Applied Thermal Engineering 56 (2013) 167–175

Contents lists available at SciVerse ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Fast oxidative pyrolysis of sugar cane straw in a fluidized bed reactor

Juan Miguel Mesa-Pérez [a], José Dilcio Rocha [b], Luis Augusto Barbosa-Cortez [c], Margarita Penedo-Medina [d], Carlos Alberto Luengo [e], Esther Cascarosa [f],*

[a] Bioware Tecnologia, Av. Martinho Lauer Filho 511, Real Parque, Barão Geraldo, Campinas, SP, Brazil
[b] Embrapa-Empresa Brasileira de Pesquisa Agropecuária, Parque Estação Biológica (PqEB), Av. W3 Norte, 70770-901 Brasilia, DF, Brazil
[c] FEAGRI/UNICAMP, Ciudade Universitária "Zeferino Vaz", C.P. 6011, 13083-970 Campinas, SP, Brazil
[d] Chemical Engineering Department, Universidad de Oriente, Avda. Las Américas s/n, 90900 Santiago de Cuba, Cuba
[e] Group Alternative Fuels GCA/IFGW/UNICAMP, Ciudade Universitária "Zeferino Vaz", C.P. 6011, 13083-970 Campinas, SP, Brazil
[f] Thermochemical Processes Group, Aragón Institute for Engineering Research (I3A), I+D Building, Universidad de Zaragoza, Mariano Esquillor s/n, E-50018 Zaragoza, Spain

HIGHLIGHTS

- Pyrolysis of sugar cane straw was studied in a fluidized bed reactor.
- The product yields were evaluated.
- The composition of the liquid and solid products obtained was analyzed.
- This is an environmentally friendly use for this waste.

ARTICLE INFO

Article history:
Received 9 December 2012
Accepted 6 March 2013
Available online 22 March 2013

Keywords:
Fast pyrolysis
Sugar cane straw
Fluidized bed

ABSTRACT

This study focuses on the technical viability evaluation of the fast pyrolysis of sugar cane straw for its energy use. By means of this thermochemical process, the sugar cane straw is converted into bio-fuels (biochar, bio-oil) and non-condensable gases. The bio-fuels obtained could be used as fuel or as raw material in the chemical industry. The fast pyrolysis of sugar cane straw has been developed in a fluidized bed reactor. In order to improve this process to obtain high bio-oil yield, the influence of the operational conditions (equivalence ratio and temperature) on the product yields and on their characteristics was evaluated. The product yields of bio-oil and char were up to 35.5 wt.% and 48.2 wt.% respectively. The maximum bio-oil yield was achieved at temperature and equivalence ratio conditions of 470 °C and 0.14. The bio-oil obtained has low oxygen content (38.48 wt.% dry basis), very low water content, and a lower heating value of 22.95 MJ/kg. The gas chromatographic analyses allowed the identification of oxygenated compounds and heterocyclic aromatic hydrocarbons. The bio-oil pH ranged between 3.14 and 3.57 due to the presence of acid organic compounds. The char obtained has a high fixed carbon and volatile matter content. Its HHV value is 13.54 MJ/kg.

1. Introduction

The production of sugar cane and alcohol has reached in a significant proportion in Brazil in the last few years. This fact makes it a leading world country on this matter. In 2009–2010, the sugar harvest produced in this country was 603 million of tons. The production of sugar cane and ethanol has increased 33.0 Mt and 25.7 Ml respectively [1]. According to the Center of Strategic Studies Management (CGEE), 140 kg of straw, 140 kg of bagasse and 150 kg of sugar are produced from every one ton of clean cane cultivated [2]. The technical methods for cane straw collection are being improved, therefore, it is expected that the amount of cane straw increases in the next years in Brazil. In other countries like in South Africa, the use of the waste from the sugar production is being considered for applications in energy production through combustion, pyrolysis (slow [3], vacuum [4]) or gasification. In Brazil, the remains from the crop of the sugar cane are currently burnt in the self-land. In order to avoid the burning of the sugar cane residues before 2031, several Laws were fixed in this country [5].

---

* Corresponding author. Tel.: +34 976765483.
E-mail addresses: juan@bioware.com.br (J.M. Mesa-Pérez), jose.rocha@embrapa.br (J.D. Rocha), cortez@agr.unicamp.br (L.A. Barbosa-Cortez), mpenedo@fiq.uo.edu.cu (M. Penedo-Medina), luengo@ifi.unicamp.br (C.A. Luengo), ecascano@unizar.es (E. Cascarosa).

1359-4311/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.applthermaleng.2013.03.017

Pyrolysis is a thermochemical process used to convert biomass into bio-fuels (biochar, bio-oil) and non-condensable gases. By controlling the process conditions, this process produces different product yields and qualities [6]. Originally, the most interesting product was the charcoal [7], but nowadays, the use of the bio-oil for the chemical industry is being analyzed. After the pyrolysis study, Putun et al. [8] concluded that the bio-oil obtained from the Euphorbia Rigida biomass could be used as a potential source of renewable fuel and/or chemical feedstock. Other studies, as Amen-Chen et al. [9], go into detail about the optimal operational conditions to produce the phenols contained within the bio-oil from lignin. In the same way, Tsai et al. [10] and Lee et al. [11] analyzed the effect of several parameters, on the oil yield from rice husk and napier grass pyrolysis, respectively. Being conscious of the importance of the production of some aromatic compounds, Peng and Wu [12] studied the pyrolysis of wheat straw hemicellulose to evaluate these compounds as useful for chemicals.

Therefore, cane straw may take up an outstanding place as raw material for the fuel production and chemical products along with sugar cane bagasse by means of pyrolysis [13].

Pyrolysis of sugar cane bagasse and sugar cane straw is being researched in the last few years. These studies mainly focus on the analyses of the thermogravimetric decomposition. Erlich et al. [14] studied the thermal decomposition of sugar cane bagasse in pellets during slow pyrolysis process. They also studied the effect of the size of the pellets on the thermal degradation. Mesa-Perez et al. [15] analyzed the thermal decomposition in another reactor and under different operational conditions. Besides these studies, Ounas et al. [16] analyzed the effect of heating rate on the thermal process. Also the solid product from the sugar cane bagasse pyrolysis has been characterized [17]. Aranda-Moraes et al. [5] analyzed the chemical composition of the liquid product (bio-oil), founding the presence of a great variety of compounds, mainly oxygenated ones. These results concluded with the viability of using this raw material for energy and industrial uses. Moubarik et al. [18] studied the production of wood adhesive obtained from the lignin-phenol-formaldehyde from sugar cane bagasse. They concluded that this is other potential application for this waste. On the other hand, Uras et al. [19] obtained a biochar from the pyrolysis of sugar cane bagasse which seems to be a promising sorbent and soil conditioner due to its high surface area, high surface acidity and microporous structure. According to the results from Arni et al. [20], even the gas from the sugar cane pyrolysis process, could be used to produce electrical energy.

Despite the potential uses of the products, the fast pyrolysis of sugar cane straw has not been studied in deep up to now. In order to use the pyrolysis like an energy recovery process, the thermochemical treatment in pilot-scale reactors and with continuous feeding systems must be evaluated. Several fast pyrolysis plants are engaged in research and development for the processing of various types of biomasses [21]. The main objective of these studies is to obtain a liquid product with properties as fuel. In order to obtain a bio-oil with a high heating value, the water content has been reduced by means of a centrifugal system enclosed to the pyrolysis plant. This system allows the bio-oil and the aqueous phase separation, therefore, the water content within the bio-oil produced in this plant is very low [22].

Fast pyrolysis is a high-temperature process in which biomass is rapidly heated in absence of oxygen, optimized for high liquid yields [23]. This process is characterized by the low residence time in the reactor and the rapid removal of the volatile products formed inside the reactor, as well as the high heat and mass transfer regimes.

Lignocellulosic materials obtained in the industrial manufacturing process of the crop of sugar cane (sugar cane bagasse and sugar cane straw) show a high potential for their use in energy production, either by means of biochemical (hydrolysis) or thermochemical treatments (combustion, pyrolysis and gasification). Bio-oil obtained from fast pyrolysis of lignocellulosic materials is made up of various organic compounds, of which about 45% are oxygenates. Among organic compounds, hydroxyaldehydes, hydroxyketone, sugars, carboxylic acids, phenolics and others are found [24,25]. Therefore, the high amount of forest and agro-industrial residues in Brazil could be transformed into products of high added value [26].

In this context, the fast pyrolysis of sugar cane straw, as one of the most abundant waste in Brazil, has been evaluated in an autothermal pilot-scale plant. This study has been developed in a fluidized bed reactor and with a continuous feeding system. The continuous feeding system allows the production of enough amount of bio-oil to be chemically analyzed. The operational conditions during this process may significantly influence on the product yields and their characteristics. Thus, this study focuses on the influence of temperature and equivalence ratio on the product yields and on the chemical composition of bio-oil and char products.

2. Material and methods

2.1. Feedstock characterization

The sugar cane straw samples used in this study were dried, grinded and subjected to drying and grinding, and then, subjected to sieve analysis. For this purpose, three samples were taken from the same population, and spread on a flat surface by separating it into four quadrants. The sieve analysis was performed using sieves of mesh diameter of 3.35, 2.00, 1.68, 0.85, 0.6 and 0.35 mm. On basis of the results obtained from this analysis, the percentage of mass retained on each sieve was obtained. The particle size distribution was not uniform, predominating particles smaller than 0.85 mm (being 66.3 wt.% of the total sample). The mean particle diameter calculated from the results of the granulometric analysis was 0.55 mm.

Biomass was also characterized performing proximate, ultimate and heating values analyses. Feedstock analyses have been carried out employing standard methods: moisture according to ISO-589-1981, ash according to ISO-1171-1976, volatiles according to ISO-5623-1974, elemental analysis (CHNS) using Carlo Erba 1108, and heating value according to ISO-1928-76. These analyses are listed in Table 1.

The biomass was supplied with a high moisture content (30 wt.%), thus, it was needed to be reduced up to 10.4 wt.% by means of drying under atmosphere conditions during 48 h. After these preliminary treatments, the cane straw was ready to be subjected to the pyrolysis process.

The proximate analyses show that the sugar cane contains a high amount of volatile matter (74.0 wt.%) and ash content (16.4 wt.%). As a result, this residue has a higher heating value of 17 MJ/kg. The high percentage of ash in the raw material can have further influence on the product yields and on the characteristics of bio-oil and char obtained in the pyrolysis [27].

The nitrogen and sulfur content are low, and as it can be observed, the H/C and O/C molar ratios are high, which is characteristic of vegetal biomass [28].

The determination of inorganic compounds in the biomass was carried out by X-ray fluorescence spectrometry (see Table 1). The main component within the ash is Si, but also Al, Ca, Fe, K and Mg, that can catalyze some pyrolysis reactions. The composition of inorganic material is similar to other residues which, nowadays, are being evaluated as raw materials in pyrolysis processes (such as sewage sludge) [29].

Table 1
Proximate, ultimate and ash composition analyses of the feedstock material.

	Units	Sugar cane
Moisture	wt.%	10.4
Ash[a]	wt.%	16.4
Volatiles[a]	wt.%	74.0
Fixed carbon[a]	wt.%	13.0
C[a]	wt.%	43.2
H[a]	wt.%	6.7
N[a]	wt.%	0.3
S[a]	wt.%	0.2
O[a]	wt.%	33.2
H/C	molar ratio	1.85
O/C	molar ratio	0.58
Higher heating value (HHV)	MJ/kg	18.00
Lower heating value (LHV)	MJ/kg	17.00
Bulk density	kg/m^3	141.2
Al_2O_3	wt.% (ash)	15.32
CaO	wt.% (ash)	12.44
Fe_2O_3	wt.% (ash)	7.62
Na_2O	wt.% (ash)	0.10
K_2O	wt.% (ash)	3.04
SO_3	wt.% (ash)	4.30
MgO	wt.% (ash)	5.83
MnO	wt.% (ash)	0.33
SiO_2	wt.% (ash)	46.40
NiO	wt.% (ash)	0.01
ZrO_2	wt.% (ash)	0.03
Cr_2O_3	wt.% (ash)	0.01
ZnO	wt.% (ash)	0.02
CuO	wt.% (ash)	0.02
SrO	wt.% (ash)	0.06
TiO_2	wt.% (ash)	1.83
P_2O_5	wt.% (ash)	2.59
Cl	wt.% (ash)	0.03

[a] wt.% on dry basis.

Table 2
Operational conditions during the fast pyrolysis experiments.

	Unit	Experiment		
		P1	P2	P3
ER		0.14	0.18	0.23
Temperature	°C	470	550	600
Air flow	kg h^{-1}	85.4	94.6	87.6
Feed rate of biomass (BB)	kg h^{-1}	147.3	128.2	93.2
Organic mass	kg h^{-1}	107.9	93.9	68.3
Air flow stoichiometric	kg h^{-1}	607.8	529.0	384.6
Pyrolyzed organic biomass (PB)	kg h^{-1}	92.7	77.1	52.7

2.2. Experimental set up

The pyrolysis experiments were carried out in an auto-thermal pilot-scale plant (PPR-200) (which belongs to the University of Campinas). Fig. 1 shows a diagram of the experimental pilot plant used for developing these experiments. The pyrolysis reactor consists of a fluidized bed of 417 mm of inner diameter and 2600 high, which uses sand as inert solid. Rated of dry biomass supply capacity is 200 kg/h. The biomass was fed to the reactor by a screw, to be in contact with the hot bed of silica sand (particle diameter of 0.164 mm). Air was used as fluidization agent. A blower supplied the air flow which goes through the feeder screw and finally goes inside the reactor.

As a result of the process, the biomass was converted into charcoal, vapor and gas mixture. Volatile products (bio-oil and gas) left the reactor, entraining the finer char particles which were separated by means of two cyclones placed in series and collected in two tanks. The vapors produced were cooled and condensed with a water scrubber. A centrifugal device on top of the washing column enabled the organic and aqueous liquid phases to be collected separately. The gas fraction was led to a combustion chamber where it was burnt without any auxiliary fuel.

The feeding regime biomass to the reactor was controlled to ensure the stability of the temperature inside of the fluidized bed. The temperature and pressure were registered using thermocouples and pressure transducers located along the reactor height. This fact allowed knowing the behavior of the profiles of temperature and static pressure during operation.

2.3. Operational conditions

The operational conditions used in the sugar cane straw pyrolysis are shown in Table 2. Three experiments were carried out in this preliminary study. The experiments were performed at temperatures between 470 °C and 600 °C and at equivalence ratios

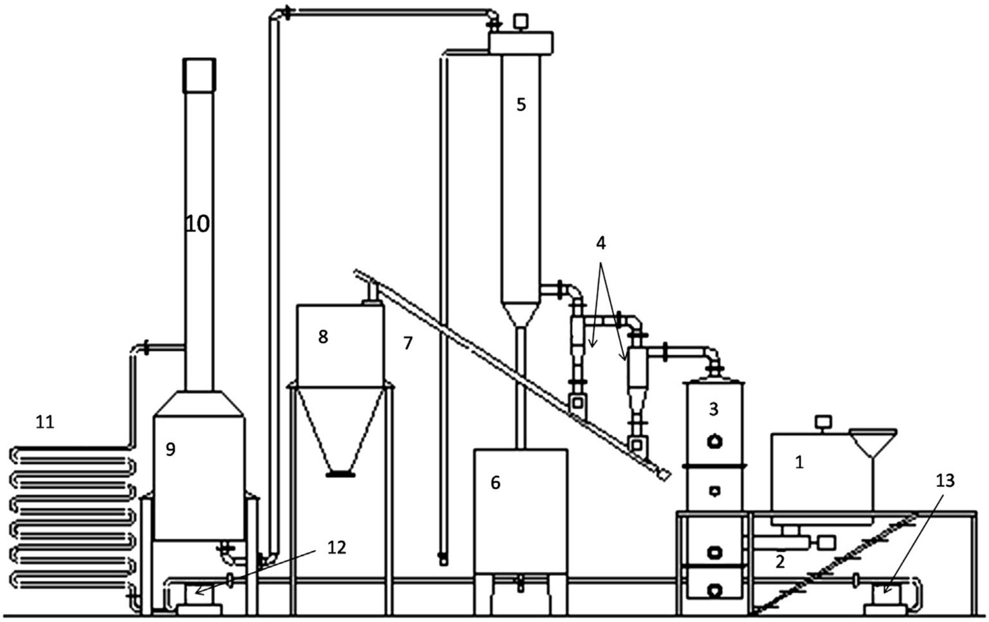

Fig. 1. PPR-200 pilot plant, flow diagram. 1) Hopper/silo; 2) screw feeder; 3) fluidized bed reactor; 4) cyclones; 5) separation system for bio-oil and acid extract; 6) reservoir for acid extract; 7) bio-oil extraction system; 8) char storage system; 9) combustion chamber; 10) chimney; 11) heat exchanger; 12) fan for hot gases; 13) fan for air.

(ERs) between 0.14 and 0.23. The equivalence ratio is defined as the ratio between the experimental flow rate of air used and the stoichiometric flow rate required for the complete fuel combustion.

The air flow was determined considering the stoichiometric amount necessary for it complete combustion. The air flow used was between 85.4 kg/h and 94.6 kg/h. The solid feed rate into the reactor was between 93.2 and 147.3 kg/h of which between 68.3 and 107.9 kg/h was organic matter. The organic matter has been determined as the total mass without moisture and ashes. As commented before, part of this organic material was combusted to obtain the heat necessary in the process. Therefore, the net organic fraction pyrolyzed (PB) is specified in Table 2.

2.4. Bio-oil characterization

The physicochemical properties and chemical composition of the organic (bio-oil) and aqueous (acid extract) fractions obtained were analyzed.

The following properties were analyzed as follows: Water content of the bio-oil samples was analyzed by Karl Fischer titration according to ASTM E 203. The pH of the samples was determined by means of a pH meter Mettler Toledo MP 120. The pH of the bio-oils was measured in the aqueous fraction extracted from each one of these samples according to the fractionation scheme established by Oasmaa and Kuoppala [30] for pyrolysis liquids. The heating value of the bio-oils was analyzed in a calorimetric bomb (C2000 Basic IKA-WERKE). Ultimate analyses were also carried out.

The chemical composition of each of the bio-oil samples was analyzed by GC/MSD (7890A GC-5975C MSD, using a DB-17ms capillary column, 60 m × 0.25 mm i.d., film thickness 0.25 μm). The injector temperature is 300 °C and 1 μl of sample was injected in splitless mode. The mobile phase was 1 ml/min of He. The MS parameters were: Acquisition mode: scan, the range of masses was between 80 and 400, the MSD Transfer line was 280 °C and the EI energy was 69.9 eV. The temperature programme was defined as: oven program 50 °C for 0 min, then 1.5 °C/min to 250 °C for 5 min, then 5 °C/min to 310 °C for 5 min, being the run time of 155.33 min. Prior to analysis, the samples were dissolved in appropriate solvents.

2.5. Char characterization

The ultimate and proximate analyses of the solid fraction produced in the pyrolysis experiments were carried out employing standard methods: moisture according to ISO-589-1981, ash according to ISO-1171-1976, and volatiles according to ISO-5623-1974. CHNS elemental analysis was carried out in a Carlo Erba 1108 apparatus.

3. Results and discussion

The pyrolysis of sugar cane straw in the pilot-scale plant was successfully carried out. The experiments carried out in the pilot-scale plant were auto-thermic. Due to the plant configuration, between 10 and 15 wt.% of the biomass fed was burnt to generate the heat necessary to warm the bed of inert material and achieve an adequate temperature for the beginning of the pyrolysis reaction of around 450–470 °C. This fact makes the reactor auto-thermal. This type of reactor has been previously tested with other residues [22].

A pyrolysis temperature between 470 °C and 600 °C was achieved with an equivalence ratio of approximately 0.14–0.23 (see Table 2). An increase in the equivalence ratio causes an increase in the temperature inside the reactor, in which the evaporation of volatiles on the feeding screw takes place. The vapors produced give rise to the suspension of the biomass reducing its bulk density. This phenomenon obstructed the entry of biomass to the reactor, which reduced the flow of biomass consumed in each experiment, being lesser than expected. This effect was most evident in experiments P2 and P3.

Table 3
Bio-oil and char product yields.

	Unit	Experiment		
		P1	P2	P3
Production rate of bio-oil	kg h^{-1}	32.9	17.3	8.8
Yield of bio-oil (PB base)	%	35.5	22.5	16.8
Yield of bio-oil (BB base)	%	22.3	13.5	9.5
Charcoal produced	kg h^{-1}	66.7	56.5	28.6
Percentage of ash in charcoal	%	33.8	39.8	63.0
Production of char ash free	kg h^{-1}	44.7	34.0	10.7
Yield of char (BB base)	%	45.8	44.1	31.2
Yield of char ash free (BB base)	%	30.3	26.5	11.5
Yield of char ash free (PB base)	%	48.2	44.1	20.3

3.1. Product yields

The product yields obtained in the experiments carried out are expressed on basis of total fed biomass (BB) and on basis of the pyrolyzed biomass (PB) (see Table 3), being the pyrolyzed biomass the total biomass excluding moisture and ash. Char and liquid yields are calculated by weighing the respective mass obtained after experiments and gas yield is calculated by the overall mass balance difference.

The values obtained of bio-oil yields, on basis of PB (PB base), are between 16.8 and 35.5 wt.%. In order to evaluate the influence of the ER on these product yields, the results are depicted in Fig. 2. The highest yield of bio-oil was reached under the conditions of the experiment P1 (35.5 wt.%), as well as the highest char yield (48.2 wt.%). This experiment was carried out at stable temperature of 470 °C and ER of 0.14. Some authors [3] studied the influence of the temperature on the bio-oil yield. Their study concluded that the bio-oil yield was optimized in the temperature range of 400–500 °C. This tendency is also observed in the present work. The operational temperature during the pyrolysis process in P2 and P3 tests was higher (550 and 600 °C respectively), resulting in an increase of the gas yield (20.4 and 42.6 wt.%), as expected [3].

The char yields fluctuated between 20.3 and 48.2 wt.% (ash free). These solid yields are similar to other char yields founded by other authors under similar operational conditions [4].

These results are also similar to the obtained in the pyrolysis of other type of biomasses processed under similar conditions and in

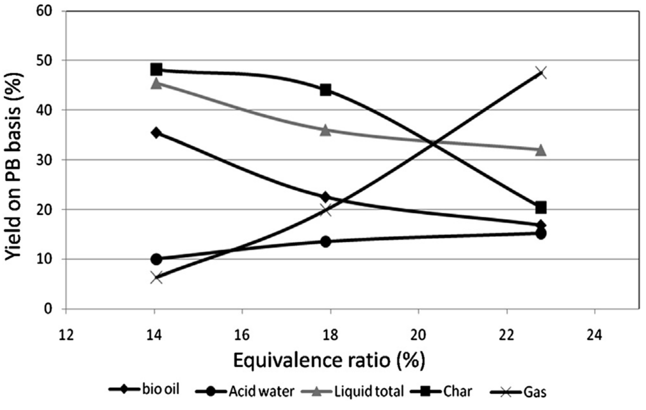

Fig. 2. Product yields in the fast pyrolysis of sugar cane straw. Influence of the equivalence ratio.

the same experimental plant. For example, the yields reported from the pyrolysis of several wastes are as follows: in the pyrolysis of sugar cane bagasse 35 wt.% of liquid, 25 wt.% of char and 40 wt.% of gas were obtained, in orange bagasse pyrolysis 40 wt.% of liquid, 20.5 wt.% of char and 39.5 wt.% of gases were produced, and in the pyrolysis of tobacco waste 31 wt.% of liquid, 40 wt.% of char and 29 wt.% of gas were obtained. Cascarosa et al. [22] studied the pyrolysis of meat and bone meal in order to evaluate the possible use of the products obtained, at the same time than manage this waste in an environmental sustainable manner. The product yields obtained in this study, under similar operational conditions (ER and temperature), are almost equal than the values obtained in the sugar cane straw pyrolysis process. In both studies, the bio-oil yield is higher than in other wastes pyrolysis processes. For instance, Fonts et al. [31] described a liquid yield of 45–50 wt.% in the pyrolysis of sewage sludge, however the water content within these liquids was between 27 wt.% and 46 wt.%. Therefore, the bio-oil yield obtained in this sugar cane straw pyrolysis process may point out the fast pyrolysis as a suitable way to this waste management.

3.2. *Chemical characterization of bio-oil and aqueous fraction*

In order to analyze the chemical composition of the bio-oil product, the first step was to evaluate the water content with it. Despite the bio-oil and the aqueous phase have been physically separated in the centrifugal system enclosed in the plant, the moisture content of bio-oil was determined by Karl Fischer method [32]. The results shown that less than 3 wt.% of water was content in the bio-oil. Regarding to the low moisture content of bio-oils, these results were attained due to the influence of the type of biomass, operational conditions and technology used. For example, it was reported that the water content within the bio-oil obtained in the pyrolysis of other type of biomasses oscillates between 35 [33], and 15 wt.% [34]. Bio-oils obtained in the pyrolysis experiments, carried out in the same plant, with sugar cane bagasse, orange bagasse, elephant grass and meat and bone meal as raw materials, have a water content between 2.4 and 19 wt.%, while the moisture of bio-oil from tobacco waste was 49 wt.% [35]. The quality of the bio-oils can be improved by reducing the water content, for this reason, Garcia-Perez et al. [36] proposed the evaporation of the lightest compounds and a portion of the water within the bio-oils, by incubation for 30 min at 45 °C in a rotator evaporator. This protocol was not necessary in this study due to the low water content in the bio-oil produced.

Proximate analyses were carried out to the three bio-oil samples obtained (see Table 4). As it can be observed, the volatile matter content decreased and the fixed carbon content increased when the ER increased. The ash content in the bio-oil was low, between 0.2 and 1.5 wt.%, and its presence can be attributed to the carbon particles, which are taken away by gases.

The pH of these bio-oils ranged between 3.1 and 3.6. These values may be due to the presence of organic acids such as formic acid and acetic acid, as well as aldehydes and phenols detected in the gas chromatographic analyses. These values are inside the limits reported for pyrolysis liquids, which generally range between 2 and 3.7. However, it also can be higher (up to 4.5 for bio-oil from cane bagasse) or even can have a basic character (such as bio-oil from tobacco waste [37], or meat and bone meal [22]).

The determination of carbon, hydrogen, nitrogen and sulfur content, and the HHV and LHV of bio-oil was carried by using a sample from the experiment P1, which displayed the highest liquid yield (Table 4). The carbon content within this sample (57.5 wt.% dry basis) was higher than the original biomass (43.2 wt.% dry basis). The sulfur and nitrogen content was very low (0.1 wt.% and 1.0 wt.% respectively), while the oxygen content of bio-oil was of 33.8 wt.% dry basis (by difference), lower than the values commonly reported in bio-oils from other materials (range between 45 and 50 wt.%), justified by the presence of about 200 oxygenated compounds [38]. The reduction in the oxygen content is desirable because its presence is indicative of the presence of many highly polar groups leading to high viscosities and boiling points as well as poor chemical stability [39].

Table 4
Proximate, ultimate and heating value analyses, moisture content and pH of bio-oils and char samples.

	Unit	Experiment		
		P1	P2	P3
Bio-oils				
Ash[a]	wt.%	0.6	0.2	1.5
Volatile matter[a]	wt.%	90.5	87.3	85.7
Fixed carbon[a]	wt.%	9.8	12.5	12.7
pH		3.1	3.3	3.6
Water content	wt.%	<3	<3	<3
C[a]	wt.%	57.5	–	–
H[a]	wt.%	7.0	–	–
N[a]	wt.%	1.0	–	–
S[a]	wt.%	0.1	–	–
O[a]	wt.%	33.8	–	–
H/C	molar ratio	1.46	–	–
O/C	molar ratio	0.59	–	–
Higher heating value (HHV)	MJ/kg	24.43	–	–
Lower heating value (LHV)	MJ/kg	22.95	–	–
Char				
C[a]	wt.%	41.3	52.4	20.7
H[a]	wt.%	2.9	2.6	1.0
N[a]	wt.%	0.4	0.5	0.1
S[a]	wt.%	0.1	0.1	0.0
O[a]	wt.%	21.5	4.5	15.2
Ash[a]	wt.%	33.8	39.9	63.0
Volatile matter[a]	wt.%	36.4	30.6	19.5
Fixed carbon[a]	wt.%	30.1	30.4	18.4
Moisture	wt.%	1.9	1.0	1.9
H/C	molar ratio	0.83	0.61	0.57
O/C	molar ratio	0.52	0.06	0.55
Higher heating value (HHV)	MJ/kg	14.15	14.48	13.08
Lower heating value (LHV)	MJ/kg	13.54	13.91	12.67

[a] wt.% on dry basis.

The H/C molar ratio in this bio-oil sample is 1.46, lower than in the bio-oil from cane straw pyrolysis (1.85). This fact may be due to the increase in carbon content in the bio-oil. The O/C molar ratio also decreased regarding the value obtained for cane straw (from 0.87 to 0.59). The low oxygen and water content, as well as the higher carbon and hydrogen contents within the bio-oil have a significant influence on their higher heating value. The higher and lower heating values (HHV and LHV) are 24.43 MJ/kg and 22.95 MJ/kg respectively. Both values are higher than the original biomass (18 MJ/kg and 17 MJ/kg), but lower than the HHV of petroleum fuels used typically in gas turbines (approximately 40 MJ/kg). Nevertheless, the highest bio-oil observed in the present study compares very well with values reported in the literature, ranging from 5.12 MJ/kg to 22.4 MJ/kg.

Both of the liquid fractions produced in the sugar cane straw pyrolysis, bio-oil and acid water, were analyzed by means of gas chromatography, which allowed the identification of the organic compounds present on these products. The samples analyzed corresponded to the experiment P1. Fig. 3(a) and (b) shows semi-volatile and volatile compounds present in the bio-oil as well as their content. Oxygenated compounds represented the 66.6% of the identified compounds. Among the volatile components, oxygenated compounds of low molecular weight were identified such as methanol (32.04 g/mol) and acetol (74.08 g/mol), as well as

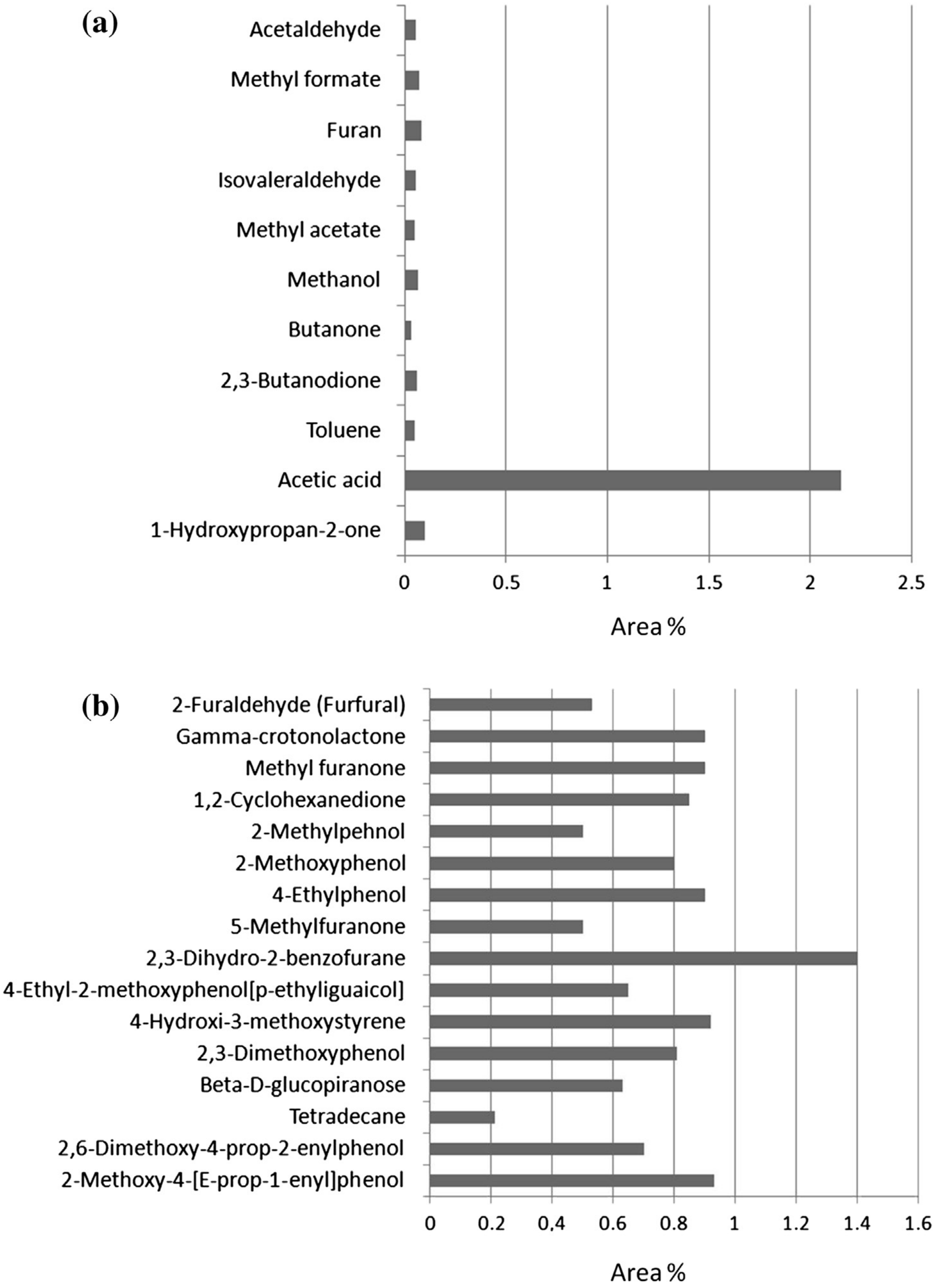

Fig. 3. (a) Content of organic volatile compounds in bio-oil of fast pyrolysis of cane straw. (b) Content of semi volatile organic compounds in bio-oil of fast pyrolysis of cane straw.

aromatic hydrocarbon such as toluene. The most abundant compound was acetic acid, followed by 1-Hydroxypropan-2-one (acetol).

Semi-volatile compounds present in the bio-oil, as well as their contents are shown in Fig. 3(b) as % of the area. Among them, aromatic oxygenated compounds predominate (27.7%), such as 2-furaldehyde (furfural), 2-methylphenol (o-cresol), 2-methoxyphenol (Guaiacol), 2.3-Dihydro-1benzofuran (Couma) and 2-methoxy-4-[(E)-prop-1-enyl] phenol (Isoeugenol). Moreover, some heterocyclic aromatic hydrocarbons (27.7%) and naphthalene, phenanthrene, pyrene, crysene and other compounds with molecular weight between 128 and 228 g/mol were identified.

The acid extract obtained from the cane straw pyrolysis, under P1 experimental condition, was also analyzed by means of gas chromatography. Both, the identified compounds and their content are shown in Fig. 4. All of the compounds detected were oxygenated compounds. An amount of 56.5% of these compounds was aliphatic and the rest of these were aromatic compounds with a molecular weight between 46.03 g/mol and 154.16 g/mol. The most abundant compounds were the Cyclopent-2-en-1-one, acetic acid, furanone and furfuric alcohol.

Bio-oil and acid extract may be used as source materials to obtain various chemical products using separation processes, or directly, as additives in the formulation of emulsifying [40], foaming [41], and extraction agents, among other applications [42].

3.3. Charcoal properties

The charcoal obtained under the three experimental conditions described before, was chemically characterized. Table 4 presents

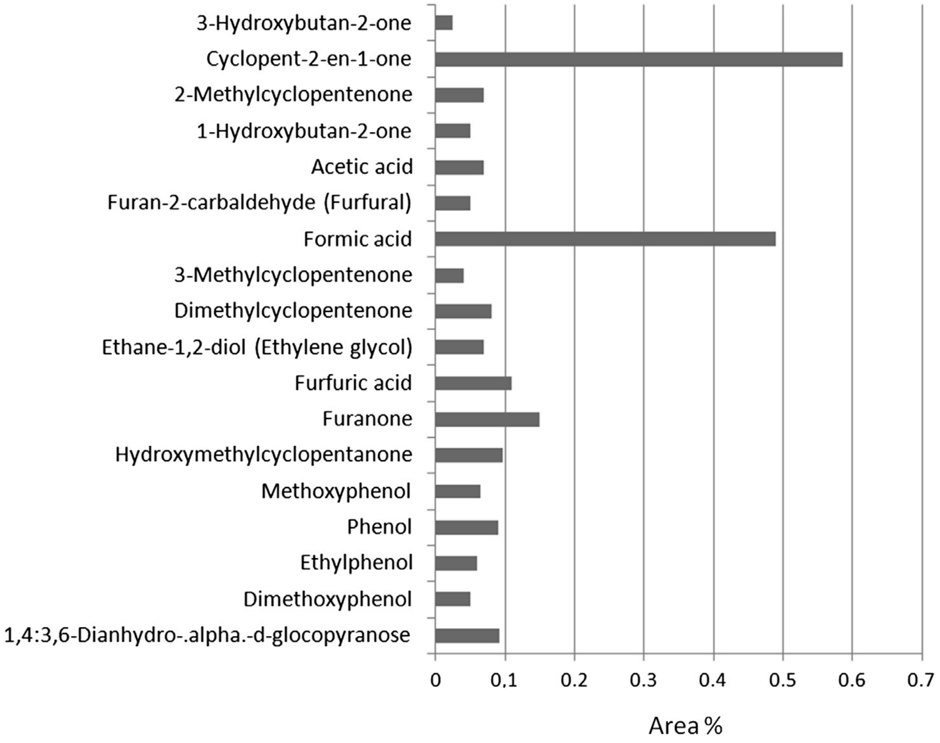

Fig. 4. Content of compounds presents in the acid extract.

the proximate and ultimate analysis of the three charcoal samples obtained. When the pyrolysis of the biomass takes place, the carbon concentration within the product and the release of oxygen occurs. In the experiments carried out it could be noted that the fixed carbon content in the char product decreased from experiments P1 and P2, to P3. While the ER gradually rose, a higher charcoal consumption occurred due to the increase of the oxygen supply. The volatile matter also decreased.

The ash content was high in the char products due to the retention of the organic compounds. Therefore the ash content becomes higher in charcoal than that in the bio-oils.

The ash content within the char samples decreased while the char yield increased, being higher at high equivalence ratios (see Fig. 5).

The higher caloric value of the char obtained, varied between 13.08 and 14.48 MJ/kg. These values are similar to those reported by Carrier et al. [3]. The high ash content influences on a series of charcoal properties, particularly its heating value.

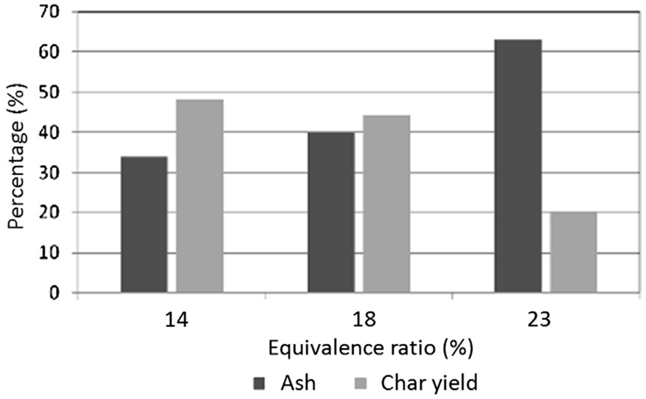

Fig. 5. Influence of the equivalence ratio on the relation between char yield and its ash content.

Other authors also analyzed the density of the char product (637 kg/m^3) and the BET surface area (259 m^2/g) [4].

In order to find a potential use for this product, Carrier et al. [4] evaluated the char obtained from the sugar cane bagasse pyrolysis as an activated carbon and as a soil amendment. The results show their optimal use as an activated carbon but unfortunately, the biochar could not be considered as a balanced fertilizer on its own, as it contains relatively low levels of water soluble nutrients.

3.4. *Energy efficiency*

As it was feasible to observe, the bio-oil and charcoal obtained from cane straw by means of fast pyrolysis in fluidized bed, reached characteristic HHV and LHV values of these types of substances. In the case of bio-oil these values are slightly higher than bio-oils from biomasses reported by other authors (14–18 MJ/kg). Considering the calorific values of bio-oil and char products, and being aware of these product yields, the energy output was determined. This was considered as a relationship between the energy content within bio-oil and charcoal per unit of fed biomass. The results are shown in Table 5. The energy content of bio-oil was 5.12 MJ/kg fed biomass, and the charcoal of 6.20 MJ/kg fed biomass.

Table 5
Equivalent energy content within bio-oil and char products. Energy efficiency.

	Cane straw	Bio-oil	Char
LHV (MJ/kg)	17.00	22.95	13.54
Yield (%)		22.3	45.8
Energy content (MJ/kg of biomass)		5.12	6.20
Energy efficiency (%)	On basis of bio-oil	**30.1**	**66.6**
	On basis of char	**36.5**	

In the case of the energy content of bio-oil, it can be stated, that is comparable with the values obtained for cane waste reported by Xu et al. [43] whose results were 4.3 and 6.0 MJ/kg of fed biomass.

The energy efficiency of this experimental pyrolysis process, defined as explained, was 66.6%. Thus, the 66.6% of the energy content in the raw material is recovered into the char and bio-oil products. In this study, the energy value of the gases was not analyzed. Therefore, by using the pyrolysis process, not only the energy value of the raw material has not been lost but also, we are recovering an important part of this energy value.

4. Conclusions

In Brazil, million of tons of sugar cane straw and bagasse are produced. Currently, significant parts of this waste are burnt. Several Laws were fixed in this country in order to avoid the burning of wastes before the 2031 year. Thus, other environmental friendly processes must be analyzed. Pyrolysis is a thermochemical process used to convert biomass into products, which can be used as fuels or for chemicals production. Therefore, by means of the pyrolysis, it can be achieved to convert the waste into products.

The pyrolysis experiments were developed in a pilot-scale plant of 200 kg h^{-1} of capacity. The maximum bio-oil yield was achieved at 470 °C and ER of 0.14. The bio-oil obtained has a low oxygen content and high heating value.

The gas chromatographic analyses showed numerous oxygenated compounds. The presence of organic acids compounds confers an acidic character to bio-oil.

The technical viability of the fast pyrolysis of sugar cane straw has been demonstrated on basis of the results obtained in this work. Fast pyrolysis has been proved as a potential treatment to the management of this residue since Brazil produces thousands of tons of straw a year, generating agricultural residues with a considerable environmental impact.

Acknowledgements

The authors thank FAPESP under process number 03/13313-5, to the Conselho Nacional de Desenvolvimiento Científico e Tecnológico (CNPq) (Process 1506604/2009-2) and Coordenaçáo de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), for the financial support to this work.

References

[1] Ministério daAgricultura, Brasil, www.agricultura.gov.br/arq_editor/file/Desenvolvimento_Sustentavel/Agroenergia/estatisticas/producao/atualizacao_20_01_2011/Producao_Acucar_Brasil.pdf (accessed July 2012).
[2] BNDES-CGEE, Centro de Gestão e Estudos Estratégicos, Sugarcane-based Bioethanol: Energy for Sustainable Development, first ed., Rio de Janeiro (Brazil), 2008.
[3] M. Carrier, T. Hugo, J. Gorgens, H. Knoetze, Comparison of slow and vacuum pyrolysis of sugar cane bagasse, Journal of Analytical and Applied Pyrolysis 90 (2011) 18–26.
[4] M. Carrier, A.G. Hardie, Ü. Uras, J. Görgens, H.J. Knoetze, Production of char from vacuum pyrolysis of South-African sugar cane bagasse and its characterization as activated carbon and biochar, Journal of Analytical and Applied Pyrolysis 96 (2012) 24–32.
[5] M.S. Aranda Moraes, F. Georges, S. Rodrigues Almeida, F. Cardoso Damasceno, G. Pereira da Silva Maciel, C. Alcaraz Zini, R. Assis Jacques, E.B. Caramao, Analysis of products from pyrolysis of Brazilian sugar cane straw, Fuel Processing Technology 101 (2012) 35–43.
[6] L. Petrus, M.A. Noordermeer, Biomass to biofuels, a chemical perspective, Green Chemistry 8 (2006) 861–897.
[7] M.J. Antal, M. Gronli, The art, science, and technology of charcoal production, Industrial and Engineering Chemical Research 42 (2003) 1619–1640.
[8] E. Putun, F. Ates, A.E. Putun, Catalytic pyrolysis of biomass in inert and steam atmospheres, Fuel 87 (2008) 815–824.
[9] C. Amen-Chen, H. Pakdel, C. Roy, Production of monomeric phenols by thermochemical conversion of biomass: a review, Bioresource Technology 79 (2001) 277–299.
[10] W.T. Tsai, M.K. Lee, Y.M. Chand, Fast pyrolysis of rice husk: product yields and compositions, Bioresource Technology 98 (2007) 22–28.
[11] M.K. Lee, W.T. Tsai, Y.L. Tsaic, S.H. Lin, Pyrolysis of napier grass in an induction-heating reactor, Journal of Analytical and Applied Pyrolysis 88 (2010) 110–116.
[12] Y. Peng, S. Wu, The structural and thermal characteristics of wheat straw hemicellulose, Journal of Analytical and Applied Pyrolysis 88 (2010) 134–139.
[13] L.A. Barbosa, Sugar Cane Bioethanol. P&D for Productivity and Sustainability, first ed., Edgar Blucher Ltd., Sao Paulo, (Brazil), 2010 (in Brazilian).
[14] C. Erlich, E. Björnbom, D. Bolado, M. Giner, T.H. Fransson, Pyrolysis and gasification of pellets from sugar cane bagasse and wood, Fuel 85 (2006) 1535–1540.
[15] J.M. Mesa-Perez, L.A.B. Cortez, J.D. Rocha, L.E. Brossard-Perez, E. Olivares-Gómez, Unidimensional heat transfer analysis of elephant grass and sugar cane bagasse slow pyrolysis in a fixed bed reactor, Fuel Processing Technology 86 (2005) 565–575.
[16] A. Ounas, A. Abulkas, K. El harfi, A. Bacaoui, A. Yaacoubi, Pyrolysis of olive residue and sugar cane bagasse: non-isothermal thermogravimetric kinetic analysis, Bioresource Technology 102 (2011) 11234–11238.
[17] C. Erlich, M. Öhman, E. Björnbom, T.H. Fransson, Thermochemical characteristics of sugar cane bagasse pellets, Fuel 84 (2005) 569–575.
[18] A. Moubarik, N. Grimi, N. Boussetta, A. Pizzi, Isolation and characterization of lignin from Moroccan sugar cane bagasse: production of lignin-phenol-formaldehyde wood adhesive, Industrial Crops and Products 45 (2013) 296–302.
[19] Ü. Uras, M. Carrier, A.G. Hardie, J.H. Knoetze, Physico-chemical characterization of biochars from vacuum pyrolysis of South African agricultural wastes for application as soil amendments, Journal of Analytical and Applied Pyrolysis 98 (2012) 207–213.
[20] S.A. Arni, B. Bosio, E. Arato, Syngas from sugarcane pyrolysis: an experimental study for fuel cell applications, Renewable Energy 35 (1) (2010) 29–35.
[21] A.V. Bridgwater, G.V.C. Peacocke, Fast pyrolysis processes for biomass, Renewable and Sustainable Energy Reviews 4 (2000) 1–73.
[22] E. Cascarosa, I. Fonts, J.M. Mesa, J.L. Sánchez, J. Arauzo, Characterization of the liquid and solid products obtained from the oxidative pyrolysis of meat and bone meal in a pilot-scale fluidized bed plant, Fuel Processing Technology 92 (2011) 1954–1962.
[23] D. Mohan, C.U. Pittman Jr., P.H. Steele, Pyrolysis of wood/biomass for bio-oil: a critical review, Energy & Fuels 20 (2006) 848–889.
[24] A. Effendi, H. Gerhauser, A.V. Bridgwater, Production of renewable phenolic resins by thermochemical conversion of biomass: a review, Renewable and Sustainable Energy Reviews 12 (2008) 2092–2116.
[25] R. Fahmi, A.V. Bridgwater, I. Donnison, N. Yates, J.M. Jones, The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability, Fuel 87 (2008) 1230–1240.
[26] L.D. Rocha, J. Mesa, E. Olivares, A. Fiovanelli, L.A. Cortez, Potential of the Biomass Fast Pyrolysis Technology to Bio-oil Production in Brazil, in: A.V. Bridgwater, D.G.B. Boocock (Eds.), Science in Thermal and Chemical Biomass Conversion, ISBN 1-872691-97-8. Newbury, Berks (UK), 2006.
[27] R. Fahmi, A.V. Bridgwater, L.I. Darvell, J.M. Jones, N. Yates, S. Thain, I.S. Donnison, The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses, switch grass and willow, Fuel 86 (2007) 1560–1569.
[28] J.M. Jones, A. Williams, L.I. Darvell, M. Nawaz, X. Baxter, The role of metal in biomass pyrolysis, char formation and char properties, in: A.V. Bridgwater (Ed.), Fast Pyrolysis of Biomass: a Handbook, vol. 2, CPL Press, Newbury (UK), 2006, pp. 1203–1214.
[29] G. García, E. Cascarosa, J. Ábrego, A. Gonzalo, J.L. Sánchez, Use of different residues for high temperature desulphurisation of gasification gas, Chemical Engineering Journal 174 (2011) 644–651.
[30] A. Oasmaa, E. Kuoppala, Fast pyrolysis of forestry residue. 3. Storage stability of liquid fuel, Energy & Fuels 17 (2003) 1075–1084.
[31] I. Fonts, M. Azuara, G. Gea, M.B. Murillo, Study of the pyrolysis liquids obtained from different sewage sludge, Journal of Analytical and Applied Pyrolysis 85 (2009) 184–191.
[32] Th. Cachet, J. Hoogmartens, The determination of water in erythromycin by Karl Fischer titration, Journal of Pharmaceutical and Biomedical Analysis 6 (1988) 461–472.
[33] G. Dobele, T. Dizhbite, I. Urbanovich, A. Andersone, J. Ponomarenko, G. Telysheva, Pyrolytic oil on the basis of wood and the antioxidant properties of its water-soluble and insoluble fraction, Journal of Analytical and Applied Pyrolysis 85 (2009) 81–86.
[34] A. Oasmaa, D. Meier, Pyrolysis liquids analysis. The results of IEA-EU round robin, in: A.V. Bridgwater (Ed.), Fast Pyrolysis of Biomass: a Handbook, vol. 2, CPL Press, Birmingham, Newbury (UK), 2002, pp. 41–58.
[35] M. Asadullah, M.A. Rahman, M.M. Ali, M.S. Rahman, M.A. Motin, M.B. Sultan, M.R. Alam, Production of bio-oil from fixed bed pyrolysis of bagasse, Fuel 86 (2007) 2514–2520.
[36] M. Garcia-Perez, A. Chaala, C. Roy, Vacuum pyrolysis of sugarcane bagasse, Journal of Analytical and Applied Pyrolysis 65 (2002) 111–136.
[37] A. Oasmaa, D. Meier, Analysis characterization and test methods of fast pyrolysis liquids, in: A.V. Bridgwater (Ed.), Fast Pyrolysis of

Biomass: a Handbook, vol. 2, CPL Press, Birmingham, Newbury (UK), 2002, pp. 23–40.

[38] S. Czernik, A.V. Bridgwater, Overview of applications of biomass fast pyrolysis oil, Energy & Fuels 18 (2004) 590–598.

[39] I. Demiral, E.A. Ayan, Pyrolysis of grape bagasse: effect of pyrolysis conditions on the product yields and characterization of the liquid product, Bioresource Technology 102 (2011) 3946–3951.

[40] S.J. Falcón, J. Carbonell, Fuel emulsions using biomass pyrolysis products as an emulsifier agent, Energy & Fuels 17 (2) (2003) 302–307.

[41] M.M. Penedo, N. Serret, J. Milán, S. Ariza, J. Falcón, Bench scale leach tails of technology pyroligneous acid ammonium carbonate sugar cane bagasse, Revista Tecnología Química 29 (3) (2009). Santiago de Cuba, (Cuba) (in Spanish).

[42] Q.N. Varela, L. Brossard, B. Dupotey, M. Penedo, Influence of the alkali solutions in the flotation of the copper minerals, Parte I, Tecnología Química XXII (1) (2002) 93–101. Santiago de Cuba, (Cuba) (in Spanish).

[43] R. Xu, L. Ferrante, C. Briens, F. Berruti, Bio-oil production by flash pyrolysis of sugarcane residues and post treatments of the aqueous phase, Journal of Analytical and Applied Pyrolysis 91 (2010) 263–272.