

Energy and exergy analysis of the integrated use of jatropha curcas biomass as energy agent

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Abstract

Jatropha Curcas is a tropical plant suitable for reforestation with high agro-industrial potential, mainly in the production of biofuels coming from the extraction of oil from its fruit, making it possible to process and produce biodiesel for its use in internal combustion engines.

However, few studies have focused on the production of energy from the biomass waste remaining after oil extraction. In this article, an energy and exergy analysis of the integral use of Jatropha Curcas for the production of biodiesel and the use of the resulting residual biomass is carried out, comparing different alternatives to study which of these presents the highest energy and exergy efficiency.

The alternatives compared refer to thermochemical and biological processes for transforming the residual biomass such as: direct combustion of the shells of Jatropha Curcas for energy generation in a cogeneration process; the gasification using a bubbling fluidized bed reactor with recirculation of solids fed with torrefied biomass, and the use the biogas obtained by the energy production in a combined cycle; production of bioethanol, using the polysaccharides present in the biomass through hydrolysis, fermentation, distillation and burning of ethanol produced in an internal combustion engine. Finally, biodigestion submitting the seed cake to the action of hydrolytic, acidogenic and methanogenic bacteria for a production of methane which is burned in a combined cycle. Of all these alternatives, biogas obtained through the gasification is the best production route with an energy efficiency of 62.14% and 89.71% of exergy efficiency.

Additionally, the wastes of all the processes described above is used in the production of compost in order to improve soil conditions of plant cultivation, mainly emphasizing on the fact that all processes are energetically viable and environmentally sustainable at the same time.

Keywords: Energy; Exergy; Biomass; Biofuel

1. Introduction

Due to the preoccupation with the climate change, the exhaustion of the fossil fuels, and the concern for the energetic independence of the countries, new strategies for energy generation have arisen, such as the use of renewable energy. Among these, the use of biomass as an energy source stands out.

Countries located in the tropical region as Colombia, have the advantage of enjoying a higher percentage of insolation and also available arable land, which is translated on the possibility to use biomass as an energetic source.

Jatropha Curcas is a small multipurpose tree found in tropical regions which is native to Mexico and Central America, but is widely distributed in semi cultivated and wild lands of Latin America, Africa, India and South East Asia [1]. The *Jatropha Curcas* has the advantage of growing on arid lands and therefore it can be used for the reforestation. This investigation is based on the possibility to create *Jatropha Curcas* crops in different places of Colombia [2].

This paper presents the energy and exergy evaluation of the integrated use of the fruit of *Jatropha Curcas*. The extracted oil of the fruit is used for biodiesel production, and the use of its residual biomass is analyzed through different production routes. First, one contemplates the biodiesel and ethanol production from the residual biomass. The second one is centered on biodiesel production and the syngas production through torrefaction and gasification. The third one is biodiesel production and the use of residual biomass for biogas production through anaerobic digestion and the production of organic fertilizers through the composting process.

In addition to the energy accounting method based on the first law of thermodynamics, exergy concept is used, which is a tool to analyze a production process from an integral point. Exergy is defined as the maximum amount of work that can be extracted from a mass in a system when it goes from one thermodynamic state to one in a chemical, mechanical, thermal equilibrium with the environment in a reversible way, only interacting with the environmental components. Therefore, any deviation from the reference state can be assumed as exergy content. When the exergetic analysis is performed, the thermodynamic irreversibility can be quantified as destroyed exergy, which is a wasted potential to produce work. [3].

2. Methodology

The development of this work takes as its basis *Jatropha* fruit production planted at the Colombian Orinoquia, where there are obtained yields of 5000 kg/ha-year of *Jatropha* fruit, with humidity of 24,3%; this is subjected to the oil extraction which originates three by-products: oil (1159 kg), seedcake (1891 kg) and shell (1950 kg). [4] The additional biomass produced by the *Jatropha* bush, will be left on the land as topsoil.

2.1. Thermodynamics model

Process analysis is carried out based on the energy and exergy concepts. The thermodynamic systems analyzed are assumed in steady state, at constant volume. The velocity, height changes are negligible, therefore the corresponding energy balance equations for the system, and the exergy equation are [5]:

$$\sum_{in} m_{in} h_{in} + \dot{Q} = \sum_{out} m_{out} h_{out} + \dot{W}, \quad (1)$$

$$\sum_{in} m_{in} b_i + \dot{Q} = \sum_{out} m_{out} b_{out} + \dot{W} + B_D, \quad (2)$$

For biomass compounds only the specific chemical exergy of the biomass calculated is being considered, based on the model proposed by Szargut. [6]. For thermodynamic properties of the gas produced on different processes, the model of ideal gases mixture is used. The thermochemical characteristic of biomass is related with its elemental composition, and volatiles and ash content. The chemical expression of biomass can be represented as CH_xO_y . This expression is used, among other uses, to calculate the heat capacity of biomass (C_p), using the methodology proposed by Wei Yan [7].

$$C_p \left(\frac{J}{molK} \right) = 7.524x + 9.614y + 16.720z, \quad (3)$$

$$x = 1, \quad y = \left(\frac{H}{C} \right) * \left(\frac{PMC}{PMH} \right), \quad z = \left(\frac{O}{C} \right) * \left(\frac{PMC}{PMO} \right)$$

The biomass higher heat value (HHV) is calculated in accordance to the elemental composition. [8]

$$HHV = 349,1C + 1178,3H + 100,5S - 103,4O - 151N - 21,1A, \quad (4)$$

Where C, H, S, O, N and A are the respective mass percentage of: carbon, hydrogen, sulfur, oxygen, nitrogen and the fuel ash. The lower heat value (LHV) is calculated assuming that the water formed by hydrogen which is part of the fuel is in steam phase. [9]

$$LHV = HHV - (0,0894 \cdot 2442,3H), \quad (5)$$

The $\Delta h_{f,298}^0$ is calculated using the next expression [10]:

$$\Delta h_{f,298}^0 = HHV - (327.63C + 1417.94H + 92.57S + 158.67H_2O), \quad (6)$$

The thermodynamic properties and chemical exergy of other substances, like: NaOH, H₂SO₄, Na₂SO₄, CaOH, CaO, CH₃OH, NH₄NO₃, CH₄N₂O, KH₂PO₄, (NH₄)₂SO₄, P₂O₅, and KCl, were obtained from different bibliographic sources. [5], [6], [11], [12]

This model was implemented and simulated in EES software, using thermodynamic properties for H₂O, CH₃OH, C₂H₅OH and ideal gases such as CO₂, H₂O, O₂, CO, N₂, CH₄, C₂H₆. [13]

2.2. Biomass characterization

Generally, *Jatropha Curcas* starts to bear fruit in about a year and reaches a stable harvest phase after five years, and has an estimated economically productive period of 25 – 30 years. But the production curve is practically unknown, as there are no current results of actual production on a commercial basis. [14].

Table 1. Chemical characterization of Jatropha Curcas fruit, seed cake, shell and oil.

	Fruit [15]	Seed Cake [16]	Shell [17]	Oil [18]
Elemental Analysis				
% C	60.71	45.50	50.3	83.48
% H	8.19	7.2	6.6	12.54
% N	1.67	4.0	1.8	0.0
% O	25.33	43.30	41	3.98
Proximate Analysis				
% Ash content	4.4	1.50	3.0	-
% Moisture	24.3	66	8.0	-
% Fixed Carbon	-	18.86	-	-
% Volatile Material	-	79.20	-	-
HHV(kJ/Kg)	28225	19983	21097	45507
LHV(kJ/Kg)	26437	19967	19656	40769
b (kJ/Kg)	-	20426	20729	39990

The plant can be used to prevent and/or control erosion, to reclaim lands; it grows as a live fence and especially to contain or exclude farm animals and can be planted as a cash crop [19].

The general characterization of the *Jatropha Curcas* fruit is presented in Table 1.

2.3. Production processes using *Jatropha Curcas* fruit

The biomass is processed simulating three different routes of transformation of the chemical energy of biomass. In all cases the oil is used for the biodiesel production, and the residual biomass is submitted to three different production routes.

2.3.1. Biodiesel production from *Jatropha Curcas* fruit oil

Around the world, there is a great awareness of the need for a clean renewable fuel, like biodiesel, which has many technical advantages over fossil fuels such as low greenhouse gas emissions, biodegradability, its production from renewable and domestic raw materials, minimal sulphide content, higher flash point and higher combustion efficiency [20].

The biochemical composition of oil is taken as a mixture of fatty acid (palmitic 14.2, oleic 43.1, stearic 6.9 and linoleic 34.3%). [14]

Figure 1 represents a schema of the biodiesel production process. The first stage is focused on the extraction process where dry *Jatropha* fruit is deposited in a debarker to remove the fruit shells and extract the seeds. The seeds are conditioned with steam to favor oil extraction. The conditioned seeds pass through a screw extractor obtaining seed cake and oil.

The second stage is focused on the esterification process where initially methanol and sulphuric acid are mixed, the mixture and oil react in the esterification reactor which is heated by steam, water-H₂SO₄ mixture, biodiesel-methanol mixture and triglycerides are the products of the esterification reaction which are separated by decantation, based on the next reaction.

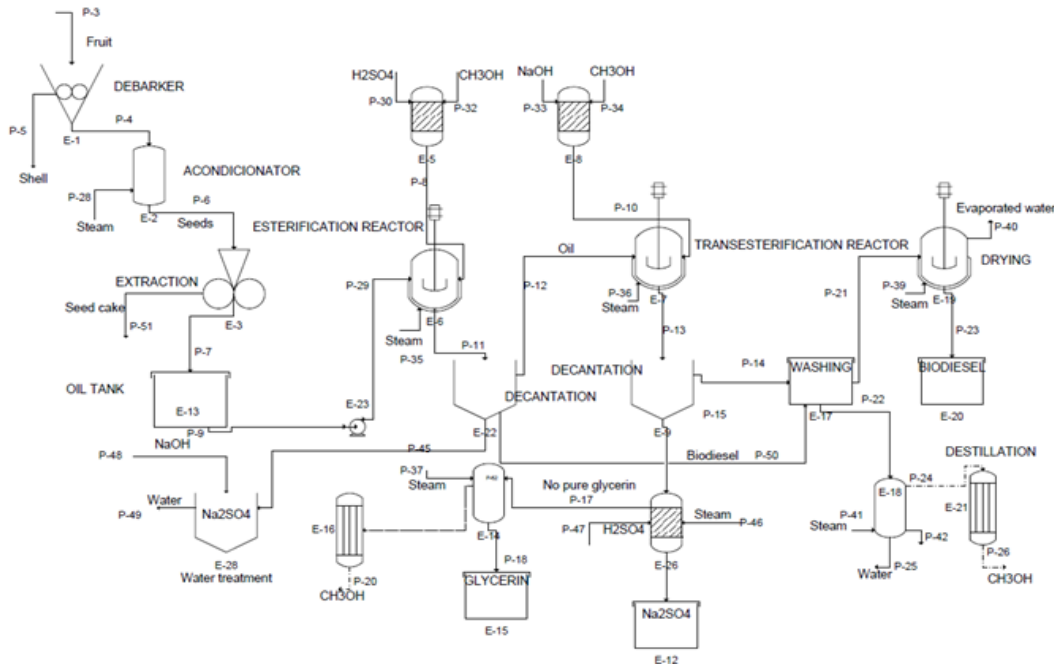
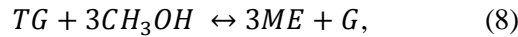


Figure 1. Biodiesel production process. [21]

The acid water (sulphuric acid and water mixture) is sent to a water treatment stage where NaOH is added to control pH; in this step Na₂SO₄ and water are obtained. The third stage is focused on the

transesterification process where oil reacts with a mixture of methanol and NaOH in a steam heated reactor, based on the following reaction:



As a result of this reaction, a biodiesel, methanol, NaOH and glycerin mixture is obtained, the glycerin-NaOH-methanol mixture and biodiesel-methanol are separated by decantation. The glycerin is purified in two steps; first NaOH is eliminated adding H₂SO₄ in a steam-heated reactor to obtain Na₂SO₄. Finally, glycerin is purified by distillation obtaining methanol and pure glycerin. The biodiesel-methanol mixture is washed with water obtaining wet biodiesel: a water-methanol mixture. The wet biodiesel is dried in a steam-heated reactor to obtain pure biodiesel. Methanol is separated from water by distillation. [21]

2.3.2. Use of the residual biomass by torrefaction and gasification

In this process, both the *Jatropha Curcas* shell and the seed cake, that are residual biomass from oil extractions, are used for the syngas production. The process diagram is shown in Figure 2.

The torrefaction process is carried out in an inert atmosphere at temperatures between 200-300°C, at low heating velocities (<20°C/min) [22]. On the torrefaction process, a biomass loss takes place until 40%, and energy between 10-15%. Nevertheless, a higher HHV is obtained. [23]–[25].

Due to the low humidity of seed cake, it will be directly used on the torrefaction process as it is shown in Figure 2. Volatile fuels that are released due to the heating rate will be deposited in a combustor that, along with the shell, will generate hot gases for pre-heating in the gasification process.

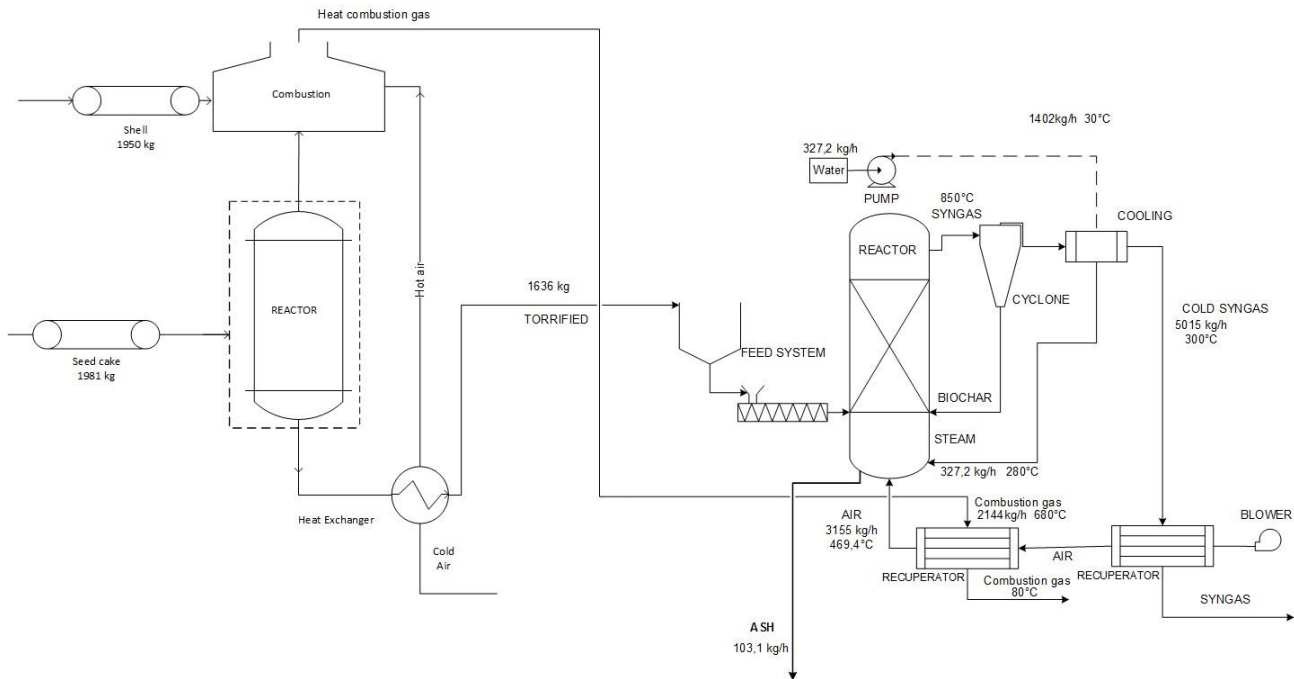


Figure 2. Torrefaction and gasification processes

The torrefied product enters to a heating exchange phase, aiming at taking advantage of the available energy to pre-heat the air entering the combustor. The torrefied product is transformed into a combustible gas (Syngas) by air and steam action in a gasification process. This process is carried out in a bubbling fluidized bed gasifier that operates at 850°C (1123,15 K) and atmospheric pressure. The air/fuel (AF) and steam/fuel (SB) ratios are fixed in 0,3 and 0,2 respectively. The required airflow on the gasification reactor is preheated in a heat exchanger, using the hot combustion gases generated on

combustion of shell in torrefaction process. The syngas obtained in cooling and the released energy are used to produce the water steam necessary on gasification process.

The biochar is recirculated for improving the conversion, and finally the syngas is obtained with 10% humidity. The gasification process heat losses are among 20-25%, taking into account that it is autothermal and it is necessary to keep the temperature of the operation. This heat loss can represent 25% of the syngas energy.

2.3.3. Ethanol production of amillaceous material

Hydrolysis is a biochemical process, which allows the production of reducing sugars from starch and lignocellulose. It is an indispensable and intermediate step in ethanol production since microorganisms that promote fermentation are not able to directly metabolize the original raw materials. Hydrolysis will be carried out in enzymatic (biochemical via) [26]. Because of its low cost and availability, sulfuric acid (H_2SO_4) is used to modify the pH, enzymes commonly used in the enzymatic hydrolysis are α -amylas and cellulases. In general, the cellulose is converted to glucose, and hemicellulose to pentose and hexose. The chemical reaction representing hydrolysis is given by:

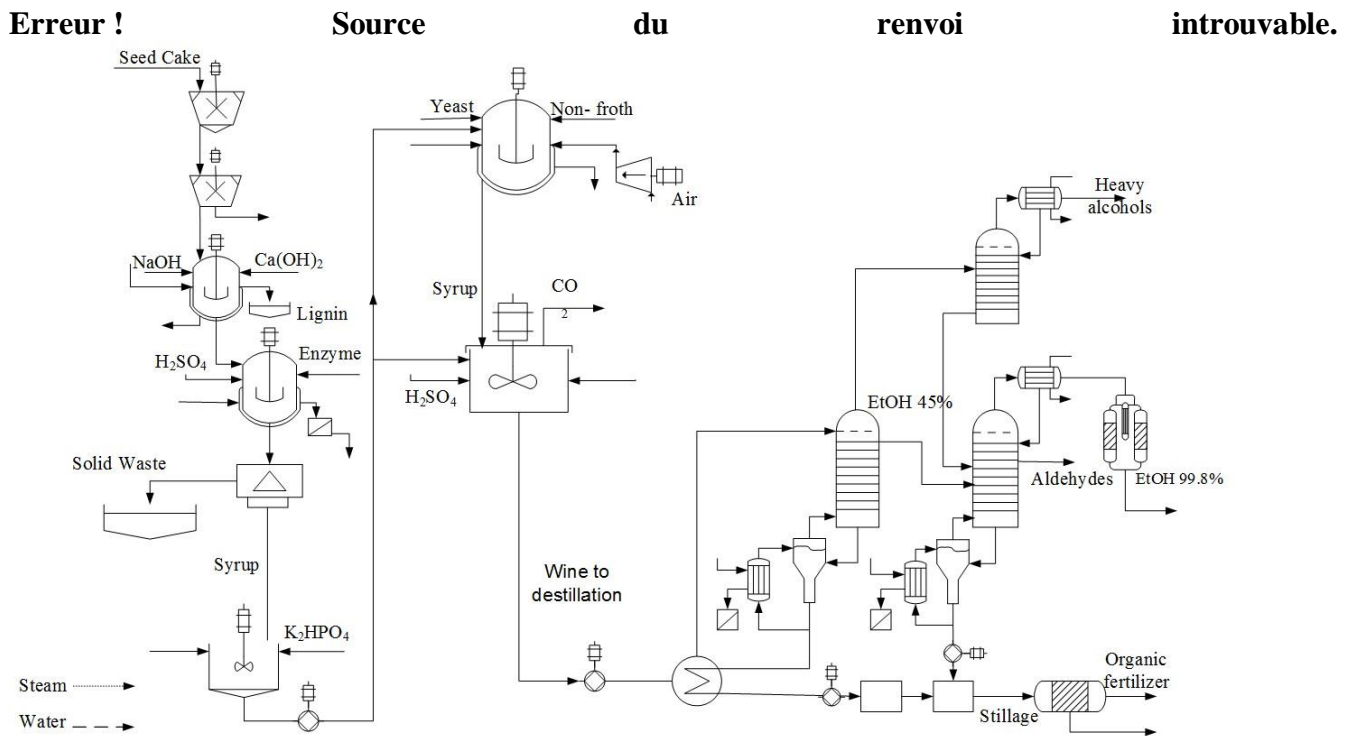
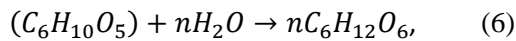
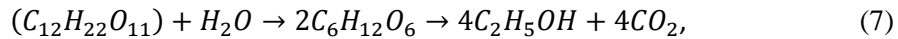


Figure 3. Ethanol production processes

Figure 3 shows the different stages that biomass (seed cake of Jatropha fruit) has to undergo in order to transform its cellulosic material content into sugars by enzymatic hydrolysis. The lignocellulosic material is shattered and crushed before passing through a delignification process, which is carried out at ambient temperature using NaOH. Then, the material is hydrolyzed adding sulfuric acid and the enzyme for 5 hours at 50°C. Finally, the mixture is also neutralized and filtered before fermentation.

Fermentation is a process whereby yeast modifies its metabolic route to convert sugars into ethanol as it is shown in the following chemical irreversible reaction:



The sucrose in the presence of enzymes absorbs one water molecule and splits into reducing sugars (glucose and fructose), which are finally converted into ethanol releasing CO₂.

The fermentation process is divided in two parts: yeast growing and syrup fermentation. Yeast growing requires an initial syrup supply and a constant oxygenation to guarantee aerobic conditions. Additionally, agitation and refrigeration are required to maintain a constant temperature in the reactor (33°C).

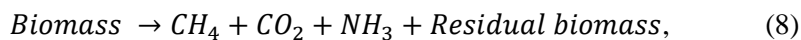
Ethanol at 96% w/w is produced in the distillation process. Normally, two distillation columns are used and some by-products such as aldehydes and heavy alcohols are recovered. After separation, the stillage is sent to the composting plant where they are mixed with ashes and other biomass residues to obtain an organic fertilizer. In a final purification stage, the product stream is dehydrated using molecular sieves to produce anhydrous ethanol of 99.8% w/w purity.

In this process, the shell of *Jatropha* fruit is used in a power plant to produce the work and heat necessary for ethanol production.

2.3.4. Use of residual biomass whereby anaerobic digestion and composting

Seed cake contains a high percentage of protein and carbohydrates, which can be bioconverted to biogas. This conversion takes place mainly by a bacterial consortium, in three different stages (Hydrolytic, acidolytic, methanogenic), where a series of intermediate chemical compounds are produced, and which will finally transform carbon dioxide, ammonium and trace amounts of other compounds such as hydrogen sulphide.

Total mass balances are present, and by component, energy balances of a sealed bioreactor, without agitation, to ensure anaerobiosis during the process; this operates in a continuous temperature range of 25°C in the input and 35°C during the output, taking into account that the treatment is thought to contain mesophilic bacteria, whose ideal working temperatures are between this range. PH will be self-regulated by the process, taking into account that if it remains around 6, it is being carried out appropriately. Thus, the global chemical reaction will be:



It is supposed that methane production is limited to the amount of hydrogen in the biomass, dividing it: 67% becomes methane, 13% becomes ammonium, and 20% is left as residual biomass. CO₂ production is 20% of the biomass total carbon.

To elaborate the compost, the fruit shell is used. The composting is carried out outdoors, since it is an aerobic process, it is necessary that the adequate carbon/nitrogen relation (C/N) is present, approximately 30:1 [27]. Besides, it requires trace amounts of potassium, calcium, sulfur and phosphorous. The process temperature increases as the organic decomposition of the material takes place.

For the *Jatropha* growing, superphosphates and urea are used as fertilizers (Corpoica). In the following amount: 112 CO(NH₂)₂, KCl 1445, B 0.5, Zn:0.5, Mg 9, and pesticides 0.5g/ha year. These values will be used to calculate the energy saved when the produced composting is used [28].

3. Results

Table 2 shows the products characterization and the high and low heat value for the torrefaction process, the biodiesel production, the gasification production and the anaerobic digestion.

Figure 4 shows the results of the mass and energy balance of first analyzed route, the production of biodiesel and ethanol. The proximate analysis of seed cake reported by Salviano dos Santos is used, [29] and it is considered that 80% of the matter possible to hydrolyze, has a reaction [30].

It is observed that 1181 kg/ha/year of biodiesel are obtained using the fruit oil, and of ethanol, 213.9 kg/ha-year are obtained using the filter cake. Shell was used for producing the necessary (Thermal and mechanical) energy for the process. It is also observed that the process is not energetically self-sufficient, requiring additional 4.7 MJ of energy.

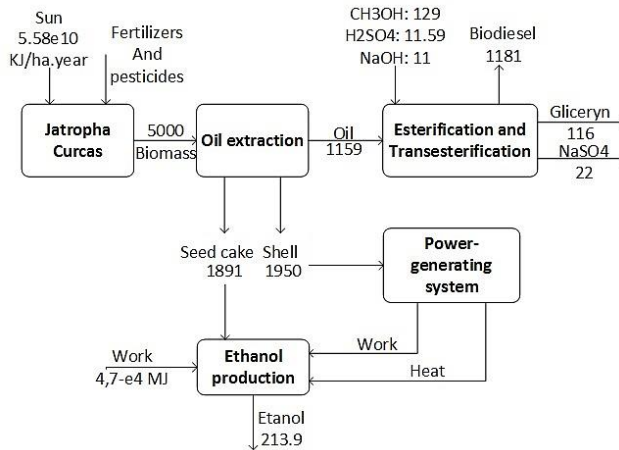


Figure 4. Route 1: Biodiesel and ethanol production

Figure 5 presents the balances for the gasification process carried out from 1636 kg of torrefied biomass, where 4514 kg/ha/year of syngas were obtained, with the composition and heating value present in table 2.

Figure 6 displays the results of the biogas and compost production. 167,7Kg de methane/ha year, 34,04 Kg of ammonium/ha-year and 50,47 Kg of CO₂/ha-year were obtained from 832,04 kg/ha-year of dry seed cake.

Table 2. Products characterization

	Torrefaction process	Biodiesel	Gasification (%v/v)	Anaerobic digestion (%p/p)
%C	53.05	73.08	H ₂ 18	CH ₄ 167.7
%H	5.17	9.68	CO 21	CO ₂ 50.47
%O	0.69	16.95	CH ₄ 0.7	NH ₃ 34.04
%N	34.80	0.29	C ₂ H ₆ 0.1	
%Ash	34.80	-	N ₂ 48.2	
			CO ₂ 12	
HHV (kJ/kg)	24540	-	HHV (kJ/kg) 4717	HHV (kJ/kg) 39947
LHV (kJ/kg)	23411	37270	LHV (kJ/kg) 4023	LHV (kJ/kg) 35769
b (kJ/kg)	-	42934	b (kJ/kg) 3000	b (kJ/kg) 39346

According to the PAHO (Pan-American Health Organization) manual for compost production, 35% of organic matter becomes fertilizer, this corresponds to 681kg of compost/ha-year, and 21% becomes CO₂, this corresponds to 376,7Kg de CO₂/ha-year from 1794Kg of shell/ha-year [31].

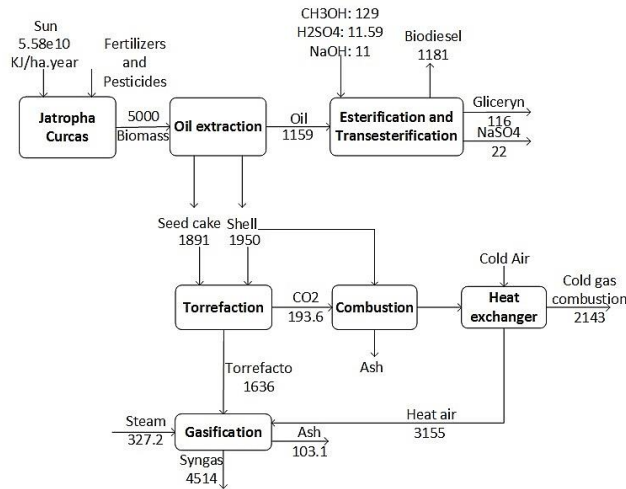


Figure 5. Route 2: Biodiesel and Syngas production

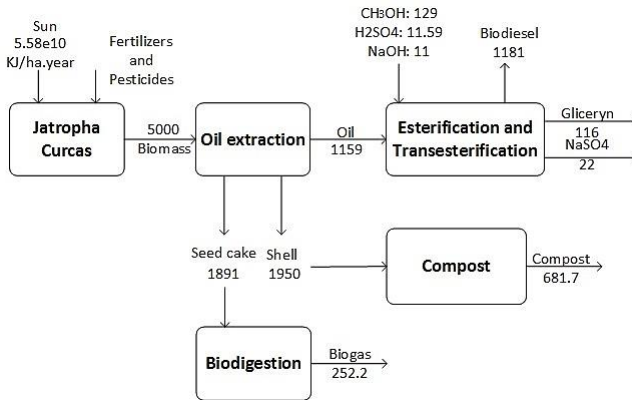
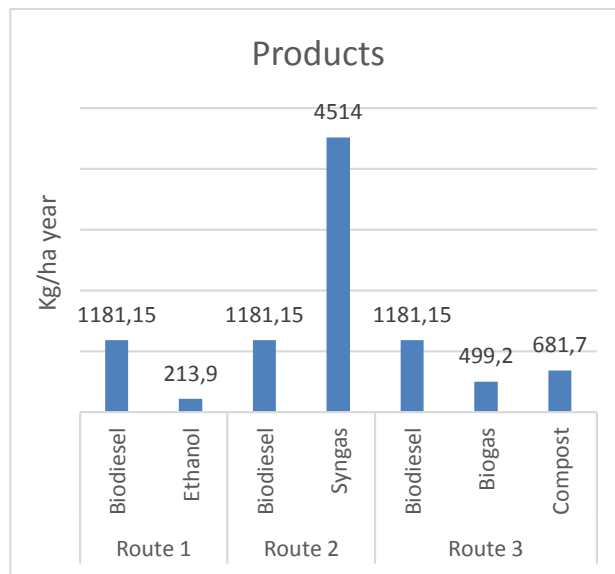


Figure 6. Route 3: Biodiesel, compost and gas mixture production

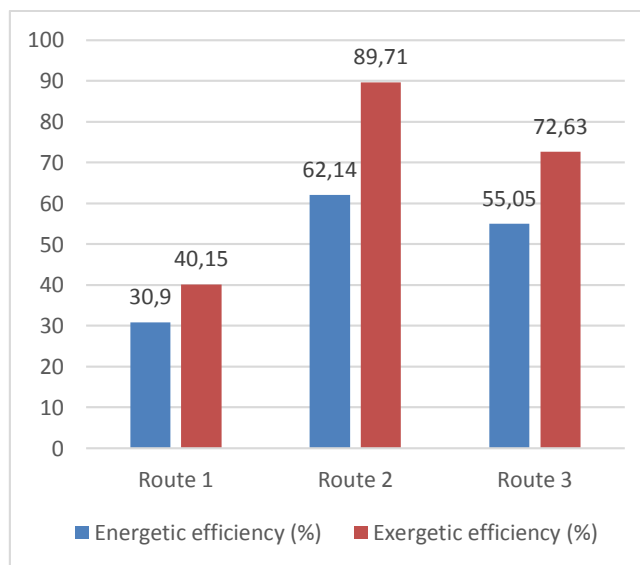
In *Graphic 1*, the results of the mass yield of the three analyzed production routes can be observed. It is concluded that the major option is the combined production of biodiesel and syngas by torrefaction and gasification. Although the biodigestion yield is not the most optimal, it presents an advantage of producing an organic fertilizer that, when returning to the crop, avoids the use of chemical fertilizers. Due to the low yield, ethanol production it is not considered to be a viable route for the use of residual biomass.



Graphic 1. Product mass of each process in its route of production

For each route, the energetic and the exergetic efficiency was calculated, apart from the products mass for all routes, these data are shown in the Graphic 2. Both energetically and exergetically speaking, it can be concluded that the best route for the use of biomass is biodiesel and syngas production from torrefaction and gasification, followed by the biogas and biodiesel production. It was observed that the least efficient process corresponds to the use of residual biomass for ethanol production, due to the intensive use of energy in ethanol production.

Assessing the energy saving when using compost by means of a life-cycle analysis, it was evidenced that when fertilizers and pesticides are no longer used, a saving of MJ/ha.year of energy and 248 MJ/ha.year of exergy is obtained.



Graphic 2. Energetic and exergetic efficiency of three production routes

4. Conclusions

Jatropha is an energetic crop with a great potential for clean energy generation, by integrating several processes it is possible to obtain biodiesel from oil, and the use of biomass waste for obtaining other energy sources.

As it was possible to evidence, the best route for the use of *Jatropha Curcas* as an energy agent is the production of biodiesel and Syngas by torrefaction and gasification, with an energetic and exergetic efficiency of 62% and 89,7%, respectively. This is due to the use in gasification of raw material with a high heating value (torrefied), compared to the initial biomass; since it is an autothermal process, the energetic efficiency is not greater than the exergetic efficiency, and to the utilization of a secondary current for the required air pre-heating. The heating value and the thermal capacity generated by the Syngas, can be usable in an internal combustion engine adapted to work with a lean fuel, or even more, in a combined cycle process of energy generation.

Ethanol production from *Jatropha Curcas* cake is not appealing due to its low production per hectare (213,9 kg/ha.year), and the energetic efficiency compared to the one of studied processes, this is mainly due to the low percentage of cellulosic material that the cake contains, 30% approximately, the low yield of hydrolysis and fermentation processes, and the high consumption of thermal and mechanical energy of the process.

Even though biogas and compost production do not present the greatest energetic efficiency, they have the advantage of avoiding the use of chemical fertilizers, which leads to energy saving and environmental benefits.

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