

# Removal of Petrochemical Wastes by arc Plasma Pyrolysis

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## Abstract

In this study the petrochemical wastes via plasma arc technology by converting the wastes into combustible gases. The wastes are completely decomposed into simple molecules in a near vacuum environment. The wastes were converted to hydrogen, and from petrochemical wastes a recycled energy was produced in the form of renewable fuel free from toxic chemicals.

**Key words:** plasma pyrolysis; petrochemical waste; hydrogen production

## Introduction

During the plasma interaction with waste, the waste is placed inside the plasma environment and directly exposed to active species at high temperatures. As a result, it undergoes various chemical reactions. The type of waste, its chemical compounds, and the plasma parameters, such as the amount and type of active species and temperature, are the key factors determining the nature of such reactions. In general, waste undergoes three main types of chemical reactions, which play a fundamental role in destroying unique waste compounds and ensuring other remarkable benefits of this method. The first reaction is pyrolysis [1,2], which can be defined as the chemical decomposition in an environment devoid of Oxygen at considerably high temperatures. In other words, when materials are exposed to an environment at temperatures higher than about 10,000 K in the absence of Oxygen, they undergo thermochemical decomposition, which, as an extremely powerful chemical reaction, converts all molecular and chemical bonds into their constituent elements [3]. The second reaction is gasification, which occurs when the specific conditions of the thermal plasma affect the organic materials in the waste and change them [4]. The output product of this chemical reaction is a combustible gas called syngas, mainly composed of carbon monoxide and hydrogen [5]. Syngas has a high heat value and, consequently, a high energy production rate; hence, it is commonly used to generate electricity in large and advanced facilities [6]. The gasification process is carried out in the temperature range of 4000–5000 °C in the core of the plasma reactor. This temperature range makes it feasible to speed up the reactions in the reactor and obtain valuable products. The third stage is vitrification. In this stage, inorganic waste materials such as metals, glass, and soil are transformed into vitrified slag using thermal plasma. These materials are of high economic value and are commonly used as raw materials in the road and construction industries [7,8]. Thermal plasma is the only method among other waste disposal methods that can efficiently dispose of unique waste compounds in most cases. The hazardous waste components are usually so strong that other methods typically fail to break them down, and only plasma pyrolysis proved to be able to neutralize and disintegrate these compounds. Owing to their beneficial functions, plasma facilities have been set up with high energy efficiency and relatively small sizes, thus

making it possible to transfer the facilities to waste production or collection sites. In this case, there is no need to transport special wastes that require special facilities with high costs [9,10].

A thermal plasma torch serves as an example of a thermal plasma generator capable of providing suitable conditions for converting various types of waste owing to its high temperature. The shape and material of the electrodes, as the primary components in the plasma torch, vary depending on their industrial applications. Historically, Graphite was predominantly used in electrode manufacturing, and cooling methods were not usually employed in the manufacturing process. For this reason, its corrosion rate was relatively high during the operation, increasing the need for their replacement after a short period. In addition, pollution in the operating environment is an inevitable result of such corrosion, which is undesirable in some industrial applications, especially in surface engineering [11,12]. The current study also implemented this technique in the plasma waste disposal systems due to the significant advantages of torches and available facilities and equipment [13,14]. The main objective the research is to produce H<sub>2</sub> from petrochemical wastes to produce a clean fuel and fuel of the future.

## Materials and methods

Gasification and pyrolysis are non-combustible thermal processes where high temperatures in an oxygen-free or partial oxidation environment contribute to breaking down the inlet waste materials into simple molecules such as CH<sub>4</sub>, H<sub>2</sub>, CO<sub>2</sub>, CO, etc., and also transforming them into ash and slag. Given that CO<sub>2</sub> in the syngas is of low value, its amount should be kept as low as possible to enhance the system's efficiency. The CO/CO<sub>2</sub> ratio is considered a determining parameter in controlling the gasification process, and it increases upon increasing the temperature [15]. Tar, characterized by its dark, dense, and viscous nature, originates from diverse organic sources such as wood, coal, peat, and petroleum. The term 'Tar petrochemical waste' specifically denotes waste materials encompassing tar compounds generated as byproducts of petrochemical processes. The petrochemical industry constituting an intricate blend of organic compounds encompassing aromatic

hydrocarbons, phenols, and heterocyclic compounds. Usually, it comprises diverse organic substances, encompassing hydrocarbons, aromatic compounds, and other organic contaminants, alongside inorganic elements like metals, salts, and mineral remnants. This research used a thermal transferred arc plasma reactor [2,3, 16]. The temperature of the transferred arc plasma exceeds that of the non-transferred one. In this reactor, the waste is directly processed by the arc. The fundamental distinction between transfer arc and to investigate the experiments further, the collected gas products in all the experiments were injected into a gas chromatography (GC) device. Equipped with specific columns and detectors, this device can determine the type of produced products in molar percentage. In this study, a chromatography device called Agilent Technologies-7890A System was employed. Following completing the above steps and closing the chamber lid, Argon gas is first injected with a flow of 30 SLM and for 3 min until the volume of the reactor chamber, which is about 50 L, is emptied of air, and there is no Oxygen in the environment. Since the reactor is large and has non-isolated inlets and outlets, remaining a small amount of air inside it is still inevitable. Upon turning on the power source and then forming the plasma, the plasma was kept on for 1 min, and during this time, the Argon gas flow was reduced to 10 SLM to make the formed plasma a little stable and prevent shutting down during the operation. Then, feed injection begins at a constant rate while simultaneously taking the injection time. The feed was injected with Peristaltic pumps at a constant flow of 10 cc/ min for 2 min on the graphite crucible where the plasma is exactly produced. In order to make the amount of injection visible, a feed injection burette was used. After injecting half of the feed (1 min), sampling begins and continues until the end of the sample injection. After completing the sampling and separating the balloon from the silicone hose, the system will be shut down. Due to the very high temperature of the plasma flame that is created inside the graphite crucible, we see the corrosion of the graphite electrodes, which leads to a change in the distance between the electrodes and, as a result, the

characteristics of the plasma. Due to the fact that it was not possible to keep the electrode distance constant in long-term operations, we considered the total test time to be 3 min (1 min for flame stability and 2 min for feed injection). The most of the flame radiation was absorbed by the graphite crucible, and as a result, the steel wall, which plays the role of the reactor wall, eventually reaches about 40 °C. To prevent interference between the previous and next experiments, the chamber lid will be opened to return the initial conditions of the test to the last state.

## Results

The petrochemical sample was extracted from the outlet gases using balloons evacuated in advance by a rotary vacuum pump to prevent variations in the results of the conducted tests. As already mentioned, a GC device was used to analyze the sample. The result obtained from the gas analysis was quite interesting; a significant proportion of the feed amount was converted into Hydrogen gas and the rest into Carbon monoxide, Carbon dioxide, and Hydrocarbons. During the experiments, attempts were made to keep constant the values of the amount of injected feed, reaction time, total energy given to the plasma and consequently to the feed, inlet gas flow, and gap distance between the anode and cathode. However, in the case of any variation in the mentioned variables, the results were re-evaluated.

Table 1 show the composition and components of the petrochemical waste material used in this research. The petrochemical waste contains nitrobenzene, aniline. The latter refers to a condition where the amount of energy obtained from burning a mass unit makes water exit the combustion chamber in the form of steam at the end of combustion. Other parameters, such as the humidity, amounts of combustible materials, and ash, can affect the heating value. In this research, only the LHV of petrochemical waste was available

Petrochemical components	Nitrobenzene	Aniline	Toluidin	Toluidin diamine	Water
WV	60	21	10	15	9
Waste flow (kg/s)	9	16	22	24	17
Wt(%)	60	12	8	12	8

**Table 1: Composition and components of the petrochemical wastes**

Table 2 presents the physical characteristics of the petrochemical wastes. In this table, the heating values refer to the amount of energy obtained from burning a unit of mass, which is classified into two groups: low heating value (LHV) and high heating value (HHV) [16,17]. The former refers to a condition where water remains as a liquid in the combustion chamber at the end of the combustion process. During waste plasma interaction, the waste undergoes direct exposure to high-temperature active species within the plasma environment, leading to various chemical reactions. The attributes of the waste, including its chemical composition, along with the plasma parameters, such as the abundance and type of active species, as well as temperature, play a critical role in defining the precise nature of these reactions [18,19].

The current and applied voltage in all tests equals 180 A and 35 V, respectively (data not shown). As a result, the power applied to the plasma

is 6.3 KW. According to the results given in Table 3, Hydrogen is the main product of the plasma pyrolysis process, which accounts for 98.01 % of the products in petrochemical waste disposal. The percentages of the Carbon monoxide gas production in the experiments are 9 %. The percentage of Carbon dioxide production in all tests was below 2 %, confirming that the combustion process did not occur. Based on the data of this research, it can be concluded that applying thermal plasma for waste disposal leads to the production of methane, ethanol, ethylene, propane, n-butane, and n-C4. As a notably important parameter, the ratio of Hydrogen to Carbon monoxide was calculated to determine whether or not the produced syngas was of high quality. Given the high efficiency of syngas, its production from hazardous petrochemical industry, can be considered a great advantage. Syngas formation occurs through diverse thermochemical methodologies, such as steam reforming of hydrocarbons, gasification.

parameters	
Opt tem (0c)	145
Density (kg/m3)	1080
Specific heat Kj/KgK)	2,99
Viscosity (mPa.s)	3,84
Entalpy (kj/kg)	765
Ash	0,2
Max flow(m3/h)	1203
Pressure (bar)	4,2

**Table 2: Physicochemical properties of petrochemical wastes**

H2 (%)	99
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CO (%)	8
CO <sub>2</sub> (%)	2
Methane (%)	1
Ethane (%)	2
Ethylene (%)	2
Methane (59	3
Buthene (%)	1
H <sub>2</sub> /CO ratio	3,71

**Table 3: Produced gases and metabolites**

In this research, only the LHV of Tar waste was available. During waste plasma interaction, the waste undergoes direct exposure to high-temperature active species within the plasma environment, leading to various chemical reactions. The attributes of the waste, including its chemical composition, along with the plasma parameters, such as the abundance and type of active species, as well as temperature, play a critical role in defining the precise nature of these reactions [20–24]. The power applied to the plasma is 6.3 KW. The percentage of Carbon dioxide production in all tests was below 3 %, confirming that the combustion process did not occur. Based on the data of

this research, it can be concluded that applying thermal plasma for waste disposal leads to the production of methane, ethanol, ethylene, propane, n-butane, and n-C<sub>4</sub>. As a notably important parameter, the ratio of Hydrogen to Carbon monoxide was calculated to determine whether or not the produced syngas was of high quality. Given the high efficiency of syngas, its production from hazardous wastes which are all threats to the environment and challenges to the petrochemical industry, can be considered a great advantage. The gas composition measured in GC was tabulated in Table 4.

H <sub>2</sub> (mol %)	99
CO (mol %)	8
CO <sub>2</sub> (mol %)	2
Methane (mol %)	1
Ethane (mol%)	2
Ethylene (mol%)	2
Methane (mol %)	3
Buthene (mol %)	1

**Table 4: GC analysis of gases**

## Conclusion

The present research employed thermal arc plasma as a novel disposal method for hazardous non-decomposable petrochemical wastes to H<sub>2</sub> gas. The production percentage of hydrogen in petrochemical waste was obtained to be about 98 %, which was favorable. In this regard, plasma is among the few methods yield Hydrogen at high ratios. Considering the broad applications of syngas, this research confirmed that the transferred thermal plasma torch would be an advantageous method for the disposal of industrial petroleum derivated wastes.

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