ENVIRONMENTAL COMPARISON OF THERMOCHEMICAL AND BIOCHEMICAL WAYS FOR PRODUCING ENERGY FROM AGRICULTURAL SOLID RESIDUES: COFFEE CUT-STEMS CASE

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ABSTRACT

Coffee Cut-Stems (CCS) are an abundant wood waste in Colombia obtained generally from crops renovation. However these residues are used directly in combustion processes for heating and cooking in coffee farms where their energy efficiency is very low. In the present work, an energy and environmental assessments for two energy production processes (ethanol fermentation and gasification) using CCS as raw material were performed and compared. The potential environmental impact (PEI) was evaluated by the Waste Reduction Algorithm (WAR algorithm) which allows determining the process with the best performance from the point of view of the Potential Environmental Impact (PEI). Besides, the performance of the two processes were compared based on the productivity and the energy efficiency. Biomass gasification seems to be the most promising technology for the use of Coffee Cut-Stems with high energy yields and low environmental issues.

KEY WORDS: Thermochemical processes, Coffee Cut-Stems, Energy and Environmental Assessment

INTRODUCTION

Colombia is the fourth largest coffee producer in the world after Brazil, Vietnam and Indonesia. According to the National Coffee Growers Federation [1], the green coffee production in Colombia was 9.9 million of bags (60 kg-bag) in 2013. In coffee-producing countries such as Colombia, coffee tree wood as waste is abundant, either from cuts or renovations, because between 80,000 and 90,000 coffee hectares are renovated per year from which on average 17 tonnes of dry wood per Hectare can be obtained. These residues would serve to produce, approximately, 690 GWe every year [2]. Currently, most of the forest residues are used directly in combustion processes for cooking and heating in rural areas; despite that the energy content of the biomass is not properly used and the emissions that are generated.

There are different methods for the transformation of wood residues into energy products. Thermochemical and biochemical processes are the most used technologies for this purpose. Thermochemical processes such as pyrolysis, combustion and gasification are the most interesting concepts, focused on the use of biomass as an energy source. From these processes, gasification has attracted more attention because it offers better efficiencies than combustion and pyrolysis [3][4]. During the gasification, biomass is subjected to a thermo-chemical treatment in the presence of a gasification agent such as air, oxygen, steam, or a mixture of these to produce a gaseous fuel known as synthesis gas, which consists mainly of carbon monoxide, carbon dioxide, methane, hydrogen, steam, and some light hydrocarbons. The synthesis gas can be used as fuel for engines and gas turbines or as a chemical platform to produce fuels such as liquid fuels, hydrogen, and chemistry compounds with carbon content [5].

In the other hand, biochemical processes use the lignocellulosic biomass to produce C5-C6 sugar fractions that are transformed into biochemical products through fermentative processes. Among the processes commonly used to convert these sugars into biochemical products are: ethanol, ABE, lactic and dark fermentation processes. Bioethanol is a promising renewable alternative for the partial replacement of fossil fuels. Ethanol is produced commonly by the *S. Cerevisiae* from the hexoses obtained in the pretreatment stage of the lignocellulosic residue. However, the production of ethanol was also evaluated using the recombinant *Z. mobilis* that can degraded both pentoses and hexoses [6]. Currently, the worldwide production of bioethanol is mainly derived from starch and sugar based feedstocks such as beets, sugarcane and corn [7]. Lignocellulosic ethanol is not commercially available yet, since it is still hampered by economic and technical obstacles [8].

The aim of this study is to evaluate and compare the energy and environmental assessment of two processes of energy production (ethanol fermentation and gasification) from Coffee Cut-Stems. For this, experimental and simulations procedures were carried out. The physicochemical characterization of the CCS was performed based on International Standards. The generation of electricity through gasification was performed in a pilot-scale downdraft gasifier connected directly to a portable gas analyzer for real-time measurement of the synthesis gas composition. The bioethanol production considers the pretreatment of the CCS to obtain C5 and C6 fractions and subsequently their fermentation using *Z. mobilis*. The results from the experimental procedure were used as starting point of the simulation procedure in order to generate the mass and energy balances, which are inputs of the energetic and environmental assessment.

2. METHODOLOGY

The results from the experimental and simulation procedure were used in the energetic and environmental assessment of the processes. In order to compare the thermochemical and biochemical pathways, two methodological approaches are proposed. First, the productivity of the processes was evaluated based on the produced platform. Synthesis gas was selected as the platform for the electricity generation through gasification. In the other hand, C5 and C6 sugars were the platforms for the bioethanol production through alcoholic fermentation. Finally, the energy and process performance was evaluated considering the final products of each process. Electricity and ethanol were considered as the final bioenergy products in the gasification and alcoholic fermentation, respectively.

2.1 Experimental Procedure

2.1.1 Raw Material

The physicochemical characterization of CCS was performed in order to determine the cellulose, hemicellulose, lignin, extractives and ash content according to International Standards. The extractives content was determined using two solvents (water and ethanol) following the procedure NREL/TP-510-42619 reported by the National Renewable Energy Laboratories. Cellulose content was performed after the holocellulose determination in search of the purest form of the fiber [9]. Then, the hemicellulose content was calculated as the subtraction between the holocellulose and cellulose content. Lignin content was determined using concentrated sulfuric acid as described in TAPPI T222. Finally, the ash content through total calcination of the material was carried out following the procedure reported in NREL/TP-510-42622.

2.1.2 Gasification

A pilot – scale downdraft gasifier using Coffee Cut – Stems was used to produce synthesis gas as main product. The experimental set up for the syngas production was based in the use of a GEK Gasifier (All Power Labs, Berkeley, California) with a capacity of 10kWh. Prior to the gasification, the raw material was dried until a moisture content between 10 – 15% was reached and subsequently, the dried feedstock was milled and grounded to obtain a particle size between 1 and 2 cm. The previously chipped and dried raw material undergoes into the reactor by means of an endless screw, where the gasification takes place using air as gasifying agent. Then, the ashes were removed from the synthesis gas using a cyclone. Subsequently, the generated gas passes through a filter of wood scraps to retain moisture and other impurities. The gas composition was determined using a portable gas analyzer (GASBOARD 3100-p, Wuhan Cubic Optoelectronics Co., Ltd, China). With this equipment, the content of H_2, CO, CO_2, CH_4, O_2 and the calorific value of the gas was calculated. Finally, the filtered gas was used as fuel for electricity generation through a gas engine.

2.1.3 Ethanol fermentation

The experimental procedure for ethanol production was divided in five stages: milling and drying, acid hydrolysis, detoxification, enzymatic saccharification and fermentation. A brief description of the methods used in each stage of the experimental procedure is presented. First, the material was dried for 5 hours at 60°C in order to remove the moisture content and facilitate the milling process. Then, the dried material was submitted to a blade mill aiming to obtain a particle size of 1 mm. Subsequently, the dried and grounded material was mixed with a diluted acid sulfuric solution 2% (w/w) in a solid: liquid ratio of 1:10. The pretreatment conditions was set at 135°C for 4 hours. From this procedure, a liquid and solid fraction were obtained. The liquid fraction was sent to a detoxification stage in which $Ca(OH)_2$ was added in order to remove the furfural and HMF formed in the acid hydrolysis stage. The operation conditions of this stage were: 60°C, pH 11 and a residence time of 30 min. Afterwards, the solution was neutralized with sulfuric acid until pH 5 was reached and the formed salts were removed by filtration. The remaining solid fraction from the acid hydrolysis was submitted to the enzymatic hydrolysis stage in which the solid was mixed with a citrate buffer solution in a relation 1:10. The enzyme (celluclast 1.5L) was added in a relation 1.5:10 with respect to the solids from the acid hydrolysis. The operation conditions of this stage were: 60°C, residence time of 120 hours and 120 rpm. The fermentation was the last stage of the experimental procedure in which the streams from the acid and enzymatic hydrolysis were mixed in order to obtain a stream rich in glucose and xylose.

The recombinant *Z. mobilis* was used as microorganism for the bioethanol production due to its capacity to degrade glucose and xylose [6]. The operation conditions of the fermentation were set at 33°C and a residence time of 30 hours.

2.1.4 Quantification Methods

The concentration of the produced sugars in the pretreatment stages were measured based on the determination of reducing sugars concentration using the dinitrosalicylic acid (DNS) method, where the absorbance was measured at different wave-lengths depending on the sugar concentration, following the protocol proposed by [10]. For the ethanol determination, Gas Chromatography (GC) was used to measure the concentration of ethanol in the fermentation broth. For this method, a *PERKIN ELMER Autosystem XL* GC with a FID (Flame ionization Detector) was used considering the following operational conditions: the temperature of the detector was fixed at 250°C, the pressure of the carrier gas was 8.3 psi, and the temperature of the furnace 1 and 2 were 70 and 250°C, respectively.

2.2 Simulation procedure

Based on the data provided from the experimental procedure, the simulation of the synthesis gas and bioethanol production were accomplished. In the gasification case, the operation conditions and the syngas composition was used as starting point for the simulation procedure. In the same way, the yields of the acid hydrolysis, enzymatic saccharification and ethanol fermentation were used as first inputs in the simulation. A brief description of the two simulated processes is presented below.

2.2.1 Gasification

Gasification is the conversion of materials with high carbon content into synthesis gas rich in hydrogen, carbon monoxide, carbon dioxide and methane by using a gasifying agent. Gasification using air is cheapest and its main application is the synthesis gas production of moderate calorific value, ideal for electricity generation [11].

The reaction mechanism of gasification can be divided into three stages: Devolatilization (pyrolysis) of the feedstock into its constituent components. Then, all the components from pyrolysis zone goes into the combustion chamber where they react with oxygen to produce CO_2, CO, H_2O and heat. The char produced in the pyrolysis and the combustion zone passes to the reduction zone where char gasification takes place to produce CO_2, CO, H_2 and CH_4. Ash and the remaining char are separated from the syngas using a cyclone. The synthesis gas obtained from the gasifier can be used as fuel to generate electricity through a gas engine. Figure 2 shows the overall scheme used for the generation of electricity through gasification.

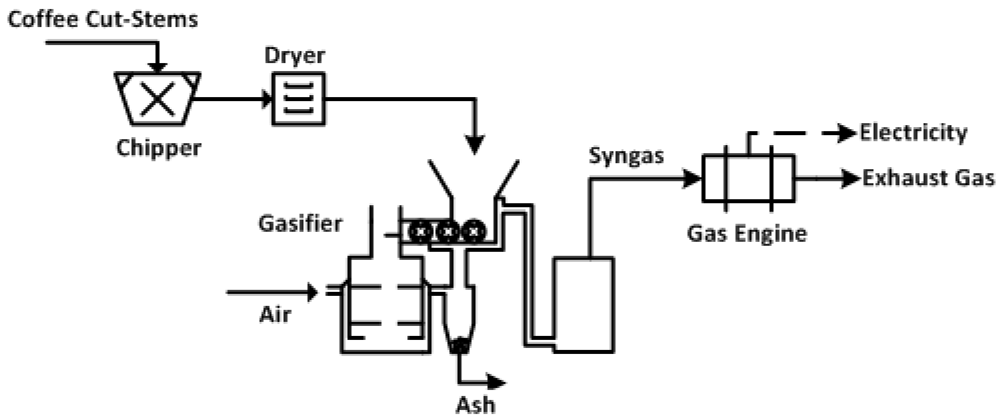

Figure 1. Flowsheet of the biomass gasification process

2.2.2 Bioethanol production

The same described processes in the experimental procedure for the ethanol production are considered in this section. Acid hydrolysis, enzymatic saccharification, detoxification and ethanol production were simulated based on the conditions of the section 2.1. Figure 2 presents the process scheme of the ethanol production using as microorganism the recombinant *Z. mobilis* from CCS. Additional to the procedure described in the experimental section, the downstream processing of the fermentation broth was proposed. The fermentation broth with an ethanol concentration of 5 – 6 % by weight, is sent in a downstream process which consists of two distillation columns and molecular sieves. In the first column, the ethanol is concentrated up to 60%. Then, the ethanol is concentrated until the azeotropic point (96 %wt). Finally, a dehydration stage is required in order to obtain ethanol at 99.6 %wt using molecular sieves [7].

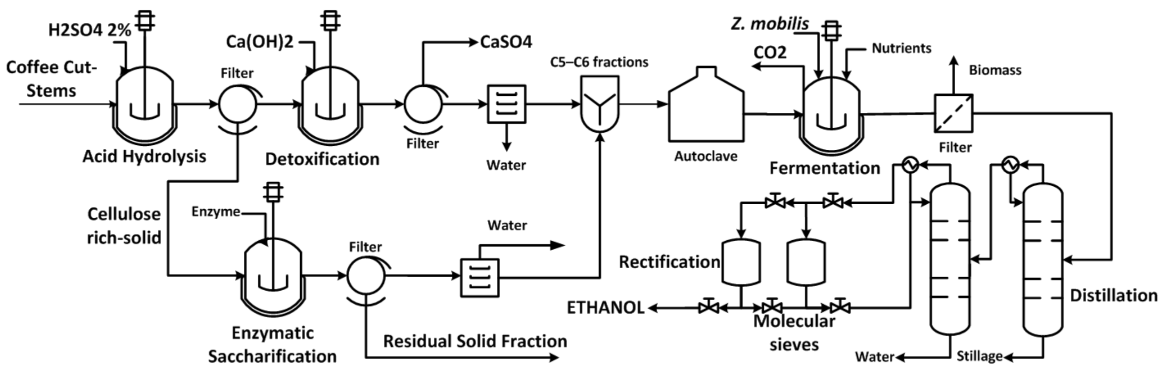

Figure 2. Flowsheet of the bioethanol production process

2.3 Process Simulation

The commercial software Aspen Plus v8.0 was used as simulation tool in order to calculate mass and energy balances of each evaluated processes (ethanol production and gasification). Subsequently, the productivities of the process based on the platforms (sugar and syngas) and the energy content of the principal products (ethanol and electricity) was calculated aiming to determine the best stand-alone process to produce bioenergy. Finally, the environmental assessment was performed using the WAR algorithm which involves the inputs and outputs of the simulation procedure.

2.4 Environmental Assessment

Waste Reduction Algorithm WAR, developed by the National Risk Management Research Laboratory of the U.S. Environmental Protection Agency (EPA) evaluates processes in terms of potential environmental impacts. The PEI balance is a quantitative indicator of the environmental friendliness or unfriendliness of a process. War Algorithm evaluates the PEI in terms of eight categories: Human toxicity by ingestion (HTPI), human toxicity by dermal exposition or inhalation (HTPE), aquatic toxicity potential (ATP), Global warming (GWP), Ozone depletion potential (ODP), Photochemical oxidation potential (PCOP) and acidification Potential (AP).

3. RESULTS

3.1 Physicochemical characterization

Table 1 presents the chemical characterization of the CCS in terms of the cellulose, hemicellulose, lignin, extractives and ash content. The high cellulose and hemicellulose content of the raw material evidence the possibility to recover fermentable sugars from the CCS. The high extractives content can be an issue due to the formation of inhibitory compounds during the pretreatment stages, especially in the acid hydrolysis. These compounds are removed through the detoxification process in which calcium sulfate is mainly produced. However, the environmental impact related to these emissions has to be considered.

Table 1. Physicochemical characterization of CCS

Component	Coffee Cut-Stems
Moisture Content (%wt dry basis)	8.7
Cellulose	40.39
Hemicellulose	34.01
Lignin	10.13
Extractives	14.18
Ash	1.27

3.2 Gasification

The main objective of the air gasification is to produce a synthesis gas with carbon monoxide, carbon dioxide, hydrogen, methane and oxygen. Table 2 presents the composition of the main species involve in the CCS gasification. When air is used as gasifying agent, the concentration of the fuel gases (hydrogen and carbon monoxide) decreases due to the excess of nitrogen supplied by the air. The average product gas composition in the air gasification ranges from 15% H_2, 20% CO, 15% CO_2, 2% CH_4 and 48% N_2 [12]. The results obtained in the pilot-scale downdraft gasifier are in agreement with those reported.

Table 2. Composition of the obtained synthesis gas in a pilot-scale downdraft gasifier

Composition (%Vol)	Coffee Cut-Stems

Hydrogen	17.41
Methane	3.13
Carbon Monoxide	12.88
Carbon Dioxide	15.8
Nitrogen	49.6
Calorific Value (Mj/Nm^3)	11.19

3.3 Ethanol Fermentation

As previously described, the dried and grounded raw material was submitted to different pretreatment stages. The first stage involves the dilute acid hydrolysis aiming to convert most of the hemicellulose into xylose and other by-products such as furfural and HMF. Besides, a fraction of the cellulose is also degraded to produce glucose, however this treatment is not very efficient in the transformation of cellulose. From this stage a reducing sugar concentration and hydrolysis yield of 33.4 g/l and 74% were obtained. However, due to the presence of inhibitory compounds that may hinder the ethanol production, the hydrolysate was treated with $Ca(OH)_2$ to remove acid, furfural and phenolic compounds. As a consequence, the reducing sugars concentration and hydrolysis yield (19.5 g/l and 43%, respectively) were reduced drastically. The effect of the temperature and pH of the solution in the detoxification process has been evaluated by different authors [13]–[15]. At high temperatures, the removal of toxic compounds is increased however the decomposition of sugars is also increased. The same behavior can be observed in the pH of the solution. High temperatures and pH values reduce the concentration of sugars up to 60% [13]. The last pretreatment stage considers the enzymatic saccharification of the solid fraction from the acid hydrolysis in order to convert the unreacted cellulose to glucose. From this stage, reducing sugar concentration and saccharification yield of 18.3 g/l and 45%, respectively was obtained. The yields from the acid hydrolysis and enzymatic saccharification (43% and 45%, respectively) are lower than those reported for the same raw material [16].

The fermentable sugars from the acid hydrolysis and enzymatic saccharification are used as feedstock for the recombinant *Z. mobilis* to produce ethanol. The yield of ethanol in the experimental procedure was 0.41 g ethanol/ g consumed substrate, which is lower than that reported from the same raw material (0.495 g ethanol/g consume substrate) [16]. This can be explained due to the low fermentable sugars yield from the acid hydrolysis stage.

3.4 Process Simulation

The comparison between the thermochemical and biochemical technologies to produce bioenergy was performed based on decision criteria: the performance of the process to produce the chemical platform (synthesis gas in the case of gasification and sugars in the bioethanol case) and the global performance of the processes considering the amount of energy that can be obtained from each product (electricity through gasification and ethanol through fermentation). Table 3 shows the results from the simulation procedure in terms of the platforms productivity of each evaluated process. The direct use of CCS to produce synthesis gas through gasification has a high performance in terms of the amount of syngas that can be obtained per kg of raw material. On the other hand, the production of fermentable sugars from CCS, which can be used in fermentation processes, is hindered mainly by the raw material and the pretreatment methods.

Table 3. Productivity of the two evaluated platforms to produce electricity and ethanol.

Platform	Yield	Units
Synthesis gas	2.84	kg syngas/kg CCS
Fermentable sugars	0.38	kg sugars/kg CCS

Based on the amount of synthesis gas that is generated from the gasification, the theoretical approach to determine the electricity generation using a gas engine was performed. First, the mass composition of the syngas was calculated considered as main fuel gases H_2, CO and CH_4 and its corresponding lower heating content (LHV). This data was used to determine the gross energy value that is the amount of energy that can be obtained from the generated synthesis gas. The amount of useful available energy that can be obtained from the raw material depends on the transformation technology and its efficiency. According to the Mining-Energetic Planning Unit (UPME), the efficiency for a gas engine that uses a gas as fuel is approximately between 29 – 38%. Based on this calculation, the amount of electricity that can be generated from CCS was estimated as can be observed in Table 4. The use of CCS in a stand-alone gasification process to produce electricity can generate 7.09 MJ per kg of CCS, in comparison to a biorefinery scheme using other lignocellulosic residue from which approximately between 0.3 to 0.55 MJ per kg of lignocellulosic material can be obtained [17]. This behavior can be explained since the stand-alone process uses the raw material directly to produce electricity, meanwhile the biorefinery way uses the solid residues from the pretreatment and further processing stages as fuel in cogeneration systems.

Several authors have evaluated the performance of different lignocellulosic residues to produce ethanol. Olive stone is one of the most important residues from the olive oil extraction, which is mainly compose of lignin (39%), cellulose and hemicellulose (49%). This residue was used as raw material in a biorefinery scheme to produce ethanol with a productivity of 598.3 kg/h which is lower than that in this study due to the low content of cellulose and hemicellulose in the olive stone compare to the composition of CCS [18]. In Colombia, it is widely used the sugarcane to produce biochemical and bioenergy. From this procedure, sugarcane bagasse is obtained as main residue of the process. Normally, this bagasse is used in cogeneration processes in order to supply the energy requirements of the sugarcane process and the surplus is sold to the national grid. However, this residue can also be used in the production of bioethanol under the biorefinery concept with a productivity between 4,100 to 10,400 kg/h which is higher than that for CCS [19].

Aiming to compare the amount of energy that is released from the combustion of the synthesis gas and ethanol, the yields of both processes were evaluated considering their lower heating value, which are 6.57 and 28.9 MJ/kg, respectively. Despite the higher energy content of the ethanol, the production yield of electricity is higher due to the high productivity of synthesis gas from CCS.

Table 5. Global performance of the evaluated processes

Product	Productivity		Yield	
	Value	**Units**	**Value**	**Units**
Electricity	21.5	MW	7.09	Mj/kg CCS
Ethanol	2,056.52	kg/h	5.44	Mj/kg CCS

3.5 Environmental Assessment

The potential environmental impact (PEI) was evaluated by the WAR algorithm which allows determine the process with the best performance from the point of view of PEI. Figure 3 summarizes the environmental impact of the ethanol and electricity production. It is evidence that the process that has the highest environmental impact is the ethanol production. The categories that has the most representative contribution to the PEI of the process are the potentials of terrestrial toxicity (TTP), human toxicity by ingestion (HTPI) and Photochemical oxidation potential (PCOP). The first two categories (TTP and HTPI) are estimated in the algorithm based on the LD_{50} (lethal-dose that produced death in 50% of rats by oral ingestion) and their high contribution could be attributed to the final disposition of the stillage from the downstream processing.

On the other hand, the most important category that affects the environmental performance of the gasification is the Global Warming Potential (GWP) which is related to the CO_2 emissions as a consequence of the synthesis gas combustion. Nevertheless, the gasification process to generate electricity has the lowest PEI.

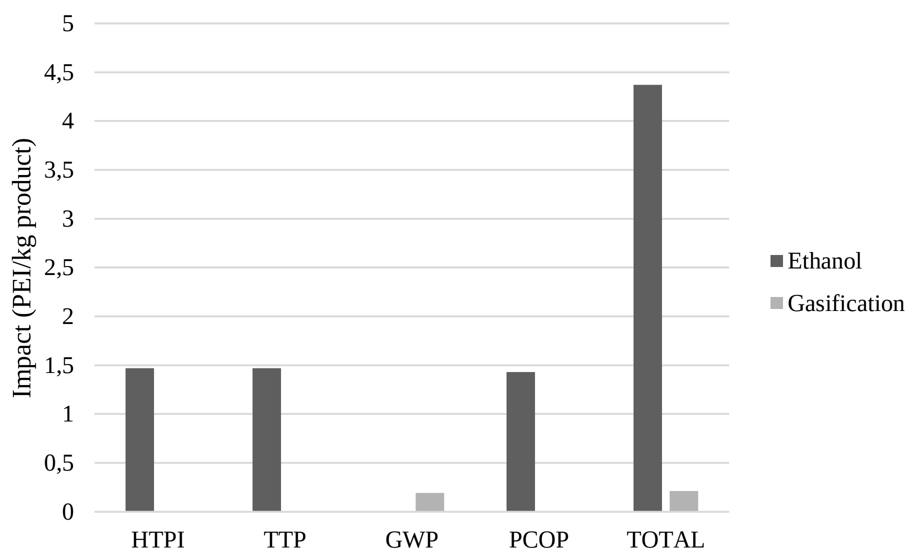

Figure 3. Environmental assessment of the two evaluated processes

4. CONCLUSIONS

Colombia is a country with a great diversity of residues from its long agricultural tradition that makes it a country with huge potential to transform these residues into high value-added products that not only promote economic sector but at the same time integrate social and environmental aspects. Currently, much of these residues are being used in rural areas as fuel for heating processes and/or cooking, where the energy potential of these residues is not exploited.

This work evaluated a thermochemical and biochemical route to obtain bioenergy (ethanol and electricity) from the environmental point of view. The most promising technology to produce bioenergy seems to be the gasification due to the high syngas/biomass ratio in comparison to the platform to obtain sugars to be used in a fermentation. Besides, the amount of energy that can be obtained from the direct use of CCS to generate electricity through the synthesis gas platform presents a novel scenario for its implementation in zones where the power supplied is not carried out. The generation of electricity through gasification can be considered as a zero emission process since part of the energy is used in the same process and the remainder can be sold to the grid.

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