Process Design & Economic Analysis of Methane Pyrolysis for Production of Hydrogen from Natural gas

by



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Abstract

There is an increase in the amount of CO₂ emissions in the past few decades and the process of capturing it back is at a much lower rate. The need of the hour is to reduce the emission rate or even avoid producing them in certain aspects. There is a transition towards renewable energy sources that could help us maintain the balance required. Hydrogen is one of the energy sources that are at the forefront of this transition in the manufacturing and automotive industry, but without sustainable methods for producing hydrogen, it would not be a great alternative to existing energy sources like fossil fuels. Presently the most used method for hydrogen production is steam methane reforming from natural gas, which produces a significant amount of CO₂ during the process and needs to be captured which reduces the efficiency and thus higher energy requirements. To tackle the existing problems of CO₂ emissions and help in the transition towards sustainable hydrogen is the main goal of this study. The project focuses on producing low-emission CO₂ hydrogen from natural gas and biomethane by using a process called methane pyrolysis, an innovative process that does not produce any GHG emissions during the process, the produced hydrogen is called Turquoise Hydrogen. Here the study focuses on different types of hydrogen production methods and different methods within methane pyrolysis. This research helped in understanding and choosing the right type of methane pyrolysis method for further study and analyzing its process and economic advantages over traditional methods like the steam methane reforming process.

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Contents

1	Introduction 1							
2	Lite	rature Review 4						
	2.1	Hvdrogen & Applications						
	2.2	Natural Gas						
	2.3	Steam Methane Reforming						
	2.4	Water Electrolysis						
		2.4.1 Polymer Electrolyte Membrane Electrolyzers						
		2.4.2 Alkaline Electrolyzers						
		2.4.3 Solid Oxide Electrolysis						
	25	Biological Hydrogen Production 9						
		2.5.1 Direct biophotolysis						
		2.5.2 Indirect Biophotolysis 10						
	26	Methane Pyrolysis						
	2.0	2.6.1 Plasma pyrolysis 11						
		2.6.2 Thermal process or Thermal catalytic process						
		2.6.2 Anternal process of Anternal outdry to process						
		2.6.6 Carbon product						
	27	Process Selection 16						
	2.1	271 Design & Requirements						
	28	Intial Design						
	2.0	2.8.1 Main Reactor 18						
		2.8.2 Cyclone 18						
		2.0.2 Cyclone						
		2.0.3 FOR						
3	Proc	cess Simulation & Analysis 21						
	3.1	Thermal Methane Pyrolysis						
		3.1.1 Components Design						
		3.1.2 Mass and Energy Balance						
		3.1.3 Fuel consumption						
	3.2	Techno-Economic analysis						
		3.2.1 Evaluation of investment costs						
		3.2.2 Sensitivity Analysis						
	C ~ n	valuation and Recommandation 27						
4		Iclusion and Recommendation 37						
	4.I							
	4.2	Fulure work						
Re	ferer	nces 40						

Introduction

There has been a growing need for the reduction of Greenhouse gas(GHG) emissions, especially CO_2 emissions. The vast effects of CO_2 on the climate change due to its greenhouse effect have been an issue of concern. The main contributors to these emissions are fossil fuels. Continuous burning of fossil fuels for energy consumption has caused an imbalance in the amount of CO_2 present in the atmosphere. This can cause some irreversible effects like seasonal and climate changes that can affect the ecosystem. Renewable energy sources have been the best alternative for our energy demand due to their ability to generate energy that produces no greenhouse gas emissions from fossil fuels and reduces some types of air pollution [1].

Based on the grand strategy presented by Kaya at Tokyo Conference on Global Environment, a generalized equation called the Kaya equation was developed in tackling the CO_2 emissions. Based on this general equation, the following mitigating paths are possible to limit CO_2 emissions [2]:

- Limit population growth
- · Improve the efficiency of conversion and utilization of energy
- · Utilize non-fossil energy sources(nuclear, solar wind, hydro and geothermal energy)
- Increase biomass production and utilization including forestation agriculture and aquaculture (algae, etc).
- · Decarbonization of fossil fuels
- · Sequestration of carbon from fossil fuels
- Reduce Energy consumption

But to implement this and achieve the above scenarios takes time due to the scarcity and cost factors of non-fossil fuels and there is a need for short-term solutions to tackle the fast-growing problems related to GHG emissions. This can either be by not producing CO_2 at all or by decarbonization. There are two methods of preventing CO_2 from entering the atmosphere due to the utilization of fossil fuels as an energy source. Remove carbon before combustion or remove carbon after combustion. Removal of carbon from fossil fuels prior to combustion requires removal and sequestration of carbon either as CO_2 or as elemental carbon. Removal of carbon post-combustion requires sequestration of carbon only as CO_2 . These methods are called decarbonization [2].

To overcome the limitations of current H_2 production methods, the concept of thermal methane pyrolysis (TMP), where H_2 and carbon (C) are directly produced in the gas phase, has been paid attention to as an alternative, novel H_2 production method owing to several technical, economic, and environmental benefits as follows [3]:

- There is no oxygen (O₂) in the reaction leading to no CO₂ emissions or additional separation process, theoretically
- The process can be relatively simplified and lower energy is required than other methods such as reforming or partial oxidation
- The reactant of the process, methane, is abundant and cheap leading to a cost-effective operation of the process
- C products can be marketed because they are usually used as raw materials in various valuable materials such as rubber, tires, and pigments, etc.
- the separation of C is much easier than the separation of CO2

This study will focus on the hydrogen industry and how we could implement decarbonization into hydrogen production methods while keeping it safe and economical. Hydrogen as fuel could be a game changer in the energy sector due to its zero carbon emissions, but a major setback presently is the production methods for hydrogen. These production methods contribute to a significant amount of CO_2 emissions and there is a need for tackling this issue. This is an important step in making hydrogen a truly sustainable fuel for the future and contributing to the energy sectors.

To meet the demands of hydrogen we need to have a continuous production method that is sustainable, economical, and easy to produce. Hydrogen is the ultimate form of decarbonized fuel. The most used method for hydrogen production is steam methane reforming. 98% of the hydrogen production comes from fossil fuels reforming with huge direct impacts on CO_2 emissions corresponding (world average, source DOE 2013) to 12 kg CO_2 eq. per kg of H₂.Giving rise to 720 Million tons CO_2 eq. emissions per year representing by itself no less than 2.25% of the total worldwide CO_2 emissions [4].

To avoid these emissions, technologies like water electrolysis have been of immense interest for producing hydrogen, but due to its high energy demand, its difficult to produce the required energy from renewable sources. Until there is a continuous way to produce this energy, it's not viable for producing hydrogen. This also depends on the location where the hydrogen production method is present. Thus there is a need for a quick solution to avoid CO_2 emissions without major changes.

Therefore, the study and the project of the chosen technology need to answer the following research questions for a better perspective on the feasibility of the technology and why it could be the best alternative to the existing processes:

- What could be an immediate alternative for producing H₂ that could solve the GHG emission issues and compete in energy usage with conventional methods?
- What alternative can be used with fewer design complexities and competing economically with all types of hydrogen production methods?
- Can this alternative compete with sustainable green hydrogen production methods in the long run?
- Could methane pyrolysis be feasible in terms of practicality, costs, and GHG emission issues for the selected target output?
- What kind of kinetic model needs to be used for designing the main reactor if the process?
- What are the effects of carbon catalyst in the process and regeneration of the catalyst for the design made?
- · How can the solid particles be separated effectively from the gas?

The study also focuses on choosing the right hydrogen technology for producing hydrogen in a sustainable and cost-effective manner. The right technology will help in the transition from grey hydrogen technologies to green hydrogen technologies. The method that is chosen is methane pyrolysis where methane is decomposed to form solid carbon and hydrogen without any CO_2 during the process thus eliminating emissions and implementing decarbonization.

The study will also give a brief intro to hydrogen and its applications and the existing hydrogen technologies. Methane pyrolysis & its types will be the focus of the study since this is the chosen technology for tackling CO_2 emissions. An initial design of Thermal methane pyrolysis is made which is simulated in Aspen Plus to find its techno-economic aspects. Methane/natural gas is chosen as the main feed for the majority of hydrogen production methods and is also the main feed in methane pyrolysis as well.

\sum

Literature Review

This chapter gives brief details on hydrogen and its existing technologies in the present market along with the feasibility of these technologies. The type of process used also determines the color spectrum of hydrogen produced, which will be mentioned in detail.

2.1. Hydrogen & Applications

Hydrogen (H_2), is a colorless, odorless, tasteless, flammable gaseous substance that is the simplest member of the family of chemical elements. Even though hydrogen is the most abundant element in the universe, it exists more in carbon compounds than as a separate element [5]. That is why to unlock the full potential of hydrogen as an energy alternative we need to extract this hydrogen based on the demands.



Figure 2.1: Applications of Hydrogen [6]

There are several applications of hydrogen in the modern day and also been used for decades safely. The industry has safely used hydrogen for decades in the following applications[7]:

- · Petroleum refining
- · Glass purification

- · Semiconductor Manufacturing
- · Aerospace applications
- · Fertilizer production
- · Welding, annealing and heat-treating metals
- · Pharmaceuticals
- · As a coolant in power plant generators
- · For hydrogenation of unsaturated fatty acids in vegetable oil

New markets are emerging for industrial trucks (e.g., forklifts) and passenger cars powered by hydrogen fuel cells. Indoor and outdoor hydrogen fueling stations are being built in support of these vehicles. A fuel cell is a device that combines hydrogen with oxygen from the air in an electrochemical reaction to create electricity, which can power an electric motor and propel a vehicle. Fuel cells are twice as energy-efficient as combustion engines, and the hydrogen used to power them can come from a variety of sources, including renewable energy resources. A hydrogen fuel cell emits only heat and water, without producing any air pollutants or greenhouse gases [7].

For transportation in particular, hydrogen would offer immediate benefits in terms of reduced pollution and a cleaner environment [8]. Hydrogen is majorly used for the synthesis of ammonia and other nitrogenated fertilizers, refining and desulphurization (hydrogenation reactions, hydrodesulfurization), hydrogenation of hazardous wastes (dioxins, PCBs), chemical plants, food preparation, synthesis of methanol, ethanol, dimethyl ether (DME), alternative fuels synthesis by Fischer–Tropsch (FT) synthesis, gas to liquid (GTL) synthesis technology, rocket fuel, IC engine fuel, high-temperature industrial furnaces fuel, etc. Primarily, hydrogen is consumed for the production of ammonia, and other chemicals, and in petro-chemistry [9].



Figure 2.2: Types of hydrogen production methods [10]

Hydrogen can be extracted from various sources like fossil fuels and biomass, or from water. Around 275 Mtoe of energy is used for the production of hydrogen today (2% of global total primary energy demand). Out of all these sources, natural gas is currently the primary source of hydrogen production, and the steam methane reforming process contributes towards the major share of hydrogen production in the ammonia and methanol industries and in refineries. Natural gas accounts for around three-quarters of the annual global dedicated hydrogen production of around 70 million tonnes of hydrogen (MtH₂), using around 205 billion cubic meters (bcm) of natural gas (6% of global natural gas use). Coal comes next, due to its dominant role in China: it accounts for an estimated 23% of global dedicated hydrogen production and uses 107 Mt of coal (2% of global coal use). Oil and electricity account for the remainder of the dedicated production [11].

2.2. Natural Gas

The main source for producing most of the hydrogen in the world is Natural gas. Natural gas is a fossil energy source that formed deep beneath the earth's surface. Natural gas contains many different compounds. The largest component of natural gas is methane, a compound with one carbon atom and four hydrogen atoms (CH₄). Natural gas also contains smaller amounts of natural gas liquids (NGLs, which are also hydrocarbon gas liquids), and nonhydrocarbon gases, such as carbon dioxide and water vapor. We use natural gas as a fuel and to make materials and chemicals [12]. Natural gas is essentially methane (83 to 97% volume depending on origin) and therefore difficult to liquefy and it is chemically quite unreactive [13]. Table 2.3 gives the description of the composition of natural gas [14].

Components	Chemical composition	Range (mole %)
Methane	CH ₄	70-90
Ethane	C_2H_6	0-20
Propane	C_3H_8	0-20
Butane	$C_{4}H_{10}$	0-20
Carbon dioxide	CO_2	0-8
Oxygen	O_2	0-0.2
Nitrogen	N_2	0-5
Hydrogen sulhide	H_2S	0-5
Rare gases	A, He, Ne, Xe	trace

Figure 2.3: Composition of natural gas [14]

The processes require H_2S removal to avoid damage to the components and to provide better efficiency. Natural gas with a higher percentage of H_2S is usually referred to as Sour gas.

2.3. Steam Methane Reforming

Steam Methane Reforming is a mature production process in which high-temperature steam $(700^{\circ}\text{C}-1,000^{\circ}\text{C})$ is used to produce hydrogen from a methane source, such as natural gas. In steam-methane reforming, methane reacts with steam under 3–25 bar pressure (1 bar = 14.5 psi) in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. Steam reforming is endothermic, that is, heat must be supplied to the process for the reaction to proceed [15]. The heat required for this process is obtained by burning fossil fuels which produce a huge amount of CO₂. Venting of CO₂ generated during steam reforming process to atmosphere causes global warming [16].

There are multiple reactions involved within the steam methane reforming process for the production of hydrogen from natural gas.

$$CH_4 + H_2O < - > CO + 3H_2$$
, $\Delta H_{298} = 206 \text{ kJ/mol}$ (2.1)

$$CH_4 + 2H_2O < -> CO_2 + 4H_2$$
, $\Delta H_{298} = 164.9 \text{ kJ/mol}$ (2.2)

$$CO + H_2O < - > CO_2 + H_2$$
, $\Delta H_{298} = -41 \text{ kJ/mol}$ (2.3)

Reactions (2.1) and (2.2) are strongly endothermic whereas reaction (2.3) is mildly exothermic. The stochiometric balance indicates that the first two equations (2.1) and (2.2) are favored by a decrease in pressure whereas equation (2.3) remains unaffected as per Le Chatelier's principle. The first step is reforming[reactions (2.1) and (2.2)] and is carried out at 750–800°C to produce synthesis gas (mixture of CO and H₂). The second step is the water gas shift (WGS) reaction(2.3), which involves the catalytic reaction of CO with steam to form H₂ and CO₂. This step essentially involves a high-temperature shift (HTS) at 350°C followed by a low-temperature shift (LTS) at 190–210°C [17].



Figure 2.4: Process flow diagram of SMR [18]

In a final process step called "pressure-swing adsorption," carbon dioxide and other impurities are removed from the gas stream, leaving essentially pure hydrogen. Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane, or even gasoline [19]. The type of hydrogen produced is grey hydrogen since it is produced using natural gas. There is also a gasification process that uses coal as feedstock, which produces brown hydrogen.



Figure 2.5: Hydrogen types [20]

Blue hydrogen uses the same process as grey, except this time the carbon is captured and stored. This makes it much more environmentally friendly but comes with added technical challenges and a big increase in cost. Carbon capture and storage (CCS) has been around for a while, with the technology being used by heavy industry and power generation companies burning fossil fuels. The technology can capture almost all of the CO_2 produced, so it isn't perfect but clearly a massive improvement. CCS can be implemented with the SMR process, but there needs to be a fine line between the costs with respect to reducing the CO_2 emissions [20]. Figure 2.6 refers to the processes that use methane for producing hydrogen. The figure gives insight into the amount of hydrogen we get from SMR, which is way less efficient than methane pyrolysis. One of the many reasons why there is a need for an alternative for SMR is that it produces CO and CO_2 , which is more of a liability than an asset, Whereas we can see that we get carbon black powder from methane pyrolysis which can be another product to sell without extra worries about emissions.

Methane based hydrogen production processes								
Process	Steam methane reforming	Methane pyrolysis (splitting or cracking)	Methane partial oxidation (gasification)	Methane combustion (thermal oxidation)				
Oxygen feed	From steam	None	From ASU	Air				
Catalyst	Usually nickel	None	None	None				
Carbon product	as CO and CO	Carbon black powder	as CO and CO	CO,				
Hydrogen in product	70% -	95%	60%	None				
Product gas pressure, bar	15-40	15	40-80	15				
Product gas temp, °C	850	1700	1400	1400				

Figure 2.6: Methane based hydrogen production [21]

2.4. Water Electrolysis

Electrolysis of water is one of the most capable methods for the production of hydrogen because it uses renewable H_2O and produces pure oxygen as a by-product. Additionally, in the electrolysis process, it utilizes the DC power from sustainable energy resources i.e solar, wind, and biomass. During the electrolysis process, the water molecule as the reactant is dissociated into hydrogen (H_2) and oxygen (O_2) under the influence of electricity. Water electrolysis can be classified into four types based on their electrolyte, operating conditions, and ionic agents (OH^- , H^+ , O_2^-). The four kinds of electrolysis methods are [10]:

- Alkaline water electrolysis (AWE)
- Solid oxide electrolysis (SOE)
- Microbial electrolysis cells (MEC)
- · PEM water electrolysis

Eco-friendly and high-purity of hydrogen (99.999%) can be obtained from the electrolysis of water to produce pure hydrogen and oxygen. The basic reaction is described in (2.4) [10].

$$H_2O + Electricity(237.5 \text{ KJ/mol}) < - > H_2 + 1/2O_2 + Heat(48.6 \text{ KJ/mol})$$
 (2.4)

Like fuel cells, electrolyzers consist of an anode and a cathode separated by an electrolyte. Different electrolyzers function in different ways, mainly due to the different types of electrolyte material involved and the ionic species it conducts.

2.4.1. Polymer Electrolyte Membrane Electrolyzers

In a polymer electrolyte membrane (PEM) electrolyzer, the electrolyte is a solid specialty plastic material[22].

- Water reacts at the anode to form oxygen and positively charged hydrogen ions (protons).
- The electrons flow through an external circuit and the hydrogen ions selectively move across the PEM to the cathode.
- At the cathode, hydrogen ions combines with electrons from the external circuit to form hydrogen gas.
- Reactions: Anode Reaction: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ Cathode Reaction: $4H^+ + 4e^- \rightarrow 2H_2$

2.4.2. Alkaline Electrolyzers

Alkaline electrolyzers operate via transport of hydroxide ions (OH⁻) through the electrolyte from the cathode to the anode with hydrogen being generated on the cathode side. Electrolyzers using a liquid alkaline solution of sodium or potassium hydroxide as the electrolyte have been commercially available for many years. Newer approaches using solid alkaline exchange membranes (AEM) as the electrolyte are showing promise on the lab scale [22].

2.4.3. Solid Oxide Electrolysis

Solid oxide electrolyzers, which use a solid ceramic material as the electrolyte that selectively conducts negatively charged oxygen ions (O_2^-) at elevated temperatures, generate hydrogen in a slightly different way[22].

- Steam at the cathode combines with electrons from the external circuit to form hydrogen gas and negatively charged oxygen ions.
- The oxygen ions pass through the solid ceramic membrane and react at the anode to form oxygen gas and generate electrons for the external circuit.

Solid oxide electrolyzers must operate at temperatures high enough for the solid oxide membranes to function properly (about 700°–800°C, compared to PEM electrolyzers, which operate at 70°–90°C, and commercial alkaline electrolyzers, which typically operate at less than 100°C). Advanced lab-scale solid oxide electrolyzers based on proton-conducting ceramic electrolytes are showing promise for lowering the operating temperature to 500°–600°C. The solid oxide electrolyzers can effectively use heat available at these elevated temperatures (from various sources, including nuclear energy) to decrease the amount of electrical energy needed to produce hydrogen from water[22].

But for electrolysis to be adapted on a larger scale and compete with existing processes like steam methane reforming process it needs to address the following aspects:

- · Reducing capital costs for the electrolysis system
- continuous and cheap electricity for the energy demand should be provided from renewable sources
- Improving energy efficiency for converting electricity to hydrogen over a wide range of operating conditions.
- Improving its operational life.

2.5. Biological Hydrogen Production

2.5.1. Direct biophotolysis

This method is similar to the processes found in plants and algal photosynthesis. In this process solar energy is directly converted to hydrogen via photosynthetic reactions (2.5).

$$2H_2O + \text{'light energy'} \rightarrow 2H_2 + O_2.$$
 (2.5)

Algae split water molecules to hydrogen ion and oxygen via photosynthesis. The generated hydrogen ions are converted into hydrogen gas by hydrogenase enzyme. Chlamydomonas reinhardtii is one of the well-known hydrogen producing algae. The advantage of this method is that the primary feed is water, which is inexpensive and available almost everywhere [23].

A direct biophotolysis method must operate at a partial pressure of near one atmosphere of O_2 , which is a thousand-fold greater than the maximum likely to be tolerated. Thus, the O_2 sensitivity of the hydrogenase enzyme reaction and supporting reductant generating pathway remains the key problem, as it has been for the past 30 years. Hydrogen production by direct photolysis using green algae is currently limited by three parameters:

· Solar conversion effciency of the photosynthetic apparatus

- H₂ synthesis processes (i.e. the need to separate the processes of H₂O oxidation from H₂ synthesis)
- · Bioreactor design and cost

A number of approaches to improve H2 production by green algae are currently under investigation. These include genetic engineering of light gathering antennae,optimization of light input into photo bioreactors, and improvements to the two-phase H₂ production systems used with green algae [23].

2.5.2. Indirect Biophotolysis

In indirect biophotolysis, problems of sensitivity of the hydrogen evolving process are potentially circumvented by separating temporally and/or spatially oxygen evolution and hydrogen evolution. Thus indirect biophotolysis processes involve separation of the H_2 and O_2 evolution reactions into separate stages, coupled through CO_2 fixation/evolution. Cyanobacteria have the unique characteristics of using CO_2 in the air as a carbon source and solar energy as an energy source. The cells take up CO_2 first to produce cellular substances, which are subsequently used for hydrogen production. The overall mechanism of hydrogen production in cyanobacteria can be represented by the following reactions[23]:

$$12H_2O + 6CO_2 + \text{`light energy'} \rightarrow C_6H_{12}O_6 + 6O_2$$
 (2.6)

$$C_6H_{12}O_6 + 12H_2O + \text{'light energy'} \rightarrow 12H_2 + 6CO_2$$
 (2.7)

2.6. Methane Pyrolysis

The above methods either have problems with CO_2 sequestration or high energy requirements that cannot be met by sustainable methods, Thus we require a solution that can tackle these issues and Methane pyrolysis could be the answer to the above problems.

Methane Pyrolysis is a zero CO/CO_2 -emitting process. Hence, this process cancels the need for CCUS. The only byproduct recovered with the hydrogen is the solid carbon that is normally valuable and could be commercialized after purification. Thereafter, it can be used in many applications, such as double-layer capacitors, polymers (e.g., rubber reinforcement for the tire industry), carbon nanofiber-based composites, precursors of graphitic materials to be used as anodes in Li-ion batteries, etc. However, the current carbon market is still highly limited and most carbon byproduct has to be stored until new applications are found [24]. The reaction is represented by:

$$CH_4 \to C(s) + H_2 \tag{2.8}$$

Methane pyrolysis reaction is moderately endothermic. The energy requirement for methane pyrolysis process (37.8 kJ/mole of H_2) is less than that for steam reforming process (63.3kJ/mole of H_2). Due to this relatively low endothermic nature of methane cracking process, less than 10% of methane combustion heat is needed to drive this process [4]. Alternatively the heat required for the methane pyrolysis can be supplied by burning 10 - 15 wt% of hydrogen produced. Also methane pyrolysis process doesn't require water gas shift reaction and CO₂ removal stages which significantly simplifies the process. As a by product it also produces clean carbon which can be utilized in metallurgical industries. The methane cracking reaction is carried out in the presence of either a carbon catalysts at 850°C or nickel based catalysts at 550°C [16].

There are different configurations of reactors for methane pyrolysis based on years of research to find solutions to the problems that have occurred during this process. The figure 2.7 refers to the configurations of the reactors that are in process or being researched. Based on the requirements of the output, a method is chosen from the Figure 2.7 for further analysis.

Methane pyrolysis processes								
Process	Plasma pyrolysis	Fluidised bed	Moving carbon bed	Molten metal or molten salt				
Developer	Monolith materials	Hazer	BASF	C-Zero				
Hydrogen at outlet	95%	92%	92%	95%				
Carbon production	Carbon black powder/ Granules	80-95% graphite + catalyst dust	Carbon black powder/ granules	Carbon granules				
Catalyst	None	Iron oxide	Carbon bed	Molten manganese chloride				
Reactor temp, °C	1700	900	1000-1400	650				
Reactor pressure	Close to atmospheric	Close to atmospheric	Close to atmospheric	Up to 5 bar				

Figure 2.7: Methane pyrolysis reactors configurations [21]

There are different options for the external heat supply. Indirect heating using burners fuelled by hydrogen or natural gas as a fuel. It is also possible to use indirect electrical heating or direct heating with an electrical plasma. These heating modes could use renewable electricity, biomethane, or low carbon hydrogen to minimise CO_2 emissions from the process [21].

Methane pyrolysis can be performed with or without a catylyst. Methane decomposition in the absence of catalyst requires high temperature, i.e. 1200°C for a practically good yield of hydrogen. The difficulty in direct methane conversion by catalytic and/or thermal processes is the strength of the methane C|H bond. The Gibbs free energy of methane is less than that of the products. The employment of catalyst significantly reduces reaction temperature, and also controls properties and type of co-products i.e. carbon species. There are three different types of catalysts for the methane decomposition (1) noble metals such as (Rh, Ru and Pt), metals from group VIII of transition elements and (3) carbonaceous materials. One of the main challenges accompanying with metal catalysts is the deactivation and recovery; the deposition of carbon formed covers the active sites during the reaction. The carbon formed in this reaction is one of the products, which means its production cannot be stopped. So reaction system and catalyst should be structured to retain good activity and stability despite the formation of substantial amounts of carbon [25].

2.6.1. Plasma pyrolysis

In this method, methane is heated to 1650°C using an argon plasma generated by electrodes powered by renewable energy sources. This method was adopted and implemented by Monolith Materials in 2012. At this temperature, the methane molecule splits. This eventually leads to the formation of carbon black, while the protons split off from the methane molecule and recombine to form hydrogen molecules. The graphite electrodes may provide some catalytic effect and the initially formed carbon black granules catalyse the production of additional carbon black. In various papers related to methane pyrolysis, various additives to the methane have been identified that can either stimulate the reaction or enhance the physical properties of the carbon black. The reaction takes place without the need for an additional solid catalyst. The prospect of producing turquoise hydrogen from renewable electricity means that this will be a carbon neutral hydrogen generation process, if the process can cope with the volatility of wind and solar electricity supply. If the electricity is sourced via a power purchase agreement (PPA) then the operation would need to follow the electricity supply of the associated wind and solar farms, which seems to be challenging [21].

Although thermal plasma sources have typically high energy consumption, the parameters of the process can be set such that the hydrogen of high purity and carbon particles of high quality are produced. Several authors reported plasma-assisted methane pyrolysis accompanied by hydrogen and carbon black production. Fincke et al. described the pyrolysis of methane to hydrogen and carbon black in a thermal plasma reactor in detail [26].



Figure 2.8: Types of methane pyrolysis methods [27]

Figure 2.8 represents a general design of plasma pyrolysis. Most of the authors conclude that the main advantage of the thermal plasma application for methane pyrolysis is the production of carbon black, carbon nanotubes, graphene nanosheets and other carbon structures of high quality, with the possibility of variations of its parameters. In most of the mentioned papers, acetylene is considered as a product, which may complicate the efficient hydrogen and carbon production. Two main reasons are mentioned: Firstly, acetylene can be easily produced also at high temperatures, which are typical for plasma processes. The second reason has to do with the residence time of the reactants in the reactor and achieving the equilibrium state [28].

2.6.2. Thermal process or Thermal catalytic process

In thermal pyrolysis, methane dissociates into hydrogen and carbon at temperatures between 1,000 °C and 1,500 °C. Differentiation revolves around the type of reactor used in the process. BASF utilizes an electrically heated moving bed reactor where carbon granules flow counter to the gas phases and methane pyrolyzes directly on the granules at 1,400 °C. KIT passes methane through a liquid tin bubble column reactor at 1,200 °C, where the solid carbon formed floats on top of the liquid and can be separated through undisclosed means. TNO also uses a molten metal reactor operating above 1,000 °C and separates out the carbon black from the liquid metal using molten salt [29].

The technology developed by BASF uses a moving bed reactor. In a moving-bed reactor, carbon granules are conducted in counterflow to the gas phase at temperatures of up to 1400°C. The cold gas flow is preheated by the hot granules leaving the reactor. In the reaction zone, the carbon bed is directly heated by electrodes. It is postulated that the pyrolysis reaction takes place mainly at the surface of the granules. This assumption is supported by the observed growth of the carbon granule particles passing through the reactor. The hot product gas leaving the reactor finally heats the cold carbon granules entering the reactor. Depending on the desired hydrogen quality, treatment of the product gas by pressure swing adsorption (PSA) is suggested [27].

An alternative approach for the continuous decomposition of hydrocarbons is the utilization of liquid metals as a heat transfer fluid in a bubble column reactor, together with the Institute for Advanced Sustainability Studies e. V. (IASS), a research group at the Karlsruhe Institute of Technology (KIT) developed a process for methane pyrolysis in liquid metal to produce hydrogen. In this process, methane is thermally decomposed at temperatures of up to 1200°C when passing through a liquid tin filled bubble column reactor [27].

In this process, methane gas is injected into a liquid metal bubble column and decomposes inside of the formed bubbles which are rising up in the reactor. The bubble opens at the upper interface of the liquid metal, releasing the produced carbon and hydrogen but also the remaining methane gas and the formed gaseous intermediates. The energy efficiency for such a methane pyrolysis process in a



Figure 2.9: Types of methane pyrolysis methods [21]

liquid metal bubble column reactor cannot be reliably established, based on existing laboratory scale experiments as the design for a large scale facility is not yet clear. In general, depending on the feed gas stream, energy is necessary for the endothermic reaction as well as for heating the methane gas and to maintain the liquid tin at reaction temperature, while the hot product gases and the produced carbon leave the reactor. Additionally, the application of carbon and product gas separation technologies consume an unknown amount of energy, whereas heat recuperation could counteract. Also the energy needed to cover the heat loss of the liquid bubble column strongly depends on the insulation and finally on the future reactor design [30].

2.6.3. Catalytic process

In catalytic pyrolysis, methane breaks down into hydrogen and carbon over a metal catalyst, which is typically nickel- or iron-based, at temperatures of less than 1,000 °C. The carbon from the methane forms graphite on the catalyst surface and hydrogen is released. Subsequently, the carbon-covered catalyst exits the reactor together with the hydrogen gas. The reactors used for this presently are fluidized bed reactor and bubble reactor and the catalysts used are carbon, or metals like nickel, iron ore [29],[27].

Some of the issues while using metal catalysts are the separation of produced carbon black from the molten metal catalyst and the technical difficulties in regenerating the catalyst. The regeneration of catalyst is also a factor that needs to be focused in further research.

Metal Catalysts: Transition metals like Ni, Fe, and Co have been widely studied as active species for methane pyrolysis due to their high activity, moderate operating temperature, and the possibility of producing valuable carbon nanotubes as by-product [31] [32] [33]. Their 3d orbitals are partially filled and can accept electrons from the C–H bonds of methane, which facilitates its decomposition [31] [32]. These metals also offer high solubility and carbon diffusion through their crystalline structure [34]. Nickel-containing catalysts have been extensively investigated since Ni is considered the most active metal for this process [35] [36]. However, nickel-based catalysts deactivate rapidly at temperatures above 600°C because the active metal sites are encapsulated within the carbon formed during the reaction [37] [31]. In the case of cobalt catalysts, their activity is lower compared to nickel catalysts. In addition to this, cobalt has toxicity issues and a higher cost than nickel. since the carbon by-product is contaminated with the active metal, the use of nickel or cobalt catalysts should be avoided due to their high toxicity. Consequently, cheaper and safer catalysts, such as iron materials, are needed for the industrial application of methane pyrolysis [38].

Carbon Catalysts: The main problem associated with the use of metal catalysts in the pyrolysis of methane is their rapid deactivation. This is a consequence of the encapsulation of the active sites by the carbon produced during the reaction. To tackle this issue carbon catalysts can be good alternative.Carbon materials usually exhibit lower catalytic activity than metal catalysts and must operate at relatively high temperatures of around 800–1,100°C to achieve good hydrogen yields. Despite this the carbon catalysts have various advantages [38].

Some of the advantages that we see in a carbon catalyst are [38]:

- · Lower in cost than metal catalysts
- · Have much better resistance to temperature and better stability among the catalysts.
- · Safe storage of the carbon product due to non-toxicity.
- Tolerance to impurities, e.g., the presence of H₂S in natural gas can be tolerated by carbon.
- · No contamination of the carbon by-product with metal particles.
- Mitigation of CO₂ emissions (unlike metal catalysts: the regeneration of metal catalysts by burning the carbon accumulated on the catalyst surface produces significant amounts of CO_x).
- The produced carbon may also have some catalytic effects.
- No need for catalyst regeneration in most cases.

The reason for choosing a catalyst along with the thermal decomposition process is to reduce the reaction temperature and speed up the process. The benefits of going with carbon-based thermal methane pyrolysis (TMP) over other catalytic processes are:

- Purification of natural gas is not required as impurities such as N₂ are inert and Carbon black is resistant to H₂S when present in small quantities.
- The carbon black produced can be used as a catalyst for the process, thus removing the separation step required when using metal catalysts.
- · Carbon products are cheaper and more abundant than metal catalysts.
- Working in the temperature range of 1000-1400°C makes sure of complete conversion of other hydrocarbons like ethane and propane as this temperature range is the ideal range for carbon TMP.

Catalyst Regeneration: Catalyst deactivation can be regarded as the transformation of the catalyst surface from an active state in the fresh sample to an inactive/inert state in the used sample. The carbon that is produced during methane pyrolysis deposits on the catalyst surface usually has a lower surface area and catalytic activity than the original carbon catalyst owing to the structure of the former tends to be more graphitized. The process of new carbon phase build-up is assumed to be a combination of two steps: carbon-nuclei formation and carbon-crystallite growth. And the rate of catalyst deactivation is considered to be the sum of the two steps. Various carbon materials have been evaluated as catalysts for methane pyrolysis in the last decades, such as activated carbon (AC), carbon black (CB), glassy carbon, acetylene black, graphite, diamond power, coal char, soot, fullerenes, carbon nanotubes (CNTs), carbon nanofibers (CNFs), and ordered mesoporous carbon. Among these carbon materials, AC and CB are the two most common carbon catalysts that are used for the process. Combustion and gasification of the carbon deposits are the two common approaches for catalyst regeneration. Oxygen (or air), steam, and carbon dioxide are the most popular activating agents by equations 2.9 respectively [39].

 $\begin{array}{c} \textbf{C} + \textbf{O}_2 \rightarrow \textbf{CO}_2 \ ; \\ \textbf{C} + \textbf{H}_2 \textbf{O} \rightarrow \textbf{CO} + \textbf{H}_2 \ ; \\ \textbf{C} + \textbf{CO}_2 \rightarrow 2\textbf{CO} \end{array} ;$

Regeneration of the deactivated carbon catalysts can be carried out by pulsed or continuous injection of the activating agents [119] at the same temperature as that of the methane pyrolysis process reaction or the elevated temperatures. However, the regeneration process is not limited to the deposited carbon part of the initial carbon catalyst can be also gasified or burned off, especially at the elevated regeneration temperature. Larger surface area and more oxygenated surface groups even can be obtained at some severe regeneration conditions, but a progressive decrease in the burn-off, surface area, and oxygenated surface groups was observed during the successive deactivation-regeneration cycle. It is probably attributed to the graphite-like structure of the deposited carbon, which is more resistant to gasification/burn-off than the initial carbon catalyst. As a result, generally, regeneration of the deactivated catalyst could not succeed in reactivating the original activity of the initial carbon catalyst in methane pyrolysis [40] [41] [42].

The reactor for catalyst regeneration is modeled as a Gibbs energy reactor. The reactor will be used for the regeneration of the carbon catalyst as well as some of the produced carbon to act as catalysts. The regeneration process is done through the gasification of carbon with steam.

2.6.4. Carbon product

Carbon is a major product of methane pyrolysis, so an economic benefit could be created depending on its quality. Different carbon structures have been reported over metal and carbon catalysts. The kind and quality of the obtained carbon strongly depends on the reaction conditions and the catalyst applied. The formation of carbon nanotubes and carbon nanofibers generally occurs over metal catalysts [43]. Carbon nanotubes have also been used as a catalyst in the pyrolysis of methane. Here, the growth of the nanotube walls is favored and the formation of multi-walled carbon nanotubes takes place [43]. The characteristics and grade of the carbon by-product determines its selling price and subsequent commercialization.

Therefore, obtaining a valuable carbon product may generate profits and improve the economics of the process on an industrial scale [44].Nevertheless, if methane pyrolysis is implemented industrially, the current market will not be able to absorb the large amounts of carbon produced [45]. In addition, since the carbon market is unlikely to increase in the coming years, the economic viability of the process cannot depend on carbon commercialization [38].

Different types of carbon products can be formed during methane pyrloysis. The reaction and process parameters dictates the type of carbon produced. The parameters are: reaction temperature and presence of catalyst. The graph 2.10 displays the type of carbon formed with respect to the temperature and different types of catalysts present during thermal decomposition of methane(TDM).

Metal catalysts in TDM have a tendency to produce filamentous carbon products whereas the carbon catalyzed or thermal decomposition of methane produce mainly graphite-like carbon or carbon black. The properties of carbon products (such as quality, purity and morphology) arising from TDM have been studied in more depth during recent years. Especially studies reporting nanotubes and their formation mechanisms have been presented more during the last ten years. Although the main component in the catalyst (metal/carbon) defines the morphology of the product carbon, the other catalyst properties (such as the catalyst pretreatment, support material, particle size and phase of the catalyst) are also important. The nanofibers and nanotubes that can be produced by metal catalysts have a higher value if the metal residues in the carbon product can be separated [46].



Figure 2.10: Types of carbon products produced based on the reaction parameters [46]

This chapter focuses on choosing the type of process for production of hydrogen and developing a initial design for the process that would be studied further for doing a techno-economic analysis. The conventional processes like steam methane reforming and future technologies like water electrolysis have a lot of problems associated with them. So we require a process that has the potential to tackle these problems

2.7. Process Selection

Before the design, first a right process needs to be selected which has potential to solve some of the problems faced by existing processes. The process selected needs to solve/ answer the research questions mentioned in Chapter-1.

Methane pyrolysis could answer the above questions and there have been several studies and comparisons done between the existing options and pyrolysis. The table 2.1 shows the CAPEX and OPEX Costs were each process. The H_2 production processes were analyzed in this study are [47]: small-scale TDM(Thermal decomposition of methane) (TDM-SS), small-scale TDMG(Thermal decomposition of methane) (TDMG-SS), small-scale water electrolysis (Electrol.-SS), small-scale SMR (SMR-SS), large-scale SMR (SMR-LS), and large-scale SMR with a CCS coupling (SMR-LS-CCS). In this study natural gas was assumed to contain 100% of methane. But in reality natural gas consists of more components like higher hydrocarbons etc, along with methane [47].

The table 2.1 is a small analysis (Tiina Keipi,pp 264-273) on the possible cost and sustainable benefits that can come with methane pyrloysis when compared to other methods [47]. The authors took technical and economic assumptions for each H_2 production technology along with operational costs assumptions to formulate this table [47].

It helps in understanding the potential of methane pyrolysis when compared to other technologies. When the scaling of the process increases, SMR seems quite reliable in terms of costs but still

significantly contributes in CO_2 emissions. Whereas in Electrolysis, the operating costs(OPEX) is quite high despite having cheaper overall hydrogen production cost than TDM-SS, but in the longer run TDM process is more sustainable and cheap and if the electricity supply is not produced by renewable energy, then it would also significantly contribute to CO_2 emissions indirectly.

	TDM-SS	TDMG-SS	Electrol-SS	SMR-SS	SMR-LS	SMR-LS +CCUS	
OPEX							
Methane	780	547	_	618	61,753	64,546	kEUR/a
CO_2 emission allowances	8	42	_	61	6099	2778	kEUR/a
Electricity		6	982	11	1064	1064	kEUR/a
Other O&M	27	24	15	87	1089	1089	kEUR/a
TOTAL OPEX	815	620	997	776	70004	97662	kEUR/a
CAPEX							
Equipment	3233	2361	2974	10,705	133,815	162,000	kEUR
Contingency(30%)	970	708	_	_	_	_	kEUR
TOTAL CAPEX	4203	3069	2974	10,705	133,815	162,000	kEUR
TOTAL H_2 production cost	72.0	53.8	71.1	117.0	44.1	57.4	EUR/MWh

Table 2.1: The annual OPEX and the total CAPEX for the evaluated H_2 production processes. SS = small scale, LS = large scale [47].

Based on the cost benefits in 2.1 and CO_2 emission reduction, the process chosen was methane pyrolysis. Since this process can be easily adapted with existing feed source like natural gas or bio-methane. The type of methane pyrloysis process will be thermal decomposition with help of a catalyst(TCDM).

2.7.1. Design & Requirements

This section consists of the various components to use for achieving the desired results along with requirements of our design. The process design was made from similar to the process that is being presently researched by BASF [48].

Application type	Estimat	ed amou	nt of hydrogen
	bcm/y	kton/y	PJ/y(LHV)
Ammonia	5.3	480	58
Refinery	6.0	544	65
Other pure hydrogen use	1.6	143	17
Methanol	1.1	102	12
Fuel gas	2.6	231	28
Total	16.7	1500	180

Table 2.2: The estimated amount of hydrogen required in Netherlands [49]

Table 3.1 refers to requirements of hydrogen in various industrial applications in the Netherlands. This data helps in understanding the different demands of hydrogen across various industries and focus on targetting one of the industries above can give us a better analysis on the hydrogen costs and see comparisons with existing technologies. In the case of the design in this project, the target is the methanol industry.

The requirements in the process design are:

- Target: Contributing to Methanol production in the Netherlands.
- Main Product H₂: Around 3 kton/yr
- By Product C(s): Around 9 kton/yr
- · Feedstock of natural gas required: 14 kton/yr
- Typical energy requirement : 75.3 kJ/mol

Purification of natural gas by removing H₂S using membranes or H₂S scavengers. (only if H₂S is significantly present)

Based on this, an initial design is developed and there will be further kinetic analysis to design the reactor and a techno-economic analysis to compare the feasibility of the design. The data from BASF was taken as a reference for operating conditions. The operating requirements are:

- Temperature: 1000-1400 °C
- Pressure: 1 bar
- · Purifying hydrogen as per requirement

2.8. Intial Design

The initial design was made for Thermal decomposition with carbon as a catalyst and was designed based on the requirements and the data from the literature review. But the simulated process model had a few changes and didn't consist of a catalyst and focused more on non-catalytic process model simulation to understand the process capabilities for hydrogen production.



Figure 2.11: Initial process design of CMP with carbon as catalyst [49]

Figure 2.11 shows the initial design of the catalytic methane pyrolysis(CMP) process made for techno-economical analysis and this model will be further developed in the upcoming months and modeled in Aspen Plus and whether this process is viable with or without a catalyst for simulation. The main components that are part of the design of CMP are the reactor, catalyst regeneration reactor, Pressure swing adsorption, and source of the heat supply.

2.8.1. Main Reactor

The reactor that is chosen is a moving bed reactor. In moving bed reactors, fresh solids can be fed from the top while a gas stream that is much lower in flow rate in comparison to a fluidized bed operating under a similar solids flow rate, is fed from the bottom. These solid particles slowly move down the reactor and are withdrawn from the bottom of the bed. In addition to providing near counter-current contact, this approach can also reduce attrition of the particles compared with fluidized beds. To achieve counter-current operation in a moving bed, the gas velocity must be kept low enough to prevent the solids from becoming fluidized. Thus moving bed reactor is a good option since the process chosen is also a combination of gas and solid reactions [50].

2.8.2. Cyclone

A cyclone separator is a type of separator used in industrial processes to separate particles from a fluid stream by centrifugal force. The typical axial cyclone separator consists of a cylindrical chamber with a tangential inlet at one end and an axial outlet at the other end. The fluid enters the chamber through the tangential inlet, creating a spiral flow pattern that generates a centrifugal force, causing the heavier particles to migrate towards the outer wall of the chamber, while the lighter fluid flows towards the center and exits through the axial outlet. There are different types and designs of cyclone separators, each with its own advantages and limitations depending on the specific application. The

dimensions and geometry of the separator, as well as the flow rate and particle size, are important factors to consider in the design [51].

In a gas-solid axial cyclone separator, the gas enters the separator through the tangential inlet and creates a swirling motion inside the cylindrical chamber. The solid particles in the gas stream are forced towards the outer wall of the chamber due to the centrifugal force generated by the swirling motion, while the cleaned gas exits through the axial outlet. To improve the separation efficiency and reduce the pressure drop across the separator, some axial cyclone separators may include additional features such as a conical or inverted cone shape at the bottom of the chamber to promote particle settling, a vortex finder at the top of the chamber to guide the cleaned gas towards the outlet, and a dust hopper or collector at the bottom to collect the separated particles [52].

2.8.3. PSA

Pressure swing adsorption(PSA) is needed for separating the unreacted gases along with the main product, hydrogen. It is possible to fully purify the mixture and obtain pure hydrogen in ideal conditions. The purity of the hydrogen will depend on the application it will be used for. The mixture gas needs to be free of any solid particles and will need to be purified before it enters the PSA system. If this is not done properly it could damage the system. Solid separators like cyclone separators are needed to be used for separating carbon black from the gas mixtures. If needed guard filters are set up to ensure the full removal of carbon particles.

Adsorption is used in the pressure swing adsorption (PSA) process. The primary function of the PSA is to separate or purify the gases in a mixture by adsorbing one or more gases to an absorbent material. The adsorbed gas is regenerated by reducing the partial pressure. This is a low-cost and energy-efficient separation technology often used in industry. The following sections describe the various designs of the PSA process, starting with the Skarstrom cycle and the Guerin-Domin cycle, which marked the beginning of the development of the PSA process. Early practical use of Skarstrom's PSA cycles focused on air drying. Another early application is air separation to produce O_2 or N_2 [53] [54]. The key design parameters to consider when designing and optimizing the PSA process, purity, and recovery are discussed below.

The Scarstrom cycle dating back to 1958 is known as the introduction of the PSA process [55]. The cycle is designed for the equilibrium separation process and is schematically shown in the figure. The design consists of two connected layers that follow a 4-step cycle.

- Pressurisation
- Adsorption
- Countercurrent blowdown
- · Countercurrent purge

In the first step, column A is pressurized with feed gas, and column B is depressurized to atmospheric pressure, also known as a countercurrent purge. The adsorption phase begins when column A is pressurized. A small product gas stream is fed countercurrent to feed to column B to purge the bed. When the purge phase is complete, the bed is ready for a new adsorption cycle. Bed B is now pressurized with the feed stream while bed A is depressurized to atmospheric pressure and the cycle can be repeated. During the adsorption, a continuous stream of feed gas enters the column. The transit time depends on the breakthrough of the most strongly absorbing gas. As soon as the impurity content of the outgoing gas stream exceeds a predetermined acceptable limit, the adsorption step ends and the feed gas supply is stopped. After the adsorption step, the bed is saturated with strongly adsorbing particles. It is restored in two successive stages: backflow purge and backflow purge. Countercurrent flow regenerates the final product so that the next adsorption step minimizes product gas contamination. The purge serves as an initial stripping and reduces the amount of purge required for bed regeneration. Purge is used to flush pores in absorbent materials. Since a portion of the product is used in the purification step, a compromise must be found between reduced product recovery and product purity. Scarstrom cycles were originally developed for air separation and are widely used for air drying [54].

Skarstrom defined some basic rules for the design of a PSA cycle. First of all, the heat of adsorption produced during the cycle should be controlled by using a short cycle with a low throughput per cycle, in order to maintain an isothermal operation. Secondly, for increased product purity, the amount of purge used must comply with the 1:1 volume ratio of purge to feed, which ensures a complete displacement of the gas in the bed and thus enhances the product purity achieved. Thirdly, purity is also controlled by the absolute pressure ratio, which should be greater than the reciprocal of the mole fraction of product in the feed stream [54] [53].



Figure 2.12: Skarstrom cycle(left) and Guerin-Domine cycle(right) [54]

The Guerin-Domine cycle, which is schematically depicted in Figure 2.12 as a two-column cycle, was approximately filed at the same time as the Skarstrom cycle. Each bed follows a three-stage cycle of pressurization, decompression, and venting. As with the Scarstrom cycle, Bed A is pressurized and the feed stream enters the top of the bed. Once the required pressure is reached, the top of the bed is closed and bed A is simultaneously evacuated by connecting the bottom of bed A to the top of bed B while the effluent is recovered as an O_2 raffinate product. When medium pressure is reached, the bottom of the bed closes and the A bed is evacuated using the vacuum line connected to the center of the bed. By depressurizing the bed to vacuum, the bed is regenerated to remove any adsorbed N_2 . A significant improvement in product recovery can be achieved compared to the Scarstrom cycle which uses a clarification step to regenerate the bed. The same steps are performed sequentially on beds A and B to ensure consistent product output [56].

3

Process Simulation & Analysis

This study consists of modeling and simulating methods, Thermal Methane Pyrolysis (TMP). Before we simulate the results from these simulations need to be validated with existing experimental results to replicate accurate values for our conditions. The reactor temperatures were selected based on the literature values [57]. The degree of methane conversion and reaction time in each concept was selected based on experimental research and calculations conducted at Tampere University of Technology and Plevan's Experiments. The degree of methane conversion as a function of temperature and residence time has been experimentally studied and the results have been used to determine the reactor dimensions of TMP. Heat losses for the concepts were assumed to be zero as this simulation was done in ideal conditions.

3.1. Thermal Methane Pyrolysis

The TMP is modeled in Aspen Plus and the optimized kinetics was developed by Keipi et al based on the experimental values obtained from their experimental setup. The reaction rate r (mol/s) was defined as:

$$r = \frac{dn_{\mathsf{CH}_4}}{dt} = k_{forward} * c^n_{\mathsf{CH}_4} - k_{backward} * c^m_{\mathsf{H}_2};$$
(3.1)

following standard formulations where n_{CH_4} is the amount of CH₄ (mol), t is time (s), c_{CH_4} and c_{H_2} are the concentrations of CH₄ and H₂ (mol/cm³), $k_{forward}$ and $k_{backward}$ are rate constants and n and m are the reaction orders for forward and backward reactions, respectively. The rate constants for forward and backward reactions were assumed to follow the Arrhenius law [58]:

$$k = A * exp[E_a/(R_uT)], \tag{3.2}$$

where A is the frequency factor, E_a is the activation energy (kJ/mol), R_u is the gas constant (8.314 J/molK) and T is the temperature (K). The rate constants and frequency factors use units of cm³, J, mol, and s.

The kinetic parameters were achieved by optimization of the global TDM reaction parameters to correspond to the experimental data produced by Keipi et al [57].

	A	Ea (kJ/mol)	n	m
Forward Reaction	8.5708*10 ¹²	337.12	1.123	-
Backward Reaction	1.1190*10 ⁷	243.16	-	0.929

Table 3.1: Global Kinetic Parameters. The reaction rate uses the units cm3, J, mol, and s.

Some of the assumptions made for TDM modeling are:

- A constant pressure plug flow reactor.
- · No Heat losses.

• Pure methane is used as inlet gas at 273.15k.

These kinetic factors need to be validated with other experiment values that have used the TDM process for hydrogen production as the global kinetics was developed based on one experiment setup. To validate these values, they are compared with Plevan's experiments [59] since this setup was very similar to Keipi's experiments [57]. The temperatures at which the Plevan's experiments were conducted were 1023k, 1123k, and 1173k.



Figure 3.1: Block flowsheet of the TDM Model

Plevan's experiment consisted of different axial temperatures along the tube/ reactor and these same values were taken for the Aspen model as well to produce values as similar as possible. Figure 3.2 represents the validation of the kinetics used in the aspen model with the experimental values taken at temperatures of 1023K, 1123K, and 1173K.



Figure 3.2: Kinetic Validation of Aspen model

The feed (CH₄) entered the validated reactor in different temperature ranges ranging between 1073 and 1273 K. The product stream containing the remaining CH₄ and produced H₂ and C is passed through the units of cyclone and pressure swing adsorption (PSA) for separating solid C and H₂, respectively as shown in the figure 3.1. We assumed the pressure drop of the cyclone as 0.01 bar

and the number of cyclones as only one and assumed the separation efficiency of PSA as 99%. Based on the process simulation results, the most conversion and accurate material balance were achieved at 1273k. Thus simulating temperature is considered to be 1273k in this study.

3.1.1. Components Design

The reactor chosen for this process is a plug flow reactor as it is a continuous process. The process was assumed to be done in a steady state and the reactor design was also based on this assumption. The TDM reactor can be powered with electrical heating elements or alternatively with a plasma torch. The heat of conversion can be provided by utilizing, for example, heating elements based on materials such as silicon carbides (SiC) or molybdenum-disilicates ($MOSi_2$). These materials can typically handle temperature ranges up to 1300–1600 °C [60]. Figure 3.3 shows a clear description of how the reactor is designed.

Electrical heating elements were chosen to provide the heat of conversion. The input methane is preheated by hot product gas before being fed to the reaction chamber. The reaction chamber is refractory-lined from the inside and is operated at atmospheric pressure. The product carbon is separated from the product gas with a cyclone and a fabric filter. The product gas is cooled down to a temperature suitable for fabric filters. The product carbon is cooled to a temperature that is below its self-ignition temperature before being exposed to air. This concept was taken in reference to model 2 in [60] and helped in designing the Aspen simulation model for the TDM process.



Figure 3.3: Schematic of TDM Reactor(left) and Cyclone(Right)

The reactor dimensions and parameters were designed for three scales, i.e, small, medium, and large-scale production. The following parameters were common for all three as given:

- Temperature: 1273k
- Pressure: 1 bar / 101.325kPa

The diameter & length of the tube along with the number of tubes required in the multi-tube reactor differ for different scales of reactors. Table 3.2 represents the changing parameters for these three sizes of reactors. These parameters were determined using the Aspen optimization tool. The tool helped in understanding the best design scenario in terms of sizing the tubes.

	Inlet Flow rate (Kmol/hr)	Tube length (m)	Tube Diameter (m)	No of tubes
TMP-1	1	2.71279	0.337381	7
TMP-2	10	9.045	0.2	60
TMP-3	100	5.1824	0.864921	56

Table 3.2: Tube Parameters of the reactor

The conversion rate of methane to hydrogen achieved for the large-scale reactor was around 85%. Even though there was the possibility to increase this conversion, the pros of increasing conversion were outweighed by the cost of the equipment and energy consumption. For equal comparison, the conversion rate for all the 3 reactor sizes was chosen to be 85% conversion.

The cyclone is assumed to be one cyclone and is designed in an ideal condition of removing 100% of the carbon from the post-reaction stream. The specifications of the cyclone in TDM-3 are mentioned in the table 3.4. These specifications were calculated from the design model in the Aspen Library based on the Leith-Licht calculation model [61] using a Stairmand HT-type cyclone which has a rectangular-shaped inlet. A rectangular inlet cyclone separator is a type of cyclone separator that uses a rectangular-shaped inlet rather than a circular inlet. The rectangular shape is designed to promote more even distribution. The TDM-3 model cyclone is mentioned in table 3.4 to help us understand the sizing of the cyclone based on scaling. The configuration of a general Stairmand HT type model is given below in fig 3.3 which shows the ratio values of these parameters with respect diameter of the cyclone D_c . The diameter range for this model is between 0.1 to 5m [62].

	STAIRMAND HT	
Inlet type		rectangular
D _c	Body diameter	1
а	Inlet height	0.75
b	Inlet width	0.375
D _i n	Inlet diameter (for round inlet)	N/A
S	Height of overflow exit (vortex finder)	0.875
D _e	Diameter of overflow exit	0.75
h	Cylinder height	1.5
Н	Overall height	4
В	Diameter of underflow (dust outlet)	0.375

Table 3.3: Stairmand-type cyclone configuration [62].

The diameter of the cyclone helps in determining the other factors of the cyclone configuration from ratio data in table 3.3. The Diameter of the cyclone is calculated based on equation 3.3 [63],

$$D_c = 0.0502 \left[\frac{Q * \rho^2}{\mu(\rho_p - \rho_f)} * \frac{1 - b/D_c}{(a/D_c)(b/D_c)^2 \cdot 2} \right]^{0.404}$$
(3.3)

where Q is overflow gas flow rate ρ_f and ρ_p are densities of fluid and particle respectfully. μ is the viscosity of the fluid.

Specifications	
Calculated number of cyclones	1
Calculated pressure drop [bar]	0.00037
Calculated diameter of cylinder [meter]	0.82
Calculated efficiency	0.99
Calculated length of vortex [meter]	2.17
Calculated length of cylinder [meter]	1.24
Calculated length of cone [meter]	2.06
Calculated diameter of gas outlet [meter]	0.62
Calculated length of gas outlet [meter]	0.72
Calculated width of gas inlet [meter]	0.31
Calculated height of gas inlet [meter]	0.62
Calculated diameter of solids outlet [meter]	0.31
Calculated number of gas turns	4
Axial Inlet Gas Velocity [m/s]	11.09
Calculated inlet/saltation velocity ratio	0.14

Table 3.4: Specifications of Cyclone for TMP-3

3.1.2. Mass and Energy Balance

The tables 3.5 represent the total material balance throughout the process for all three sizings of this model. Mass and energy balance calculations were conducted with the aforementioned calculation assumptions. All the concepts have a methane conversion rate of 85% for ideal comparison purposes. It helped in understanding the amount of hydrogen produced every operational year and

	1	2	3	4	5	6	7	8
Temperature (K)	273.15	1273	1272.99	298.15	298.15	298.15	298.15	298.15
Pressure (bar)	1.01325	1	1.013	1	0.99	0.99	1	1
Mole Flows (kmol/hr)	1	1	2.69	2.69	1.85	0.84	1.68	0.16
Mole Fractions								
H2	0	0	0.62	0.62	0.91	0	1	0.053
С	0	0	0.31	0.31	0.00046	1	0	0.0054
CH4	1	1	0.055	0.055	0.081	0	0	0.94

	1	2	3	4	5	6	7	8
Temperature (K)	273.15	1273	1272.99	298.15	298.15	298.15	298.15	298.15
Pressure (bar)	1.01325	1	1.01325	1	0.99	0.99	1	1
Mole Flows (kmol/hr)	10	10	26.99	26.99	18.5	8.4	16.91	1.59
Mole Fractions								
H2	0	0	0.62	0.62	0.91	0	1	0.053
С	0	0	0.31	0.31	0.00046	1	0	0.0054
CH4	1	1	0.055	0.055	0.081	0	0	0.94

	1	2	3	4	5	6	7	8
Temperature (K)	273.15	1273	1272.99	298.15	298.15	298.15	298.15	298.15
Pressure (bar)	1.013	1	1.01325	1	0.99	0.999	1	1
Mole Flows (kmol/hr)	100	100	269.98	269.98	185.07	84.91	169.13	15.93
Mole Fractions								
H2	0	0	0.629	0.629	0.918	0	1	0.053
С	0	0	0.314	0.314	0.000453	1	0	0.005
CH4	1	1	0.055	0.055	0.081	0	0	0.94

Table 3.5: Total Material Balance for three different scalings of TMP (top to bottom)

3.1.3. Fuel consumption

To investigate the amount of fuel combusted to cover the total heat required in each system, the required amount of fuel was obtained. The fuel in this case is the amount of methane consumed to provide the required temperature for the reaction to happen. When calculating the amount of consumption we keep every conversion rate the same. The heat of conversion (Q) is the total energy requirement of the conversion process in the concepts. The heat of conversion is the sum of the required reaction enthalpy (ΔH_r) and the sensible heat of methane [60]:

$$Q = N_{CH_4} * cp, CH_4 * M_{CH_4} * \Delta T_{CH_4} + a * N_{CH_4} * \Delta H_r$$
(3.4)

where N_{CH_4} is the molar flow rate of input methane, c_{p,CH_4} the specific heat capacity of methane, M_{CH_4} the molar mass of methane, and ΔT_{CH_4} the difference between the reaction temperature and the temperature of the input methane stream. The reaction enthalpy ΔH_r depends on the reaction temperature. The mass flow rate of methane which is combusted to supply the energy demand is calculated according to the following equation[60].

$$m_{comb,CH_4} = \frac{Q}{LHV_{CH_4}} \tag{3.5}$$

Table 3.6 shows the energy requirements for the process to occur at different temperatures, this gives a better understanding of the difference in increasing our temperatures and how this can affect the cost of production of hydrogen. In TDM-1 the energy requirement is 6094.7,6327.9,6561.5 cal/s at reaction temperatures of 1073k, 1173k, and 1273k, when it came to catalyst methane pyrolysis(CMP), studies that were analyzed temperatures were lower and required lesser energies. The values of TDM-2 and TDM-3 are in the factor of 10 and 100 times TDM-1 energy requirement values since these models are scaled without major differences.

At 1073k, the CMP required around 3941 cal/s [64] whereas in TDM-1 it was 6327.9 cal/s. This showed that we require a higher amount of heat for TDM-1 than CMP due to its higher reaction temperature and the technical benefit of the catalyst-based MP. But in the TDM process, we do not face any issues with catalyst separation issues with product carbon whereas this is a major issue in CMP.

We can reduce the consumption of methane for fuel by using partly using the product hydrogen obtained. But this ratio needs to be determined where the economic benefit is not outweighed by the reduction of methane consumption for fuel. The hydrogen consumption could significantly increase in the methane and hydrogen fuel mixture when temperatures increase thus affecting our final costs [64]. This needs to be kept in check when attempting heat integration.

	TDM-1	TDM-2	TDM-3			
Flow rate(kmol/hr)	1	10	100			
Flow rate(kg/s)	0.0044	0.044	0.44			
Total Heat Required(kJ/s)						
1073k	25.51791	255.1791	2551.7			
1173k	26.49429	264.9429	2649.4			
1273k	27.47214	274.7214	2747.2			
Amount of fuel(kmol/hr)						
1073k	0.114544	1.14	11.45			
1173k	0.118927	1.18	11.89			
1273k	0.123316	1.23	12.33			

Table 3.6: Energy requirements for models at different temperatures

3.2. Techno-Economic analysis

This section presents the calculation criteria and assumptions made in the Analysis. The analysis presented in this report is a preliminary assessment of the viability of these concepts. Figure 3.4 gives a description of the steps followed for the economic analysis.

The technology solution selected in this study represents currently available technologies. The product gas, which is purified hydrogen, is burned after the TDM process and can be used to generate electricity with a steam power cycle. It may also be possible to connect the TDM process to an existing power or thermal boiler. The possible end use of the product gas was considered for the production of methanol during the literature study and to reduce CO_2 emissions and hydrogen cost [60].

The reference case in this study is the direct combustion of natural gas, which is for the sake of clarity replaced with methane in all calculations, to produce electricity with a steam power cycle. The reference plant is assumed to be an operating plant that still has operation time left and whose investment costs have been paid back already.

In this study, the produced carbon is assumed to be sold in the carbon black market with a price of $500 \notin t_{carbon}$. The effect of a carbon product price on the feasibility of the concepts was studied with a sensibility analysis. The cost of producing electricity, therefore, includes the cost of emission allowances (assuming a reasonable value of $20 \notin t_{CO_2}$) [60]. It was decided that the generated gas would be used only for electricity generation, not for example additional heat. It is important to note that the results obtained in this study are not general because they are highly dependent on the assumptions made in the analysis. However, the results can be used to compare certain aspects to other types of processes for hydrogen production.



Figure 3.4: Analysis methodology[60]

3.2.1. Evaluation of investment costs

The investment costs for the process equipment were based on nominal price approximations in existing similar devices found in the power industry. Cost distribution for total capital expenditure (CAPEX) was assumed to be similar to the reference values taken from various sources for each component. For simplicity, the cost of the preheaters and coolers is approximated according to the price data from non-pressurized air-to-air shell and tube heat exchangers.

The method used to calculate the economic aspects was taken in reference from Cheon et al [64]. In this method, the unit H_2 production cost (USD /kg H_2) is obtained from the sum of the total cost (USD/ yr) divided by the total amount of H_2 produced (kg/yr).

The total CAPEX in each sizing was divided into an annual capital cost for the investment (Annual capital cost = CRF*Total capital cost) by using the capital recovery factor (CRF) which is defined as:

$$CRF = \frac{i(i+1)^N}{(i+1)^N - 1}$$
(3.6)

where i is the interest rate (–), and N is the investment period in years [47]. An interest rate of 10% and an investment period of 10 years were assumed. These costs are evaluated based on reference capital costs and technical assumptions which are shown in the table 3.7.

CAPEX Parameters				
Feed Input(Kg/s) [57]	0.1			
TMP Reactor [57]	EUR 2740 k			
PSA [65]	CEPCI/392.6 x 1, 510, 000 x (Inlet flow rate/500)^0.6 (USD)			
Cyclone [64]	USD 31,400			
Supplement [64]	20% of (Capital cost-Supplement) (USD)			
CEPCI(oct 2022)	816.3			
i	0.1			
Exchange rate	USD 1 = EUR 0.85			
Ν	10			
Stream factor	0.95			

OPEX Parameters				
CH4 [57]	USD 0.005 MJ _{LHV⁻¹}			
Labor[3]	USD 11 hr-1			
PSA operating cost [65]	6.11 × 100 × (inlet flow rate except H2) (USD)			
C selling price [60]	EUR 500 ton-1			
Maintenance [66]	2% of (Total Capital cost) (USD y−1)			
Other cost [66]	1% of (Total Capital cost) (USD y−1)			

Table 3.7: Economic parameters and assumptions for cost estimation

Based on these parameters, hydrogen cost per kg produced is evaluated for all three models discussed in the study. Key economic parameters of each system of TMP and future unit H_2 production cost with varied C selling prices, which can be advantages for economic feasibility, were quantified as well.

The specific H_2 production costs in each process were analyzed. The main process components were listed and the capital expenditure (CAPEX) of each component was estimated based on the reference costs presented in table 3.7. The costs were evaluated by applying the equation:

$$C_2 = C_1 \left(\frac{S_2}{S_1}\right)^n \tag{3.7}$$

where C_2 is the CAPEX of a component with capacity S_2 , C_1 is the CAPEX of a component with capacity, S_1 , and n is the exponent that most typically has a value between 0.4 and 0.9, the value taken in the study is 0.6 [67]. The reactor CAPEX evaluation in the TDM process was carried out by using the reactor cost estimate in the study [57] as a reference.

Based on the results from the process simulation, the itemized cost estimation for each MP system using only CH_4 and H_2 as fuel was conducted to investigate unit H2 production cost at the temperature of 1273 K.

For all the models, the unit H_2 production cost was estimated considering the capital cost of the MP reactor, PSA, cyclone, and supplement, and the operating cost of reactant, fuel, labor, PSA operating cost, maintenance, carbon emission allowance which is 85.22 Eur/kg of CO₂ produced and other costs. In this estimation, the production cost is calculated by considering the C selling price.

In the current market situation, large-scale SMR is the most inexpensive process for H_2 production. TDM cannot compete with large-scale SMR in an economic sense in a case where the TDM product carbon does not have a market value. By contrast, the small-scale SMR process is more expensive than any other process studied here. The CAPEX of electrolysis is currently relatively high but is expected to decrease by around 50% until 2030 as the technology develops [47].

The OPEX in each TDM process was divided into components in 3.8. Methane is the major OPEX component in H_2 production costs in this process as it is used as the reactant and fuel. This is the same case for the SMR process as well. But in Electrolysis, Electricity is the major OPEX component.

	TDM-1	TDM-2	TDM-3			
Items	Annual cost(Eur/Yr)					
CAPEX						
Reactor	49777	274567	1093072			
PSA	10433	41535	165356			
cyclone	4316	17182	68404			
Heater	8137	16274	40686			
cooler	8137	16274	40686			
Supplement	61112	204054	802715			
C	PEX					
Feed	29864	298640	2986404			
Fuel	3682	36820	368205			
Labour	17017	67745	269701			
PSA OPEX	78	779	7790			
Maintenance	12288	44957	173056			
Other	6144	22478	86528			
C selling price	-44676	-446760	-4467600			
Carbon emission allowance	1549	15497	154973			
Hydrogen(kg/yr)	29376	293760	2937600			
Total	126746	479161	1268907			
Hydrogen cost(Eur/kg)	4.31	1.63	0.43			

Table 3.8: Results of itemized cost estimation for methane pyrolysis (MP) systems TDM-1, TDM-2, and TDM-3

In the current market situation, large-scale SMR is the most inexpensive process for H_2 production. TDM cannot compete with large-scale SMR in an economic sense in a case where the TDM product carbon does not have a market value. By contrast, the small-scale SMR process is more expensive than any other process studied here. The CAPEX of electrolysis is currently relatively high but is expected to decrease by around 50% until 2030 as the technology develops [47].

The OPEX in each TDM process was divided into components in 3.8. Methane is the major OPEX component in H_2 production costs in this process as it is used as the reactant and fuel. This is the same case for the SMR process as well. But in Electrolysis, Electricity is the major OPEX component.



Figure 3.5: CO₂ emissions of TDM models and SMR

For TDM-1, unit H₂ production cost obtained was around 3.76 Eur/kg H₂, in this estimate, the costs of the MP reactor and reactant account for 29% and 17% of the production cost with no consideration of the C selling price per year. In TDM-2 costs of the reactor and reactant account for 30% and 32% of the total production cost, Lastly in TDM-3 the cost of the reactor and reactant account for 19% and 52% of the total production cost.

When the carbon selling price has been included, the cost of hydrogen per kg is decreased by about 35% in TDM-1, 93% in TDM-2, and 352% TDM-3. This shows the effect of carbon selling price affecting the cost of production of hydrogen by a drastic margin. In the scenario where carbon selling is assumed to be at a fairly higher cost and despite a huge amount of carbon being produced, we assume that the whole carbon produced is sold.

The CO₂ emissions are solely produced due to the burning of methane for producing the heat required to obtain the required temperature in the reactor for decomposition to occur. The CO₂ emissions from the models are compared with existing hydrogen production processes. We can clearly see a vast difference in the reduction of CO₂ emissions in comparison to traditional processes like Steam Methane Reforming(SMR) in figure 3.5 even tho SMR has adopted carbon capture with the process. The SMR values were obtained from other studies [47]. The reduction is due to the formation of solid carbon in TDM. The table 3.9 helps us in understanding the scaling of each of these processes to get a better understanding of the TDM models emissions.

Among economic parameters, it is clear that the costs of the MP reactor and reactant are the most influential economic factors in CAPEX and OPEX respectively. This shows in smaller scales the reactor cost affects the total cost of hydrogen production by a greater margin and cost efficiency can be obtained by reducing the reactor price alone. But as the scaling increases the reactant cost plays a similar role as the reactor in the production cost of hydrogen and needs to be effectively reduced to achieve economic optimization. The results indicated that selling produced carbon can be a very effective way to obtain economic competitiveness through the concept of MP, and showed the importance of the cost of the MP reactor and reactant for economic feasibility.

3.2.2. Sensitivity Analysis

To investigate key economic parameters in each system and the possibility of the commercialization of each system, sensitivity, and scenario analyses were conducted. In this study, one economic parameter was varied in the range of $\pm 20\%$ with the remaining parameters fixed, and variations of unit H₂ production cost for each system were obtained with key factors showing high variation remarked.

Accordingly, the effect of varying the scale factor in the TDM cost analysis was studied by applying values between 0.4 and 0.9. As a result, the H_2 production costs in TDM processes respectively increased or reduced by 20% [47]. This is the reason for selecting the variation of 20% to see the range of variation of hydrogen cost.

The figure, a,b, and c show the effect of the cost of hydrogen with respect to every component that contributes to the process. The major factors that change the hydrogen pricing in a larger margin are Reactor, Reactant/feed, and C selling price. In TDM-1, the reactor affects the change in the price of hydrogen by 8%, the carbon price affects it by 7.5% and the reactant price affects it by around 4.7%.

As the scaling of this process is increased, the Carbon selling price and the cost of the reactant played a more vital role in varying the cost of production as compared to the reactor. Thus these results portray the enormous importance of reactant and carbon selling prices for obtaining economic feasibility. By contrast, electrolytic H2 production costs are highly dependent on electricity costs. Additionally, the product carbon value was found to cause the greatest uncertainties in H₂ production costs by TDM.

Technical values	Electrolysis	SMR-SS	TDM-1	TDM-2	TDM-3
Reactor Temperature(K)	-	1173	1273	1273	1273
H ₂ purity	0.998	0.99	0.99	0.99	0.99
H ₂ produced(kg/s)	0.02	0.02	9.44E-04	9.44E-03	0.0944
methane feed(kg/s)	-	0.07	0.0044	0.044	0.44
water(kg/s)	0.22	-	-	-	-

 Table 3.9: Technical values for understanding the scalings of processes of hydrogen production in TDM and other production methods.

We can also understand the scaling of the process has helped in the economic feasibility of the hydrogen production process. Table 3.9 shows us the values of each TDM model along with electrolysis and SMR values. The values for electrolysis and SMR were taken in reference from et Keipi [47]. The table helps in understanding the scalings based on the hydrogen produced per second. The major factors that affect the economics of the process are Reactor, methane, and carbon selling price. So more detailed plots of these factors affecting the price are plotted to understand the range of change in hydrogen price. The graphs 3.9 show the variation of prices with respect to the major factors in all the models.

From the graphs 3.9, it is observed that when varying major factors, the price of hydrogen in TDM-1, TDM-2 & TDM-3 ranged between 3.82-4.82 EUR/kg H_2 , 1.18-2.1 EUR/kg H_2 & 0.057-0.89 EUR/kg H_2 . We can observe that as the scaling increased, the variation in the price of hydrogen increased when the methane price was varied, thus showing how the cost of natural gas/methane can affect the process costs as inflation and prices rise as the years pass by. The variation in the reactor prices stayed in a similar range in all three scalings, the range of variation got more stable as the scaling increased.







Figure 3.7: Results of sensitivity analysis of TDM-2, which depicts the price change of hydrogen cost with respect to a price change in each item that contributes to the total costs. The maximum variations of costs observed were up to 18% and the factor where this occurred was at the product carbon selling price.



Figure 3.8: Results of sensitivity analysis of TDM-3, which depicts the price change of hydrogen cost with respect to a price change in each item that contributes to the total costs. the maximum variations of costs observed were up to 70% and the factor where this occurred was at the product carbon selling price.



Figure 3.9: Variation of hydrogen costs in TDM-1, the plot represents a change in factors of C selling price, reactor price, and methane price. The range of variation of costs is between -30% to 30%



Figure 3.10: Variation of hydrogen costs in TDM-2, the plot represents a change in factors of C selling price, reactor price, and methane price. The range of variation of costs is between -30% to 30%



Figure 3.11: Variation of hydrogen costs in TDM-3, the plot represents a change in factors of C selling price, reactor price, and methane price. The range of variation of costs is between -30% to 25%

Scenario analysis for H_2 production showed a cost reduction in capital cost. The different C selling prices in the TDM models, which is a very crucial economic factor as reported by the sensitivity analysis, a pessimistic price fluctuation, and low product quality of C were assumed in consideration and compared to conventional H_2 production methods of Steam Methane Reforming(SMR) and how the pricing changes can affect in the longer run.



Figure 3.12: Comparision of SMR H₂ process with TDM process. The factor that affects the cost of the hydrogen produced is product carbon sales and this checks the effect on the price of hydrogen and whether this could be feasible to compete with SMR and SMR with carbon capture(CCS)

The graph 3.12 shows us a clear comparison of SMR and the TDM models.SMR (EUR 0.94–1.78 kg/H₂) and SMR with CCS (EUR 1.45–2.38 kg/H₂) From the graph results we can understand that scaling of the models beyond 75 kg/hr production can compete with SMR+CCS cost production cost but is still quite away from SMR alone. At lower scales, TDM can compete with the SMR+CCS method when there are at least 50% sales of the product carbon.

The price change is about 7%, 13%, and 20% for TDM-1, TDM-2, and TDM-3 respectively when 50% of the carbon product is sold at 500 Euro/ton price and the price change is about 26%, 48%, and 77% for TDM-1, TDM-2, and TDM-3 respectively when 100% of the carbon product is sold at 500 Euro/ton price. We can also observe from this that the price variation percentage has been increased as the scaling of the process increased, this is due to the fact that a larger portion of the carbon is produced and sold as scaling is increased. Their economic competitiveness with conventional commercialized H₂ production methods of SMR and SMR with CCS has been shown in the graph. High scaling and full carbon sales prices can help with competing and producing at the same price as SMR.

The key economic parameters like C selling price, costs of TDM reactor, and reactant were calculated and the future economic competitiveness for all models of H_2 production and C selling prices, even pessimistic prices, was confirmed. TDM could be an especially suitable technology for peak-load power plants. In these plants, it is not cost-efficient to apply conventional CCS technologies that require large investments in the infrastructure. More research and optimization are required in order to achieve high conversion rates and product carbon with suitable quality in the TDM process. The price of the product carbon has a crucial effect on the feasibility, and therefore more research on the utilization of thermal black is required as well.



Conclusion and Recommendation

This project focuses on the feasibility of Methane pyrolysis as compared to conventional processes like Steam Methane Reforming(SMR) in order to develop an effective hydrogen production process with the least environmental consequences and readily available raw material. Chapter 1 focused on the overview of CO-2 emissions and how hydrogen can combat this and also discussed some of the factors to be studied to obtain a feasible hydrogen production process. Chapter 2 focused on hydrogen and its uses and also focused on the production method of hydrogen, its evolution, and the thermodynamics related to them. Chapter 3 focused on the modeling of the system in Aspen, with all the conditions, assumptions, and constraints. This chapter focused on component design and techno-economic analysis of three TDM models and also focused on the effects of scaling TDM and sensitivity analysis was conducted on these TDM models.

4.1. Conclusion

This study presents and analyses three scaling concepts that utilize the thermal decomposition of methane to reduce CO_2 emissions in natural gas/Methane combustion which was technically and economically investigated by preliminary techno-economic analysis consisting of a process simulation using Aspen Plus®, itemized cost estimation, and sensitivity and scenario analysis for various parameters such as temperature and scaling change. Based on the results of the techno-economic analysis with the current assumptions, applying TDM reduces the CO_2 emissions in the hydrogen production process when compared to processes like SMR. The CO_2 emissions decrease when a part of the carbon is taken out from the feedstock/reactant in a solid form. Furthermore, the cost of avoided CO_2 decreases rapidly when more solid carbon is taken out from the feedstock/reactant.

The major technical and economic parameters the reactor temperature and the carbon selling price respectively have dictated the overall performance of all designed models where theoretical yields have been obtained based on kinetics developed from experimental data. The study also helped in designing the reactor and cyclone. Three reactor sizings have been designed and have been analyzed in Aspen Plus based on the theoretical data and kinetics to help in designing for real-life modeling of the process. We were able to answer many of the research questions mentioned in the introduction chapter. The conclusions we obtained in this study based on the analysis are:

- Thermal decomposition of Methane could be an immediate alternative to traditional processes like SMR for producing hydrogen for a certain scaling, due to its low CO₂ emissions and cost reduction due to the selling of the by-product solid carbon.
- We can also understand that TDM can compete with green hydrogen production methods if the fuel/electricity for producing the high temperatures can be obtained from renewable sources in the coming decades as the emissions of CO₂ are totally eliminated.
- The kinetic model used to analyze the process was the optimized kinetic parameters and the derived Arrhenius parameters for the forward and backward reaction of methane

decomposition. The kinetic parameters were referred to based on the results of the lab experimental setup of methane pyrolysis.

• The solid particles are separated using a moving bed reactor in real-life conditions and exit through the bottom of the reactor. In the Aspen model, the solid carbon is separated using a cyclone from the product gas. The cyclone in the model is assumed to have a 100% conversion rate for a smoother separation of gases in PSA.

The amount of H₂ produced and the fuel used in TDM-1 is 29 tons H₂/yr & 7274.06 kg/yr of fuel. The other two models have obtained values scaled up to 10 and 100 times TDM-1 results. The CO₂ emissions in TDM-3 despite scaling up higher than the SMR model, were lesser than SMR, showing the environmental benefit of opting for the TDM process. The CCS coupling reduces the CO₂ emissions from the H₂ production by SMR, but lower emissions than in TDM cannot be achieved if CO₂ is captured exclusively from the syngas.

The study also proved to show the advantages of the usage of TDM process in the transition to clean energy process like electrolysis as it has the ability to utilize the current natural gas network for the feedstock supply and a good feedstock availability that enables demand-driven H_2 production while reducing CO_2 emissions and a secondary product(Solid Carbon) to obtain economic benefits. According to the analysis, TDM could be a cost-efficient technology in small or medium industrial-scale on-site H_2 production which was observed in the costs of TDM-1 and TDM-2 models. A break-even value for the TDM product carbon was found as 250 EUR/ton C for a hydrogen production scale of 100 kg/hr to be competing with the SMR process. The break-even value for the TDM product carbon market price of carbon black which varies between 500 EUR/t and 2000 EUR/t C depending on the quality of carbon.

4.2. Future work

Some of the parameters that can be researched in further studies would be:

- Addition of Carbon catalyst with the scaling models and Catalyst regeneration.
- Research on utilization and quality assurance of the produced solid carbon during this process.
- Usage of green methane as feedstock and fuel for the TDM process.
- · Heat integration(usage of product hydrogen to meet the fuel consumption demand)

Catalyst in this process essentially helps in increasing productivity and the ability to perform this process at lower temperatures thus providing a more energy-efficient way to produce hydrogen. Carbon catalyst is promising due to their cheap costs and easier separation of the catalyst from the product carbon. This is the area where some of the parameters can be studied at a deeper scale. The Catalyst also can be reused by using the regeneration process which is much easier with carbon catalysts when compared to metal catalysts.

The Quality of solid carbon produced has not been studied very deeply and this process could be studied further to understand the quality of carbon produced based on the parameters like temperature, flow rate, and pressure. A research study on producing quality carbon can help in developing a very good product of carbon.

Methane pyrolysis in this study works with natural gas as feed and uses nonrenewable sources for its energy usage. The usage of green methane for this process is a very promising parameter in this process to further eliminate CO_2 emissions. Presently to meet the demand in larger scales of hydrogen production, there is not enough green methane. This could be a focused study in the near future.

Heat integration is a very crucial process in any chemical process. The ability to transfer any unused heat can help in making it more efficient and cost-effective. In this case, some part of produced hydrogen can be used to provide for the energy required by the reaction and also be able to use the heat obtained from the gases post-reaction cooling where the reactant could be partially preheated from the heating obtained from cooling of the methane and hydrogen mixture pre PSA.

The work on these can give us further insights and more depth research on this unique process that will help us in transitions from the traditional hydrogen production process.

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