

THERMODYNAMIC ANALYSIS OF
PLASMA-ASSISTED REFORMING OF METHANE

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THERMODYNAMIC ANALYSIS OF
PLASMA-ASSISTED REFORMING OF METHANE

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ABSTRACT

THERMODYNAMIC ANALYSIS OF PLASMA-ASSISTED REFORMING OF METHANE

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Conventional techniques of syngas production use the exhaust gas of combustion of fossil fuels or feedstock like biomass itself. High temperatures are required for this process. To achieve necessary high temperatures, about 30% of feedstock is used initially. Another disadvantage of these conventional techniques is the tar formation which can damage the system by blocking the equipment. On the other hand, plasma processes are more efficient techniques to convert energy like solar, electrical, etc. into chemical energy by breaking the bonds of feedstock. Since the plasma processes do not need to increase the temperature of the feedstock, syngas can be produced from any gas (natural gas, biogas, etc.) that contains methane. In addition, produced syngas is free of toxic waste and reduced amount of pollutant gases such as CO_2 , NO_x , SO_x , etc. This study focuses on the system-level, thermodynamic modeling of the plasma-assisted reforming of methane. This analysis has three main important steps. First step is the comparison of conventional and plasma technologies for methane reforming. Second step is finding the theoretical limits in terms of efficiencies and production rates, as well as, figuring out the theoretical improvement capabilities of each individual system. The last step is suggesting the best system, among the studied ones, which has the

maximum efficiency and productivity, besides obtaining the reaction quotient higher than the equilibrium constant. The main contribution of this study is comparison of plasma processes among themselves and with other conventional techniques through thermodynamic modeling. As results of the study suggest, plasma technologies have better energy efficiencies than conventional methods. Among themselves, although thermal plasma technologies have higher energy efficiency values, non-thermal plasma technologies exhibit greater specific energy values. In addition, non-thermal plasmas show better performance in the equilibrium constant analysis which represents they provides good ratio of products to reactants in terms of their mole fractions.

Keywords: Syngas production, methane reforming, performance assessment, plasma reactors

ÖZ

PLAZMA DESTEKLİ METAN DÖNÜŞÜMÜNÜN TERMODİNAMİK ANALİZİ

Maşera, Kemal

Yüksek Lisans, Sürdürülebilir Çevre ve Enerji Sistemleri

Tez Yöneticisi: Yrd. Doç. Dr. Onur Taylan

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Geleneksel teknikler, sentetik gaz üretmek için fosil yakıtların yanması sonucu ortaya çıkan egzoz gazını veya biyokütle gibi hammaddeleri kullanırlar. Bunu yapabilmek için yüksek sıcaklıklara gerek vardır. Kullanılacak olan hammaddenin yaklaşık %30'luk bir kısmı gerekli olan sıcaklığa ulaşmak için harcanır. Bu tekniklerin diğer bir dezavantajı ise katran oluşumudur. Oluşan bu katran sistemde kullanılan ekipmanları tıkayarak ciddi zararlara yol açabilir. Bunun tam aksine, plazma işlemleri, güneş ve elektrik benzeri enerjilerin kimyasal enerjiye dönüşümlerinde daha verimlidirler. Bu dönüşüm hammaddenin kimyasal bağlarının kırılması şeklinde düşünülebilir. Hammaddeyi ısıtmak gerekmediği için, plazma tekniklerini kullanarak metan içeren herhangi bir gazdan (doğal gaz, biyogaz, vb.) düşük sıcaklıklarda sentetik gaz elde edilebilir. Buna ek olarak, üretilen sentetik gaz zehirli atıklar içermez ve CO_2 , NO_x , SO_x gibi kirletici gazların salınımı azaltılır. Bu araştırma sistem seviyesinde metan dönüşümünü termodinamik açıdan modellemeyi amaçlamaktadır. Bu analizin üç ana önemli adımı vardır. Bunlardan ilki geleneksel ve plazma teknikleri için farklı sistem ve işlemlerini metan dönüşümü için karşılaştırmaktır. İkinci adım ise, verim ve üretim oranı açısından teorik limitleri bulmak, bunun yanında araştırılan her bir sistemin teorik olarak ne kadar

geliştirilebileceğini ortaya çıkarmaktır. Son adım ise, maksimum verimliliği ve üretimi sağlayan, bunun yanında reaksiyon oranının, denge sabitinin üzerinde olan sistemi bulmaktır. Özetleyecek olursak, bu araştırmanın ortaya koyduğu temel katkı, metan ayrıştırması için plazma yöntemlerini kendi içlerinde ve diğer geleneksel yöntemlerle termodinamik açıdan karşılaştırmaktır. Çalışmanın sonucu olarak, plazma teknolojileri geleneksel yöntemlere göre daha yüksek enerji verimine sahiptirler. Kendi içlerinde, termal plazmaların daha yüksek enerji verimleri olmasına rağmen, termal olmayan plazmalar daha yüksek spesifik enerji değerleri gösterirler. Ek olarak, termal olmayan plazmalar denge sabiti analizinde daha iyi performans göstermektedirler. Bu analiz, termal olmayan plazmaların mol sayıları açısından yüksek ürünler-girenler oranı sağladığını gösterir.

Anahtar Kelimeler: Sentetik gaz üretimi, Metan dönüşümü, Performans değerlendirmesi, Plazma reaktörleri

To My Family and Fiancée

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LIST OF SYMBOLS

$K(T)$	Chemical equilibrium constant as a function of temperature
\dot{m}	Mass flow rate
\dot{n}	Molar flow rate
n	Total number of moles
P	Pressure
P_{ref}	Reference pressure (<i>1 atm</i>)
S_i	Selectivity of component i
T	Temperature
\dot{V}	Volumetric flow rate
V_{total}	Total volumetric flow rate
$W_{catalyst}$	Bulk weight of the catalyst bed
X_i	Conversion of component i
Y_i	Yield of component i
y_i	Mole fraction
Δh	Heat of formation
η	Efficiency
ρ	Density
v_i	Stoichiometric coefficient of component i

CHAPTER 1

INTRODUCTION

1.1 Motivation

As the world grows and population of human being dramatically increases for the last few decades, energy demand also increases. Increasing trend of the human population as well as developments and inventions on technology requires more and more energy. This energy requirement is generally supplied by using fossil fuels like oil, natural gas etc. However, fossil fuels have greenhouse gas emissions. In other words, these types of energy sources pollute our world and cause global warming. It is a well-known fact that the earth is under a threat of climate change. The main cause of the global warming is the use of fossil fuels which produce greenhouse gases such as CO_2 when combusted for energy generation. Furthermore, fossil fuels are limited and they are expected to be extinct, at least they will not be available in large amounts in the future. Considering all of those effects, alternative energy sources need to be found to meet the increasing energy demand of world. Alternative energy sources have to be environment friendly and sustainable which would allow today's generation to meet their needs without destroying the environment of future generations.

Carbon dioxide is one of the greenhouse gases that contribute significantly to increase in earth temperature and resulting climate change. According to related finding, 31.6 gigatonnes of carbon dioxide released to air as a combustion product of fossil fuels in 2011 [1]. This amount of carbon dioxide emission would yield approximately $2^{\circ}C$ increase in the average temperature of the earth [1]. Considering the negative effect of carbon dioxide to the nature; supplementing conventional methods with sustainable methods to generate electricity is inevitable. Although, currently it seems not possible to completely replace all conventional methods with

the renewables due to some technical restrictions, it could be realizable in the future. On the other hand, there are some alternative technologies which use or reutilize the carbon dioxide in the process of alternative fuel production. To illustrate, dry reforming uses carbon dioxide and methane to generate syngas. Syngas is the short version of synthesis gas which is made up from combination of hydrogen and carbon monoxide gases. This type of carbon dioxide demanding alternative fuel production methods, like plasma technologies, is increasing the diversity of alternative fuels and has a positive contribution on caring the environment in two manners. Initially, plasma can be used for producing syngas which is essential for fuel production for many areas. In addition, during this production of syngas carbon dioxide is consumed. This consumption of carbon dioxide prevents the new carbons sources to add carbon recycle in the nature.

As the syngas both can be directly used as a source of energy and can be used in the production stage of other synthetic fuels, it is considered as a promising subject to investigate. In order to produce syngas there are some conventional thermochemical processes exist. These methods can be inserted under the processes of dry reforming [2]–[5], partial oxidation [6]–[8] and steam reforming (wet reforming) [9]. Although, with help of different catalyses these processes are capable of producing syngas in high selectivity or yield values, they have some disadvantages and technical difficulties. (i) In general conventional methods are accepted as energy intensive processes [7]. (ii) Due to the inappropriate H_2/CO ratio (some has very high, some has very low), produced gas cannot be directly used in the subsequent processes like methanol synthesis [7]. (iii) Due to the heating requirements of the system, some of the feedstock is used solely reaching to the required temperature for the process [1].

1.2 Objective of the Thesis

As the day passes, the fact of increasing energy demand of world pushes human being to produce more and more energy. However, knowing all situations, which our earth faces with such as global warming and climate change, make people to come up with new reasonable, sustainable and renewable solutions in the energy production sector. The main aim of this thesis is to contribute the today's technology in order to supply its demand in more efficient, sustainable and renewable manner. To be more specific, thermodynamically analysing the performance of both conventional and relatively new techniques which are plasma assisted reforming of gases that contains methane.

Popular renewable energy sources like wind and solar energy are going to be much more effective if they are supported with the other alternative energy harvesting technologies. Beside, electricity should not be considered as an only energy type, since other types of energy are also used for different purposes. To illustrate, for heating purposes, as one can heat the water (or working fluid) with the sunlight and circulate it around the building to get it warmed up, same application can be applied only by heating the water (or working fluid) by another fuel like natural gas, biogas, synthesis gas etc. So that, the solar energy can be used for other purposes and the existence of the additional energy source can be considered as a gain in total system. Consequently, in order to supply enough amount of sustainable energy to meet the world energy demand, popular renewable energy harvesting technologies, that are wind, solar and hydro, seems like insufficient without the help of other renewable energy sources like bio energy.

There are lots of plasma related technologies exist in the literature for reforming syngas. Several examples are studied in this paper. It can be seen that, project related this topic is relatively new on the literature and they are generally based on

experimental analysis. Although, experimental results and technically detailed reports and papers exist, it is difficult to find any work regarding to theoretical analysis in the literature. The main focus of this thesis is to make a thermodynamic analysis of different syngas production methods. By doing this, data of the experiments that are conducted different operation conditions collected from the literature and prepared for the analysis. Not only the comparison of solely the plasma assisted technologies but also the conventional methods are examined. As a result of these thermodynamic analyses related technologies can be compared on the same base among themselves. Moreover, it will be possible to compare the conventional technologies with the plasma assisted methods. The major objective steps of this thesis can be summarized as follows

- Gathering the experimental data that are all conducted different operating conditions and regulating the data sets at the same base
- Comparing the calculated thermodynamic parameters like energy efficiencies, specific energies, selectivity's of the products and H_2/CO ratio
- Figuring out the improvement capabilities of the selected samples of thermal and non-thermal technologies by doing the equilibrium constant, K analysis

1.3 Organization of the Thesis

This study consists of five chapters in total. Chapter 1 includes basically the motivation and the objective of the research. In Chapter 2 generally the background of the syngas explained. In the beginning, conventional techniques and the comparison of them examined. On the other hand, plasmas analyses both at the plasma as a phase and its system level applications are reported. Moreover, the

examples of plasma technologies and some related studies from the literature summarized. Chapter 3 presents the overall methodology of the research. The used governing equations to figure up missing parameters and to develop the thermodynamic results are given and explained. Chapter 4 provides the results and discussions of the research. The conventional methods and the plasma processes are compared among themselves through thermodynamic parameters. Energy efficiencies, selectivity's, conversion rates and specific energy values are some examples of the parameters that are supplied as a result. Furthermore, the equilibrium constant analysis can be found in chapter 4 which compares samples of non-thermal and thermal plasma technologies. Finally, chapter 5 summarizes the major outcomes of the thesis and provides some remarks and recommendation for the future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Conventional Reforming of Syngas

2.1.1 Synthesis gas

The mixture of carbon monoxide (CO) and hydrogen (H_2) is called synthesis gas, shortly syngas. There are lots of possibilities in terms of syngas usage. One of the most critical usages of syngas is synthesizing the environment friendly fuels and some chemicals like methanol, diesel and synthetic gasoline. Different products can be synthesized based on the ratio of H_2 and CO in syngas; thus, this ratio is an important parameter [3].

According to Tao *et al.* [3] syngas can be obtained from coal, petroleum coke, natural gas, biomass and organic waste. Among those, natural gas is the mostly used source for producing syngas. Again according to Tao *et al.* [3], it is the largest source of energy because of its environment-friendship and its cost. Methane is the main substance of mentioned feedstock. When their compositions are compared it can be clearly analysed that natural gas has highest methane percentage among other candidates. Considering the conversion, hydrogen is the crucial component of the synthesis gas and it is supplied from the methane. Thus, natural gas generally preferred to use in the production of syngas or hydrogen.

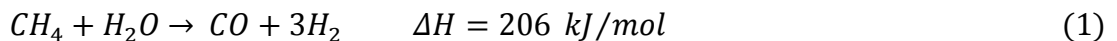
2.1.2 Conventional synthesis gas production methods

Depending on the purpose of application there are several techniques to produce syngas. Steam reforming of CH_4 (also known as wet reforming), partial oxidation

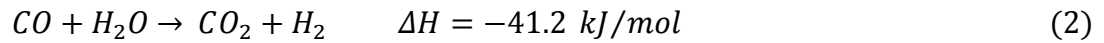
and CH_4 - CO_2 reforming (also known as dry reforming) are the most known technologies in syngas production. Rather than the direct usage of steam reforming, partial oxidation or dry reforming, catalytic assisted versions are preferred in synthesis gas production. Since, catalysis makes the chemical reaction faster it is very useful in hydrogen or syngas production processes as well. It should be noted that, there are significant amount of studies in the literature which are trying to figure out to obtain better out comes (yield, efficiency, etc...) by combining these methods or using different types of catalysts.

2.1.3 Steam reforming

Steam reforming of CH_4 can be accepted as traditional way of syngas production equation 1 [7]. As it is mentioned before H_2/CO ratio is an important parameter. This process ends up with a syngas at a ratio of 3 or higher [3]. It can be seen from the reaction 1, that methane and the water are the reactants of the reaction and it produces carbon monoxide and hydrogen which we call syngas.



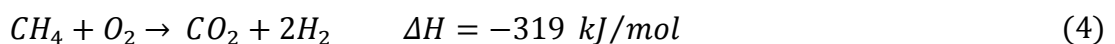
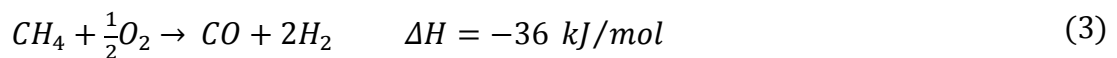
There is another step for steam reforming which is called water gas shift as in equation (2) [9]. The purpose of this step is to produce hydrogen from steam. However, at the same time CO is converted to CO_2 which is one of the most important greenhouse gases. This conversion was defended by M. Komiyama (2006) [9] as “While CO_2 is also an important greenhouse gas, this conversion (1 mole of CO_2 from 1 mole of CH_4) is favourable as CH_4 has the higher global warming potential than CO_2 . If H_2 is the objective, equations together will produce 4 moles of H_2 from 1 mole of CH_4 .”



2.1.4 Partial oxidation

Another technique to produce syngas is partial oxidation, also known as oxy-reforming. It can provide the product (syngas) with the desired CO/H_2 ratio by using oxygen or air. There are two major industrial applications in use for partial oxidation of hydrocarbons. Both of them are using natural gas and heavy hydrocarbons to produce syngas. First one is Texaco process which developed in 1954 [6]. Another one is Shell gasification process which is developed later in 1956 [6]. Comparing the partial oxidation with the steam reforming, partial oxidation has capability to operate at much higher temperatures and pressures which gives an advantage to partial oxidation. Another advantage is explained by Ann M. and Gilbert F. (1996) [6] as "Indeed, the overall exothermicity of the process permits adiabatic operation, in refractory lined vessels, thus, avoiding metallurgical problems."

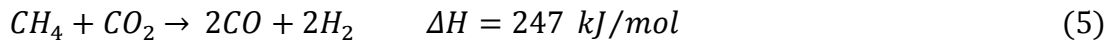
Equations (3) and (4), are showing the two possible partial oxidation reactions with different stoichiometric coefficients [10] and change on the products with respect to initial mole of O_2 .



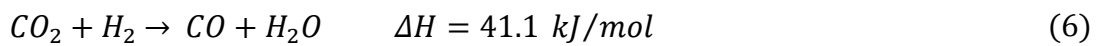
2.1.5 Dry reforming

Dry reforming (CH_4 - CO_2 reforming) Equation (5), has play huge impact on the environment in positive manner [5]. In terms of thermodynamic characteristics, dry reforming is very similar to steam reforming. The major outcome between them is

carbon formation bring higher in dry reforming. This situation is a consequence of lower H/C ratio of dry reforming process [2].



Since this process consumes CO_2 during the syngas production it has widely open future as it reduces CO_2 as a greenhouse gas. Direct consumption of CO_2 , via obtaining CO_2 in the reactants of the chemical reaction makes dry reforming more popular among conventional methods. In addition, this type of reforming results with synthesis gas having a H_2/CO ratio of less than 1 or 1 [2], [3]. However, this ratio can be arranged by adjusting the CH_4/CO_2 ratio at the feedstock. Generally, dry reforming process is continued (or simultaneously) with the reverse water-gas shift reaction equation 6 [2].



Dry reforming is a reaction which requires high (247 kJ/mol) energy from its surroundings which makes it an endothermic process.

2.1.6 The evaluation of the conventional methods

Table 1 illustrates the conventional syngas production methods with their major comparisons. For each process reaction chemistry and ΔH values are given. The main use of the Table 1 is summarized advantages and disadvantages of the processes as well as their general production purpose that has been using in the industry.

Table 1: Comparison of syngas production from different routes [7]

Conventional Method	Reaction	ΔH_{298} (kJ/mol)	Industrial Application	Advantages	Associated Problems
Steam reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	206	H ₂ production, syngas production	Low carbon deposition, suitable for high-pressure processes, easy separation of the products	High H ₂ /CO ratio, need separation for follow-up F-T or methanol synthesis, energy-intensive process
Dry reforming	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	247	Synthesis gas or H ₂ production	Use of two greenhouse gases, i.e. CO ₂ as the feedstock, high availability in some gas fields	Energy-intensive process, low H ₂ /CO ratio, more H ₂ is needed for follow-up F-T or methanol process, easy carbon deposition
Partial oxidation	$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$	-36	Synthesis gas or H ₂ production	Mild exothermic reaction, energy saving, H ₂ to CO ratio around 2 (suitable for methanol and F-T synthesis)	Hot-spot may occur in the catalyst bed
Methanol steam reforming	$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$	49	H ₂ production	High yield of H ₂	Energy-intensive process
Methanol oxy-reforming	$CH_3OH + \frac{1}{2}O_2 \rightarrow CO_2 + 2H_2$	-192	H ₂ production	Exothermic reaction, save energy	Hot-spot may occur in the catalyst bed

These conventional methods are in use since the middle of 20th century. Previously, real focus or question of scientists was how to improve the conventional methods. However, to the best of my knowledge there is no study that compares them. Although, steam reforming, partial oxidation and dry reforming are all used for synthesis gas production, they are not like each other in terms of thermodynamics. This brings a difficulty on comparison of these conventional methods. Not only their reaction chemistry but also their operation conditions can vary. In addition, as mentioned before, during the improvement process of these technologies new methods and extra components have been added on their systems that are very different from each other. In other words, each improvement, such as catalysts, on one technology makes it more different than the others. In the light of this issue, detailed review on literature was essential to collect relevant data such as experiment conditions, used techniques, thermodynamic parameters and substances like carrier gas, cooling fluid etc.

2.2 Plasma Processes

2.2.1 Plasma

There are three well known states of matter which are solid, liquid and gas states. Plasma is accepted as the fourth state of matter. Obviously, transition from gas to plasma state requires energy. Generally, with the help of voltage difference, electrical energy is used for ionization and reaching to plasma state. In this state, matter made up from electrons, ions, neutral particles etc. when they are considered on mass bases, ions and neutral particles are heavier than those of electrons in plasma. For that reason, ions and neutral particles are called as heavy particles and electrons are called as light particles.

“Plasma is considered as a 4th state of the matter with unique properties that cannot be found in the nature” [11]. Direct current torches (DC) and alternating current (AC) torches are mainly categorized group of plasma generators in terms of their designs. In DC plasma torches, water is used as a cooling medium to cool down the two electrodes and they have a nozzle shaped anode. The usage of this type of torches provides some advantages in gasification. To illustrate, when compared with other thermal technologies they are providing high temperatures and heating rates. In addition, decomposition of feedstock can be achieved via pyrolysis. This progress is starting by the exposing waste to plasma and increasing the temperature of the waste above 2000°C [11]. Consequently, simple atoms and molecules, which are H_2 , CO , CO_2 and CH_4 , are produced from the organic compound which consists in the waste, with the effect of extremely high heat exchange. This can be solution to problems in conventional pyrolysis processes [11].

Both, pyrolysis and gasification can be used for utilizing the biomass efficiently. Considering the pyrolysis, with the conventional systems it is expected to obtain below 40wt% yield of gas from feed biomass [12]. The conventional pyrolysis technologies have also another disadvantage of creating fouling on the used equipment since it has high content of tar vapour in its content. On the other hand, plasma pyrolysis is in a more advantageous shape. Producing the gas with low tar content and high heating value, makes the product being able to use in the gas turbine for producing the power as well as it can be used like syngas for different purposes [12]. The bigger portion of the plasma processes, which are used for waste treatment, uses direct current (DC) and arc plasma generators (torches) to focus on the destruction of the waste. DC plasma generators do not have a long life period. Moreover, they need regular maintenance in frequent time intervals. Beside of their high initial cost, in these systems high amount of thermal losses observed due to the cooling of arc-constricting parts. For achieving the stable plasma and distributing the heat to the materials huge amount of gas is needed. Argon can be

considered as the most common example of these gases in the literature. When the thermal plasma compared with the biomass pyrolysis, it can be clearly seen that temperature requirements of thermal plasmas are much higher (generally 3000-10000 K) [12]. The bigger part of this temperature is transferred to surroundings by radiation and convection.

2.2.2 Working principle of the plasma

In the earlier steps of plasma generation, electrical power is required to generate electrical field. The voltage difference between two electrodes needs to be provided via help of the electrical power. The voltage difference between anode and cathode will generate an electric field. Since the electron located at the surface of the cathode will be exposed to electric field, it will start to accelerate towards anode due to presence of electrical field and it will start to collide with molecules. When the electron has enough energy it will cause ionization as it collides with the molecules. After that, electrons that are appear after the ionization of the molecules starts to accelerate under the electric field and start to collide with other molecules which makes the electron avalanche. Break down occurs when the electrons reach to the anode. In addition, positive ions will accelerate towards exactly the opposite direction and move to cathode. As a result, the medium become neutral between the electrodes. If the electric field still exists another cascade of ionization starts to form [1].

2.2.3 Non-thermal and thermal plasmas

Plasma technologies are divided into two in itself. Energy density level and electron density are the two crucial parameters to differentiate whether it is cold or thermal plasma. The first one is cold plasma, also known as thermodynamic non-equilibrium plasma. In this type of plasma, average bulk temperature is in the range of room temperature to hundreds of Celsius degrees [13]. The kinetic energy of the light

particles, electrons, is well higher than those of ions and neutral particles. The electrons having enough amount of energy induce the reaction. Under the effect of voltage difference electric field occurs; those electrons subjected to electric field accelerates and gain energy. While electrons are accelerating, electron-impact dissociation, ionization and excitation take place. As a result, with the help of inelastic collisions, energized light particles transfer energy to flowing gas molecules. At the end, excited particles, ions, free radicals and additional energized electrons become products [14]. The other plasma type is the thermal plasma which is also known as thermodynamic equilibrium plasma. As the name refers, in thermal type of plasma, temperature is much higher than the cold plasma. The electron density is higher than the cold plasma and the temperature is on the order of thousands of Kelvin. Moreover, impact between heavy and light particles causes energy transfer from electrons to heavy particles. This situation creates the thermodynamic equilibrium.

2.2.4 Non-thermal plasma technologies

There are different types of cold plasma exist for reforming. Microwave discharge, dielectric barrier discharge (DBD), glow discharge, corona discharge, and gliding-arc discharge are suitable techniques for creating cold plasma. In cold plasma, electron temperature changes from 1 to 10 eV (8.6×10^{-5} to 8.6×10^{-4} K) because of varying discharge modes. Beside, temperature of the heavy particles reaches to hundreds of Kelvin and the electron density can vary from 10^{15} to 10^{20} m^{-3} [3].

2.2.5 Corona discharge

This type of cold plasma works with low current density around 6 kV and exhibits an inhomogeneous discharge [15]. Electric intensity of corona discharge type plasma is high so ionization of feedstock gas particles can occur. It has capacity to operate at atmospheric pressure. This cold plasma type generally consists two electrodes

which are not symmetrical. One of these electrodes has to obtain high curvature like a small diameter wire whereas the other has to obtain low curvature like a plate. When the enough amount of voltage difference is supplied, this geometry allows electric breakdown to appear at closer place to electrode having high curvature. The gas temperature in the corona discharge plasma is less than 400 K while the electron temperature changes in the range of 3.5-5 eV (30×10^{-5} to 40×10^{-5} K) [3]. Due to the location of electric breakdown, density of the electrons tends to accumulate location closer to curvy electrode and it can vary from 10^{15} - 10^{19} m^{-3} in magnitude[16].

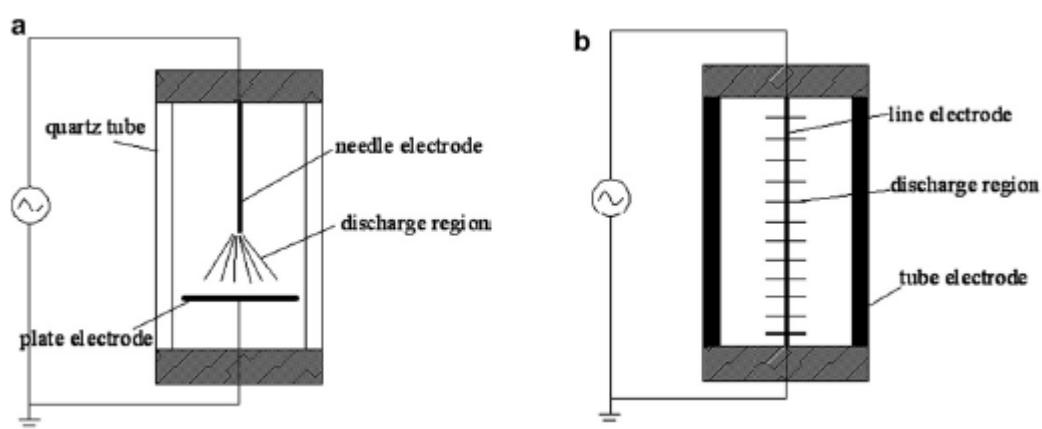


Figure 1: Schematic of some examples for corona discharge reactor [3]

2.2.6 Dielectric barrier discharge

Dielectric barrier discharge (DBD) is a type of cold plasma which is also known as silent discharge. It generally used for ozone production. It includes two planar electrodes located parallel with a distance of few millimetres. The electrodes, at least one of them, have to be covered with dielectric thickness of few millimetres. Properties of the dielectric material such as low electric loss and high breakdown strength are two important characteristics in DBDs. Glass, quartz and ceramics are some examples of dielectric material [16]. The purpose of dielectric is to prevent

the spark or arc formation by restricting the discharge gap [17]. Being inhomogeneous at 1 *atm* and demanding varying voltages to operate are the other properties of DBD type plasmas. There are also micro level discharge channels with the diameters of 0.1 to 0.2 millimetres which are characterizing the discharge [3].

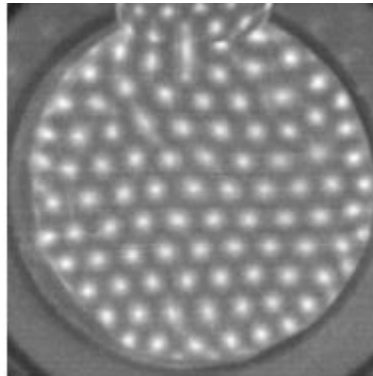


Figure 2: The pattern of discharge imprint [3]

The magnitude of gas temperature in the gap is hundreds of Kelvin. Whereas, the electron temperatures at micro discharge channels vary between 1 to 10 eV, the electron density is about $10^{18} - 10^{21} \text{ m}^{-3}$ [3]. It should be noted that the DBD can only work with Alternating current.

Simple schematic of a DBD, which includes the basic components of the system, is given in Figure 3.

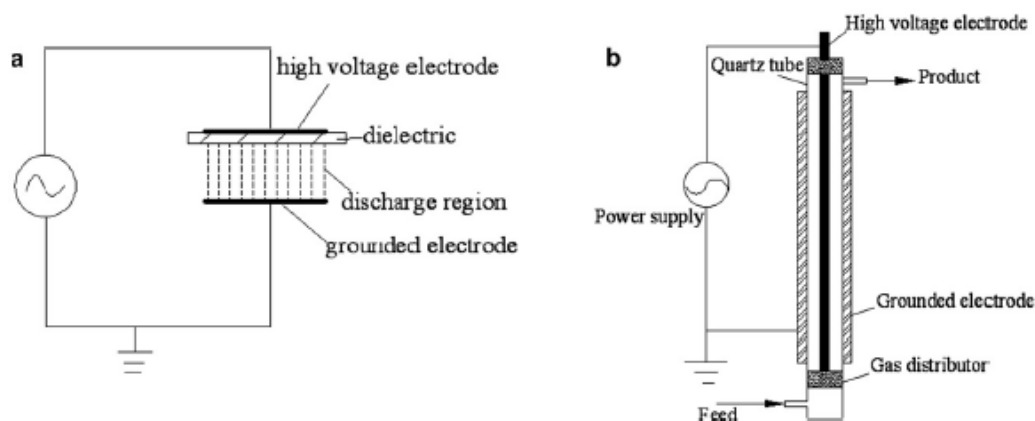


Figure 3: Schematic diagram of the DBD reactor [3]

2.2.7 Microwave discharge

Microwave plasma is a cold type of plasma technology. The reactor of microwave plasma includes a microwave generator, waveguides and tube that is usually made up from quartz material placed into resonance cavity. About its operation properties, the frequency is in magnitude of GHz and pressure can vary in wide range. Comparing microwave discharge with DBD and corona discharge, it has better discharge uniformity and larger discharge space [3]. The electron temperature can vary between 0.4 to 0.6 eV and temperature of the heavy particles is approximately 2000 K [18].

CH_4 - CO_2 reforming has been performed in microwave discharge. Due to its advantages like its large discharge capacity and good uniformity on discharge; it has higher conversion, selectivity, energy efficiency and larger treatment capacity. High gas temperature and the energetic electrons are the inducer of the reaction in the microwave plasma. The main disadvantage of this technology can be considered the unsuitableness for the industrial usage. Since the equipment is complicated and bulky, it is not practical to obtain huge equipment for industrial purpose.

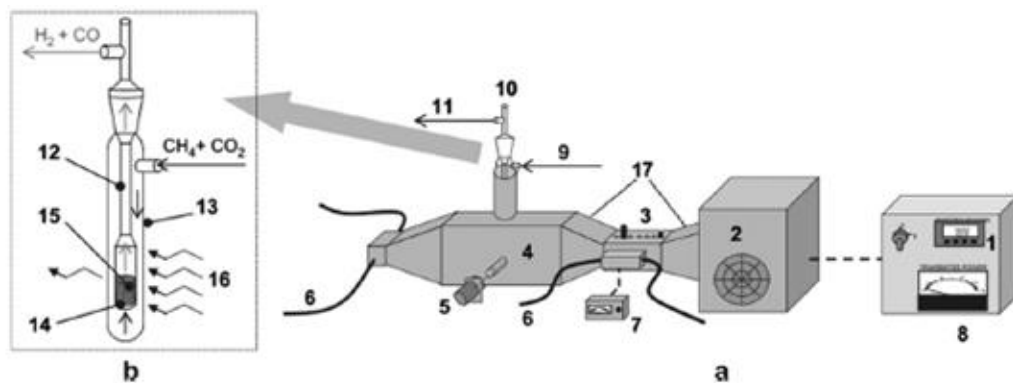


Figure 4: a) Components of Microwave discharge. b) Enlarged schematic of the set quartz reactor jacket [3]

Defining the components in Figure 4, 1 is the input power controller, 2 microwave generator, 3 manual 2-stub unit, 4 cavity of the resonance, 5 optical pyrometer, 6 water sink, 7 reflected power controller, 8 transmitted power controller, 9 inflow gas duct, 10 set quartz reactor jacket, 11 outflow gas line, 12 quartz reactor, 13 quartz jacket, 14 porous plate, 15 catalyst and microwave receptor bed, 16 microwave radiation, 17 waveguide.

2.2.8 Atmospheric pressure glow discharge

The word of glow means observing luminous discharge. Atmospheric pressure glow discharge can operate at different pressures. As the name of luminous refers it is an arc-like discharge.

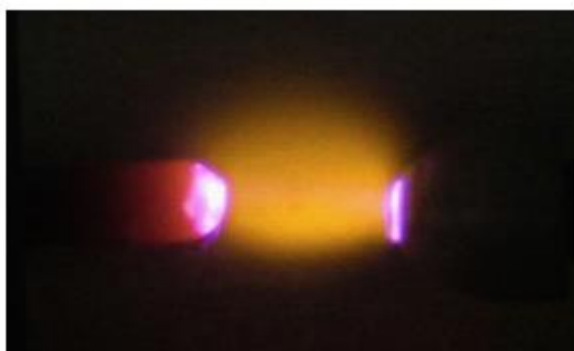


Figure 5: Atmospheric pressure glow discharge in process [3]

Atmospheric pressure glow discharge occurs between the electrodes as a consequent of voltage supply which is in the magnitude of kilo volts. The benefit of ballast circuit prevents the glow being transmitted to arc. In this technology electron temperature changes in the range of 1 to 2 eV, gas temperature 2000 K and the electron density changes 10^{18} to 10^{19} m^{-3} [3].

H. Koinuma *et al.* [19] produced a new kind of atmospheric pressure glow discharge and named it as cold plasma jet. Comparing this new type of atmospheric pressure glow discharge (APGD) cold plasma with the aforementioned cold plasma technologies, one can notice the significant raise on energy conversion efficiency. This positive invention was a result of better design of reactor configuration and the usage of plasma mode.

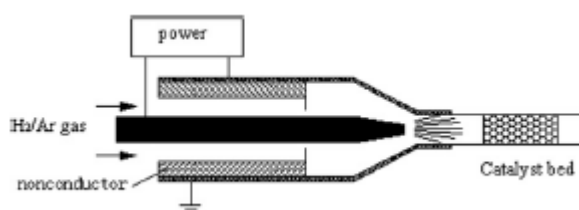


Figure 6: Schematic diagram of APGD plasma jet [3]

As the reactor configuration makes the feed gas confined, it makes all the feed gas exposed to plasma discharge region. In terms of electron density and plasma temperature, AC cold plasma jet of 20 kHz has high values that of corona and dielectric barrier discharges.

2.2.9 Gliding arc discharge

This technology was developed by Czernichowski *et al.* [17] and was patented by Lesueur *et al.* in 1988.

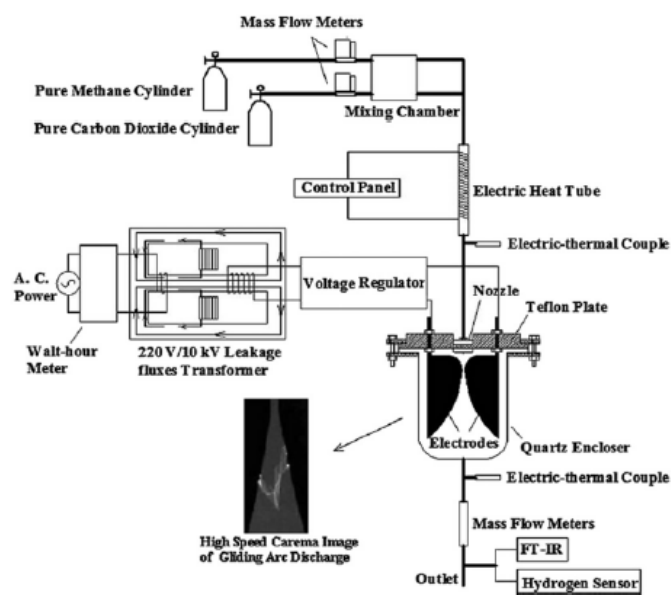


Figure 7: Gliding arc discharge setup [3]

There are at least two diverging metallic electrodes are located inside the reactor. When the high voltage difference supplied on the electrodes, comparatively low current occurs on the electrodes. The appearance of the arc flame plays a crucial role on the distinguishing the gliding arc discharge. The discharge phenomena start at the closest gap, then it starts to expand through the electrodes by the help of the flowing working gas till extinguishes at the downstream. The gas flow rate and the discharge power are two crucial parameters in gliding arc discharge technology, since upon these parameters it could be cold or thermal plasma. In other words, by changing the mentioned parameters one can use gliding arc discharge not only the cold plasma but also the thermal plasma.

2.3 Examples from the Literature

Although in the scope of this study plasma assisted dry reforming of CH_4 is analysed thermodynamically, there are other techniques and feedstock in the literature. The aim of this chapter is to basically demonstrate the similar plasma assisted reforming of different feedstock that are not analysed thermodynamically. The main

difference of selected examples for this chapter, with the cases that are going to be analysed in the main scope of thesis, is the phase of feedstock. In the section 2.3 solid or liquid feedstock application of plasma reforming to generate syngas or synthetic fuel selected, where as in the main thermodynamic analysis CH_4 gas is used. Waste cooking oil (WCO) and wood particles are two examples of biomass that are used as a feedstock in summarised studies.

Biomass can be considered as a renewable energy source. In addition, it can also easily storable and transportable. Different forms of biomass exist in the nature like garbage, wood, agricultural, forest and industrial residues. This source of energy is carbon natural and eases the greenhouse gas emission effect which is caused by fossil fuel based non-renewable energy sources. In most locations on earth the agricultural residues are cheap. Rice straw and corn stalk can be considered as the most possible two candidates of the feedstock of the biomass energy source that can reduce the non-renewable energy source usage.

Rafiq *et al.* [20] studied auto thermal reforming of waste cooking oil. Used reactor is a plasma-assisted gliding arc reactor. Resources like WCO are considered attractive through the literature since they are renewable, reliable and CO_2 natural. In addition, it is claimed that waste cooking oil production is about millions of tons per year in European countries. It can be understood that if the waste cooking oil is used as a feedstock, harm of waste cooking oil disposal to the environment can be reduced or prevented. Furthermore, WCO conversion processes can be done with low cost facilities and environment friendly bioenergy production can be obtained at the end.

Van Oost *et. al.* [21] mainly focused on the transportation sector. They figured out that 30% of energy consumption accounts on transportation sector in Europe.

Considering the CO_2 emissions of fossil fuel based energy source, most of the countries have to find alternative ways of energy that can be used in transportation sector. One of the main causes of this situation is Kyoto protocol argument. This argument forces the countries not to extend certain amount of CO_2 emissions.

2.3.1 Using Waste Cooking Oil (WCO) to Produce Bio Syngas

The actual objective of the study [20] is to generate a bio-syngas with the using waste cooking oil with the existence of C_3H_8 and air. Initially, test has been performed with propane and water. The main purposes of test are finding out the maximum flow rate of water which would be suits with the stability of the operation and producing a soot free gas production. In other words, operating capacity of reactor, which is gliding arc reactor, has been found for the water and WCO rates. In the experiment, effects of important parameters like flow rates of WCO and water, axial temperature distribution, product concentration, reactant conversion, product yield, H_2/CO ratio, and thermal efficiency have been analysed under the presence of constant propane and air flow. K type thermo-couples were inserted into the thin hollow pipe at different places to measure the temperature. It was also noted that there was no need of another energy supply to heat the catalyst bed. The reaction temperature and the temperature of the hot gases inside plasma region were enough to meet required temperature. In addition, it could be difficult to use WCO as a feedstock in processes. To overcome this difficulty, blend of feedstock with other hydrocarbons such as CH_4 , C_2H_6 , and C_3H_8 increases the speed of the reaction and make the operation more sustainable.

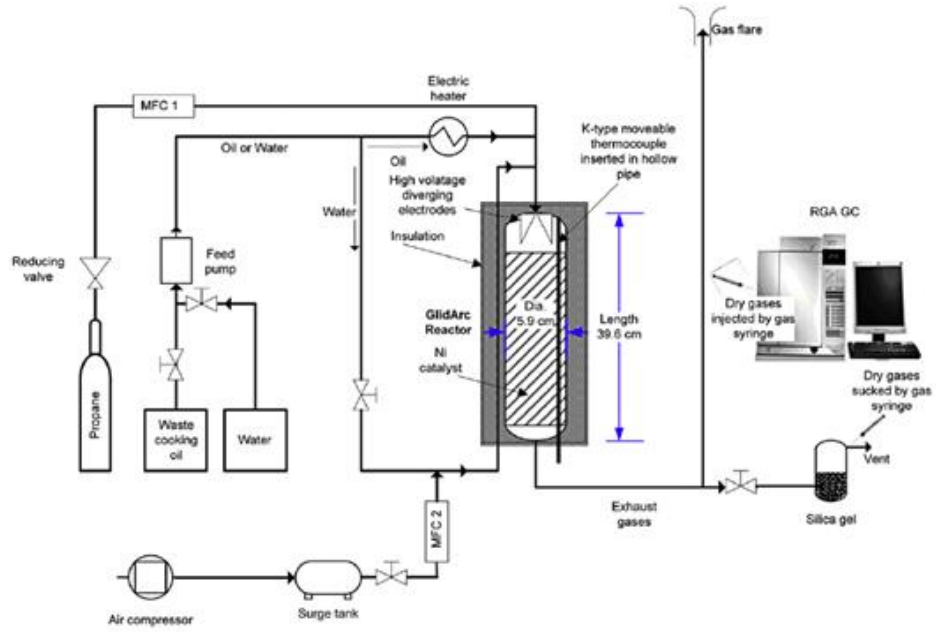


Figure 8: Non-thermal plasma assisted gliding arc reforming technique [20]

Elemental balance of N_2 gives the total dry molar flow rate of products that is coming out from the gliding arc reactor. It can be formulised as follows Equation (7) [20]:

$$F_{dry,out} = \frac{F_{N_2,in}}{y_{N_2,in}} \quad (7)$$

Carbon and oxygen conversions can be calculated from Equation (8) [20];

$$X_C = \frac{F_{dry,out} \sum y_{C,out}}{F_{C,in}} \quad (8)$$

$$X_{O_2} = \frac{F_{O_2,in} - F_{O_2,out}}{F_{O_2,in}} \quad (9)$$

where Y is the mole fraction and F is the molar flow in mole per minute.

In addition to the conversion, yield is an important parameter. For calculating the yield of the i product from species j , Equation (10) can be used as [20]:

$$Y_{i,j} = \frac{v_{i,j} F_{i,out}}{\sum_k v_{i,j} F_{k,in}} \quad (10)$$

The chemical ratio (stoichiometric amount) of i component in species j is defined as, $v_{i,j}$. The denominator of Equation (10) is the summation of all species k .

One of the most important parameters of any system is the thermal efficiency. In this study the thermal efficiency of the gliding arc reactor can define as Equation (11) [20]:

$$\eta = \frac{F_{syngas} LHV_{syngas}}{F_{C_3H_8,in} LHV_{C_3H_8} + F_{WCO,in} LHV_{WCO} + E_P + E_H} \quad (11)$$

Where LHV stands for lower heating values of the, synthesis gas, propane and waste cooking oil in kJ per minute. E_P is the electrical energy which is necessary for the high voltage electrodes of GlidArc in kJ per minute. E_H is the heating energy for the WCO electric heater in kJ per minute.

Last parameter is the space velocity SV , which is the ratio of total volumetric flow rate to total weight of the catalyst [20]:

$$SV = \frac{V_{total}}{W_{catalyst}} \quad (12)$$

where, V_{total} is the total volumetric flow rate of the both gas and waste cooking oil or water and $W_{catalyst}$ is the bulk weight of the catalyst bed given in grams.

2.3.2 Using Crushed Wood to Produce Synthetic Fuel

In the paper of Van Oost et. al. [21], Pyrolysis/Gasification of biomass for synthetic fuel production using a hybrid gas-water stabilized plasma torch analysed.

Conventional biomass gasification occurs between the carbon source which is heated and a fixed amount of oxygen and steam. In addition, thermal plasma can decompose biomass in the absence of oxygen. The higher heat capacity of the gas the less unwanted contaminants (like CO_2 , tar etc.) occur in the product.

Figure 9 illustrates the schematic of the reactor that is used in the production of Synthetic fuel from the crushed wood. This reactor is called as plasma-chemical reactor.

The wall temperature of the reactor has been given as 1700°C. Such systems having a high temperature have to be cooled. In this specific case, the system is cooled with water circulated around the reactor. Inner portions of the reactor were ceramic for being able to survive in extremely high temperatures. The other concern was the pressure; there was continuous flow to material container under controlled flow rate. The pressure inside the supply container was automatically will

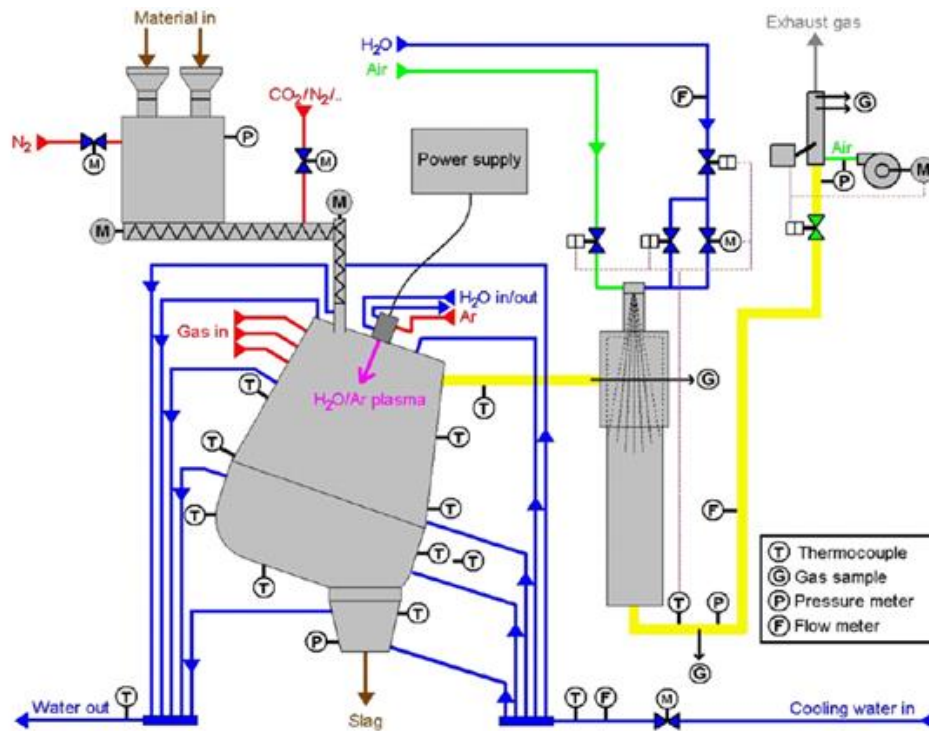


Figure 9: Schematic of experimental reactor for plasma pyrolysis and gasification [21]

be kept higher than the pressure inside the reactor by controlled nitrogen flow. Thus, gas flow from the reactor to the supply unit was prevented. As a feedstock, crushed wood with the dimensions of few mm was sent to the reactor from the downstream 30 cm distance to entrance nozzle in which located at the top of the system. During the jet flight some particles gasified and the other non-gasified particles fell down to the bottom of the reactor and they gasified under the effect of hot gas flow. The exit zone of the reactor was located at the upper part of the reactor in order to force the product gas to pass inside or near by the high temperature area in which plasma jet occurred. The UV radiation of plasma jet had a gas cleaning property as well. As it can be observed from Figure 9, there were three different gas entrances to the reactor located at top. These places were for the additional gas injection to the reactor for controlling the atmosphere of the system.

The used torches which can generate oxygen-hydrogen-argon plasma jets were located at the top, and it was having high plasma enthalpy and temperature. The anode of the torch was consisting of rotating water-cooled disc, and it was located arc chamber downstream of the torch exit nozzle. The argon gas was given to the chamber from the torch for protecting the anode from the movement of the reaction gases.

As it can be seen from Figure 10, the main components of produced gas were hydrogen (28-46% vol.), CO (46-68%), CO₂ (2-8%) and Ar (0.2-8%) and the content of complex hydrocarbons and tar can be neglected due to their low amount (1 mg/Nm³). During the experiment feedstock (wood) feeding rate was 47 kg/h, humidity was 6.5%, stem plasma flow rate was 22.4 L/min, argon 13.6 L/min, carbon dioxide 115 L/min and oxygen was 30 L/min [21].

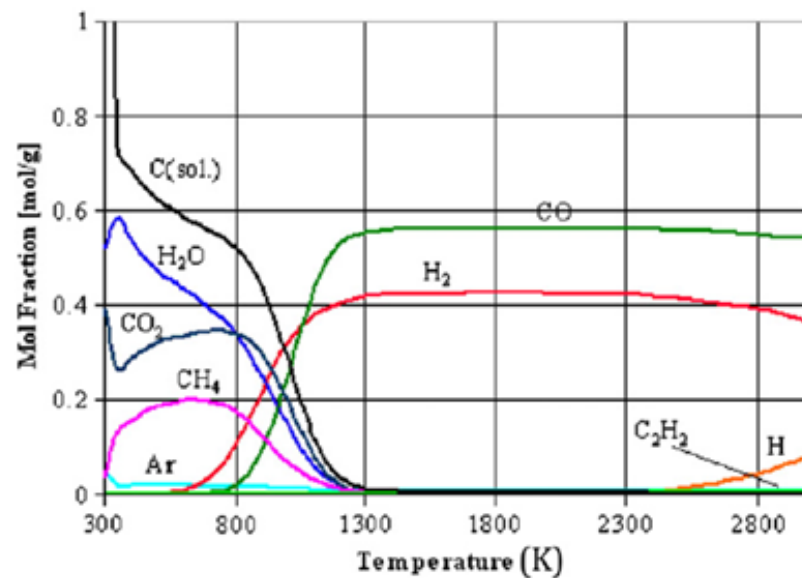


Figure 10: Gasification of wood in a H₂O/Ar plasma: Mole fraction of products as a function of the temperature in the reactor [21]

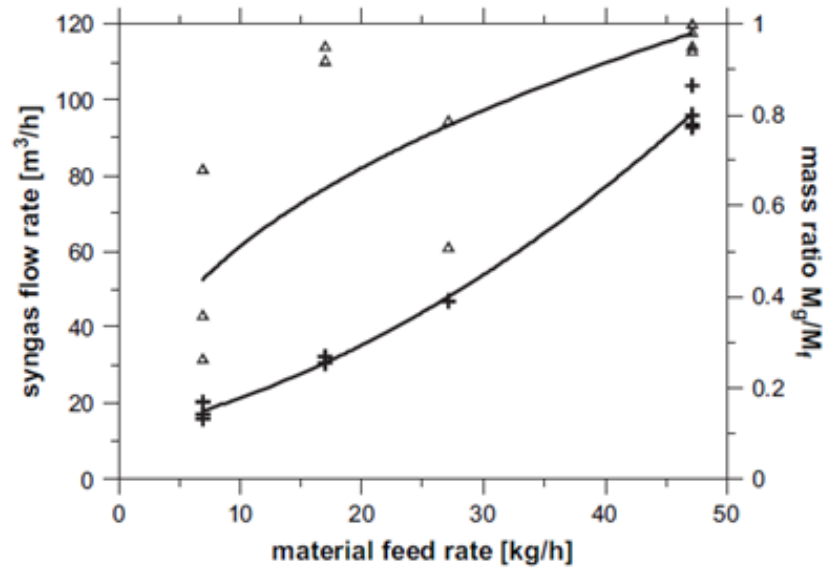


Figure 11: Synthesis gas flow rate (+) and the mass of synthesis gas over total mass ratio (Δ) vs. feed rate of the material [21]

Feedstock feed rate to the reactor is an important parameter since it has significant effect on flow rate of products, i.e., synthesis gas. Moreover, the mass ratio of product syngas to overall input mass is effected by material feed rate. Figure 11, illustrates the relations between parameters.

2.3.3 Using Biomass to Produce Synthetic Gas

According to Grigaiten et. al. [11] biomass per one habitant ratio is really high in European countries. So that use of biogas will not only reduce the waste material but also supply a benefit to the society in terms of energy. Plasma gasification technology is mentioned as one of the latest and less explored technology to achieve this goal.

The Figure 12 shows the system that had been used during the test of water vapour plasma technology for biomass conversion to synthetic gas. The DC plasma torch

had been used. It was 30-40 kW power and cathode were button type hot tungsten and anode was a step-formed copper. The system also contains the units like supplying and regulating kits, coolant kit for preventing the torch to reach extreme temperatures, feeding kits for gases like water vapour. The insulation rings were used for the electrodes which also take a separation role. The electrodes were the place of shielding and main reforming gases supply to the system.

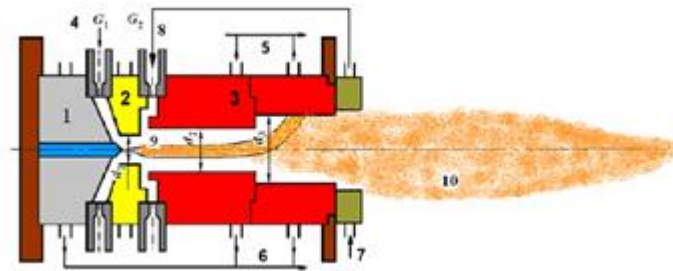


Figure 12: Schematic of water vapour plasma torch [11]

The sections of Figure 12, refers to; “(1) cathode junction, (2,4,8) neutral section, (3) step formed anode, (5) cooling water supply, (6) water exhaust, (7) water vapour supply, (8) overheated water vapour, (9) electric arc, (10) plasma jet, (G1) argon gas supply, (G2)water vapour supply” [11].

The high velocity plasma jet automatically occurred by the meeting of feeding gas with the DC arc ignition between the cathode and anode at the reaction chamber of plasma torch. Argon gas had been used as a shielding gas in order to dynamical stabilization of electric arc and protection of the cathode from erosion. Depending up on the type of used plasma forming gas and the strength of the current, total mass flow rate of argon can be vary from 10% to 20% for achieving sufficient shielding. One of the most commonly used plasma forming gas was the water vapour. It is critical that water vapour had to be overheated. This plasma forming gas could be obtained by exposing the H_2O to water steam generator under 5 bar pressure.

Thanks to the energy conversion equation, variables of plasma jet and the plasma torch characteristics can be calculated with the help of reading the three parameters which are current strength drop on the voltage and the flow rates of the gases. Crucial engineering variables like heat loss to the cooling water, average temperature of the flow and the velocity can be calculated. In addition, efficiency of the plasma torch can be found.

In the selection of the anode of the reactor Equation (13) can be used to figure out dimensions like diameter and length. Total gas flow rate, arc current and pressure have a direct effect on the selection of the anode [11];

$$\frac{U d}{I} = A \left(\frac{I^2}{G d} \right)^m \left(\frac{G}{d} \right)^n (p d)^2 \left(\frac{l}{d} \right)^r \quad (13)$$

where, I is the arc current in ampere; d is de anode diameter in meters; U is the arc voltage in voltage; G is the total gas flow rate in kg per second; p is the pressure in Pascal; l is the length of the anode in meters and A, m, n, k, x are the values which are depends on the plasma torch construction and operating regime.

2.3.4 Using Wood and Char to Produce Synthetic Gas

The experimental setup of the study of Tang and Huang [12] is given in the Figure 13. The source of the plasma having a radio frequency of 13.56 MHz has 0-2000 W power output. The other component of the system is pyrolysis reactor. It is a quartz tube in cylindrical dimensions which has inner diameter and length of 16 mm and 500 mm respectively. There are two copper rings which are surrounding the electrodes with a width of 25 mm. The purpose of these copper rings is transferring the power from the RF power source to gas flowing inside the tube. The locations of

these two copper rings are as important as their function. As the plasma zone is going to appear between those rings, the best distance between them must be found. To achieve this goal, in this specific experiment, space between them changed from 3 to 9 cm. Furthermore, an additional copper ring couple, used for generating two plasma zones. At this situation, distance between each set of electrodes was 10 cm and the spacing of two electrodes on the same side was 3 cm.

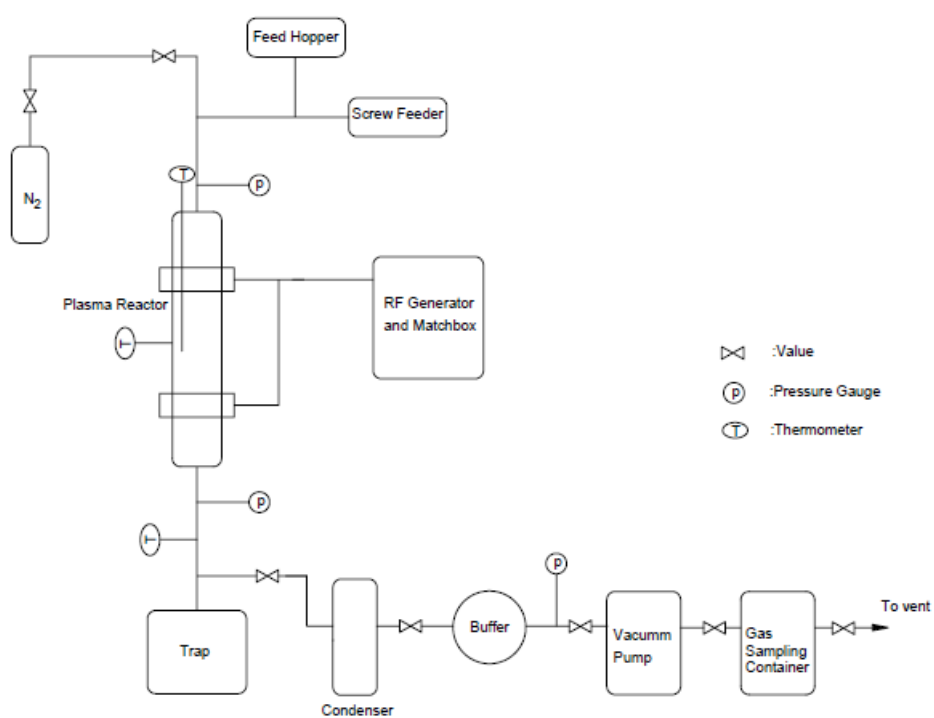


Figure 13: Schematic of the RF plasma reactor system [12]

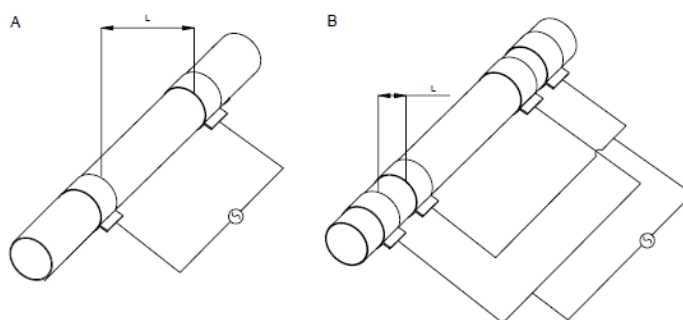


Figure 14: Schematic of electrodes with copper rings [12]

Other issue is the purging the system. In order to do this, the entrance of the gas is located in the reactor. Other than the purging, inert gas flows into the system from this location and serves to system for generating the plasma. As it can be seen from Figure 13, screw feeder is placed on top of the plasma reactor (quartz tube). This provides not only the supplying necessary amount of biomass feedstock to obtain continues production, but also guides the biomass particles to fall in to the centre of the cylindrical tube so that feedstock particles can ionized easily by being exposed to plasma. The temperature measurement device was platinum-rhodium thermocouple in this experiment.

The type of the biomass that used in this experiment was fir sawdust with the average size of 200 μm . Further details of the experiment have given in Table 1.

Table 2: Analysis of wood and char samples [12]

Material	Proximate Analysis (wt%)			Ultimate Analysis (wt% dried)					Heat Value (MJ/kg)
	Volatile	Fixed Carbon	Ash	C	H	O	N	S	
Wood	78.82	18.83	2.35	47.1	6.4	46.5	<0.3	<0.5	17.53
Char			14.62	83.17	2.21	<0.5	<0.3	<0.5	29.03

The velocity of the feedstock particles during the entrance of the system was 0.3 g/min. In order to obtaining stable condition at the biomass feedstock injection to the system, nitrogen carrier gas with the velocity of 0.8 L/min has been used. The variable speed rotary vacuum pump has been used for evacuating the pyrolysis product vapour from the system.

2.3.5 Summary

As it is clearly understood from the summarized examples, plasma reforming processes are all case specific, and do not allow the reader to compare and contrast the plasma types and reactor for biomass conversion. As it is mentioned before, in the thermodynamic analysis of this thesis, rather than the biomass feedstock in solid or liquid phases, mainly the CH_4 (methane) gas is going to be reformed via different technologies. One of the reasons of this chapter is to show that, plasma reforming is not limited with the gas phase feedstock but biomass in the phases of solid and liquid can be converted in similar technologies. On the other hand, the reason of selecting CH_4 (gas) reforming for the thermodynamic analysis is the existence of CH_4 gas in the many of the gases that can be used as a fuel such as natural gas and biogas.

CHAPTER 3

METHODOLOGY

3.1 Conventional Methods

In this part of the study, experimental data of conventional methods are gathered from the literature. Table 3 summarizes the raw data that directly gathered from the literature.

Table 3 represents the accessed parameters for related technologies from the literature with their references. Based up on the table, thermodynamic analysis of conventional methods is going to be performed. However, as it can be seen on Table 3, there are missing values for the further analysis. So, initial task is to find unknown parameters.

In order to figure out the thermodynamic properties of the conventional methods, necessary parameters have to be calculated. Both of before reaction and after reaction moles of CH_4 and CO_2 need to be cleared out as well as mole of the product CO . For finding these parameters, conversion values that are given from the studies can be used. Note that, given parameters were different in each study. However, there is enough information to calculate the not given parameters. For example, to find mole flow rate of methane Equation (14) can be used [4];

$$\dot{n}_{CH_4,in} = \frac{\dot{n}_{CH_4,out}}{1 - \dot{n}_{CH_4,converted}} \quad (14)$$

Table 3: Data collected from the literature for the conventional methods to produce syngas

Conventional Technology	Flow Rate	O ₂ /CH ₄	H ₂ O/CH ₄	T _{max} (K)	Pressure (bar)	mole input %			mole output %			%CH ₄ converted	%CO ₂ converted	%CO selectivity	%H ₂ selectivity	H ₂ /CO Reference	
						H ₂	CO	CH ₄	CH ₄	CO ₂	CO						H ₂
CO ₂ reforming	1.5 h ⁻¹			1173	1	60	8	27				64	60		70	2.69	[22]
CO ₂ reforming	80000 h ⁻¹			1023		58	6	26				65	80	100	100	2.25	[23]
Steam reforming	1 m ³ /s		3	1173	1				5	12	10	78					[10]
Steam reforming	4000 h ⁻¹		3	1073		60.2		39.8	16.9	19.5	63.6	100					[9]
Steam reforming	4000 h ⁻¹		3	873		60.2		39.8	6	24.4	10	59.6	75				[9]
Partial Oxidation	3483 m ³ /s	0.6	1.4	1444	25							95					[6]
Partial Oxidation	417 mL/min	0.5		723					8			31		25.8		8.3	[24]
Partial Oxidation	8667 mL/min	0.5		1046					61.2			76		80.5		2.1	[24]
Partial Oxidation	200556 L/kg/h	0.5		1285				91.1				80.1		91.5	87.3	1.91	[8]
Partial Oxidation	500000 L/kg/h	0.5		1360				91.1				85		94.2	88.5	1.88	[8]

While completing the missing parameters on the table, for some references $\dot{n}_{CH_4,in}$ was the missing parameter but for some other it was given and $\dot{n}_{CH_4,out}$ was the missing parameter. Obviously, for finding the $\dot{n}_{CH_4,out}$, same equation can be used for rearranging Equation (14).

After completing the table for methane, only remaining parameter is to find is $\dot{n}_{CO,out}$ values for the partial oxidation case. In order to find this parameter, CO selectivity can be used as described in Equation (15) [4];

$$S_{CO} = \frac{\dot{n}_{CO,out}}{\dot{n}_{CH_4,in} - \dot{n}_{CH_4,out} + \dot{n}_{CO_2,in} - \dot{n}_{CO_2,out}} \quad (15)$$

For the case in reference [8] CO_2 did not exist in the reaction so they are taken as zero. Both, in and out molar flow rate of methane values were known and the selectivity value was given. Thus, molar flow rate of CO can be calculated from equation 3.

Using the equation 16, selectivity of H_2 , it is possible to find $\dot{n}_{H_2,out}$ value from using following equation or directly the H_2/CO ratio can be used [4].

$$S_{H_2} = \frac{0.5 \dot{n}_{H_2,out}}{\dot{n}_{CH_4,in} - \dot{n}_{CH_4,out}} \quad (16)$$

It should be noted that, selectivity equation has some modification for dry reforming process because of existence of H_2 gas at the composition of the inlet gas. For the case studied in this paper coke oven gas were used [23]. Since it

contains H_2 in its content, selectivity equation is modified as follows on Equation (17) [23];

$$S_{H_2} = \frac{\dot{n}_{H_2,out}}{\dot{n}_{H_2,in} + 2(\dot{n}_{CH_4,in} - \dot{n}_{CH_4,out})} \quad (17)$$

The equations which are used for evaluating the missing parameters are not limited with given above. There are equations for conversions and yield parameters as well. Such as conversion of methane Equation (18) [23], conversion of carbon dioxide Equation (19) [23] and yield of hydrogen and carbon monoxide are given in Equations (20) [25] and (21) [25] respectively.

Conversion of CH_4 Equation (18) can be calculated simply by taking the ratio of difference of inlet and exit molar flow rate values of CH_4 to the inlet molar flow rate value of the CH_4 .

$$X_{CH_4} = \frac{\dot{n}_{CH_4,in} - \dot{n}_{CH_4,out}}{\dot{n}_{CH_4,in}} \quad (18)$$

Similar to the Equation (18), conversion of CO_2 Equation (19) can be calculated simply by taking the ratio of difference of inlet and exit molar flow rate values of CO_2 to the inlet molar flow rate value of the CO_2 .

$$X_{CO_2} = \frac{\dot{n}_{CO_2,in} - \dot{n}_{CO_2,out}}{\dot{n}_{CO_2,in}} \quad (19)$$

Yield of H_2 can be calculated by dividing the exit molar flow rate of H_2 to two times of inlet molar flow rate of CH_4 .

$$Y_{H_2} = \frac{\dot{n}_{H_2,out}}{2 \dot{n}_{CH_4,in}} \quad (20)$$

Yield of CO can be calculated by dividing the exit molar flow rate of CO to inlet molar flow rate value of CH_4 .

$$Y_{CO} = \frac{\dot{n}_{CO,out}}{\dot{n}_{CH_4,in} + \dot{n}_{CO_2,in}} \quad (21)$$

Although, yield and selectivity parameters are different in terms of equation, it is enough to illustrate one of them in the results, since; they are both related with the amount of products. However, both of them have to be used during the thermodynamic analysis since some references uses yield and others use selectivity values. In other to create correlation, Equation (22), between the yield Equations (20) and (21) and the selectivity Equation (15) and (16); conversion Equations (18) and (19) can be used.

$$S_i = \frac{Y_i}{X_i} \quad (22)$$

Table 4: Completed table with essential parameters for thermodynamic analysis

Conventional Technology	Flow Rate	T_{max} (K)	Pressure (bar)	mole input			mole output			mol fraction			%CH ₄ converted	%CO ₂ or %O ₂ converted	CO yield	H ₂ yield	H ₂ /CO reference	
				H ₂	CO	CH ₄	CH ₄	CO ₂	CO	H ₂	CH ₄	CO ₂						CO
CO2 reforming	1.5 h ⁻¹	1173	1.013	60	8	27	9.72	24.61	66				64	60	0.46	1.23	2.69	[22]
CO2 reforming	80000 h ⁻¹	1023		58	6	26	9.1	16.9	92				65	80	0.33	1.77	2.25	[23]
Steam reforming	1 m ³ /s	1173	1.013	25	5	12	5	12	78	0.048	0.114	0.095	80		0.2	1.56	7.8	[10]
Steam reforming	4000 h ⁻¹	1073		60	39.8	0	0	16.9	19.5	64	0	0.169	0.195	100	0.16	0.53	3.26	[9]
Steam reforming	4000 h ⁻¹	873		60	39.8	6	24.4	10	60	0.06	0.244	0.1	75		0.08	0.5	5.96	[9]
Partial Oxidation	3483 m ³ /s	1444	25	11	0.55	6	15.6	46	0.006	0.006	0.156	0.458	95	99.81	0.71	2.08	2.94	[6]
Partial Oxidation	200556 L/kg/h	1285		91	18.13	66.77	127	0.085		0.314	0.6		80.1	99.9	0.37	0.7	1.91	[8]
Partial Oxidation	500000 L/kg/h	1360		91	13.67	72.94	137	0.061		0.326	0.613		85	99.6	0.4	0.75	1.88	[8]

Values that are in bold and underlined are the calculated

It can be noticed that there are still missing values exist in the Table 4, the reason is the unnecessary of those values in the calculation of related result. It should be noted that, each process in the Table 4 was case specific so same parameter is going to be calculated by using different parameters. Consequently, if the parameter is not required for finding the result, it is not calculated and tabulated in the Table 4. However, if it is calculated for another line (other process) it means that, that parameter is crucial for the further thermodynamic analysis.

Table 4 also illustrates the yield of CO and H_2 values. Although, the technologies going to be compared based up on selectivity values, during the thermodynamic analysis yield values is going to be used. As it is mentioned earlier both selectivity and yield parameters represent the magnitude of products in different manner. As the referred references used yield values, for the simplicity of the calculations, yields used in the calculation stage then they can be converted to the selectivity by using Equation (22) for the comparison.

Filling the necessary columns of the data Table 4, next step is to figuring out the total energy consumption of each case that is needed to run the system properly. It is frequently seen on some research papers that efficiencies of the similar studies can vary a lot from paper to paper. This is mainly caused by missing any energy consumption parameter during the efficiency analysis. The main conditions that can affect the energy efficiency of the system are electric energy consumption for running the system, heating the system, pre-heating the working or carrier gas and any secondary devices for running the system. Beside, thermal energy for different purposes can sometimes is used for proper operation of the systems. In other words, regardless of its type or purpose, all energy consumption has to be taken in to consideration to obtain a correct result and to compare the systems on the same bases.

Other important parameter is lower heating value, *LHV*, which can be found from thermodynamic tables. Once the raw data completed, thermodynamic analysis can be started to compare conventional syngas production methods. Equation (23) illustrates the general form of the energy efficiency equation.

$$\eta = \frac{\dot{m}_{syngas} LHV_{syngas}}{\dot{m}_{fuel} LHV_{fuel} + \dot{m}_{carrier\ gas} \Delta h_{carrier\ gas} + E_{pre-heating} + E_{cooling} + E_{other}} \quad (23)$$

3.2 Plasma Methods

Like in conventional methods, experimental data have to exist in order to make any analysis or calculations. Literature research has been done in detail to obtain experimental results. Table 5 shows the data gathered from the literature.

As it can be understood from the empty spaces on Table 5, there are lots of unknown values on the gathered data from the literature. It should be noted that, references are selected among many different papers. The most of the studies were not taken into account since they have not provided sufficient amount of data from the experiment. Thus, the studies that are listed on Table 5 are the ones either necessary parameters like conversions, yields and efficiencies given or the parameters which are sufficient to calculate efficiency in their definition are provided.

Table 5: Data gathered from the literature

Plasma Technology	Feed	Flow Rate $\times 10^4 (\text{m}^3/\text{s})$	T_{in} (K)	P_{in} (kPa)	Power Input (W)	T_{out} (K)	mole output %			Converted	CO Yield	H ₂ Yield	%CO Selectivity	%H ₂ Selectivity	H ₂ /CO	Efficiency (%)	Reference
							H ₂	CO	CH ₄								
Pulsed corona (NT)	methane	0.25	300	161.4	300	523	25	60	19				64	4		[26]	
Thermal DC water (T)	methane	0.67	500	100	1050	5250	0.55	0.3	0.05	0.11	59		78	1.8		[27]	
Thermal N ₂ (T)	methane	5	333	100	9600	1073			90		80		69	1.16	48	[27]	
Thermal Ar (T)	methane	12.22		100	18000	1073			79		65		97	1.39	57	[27]	
DBD (NT)	methane	0.03	423	100	500				64		39		43	0.67		[28]	
DBD (NT)	methane	0.1	423	100	500				30		13		42	0.7		[28]	
Microwave (T)	methane	3.33	1073		120	2750			71		69		75		25	[27]	
Gliding Arc (NT)	propane	2.33	923		1370		44.4	18.2	11.2	21	23			2.4	63	[29]	

T: Thermal, NT: Non-thermal

The next step is calculating the ungiven values of each plasma technology by using the other given parameters.

Initially, if the H_2 yield and CH_4 conversion values are known, H_2 selectivity value can be calculated by using the following Equation 24 [30].

$$S_{H_2} = \frac{H_2 \text{ yield}}{CH_4 \text{ conversion rate}} \quad (24)$$

The efficiency given on the references were simply calculated by taking the ratio of energy of the produced syngas to input energy [26]. At this stage, aim was to fill efficiency values for not given references according to given definition of efficiency [26].

$$\eta_{given} = \frac{\dot{m}_{syngas} LHV_{syngas}}{W} \quad (25)$$

Investigating the given efficiency definition and equation, LHV is a constant and input power is known parameter on every case on selected studies. The mass flow rate of syngas [kg/s] is the critical parameter at this stage since it is not known. However, it can be calculated if the mole output of H_2 is known, by using continuity Equation (26).

$$\dot{m} = y_{H_2, out} \dot{V} \rho \quad (26)$$

Volumetric flow rate [m^3/s] is given in all studies and the density [kg/m^3] can be found easily since the working fluids are known in each experiment. Thus, out flow mole fraction of H_2 is the only unknown. In order to figure out the mole fraction of H_2 , the mole fraction of CO has to be known so that the ratio of H_2 to CO can be used. However, the only known value is their ratio in all cases. Consequently, the other parameters including the out flow mole fraction of H_2 or the out flow mole fraction of CO need to be considered. In the light of this issue, the equations of conversion rate Equations (18) and (19), H_2 selectivity Equation (27) [26] and CO selectivity Equation (28) [26] can be used. Taking those equations in to account brings additional unknowns which are in and out mole fractions of CH_4 . As a result of this, there are four equations which are CH_4 conversion rate, CO selectivity, H_2 selectivity and H_2/CO ratio; and four unknowns which are the in and out mole fractions of CH_4 , the out flow mole fraction of H_2 and the out flow mole fraction of CO .

$$S_{H_2} = \frac{0.5 \dot{n}_{H_2,out}}{\dot{n}_{CH_4,in} - \dot{n}_{CH_4,out}} \quad (27)$$

$$S_{CO} = \frac{\dot{n}_{CO,out}}{\dot{n}_{CH_4,in} - \dot{n}_{CH_4,out}} \quad (28)$$

Completing the necessary calculations, that are explained above, with using the data supplied in Table 5, important parameters (especially the energy efficiencies) of the selected systems are calculated and tabulated in Table 6;

Table 6: Data gathered from the literature after completing the missing values of efficiencies

Plasma Technology	Feed	Flow Rate $\times 10^{-4}$ (m ³ /s)	T _{in} (K)	P _{in} (kPa)	Power (W)	T _{out} (K)	%CH ₄ Converted	%CO ₂ Converted	%CO Selectivity	%H ₂ Selectivity	H ₂ /CO	%Efficiency (η)	Reference
Pulsed corona (NT)	methane	0.25	300	161.4	300	523	19		0	64	4.00	20	[26]
Thermal DC water (T)	methane	0.67	500	100	1050	5250	75	59	78	71	1.80	34	[27]
Thermal N ₂ (T)	methane	3.61	333	100	9600	1073	90	80	88	69	1.16	48	[27]
Thermal Ar (T)	methane	5.00		100	18000	1073	79	65	97	83	1.39	57	[27]
DBD (NT)	methane	12.22	423	100	500		64	39	43	24	0.67	1	[28]
DBD (NT)	methane	0.03	423	100	500		30	13	42	20	0.70	16	[28]
Microwave (T)	methane	0.10	1073		120	2750	71	69	75	0		25	[27]
Gliding Arc (NT)	propane	3.33	923		1370		62	23	0	0	2.40	63	[29]

T: Thermal, NT: Non-thermal

Table 6 illustrates the given efficiencies of different plasma processes. As it is mentioned before, those efficiency values not exist on Table 5, which was not given on related reference, were determined by using Equation (25) according to given definition of efficiency. Other than the efficiency values, feed gas, the operating conditions, power consumed for generating the plasma, methane and carbon dioxide conversions for different plasma technologies are also included in Table 6.

Since the major purpose of this thesis is to analyse and compare different plasma technologies thermodynamically, the parameter of efficiency has to be calculated in detail as much as possible. The main obstacle on this issue is the limited information about the conditions and lack of detailed data on the studies in the literature. The cited references on this thesis are the ones supplying the most data and related conditions of plasma relevant experiments. Even so, since the experiments were conducted by different researchers, it is not guaranteed that we have captured all components of the processes perfectly. Any simple single process may contribute effect on efficiency. Consequently, in the light of the detailed efficiency analysis, every energy consumption cases taken into account to come up with accurate efficiency values. In other words, not only the power input for generating the plasma, but also other energy consumptions added into efficiency analysis.

$$\eta_{calculated} = \frac{\dot{m}_{syngas} LHV_{syngas}}{W + \dot{m}_{fuel} LHV_{fuel} + \dot{m}_{carrier\ gas} \Delta h_{carrier\ gas} + E_{cooling} + E_{other}} \quad (29)$$

3.3 The Equilibrium Constant, K, Analysis

In this part of the study, main focus is to observe the chemical equilibriums of plasma processes. Thermodynamically, it is possible to estimate the equilibrium compositions of the system at a specified temperature and pressure [31]. In order

to check whether the system reached to equilibrium or not Equation (30) can be used [31],

$$K(T) = \frac{y_C^{v_C} y_D^{v_D}}{y_A^{v_A} y_B^{v_B}} \left(\frac{P}{P_{ref}} \right)^{v_C+v_D-v_A-v_B} \quad (30)$$

Where A and B stands for reactants, C and D for products; v_i represents the stoichiometric coefficients; P is the pressure and P_{ref} equals to 1 atm. As it can be seen from the Equation (31) the equilibrium constant, K is a function of temperature [31].

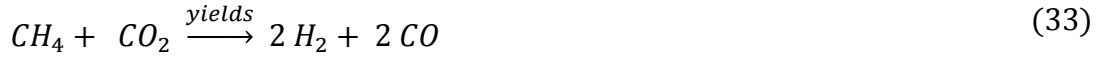
It is possible to express Equation (30) in terms of the number of moles that would be present in the equilibrium [31]. The number of moles can be related to mole fraction as $y_i = n_i/n$, where n is the total number of moles in the mixture.

$$K = \frac{n_C^{v_C} n_D^{v_D}}{n_A^{v_A} n_B^{v_B}} \left(\frac{P/P_{ref}}{n} \right)^{v_C+v_D-v_A-v_B} \quad (31)$$

$$n = n_A + n_B + n_C + n_D + n_E \quad (32)$$

The importance of equation 30 can be understood when there is inert component exists in the reaction. Although this inert component does not affect the reaction chemistry, it has to be taken into account since it has contribution in the mole fraction. This was expected situation as it is known that catalysts have effect on the time, for reaction to reach equilibrium condition.

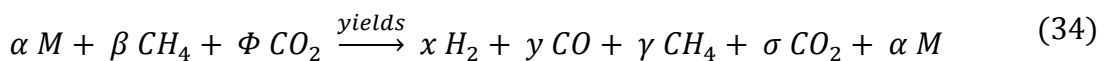
Considering the two cases of this study, which are DBD non thermal plasma and DC water thermal plasma, same stoichiometric reaction applies for both of them since the reactants and products are same.



Recalling the conventional methods, this reaction is dry reforming. In Plasma application to dry reforming, plasma can be considered as a catalyst and its usage reduces the required activation energy. As a result of this, in the analysis of plasma process dry reforming accepted as a stoichiometric reaction. According to this reaction, Equation (33), one can set $v_A = v_{CH_4} = 1$; $v_B = v_{CO_2} = 1$; $v_C = v_{H_2} = 2$ and $v_D = v_{CO} = 2$.

In order to make use of Equation (30), mole fractions of both reactants and products need to be known. These parameters were not totally given in the reference studies but the necessary data and information exist for calculating unknown mole fractions.

Equation (34) represents the complete version of dry reforming which is applicable for plasma assisted reforming of methane.



Although the crucial reactants and products are known, certainly there are other components in the system as well. Due to the lack of information from literature it

is not possible to add them into stoichiometric reaction. However, since they have an influence on the thermodynamic of the system like contribution in molar flow rate, they need to be taken into account. Therefore, M is added to reaction as unknowns. After obtaining the values for all parameters, Equation (30) can be used for finding the equilibrium constant. The physical interpretation of the K value obtained at the end of the production can be understood only if the K value at the equilibrium is known. For estimating K value at the equilibrium, tables exist in the literature which provides the equilibrium constants of different reactions in \log_{10} scale [31].

To be able to obtain physical interpretation of those results, the equilibrium constant needs to be compared with the reaction quotient of known reaction. According to the known information either K value for the given case can be computed or if it is possible to capture K value from the tables, mole fractions at the equilibrium can be calculated. In other words, in addition to checking of whether the system is at the equilibrium or not, it is also possible to calculate the magnitude of the products in the case of equilibrium, known mole fractions of reactants, temperature and pressure of the reaction.

After completing the all described methodology in this section, it will be possible to;

- (i) compare the conventional methods to produce syngas in terms of their selectivity's and energy efficiencies among themselves.
- (ii) Compare the selected plasma assisted methane reforming technologies in terms of their conversions, selectivity's, energy efficiencies that are all calculated on same base.
- (iii) Since the energy efficiencies of the both conventional methods and plasma assisted technologies are going to be calculated on similar methodology, it is also going to be possible to compare the relatively new plasma technologies with the conventional ways of syngas production.
- (iv) As a result of, K analysis, further improvement possibilities going to be clarified for the future analysis. In addition,

solid recommendations for the existing productions will be done for having better thermodynamic performance from current design of plasma assisted syngas production technologies.

3.4 Verification of Results

This section explains the validation of the modeling and analyses. The analyses explained in detail in Chapter 3 were performed via Microsoft Excel software. During the thermodynamic analyses, a lot of different case-specific technologies were investigated that were found in the literature. As a first step, the parameters provided in the literature were input to the model. This comparison includes, but not limited to the calculated selectivity values for the CO and H_2 given in Table 7 for the conventional methods.

For some cases, that are shown in Table 3, the selectivity values were already provided by the reference. Moreover, all of the selectivity values in Table 7 were calculated in the scope of this study. The results of the model were in agreement with the given results in the literature within 1% based on the relative difference between the calculated and given values. Similar validation is also applied for the given efficiency analysis of the plasma technologies. When the method for finding the efficiency values, the efficiency values given in Table 5, that are obtained from the literature, were compared with the ones in Table 8 that are calculated in this study. The comparison showed that the relative error was less than 1%.

Furthermore, the equilibrium constant calculations were checked and validated against the given cases in Moran *et al.* [31]. The given and calculated K values were exactly matched.

CHAPTER 4

RESULTS AND DISCUSSION

In this thesis, seven different plasma technologies and three different conventional methods have been investigated thermodynamically in total for the production of syngas. These are namely plasma technologies: Pulsed corona, Thermal DC water, Thermal N_2 , Thermal Ar , DBD, Microwave and Gliding arc; conventional methods: CO_2 reforming, Steam reforming and Partial oxidation. As there was not possibility to conduct all of mentioned processes and gather the data, it should be noted that, all the data used in this research is taken from the literature, previously conducted experiments.

4.1 Conventional Methods

Initially, the conventional methods analysed. The main reason to investigate the conventional methods is to check the order of energy efficiencies, then comparing the order of magnitude with the plasma technologies. In order to find order of magnitude of energy efficiencies, the exact values have to be calculated. Consequently, since the exact energy efficiency values of those conventional methods, they can be compared among themselves as well.

Table 7 illustrates the energy efficiencies, CO and H_2 yields of different conventional syngas production methods. Additionally, fuel type and its properties are shown for each technology. Mass flow rate is crucial in the calculation of efficiency. Using the volumetric flow rate, mass flow rate of each case has been calculated and is given in Table 7.

Table 7: The tabulation for different conventional syngas production methods in terms of energy efficiencies and selectivity of products

Conventional Technology	Flow	Fuel			Syngas			CO % selectivity	H ₂ % selectivity	Reference
	Rate (m ³ /s)	Flow Rate (kg/s)	LHV (kJ/kg)	Name	Flow Rate (kg/s)	LHV (kJ/kg)	Efficiency (η) %			
CO ₂ reforming	4.1 x 10 ⁻⁶	7.9 x 10 ⁻⁵	85631	COG	3.8 x 10 ⁻⁴	90000	1.94	100	70	[22]
CO ₂ reforming	22.2	404	85631	COG	2.4 x 10 ³	90000	1.61	100	100	[23]
Steam reforming	2.8 x 10 ⁻⁴	4.9 x 10 ⁻³	47141	NG	2.4 x 10 ⁻²	90000	2.01	50	100	[10]
Steam reforming	1.11	46.8	30012	BG	92.3	90000	2.04	32	53	[9]
Steam reforming	1.11	46.8	30012	BG	77.3	90000	1.20	26	55	[9]
Partial Oxidation	0.97	7.45	50020	CH ₄	59.4	90000	5.25	81	100	[6]
Partial Oxidation	3.3 x 10 ⁻³	0.21	47141	NG	0.64	90000	2.71	92	87	[8]
Partial Oxidation	8.3 x 10 ⁻³	0.53	47141	NG	1.75	90000	2.96	94	89	[8]

COG: Cook oven gas, NG: Natural gas, BG: Biogas

The most important issue on the results in Table 7 is the values that were taken into account during the efficiency analyses. As it is clearly seen on Table 7, only the fuel consumption was considered. This is because of the difficulty of capturing the necessary data for the calculation of pre-heating, heating, cooling and drying processes from the literature. In other words, once the energy consumption of mentioned conditions is included, the efficiency value will decrease, and this decrease could be very dramatic depending up on the magnitude of the additional energy consumption.

As a result of conventional method analysis, according to Table 7, it could be noted that generally the energy efficiencies varies between 1% and 5%. Except the one condition which is partial oxidation of CH₄ having a higher flow rate with respect to other partial oxidation cases. On the other hand, when the conventional methods compared in terms of CO and H₂ selectivity's; CO₂ reforming exhibits the best performance, whereas syngas production by steam reforming provides the lowest percentage of CO and H₂ selectivity's. The last but the not least outcome of this first analysis is the order of magnitude of selectivity percentages of conventional methods.

It is given that highest selectivity values are observed on dry reforming and the lowest on steam reforming. The reason of this underlies on their stoichiometric reactions. To illustrate, considering the selectivity, recalling stoichiometric reactions of dry reforming Equation (5) and steam reforming Equation (1) all H_2 that exist in the product is coming from the dissociation of CH_4 . Whereas, in steam reforming, the H_2 obtained at the product is not solely coming from the methane dissociation but also the dissociation of H_2O also contributes. In the light of this issue, H_2 production in steam reforming requires higher time when compared to dry reforming.

4.2 Plasma Methods

After the conventional methods, plasma technologies investigated thermodynamically. In the light of their operating conditions and their technologies; their specific energies, CH_4 or C_3H_8 conversion percentages, CO_2 conversion percentage, CO and H_2 selectivity's and different efficiency values are calculated and tabulated on Table 8 for analysed plasma technologies.

The critical parameters for comparing different technologies can vary a lot. Since, at this stage, the scope of this study is to compare selected plasma technologies in terms of thermodynamic properties, energy efficiency value can be considered one of the most crucial parameter to investigate. As it is explained previously, plasma technologies in Table 8 have been selected with respect to data availability. Thus, the model of this study is not only limited with those mentioned technologies but also it is able to calculate the same parameters for other plasma technologies.

Table 8: Efficiency comparison table for different plasma technologies

Plasma Technology	Feed	Flow Rate $\times 10^4$ (m ³ /s)	T _{max} (K)	P _{in} (kPa)	Specific Energy (MJ/kg)	%CH ₄ Or %C ₃ H ₈ Converted	%CO ₂ Converted	%CO Selectivity	%H ₂ Selectivity	H ₂ /CO	Efficiency (η)		Reference
											%Given	%Calculated	
Pulsed corona (NT)	methane	0.25	300	161		19			64	4.00	20.3	5.5	[26]
Thermal DC water (T)	methane	0.67	5250	100	26	75	59	78	71	1.80	34.4	11.1	[27]
Thermal N ₂ (T)	methane	5.00	1073	100	21	90	80	88	69	1.16	48.0	17.7	[27]
Thermal Ar (T)	methane	12.22	1073	100	18	79	65	97	83	1.39	57.2	17.5	[27]
DBD (NT)	methane	0.03	423	100	670	64	39	43	24	0.67	0.6	0.5	[28]
DBD (NT)	methane	0.10	423	100	710	30	13	42	20	0.70	16.1	9.7	[28]
Microwave (T)	methane	3.33	2750			71	69	75			25.0	0.3	[27]
Glowing Arc (NT)	propane	2.33	923			62	23			2.40	62.6	4.0	[29]

T: Thermal, NT: Non-thermal

Obviously, the model demands data of the experiment in order to calculate energy efficiency values on the same bases of given in Table 8.

There are two efficiency values exist in Table 8, which are given and calculated efficiencies. The given efficiency is the value that is stated on the related reference in the literature. It would not be correct to compare those plasma systems based up on given efficiency values since they are all calculated in different manners. In other words, since the main focuses of the different studies were not the same, it is expected to have different parameters that are pay more attention in the calculation of efficiency value. This situation can cause significant variance from case to case. In the light of this fact, the efficiency values calculated for each technology in the same way to be able to compare them on same bases Equation (29). This efficiency value given in Table 8 as calculated. Calculated efficiencies decreased when they are compared with the given values in all cases. It should be noted that, this reduction is not caused by the single parameter in all cases. The main factors are the effect of the carrier gas, used fuel and the auxiliary energy demanded processes like cooling, pre-heating, drying etc. It is not possible to reach significant quantitative information, related to auxiliary processes but referred references states the existence of them, during the syngas production process. In other words, it is quite likely to observe slight decrease on the calculated energy efficiencies. Obviously, the magnitude of the decrease would be directly proportional to the unconsidered energy consumption of the auxiliary process. Apart from auxiliary energy consumption, effects of carrier gas and the used fuel successfully taken into account in the calculation of energy efficiencies. To sum up, different energy injection to the system or energy production of the system affected the efficiency calculation.

Considering only the non-thermal DBD cases one at higher flow rate than the other; it could be concluded that having a higher flow rate results in higher efficiency but lower conversion rates. Consequently, in plasma systems if the aim is to get more conversion so as selectivity it can be recommended to operate the system in lower flow rate values. However, if the energy efficiency is more important, having a higher flow rate values would definitely increase the efficiency. This was an expected situation and can be explained as follows: When the flow rate is low, reactants will have more retention time so they will more exposed to plasma process and deionised more whereas in the higher flow rate values reactant molecules will exposed to plasma process in shorter amount of time. On the other hand, at the lower flow rates system will require more time to operate same amount of reactants so consumed energy will increase accordingly and this increase in the energy consumption will directly contributes to energy efficiency decrease.

According to another outcome listed in Table 8, non-thermal technologies have much higher specific energy when compared with the thermal plasma technologies. This can be explained as follows, in thermal plasmas some of the energy consumes for heating gas in order to reach desired temperature rather than the reaction which reduces the specific energy. Specific energy simply explained as a ratio of input power to mass flow rate of the produced syngas.

One of the main purposes of analysing the conventional methods to produce syngas in this thesis is to compare them with plasma technologies. According to their energy efficiencies, it is going to be scientifically proved that plasma technologies should be use in the syngas production processes. Table 9 shows the efficiencies of both conventional and plasma technologies in the syngas production process.

Table 9: Energy efficiency comparison of conventional methods with plasma methods

Plasma Technology	Efficiency (η)		Conventional Technology
	%	%	
Pulsed corona (NT)	5.5	1.9	CO ₂ reforming
Thermal DC water (T)	11.1	1.6	CO ₂ reforming
Thermal N ₂ (T)	17.7	2.0	Steam reforming
Thermal Ar (T)	17.5	2.0	Steam reforming
DBD (NT)	0.5	1.2	Steam reforming
DBD (NT)	9.7	5.3	Partial Oxidation
Microwave (T)	0.3	2.7	Partial Oxidation
Gliding Arc (NT)	4.0	3.0	Partial Oxidation

T: Thermal, NT: Non-thermal

As it can be clearly seen in Table 9, plasma technologies have better efficiencies in most of the cases. This makes the usage of plasma technologies in the syngas production sector a promising subject. For the plasma technologies which have energy efficiency less than 1% has a reason. To illustrate in the case of DBD (efficiency 0.5%), process completed under low flow rate to increase the magnitude of the products. However, as it can be seen from the case DBD having efficiency of 9.7%, efficiency can be increased by increasing the flow rate.

4.3 The Equilibrium Constant, K, Analysis

The efficiencies are studied and clearly tabulated for each example of different plasma technologies. By doing this further analysis, this study will be able to come up with the solid conclusions therefore certain recommendations about the examined processes. Consequently, based up on the result of K analysis, the necessary things will be clear in order to improve each technology.

For conducting the equilibrium analysis, one example from non-thermal plasma and one example from thermal plasma have been selected based up on efficiencies. Both methods have relatively low efficiencies when compared to other methods. Having low efficiency values makes them most promising methods to conduct further improvement analysis in the scope of this thesis. Note that low efficiency value is not the representation of capacity for the improvement but two samples had to be selected for K analysis. This study can be conducted for every reaction as it is described in the Methodology chapter and every method given in Table 8.

Initially, for the example of non-thermal plasma technology, DBD and for the example of thermal plasma technology DC water thermal have been selected. According to the Equation (25), mole fractions at the reactants and the products need to be known in addition to temperature, pressure and the stoichiometric coefficients. Temperature and pressure values are given in Table 8. Moreover, coefficients of stoichiometric reaction have been analysed and illustrated in the Methodology chapter. The only unknown parameters are the mole fractions. Table 10 examines the unknown mole fractions which have to be figured out before conducting the equilibrium analysis. Additionally, Table 10 also gives the crucial parameters which make the calculation of unknown mole fractions possible.

Table 10: Known parameters for the equilibrium constant analysis for non-thermal DBD (adapted from [28])

Non-Thermal DBD								
mole fractions								ratio
CH _{4,in}	CO _{2,in}	H _{2,out}	CO _{out}	CH _{4,conversion}	CO _{2,conversion}	H _{2,selectivity}	CO _{selectivity}	H ₂ /CO
0.29	?	0.086	?	0.64	0.39	0.24	0.43	0.67

For DBD case, after doing necessary calculations by using the conversion, selectivity equations and the H₂ to CO ratio; unknown mole fractions obtained. Table 11 shows

the required parameters to calculate the equilibrium constant by using equation 25. On the other hand, for the case of thermal plasma, all mole fractions were directly given in the related reference.

Table 11: Mole fractions to calculate the equilibrium constant for non-thermal DBD & thermal DC water

Non-Thermal DBD								
mole fractions								ratio
CH _{4,in}	CO _{2,in}	H _{2,out}	CO _{out}	CH _{4,conversion}	CO _{2,conversion}	H _{2,selectivity}	CO _{selectivity}	H ₂ /CO
0.29	0.46	0.086	0.128	0.64	0.39	0.24	0.43	0.67

Thermal DC water								
mole fractions								ratio
CH _{4,in}	CO _{2,in}	H _{2,out}	CO _{out}	CH _{4,conversion}	CO _{2,conversion}	H _{2,selectivity}	CO _{selectivity}	H ₂ /CO
0.05	0.11	0.55	0.30	0.75	0.59	0.71	0.78	1.8

Then, the calculated equilibrium constants for DBD and Thermal DC water technologies found based on Equations (30) and (31);

The results obtained for non-thermal DBD from Equation (31) as 0.00269 and for thermal DC water from Equation (30) as 4.95. These results illustrate the reaction quotient that systems have at the end of the reaction which is calculated by using the supplied data in the references. At this stage the equilibrium constant, at the equilibrium case, under the specified temperature, has to be known to compare the results.

In order to find the equilibrium constant one can refer to the figures that present in the literature. There are few important issues that need to be pay attention while capturing the equilibrium constant from the figures. Initially, the correct reactions

have to be selected in correct direction. If the reaction exists in the figure in reverse direction than the seeking one, the negative of the given value has to be chosen.

Considered reaction is same in the cases of both DBD and thermal DC water. In this reaction methane and carbon dioxide are present at the reactant to form hydrogen and carbon monoxide, syngas. Analysing the chemical compositions is important, since they need to be selected exactly from the thermodynamic tables. Table 12 illustrates the K values for the related reactions read from the thermodynamic tables at the temperatures of 423 K and 5250 K for the DBD and thermal DC water technologies, respectively.

Table 12: log K values read from the tables in the literature

Plasma technology	Temperature (K)	log K(T)		
		ref [32]	ref [31]	
		$C + 2H_2 \leftrightarrow CH_4$	$CO_2 \leftrightarrow CO + 1/2O_2$	$C + 1/2O_2 \leftrightarrow CO$
DBD	423	3.395	-32.6	18
DC water	5250	-4.8	2	5.4

Initially, considering Equation (28) reactants it could be said that; reactions of $C + 2H_2 \leftrightarrow CH_4$ and $CO_2 \leftrightarrow CO + 1/2O_2$ are going to be used for the equilibrium constant analysis. However, it is clear that the products of the selected reactions are not same with the one in equation 27. Thus, as it can be understood from the Table 12, the K value of an additional reaction $C + 1/2O_2 \leftrightarrow CO$ has to be taken into consideration in order to obtain a correct result.

Table 13 summarises the equilibrium constant analysis of non-thermal DBD and thermal DC water plasma technologies. Comparing the equilibrium constants in logarithmic scale, it can be said that, under the given operating conditions;

Table 13: Equilibrium constant values for comparison

Plasma technology	Temperature (K)	Pressure (atm)	Equilibrium Constant		
			$K_{\text{calculated}}$	$\log K_{\text{calculated}}$	$\log K_{\text{read}}$
DBD	423	1	0.00269	-1.57	-18.1
DC water	5250	1	4.95	0.69	12.2

- For non-thermal case, calculated reaction quotient which represents the situation at the end of plasma process captured from the previous experimental studies is higher than the equilibrium constant at the equilibrium case. Referring to definition of the K value (or see equation 29), products are higher than their equilibrium values in terms of mole fraction.
- For thermal case, calculated reaction quotient which represents the situation at the end of plasma process captured from the previous experimental studies is lower than the equilibrium constant at the equilibrium case. Referring to definition of the K value (or see equation 29), products are lower than their equilibrium values in terms of mole fraction.

According to highlighted out comes several solid recommendations/comments can be made for both non-thermal and thermal plasma technologies.

i) For non-thermal DBD plasma technology it could be concluded that system is able to supply methane formation to syngas in good ratio of products to reactants. In

other words, the operating conditions are suitable for this formation in terms of the equilibrium constant. It should be also noted that, since the equilibrium constant is well above the equilibrium case, increasing the retention time and keeping the exit pipe of the system is not recommended. Because, the products will tend to reach to the equilibrium by reverse reaction which means syngas will start to decrease.

ii) For Thermal DC water plasma technology it is clear that reaction is not reached to equilibrium. Thus, improvements can be done. At this stage of the research, increasing the pressure seems an opportunity to achieve this goal. However, this idea is not recommended because of two reasons. Firstly, reaching to the equilibrium is not the primary goal of this study. In other words, increasing the pressure may carry system to the equilibrium but it is not going to increase the yield of syngas. Secondly, according to Table 14, by solely increasing the pressure system will reach to equilibrium at dramatic pressure.

Table 14: Equilibrium constant values with increasing the pressure

Pressure (atm)	Equilibrium constant	
	log $K_{\text{calculated}}$	log K_{read}
900000	12.60	12.2
600000	12.25	12.2
50000	10.09	12.2
4000	7.90	12.2
300	5.65	12.2
40	3.90	12.2
30	3.65	12.2
20	3.30	12.2
1	0.69	12.2

iii) For Thermal DC water plasma technology it could be suggested to increase the retention time, decrease the flow rate and if it is possible keeping the plasma

reactor as long as possible. All of these mentioned conditions will expand the time which the reactants exposed to plasma process and have more ionization. This recommendation has been done according to the equilibrium constant analysis. The calculated reaction quotient value is less than the equilibrium constant at the equilibrium which means more of reactants can be turned into syngas. However, it should be kept in mind that, this recommendation is valid only if the interest is to increase selectivity of the system. Because, in the case of, increasing the running time of the system would decrease the energy efficiency.

CHAPTER 5

CONCLUSIONS

This study focuses on analysing the plasma reforming of methane to obtain syngas in thermodynamic point of view and comparison of the plasma reforming with conventional methods. Initially, conventional methods for producing syngas have been examined. Their advantages and disadvantages are summarised and tabulated for generating a chance of quick comparison of mentioned methods. Then, their thermodynamic performances such as yields of syngas as products and their energy efficiencies were calculated on the same bases. Thus, one can easily compare those conventional processes among themselves. However, what is more important for this study is to be able to compare the general conventional syngas production methods with the plasma reforming which is the real scope of this research. In the light of this issue, it is clearly represented in the paper that relatively new technology of plasmas is better than the conventional methods, in terms of their efficiencies, for producing syngas.

As a second and main analysis of the research was analysing the different plasma technologies. In the scope of thermodynamic analysis; Pulsed Corona, Thermal DC water, Thermal N_2 , Thermal Ar , DBD, Microwave and Gliding Arc (non-thermal) plasma technologies analysed. Several similar examples of plasma related studies were also illustrated.

In the thermodynamic analysis of plasma technologies, the difficulty was the availability of experimental data. It is highly crucial that accurate and real data have to be used in the analysis. Since it was not possible to conduct the experiments within the scope of this study, the related data were captured from the literature. While gathering the data, experimental conditions, ambient conditions, pre stages,

type and rate of the cooling and any other gases that had been used during the experiment were all important since they directly affected the results. Consequently, after long and detailed literature review data those are suitable for the analysis shortlisted. Moreover, some missing data values were calculated by the governing equations. Once the all necessary data completed, the performance assessment metrics, such as energy efficiencies, were calculated. As a result of this analysis, it was observed that energy efficiencies of the thermal plasma technologies are higher than non-thermal technologies. This is simply because of the dramatic high temperatures of operating condition of thermal plasmas. However, it can be also said that, for the non-thermal plasmas it is possible to increase the efficiency of the system by operating the system relatively higher flow rates. Definitely increasing the flowrate is going to decrease the conversion rates since the particles will be exposed to plasma process shorter time. Another outcome of the efficiency analysis is finding the systems availability for the improvement.

In addition to efficiency analysis, the equilibrium analysis was also done for two sample of which non-thermal and thermal technologies. In the scope of this analysis, the equilibrium constant was calculated based up on the data for given technologies. Then these values were compared with the values at the exact equilibrium captured from the literature. As a result of this analysis, non-thermal plasma technology showed good performance since it exhibited higher K value than at the equilibrium case. On the other hand, for thermal plasma technology the situation was exactly the opposite.

In the light of all of these results, it could be concluded that thermal plasmas are better than non-thermal plasmas in terms of energy efficiency. However, as the equilibrium analysis illustrated, non-thermal plasma has better products to

reactants ratio in terms of molar flow rates. Thus non-thermal plasma technology (DBD) has better yield value when they are compared on same bases.

As a future work, this study can be expanded related to improvement of plasma technologies to become more efficient. The possible ways can be incorporated to this study to quantify the possible changes in the performance of the systems. Not only the possibility of improvement but also the contribution on sustainability and the better performance than the conventional methods makes this subject promising.

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