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# Assessment of sugarcane trash for agronomic and energy purposes in Brazil

Henrique Coutinho Junqueira Franco[1]*, Maria Teresa Borges Pimenta[1], João Luís Nunes Carvalho[1], Paulo Sérgio Graziano Magalhães[1,2], Carlos Eduardo Vaz Rossell[1], Oscar Antonio Braunbeck[1], André Cesar Vitti[3], Oriel Tiago Kölln[1], João Rossi Neto[1]

[1]CNPEM/CTBE – Laboratório Nacional de Ciência e Tecnologia do Bioetanol, Polo II de Alta Tecnologia, R. Giuseppe Máximo Scolfaro, 10.000 – 13083-970 – Campinas, SP – Brasil.
[2]UNICAMP/FEAGRI, Cidade Universitária "Zeferino Vaz" – 13083-970 – Campinas, SP – Brasil.
[3]APTA – Agência Paulista de Tecnologia dos Agronegócios, Rod. SP 127, km 30 – 13400-970 – Piracicaba, SP – Brasil.
*Corresponding author <henrique.franco@bioetanol.org.br>

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ABSTRACT: Due to new possibilities for using sugarcane (*Saccharum* spp.) trash for electricity generation, and the production of 2nd generation ethanol and others chemicals, the interest for its recovery has increased. However, the question of how much trash can be removed from sugarcane field still needs to be clarified. This study evaluated the amount of dry matter, nutrients content, structural compounds and efficiency of the enzymatic hydrolysis of the hydrothermal pretreated materials for tops and dry leaves in samples from sugarcane varieties. Tops and dry leaves present differences in nutrients content and moisture. Therefore, the amount of trash to be collected should not be simply based on percentages, but also should take into account the different fractions of the crop residues. For instance, around 80 % of N, P and K were derived from tops. Therein, the environmental indicators of the entire chain of sugarcane could be benefited because more nutrients would be recycled and less mineral fertilizers might be used for sugarcane production if tops are left on the field. Further, the tops have seven times more moisture than dry leaves and higher amounts of extractives (organic compounds of low molecular weight). Moreover, as the result of yield obtained in the pretreatment steps for dry leaves were superior to the tops and the glucose yields obtained in the enzymatic hydrolysis step were similar, it can be predicted that for second generation ethanol production, it is more viable to recover parts of the dry leaves fraction, leaving the tops on the field.
Keywords: *Saccharum* spp., enzymatic hydrolysis, sugarcane crop residues

## Introduction

Sugarcane (*Saccharum* spp.) has significant importance in the tropical and subtropical regions of the world, especially due to the sugar and ethanol production. Recently, the sugarcane crop has drawn global interest as a raw material for the production of energy, since it presents highly positive energy and greenhouse gases balances (Macedo et al., 2008; Renouf et al., 2008; Smeets et al., 2009).

In Brazil, with the advancement of mechanized harvesting of sugarcane without previous burning, a substantial portion of crop residues, composed by plant tops and dry leaves, is left on the soil, thus generating a residue known in the sugarcane industry as trash. At the beginning, the most common action was to windrow and burn this biomass in the field, in order to maintain the cultivation practices of the ratoons. As experience accumulates in the handling of the crops with the presence of trash, many farmers have begun to leave the residue on the soil, aiming mainly at conservation of the soil and water. Currently, around 85 % of sugarcane area is mechanically green harvested in the state of São Paulo (Canasat, 2012). Recently, a substantial group of companies have started to consider alternative uses for this crop residue, which may represent between 10 to 30 t $ha^{-1}$ $year^{-1}$ dry biomass, depending on the sugarcane yield (Trivelin et al., 1995; Vitti et al., 2011; Fortes et al., 2012).

Due to the possibilities of industrial use of sugarcane trash in boilers to cogenerate electricity and, in the near future, in the production of second generation ethanol and high added value building blocks for chemicals, the use of this residue in biorefineries may became a very attractive option.

From the agronomic point of view, the practice of maintaining the post-harvest sugarcane residues on the field brings evident benefits to the agricultural production, such as the protection of soil against erosion, the reduction of variation in the soil temperature, as a result of protection from direct radiation, an increase in the biological activity, higher rate of water infiltration and availability due to smaller evapotranspiration, improvement in weed control (Rossetto et al., 2008), increase of the soil carbon stock (Cerri et al., 2011) and nutrients cycling (Oliveira et al., 1999). However, some negative effects have also been associated with the maintenance of large amounts of trash over the soil such as the reduction of ratoon sprouting, increased risk of fire (Rossetto et al., 2008), greater incidence of sugarcane pest and disease (Macedo et al., 2003), and difficulties in the mechanized cultivation (Magalhães et al., 2012).

The Brazilian sugarcane sector has recurrently questioned how much trash should be left on the soil to improve sustainability and sugarcane yield, against the claiming demand to use this biomass for energy purposes. Regardless of the point of view of trash preservation or energy generation, all estimation have been done based just on the amount of crop residues, without taking into account the biomass composition. Sugarcane trash is a heterogeneous material formed by tops and dry leaves, which presents quite different physical-chemical composition (Franco et al., 2008; Franco et al., 2010).

Regarding to the competing dual use of sugarcane trash (for energy and agronomic purposes), the prevalent natural idea is that of partial recovery of this material from the field for industrial use. Nevertheless, the question of how much trash can be removed from sugarcane fields still has to be scientifically clarified. Therefore, this study aimed to assess a preliminary sustainable option for the partial removal of the trash from green harvested sugarcane based on trash composition.

## Materials and Methods

### Field experiment characterization

Samples of crop residues (dry leaves and tops) from eight sugarcane varieties were collected from a sugarcane area located in Piracicaba (22°42′ S; 47°38' W), São Paulo State, Brazil. The climate according to Köppen classification is Cwa (humid subtropical), with dry weather in the winter and average temperature below 18 °C in the coldest month, and above 22 °C in the warmest month (Rolim et al., 2007). The soil is an Oxisol (chemical characteristics presented in Table 1) where sugarcane has been cultivated for over 30 years.

The experiment was performed in randomized block design with three replications. The treatments were eight varieties of sugarcane: SP80-1842, SP80-3280, SP81-3250, IAC87-3396, IAC92-1099, IAC93-3046, RB86-7515 and RB85-5453. All varieties were planted in March 2009, in plots of five rows, 20 m long and 1.5 m apart (row space). At the planting, 40 kg $ha^{-1}$ N, 120 kg $ha^{-1}$ $P_2O_5$ and 120 kg $ha^{-1}$ $K_2O$ were applied. The stalks yield and the amount of crop residues compartments were evaluated in July 2010.

### Biomass production and nutrients content

The determination of stalk yield, dry matter and nutrients accumulation (N, P, K, Ca, Mg and S) in the aboveground of sugarcane was done in 2-m section of sugarcane rows. The aboveground plants parts were separated in stalks, tops and dry leaves. After that, the samples were weighed, chopped in forage chopper and then, subsamples of each plant compartment were sent to the laboratory to determine the level of moisture by means of weighing before and after drying in oven of forced air circulation. Afterwards, these materials were ground, and 10 g of samples were analyzed for macronutrients (N, P, K, Ca, Mg and S) using the methodology described by Malavolta et al. (1997).

### Compositional analysis of crop residues

Samples of dry leaves and tops were analyzed for lignocellulosic components and were submitted to hydrothermal pre-treatment process to assess the yield of glucose obtained by enzymatic hydrolisys.

In order to determine lignin, cellulose and hemicellulose contents of the trash organic compounds of low molecular mass, known as extractives (e.g. aromatic phenolic compounds, terpenes, saturated and unsaturated higher fatty acids, flavonoids and proteins) must be removed. Therefore, the integral raw materials were submitted to the pre-extraction process as described in the TAPPI T204 cm-97 modified method (Tappi, 1997) using ethanol-benzene. After the extraction step, samples were dried, weighed to determine the extractives content and reserved for later analyses.

Cellulose, hemicelluloses and insoluble lignin were determined both in the integral material (after removal of extractives) and in the trash that underwent the hydrothermal pre-treatment, according to Sluiter et al. (2008), using the acid hydrolysis procedure employing $H_2SO_4$ 72 % for 60 min at 35 °C, followed by dilution to $H_2SO_4$ 4 % and an additional hydrolysis step at 121 °C for 30 min. After the hydrolysis process, the resulting suspension was filtered and the solid residue was dry-ashed for gravimetric determination of the mineral content. Insoluble lignin was determined as the solid residue from hydrolysis, subtracted from its ash content. The filtered residue was stored for analysis of soluble lignin, carbohydrates, organic acids, furfural and hydroxymethylfurfural (HMF).

Soluble lignin concentration was determined by measuring of absorbance at 280 nm in a UV/Vis spectrometer, according to Gouveia et al. (2009). Cellulose and hemicelluloses contents were obtained by chromatography (HPLC) through the determination of concentrations of cellobiose, glucose, HMF, formic acid, and glucuronic acid (which were converted into cellulose); and xylose, arabinose, furfural and acetic acid (which were converted into hemicelluloses). Ash content was determined by the quantity of inorganic residues resulting from the total burning of the materials according to Sluiter et al. (2005).

### Hydrothermal Treatments

The hydrothermal treatments were performed in custom-made 200 mL stainless steel reactors in a static mode. A solid: liquid ratio of 1:10 (m:v) was used, with 12 g (dry basis) of integral trash and 120 mL of water. The hydrothermal treatment was performed for 10 min at 190 °C by heating the reactors, immersed in a glycerin bath. After the established reactional time, each reactor was quickly cooled on ice bath so as to cease the reaction

Table 1 – Chemical characteristics of soil in the experimental area.

| Layer | pH ($CaCl_2$) | SOM | Resin P | S-$SO_4$ | K | Ca | Mg | H+Al | Al | BS | CEC | V |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| cm | | g $dm^{-3}$ | mg $dm^{-3}$ | mg $dm^{-3}$ | mmol$_c$ $dm^{-3}$ | | | | | | | % |
| 0 - 25 | 5.0 | 33 | 19 | 35 | 1.2 | 30 | 16 | 47 | 1 | 47.2 | 94.2 | 50 |
| 25 - 50 | 4.5 | 21 | 5 | 42 | 0.5 | 13 | 6 | 42 | 1 | 19.5 | 61.5 | 32 |

Analysis performed according to the Van Raij et al. (2001). SOM: organic matter. BS: base saturation. CEC: cation exchange capacity.

in the immediate determined time. After the reactors were cooled, depressurized and opened, the solid treated material (cellulignin) was separated from the liquor rich in hemicelluloses. A fraction of the cellulignin was separated for compositional analysis (previously described) and for enzymatic hydrolysis. The determination of the initial and final mass was employed in the percentage calculation of mass loss occurred in the treatment.

**Enzymatic hydrolysis**

For the enzymatic hydrolysis step, a commercial cellulase was employed (Celluclast 1.5L), supplemented by β-glucosidade (Novozym 188), both from Novozymes Latin America Ltda. The reaction conditions were: sodium citrate buffer 0.05 mol $L^{-1}$ at pH 4.8 under agitation at 150 rpm in a shaker at 50 °C for 72 h (samples being extracted every 24 h) with 10 % of solid levels. The enzymatic loads were 10 Filter paper unit/g of cellulosic pulp (dry basis) for the complex celluclast 1.5 L and 20 enzyme international unit/g of cellulosic pulp (dry basis) for the enzyme β-glucosidade. After the end of the reaction, the hydrolisates were kept in flasks, cooled in ice to stop the enzymatic activity, and subsequently centrifuged, frozen and kept for chromatography analysis (HPLC). The total cellulolitic activity (FPase) was determined by the standard method (Ghose, 1987) and the glucose released was determined by the DNS method described by Miller (1959). The activity of the enzyme β-glucosidade was determined by the methodology described by Wood and Bhat (1988).

**Statistical Analysis**

The results were submitted to variance analysis (ANOVA), using F test at $p < 0.05$, the averages being compared by Tukey test ($p < 0.1$).

## Results and Discussion

**Biomass production and nutrient stock in crop residues**

In general fresh matter of aboveground biomass (average of all varieties evaluated) was 152 t $ha^{-1}$ with 87.5 % of stalks (133 t $ha^{-1}$). The analysis of the fresh samples has shown that 67 % of trash was composed by tops (12.8 t $ha^{-1}$), and 33 % by dry leaves. Only the fresh matter of the tops have presented differences between the varieties, with emphasis on RB85-5453, which produced more than 15 t $ha^{-1}$, while the varieties SP80-1842 and SP81-3250 produced around 10 t $ha^{-1}$.

The average of trash dry matter yield (Table 2) was 10.7 t $ha^{-1}$ (54 % of dry leaves and 46 % of tops). The percentage of tops dry matter in our study was slightly higher than those observed by Franco et al. (2010) with SP81-3250 in plant cane experiments in which the proportion of tops were in the range of 30 to 35 %. The amounts of trash produced did not vary among the eight sugarcane varieties as also found in the studies with post harvest residues of sugarcane in Brazil (Gava et al., 2001; Vitti et al., 2007; Fortes et al., 2011) and in Australia (Robertson and Thorburn, 2007a).

Tops have approximately seven times more moisture than dry leaves (Table 2). Taking moisture into consideration, it is possible to infer that collecting only dry leaves as opposed to the whole trash would be more interesting, if the trash should be removed at the same time as the stalks, since this would avoid the transportation of the biomass with high level of moisture from the field to the industry.

There are currently different alternatives to remove the trash from the field: i) windrow the residues a few days after harvesting for latter collection using a forage chopper; ii) baling after windrowing; iii) the integral harvest gathering stalks, dry leaves and tops all together. In this case, the residues separation takes place in the industrial plant by stationary dry cleaning (Magalhães and Braunbeck, 2010). The three alternatives are currently adopted in some sugarcane producing companies in Brazil where electricity is cogenerated.

In one of the few analysis of trash collection routes currently used (Project BRA/96/G31, CGEE, 2009), the lowest cost of collection and transportation of the trash to the biorefinery was obtained via integral harvest ( US$ 7.6 $t^{-1}$ of trash recovered) with retrieval of 70 % of the residues (harvester cleaning efficiency around 30 %), whereas in baling system and in integral harvest without cleaning separation of trash the costs was higher (US$ 10.5 and US$ 26.9 respectively). These differences are due to the light amounts of trash harvested together with the stalks (integral harvest) that causes a decrease of the loading density which require more trucks and wagons to transport stalks and crop residues. Therefore the cost of trash recovery is high in this model than when a lower amount of trash is collected (30 %) or when the bailing system is adopted.

The estimated cost of collecting trash varies according to particular condition. In the economic simulation of Michelazzo and Braunbeck (2008) baling presented higher costs (US$ 14.9) and the integral harvest presented substantially smaller recovery cost (US$ 6.9) than those report in CGEE (2009) study.

All these systems of trash recovery and transportation to the biorefineries have drawbacks, especially in the economic and energetic balance, since the removal of this material in the field requires many hours of machinery work (Magalhães et al., 2012). For example, Sokhansanj et al. (2008) evaluated the energetic balance and GHG fluxes in the operations of harvest and transportation of wheat residues destined to produce energy in five scenarios. These authors observed that the demand of energy and GHG was proportional to the cost of the operations used in the harvest. These emissions varied between 20 and 40 kg $CO_2$ by ton of dry matter. Additionally, the removal of residues from the field after the sugarcane harvest, as it is done through baling, results in large amounts of mineral impurities taken to the industry, which may impair damage to the boilers and

Table 2 – Biomass production and nutrient content of sugarcane straw from eight Brazilian varieties.

| Sugarcane Variety | Fresh Matter | Dry Matter | Moisture | Nutrients content | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | N | K | P | Ca | Mg | S |
| Tops | | | | | | | | | |
| | t ha$^{-1}$ | | % | g kg$^{-1}$ | | | | | |
| SP80-1842 | 10.9 c | 3.9 | 64 | 7.2 ab | 11.5 bc | 0.70 c | 6.3 ab | 2.2 ab | 1.6 b |
| SP80-3280 | 11.6 bc | 4.6 | 60 | 7.6 a | 13.1 ab | 0.77 bc | 5.4 abc | 1.2 b | 1.2 b |
| IAC87-3396 | 15.4 ab | 6.0 | 61 | 8.2 a | 12.3 b | 1.00 a | 5.8 ab | 1.5 b | 1.4 b |
| RB86-7515 | 13.5 abc | 5.7 | 58 | 8.0 a | 12.4 b | 0.90 bc | 4.6 bc | 1.8 b | 1.6 b |
| RB85-5453 | 16.2 a | 6.4 | 61 | 6.3 b | 11.3 bc | 0.77 bc | 3.4 c | 1.3 b | 1.1 b |
| SP81-3250 | 9.6 c | 3.5 | 63 | 7.1 ab | 13.6 ab | 0.93 a | 4.7 bc | 1.2 b | 1.2 b |
| IAC92-1099 | 12.7 abc | 4.6 | 63 | 8.2 a | 15.2 a | 1.03 a | 6.9 a | 2.9 a | 2.3 a |
| IAC93-3046 | 12.4 abc | 4.4 | 65 | 7.6 a | 9.7 c | 0.77 bc | 5.0 abc | 1.6 b | 1.6 b |
| LSD | 4.0 | NS | NS | 1.1 | 2.5 | 0.14 | 2.2 | 1.0 | 0.5 |
| Dry Leaves | | | | | | | | | |
| SP80-1842 | 6.2 | 5.7 | 8.3 | 3.4 ab | 2.3 | 0.10 b | 6.5 | 2.4 ab | 1.6 |
| SP80-3280 | 7.4 | 6.8 | 9.0 | 3.4 ab | 1.7 | 0.13 ab | 6.6 | 2.5 ab | 1.7 |
| IAC87-3396 | 7.7 | 6.8 | 12.0 | 3.5 ab | 1.6 | 0.20 ab | 6.9 | 2.3 ab | 1.3 |
| RB86-7515 | 5.2 | 4.8 | 7.1 | 3.6 ab | 2.4 | 0.20 ab | 7.1 | 3.0 a | 1.6 |
| RB85-5453 | 6.0 | 5.4 | 10.4 | 2.9 b | 1.2 | 0.10 b | 6.9 | 2.6 ab | 1.2 |
| SP81-3250 | 7.0 | 6.5 | 9.4 | 3.0 ab | 1.3 | 0.13 ab | 7.0 | 1.9 b | 1.2 |
| IAC92-1099 | 5.4 | 5.0 | 8.3 | 4.1 a | 2.2 | 0.20 ab | 6.2 | 3.1 a | 1.7 |
| IAC93-3046 | 5.6 | 5.1 | 8.9 | 3.5 ab | 1.8 | 0.27 a | 7.2 | 2.3 ab | 1.5 |
| LSD | NS | NS | NS | 1.1 | NS | 0.14 | NS | 1.0 | NS |
| Average of Parts of Sugarcane Straw | | | | | | | | | |
| Tops | 12.8 a | 4.9 b | 62 a | 7.5 a | 12.4 a | 0.86 a | 6.8 a | 1.7 b | 1.5 |
| Dry Leaves | 6.3 b | 5.8 a | 9.2 b | 3.4 b | 1.8 b | 0.17 b | 5.3 b | 2.5 a | 1.5 |
| LSD | 0.8 | 0.6 | 1.6 | 0.2 | 0.5 | 0.03 | 0.44 | 0.21 | 0.12 |
| *p > n straw p.* | 0.000 | 0.018 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | NS |
| *p > n variety* | 0.020 | NS | NS | 0.001 | 0.002 | 0.000 | NS | 0.000 | 0.000 |
| *p > n S x V* | 0.001 | NS | NS | NS | 0.004 | 0.000 | 0.007 | NS | 0.020 |
| CV (%) | 17 | 22 | 9 | 9 | 14 | 11 | 15 | 20 | 15 |

V: variety. S: straw. $p > n$: probability of ANOVA test. Tukey test at $p < 0.1$. LSD: least significant difference. CV = coefficient of variation.

their energy performance (Magalhães and Braunbeck, 2010). On the other hand, the current technology for the integral cane harvest causes the overall load density of the trucks to be reduced considerably, raising the costs of transportation of raw material for the production of sugar and ethanol (Magalhães and Braunbeck, 2010).

To contribute the comparative analysis between the crop residues compartments, the levels of macronutrients present in the tops and dry leaves in the sugarcane harvest were analyzed (Table 2). The tops presented the largest content of N, K, P and Ca, whereas the dry leaves had the highest concentration of Mg. Considering the main macronutrients in fertilizer formulation, tops contain around two, seven and five times more N, K and P than the dry leaves, respectively. That is justifiable because these three macronutrients are mobile in the plants phloem (Epstein and Bloom, 2006), and part of them are remobilized to the active parts of the plants (tops and roots system) along the sugarcane growth cycle.

In terms of quantity, a considerable fraction of K and P is present in the tops (80 %), which will represent an important source of these nutrients to be recycled in

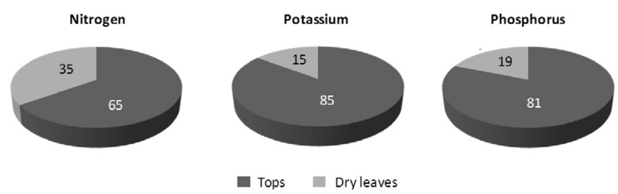


Figure 1 – Percentage distributions of N, K, and P in the sugarcane crop residues (tops and dry leaves).

soil-plant system (Figure 1). As K is not a part of any organic structure that constitutes the plant, after the death and breakdown of the cell membrane, this nutrient is released to soil solution, and may be readily reused by ratoon. Currently, some sugarcane producers are reducing the amount of K fertilizer application due to the maintenance of trash on the soil. Generally, around 40 to 60 kg ha$^{-1}$ $K_2O$ are suppressed from the K fertilizer to be applied in ratoons (Vitti et al., 2010a). Nevertheless, our results indicate that this reduction could be even great, because in average, the sugarcane varieties have accumulated in the trash around 80 kg ha$^{-1}$ K (equivalent to 96 kg ha$^{-1}$ $K_2O$). It is useful to highlight the value fertilizer of sugarcane trash. For instance, considering the price of KCl (50 % of K; main source of K in Brazil) of US$ 600.00 t$^{-1}$, it is possible to infer that 10.7 t ha$^{-1}$ of sugarcane trash as a K source for ratoon is worth US$ 96.00 (considering 80 kg ha$^{-1}$ K in trash) or US$ 9.00 t$^{-1}$.

The tops contained 65 % of the total N present in crop residues, which is equivalent to 40 kg ha$^{-1}$. Depending on the mineralization level, part of this N will be released in the soil system to be used by the crop, which could decrease the consumption of N fertilizers and increase the sustainability of the sugarcane production system. Fortes et al. (2011) showed that the utilization of N present in the trash by the subsequent ratoon was low, around 20 % after maintaining residues in the field for three years. Small N recoveries from sugarcane trash also was reported by Oliveira et al. (1999), Gava et al. (2003), Trivelin et al. (2002), Basanta et al. (2003), Vitti et al. (2010b), Vitti et al. (2011), Fortes et al. (2011) and Fortes et al. (2012). Moreover, Robertson and Thorburn (2007b) verified that the supply, to sugarcane, of N from trash will increase until it achieves the balance into the soil about 40 kg ha$^{-1}$ year$^{-1}$ N, with 90 % of the balance being reached after around 30 years of continuous trash preservation.

In spite of biomass of sugarcane parts did not differ among varieties, the nutrient content changed remarkably (Table 2). Therefore, some varieties evaluated had substantial by higher nutrient accumulation than others. For instance, IAC92-1099 showed the highest N content in tops (8.2 g kg$^{-1}$) and dry leaves (4.1 g kg$^{-1}$), whereas RB85-5453 had the lowest N content (Table 2). Such differences related to the nutritional aspects of sugarcane are expected, as shown by Oliveira et al. (2010), with varieties cultivated under irrigation in Northeastern of Brazil. Similar results were found by Robinson et al. (2007) testing nitrogen use efficiency by Australian sugarcane genotypes.

From point of view of industrial purposes separating tops from dry leaves and keeping the tops on the field may also improve combustion and preserve the boilers in case plant material is used to produce heat and electricity. Tops have a lower quality, as compared to the dry leaves, as feedstock for combustion in boilers. The tops of sugarcane plants are high in K, chlorine, and other inorganic nutrients. High alkali content in the fuel causes the formation of partially fused deposits (slagging) on the boilers and on convection heat surfaces (fouling) during dry combustion, which is detrimental to the whole process (Jenkins et al., 1998; Hassuani et al., 2005; Suramaythangkoor and Li, 2012). High chlorine content in the burning material can also cause fouling and corrosion (Jenkins et al., 1998; Suramaythangkoor and Li, 2012).

## Crop residues to produce bioethanol

A small variation in the content of the macromolecules (cellulose, hemicelluloses and lignin) was observed in the different parts of the crop residues (Table 3 and 4): 21.7 % and 22.7 % for lignin, 39.7 % and 40.8 % for cellulose, and 32.0 % and 28.7 % for hemicelluloses in tops and dry leaves, respectively. This is expected, since the comparison was done with commercial sugarcane varieties grown in the same field. These values are fundamentally dependant, for example, on geographic location and the weather where the plants are cultivated (Fengel and Wegener, 1984). However, for the produc-

Table 3 – Chemical composition of integral sugarcane trash compartments (dry leaves and tops).

| Treatment | Ash | Extratives# | Lignin | Cellulose | Hemicelluloses |
|---|---|---|---|---|---|
| Variety | | | % | | |
| SP80-1842 | 5.3 a | 19.8 | 21.6 b | 40.9 ab | 30.4 a |
| SP80-3280 | 5.0 ab | 18.5 | 21.8 ab | 40.7 ab | 29.9 a |
| IAC87-3396 | 4.9 ab | 18.4 | 23.0 ab | 39.3c | 29.8 a |
| RB86-7515 | 4.8 abc | 19.3 | 21.8 ab | 40.4 abc | 30.3 a |
| RB85-5453 | 4.1 cd | 18.9 | 21.5 b | 39.2 c | 31.3 a |
| SP81-3250 | 4.0 d | 19.7 | 21.9 ab | 41.6 a | 30.4 a |
| IAC92-1099 | 5.3 a | 21.5 | 23.3 a | 40.0 bc | 30.6 a |
| IAC93-3046 | 4.4 bcd | 19.9 | 22.5 ab | 40.0 bc | 30.3 |
| LSD | 0.7 | – | 1.6 | 1.3 | 1.6 |
| *p > n* | 0.000 | – | 0.020 | 0.000 | 0.196 |
| Trash parts | | | | | |
| Tops | 4.7 | 25.7 | 21.7 b | 39.7 b | 32.0 a |
| Dry Leaves | 4.7 | 13.7 | 22.7 a | 40.8 a | 28.7 b |
| LSD | 0.2 | – | 0.5 | 0.4 | 0.4 |
| *p > n straw p.* | 0.680 | – | 0.002 | 0.000 | 0.000 |
| *p > n variety* | 0.036 | – | 0.132 | 0.000 | 0.417 |
| *p > n S x V* | 0.283 | – | 0.358 | 0.749 | 0.245 |
| CV (%) | 9 | – | 3 | 2 | 2 |

#For extractives only one replicate was used per treatment. Extractives are removed from the trash just for composition analysis. V: variety. S: straw. *p > n*: probability of ANOVA test. Tukey test at *p* > 0.1 LSD: least significant difference. CV = coefficient of variation.

Table 4 – Chemical composition and mass balance of the samples of the integral and the hydrothermically-pretreated tops and dry leaves. Hydrothermal treatment was carried out at 190 °C, 10 minutes of reaction time and 1:10 (m:v) solid liquid ratio.

| Composition | Integral trash# | Pretreated trash | | Integral trash# | Pretreated trash | |
|---|---|---|---|---|---|---|
| | Tops | Tops | Tops* | Dry Leaves | Dry Leaves | Dry Leaves* |
| Yield (%) | - | - | 52.5 ± 1.0 | - | - | 62.4 ± 0.6 |
| Ash (%) | 4.7 | 1.4 ± 0.1 | 0.7 | 4.7 | 3.5 ± 0.1 | 2.2 |
| Total Lignin (%) | 21.7 | 30.0 ± 0.4 | 15.8 | 22.7 | 29.5 ± 0.2 | 18.4 |
| Cellulose (%) | 39.7 | 51.6 ± 1.3 | 27.1 | 40.8 | 53.9 ± 0.3 | 33.6 |
| Hemicelluloses (%) | 32.0 | 16.8 ± 0.3 | 8.8 | 28.7 | 12.3 ± 0.2 | 7.7 |

# Data of lignin, cellulose and hemicelluloses in the integral trash reflect concentrations after removal of extractables. *Values corrected by the yield. Pretreatments were carried out in six replicates.

tion of cellulosic ethanol and/or building blocks for other chemicals, the variation found in the concentration of these macromolecules is little significant, that is, both tops and dry leaves may be used with this objective. In these cases, the processes of macromolecules separation, which must be selective and efficient, and the purification steps are extremely challenging factors.

The low molecular mass substances (micromolecules) may be divided into organic compounds, generically called extractives (e.g. aromatic phenolic compounds, terpenes, saturated and unsaturated higher fatty acids, flavonoids and proteins), and inorganic substances, referred to as ashes. The levels of ashes (4.7 % on average) are similar in both the tops and the dry leaves (Table 4). However, the extractives content is 88 % higher in tops (25.7 %) then in dry leaves (13.7 %). This difference can be explained by the fact that the extractives have a defense role in plants against microorganisms and some insects. As the dry leaves are dead tissues the protective function of such molecules is not necessary (ICIDCA, 1999). Extractives may be used, for example, as new materials for cosmetics or pharmaceutical industry; therefore, the tops could offer a greater variety of substances to obtain products of high added value.

The amounts of lignin and cellulose in the pretreated fractions increased in relation to those of the original integral trash (Table 4). This proportional increase of lignin and cellulose content was due to the high solubility of the hemicellulosic fraction, partially removed during the hydrothermal pretreatment – tops: from 21.7 % to 30.0 % lignin and from 39.7 % to 51.6 % cellulose; and dry leaves: from 22.7 % to 29.5 % lignin and from 40.8 % to 53.9 % cellulose. As expected, the hemicellulose fraction decreases after the hydrothermal processing. Nevertheless, after correcting by the yield of the hydrothermal pretreatment reactions (Table 4), the amounts of these components are reduced, when expressed as a percentage in the original trash, because of the loss of the plant components solubilized during the pretreatment. Therefore, the available feedstock that can be effectively used for industrial processing (e.g. second generation ethanol from cellulose or co-generation from lignin) as a proportion of the original trash is 15.8 % lignin and 27.1 % cellulose in tops; and 18.4 % lignin and 33.6 % cellulose in dry leaves.

The pretreatment of the trash caused a solubilization of hemicelluloses: 72.5 % in the tops (from 32.0 % to 8.8 %) and 73.2 % in the dry leaves (from 28.7 % to 7.7 %). Due to the relatively amorphous character and lower level of polymerization of the hemicelluloses, if compared to cellulose, that fraction becomes more susceptible to hydrolysis in the hydrothermal pretreatment (Fengel and Wegener, 1984). The pretreatment cause high solubilization of the cellulosic fraction as well: 31.7 % for the tops and 17.6 % for the dry leaves (tops: from 39.7 % to 27.1; dry leaves: from 40.8 % to 33.6 %). These values show that the process, at least in the conditions employed in this study, is not selective for the removal of hemicelluloses.

The two trash fractions presented small differences in the levels of residual lignin and hemicelluloses after the pre-treatment (Table 4). These small differences did not interfere in the efficiency of the enzymatic conversion (Table 5).

The glucose yields obtained in the enzymatic hydrolysis steps did not present differences between dry leaves and tops (Table 5). After 48 h of reaction, the maximum glucose yield was achieved (reaching values close to 60 % yield), making it evident that there is no need to employ a 72-h enzymatic hydrolysis.

Comparing the data obtained with those found in literature (Silva, 2010), in which on average glucose yield values of 7.7 % are found for integral sugarcane trash, the conversion obtained after the hydrothermal pretreatment employed in this study was a lot superior, showing that the removal of a large fraction of hemicelluloses and partial removal of lignin considerably increases the cellulose conversion to sugars. Both hemicelluloses and lignin form a physical barrier against the enzymatic attack to cellulose. The results corroborate others reported in the literature, making it evident that the removal of these components by the pre-treatment step results in a change in the morphological structure of the lignocellulosic biomass, making it more accessible to the cellulolitic enzymes, and therefore providing an increase in the enzymatic digestibility in the conversion processes of the lignocellulosic biomass into glucose and consequently in ethanol (Öhgren et al., 2006; Liao et al., 2005).

As the yields obtained in the pretreatment steps for dry leaves (Table 4) were superior to those of the

Table 5 – Glucose yields obtained after different time intervals of enzymatic hydrolysis of tops and dry leaves submitted to hydrothermal pre-treatment.

| Time of enzymatic hydrolysis (h) | Glucose yield* (%) | |
|---|---|---|
| | Tops | Dry leaves |
| 24 | 51.8 ± 0.2 | 50.4 ± 1.6 |
| 48 | 60.8 ± 1.3 | 61.7 ± 1.2 |
| 72 | 63.6 ± 1.7 | 61.0 ± 1.0 |

*Pretreated material basis.

tops (62.4 % and 52.5 %, respectively) and the glucose yields obtained in the enzymatic hydrolysis step were similar, it can be predicted that from the point of view of production of second generation ethanol, it may be preferable to employ the dry leaves fraction, leaving the tops on the soil. Although, these are preliminary results, they provide relevant data to the debate on how much trash can be removed from sugarcane field to produce energy without jeopardizing long term soil productivity.

## Conclusions

The decision about how much sugarcane trash can be removed from the field to produce energy in biorefinaries should not be based just on percentage of the whole mass of plant residue because dry leaves and tops present substantial differences in their composition. The tops contain more valuable nutrients than dry leaves, and therefore could be the preferable part to preserve on the field. In addition, as the yields obtained in the pretreatment steps for dry leaves were superior to tops and the glucose yields verified in the enzymatic hydrolysis step were similar, it can be predicted that from the point of view of the second generation ethanol production, it is more viable to use the dry leaves fraction, leaving the tops in the sugarcane fields.

## References

Basanta, M.V.; Dourado Neto, D.; Reichardt, K.; Bacchi, O.O.S.; Oliveira, J.C.M.; Trivelin, P.C.O.; Timm, L.C.; Tominaga, T.T.; Correchel, T.; Cássaro, F.A.M.; Pires, L.F.; Macedo, J.R. 2003. Management effects on nitrogen recovery in a sugarcane crop grown in Brazil. Geoderma 116: 235-248.

CANASAT. 2012. Monitoring of sugarcane. Available at: http://www.dsr.inpe.br/laf/canasat/colheita.html [Accessed Jul. 12, 2012].

Centro de Gestão e Estudos Estratégicos [CGEE]. 2009. Bioetanol Fuel: An Oportunity for Brazil = Bioetanol combustível: uma oportunidade para o Brasil. CGEE, Brasília, DF, Brazil. (in Portuguese).

Cerri, C.C.; Galdos, M.V.; Maia, S.M.F.; Bernoux, M.; Feigl, B.J.; Powlson, D.; Cerri, C.E.P. 2011. Effect of sugarcane harvesting systems on soil carbon stocks in Brazil: an examination of existing data. European Journal of Soil Science 62: 23-28.

Epstein, E.; Bloom, A. 2006. Mineral Nutrition of Plants: Principles and Perspectives. 2. ed. Planta, Londrina, PR, Brazil.

Fengel, D.; Wegener, G. 1984. Wood: Chemistry, Ultrasctructure, Reactions. Walter de Gruyter, New York, NY, USA.

Fortes, C.; Trivelin, P.C.O.; Vitti, A.C. 2012. Long-term decomposition of sugarcane harvest residues in São Paulo state, Brazil. Biomass and Bioenergy 42: 189-198.

Fortes, C.; Trivelin, P.C.O.; Vitti, A.C.; Ferreira, D.A.; Franco, H.C.J.; Otto, R. 2011. Recovery of nitrogen ($^{15}N$) by sugarcane from previous crop residues and urea fertilisation under a minimum tillage system. Sugar Tech 13: 42-46.

Franco, H.C.J.; Trivelin, P.C.O.; Faroni, C.E.; Vitti, A.C.; Otto, R. 2008. Utilization by sugar cane of nitrogen applied at planting. Revista Brasileira de Ciência do Solo 32: 2763-2770 (in Portuguese with abstract in English).

Franco, H.C.J.; Trivelin, P.C.O.; Faroni, C.E.; Vitti, A.C.; Otto, R. 2010. Stalk yield and technological attributes of planted cane as related to nitrogen fertilization. Scientia Agricola 67: 579–590.

Gava, G.J.C.; Trivelin, P.C.O.; Oliveira, M.W.; Penatti, C.P. 2001. Growth and accumulation of nitrogen by sugarcane cultivated in soil covered with cane trash. Pesquisa Agropecuária Brasileira 36: 1347-1354 (in Portuguese with abstract in English).

Gava, G.J.C.; Trivelin, P.C.O.; Vitti, A.C.; Oliveira, M.W. 2003. Recovery of nitrogen ($^{15}N$) from urea and cane trash by sugar cane ratoon (*Saccharum* spp.). Revista Brasileira de Ciência do Solo 27: 621-630 (in Portuguese, with abstract in English).

Ghose, T.K. 1987. Measurement of cellulose activities. Pure Apply Chemistry 59: 257-268.

Gouveia, E.R.; Nascimento, R.T.; Maior, A.M.S.; Rocha, G.J.M. 2009. Validation of methodology for the chemical characterization of sugar cane bagasse. Química Nova 32: 1500-1503 (in Portuguese with abstract in English).

Hassuani, S.J.; Leal, M.R.L.V.; Macedo, I.C. 2005 Biomass Power Generation: Sugar Cane Bagasse and Trash. CTC/PNUD, Piracicaba, SP, Brazil.

Instituto Cubano de Investigaciones de los Derivados de la Caña de Azúcar [ICIDCA]. 1999. Manual de Derivados = Derivatives Manual. ICIDCA, Habana, Cuba (in Spanish).

Jenkins, B.M.; Baxter, L.L.; Miles Jr., T.R.; Miles, T.R. 1998. Combustion properties of biomass. Fuel Processing Technology 54:17-46.

Liao, W.; Wen, Z.; Hurley, S.; Liu, C.; Chen, S. 2005. Effects of hemicellulose and lignin on enzymatic hydrolysis of cellulose from dairy manure. Applied Biochemistry and Biotechnology 121-124: 1017-1030.

Macedo, I.; Seabra, J.E.A.; Silva, J.E.A.R. 2008. Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: the 2005/2006 averages and a prediction for 2020. Biomass and Bioenergy 32: 582-595.

Macedo, N.M.; Botelho, P.S.M.; Campos, M.B.S. 2003. Chemical control of the leafhopper-root sugarcane and impact on the population of arthropods. = Controle químico de cigarinha-da-raiz em cana-de-açúcar e impacto sobre a população de artrópodes. STAB - Açúcar, Álcool e Subprodutos 21: 30-33 (in Portuguese).

Magalhães, P.S.G.; Braunbeck, O.A. 2010. Sugarcane and straw harvesting for ethanol production. p. 465-475. In: Cortez, L.A.B., ed. Sugarcane bioethanol. Blucher, São Paulo, SP, Brazil.

Magalhães, P.S.G.; Nogueira, L.A.H.; Canatarella, H., Rossetto, R.; Franco, H.C.J.; Braunbeck, O.A. 2012. Agro-industrial Technological Paths, in Sustainability of Sugarcane Bioenergy by Center of Strategic Studies and Management. CGEE, Brasília, DF, Brazil.

Malavolta, E.; Vitti, G.C.; Oliveira, S.A. 1997. Nutritional Status of Plants: Principles and Applications. 3ed. Potafos, Piracicaba, SP, Brazil.

Michelazzo, M. B.; Braunbeck, O. 2008. Analysis of six systems of trash recovery in mechanical harvesting of sugarcane. Revista Brasileira de Engenharia Agrícola e Ambiental 12: 546-552 (in Portuguese with abstract in English).

Miller, G.L. 1959. Use of dinitrosalicylic acid reagent for determination of reducing sugar. Analytical Chemistry 31: 426-428.

Öhgren, K.; Bura, R.; Saddler, J.; Zacchi, G. 2006. Effect of hemicellulose and lignin removal on enzymatic hydrolysis of steam pretreated corn stover. Bioresource Technology 98: 2503-2510.

Oliveira, E.C.A.; Freire, F.J.F.; Oliveira, R.I.; Freire, M.B.G.S.; Simões Neto, D.E.; Silva, S.A.M. 2010. Nutrient extraction and export by fully irrigated sugarcane varieties. Revista Brasileira de Ciência do Solo 34: 1343-1342 (in Portuguese with abstract in English).

Oliveira, M.W.; Trivelin, P.C.O.; Gava, G.J.C.; Penatti, C.P. 1999. Sugarcane trash degradation. Scientia Agricola 56: 803- 809 (in Portuguese with abstract in English).

Renouf, M.A.; Wegener, M.K.; Nielsen, L.K. 2008. An environmental life cycle assessment comparing Australian sugarcane with US corn and UK sugar beet as producers of sugars for fermentation. Biomass Bioenergy 32: 1144–1155.

Robertson, F.A.; Thorburn, P.J. 2007a. Decomposition of sugarcane harvest residue in different climatic zones. Australian Journal of Soil Research 45: 1-11

Robertson, F.A.; Thorburn, P.J. 2007b. Management of sugarcane harvest residues: consequence for soil carbon and nitrogen. Australian Journal of Soil Research 45: 13-23.

Robinson, N.; Fletcher, A.; Whan, A.; Critchley, C.; Wirén, N. von; Lakshmanan, P.; Schmidt, S. 2007. Sugarcane genotypes differ in internal nitrogen use efficiency. Functional Plant Biology 34: 1122-1129.

Rolim, G.S.; Camargo, M.B.P.; Lania, D.G.; Moraes, J.F.L. 2007. Climatic classification of köppen and thornthwaite sistems and their applicability in the determination of agroclimatic zonning for the state of São Paulo, Brazil. Bragantia 66: 711-720.

Silva, V.F.N. 2010. Study of pretreatment of sugarcane bagasse and enzymatic saccharification of biomass for obtaining bioethanol = Estudo do pré-tratamento do bagaço de cana e sacarificação enzimática da biomassa para obtenção de bioetanol. Dissertation (MS) - Escola de Engenharia de Lorena, Universidade de São Paulo, Lorena, SP, Brazil (in Portuguese).

Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D. 2005. Determination of Ash in Biomass. National Renewable Energy Laboratory, Washington, DC, USA. (Technical Report, NREL/TP 510-42622).

Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. 2008. Determination of Structural Carbohydrates and Lignin in Biomass. National Renewable Energy Laboratory, Washington, DC, USA. (Technical Report, NREL/TP-510-42618).

Smeets, E.M.W.; Bouwmanw, L.F.; Stehfest, E.; Van Vuuren, D.P.; Posthuma, A. 2009. Contribution of $N_2O$ to the greenhouse gas balance of first generation biofuels. Global Change Biology 15: 1-23.

Sokhansanj, S.; Turholow, A.F.; Stephen, J.; Stumborg, M.; Fenton, J.; Mani, S. 2008. Analysis of five simulated straw harvest scenarios. Canadian Biosystems Engineering 50: 27-35.

Suramaythangkoor, T.; Li, Z. 2012. Energy policy tools for agricultural residues utilization for heat and power generation: a case study of sugarcane trash in Thailand. Renewable and Sustainable Energy Reviews 16: 4343-4351.

Technical Association of the Pulp and Paper Industry [TAPPI]. 1997. T204 cm-97: Solvent Extractives of Wood and Pulp. TAPPI, Englewood, CO, USA.

Trivelin, P.C.O.; Victoria, R.L.; Rodrigues, J.C.S. 1995. Utilization by late harvest sugar cane ratoon of nitrogen from $^{15}$n-aqua ammonia and $^{15}$n-urea applied to the soil as vinasse n-complement. Pesquisa Agropecuária Brasileira 30: 1375-1385 (in Portuguese with abstract in English).

Van Raij, B.; Andrade, J.C.; Cantarella, H.; Quaggio, J.A. 2001. Chemical Analysis for the Evaluation of Fertility of Tropical Soils. Instituto Agronômico, Campinas, SP, Brazil.

Vitti, A.C.; Ferreira, D.A.; Franco, H.C.J.; Fortes, C; Otto, R.; Faroni, C.E.; Trivelin, P.C.O. 2010a. Utilisation of nitrogen from trash by sugarcane ratoons. Sugar Cane International 28: 249-253.

Vitti, A.C.; Franco, H.C.J.; Trivelin, P.C.O.; Trivelin, P.C.O.; Ferreira, D.A.; Otto, R.; Fortes, C.; Faroni, C. E. 2011. Nitrogen derived from fertilization and straw for plant cane nutrition. Pesquisa Agropecuária Brasileira 46: 287-293 (in Portuguese with abstract in English).

Vitti, A.C.; Trivelin; P.C.O.; Gava, G.J.C.; Penatti, C.; Bolonga, I.R.; Faroni; C.E.; Franco; H.C.J. 2007. Sugar cane yield related to the residual nitrogen from fertilization and the root system. Pesquisa Agropecuária Brasileira 42: 249-256 (in Portuguese with abstract in English).

Vitti, G.C.; Luz, P.H.C.; Altran, W.S. 2010b. Nutrition and fertilization = Nutrição e adubação. p. 73-117. In: Santos, F.; Borém, A.; Caldas, C., eds. Sugarcane: bioenergy, sugar and ethanol; technologies and perspectives = Cana-de-açúcar: bioenergia, açúcar e álcool – tecnologias e perspectivas. UFV, Viçosa, MG, Brazil (in Portuguese).

Wood, T.M.; Bhat, K.M. 1988. Methods for measuring cellulase activities, p. 87-116. In: Wood, W.A.; Kellog, S.T., eds. Methods in enzymology. Academic Press, San Diego, CA, USA.