Gasification, pyrolysis and combustion technologies as process alternatives for woody biomass valorization.

Juan Camilo Solarte-Toro[1], Jose Andrés González-Aguirre[1], Carlos Andrés García-Velásquez[2], Carlos Ariel Cardona-Alzate[1]

[1]Instituto de Biotecnología y Agroindustria, Departamento de Ingeniería Química, Universidad Nacional de Colombia – Sede Manizales, Manizales, Zip Code: 170003, Colombia.

[2]Department of bio-based materials, Maastricht University, Maastricht, P.O. Box 616 6200 MD, Netherlands

Corresponding author: ccardonaal@unal.edu.co.

Abstract.
Energy and chemical compounds production at different scales has been addressed mainly by the use of non-renewable resources such as crude oil, natural gas and coal in the last years [1]. On the other hand different ways are used to valorize a wide variety of second generation biomass such as rice husk, sugarcane bagasse, empty fruit bunches, coffee grounds, corn cobs and so others, which are residues obtained from the agro-industrial processing of first generation raw materials (e.g., sugarcane, oil palm, corn) [2,3]. Nevertheless, these potential raw materials could have a limited application in thermochemical industry due to the high moisture content, the high content of silica in their mineralogical composition as well as their fuel properties such as calorific value and elemental oxygen content [4]. Therefore, the raw materials more suitable to be used in thermochemical conversion routes such as gasification, combustion and gasification are the woody biomass due to the inherent potential fuel use that this type of biomass has. In this way, this work evaluates the fuel properties of the Pinus Patula as woody raw material to be used in thermochemical conversion processes as well as to evaluate from an energy, economic and environmental point of view the potential value-added products obtainment and the energy vectors production using gasification, pyrolysis and combustion as processing technologies.

1. Introduction.

Valorization of biomass has become important in recent years for replacing fossil fuels energy generation and reducing pollution levels in the atmosphere. Woody biomass appears though, as a suitable material used in thermochemical conversion routes such as gasification, combustion and pyrolysis, for producing bioenergy and chemical platforms due to their low density and high supply availability. The average majority of energy produced from biomass comes from wood and wood residues (64%), followed by municipal solid waste (24%), agricultural waste (5%), and landfill gases (5%) [2][3], which provide 4 % of the industrialized countries energy [2]. In general, woody biomass can be used directly (e.g. burning for heating or electricity) or indirectly by converting it into a liquid or gaseous fuels (e.g. bioethanol or biogas). The net energy available (calorific value) from biomass when it is combusted ranges from about 8 MJ/kg for green wood, to 20 MJ/kg for dry plant matter [2,6], 29.3 MJ/kg for bioethanol, to 55 MJ/kg for methane, as compared with about 27 MJ/kg for coal [7] [8].

The thermochemical conversion technologies include direct combustion, pyrolysis, gasification and liquefaction [11,12]. In order to extract the energy contained in biomass directly as heat, combustion/co-firing is the most used direct method; or could be converted into a solid (e.g., biochar), liquid (e.g., bio-oils), or gaseous (e.g., syngas) fuels through pyrolysis and gasification respectively. The headline of this work is to assess these technologies by means of techno-economic and environmental assessment. A case of study will be formulated and carried out in order to illustrate the significance of the work.

2. Methodology.

2.1. Experimental procedure.

The *pinus patula* characterization is based on physicochemical analysis, which involves chemical, proximate and elemental analysis and calorific value. The methods used to perform these analyses are described in the following sub-sections:

2.1.1. Chemical characterization.

Samples were collected in Manizales, Colombia, dried directly to the sunlight along two or three days until the moisture < 10% was reached and milled and grounded to pass 40 mesh (0.4 mm).

Chemical Characterization Determination

The extractives content was measured based on the National Renewable Energy Laboratories (NREL/TP-510-42619) [5]. 250 mL of distilled water, 250 mL of anhydrous ethanol and 10 grams of raw material were used for performing the extractives in water and ethanol. Holocellulose content is based on the ASTM standards (D-1104) [6], "The chlorination method". For cellulose determination, alkaline treatment described in ASTM standards (D-1695) [7] was used. The hemicellulose content was calculated from the subtraction between the holocellulose and cellulose content. The procedure for the lignin content determination was based on a modified version of the TAPPI T222 acid-insoluble lignin in wood and pulp [8].

2.1.2. Proximate analysis.

The moisture, ash and volatile matter determination were performed. For this, a Shimadzu moisture balance MOC - 120H was used for measuring the moisture content according to ASTM standards (D-3173) [9]. Ash was determined according to National Renewable Energy Laboratories (NREL/TP-510-42622) [10]. Thereafter, the volatile matter was determined using the American Society of Testing and Materials (ASTM D3175-11) standard method [11]. Finally, the fixed carbon content was calculated from the subtraction between the volatile matter, the moisture and the ash content of the biomass. Once these fractions were obtained the HHV content of the Pinus Patula was calculated using the correlation described by Sheng et al., [12]

2.1.3. Elemental analysis.

In this work, the main identified and quantified elements were carbon, hydrogen, oxygen and nitrogen (often referred as CHON). This procedure was performed by a CHNS elemental microanalyzer with Micro detection system TruSpec (LECO, USA). The samples should be grounded to a uniform consistency. This data was used to calculate the empiric formula of Pinus Patula.

2.1.4. Pinus Patula gasification.

Pinus Patula were gasified using a 10-kWe pilot-scale air-downdraft gasifier. The raw material was chipped until reach a particle size from 1.0 to 3.0 cm as pretreatment of this process. Then, the syngas composition was measured using a portable gas analyzer (Gasboard—3100P, Wuhan, China). From this process, the volumetric compositions of O_2, CO, CO_2, H_2, CH_4 and C_nH_m were determined. Finally, the carbon conversion and cold gas efficiency of the process were calculated using the mass balances derived from the equipment. Moreover, a global energy balance was performed using the heating value of the produced syngas and the raw material to identify the energy losses during the process. The electricity production was carried out burning the syngas in a spark gas engine Kubota model DG972 and electrical generator Mecc-Alte ECO3N-4.

2.2. Simulation approach.

The gasification, combustion and pyrolysis processes were simulated using the experimental data obtained from the chemical characterization, proximate and ultimate analysis to complete the mass balances of these processes. Moreover, the pilot-scale air-downdraft gasification of Pinus Patula was carried out to validate the syngas composition obtained from the simulation process.

2.2.1. Processes description.

The simulated thermochemical conversion process are composed by three different stages, which are biomass pretreatment, thermochemical upgrading process and power generation section. In the biomass pretreatment, Pinus Patula is dried and milled until reach an appropriate particle size. Then, the thermochemical conversion of the raw material is done and fuel gases used to produce energy in a combustion chamber in the case of the pyrolysis and gasification processes. The process flow diagram of the gasification, combustion and pyrolysis processes are presented in Figures 1, 2 and 3.

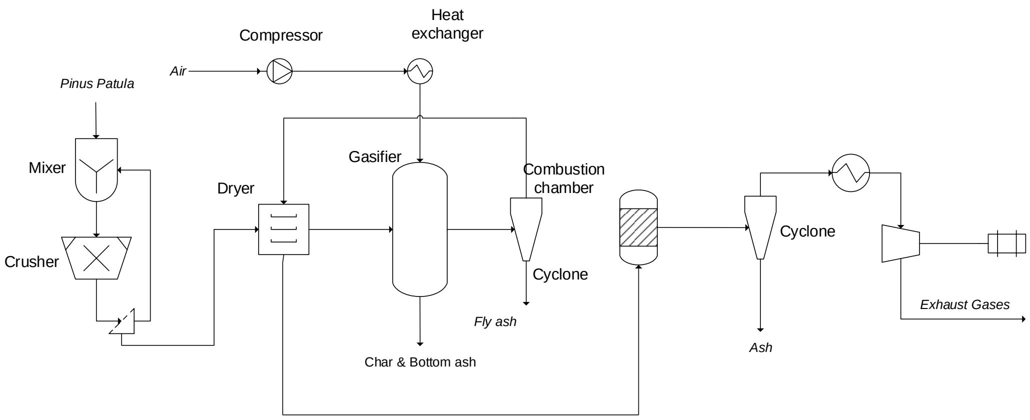


Figure 1. Process flow diagram of woody biomass gasification process for power generation.

The gasification process involves the production of syngas, tars, char and ash. In this process, char and ash are evaluated as possible value-added products to be commercialized. On the other hand, the syngas produced from this process is used as fuel to produce power in a steam turbine. The gasification process is carried out at 800°C using pressurized air as oxidizing agent. In addition, the combustion of the syngas was designed to reach the adiabatic flame temperature at outlet of the combustion chamber. Finally, the process exhaust gases are used to preheat the inlet air to the combustion chamber.

On the other hand, the pyrolysis process flow diagram is presented in Figure 2. This process involves the production of bio-oil, char and electricity. The pyrolysis process is carried out at 400°C and the residence time of the raw material is fixed in 20 minutes. Nitrogen is used to guarantee a non-oxidizing atmosphere in the pyrolysis reactor. In this process, the pyrolysis gases (i.e., CO, H_2, CH_4, and CO_2) are combusted to produce electricity.

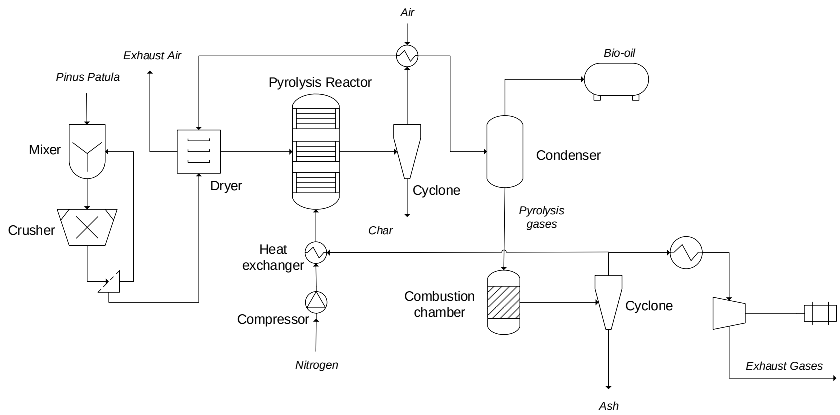
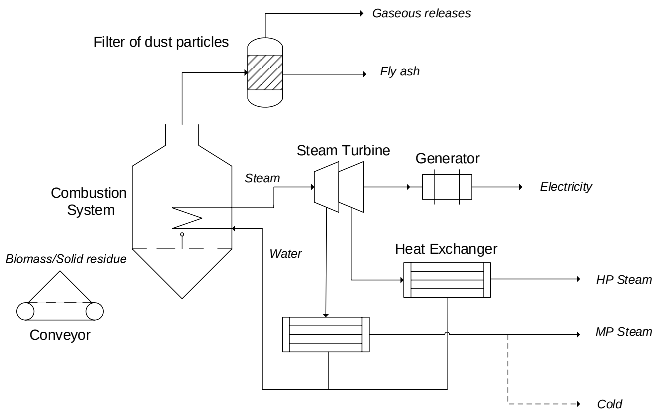


Figure 2. Process flow diagram of woody biomass pyrolysis process for power generation

Finally, the combustion process was simulated using the flowsheet presented in Figure 3. This process involves was designed considering an oxygen excess of 5% to ensure complete combustion, a temperature of 900°C and pressure of 1 atm.



2.2.2. Mass, energy and economic assessment

The thermochemical processes were evaluated in terms of mass and energy indicators. For this, the mass and energy balances of the gasification, pyrolysis and combustion processes were obtained from the Aspen Plus v 9.0 simulation software. The mass metrics are related to the conversion of the raw material to the desired products. For instance, the carbon conversion efficiency (CCE) indicator is calculated to evaluate the amount of the carbon contained in the main outlet streams from the process. Moreover, energy indicators related to energy conversion efficiency of each process are calculated. On the other hand, the economic assessment was performed using the commercial software Aspen Process Economic Analyzer v8.4 (Aspen Technology Inc., USA) to calculate the capital and operational expenditures of each process. The mass and energy balances from the simulations were used in the sizing of the process equipment. As input data to perform the economic evaluation, a 10-years period with an annual interest rate of 17% was considered. In addition, the straight-line method for the capital depreciation calculation and a 25% of tax rate, also were considered. The operator and supervisor labor costs were 2.14 USD/h and 4.29 USD/h, respectively, considering the Colombian context [13], [14]. Moreover, the raw materials costs only involves the acquisition costs of the raw material, which is 19.40 USD/ton [15]. Finally, a period of 8000 h was considered to perform the calculations.

3. Results and discussion.

3.1. Chemical characterization.

The chemical characterization results of the *Pinus Patula* are presented in Table 1. Moreover, in this table a comparison of this characterization with other woody biomass is presented.

Table 1. Chemical characterization of *Pinus Patula* and other woody biomass.

Item	Pinus Patula	Coffee cut stems	Wood bark	Spruce bark
Moisture	9.21	8.7	8.8	7.6
Extractives	11.0	14.18	N.R	N.R
Cellulose	44.78	40.39	24.8	50.8
Hemicellulose	23.75	34.01	29.8	21.2
Lignin	20.22	10.13	43.8	27.5
Ash	0.25	1.27	1.6	0.5

The ash content of *Pinus Patula* is lower than the other woody biomass examples in Table 1. This low ash content allows discerning a low clinker formation during the thermal degradation of the raw material. This fact is explained due to low ash content means low Na^+ and K^+ compounds to be incrusted in the combustion chambers, pyrolysis equipment and gasifier reactor. Therefore, this low ash content of this raw material can be seen as advantage over other type of woody biomass. Nevertheless, this fact not limits the use of woody biomass in thermochemical applications only increases the safety and prevention protocols to operate this type of equipment.

3.2. Fuel properties of *Pinus Patula.*

The volatile to fixed carbon ratio of the *Pinus Patula* was 4.66. This ratio gives an idea of the feedstock volatilization in a thermochemical upgrading process. In fact, the VM/FC ratio provides an idea of the possible temperatures reached in the thermochemical processing. In this way, raw materials with high volatile matter to fixed carbon ratio trend to have low temperatures of combustion, pyrolysis and gasification. Meanwhile feedstocks with low ratios trend to have high temperatures. The range of the VM/FC thermochemical processing is 3 – 4, which means that the thermochemical processing of *Pinus Patula* requires lower temperatures to be burned completely. This suggests that the raw material trend to burn too cool to support efficient tar cracking and temperatures below of 1000°C in any thermochemical process are expected. Other important aspect is the high heating value (HHV) of the *Pinus Patula*, which was 19.97 MJ/kg. In comparison to other woody biomass residues, this raw material has a relative high heating value. Therefore, the implementation of *Pinus Patula* for energy purposes through thermochemical upgrading is reasonable.

Regarding to the *Pinus Patula* elemental composition, this raw material has an atomic H/C ratio of 1.47 and O/C ratio of 0.68. These values of H/C and O/C ratios comparable with the results obtained for different raw materials such as aspen wood, poplar, *Eucalyptus globulus,* and coffee cut stems, which varies from 0.6 to 1.2 in the O/C case and 1.4 to 1.6 in the H/C case. Moreover, the high oxygen content in the raw material can be seen as a drawback in thermochemistry. This fact is due to high oxygen content means low heating values compared to non-renewable resources such as natural gas and gasolines. For this reason, the electricity production at low scales is considered as an option to upgrade woody biomass.

3.3. Mass and Energy evaluation.

Mass yields of each process as well as three energy indicators were calculated to compare the performance of each process. The results of these evaluations can be seen in Table 2. The carbon version efficiency was calculated for the gasification and pyrolysis cases. A 94.96% value was obtained in the gasification case, which is higher than the value calculated for the pyrolysis case (i.e., 75.63%). This difference can be explained due to the distribution of molecular carbon into char, bio-oil and pyrolysis gases depends of the operating conditions, mass and heat transfers effects that the pyrolysis process involves, which were not considered in the simulation process. On the other hand, the obtained yields from the simulations are in agreement with the yields reported for each process in the open literature [16].

Table 2. Mass yields of the combustion, gasification and pyrolysis processes.

Process	**Mass yield (g/g)**				
	Ashes	**Biochar**	**Gases**	**Bio-oil/Tars**	**Carbon conversion efficiency (%)**
Combustion	0.021	N.A	3.56	N.A	N.A
Gasification	0.01	5.93	2.22	0.27	94.98
Pyrolysis	0.005	0.13	0.31	0.48	75.63

The energy assessment was done calculating the energy efficiency, specific energy generation and exergy losses in each process. The results of this analysis are summarized in Table 3.

Table 3. Energy indicators of the combustion, gasification and pyrolysis processes.

Process	**Energy efficiency (%)**	**Specific energy generation (kW/kg)**	**Exergy losses (kW)**
Combustion	45.02	1.72	194.85
Gasification	29.69	0.83	122.57
Pyrolysis	18.42	0.61	201.31

The combustion process has the highest process efficiency due to the higher temperature of this process allows obtaining more energy as electrical output. Instead, the gasification and pyrolysis process have low energy efficiency due to part of the raw material is converted into biochar and bio-oil, which reduces the flow of obtained gases. This fact also can be observed in the specific energy generation indicator, which is expressed as the ratio of energy produced per unit of feedstock. The combustion process has the highest specific energy generation in comparison to the pyrolysis and combustion processes. Finally, the exergy losses were calculated to identify the amount of wasted energy in each process. As can be seen in Table 3, the pyrolysis process has the highest energy losses due to the unit operation involved in this process.

3.4. Economic evaluation.

The economic evaluation was done to evaluate the profitability of the combustion, gasification and pyrolysis process considering a low scale application with a mass flow of raw material of 250 ton/day. This evaluation was done in terms of the net present value of the process over the years and calculating the distribution costs of these processes. In fact, the NPV of each project for ten years of lifetime is presented in Figure 4.

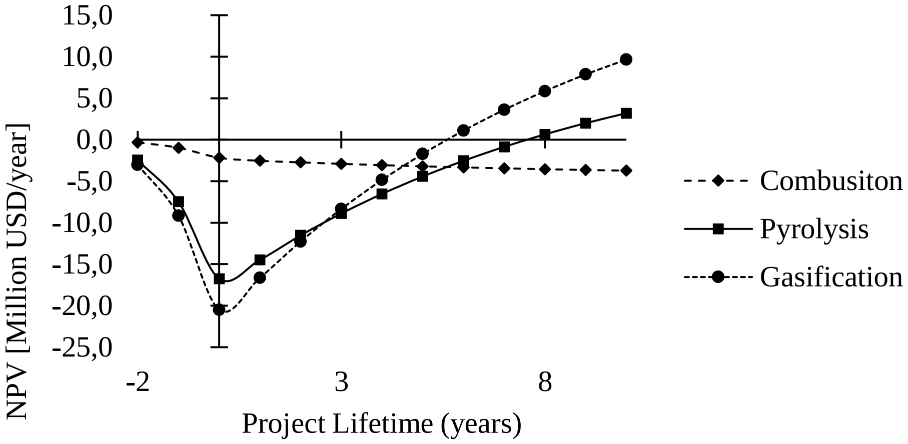


Figure 4. Net present value of the project for ten years of lifetime.

In Figure 4 is presented the NPV of each transformation technology for ten years of lifetime. The gasification pathway shows the highest NPV over the other two technologies which represents the shortest payback period in 5.7 years. Pyrolysis presents 7.5 years of payback period on account of the industrial services expenses and the handling of special chemicals such as nitrogen. Combustion, is not a profitable pathway due to the NPV never reach or exceed the equilibrium point. This result can be explained due to the energy derived from the combustion process has a similar cost than the other thermochemical routes. Nevertheless, the combustion process does not offer any other product t increase the incomes of this process. Moreover, the economic results for the three scenarios suggest that the gasification process is the more suitable technology to be used at low scales for the woody biomass valorization. In accordance with above-mentioned, the most profitable pathway is given to gasification, followed by pyrolysis, which need an improvement in the products conversion for saving expenses in services. On the other hand, the distribution costs of the combustion, pyrolysis and gasification processes are showed in Figure 5.

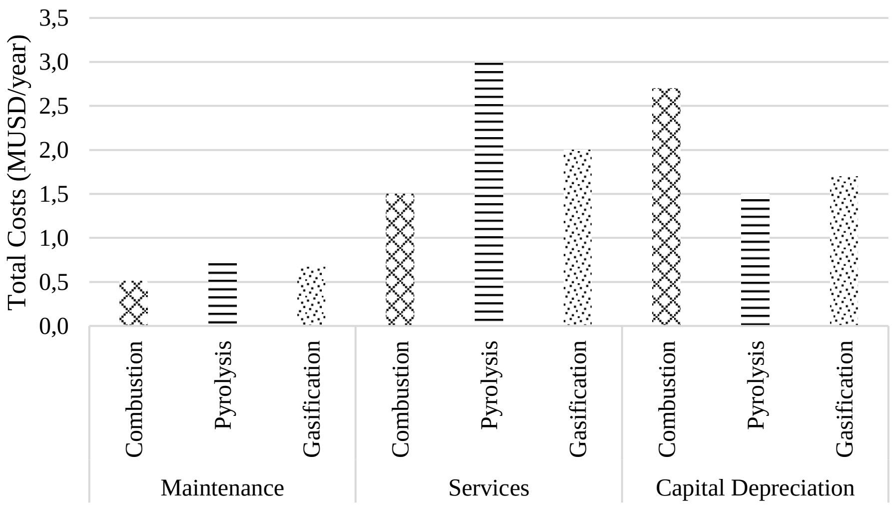


Figure 5. Distribution cost of the combustion, pyrolysis and gasification processes.

In Figure 5 is presented the net present value NPV of each transformation technology for ten years of lifetime. The gasification pathway shows the highest NPV over the other two technologies which represents the shortest payback period in 5.7 years. Pyrolysis presents 7.5 years of payback period on account of the industrial services expenses and the handling of special chemicals such as nitrogen. Combustion, is not a profitable pathway due to the NPV never reach or exceed the equilibrium point. In accordance with abovementioned, the most profitable pathway is given to gasification, followed by pyrolysis, which need an improvement in the products conversion for saving expenses in services. Finally, the environmental assessment of each process leads to establish the combustion process as the most polluting thermochemical route due to the higher amounts of carbon dioxide released to the atmosphere.

4. Conclusions.

The results of this work were significant to comprehend the energy and economic feasibility of thermochemical conversion pathway to upgrade wood biomass (*Pinus Patul*a). In fact, the gasification process can be profiled as a technology to be applied in low scale scenarios due to the energy efficiency in the electricity production and the obtaining of bio-char as soil improver. On the other hand, the combustion and pyrolysis processes can be implemented in higher scales than gasification.

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