THERMODYNAMIC EQUILIBRIUM MODELING OF THE THERMAL PLASMA GASIFICATION PROCESS USING ASPEN PLUS

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Abstract: Aspen Plus has become one of the most widely used process modeling and simulation tools, which finds application in both academia and industry. Studies conducted using the Aspen Plus simulator have been widely applied to various technologies and feedstock. This paper aims to summarize advances and emphasize the significance of Aspen Plus in designing thermodynamic equilibrium models for the plasma gasification process and its application. We will present the characteristics of the thermal plasma gasification process, and modeling approaches, introduce thermodynamic equilibrium system modeling in Aspen Plus simulator, and highlight a review of developed models from the literature, emphasizing non-stoichiometric equilibrium models. The literature review points out the novelties in the recent developed models, as well as the influence of the most important operating parameters, such as temperature, equivalence ratio, selection of the gasifying medium, plasma power, and steam-to-feedstock ratio on the performance of the gasification process.

Keywords: plasma gasification, thermodynamic modeling, Aspen Plus

1. INTRODUCTION

The increase of the world population in recent decades, along with the improved living standards, has resulted in the generation of huge amounts of waste from households, as well as various types of industrial waste [1]. Therefore, finding a suitable way to dispose the generated waste became one of the major challenges of modern society [2], considering that the conventional pathways of waste disposal pose a great risk to human health and the environment. On the other side, there is a trend of increased demand for energy worldwide. A significant amount of energy is still produced from fossil sources [1], further increasing environmental concern. Such developments have encouraged communities to seek a solution to the excessive depletion of fossil fuels by substituting them with clean energies from renewable sources. Developing optimal technologies based on the utilization of renewable energy sources that supply the energy demands of the entire population is a big challenge nowadays. Wind, hydro, solar, and biomass energy sources have been extensively researched, along with the waste as another alternative to fossil fuels that can be converted into syngas, biogas, or liquid fuels [3].

Technologies to convert waste materials into producer gas include thermochemical and biochemical methods [4]. Energy recovery from waste via thermochemical conversion includes several routes, e.g. incineration, pyrolysis, and gasification. Among those, incineration is the most commonly used method [2], and can be considered a conventional technique of waste materials processing. Although incineration reduces a significant amount of waste, an issue occurs as a result of hazardous pollutants emissions during the process, such as dioxins and furans. Gasification technology has recently come up as a more viable and promising alternative to incineration [1]. It is a thermochemical route that converts feedstock into fuel gas, which is mainly composed by carbon monoxide (CO), hydrogen (H_2), water vapor (H_2O), carbon dioxide (CO_2), tar and ash. The final product of the gasification process is named syngas, and is obtained after the removal of ashes and tars. Gasification consists of four stages called drying, pyrolysis, combustion, and gasification reactions [3], [5]. The most important gasification reactions are given in Table 1.

Table 1. Major reactions in the gasification process [6]

Reaction name	Chemical reaction	
Partial Oxidation	$C+0.5O_2 \rightarrow CO$	$\Delta H^0_{298} = -111 kJ/mol$
Boudouard Reaction	$C+CO_2 \rightarrow 2CO$	$\Delta H^0_{298} = 172 kJ/mol$
Steam-Carbon Reforming	$C+H_2O \rightarrow CO+H_2$	$\Delta H^0_{298} = 131 kJ/mol$
Methanation	$C+2H_2 \rightarrow CH_4$	$\Delta H^0_{298} = -74 kJ/mol$
Hydrogen Combustion	$H_2+0.5O_2 \rightarrow H_2O$	$\Delta H^0_{298} = -484 kJ/mol$
CO Combustion	$CO+0.5O_2 \rightarrow CO_2$	$\Delta H^0_{298} = -284 kJ/mol$
Water-Gas Shift Reaction	$CO+H_2O \rightarrow CO_2+H_2$	$\Delta H^0_{298} = -42 kJ/mol$
Steam-Methane Reforming	$CH_4+H_2O \rightarrow CO+3H_2$	$\Delta H^0_{298} = 206 kJ/mol$

The introduction of plasma torches during the gasification process marked an important breakthrough in gasification technology. Plasma is considered the fourth state of matter. It consists of electrons, ions, neutral particles, exited atoms, photons, and other particles, and it is electrically neutral [7]. Plasma is formed when energy is applied to a gas in order to reorganize the electronic structure of the species as atoms and molecules, and to produce excited species. This energy might be thermal, or it can be transmitted by an electric current or electromagnetic radiations [8]. The plasma provides high temperature heat to the system [5]. Due to high temperatures, all chemical bonds are destroyed and a large amount of radicals, electrons, ions and excited molecules are formed in the system. Because of these active species, and the high radiation intensity from the plasma, the process has the benefit of significanty increasing the rates of the reactions. Through plasma gasification process, the organic fraction of feedstock is converted into high calorific value syngas, that can be used as fuel or chemical. The inorganic fraction is vitrified into a non-leachable slag, that is later used as a construction material [9]. Because of high process temperatures, tars, char, and dioxins are decomposed, making plasma gasification one of the thermochemical pathways that can be used to generate cleaner fuel in comparison with conventional treatments [8].

2. PLASMA GASIFICATION PROCESS MODELING

During the plasma gasification process, there is simultaneous participation of fluid dynamics, and transport phenomena, along with numerous homogeneous and heterogeneous reactions occurring inside the plasma reactor, which makes the process extremely complex [10]. Considering that the consumption of electricity is high during the process [9], and that experiments are expensive and time-consuming, the application of computational models is crucial for understanding the process behavior [11]. Mathematical and numerical models are developed and applied to study the influence of different variable parameters on process performance. It is worth noting that integrating computational modeling and simulation with experimental work leads to improved process and economic efficiency [12]. An adequate model should accurately represent the physical and chemical phenomena occurring inside a gasification reactor, provide a set of optimal operating parameter values, recognize system limitations and undesirable working conditions, and predict experimental results, as well as provide assistance in their understanding and interpretation. [12], [13].

2.1. Modeling approaches

Modeling of the plasma gasification process is performed using different approaches. The four fundamental modeling approaches are the following: thermodynamic approach, kinetic approach, computer fluid dynamics (CFD), and artificial neural networks (ANN). The choice of a model that would most accurately represent the behavior inside the gasification reactor depends on the goals defined and existing experimental data [14].

Table 2. Comparison of the four modeling approaches [10], [11], [13], [15]

	Thermodynamic approach	Kinetic approach	CFD	ANN
Input	– feedstock characteristics (ultimate and proximate analysis) – gasifier parameters	– feedstock composition, density, and particle size – reactor geometry – reaction kinetic parameters	– feedstock characteristics – reaction kinetic parameters –reactor geometry – gasifier parameters	–a large number of experimental data (input data sets)
Output	– gas composition – maximum achievable yield	– gas composition at different positions along the reactor – conversion yield and temperature distribution along the reactor	– syngas yield – temperature and concentration profiles along the reactor	– numerical results
Background	– mass and energy balances of the entire reactor – calculation of Gibbs free energy minimum, or equilibrium constants	– based on reactor hydrodynamics and geometry	– based on mass, heat, and momentum conversion equations	– based on input-output correlation developed from a large set of experimental data
Characteristics	– the result is achieved after infinite time – the components react in a completely mixed state	– includes reaction kinetics, system hydrodynamics, particle size distribution – finite time – description of kinetic mechanisms	– includes system hydrodynamics – usually includes various sub-models	– imitates the working of the human brain to process information through a system of neural networks

2.2. Thermodynamic Equilibrium Modeling

When chemical equilibrium is reached, the reactor is in its most stable composition, which corresponds to the state when the minimum Gibbs free energy and maximum entropy are achieved. [15]. At the mentioned equilibrium conditions, the thermodynamic approach can be applied for modeling and simulation of the gasification process. As the fundamentals of chemical equilibrium are based on the Second law of thermodynamics, a thermodynamic equilibrium model can be formulated using the governing equations that describe the behavior of such a state [13].

The thermodynamic equilibrium model is known as the zero-dimensional model. It represents an effective approach that enables the estimation of optimal working conditions and the maximum achievable conversion yield. Processes with long residence time, or with a temperatures higher than 800 °C can be successfully simulated using the thermodynamic modeling approach, because these are the conditions that allow the system to reach an equilibrium state [10]. The components are assumed to react in a fully mixed state and for an infinite period of time that allows the composition to stabilize.

Equilibrium models can be classified into two types, namely stoichiometric and non-stoichiometric models. The non-stoichiometric approach takes into account all chemical species included in the process, while the non-stoichiometric approach includes all the chemical reactions assumed to take place in the process. It is based on the equilibrium constants of an independent set of reactions [12]. The steps of stoichiometric and non-stoichiometric modeling approaches are given in Table 3. In their study, Ramos et al. [13] have summarized the fundamental equations necessary to formulate a thermodynamic equilibrium model by employing one of the mentioned modeling approaches. According to Safarian et al. [12], stoichiometric and non-stoichiometric approaches are considered to be two different methods that converge to the exact predicted composition. Ajorloo et al. [10] stressed out that in some cases, there are reported deviations between experimental results and the results obtained by simulation due to the introduction of many simplifying assumptions and the ignoring of certain parameters.

Table 3. The steps for the non-stoichiometric and stoichiometric approaches [12]

Non-stoichiometric approach	Stoichiometric approach
1) selection of chemical species to be included in the simulation 2) calculation of the minimum Gibbs energy at the reaction temperature and pressure for the given input composition of the feedstock	1) selection of a set of chemical reactions to be included in the simulation 2) calculation of equilibrium constants for selected chemical reactions at the reaction temperature 3) calculation of the equilibrium composition for a given input composition of the feedstock

2.3. System Modeling with Aspen Plus

In general, Aspen Plus may use equilibrium or kinetic approach for modeling and simulation. For the plasma gasification process, the equilibrium approach is more applicable because of high gasification temperatures, considering that the thermodynamic equilibrium is not fully achieved on relatively lower temperatures [16]. Aspen Plus has become one of the most significant and widely used simulators for thermodynamic analysis. Simulator functions are based on mass and energy balances, and phase equilibrium data [10]. Aspen Plus provides high flexibility in the terms of designing different process configurations. Namely, the integral process scheme consists of different modules (units), which are interconnected by material and heat flow streams [16]. Each unit's output stream properties depend solely on the properties of its input stream, implying that each unit can be studied individually. A significant benefit of Aspen Plus is its ability to carry out analysis and optimization of a wide range of working conditions, as well as to determine process limitations that depend on changes in those conditions. The main limitations in the process modeling and simulation using Aspen Plus arise from the simplified assumptions that are introduced, which can lead to the generalization of the developed model to other process configurations [10].

Within the Aspen Plus simulator, solids involved in process technology can be categorized as conventional and non-conventional solids. Components such as C, S, O_2, H_2, N_2, H_2O, CO, CO_2, CH_4, and so on are considered conventional, while coal, biomass, waste materials, ash, etc. are considered non-conventional solids, due to their heterogeneous nature. Aspen Plus characterizes non-conventional solids in terms of empirical factors called *Component Attributes*, which represent component composition by one or more constituents. In other words, non-conventional materials are assigned based on proximate and ultimate analysis. Simulation of processes involving non-conventional components faces certain limitations due to lack of equilibrium and physical property data. It is important to note that until non-conventional solids are converted to conventional compounds, they cannot participate in phase or chemical equilibrium calculations [17].

Modeling of the plasma gasification process with the Aspen Plus simulator usually consists of the following stages: feedstock drying, feedstock decomposition, and gasification reactions inside the plasma reactor, as shown in Figure 1.

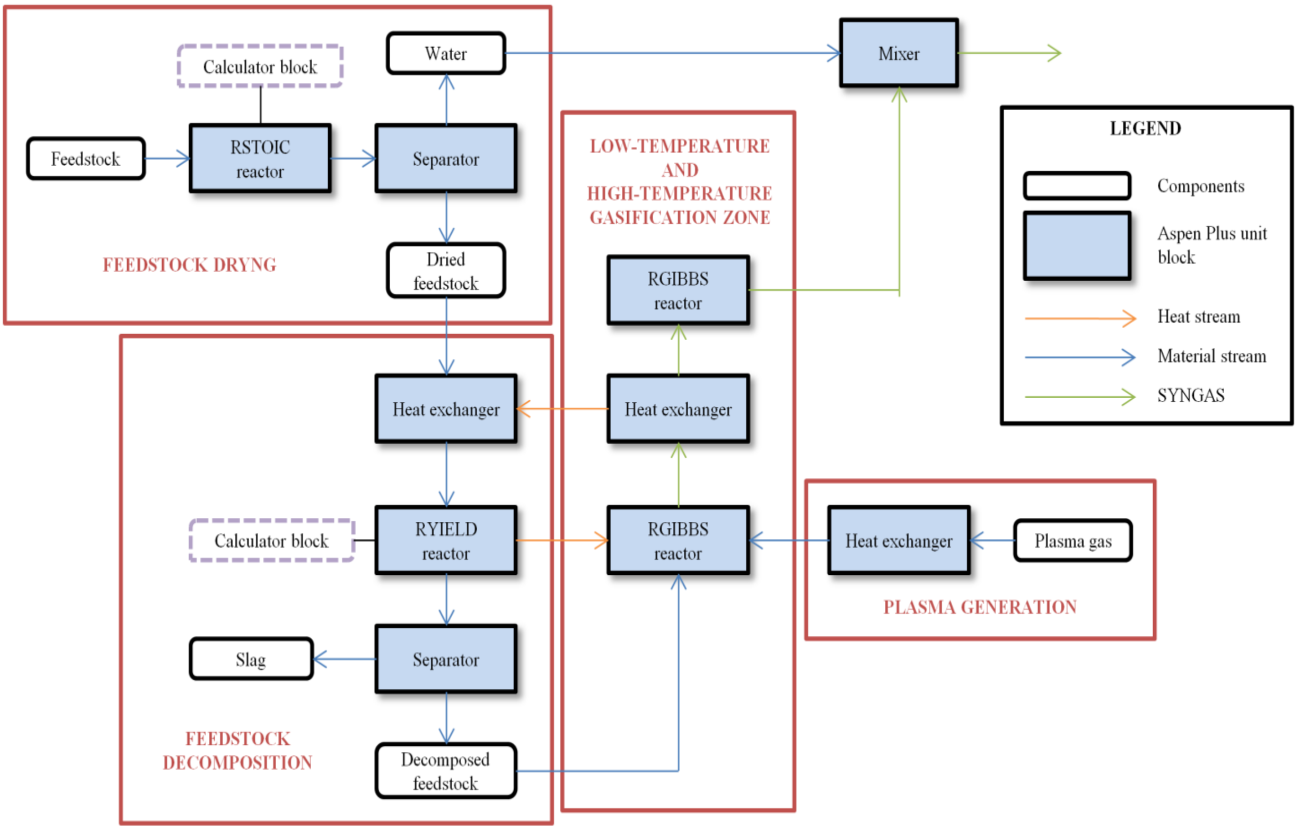

Figure 1. Block diagram of a plasma gasification reactor model

Creating a model in Aspen Plus involves introducing assumptions to simplify the model. The most common assumptions in studies based on the thermodynamic equilibrium approach are the following [5], [18], [19]:

- the model is zero-dimensional;
- temperature and pressure are stable and uniform;
- process is steady-state and stationary;
- the process is considered isobaric and adiabatic;
- heat losses are neglected;
- the process takes place at atmospheric pressure, without pressure drop;
- mixing within the reactor is ideal;
- residence time inside the reactor is long enough to reach thermodynamic equilibrium;
- tar formation is neglected.

3. A SURVEY OF THE MODELS IN THE LITERATURE

As previously mentioned, models created in the Aspen Plus environment usually use a kinetic or thermodynamic equilibrium setup for simulation. Equilibrium models have simple input data consisting of ultimate and proximate analysis of the feedstock, therefore are significantly more used in the literature, while kinetic models are suitable for that feedstock where kinetic reactions are known and well explained. Ferreira et al. [11] in their work stressed that one of the main limitations of thermodynamic equilibrium models is that they overestimate CO and H_2 concentrations while underestimating CH_4, CO_2, light hydrocarbons, and tar. Therefore, Okati et al. [6] attempted to solve the issue by developing a quasi-equilibrium model where the reaction temperature is lowered which should result in a better estimation of these species. Therefore, the RESTRICT block was included where the equilibrium temperatures of the Water-Gas-Shift reaction and Steam-Methane Reforming were assumed to be less than the theoretical equilibrium temperature. The feedstocks used for the simulation were pine sawdust and coal and they were defined as unconventional components in Aspen Plus using proximate and ultimate data and high heating value (HHV). Authors assumed that the chemical reactions reach the equilibrium state, char was composed of carbon, ash was an inert material, produced gas consisted of CO, H_2, CO_2, CH_4, and N_2, while tar formation was neglected. The authors concluded that their quasi-equilibrium model presented better results compared to the thermodynamic equilibrium model, since the mean error of the calculation was 2.0%, compared to the numerical model of 2.11%. The negative effect of tar presence in the gasification process is widely known, but because of the specific tar composition and the mechanism of its formation, it still presents a great challenge to simulate this process. Hu et al. [20] presented a multi-stage co-gasification process that considers the presence of tar. The authors concluded that the addition of steam increases tar decomposition, gas yield, and H_2 production. Tungalag et al. [21] presented a stoichiometric steady-state model to simulate steam plasma gasification of MSW with an emphasis on the hydrocarbons and tar formation during pyrolysis. Authors also considered highly undesired corrosive gas such as tetrachlorodibenzo dioxin (2,3,7,8), while tar was modeled as phenol (C_6H_6O) and pyrene ($C_{16}H_{10}$). Results showed that the concentration of dioxin during plasma gasification is lower than the maximum tolerable amount which suggests that plasma is capable of treating MSW. When comparing the experimental and numerical results, the authors concluded that there is a noticeable difference in syngas yield whereas the Aspen Plus simulation showed a higher syngas yield. Chen et al. [22] presented a novel hybrid design of an integrated system where the syngas generated by the plasma gasification of medical waste is first burned which drove the gas turbine for power generation, while gas turbine exhaust was taken from the system to heat the steam and feedwater of MSW incineration plant. The plasma gasification process was modeled as a non-stoichiometric model in Aspen Plus, while the incineration plant and gas turbine subsystem were simulated in EBSILON Professional. The model in Aspen Plus considered 2 undesirable gasses such as H_2S and COS, therefore, a syngas cleaning component was used to remove them.

3.1. Effects of operating parameters on the gasification process

Temperature. Gasification is a process highly influenced by temperature**.** This influence has two main goals which are increasing the hydrogen and carbon monoxide yields in the produced syngas and improving the tars decomposition. The temperature changes in the process are related to Le Chatelier's principle where the increase in temperature favors the forward direction of endothermic reactions like the Boudoard reaction, Water-Gas, and Steam Reforming reaction, which consequently causes the H_2 and CO increase and CO_2 and CH_4 decrease in syngas composition [5], [6]. From this observation, it can be concluded that the increase in temperature also has a positive impact on the heating value of the obtained syngas, since the main components that increase its heating value are precisely H_2 and CO [3]. The authors reported that higher temperatures are more suitable for tars, dioxins, and furans removal [18], where tars are an inevitable product during the thermochemical conversion of fuel which can have a negative effect on the process and equipment, therefore present one of the most undesirable products, the term "dioxins" refers to chlorinated dibenzo-p-dioxins (CDDs) and "furans" to chlorinated dibenzofurans (CDFs). Dioxins and furans are also highly toxic and potentially human carcinogen compounds [23]. Tungalag et al. [21] varied the gasification temperature in the range of 600-1000 °C and reported a sharp increase in CO fraction until the system reached the optimal temperature of 850 °C, afterward the increase was negligible. A similar pattern was presented in the case of H_2 fraction, while the higher temperature caused the decrease in CH4 fraction due to the exothermic methanation reaction, which was also reported in the work of Hu et al. [20]. Temperature indeed plays an important role in the gasification process because it affects the equilibrium reactions involved in the process, but it is also a parameter that cannot be directly controlled in real-life systems. Temperature is determined by equivalence ratio (ER), where the higher the ER, the higher the temperature [24].

Equivalence Ratio. The equivalence ratio (ER) presents the ratio between the air content in the real operating conditions and the one required for complete stoichiometric combustion of the feedstock.

$$ER = \frac{\left(\dot{m}_{air} / \dot{m}_{feedstock}\right)}{\left(\dot{m}_{air} / \dot{m}_{feedstock}\right)_{stoic}}$$

ER can obtain different values, where the ones close to 0 correspond to pyrolysis conditions, between 0 and 1 correspond to gasification and greater than 1 to combustion conditions. During the gasification process, lower ER values are desirable since they maximize the H_2 and CO yield, but at the same time, extremely low ER values may leave the char and tar unconverted which would present a problem. Also, higher ER values lead to the lower heating value of the produced syngas since they increase the CO_2 yield. The effect is explained with the assumption that the increase in O_2 concentration in the reactor which originates from the air enhances combustion reactions like Partial oxidation, H_2 combustion, and CO combustion [5]. Therefore, the ER for traditional gasification is around 0.3, while in the case of plasma gasification that value is significantly lower (0.04-0.1) [24]. The effects of ER on the gasification process can be considered from two aspects. On one side, higher ER provides more chemical heat by combustion which is beneficial for both syngas yield and heating value of the syngas, therefore presenting a positive impact on the process. On the other side, higher ER also means more combustion reactions in the reactor, which on the other hand will consume some combustible gases such as CO and H_2. Additionally, higher ER will increase the N_2 content introduced into the reactor which will dilute the content of combustible gases as well [25]. Pan et al. [26] varied the ER in the range of 0.15 to 0.40 and concluded that it caused the gasification efficiency to drop from 72.36% to 47.53%. Okati et al. [18] in their work presented the impact of ER in the range of 0.1 to 1.0 at the temperature of 1500 °C, and PCB as a feedstock mass flow rate of 10 kg/h. The authors concluded that the increase in ER caused the H_2 fraction to decrease from 58% to 6%. It is worth noting that the optimal ER value highly depends on the feedstock composition [10].

Gasifying medium. Different gasifying mediums can be used for the gasification process but the most common ones are air, steam, pure oxygen, CO_2, or a mixture of them. Air is the medium widely used in the gasification process since it presents a cheap and abundant source that produces syngas from the gasification process with LHV=4-7 MJ/Nm^3 [27]. Compared to the syngas obtained from oxygen gasification this is a low-quality syngas since oxygen gasification yields syngas with LHV=10-18 MJ/Nm^3. The main reason is the presence of N_2 which dilutes the syngas. The use of oxygen as a gasifying medium on the other hand is rather expensive since the first step would be to obtain high-purity oxygen from the air using an air separation unit which also adds to the complexity of the system. Steam presents a possible solution to these problems since it yields syngas with a high heating value and at the same time is a cheap source. Also, considering economic and operating parameters, introducing oxygen and steam simultaneously is an efficient approach for biomass valorisation within the gasification process [10]. Okati et al. [6] reported that the highest H2 concentration in air plasma gasification was around 39%, in the case of oxygen plasma gasification around 58%, and the case of steam plasma gasification around 60%.

Plasma power. Plasma supplies heat for the gasification process and the amount of plasma that is provided to the system can be presented by plasma-energy-ratio (PER).

$$PER = \frac{P_{pla}}{LHV_{feedstock} \cdot \dot{m}_{feedstock}}$$

With the increase in PER, the temperature of the process increases as well which favors the generation of CO and H_2 and tar and char conversion, causing the increase in the heating value of produced syngas. At the same time, the increase in PER means higher electricity consumption to generate plasma which might not be economically benefical and will cause a decrease in gasification efficiency [26]. Also, too high temperatures caused by the increase in plasma power may lead to the formation of high-temperature zones which might challenge the thermostability of the reactor wall [24]. Zhang et al. [24] reported that the increase in PER from 0.098 to 0.137, increased the syngas yield from 0.96 to 1.08 Nm^3/kg_{MSW} and LHV of syngas from 7.32 to 9.31 MJ/Nm^3.

Steam-to-Feedstock ratio (SFR). The steam-to-feedstock (SFR) ratio is used to represent the amount of steam by the amount of feedstock when the gasifying agent contains steam (pure or mixture).

$$SFR = \frac{Steam\ mass\ \ flow}{Feedstock\ mass\ \ flow}$$

The authors [5] reported that the use of steam as a gasifying medium increases the partial pressure of water vapor inside the reactor which favors the Water-Gas Shift and Steam Reforming reactions, leading to increased H_2 production. Similar results can be obtained in [6] where in the case of steam plasma gasification H_2 and CO_2 increase, 10.96 vol% to 12.24 vol% and 12.41 vol% to 13.66 vol%, respectively, while CO and CH_4 decrease. Also, steam affects the tar conversion, where in the case of steam gasification tar yield decreases by 4.1%, from 16.08 to 15.41 g/Nm^3 [20]. The negligible reduction of tar yield by the increase in SFR is explained by the slight promotion of tar cracking/reforming reactions at a constant temperature. The increase of steam in the reactor caused the gas yield to increase from 1.35 to 1.39 Nm^3. The effect is explained by the possible promotion of Steam Reforming of condensable materials such as tar, and the increase of endothermic Char Gasification reactions [20].

4. CONCLUSION

This paper presents a review and analysis of literature ralated to the use of plasma gasification as the method of waste treatment. To assist the development of the plasma gasification facilities, modeling is required as a way to optimize the experimental conditions, with the goal of achieving higher efficiency of the process. The review of the literature showed that Aspen Plus the most commonly used software for modeling and simuation of the plasma gasification process. The non-stoichiometric equilibrium method, in which the input data for the model is provided from proximate and ultimate analysis, is the most frequently applied approach in the literature. The behavior of different feedstock was simulated, such as biomass, MSW, hazardous waste, and different mixtures of feedstocks. The influence of various parameter on the process performance was investigated. The main observations derived from the literature review are the following:

- The increase in temperature has positive effect on the production of combustible chemical species such as H_2 and CO, and, consequently, on the heating value of syngas. High temperatures are also suitable for the destruction of harmful chemical species from syngas.
- H_2 and CO yield increase at lower values of equivalence ratio, but at the same time, the negative effect on conversion of tars and char is present.
- The increase of plasma-energy ratio also causes the increase of temperature, and higher amounts of H_2 and CO are obtained, as previously mentioned.
- The use of steam as the gasifying medium is favorable for H_2 production.

From the above it can be concluded that the use of Aspen Plus is the future for process modeling, as well as for the analysis of vaious operating parameters in order to achieve the best performance of the plasma gasification system.

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