A Review of Physical Properties of Biomass Pyrolysis Oil

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Abstract- The article has made a discussion and review on the physical properties and behaviour of the bio-oil produced by the pyrolysis process from various biomasses at different operating conditions. An attempt has also been done to suggest and mention the various causes for the poor quality of bio-oil which requires up-gradation to make it suitable for transportation fuel. The effects of various parameters such as type of biomass, particle size of the biomass, type of reactor, pyrolysis temperature, condensing temperature, use of hot filter, type of reactor etc. on the behaviour of the bio-oil are also discussed. The summary of the discussion pertains a need of optimisation of various parameters to get a suitable fuel, as controlling of one parameter although improves a particular property of the bio-oil, at the same time it may lead to deteriorate another property.

Keywords—Pyrolysis; biomass; reactor; physical properties; hot filter; electrostatic precipitator; heating vale; pH value; ash content; hydrodeoxygenation.

1. Introduction

Today, the world is facing a great demand of fuel and on the other hand, the crisis of it at the same time is another burning problem. The fossil fuel available in the earth will no more be able to support this increased amount of energy demand in the near future. Pollution is another serious matter of concern across the world for which the production and use of fossil fuel is mainly responsible. So, the researchers are now searching and trying to produce the alternate fuel so that it can fulfil the increasing demand of energy and can keep the world clean for the upcoming generation. Out of many renewable energy resources, biomass is one of the sources of energy which is abundantly available in each part of the world. The biomass can be used as energy in many ways, e.g. just burning or by converting it into gaseous and liquid form. As compared to conventional fuel, the biomass has negligible emission of CO_2 to the environment. The biomass can be converted into liquid using different methods such as, biochemical and thermochemical. In biochemical method, the biomass conversion is carried out using metabolic action of microorganism or bacteria. The thermochemical conversion of biomass, which includes pyrolysis and hydrothermal liquefaction, has found to be more convenient and economical than the other methods. Pyrolysis is the technique of biomass conversion into gaseous form with the application of heat in oxygen free condition. The vapour produced in the pyrolysis, can be converted into liquid by condensing this vapour which is known as bio-oil or pyrolysis oil. Pyrolysis can process all type of biomasses and some other substances such as rubber, plastic etc., which cannot be done by any other methods. There are many advantages of liquid over the solid form of biomass, as the liquid contains more energy and it is easier for the transportation and storage compared to the solid biomass. Pyrolysis process can be broadly divided into two categories: fast and slow pyrolysis. Xiu and Shahbazi [1] found that the quality of bio-oil obtained from hydrothermal liquefaction is higher than that of pyrolysis oil; however it appears inferior as compared to the conventional fuel, so, it is still requires some up-gradation to make it suitable for the use. Blin et al. [2] carried out the biodegradability test on the pyrolysis oil and found it as biodegradable. The quality of the bio-oil has the impacts on its performance when it is used for various purposes. Therefore it is very essential to check the properties of the bio-oil to make it ready before use. The behaviour and the properties of bio-oil depend on many factors such as, size of the feed stocks, rate of feeding, type of biomass, moisture content in the sample, type of reactor used, heating rate and temperature, type of condensation etc. Researchers have already been done many works related to analyses of the pyrolysis oil and up-gradation of its properties but still it seems some needs for the optimum application of the various parameters to get a suitable liquid fuel. In this article an overall discussion and review has been made on the physical properties of the pyrolysis oil produced from various biomasses at different conditions used so far.

2. Review of the Pyrolysis Oil Properties

The analysis of behaviour of the bio-oil properties is very important as the quality of any oil depends on its physical and chemical properties and the suitability of the oil for a specific work can be identified from these. The physical properties include viscosity, heating value, density, water content, oxygen content, pH value, density and solid contents etc., whereas the identification of various chemical compounds present in the bio-oil, various functional group and their chemical bonding etc. are included in the chemical properties. In a number of publications, the various physical properties of the pyrolysis oil from different biomasses, in various conditions has been presented and from all these **data**, it is clear that, the pyrolysis oil cannot be used directly as transportation fuel and needs further treatment and up-gradation, for example, Bertero et al.[3] compared the characteristics of the pyrolysis oil and the thermally treated pyrolysis oil of pine saw dust, mesquite saw dust and wheat shell, and the special observation was that, in the treated oil, the conradson carbon residue (CCR) was very less, on the other hand, the effective hydrogen index was found very high as compared to the untreated bio-oil. There are lots scopes for study in the optimization of various parameters and operating conditions and application of different process to get a suitable oil product. A review of the physical properties of different types of pyrolysis oil at various conditions has been made and some probable solutions are suggested based on these.

2.1. Viscosity

Viscosity is a very important property of bio-oil, which determines the flow quality or fluidity of the liquid. It has a big role on the design and manufacturing of engines where a liquid fuel is used. As the viscosity of a liquid increases, it creates some disturbances in pumping and atomization. Many techniques or processes such as addition of polar solvents like methanol or acetone can be applied to reduce the viscosity but at the same time, it effects on some **other** properties also [4].

The viscosity of the pyrolytic oil varies in a wide range as it is produced from various biomasses, at different operating conditions using different parameters. It is obvious that the viscosity of the pyrolysis oil varies with the type of biomasses as the biological and chemical compositions are not same in all biomasses. The percentage of three main constituents of biomass: cellulose, hemicelluloses and lignin are not same in the biomasses, where the cellulose and hemicelluloses are easily decomposed on heating; however lignin is difficult to break, as it is a 3D complex polymer and enhance in producing tar in pyrolysis. Further, the viscosity depends on many factors which can be observed from detailed literature reports of pyrolytic oil production from biomasses, some of which are discussed below.

The bio-oil produced from two different type of biomasses often shows different viscosity although it is produced at the same conditions e.g. in the publication of Sipila et al. [5], the viscosity of the pyrolysis oil from the biomasses such as wheat straw, pine and ensyn (hard wood) were found as 11 cSt, 46 cSt and 50 cSt respectively at 50 ^{0}C. According to Feng et al. [6], the viscosity of the bio-oil obtained from saw dust is higher as compared to rice husk which were found to be as 240 cSt and 128 cSt respectively; however in the bio-oil from the mixture of rice husk and saw dust, the viscosity lies in between these two, when the particle size for both the feedstock was around 0.3 mm. The viscosity of the bio-oil obtained from the biomasses of particle size 0.1-0.5 mm, were determined by Lu et al. [7] and Lu [8], and found as 125 mm^2/s and 138 mm^2/s respectively, but when the particle size was taken as 1.5-5 mm, the viscosity was found in the range of 36-71 cSt according to Sundaram and Natarajan [9], and Park et al. [10]. From these reported data it can be presumed that the smaller size biomass feedstock gives high viscous oil. It can be noted that viscosity does not depend much on the type of reactor rather than other parameters, as the bio-oil from pine and oak wood shows the viscosity as 60.9 cSt and 41.6 cSt at 50 ^{0}C, which are similar with other bio-oils when these were produced using an auger reactor according to the research work of Ingram et al. [11]. Similarly, the viscosities of the bio-oil from rapeseed and soybean oil cake using same type of reactor, were found as 42.6 cSt and 72.38 cSt measuring at 50 ^{0}C [12, 13]. The bio-oil which is kept or stored for certain period is known as ageing of bio-oil and the its quality changes due to this ageing effect. Qiang et al. [14] found that viscosity significantly increases continuously with the increase of duration of storage time, since during storage the volatile substance and the water present in the bio-oil get the opportunity for evaporation and thus the liquid becomes more viscous; for example, in fresh pyrolysis oil obtained from rice husk using fluidised bed reactor, the viscosity was found as 128 cSt, at 20 ^{0}C; however its value further increases up to 220 cSt when it is stored for 80 days, similarly the viscosity of the bio-oil was found in the range of 40-90 cSt at 60 ^{0}C, when it was stored for 30 days [6,15]. The use of hot vapour filter could be one technique for reduction of viscosity in the pyrolysis oil. It can reduce the viscosity to around 13-38 % in fresh bio-oil whereas in case of aged bio-oil it can reduce up to 95 %. The variation of viscosity of bio-oil from two biomasses with and without hot filter in fresh and aged bio-oil is shown in figure 1 [16]. From this figure, it has been observed that due to ageing, the viscosity tremendously increases which can be prevented by the help of using hot vapour filter.

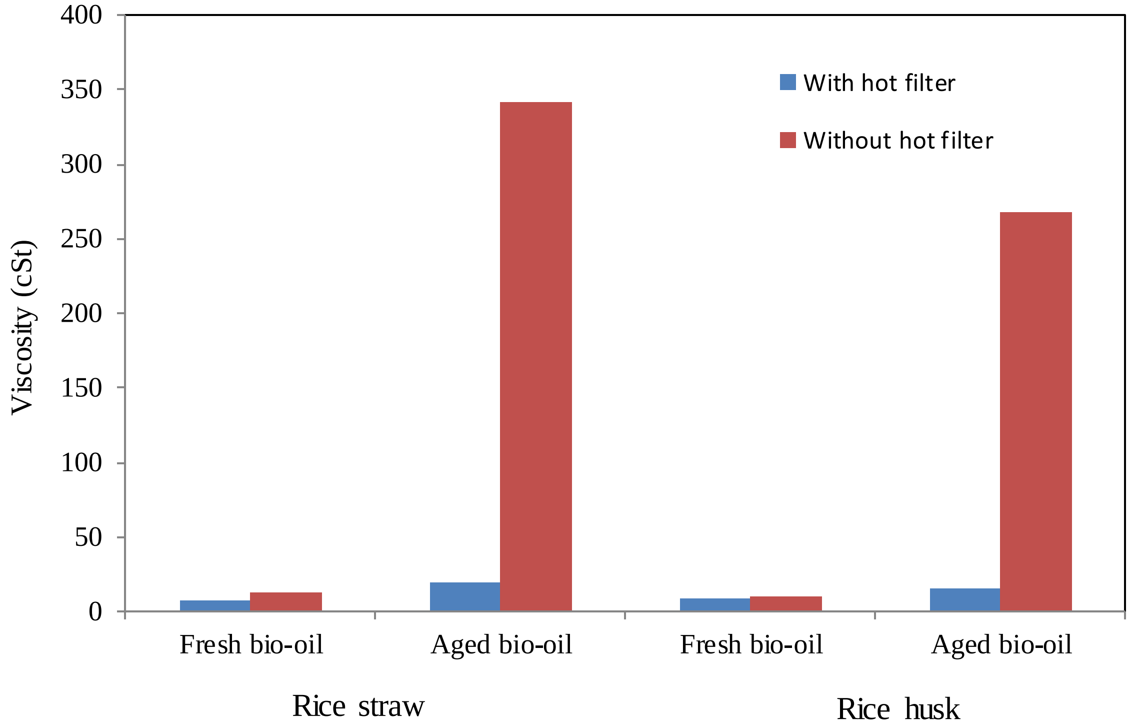

Figure 1. Variation of viscosity fresh and aged bio-oil with and without hot filter.

According to Parez et al.[17], in sugarcane bagasse pyrolysis oil, the viscosity was 116.5 cSt and 26.7 cSt at 20 ^{0}C and 40 ^{0}C respectively, again it decreased up to 4.1 cSt, when the temperature was increased to 90 ^{0}C, which is similar to the viscosity of oil used in gas turbine application (3-4 cSt at 90 ^{0}C). Qiang et al.[14] showed the similar effect of viscosity with the temperature as the kinematic viscosity of the bio-oil from the rice husk, which was found as 13.2 cSt measured at 40 ^{0}C and continuously decreased up to 2 cSt, when the temperature was increased to 90 ^{0}C. So from these reports, it is found that the bio-oil shows more viscosity at low temperature and less at higher temperature. By condensing the vapour at very lower temperature such as − 5 ^{0}C helps in reducing the viscosity as compared at high temperature like 60 ^{0}C [17]. The effect of multiple condensers and electrostatic precipitator (ESP) on viscosity has shown in Table 1. The aim of installation of ESP was to improve the quality of bio-oil in terms of calorific value, but it badly affected the viscosity as the viscosity increased to a very high value [19].

Table 1. Viscosity of sweet sorghum bagasse bio-oil using multiple condensers at different condensing temperatures.

Temperature (^{0}C)	Viscosity in mm^2/s (cSt)			
	C-1* (37 ^{0}C)	C-2* (25 ^{0}C)	C-3* (24 ^{0}C)	ESP
30	2.04	124.35	277.02	1093.03
40	1.89	41.39	90.15	445.86
50	1.48	23.46	45.21	224.57
60	1.23	11.25	32.15	91.68

C-1*: condenser 1
C-2*: condenser 2
C-3*: condenser 3

Xiu et al. [20] investigated the properties of bio-oil using hydrothermal pyrolysis from swine manure and the viscosity at 50 ^{0}C was found as 843 cSt which is a very high value as in hydrothermal pyrolysis, the decomposed fragments repolymerize and produce a heavy tarry oily product with high viscosity. The amount of water content present in the bio-oil affects many properties, out of which the viscosity is one of them, such that higher water content reduces the viscosity of the bio-oil very significantly, even the bio-oil from same biomass (rice husk) at same operating conditions may have different viscosity due to the variation of water content present in the bio-oil [21, 22]. The pyrolysis oil from alga in a continuous fluidised bed reactor was investigated by Guo et al. [23] and a very low viscosity i.e. 1.15 cSt, was found at 40 ^{0}C, where the moisture content was as high as 86.1 %; but the high water content has bad impact on the bio-oil quality such as reducing calorific value. The whole sugarcane and sugarcane straw was pyrolysed and bio-oil was produced in a fluidised bed reactor pilot plant for the comparative study and the viscosity of the bio-oil measuring at 60 ^{0}C for sugarcane straw and the whole sugarcane were found as 0.5 pa.s and 0.4 pa.s respectively [24]. The heating rate and pyrolysis temperature has less impact on the viscosity of the bio-oil, as variation of temperature and heating rate do not show significant variation of viscosity, although because of some other parameters, it shows some difference [9, 12, 13, 22].

2.2. Heating Value

The heating value or the calorific value of any oil indicates the energy content present in it, which is an important parameter for the selection of the oil for a particular application. As the calorific value increases, the oil becomes more efficient and useful. So, the determination of the calorific value is very essential before selecting it for any purpose. The heating value can be determined using bomb calorimeter or using Dulong formula based on ultimate analysis of the sample. There are two types of heating value: higher heating value (HHV) and lower heating value (LHV). The relation between these two heating values can be expressed as $LHV_{dry} = HHV_{dry} — 2.442(8.936H/100)$, where H is the weight percentage of hydrogen on dry basis [25]. The heating value of a bio-oil depends mainly on some factors, such as water content, oxygen content and the operating conditions of the pyrolysis process. According to literature, the calorific value in most of the bio-oils are found within 15-36 MJ/kg [26, 27, 28, 29] which is always lower than that of conventional petroleum fuels (40-50 MJ/kg).

According to Xiujuan et al. [21], both water and oxygen content has negative impact on the heating value. Because of high oxygen content (>50 %) and water content (>30 %) the heating value of the bio-oil reduces to around 30-40% (i.e. 13-15 MJ/kg) of the fossil fuel. Whenever the oxygen and water content present in the biomass feedstock are less (<10 %), it obviously results a good calorific value in the bio-oil obtained from it, which is observed from many researcher's report such as Greenhalf et al. [30] and Uzun et al. [31]. When the liquid product obtained in pyrolysis process is measured on wet basis, the calorific value is found very less, irrespective of temperature and heating rate, as the liquid is mainly composed of water and less amount of oil [32]. The water content present in the bio-oil takes the heat to evaporate during combustion and thus the heating value of the bio-oil reduces. So the calorific value of a bio-oil on dry basis is higher as compared to the wet basis [16]. The oxygen present in the bio-oil helps in increasing the water content and reduces the amount of hydrocarbon. Mahanty et al. [33] discussed some techniques for the upgradation of pyrolysis oil such as hydrotreating, reforming, catalytic upgradation etc. and listed some calorific values of the upgraded oils from eucalyptus wood, rice straw and waste bamboo etc. which are found as 16-19 MJ/kg, but this is not found much effective as these could not increase the calorific values significantly [34, 35]. Hydrothermal pyrolysis has been found a promising method for the upgradation of bio-oil quality, as by using this method the calorific value can be increased up to 36-39 MJ/kg [20, 36] which is much better than many other pyrolysis oil. The soybean oilcake, coconut shell and sunflower pressed bagasse can be considered as the energy efficient biomasses, since the pyrolysis oil derived from these have very high heating value such as 33.6-38.6 MJ/kg; It can be noted that the heating rate used in these pyrolysis processes was very high (50-300 ^{0}C/min) and the water content present in both the biomasses and bio-oils were very less, so these could be assumed as the deciding factors for getting such a high heating value [9, 37, 13]. When the pyrolysis process is carried out in nitrogen atmosphere along with product gas by recycling in it, the calorific value of the bio-oil can be increased as compared to 100 % N_2 atmosphere, further it also depends upon the percentage of product gas concentration [38]. The heating value of the bio-oil obtained at different condensation temperature shows different calorific value such that condensing at lower temperature, the bio-oil contains higher calorific value as compared to the bio-oil condensing at higher temperature [18, 19]. It could be concluded that, at high condensation temperature some of the gaseous elements having energy content left out in the form of incondensable gas. According to Pattiya and Suttiback [39], the heating value of bio-oil has reduced up to 20 % when hot filter is used; on the other hand, Yin et al. [19] found that the use of ESP helps in increasing the heating value. It is very difficult to find a general pyrolysis temperature for optimum heating value because it depends upon many factors, such as type of biomass, heating rate, moisture content etc., but still the temperature between 400 ^{0}C and 500 ^{0}C are suggested for the optimum heating value for the common biomasses as per Gang et al. [40]. It has been observed that the type of reactors do not have much impact on the quality of bio-oil such as using auger reactor also have the same range of calorific value as fluidised or fixed bed reactor [11].

2.3. Water Content

The water content in the pyrolysis oil depends on moisture content present in the feedstock and also on the dehydration reaction that takes place during the fast pyrolysis process. Generally the water content in the bio-oil is determined by the Karl-Fischer titration method or by the help of Dean and Stark apparatus. The higher amount of water content present in the bio-oil leads to phase separation between aqueous phase and a heavier organic phase and the bio-oil becomes difficult for application [41]. Therefore, it is very important to reduce the water content in feedstock below 10 wt.%. Some other adverse impacts of water content in the bio-oil can be summarised as- (i) it lowers the heating value of the liquid, (ii) increases ignition delay (iii) reduces combustion rate by decreasing adiabatic flame temperature (iv) it also results the premature evaporation and subsequent injection difficulties during preheating [41]. Apart from these effects, however; it has some positive aspects also, such as an increased amount of water leads to reduction in viscosity which helps in pumping and atomization. It also leads to a more uniform temperature distribution in diesel engine cylinder and lowers the NO_x emissions and thus reduces pollution during combustion and emission. It also leads to micro explosion of droplets which is helpful for proper combustion [4, 42, 43]. In general the water content present in the pyrolysis oil from most of biomasses is found between 10 wt.% to 40 wt.%. The variation of water content in the bio-oil entirely depends on many factors such as type of biomass, moisture content present in the biomass, temperature, heating rate, rate of sweeping gas flow, vapour residence time etc. Since high water content is always undesirable in the bio-oil, so some methods have been developed for the reduction of water content; hydrodeoxygenation can be mentioned in this regard [44]. According to Heo et al. [45], water content in the bio-oil gradually increases with the increase in temperature, it is also found in their research work that presence of some additives in the biomass might be a reason of higher water (approx. 60 wt. %) content in the bio-oil. The same effect was found by Gang et al. [40], as the water content in tar increased from 13.88 % to 20.46 % when the temperature was increased from 400 ^{0}C to 700 ^{0}C, it can be mentioned that the temperature 400-500 ^{0}C is the optimum from the heating value and water content point of view, as in this temperature range heating value is highest and water content is lowest, and the same can be interpreted from the figure 2.

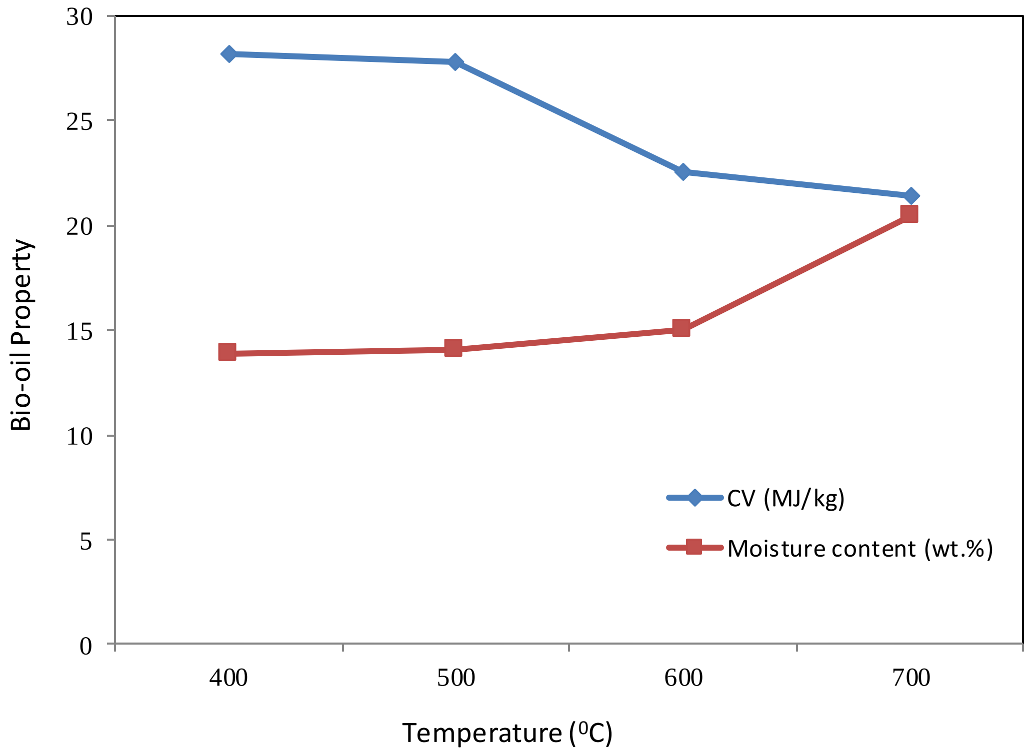

Figure 2. Variation of CV and moisture content with temperature.

The addition of solvent such as methanol can improve the flow quality of the oil, but due to this, water content also increases, so an optimal addition of solvent could be an advisable method [14]. The bio oil collected from very lower temperature (e.g. -5 ^{0}C) condenser is advantageous as it contains less water content as compared to the higher temperature condenser [18]. In the pyrolysis oil from some biomasses such as rapeseed cake and soybean oil cake contains very less amount of water which can be neglected as compared to other bio-oil [13, 22]. However some bio-oils derived from the biomasses such as chanar fruit, white palm fruit, white palm seed and alga, contains large amount of water content i.e. 44 wt.% to 86 wt.%. These type of bio-oils although reduces the heating value of the bio-oil, it improves the fluidity of the bio-oil as it reduces the viscosity [28, 23]. The bio-oil where two phases i.e. top and bottom phase is found contains different water content. It is found that the bottom phase have lower water content as compared to the top phase [34]. Pattiya and Suttibak [12] found that the use of hot filter also a factor for the increase of water content in bio-oil, on the other hand, using ESP, the water content in the bio-oil can be reduced very significantly [19].

2.4. Oxygen Content

The amount of oxygen content in the bio-oil results from the water content present in it. The oxygenated compound in the bio-oil makes the oil polar due to which it becomes non-miscible with non-polar petroleum fuel [41]. The oxygen content in the oil has some negative effects such as, it reduces the heating value of the liquid; it is also responsible for corrosive nature and instability of the bio-oil. Because of the complex composition of bio-oil, it shows a wide range of boiling point temperature. During distillation, the bio-oil starts boiling below 100 ^{0}C and stops at 280 ^{0}C which leads to leave 35-50 wt.% as solid residue [46]. Therefore; it becomes necessary to remove oxygen from the bio-oil so that it can be economical and attractive worldwide. Two processes can be applied for the elimination of oxygen, i.e., hydro-treating and catalytic cracking. In hydro-treating, the oxygen is eliminated in the form of water, whereas in the latter case, the oxygen is removed in the form of water and carbon oxides using some catalysts. In catalytic cracking, zeolite can be used as the catalyst for the up-gradation of the bio-oil which removes the oxygen significantly from the organic compound and converts it into hydrocarbon [47]. The oxygen is the element present in all the biomasses which is determined by the help of ultimate analysis, where basically a CHN analyser is used to determine and carbon, hydrogen and nitrogen and then the oxygen content is determined by taking the difference. The increased amount of oxygen in the biomass indicates the low heating value of the sample, so in the pyrolysis process, it is always essential to reduce it, so that it cannot effect badly in the quality of the bio-oil. Different amount of oxygen content present in the bio-oil derived from various biomasses at different conditions can be found in the literature. It has been found that in most of the bio-oil, the oxygen content remains in the range of 10- 50 wt.% [47, 48, 49], but the pyrolysis oil from few biomasses, for example in rice husk, the oxygen content has been found more than 50 wt.%, hence results in low calorific value [15, 21]. This higher amount of oxygen content is due to the presence of many highly polar groups in the bio-oil. Because of this high oxygen content and hydrophilic character, it is mostly insoluble in hydrocarbon solvent and also it leads to low calorific value [7, 8]. The use of hot filter could be one of the reasons for the increase of oxygen in the bio-oil around 7 %-16 %. Condensing the vapour at low temperature is very useful in reducing the oxygen content, for instance, condensing at 24 ^{0}C, around 45 % oxygen content can be reduced as compared at 37 ^{0}C [19]. The bio-oil, which shows the phase separation, contains different oxygen amount in different phases. It has been observed that the upper phase of the bio-oil contains comparatively more oxygen than the lower phase [34].

2.5. Acidity / pH Value

The bio-oils mostly contain organic acids, like acetic acid, carboxylic acid and formic acid. As the pH value of bio-oil becomes less, the oil becomes more acidic. Because of the higher acidity, the bio-oil becomes corrosive and hence corrosion resistance material should be used in the bio-oil production and storage system. The pH value in the bio-oil depends on many factors including the type of biomass used for the bio-oil production. From the literature report, it is found that in most of the bio-oil, the pH value is within the range of 2-4. But few biomasses are also there, which give the pyrolysis oil having higher pH value (>4) such as rice straw [10], wheat straw [30] etc. On the other hand, some bio-oils are highly acidic as the pH value is found within 1.8-2.9 from the biomass like eucalyptus wood [33, 35]. Till date so much techniques has not been developed so far for the increase of pH value significantly, but only a slight increase becomes possible. Condensing the vapour at low temperature (e.g. -5 ^{0}C) by the help of ice water mixed with some solution such as NaCl, instead of condensing at higher temperature (50-60 ^{0}C), the pH value can be increased up to 4.5 [18]. Yin et al. [19] also found the same effect as the pH value gradually increases with decrease in condensing temperature; however this value can be further increased when the bio-oil is collected by using an ESP. The use of hot vapour filter might have a negative impact on pH value as due to this accessory, the pH value slightly decreases [39]. Dehydroxygenation could be a method to improve the quality of bio-oil in which the pH value increases by little amount [44]. Heating rate could be an approach for the increase of pH in the bio-oil, as Tsai et al. [32] found that bio-oil obtained at the heating rate of 400 ^{0}C/min has higher pH value as compared to 200 ^{0}C/min. When the bio-oil shows two phases: top and bottom, generally it is seen that top phase bio-oil have slightly higher pH value as compared to bottom phase [34].

2.6. Density

The density of the bio-oil affects the energy value of the oil or fuel. The two fuels having same heating value may have different energy quantity due to the variation of density. As the density increases, the energy content also increases. The normal range of density of pyrolysis oil is found as 1000-1240 kg/m^3 measured between the temperature of 15 ^{0}C and 40 ^{0}C, found from the most common biomasses and this variation comes mainly due to the type of biomasses, but from few biomasses like saw dust, density may raise up to 1300 kg/m^3 [6]; However bio-oils derived from biomasses such as rapeseed cake, palm fruit etc. [12, 28] have lower density (<1000 kg/m^3). It has been observed that density of bio-oil always decreases with increases in temperature which is found by measuring the density at various temperatures [17]. The density of the bio-oil is found less when the bio-oil is obtained by condensing at low temperature [18, 19]. It is interesting to note that unlike other properties, density was found to remain same within the normal range i.e. 1100 kg/m^3, irrespective of the installation of the hot vapour filter [39], although by the use of ESP the density of the bio-oil could be increased to a higher value [19].

2.7. Solid Content

The solid content in the bio-oil has many adverse effects, particularly during storage and combustion. It leads to increase the viscosity. It also creates blockage in the engines, particularly in the fuel ignition system. It also creates a phase separation in the bio-oil and delays the burning process. The solid particles are formed by the hydrocarbons derived from ash content in the bio-oil. It has been found that solid content in the pyrolysis oil can be reduced by the use of cyclone separator of the particle size greater than the 10μm. The normal range of solid content found in the bio-oil is 0.01-0.5 wt.%. [39, 50]. It is a general concept that when few cyclones are employed in the pyrolysis plant so that the vapour produced passes through it and separates the solid content as much as possible and thus the bio-oil becomes solid content free. Bio-oil obtained by condensing at lower temperature contains more solid content, it can also be mentioned that bio-oil collected at ESP contains large amount of solid content [19]. On the other hand the use of glass wool vapour filter is very useful in reducing the solid content in the bio-oil to approximately 85-86 % [39]. It has been noticed that the solid content in the bio-oil is much higher when it is produced from the bark portion rather than the wood portion from the same tree [11].

2.8. Ash Content and Alkali Elements

The ash is associated with char produced during the pyrolysis process. The char acts as a vapour cracking catalysts, so the rapid and effective removal or separation of product vapour from the char becomes very important. As the alkali metals increases, the ash content in the bio-oil also increases [51]. Many char removal techniques have already been developed, such as cyclones, hot vapour filter, pressure filtration of the liquid etc. [4]. The ash content in the bio-oil is mainly responsible for erosion, corrosion and kicking problem in the engine [46]. As the lignin content increases, alkali metals such as potassium and sodium also decreases [51]. Some other common alkali elements found in ash are Na, Ca, Mg, K, Si, P, V etc.

The biomass is constituted of many inorganic elements which results the presence of alkali metals in the bio-oil. The highest amounts of alkali elements found in the bio-oil are Ca, S, K and Na which are found in the range of 6-46 ppm [19, 34, 52]. In most of the pyrolysis oil the ash content varies in between 0.01 wt.% and 0.5 wt.%. [53, 54, 55, 56]. Park et al. [10] found that the bio-oil derived from peculiar biomass like rice straw contains very negligible ash content (0.007 wt.%); however, some other bio-oils contains approximately 0.1 wt.%, which is equivalent to heavy petroleum fuel [12,40]. In hydrothermal pyrolysis oil, the ash content is generally found high (~1.3 wt. %) is very high compared to heavy petroleum fuel [20, 46]. Condensing the vapour at much lower temperature to get the bio-oil, is not very effective in terms of ash content, since it contains almost same ash content in both the situations [18]. Using hot filter, the ash content in the bio-oil can be reduced significantly as compared to the absence of hot filter [34,16]. In the elemental analysis of the pyrolysis oil obtained from sweet sorghum bagasse in fractional condensers are plotted in the column diagram as shown in the figure 3 [19].

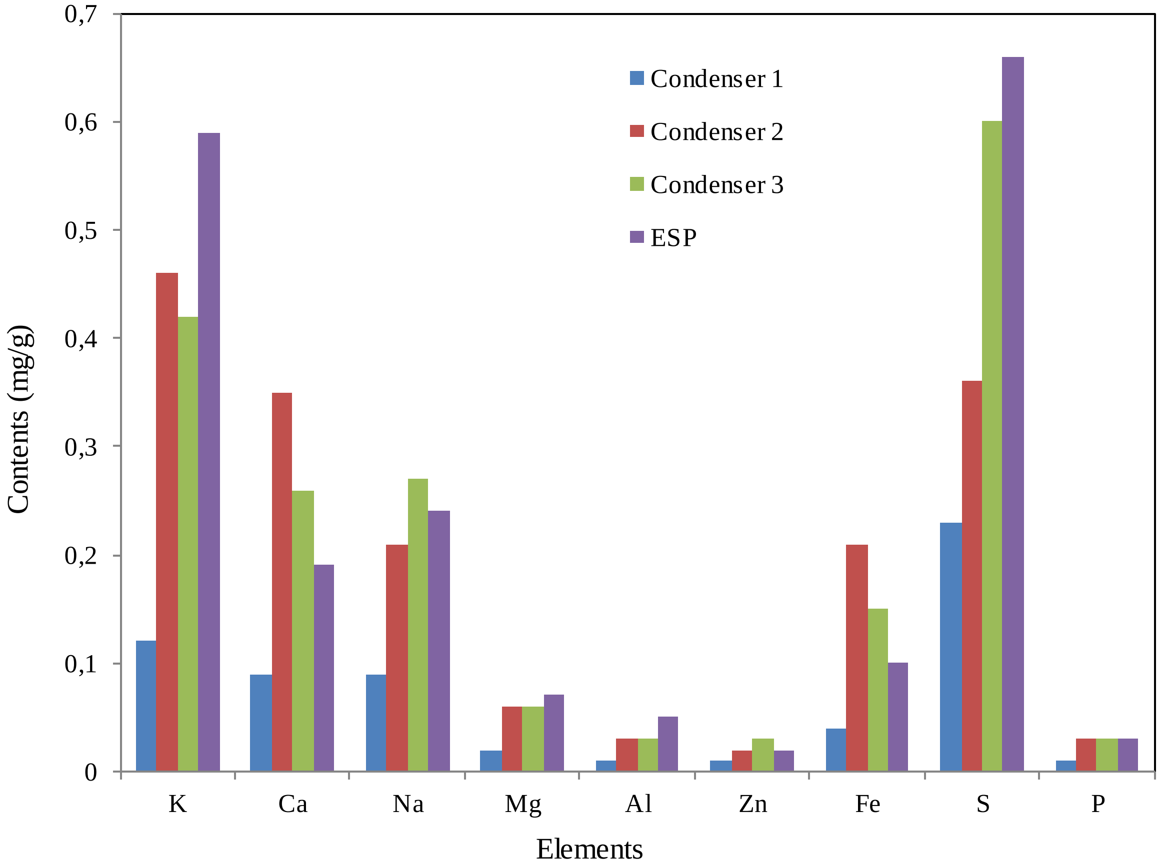

Figure 3. Elements presents in the bio-oil from different condensers.
(Condenser 1 at 37 ^{0}C, Condenser 2 at 25 ^{0}C and condenser 3 at 24 ^{0}C)

3. Conclusion

From the detailed discussions on the properties of biomass pyrolysis oil, it can be concluded that the physical properties of the bio-oil produced from the various biomasses depend on the many factors. The use of different catalysts may help in increase the bio-oil yield and improvement of the oil quality. There should be a details observation of the effects of different parameters during pyrolysis. For example, the bio-oil collected from ESP shows higher heating value and lower oxygen and water content, but at the same time it leads to increase the viscosity and solid content in the bio-oil; again with the use of hot filter, the viscosity of the bio-oil can be reduced, but it deteriorates the quality of the bio-oil by reducing the heating value and by increasing the water as well as oxygen content in the bio-oil. In phase separation bio-oil, the bottom phase of the bio-oil contains less water and oxygen and has higher calorific value, but in this phase, the bio-oil density becomes higher. So, there must be an optimum selection of the parameters during pyrolysis oil production and collection as well as for storage, so that the obtained bio-oil can be used as a useful alternate fuel in the near future.

References

[1] S. Xiu, and A. Shahbazi, “Bio-oil production and upgrading: A review”, *Renewable and Sustainable Energy Reviews*, vol. 16, pp. 4406-4414, 2012. (Article)

[2] J. Blin, G. Volle, P. Girard, T. Bridgwater and D. Meier, “Biodegradability of biomass pyrolysis oils: Comparison to conventional petroleum fuels in current use”, *Fuel*, vol. 86, pp. 2679-2686, 2007. (Article).

[3] M. Bertero, G. Puente, and U. Sedran, “Fuel from bio-oils: Bio-oil production from different residual sources, characterization and thermal conditioning”, *Fuel*, vol. 95, pp. 263-271, 2012. (Article)

[4] A.V. Bridgwater, “Biomass fast pyrolysis”, Thermal Science, vol.8, pp. 21-49,2004. (Article)

[5] K. Sipila, E. Kuoppala, L. Fagernas, A. Oasmaa, “Characterization of biomass-based flash pyrolysis oils”, Biomass and Bioenergy, vol.14, No. 2, pp. 103-113, 1998. (Article)

[6] Z.X. Feng, Z.J. Lu, G.Q. Xiang, and Z.Q. Shi, “Pyrolysis of rice husk and saw dust for liquid fuel”, Journal of Environmental Science, vol.18, No. 2, pp. 392-396, 2006. (Article)

[7] Z.J. Lu, Y.W. Ming, and W.N. Na, “Bio-oil production from cotton stalks”, Energy Conversion and Management, vol. 49, pp. 1724-1730, 2008. (Article)

[8] Z.J. Lu, “Pyrolysis oil from fast pyrolysis of maize stalks”, J. Anal. Appl. Pyrolysis, vol. 83, pp. 205-212, 2008. (Article)

[9] E.G. Sundaram, and E. Natarajan, “Pyrolysis of coconut shell: An Experimental Investigation”, The Journal of Engineering Research, vol.6, No. 2, pp. 33-39, 2009. (Article)

[10] Y.K. Park, J.K. Jeon, S. Kim, and J.S. Kim, “Bio-oil from rice straw by pyrolysis using fluidised bed and char removal system”, American Chemical Society, Div. Fuel Chem. vol. 49, No. 2, pp. 800, 2004. (Article)

[11] L. Ingram, D. Mohan, M. Bricka, P. Steele, D. Strobel, D. Crocker, D. Mitchell, J. Mohammad, K. Cantrell, and C.U. Pittman, “Pyrolysis of wood and bark in an auger reactor: Physical properties and chemical analysis of the produced bio-oils”, Energy & Fuels, vol. 22,pp. 614-625, 2008. (Article)

[12] E. Culcuoglu, E. Unay, F. Karaosmanoglu, D. Angin, and S. Sensoz, “Chracaterization of bio-oil of rapeseed cake”, Energy Sources, vol. 27, No. 13, pp. 1217-1223,2005. (Article)

[13] S. Sensoz, and I. Kaynar, “Bio-oil production from soybean (Glycine max L.); Fuel properties of bio-oil”, Industrial Crops and Products, vol. 23, pp. 99-105, 2006. (Article)

[14] L. Qiang, Y.X. Lai and Z.X. Feng, “Analysis on physical and chemical properties of bio-oil pyrolyzed from rice husk”, J. Anal. Appl. Pyrolysis, vol. 82, pp.191-198, 2008. (Article)

[15] Z. Ji-lu, “Bio-oil from fast pyrolysis of rice husk: Yield and related properties and improvement of the pyrolysis system”, Journal of Analytical and Applied Pyrolysis, vol. 80, pp. 30-35, 2007. (Article)

[16] S. Suttibak, K. Sriprateep, and A. Pattiya, “Production of bio-oil via fast pyrolysis of cassava rhizome in a fluidised-bed reactor”, Energy Procedia, vol. 14, pp. 668-673, 2012. (Article)

[17] M.G. Perez, A. Chaala, and C. Roy, “Vacuum pyrolysis of sugarcane bagasse”, Journal of Analytical and Applied Pyrolysis, vol. 65, pp. 111-136, 2002. (Article)

[18] M. Asadullah, M.A. Rahman, M.M. Ali, M.S. Rahman, M.A. Motin, M.B. Sultan, and M.R. Alam, “Production of bio-oil from fixed bed pyrolysis of bagasse”, Fuel, vol. 86, pp. 2514-2520, 2007. (Article)

[19] R. Yin, R. Liu, Y. Mei, W. Fei, and X. Sun, “Characterisation of bio-oil and bio-char obtained from sweet sorghum bagasse fast pyrolysis with fractional condensers”, Fuel, vol. 112, pp. 96-104, 2013. (Article)

[20] S. Xiu, A. Shahbazi, V. Shirley, and D. Cheng, “Hydrothermal pyrolysis of swine manure to bio-oil: effects of operating parameters on products yield and characterization of bio-oil”, Journal of analytical and applied pyrolysis, vol. 88, pp. 73-79, 2010. (Article)

[21] G. Xiujuan, W. Shurong,W. Qi, G. Zuogang, L. Zhongyang, “Properties of bio-oil from fast pyrolysis of rice husk”, Chinese Journal of Chemical Engineering, vol. 19, No.1, pp. 116-121, 2011. (Article)

[22] M. Ertas and M.H. Alma, “Pyrolysis of laurel (Laurusnobilis L.) extraction residues in a fixed-bed reactor: Characterisation of bio-oil and bio-char”, J. Anal. Appl. Pyrolysis, vol. 88, pp. 22-29, 2010. (Article)

[23] X. Guo, S. Wang, Z. Guo, and Z. Luo, “Properties of bio-oil from alga fast pyrolysis”, IEEE, vol. 978, No. 1, pp. 4244-6255, 2011. (Article)

[24] J.A.C. Durange, M.R.L. Santos, M.M. Pereira, L.A.P. Jr. Feranadaes, M.N. Souza, A.N. Mendes, L.M. Mesa, C.J. Sanchez, E.M.S. Sanchez, J.M.M. Perez, and N.M.F. Carvalho, “Physicochemical properties of pyrolysis bio-oil from sugarcane straw and sugarcane in Natura”, Journal of Biomaterials and Nano biotechnology, vol. 4, pp. 10-19, 2013. (Article)

[25] A. Pattiya, J.O. Titiloye, and A.V. Bridgwater, “Fast pyrolysis of agricultural residue from cassava plantation for bio-oil production”, The 2ndJoint International Conference on Sustainable Energy and Environment, Bangkok, Thailand SEE, 2006. (Conference paper)

[26] B. Biswal,S. Kumar, and R.K. Singh, “Production of hydrocarbon liquid by thermal pyrolysis of paper cup waste”, Journal of Waste Management, vol.7. ID 731858, 2013. (Article)

[27] C.Z. Mullen, A.A. Boateng, N.M. Goldberg, I.M. Lima, D.A. Laird, and K.B. Hicks, “Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis”, Biomass and Bioenergy, vol.. 34, pp. 67-74, 2010. (Article)

[28] M. Bertero, H.A. Gorostegui, C.J. Orrabalis, C.A. Guzman, E.L. Caladri, and U. Sedran, “Chararatersiation of the liquid products in the pyrolysis of residual chanar and palm fruit biomasses”, Fuel, vol.116, pp. 409-414, 2014. (Article)

[29] I. Demiral, A. Eryazici, and S. Sensoz, “Bio-oil production from pyrolysis of corn cob (Zea mays L.)”, Biomass and Bioenergy, vol. 36, pp. 43-49, 2012. (Article)

[30] C.E. Greenhalf, D.J. Nowakowski, A.B. Harms, J.O. Tililoye, and A.B. Bridgwater, “A comparative study of straw, perennial grasses, and hard woods in terms of fast pyrolysis products”, Fuel, vol. 108, pp. 216-230, 2013. (Article)

[31] B.B. Uzun, E.A. Varol, F. Ates, N. Ozbay, and A.E. Putun, “Synthetic fuel production from tea waste: characterisation of bio-oil and bio-char”, Fuel, vol. 89, pp. 176-184, 2010. (Article)

[32] W.T. Tsai, M.K. Lee, and Y.M. Chang, “Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an

induction- heating reactor", J. Appl. Pyrolysis, vol.76, pp. 230-237, 2006. (Article)

[33] P. Mohanty, K.K. Pant, S.N. Naik, L.M. Das, and P. Vasudevan, "Fuel production from biomass: Indian perspective for pyrolysis oil", Journal of Scientific & Industrial Research, vol.70, pp. 668-674, 2011. (Article)

[34] S.H. Jung, B.S. Hang, and J.K. Kim, "Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system", J. Aanl. App. Pyrolysis, vol.82, pp. 240-247, 2008. (Article)

[35] G. Kumar, A.K. Panda, and R.K. Singh, "Optimization of process for the production of bio-oil from eucalyptus wood", Journal of Fuel Chemistry Technology, vol.38, pp. 162-167, 2010. (Article)

[36] A.E. Puttun, O.M. Kockar,S. Yourgun, H.F. Gercel, J. Andresen, C.E. Snape, and E. Puttun, "Fixed- bed pyrolysis and hydropyrolysis of sunflower bagasse: product yields and compositions", Fuel Processing Technology, vol. 46, pp. 49-62, 1996. (Article)

[37] H.F. Gercel, "Production and characterization of pyrolysis liquids from sunflower pressed bagasse", Bioresource Technology, vol. 85, pp. 113-117, 2002. (Article)

[38] C.A. Mullen, A.A. Boateng, and N.M. Goldberg, "Production of deoxygenated biomass fast pyrolysis oils via product gas recycling", Energy and Fuels, vol. 27, pp. 3867-3874, 2013. (Article)

[39] A. Pattiya, and S. Suttibak, "Influence of glass wool hot vapour filter on yields and properties of bio-oil derived from rapid pyrolysis of paddy residue", Bioresource Technology, vol. 116, pp. 107-113, 2012. (Article)

[40] X. Gang, N.M. Jiang, H. He, C. Young, X. Rui, Z.Z. Ping, and C. Ke-fa, "Fluidised-bed pyrolysis of waste bamboo", Journal of Zhejiang University Science A, vol.8, No. 9, pp. 1495-1499, 2007. (Article)

[41] L. Qiang, L.W. Zhi, and Z.X. Feng, "Overview of fuel properties of biomass fast pyrolysis oils", Energy Conversion and Management, vol. 50, pp. 1376-1383, 2009. (Article)

[42] R. Calabria, F. Chiariello, and P. Massoli, "Combustion fundamentals of pyrolysis oil based fuels", Exp Therm Fluid Sci. vol.31, pp. 413-420, 2007. (Article)

[43] A.E. Puttun, A. Ozcan, and E. Puttun, "Pyrolysis of hazelnut shells in a fixed- bed tubular reactor: yields and structural analysis of bio-oil", J. Anal. Appl Pyrolysis, vol.52, pp. 33-49, 1999. (Article)

[44] J. Wildschut, F.H. Mahfud, R.H. Vederbosch, and H.J. Heeres, "Hydrotreatment of fast pyrolysis oil using Heterogeneous noble-metal catalysts", Ind. Eng. Chem. Res, vol.48, pp. 10324-10334, 2009. (Article)

[45] [H.S. Heo, H.J. Park, Y.K. Park, C. Ryu, D.J. Suh, Y.W. Suh, J.H. Yim, and S.S. Kim, "Bio-oil production from fast pyrolysis of waste furniture saw dust in a fluidised", Biosource Technology, vol. 101, pp. S91-S96, 2010. (Article)

[46] Q. Zhang, J. Chang, T. Wang and Y. Xu, "Review of biomass pyrolysis oil properties and upgrading research", Energy Conversion and Management, vol. 48, pp. 87-92, 2007. (Article)

[47] R. Frensh, and S. Czernik, "Catalytic pyrolysis of biomass for biofuels production", Fuel Processing Technology, vol. 91, pp. 25-32, 2010. (Article)

[48] F. Ates, E. Putun, and A.E. Puttun, "Fast pyrolysis of sesame stalk: yields and structural analysis of bio-oil", J. Anal. Appl. Pyrolysis, vol. 71, pp. 779-790, 2004. (Article)

[49] L. Li, H. Zhang, and X. Zhuang, "Pyrolysis of waste paper: characterization and composition of pyrolysis oil", Energy Sources, vol.27, No. 9, pp. 867-873, 2005. (Article)

[50] K.H. Lee, B.S. Kang, Y.K. Park, and J.S. Kim, "Influence of reaction temperature, pre-treatment, and a char removal system on the production of bio–oil from rice straw by fast pyrolysis, using a fluidised bed", Energy & Fuels, vol.19, pp. 2179-2184, 2005. (Article)

[51] R. Fahmi, A.V. Bridgwater, L.I. Darvell, J.M. Jones, N. Yates, S. Thain, and I.S. Donnison, "The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses, switch grass and willow", Fuel, vol. 86, pp. 1560-1569, 2007. (Article)

[52] M.E. Boucher, A. Chaala, and C. Roy, "Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbine. Part1: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase", Biomass and Bioenergy, vol.19, pp. 337-350, 2000. (Article)

[53] D.L. Larson and E. Olivares, "Energy loses due to elutriation in fluidised bed gasification of sugarcane bagasse, in: R.P. Overend, E. Chornet (Eds.)", Proc. of the fourth biomass conference of the Americas, Oakland, Elsevier science Ltd., UK., August 29-September 2, 1999.

[54] R.G. Graham, A. Barry, and D.R. Huffman, "Application of rapid thermal processing of biomass, in: A. V. Bridgwater (Ed.)", Proc. of Advances in thermochemical biomass conversion, Interlaken, Blackie academic and professional, London, pp. 1275-1288, 1994.

[55] M.G. Perez, A. Chaala, and C. Roy, "Co-pyrolysis of sugarcane bagasse with petroleum residue. Part I: Thermogravametric analysis", Fuel, vol. 80, pp. 1245-1258, 2001. (Article)

[56] H. Pakdel, C. Roy, and W. Kalkrueth, "Oil production by vacuum pyrolysis of Canadian oil shales and fate of the biological markers", Fuel, vol. 78, pp. 365-375, 1999. (Article)