

# A toolbox to tackle the technological and environmental constraints associated with the use of biomass for energy from marginal land

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## **Abstract:**

Biomass is a renewable and sustainable feedstock for energy, contributing to diversify the energy supply, to reduce the dependence on fossils fuels, and to greenhouse gas (GHG) mitigation. Nevertheless, the mandatory renewable energy targets are also contributing to a higher demand on biomass, which increases competition for land, threatening food security. Therefore, production of biomass in marginal soils is being recommended to lessen land use change ethical issues linked with competition with food crops. But, the marginal conditions of the soils (e.g. contaminated soils) may hinder the technological and environmental performance of the bioenergy production chain. Despite the potential amount of energy content, yields are reduced, and biomass characteristics may change, affecting processes and equipment's chosen. Reduced yields force the energy balance to decrease, once outputs will be lower, decreasing the amount of fossil energy saved/conserved. Moreover, lower yields imply a lower abatement of GHG, due to lower carbon sequestration by the biomass, which may limit future applications of biomass according to the European policies. In addition, the increment of nitrogen, potassium and ash content in the biomass, induced by the decreased production, may harm the equipment's performance, and implicate in the environmental life cycle benefits driven by the biomass use. In this scenario, the main goal of this study is to provide an identification of the technological and environmental constraints and challenges associated with the use of biomass obtained from marginal soils through thermochemical processes and to provide a toolbox to tackle it. Implementation pathways will be presented based on a decision tree, supported by the current knowledge.

## **Keywords:**

Biomass Conversion, Bioenergy, Sustainability, Marginal soils, Thermochemical processes.

## **1. Introduction**

Consequences of the increase in world population, which is expected to exceed 9 billion by 2040 according United Nations [1], will be related to the increase in the demand for essential goods and services, such as food, energy and others associated with them. Concerning energy, as fossil fuels are limited, the generation of energy through renewable sources becomes essential. Among the current strategies, the use of solar and wind energy are promising options, but being considered a basic form of energy, biomass becomes a source of safe generation, and can respond quickly to variations in demand [1].

The versatility of biomass is another aspect to be highlighted. Due to the possibility of transformation into solid, liquid and gaseous fuels, biomass can complement or even replace fossil fuels (coal, oil and natural gas). The use of ethanol for example, can be added to gasoline or used as its substitute. The replacement of fossil fuels by biomass and consequently the reduction of the share of fossil fuels in the energy matrix represent an important step in the fight against global warming. In fact, in 2015, approximately 56% of GHGs emitted were generated by the transportation sector (27%) and electricity generation (29%), both predominantly dominated by

fossil fuels. Fossil fuels represent around 90% of the transport sector, and the combustion process of coal in electricity generation was responsible for 70% of the sector's CO<sub>2</sub> emissions [2].

The energy potential of biomass comes from the chemical energy stored in plants through the process of photosynthesis storing energy in the form of carbohydrates. Although biomass conversion processes to energy also produce GHG, emission of GHG by biomass is lower than the one associated with fossil fuels. This is due to the carbon cycle which, released in the form of CO<sub>2</sub> during the biomass conversion processes, is absorbed again by crops in the photosynthesis process, causing a reduction in the final GHG emission balance [3].

Production of energy from biomass on a larger scale will increase the need of feedstock, which, consequently, will require a larger area for cultivation. At this point, the production of energy crops becomes a competitor to the production of crops for food and feed. Thus, to guarantee the safety of food production, several policies have been implemented, such as encouraging the use of biomass from agricultural and urban waste, but a promising alternative is the use of marginal soils to produce energy crops [3-5]. Marginal soils are defined according to EEA (European Environmental Agency) [6] as low-quality soils for agriculture, being economically unviable for food production. Benefits from the introduction of energy crops in marginal soils are linked with ecosystem services and soil function restoration (fertility, structure, organic matter), along with soil erosion control and increment of biological and landscape diversity [6-7]. However, above and below ground productivity of energy crops in marginal land may be reduced due to the marginality conditions of the soil, which may compromise its environmental and technical exploitation for bioenergy production.

Therefore, the study aims to present the environmental and technological obstacles and challenges associated with the exploitation of biomass obtained from marginal land through thermochemical processes. The ultimate goal is to provide an informative guide, based on a decision tree, to help the sector on pathways to follow.

## **2. Exploiting the biomass from marginal land through Thermochemical Conversion Processes – what are the environmental and technological challenges?**

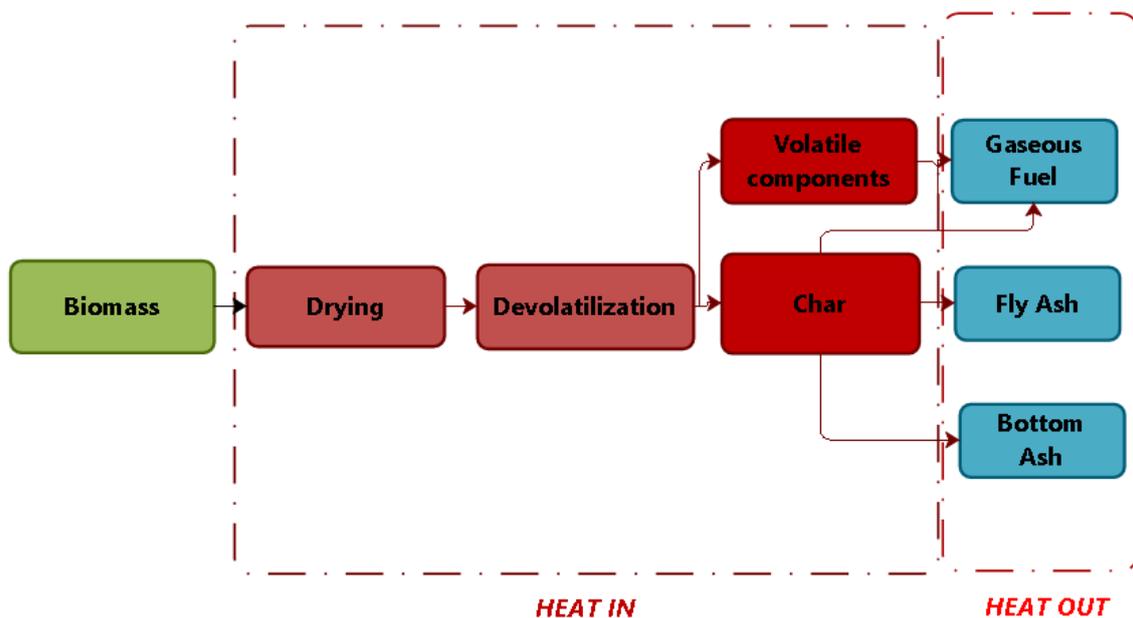
Producing biomass in marginal land may contribute to reduce the ethical issues related with the food versus fuel competition. Yet, the productivity loss diminishes the energy, and the greenhouse savings, and the decreased production may concentrate nitrogen, potassium and ash content in the biomass, which may harm the equipment's performance, and implicate in the environmental life cycle benefits driven by the biomass use [8-12]. In fact, establishing vegetation on marginal land contributes to the capture of CO<sub>2</sub>, incrementing the abatement of GHG emissions. But, the marginality of the soils can affect the biomass growth, lowering yields, and forcing the energy balance to decrease, as outputs will be lower, reducing the amount of fossil energy saved/conserved [9]. Moreover, lower yields also imply a lower abatement of GHG, due to lower carbon sequestration by the biomass [10]. This may limit future applications of biomass produced in less productive land according to the European policies. In addition, lower yields also contribute to a higher need of land in order to produce an amount of feedstock equivalent to the one obtained in standard soils.

Concerning the characteristics of the biomass, nitrogen, potassium, and ash content increments in the biomass, due to the concentration effect of the reduced yields, may hamper the industrial exploitation of the biomass. Higher nitrogen content in the biomass may increase NO<sub>x</sub> emissions from the combustion of biomass, contributing to acidification; a higher ash content produced has consequences on the handling and use/disposal of ash residues from biomass combustion plants; and higher potassium contribute to the increment of fused agglomerates and slag

deposits, accelerating metal wastage of furnace and boilers components, reducing equipment's life [13-15]. Moreover, the increment of non-carbonaceous elements may require not only extra maintenance but also adaptation of the equipment and alteration of the biomass energy conversion processes (pretreatment processes), adding costs to the system and making it economically unfeasible [16].

## 2.1. Combustion

Considering the thermochemical processes to convert biomass into energy, the combustion of biomass and its technologies are an important topic of research. The biomass combustion occurs in five phases: heating-up, drying, devolatilization (which produce volatiles and char), combustion of volatiles and combustion of char [17] as demonstrated in fig.1. Each biomass composition is different, with variable values for organic and inorganic compounds and this composition has an effect on the behavior of biomass fuels during the combustion process.



*Fig. 1. Combustion phases. Heat in represent the phases where heat is necessary in the combustion process and Heat out indicates the heat produced by the combustion process*

In the combustion process, the components of biomass can step out of the combustion chamber as a gas or remain as solid particle (ash). The complete combustion process of biomass always produces CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, HCl, metal compounds and solid particles. In most of the cases, the metals are founded in elemental, oxides, sulfites or chlorides form. When the combustion is not complete, the amount of solid particles produced is higher, and some non-oxidized elements are produced too [17-18]. The gas and some fly ash particles which steps out of the combustion system could contain inorganic components in different forms, which can cause environmental problems depending on the quantity and oxidation state of the contaminants [17-19]. When the biomass is contaminated by hazardous metals compounds through contaminated soils, contaminated ash will be obtained after biomass combustion, demanding a decontamination treatment before being discarded; the small particles of contaminated ash (solid phase) which steps out of the combustion with the gaseous phase may contaminate the soil by deposition and the gaseous fraction [18][20]. When the ash is not discarded with the appropriate treatment, the metals present in it could be leached by the rain, contaminating soil and groundwater. Despite this problem, the ash could

receive treatment. The biggest problem is to treat the flue gas, which is emitted with a high amount of contaminants [21-22].

Due to the damaging effects of some components in boilers and pipes, some elements need to respect a concentration limit in biomass and in the ashes. Elements such as Cl, S, K and Na are responsible for direct and indirect corrosion of the combustion equipment. Elements may cause corrosion caused principally by complex oxide-slag with low melting points. Besides oxidation, corrosion on heat transfer surfaces can be also caused by sulfidation and chlorination. The sulfidation reaction is a reaction involving sulfur and oxygen, which results in  $\text{SO}_x$  formation and the chlorination can be defined as the reaction where HCl is formed during the combustion process damaging the walls of boilers, combustion chambers and pipes [23-25].

The high presence of  $\text{SO}_x$  compounds can also cause the temperature decrease of the flue gas which increase the Cl release and as consequence, the production of HCl. This HCl can react with Fe and Zn, producing  $\text{FeCl}_2$  ou  $\text{ZnCl}_2$ , which volatize at the combustion temperature causing damage in the pipes. So in order to control the corrosion problem, the concentration of Cl an S in biomass needs to be lower than 0.1% (dry base). When biomass present higher concentrations of these elements, alternatives encompass coating of boiler tubes, automatic heat exchange cleaning systems, appropriate material selection and fuel leaching [23-25]. Yet, one of the advantages of combusting biomass is its lower Cl and S contents, by comparison with coal, for example [26]. Therefore, technological and environmental problems associated with S and Cl emissions are of minor importance.

Other elements, such as K and Na, remain in the ash but, since they decrease the ash melting point and can volatize at lower temperatures, causing deposits formation in the walls of the equipment, a limit concentration for those elements in the ash was suggested by Bierdermann & Obernberger [24], where K concentration needs to be lower than 7% and Na concentration needs to be lower than 2%. This process also reduces plant availability and lifetime. Moreover, hard deposit formation due to sticky fly ash particles can be accelerated by alkali and heavy metal salt mixtures. Therefore, the influence of increased potassium and sodium contents and heavy metals is of special relevance when biomass from contaminated soils is utilised [24]. To avoid the corrosion problems some procedures can be applied such as: lowering the oxygen content during the combustion process, maintaining an uniform distribution of air and fuel in the combustion chamber or using additives [23-25].

Clery and collaborators [27] studied the influence of aluminosilicate in the potassium behavior during the combustion of biomass, to mitigate slagging and fouling problems in boilers and furnaces. To run the experiment, three different biomasses were studied: softwood, wheat straw and olive residues. For the softwood without the aluminosilicate, the fraction of potassium in gas phase was large, and was released during the volatile and char combustion stage during the combustion process. The wheat straw releases potassium during the combustion process and after that, during the ash cooking period. Olive residues showed a higher fraction of potassium fixed in the ash. When the additive was added, the retained potassium in the ash increased to the levels of 70-100% for softwood, 60-80% to wheat straw and 70-100% to olive pellet. This is because high Si+Al helps to fix K in the solid phase.

Seeking an alternative to the potassium problem, Xue and collaborators [28] analyzed the potassium migration and transformation in biomass combustion through a co-combustion experiment with coal. The biomass combustion was conducted in a horizontal furnace and the studied temperatures were from 600°C to 1000°C. The analysis of the combustion indicated that high temperature improved the release of K to the gaseous phase and promoted the generation of insoluble K compounds in the bottom ash. Co-combustion with coal showed that Al from coal formed a steady and high-melting point potassium aluminosilicate, increasing the melting temperature of ash effectively. In contrast, combustion of rice straw, showed a much lower ash melting temperature.

## 2.2. Gasification

The process of converting a solid or liquid fuel (composed of carbon) into synthesis gas (gaseous fuel) using a thermochemical conversion route is called gasification. This process occurs through partial oxidation of the initial fuel, which can be carried out at atmospheric pressure or at high pressures, and at a temperature varying between 800°C to 1100°C [29].

According to Genehr [30] biomass gasification can be understood as the process after the pyrolysis process, where the biomass is transformed into charcoal, and prior to combustion, as shown in Figure 1, and differs from combustion due to the partial oxidation of the biomass, while in the combustion the total biomass oxidation occurs [30-31].

The gasification process can be influenced by the following factors: air factor (or equivalence ratio); the gaseous agent used; residence time; the physical, chemical and energetic characteristics of the biomass used in the process and the use or not of catalysts [31]. According to those authors [31], the variables involved in the gasification process are the equivalence ratio, the temperature, the gas production capacity, the composition and calorific value of the gas produced and the efficiency of the gasification. The air factor, or equivalence ratio, is calculated by the actual gas / fuel ratio used in the process by the theoretical actual gas / fuel, thus describing the proportion of fuel that has undergone complete combustion with the fuel that has been gasified. The temperature is a variable defined by the physical, chemical and energetic properties of the biomass (such as volatile content, fixed carbon, grain size, humidity) and the proportion of air / fuel used, that is, the air factor. The gas production capacity is directly influenced by the air factor of the system, as well as the residence time of the gas in the reduction zone inside the reactor. The composition and calorific value of the gas produced is directly affected by the gas used as the gasification agent. The gasification agents used in the process may be air, water vapor, CO<sub>2</sub>, O<sub>2</sub> or even a mixture of these gases.

Gasifiers are reactors where the thermochemical conversion of the raw material into gas takes place. Fixed bed gasifier, fluidized bed gasifier and indirect gasifier are the three main types [29]. The fixed bed gasification reactors, also called moving bed, since in continuous operation, as the fuel is fed and the ashes removed, the bed moves from the top to the bottom of the reactor, they are easy to design and operate and has high efficiency when used with high density and coarse granulometry fuels. These reactors can be classified according to the movement of the fluid through the reactor: updraft, downdraft and cross-flow [29-31]. Fluidized bed gasifiers were initially developed to minimize operational issues of fixed bed gasifiers such as high ash content, and therefore are equipment's that might fit well to biomass from marginal soils. In addition, the efficiency of a fluidized bed gasifier is about five times greater than that of a fixed bed gasifier [32]. Unlike fixed bed reactors, fluidized bed reactors do not have differentiated zones of reaction. These gasifiers operate with an isothermal bed, with temperatures ranging from 700-900 °C [32-34].

The technological and environmental problems associated with the use of biomass from marginal soils in a gasifier are similar to those reported for combustion. Woolcock and Brown [35] defined some limits to contaminants in syngas when applied to different systems (Table 1).

*Table 1. Limits for contaminants in syngas [35]*

Contaminant	IC Engine	Gas Turbine	Methanol Synthesis	FT Synthesis
Particulate	<50 mg/m (PM10)	<30 mg/m (PM5)	<0.02 mg/m	
Tars	<100 mg/m		<0.1 mg/m	<0.1-1 µL/L
Sulfur		<20 µL/L	<1 mg/m	<0.01 µL/L
Nitrogen		<50 µL/L	<0.1 mg/m	<0.02 µL/L
Alkali		<0.024 µL/L		<0.01µL/L
Halides (primarily HCl)		<1 µL/L	<0.1 mg/m	<0.01µL/L

Elements, such as potassium and calcium, can also interfere, positively or negatively, in the gasification process. Kramb and collaborators [36] studied the influence of potassium and calcium during the gasification of birch wood in a bubbling fluidized bed reactor. Samples were first pyrolyzed with N<sub>2</sub> and then gasified with CO<sub>2</sub>. It was observed that the presence of potassium did not have an observable catalytic effect on the overall gasification reaction rate with CO<sub>2</sub> due to the formation of an unreactive coke layer on the char surface. In contrast, calcium did increase the char conversion rate and is likely the primary active catalyst in gasification of birch wood with CO<sub>2</sub>.

## 2.3. Pyrolysis

Pyrolysis can be defined as a process in which organic materials are processed into solid, liquid or gaseous fuels, in the absence of oxygen. Instant pyrolysis is done through a high heating rate, in addition to a moderate process temperature and a short residence time of the vapours [37]. The solid fuel obtained is the biochar, while the liquid fuel is known as pyrolytic oil or bio-oil. In cases where the feedstock to be used in the pyrolysis is lignocellulosic biomass, the process disintegrates the structural components (cellulose, hemicelluloses and lignin) into small molecules in the form of a gas. The condensation of this gas generates the pyrolytic oil and the mass of biomass that was not gasified, remaining solid, is the biochar [38-39].

The biomass pyrolysis process is based on the heating of the organic matter under controlled temperature, residence time and oxidant rate, allowing inhibition of inflammatory ignition during the process. The products generated by the pyrolysis (solid, liquid and gaseous), can be used as fuels with higher energy density. The volume and quality of the products depend on the characteristics of the initial biomass and the process parameters [38-39].

The moisture content and the chemical composition determine the operating conditions, which are fundamental for the quality and composition of the final product. When pyrolysis occurs at a low or intermediate temperature, the solid fraction will be higher than if the process occurred at high temperature. This process happens in a few minutes, being called slow pyrolysis and due to the low temperature, the chemical bonds remain more stable and, therefore, the liquid and gas fractions are lower [38-39]. The process that uses high temperature and low residence time is called fast pyrolysis. In a process like fast pyrolysis a pre-treatment is used which consists of drying and fine grinding of the raw material.

Since biomass from marginal soils, e.g. contaminated soils with heavy metals, will generate products with distinct characteristics compared to those from biomass not been exposed to soils marginality, the conversion process may need some adaptations. Treating metal-rich biomass is challenging since the objective is to disintegrate the contaminants in the feedstock and to recover them later, as well as to produce other products of high added value, such as bio-oil, volatile condensable fraction and non-condensable gas fraction [19]. Fast or flash pyrolysis is a good technique, selected to add value to biomass obtained from heavy metal contaminated soils. In this case, pyrolysis apparatus used are generally reactors which transfer heat from the reactor wall (ablative reactors) or fluidized bed reactors which transfer heat from hot gases or fire tubes. The standard temperature used for bio-oil production ranges from 673K to 773K. Steam residence time for the maximum production of fuel is 1 s or less for contaminated or uncontaminated wood and up to 5 s for other types of biomass [40]. In the work of Lievens and collaborators [40], a pyrolysis reactor was used to process a feedstock composed of biomass contaminated with Cu, Cd, Pb and Zn. The temperature of 623 K was considered ideal to avoid the volatilization of elements such as Cd and Zn, whereas Cu and Pb may remain immobilized in the solid fraction in a temperature range of 623 K to 873 K. A high temperature treatment increases the pH of the liquid fraction, decreasing the solubility of heavy metals and the concentration of Cu and Ni extractable with water. According to Lievens et al. [40], a technique complementary to the pyrolysis process is to promote the

thermodynamically favoured bonding of heavy metals with SiO<sub>2</sub> by mixing a silica rich heat carrier, particularly fumed silica, with the starting feedstock prior to pyrolysis. This technique minimizes the probabilities of contamination of the liquid and gaseous fractions through the volatilization of the elements [40].

To study the effects of heavy metals from the biomass produced in marginal lands in the final product of fast pyrolysis, Stals et al. [41] used contaminated willow (wood and leaves) as raw material to the process. The biomass was produced in a land contaminated by Zn, Cd, Pb and Cu. Using a stainless-steel reactor, the pyrolysis was done at three different temperatures 623K, 723K and 823K for willow wood, and 723k for willow wood and leaves. At higher temperature, the concentration of Cd in bio-oil was considerate toxic, 16 ppm, while at 723K the concentration significantly decreased to 0.9 ppm, still above the normal value but not excessive. For Zn, the concentration at the higher temperature was 10.8 ppm while at 723K was 4 ppm and using 623K was 4.3 ppm. The experiment showed that when temperature increased, the contamination of biochar by heavy metals contaminants increased too [41].

He et al. [42] studied the influence of temperature in pyrolysis products and how the composition of these products was affected. In the experiment, temperatures ranged from 300°C until 600°C, and the results showed that at higher temperatures, volatile matter in biochar decreased, while the content of ash, K and P increased.

Zhang et al. [43] studied the effects of potassium on biomass pyrolysis and found that the presence of K produced a greater quantity of phenols and acids, reducing the yield of aldehydes and increasing furfural. One of the factors that cause potassium to have a great effect on the characteristics of the bio-oil obtained is its strong catalytic effects during the pyrolysis of biomass. The presence of potassium during pyrolysis of biomass was also studied by Guo et al. [44]. Results showed that the presence of potassium promoted the decomposition process of biomass, as K is a well-known catalyst in the thermal reactions of biomass. The gas yield was also significantly increased with the increasing of potassium concentration, especially, the yield of H<sub>2</sub> and CO<sub>2</sub>, and the tar yield quickly decreased.

### 3. Exploiting the biomass from marginal land through Thermochemical Conversion Processes – what are the boundaries?

According to S2BIOM [45] data bases, the current operational plants defined some maximum limits for contaminants, which allow us to create boundaries for the different technologies. Tables 2 to 4 were constructed based on the data collected and reported by more all the operational plants signed in the S2BIOM data base.

*Table 2. Maximum contaminant concentration for direct combustion of biomass*

	Ash [% db]	Nitrogen [wt %, db]	Sulphur [wt %, db]	Chlorine [wt %, db]
Domestic residential batch fired stoves for heat	3	3	0.3	0.03
Domestic pellet burners for heat	3	3	0.3	0.03
Fixed bed combustion for CHP (steam cycle)	10	15	0.3	0.03
Fixed bed combustion for heat	10	15	0.3	0.03

db – dry base

*Table 3. Maximum contaminant concentration for biomass gasification*

	Ash [% db]	Nitrogen [wt %, db]	Sulphur [wt %, db]	Chlorine [wt %, db]
Fixed bed (downdraft) for CHP (gas engine)	2	1	0.3	0.1
Bubbling fluidized bed for syngas production	5	1	0.3	0.3
Bubbling fluidized bed for IGCC	5	1	0.3	0.3
Dual Fluidized bed for syngas production	5	1	0.3	0.3
Dual Fluidized bed for CHP (gas engine)	5	1	0.3	0.3
Circulating Fluidized bed for IGCC	5	1	0.3	0.3
Circulating Fluidized bed for CHP (gas engine)	5	2	0.3	0.3
Fixed bed (updraft), direct combustion	10	1	0.3	0.5
Circulating Fluidized bed for syngas production	10	2	0.3	0.5
Bubbling fluidized bed for CHP (gas engine)	10	1	0.3	0.3
Entrained flow for syngas production	20	1	10	1

db – dry base

*Table 4. Maximum contaminant concentration for biomass pyrolysis*

	Ash [% db]	Nitrogen [wt %, db]	Chlorine [wt %, db]
Pyrolysis oil and diesel engine for electricity	3	2.5	0.3
Pyrolysis and hydrogenation for diesel fuel	3	2.5	0.3
Pyrolysis plus boiler for heat and steam	3-9	0.25-2.5	0.3

db – dry base

## 4. Decision's tree and conclusive remarks

A decision tree based on the composition of the biomass, can be made through the use of the tables constructed in this work (tables 2-4). Specifically, the biomass characteristics in terms of ash, nitrogen, sulphur and chlorine content should be determined, and based on the results obtained, the best technology should be chosen. For example, if the ash content of the biomass is 7%, with a nitrogen content of 2% and a chlorine content of 0.3%, the technologies best fitted to add value to the biomass are. Gasification through Circulating Fluidized bed (syngas production), or Pyrolysis plus boiler for heat and steam.

Based on the limits it is possible to decide according to biomass composition, which is the best alternative for conversion. The limits for ash are higher in some gasification processes while nitrogen limits are higher to combustion processes. There is no described limit for sulfur in pyrolysis which can simplify the decision.

According with the tables 2, 3 and 4 values, based in the contaminants contents it is possible to define which process is better for biomass to energy conversion. It is important to see that besides the amount of energy production, the composition of biomass have an important part in the biomass conversion. A bad decision in the conversion process chosen can cause injuries in the equipment increasing the maintenance costs and decreasing the energetic biomass utilization and its economic viability.

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