# From Biomass to Bio-oil: Processes and Treatments to Convert Raw Material into Energy

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#### Abstract

Bio-oil is a potential fuel obtained from pyrolysis of biomass. This work provides a discussion about the different processes used to obtain this product, evidencing the factors that influence its properties and characteristics. A comparison of the properties of bio-oils with traditional fuels is presented. As well as this, the main treatments to upgrade biooil are also discussed.

Keywords - biomass, pyrolysis, bio-oil.

## I. INTRODUCTION

The environmental impacts caused by the burning of fossil fuels, the increase in energy demand associated with population and economic growth, the energy geopolitics that subordinate countries that do not have the minimum reserves of fossil; justify and impel the energy matrixes in the world to employ the gradual insertion of sources of renewable energies. Among the renewable energy sources are biofuels, and hydroelectric, wind, solar, photovoltaic, and geothermal energies [1].

Controversies involve the pros and cons in regard to the production of biofuels to the detriment of food safety. This gives rise to the stimulation of secondgeneration energy production and, essentially, the sustainable production of biomass, where secondgeneration biofuels are produced from non-food crops, such as lignocellulosic materials, and agricultural and forestry waste [2].

All organic material that comes from plants, such as wood and wood wastes, crops and their by-products, waste from food processing and aquatic plants and algae can be a biomass to be used as a raw material in energy production [3], [4]. The use of biomass products as a source of energy dates from prehistory with the discovery of fire, where wood was used as an energy source. Biomass products have increasingly gained more importance as an energy source. The great advantage of obtaining energy sources from biomass is that it is a renewable product and contributes to the reduction of environmental impacts, mainly in regard to the absorption of  $CO_2$  by biomass insofar as it serves as source of raw material, for energy purposes.

Concerns and current needs regarding the insertion of biomass into the production of biofuels drive the development and expansion of biorefineries. A biorefinery is a concept analogous to the oil refinery, changing in the sense that it is based on the exploitation of large amounts of waste and natural resources, where biomass is converted into biofuels, energy and chemicals. A biorefinery encompasses thermochemical. biochemical. mechanical and chemical processes. The biomass allied to the concepts of agro-energy and bio-refineries is then a substitute for future oil depletion. In this context, challenges arise, such as: to produce raw material in large scale and at competitive costs; developing efficient and low-cost transformation processes; promote additional value in the chain with the use of co-products and with the implementation of processes focused on biorefineries [5].

Among the technologies for energy production from biomass and residues are biological processes (anaerobic digestion and fermentation), thermochemical (gasification, liquefaction, combustion and pyrolysis) and mechanical (Fig. 1). The literature has shown that studies focused on the development and improvement of more efficient conversion technologies, such as gasification and pyrolysis, are related to increased process efficiency and reduction of socio-environmental impacts [6].

Gasification is a thermochemical process in which solid or liquid fuels are converted into a mixture of gases that can be used as energy production (known as synthesis gas or syngas), or used as raw material for the production of other chemical compounds. This transformation occurs through the partial oxidation of biomass under high temperature conditions [7], [8]. The main components of syngas are CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O and N<sub>2</sub>, and this mixture can be burned to produce heat or synthesized to produce liquid fuels for transport [9]-[12].

Combustion is a process of burning biomass in ovens, boilers or stoves, involving reactions in which carbon and hydrogen, present in the fuel, react with oxygen forming CO<sub>2</sub>, water and generating energy.

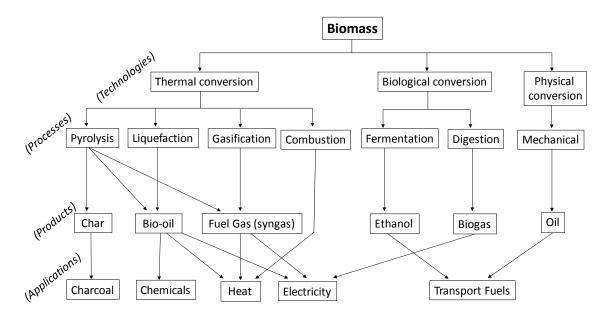


Fig 1: Processes for obtaining fuels from biomass. Based on [7].

This is a well-established and widely applied process in sugarcane mills. Even though it is considered the simplest process to convert biomass to energy and is widely practiced commercially, combustion is not an ecological method [13], [14].

In the case of liquefaction this is a process that allows for the transformation of biomass with high moisture content (above 50% w/w) into liquid products using solvents in the process under conditions of high pressures (2-20 MPa) and lower and moderate temperatures (250- 450 °C) [15]. It is also called hydrothermal liquefaction (HTL) when water is used as solvent. The operational conditions are performed in order to keep the water in supercritical conditions. Although it is a good process to obtain bio-oils, it has considerable costs of implantation [16].

Pyrolysis consists of the decomposition of dry biomass (containing a moisture content below 10% w/w) in a heated atmosphere, controlled (350- 550 °C) at atmospheric pressure (0.1-0.5 MPa) in the total or partial absence of oxygen, with the formation of three products: coal, bio-oil and fuel gas [13], [17], [18]. One of the advantages of this method is the obtaining of products that can be used in the generation of heat and electricity, or after treatment are used with fuel and / or other chemical products. Moreover, high efficiency in the transformation phase (bio-oil with up to 70% yield) and low investment cost makes this process a differential in obtaining energy [19].

As seen, among the thermochemical conversion processes, pyrolysis has the clear advantage of generating solid, liquid and gaseous products and has generate great interest in the current scenario. The liquid product of pyrolysis, called bio-oil, is a renewable liquid fuel, and its production as well as its different applications is still under development, so a study supporting the production and processing of this product is essential.

In this sense, this article presents an overview of the liquid product of the thermochemical conversion of biomass through the pyrolysis reaction, explaining the catalytic and non-catalytic processes, the types of biooil treatment and the types, aspects and peculiarities of the raw material for conversion.

## II. PYROLYSIS AND THE BIO-OIL OBTAINING PROCESSES

The thermochemical conversion of pyrolysis often occurs in a temperature range of 400 to 800 °C, generating as by-products fuel gases, bio-oil and coal. The liquid product of pyrolysis, called a bio-oil, is a renewable liquid fuel, formed by a complex mixture of organic compounds, including aromatic hydrocarbons, acids, esters, ether, alcohols, ketones, aldehydes, furans, sugars, amines, phenols, and water, as well as inorganic species, such as K, Fe, Al, Na, S, Ti, Mn, Ln, Ba and others [20].

Bio-oil is the dark brown color liquid fraction and with a characteristic odor of smoke resulting from the pyrolysis process. This complex mixture contains compounds with a varying molecule size resulting from the depolymerization and fragmentation reactions of the major constituents of the biomass: cellulose, lignin and hemicellulose. One of the characteristics of this mixture is its oxidative instability, which is caused by the presence of oxygenated compounds which makes it easy for aging and low energy density [21], [22].

Although bio-oil presents interesting characteristics for the production of energy, some properties of the bio-oil are still quite distinct from the properties of petroleum products, which makes it impossible to use them directly as fuel in vehicles. Table 1 presents a comparison between the properties of bio-oil and other fuels.

Even possessing properties that make it impossible for direct use as fuel in vehicles, such as high viscosity, high oxygen content, and oxidative instability, bio-oil has similar physical properties to diesel oil, and is therefore a great alternative to use as fuel in boilers, ovens, engines and turbines to generate energy as a substitute for diesel [7], having the advantage of being a fuel that generates energy comparable to fossil fuels characterized by producing compounds such as CO<sub>2</sub>, SOX, and NOX [31], [32]. As well as this, it can partially replace petrochemical phenol for the production of phenolic resins, which is the basis of all adhesives for compensated woods; and thus can be used as an additive in the manufacture of cellular cement, acting as an air incorporator in the mortar; or even be an additive for the transport of high viscosity petroleum; be present in emulsions for burning or emulsions for asphalt; and finally, it can be fractionated by distillation to obtain fractions used as a food additive and in the use of the production of slow release fertilizers [33]. These and other applications are indicated in Fig. 2.

The nature and properties of the products obtained by biomass pyrolysis are strongly affected by the raw material and procedure used. The bio-oil consists basically of 20-30% of water and 70-80% of polar organic [34] and the composition and yield of the biofuel are influenced by the type of material and the technology used in the pyrolysis process. The pyrolysis processes can be classified according to the conditions employed, such as temperature, pressure, type of atmosphere, residence time, heating rate, catalyst and also the type of catalyst, as will be seen

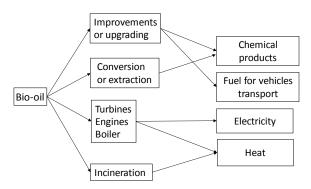


Fig 2: Applications of bio-oil. Based on [7].

below. These factors influence the quality of the products and by-products of pyrolysis [35].

#### A. Slow Pyrolysis

In pyrolysis, three products are always produced, but the proportions can be varied over a wide range of parameters due to process adaptation. Slow pyrolysis is characterized by slow heating rates favoring a higher yield of the solid product. Coal has several applications such as: fuel of heaters, catalytic converter, soil correction, adsorbent of contaminant, and activate carbon, etc. [36]-[39].

Shaaban et al. [40] and Chen et al. [41] evaluated the effects of the heating rate of slow pyrolysis of sawdust of rubber and bamboo wood, respectively. These studies concluded that the heating rate significantly influences the physicochemical properties of coal and other by-products.

Thermophysical properties of different fuels ([23]-[29] apud and based on [30]).									
Properties		Bio-oil Diesel		Heavy fuel oil	Gasoline type C	Ethanol (anhydrous)			
Density (kg/m <sup>3</sup> at 15 °C)		1220	854	963	740	790			
Ignition	point (°C)	-27	-20	21	-40	-23			
Viscosity (cSta, 50 °C)		13	2.5	3.51	-	—			
HHV (MJ/kg)		16-19	429	40.7	401	26.8			
Latent heat of vaporization (kJ/kg)		_	-	_	498	904			
Composition	% C	55-58	86.3	86.1	76.6	52.0			
	% H	6.2	12.8	11.8	15.3	13.0			
	% O	37.3	-	_	8.1	35.0			
	% S	-	0.9	2.1	_	_			
Ashes (wt %)		0-0.2	< 0.01	0.03	—	—			
Water (wt %)		15-30	0.1	0.1	-	-			
Acidity (pH)		2.5	-	_	_	_			

 TABLE I

 Chermonhysical properties of different fuels ([23]-[29] anud and based on [30])

Chen et al. [41] also studied the kinetic parameters of the slow bamboo pyrolysis, where the increase of the heating rate increased the activation energy values in relation to the content of bio-oil phenolic substances,  $CH_4$  concentrations in non-condensable gas, and the specific surface area of coal, while reducing the yield of coal, viscosity and water content of bio-oil and concentration of  $CO_2$ .

Lee et al [42] investigated the production of coal from the slow pyrolysis of Geodae-Uksae 1 for soil applications in order to sequester carbon from the atmosphere and improve crop productivity. The temperature of the pyrolysis ranged from 300 to 700 °C, where the yield of the coal decreased with an increase in the temperature to 500 °C, above this temperature the decrease in solid yield was very small. In relation to the characteristics of the coal obtained, it became increasingly carbonaceous high at temperatures, releasing H and O. The coal produced exhibited a rapid increase in the surface area, which can conserve the nutrients in the soil preventing them from being washed away by water and thus reducing the need for fertilizer.

Crombie & Masek [43] studied the feasibility of a self-sustaining slow pyrolysis system. Calculations based on the gaseous product composition of the pyrolysis showed that the process can be sustained by the energy contained within the pyrolysis gases. In this study, the energy balance showed the real possibility of slow pyrolysis as a self-sustaining system for the production of coal and bio-oil.

## B. Fast Pyrolysis

When the liquid pyrolysis product is desirable in higher yields, the pyrolysis reaction should occur at a rapid rate of heating. The rate of heating in fast pyrolysis is generally about 300 °C min, less than the flash pyrolysis heating rate, and fast enough to obtain a larger amount of bio-oil [44]. Fast pyrolysis is also characterized by temperature control at approximately 500 °C, short residence time (less than 2 s) and biomass with particle size less than 3 mm. In fast pyrolysis, the high yield of bio-oil is favored when a low ash content biomass is used. The liquid formed has half the calorific value of conventional fuel oil, which implies the need to treat the bio-oil so it can be applied as fuel for vehicles [8].

Ben & Ragauskas [45] carried out a comparison study for the characterization of oils obtained by fast and slow pyrolysis through characterization by Gel Permeation Chromatography (GPC), Nuclear Magnetic Resonance (NMR) and Heteronuclear Single Quantum Correlation- NMR. The raw materials employed were the soft wood kraft lignin and pine wood. The results indicated, for both lignin and pine wood, that the fast pyrolysis process produced less coal and that the gas yield was higher in the fast pyrolysis process, indicating that a higher heating rate could improve the decomposition of small oil components in pyrolysis. The significant difference

between the fast and slow pyrolysis oil was the content of the methoxyl group. This content decreased by 76% for pine wood and 70% for lignin when using the fast pyrolysis system at 600 °C, indicating that the fast pyrolysis process will improve the cleavage of methoxyl groups. The fast pyrolysis process provides higher yield of liquid product, however, the higher content of polyaromatic hydrocarbons (PAH) and molecular weight of the fast pyrolysis oil create barriers to the subsequent treatment process.

Kim & Agblevor [46] studied the characteristics of the fast pyrolysis of milkweed and carried out thermogravimetric analyzes designed for biofuels from high density raw material. The reaction temperature of the fast pyrolysis was determined from the analyzes of thermogravimetry (TG) and differential thermogravimetry (DTG) of the milkweed. When the reaction temperature reached 425 °C, the average conversion was 86.92%, at each heating rate it was assumed that most of the hemicellulose, cellulose and natural rubber had decomposed between 425 °C and 550 °C for fast pyrolysis. The total net yield was higher (44.19% by weight) at 425 °C, the gas yield was higher (33.33% by weight) at 550 °C, while the higher coal yield (24.5% by weight) was at 475 °C. The calorific value of the bio-oil of milkweed was between 30.33 MJ/kg and 32.04 MJ/kg, which is much higher than those of most lignocellulosic biomasses pyrolysed under similar conditions.

Czernik et al. [47] evaluated the effects of storage conditions on the physical and chemical properties of fast biomass (biomass) pyrolysis oil (wood) exposed at elevated temperatures and for extended periods of time. The chemical changes in the bio-oil were measured using GPC and Fourier-transform infrared (FTIR) spectroscopy. The pH of the oil was not affected by storage, while the water content increased and aging progressed, suggesting that the condensation reactions occurred in the oil. The viscosity and molecular weight of the bio-oil also increased with time and storage temperature.

Bai et al. [48] studied the origin of phenolic oligomers (a compound of difficult application, low volatility, high viscosity and quite reactive) during fast pyrolysis. Phenolic Oligomers are the most abundant products in the bio-oil from lignin pyrolysis. Pyrolysis products were investigated using gas chromatography / mass spectrometry, GPC and atmospheric pressure photoionization to minimize secondary reactions. A significant fraction of the primary products during lignin pyrolysis are monomers and dimers, but they reoligomerize rapidly to form phenolic oligomers.

Kiliç et al. [49] optimized the experimental conditions for obtaining the fast Euphorbia rigid biooil by fast pyrolysis using the RSM based on experimental planning. The parameters evaluated were temperature, heating rate and nitrogen gas flow rate. The maximum yield of bio-oil was 35.3% in the optimum condition where the temperature was 600 °C, the heating rate 200  $^{\circ}\text{C/min}$  and the nitrogen flow was 100 mL/min.

In view of its multiple applications, the interest in the liquid pyrolysis product has increased in the last 30 years. Thus, studies in fast pyrolysis have been growing, in which there have been investigations into the influence of the type of reactor; different biomasses such as sewage sludge, wood, rice husk, and swine manure; the variations in the conditions of fast pyrolysis have also been studied in order to optimize the reaction that is particular to each type of reactor and biomass in terms of the composition of the bio-oil [50]-[54].

## C. Flash Pyrolysis

Flash pyrolysis is characterized by a very short reaction time and very high heating rate. Although flash pyrolysis can be performed with any type of biomass, this reaction requires an even smaller particle size, in the range of 105-250  $\mu$ m. Using temperatures below 650 °C this reaction favors the formation of bio-oil, when using temperatures above 650 °C the gas yield tends to be higher [55]. Flash pyrolysis is further subdivided into certain types such as hydro pyrolysis and vacuum flash pyrolysis [18].

Pütün et al. [56] evaluated the effects of mass transfer and hydrogen pressure on the production and quality of bio-oil in the hydro-pyrolysis reaction of rigid Euphorbia. Hydro-pyrolysis is carried out under a pressurized hydrogen atmosphere, in order to reduce the oxygen content present in the bio-oil.

Pakdel et al. [57] investigated the production of oil from bituminous shales through the vacuum pyrolysis reaction. Vacuum pyrolysis provides a higher yield in bio-oil in that it limits the secondary decomposition reactions. This study also compared vacuum pyrolysis with other traditional extraction processes, in which vacuum pyrolysis showed the highest oil yield.

A study of the comparison of slow and flash of the raspberry seed was performed by Smets et al. [58]. The types of pyrolysis influenced the yield and properties of the products. Flash pyrolysis provided a higher liquid yield (53.6%) with high water content (26.2%) and higher heating values (HHVs) of 18.6 MJ/kg. In the slow pyrolysis, the liquid product was collected in three fractions as a function of temperature, where fraction 1 (220-320 °C) and 2 (320-350 °C) had a high water content different from fraction 3 (350-450 °C), which spontaneously separated into two fractions and had low water content and the organic fraction had a HHV of 27.0 MJ / kg.

Table 2 show the types of pyrolysis associated with biomass, particle size, temperature and yield of the products.

Types of pyrolysis related to biomass, temperature, particle size and yield.									
Biomass		Temperature (°C)	Particle size	Produced Fuel (%)			Ref.		
			( <b>mm</b> )	Coal	Bio-oil	Gas	Kel.		
Slow Pyrolysis	Geodae-Uksae 1	300	4-12	49.54	30.7	19.75	[42]		
	Sugar cane residue	500	<1	24.5	55.1	20.4	[59]		
	Coconut fiber	500	<1	38.7	39.1	22.2	[59]		
	Oryza sativa	500	<1	41	37.2	21.8	[59]		
wF	Palm kernel shell (PKS)	500	<1	32.2	51.4	16.4	[59]		
Slo	Wood rod of Maesopsis eminii	500	<1	22.3	59.5	18.2	[59]		
	Bark of Maesopsis eminii	500	<1	31.9	50.5	17.6	[59]		
	Rice straw	300	-	50.2	33	16.8	[59]		
Fast Pyrolysis	Linseed	550	0.6-1.8	12.5	62.7	24.8	[44]		
	Rice husk	450	0.63-1	26	70	4	[50]		
	Cotton seed	500	0.92	22	59.5	18.5	[51]		
	Sludge	500	0.42	24	45.3	17.7	[53]		
	Swine	600	0.6-1	6	18.48	36.15	[54]		
	Wilkweed	425	<2	27.91	44.19	27.90	[46]		
Flash Pyrolysis	Waste wood	550	<1	16.7	67.8	15.7	[55]		
	Euphorbia rigida	550	< 0.55	16	43	11	[56]		
	Raspberry seed	350	0.125-0.5	52.1	27	20.9	[58]		
		450	0.125-0.5	25.6	53.6	20.8	[58]		
FI		550	0.125-0.5	18.8	45	36.2	[58]		

TABLE II vpes of pyrolysis related to biomass, temperature, particle size and yield.

In the studies performed by Jeong et al. [54], it can be seen that the sum of oil, coal and gas yield does not reach 100% by weight because of the high ash content of the biomass. Also, according to Lee et al. [59] the yield was significantly influenced by the ash and lignin contents of the biomass which explains great differences in the yields of the products.

#### D. Catalytic Pyrolysis

Due to the fact that the pyrolysis bio-oil is not suitable for direct use as a fuel, pyrolysis is carried out in the presence of a catalyst with the main objective of improving the quality of the oil produced by the processes of slow, fast and flash pyrolysis [18].

Zeolites have often been used in catalytic pyrolysis of biomass. Samolada et al. [61] used zeolites (HZSM-5), transition metal catalysts (Fe/Cr) and aluminas to select catalysts capable of maintaining the amount of the liquid product with a minimum water production and also achieving a reduction of carbonyls during pyrolysis catalytic flash of biomass. HZSM-5 was the one that achieved the complete conversion of the carbonyl compounds of raw material into hydrocarbons and phenolic compounds. In relation to the minimum obtaining of water in the process, the optimum catalyst was the transition metal catalyst containing Fe and Cr through the form of oxides. All the catalysts employed showed increased gas yield.

Wang et al. [62] hydrotreated the bio-oil obtained from catalytic and non-catalytic pyrolysis. The results indicated that hydrodeoxygenation is facilitated in the catalytic pyrolysis bio-oil and that there is good synergy between catalytic pyrolysis and hydrotreated bio-oil for applicability as biofuel. In regard to the Pt / MZ-5 and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, the former showed the best performance in reducing the oxygen content in the bio-oil, this performance in justified by the mesoporous structure of the catalyst.

Xie et al. [63] studied the catalytic fast pyrolysis of microwave assisted sewage sludge using HZSM-5 as a catalyst. The temperature had a great influence on the pyrolysis process, in which the maximum yield of biooil and the lowest proportions of oxygen and nitrogen compounds in the bio-oil were obtained at 550 °C. The use of the catalyst decreased the yield of the biooil, however, it significantly reduced the proportions of oxygen and nitrogen-containing compounds. The HZSM-5 catalyst still showed good stability during pyrolysis.

Lu et al. [64] studied a new technique to obtain biooil rich in phenolic compounds from the fast catalytic pyrolysis of biomass impregnated with K3PO4. The presence of K3PO4 inhibited the devolatilization of holocellulose to form volatile organic compounds and promote the decomposition of lignin to form phenolic compounds, confirming positive results of  $K_3PO_4$  as a catalyst to selectively produce phenolic compounds of biomass.

A study of the catalytic effect of magnesium on fast pyrolysis in relation to the products obtained was carried out by Hwang et al. [65]. Table 3 shows the yield of the pyrolysis products as a function of the magnesium content in the biomass and the temperature.

Huber et al. [15] mentioned that bio-oil produced by pyrolysis has problems that limit its applications, among them, as already mentioned, high viscosity, and others such as poor volatility, coke, and corrosivity. However, as shown in Figure 2, bio-oil has a number of applications and can be treated for the purpose of being used as carrier fuel or as a chemical substance.

#### **III. BIO-OIL UPGRADING PROCESSES**

As commented previously, the direct use of bio-oil as fuel in transportation vehicles is not viable due to its high viscosity, high oxygen content, and oxidative instability. Therefore, in order to make bio-oil useful as a transport fuel, additional treatment is necessary [8]. There are basically seven types of treatments/upgrades for bio-oils: hydrotreating, hydrocracking, supercritical fluids, solvent addition, emulsification, steam reforming, and extraction [16].

Tield of biolinuss pyrotysis products impregnated with magnesium (Mg) [65].									
wt %	Bio-oil			Coal			Gas		
	450 °C	500 °C	550 °C	450 °C	500 °C	550 °C	450 °C	500 °C	550 °C
YP	59.7	52.6	46.8	9.6	8.4	5.8	30.7	39	47.5
D-YP	59.6	55.5	46.7	6.2	4.7	3.3	34.2	39.8	50
Mg-0.5	53.3	56.7	45.9	8.1	5.1	5.1	38.6	38.2	49
Mg-1.0	54	52.3	47.2	8.2	6.7	6.2	37.8	41	46.6
Mg-2.0	55.8	54.8	44.6	8.3	7.7	7	35.7	37.5	48.4

 TABLE III

 Yield of biomass pyrolysis products impregnated with magnesium (Mg) [65].

YP: Liriodendron tulipifera.

The most widely used process in the petroleum industry is hydrotreating. This process is a simple hydrogenation characterized by providing improvement in the quality of bio-oil without altering the boiling properties and it also is a non-destructive process. However, this process produces a high amount of coke (8-25%) and other products such as char and tar, and the quality of the fuel is inferior when compared to the other treatments [16].

Hydro-cracking is a thermal process in which besides hydrogenation, the biomass goes through a cracking process. This process occurs at moderatehigh pressures (0.7 to 14 MPa) [66]. The advantage of this process is the production of large quantities of light products. However, the costs involved in this process and the necessity of deactivating the catalyst are inconvenient elements of this treatment [16].

Among the new methods, supercritical fluid technology has been shown good results in the treatment of bio-oils [67]. Water is one of the compounds used for this treatment. Carbon dioxide (CO<sub>2</sub>) also has several advantages, such as easy obtention, cheapness, non-flammability, non-toxic and it exhibits supercritical behavior under mild conditions of temperature and pressure (31°C and 7.38 MPa) [68]. The characteristics of the solvent at supercritical conditions of gas-like diffusivity and liquid-like density promote good effects in the reaction, resulting in higher bio-oil yields and fuel of better quality (lower oxygen content, lower viscosity). As well as this, other solvents such as methanol [69], [70] and ethanol [71]-[73] have been used to improve the quality and yield of the final product.

Another type of treatment used is based on the use of solvent to change physical characteristics of the bio-oil, such as viscosity, and at the same time promote a reaction of esterification with oil components that prevent further chain growth [74]. This is a simple method used to decrease the viscosity of the bio-oil produced by pyrolysis and increase stability and heating value. Ethanol, methanol and acetic acid have been used for this propose [75]-[81]. Solid acid catalysts, solid base catalysts [82], ionic liquid catalysts [78], HZSM-5, and aluminum silicate catalysts have also been evaluated for esterification of bio-oils [83]-[85].

Emulsification is another possibility in the upgrading of bio-oil. The production of stable microemulsions, with 5–30% of bio-oil in diesel was investigated showing good results in the stability of bio-oil [86]-[89]. The emulsions produced by this mixture is less corrosive and show good properties of ignition. However, the heating value, water content, density, pH value, and ash content did not change, indicating that this process needs further research to show good improvements in other properties of the bio-oil

Steam reforming is also a possibility to be used in the upgrading of bio-oil. Production of hydrogen from

reforming bio-oil has been investigated showing good results in treated bio-oil. Reforming refers to the process of conversion of hydrocarbon gases and vaporized organic compounds into hydrogen and syngas [16].

Finally, the last possibility is the direct extraction of compounds from bio-oils, allowing for new possibilities for the co-products removed from this liquid fuel, such as phenols, volatile organic acids, nitrogen and n-alkanes [90], [91].

#### **IV.CONCLUSIONS**

Bio-oil is a product obtained from the pyrolysis of biomass that has important energy applications, which vary from its direct application in furnaces, boilers and turbines, to the production of chemicals of high added value. There are 3 types of pyrolysis (slow, fast, flash), and the characteristics of the bio-oil produced depends on several factors such as the composition of the original lignocellulosic material, content of inorganic material, characteristic of the raw material, and operating conditions.

To be used directly as a fuel in transportation vehicles, a treatment of bio-oil is required, and seven types of processes has been considered for this goal: hydrotreating, hydro-cracking, supercritical fluids, solvent addition, emulsification, steam reforming, and extraction. In all of these, research and investment are necessary to improve the products obtained, and to reduce the costs involved in the process.

It is observed that there are many studies involving pyrolysis and processes of upgrading of bio-oil, showing the great importance of thermo-conversion to overcome the great need of energy and the need to reduce the use of fossil fuels by using a raw material of cheap origin, as is biomass. The search for renewable energy solutions with the use of biomass has increased in recent years, and the need for studies is strengthened due to the need to know and improve the already established processes.

In this sense, the present work showed the great range of possibilities and the different ways of obtaining the bio-oil with the advantages and limitations observed in each case. There is still a need for research and investments to develop and disseminate knowledge and advances in this area, since the discovery of bio-oil brings new perspectives and new routes to obtain renewable energy for the whole world.

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#### REFERENCES

[1] U. Schuchardt, M. L. Ribeiro, and A. R. Gonçalves, "A indústria petroquímica no próximo século: como substituir o

petróleo como matéria-prima?", Quím. Nova, vol. 24, pp. 247-251, 2001.

- [2] F. Cherubini, N. D. Bird, A. Cowie, G. Jungmeier, B. Schlamadinger, and S. Woess-Gallasch, "Energy and greenhouse gas-based LCA of biofuel and bioenergy systems: Key issues, ranges and recommendations", Resour. Conserv. Recycl., vol. 53, pp. 434–447, 2009.
- [3] A. Demirbas, "Biomass resouce facilities and biomass conversion processing for fuels and chemicals", Energy Convers. Manag., vol. 42, pp. 1357–1378, 2001.
- [4] H. B. Goyal, D. Seal, and R.C. Saxena, "Bio-fuels from thermochemical conversion of renewable resources: a review", Renew. Sustain. Energy Rev., vol. 12, pp. 504–517, 2008.
- [5] F. Cherubini, "The biorefinery concept: Using biomass instead of oil for producing energy and chemicals", Energy Convers. Manag., vol. 51, pp. 1412–1421, 2010.
- [6] J. M. M. Perez, "Tests in a fast pyrolysis plant biomass fluidized: criteria for optimization" (Original title: Testes em uma planta de pirólise rápida de biomassa em leito fluidizado: critérios para sua otimização). Thesis. Faculty of Agricultural Engineering, State University of Campinas, Campinas, Brazil, 2004.
- [7] A. V. Bridgwater, "Biomass for energy", J. Sci. Food Agr., vol. 86, pp.1755-1768, 2006.
- [8] A. V. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading", Biomass Bioenerg, vol. 38, pp. 68-94, 2012.
- [9] C. V. Huynh, and S. Kong, "Performance characteristics of a pilot-scale biomass gasifier using oxygen-enriched air and steam", Fuel, vol. 103, pp. 987–996, 2013.
- [10] C. Hindsgaul, J. Schramm, L. Gratz, U. Henriksen, and J. Dall Bentzen, "Physical and chemical characterization of particles in producer gas from wood chips", Bioresour. Technol., vol. 73, p. 147–155, 2000.
- [11] N. S. Barman, and S. Ghosh, "Gasification of biomass in a fixed bed downdraft gasifier: a realistic model including tar", Bioresour. Technol., vol. 107, pp. 505–511, 2012.
- [12] R. C. Brown, "Biorenewable resources: engineering new products from agriculture. Iowa State Press 2003.
- [13] A. V. Bridgwater, "Renewable fuels and chemicals by thermal processing of biomass", Chem. Eng. J., vol. 91, pp. 87–102, 2003.
- [14] H. V. Ly, J. Kim, and S. S. Kim, "Pyrolysis characteristics and kinetics of palm fiber in a closed reactor", Renew. Energy, vol. 54, pp. 91–95, 2013.
- [15] G. W. Huber, S. Iborra, and A. Corma, "Synthesis of Transportation Fuels From Biomass: Chemistry, Catalysts, and Engineering", Chem. Rev., vol.106, pp.4044-4098, 2006.
- [16] S. Xiu, and A. Shahbazi, "Bio-oil production and upgrading research: A review" Renew. Sustain. Energy Rev, vol. 16, pp. 4406-4414, 2012.
- [17] D. Meier, and O. Faix, "State of the art of applied fast pyrolysis of lignocellulosic materials a review", Bioresour. Technol., vol. 68, pp. 71-77, 1999.
- [18] H. B. Goyal, D. Seal, and R. C. Saxena, "Bio-fuels from thermochemical conversion of renewable resources: A review", Renew. Sustain. Energy Rev., vol. 12, pp. 504–517, 2008.
- [19] A. Oasmaa, and S. Czernik, "Fuel Oil Quality of Biomass Pyrolysis Oils-State of the Art of The End Users", Energ. Fuels, vol.13, pp.914-921,1999.
- [20] Z. Luo, S. Wang, Y. Liao, J. Zhou, Y. Gu, and K. Cen, "Research on biomass fast pyrolysis for liquid fuel", Biomass Bioenerg., vol. 26, pp. 455 – 462, 2004.
- [21] A. V. Bridgwater, and K. Maniatis, K, "Chapter 10. The production of Biofuels by the Thermochemical Processing of Biomass", Archer MD, Barber J. Molecular to Global Photosynthesis. IC Press, p.521-612, 2004.
- [22] A. V. Bridgwater, "Biomass Fast Pyrolysis", Therm. Sci., vol. 8, pp.21-49, 2004.
- [23] A. V. Bridgwater, and S. A. Bridge, "A review of Biomass Pyrolysis and Pyrolysis Technologies", In: A. V. Bridgwater, G. Grassi (Eds.). Biomass pyrolysis liquids upgrading and utilization. London: Elsevier Applied Science, 1991.

- [24] A. V. Bridgwater, S. Czenick, and J. Piskorz, "An Overview of Fast Pyrolysis", In: (Ed.). Progress in Thermochemical Biomass Conversion. [S.1] IEA Bioenergy; Blackwell Sciences, 2001.
- [25] A. V. Bridgwater, S. Czernik, and J. Piskorz, "The Status of Biomass Fast Pyrolysis", Fast Pyrolysis of biomass: A Handbook. [S. l.:] A. Bridwater Editor, IEA Bioenergy, 2002.
- [26] ANP (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis). (2007). Available:<a href="http://www.anp.gov.br">http://www.anp.gov.br</a>>.
- [27] CETESB (Companhia de Tecnologia de Saneamento Ambiental do Estado de São Paulo). (2006). Available: < http://www.cetesb.sp.gov.br/emergencia/acidentes/vazament o/oleo/a\_fisicos.asp>.
- [28] P. Penido Filho. <sup>4</sup>Os motores de combustão interna", Ed. Lemi, 1983.
- [29] D. Vlassov, "Combustíveis, combustão e câmaras de combustão", Ed. UFPR, 2001.
- [30] M. R. P. Samaniego, "Use of biofuels from the rapid pyrolysis of sugarcane straw in an Otto cycle engine" (Original title: Uso de biocombustível da pirólise rápida da palha de cana em um motor de ciclo Otto). Master Diss., Faculty of Mecanical Engineering, State University of Campinas, Campinas, Brazil, 2007.
- [31] E. O. Gómez. "Study of the rapid pyrolysis of elephantgrass in bubbling fluidized bed by characterization of coal fines" (Original title: Estudo da pirólise rápida de capim elefante em leito fluidizado borbulhante mediante caracterização dos finos de carvão), Thesis, State University of Campinas, Campinas, Brazil, 2002.
- [32] L. O. Santos. "Study to obtain bio-oil of 2nd generation through the pyrolysis of aquatic plants" (Original Title: Estudo para obtenção de bio-óleo de 2ª geração através da pirólise de plantas aquáticas). Master Diss., Federal University of Sergipe, Aracaju, Brazil, 2013.
- [33] J. M. M. Perez. "Tests in a fast pyrolysis plant of fluidized bed biomass: criteria for its optimization" (Original title: Testes em uma planta de pirólise rápida de biomassa em leito fluidizado: critérios para sua otimização). Thesis, Faculty of Agricultural Engineering, State University of Campinas, Campinas, Brazil, 2004.
- [34] M. B. B. Almeida. "Bio-oil from rapid, thermal or catalytic pyrolysis of sugarcane and its co-processing with gas oil in catalytic cracking" (Original title: Bio-óleo a partir da pirólise rápida, térmica ou catalítica da cana-de-açúcar e seu co-processamento com gasóleo em craqueamento catalítico). Master Diss. Chemistry School, UFRJ, Brazil, 2008.
- [35] D. A. Bulushev, and J. R. H. Ross, "Catalysis for conversion of biomass to fuels via pyrolysis and gasification: A review", Catal. Today, vol. 171, pp. 1–13, 2011.
- [36] A. M. Dehkhoda, A. H. West, and N. Ellis, "Biochar based solid acid catalyst for biodiesel production", Appl. Catal., A. vol. 382, pp. 197–204, 2010.
- [37] J. Lehmann, M. C. Rillig, J. Thies, C. A. Masiello, W. C. Hockaday, and D. Crowley, "Biochar effects on soil biota - A review", Soil Biol. Biochem. vol. 43, pp. 1812-1836, 2011.
- [38] M. Ahmad, A. U. Rajapaksha, J. E. Lim, M. Zhang, N. Bolan, D. Mohan, M. Vithanage, S. S. Lee, and Y. S. Ok, "Biochar as a sorbent for contaminant management in soil and water: A review", Chemosphere, vol. 99, pp. 19–33, 2014.
- [39] O. Ioannidou, and A. Zabaniotou, "Agricultural residues as precursors for activated carbon production—A review. Renew", Sustain. Energy Rev. 11 (2007) 1966–2005.
- [40] A. Shaaban, S. Se, M. F. Dimin, J. M. Juoi, M. H. M. Husin, and N. M. M. Mitan, "Influence of heating temperature and holding time on biocharsderived from rubber wood sawdust via slow pyrolysis", J. Anal. Appl. Pyrolysis, vol. 107, pp. 31–39, 2014.
- [41] D. Chen, J. Zhou, and Q. Zhang, "Effects of heating rate on slow pyrolysis behavior, kinetic parameters and products properties of moso bamboo", Bioresour. Technol., vol. 169, pp. 313–319, 2014.
- [42] Y. Lee, P. Eum, C. Ryu, Y. Park, J. Jung, and S. Hyun, "Characteristics of biochar produced from slow pyrolysis of Geodae-Uksae 1". Bioresour. Technol., vol. 130, pp. 345– 350, 2013.

- [43] K. Crombie, and O. Masek, "Investigating the potential for a self-sustaining slow pyrolysis system under varying operating conditions", Bioresour. Technol., vol. 162, pp. 148–156, 2014.
- [44] C. Acıkgoz, O. Onay, and O.M. Kockar, "Fast pyrolysis of linseed: product yields and compositions", J. Anal. Appl. Pyrolysis, vol. 71, pp. 417–429, 2004.
- [45] H. Ben, and A. J. Ragauskas, "Comparison for the compositions of fast and slow pyrolysis oils by NMR Characterization", Bioresour. Technol., vol. 147, pp. 577– 584, 2013.
- [46] S. Kim, and F. A. Agblevor, "Thermogravimetric analysis and fast pyrolysis of Milkweed", Bioresour. Technol., vol. 169, pp. 367–373, 2014.
- [47] S. Czernik, D. K. Johnson, and S. Black, "Stability of wood fast pyrolysis oil", Biomass Bioenerg., vol. 7, pp. 187-192, 1994.
- [48] X. Bai, K. H. Kim, R. C. Brown, E. Dalluge, C. Hutchinson, Y. J. Lee, and D. Dalluge, "Formation of phenolic oligomers during fast pyrolysis of lignina", Fuel, vol. 128, pp. 170–179, 2014.
- [49] M. Kiliç, E. Pütün, and A. E. Pütün, "Optimization of Euphorbia rigida fast pyrolysis conditions by usingresponse surface methodology", J. Anal. Appl. Pyrolysis, vol.110, pp.162-171, 2014.
- [50] J. Alvarez, G. Lopez, M. Amutio, J. Bilbao, and M. Olazar, "Bio-oil production from rice husk fast pyrolysis in a conical spouted bed reactor", Fuel, vol. 128, pp. 162–169, 2014.
- [51] E. Apaydin-Varol, B. B. Uzun, E. Önal, and A. E. Pütün, "Synthetic fuel production from cottonseed: Fast pyrolysis and a TGA/FT-IR/MS study", J. Anal. Appl. Pyrolysis, vol. 105, pp. 83–90, 2014.
- [52] M. Atienza-Martinez, I. Fonts, L. Lazaro, J. Ceamanos, and G. Gea, "Fast pyrolysis of torrefied sewage sludge in a fluidized bed reactor", Chem. Eng. J., vol. 259, pp. 467–480, 2015.
- [53] X. Huang, J. Cao, P. Shi, X. Zhao, X. Feng, Y. Zhao, X. Fan, X. Wei, and T. Takarada, "Influences of pyrolysis conditions in the production and chemical composition of the bio-oils from fast pyrolysis of sewage sludge", J. Anal. Appl. Pyrolysis, vol. 100, pp. 353-362, 2014.
- [54] Y. W. Jeong, S. K. Choi, Y. S. Choi, and S. J. Kim, "Production of biocrude-oil from swine manure by fast pyrolysis and analysis of its characteristics", Renew. Energy, vol. 79, pp. 14-19, 2015.
- [55] P. A. Horne, and P. T. Williams, "Influence of temperature on the products from the flash pyrolysis of biomass", Fuel, vol. 75, pp. 1051-1059, 1996.
- [56] A. E. Pütün, H. F. Gerçel, O. M. Koçkar, O. Ege, C. E. Snapet, and E. Pütün, "Oil production from an arid-land plant: fixed-bed pyrolysis and hydropyrolysis of Euphorbia rígida", Fuel, vol. 75, pp. 1307-1312, 1996.
- [57] H. Pakdel, C. Roy, and W. Kalkreuth, "Oil production by vacuum pyrolysis of Canadian oil shales and fate of the biological markers", Fuel, vol. 78, pp. 365-375, 1999.
- [58] K. Smets, S. Schreurs, R. Carleer, and J. Yperman, "Valorization of raspberry seed cake by flash and slow pyrolysis: Product yield and characterization of the liquid and solid fraction", J. Anal. Appl. Pyrolysis, vol. 107, pp. 289– 297, 2014.
- [59] Y. Lee, J. Park, C. Ryu, K. S. Gang, W. Yang, Y. Park, J. Jung, and S. Hyun, "Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500 °C", Bioresour. Technol., vol. 148, pp. 196–201, 2013.
  [60] J. Park, Y. Lee, C. Ryu, and Y. Park, "Slow pyrolysis of rice
- [60] J. Park, Y. Lee, C. Ryu, and Y. Park, "Slow pyrolysis of rice straw: Analysis of products properties, carbon and energy yields", Bioresour. Technol. vol. 155, pp. 63–70, 2014.
- [61] M. C. Samolada, A. Papafotica, and I. A. Vasalos, "Catalyst Evaluation for Catalytic Biomass Pyrolysis", Energ. Fuel., vol. 14, pp. 1161-1167, 2000.
- [62] Y. Wang, T. He, K. Liu, J. Wu, and Y. Fang, "From biomass to advanced bio-fuel by catalytic pyrolysis/hydro-processing: Hydrodeoxygenation of bio-oil derived from biomass catalytic pyrolysis", Bioresour. Technol. vol. 108, pp. 280– 284, 2012.

- [63] Q. Xie, P. Peng, S. Liu, M. Min, Y. Cheng, Y. Wan, Y. Li, X. Lin, Y. Liu, P. Chen, and R. Ruan, "Fast microwave-assisted catalytic pyrolysis of sewage sludge for bio-oil production", Bioresour. Technol. vol. 172, pp. 162–168, 2014.
- [64] Q. Lu, Z. Zhang, X. Yang, C. Dong, and X. Zhu, "Catalytic fast pyrolysis of biomass impregnated with K3PO4 to produce phenolic compounds: Analytical Py-GC/MS study", J. Anal. Appl. Pyrolysis, vol. 104, pp. 139–145, 2013.
- [65] H. Hwang, S. Oh, I. Choi, and J. W. Choi, "Catalytic effects of magnesium on the characteristics of fast pyrolysis products – Bio-oil, bio-char, and non-condensed pyrolytic gas fractions", J. Anal. Appl. Pyrolysis, vol. 113, pp. 27-34, 2015.
- [66] J. Ancheyta, and J.G. Speight, "Hydroprocessing of Heavy Oils and Residua". FI U.S.A., CRC press, 2007.
- [67] S. R. C. Sena, and C. G. Pereira, "Bio-Oil Upgrading by Supercritical Technology and Conventional Processes", IV Prosciba, Cartagena das Indias, Chile, 2016.
- [68] C. G. Pereira, and M. A. A. Meireles, "Supercritical Fluid Extraction of Bioactive Compounds: Fundamentals, Applications and Economic Perspectives", Food Bioprocess. Tech., vol.3, pp. 340-372, 2009.
- [69] S. Cheng, L. Wei, J. Julson, K. Muthukumarappan, and P.R. Kharel, "Upgrading pyrolysis bio-oil to hydrocarbon enriched biofuel over bifunctional Fe-Ni/HZSM-5 catalyst in supercritical methanol", Fuel Process. Technol., vol. 167, pp. 117-126, 2017.
- [70] S. Cheng, L. Wei, J. Julson, K. Muthukumarappan, and P.R. Kharel, "Upgrading pyrolysis bio-oil to biofuel over bifunctional Co-Zn/HZSM-5 catalyst in supercritical methanol", Energ. Convers. Manage., vol. 147, pp. 19-28, 2017.
- [71] S. Brand, and J. Kim, "Liquefaction of major lignocellulosic biomass constituents in supercritical ethanol", Energy, vol. 80, pp. 64-74, 2015.
- [72] H. Jo, D. Verma, J. Kim, "Excellent aging stability of upgraded fast pyrolysis bio-oil in supercritical ethanol", Fuel, vol. 232, pp. 610-619, 2018.
- [73] W. Chen, Z. Luo, C. Yu, G. Li, and H. Zhang, "Upgrading of bio-oil in supercritical ethanol: Catalysts screening, solvent recovery and catalyst stability study", J Supercrit. Fluid., vol. 95, pp. 387-393, 2014.
- [74] A. Oasmaa, E. Kuoppala, J.F. Selin, S. Gust, and Y. Solantausta, "Fast pyrolysis of forestry residue and pine. 4. Improvement of the product quality by solvent addition", Energ. Fuel., vol. 18, pp. 1578–1583, 2004.
- [75] F. Mahfud, I. Meli\_An-Cabrera, R. Manurung, and H. Heeres, "Biomass to fuels: Upgrading of flash pyrolysis oil by reactive distillation using a high boiling alcohol and acid catalysts", Process. Saf. Environ., vol. 85, pp.466–472, 2007.
- [76] J. Xu, J. Jiang, Y. Sun, and Y. Lu. "Bio-oil upgrading by means of ethyl ester production in reactive distillation to remove water and to improve storage and fuel characteristics", Biomass Bioenerg., vol., 32, pp. 1056–1061, 2008.
- [77] Y. Tang, W. Yu, L. Mo, H. Lou, and X. Zheng. "One-step hydrogenation-esterification of aldehyde and acid to ester over bifunctional pt catalysts: A model reaction as novel route for catalytic upgrading of fast pyrolysis bio-oil", Energ Fuel., vol. 22, pp. 3484–3488, 2008.
- [78] W. M. Xiong, M. Z. Zhu, L. Deng, Y. Fu, and Q.X. Guo, "Esterification of organic acid in bio-oil using acidic ionic liquid catalysts", Energ Fuel., vol. 23, pp. 2278–2283, 2009.
- [79] J. Wang, J. Chang, and J. Fan, "Upgrading of bio-oil by catalytic esterification and determination of acid number for evaluating esterification degree", Energ. Fuel., vol. 24, pp. 3251–3255, 2010.
- [80] R. N. Hilten, B. P. Bibens, J. R. Kastner, and K. C. Das, "Inline esterification of pyrolysis vapor with ethanol improves bio-oil quality", Energ. Fuel., vol. 24, pp. 673–682, 2010.
- [81] W. Yu, L. Mo, H. Lou, and X. Zheng, "One-step hydrogenation-esterification of aldehyde and acid to ester over bifunctional pt catalysts: A model reaction as novel route for catalytic upgrading of fast pyrolysis bio-oil", Energ. Fuel., vol. 22, pp. 3484–3488, 2009.

- [82] Q. Zhang, J. Chang, and T.J. Wang, "Upgrading bio-oil over different solid catalysts", Energ. Fuel., vol.20, pp. 2717– 2720, 2006.
- [83] J. Peng, P. Chen, H. Lou, and X. Zheng, "Upgrading of biooil over aluminum silicate in supercritical ethanol", Energ. Fuel., vol. 22, pp. 3489–3492, 2008.
- [84] J. Peng, P. Chen, H. Lou, and X. Zheng, "Catalytic upgrading of bio-oil by HZSM-5 in sub- and super-critical ethanol", Bioresource Technol., vol.100, pp. 3415–3418, 2009.
- [85] D. Chiaramonti, M. Bonini, E. Fratini, G. Tondi, K. Gartner, A.V. Bridgwater, H.P. Grimm, I. Soldaini, A. Webster, and P. Baglioni, "Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines — Part 1: Emulsion production", Biomass Bioenerg., vol. 25, pp. 85– 99, 2003.
- [86] D. Chiaramonti, M. Bonini, E. Fratini, G. Tondi, K. Gartner, A.V. Bridgwater, H.P. Grimm, I. Soldaini, A. Webster, and P. Baglioni, "Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines — Part 2:

Tests in diesel engines", Biomass Bioenerg., vol. 25, pp. 101-11, 2003.

- [87] M. Ikura, M. Stanciulescu, and E. Hogan, "Emulsification of pyrolysis derived bio-oil in diesel fuel", Biomass Bioenerg., vol. 3, 221–232, 2003.
- [88] X. Jiang, and N. Ellis, "Upgrading bio-oil through emulsification with biodesel: Mixture production", Energ. Fuel., vol. 24, pp. 1358–1364, 2010.
- [89] M. Garcia-Perez, J. Shen, X. Wang, and C. Li, "Production and fuel properties of fast pyrolysis oil/bio-diesel blends", Fuel Process. Technol., vol. 91, pp. 296–305, 2010.
- [90] A. B. Ross, P. Biller, M. L. Kubacki, H. Li, A. Lea-langton, and J. M Jones, "Hydrothermal processing of microalgae using alkali and organic acids", Fuel vol. 89, pp. 2234–2243, 2010.
- [91] R. M. Gallivan, and P. K. Matschei, "Fraction of oil obtained by pyrolysis of lignocellulosic materials to recover a phenolic fraction for use in making phenolic fraction for use in making phenol-formaldehyde resins", US Patent No. 42009647; 1980.