CHAPTER 1

INTRODUCTION

1.1 Background

Pyrocarbon is a carbon-based material that is formed by the pyrolysis of a hydrocarbon gas at high temperatures. It is a hard, wear-resistant, and biocompatible material that is often used in biomedical and aerospace applications (Tan et al., 2016). Because of its outstanding electrochemical characteristics and electrical conductivity, low friction, chemical inertness, and anisotropic dense and controlled microstructure (Bourrat et al., 2006a), it is a potential coating material. It has lately gained popularity due to its ability to substitute silicon in microelectromechanical systems. Moreover, the superior impermeability of isotropic PyC makes it the best candidate for the mechanical sealing devices used extensively in the aerospace and shipping industries (Beigi-Boroujeni et al., 2019).

Methane pyrolysis is a promising process for the production of carbon-based materials such as pyrocarbon, graphene and carbon nanotubes (Sanchez-Bastardo et al., 2021). Chemical vapour deposition (CVD) is a method of depositing thin layers of material onto a substrate. It involves the decomposition and reactivity of volatile precursor gases in a heated chamber to generate a solid coating on the substrate surface. It is widely utilized in various industries, including semiconductor manufacturing, coating technologies, and nanomaterial synthesis, to produce high-quality and controlled thin films with precise thickness and composition. The understanding of CVD reactors is a complex and challenging task, as it involves multiple interacting factors such as reactor geometry, temperature, pressure, gas flow etc. (Komiyama et al., 1999; Ogawa et al., 2023). The film morphology in CVD is also influenced by these parameters. Temperature affects growth rate and surface quality, while pressure impacts gas diffusion and film quality (Hu, 2012). Gas flow rate determines precursor concentration and uniformity, and reactor geometry affects deposition uniformity and nucleation density. These parameters are interrelated and require optimization to achieve the desired film morphology, considering the specific CVD system and precursor materials. Careful control and optimization of these parameters are crucial for successful CVD processes. In addition, the current process suffers from low yield, low quality, and high energy consumption, which limit its commercial viability. Therefore, there is a pressing need to optimize the process parameters to improve its efficiency and environmental impact (Jabar, 2021; Timmerberg et al., 2020). Traditional optimization techniques based on trial and error can be time-consuming and costly, and may not guarantee the optimal solution (Dong and Huttinger, 2002; Hu and Hüttinger, 2001).

CFD plays a crucial role in understanding CVD processes by simulating the complex fluid dynamics and heat transfer phenomena involved. CFD models help analyze the gas flow patterns, temperature distribution, and species transport within the CVD reactor (Ogawa et al., 2023). By providing insights into gas mixing, reactant concentration, and residence time, CFD allows the optimization of reactor design and process parameters, leading to enhanced film quality and deposition rates. It also aids in predicting and mitigating issues such as gas phase reactions, particle transport, and deposition non-uniformity, contributing to the overall understanding and improvement of CVD processes (Ali and Ürgen, 2011a; Yang et al., 2009).

Traditional optimization algorithms often struggle to solve complex problems with many variables and constraints. Machine learning can overcome these challenges by learning from data to find optimal solutions more efficiently (Weichert et al., 2019). One way machine learning is used for optimization is to train a model to predict the objective function value for a given set of decision variables. This model can then be used to guide the search for an optimal solution. Another approach is to use machine learning to learn a good initialization for a traditional optimization algorithm (Kubat, 2017). This can help the algorithm to converge to a better solution more quickly. Therefore, the motivation for this thesis is to analyze and optimize the pyrolysis of methane in a commercial hot-wall CVD reactor using CFD simulations. The goal is to achieve high-quality pyrocarbon by combining the support vector machine (SVM) and the Nelder-Mead algorithm by simultaneously maximising the average deposition rate and uniformity index.

1.2 Thermal decomposition of methane

The thermal decomposition of methane, also known as methane pyrolysis or methane cracking, is a chemical process in which methane (CH_4) is broken down into its constituent elements, typically hydrogen (H_2) and solid carbon (C). The reaction is endothermic, requiring the input of heat to drive the process. The overall reaction can be represented as follows:

$$CH_4 \rightarrow C + 2H_2 \qquad (1)$$

The thermal decomposition of methane is typically carried out at high temperatures, typically in the range of 900 to 1200^0C, and in the presence of a catalyst to enhance the reaction rate. The reaction can occur in both homogeneous and heterogeneous systems. The thermal decomposition of methane has a variety of applications in industry and is interesting for several reasons, some of which are briefly discussed below:

1. **Hydrogen production:** Methane pyrolysis is a potential method for hydrogen production. Hydrogen is a clean and efficient fuel that can be used in fuel cells and various industrial processes. By decomposing methane, hydrogen can be obtained as a valuable byproduct (Sánchez-Bastardo et al., 2021; Timmerberg et al., 2020).

2. **Carbon materials synthesis**: The solid carbon produced during methane pyrolysis can be utilized for the synthesis of various carbon-based materials (Dadsetan et al., 2023). These include carbon black, carbon nanotubes, graphene, and other forms of carbon with unique properties and applications. It is used in advanced composite materials for improving mechanical strength and thermal conductivity in industries such as automotive and aerospace (Tan et al., 2016).

3. **Decarbonization:** Methane, a potent greenhouse gas, is a major component of natural gas. The thermal decomposition of methane offers a potential pathway for reducing greenhouse gas emissions by converting methane into useful products like hydrogen and carbon, thereby mitigating its impact on climate change (Parkinson et al., 2018).

4. **Chemical industry:** Methane pyrolysis can be used as a precursor for the production of various chemicals like ethylene benzene, toluene, xylene, and other hydrocarbons (Jabar, 2021). By selectively controlling the reaction conditions and catalysts, specific chemical intermediates or end products can be obtained. The specific chemicals that are produced from methane pyrolysis depend on the reaction conditions and catalysts used. For example, high temperatures favour the production of ethylene, while lower temperatures favour the production of benzene (Fau et al., 2013).

However, there are challenges associated with methane pyrolysis, including high energy requirements due to the endothermic nature of the reaction, catalyst deactivation or degradation, and the need for efficient heat transfer and reactor design. The design of a CVD reactor presents engineering challenges such as achieving uniform deposition, maintaining stable gas flow, and controlling temperature distribution. Addressing these issues is crucial for ensuring consistent film growth and properties, as well as for optimizing safety and scalability in CVD processes (Komiyama et al., 1999; Ogawa et al., 2023). Research efforts are focused on developing optimized process conditions, exploring new catalyst materials, and improving the energy efficiency of methane pyrolysis to make it commercially viable and environmentally sustainable (Becker et al., 2000; Dong and Hüttinger, 2002) Continued research and development in this field hold promise for advancements in CVD process and sustainable materials development.

1.3 Types of pyrolytic carbon and their importance

Pyrolytic carbon is a form of carbon material that is synthesized through the process of pyrolysis, which involves the thermal decomposition of a carbon-containing precursor. Pyrolytic carbon possesses unique properties and finds important applications in various fields. Here are some types of pyrolytic carbon and their significance:

1. **Pyrolytic graphite (PG)**: Pyrolytic graphite is a highly oriented form of pyrolytic carbon with a layered structure similar to graphite (Gulyaev and Shushkov, 2022). It is produced by depositing carbon vapour onto a substrate at high temperatures. It exhibits excellent thermal conductivity, electrical conductivity, and lubricating properties. Padnya et. al. found that the carbon black layer consisted of roundish particles 30-50 nm in size (Padnya et al., 2018). It is used in applications such as thermal management, electrodes, crucibles, and as a lubricant in high-temperature environments.

2. **Pyrolytic carbon fibre (PyCF):** Pyrolytic carbon fibres are produced by the pyrolysis of carbon-rich precursor fibres, such as polyacrylonitrile (PAN) or rayon, in a controlled environment. Tan et al., 2016 showed that PyCF has high-density isotropic pyrocarbon and exhibits fine grains resembling wrinkled sheets, with a significantly smaller average grain size compared to the substrate's graphite grains. Moreover, Figure 1.2 (i) demonstrates a schistose appearance at the specimen's edge, indicating a layer-by-layer deposition mechanism in that region, consistent with the growth of anisotropic pyrocarbon. PyCF possesses high strength, stiffness, and thermal stability. It finds applications in aerospace, automotive, and sporting goods industries for lightweight structural components, reinforcing materials, and conductive composites (Tan et al., 2016).

3. **Pyrolytic carbon coating (PyCC)**: Pyrolytic carbon coatings are thin layers of pyrolytic carbon deposited on various substrates using CVD techniques. Li et al., 2010 discovered that pyrocarbon is made of granular particles with uniform dimensions of about 1.5 µm (Li et al., 2020). These coatings provide a range of desirable properties, like excellent chemical resistance, biocompatibility, low friction, and electrical conductivity (Bourrat et al., 2006a). PyC is used in applications such as biomedical implants, protective coatings, and electrical contacts (Li et al., 2010).

4. **Pyrolytic carbon electrodes (PCE):** Because of its high electrical conductivity and corrosion resistance, pyrolytic carbon electrodes are widely employed in electrochemical applications. They are employed in fuel cells, batteries, sensors, and other electrochemical devices for efficient electron transfer and stable performance. In Fig 1.2 (iv) Rezaei et. al. found that fast pyrolysis leads to non-isotropic shrinkage and distorted mesh holes, while slow pyrolysis retains the cubic shape with gradual degradation and degassing. Pyrolysis conditions affect both the macro-structure and surface topography of carbonized materials (Rezaei et al., 2020).

5. **Pyrolytic carbon foam (PCF)**: is a porous form of pyrolytic carbon with a three-dimensional interconnected network structure. It exhibits a combination of low density, high thermal conductivity, and excellent mechanical strength. Pyrolytic carbon foam is used in heat exchangers, thermal insulation, catalyst supports, and as a substrate for energy storage devices (Rodríguez et al., 2021).

The importance of pyrolytic carbon lies in its unique combination of properties, including high thermal and electrical conductivity, mechanical strength, chemical stability, and biocompatibility. These characteristics make pyrolytic carbon suitable for a wide range of applications, ranging from aerospace and automotive industries to biomedical and energy sectors. The different types of pyrolytic carbon offer tailored properties to meet specific application requirements and contribute to advancements in various fields of technology and engineering.

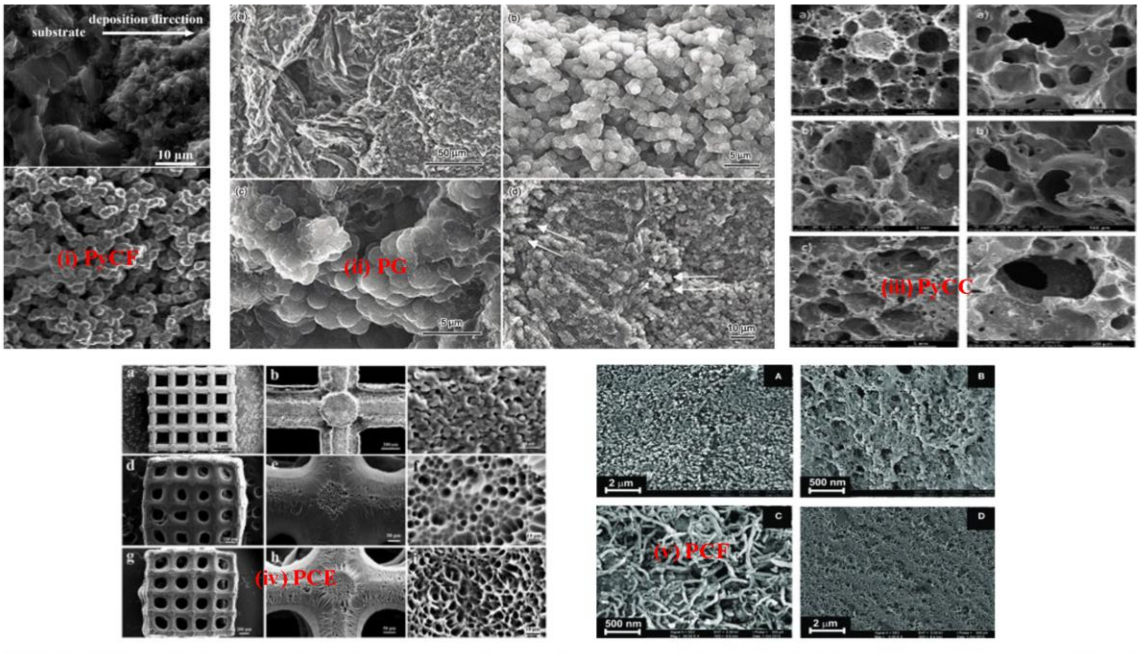

Fig. 1.1 SEM images of different types of PyC

(Li et al., 2020; Padnya et al., 2018; Rezaei et al., 2020; Rodríguez et al., 2021; Tan et al., 2016)

1.4 Various manufacturing processes of pyrocarbon

Pyrocarbon is a high-performance carbon material that finds applications in various industries, including aerospace, automotive, and medical. The manufacturing processes of pyrocarbon involve the deposition of carbon from a gaseous precursor onto a substrate under controlled conditions. The following list of frequently employed pyrocarbon production techniques includes information on each process's benefits and drawbacks:

1. **Chemical Vapor Deposition (CVD)**

   Chemical vapour deposition (CVD) is a process for coating surfaces with a thin film of material from a gas. The type of gas used depends on the application. For example, coating carbon fibres with pyrocarbon can help prevent them from sticking together in carbon fibre-reinforced carbon composites.

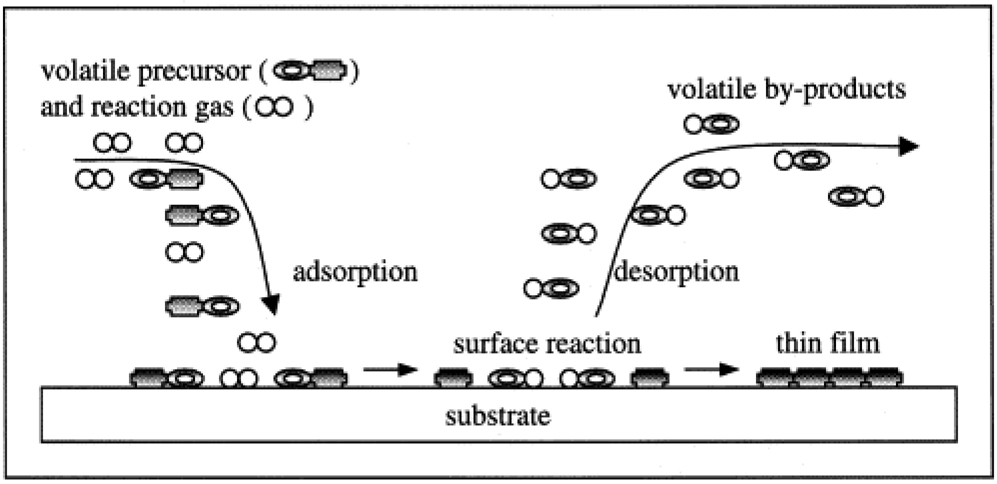

Fig. 1.2 A schematic representation of the CVD reaction (Dahmen, 2003)

Advantages:

i. Allows precise control over deposition parameters such as temperature, pressure, and gas composition, resulting in tailored material properties.
ii. High purity and uniformity of the deposited carbon.
iii. Provides excellent adherence to complex-shaped substrates.
iv. Enables the deposition of thick coatings or bulk materials.

Limitations:

i. Requires specialized equipment and precise process control.
ii. Relatively longer deposition times compared to other processes.
iii. Susceptible to variations in process conditions leading to non-uniform deposition.
iv. Sensitive to impurities in the precursor gases.

2. **Polymer Pyrolysis:**

Polymer pyrolysis is the thermal decomposition of polymers in the absence of oxygen. It is a complex process that involves a variety of chemical reactions, including chain scission, crosslinking, and cyclization. The products of polymer pyrolysis depend on the type of polymer, the pyrolysis temperature, and the heating rate (Yansaneh and Zein, 2022).

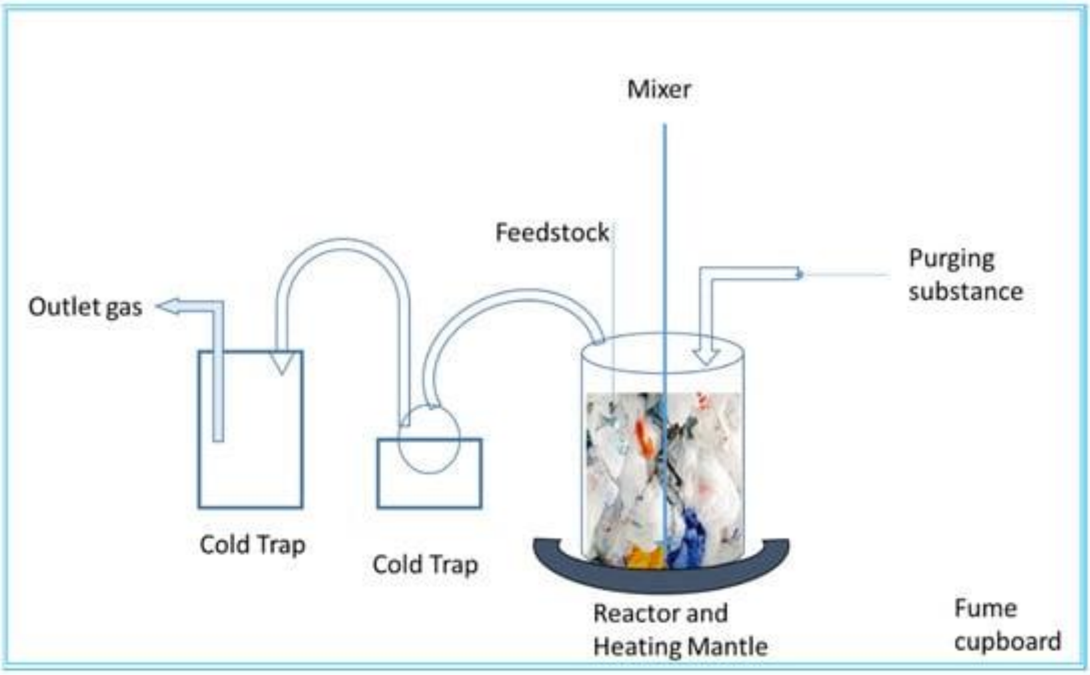

Fig. 1.3 A polymer Pyrolysis setup
(Yansaneh and Zein, 2022)

Advantages:

i. Flexibility in material selection.
ii. Low-temperature operation.
iii. Offers scalability and cost-effectiveness.
iv. Suitable for producing thin coatings and fibres.

Limitations:

i. Generally, produces lower densities compared to CVD.
ii. Limited control over the resulting material properties.
iii. May require additional steps, such as carbonization and graphitization, for enhanced performance.
iv. Polymer precursors may contain impurities that affect the quality of the final pyrocarbon.

3. **Carbonization:** Carbonization involves the formation of C–C bonds and typically occurs in the temperature range of 800°C to 2000°C. When the material undergoes further heating, specifically in the range of 2000°C to 3000°C, this process is termed graphitization (Devi et al., 2020). An illustrative instance of this is observed in the

pyrolysis of coal, leading to the extraction of tars, volatile organic compounds (VOCs), and char (carbon with impurities).

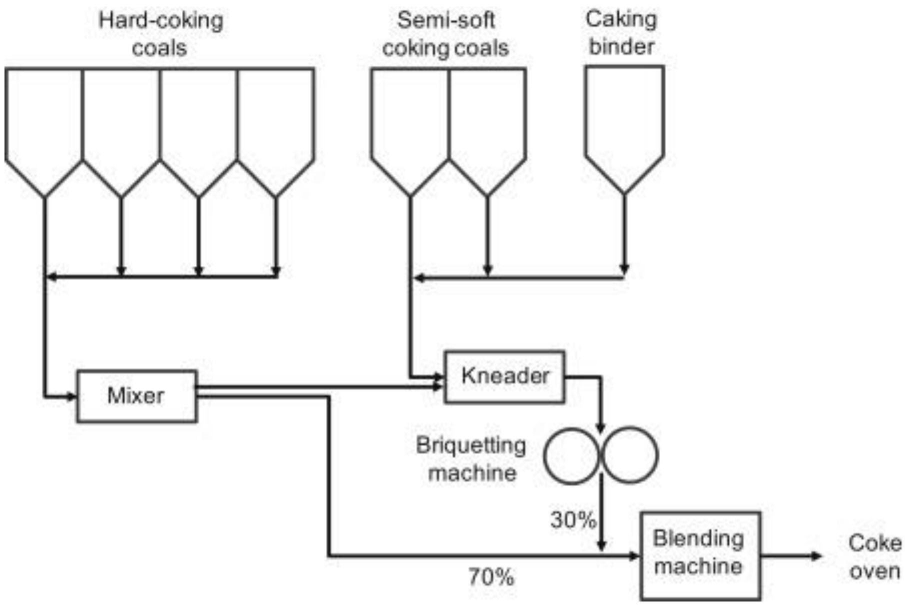

Fig. 1.4 Process flow of briquette blending carbonization process (Nomura, 2019).

Advantages:

i. Involves the heat treatment of carbon-rich materials, such as organic fibres or carbonaceous powders, to convert them into pyrocarbon.
ii. Moderate temperatures and atmospheric pressure.
iii. A relatively simple process requiring minimal equipment.
iv. Suitable for small-scale production or prototyping.

Limitations:

i. Limited control over the resulting material properties.
ii. Formation of amorphous carbon or incomplete conversion to pyrocarbon.
iii. Tends to produce lower densities and mechanical properties compared to other processes.
iv. Require post-treatment steps, such as graphitization, to enhance the performance.

It is important to select the appropriate manufacturing process based on the desired pyrocarbon properties, substrate characteristics, production scale, and cost considerations. Additionally, process optimization and quality control are essential to ensure consistent and reliable pyrocarbon production.

1.5 Advantages of CVD over another manufacturing process

CVD offers several advantages over other manufacturing processes, making it a widely used technique in various industries. Here are some key advantages of CVD:

1. **Conformal deposition:** CVD provides excellent conformal deposition, meaning the thin film uniformly covers the surface of complex three-dimensional structures (Pierson, 1999). This is particularly advantageous for applications where precise and uniform coating on intricate geometries is required, such as microelectronics, MEMS devices, and optical coatings. Other deposition techniques, such as physical vapour deposition (PVD), may struggle to achieve the same level of conformality.

2. **Tailored film composition:** CVD allows for fine control of the deposited film's composition. By selecting appropriate precursor gases and adjusting process parameters, the film's elemental composition, stoichiometry, and doping levels can be precisely tailored (Seo et al., 2016). This flexibility is highly advantageous for applications where specific material properties, such as electrical conductivity, optical transparency, or chemical reactivity, are required (Bourrat et al., 2006b).

3. **A wide range of materials:** Metals, semiconductors, ceramics, oxides, nitrides, and polymers can all be deposited using CVD. This versatility allows for the deposition of various functional coatings and thin films with tailored properties (Beigi-Boroujeni et al., 2019; Bérard et al., 2016; Seo et al., 2016). In contrast, some other deposition methods may be limited to specific material types or have restrictions on the range of materials that can be deposited.

4. **High purity and density:** CVD processes can produce films with high purity and density. The chemical reactions occurring during CVD allow for the formation of dense and highly crystalline films, resulting in improved physical and mechanical properties.

Additionally, CVD can achieve low levels of impurities and contaminants, making it suitable for applications where material purity is crucial, such as semiconductor manufacturing and high-performance coatings (Beigi-Boroujeni et al., 2019; Tan et al., 2016).

5. **Scalability and production efficiency:** CVD can be easily scaled up for large-scale production. CVD reactors can be designed with multiple deposition chambers, enabling high throughput and efficient manufacturing (Chen et al., 2018). Continuous CVD processes allow for the deposition of films over large areas, making them well-suited for industrial-scale production. This scalability and production efficiency make CVD an attractive choice for commercial applications (Lin et al., 2009a).

6. **Film customization and complexity:** CVD allows for the deposition of films with complicated architectures and customised characteristics. By manipulating process parameters, multiple precursor gases, and deposition conditions, it is possible to create multi-layered films, graded compositions, nanostructured coatings, and other advanced structures (Pierson, 1999). This level of customization and complexity is often difficult to achieve with other deposition methods.

7. **Compatibility with substrate materials:** CVD is compatible with a wide range of substrate materials, including metals, ceramics, glass, and polymers. This versatility allows for the deposition of thin films on diverse substrates, expanding the range of applications (Pierson, 1999). Other techniques, such as sputtering or evaporation, may have limitations in terms of substrate compatibility.

1.6 CVD of pyrocarbon (PyC)

PyC can be deposited on a substrate using a variety of methods, including CVD and PVD. CVD is considered better than PVD in certain applications where precise and uniform coatings are required on complex shapes or structures, such as semiconductor fabrication, optical coatings, and thin film deposition for electronic devices due to its ability to create conformal coatings with excellent step coverage and uniform thickness (Sharma et al., 2020; Sun et al., 2021). CVD also allows for the deposition of a wider range of materials, including complex compounds and alloys. Additionally, CVD can produce coatings with superior adhesion and can be performed at lower temperatures, reducing the risk of substrate damage.

In CVD, a hydrocarbon gas is introduced into a reactor and is heated to a high temperature, where it decomposes to form a solid film of pyrocarbon on the substrate. PyC is generally deposited by CVD, in which light hydrocarbon gases are pyrolysed over the substrate at high temperatures (ca.1050-1450°C) (Sharma et al., 2020). It is generally operated at low pressure to increase the molecular mean free path and diffusion of gases. As a result, more gas molecules collide with a substrate than with other gas molecules.

1.6.1. A sequence of events during CVD of PyC

The gas mixture undergoes intricate flow patterns as it passes through pipes, valves, and chambers, experiencing significant temperature variations and, to a lesser extent, pressure changes. Finally, the gas makes contact with the substrate, when the heterogeneous deposition reaction takes place, converting the gas to a solid. Additionally, in certain cases, the reaction may occur before reaching the substrate, known as gas-phase precipitation. The CVD reaction sequence, represented in Fig. 1.5, is as follows: reactant gases enter the reactor by forced flow and subsequently diffuse through the boundary layer. Upon reaching the substrate surface, the gases come into contact and undergo a deposition reaction. After the reaction, the gaseous byproducts diffuse away from the surface and go through the boundary layer (Sun et al., 2021).

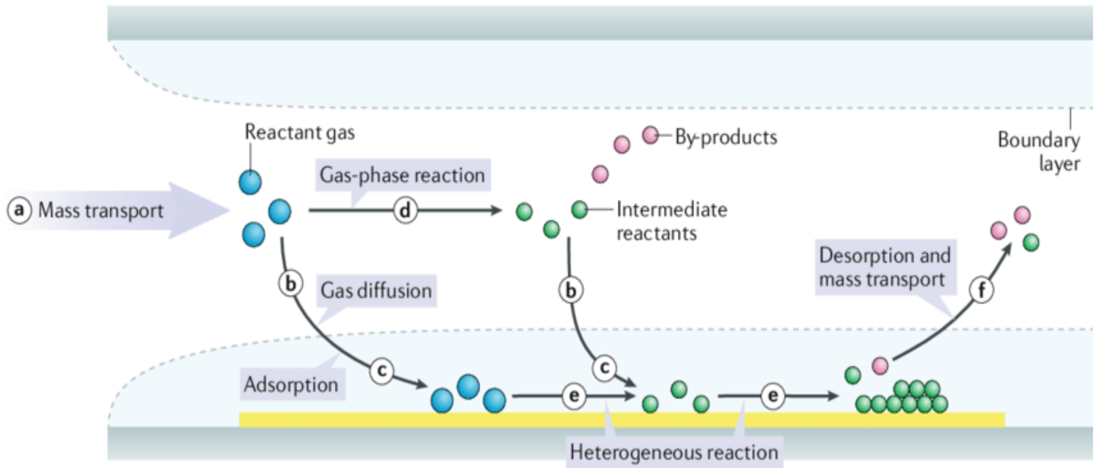

Fig. 1.5 Sequence of events during the CVD process (Sun et al., 2021)

i. Gas-phase transport of reagents (e.g., CH_4, BCl_3, H_2) to the reaction zone (frequently with carrier gas). Diffusion (or convection) through the boundary layer.
ii. Precursor adsorption on the substrate.
iii. Precursor surface diffusion to growth sites. Reaction without diffusion is undesirable because it may result in a rough growth surface.
iv. Surface chemical reaction, solid film formation, and byproduct generation.
v. By-product desorption.
vi. Removal of gaseous byproducts from the reactor.

1.6.2. Types of CVD

CVD is a flexible process for depositing thin films of different materials onto substrates. There are several types of CVD methods, each with its specific characteristics and applications. Here are some common types of CVD:

1. **Thermal CVD**: It is also known as conventional or atmospheric pressure CVD; thermal CVD involves the deposition of films by introducing precursor gases into a reactor at elevated temperatures. The thermal energy initiates chemical reactions that lead to the deposition of the desired material onto the substrate (Pierson, 1999).

Advantages:

i. Simple and cost-effective process.
ii. Suitable for large-area deposition.
iii. Can be performed at atmospheric pressure, eliminating the need for vacuum systems.

Limitations:

i. Limited control over film thickness and uniformity.
ii. High-temperature process, which may restrict the use of temperature-sensitive substrates.
iii. Lower deposition rates compared to other CVD methods.

2. **Low-pressure CVD (LPCVD):** LPCVD operates at reduced pressures compared to atmospheric pressure CVD. To optimise the deposition process, the precursor gases are

delivered into a vacuum chamber and the pressure is adjusted. Materials such as silicon nitride (Si_3N_4), polysilicon, and silicon dioxide (SiO_2) are typically deposited using LPCVD. Microelectronics, MEMS devices, and thin film coatings benefit from LPCVD's ability to provide fine control, homogeneous film deposition, and enough step coverage at lower temperatures (Pierson, 1999; Wang et al., 2013).

Advantages:

i. Allows for better control over film thickness, uniformity, and composition.
ii. Low temperatures compared to other CVD methods.
iii. Offers higher deposition rates compared to APCVD.

Limitations:

i. Requires a vacuum system, increasing equipment complexity and cost.
ii. Limited scalability for large-area deposition.
iii. Poorer step coverage on complex substrate topographies.

3. **Plasma-enhanced CVD (PECVD):** Plasma is used to improve chemical reactions and deposition processes in PECVD. Plasma is generated by applying a high-frequency electric field to a precursor gas or gas mixture. The plasma provides energy to break down the precursor molecules, creating reactive species that contribute to film deposition. PECVD is suitable for depositing various materials, including silicon-based compounds, amorphous silicon and carbon-based films (Mankelevich and May 2008a, 2008b).

Advantages:

i. Lower process temperatures, enabling the use of temperature-sensitive substrates.
ii. Better control over film aspects like composition and structure.
iii. Can deposit films with high conformality on complex geometries.

Limitations:

i. Requires a plasma source, which adds complexity and cost to the system.
ii. Higher susceptibility to plasma damage, which may affect film quality.
iii. Limited scalability for large-area deposition.

4. **Metal-organic CVD (MOCVD):** MOCVD, also known as organometallic CVD, is specifically used for depositing thin films of metal compounds, such as oxides, nitrides, and semiconductors. It involves the use of metal-organic precursors, which are vaporized and decomposed to deposit the desired material onto the substrate. MOCVD is widely used in the production of compound semiconductors for electronic and optoelectronic devices (Chuang and Chen, 2014; Kadinski et al., 2004; Liu et al., 2007).

Advantages:

i. Enables the deposition of compound semiconductor materials.
ii. Offers precise control over film composition and doping.
iii. Suitable for growing thin films for electronic and optoelectronic devices.

Limitations:

i. Requires highly reactive and expensive precursor materials.
ii. Complex gas handling and safety considerations.
iii. Limited to specific materials and applications.

5. **Atomic layer deposition (ALD):** ALD is a form of CVD that allows for atomic-level control of layer thickness and composition. It is accomplished by sequentially exposing the substrate to two or more precursor gases. Each precursor reacts with the surface in a self-limiting manner, allowing for the controlled growth of ultra-thin films with excellent conformality. ALD is commonly used in nanotechnology, semiconductor manufacturing, and advanced materials research (Pierson, 1999).

Advantages:

i. Allows for atomic-level control over film thickness.
ii. Excellent conformal deposition on complex geometries.
iii. Enables high-uniformity deposition of ultra-thin films.

Limitations:

i. Slow deposition rates, resulting in longer processing times.
ii. Requires alternating exposure of precursors, increasing process complexity.
iii. Limited scalability for large-area deposition.

6. **Hot Wall CVD:** The hot wall CVD is a CVD procedure in which the substrate is directly heated, often by placing it on a hot susceptor or heater. The reaction chamber is often cooler than the substrate in this process, and heat is transmitted from the substrate to the reactant gases. When the reactant gases are delivered into the chamber, chemical reactions take place on the heated substrate surface, resulting in the deposition of the desired material (Creighton and Ho, 2001).

Advantages

i. **Higher temperature capability:** Hot wall CVD allows for higher temperature operation compared to cold wall CVD. This enables the deposition of materials that require high temperatures for their growth or for achieving desired properties.
ii. **Enhanced reaction rates:** The elevated substrate temperature in hot wall CVD promotes faster reaction rates, leading to improved deposition kinetics. This can result in higher growth rates and improved film quality.
iii. **Reduced parasitic deposition**: With hot wall CVD, the chamber walls are typically cooler than the substrate. This temperature gradient helps to minimize undesired deposition on the chamber walls, reducing contamination and improving process efficiency (Li et al., 2010).

Limitations

i. **Limited control over temperature distribution**: In hot wall CVD, controlling the temperature distribution across the substrate can be challenging. Variations in temperature across the substrate surface may lead to non-uniform film deposition, impacting the film's quality and thickness uniformity.
ii. **Higher thermal stress:** The direct heating of the substrate in hot wall CVD can result in higher thermal stress on the substrate and deposited films. This can potentially cause cracking, delamination, or other defects in the deposited layers.

7. **Cold wall CVD:** Cold wall CVD is a type of CVD process where the reactor walls are maintained at a lower temperature compared to the substrate. In this method, the reactant gases are introduced into the chamber, and the deposition occurs on the

substrate surface without direct heating from the walls (Creighton and Ho, 2001; Pierson, 1999)

Advantages

Better temperature control: Cold wall CVD provides better control over the temperature distribution across the substrate. Maintaining a temperature gradient allows for more uniform deposition and more exact control of the growth parameters.

i. **Reduced thermal stress:** Compared to hot wall CVD, cold wall CVD imposes lower thermal stress on the substrate and the deposited films. This can lead to improved film quality and reduced likelihood of cracking or delamination.
ii. **Compatibility with sensitive substrates:** Cold wall CVD is often preferred for substrates that are sensitive to high temperatures. By avoiding direct heating, the temperature of the substrate can be kept within a safe range without causing damage or undesirable consequences.

Limitations

Lower temperature capability: Cold wall CVD typically operates at lower temperatures compared to hot wall CVD. This can limit the growth of materials that require higher temperatures for their deposition or for achieving specific properties.

i. **Slower reaction rates:** The lower substrate temperature in cold wall CVD can result in slower reaction rates compared to hot wall CVD. This may lead to slower growth rates and longer deposition times.
ii. **Potential for parasitic deposition:** In cold wall CVD, the chamber walls are generally colder than the substrate. This temperature gradient can sometimes lead to parasitic deposition on the walls, which can cause contamination and reduce the efficiency of the process.

These are just a few examples of the types of CVD methods commonly used in various industries and research fields. Each process has distinct advantages and is best suited to certain applications, allowing for the deposition of a diverse spectrum of materials with customised features. The suitable CVD process is determined by the desired material, film properties, deposition parameters, and unique application needs. The selection of a CVD method depends on the desired film properties, substrate compatibility, process scalability, and cost considerations. Each approach has advantages and disadvantages, and the choice should be based on the unique deposition process requirements and desired film properties.

1.6.3. Critical components in CVD

CVD critical components are required for the successful fabrication and deposition of high-quality thin films or coatings. These elements are critical in managing deposition parameters, guaranteeing uniformity, and achieving the desired film characteristics (Pierson, 1999). Some of the most important components of CVD systems are:

1. **Reactor chamber:** The reactor chamber provides a controlled environment for the CVD process. It typically consists of a heated chamber where the precursor gases are introduced and the deposition occurs. The chamber design and materials used should be compatible with the process conditions and the desired film characteristics.

2. **Gas delivery system**: The gas delivery system is in charge of bringing the precursor gases into the reactor chamber exactly. To obtain the appropriate gas composition and flow rates, it often incorporates mass flow controls, gas lines, and gas mixing capabilities. Controlling film thickness, composition, and uniformity requires precise control of precursor gas flow.

3. **Substrate holder**: The substrate holder or stage holds the substrate on which the film is deposited. It should provide proper mechanical support, thermal stability, and temperature control during the deposition process. The substrate holder may also have rotation or translation capabilities to ensure uniform deposition across the substrate surface.

4. **Heating system:** Temperature control is vital in CVD processes to promote the desired chemical reactions and achieve the desired film properties. A heating system, such as resistive heaters or induction coils, is used to heat the substrate and/or reactor chamber to the required temperature. Precise temperature control is essential to maintain process stability and repeatability.

5. **Vacuum system**: A vacuum system is employed to evacuate the reactor chamber and maintain the desired process pressure. It typically consists of vacuum pumps, pressure gauges, and valves. Proper control of the process pressure is critical for gas flow, precursor decomposition, and the prevention of unwanted reactions or contaminations.

6. **Exhaust system**: The exhaust system removes the byproducts and unreacted gases from the reactor chamber. It helps maintain a clean environment and prevents the accumulation of unwanted species that can affect film quality. It usually includes a vacuum pump and appropriate gas scrubbing or filtration systems.

7. **Gas exhaust analysis**: Analytical tools, such as mass spectrometers or gas analyzers, may be integrated into the CVD system to monitor and analyze the exhaust gases. These tools provide valuable information about the process chemistry, gas consumption, reaction kinetics, and the presence of impurities.

8. **Safety and process monitoring systems**: CVD systems often include safety features and monitoring systems to ensure operator safety and process control. These may include temperature and pressure sensors, gas leak detectors, interlocks, and alarms.

1.6.4. Advantage of vertical over horizontal CVD reactor

A vertical CVD reactor can have several advantages over a horizontal one. Some of these advantages include:

- **Greater surface area to volume ratio**: A vertical reactor can have a larger surface area for a given volume, which can lead to better heat and mass transfer.
- **Easier to scale up**: A vertical reactor can be scaled up more easily than a horizontal one, as the reactor can simply be made taller rather than wider.
- **Reduced risk of contamination:** A vertical reactor can have a reduced risk of contamination, as the reactants can be fed into the reactor from the top and the products can be removed from the bottom, minimizing the chance of cross-contamination.
- **More efficient use of space:** A vertical reactor can be more space efficient than a horizontal one, as it can be placed in a smaller footprint.

1.7 Importance of CFD in designing CVD reactor:

Computational Fluid Dynamics (CFD) is a valuable tool for developing CVD reactors. CFD can assist in optimising reactor design and operation, increasing process efficiency, and lowering costs. Some of the primary advantages of employing CFD in CVD reactor design are as follows:

1. **Understanding the flow patterns and heat transfer mechanisms**: CFD models can provide precise information on reactor flow patterns and heat transfer mechanisms (Cheng and Hsiao, 2008). This data can be utilised to optimise the reactor's design and increase the process's efficiency.

2. **Optimizing reactor geometry and operating conditions**: CFD simulations can be used to evaluate the performance of different reactor geometries and operating conditions and identify the optimal design that maximizes the production rate and quality of the target material. Jia et al studied the optimal design for dividing wall columns using SVM and PSO. They learn several parameters on their own by fitting the data. In addition, they are also computationally efficient and can be used in real-time prediction (Jia et al., 2017a).

3. **Reducing experimental costs and time**: CFD simulations can provide a cost-effective and time-efficient alternative to experimental testing. By simulating different scenarios and analyzing the results, engineers can reduce the number of experiments needed and optimize the process parameters more quickly and efficiently (Haddadi et al., 2017).

4. **Improving process safety**: CFD simulations can help to identify potential safety hazards, such as high temperatures, pressure drops, and flow instabilities, and design the reactor to mitigate these risks (Szpicer et al., 2023).

5. **Enhancing product quality and consistency**: CFD simulations can aid in the improvement of product quality and consistency by detecting and addressing probable sources of non-uniformity in the reactor.

1.8 Optimisation of CVD

The optimization of CVD processes is of paramount importance to ensure the successful fabrication of high-quality films and coatings. Failure to optimize the CVD process can lead to various undesirable outcomes. Without optimization, the deposition may result in inconsistent film quality, with variations in thickness, composition, and properties from batch to batch or across the substrate surface. This lack of control over film properties can severely limit the range of applications and compromise the performance of the deposited films. Inefficient material utilization is another consequence of poor optimization, leading to the wastage of expensive precursor gases and higher production costs. Additionally, non-uniform film growth, defects, or incomplete coverage can reduce the production yield and increase rejection rates. This not only impacts overall efficiency but also leads to increased costs and time consumption. Inadequate optimization may also result in films that do not adhere to the required specifications and fail to meet the desired performance criteria. Such deficiencies can lead to customer dissatisfaction, rejection of films, and potential loss of business opportunities. Therefore, optimization of the CVD process is essential to achieve consistent film quality, maximize material utilization, reduce costs, improve production yield, and ensure compliance with specifications and performance requirements (George et al., 2006; Lin et al., 2009b; Ramadan and Im, 2019a; Wissmann and Grover, 2010).

1.8 Techniques used for optimisation of CVD

There are several techniques and methods available for CVD processes (Chen, 2007; Creighton and Ho, 2001; del Coso et al., 2008; Hwang et al., 2021a; Jia et al., 2017a; Myers, 2018, 1999; Pierson, 1999; Teixeira et al., 2020; Wissmann and Grover, 2010). Here are some commonly used approaches:

1. **Response surface methodology (RSM):** Response Surface Methodology (RSM) in the Design of Experiments (DoE) is a statistical approach that systematically varies process parameters to analyze their impact on the deposition process. This method efficiently explores a broad parameter space, facilitating the identification of optimal conditions. Through statistical analysis, DoE assists in pinpointing key process variables and their interactions, leading to the development of predictive mathematical models for film properties and informed optimization strategies (Kober et al., 2022). RSM, as a statistical technique, utilizes mathematical models to optimize process parameters. It entails the design of a series of experiments based on a predefined set of input variables,

with the measurement of the response of interest. By fitting a mathematical model to the experimental data, RSM enables the prediction of optimal process conditions for desired film properties. This approach aids in determining the optimal combination of parameters that maximizes both film quality and process efficiency.

2. **Genetic Algorithms (GA):** The GA modelling technique is made up of two steps: computing the predicted outcomes from the reaction model candidates and updating the candidates based on the difference between experimental and anticipated results (Takahashi et al., 2005). Takahiro and colleagues demonstrated the efficacy of this methodology by successfully identifying suitable reaction models using both synthetic and authentic experimental data obtained during the thermal chemical vapour deposition (CVD) of tetraethylorthosilicate (Takahashi et al., 2005).

3. **Machine learning (ML) based techniques:** To model and optimise CVD processes, ML approaches like support vector machines, random forests and neural networks can be used. ML algorithms learn from historical data and develop predictive models to guide the optimization process. These models can help in understanding the complex relationships between process parameters and film properties, enabling efficient optimization of the CVD process (Hwang et al., 2021a; Jia et al., 2017a; Kadinski et al., 2004).

4. **Sequential Optimization and Response Surface Optimization (SORO):** SORO is a method that combines the principles of sequential optimization and response surface methodology. It involves multiple stages of optimization, where the output from one stage serves as the input for the next stage. By iteratively refining the process parameters based on response surface models, SORO helps in achieving progressively better results (Ramadan and Im, 2019b).

It is important to note that the selection of the optimization technique depends on various factors, including the complexity of the CVD process, available resources, and desired objectives. The combination of multiple techniques may also be employed for a comprehensive optimization approach (Chuang and Chen, 2014; Gupta et al., 2022a; Jia et al., 2017b; Ramadan and Im, 2019b). In summary, the use of CFD in the design of CVD reactors can provide a powerful tool for optimizing the reactor design and operation, improving process efficiency, reducing costs, and enhancing product quality and consistency.

1.9 Machine learning

Machine learning (ML) is a subset of artificial intelligence that enables computers to learn from data without being explicitly taught (Hwang et al., 2021a, 2021b; Kubat, 2017). ML algorithms have recently attracted significant attention in process modelling. They learn several parameters on their own by fitting the data. In addition, they are also computationally efficient and can be used in real-time prediction (Jia et al., 2017a). Several applications of ML are reported in the area of chemical and material process engineering. For example, the optical properties of the materials were predicted using ML and the relationship among various process parameters that were hard to establish using physics-based models (Wu et al., 2020a). Masoumi et al. integrated the wavelet neural network (WNN) and an experimental design to optimise the 2-litre bioreactor (Fard Masoumi et al., 2014). Recently, Chuang et al. proposed a data-driven optimisation technique that coupled a uniform design method, an artificial neural network, and a genetic algorithm to improve the GaAs growth. They observed that the proposed correlated the experimental data reasonably well and improved the performance of the film. In addition, the advantage of using ML, particularly the support vector machine (SVM) for optimising chemical processes, is high speed, accuracy, and robustness, and requires no or fewer human interventions (Chuang and Chen, 2014). Therefore, the rigorous model-based strategy can be framed using the ML method. It can then be coupled with an efficient optimisation technique to explore the optimal solution of the exceptionally complex process. There are several different types of machine learning, including:

1. **Supervised learning**: This is the most common sort of machine learning, in which a model is trained on labelled data and then used to predict unlabeled data.
2. **Unsupervised learning**: The model does not provide labelled data in this sort of machine learning, but rather is used to detect patterns or relationships within the data.
3. **Reinforcement learning:** This sort of machine learning is used to train models to make decisions or execute actions in a given environment to maximise a reward or achieve a goal.
4. **Deep learning:** This is a branch of machine learning in which neural networks are used to represent the structure of the human brain. Deep learning models are particularly

beneficial for applications such as image recognition, audio recognition, and natural language processing.

1.9.1 Advantages of Machine Learning

1. **Data-driven insights:** ML algorithms can extract valuable insights and patterns from large and complex datasets that may be difficult for humans to discern. They can uncover hidden relationships and correlations, leading to a deeper understanding of the data and enabling data-driven decision-making.

2. **Automation and efficiency**: ML automates repetitive and time-consuming tasks, reducing manual effort and increasing efficiency. Once trained, ML models can process and analyze large amounts of data quickly, allowing for faster decision-making and enhanced productivity.

3. **Predictive capabilities**: Based on historical data trends, ML models may make accurate predictions and forecasts. These predictive capabilities can be used to forecast sales patterns, predict equipment faults, or estimate client behaviour, allowing for proactive decision-making and enhanced planning.

4. **Adaptability and generalization:** ML algorithms can adapt to new data and changing conditions, allowing for continuous improvement and adaptation to evolving environments. They can generalize from training data to make predictions on unseen data, providing valuable insights beyond the available training set.

5. **Handling complex and large-scale data:** ML techniques excel in handling complex and large-scale data. They can handle diverse data types, including structured, unstructured, and multi-modal data, and effectively extract meaningful information from them.

1.10 Support vector machines (SVM)

The advantage of SVM for optimising chemical processes is its high speed, accuracy, and robustness, and it requires no or fewer human interventions saving considerable time and cost of performing actual experiments. The accuracy of SVM is better than the linear regression model. Some more advantages are given below:

1. **Effective in High-Dimensional Spaces:** Even in high-dimensional feature spaces, SVM works effectively. It is capable of handling datasets with a large number of features, making it appropriate for situations involving complicated and diverse data.
2. **Robust to Overfitting**: SVM employs a regularisation parameter (C) to help reduce overfitting, which is a prevalent issue in machine learning. SVM can generalise well to unknown data by regulating the trade-off between the model's complexity and its ability to fit the input.
3. **Versatility in Kernel Functions:** SVM is compatible with a wide range of kernel functions, including linear, polynomial, radial basis function (RBF), and sigmoid. SVM can capture nonlinear relationships in data and manage difficult decision limitations as a result of its adaptability.
4. **Global Optimization:** SVM aims to find the global optimum solution by minimizing the empirical risk, which helps in avoiding local minima. This property contributes to the model's stability and robustness.
5. **Ability to Handle Outliers:** In comparison to other algorithms, SVM is less sensitive to outliers. SVM's usage of the margin notion allows it to focus on support vectors, which are the data points closest to the decision border, rather than all data points.
6. **Memory Efficiency:** SVM uses a subset of training data called support vectors, which reduces memory requirements. Only the support vectors are used to define the decision boundary, making SVM memory-efficient, especially when dealing with large datasets.

1.11 Objectives of the thesis

The detailed research objectives are as follows:

1. To identify the most efficient and effective process parameters for producing high-quality pyrocarbon. This would involve analyzing the effects of various process variables, such as temperature, pressure, and reactant flow rate.
2. To achieve high-quality pyrocarbon by combined support vector machine (SVM) and Nelder-Mead algorithm by simultaneously maximising the average deposition rate and the uniformity index.

1.12 Thesis organisation

This thesis is organised into four sections, each of which focuses on optimising methane pyrolysis in a commercial CVD reactor using support vector machines and the Nelder-Mead algorithm. (a) process modelling and simulation; (b) assimilation of detailed gas and surface chemistry; (c) effect of process parameters; (d) machine learning-based optimization;
This thesis contains five chapters.

- Chapter 1 discusses the introduction, motivation, different types of CVD, the importance of CFD in designing the CVD reactor, the basics of machine learning technique and its types.
- Chapter 2 explains the history of CVD and its modelling and optimization technique, and discusses the pyrolysis of methane in CVD reactors using various machine learning methods.
- Chapter 3 shows the equations governing the modelling of physical and chemical phenomena for the CVD reactor, the gas and surface reaction model and the solution procedure. Subsequently, the optimization technique of NMA and SVM is explained.
- Chapter 4 examines the impact of reactor operating variables such as temperature, pressure, flow rate, and reactant concentration. And how these variables influence thickness and film uniformity.
- Chapter 5 presents the key observations and conclusions derived from the current research, highlighting the significance of SVM and Nelder-Mead Algorithm (NMA) in optimizing methane pyrolysis in a CVD reactor. Furthermore, it outlines the potential for future research in the field, aiming to further enhance the understanding and application of these techniques.

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