The effect of citric acid pretreatment on composition and stability of bio-oil from sugar cane residues using a continuous lab-scale pyrolysis reactor

L. Rodríguez-Machín[a,b], L. E. Arteaga-Pérez[c], R. Manrique[c], M. Pala[b], J. Feys[b], S. Ghysels[b], W. Prins[b], F. Ronsse[b,*]

[a] Center for Energy and Environmental Technologies Assessments (CEETA), Faculty of Mechanical and Industrial Engineering. Universidad Central "Marta Abreu" de Las Villas, Cuba. E-mail: lizetr@uclv.edu.cu

[b] Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Belgium. E-mail: Mehmet.Pala@UGent.be; Jeroen.feys@hotmail.com; Stef.Ghysels@UGent.be; Wolter.Prins@UGent.be; Frederik.Ronsse@UGent.be

[c] Laboratory of Thermal and Catalytic Processes (LPTC-UBB). Wood Engineering Department, University of Bío-Bío, Concepción, Chile. E-mail: larteaga@ubiobio.cl

[*] Corresponding author

Abstract

This study outlines the effect of citric acid leaching on the quality and stability of fast pyrolysis bio-oils from sugarcane bagasse (SCB) and sugarcane trash (SCT). The quality of bio-oil was probed by GC-MS analysis, elemental composition, higher heating value, water and solids content, pH, dynamic viscosity and stability (ageing). Pyrolysis was performed at 500 °C in a fully controlled, continuously operated plant with a biomass throughput of ca. 300 $g.hr^{-1}$. While citric acid leaching causes a decrease of the average bio-oil yield with 5 %, it does not lead to a bio-oil with improved fuel-related properties. However, the bio-oil composition became more advantageous in light of its biorefining. Indeed, citric acid leaching led to an increased levoglucosan concentration – a promising platform chemical – of 17 % for SCB and of to 35 % for SCT (based on relative abundance in GC-MS). In tandem, the concentration of carboxylic acids and phenols in the bio-oil decreased after citric acid leaching, which is beneficial for downstream purification of levoglucosan. Regarding the non-condensable gases, CO and CO_2 represented between 88 and 91% by weight of the total non-condensable gases produced in pyrolysis. Therefore, the results of this study demonstrate that optimized biomass demineralization pretreatment with citric acid could produce bio-oil at high yield and rich in high-value chemical compounds like levoglucosan. Biomass demineralization pretreatment however, does not result in bio-oil with improved quality for fuel purposes, nor does it necessarily lead to bio-oil having higher stability.

Keywords: Bio-oil, Composition, Leaching, Stability, Sugarcane bagasse, Sugarcane trash

1. Introduction

Fast pyrolysis is one of the most studied processes to convert biomass into liquid biofuels. Pyrolysis involves heating the biomass in the absence of oxygen to produce bio-oil, biochar and permanent gases. Bio-oil, the liquid product of pyrolysis, is considered a renewable fuel. There are only a limited number of scenarios in which these biomass-derived liquids can be applied directly with minor modifications to the equipment in which the bio-oil is being consumed, which is the case when bio-oil is used as boiler fuel. However, bio-oil has technical and physico-chemical characteristics that hinder its application in most fuel scenarios, e.g. as a transportation fuel, thus requiring the design of bio-oil upgrading strategies [1].

Bio-oils are typically rich in water (15-30 wt.% on dry basis) [2-4], can have substantial levels of suspended solids ranging from 0.01 to 3 wt.%, have a density higher than conventional fossil fuels (1.0-1.3 kg·m^{-3} measured between a temperature of 15 ˚C and 40 ˚C and depending on the raw materials and pyrolysis conditions [2,5]), are acidic (pH value in the range of 2-4) and mostly contain carboxylic acids and phenolics. Bio-oils have a heating value in a range of 15-26 MJ·kg^{-1} [6,7] which is about half of that of mineral oils (40-46 MJ·kg^{-1}) and are chemically unstable when heated or stored for prolonged periods of time. Moreover, bio-oils are highly polar, containing about 35–40 wt.% oxygen (dry basis), while mineral oils contain oxygen at ppm levels. Bio-oils are not miscible with mineral oils without a pretreatment. Therefore, these issues must be taken into careful consideration prior to their use in a range of applications.

For example, the high-water content in bio-oils is detrimental for combustion engines and may lead to phase separation: a supernatant phase rich in extractives and water-soluble compounds [8] and a bottom phase containing heavier organic compounds, including pyrolytic lignin. Consequently, such phase separation may hinder the direct application of bio-oils [9]. Moreover, the pH of bio-oil makes it a highly corrosive liquid, directly hindering its use as a fuel in existing, conventional systems and imposing the need for special metals when constructing equipment destined for processing and consuming bio-oil. Moreover, solid particles in bio-oil (char fines that escaped the solids separation system) have the potential to cause equipment blockages like in injectors [10,11] and can erode turbine blades [3]. During storage, some reactive components in the bio-oil undergo polymerization leading to the formation of larger molecules that result in higher viscosity of the bio-oil, phase separation and lower combustion efficiency [3,10,12].

In entrained bed reactors, and some fluidized bed processes, some sand may also end up in the product liquid along with the char, due to bed attrition phenomena. Thus, the solids content in the bio-oil depends on the feedstock (type and particle size distribution), process type (fluidized bed, entrained bed, etc.), and also on the particle separation systems downstream the pyrolysis reactor. Most of these systems are provided with cyclones, among which, those able to operate at high temperatures with a high efficiency for separating low-density solid particles, are the desired ones. Depending on the densities and storage time, solids can be found on the surface or at the bottom of the pyrolysis liquid [1,12].

Several studies have properly documented that inorganics catalyze dehydration and cracking reactions during pyrolysis, lowering the bio-oil quality [13]. Inorganics are present in at least two forms in biomass: either soluble salts (e.g. oxides, carbonates, oxalates and chlorides) deposited in cells or pores after drying [14] or as cations bound to reactive ionic sites in biomass. Soluble salts can be removed through simple water leaching[15], while inorganics in the form of cations which are bound to negatively charged functional groups associated to lignin, hemicellulose, cellulose and extractives, thus require an acid for ion exchange to occur [15-17].

Washing with water or a dilute acid (either mineral or organic acid) are typical leaching methods used in biomass demineralization to reduce the inorganic content (ash) [14,18,19]. The removal or passivation of the alkali and alkaline earth metals (AAEMs) in biomass is required for controlling the fast pyrolysis reaction and improving bio-oil quality and stability [20]. Additionally, in closed loop systems where the heat carrier in fast pyrolysis is continuously being recycled, the ash-forming minerals in the biomass tend to accumulate in the process, thereby jeopardizing the long-term stability of process operation. Finally, elements like AAEMs could also deactivate or poison the heterogenous catalysts used in catalytic fast pyrolysis [21]. Recent fast pyrolysis research focuses more towards the use of residual, as-of-yet non-valorized biomasses (e.g. agricultural residues) which typically have higher ash contents compared to clean wood-based feedstock, hence the importance of prior demineralization with either mineral [22-27] or organic acids [28-30]. According to Rodríguez-Machín et al. the effect of hydrolysis promoted by the acids during the leaching process on the thermal degradation behavior appears to be dominant over any suppression or passivation of the catalytic effect of AAEMs. Hence the importance of using organic acids that are more mild (towards the lignocellulosic structure of the biomass) but are able to achieve high demineralization efficiencies, like citric acid [31].

Nonetheless, thermochemical valorization of sugarcane lignocellulosic biomass has arisen as one of the strategic research areas concerning biorefinery concepts because of its potential to produce fuels and high value-added chemicals [32]. However, further investigation is required to achieve cost-effective procedures, to fully exploit the potential of the bio-oil as a source of chemicals and biofuels. In more recent times, several chemicals derived from bio-oil are being considered as platform molecules for biorefineries (e.g., furans, phenolics, C_5 and C_6 anhydrosugars, etc.). Thus, developing process strategies to obtain a bio-oil rich in those platform molecules and with low levels of impurities (such as solids) and high stability (low reactivity, improved aging behavior) is of paramount importance for establishing a bio-oil biorefinery [33]. In that regard, mineral removal is not only meaningful to envisage better bio-oil stability, it also enhances the yield in compounds of interest like levoglucosan. Indeed, these minerals catalyze the cracking of levoglucosan into smaller oxygenated compounds, like acetic acid.

The analytical-scale and lab-scale results reported in previous papers [34,35] are the knowledge basis supporting the bench-scale attempt in this study for producing a bio-oil from demineralized sugarcane residues. The stability of the bio-oil is assessed by rheological characterization and aging tests. The bio-oil quality was assessed by elemental composition, pH, higher heating value, water and solids content, viscosity and GC-MS analysis.

2. Materials and Methods

2.1 Raw sugarcane residues

Sugarcane trash (SCT) and sugarcane bagasse (SCB) of the Cuban´s 1051-73 variety were used in this work and were provided by the Ifraín Alfonso sugar mill, located in Villa Clara, Cuba. SCT was manually harvested and SCB was sampled two hours after milling. Both materials were naturally dried in ambient atmosphere for three days. Afterwards, they were ground into particles ranging from 1 to 2 mm in size using a Retsch mill. The water mass fraction on an as received basis was 32 $g \cdot kg^{-1}$ in SCT and 51 $g \cdot kg^{-1}$ in SCB.

2.2 Pretreatment

The pretreatment experiments of both biomasses were conducted according to procedures reported elsewhere [35]. In brief, citric acid (CA, in an aqueous solution of a concentration of 0.096 $kg \cdot dm^{-3}$) was used as the leaching solution at 25 ºC, wherein the biomass was soaked with 1 h of residence time in a 10 dm^3 glass vessel. For SCT, each leaching batch contained 0.608 kg of biomass, while for SCB it was 0.633 kg of biomass, both keeping the same liquid-to-solids ratio as previously reported (12 dm^3 leaching solution per kg of biomass) [31]. To reach an adequate dispersion of biomass-leaching solution and have proper mixing, the rotational speed of the stirrer was set at 350 and 470 rpm for SCB and SCT, respectively.

During citric acid pretreatment, not only inorganic constituents but also organic compounds are removed from the biomass matrix. Accordingly, the leaching losses (in wt.%) in pretreatment are quantified as,

$$\eta_{total} = \frac{m_u - m_t}{m_u} \cdot 100\% \qquad (1)$$

Where m_u and m_t are the masses of the untreated and treated samples (dry basis, in kg) respectively.

2.3 Lab-scale fast pyrolysis experiments

Fast pyrolysis experiments of raw and pretreated sugarcane residues were carried out in a fully controlled, continuously operated plant (see Fig. 1). The plant was designed and constructed by Biomass Technology Group (Enschede, The Netherlands) and is based on auger reactor technology [21] and described in detail in [36]. The reactor was designed for continuous production of ca. 0.3 $kg \cdot h^{-1}$ bio-oil.

Below, a brief description of the setup operation is given.

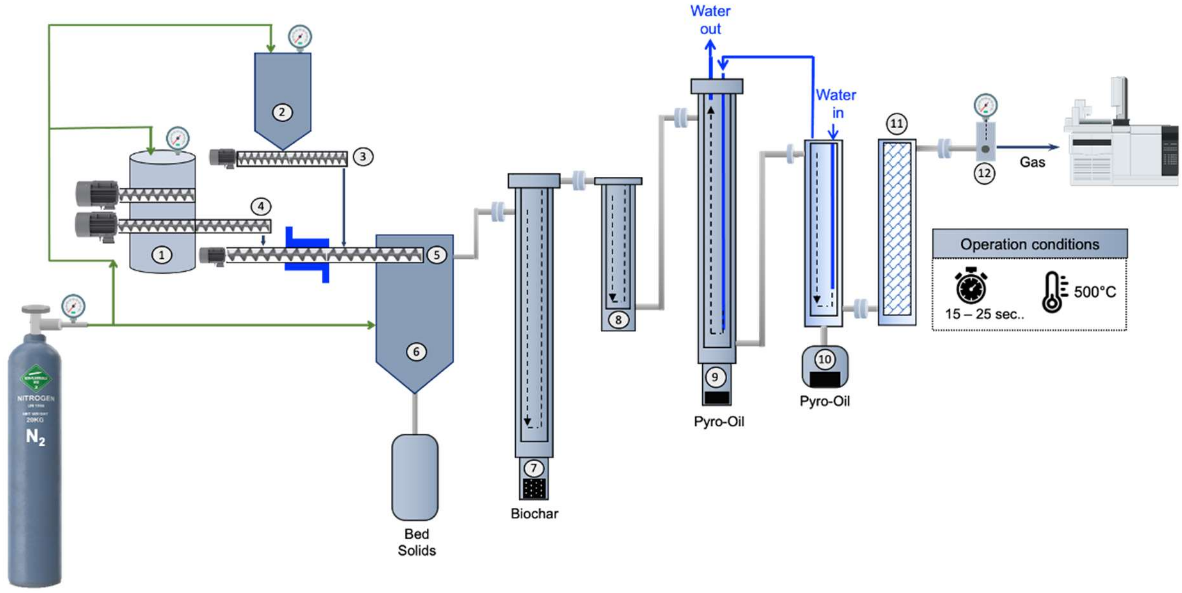

Figure 1. Schematic diagram of the mini-plant used for the pyrolysis experiments. Adapted from [36]. (1) biomass storage hopper; (2) heat carrier storage hopper; (3) heat carrier conveyor; (4) biomass conveyor; (5) reactor auger/screw; (6) downer; (7) solids collection vessel; (8) knock-out vessel; (9) ESP; (10) glass condenser; (11) cotton filter; (12) gas flow meter; green lines: N_2.

After being weighted, the biomass is introduced into a hopper (1) with a storage capacity of 4 kg. The hopper includes an agitator to prevent the formation of aggregates and biomass lumps. A feed screw (4) transports the biomass into the reactor screw (5). A water-cooled stainless-steel jacket was placed around the front section of the auger to prevent biomass thermal decomposition before contacting with the heat carrier. In this work, the feed rate of biomass was slightly changed (270 - 300 $g{\cdot}h^{-1}$) depending on the biomass type (SCT or SCB) due to the differences in density. The heat carrier was silica sand with a mean diameter of 250 µm, was provided by PTB-Compaktuna (Gent, Belgium) and was stored in a hopper (2) with 25 kg of capacity. Next to a knock-out vessel (8), the setup has an ex situ reactor (for vapor phase upgrading) that was not used (*i.e.* kept empty) in the experiments carried out in this work.

The heat carrier is transported to the reactor through a 1.1 m long heated screw (3) at a flow rate of 8.3 $kg{\cdot}h^{-1}$. Heat carrier-to-biomass mass ratio was about 34:1. The last section of the reactor screw serves as the biomass fast pyrolysis reactor, this section starts at the point where the biomass and the heat carrier are intensively mixed and ends when the mixture drops into a conical downer. In this section, the solid material's residence time is approximately 1 s. After this screw section, the mixture flows into a conical downer (6) containing a bed of sand plus reacting biomass of a specific height where the biomass further undergoes and completes pyrolysis at 500 °C. The height of the bed in the downer is controlled by a sluice system which is placed at the bottom of the downer. The time of opening and closing of both sluices was optimized by trial and error and found to be in the range of 15-25 seconds. The timing depends on the biomass type and screw reactor throughput. The downer has five thermocouples to indirectly monitor the height of the bed.

The vapors produced in the reactor and in the downer are entrained to a knock-out vessel (8) by a continuous inert gas (N_2) stream flowing at 750 $dm^3 \cdot h^{-1}$. The nitrogen flow can be adjusted using the KDG-type flow controllers (Kobold Instrumentation N.V., Strombeek-Bever, Belgium). Although most of the solid particles (char and sand) fall into the solids collection vessel (7) placed below the downer, some of the finer particles might be carried over or be entrained into the vapors. The latter are then trapped in the knock-out vessel, which is filled with steel wool, thus acting as a particulate filter. After the knock-out vessel, the vapors are then condensed using a water-cooled electrostatic precipitator (ESP, operated at 15 kV) (9) whose inner wall was kept at a constant temperature of 5°C and where the bio-oil is collected in a Schott glass bottle. A second condenser (glass Graham condenser) (10) was placed to ensure additional condensation. After the experiment, the collected bio-oil was kept in a freezer at –9°C until the samples were analyzed for stability and composition. Furthermore, a cotton filter (11) is placed at the outlet of the second condenser avoiding residual aerosols entering in the gas flow meter (12) in which the volumetric flow rate of the outgoing non-condensable gases (NCGs) is measured. Finally, the NCGs are released through the vent system. At least three experimental pyrolysis runs of 80 min were carried out for each biomass, followed by cleaning the entire reactor before a subsequent run.

2.4 Characterization of pyrolytic products

2.4.1 Water content

The water content of the bio-oil fractions – either whole bio-oil, or in case phase separation occurred, the organic (OP) and aqueous (AP) phases – were determined by Karl-Fischer (KF) titration according to ASTM E203-16 standard method.

2.4.2 Solids content

The pyrolysis oil solids content (*PS*) was determined by ASTM D7579−09(2019) standard method. The solids content as a percentage is calculated using equation 2. The procedure, for a given sample, was carried out at least in duplicate, and the reported values represent averages.

$$PS\ (wt.\%) = \frac{m_{s,oil}}{m_{bio-oil}} \cdot 100\% \qquad (2)$$

Where $m_{\text{s,oil}}$ is the weight of pyrolysis solids retained on a 1 μm filter paper (g), and $m_{\text{bio-oil}}$ is the weight of pyrolysis bio-oil sample taken for analysis (g).

2.4.3 Elemental composition, pH, and higher heating value

The elemental composition of the bio-oil was determined using a Flash 2000 CHNS-O analyzer (Thermo Scientific, US). Oxygen content was calculated by difference as O = 100 – Ash – (C + H + N + S). The elemental composition is reported on a dry basis (in wt.%). The ash mass fraction was determined following ASTM E1755-01(2015) standard method. The analyses were performed in quintuple and the average is reported. The pH measurement was done according to the standard test method described in ASTM E70-07(2015) standard method. In order to calibrate the pH meter, two standard buffer solutions (pH 7 and 4) were used. The higher heating value (HHV) of the bio-oil fractions was determined in an E2K bomb calorimeter system (Digital Data Systems, South Africa) according to ASTM D240 standard method. The detailed procedure can be consulted in a previous publication [35].

From the elemental analysis data, the carbon yields in the bio-oil, on pretreated and raw-feedstock basis were calculated as;

$$C^{*}_{yield} = \frac{Yield^{*}_{bio-o} \cdot C_{bio-oil}}{C^{*}_{biomass}} \qquad (3)$$

$$C_{yield} = \frac{Yield_{bio-oil} \cdot C_{bio-oil}}{C_{biomass}} \qquad (4)$$

Where C^{*}_{yield} and C_{yield} (%) are the carbon yield based on pretreated and raw feedstock basis, respectively; $Yield^{*}_{bio-o}$ and $Yield_{bio-o}$ are the bio-oil yields on pretreated and raw feedstock basis, respectively (in wt.%); $C_{bio-oil}$ (wt.%) is the carbon mass fraction in the bio-oil; while $C^{*}_{biomass}$ and

$C_{biomass}$ are the carbon mass fractions in the pretreated and raw biomass, respectively. Distinction between raw and pretreated feedstock basis is made, as the pretreatment process induces loss of organics (hence carbon) as demonstrated in a previous study [31].

2.4.4 Chemical composition by gas chromatography mass spectrometry (GC-MS)

Gas chromatography-mass spectrometry (Thermo-Fisher Scientific Trace-GC Ultra Gas Chromatograph) analysis was conducted to identify the main pyrolytic compounds in each bio-oil sample. The produced bio-oils were diluted in methanol (10 wt.% bio-oil solution), then filtered through a 0.25 μm pore size filter to remove solids, thereafter 2 μL were injected into the GC. A more detailed explanation on the GC-MS method and equipment can be found in a previous publication by the authors [31].

2.4.5 Viscosity measurement

The dynamic viscosity of the bio-oil was measured using a rotational viscometer, Brookfield LVDV II+ Pro Digital Viscometer (Scinteck Instruments). The device is equipped with a sample container, a spindle set and an external temperature controller. The spindle (in this work: SC4-18) is driven by a motor through a calibrated spring; deflection of the spring is indicated by a digital display. A multiple speed transmission was used (i.e. 10; 48; 86; 124; 162 and 200 min^{-1}).

The data was processed with the Rheocalc v3.3 software and the measurements were performed at 40 °C following the ASTM D445 standard method. This allows classifying the bio-oil as Newtonian or non-Newtonian fluid, according to its flow behavior index by applying the power law of Ostwald–de Waele.

The Ostwald–de Waele's power law is a mathematical relationship describing the behavior of a real non-Newtonian fluid for which the shear stress, τ ($\text{N}\cdot\text{m}^{-2}$), is given by the following equation,

$$\tau = \mathrm{K}\left(\frac{\partial v}{\partial y}\right)^{n} \qquad (5)$$

Where K is the flow consistency index (mPa.s), which is a product's viscosity at one reciprocal second; $\partial v/\partial y$ is the shear rate or the velocity gradient perpendicular to the plane of shear (s^{-1}), and n is the flow behavior index (dimensionless) which indicates the degree with which a material exhibits non-Newtonian flow behavior [37]. Applying a natural logarithm to both members of the Ostwald–de Waele's power law, a linear equation is obtained,

$$ln\tau = lnK + n\ ln\left(\frac{\partial v}{\partial y}\right) \tag{6}$$

The value of K and n can be obtained from the graph of $\ln\tau$ vs ln ($\partial v/\partial y$) b y regression analysis. The slope of the regression line gives the value of n while the intercept at ln ($\partial v/\partial y$) = 0 gives the value of K.

2.4.6 Stability of bio-oil

The stability of the bio-oil was determined by measuring the change in viscosity and water content after a thermally-accelerated aging process. Two glass bottles (50 mL) per oil sample were used. Each bottle was filled up to 90% of its volume with the bio-oil sample, which was previously homogenized and left to stand until air bubbles are removed. Then, the bottles are sealed and pre-weighted before being placed in an oven at 80 °C (± 1 °C) for exactly 24 h. After 24 h, the bottles containing the samples are cooled to room temperature for 1.5 h, weighted and the samples are taken for analysis [38].

2.4.7 Non-condensable gas flow rate and composition

During fast pyrolysis experiments, gas samples were taken after the NCGs volumetric flowmeter (point 12 in Fig. 1) and then analyzed off-line using a micro-GC (Varian 490-GC), for more details on the procedure, the reader is referred to a previous study [35].

2.4.8 Char quantification

The char/sand mixture collected was sieved using an stainless steel test sieve with 0.25 mm aperture and then it was subjected to loss-on ignition analysis (burning under air atmosphere in a Carbolite muffle oven AAF 1100, at 600 °C during 6 h) to determine the produced amount of char. More details are provided in a previous publication [35].

2.4.9 Mass balance

The mass balance (in wt.%) in pretreatment and pyrolysis was calculated by using the equation below:

$$Y_{total} = \frac{(m_{bio-oil} + m_{NCGs} + m_{char} + m_{p,loss})}{m_{bm}} \cdot 100\% \qquad (7)$$

Where $m_{bio\text{-}oil}$ (g) is the bio-oil mass, m_{NCGs} (g) is the mass of non-condensable gases, m_{char} (g) is the mass of produced char, $m_{p,loss}$ (g) is the mass loss that occurs in the acid leaching of the biomass, m_{bm} (g) is the mass of raw biomass. Mass balance data from pyrolysis of the different pretreated and raw feedstock was also analyzed statistically by performing one-way ANOV. To indicate which groups (i.e. yield data from a specific feedstock) were statistically significant from another, the Tukey-HSD post hoc test was performed.

3. Results and Discussion

3.1 Properties of pretreated samples

The characterization of the raw feedstocks in terms of proximate analysis, elemental composition, and higher heating value (HHV) is listed in Table 1 whereas Table 2 presents the characterization of leached sugarcane trash (SCT) and sugarcane bagasse (SCB). The elemental composition and higher heating value (HHV) of the pretreated biomass samples showed minimal changes in comparison to their respective raw biomasses, as shown in Table 1. The reduction in mass of the biomass samples after leaching was found to be 16.5% and 15.2% for SCT and SCB, respectively. This mass loss can be attributed to the removal of ash and extractives and, to a certain extent, mild hydrolysis of the feedstock yielding water-soluble intermediates during pretreatment.

Table 1. Compositional analysis results of the raw SCT and SCB in wt.%, dry basis (unless otherwise stated).

	raw SCT	**raw SCB**
volatile matter	71.8 ± 0.1	79.5 ± 0.1
fixed carbon[a]	20.8 ± 0.1	18.6 ± 0.1
ash	7.4 ± 0.2	1.9 ± 0.1
carbon	41.5 ± 0.8	46.2 ± 0.3
hydrogen	5.1 ± 0.1	5.5 ± 0.4
nitrogen	0.6 ± 0.6	0.3 ± 0.1
oxygen[b]	45.4 ± 0.3	46.1 ± 3.1
sulfur	– [c]	– [c]
HHV, MJ·kg^{-1}	16.3 ± 0.0	17.1 ± 0.0

[a] fixed carbon (wt. %, dry basis) = 100 – ash – volatile matter

[b] calculated by difference.

[c] below detection limit

Table 2. Compositional analysis results of the pretreated SCT and SCB in wt.%, dry basis (unless otherwise stated).

	CA–leached SCT	**CA–leached SCB**
volatile matter	76.5 ± 0.3	80.4 ± 0.1
fixed carbon[a]	17.7 ± 0.1	18.5 ± 0.2
ash	5.8 ± 0.1	1.1 ± 0.3
carbon	42.6 ± 0.3	45.8 ± 0.2
hydrogen	5.7 ± 0.0	5.9 ± 0.1
nitrogen	0.4 ± 0.3	0.2 ± 0.1
oxygen[b]	45.5 ± 0.6	46.9 ± 0.3
sulfur	– [c]	– [c]
HHV, MJ/kg	17.2 ± 0.1	17.8 ± 0.1

[a] fixed carbon (wt.%, dry basis) = 1 – ash – volatile matter

[b] calculated by difference

[c] below the detection limit

3.2 Effect of pretreatment on pyrolysis products distribution

The average yields of bio-oil, non-condensable gases and biochar on raw-feedstock basis are reported in Fig. 2 and also tabulated in Table B.1 in Supplementary Materials. The mass balance closure of the pyrolysis experiments ranged between 89.1–93.4 wt.% for raw SCB and SCT, respectively. On the other hand, the mass balance closure was between 96.3–96.6 wt.% for the pretreated biomasses. The lower mass balance closure in the pyrolysis of raw biomasses as compared to the pyrolysis of leached biomass can be attributed to the composition of the respective bio-oils. Levoglucosan condenses more readily than low molecular-weight degradation products thereof, like acetic acid, acetol, etc. Therefore, bio-oils that contain more lighter oxygenates (from untreated sugarcane residues) are more likely to suffer from small imperfections in the condensation steps. The variation on the yields of bio-oil, char, and NCGs is less than 3%, denoting that the reproducibility of the pyrolysis experiments is acceptable, thus the results can be used to analyze trends.

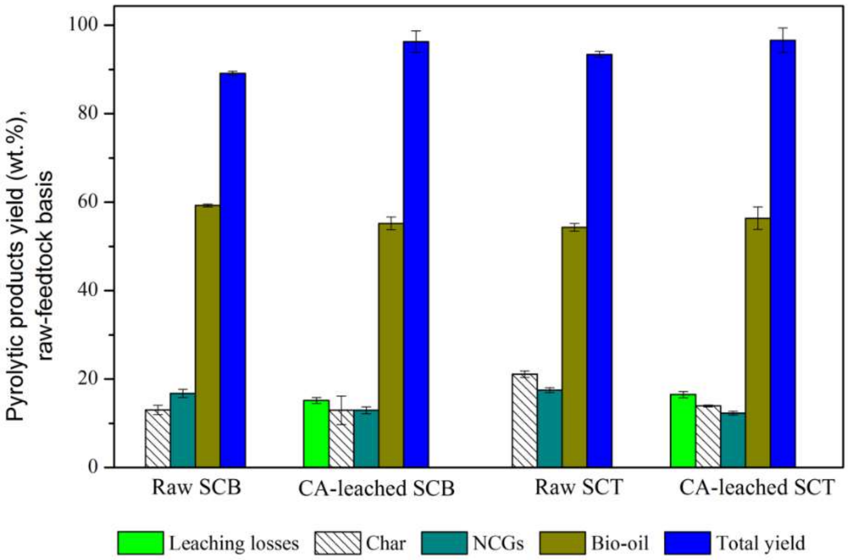

Figure 2. Average yields of pyrolysis products from raw and pretreated (25 °C and 1 h) sugarcane trash (SCT) and sugarcane bagasse (SCB) pyrolyzed at 500 °C.

Statistically significant differences ($p < 0.05$) in the average mass yields obtained for raw and CA–pretreated SCT were in the biochar (21.1 and 14.0 wt.%, respectively) and NCGs (17.5 and 12.3 wt.%, respectively). However, for SCB the statistically significant differences between raw and treated samples were only found for the NCG yield but not for the char yield, owing to its lower content of ashes which could act catalytically in the production of gases.

From these results (Fig. 2), it can be observed that despite some loss in the organic fraction upon leaching (with no significant differences between mass loss in SCB and SCT during pretreatment, $p < 0.05$), the overall yield in bio-oil is not affected by the leaching pre-treatment. No significant difference was found between the bio-oil yield of raw and leached SCT ($p > 0.05$) whereas the difference in bio-oil yield between raw SCB and leached SCB was somewhat significant ($p = 0.044 < 0.05$). This means that the pyrolysis process is yielding more bio-oil per incoming feedstock, but this is compensated by the higher mass losses during the CA pretreatment. Previous reports of fast pyrolysis experiments of pine wood in an auger reactor at 500 °C, resulted in similar yields of bio-oil, NCGs and biochar [39].

Moreover, these results are similar to those reported by Oudenhove et al. [40] who observed a large increase in the yields of pyrolysis oil for acid-leached biomasses (pine wood, straw, bagasse and hay) using a fluidized bed reactor operated at 530 °C. Nevertheless, these differ from the results published by Rodríguez-Machín et al. [35] who reported between 38–45 wt.% yields of the organic fraction of bio-oils produced from acid-leached SCB and SCT, respectively.

However, comparing liquid yields alone does not account for the differences in water content that may occur between the various pyrolysis bio-oils, as is also detailed in Section 3.3.1.1. Some of the inorganic constituents are known to promote dehydration reactions, so bio-oils stemming from demineralized biomass could have lower water concentrations. Hence, it makes more sense to compare the liquid yields among the different pretreated and raw feedstock in terms of organic liquid yields or C yields. The carbon yield in the pyrolysis oils is demonstrated in Table 3, where C_{yield} is the carbon yield in the liquid based on carbon in the raw feedstock, whereas C^{*}_{yield} is the carbon yield in the pyrolysis liquid based on carbon in the pretreated feedstock. Although the carbon yield of the fast pyrolysis process (C^{*}_{yield}) is higher (78.2 – 80.6 %) when using a citric acid pretreated feedstock compared to the corresponding raw feedstock (71.8 – 75.9 %), which also coincides with a minor drop in water content in the bio-oil, the overall carbon yield (C_{yield}) is lower (66.3 – 70.1 %). The latter can be explained as, on average, the citric acid leaching process also removes 10 to 12 % of the feedstock carbon (i.e. in the form of extractives and partial hydrolysis of the lignocellulose).

3.3 Characterization of pyrolytic products

3.3.1 Fast pyrolysis bio-oil

Main physical properties of the bio-oils are listed in Table 3. The bio-oils obtained from raw SCT separated into two phases upon collection, an upper layer corresponding to a water-rich fraction (48.5 wt.%) which is named as aqueous phase (AP), and a bottom thick oil layer (51.5 wt.%) which is labeled as organic phase (OP) – all other bio-oil samples were obtained as single-phase liquids.

3.3.1.1 Water content

The bio-oil samples had a global water content within the range of 26–38 wt.%. However, the bio-oil from raw SCT had a water content above 30 wt.% leading to phase separation into two fractions (AP and OP) [3,41]. The herein reported range of water content is in line with what was previously reported in the literature (15–30 wt.%) for different sources of biomass [3,4,41]. Within this water yield range, bio-oils are generally single-phase liquids due to the presence of polar carboxyl and hydroxyl compounds. In addition, it was observed that the water content of the bio-oil slightly decreased when the biomass was leached with CA. This can be attributed to the removal of ash from both sugarcane lignocellulosic residues upon pretreatment, especially in SCT. Thus, reducing the possibility of dehydration reactions that can occur during biomass pyrolysis promoted (catalyzed) by the presence of AAEMs [11].

Table 3. Physical and chemical properties of bio-oil from pyrolysis (500 °C).

parameter	**SCT**			**SCB**	
	raw		**CA–leached**	**raw**	**CA–leached**
	AP	OP			
water content (wt.%)	59.1 ± 1.4	17.8 ± 0.5	26.8 ± 2.0	34.9 ± 1.0	33.5 ± 2.3
solids content (wt.%)	0.02 ± 0.01	2.0 ± 0.3	1.9 ± 0.1	0.9 ± 0.1	0.9 ± 0.2
pH	3.3 ± 0.3	n.d.	2.9 ± 0.2	2.5 ± 0.1	2.4 ± 0.1
elemental composition (wt.%, *d.b*)					
carbon	32.0 ± 2.3	57.8 ± 1.4	53.4 ± 1.9	56.4 ± 1.2	53.9 ± 2.5
hydrogen	8.9 ± 0.2	7.6 ± 0.2	6.8 ± 0.2	6.7 ± 0.1	6.3 ± 0.3
nitrogen	0.6 ± 0.1	1.0 ± 0.1	3.3 ± 0.1	2.1 ± 0.3	2.4 ± 0.1
oxygen	58.5 ± 4.1	33.6 ± 1.3	36.6 ± 2.3	34.8 ± 1.4	37.4 ± 3.3
HHV (MJ/kg)	8.6 ± 0.3	18.2 ± 0.1	12.8 ± 0.1	12.0 ± 1.1	13.2 ± 0.3
$\boldsymbol{C_{yield}}$, % (*d.b*)	75.9		70.1	71.8	66.3
$\boldsymbol{C^{*}_{yield}}$, % (*d.b*)	75.9		80.6	71.8	78.2
C_{loss}, %	n.a.		10.5	n.a.	11.9

sulfur: *below detection limit*
C_{loss}: carbon loss by pretreatment
note: the water content of the raw SCT oil sample is 38 wt.%. HHV expressed on as-produced basis.

3.3.1.2 Solids content

The solids content in bio-oil leads to an increase in the viscosity. It also creates phase separation in the bio-oil and delays the combustion process in thermal applications [42,43]. The solids content (i.e. heat carrier and char), measured as a MeOH – DCM insoluble fraction, indicated that there were no differences in the mass of particles carried over from the same biomass (i.e. 0.9 wt.% for SCB and in a range within 1.9 and 2.1 wt.% for SCT) irrespective whether the pretreatment process was carried out or not. The differences between the biomasses can be attributed to the higher ash content of SCT with respect to SCB and to a higher percentage of char produced in pyrolysis of the former. Independently of the operational conditions, some fine char is inevitably carried over through cyclones or other solids separators. The char particles also contribute to secondary cracking by catalyzing the cracking reactions in the vapor phase. Thus, rapid and complete char separation is therefore desirable [44].

3.3.1.3 Acidity

The pH represents the corrosiveness of the bio-oil, but it does not directly indicate a concentration of acidic constituents such as strong carboxylic acids and weak acids (e.g. phenols) [44]. Carboxylic acids are suspected of catalyzing reactions that negatively affect bio-oil stability [11]. The pH value in the bio-oil depends, amongst others, on the type of biomass used [2].

The pH values of bio-oil samples in Table 3 showed negligible differences between the bio-oil from raw and CA–leached SCB, while the bio-oil from CA–leached SCT is slightly more acidic (pH=2.9) than that from its parent raw biomass (pH=3.3). This is in agreement with prior publications [2,44,45] in which reported values of pH for typical bio-oils range from 2 to 4. These bio-oils are acidic because of the presence of some acids such as acetic and propanoic acid, especially acetic acid that was found in higher concentrations compared to propanoic acid (see Table A.1 of Supplementary Material). The degradation of hemicelluloses in pyrolysis has been reported as the origin of these acids in bio-oil [1]. The hydrolysis of hemicellulose in the prior leaching process [31] could be the reason of lower concentrations of acids in the bio-oil from CA–leached biomasses (though not reflected in the observed pH values). Thus, acid pretreatment may contribute to improve the stability of the bio-oil during storage.

3.3.1.4 Elemental composition

Table 3 provides the elemental composition (CHNS-O) of the bio-oils. The bio-oil also contains trace elements such as Na, K, Ca, Mg, P and Si, grouped in the form of ash, which can range between 0.01–0.2 wt.%, but were not measured in this study. The bio-oil from sugarcane residues contained higher concentrations of nitrogen (1.0–3.3 wt.%) than bio-oils derived from straw and other forestry residues which are within the range of 0.2 to 0.4 wt.% [44]. The oxygen concentration contained in the bio-oil from the sugarcane residues was between 34 to 38 wt.% showing that the bio-oils were highly polar. However, the oxygen content of the organic (OP) and aqueous (AP) phases of the crude SCT bio-oil differed significantly. The AP contained about 60 wt.% oxygen due to the higher concentration of oxygenated compounds in this phase. While the OP contained much less oxygen (33.6 % by weight) and less water after separation. As mentioned in Section 3.2, the pretreatment results in a higher carbon yield in both produced bio-oils, and therefore, more valuable chemical products can potentially be obtained. Additionally, the carbon yields from raw and pretreated SCT were slightly higher than those of SCB.

3.3.1.5 Higher heating value

The heating value indicates the combustion energy present in bio-oil. The higher heating value (HHV) in the majority of bio-oils is between 15 and 26 $\mathrm{MJ \cdot kg^{-1}}$ [46,47], which is lower than the HHV of conventional fossil oil (41-46 $\mathrm{MJ \cdot kg^{-1}}$) [48]. The bio-oil produced from SCB treated with CA showed values of HHV's ranging from 12.1 to 13.2 $\mathrm{MJ \cdot kg^{-1}}$, which are somewhat lower than those for other typical bio-oils like from pine (21.9 $\mathrm{MJ \cdot kg^{-1}}$) and oak (18.7 $\mathrm{MJ \cdot kg^{-1}}$) [44]. These low values of HHV with respect to conventional petroleum fuels result from both the high water content (26–38 wt.%) and the high oxygen content (33–38 wt.%) of the bio-oils from sugarcane residues at the pyrolysis conditions tested. However, the HHV of the organic phase in the bio-oil obtained from raw SCT had the highest value (i.e. 18.2 $\mathrm{MJ \cdot kg^{-1}}$), which is higher than that of the original biomass (17.2 $\mathrm{MJ \cdot kg^{-1}}$). This could be a result of the lower water content of the separated organic phase (17.8 wt.%).

3.3.1.6 Viscosity and stability

Viscosity of a bio-oil is the measure of its internal friction which resists flow. It is an important fuel property that should be considered when attempting to design and select handling, processing and transportation equipment [49]. The viscosity of bio-oil affects the operation of fuel injection equipment, particularly when the increase in viscosity affects the fluidity of fuel at low temperatures [50].

From the rotational viscometer, the values of dynamic viscosity (40 °C) and the shear stress for each speed applied were obtained. The relationship between shear stress and shear rate, plotted in a *ln-ln* diagram, is approximated by a straight line over an interval of the shear rate between 13 to 264 s^{-1}. Rheological data of shear rate and shear stress of the bio-oil were fitted according to the Ostwald–de Waele power law (Eq. 5) allowing the classification of the bio-oil samples from a rheological point of view. The Ostwald–de Waele constants, as well as the viscosity range of fresh and aged bio-oil are presented in Table B.2 in Supplementary Materials. The values from raw SCT were not reported due to phase separation in this bio-oil sample.

According to the flow behavior index n, the measured samples exhibited shear-thinning or pseudoplastic fluid behavior in the shear rate range of 13 to 264 s^{-1}, since all CA–leached and raw SCB bio-oils have values of n below 1. This means that the viscosity decreases as shear rate increases [51,52]. Hence, the closer n is to 0, the more shear-thinning the material is. For these types of fluids, the viscosity may change with time as has been seen in the aged samples.

From Table B.2 in Supplementary Materials it can be seen that the viscosity of raw SCB is the lowest among the measured samples, which is reduced slightly with aging. On the other hand, the viscosity of bio-oil of CA–leached biomasses increased during aging, which can be attributed to more reactive compounds in bio-oil that during aging, can react to form larger molecules [53]. Most likely, this could be attributed, amongst others, to the high (anhydro)sugar content in bio-oils obtained from CA-leached feedstock and other compounds that polymerize upon aging to result in a more viscous oil.

Chemical reactions of polymerization of double-bonded compounds, as well as etherification and esterification occurring between hydroxyl, carbonyl and carboxyl groups containing components could be responsible for the increase in viscosity but also in the formation of water as a byproduct during ageing [54,55].

Water improves the stability of the bio-oil until it starts to separate out [38]. Differences in the water content of fresh and aged bio-oil are presented in Fig. 3, from which it can be observed that bio-oil from CA–leached biomass had an increase in the water content during aging, which is to be expected according to literature [3,44] and given the higher (anhydro)sugar content which may result in more extensive polymerization and production of water as a side reaction product.

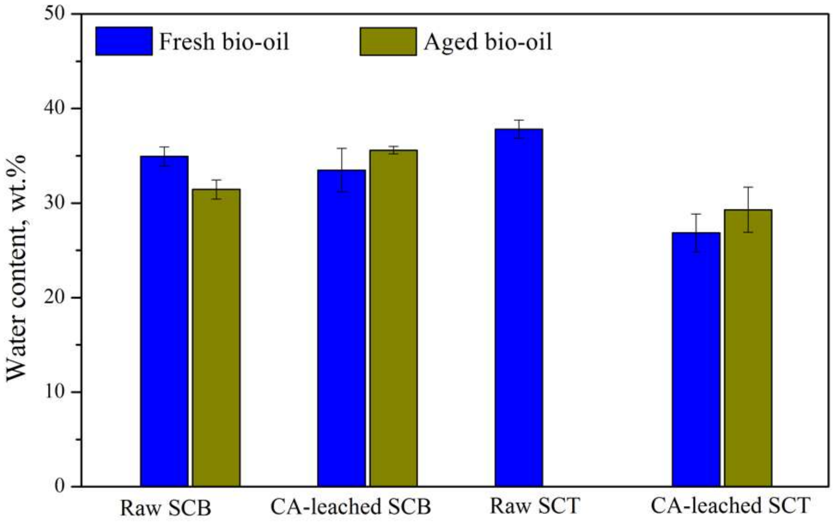

Figure 3. Comparison of the water content of fresh and aged bio-oil from fast pyrolysis (500 °C) of raw and CA–leached sugarcane residues.

However, this trend of increasing water upon ageing was not found in pyrolysis oil derived from raw SCB, which could be due to the lower (anhydro)sugar content in this oil.

3.3.1.7 Chemical composition, gas chromatography–mass spectrometry results

Four bio-oil samples, in triplicate, obtained from the two types of sugarcane lignocellulosic residues produced at a reactor temperature of 500 °C were examined by means of GC-MS in order to identify their chemical composition. Typical chromatograms from bio-oil resulting from raw and leached SCT are shown in Fig. C.1 of Supplementary Materials and those from SCB are presented in Fig. C.2 of Supplementary Materials. In the chromatograms from bio-oil in both fresh and aged form, 34 major peaks were identified.

Peak identification is listed in Table 4 from which 67.6% are pyrolysis compounds derived from carbohydrates (i.e. from cellulose and hemicellulose), 23.8% are lignin decomposition products and 8.6% compounds are from unspecified origin. Most of the identified peaks are oxygenated compounds including acetals, aldehydes, alcohols, ketones, furans/pyrans, acids, phenols and sugars.

Table 4. Compounds identified by GC-MS at 500 °C of *bio-oil* (fresh and aged) from raw or CA–leached (25 °C and 1 h) SCT and SCB.

Id#	Rt (min)	Source[a]	Formula	Compound name	Group[b]
1	8.2	C	$C_5H_{12}O_2$	1,1-dimetoxypropane	AT
2	8.4	C	$C_2H_4O_2$	2-hydroxyacetaldehyde (glycolaldehyde)	AH
3	9.5	C	$C_2H_4O_2$	acetic acid	CAs
4	10.5	C	$C_5H_{10}O_2$	2-methoxytetrahydrofuran	FU
5	10.8	C	$C_3H_6O_2$	1-hydroxy-2-propanone (hydroxyacetone)	KE
6	12.7	UN	$C_3H_6O_2$	propanoic acid	CAs
7	13.9	UN	$C_2H_6O_2$	ethylene glycol	ALC
8	14.3	UN	$C_4H_8O_3$	2-hydroxyethyl acetate	ALC
9	14.9	C	$C_6H_{12}O_3$	2,5-dimethoxytetrahydrofuran	FU
10	16.2	C	$C_6H_{12}O_3$	2,5-dimethoxytetrahydrofuran	FU
11	16.3	C	$C_5H_4O_2$	2-furaldehyde/furfural	AH
12	18.2	C	C_6H_8O	2-methyl-2-cyclopenten-1-one	KE
13	18.6	C	$C_7H_{10}O_3$	2-(2-furyl)-2-methoxyethanol	ALC
14	21.5	C	C_6H_8O	3-methyl-2-cyclopenten-1-one	KE
15	21.7	C	$C_4H_6O_2$	butyrolactone	FU
16	22.0	C	$C_4H_4O_2$	2(5H)-furanone	FU
17	23.1	C	$C_6H_8O_2$	3-methyl-1,2-cyclopententadione	KE
18	24.1		C_6H_6O	phenol	PH
19	24.6	C	$C_6H_{18}O_2$	hexanal dimethyl acetal	AT
20	26.5	L	C_7H_8O	4-methylphenol (*p*-cresol)	PH
21	26.6	L	C_7H_8O	3-methylphenol (*m*-cresol)	PH
22	26.8	L	$C_5H_6O_2$	4-methyl-5H-furan-2-one	KE
23	27.6	L	$C_8H_{10}O$	2-ethylphenol	PH
24	28.9	L	$C_8H_{10}O$	4-ethylphenol (*p*-ethylphenol)	PH
25	30.9	C	$C_6H_8O_4$	1,4:3,6-dianhydro-α-D-glucopyranose	SU
26	31.3	L	C_8H_8O	2,3 dihydrobenzofuran (coumaran)	FU
27	31.4	C	-	unidentified sugar	SU
28	31.6	C	$C_8H_{12}O_4$	5-(hydroxymethyl)-2-(dimethoxyme)	ALC
29	32.5	C	$C_6H_6O_3$	5-(hydroxymethyl)-2-furaldehyde	AH
30	32.6	L	$C_6H_6O_2$	1,2-benzenediol (catechol)	PH
31	33.2	C	-	unidentified sugar	SU
32	34.8	C	-	unidentified sugar	SU
33	40.8	C	$C_6H_{10}O_5$	levoglucosan	SU
34	44.0	C	-	unidentified sugar	SU

([a]) C: carbohydrate derivatives; L: lignin derivatives; UN: unspecified origin

([b]) AT: acetals; AH: aldehydes; ALC: alcohols; KE: ketones; FU: furans/pyrans; CAs: carboxylic acids; PH: phenols; SU: sugars

A semi-quantitative assessment of the changes in the chemical composition of the bio-oil from raw and CA–leached feedstocks can be made via GC-MS analysis. In Fig. 4, the product distribution in bio-oil samples is shown. The compounds are grouped according to their chemical functionality; i.e. alcohols (ALC), aldehydes (AH), carboxylic acids (CAs), furans/pyrans (FU), ketones (KE), phenols (PF) and sugars (SU). Concentrations are expressed in relative abundance. In addition, the composition by GC-MS analysis of identified pyrolytic compounds in the bio-oil fraction can be seen in Table A.1, while those of aged bio-oil are shown in Table A.2, both in Supplementary Materials.

As can be seen in Fig. 4, the chemical composition of all groups is significantly influenced by leaching with the CA solution used in the pretreatment process. The most important observations related to the effect of leaching with CA at the tested concentration on the bio-oil's chemical composition are a significant increase in the anhydrosugars, as well as a decrease in the carboxylic acids and phenols with respect to the raw biomass derived bio-oil.

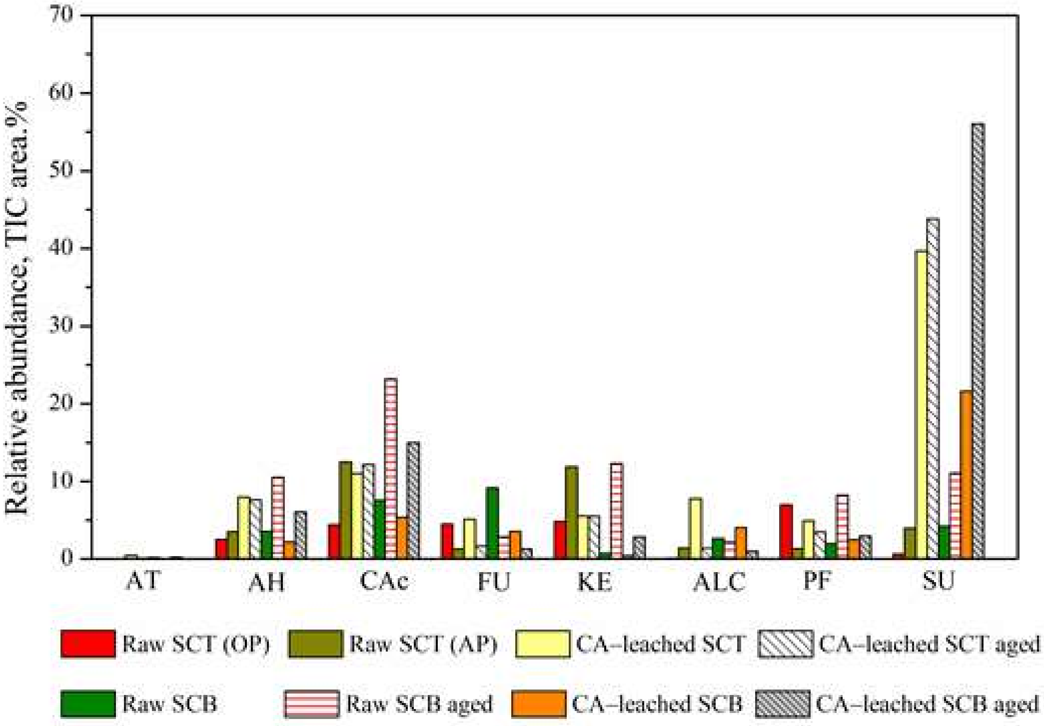

Figure 4. Effect of leaching (25 °C and 1 h) with CA on bio-oil chemical composition obtained by fast pyrolysis in a mini-plant at 500 °C of sugarcane trash (SCT) and sugarcane bagasse (SCB) and analyzed by GC-MS – grouping of chemical compounds according to Table 4 and averages are reported. The composition of aged samples is also included.

This observation could be associated with the suppression of the catalytic influence of AAEMs (i.e. by their removal). Typically, AAEMs reduce the production of levoglucosan out of cellulose, while favoring the production of lighter oxygenates [56]. In addition, when comparing SCT with SCB biomasses, differences in the polymeric structures of the cell walls of trash and bagasse should be considered [57].

The results of the stability test showed that aging increases the relative content of chemical groups including anhydrosugars, aldehydes, carboxylic acids, ketones and phenols in bio-oil, especially in SCB aged either from raw or leached with CA. Aldehydes and ketones have been identified [58,59] as the main reason for the instability in bio-oil. During aging, aldehydes can react with each other to form polyacetal oligomers and polymers. For example, poly(oxymethylene) polymer has limited solubility in water [60]. So, the increases observed (like sugars) upon ageing may be purely relative: ageing reactions consume (GC-detectable) aldehydes and ketones to produce heavier (hence GC-undetectable) compounds. The increase in sugars may cause some negative properties, for example, stickiness of bio-oils which can be problematic.

3.3.2 Non-condensable gases

The composition of non-condensable gases from the pyrolysis of raw and CA–leached sugarcane residues was measured by a micro-GC (Varian 490-GC) and presented as average values in Fig. 5.

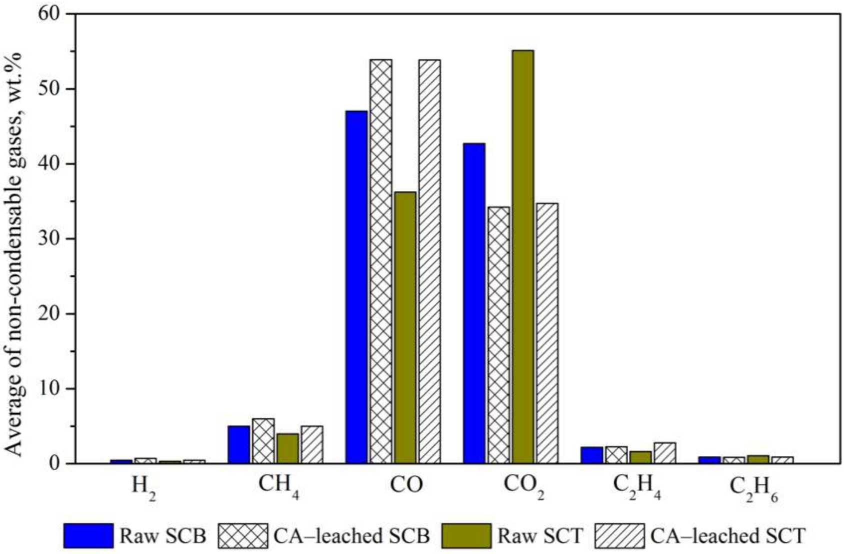

Figure 5. Average (wt.%) of non-condensable gases from the pyrolysis of raw and CA pretreated sugarcane residues.

The gas yields reported varied in a range of 12–18 wt.%. Bridgwater [61] stated that fast pyrolysis itself requires only about 15% of the total energy contained in the feedstock. The energy for the process can be provided by burning (in combustors) the non-condensable gases and the char.

From Fig. 5 it can be concluded that, by far, CO and CO_2 are the main components in the NCGs, representing between 88 and 91% by weight of the total non-condensable gases produced during pyrolysis. According to multiple studies [61,62-64], CO can be produced from the decomposition (decarbonylation reactions) of cellulose, hemicellulose and lignin, while CO_2 mostly originates from hemicellulose and lignin by decarboxylation reactions.

Considering the high contents of CO, the non-condensable gases can be considered to be used for energy production by their combustion. It can be seen that the results for CA–leached sugarcane residues in terms of NCGs production were mostly similar to their non-pretreated counterparts, with the major difference being an increase in CO concentration (representing more than half the mass fraction of the NCG's derived from CA-treated sugarcane residues) at the expense of CO_2. Most likely, the hydrolysis of hemicellulose occurring upon pretreatment and thus hemicellulose being less of a source of CO_2 in pyrolysis might be explain this shift in gas composition when pyrolyzing the CA-pretreated biomasses. As for the minor constituents in the NCG's (like CH_4, H_2, lighter alkanes/alkenes), no significant differences were observed with or without CA pretreatment of the feedstock.

3.4. Overarching discussion

Alkali and alkaline earth metals (AAEM's) are known to have a negative impact on the quality and stability of bio-oil because of their catalytic role in biomass fast pyrolysis [13]. Amongst others, dehydration reactions are promoted, leading to higher water concentrations in the bio-oil. As such, the initial research question was to demineralize the biomass (in here sugarcane residues) in order to demonstrate an improvement in yield and quality of the bio-oil with respect to its fuel application. The question is still relevant, as fast pyrolysis research currently focuses more on the use of residual, not-yet-valorized feedstocks (like agricultural residues) which also happen to be characterized by a higher ash (and AAEM) content, and the problem associated with the presence of the later in fast pyrolysis is thus exacerbated.

Despite the promise of demineralizing biomass prior to fast pyrolysis, a problem that is often overlooked is that the pretreatment process itself is associated with significant mass losses, as extractives are removed, and in the case of using stronger acids, partial hydrolysis of the cell wall constituents (lignocellulose) additionally solubilizes and removes organic matter. Hence, the use of mild organic acids, like citric acid have been proposed [31]. Despite the use of citric acid, total mass losses in pretreatment of sugarcane trash (SCT) and bagasse (SCB) were over 10 wt.% which, despite bio-oil yield improvements using pretreated feedstock of 5 to 10 wt.%, could not be compensated in the overall mass balance. One benefit that was noted however, was the demineralized feedstock produced less water in pyrolysis due to dehydration reactions (otherwise catalyzed by AAEM species) being suppressed which in the case of SCT led to a single phase pyrolysis oil whereas the raw feedstock yielded a two-phase pyrolysis oil. In terms of pyrolysis oil quality and next to the minor reduction in water content, no discernable effect on pH was noticed after biomass demineralization. The carbon concentration in the bio-oil increased, which also led to a minor improvement in HHV. But in general, the improvement in any quality indicator of the bio-oil (both SCB and SCT) was around 10% or less when comparing between pyrolysis of demineralized and of raw feedstock. Finally, demineralized biomass yielded a more viscous bio-oil, of which the viscosity more rapidly increased in accelerated aging, demonstrating higher instability.

So, in terms of yield and properties relevant to its use as fuel (i.e. in boilers), there was no demonstrable major improvement stemming from mild acidic demineralization of the biomass. However, most of the aforementioned minor changes can be linked to a much larger change in the chemical composition of the resultant pyrolysis oil: whereas the increase in alcohols and ethers in demineralized SCB and SCT as well as the reduction in carboxylic acids and phenolics was limited, there was an increase in anhydrosugars of about one order of magnitude, in particular levoglucosan. Anhydrosugars are unstable, especially in the presence of AAEM [65] and will react to produce smaller (and more stable) lighter oxygenates in fast pyrolysis. When using demineralized biomass, the anhydrosugars (levoglucosan in particular) will thus end up in the pyrolysis oil, at the same time rendering the bio-oil less stable and more viscous. Despite these major changes in the chemical makeup of the bio-oil not favoring its use as a fuel, a compound like levoglucosan has been identified as a valuable bio-based platform molecule

[66]. Hence, biomass pretreatment by demineralization could hold a key role in biorefining towards renewable chemicals.

4. Conclusions

The acidic pretreatment was effective for removing alkali and alkaline earth metals from sugarcane residues. Raw and pretreated biomasses were pyrolyzed in a continuous lab-scale pyrolysis unit at 500 °C. The overall yield in bio-oil, on incoming feedstock basis, is not affected by the leaching and the losses in organic carbon in the pretreatment were offset by higher C-yields of fast pyrolysis of the pretreated versus the raw sugarcane residues. The rheological characterization of bio-oils revealed that all samples behaved as shear-thinning fluids. The stability test showed that fresh and aged SCB bio-oils (raw or leached with CA) have lower viscosities than those from SCT and that the more reactive nature of the sugar-derived pyrolysis compounds stemming from CA-leached biomass led to a more unstable bio-oil compared to the bio-oil stemming from raw (not pretreated) sugarcane biomass. Bio-oil samples from either raw or CA–leached SCT and SCB may thus not be suitable for direct use as a fuel (low HHV, high solids content, low pH). While the CA-leaching process does not improve the quality of the resulting bio-oil for fuel purposes, it does leads to an increase of key-chemicals of interest, like levoglucosan.

Acknowledgements

We gratefully acknowledge the financial support of “Special Research Fund” (BOF) from Ghent University.

Appendix A. Supplementary data

Supplementary data related to this article can be found at *****.

a

References

[1] A. Oasmaa, D.C., Elliott, J. Korhonen, Acidity of biomass fast pyrolysis bio-oils, *Energ. Fuels*, 24 (2010), 6548-6554. https://doi.org/10.1021/ef100935r

[2] M. Bardalai, A review of physical properties of biomass pyrolysis oil, *Int. J. Renew. Energy Res.*, 5 (2015). https://doi.org/10.20508/ijrer.v5i1.1989.g6495

[3] A. Oasmaa, S. Czernik, Fuel oil quality of biomass pyrolysis oils - State of the art for the end user, *Energ. Fuels*, 13 (1999), 914-921. https://doi.org/10.1021/ef980272b

[4] A. Oasmaa, J. Lehto, Y. Solantausta, S. Kallio, Historical review on VTT fast pyrolysis bio-oil production and upgrading, *Energ. Fuels*, 35 (2021), 5683-5695. https://doi.org/10.1021/acs.energyfuels.1c00177

[5] Y. Xu, X. Hu, W. Li, Y. Shi, Preparation and characterization of bio-oil from biomass, in: S.S. Shaukat (Ed.), Progress in biomass bioenergy production, InTech, 2011. https://doi.org/10.5772/16466

[6] C.A. Mullen, A.A. Boateng, Chemical composition of bio-oils produced by fast pyrolysis of two energy crops, *Energ. Fuels*, 22 (2008), 2104-2109. https://doi.org/10.1021/ef700776w

[7] I. Demiral, A. Eryazici, S. Sensoz, Bio-oil production from pyrolysis of corncob (Zea mays L.), *Biomass Bioenerg.*, 36 (2012), 43-49. https://doi.org/10.1016/j.biombioe.2011.10.045

[8] S. Harinen, Analysis of the top phase fraction of wood pyrolysis liquids, University of Jyväskylä, 2004, p76.

[9] Q. Lu, W.-Z. Li, X.-F. Zhu, Overview of fuel properties of biomass fast pyrolysis oils, *Energ. Convers. Manag.*, 50 (2009), 1376-1383. https://doi.org/10.1016/j.enconman.2009.01.001

[10] A.V. Bridgwater, Production of high grade fuels and chemicals from catalytic pyrolysis of biomass, *Catal. Today*, 29 (1996), 285-295. https://doi.org/10.1016/0920-5861(95)00294-4

[11] A.S. Pollard, M.R. Rover, R.C. Brown, Characterization of bio-oil recovered as stage fractions with unique chemical and physical properties, *J. Anal. Appl. Pyrol.*, 93 (2012), 129-138. https://doi.org/10.1016/j.jaap.2011.10.007

[12] M.I. Jahirul, M.G. Rasul, A.A. Chowdhury, N. Ashwath, Biofuels production through biomass pyrolysis-a technological review, *Energies*, 5 (2012), 4952-5001. https://doi.org/10.3390/en5124952

[13] S.A. Rollag, J.K. Lindstrom, R.C. Brown, Pretreatments for the continuous production of pyrolytic sugar from lignocellulosic biomass, *Chem. Eng. J.*, 385 (2020), 123889. https://doi.org/10.1016/j.cej.2019.123889

[14] A.V. Barker, D. Pilbeam, Handbook of plant nutrition, CRC Press, Boca Raton, 2006, p632. https://doi.org/10.1201/b18458

[15] T. Wigley, A.C.K. Yip, S. Pang, The use of demineralisation and torrefaction to improve the properties of biomass intended as a feedstock for fast pyrolysis, *J. Anal. Appl. Pyrol.*, 113 (2015), 296-306. https://doi.org/10.1016/j.jaap.2015.02.007

[16] D.S. Scott, L. Paterson, J. Piskorz and D. Radlein, Pretreatment of poplar wood for fast pyrolysis: rate of cation removal, *J. Anal. Appl. Pyrol.*, 57 (2001), 169-176. https://doi.org/10.1016/S0165-2370(00)00108-X

[17] R. Kumar, V. Strezov, H. Weldekidan, J. He, S. Singh, T. Kan, B. Dastjerdi, Lignocellulose biomass pyrolysis for bio-oil production: A review of biomass pre-treatment methods for production of drop-in fuels, *Renew. Sust. Energ. Rev.*, 123 (2020), 109763. https://doi.org/10.1016/j.rser.2020.109763

[18] S. Vassilev, D. Baxter, L. Andersen, C. Vassileva, T. Morgan, An overview of the organic and inorganic phase composition of biomass, *Fuel*, 94 (2012), 1-33. https://doi.org/10.1016/j.fuel.2011.09.030

[19] K.H. Cen, X.B. Cao, D.Y. Chen, J.B. Zhou, F. Chen, M. Li, Leaching of alkali and alkaline earth metallic species (AAEMs) with phenolic substances in bio-oil and its effect on pyrolysis characteristics of Moso bamboo, *Fuel Process. Technol.*, 200 (2020), 106332. https://doi.org/10.1016/j.fuproc.2019.106332

[20] S.R.G. Oudenhoven, Improving the selectivity of pyrolysis by pyrolytic acid leaching of biomass. The role of AAEMs, anhydrosugar production and process desing & evaluation, University of Twente, The Netherlands, 2016, p312.

[21] G. Yildiz, F. Ronsse, R. Venderbosch, R.v. Duren, S.R.A. Kersten, W. Prins, Effect of biomass ash in catalytic fast pyrolysis of pine wood, *Appl. Catal. B-Environ.*, 168 (2015), 203-211. https://doi.org/10.1016/j.apcatb.2014.12.044

[22] K. Meile, A. Jermolajeva, E. Volkova, A. Zhurinsh, Solid-phase extraction of the aromatic by-products obtained by fast pyrolysis of pretreated lignocellulose, *Chem. Eng. Technol.*, 46 (2023). 1212-1217. https://doi.org/10.1002/ceat.202200512

[23] A. Alcazar-Ruiz, F. Dorado, L. Sanchez-Silva, Bio-phenolic compounds production through fast pyrolysis: Demineralizing olive pomace pretreatments, *Food Bioprod. Process,* 137 (2023), 200-213. https://doi.org/10.1016/j.fbp.2022.12.002

[24] G.D. Valdez, F.P. Valois, S.J. Bremer, K.C.A. Bezerra, L.H.H. Guerreiro, M.C. Santos, L.P. Bernar, W.P. Feio, L.G.S. Moreira, N.M. Mendonça, D.A.R. de Castro, N.T. Machado, Improving the bio-oil quality of residual biomass pyrolysis by chemical activation: effect of alkalis and acid pre-treatment, *Energies*, 16, 3162. https://doi.org/10.3390/en16073162

[25] E. Pienihakkinen, C. Lindfors, T. Ohra-aho, A. Oasmaa, Improving fast pyrolysis bio-oil yield and quality by alkali removal from feedstock, *Energ. Fuels*, 36 (2022), 3654-3664. https://doi.org/10.1021/acs.energyfuels.1c04331

[26] Z.H. Liu, X.S. Tan, X.S. Zhuang, H.P. Yang, X. Chen, Q.F. Wang, H.P. Chen, Coupling of pretreatment and pyrolysis improving the production of levoglucosan from corncob, *Fuel Process. Technol.*, 228 (2022), 107157. https://doi.org/10.1016/j.fuproc.2021.107157

[27] P. Li, X.P. Shi, L.Y. Jiang, X.H. Wang, J.D. Song, S.Q. Fang, J. Bai, C. Chang, S.S. Pang, Synergistic enhancement of bio-oil quality through hydrochloric or acetic acid-washing pretreatment and catalytic fast pyrolysis of biomass. *Ind. Crop Prod.*, 187 (2022), 115474. https://doi.org/10.1016/j.indcrop.2022.115474

[28] S.J. Liu, Z.S. He, Q. Dong, A. Zhao, F.P. Huang, D.M. Bi, Comparative assessment of water and organic acid washing pretreatment for nitrogen-rich pyrolysis: Characteristics and distribution of bio-oil and biochar, *Biomass Bioenerg.*, 161 (2022), 106840. https://doi.org/10.1016/j.biombioe.2022.106840

[29] E.G. Silveira, T.D. Silveira, V.H. Perez, O.R. Justo, G.F. David, S.A. Fernandes, Fast pyrolysis of elephant grass: Intensification of levoglucosan yield and other value-added pyrolytic by-products, *J. Energy Inst.,* 101 (2022), 254-264. https://doi.org/10.1016/j.joei.2022.02.003

[30] I.G. Hakeem, P. Halder, M.H. Marzbali, S. Patel, S. Kundu, J. Paz-Ferreiro, A. Surapaneni, K. Shah, Research progress on levoglucosan production via pyrolysis of lignocellulosic biomass and its effective recovery from bio-oil. *J. Env. Chem. Eng.*, 9 (2021), 105614. https://doi.org/10.1016.j.jece.2021.105614

[31] L. Rodríguez-Machín, L.E. Arteaga-Pérez, R.A. Pérez-Bermúdez, Y. Casas-Ledón, W. Prins, F. Ronsse, Effect of citric acid leaching on the demineralization and thermal degradation behavior of sugarcane trash and bagasse, *Biomass Bioenerg.*, 108 (2018), 371-380. https://doi.org/10.1016/j.biombioe.2017.11.001

[32] C.C. Schmitt, R. Moreira, R.C. Neves, D. Richter, A. Funke, K. Raffelt, J.-D. Grunwaldt and N. Dahmen, From agriculture residue to upgraded product: The thermochemical conversion of sugarcane bagasse for fuel and chemical products, *Fuel Process. Technol.*, 197 (2020), 106199. https://doi.org/10.1016/j.fuproc.2019.106199

[33] R.H. Venderbosch, W. Prins, Fast pyrolysis technology development, *Biofuel Bioprod. Bior.*, 4 (2010), 178-208. https://doi.org/10.1002/bbb.205

[34] L. Rodríguez-Machín, L.E. Arteaga-Pérez, J. Vercruysse, R.A. Pérez-Bermúdez, W. Prins, F. Ronsse, Py-GC/MS based analysis of the influence of citric acid leaching of sugarcane residues as a pretreatment to fast pyrolysis, *J. Anal. Appl. Pyrol.*, 134 (2018), 465-475. https://doi.org/10.1016/j.jaap.2018.07.013

[35] L. Rodríguez-Machín, L.E. Arteaga-Pérez, M. Pala, K. Herregods-Van De Pontseele, R.A. Pérez-Bermúdez, J. Feys, W. Prins, F. Ronsse, Influence of citric acid leaching on the yield and quality of pyrolytic bio-oils from sugarcane residues, *J. Anal. Appl. Pyrol.*, 137 (2019), 43-53. https://doi.org/10.1016/j.jaap.2018.11.006

[36] G. Yildiz, M. Pronk, M. Djokic, K.M. Van Geem, F. Ronsse, R. van Duren, W. Prins, Validation of a new set-up for continuous catalytic fast pyrolysis of biomass coupled with vapour phase upgrading, *J. Anal. Appl. Pyrol.*, 103 (2013), 343-351. https://doi.org/10.1016/j.jaap.2013.02.001

[37] I.H. Shames, Mecánica de fluidos, McGraw-Hill, Colombia, 1995, p824.

[38] A. Oasmaa, C. Peacocke, A guide to physical property characterisation of biomass-derived fast pyrolysis liquids, Valtion teknillinen tutkimuskeskus (VTT), Otamedia Oy, 2001, p102.

[39] G. Yildiz, Catalytic fast pyrolysis of biomass, Ghent University, Ghent, Belgium, 2015, p238.

[40] S.R.G. Oudenhoven, R.J.M. Westerhof, S.R.A. Kersten, Fast pyrolysis of organic acid leached wood, straw, hay and bagasse: Improved oil and sugar yields, *J. Anal. Appl. Pyrol.*, 116 (2015), 253-262. https://doi.org/10.1016/j.jaap.2015.09.003

[41] 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, *J. Anal. Appl. Pyrol.*, 85 (2009), 81-86. https://doi.org/10.1016/j.jaap.2008.12.006

[42] K.-H. Lee, B.-S. Kang, Y.-K. Park, J.-S. Kim, Influence of reaction temperature, pretreatment, and a char removal system on the production of bio-oil from rice straw by fast pyrolysis, using a fluidized bed, *Energ. Fuels*, 19 (2005), 2179-2184. https://doi.org/10.1021/ef050015o

[43] A. Pattiya, S. Suttibak, Influence of a glass wool hot vapour filter on yields and properties of bio-oil derived from rapid pyrolysis of paddy residues, *Bioresource Technol.*, 116 (2012), 107-113. https://doi.org/10.1016/j.biortech.2012.03.116

[44] A. Oasmaa, C. Peacocke, Properties and fuel use of biomass-derived fast pyrolysis liquids. A guide. VTT publications 731, 2010, p79.

[45] J.M. Mesa-Pérez, J.D. Rocha, L.A. Barbosa-Cortez, M. Penedo-Medina, C.A. Luengo, E. Cascarosa, Fast oxidative pyrolysis of sugar cane straw in a fluidized bed reactor, *Appl. Therm. Eng.*, 56 (2013), 167-175. https://doi.org/10.1016/j.applthermaleng.2013.03.017

[46] C.A. Mullen, A.A. Boateng, N.M. Goldberg, I.M. Lima, D.A. Laird, K.B. Hicks, Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis, 34 (2010), 67-74. https://doi.org/10.1016/j.biombioe.2009.09.012

[47] B. Biswal, S. Kumar, R.K. Singh, Production of hydrocarbon liquid by thermal pyrolysis of paper cup waste, *J. Waste Manage.*, 2013 (2013), 731858. https://doi.org/10.1155/2013/731858

[48] A.V. Bridgwater, D. Meier, D. Radlein, An overview of fast pyrolysis of biomass, *Org. Geochem.*, 30 (1999), 1479-1493. https://doi.org/10.1016/S0146-6380(99)00120-5

[49] M. Ertas, M.H. Alma, Pyrolysis of laurel (Laurus nobilis L.) extraction residues in a fixed-bed reactor: Characterization of bio-oil and bio-char, *J. Anal. Appl. Pyrol.*, 88 (2010), 22-29. https://doi.org/10.1016/j.jaap.2010.02.006

[50] C. Karunanithy, K. Muthukumarappan, Rheological characterization of bio-oils from pilot scale microwave assisted pyrolysis, in M.A.d.S. Bernardes (Ed.), Biofuel's Engineering Process Technology, InTech, 2011. https://doi.org/10.5772/961

[51] R.P. Chhabra, Non-Newtonian fluids: An introduction, in J.M. Krishnan, A.P. Deshpande, P.B.S. Kumar (Eds.), Rheology of complex fluids, Springer, New York, 2010, p. 3. https://doi.org/10.1007/978-1-4419-6494-6

[52] P.C. Barman, R.R. Kairi, A. Das, R. Islam, An overview of non-Newtonian fluid, *Int. J. Appl. Sci. Eng.*, 4 (2016), 97-101. https://doi.org/10.5958/2322-0465.2016.00011.3

[53] M. Polk, M. Phingbodhippakkiya, Characterization of the pyrolytic oils, *Nuclear Chem. Waste Manag.*, 1 (1980), 111-118. https://doi.org/10.1016/0191-815X(80)90005-4

[54] R.K. Sharma, N.N. Bakhshi, Upgrading of wood-derived bio-oil over HZSM-5, *Bioresource Technol.*, 35 (1991), 57-66. https://doi.org/10.1016/0960-8524(91)90082-U

[55] A. Oasmaa, E. Kuoppala, Fast pyrolysis of forestry residue. 3. Storage stability of liquid fuel, *Energ. Fuels*, 17 (2003), 1075-1084. https://doi.org/10.1021/ef030011o

[56] P.R. Patwardhan, Understanding the product distribution from biomass fast pyrolysis, Iowa State University, Ames, 2010, p162.

[57] L. Rodríguez Machín, L.E. Arteaga-Pérez, Y. Chenaf, J. Feys, N.V. Rodriguez, W. Prins, F. Ronsse, Effect of citric acid concentration on demineralization and pyrolysis of sugarcane residues as analyzed by analytical pyrolysis, *Afinidad*, 78 (2021), 23-32.

[58] R.H. Venderbosch, A.R. Ardiyanti, J. Wildschut, A. Oasmaa, H.J. Heeres, Stabilization of biomass-derived pyrolysis oils, *J. Chem. Technol. Biot.*, 85 (2010), 674-686. https://doi.org/10.1002/jctb.2354

[59] A. Oasmaa, J. Korhonen and E. Kuoppala, An approach for stability measurement of wood-based fast pyrolysis bio-oils, *Energ. Fuels*, 25 (2011), 3307-3313. https://doi.org/10.1021/ef2006673

[60] J.P. Diebold, A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils, in: A.V. Bridgwater (Ed.), Fast pyrolysis of biomass: A handbook, volume 2, CPL Press, Newbury, UK, 2002, p243.

[61] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, *Biomass Bioenerg.*, 38 (2012), 68-94. https://doi.org/10.1016/j.biombioe.2011.01.048

[60] P.R. Patwardhan, J.A. Satrio, R.C. Brown, B.H. Shanks, Product distribution from fast pyrolysis of glucose-based carbohydrates, *J. Anal. Appl. Pyrol.*, 86 (2009), 323-330. https://doi.org/10.1016/j.jaap.2009.08.007

[63] P.R. Patwardhan, R.C. Brown, B.H. Shanks, Understanding the fast pyrolysis of lignin, *ChemSusChem*, 4 (2011), 1629-1636. https://doi.org/10.1002/cssc.201100133

[64] P.R. Patwardhan, D.L. Dalluge, B.H. Shanks, R.C. Brown, Distinguishing primary and secondary reactions of cellulose pyrolysis, *Bioresource Technol.,* 102 (2011), 5265-5269. https://doi.org/10.1016/j.biortech.2011.02.018

[65] R. Ronsse, X.L. Bai, W. Prins, R.C. Brown, Secondary Reactions of Levoglucosan and Char in the Fast Pyrolysis of Cellulose, *Environ. Prog. Sustain.*, 31 (2012), 256-260. https://doi.org/10.1002/ep.11633

[66] I. Itabaiana, M.A. do Nascimento, R.O.M.A. de Souza, A. Dufour, R. Wojcieszak, Levoglucosan: a promising platform molecule ? *Green Chem..,* 22 (2020), 5859-5880. https://doi.org/10.1039/D0GC01490G