COMPARISON OF PROCEDURES FOR IMMEDIATE CHEMICAL ANALYSIS OF CHARCOAL[1]

Artur Queiroz Lana[2*], Thiago Taglialegna Salles[3], Angélica de Cássia Oliveira Carneiro[4], Marco Túlio Cardoso[5] and Ramon Ubirajara Teixeira[6]

[1] Received on 29.11.2013 accepted for publication on 03.12.2015.
[2] Universidade Federal de Viçosa, Mestrado em Ciência Florestal, Viçosa, MG - Brasil. E-mail: <artur.lana@ufv.br>.
[3] Universidade Federal de Viçosa, Programa de Pós-Graduação em Ciência Florestal, Viçosa, MG - Brasil. E-mail: <thiago.salles@ufv.br>.
[4] Universidade Federal de Viçosa, Departamento de Engenharia Florestal, Viçosa, MG - Brasil. E-mail: <cassiacarneiro@ufv.br>.
[5] Universidade Federal de Viçosa, Doutorado em Ciência Florestal, Viçosa, MG - Brasil. E-mail: <mtulio_cardoso@yahoo.com.br>.
[6] Universidade Federal de Viçosa, Mestrado em Ciência Florestal, Viçosa, MG - Brasil. E-mail <ramon_ufv@yahoo.com.br>.
*Corresponding author.

ABSTRACT – The climate change, the quest for sustainability and the strong environmental pressures for alternatives to traditional fossil fuels have increased the interest in the search and use of renewable energy sources. Among them stands out the biomass of charcoal coming from renewable forests, widely used as a thermal reductant in the steel industry in the detriment of the use of mineral coal coke. This study aimed to compare different operating procedures of immediate chemical analysis of charcoal. Seven essays to immediate chemical analysis were compared, spread between procedures performed by Brazilian companies and laboratories, the test described by NBR 8112 and one realized with a thermogravimetric analyzer (TGA) using the parameters of the NBR 8112. There were significant differences in the volatiles matter content and consequently in the fixed carbon contents found. The differences between the procedures and the NBR 8112 were caused by an excess burning time, a mass sample above or below the standard or inappropriate container used for burning. It observed that the TGA appraisal of the volatiles content must be carried out with a burning time equal to 2 minutes to obtain results similar to those of the NBR 8112 norm. Moreover, the ash content values were statistically identical and the particles size did not influence the differences between means.

Keywords: Carbonization; Thermogravimetric analysis; NBR 8112.

COMPARAÇÃO DE PROCEDIMENTOS PARA ANÁLISE QUÍMICA IMEDIATA DE CARVÃO VEGETAL

RESUMO – As mudanças climáticas, a busca pela sustentabilidade, e as fortes pressões ambientais por alternativas aos tradicionais combustíveis fósseis aumentaram o interesse na pesquisa e utilização de fontes renováveis de energia. Dentre elas se destaca a biomassa do carvão vegetal, advindo de florestas renováveis, amplamente utilizado como termorredutor na indústria siderúrgica em detrimento ao uso do coque de carvão mineral. O objetivo deste estudo foi comparar diferentes procedimentos operacionais de análise química imediata de carvão vegetal. Foram comparados sete ensaios para análise química imediata praticados por empresas e laboratórios brasileiros; o ensaio descrito pela NBR 8112; e um ensaio realizado em analisador termogravimétrico (TGA) com os parâmetros presentes na NBR 8112. Houve diferenças significativas nos teores de materiais voláteis e por consequência nos teores de carbono fixo encontrados. As diferenças entre os ensaios e a NBR 8112 tiveram como causas: tempo de queima em excesso, massa da amostra acima ou abaixo do padronizado, ou recipiente inadequado usado para queima. Observou-se que a determinação do teor de materiais voláteis em TGA deve ser realizada com

tempo de queima igual a 2 minutos para atingir resultados equivalentes aos do procedimento da NBR 8112. Os valores obtidos para os teores de cinzas foram estatisticamente iguais e a granulometria não influenciou as diferenças entre as médias.

Palavras-chave: Carbonização; Analisador termogravimétrico; NBR 8112.

1. INTRODUCTION

The last decade has seen an increased demand for renewable energy sources, especially biomass. In this domain, the charcoal is a protagonist in Brazil, being used not only as source of energy, but also as main reducing agent in iron ore reduction process in steelmaking mills. According to the National Energy Balance for the reference year of 2013, 33% of the wood produced in the country was transformed into charcoal, 1.4% was used directly for electricity production and the rest of wood consumed in the industrial, agricultural and residential (EPE, 2014).

Brazil is the only country producing large-scale charcoal for industry use. Its consumption is concentrated on the domestic market and the main targets are the pig iron and steel industry, which consumes 72% of the charcoal product, whereas ferrous alloys occupy themselves 12% of the charcoal market. Next are the residential areas and off-steel industries, especially for the production of cement, chemicals, food and ceramic (ABRAF, 2012; EPE, 2011). According to Rezende and Santos (2010), it is estimated that in Brazil, about a third of the production of pig iron and more than half of the production of ferroalloys make use of charcoal as thermal reducer.

The knowledge of the chemical composition of charcoal is crucial for estimating the quality and thus controlling process characteristics that is employed, since each application demands specific features of the charcoal. In order to determine its chemical composition is performed, among others, the immediate chemical analysis. This analysis helps to quantify constituents such as fixed carbon, volatiles matter and ash.

The fixed carbon ratio is determined by the amount of carbon in the charcoal. In a blast furnace with specific operating conditions, the higher the fixed carbon content, the greater the useful volume, in other words, the lower is the volume occupied by the charcoal into the metallurgical furnace (Rocha and Klitzke, 1998). The volatiles materials are given off substances from wood such as gas, during carbonization and/or burning charcoal. The greater the volatiles content, the higher the gaseous expansion will be during the descent of the charcoal into the furnace, generating over cracks and increasing the porosity (CARDOSO, 2010). Ash, on the other hand, is an inorganic residue mineral resulting of wooden and bark components. A high ash content, as much as the minerals entering its composition, may adversely affect the production of pig iron, ferrous alloys and non-ferrous metals (BARCELLOS, 2007).

In Brazil, the method for performing immediate chemical analysis of charcoal is the one prescribed by the NBR 8112 (ABNT, 1986). However, companies and laboratories in the country choose to make adjustments in the standard and developed their own procedures for the same purpose. Thus, the objectives of this study were to compare the results of these procedures with those obtained by NBR 8112, and to evaluate the pertinence of the NBR 8112 in a thermogravimetric analyzer (TGA).

2. MATERIAL AND METHODS

Five operational assays of immediate chemical analysis carried out by Brazilian companies (Companies A to G), being that three companies use the same procedure (Company A, B and C); Two procedures applied by laboratories at the Federal University of Lavras - UFLA and the Federal University of Viçosa - UFV, both in the Minas Gerais state; the procedure described by the NBR 8112; and one last procedure was done using a thermogravimetric analyzer (TGA), according to the parameters of the NBR 8112 and a heating ramp equal to 32°C/min. Apart from the latter carried out with 15 ml of iron crucibles, the other tests were conducted in the muffle furnace with 20 ml porcelain crucible. They were performed on samples of the same batch of charcoal of *Eucalyptus* sp. and each procedure (Tables 1 and 2) was replicated four times. The charcoal samples were previously dried at 105°C for 14 hours, then cooled on in a silica desiccator and weighed on an analytical balance precision (0.001 g).

Table 1 – Description of the nine operating procedures performed to determine the content of volatiles matter in charcoal.
Tabela 1 *– Descrição dos nove procedimentos operacionais realizados para determinação do teor de compostos voláteis de carvão vegetal.*

Operational routine	Sample preparation		Determination of volatiles compounds		
	Granulometry (mesh)	Mass (g)	Temperature (ºC)	Acclimatization time (min)	Burning time (min)
UFLA	40 > sample > 60	1.0	950	5.0	6.0
UFV	40 > sample > 60	1.0	950	2.0	9.0
Companies A/B/C	40 > sample > 60	1.0	900	3.0	7.0
Company D	40 > sample > 60	2.0	950	1.0	7.0
Company E	40 > sample > 60	1.0	950	4.0	7.0
Company F	80 > sample	1.0	900	0.0	7.0
Company G	40 > sample > 60	1.0	800	0.0	10.0
ABNT	70 > sample > 100	1.0	900	3.0	7.0
TGA (ABNT)	70 > sample > 100	1.0	900	0.0	7.0

Table 2 – Description of the nine operating procedures carried out for the determination of the ashes content in charcoal.
Tabela 2 *– Descrição dos nove procedimentos operacionais realizados para determinação do teor de cinzas de carvão vegetal.*

Operating Procedures	Sample Preparation		Ash content estimation	
	Granulometry (mesh)	Mass (g)	Temperature (ºC)	Burning time (h)
UFLA	40 > sample > 60	1.0	750	6.0
UFV	40 > sample > 60	1.0	600	6.0
Companies A/B/C	40 > sample > 60	1.0	700	7.0
Company D	40 > sample > 60	2.0	750	2.0
Company E	40 > sample > 60	1.0	600	6.0
Company F	80 > sample	1.0	600	1.5
Company G	40 > sample > 60	0.1	800	Till constant mass
ABNT	70 > sample > 100	1.0	700	Till constant mass
TGA (ABNT)	70 > sample > 100	1.0	700	Till constant mass

The calculation of volatiles matter (*VM*), ashes (*As*) and fixed carbon (*FC*) were done according to the equations: $VM = 100\ [(P_1-P_2) / P]$, $As = 100\ [(P_2- P_0)/P]$ and $FC = 100 - As-VM$. Wherein: P_1 is the initial mass of the crucible + mass of sample in grams (g); P_2 is the final mass of the crucible + mass of sample in g; P is the original mass of sample in g; P_0 is the initial mass of the crucible, in grams; *VM* is the content of volatile matter, in %; *As* is the ash content in %; and *FC* is the fixed carbon content in %. Comparisons of the results were made via ANOVA and Tukey mean test.

The UFLA proceeding for the volatiles matter content was done within a 2 minutes acclimatization at the door and a 3 minutes delay on the edge of the front opening of the muffle. To test the Company E procedure, a 2 minutes acclimatization was made at each of these locations. For the other assays the acclimatization time was done on the sole muffle door. The procedure for *VM* of the Company F, a 20 ml crucible containing the sample was introduced into the furnace inside a larger crucible of 30 ml. For the TGA test (ABNT), the crucibles were connected to the equipment inside the chamber and a heating ramp of 40 minutes to reach a temperature of 900 ° C was done before starting the burning time count.

To determine the ash content, one had to prolong the burning time in some procedures in order to burn completely the fixed carbon and the volatiles matters in the sample.

3. RESULTS

The volatiles matters content (*VM*) estimation was submitted to the ANOVA test under the hypothesis H_0, or null hypothesis, suggesting none significant variance between the volatiles contents. The test F ($p<0.05$) rejected the hypothesis which impose to operate the means test in order to compare the procedures (Table 3).

The ideal burning time for *VM* in the TGA procedure (ABNT) was determined from the averaged weight loss

Table 3 – Groups of means generated by applying the Tukey test ($\alpha = 0.05$) to the results of the volatiles matter (*VM*).

Tabela 3 *– Grupos de médias gerados pela aplicação do teste Tukey (α =0,05) aos resultados de teores de materiais voláteis (MV).*

Operating Procedure	Averaged content of *VM* (%)	Homogeneous Groups
Company D	15.96	d
Company F	17.32	e
Companies A/B/C	18.12	a
UFLA	18.24	a b
ABNT	18.33	a b
Company G	18.60	a b c
Company E	18.67	b c
UFV	18.89	c
TGA (ABNT)	19.78	f

* Means followed by the same letter are not statistically different from each other.
** Médias seguidas de uma mesma letra não diferem estatisticamente entre si.*

values generated by the thermal gravimetric analyzer (Figure 1). It is to notice that an 18.60% degradation of the sample mass was recorded 2 minutes after reaching 900 ° C.

On the other hand, for the ash content (*As*), the hypothesis H_0 was verified by the test F of ANOVA and it was not rejected, with p = 0.17. For the D and F companies protocols, the samples still remained four hours in the muffle to complete the coking process. The averages of *As* content for each procedure are 0.8% for ABNT; 0.76% for TGA (ABNT); 0.77% for Company F; 0.72% for Company E; 0.81% for UFV; 0.74% for UFLA; 0.81% for Company D and 0.74% for Companies A/ B/ C. It was not possible to get any consistent results using the methodology of the company G, whose tests repetition showed values between 0.09 and 2.27%.

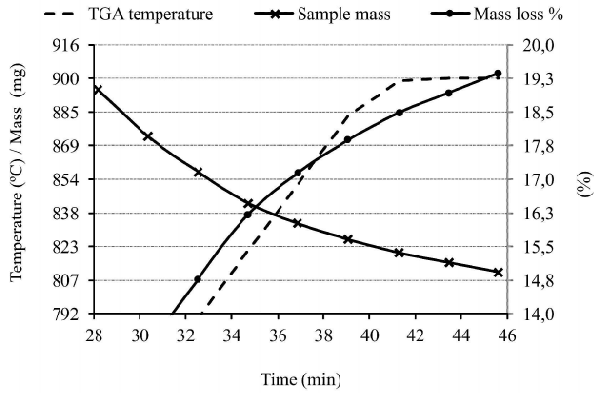

Figure 1 – TGA curves of average temperature, burning time and weight loss of the sample during an interval of the TGA (ABNT) procedure.

Figura 1 *– Curvas médias de temperatura no TGA, tempo de queima e perda de massa da amostra durante a execução do procedimento TGA (ABNT).*

The hypothesis H_0 having been rejected in the F test ($p < 0.05$), the Tukey test was performed to compare procedures for fixed carbon values (*FC*) (Table 4). The *FC* content of the company G protocol was not calculated as there was no *As* content for it.

No significant difference was observed in the averaged test results, both in the content of volatiles matters as in the ash content related to the samples particle size.

4. DISCUSSION

The values gotten from the implementation of these operational procedures are in the same range of values found in recent studies on *Eucalyptus* sp charcoal. In the immediate chemical analysis of charcoal, Oliveira et al. (2010), Oliveira et al. (2012) and Santos et al. (2011) reported *VM* rates ranging between 9.71 and 26.43%, *As* rates between 0.39 and 2.60% and *FC* rates between 73.05 and 88.17%.

A significant statistical difference is noticed between the average volatiles matter of the treatments. The *VM* content values of companies D and F stayed below the ABTN one. Regarding the procedures of UFV and

Table 4 – Groups of means generated by applying the Tukey test ($\alpha = 0.05$) to the results of the fixed carbon contents (*FC*).

Tabela 4 *– Grupos de médias gerados pela aplicação do teste Tukey (α =0,05) aos resultados des teores de carbono fixo (CF).*

Operating procedure	Averaged content of *FC* (%)	Homogeneous Groups
TGA (ABNT)	79.5	c
UFV	80.3	b
Company E	80.7	a b
ABNT	80.9	a b
UFLA	81.0	a
Companies A/B/C	81.1	a
Company F	81.9	d
Company D	83.2	e

* Means followed by the same letter are not statistically different from each other.
** Médias seguidas de uma mesma letra não diferem estatisticamente entre si.*

TGA (ABNT), the *VM* values were higher than the ABNT. The low values ones can be explained by a sample mass twice larger than the standard (Company D) and the use of a bigger crucible (Company F), which did not permit to burn properly the entire *VM* during testing. However, the highest values can be explained by a longer burning time in the UFV and TGA procedure (ABNT). The fact that the sample remained in the TGA equipment until the temperature of 900 ° C has been reached, indicating a combustion of fixed carbon for the entire procedure, its mass loss being then taken into account in the *VM* content calculation.

In the case of the TGA procedure (ABNT) for determining *VM*, it was verified that if the combustion time was changed to 2 minutes, it resulting in a rate of 18.60% close to the reference ABNT value found. The *FC* value recalculated for the TGA (ABNT) would be equal to 80.64% and *As* should remain equal to 0.76%. This procedure, as shown in Tables 3 and 4, the volatiles matter, ash and fixed carbon contents appears to conform to the results obtained by applying the NBR 8112 standard.

Besides, the ash contents analysis has shown that a 6 hours duration at 600 ° C was enough to burn the entire sample. Discarding the company G procedure and considering an additional burnig time for D and F companies procedures, the treatment means were statistically considered equals. In the case of the Company G procedure, the use of a 0.1 g sample entails working with a very high sensitivity. Actually the differences of initial weight and of final mass below 0.01 g, may compromise the accuracy of the test. For the D and F companies procedures, the given combustion time was not sufficient. The graphical analysis of the TGA weight loss data acquired according various routines of *As* content determination in the lab where was driven the study, concluded that a 1g of charcoal needs more than 3 hours at 700 °C to burn completely.

The means were statistically different to fixed carbon content. As the *FC* content is obtained indirectly through *VM* and *As* contents, and *As* was statistically the same for all procedures, it ensures that the mean test for *FC* followed the *VM* test trend, except for the UFV test whose *FC* content obtained was statistically equal to ABNT.

It is worth to emphasize that the results of the average tests involving the *VM* determination procedures with respect to the reference values of the ABNT test, were consistent with NBR 8112. Knowing that the NBR 8112 is rejecting any analogous estimations differing in relative value for more than 2% between them. Similarly for the *As* assessment procedures, the limit is 10% difference in relative values.

Moreover, between the companies A/ B/ C and ABNT protocols, the only difference noted for the *VM* and *As* contents appraisal is the particle size, since for determining the content of *As*, a 6 hours burning time at 600 °C was sufficient. At this point, the constituents concentrations of these two procedures were identical. Hence, it let appear that the size of the particles caused no statistical differences between treatment means.

The driven assays of companies A/B/C, company E and the UFLA laboratory generated results equivalent to the tests carried out on the basis of NBR 8112. The other procedures studied did not give values similar to those obtained by applying the ABNT. The results exhibited the need to adopt a single procedure between companies and research institutions in Brazil, aiming to standardize the immediate chemical analysis method of charcoal in the country, to get comparable values within the research and production sectors.

5. CONCLUSION

The operating procedures of immediate chemical analysis of charcoal of Companies A/ B/ C, Company E, and of the UFLA´s laboratory gave results equivalent to the ABNT procedure. Similarly, the TGA procedure (ABNT) when used for the determination of volatiles matter with a burning time equal to two minutes also produces results equivalent to the procedure described by NBR 8112.

More generally, the study emphasized the need of standardization of the operating methods for immediate chemical analysis of charcoal in Brazil.

6. ACKNOWLEDGMENTS

Thanks to the Minas Gerais Research Foundation - FAPEMIG, the Charcoal Research Group G6 for its financial support, to the National Counsel for Scientific and Technological Development - CNPq and to the Brazilian Agricultural Research Corporation - Embrapa Forestry for the grants awarded to students who contributed to this research.

7. REFERENCES

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS-ABNT. **Normas técnicas NBR 8112**. Brasília: 1986.

ASSOCIAÇÃO BRASILEIRA DE PRODUTORES DE FLORESTAS PLANTADAS - ABRAF. **Anuário estatístico da ABRAF: ano base 2010**. Brasília: 2011. 130p.

BARCELLOS, D.C. **Caracterização do carvão vegetal através do uso de espectroscopia no infravermelho próximo**. 2007. 139f. Tese (Doutorado em Ciência Florestal) - Universidade Federal de Viçosa, Viçosa, MG, 2007.

CARDOSO, M.T. **Desempenho de um sistema de forno-fornalha para combustão de gases na carbonização de madeira**. 2010. 89f. Dissertação (Mestrado em Ciência Florestal) - Universidade Federal de Viçosa, Viçosa, MG, 2010.

EMPRESA DE PESQUISA ENERGÉTICA – EPE. **Balanço Energético Nacional 2014:** Ano Base 2013. Rio de Janeiro: 2014. 288p.

EMPRESA DE PESQUISA ENERGÉTICA – EPE. **Balanço Energético Nacional 2011**: Ano Base 2010. Rio de Janeiro, 2011. 266p.

OLIVEIRA, A.C.; CARNEIRO, A.C.O.; VITAL, B.R.; ALMEIDA, W.; PEREIRA, B.L.C.; CARDOSO, M.T. Parâmetros de qualidade da madeira e do carvão vegetal de *Eucalyptus pellita* F. Muell. **Scientia Forestalis**, v.38, n.87, p.431-439, 2010.

OLIVEIRA, A.C.; ROCHA, M.F.V.; PEREIRA, B.L.C.; CARNEIRO, A.C.O.; CARVALHO, A.M.M.L.; VITAL, B.R. Avaliação de diferentes níveis de desbaste nas propriedades da madeira e do carvão vegetal de *Eucalyptus grandis x Eucalyptus urophylla*. **Floresta**, v.42, n.1, p.59-68, 2012.

REZENDE, J.B.; SANTOS, A.C. **A cadeia produtiva do carvão vegetal em Minas Gerais: pontos críticos e potencialidades**. Viçosa, MG: U.R. EPAMIG ZM, 2010. 80p.

ROCHA, M.P.; KLITZKE, R.J. **Energia da madeira**. Curitiba: FUPEF, 1998. 86p.

SANTOS, R.C.; CARNEIRO, A.C.O.; CASTRO, A.F.M.; CASTRO, R.V.O.; BIANCHE, J.J.; SOUZA, M.M.; CARDOSO, M.T. Correlações entre os parâmetros de qualidade da madeira e do carvão vegetal de clones de eucalipto. **Scientia Forestalis**, v.39, n.90, p.221-230, 2011.