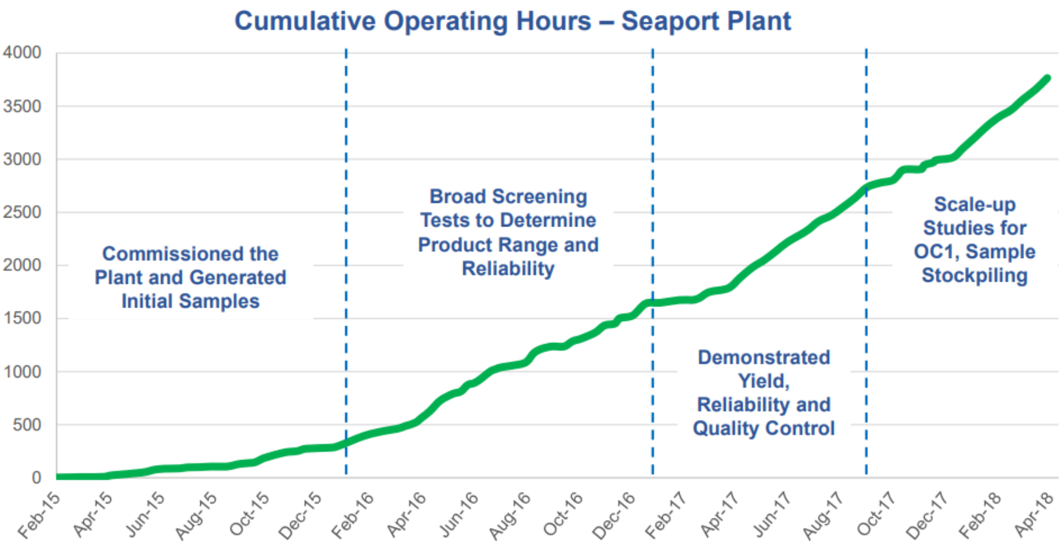


Figure 5-12. Operational history at Seaport demonstration scale pilot plant (Mesrobian, 2021).

In October 2016, construction began on a commercial-scale Olive Creek I (OC1) facility near Hallam, Nebraska (Monolith, 2016). The plant was commissioned in June, 2020, and first batch of carbon black was produced in September of that year. The plant has the production capacity of 14,000 tonnes of carbon black a year and 4,500 tonnes of hydrogen a year (Figure 5-13) (Monolith, 2020; Mesrobian, 2022). OC1 is the first commercial, carbon black facility to be built on a greenfield site in the U.S. in over 50 years, as well as the largest CO_2 free, stand-alone hydrogen plant in the country (Monolith, 2022b). The capital cost was about USD 100 million (Monolith, 2020). As for the use of hydrogen produced, it will be vented until an application for it can be found. Initially, Monolith planned to sell the hydrogen co-product to the Nebraska Public Power District (NPPD), Nebraska’s largest electric utility. The company originally chose the site next to Sheldon Station power plant because NPPD planned to replace one of Sheldon plant's coal-fired boiler with a hydrogen-fired boiler. However, in July of 2020, the two companies announced that their two years of research had shown that this idea for hydrogen utilization was not financially viable (Monolith, 2016; Monolith 2020).

Olive Creek I (OC1)	
Location	Hallam, Nebraska, USA
Reactor / Train	1/1
Feedstock Type	Natural gas
Carbon Black	14,000 tonnes/year
Hydrogen	4,500 tonnes/year
Energy	100% Renewable Electricity
Completion	June 2020
Cost	USD100 million

Figure 5-13. Monolith's Olive Creek I (OC1) commercial-scale facility (left) and project summary (right) (after Mesrobian, 2022).

Olive Creek I was the first phase of the plant. As a part of the second-phase of the plant, Monolith announced the construction of an anhydrous ammonia plant. In the ammonia plant produced hydrogen produced is combined with nitrogen from the air to produce liquid fertilizer with no additional CO_2 emissions. This is a significant venture since the anhydrous ammonia business accounts for about 1% of the global CO_2 emissions (Monolith, 2020). Olive Creek II (OC2), the second expansion stage of the plant, will have about 12 times the capacity of OC1, producing about 194,000 tonnes of clean carbon black a year (180,000 tonnes/year + 14,000 tonnes/year from OC1) and 275,000 tonnes of clean ammonia a year (Figure 5-14). The plant will cost about USD 1 billion. There is no need to scale the technology because Monolith is taking a modular approach, meaning they will replicate the reactor 12 times. This also means that the footprint of OC2 will only be about 2-3 times that of OC1 plant; so construction will not take much longer. The expansion facility will require about 1.2 to 1.5 million m^3 of water per year, which will be used for cooling. The plan is to sell the ammonia produced to farms in the region which will help offset the current 1.75 million tonne deficit in the U.S. Corn Belt (Monolith, 2020; Monolith, 2021b; Mesrobian, 2022). The construction of OC2 facility is expected to begin in the second quarter of 2023, with completion scheduled for 2025 (Monolith, 2022b).

Olive Creek II (OC2)	
Location	Hallam, Nebraska, USA
Reactor / Train	12/2
Feedstock Type	Natural gas
Carbon Black	180,000 tonnes/year + 14,000 tonnes/year (OC1)
Ammonia	275,000 tonnes/year
Energy	100% Renewable Electricity
Planned start of construction	Q2 2023
Cost	USD1 billion

Figure 5-14. Monolith’s Olive Creek II (OC2) design concept (left) and project summary (right) (after Mesrobian, 2022).

In December 2021, Monolith and The Goodyear Tire & Rubber Company, one of the biggest tire manufacturers in the world, signed a cooperation agreement and a letter of intent (LOI) for the potential use of carbon black, produced in OC2, for tire production (Monolith, 2021c). Monolith’s investors include Azimuth Capital Management, Cornell Capital LLC, Imperative Ventures, Warburg Pincus, Mitsubishi Heavy Industries America, SK Inc. and NextEra Energy Resources Inc. Monolith has also announced that it had signed a memorandum of understanding with SK Inc. to pursue a joint venture to produce clean hydrogen and carbon black products in South Korea (Monolith, 2021d).

5.3.3. Graforce's technology

Graforce GmbH was founded in 2012 by Dr. Jens Hanke and has since been located in Berlin, Adlershof. Graforce holds three patents for the application of various plasma processes: high-frequency discharge, dielectric barrier discharge and corona low-frequency discharge (Graforce, 2022b).

The Methane Plasmalyzer® technology developed by Graforce uses a non-thermal plasma, generated by a high-frequency electric field to split natural gas or biogas into hydrogen and solid carbon. As described in Section 3.3, the non-thermal plasma causes ionization of the methane. The temperature of the electrons increases from 10,000 to 100,000 K, resulting in the methane pyrolysis process, while the overall gas temperature remains as low as room temperature. The process requires very small amount of energy input. To illustrate, 4 kg of CH_4 and 10 kWh are required to produce 1 kg of hydrogen and 3 kg of solid carbon. To yield 600 Nm^3/h (about 54 kg/h) of hydrogen, 700 kWh of electricity and

300 Nm^3/h of natural gas feedstock are needed. Additionally, 150 kg/h carbon black and 250 kW/h of waste heat are generated (Figure 5-15) (Graforce, 2022a).

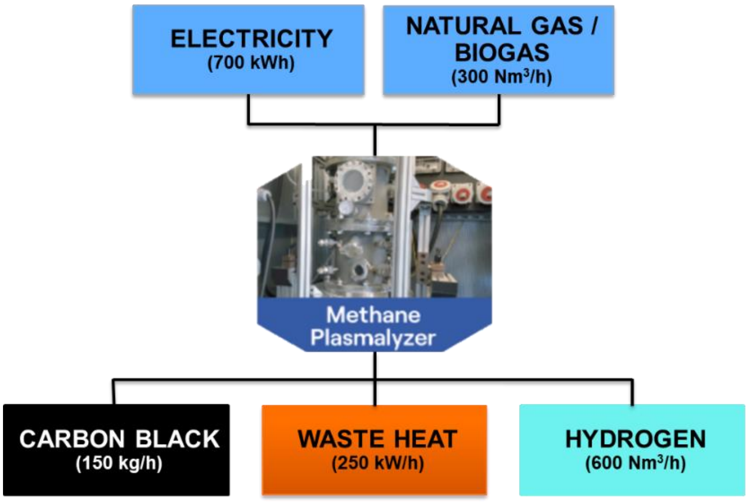


Figure 5-15. Required resources for Methane Plasmalyzer® process and final products (after Graforce, 2022a).

The purity of the hydrogen produced is about 98% vol. If a higher degree of purity is required, a PSA system can be added and hydrogen can be produced at 99,99% vol. This high purity hydrogen can be used directly in hydrogen combined heat and power plants (hydrogen CHP units), boilers or solid oxide fuel cells (SOFC) for CO_2-free heat and power generation.

The purity of produced carbon black is about 98% by weight (when natural gas is used as feed gas). Depending on the plasma parameters, the particle size ranges from 10 to 150 µm. Product forms of carbon black include compressed powder, granules or pellets (Graforce, 2022a).

Regarding the application of methane plasmalysis, plants with capacities ranging from 115 - 6,500 Nm^3 H_2/h have been developed for the following industries (Graforce, 2022a):

- heavy duty traffic,
- steel industry,
- fertilizer industry,
- energy and heat industry.

Graforce has successfully trialled their methane plasmalysis technology at MOA, a conference hotel in Berlin owned by the Mercure Group (German Energy Solutions

Initiative, 2020). Figure 5-16. illustrates the energy concept envisioned at MOA: generating heat and power with zero or even negative emissions. Renewable electricity from solar energy and biogas as feed gas are used as input to the plasma reactor. In the case of biogas utilization, the process becomes not only emission free but also carbon-negative. The hydrogen produced is used for emission-free heating (Business Wire, 2020). Initially, two of the hotel's five boilers will be fired with a mixture of 20% hydrogen and 80% biogas. Further plans call for all boilers to run on hydrogen (Hanke, 2021). Reportedly, produced carbon black will be used to make asphalt (German Energy Solutions Initiative, 2020). Further information on the current status of the project could not be found in the public domain.

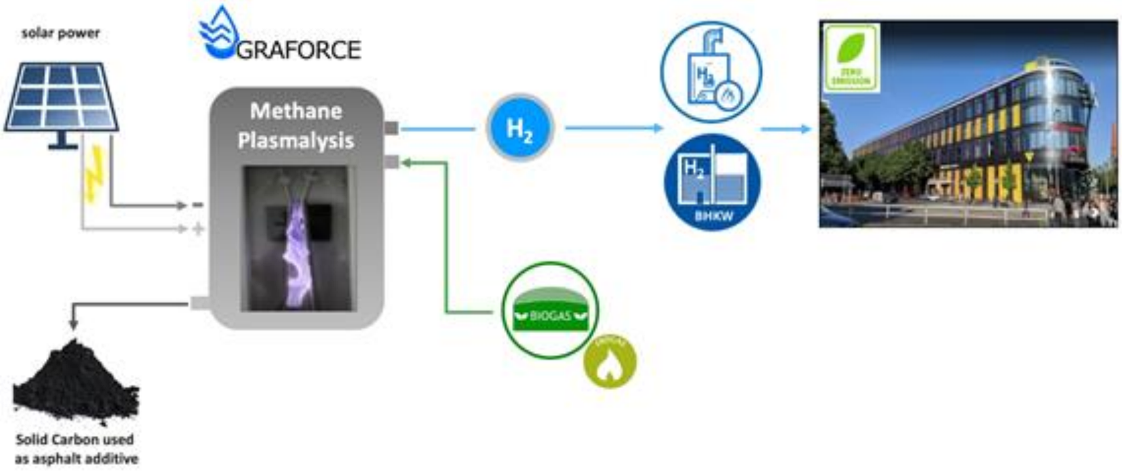


Figure 5-16. Graforce's Methane Plasmalyzer® at MOA - energy concept: heat & power with zero or even negative emissions (Business Wire, 2020).

5.3.4. Plenesys's technology

Plenesys is a small start-up company founded in 2018 and based in Valbonne, south-eastern France. According to the company it is "working to innovate the best clean hydrogen production process and develop highly performant plasma torches". Its goal is to decarbonize the industry by offering innovative products and solutions that are simultaneously cost-effective, efficient, and reliable (Plenesys, 2022).

Plenesis is developing HyPlasma® Process, a thermal plasma process that uses its patented AC plasma torch (Plenesys, 2022). Thermal plasma is generated by electric arc discharge between graphite electrodes. Figure 5-17 illustrates the operation of the HyPlasma® process (Plenesys, 2021):

2. Natural gas is injected into the plasma reactor where plasma, generated by the plasma torch at very high temperatures, splits CH_4 molecules into hydrogen and solid carbon.
3. The mixture of hydrogen and solid carbon exits the reactor and flows into a carbon filter where hydrogen is separated from the solid carbon.
4. The solid carbon is recovered from the lower outlet of the carbon filter and the hydrogen is recovered from the upper outlet.

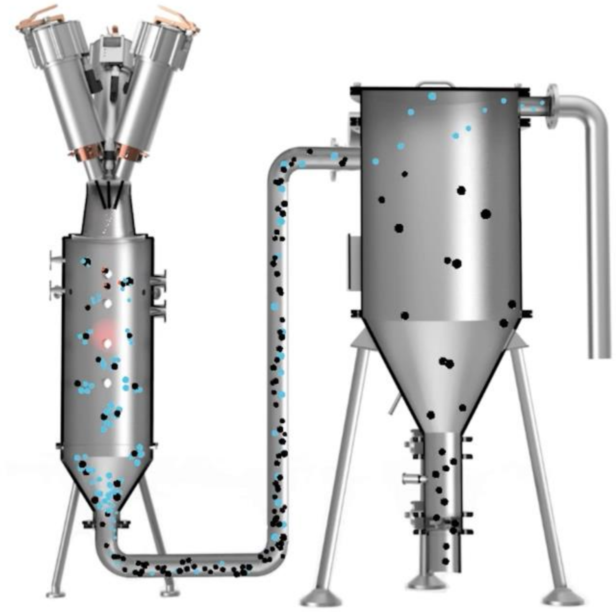


Figure 5-17. Illustration of HyPlasma® process (Plenesys, 2021).

What is unique about the HyPlasma technology is that Plenesys has developed a process to automatically replace graphite electrodes so that the system can be operated continuously; therefore, no shutdown of the process is required (Harrison, 2021). The highly automated torch is equipped with a machine learning system enabling the stabilization of plasma operation.

HyPlasma® is a modular solution that is decentralized, scalable and flexible, allowing the units to be mounted close to the end user and adapted to production requirements. The smallest unit produces 7 kg H_2/h (~50 t H_2/year) requiring about 30 kg/h of methane. For each kg of hydrogen produced, about 13 kWh of electricity is required. Figure 5-18 shows the modular HyPlasma® unit. It contains all the essential equipment for the operation of the plasma reactor and the plasma torch, including the three-phase power supply, the control and command room, the cooling system, the carbon filtration system and, if necessary, a PSA unit for the recovery of high purity hydrogen (Plenesys, 2022). Table 5-6 shows the technical specifications of the HyPlasma® demonstration unit (Plenesys, 2022).

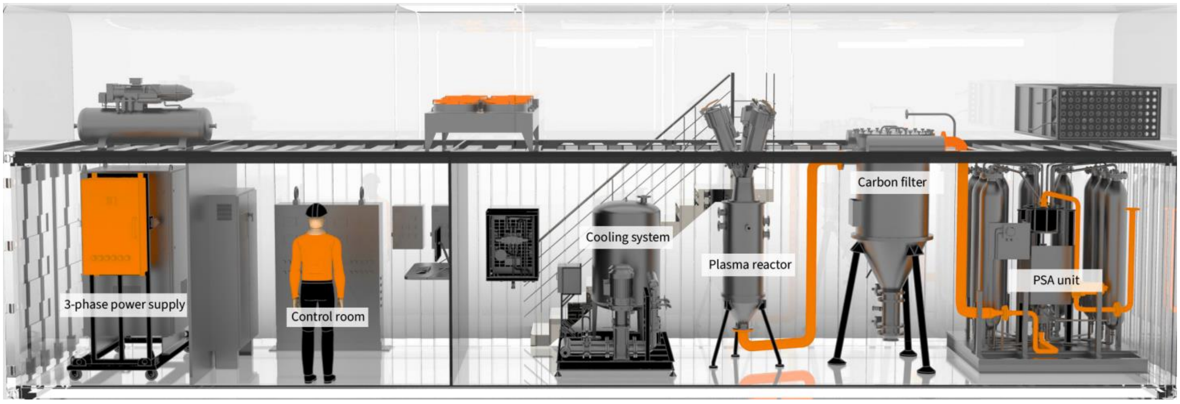


Figure 5-18. HyPlasma® containerized solution (Plenesys, 2022).

Table 5-6. Technical specifications of HyPlasma® demonstration unit under development (after Plenesys, 2022).

Hyplasma Technical Specification	
Hydrogen production capacity	7 kg/h (50 000 kg/year)
Operating time	7,200 h/year
Operating pressure	Near atmospheric pressure
Plasma torch nominal power	100 kW
Power supply	150-250 kVA
Operating range	30 to 100%
Feedstock	Natural gas
Methane flow rate	29 kg/h
Carbon powder flow rate	≈ 19 kg/h
Carbon powder description	Fluffy, nanometric to micrometric, pyrolytic powder
Main consumable	Graphite electrodes
Utilities	Nitrogen for inerting

In March 2022, Pure Hydrogen, an Australian East Coast clean energy company, signed a binding collaboration and license agreement with Plensys to collaborate on the commercialization of HyPlasma process. The collaboration will begin with a pilot plant in Brisbane to be built within 12 months from signing the agreement. Under the terms of the agreement, Pure Hydrogen will have exclusive rights to commercialize the HyPlasma process in Australia, most of South East Asia and Sub-Saharan Africa for an initial period of ten years, with the option to extend the period of exclusivity and add new regions. Pure Hydrogen will build modules, based on the Plenesys supply of the AC plasma system, and pay Plenesys a royalty for each manufactured HyPlasma module. Commercial operation is planned with capacities ranging from 1,500 kg/day to 5,000 kg H_2/day, depending on the market demand (Pure Hydrogen, 2022).

5.3.5. HiiROC's technology

HiiROC is a small start-up company founded in 2019 and based in Hull, UK. In collaboration with the University of Hull, HiiROC is developing a proprietary thermal plasma torch technology to produce hydrogen from biomethane, flare gas or natural gas (Carbon Copy, 2021; HiiROC, 2021). Further details on the technological specifics are not available to the public.

The units are flexible, scalable, mobile and can be installed at the point of need, thereby using existing infrastructure and avoiding storage and transportation costs. Multiple units (the smallest unit is $6m^2/6m^3$) can be combined to enable both local and industrial production (Carbon Copy, 2021; HiiROC, 2021).

HiiROC collaborates with large multinational companies. In November 2021, the company announced the closing of a major funding round to expand the deployment of pilot units to additional customer segments, positioning the technology for future commercialization. New investors include Melrose Industries, HydrogenOne, Centrica, Hyundai and Kia, who joined existing strategic investors Wintershall Dea and VNG (HiiROC, 2021).

Wintershall Dea and VNG announced the construction of a 400 kg/day hydrogen pilot facility in Germany using HiiROC's thermal methane pyrolysis process. The facility is expected to be operational in 2023 (Wintershall Dea, 2021). At the moment, HiiROC is intentionally not disclosing too much information to the public domain as the company is at the critical point in their strategic development (HiiROC, pers. comm. 12th October).

5.3.6. SPARK Cleantech's technology

SPARK Cleantech is the most recent deep-tech start-up to develop methane pyrolysis. The company was founded in early 2022 and is based in Gif-sur-Yvette, France (Le Figaro, 2022). Spark Cleantech's patent-pending technology uses cold, pulsed plasma discharges to convert CH_4 (in pyrolysis mode) or CO_2 and CH_4 mixtures (in biogas mode) into value added products, hydrogen and solid carbon or hydrogen and CO (Figure 5-19) (Spark Cleantech, n.d.). Cold plasma is generated by electrical pulses of very short duration, high voltage, and very high frequency. The energy is delivered in about 10 nanoseconds, at a frequency of 10 to 100 kHz (Louis, 2022).

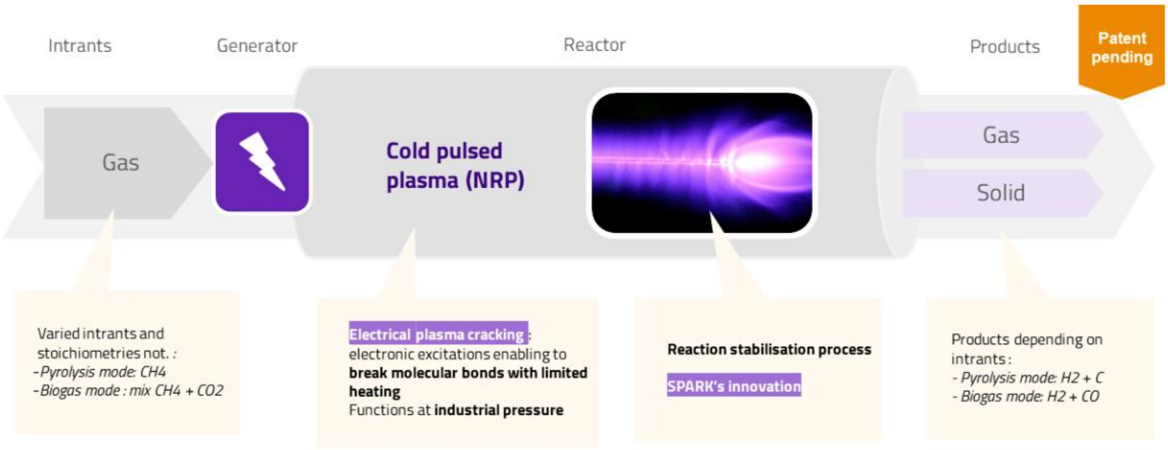


Figure 5-19. Spark Cleantech's technology (Spark Cleantech, n.d.).

The SPARK project was originally developed as a result of the doctorate of Erwan Pannier who studied at the EM2C laboratory of CentraleSupélec's at the Université Paris-Saclay. In 2019, Erwan Pannier partook in the course at Université Paris-Saclay that trains PhD students in deep tech specific entrepreneurship, i.e., projects that come directly from laboratories. When his project was complete, he approached the SATT Paris-Saclay, which granted funding within the framework of theirs “Young doctor” pre-maturation project. He then performed a technical proof of concept of his project and submitted a patent for the means for the means to stabilized the nanosecond pulsed plasma discharges in order to enable industrial application.

At the beginning of 2020, he won the innovation competition “i-PhD de Bpifrance”, aimed at young professionals who want to set up a deep tech start-up. The project has received funding as a result of SATT Paris-Saclay’s call for maturation projects, which allowed hiring of engineers experienced in the design of reactors and plasma generators, thereby accelerating the development of the idea (Université Paris-Saclay, 2021). The objective of maturation project funded by SATT Paris-Saclay was to design and techno-economically validate the plasma reactor used as a basic module for industrial installations (SAAT Paris-Saclay, n.d.).

The concept has been tested on a unit capable of producing 1 Nm^3 H_2/h. This prototype is their basic unit, which will then be mounted in parallel, as a modular concept is developed. The company plans to install a first industrial site demonstrator of about 30 kW in 2023. Their objective is to commercialize the process by 2025 (Louis, 2022). Spark Cleantech targets industrial hydrogen consumers, whose demand is less than 1,000 Nm^3 H_2/h (less than 2,000 kg H_2/day) and who want to reduce their costs by producing it on site (Louis, 2022).

5.3.7. Levidian's technology

Levidian Nanosystems Limited (also referred to as just Levidian), a Cambridge, UK based company founded in 2012, has developed a LOOP system which uses a patented low-temperature, low-pressure process to decompose methane into hydrogen and carbon in the form of graphene (Hopkins, 2022; Levidian, n.d.). The company primarily produces graphene and has recently been tapping into the growing demand for hydrogen, a by-product of the process (Levidian, 2022c). Levidian has its roots in the world-leading nanomaterials development labs at Cambridge University, which focuses primarily on graphene (Levidian, 2022b). Their Technology Centre in Cambridge also provides R&D consultancy to companies on the development of graphene-enhanced products (Levidian, n.d.).

The LOOP process uses a non-thermal microwave plasma, in which focused microwaves directly ionize methane to create a plasma. Electrons in the gas are excited by high-frequency electromagnetic microwaves, causing collisions with other molecules, which break apart and generates more free electrons and positive ion radicals. As long as microwave energy is supplied, a sustained plasma state is ensured. Exited electrons and ions exit the plasma region, cool and form stable compounds, hydrogen and graphene (Hopkins, 2022; Levidian, 2022a). When processed by LOOP, natural gas is replaced by a hydrogen-methane mixture (Levidian, 2022b). With an additional hydrogen separator, LOOP can provide hydrogen for a variety of applications directly at the point of use (Hopkins, 2022).

Levidian developed LOOP50, a contained solution shown in Figure 5-20, which produces 10 tonnes of graphite per year. Utilizing waste gas, LOOP50 removes 50 tonnes of CO_2eq emissions per year, hence the name (Levidian, 2022a). LOOP system can be installed in standard shipping containers or in fixed infrastructure as single units or larger arrays. Levidian is now expanding this technology to deploy LOOP1000+, which will remove more than 1,000 tonnes of CO2eq emissions per year (Hopkins, 2022).

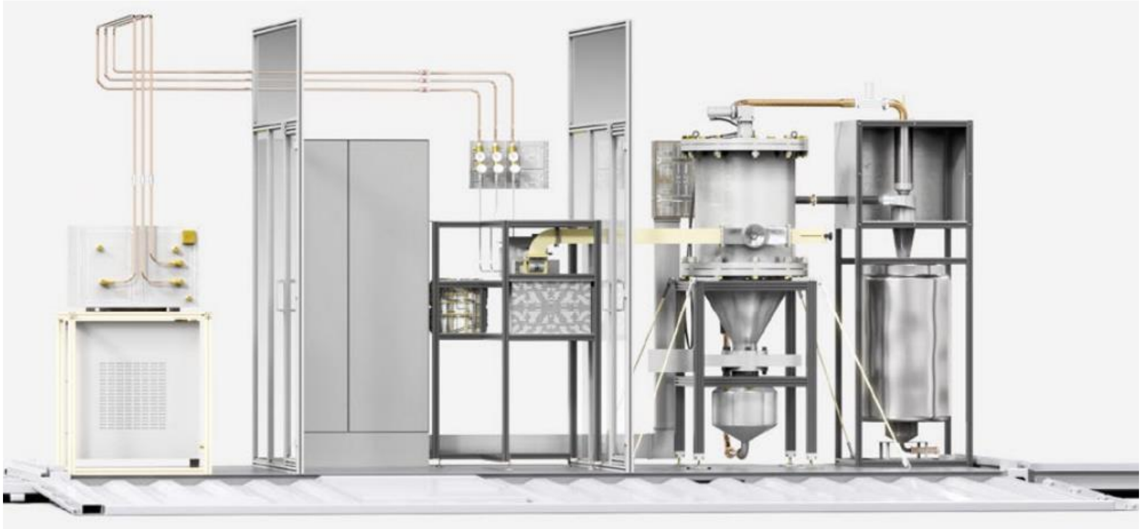


Figure 5-20. The Levidian LOOP solution (Hopkins, 2022).

In January 2022, it was announced that the UK's National Grid will test the Levidian LOOP process as part of a project to explore how graphene can be used to reinforce parts of their grid by using it as a hydrogen and corrosion-resistant coating. This could support the injection of hydrogen into the gas pipeline network (Levidian, 2022b). The trial, scheduled to begin in the first half of 2022, is expected to process 1.5 m^3 of natural gas per hour, producing 7 kg of hydrogen per day, with hydrogen making up 70% of the exhaust gas (Levidian, 2022c).

In May, 2022, Levidian announced its first customer agreement with Zero Carbon Ventures to deploy over 500 LOOP50s in the United Arab Emirates over the next ten years. LOOPs are primarily used to decarbonize waste gases at landfills and gas flaring sites rather than for industrial processes (Levidian, 2022d).

In July, 2022, Levidian and Adamant Composites Limited signed a joint development agreement to collaborate on enhancing composite materials using Levidian’s graphene (Levidian, 2022e).

5.3.8. Sakowin Green Energy's technology

Sakowin Green Energy, a start-up founded in 2017 and based in the France province of Aix-en, is developing a process that uses microwave plasma to decompose methane into hydrogen and solid carbon. Sakowin has filed three patents related to production, distribution and scaling of technology. Both natural gas and biomethane can be used as feedstock for the process (Sakowin, 2021a).

The compact, modular and stackable solution can deliver a range of energy capacities, from a few kg to several tonnes per day, and enables on-site and on-demand production of hydrogen. Figure 5-21 illustrates Sakowin's prototype unit, a 100 kW South Beach Module. The technology uses five times less energy than an electrolyzer to produce hydrogen (Sakowin, 2021b; Gatt, 2022).

Figure 5-21. Sakowin South Beach Module 100 kW (Gatt, 2022).

Sakowin is now working to improve performance and reduce production costs with the goal of commercialization in 2025 (Niedercorn, 2021).

6. SOLID CARBON PRODUCTS

Depending on the process, methane pyrolysis can yield different allotropes of solid carbon products, including carbon black, carbon nanotubes, carbon nanofibers, graphite, graphene, etc. The purpose of this chapter is to describe the most common uses for the above carbon products and potential future uses. The focus of this chapter is to explore the carbon black product, as it is the oldest and most mature market for carbon. Other carbon allotropes, such as graphite, graphene, carbon nanotubes and carbon fibers, are briefly described.

6.1. Carbon Black

Carbon black is virtually pure elemental carbon, usually 97% or more by weight, in the form of colloidal particles. It is essential ingredient in numerous everyday products, making them stronger, more colorful, and more durable. In appearance, it is a black, finely divided pellet or powder. Carbon black is produced by partial burning or pyrolysis of gaseous or liquid hydrocarbons at high temperatures under controlled process conditions. Table 6-1 shows the typical carbon black composition that applies to all carbon black grades, regardless of the production method. In terms of annual tonnage, carbon black is in the top 50 industrial chemicals produced worldwide (International Carbon Black Association [ICBA], 2016).

Different production processes produce carbon blacks with different properties, varying in particle size, structure, surface chemistry, porosity, etc. The properties of most carbon black grades are specified by industry-wide standards issued by the International Organization for Standardization (ISO), the American Society for Testing and Materials (ASTM) and German Institute for Standardization (DIN). These standards are used not only to characterize carbon black grades, but also as a quality assurance tool for the production process (Orion Engineered Carbons, 2021). Depending on the production process, carbon black is also referred to as acetylene black, channel black, furnace black, gas black, lampblack and thermal black. General information and physical properties of carbon black are summarized in Table 6-2.

Table 6-1. Typical carbon black composition (after Orion Engineered Carbons, 2015).

Element	Content (% of wt.)
Carbon	96-99.5
Hydrogen	0.2-1.3
Oxygen	0.2-0.5
Nitrogen	0-0.7
Sulfur	0.1-1.0
Residual Ash	<1

Table 6-2. Carbon black: general information and physical properties. (after Wypych, 2014; ICBA, 2016).

GENERAL INFORMATION	
Name	Carbon Black
Synonyms	Acetylene Black, Channel Black, Furnace Black, Gas Black, Lampblack, Thermal Black
Acronym	CB
CAS Name	Carbon Black
CAS Registry Number	1333-86-4
EC number:	231-153-3
Empirical formula	C
Molecular mass	12.01 g/mol
PHYSICAL PROPERTIES	
State	Solid: powder or pellet
Odor	None
Color	Black
Solubility	Water: insoluble Solvents: insoluble
Density	1.7-1.9 g/cm^3

It is important to note that carbon black is not black carbon or soot. Soot and black carbon are undesirable carbonaceous by-products that result from the incomplete combustion of carbon-containing fuels, e.g. waste oil, gasoline, diesel fuel, coal, paper, rubber, plastic, and waste material.

The term soot is used to describe carbon-rich particles produced by a number of different combustion processes, e.g. chimney soot or diesel exhaust soot. Term black carbon refers to carbonaceous particles in the air, which have been measured in many recent studies of airborne and indoor particulate matter. On the other hand, carbon black is intentionally produced for commercial use primarily in the rubber, paint, and printing industries. Most types of carbon black contain over 97% elemental carbon, while the total particulate matter of soot or black carbon typically contains less than 60% elemental carbon and up to 50% ash (ICBA, 2016; ICBA, n.d.).

Activated carbon and bone black are the two other commercial carbonaceous products that are often mistakenly used as synonyms for carbon black. Both have unique physical and chemical properties and are produced by a different process than commercial carbon black (ICBA, n.d.).

6.1.1. Carbon black properties

Standard Terminology Relating to Carbon Black, ASTM D3053-13a, includes the following definition for carbon black morphology: "*Carbon black, n — an engineered material, primarily composed of elemental carbon, obtained from the partial combustion or thermal decomposition of hydrocarbons, existing as aggregates of aciniform morphology which are composed of spheroidal primary particles which exhibit uniformity of primary particle sizes within a given aggregate*[1] *and turbo-stratic layering within the primary particles"* (ICBA, n.d.).

[1] The one exception to this general characteristic of manufactured carbon black is thermal black, in which primary particles may exist in isolation and the primary particle sizes within an aggregate are not necessarily uniform.

As shown in Figure 6-1, carbon black displays a hierarchy of morphological features (ICBA, 2016):

- particles (primary particles or spheroidal nodule): 10-300 nm,
- aggregates: 85-500 nm,

- agglomerates: 1-100+ µm.

Primary particles are the basic building blocks of carbon black, but they are practically never present in isolation but are strongly linked by covalent bonds to form aggregates [1]. Individual aggregates are then bonded together by Van der Waals forces into agglomerates. Agglomerates do not disintegrate into smaller components unless sufficient force is applied. Primary particle and aggregate sizes are distributional properties and differ depending on the carbon black grade (ICBA, 2016).

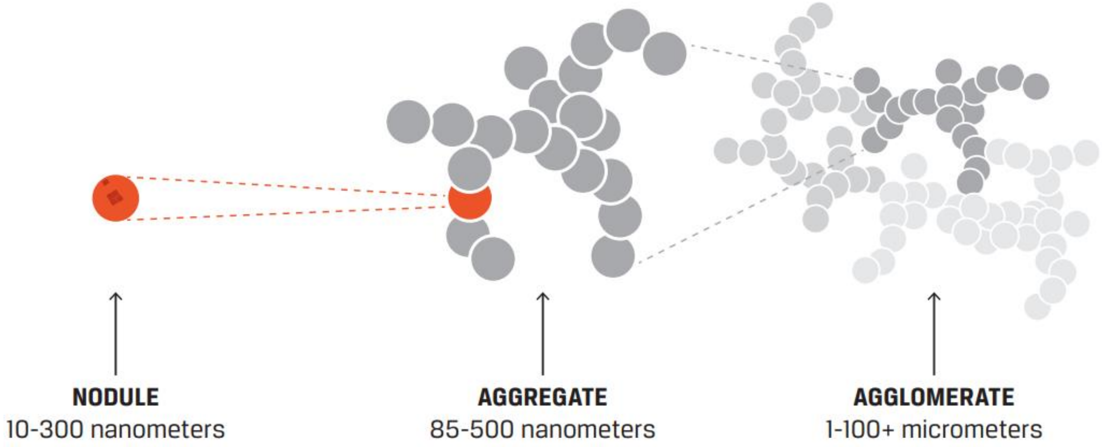


Figure 6-1. Sequence of carbon clack structure development (ICBA, 2016).

The fundamental properties of carbon black and the level of dispersion achieved determine carbon black’s application performance. The most important physical and chemical properties include (Penta Carbon, 2017; Birla Carbon, n.d.):

- particle size,
- structure or aggregate size,
- porosity,
- surface chemistry or surface activity.

6.1.1.1. *Particle size*

Particle size is the basic property that has an important effect on the rubber properties and on the color properties for specialty carbon blacks. Surface area measurement (m^2/g) provides an indirect characterization of carbon black particle size. It is used as an indicator of the fineness of the carbon black and thus of the particle size (Birla Carbon, n.d.).

For specialty carbon blacks, a smaller particle diameter results in a larger surface area, which is typically associated with greater jetness, higher conductivity, improved weatherability and higher viscosity. On the other hand, a higher dispersion energy is required. When used in rubber application, smaller particles result in higher reinforcement, increased abrasion resistance, and better tensile strength (BKT Carbon, 2021; Birla Carbon, n.d.).

6.1.1.2. *Structure or aggregate size*

Structure or aggregate size refers to the shape and degree of branching of the aggregates. Structure level has a direct impact on a number of important in-rubber properties. As the structure of carbon black increases, the modulus, hardness and electrical conductivity, increases, as does the viscosity of the compound (BKT Carbon, 2021). For specialty carbon blacks, highly structured carbon blacks result in higher viscosity, greater electrical conductivity and easier dispersion (Birla Carbon, n.d.).

6.1.1.3. *Porosity*

Porosity is a property that can be controlled during the production process. It can affect surface measurements and other tests. Conductive specialty carbon blacks tend to have a high degree of porosity. Porosity can affect certain applications and properties by increasing the effective loading of the carbon black. For instance, by increasing porosity a rubber manufacturer can increase carbon black loading while maintaining compound-specific gravity (Donnet, 1993; BKT Carbon, 2021; Birla Carbon, n.d.).

6.1.1.4. *Surface chemistry or surface activity*

Surface chemistry or surface activity generally refers to the oxygen-containing groups present on a carbon black’s surface. While properties, such as primary particle size, aggregate size, and porosity are determined in the reactor and can be changed only slightly later in the process, surface chemistry can be affected in the reactor, in the pneumatic handling system, during pelletizing and during drying (Donnet, 1996). For specialty carbon blacks, oxidized surfaces improve pigment wetting, dispersion, rheology, and overall performance. In other cases, oxidation increases electrical resistance and makes the carbon black more hydrophilic. Although surface chemistry is difficult to measure directly for rubber, it is evident through its effects on rubber properties, such as as abrasion resistance, tensile strength, hysteresis, and modulus (Birla Carbon, n.d.).

6.1.2. Commercial carbon black production processes

Depending on the absence or presence of oxygen, carbon black manufacturing processes fall into two main categories (Donnet, 1993):

1. incomplete combustion or thermal-oxidative decomposition,
2. thermal decomposition of hydrocarbons.

Incomplete combustion processes include lamp black, channel black (historic process), gas black and furnace black process. Thermal decomposition processes include acetylene black and thermal black process (Donnet, 1993). Table 6-3 shows the carbon black manufacturing processes and the type of feedstock used in each. Today, almost all carbon black is produced by the furnace black and thermal black process, with furnace black being by far the most prevalent (ICBA, 2016).

Table 6-3. Classification of carbon black production processes (after Donnet, 1993).

CARBON BLACK PRODUCTION PROCESSES		FEEDSTOCK
Incomplete Combustion (Thermal-Oxidative Decomposition)	Lamp black	Aromatic oils based on coal tar or crude oil
	Gas black Channel black (historic)	Coal tar distillates Natural gas
	Furnace black (most common)	Aromatic hydrocarbon oils
Thermal decomposition	Acetylene black	Acetylene
	Thermal black	Natural gas

Figure 6-2 shows a schematic representation of the individual process steps of a carbon black production plant. The heart of the process is the carbon black production unit, which may consist of reactor(s) or apparatus, depending on the process. The initial product exiting the carbon black production unit is a mixture of process gas and carbon black suspended in the form of an aerosol. This aerosol is first cooled and then passed to a filter where the solids are separated from the process gas. The carbon black obtained has a low bulk density and a tendency to dust. Since it cannot be handled in this form, it must be compressed in some way to facilitate further processing. It is either compacted into powder black or pelletized, and depending on the pelletizing process, dry- or wet-pelletized carbon black is obtained (Figure

6-3). The carbon black is then transported to the packaging and storage section. Powder black is always packed in bags, while pelletized black is shipped either in bags or in semibulk tankers or containers (Donnet, 1993).

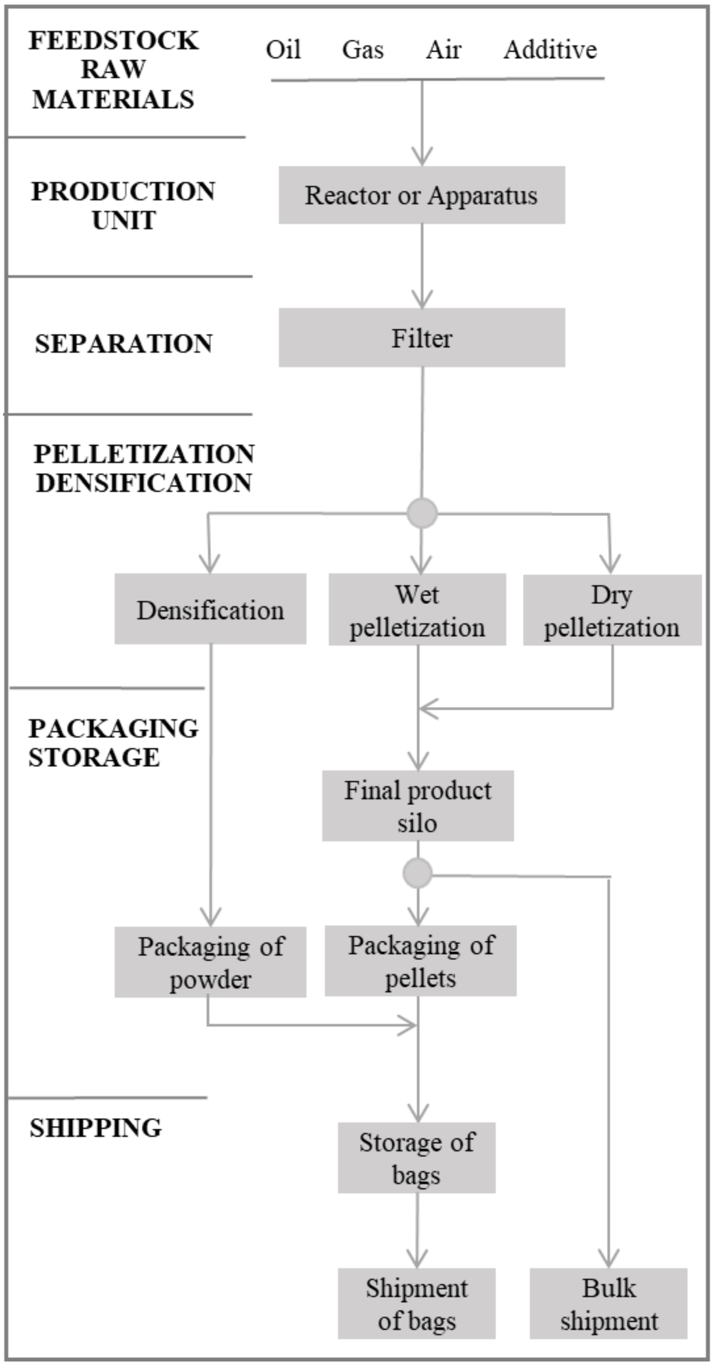


Figure 6-2. Schematic diagram of the individual process steps in carbon black manufacture (after Donnet, 1993).

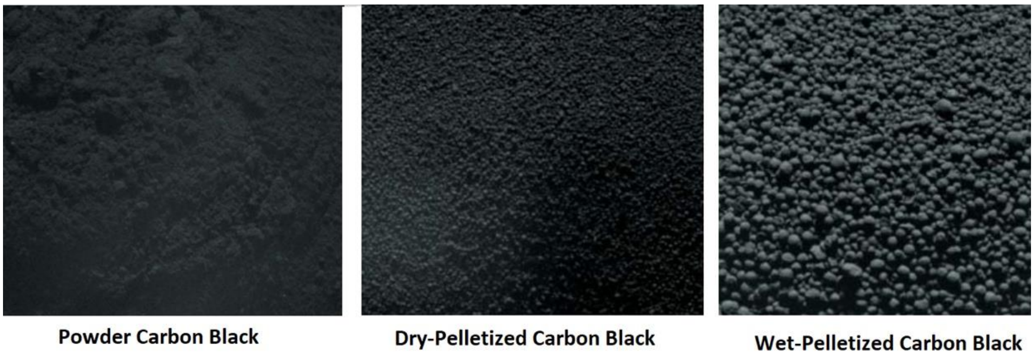


Figure 6-3. Carbon black forms obtained after densification or palletization (Orion Engineered Carbons, 2015).

6.1.2.1. *Furnace black process*

Furnace black is the most recent process for producing carbon black. It was developed in the early 1940s and revolutionized the carbon black industry by being more economical, flexible and cleaner than other commercial carbon black manufacturing processes at the time, i.e., channel black process (Hardman, 2017). Today, about 98% of the carbon black on the market is produced using the furnace black process.

The furnace black process is continuous and uses heavy aromatic hydrocarbon oils and natural gas as feedstock and heat source, respectively (Orion Engineered Carbons, 2015). Figure 6-4 shows the schematic furnace black reactor. The first section of the reactor consists of the combustion zone, where the fuel is burned in excess of process air. The following section is the mixing zone, where the carbon black feedstock is added and mixed as homogeneously as possible with the hot gases from the combustion chamber. In the third section, the reaction zone, the main portion of the feedstock is pyrolyzed under carefully controlled conditions (primarily temperature and pressure) and decomposed into carbon black and tail gas. There, a small portion of the feedstock also reacts with the residual oxygen from the combustion chamber. In the final section, the quench zone, carbon black and tail gas mixture is cooled by injection of water (Donnet, 1993). The mixture exits the reactor and is passed through a heat exchanger for further cooling, while simultaneously heating the required process air. After cooling, the carbon black is separated from the tail gas and densified or pelletized as previously described. Tail gas contains a variety of gases, such as carbon monoxide and hydrogen. Most furnace black plants use a portion of this residual gas to produce heat, steam, or electric power (ICBA, 2016).

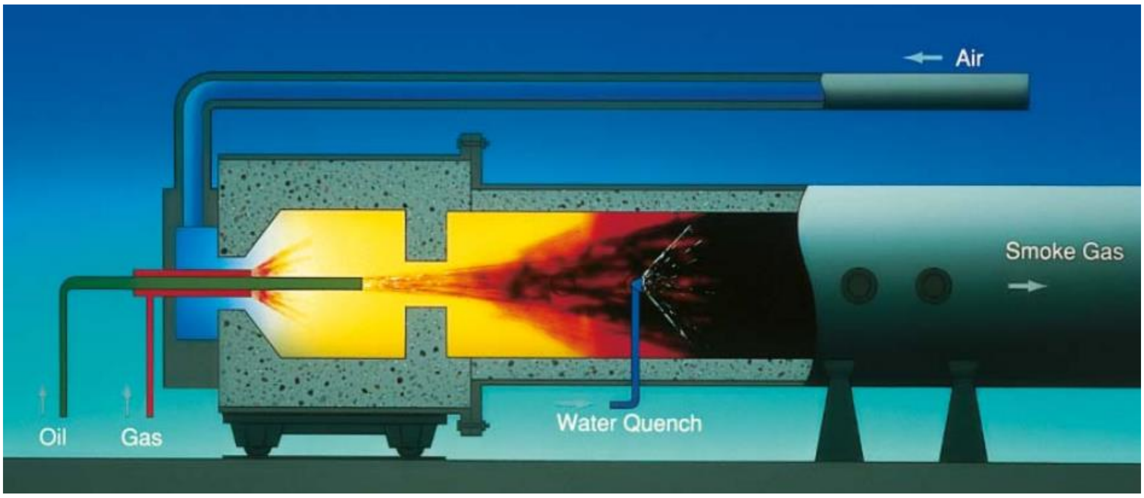


Figure 6-4. Schematic of a furnace black reactor (Orion Engineered Carbons, 2015).

The furnace black process can produce more different grades of carbon than any other method currently in use. The feedstock is precisely specified in terms of quality, type and quantity. This makes it possible to produce a wide range of carbon blacks for different applications without having to fundamentally change the process for each product variant. By choosing the right process parameters, the initial particle size or specified surface area can be easily controlled (Orion Engineered Carbons, 2015). The furnace black process produces carbon black with primary particle sizes of 10-80 nm or 8-100 nm, depending on the source (Orion Engineered Carbons, 2015; Birla Carbon, n.d.). The primary particle size is specified to determine the suitability of a product for a particular application.

6.1.2.2. *Lamp black process*

The lamp black process is the oldest commercial process for producing carbon black. However, today's lamp black production equipment has little in common with early lamp blacks first produced by the Chinese over 3,500 years ago. These early lamp blacks were not very pure and their chemical composition varied greatly compared to today's carbon blacks (Donnet, 1993; ICBA, 2016).

The lamp black process consists of a shallow cast-iron pan containing the liquid feedstock, an aromatic oil based primarily on coal tar. A fire-proof flue hood, refractory-lined with bricks, is placed above the pan, leaving an annular gap between the rim of the pan and the hood. Process air is fed into the system through this gap. The air gap between the pan and the hood, as well as the vacuum present in the system, help to control the air supply and, allowing fine-tuning of the final properties of carbon black. Even though the heat radiated by the hood causes the raw material to evaporate and partially combust, most of it is converted into carbon black (Figure 6-5). After the cooling phase, the obtained carbon black and gas mixture is conveyed through a filter to separate the carbon black. From this stage on, the process follows the steps described previously (Donnet, 1993; Orion Engineered Carbons, 2015).

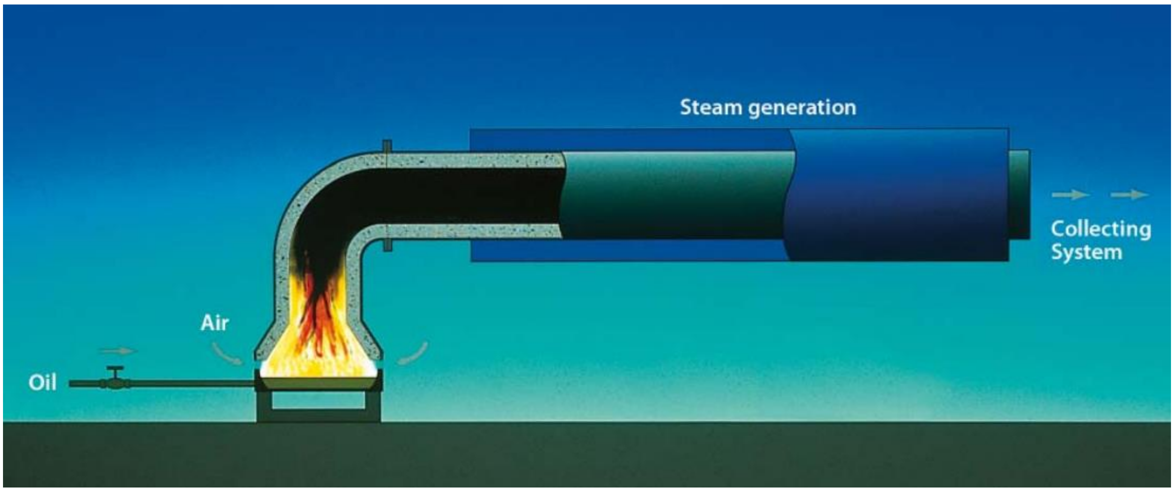


Figure 6-5. Schematic of lamp black production process (Orion Engineered Carbons, 2015).

The carbon blacks produced by the lamp black process are characterized by a broad primary particle size distribution ranging from about 60 to over 200 nm (Orion Engineered Carbons, 2015).

6.1.2.3. *Gas black and historic channel black process*

A common feature of the gas black and channel black processes is that they are both conducted in open systems in which a series of small diffusion flames burn in the air and the carbon black is deposited on water-cooled channels. Channel black process uses natural gas as a feedstock. Carbon black deposited on the underside of iron channels is scraped off into a funnel-shaped trough and collected in screw conveyors (Figure 6-6) (Donnet, 1993).

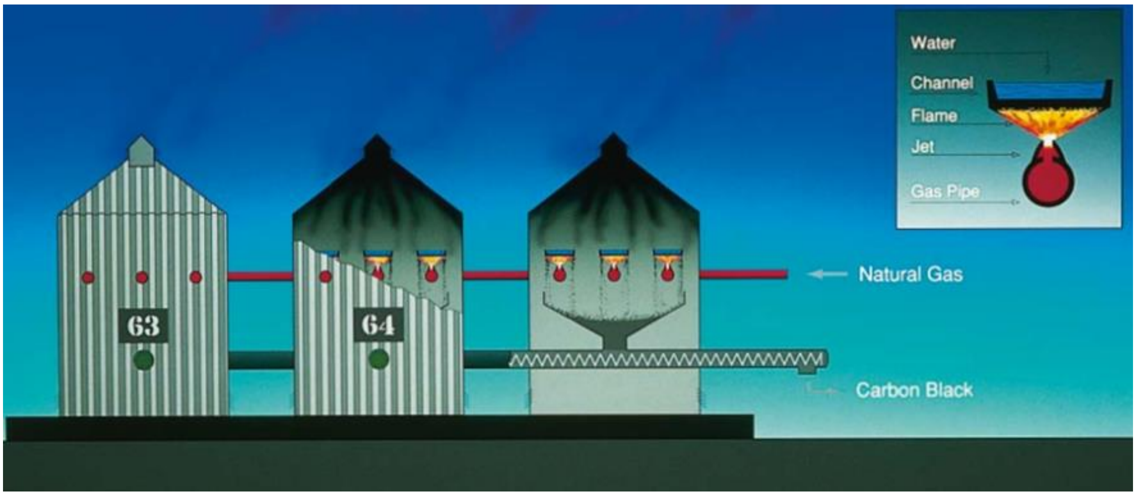


Figure 6-6. Schematic of channel black production process (Orion Engineered Carbons, 2015).

The channel black process was developed in the USA in 1872 and has historically played an important role (Donnet, 1993). Carbon black produced by the channel black process proved to have increased jetness, i.e., it was blacker. Therefore, until 1912, carbon black produced by the channel black process was used mainly as a pigment in plastics, paints, and other media. Then, in 1912, the reinforcing effect of carbon black in rubber was discovered, laying the foundation for carbon black to evolve from a small black pigment business into a global industrial specialty chemical business (Hardman, 2017).

Channel black was completely discontinued in the USA in the 1970s and replaced by the furnace black process. The main reasons were the limited yield of the feedstock (3-6%) and the environmental hazard due to emission of carbon black particles. The channel black process released a considerable amount of carbon black particles into the atmosphere, because not all of the carbon black was deposited on the iron channels and no filters were used at the time (Donnet, 1993; Orion Engineered Carbons, 2015).

In 1935, the European company Degussa developed the gas black process. It is closely related to the channel black process, but coal tar distillates are used as a feedstock instead of natural gas. Figure 6-7 illustrates the gas black production process. Coal tar distillates are heated in a vaporizer and the resulting vapors are carried by a hydrogen-rich gas into a gas tube equipped with burners. The flames from burners impinge on the surface of water-cooled rollers. Most of the formed carbon black is deposited on these rollers, while the rest is conveyed to the filtration system. In the next step, these two carbon black streams are combined. In contrast to the channel black process, the gas black process is much more environmentally friendly, as the equipment is regularly vacuum-cleaned and the carbon black is collected in sealed filter systems (Donnet, 1993; Orion Engineered Carbons, 2015).

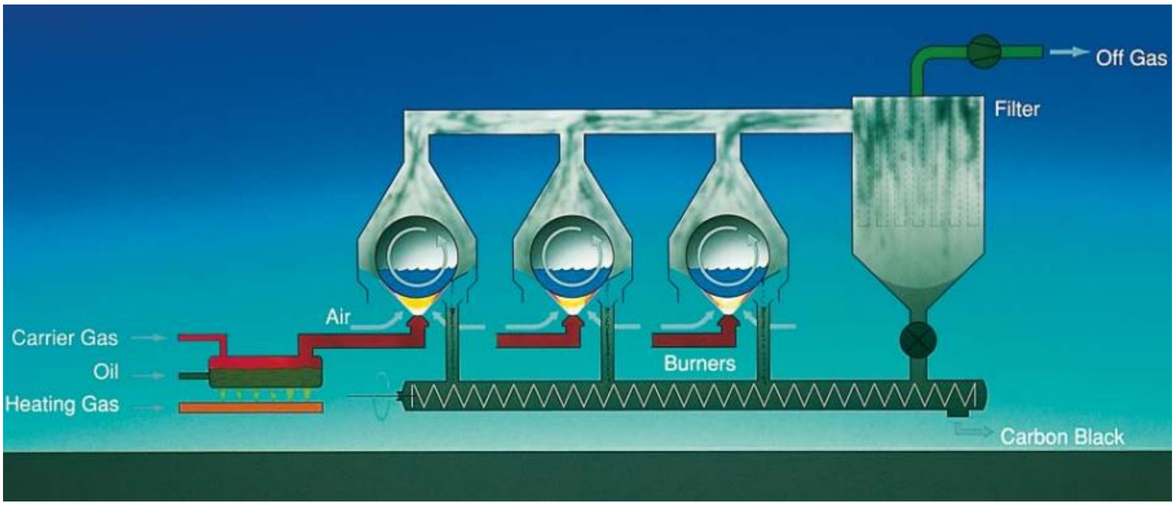


Figure 6-7. Schematic of gas black production process (Orion Engineered Carbons, 2015).

In the gas black process, fine primary particles with a size of 10 to 30 nm are produced. Gas blacks are characterized by their loose structure and exceptional dispersibility. Over the years, gas blacks have lost their importance for reinforcement applications and are now used almost exclusively for pigment applications (Donnet, 1993; Orion Engineered Carbons, 2015).

6.1.2.4. *Thermal black process*

The thermal black process is based on the thermal decomposition of natural gas in the absence of oxygen. It is a non-continuous or cyclic process that consists of a pair of vertical refractory-lined furnaces that alternate between preheating and carbon black production every five to eight minutes (Figure 6-8). During the heating cycle, the fuel is burned with air until the temperature inside a furnace reaches a predetermined temperature level. Then the air supply is stopped and the decomposition cycle begins: natural gas is fed into the hot furnace and, and in the absence of oxygen, the heat from the refractory material decomposes the natural gas into carbon black and hydrogen. The aerosol stream is quenched with water sprays and filtered in a bag house. The carbon black is further processes as previously described. The produced hydrogen tail gas is burned to preheat the second furnace. The residual heat can be utilized to generate electric power (Donnet, 1993; ICBA, 2016).

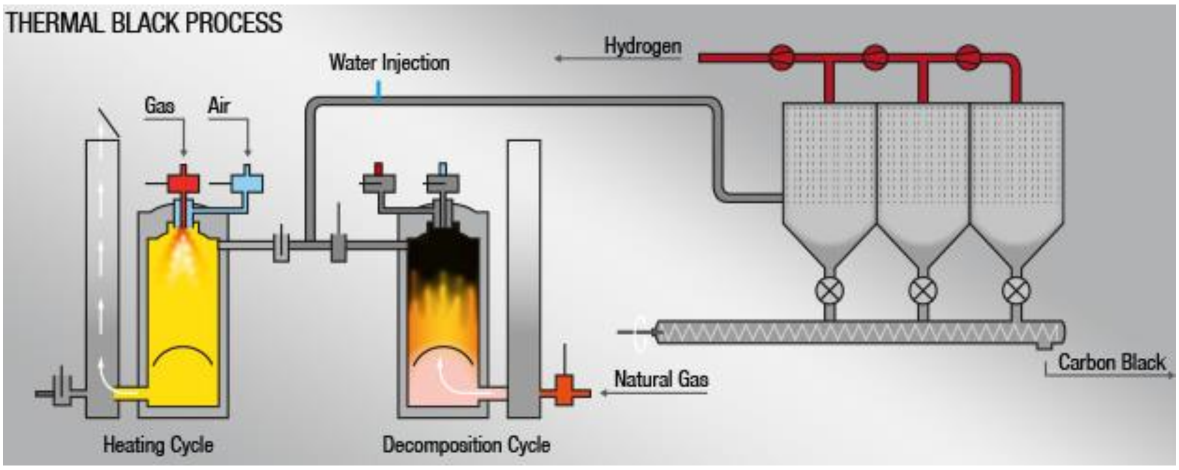


Figure 6-8. Schematic of thermal black production process (Penta Carbon, 2017).

Carbon black from the thermal black process forms relatively slowly, resulting in coarse primary particles with a size of 300 to 500 nm, referred to as medium thermal. In the past, dilution of natural gas with inert gases also produced a different thermal grade called fine thermal black. This resulted in carbon black with primary particle sizes between 150 and 200 nm.

A primary particles size of up to 500 nm gives carbon black unique compounding properties, that enable it to achieve high filler contents in rubber and plastics. As a result, the use of thermal blacks today is limited to specialty applications (Donnet, 1993).

6.1.2.5. *Acetylene black process*

In the acetylene black process, carbon black and hydrogen are produced by the exothermic decomposition of acetylene in the absence of oxygen. Once the reactor is heated by burning acetylene, the air supply is cut off, allowing carbon black to develop (Figure 6-9). Heat exchangers are used to cool a mixture of carbon black and hydrogen to ambient temperature. After separating carbon black from hydrogen, carbon black is pneumatically conveyed to a multi-stage densification process (Orion Engineered Carbons, 2019a).

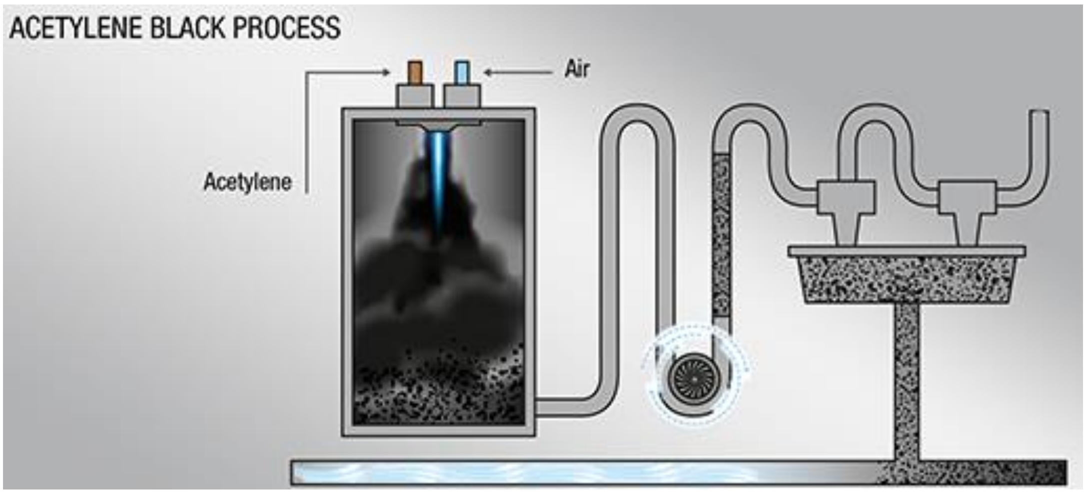


Figure 6-9. Schematic of acetylene black production process (Penta Carbon, 2017).

Carbon black produced by the acetylene black process is different from other carbon black grades. Acetylene blacks are characterized by a high structure, which is why they are available only in powder form, as since they are difficult to compact and pelletized. They have very high thermal and electrical conductivity and are therefore mainly used as conductive blacks in electrical cells, antistatic rubber and plastic applications and cable manufacturing (Penta Carbon, 2017). They are also very hydrophobic and therefore have very low moisture absorption (Orion Engineered Carbons, 2019a).

6.1.3. Applications of Carbon Black

Carbon black is one of the oldest manufactured products, its use as a pigment for the production of India inks and mural paints dates back to the ancient Chinese and Egyptians (Donnet, 1993). Since the invention of book printing in the fifteenth century, the demand for strong black pigment has gradually increased (Orion Engineered Carbons, 2019b). The most important event that had the greatest impact on the use of carbon black was the discovery of the reinforcing effect of carbon black when added to natural rubber (Donnet, 1993). Today, carbon black is used in various materials to enhance their physical, electrical and optical properties (Orion Engineered Carbons, 2015).

About 90% of carbon black produced globally is used in rubber applications, 9% is used as a pigment and the remaining 1% as an essential ingredient in numerous different applications. Of the 90% carbon black used in rubber, 70% is used by the tire industry as a reinforcing phase and pigment and 20% in other rubber industrial products, such as tubes and hoses, conveyor belts, gaskets, wiper blades, rubber flooring, seals, etc. (Figure 6-10) (Donnet, 1993; Ataman Chemicals, 2020; Kouzegaran 2020; ICBA, n.d.).

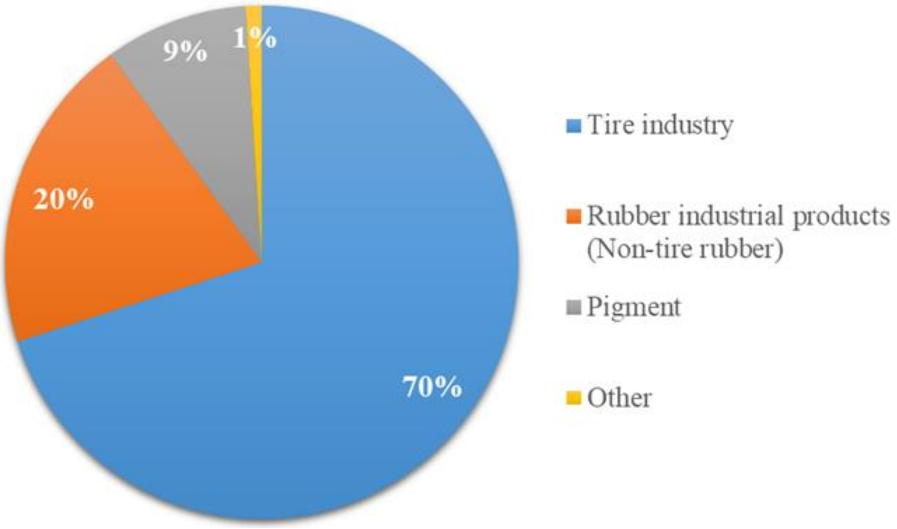


Figure 6-10. Carbon black end-use markets (after Ataman Chemicals, 2020; ICBA, n.d.).

Carbon black is by far the most important filler and reinforcing agent used in rubber compounding. It is crucial for strengthening compounds and for improving the physical properties of compounds, e.g. ultimate tensile strength, abrasion resistance, wear, and tear resistance (Dick and Rader, 2014). In tire application, besides reinforcement, the resistance of carbon black to ultraviolet (UV) radiation and its role as an ozone scavenger stabilizes the tire rubber against UV light and oxidation and prevents the rubber tire from cracking or breaking. The addition of carbon black prevents the tire from becoming electrostatically charged and helps to dissipate heat from certain hot spots on the tire, especially around the tread and bel. This reduces thermal damage and extends the life of the tire (Orion Engineered Carbons, 2019b). Table 6-4 and Figure 6-11. Examples of carbon black applicationexplain the main applications of carbon black in more detail.

Table 6-4. Applications of carbon black (after Dick and Rader, 2014; ICBA, 2021).

Application	Remarks
Tires	Carbon black is used to improve the physical properties of compounds, such as ultimate tensile strength, abrasion, wear, tear resistance and overall tire performance (especially safety), thereby increasing tire life and fuel economy.
Rubber Goods	Tubes, hoses, belts, gaskets, footwear – carbon black is used to improve mechanical properties, anti-vibration and conductivity of rubber goods.
Plastics	Carbon black imparts color, UV protection and conductivity to plastics (power cable shielding or electrostatic dissipation).
Food Contact Grades	Certain grades of carbon black meet stringent purity requirements for many regulated industrial or consumer plastic applications.
Batteries	Carbon black improves the electrochemical conductivity and charging properties of lead-acid batteries, advanced stop-start, batteries and hybrid batteries, and thus the overall battery efficiency.
High Performance Coatings	Carbon black provides jetness for coatings, protects against degradation due to UV radiation and imparts conductivity for coatings.
Pipe	Carbon black serves to protect pipes from mechanical degradation caused by harmful UV radiation.
Agricultural Irrigation, Mulch Films and Greenhouse Coverings	Carbon black enables more efficient and better farming through water management for irrigation, retention and UV protection.
Automotive Skin Contact	Low PAH carbon black provides excellent UV protection for automotive interior parts that come into contact with skin (steering wheel, gear shift, armrests, etc.).
Wire and Cable	Carbon black extends cable life and efficiency by creating exceptionally smooth and conductive insulation, conductor shielding and UV resistance.
Toner and Printing Inks	Carbon black provides pigmentation that enhances color and undertone in various ink applications.

Figure 6-11. Examples of carbon black application (after Continental Carbon, 2014; ICBA, 2016; Orion Engineered Carbons, 2019c; Kouzegaran, 2020; ICBA, 2021; Mesrobian, 2022; Tek Toner, n.d.).

6.1.4. Carbon black market

Some of the major carbon black producers include Birla Carbon, Cabot Corporation, Orion Engineered Carbons, Tokai Carbon Co. Ltd., China Synthetic Rubber (CSR), OMSK Carbon Group, Philips Carbon Black Limited, Continental Carbon Co., Mitsubishi Chemical Corporation, Asahi Carbon Co. Ltd., Bridgestone Corporation, Sid Richardson Carbon & Energy Co., OCI Company Ltd., etc. (Dick and Rader, 2014; Dagle et al., 2017; Penta Carbon, 2017; ChemAnalyst, 2021; Global Market Insights, 2022).

In 2020, the demand for carbon black amounted to 16.42 million tonnes. The key factor driving the market is the growth of the rubber and automotive industries. Demand for carbon black is expected to continue to grow, reaching approximately 18 million tonnes by 2025 or 27.21 million tonnes by 2030, depending on the source (ChemAnalyst, 2021; Grönqvis, 2021). Today, the global carbon black market is estimated at around USD 18.5 billion, while the projected value for 2030 is around USD 24 billion (Grönqvis, 2021).

6.2. Graphite

Graphite, by nature a very soft material, occurs both in its mineral form and synthetically produced. Graphite is the precursor to graphene. It has a layered, sheet-like structure; the individual layers are called graphene. The individual layers of graphene in graphite are held together by van der Waals forces, which can be overcome when graphene is exfoliated from graphite. Purified natural graphite has a higher crystalline structure and provides better electrical and thermal conductivity than synthetic material (De La Fuente, 2014; Dagle et al., 2017; Gouvernment of Canada, 2022). Due to its unique properties, graphite has numerous potential applications in almost all industries (Focus Graphite, 2021):

- excellent conductor of heat and electricity,
- maintains its stability to temperatures over 3,600 °C,
- one of the lightest of all reinforcing agents,
- natural lubricant,
- chemically inactive, with high corrosion resistance.

6.2.1. Applications of Graphite

Due to its unique thermal and structural properties, graphite is used in numerous commercial and industrial applications. Table 6-5 lists some of the most common applications of graphite, such as in the electronics, electrode, metallurgical, refractory, chemical, mechanical (including medical and aerospace) and nuclear applications (Mukhopadhyay and Gupta, 2012). Nowadays, the demand for graphite is mostly driven by the production of batteries for electric vehicles (EVs). Along with lithium, cobalt, nickel, and manganese, it is one of five materials required for the production of electric vehicles batteries, and it is the primary material for the anode, the current-absorbing part of the battery. Today, graphite is considered an important and strategic element in the developing green technology industry, which includes developments in energy storage, electric cars, and electronics (Focus Graphite, 2021).

Table 6-5. Applications of graphite (after Mukhopadhyay and Gupta, 2012; Focus Graphite, 2021).

Application	Remarks
Electronics	New application, for lithium-ion batteries.
Electrode	Synthetic graphite is used as electrodes in the electric arc furnace.
Metallurgy	Metallurgical applications are those in which graphite comes into direct contact with the molten metal being processed.
Refractory applications	The use of graphite as a refractory material dates back to the 1850s, and since then graphite refractories have been widely used in the steel and aluminum industries.
Chemical Applications	Graphite is used as construction material in the chemical process industry. Due to its chemical inertness, it can come into contact with corrosive acids, bases, and organic and inorganic substances without decomposing.
Mechanical Applications	For mechanical application, the most important properties of graphite are its strength, low friction, lubricity, and compatibility with other materials. Typical applications in this field include all types of seals for jet engines, high-temperature bearings and bushings, packing glands, pistons and piston rings, flat sliding bearings for machine bearings, turbine and rotor blades, and a variety of seals that are particularly useful at high temperatures.
Aerospace industry	In the aerospace industry, graphite is commonly used to make nose cones, rocket nozzles, leading edges on wings and turbines, and insulating components are commonly fabricated from graphite.
Medical field	In the medicine, graphite is successfully used in the manufacture of prosthetics and artificial heart valves.
Nuclear Applications	Nuclear-grade graphite is used extensively as moderator and a reflector in nuclear reactors, mainly because of its excellent thermal stability, strength at high temperatures and extremely high purity.

6.2.2. Graphite market

In 2020, global graphite consumption amounted to around 2.7 million tonnes. Synthetic and natural graphite accounted for 62% and 38% of global graphite use, respectively. Figure 6-12 shows the main global uses of natural and synthetic graphite. Natural graphite is used for refractory materials (16%), batteries (8%), foundries (5%), and other purposes (9%). Synthetic graphite is used for electrodes (32%), carburizing (10%), graphite shapes (4%), lubricants (4%), and other uses (12%) (Government of Canada, 2022).

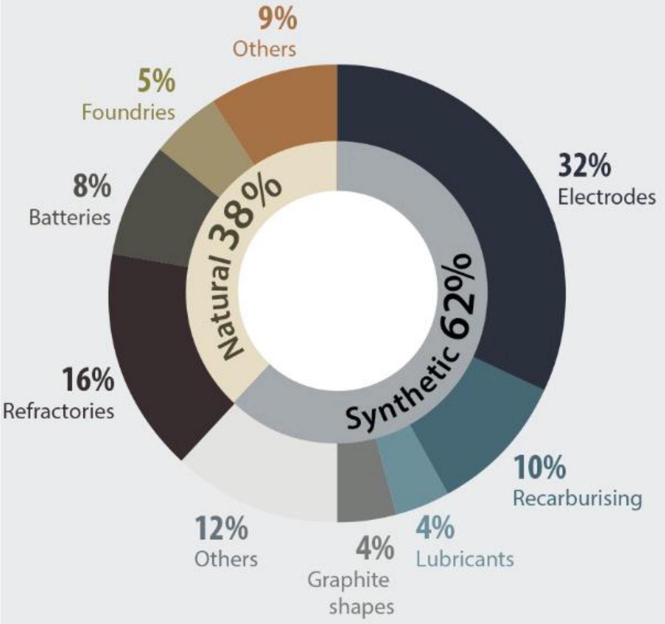


Figure 6-12. Global graphite use in 2020 (Government of Canada, 2022).

Global graphite production and demand is forecast to increase in the upcoming years, mostly due to the use of graphite in the batteries of electric vehicles. To meet the demand for electric vehicles and energy storage batteries, an additional 3.1 million tonnes of synthetic graphite is expected to be required by 2035 (Mauthner and Malkamäki, 2022). The current market size is estimated at around USD 16.13 billion. In 2030, the global graphite market is expected to reach a value of USD 31.55 billion (Grönqvis, 2021).

6.3. Graphene

Graphene is a one atom thick layer of carbon (or at most a few layers thick), tightly bound in a hexagonal honeycomb pattern (Figure 6-13) (Dagle et al., 2017; Levidian, 2021). Although the existence of single-layer graphene had been known for a long time, it was first unambiguously produced and identified in 2004 by Andre Geim and Konstantin Novoselov, for which they received the Nobel Prize in Physics. Graphene appears to be one of the most promising materials for developing new technologies in various industries (Mukhopadhyay and Gupta, 2012; PCC Group, 2022). With a thickness of one atom, graphene is the thinnest compound ever discovered. It is also one of the lightest known materials, a sheet of graphene one square meter weights 0.77 milligrams (0.001% the weight of a sheet of paper of equivalent size). It is the strongest compound discovered (40 times stronger than diamond and 100-300 times stronger than steel). In addition, graphene exhibits exceptional thermal and electrical conductivity. Other notable properties include corrosion resistance, water repellency and the ability to absorb 2.3% white light (De La Fuente, 2014; Levidian, 2021).

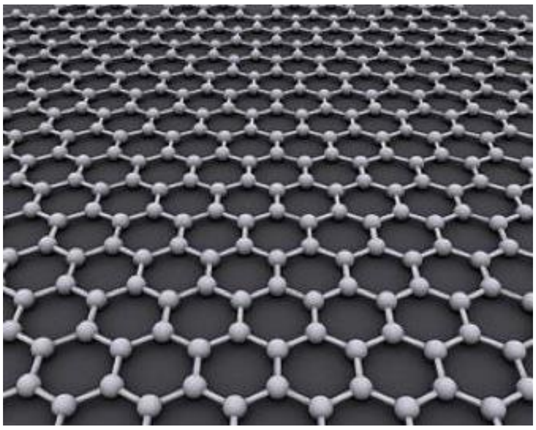


Figure 6-13. The structure of graphene (De La Fuente, 2014).

6.3.1. Applications of graphene

Since its discovery in 2004, the use of graphene has skyrocketed in different scientific fields. Major advances have been made in high-frequency electronics, biological, chemical and magnetic sensors, ultra-wide bandwidth photodetectors and energy storage and generation (De La Fuente, 2014). Similar to carbon black, one of the potential uses of graphite is to add it to tires to make them last longer (Levidian, 2022f).

Another potential application where large amounts of graphene could be used is in concrete. It is estimated that concrete is responsible for about 8% of global CO_2 emissions, making it one of the most polluting materials in the world. By incorporating graphene into concrete it can become 1.5 times stronger and reduce its carbon footprint by half (Levidian, 2022f).

Coordinated efforts are needed to steer graphene research toward commercial applications such as the EU’s billion-euro Graphene Flagship project funded by the European Commission in 2013 (De La Fuente, 2014). The Flagship researchers created a roadmap for graphene applications, shown in Figure 6-14, which identifies the most promising application areas for graphene: composites, energy, datacom, electronics, sensors and imaging, and biomedical technologies (Graphene Flagship, 2020).

Figure 6-14. The future of graphene applications (after Graphene Flagship, 2020).

6.3.2. Graphene market

Globally, more than 300 companies claim to produce graphene. Some of them are Directa Plus PLC, Talga Resources Ltd., Versarien PLC, Saint Jean Carbon Inc., Haydale Graphene

Industries, Group NanoXplore Inc., Graphene NanoChem LLC, First Graphene, 1st Graphene, Global Graphene Group, Graphene 3d Lab, Inc., Graphene One LLC, Graphenea Inc., Graphite Central, etc. (ThomasNet, 2019; Barkan, 2022).

It is difficult to get a clear picture of actual global graphite demand, supply and future projections as different sources indicate different sizes. According to Barkan (2022), the global production capacity for graphene today is about 15,000 tonnes. Looking at high-volume applications for graphene materials (concrete, plastics, coatings, batteries, elastomers and composites), the Graphene Council predicts global demand to be between 300,000 and 600,000 tonnes in the next three to five years (Barkan, 2022). According to Grönqvis (2021), the market size is around 1,000 tonnes per year, and it is predicted to grow in the future reaching 12,000 tonnes by 2030. The current estimated value of the global market for graphene is around USD 60 million and is expected to reach USD 620 million in 2030 (Grönqvis, 2021).

6.4. Carbon Nanotubes

Carbon nanotubes (CNTs) were first discovered by Sumio Iijima in 1991. A carbon nanotube can be described as a single-layer graphene rolled up into a cylinder (Figure 6-15). Many of the physical properties of carbon nanotubes are derived from graphene. Carbon nanotubes can be classified by the number of layers into single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). CNTs can have diameters ranging from 0.4 nm to several hundred nanometers (Eatemadi et al., 2014; Jäger and Frohs, 2021).

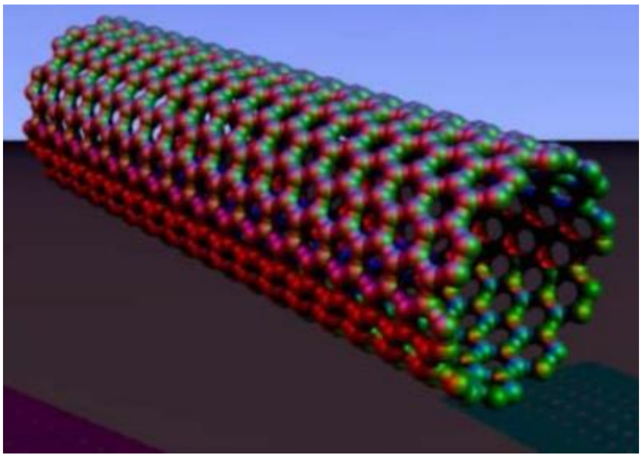


Figure 6-15. Structure of a single-walled carbon nanotube (Dagle et al., 2017).

CNTs exhibit the following properties (Cheap Tubes, 2015; Khanna and Islam, 2018):

- high stiffness (stiffer than steel),
- high electrical conductivity,
- high thermal conductivity,
- elasticity: they can be strongly bent without being damaged,
- high aspect ratio (which means that a lower concentration of CNTs is required compared to other conductive additives to achieve the same electrical conductivity),
- good electron field emitters,
- corrosion resistant.

6.4.1. Applications of carbon nanotubes

The unique composition, geometry, and properties of CNTs enable numerous potential applications, such as in polymers, electronics, plastics, and energy storage. One of the main uses for CNTs is in composite fibers in polymers to improve thermal, electrical, and mechanical properties. Moreover, CNTs are increasingly used in the production of lithium-ion batteries (Mukhopadhyay and Gupta, 2012; Cheap Tubes, 2015; Dagle et al., 2017). Table 6-6 summarizes some of the many applications for CNTs.

Table 6-6. Current and potential application of carbon nanotubes (after Mukhopadhyay and Gupta, 2012; Eatemadi et al., 2014; Cheap Tubes, 2015; Dagle et al., 2017).

Application	**Remarks**
Polymers	In composite fibers in polymers. In particular, MWCNTs are increasingly used in engineering polymers (polyetherimide, polycarbonate etc.)
Energy Storage	For lithium-ion batteries, supercapacitor electrodes.
Conductive Plastics	EMI/RFI shielding composites, coatings for enclosures, gaskets, electrostatic dissipation (ESD), and antistatic materials and conductive coatings
Molecular Electronics	For the connections in molecular electronics
Electrical Emitters	In field-emission flat-panel displays
Fabrics And Fibers	In body and vehicle armor, transmission line cables, woven fabrics and textiles (used to make textiles stain resistant)
Sensors	In in chemical sensors for environmental and health monitoring, gas sensors, etc.
Biomedical	In artificial implants, tissue engineering, cancer cell identification, drug and gene delivery by CNTs
Air & Water Filtration	CNT based air and water filtration devices. It has been reported that these filters can block the smallest particles and also kill most bacteria
Conductive Adhesives	For electronics packaging and interconnection applications (adhesives, potting compounds, and coaxial cables and other types of connectors

6.4.2. Carbon nanotubes market

Some of the major manufacturers of CNTs are LG Chem, Arkema S.A., Cheap Tubes Inc, Cabot Corporation, Toray Industries, Zeon Corporation, Showa Denko K.K., CNano Technology, Chasm Advanced Materials, Nano-C, Klean Industries, Bayer Material

Science, Nanocyl S.A, Thomas Swan and Co, Carbon Solutions Inc, SkyNano Technologies and many others (Dagle et al. 2017; Future Markets, 2020).

In recent years, global demand for carbon nanotubes has been 2,000-2,500 tons per year (Plastics Today, 2019; Future Markets, 2020). According to Temizel-Sekeryan et al. (2021), the global production volume of CNTs is expected to reach around 7,000 tonnes by 2025. Production of single-walled carbon nanotubes (SWCNTs) has now started on a large industrial scale, opening up new commercial potential in rubber, coatings, transparent conductive films, transistors, sensors, and memory devices (Future Markets, 2020). A report by Research and Markets (2022) estimates that the demand for CNTs is expected to increase to more than 50,000 tonnes per year in the next few years.

6.5. Carbon Fibers

Carbon fibers can be described as long, thin strands of material about 5 to 10 μm in diameter composed mostly of carbon atoms. They are polycrystalline, two-dimensional, planar hexagonal networks of carbon, usually containing more than >95% pure carbon. The carbon atoms are interconnected in microscopic crystals that are largely aligned parallel to the fiber axis, which provides the high stability of the fiber (Dagle et al., 2017; Lengsfeld et al., 2021; Zoltek, n.d.).

Carbon fibers are synthetic products made from a raw material called the precursor. Nowadays, two precursors are commercially available: polyacrylonitrile (PAN) and pitch. PAN is used to produce 95% of the world’s carbon fibers. This is mainly because PAN is readily available and has consistent quality. Pitch-based carbon fibers account for the remaining 5% of the global market (Lengsfeld et al., 2021).

Similar to the aforementioned carbon allotropes, graphite, graphene and carbon nanotubes, the carbon fibers are characterized by their excellent properties. Carbon fibers are ten times stronger than steel and eight times stronger than aluminum, but still weigh considerably less (Zoltek, n.d.). A summary of the typical properties of carbon fibers can be found in Table 6-7.

Table 6-7. General properties of carbon fibers (after Lengsfeld et al., 2021).

Property Type	**Characteristics**
Mechanical properties	▪ high strength and stiffness (high modulus of elasticity) up to approx. 500 °C ▪ almost fatigue-free and fatigue-proof ▪ low creep tendency ▪ good vibration damping ▪ progressive stress-strain behaviour
Chemical and physical properties	▪ chemically inert ▪ low density ▪ corrosion-resistant ▪ high resistance to acids, alkalis, and organic solvents
Thermal properties	▪ negative coefficient of expansion ▪ good to very good thermal conductivity
Electrical properties	▪ high electrical conductivity in fiber direction
Electromagnetic properties	▪ low absorption of X-rays ▪ non-magnetic

6.5.1. Applications of carbon fibers

Figure 6-16 provides an overview of the market penetration and price development of carbon fibers. In the past, they were mainly used in the space industry and for military applications, i.e., in areas where functionality overrules cost. As the price of carbon fibers has fallen, they are now finding increasing use in a variety of industrial sectors. Some of these include the civil aviation industry, sporting goods, chemical industry, wind turbines, hydrogen tanks, medical technology, automotive, carbon-reinforced composite materials, textiles etc. (further detailed in Table 6-8) (Dagle et al., 2017; Jäger and Frohs, 2021; Lengsfeld et al., 2021).

One promising application that could accommodate large quantities of carbon fibers in the future is in civil engineering, i.e., construction industry, via carbon fiber reinforced concrete (i.e., “carbon concrete”) (Dagle et al., 2017; Jäger and Frohs, 2021; Lengsfeld et al., 2021). Lightweight materials offer great potential by minimizing the consumption of raw materials for buildings. Lightweight materials not only have low in density, but also a high strength-to-density or stiffness-to-density ratio (Jäger and Frohs, 2021). Compared to steel-reinforced concrete, the application of carbon fiber reinforced concrete is more sustainable as it reduces overall material consumption, allows structures to last longer, and helps reduce CO_2 emissions (Carbocon, n.d.). In 2020, the construction began on the first building made entirely from carbon-fiber reinforced concrete. The two-story building, named Carbonhaus or CUBE, is located on the campus of the Technical University in Dresden, Germany (Caulfield, 2020).

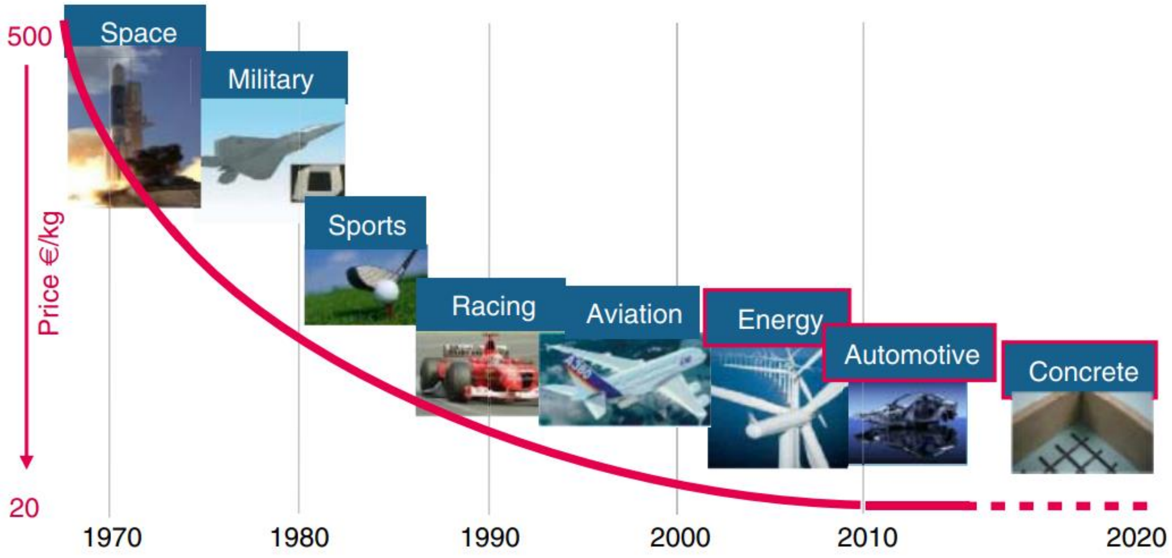


Figure 6-16. The market penetration and price development of carbon fibers (Jäger and Frohs, 2021).

Table 6-8. Examples of carbon fiber application in various industries (Dagle et al. 2017; Zoltek, 2019; Jäger and Frohs, 2021; Lengsfeld et al., 2021; SMI Composites, 2022).

Application	Remarks
Space	tank for solid-fuel rockets
Military	helmets, weapons, vehicles, planes
Sporting goods	bike frames, hockey sticks, tennis rackets, fishing rods, archery bows and arrows.
Automotive	NASCAR, Formula 1, high-end vehicles, interior and exterior components (carbon fiber composites could cut passenger vehicle weight in half and increase fuel efficiency)
Wind turbines	blades (lighter blades equal greater efficiency)
Construction industry	fiber-reinforced plastic bathtubs, doors, windows, and panels
Energy storage	hydrogen, battery electrode material for redox flow battery technology
Medical technology	reinforcement of medical equipment (e.g. radiological instruments, orthopedics), carbon fiber's lightweight, super-strength, and anti-corrosion abilities make it an ideal material for the medical industry
Concrete	concrete reinforced with carbon fibers (“carbon concrete”)

6.5.2. Carbon fiber market

Major companies manufacturing carbon fibers include Toray (including the purchase of Zoltek), SGL, Tejin Carbon, Mitsubishi Chemical, Jiangsu Hengshen Fiber Material Co., Solvay Cytec, Hexcel, DowAksa, Kemrock, Hyosung Corporation, LeMond Composites (Dagle et al. 2017; Lengsfeld et al., 2021).

According to Lengsfeld et al. (2021), in 2019, the theoretical global production capacity for carbon fibers was about 151,000 tons. This indicates a capacity growth of more than ten times compared to the 14,000 tons available in 2000. In 2019, the demand for carbon fibers was 84,500-92,000 tons (Jäger and Frohs, 2021; Lengsfeld et al., 2021). New markets for carbon fibers are expected to drive a significant increase in carbon fibers demand. By 2030, the demand is expected to reach approximately 270.000 tons (Jäger and Frohs, 2021)

7. DISCUSSION

This chapter discusses the current market for methane pyrolysis and identifies potential applications for large quantities of solid carbon that would be produced by the industrial application of methane pyrolysis. The analysis conducted as part of this thesis found that more companies and organizations are looking at different methane pyrolysis technologies.

Figure 7-1 provides an overview of all companies and organizations currently developing methane pyrolysis technologies mentioned in this thesis.

Figure 7-1. Overview of methane pyrolysis technology developers.

The statistics produced refer only to methane pyrolysis technologies currently under development, while earlier attempts to develope methane pyrolysis are not included. Technologies based on plasma pyrolysis account for about 46% of all methane pyrolysis technologies. Thermal and catalytic technologies each account for about 27% (Figure 7-2).

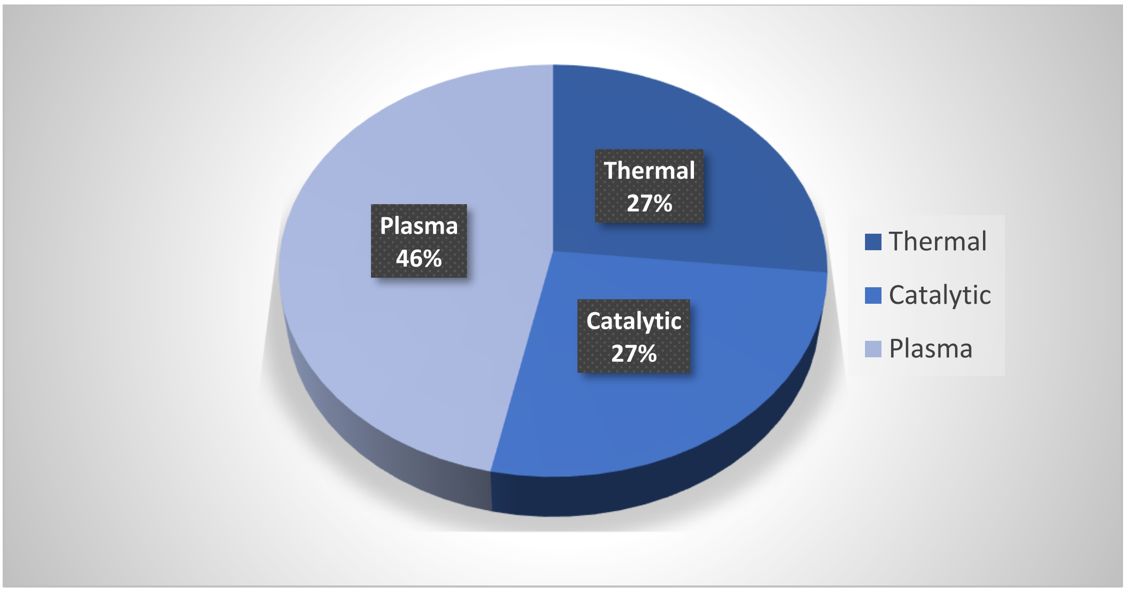


Figure 7-2. Methane pyrolysis technologies by category.

About three-quarters of all companies and organizations developing methane pyrolysis technologies are based in Europe. Those include BASF, TNO, KIT, Hycamite, Carbotopia, Graforce, Plenesys, HiiROC, SparkCleantech, Levidian and Sakowin Green Energy. Around 20% of all technologies are located in North America. More precisely, the technologies developed by Monolith and C-Zero are located in the USA, while EKONA is located in Canada. Hazer group is the only technology developed in Australia (Figure 7-3).

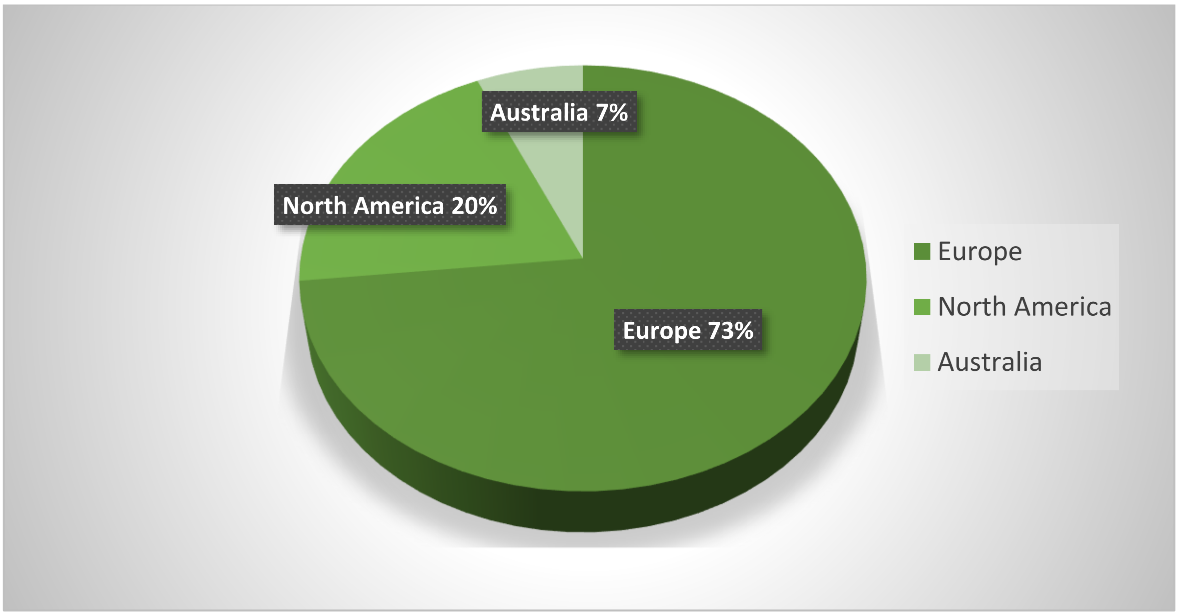


Figure 7-3. Developing methane pyrolysis technologies by region.

The methane pyrolysis market is dominated by small to medium-sized, which account for about 73% of total developing technologies (Figure 7-4). These include start-ups (Graforce, Plenesys, HiiROC, SparkCleantech, Hycamite, C-Zero, EKONA, Levidian and Sakowin Green Energy) and spin-out companies (Hazer Group, a spin-out company from the University of Western Australia). The TNO and KIT research organizations account for about 13% of all technologies. BASF is the only large corporation in the market today. Other, shown in Figure 7-4, refers to Carbotopia, a non-profit organization.

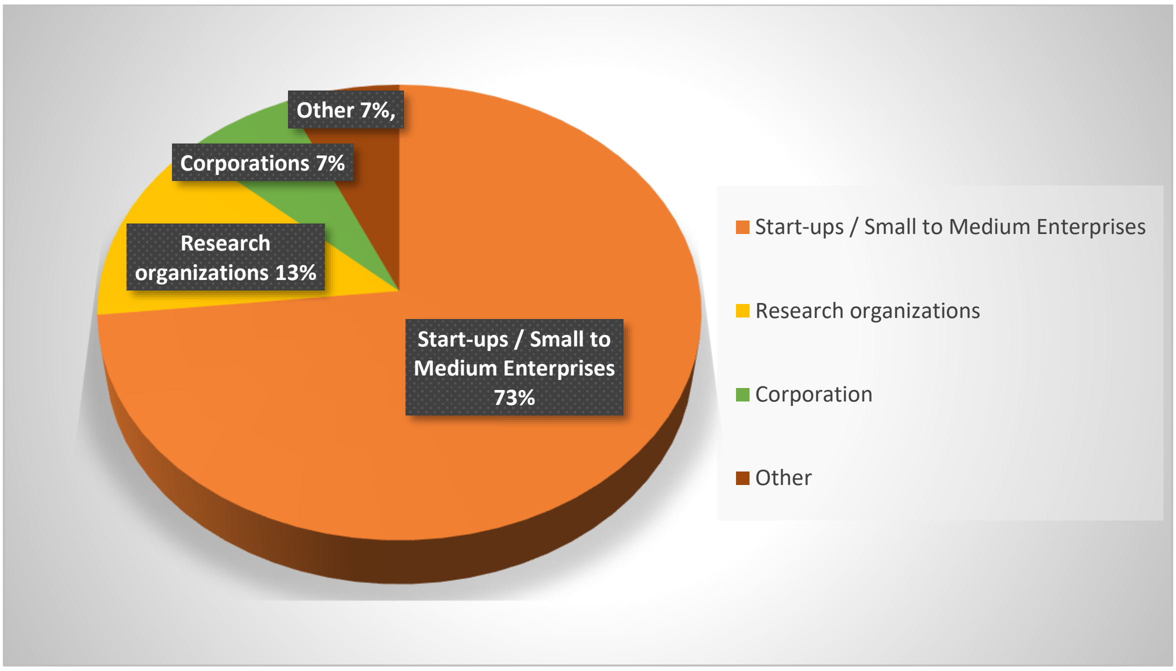


Figure 7-4. Methane pyrolysis technologies by organization type.

If methane pyrolysis is carried out on an industrial scale, huge amounts of solid carbon will be produced yearly. To put it into perspective, if 70 million tonnes of pure hydrogen produced in 2021 were produced by methane pyrolysis, around 210 million tonnes of solid carbon product would be generated. Current consumption of all carbon products mentioned in the Chapter 6 is less than 20 million tonnes and it is unlikely that it will substantially increase in the near future. Therefore, it is obvious that existing markets for different carbon products would not be able to absorb such large quantities and that new markets must be created.

One of the potential applications that could accommodate large markets is the building and construction materials field. As was previously mentioned, carbon fibers are already being used as a substitute for steel in carbon-reinforced concrete (Subchapter 6.5.1) and, according to Levidian (2022), incorporating graphene into concrete makes it 1.5 times stronger and reduces CO_2 emissions (Subchapter 6.3.1).

Another potential application is in the field of soil improvement and environmental remediation, which could provide a practically unlimited market for carbon products (Muradov and Veziroğlu, 2005).

Previous studies indicate that the addition of carbonaceous products to soil can significantly improve seed germination, plant growth, and crop yields (up to 200% increases in crop yield have been reported). It could also increase nutrient and water retention capacity and microbial abundance and activate root activity. Carbon can act as a potential slow-release fertilizer by storing nutrients from the soil, which could significantly reduce the amount of fertilizers added to the soil. Adding carbon to soil can improve CO_2 sequestration, thereby reducing CO_2 in the atmosphere and acting as a long-term CO_2 sink.

The carbon products formed during methane pyrolysis (particularly disordered carbons with relatively large surface area) are comparable to carbon materials used for soil amendment; hence, it is plausible that they would also have a positive impact on plant growth. Further long-term studies are needed to verify these claims (Muradov and Veziroğlu, 2005; Sánchez-Bastardo et al., 2021). If solid carbon produced by methane pyrolysis is to be used for soil improvement, it must not be contaminated with toxic metals (Sánchez-Bastardo et al., 2021).

8. CONCLUSION

Hydrogen can help address numerous critical energy challenges since it provides a means to decarbonize a number of sectors, including long-haul transport, chemicals, and iron and steel, where it is proving difficult to meaningfully reduce emissions. Interest in hydrogen is growing worldwide, and hydrogen technology, with its many advances, is considered one of the most promising options for the energy transition.

Methane pyrolysis has been intensively studied and reported in the literature for many years, but it is still at an early-stage technology. Only recently companies have begun to develop it for commercial use.

Currently, thermal plasma pyrolysis is the most mature technology. Thermal methane pyrolysis technologies are unlikely to be ready for commercial-scale deployment before 2030. Compared to thermal technologies, catalytic technologies are a bit more advanced. This thesis described fifteen methane technologies currently under development today and mentioned previous attempts to develop this technology. Nearly half (46%) are thermal and non-thermal plasma methane pyrolysis processes. Slightly less than three-quarters (73%) of the technologies are being developed in Europe, followed by North America (20%) and Australia (7%). Start-ups and collage spin-outs are by far the most common organizations developing methane pyrolysis (73%), followed by research institutions (13%), large corporations (7%) and non-profit organizations (7%).

Solid carbon characterization is crucial since its quality affects the process economics. One of the biggest challenges in deploying methane pyrolysis on an industrial-scale is finding a market for the vast quantities of solid carbon that would be produced yearly. Current carbon markets are not capable of absorbing such volumes, and are unlikely to increase significantly in the near future. Therefore, sufficiently large markets need to be found to address the issue of using solid carbon products and consequently reduce the cost of methane pyrolysis. Potential applications could be in soil improvement and environmental remediation or in building and construction materials.

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I declare that I wrote this thesis and performed the research myself using the knowledge and skills gained at the Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb and the cited literature.

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Sara Kesić, studentica

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Na temelju vašeg zahtjeva primljenog pod KLASOM 602-01/22-01/188, URBROJ: 251-70-12-22-1 od 5.10.2022. priopćujemo vam temu diplomskog rada koja glasi:

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Za mentoricu ovog diplomskog rada imenuje se u smislu Pravilnika o izradi i obrani diplomskog rada doc. dr. sc. Karolina Novak Mavar nastavnik Rudarsko-geološko-naftnog-fakulteta Sveučilišta u Zagrebu i komentoricu izv.prof. dr.sc. Ankica Kovač.

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