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Plasma-Arc-Flow Technology for Sustainable Treatment of High-Impact Fluid Waste: A Graphene-Based Material for Industrial-Wastewater Purification

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Abstract: The research presented aimed to address the treatment of fluid waste with significant environmental impact by utilizing plasma technology, specifically plasma arc flow (PAF). The goal was to develop a novel purification material based on graphene for industrial applications and to optimize the treatment process. Analysis and monitoring of a submerged arc plasma reactor were the main goals of this research. This entailed a careful examination of the incoming wastewater that needed to be treated with the goal of identifying its precise composition characteristics with the relative tolerances needed for the reactions that were to follow in the reactor. The focus of the analysis was on input-parameter optimization, production of characteristic curves, and analysis of the factors affecting hydrogen evolution in syngas. Additionally, the study investigated how to determine the best viscosity for a particular input matrix by carrying out an evaluation study. The effects of this parameter were thought to be reduced by preheating the incoming wastewater through heat recovery. The long-term objective of the research is to create filters that can purify the water used and produced in gasification processes as well as to characterize the fixed reside from the gasifier for potential conversion into graphene-based material. In addition, this work acknowledges that additional experiments are required to validate its purifying capacity on wastewater produced by various industrial processes. Moreover, the inclusion of plans to model the evolution of hydrogen in PAF using the CHEMCAD software® and defining guidelines for optimizing parameters for enhanced energy efficiency showcased the research's ambition to expand and refine its scope. Finding the best plant solutions that can significantly reduce electricity consumption is the ultimate goal. In summary, the study demonstrated significant advancement in the analysis and optimization of fluid-waste treatment with high environmental impact through the use of plasma technology, specifically PAF. A thorough and forward-looking approach was demonstrated by the use of modeling software, experimental studies, and plans for future research. The potential creation of graphene-based filters and the use of the fixed residue as a useful material further highlight the innovativeness of this research.

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1. Introduction

The energy sector is a nexus where all facets of public and private productive life, as well as all production consequences, converge. Agriculture and industry; primary and secondary economies; crafts; small, medium, and large industries; and transportation all deal with energy needs and the costs and benefits that national energy plans can predict and plan for. By its very nature, energy is at the heart of life for both people and the environment, determining its qualities and perspectives. The growing demand for energy resources in modern society creates a variety of issues, and the overall picture that emerges has become broader and more articulated as a result.

The Renewable Energy Directive, 2009/28/EC, has driven a rapid deployment of renewable energy. In 2012, energy from renewable sources was estimated to contribute up to 14.1% of EU final energy consumption, while the EU target for 2040 is 50% of EU primary energy [1–3]. The analyzed plant had many innovative features, and the gas produced contained hydrogen in a thicker state than under usual conditions. The project demonstrated a profitable increase in the production of energy from biomass, considering a lower energy commitment concerning the volumes of wastewater treated. An examination of the Italian and European situation in terms of management techniques related to the problem of municipal solid waste was carried out, including the reuse of old combustors and the adoption of cogeneration technology.

Innovative technologies in sustainable combustion are crucial for companies producing liquid substances with significant environmental impacts, such as oil consortia. These facilities must efficiently address global environmental impact, depletion of fossil fuel reserves, supply security, and energy distribution. The focus is on applying these methods to energy-production processes. Research that focuses on the production of energy and recycling is driven by the need for savings related to their means, their efficiency, and their effectiveness. Human activities have an unavoidable impact on the environment, which can be minimized and mitigated with proper technologies. To address this slow environmental deterioration, researchers focus on the production of renewable energies, which are not directly available energy sources, but rather, are gaseous energies derived from processes that are already useful in and of themselves.

The European Environment Agency defines pollution as the alteration of the biological, physical, chemical, or radioactive elements of the environment that endangers human health or the security and welfare of all living species [4]. The recent demographic expansion has increased the amount of trash produced, leading to an increase in contaminating species released into the environment. Researchers are working to find a solution to address the environmental impact caused by the storage and disposal of the latter.

Fossil fuels, which are still used as an energy carrier, have shown several flaws in terms of environmental and economic performance. The use of technologies aimed at improving various types of materials has been grafted into the debate over the use of low-potential fuels and the optimization of processes related to their full energy enhancement. Waste-to-energy plants demonstrate how efficiency, as measured by a cost–benefit ratio, is critical, and the necessity of establishing a circular waste economy in which garbage loses its status as such, and is instead viewed as a resource to be exploited. Various initiatives in this direction, such as pyrolysis and gasification, are aimed at integrating a part of the waste cycle into electricity generation or fuel production. Adequate cleaning of the syngas through ad hoc devices (scrubbers) is essential for containing emissions and improving the performance of processes aimed at energy production, but the water that would result from such a process is configured as special waste.

One of the characteristics of biomass that makes it suitable as an energy source is that through direct combustion it is often burned in waste-conversion plants to supply electricity [5] or in boilers to supply heat at industrial and residential levels [6]. Plasma arc gasification (PAG) is a waste-treatment technology that uses a combination of electricity and high temperatures to turn municipal waste (garbage or trash) into usable by-products without combustion. Gasification is performed by employing a gasifier agent (air, oxygen, and/or steam) to convert biomass into a combustible gas mixture by partial oxidation at high temperatures (800–1000 °C) [7,8]. The produced gas is named syngas and its composition depends on various parameters, like feedstock composition, gasification medium, operating temperature and pressure, or gasifier design. For this reason, it is very difficult to predict the precise composition of the syngas from the gasifier [9–11] and the composition of the waste stream can affect the effectiveness of the gasification procedure.

Hydrogen is a form or carrier of energy that cannot be adequately defined as an energy source. Currently, 500 billion Nm^3 of hydrogen is sold around the world, mostly from fossil fuels [12]. It is mostly created as a by-product of the chemical industry, particularly in the manufacturing of polyvinyl chloride (PVC) and crude-oil refining. Given the current state of the energy sector, large growth in hydrogen consumption is projected in the future. Hydrogen production is a major impediment to industrial development due to its high cost and selection of optimal production and storage procedures. Technology will be implemented to produce more hydrogen while also addressing the problem of disposing of harmful effluent such as leachate. This will be dictated by environmental legislation and the need to develop other energy sources.

The elimination of time-consuming and expensive experimental methods is another advantage of mathematical models [13,14]. Plasma gasification uses computational fluid dynamics (CFD) mathematical models to make more accurate predictions [15]. Thermodynamic equilibrium, kinetic simulation, computational fluid dynamics, and artificial neural networks are a few of the mathematical models for gasification that have been created [16]. In the literature, Mirmoshtaghi et al. [17] built a model for biomass gasification during a fluidized-bed gasifier by air oxidant with quasi-equilibrium temperature (QET), predicting the quantity fraction of the main components (hydrogen, carbon monoxide, CO_2, and methane) within the produced gas. The temperature range of the gasification was set to 730–815 °C, with an equivalence ratio (ER) between 0.22 and 0.53. In addition, Aspen Plus and MATLAB are two of the most-used simulation tools for biomass gasification in other papers [18–22]. Ansys Fluent was used by Ibrahimoglu et al. [23] to model a microwave plasma downdraft coal reactor using an Eulerian–Lagrangian methodology. They used the SIMPLE algorithm for velocity–pressure coupling, the k-ε model was employed as the turbulence model, and plasma conditions were derived from experimental data. According to the findings, the gasifier and syngas had average temperatures of 1350 °K and volume percentages of 18.4% H_2 and 37.2% CO.

Giuntini et al. examined the use of biomass-derived syngas in a tissue-paper drying chamber using numerical simulations by computational fluid dynamics to replace fossil fuels and decarbonize the plant [24]. It was noted that detailed kinetics and finite-rate approaches are necessary for syngas in the context of the simulation of the Favre-averaged Navier–Stokes equations because the fast-chemistry approaches, which are frequently used in the industry for conventional fuels, produced unreliable results. The combustion chamber malfunctions when powered by syngas and only partially oxidizes carbon monoxide. Numerical simulations have demonstrated how few changes to the chamber are necessary to achieve low pollutant emissions, efficient syngas feeding, and the desired flow and thermal uniformity for the drying process.

In a different study, Quintero-Coronel et al. looked into the co-gasification of biomass and coal as a potentially effective way to combine the production of syngas with various gasification feedstocks [25]. This strategy might supplement the natural gas used in commercial and residential burners. The co-gasification performance of palm kernel shell and high-volatile bituminous coal was evaluated using a top-lit updraft gasifier with a moving ignition front. The study discovered that as biomass volume rose, the ignition front spread more quickly and uniformly. Syngas–natural gas blends containing up to

15 vol% syngas can burn in atmospheric natural gas burners without any modifications, according to a gas interchangeability analysis. As a result, the top-lit updraft gasifier has great potential for co-gasifying biomass and coal.

In wastewater treatment, graphene is a suitable material for the removal of toxic compounds through adsorption, electrochemical treatment, and photocatalysis due to its large surface area, high current density, and optical transmittance [26]. It is the material known as graphene, which was found by Nobel laureates Konstantin Novoselov and Andrej Gejm [27]. Numerous studies have demonstrated the excellent potential of the millennium material as a filter element. Lin et al., for instance, used graphene quantum dots (GQDs) for wastewater nanofiltration [28]. For the electrochemical treatment of wastewater, photocatalysis, and adsorption, respectively, graphene and its derivatives have been used as efficient electrodes, photocatalysts, and adsorbents in a variety of applications [29–31]. The production of surfaces in the order of a few square centimeters can be accomplished using a variety of frequently expensive technologies. One of the most effective thermal and electrical conductors ever created, graphene is a two-dimensional material with mechanical strength 100 times greater than that of steel. Derivatives of graphene have been synthesized and used for a variety of environmental-remediation applications, particularly in wastewater treatment.

There have been previous studies of wastewater treatment and purification but there have been few studies on the usage of graphene-based material as a novel material with industrial applications, especially in wastewater purification and filter production. The purpose of this paper was to implement a method for the disposal of wastewater, which could be integrated with industrial procedures operational in the treatment of special liquid waste. Despite the environmental decline, the main target of researchers has shifted to the assembly of renewable energies, obtainable from industrial processes that are already useful and can also be useful in further particular applications. The appropriate treatment of wastewater, which is crucial to energy recovery, has been a goal in recent studies. In this paper, we propose a novel graphene material based on plasma-arc technology, that is applicable in testing produced filters for rapid reduction in pollutant concentrations and can lead to the efficient treatment of wastewater leaving the plant and the solid residue. The analysis also concentrated on input parameter optimization, using experimental data, and provided guidelines for the optimization of parameters for energy efficiency as a novel approach in the conversion of the output into electricity.

The rest of the paper is structured as follows: the theory and methods are described in Section 2, followed by a case study description. The results and discussion are included in Section 3. Finally, Section 4 provides the main conclusions of the paper and suggestions for future research.

2. Theory and Methods

We have been working on hydrogen scenarios for many years due to its low environmental impact as a fuel. Hydrogen, as a fuel, produces water vapor and traces of nitrogen oxides as reaction products, and when used in electrochemical devices, such as fuel cells, it just emits water vapor. Hydrogen is a non-competitive technology due to its high energy cost and limited valorization yields. It is found in small quantities in its pure form but is widely mixed with other elements, making it a non-competitive technology with a high energy cost (67 kWh_e/m^3 of gas generated) and limited valorization yields.

The possibility of extracting fuels from waste oils was investigated, with the crux of the issue being to determine the composition and carbon content of the fuels. Suspended particles in combustible gases have been demonstrated to be problematic, leading to the formation of NO_x, dioxins, and furans, necessitating the implementation of safeguards. Co-generators are fixed-point machines, and the presence of various contaminants has an impact on both life and operation. Proper syngas purification plays a critical role in the proper performance of energy production. Based on the National Hydrogen Program of the United States, hydrogen could account for between 1% and 14% of total energy demand in the United States, and by 2025, the United States could see a two- or four-fold increase in hydrogen demand across the nation [32]. Furthermore, in the presence of adequate extractive technologies, hydrogen would not cause problems, although it is present on the earth in extremely small quantities and combined with other elements. Extracting hydrogen from moles of generic external sources (fossil fuels, renewable energies, or nuclear energy) is one of the main obstacles that prevent its widespread use.

This work aimed to build a plant supply chain based on a large-scale hydrogen economy, with a focus on lowering production costs and increasing conversion yields, while maintaining emission control and limiting the environmental impact of the entire production chain. The future of this industry hinges on the development of energy sources that are both renewable and environmentally sustainable.

2.1. Plasma Arc Flow

The utilization of the PAF refinery, which represents a crucial factor in the energy conversion of gases recovered from wastewater treatment, would be the central element of the identified solution. The PAF plant's analyzed procedure aims to produce sterilized water, syngas/biogas with a high concentration of hydrogen, and fixed carbon residue. The findings suggest that syngas with a discontinuous calorific value in which the primary element is hydrogen can be produced at a low energy cost. The technology involves a reactor in which liquid is exposed to ultraviolet electromagnetic radiation, which sterilizes it, carbonizes suspended substances, and decomposes organic substances into molecules/base atoms. This is done through two electrodes that generate a submerged electric arc. The electrodes are driven by a high direct current (3040 V; 2500–3000 A for a 100 kWh reactor) that heats the treated fluid to extremely high temperatures (in the order of 5500 °C) to allow molecular decomposition. The atoms that are liberated naturally create PAF, which is collected and stored and can be assimilated into biogas, with a yield and efficiency comparable to any other biogas on the market. This reactor can create gas only, decontaminated water only, or create gas plus decontaminate water, according to predetermined compositions and with the inclusion of other bespoke technologies. Figure 1 is a simple scheme of the plasma arc flow gasifier.

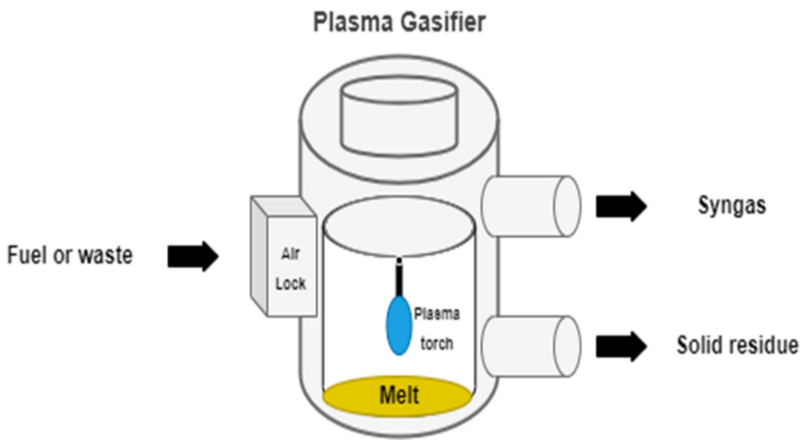

Figure 1. Plasma arc flow gasifier.

The thermal energy produced by the electric arc is recovered by the device itself. Use of the reactor should be preceded by customized testing. The reactor can dispose of all carbon-containing liquid waste, with varying productivity and efficiency depending on the quality of the liquids. When using the reactor, the following must be known:

a. Percentage of water in the liquid and TSS;
b. Conductivity (not exceeding 1%);
c. Organic content.

2.2. Case Study

The development of innovative technologies targeted at utilizing knowledge in the purification sector, as well as getting a gas that is rich in hydrogen obtained from the same purification process as we have just shown, has a wide range of applications. One of these is the possibility of purifying water waste and extracting a gas with the following energy values from the process:

a. Renewability;
b. Low cost of production;
c. Low environmental impact.

Based on a study performed on a PAF reactor that treats 5500 L/h of leachate with an energy absorption of 200 kW_e power, the machine was set to operate in total-linear mode, producing PAF (20 m^3) and decontaminated water simultaneously. When the mass of gas and solid carbon residue input flow rates were subtracted, the output flow rate was practically equal to the input flow rate (0.003% less than the incoming flow). After passing through a single passage in the reactor, the treated matrix had the following composition at input and output as illustrated in Table 1.

Table 1. Matrix composition at input and output [33].

Leachate 26 October 2013 [33]		
Parameter	**Input mg/L**	**Output mg/L**
	Linear 100 L·min	
SST	1393	630
BOD	3020	1850
COD	9073.4	4633
NH4	1355.2	1724.8
Az. N	2.2	8.6
Rs 105	700	900
Rf 550	530	600

Following the passage of the flow inside the reactor, PAF was formed with the following composition as indicated in Table 2.

Experimental evidence allowed us to determine that, depending on the density of the gas, hydrogen-thickened components could be thickened because their molecular weight was lighter. Verifying the gas density and $\sum = \rho_i * x_i$, it was observed that the density of hydrogen was 0.20 kg/Nm^3, which is about 2.3 times the density of n-hydrogen. Therefore, it was possible to deduce that the hydrogen contained in this mixture was in a more thickened state than under standard conditions. Since the PAF produced contained 49.18 percent molar hydrogen, the volumetric flow rate of hydrogen derived from this process was 9.83 m^3, resulting in a mass flow rate of 1966 g.

The energy necessary to generate this quantity, given that the moles of water are equivalent to those of hydrogen and that dissociating the water molecule requires 458.86 kJ/mol, was 450,214.58 kJ which equals 125 kWh_e. Since the density of the syngas varies depending on the matrix used, the gas's low calorific value rose when compared to the value derived only by composition analysis under standard conditions.

Table 2. PAF gas composition [34].

Composition ASTM D 1946–90 (20068)	% Molar	Density
Hydrogen	49.18% molar	0.08993 kg/Nm^3
Oxygen + argon	1.20% molar	1.607 kg/Nm^3
Nitrogen	4.09% molar	1.25 kg/Nm^3
Methane	0.57% molar	0.66 kg/Nm^3
Carbon monoxide	30.90% molar	1.15 kg/Nm^3
Carbon dioxide	12.91% molar	1.98 kg/Nm^3
Ethane	0.03% molar	1.356 kg/Nm^3
Ethylene (C_2H_4)	0.54% molar	1.26 kg/Nm^3
Propane	0.01% molar	2.003 kg/Nm^3
Propylene (C_3H_6)	0.10% molar	1.81 kg/Nm^3
Esani+superior hydrocarbons	0.06% molar	
Unidentified hydrocarbons	0.38% molar	
Pot. Callus. Sup. (UNI EN ISO 6975-06 [35])	12,085 kJ/Sm^3	
“” “	12,770 kJ/Nm^3	
Pot. Cal. Inf. (UNI EN ISO 6975-06 [35])	10,911 kJ/Sm^3	
“” “	10,514 kJ/Nm^3	
Volumetric mass	0.7404 kg/Sm^3	
Volumetric mass	0.7817 kg/Nm^3	

2.3. Energy Recovery

We investigated the possibility of achieving energy recovery on-site by employing a co-generator as a fuel, allowing for the self-consumption of the energy generated to power the process. Taking note of the gas's composition, we could see that H_2, CO, and a tiny portion of combustible gases were present in higher percentages and actively participated in the burning process. Their volumetric flow rate was 17.61 m^3 based on the proportion that they were present in the mixture. The thermal potential obtained from the combustion of the active fraction of this gas was 272.34 MJ and was instantly available. The power obtained from the same was 122.58 MJ or 34.08 kWh if a CHP unit with an electrical efficiency of 0.45 was adapted to the plant.

Assuming the machine's absorption does not alter during operation at full capacity, we may recover roughly 17% of the energy used in the entire purifying process; otherwise, a higher percentage of self-consumption is attained. It is possible to use an energy quota directly on-site without having to absorb it from the grid in this configuration, resulting in cost savings and CO_2 reduction. Note that while the energy obtained from the combustion of the gas in question was equal to 272.34 MJ, it takes 7.88 m^3 of natural gas to provide the same amount, which corresponds to 7.44 m^3 of methane as it is the predominant element in the mixture, present in a volumetric percentage of about 94.38%.

Because each mole of methane produces the same amount of CO_2 in the combustion process, obtaining the same amount of energy provided by PAF using natural gas produces around 7.44 m^3 of CO_2. Using the produced gas in the combustion chamber, however, the amount of CO_2 produced was 6.18 m^3, resulting in a CO_2 savings of 17%. The process is more energy-efficient than conventional methods if the gas generated is not used for self-consumption but rather as a processing byproduct for potential hydrogen extraction. This is because for each cubic meter of H_2 brought back to standard conditions, 5.16 kWh would be needed with the new machine that treats the same amount of waste but with a consumption halved.

The analysis of ancillary systems for the control and abatement of harmful substances, such as CO_2 and NO_x, for the environment and humans will be correlated by the identification of similarities and differences in the different processes through the study of alternative solutions currently implemented in Italy and Europe. Finally, will focus on a review of the current cogeneration and trigeneration systems for energy recovery that are suitable for syngas conversion systems. An acceptable design of solutions for the implementation of these systems associated with the plant under investigation will be realized. This study provides a cost estimate for the feasibility based on the kind of wastewater and plant used. Exploring the possibilities of using the plant in operation with these wastewaters by combining an ad hoc co-generator to optimize the process of valorization of the gases produced while recovering a portion of the energy required for the purification process through cogeneration is considered innovative. Before arriving at assessments based on detailed analysis, care must be taken to carry out a series of investigations aimed at understanding the efficiency and the operating conditions when working with an alternative material that is not endowed with particular combustible attitudes, in the sense that it does not burn in most cases and presents the not insignificant problem of emissions.

Molecular dissociation is a promising new technology that uses a plasma arc hadronic process with a low energy cost. To achieve this, the definition of BAT (best available technique) is established. BAT is a treatment that can make waste reusable or recoverable with the least amount of environmental impact. It can help explain why one solution to an environmental problem is chosen over another. Large waste-to-energy plants are more efficient than gasification machines but require more sophisticated monitoring and pollution purification equipment. This is due to the furnaces operating on oxygen and at temperatures where nitrogen can also participate in combustion, resulting in the generation of NO_x, SO_x, and chlorinated organic compounds.

2.4. Characterization of Wastewater and Filter Production

The primary objective off this research was to verify whether it is possible to extract a substance from the fixed residue to be used in the production of filters for wastewater purification, to implement circular economy technology. This part of the study focuses on two aspects:

Focus 1: Purification of water used in the production processes of fuels obtained from the gasification of industrial waste of various kinds, with different pollutant content, depending on the initial input matrix. The classification of the chemical composition of the water exiting the gasification plant is the first step in the testing process, and determines the most appropriate systems for maximum contaminant abatement and the use of innovative graphene filters.

Focus 2: Recovery and use of the solid residue, consisting mainly of carbonaceous agglomerates. This work aims to qualify the fixed residue leaving a gasifier, determine its composition, and evaluate the possibility of using it to produce graphene. A filter material has been developed using carbonaceous materials derived from eco-friendly matrices, such as sweet lignin mass. The material has produced great results in the filtration of water from various industrial environments, displaying good effectiveness for both organic and inorganic contaminants. Following the acquisition of the material, its composition is assessed and its filtering capacity on gasifier effluent is confirmed.

The water used in these activities must meet certain conditions as defined in Annex 5 of Legislative Decree No. 152/2006 before it can be discharged into the environment. To optimize and limit water use, it is important to make industrial operations as efficient as possible. The leachate's composition varies depending on the type of waste that generates it and the operational features of the syngas conversion process (pyrolysis temperature). The main issue with landfills is the production of leachate and the emission of foul-smelling gases as the organic fraction decomposes. Leachate is a liquid produced primarily by infiltrating water into a waste heap or by the breakdown of the waste mass. The average characteristics of the leachate produced by each waste sent to the landfill are usually evaluated through pH, BOD, COD, and metal-content indicators which indicate the amount of organic matter contained in the wastewater under investigation. Physical features and pollutant content, such as turbidity, surfactants, mineral oils, COD, phosphorus, suspended and sentimental materials, metals, and dyes can be used to categorize industrial wastewater. Markers such as pH, BOD, COD, and metal concentration are used to assess the average characteristics of wastewater. BOD and COD are indicators of the amount of organic matter contained in the wastewater under investigation.

Figure 2 shows FT-IR analysis of wastewater to investigate the quality and possible compositions that were used to compare with our case. Moreover, an elemental analysis was extracted and is shown in Table 3 [36].

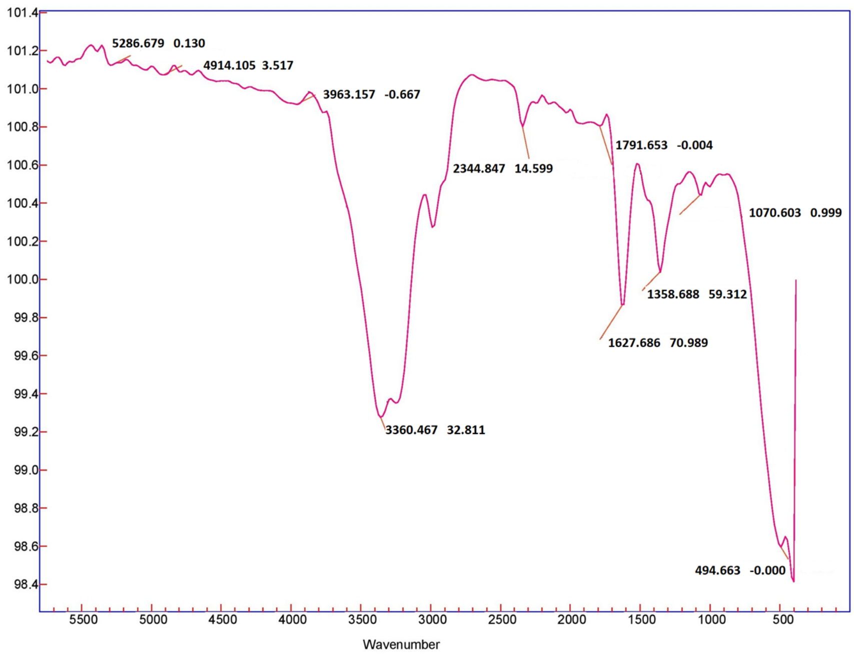

Figure 2. FT-IR analysis of the raw leachate [36].

Table 3. Wastewater characterization and elemental analysis [36].

Parameter	Substances
TC (mg L^{-1})	5868 ± 293
TIC (mg L^{-1})	2450 ± 196
TOC (mg L^{-1})	3227 ± 252
TN (mg L^{-1})	2905 ± 87
TSS (g L^{-1})	0.17 ± 0.02
TS (g L^{-1})	13.5 ± 1.7
pH	8.2 ± 0.1
Conductivity (mS cm^{-1})	32.1 ± 0.4
TC (mg L^{-1})	5868 ± 293
TIC (mg L^{-1})	2450 ± 196
N-$NH4^+$ (mg L^{-1})	2615 ± 99
Chloride (mg L^{-1})	3316 ± 60
Sodium (mg L^{-1})	3379 ± 124
Potassium (mg L^{-1})	2049 ± 88

Table 3. *Cont.*

Parameter	Substances
Magnesium (mg L^{-1})	236 ± 47
Calcium (mg L^{-1})	156.5 ± 29.4
Iron (mg L^{-1})	0.4 ± 0.04
Nitrate (mg L^{-1})	58.9 ± 1.2
Zinc (μg L^{-1})	512 ± 29.2
Chromium (μg L^{-1})	670 ± 16.8
Lead (μg L^{-1})	4.6 ± 1.1
Cadmium (μg L^{-1})	15.5 ± 2.5
Cobalt (μg L^{-1})	113 ± 17
Copper (μg L^{-1})	47 ± 12.5
Mercury (μg L^{-1})	1.2 ± 1

3. Results and Discussion

3.1. Case-Study Analysis

The evidence gathered reassures us because, in each case, the leachate in question at the exit becomes wastewater that can be used in a variety of ways, including as residential water, irrigation water, or water that can be discharged into the sewer. The composition of the liquid phase exiting the plant is shown in Table 4, indicating that the resulting water cannot be released into surface water or the sewer system, as required by Italian regulation:

The proposed solution is to install a chemical−physical purification system downstream of the gasification plant, with a capacity appropriate for the effluent produced (100 L/min). Following that, the wastewater from the purification plant will be characterized. If the legal limit values are not met, the solution is to implement a finishing filtering system that uses special filters with the innovative, graphene-based material, which is based on functionalized graphene, resulting in cost and time savings.

The filters made of graphene-based material were tested with industrial wastewater, and the measured values of pollutant concentrations entering the purification system, as well as the effects produced by the purification finesse process, following chemical−physical treatment, are reported in the following table (Table 5).

3.2. Chemical/Physical Characterization of Graphene-Based Material

The graphene-based system is a graphene composite product for water treatment that is the first and only solution for large-scale applications on the market. The graphene-based material is a micro-mesoporous filtering device made up of functionalized graphene and graphene nanosheets embedded in an activated carbon matrix containing gaps and dislocation defects. It is a material with unrivalled properties and performance in terms of contaminant-removal capacity, with extremely high efficiency for the decontamination of a wide range of pollutants. It is stable and inert regardless of the aggressiveness of the chemical matrix, making it an excellent material for use in water purification treatment to achieve concentration targets of pollutants within the limits established by law. It has also shown a particular efficacy in the treatment of prefiltration with a significant improvement compared to treatments operated with reverse osmosis and ultra-filtering membranes, with a significant reduction in fouling and biofouling phenomena (Figure 3).

Table 4. Annex 5 to Legislative Decree no. 152/200.

Parameter Number	Substances	Units of Measurement	Discharge into Surface Water	Discharge into Sewerage Network
1	PH		5.5–9.5	5.5–9.5
2	Temperature	C	−1	−1
3	Color		Not perceptible with dilution 1:20	Not perceptible with dilution 1:40
4	Smell		Must not be a cause of harassment	Must not be a cause of harassment
5	Coarse materials		Absent	Absent
6	Total suspended solids	mg/L	≤80	≤200
7	BOD (as O_2)	mg/L	≤40	≤250
8	COD (as O_2)	mg/L	≤160	≤500
9	Aluminum	mg/L	≤1	≤2.0
10	Arsenic	mg/L	≤0.5	≤0.5
11	Barium	mg/L	≤20	-
12	Bromine	mg/L	≤2	≤4
13	Cadmium	mg/L	≤0.02	≤0.02
14	Total chromium	mg/L	≤2	≤4
15	Chromium VI	mg/L	≤0.2	≤0.20
16	Iron	mg/L	≤2	≤4
17	Manganese	mg/L	≤2	≤4
18	Mercury	mg/L	≤0.005	≤0.005
19	Nickel	mg/L	≤2	≤4
20	Lead	mg/L	≤0.2	≤0.3
21	Copper	mg/L	≤0.1	≤0.4
22	Selenium	mg/L	≤0.03	≤0.03
23	Tin	mg/L	≤10	
24	Zinc	mg/L	≤0.5	≤1.0
25	Total cyanides (as CN)	mg/L	≤0.5	≤1.0
26	Free active chlorine	mg/L	≤0.2	≤0.3
27	H_2S	mg/L	≤1	≤2
28	SO_3	mg/L	≤1	≤2
29	SO_4 / −3	mg/L	≤1000	≤1000
30	Chlorides / −3	mg/L	≤1200	≤1200
31	Fluorides	mg/L	≤6	≤12
32	Total phosphorus (as P) / −2	mg/L	≤10	≤10
33	NH_4 / −2	mg/L	≤15	≤30

Table 5. Result of the graphene- based material.

	Input to Graphene-Based Material	Output from Graphene-Based Material
COD	<800 ppm	<200 ppm
BOD	<700 ppm	<150 ppm
SST	<300 ppm	<10 ppm
Heavy metals (summation)	<50 ppm	<5 ppm
Chlorinated solvents (summation)	<100 ppm	<5 ppm
Total hydrocarbons	<50 ppm	<1 ppm

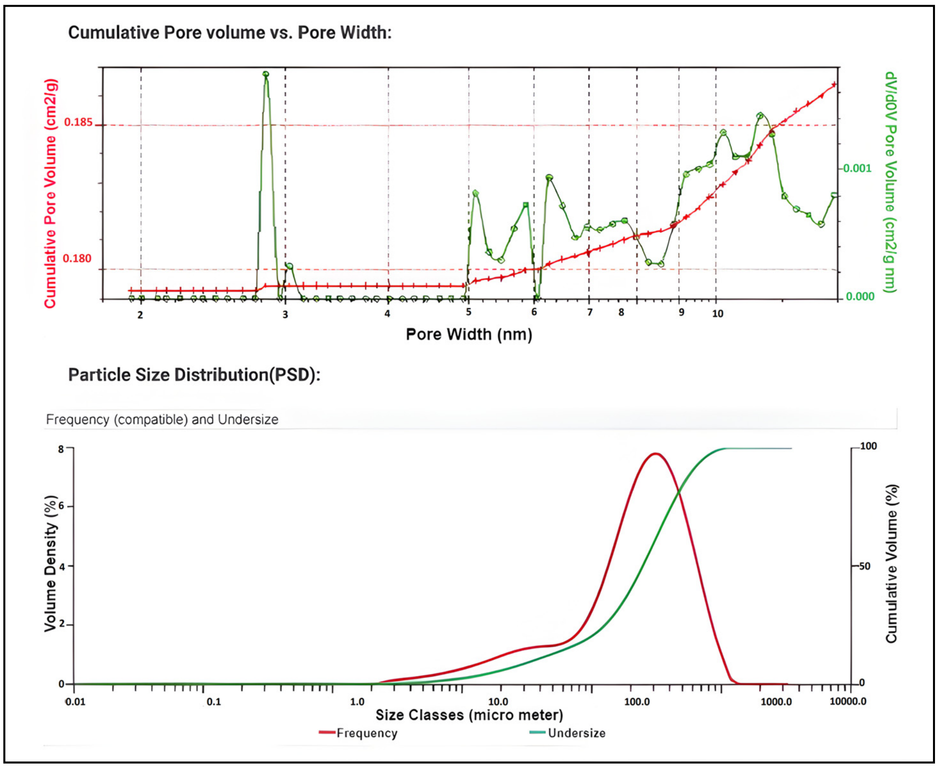

Figure 3. The result of graphene-based material characterization.

The following (Tables 6 and 7) are the key chemical−physical features of the graphene-based material, as determined by the characterization investigations:

Table 6. Physical properties.

0.20–0.25 cm^3/g total pore volume	500–560 m^2/g specific surface area (BET analyses)
0.5–0.6 cm^3/g bulk density	0.18–0.21 cm^3/g (t-plot method) micropore volume

Table 7. Chemical properties.

18–20% fewer layers of graphene in graphene-based material	<1% wt moisture content	<1% max ash content
>98% purification (X-ray fluorescence spectroscopy)		4–6 pH
94–96 atomic wt% carbon content	3–5 atomic wt% oxygen content	0.1–0.2 atomic wt% sodium content

3.3. Morphological and Compositional Investigation

The morphological and compositional investigation was performed with a scanning electron microscope in an electron microscopy laboratory in Italy. By depositing a layer of powder on the sample holder, the observed sample was obtained (Figure 4).

(a) (b)
(c) (d)

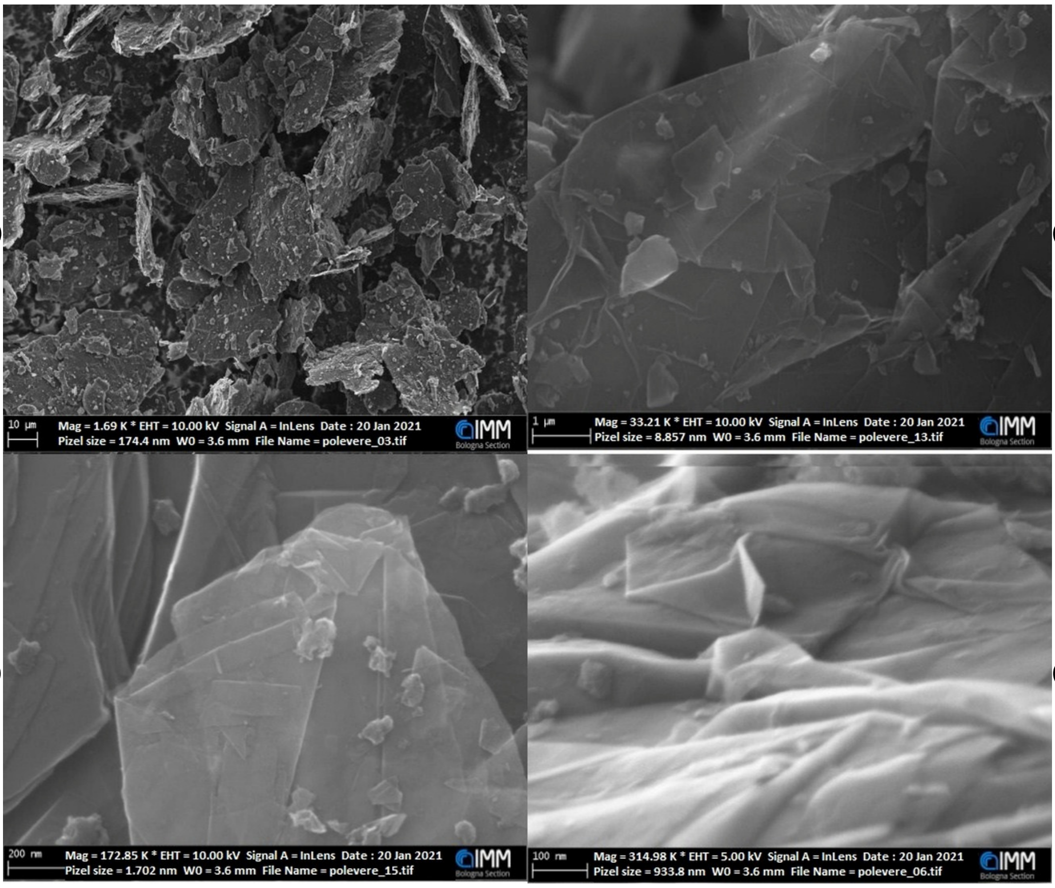

Figure 4. (**a**) Low-magnification image highlights the flake fragmentation of the material, (**b**) some 'thin' layers found on the surface of the fragment, (**c**) thin layers, and (**d**) evidence of thin stratifications.

3.4. Water Purification Mechanism from Contaminants

The graphene-based material removes the contaminant by the synergistic effect of two phenomena: by absorption (absorption, adsorption, physisorption, and chemisorption) and by its action as a separation membrane. The flow of water is conveyed into the filtering device, consisting of oxidized regions, and graphene-based material plates, alternating with pure graphene. The motion of the fluid is slowed down by hydrogen bonds between water molecules, in pristine and oxidized regions. The stages of the decontamination process are as follows:

a. Mesopores: provide a capillary effect by allowing big and small particles of contaminating substances to flow through the adsorbent surface. The main concept of the graphene-based material membrane's decontaminating activity is this propulsive influence on the fluid's motion.
b. The monolithic structure: the filter bed is prepared in a monolithic structure which ensures the geometric stability of the graphene nano-channels during the decontamination process. Therefore, the purification mechanism consists of the combined action of the absorption of mesoporous graphene and the action of membrane separation.
c. Absorption process: includes chemisorption, adsorption, absorption, and p−p interaction mechanisms between graphene sheets and sorbates, van der Waal's forces, and London forces.

d. Separation membrane effect: Some contaminants get caught inside the nano-channels produced between two or more layers of graphene, usually those with a molecular size of above 0.4 nm. The separation membrane can be thought of as a molecular sieve. Purification has a clearance effectiveness of greater than 99.9% for most pollutants.

3.5. Conceptual Filtration Model

The leachate transport channel through the filter material is formed within the functionalized graphene sheets as an interlayer of intermediate gaps, pores, and non-homogeneity (Figure 5).

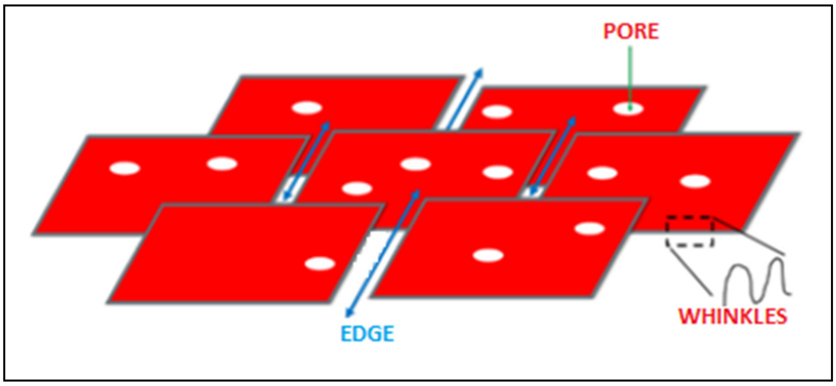

Figure 5. Filtration model with graphene-based material.

First, the graphene-based material improves the hydrophilicity of graphene nanosheets, increasing the available filtering surface of each nanosheet and therefore its ability to retain contaminants. Secondly, the surfaces of the nanosheets are modified to maximize the electrostatic interactions between graphene-based material and sorbate, improving their absorption capacity. Electrostatic interaction is the main driving factor for the adsorption of positively charged substances (such as heavy metals) by negatively charged functionalized carbon nanosheets. The effectiveness with which certain pollutants, particularly heavy metals, are removed is highly influenced by pH changes. This phenomenon is explained by the fact that the carboxylic acid groups on the material's surface have a pH of around 4–5. As a result, leachate with a pH greater than 5.5 has the highest ability to remove pollutants. The carboxyl groups are deprotonated under these conditions, resulting in a high electric charge in the substance. The graphene-based material has more negative charges on its surface at higher pHs, which dramatically improves its electrostatic interaction with positively charged dye molecules.

The functionalized graphene sheets absorb higher-molecular-weight organic compounds on the outside surface, while smaller molecules are absorbed inside the micro holes. The interlayer tunnel can boost the capillary effect and cross-flow from the pores within the graphene sheets and between the intermediate space of neighboring sheets due to the low porosity and ratio between the edge and surface of the graphene or graphene-based-material sheets. The water has a lateral blocking effect, allowing a noticeable flow transverse to the layers of uncontaminated graphene that alternate with the oxidized portions of the graphene-based sheets. The hydrogen bonds between the water molecules in the uncontaminated and oxidized portions slow down the flow during motion.

The pore size distribution and membrane effect have been extensively researched to optimize the removal of a diverse spectrum of pollutants—polar and non-polar, organic and inorganic. The material is a good fit for applications that require a quick reduction in pollutant concentrations. Its main aptitude is its use as a finishing means for the removal of a wide range of contaminants. The result of the substances test has been summarized in Table 8.

Table 8. Tested substances.

Type	Contaminants
Heavy metals and metalloids	As, Cd, Cr (III), Cr (VI), B, Ba, Tl, Sr, Cu, Zn, Mn, Fe, Se, Sb, Sn, Hg, Ti, V, Pb, Co, Hg, Mo
Hydrocarbons	All of them (BTEX, PAHs, C<12, C>12)
Chlorinated solvents	All of them (CF, DCM, CM, HCA, CM, PCA, 1,1,1,2-TeCA, 1,1,2,2-TeCA, 1,1,2-TCA, 1,1,1-TCA, 1,2-DCA, 1,1-DCA, CA, PCE, TCE, cis-DCE, trans-DCE, 1,1-DCE, VC)
Emerging contaminants	PPCPs, detergents, fire retardants, pesticides, hormones, antibiotics
Radionuclides	^{137}Cs, ^{99}Tc, ^{131}I (others not yet tested)
Others	MTBE, ETBE, TBA, pesticides, PCDF, PCDD, NOM, DBPs, anionic and nonionic surfactants, phenols and polyphenols, PFASs, COD, BOD, iodine, acetone, THF

4. Conclusions

This research aimed to analyze and optimize a procedure for treating fluid waste with high environmental impact, using plasma technology or plasma arc flow. It also aimed to find commonalities with similar technologies and create a novel graphene-based material for purification treatment in industrial applications. The goal of the research was to analyze and monitor the submerged arc plasma reactor. This involved analyzing the incoming wastewater to be treated, and identifying precise composition characteristics with relative tolerances for the reactor's next processes. The analysis focused on optimizing input parameters, producing characteristic curves, and searching for specifications that govern the evolution of hydrogen in the syngas. Additionally, guidelines were provided for optimizing parameters for energy efficiency, characterization of the syngas produced, and identification of plant solutions for the conversion of the output into electricity. In short, these phases will be generated through modeling of the gasification process using the CHEMCAD software®, which will allow the upper temperature to be limited; avoid energy waste due to unnecessary heat administration; control inlet temperatures and precipitation of the solid part; and allow optimal-temperature-range identification for the reactor to operate, based on the liquid state of the incoming wastewater

Subsequently, for a given input matrix, the investigation will be oriented to the determination of the optimal viscosity through an evaluation study aimed at reducing the effects of this parameter by preheating the incoming wastewater by heat recovery. The research phases will be developed to:

a. Identify the characteristic parameters of the molecular dissociation phenomenon;
b. Identify the energy- (e.g., self-consumption) and economic- (e.g., self-consumption for operation, maintenance, personnel) balancing assumptions;
c. Allow parametric comparative study within the incentive range of the specific input matrix;
d. Identify and resolve issues that were not apparent during the presentation phase.

Further experiments to validate its purifying capacity on wastewater produced by different types of industrial processes will be the subject of future studies, therefore the list should be regarded as incomplete. The creation of filters capable of purifying the water used and produced in the gasification processes of various types of industrial waste is the future goal of our research work. Following that, the fixed residue from the gasifier will be characterized to ensure that it can be processed and turned into graphene-based material. In the future, it is also planned to use the CHEMCAD software® to model the evolution of hydrogen in PAF, which has already been adequately characterized, as well as to define guidelines for the optimization of parameters for the best energy efficiency, to identify the best plant solutions to reduce electricity consumption.

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Abbreviations

PAF	Plasma arc flow
PAG	Plasma arc gasification
PVC	Polyvinyl chloride
CFD	Computational fluid dynamics
QET	Quasi-equilibrium temperature
ER	Equivalence ratio
GQD	Graphene quantum dots
BOD	Biological oxygen demand
COD	Chemical oxygen demand
TSS	Total suspended solids
BAT	Best available technique

References

1. Communication from the Commission to the European Parliament and the Council. Available online: https://eurlex.europa.eu/legalcontent/EN/TXT/PDF/?uri=CELEX:52014DC0330&from=EN (accessed on 5 October 2020).
2. Bocci, E.L.; Zotto, D.; Monforti, A.F.; Marcantonio, V.; Di Alessandro, C.A.; Giuliano, D.E.; Barisano, S.; Stephen, D.; Massimiliano, P.M.; Pietra, D.; et al. First Results of the H2020-Lc-Sc3-Res.-11 Blaze Project: Biomass Low Cost Advanced Zero Emission Small-To-Medium Scale Integrated Gasifier Fuel Cell Combined Heat and Power Plan. In Proceedings of the 8th European Fuel Cell Technology & Applications Piero Lunghi Conference—EFC19, Napoli, Italy, 9–11 December 2019.
3. *SET Plan Delivering Results: The Implementation Plans*, SET Plan 2018 ed; European Commission: Brussels, Belgium, 2019.
4. Inglezakis, V.; Poulopoulos, S. *Adsorption, Ion Exchange and Catalysis*; Elsevier: Amsterdam, The Netherland, 2006; Volume 3.
5. Manzano Agugliaro, F. Gasification of greenhouse residues for obtaining electrical energy in the south of Spain: Localization by GIS. *Interciencia* **2007**, *32*, 131–136.
6. Perea-Moreno, M.A.; Manzano-Agugliaro, F.; Perea-Moreno, A.J. Sustainable energy based on sunflower seed husk boiler for residential buildings. *Sustainability* **2018**, *10*, 3407. [CrossRef]
7. Bocci, E.; Sisinni, M.; Moneti, M.; Vecchione, L.; Di Carlo, A.; Villarini, M. State of Art of Small-Scale Biomass Gasification Power Systems: A Review of the Different Typologies. *Energy Proceed.* **2014**, *45*, 247–256. [CrossRef]
8. Ramzan, N.; Ashraf, A.; Naveed, S.; Malik, A. Simulation of hybrid biomass gasification using Aspen plus: A comparative performance analysis for food, municipal solid and poultry waste. *Biomass Bioenergy* **2011**, *35*, 3962–3969. [CrossRef]
9. Energy Efficiency and Its Contribution to Energy Security and the 2030 Framework for Climate and Energy Policy. In *Impact Assessment on the Energy Efficiency Directive Review*; European Commission: Brussels, Belgium, 2014.
10. Villarini, M.; Marcantonio, V.; Colantoni, A.; Bocci, E.; Villarini, M.; Marcantonio, V.; Colantoni, A.; Bocci, E. Sensitivity Analysis of Different Parameters on the Performance of a CHP Internal Combustion Engine System Fed by a BiomassWaste Gasifier. *Energies* **2019**, *12*, 688. [CrossRef]
11. Bocci, E.; Di Carlo, A.; McPhail, S.J.; Gallucci, K.; Foscolo, P.U.; Moneti, M.; Villarini, M.; Carlini, M. Biomass to fuel cells state of the art: A review of the most innovative technology solutions. *Int. J. Hydrogen Energy* **2014**, *39*, 21876–21895. [CrossRef]
12. U.S. Department of Energy (DOE). "Hydrogen Basics: Frequently Asked Questions about Hydrogen." Energy Efficiency and Renewable Energy Division, World Wide Web. 2003. Available online: http://www.eere.energy.gov/hydrogenandfuelcells/hydrogen/faqs.html#cost (accessed on 26 January 2003).
13. Sasujit, K.; Homdoung, N.; Tippayawong, N. Non-thermal plasma removal of naphthalene as tar model compound from biomass gasification. *Energy Rep.* **2020**, *8*, 97–103. [CrossRef]
14. Couto, N.; Silva, V.; Monteiro, E.; Brito, P.S.D.; Rouboa, A. Modeling of fluidized bed gasification: Assessment of zero-dimensional and CFD approaches. *J. Therm. Sci.* **2015**, *24*, 378–385. [CrossRef]
15. Ramos, A.; Teixeira, C.A.; Rouboa, A. Environmental analysis of waste-to-energy-a portuguese case study. *Energies* **2018**, *11*, 548. [CrossRef]

16. Ferreira, S.; Monteiro, E.; Brito, P.; Vilarinho, C. A holistic review on biomass gasification modified equilibrium models. *Energies* **2019**, *12*, 160. [CrossRef]
17. Mirmoshtaghi, G.; Li, H.; Thorin, E.; Dahlquist, E. Evaluation of different biomass gasification modeling approaches for fluidized bed gasifiers. *Biomass BioEnergy* **2016**, *91*, 69–82. [CrossRef]
18. Marcantonio, V.; De Falco, M.; Capocelli, M.; Bocci, E.; Colantoni, A.; Villarini, M. Process analysis of hydrogen production from biomass gasification in fluidized bed reactor with different separation systems. *Int. J. Hydrogen Energy* **2019**, *44*, 10350–10360. [CrossRef]
19. Inayat, A.; Ahmad, M.M.; Yusup, S.; Mutalib, M.I.A. 2010, Biomass Steam Gasification with In-Situ CO_2 Capture for Enriched Hydrogen Gas Production: A Reaction Kinetics Modelling Approach. *Energies* **2010**, *3*, 1472–1484. [CrossRef]
20. Liao, C.-H.; Summers, M.; Seiser, R.; Cattolica, R.; Herz, R. Simulation of a pilot-scale dual-fluidized-bed gasifier for biomass. *Environ. Prog. Sustain. Energy* **2014**, *33*, 732–736. [CrossRef]
21. Silva, V.; Rouboa, A.I. Using a two-stage equilibrium model to simulate oxygen air enriched gasification of pine biomass residues. Fuel Process. *Technology* **2013**, *109*, 111–117.
22. Moradi, R.; Marcantonio, V.; Cioccolanti, L.; Bocci, E. Integrating biomass gasification with steam injected micro gas turbine and an Organic Rankine Cycle unit for combined heat and power production. *Energy Convers. Manag.* **2020**, *205*, 112464. [CrossRef]
23. Ibrahimoglu, B.; Cucen, A.; Yilmazoglu, M.Z. Numerical modeling of a downdraft plasma gasification reactor. *Int. J. Hydrogen Energy* **2017**, *42*, 2583–2591. [CrossRef]
24. Giuntini, L.; Lamioni, R.; Linari, L.; Saccomano, P.; Mainardi, D.; Tognotti, L.; Galletti, C. Decarbonization of a tissue paper plant: Advanced numerical simulations to assess the replacement of fossil fuels with a biomass-derived syngas. *Renew. Energy* **2022**, *198*, 884–893. [CrossRef]
25. Quintero-Coronel, D.; Lenis-Rodas, Y.; Corredor, L.; Perreault, P.; Bula, A.; Gonzalez-Quiroga, A. Co-gasification of biomass and coal in a top-lit updraft fixed bed gasifier: Syngas composition and its interchangeability with natural gas for combustion applications. *Fuel* **2022**, *316*, 123394. [CrossRef]
26. Saravanan, A.; Kumar, P.S.; Srinivasan, S.; Jeevanantham, S.; Vishnu, M.; Amith, K.V.; Sruthi, R.; Saravanan, R.; Vo, D.V.N. Insights on synthesis and applications of graphene-based materials in wastewater treatment: A review. *Chemosphere* **2022**, *298*, 134284. [CrossRef]
27. Gerstner, E. Nobel Prize 2010: Andre Geim & Konstantin Novoselov. *Nat. Phys.* **2010**, *6*, 836. [CrossRef]
28. Lin, Y.; Shen, Q.; Kawabata, Y.; Segawa, J.; Cao, X.; Guan, K.; Istirokhatun, T.; Yoshioka, T.; Matsuyama, H. Graphene quantum dots (GQDs)-Assembled membranes with intrinsic functionalized nanochannels for high-performance nanofiltration. *Chem. Eng. J.* **2021**, *420*, 127602. [CrossRef]
29. Geim, A.K.; Novoselov, K.S. The rise of graphene. *Nanosci. Technol.* **2009**, 11–19. [CrossRef]
30. Choi, W.; Lahiri, I.; Seelaboyina, R.; Kang, Y.S. Synthesis of graphene and its applications: A review. *Crit. Rev. Solid. State Mater. Sci.* **2010**, *35*, 52–71. [CrossRef]
31. Lee, J.; Noh, S.; Pham, N.D.; Shim, J.H. Top-down synthesis of S-doped graphene nanosheets by electrochemical exfoliation of graphite: Metal-free bifunctional catalysts for oxygen reduction and evolution reactions. *Electrochim. Acta* **2019**, *313*, 1–9. [CrossRef]
32. The U.S. Department of Energy Hydrogen Program Plan. DOE/EE-2128. November 2020. Available online: https://www.hydrogen.energy.gov/pdfs/hydrogen-program-plan-2020.pdf (accessed on 15 June 2023).
33. Verlingeri, I. *Innovhub Stazioni Sperimentali per L'industria*; Test Report n. 201304937; Nuova Magnegas Italia s.r.l.: Benevento, Italy, 2013; Unpublished Test.
34. *ASTM D1946-90*; Standard Practice for Analysis of Reformed Gas by Gas Chromatography. ASTM International: West Conshohocken, PA, USA, 2000.
35. *ISO6975*; Natural Gas-Extended Analysis-Gas-Chromatographic Method. 2nd ed. International Organization for Standardization: Geneva, Switzerland, 1997.
36. Makhatova, A.; Mazhit, B.; Sarbassov, Y.; Meiramkulova, K.; Inglezakis, V.J.; Poulopoulos, S.G. Effective photochemical treatment of a municipal solid waste landfill leachate. *PLoS ONE* **2020**, *15*, e0239433. [CrossRef]