

Energetic improvement of tanned leather solid wastes by thermal treatment

Mejoramiento energético de residuos sólidos de cuero curtido mediante tratamiento térmico

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Abstract

The permanent increase of the world energy consumption based on fossil fuels has caused several problems around the globe, which cannot be overlooked anymore. The necessity of cleaner energy sources is mandatory; among the different possibilities, biomass and solid wastes have become remarkable materials because of the wide processes and fuels resulting of them. Annually, the leather industry in Colombia produces 3.324 tons and generates 700 tons of tanned solid wastes approximately. The lack of alternative disposal methods makes this industry hazardous, despite the different technologies evaluated worldwide, such as pyrolysis, gasification or biodigestion. This work aims to analyze the changes in the chemical composition of the remaining solid and to enhance the energetic value of tanned solid wastes after thermal treatment in the 180-280°C range. The improvement of the high heating value is about 16%. Such parameter ups from 17 to 20,5 MJ kg⁻¹. Hydrogen exhibits the highest variation after thermal treatment with a decomposition ratio of 0,102 mol C-1, while Sulfur, at 0,0021 mol C-1, is the most stable. The high concentration of the carbon content in the remaining char, about 47,8%, increases the opportunities to use this material as either a feedstock for subsequent energy systems, or as a precursor for activated carbon production.

Keywords: higher heating value, Leather industry, Pyrolysis, Tanned wastes, Thermal treatment.

Resumen

El aumento permanente de los niveles de consumo de energía a nivel mundial basados en combustibles fósiles ha causado graves problemas alrededor del planeta, los cuales son cada vez más visibles. Emplear fuentes de energía limpias y renovables es una alternativa adecuada; entre las distintas posibilidades, la biomasa y los residuos sólidos se han convertido en materiales destacables debido a la diversidad de procesos y de combustibles resultantes. Anualmente, las curtiembres en Colombia producen aproximadamente 3.324 toneladas de cuero y generan 700 toneladas de residuos sólidos de curtiembres. La falta de métodos alternativos de disposición perjudica a esta industria a pesar de las distintas tecnologías probadas como pirolisis, gasificación o biodigestión. Este trabajo pretende analizar los cambios en la composición química del material sólido y mejorar el poder calorífico de los residuos sólidos de curtiembres al llevar a cabo un tratamiento térmico en un rango de temperaturas entre 180 y 280°C. El aumento del poder calorífico es de 16% aumentando de 17 a 20,5 MJ kg⁻¹. El hidrógeno presenta la mayor variación después del tratamiento térmico con una descomposición de 0,102 mol C-1, mientras que el azufre, con 0,0021 mol C-1, resulta ser el más estable. La alta concentración de carbono en el coque, cerca de 47,8%, aumenta las oportunidades para utilizar este material como materia prima en sistemas energéticos o como precursor para la producción de carbón activado.

Palabras clave: industria del cuero, Pirolisis, Poder calorífico superior, Residuos de curtiembres, Tratamiento térmico.

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INTRODUCTION

The continuous development of humankind has a close relationship to the energy demand. Heavily industrialized countries require more thermal and electrical energy. Between 1970 and 1990, the world total primary energy supply raised up from 69780 to 93040 TWh, which is an average rate of 1163 TWh per year. Whereas, over the last 20 years such rate boosted to 2413 TWh yr⁻¹ [1]. A 200% increase during last two decades. Mainly, this energy comes from fossil fuels such as natural gas (20,9%), oil (32,8%) and coal (27,2%). Regarding the world electricity generation, the trend is similar. Between 1970 and 1990, electricity generation moved up from 6000 to 12000 TWh with a 300 TWh yr⁻¹ increase rate. In 2010, this parameter reached 20000 TWh, and the rate was 400 TWh yr⁻¹. In this field, the share of fossil fuels is not as high as on primary energy supply, but these sources are the most representative. Oil generates 5,1%, natural gas 21,4% and coal 40%. There are a lot of consequences due to the fossil fuels combustion; most of them associated with greenhouse gas emissions, global warming, and water polluting.

Based on these problems, which affect the entire globe, national governments have created severe policies to promote the use of alternative technologies such as renewable energy systems, and enhance the efficiency of fossil fuel combustion systems. Moreover, they have funded different technologies nowadays; combined cycle systems, high-efficiency electrical appliances, fossil fuel switching or renewable energy systems, which are commercially available. Each year, the global new investment in renewable energy is growing. While in 2004, it was 22 Billion USD, it surpassed 211 Billion in 2010 [2]. Renewable energy systems are remarkable because some of them harness free energy sources, such as solar radiation, wind power, kinetic and potential energy of water, or heat stored underground. As a result of this growing investment, the renewable energy power capacity in 2010 was 1320 GW within hydropower (1010 GW) and wind power (198 GW) as the major sources. Biomass, with 62 GW installed, is the third most valuable resource regarding electricity capacity, but it is the most important in terms of heating applications, with a 280 GW installed capacity.

Biomass has a lot of advantages; different processes are commercially available right now, because of the wide range of existing materials. Some of

them are direct combustion, co-firing, gasification, biodigestion, pyrolysis, fermentation, and transesterification, among others. Biomass systems have become an interesting alternative for small-scale energy generation and solid wastes upgrading. Diverse byproducts, such as agro-industrial residues or municipal solid wastes, have acquired more value due to their feasibility of usage in energy systems. Therefore, the research on biomass and solid wastes fed energy systems has gained worldwide awareness.

The leather industry generates environmental pollutants and huge amounts of both solid and liquid wastes, which could be upgraded. Some of them are tannery shavings, trimmings and buffing dusts. The management of solid wastes, especially tanned leather waste, is a challenging problem. Globally, the tannery industry generates about 0,8 million tons of chromium tanned shavings per year [3]. Europe stands first with 25% of the global tanned leather and generates about 170,000 tons of tanned leather wastes annually [4]. In the same way, this industry represents serious environmental problems in Latin America. The production of chromium containing solid waste in Brazil is 100,000 tons a year⁻¹ [5]; meanwhile, in Colombia, the leather industry produces approximately 3,324 tons of tanned leather annually, distributed around 12 states and 677 tanneries. The highest production comes from Cundinamarca and Antioquia. Nevertheless, the huge number of tanneries shows that these companies are mid- and small- scale mainly [6].

Table 1. Summary of the leather industry production by state in Colombia

| State | Tanneries | Production (ton year ⁻¹) |
|-----------------|------------|--------------------------------------|
| Cundinamarca | 190 | 840 |
| Antioquia | 7 | 744 |
| Valle del Cauca | 22 | 492 |
| Bogotá | 350 | 396 |
| Atlántico | 2 | 252 |
| Nariño | 64 | 228 |
| Quindío | 27 | 144 |
| Bolívar | 1 | 120 |
| Risaralda | 1 | 108 |
| Total | 664 | 3324 |

Source: [6]

The leather production process has multiple steps from receiving to final commercialization. According to Cámara de Comercio de Bogotá [7], this process needs approximately 15 stages, which Figure 1 summarizes. Tanning is one of the unit operations in which the tanning agents react with the collagen matrix, stabilizing the protein and the collagen [4]. Some of these stages produce solid wastes and waste water. Thus, according to Kolomaznik [8], processing one metric ton of raw hide generates 200 kg of final leather product, 250 kg of non-tanned solid waste, 200 kg of tanned wastes and 50 tons of waste water. This means that tanned wastes corresponds to 20% weight of the final production.

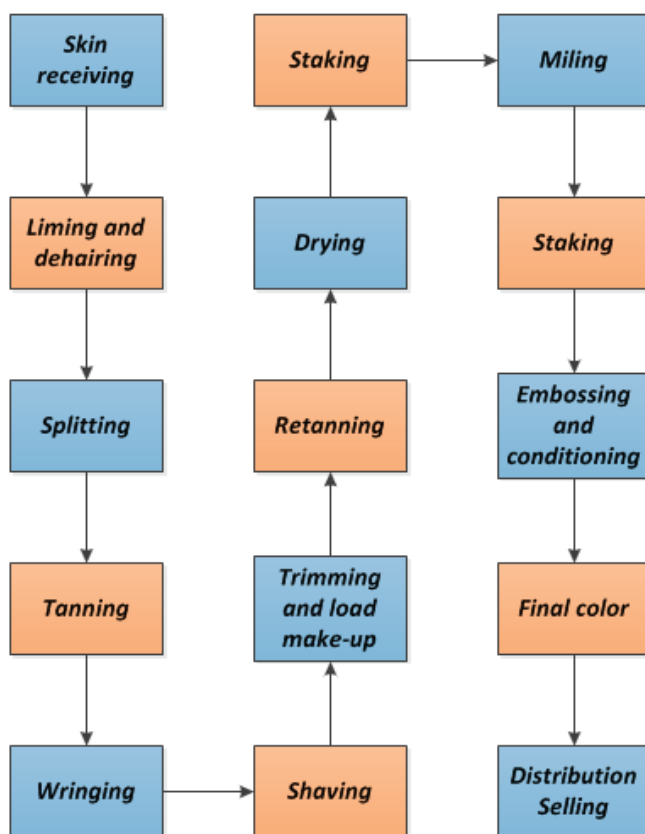


Figure 1. Scheme of the leather process followed at most Colombian tannery industries.

A wide range of works presents alternatives to upgrade these wastes and thereby mitigate their environmental impact. Some of them treated the wastes with chemical techniques such as anaerobic digestion or transesterification, although they are scarce and uncommon. Dhayalan et al [4] analyzed the biodegradability of untanned, chrome tanned and vegetable tanned leather under anaerobic conditions. Their results prove that degradation of chrome tanned leather waste is possible using anaerobic sludge and is better than vegetable tanned leather waste. Ong et al. [9] demonstrated the production of biodiesel from leather tanning waste with high free fatty acid content by methanolysis reaction at supercritical condition. They conducted the experiments at 12MPa and methanol/fatty oil molar ratios of 40:1 with temperatures between 250°C and 325°C. Moreover, they calculated the activation energy of transesterification, forward and reverse esterification reactions.

On the other hand, chromium and vegetable tanned wastes have remarkable physical and chemical characteristics for upgrading them by thermal treatments such as pyrolysis or gasification, which can result on either a rich carbonaceous solid useful as raw material of activated carbon process or a valuable gas fuel for subsequent energy systems. Caballero et al. [10] analyzed the kinetic of global primary thermal decomposition of tanned wastes using TG-DTG in strict pyrolysis conditions and with different proportions of oxygen. They varied the heating rates at 5, 10 and 20°C min⁻¹, and also fed ratios of He:Oxygen (9:1, 4:1, 2:1). Heating rates did not affect the process, whereas adding more Oxygen produced faster decomposition at temperatures between 250 and 450°C. Likewise, Gil et al. [11] established adequate conditions for the pyrolysis of leather wastes in order to recover gas and condensable fractions; thus, the solid wastes of leather industry could be converted in low cost adsorbent materials. They carried out pyrolysis of the leather waste with heating rates of 2, 5, 10, 15 and 20°C min⁻¹. In the same way as presented below, the faster decomposition was between 250 and 350°C. Finally, they prepared activated carbons with high thermal stability and surfaces areas up to 2700 m² g⁻¹. Moreover, ashes, which contain very high amounts of the metal chromium present mainly as chromium oxide (Cr₂O₃), are common products of these thermal processes. Alves [12] presented a possibility of recycling chromium contained in leather shavings incineration ashes, and utilizing it as raw material for stainless steel production. They produced a HC-FeCr alloy by carbothermal reduction at 1600°C.

Works on tanned leather wastes management are not only at lab scale; the BLC Leather Technology Center [13] developed a gasification prototype power plant 2 ton day⁻¹ capacity in UK. This system processes a wide range of leather wastes such as chromium tanned wastes, wet white shavings, vegetable tanned shavings, tallows and trimmings. Based upon the design, dry solids to gasifier are 50 kg hr⁻¹, gas volume is 129 Nm³ h⁻¹, expected gas value 4,5 - 5 MJ Nm⁻³ and 70% maximum cold gas efficiency. Syngas should be cleaned of soot and tar using dry catalysis or physical filtration. However, despite the generation of a clean syngas for reuse in boilers or other CHP applications, tannery wastes should be macerated, flash dried and densified beforehand.

In this manner, tanned solid wastes are suitable for upgrading and recycling, but the lack of research in Colombia has given tanners no more possibilities than landfill disposal and wrong environmental practices. This preliminary study aims to analyze the changes in the chemical composition of the remaining solid and thereby enhance the energetic value of tanned solid wastes after thermal treatment in the 180-280°C range. In this manner, Colombian tannery industries would identify alternative methodologies for adding value to their solid wastes and decreasing the environmental impact.

METHODOLOGY

Solid wastes from the shaving stage after tanning and wringing were gathered from a leather industry placed in San Benito Bogotá, Colombia. Afterwards, they were crushed and some physical properties from these tanned wastes were measured. The proximate analysis, which includes the measurement of moisture content, volatile matter, ash content, and fixed carbon was done in accordance with Forero-Núñez [14]. Moisture content is evaluated by following ASTM E871-82, so the sample is dried in an oven at 105°C until the final weight varied less than 0,2%. Volatile matter was measured by recording the final weight of the sample after placing them in an oven during seven minutes at 950°C, in accordance with ASTM E872. Ash content was defined by ASTM E1755-01 as the remaining material after burning the sample in an oven at 800°C. Finally, the fixed carbon is calculated by mass balance according to ASTM 1756-08.

Both, ultimate analysis and heating value evaluation were developed at the coal laboratory of Servicio Geológico Colombiano in Bogotá Colombia. A LECO Truspec CHN Analyzer was employed to determine carbon, hydrogen and nitrogen content by ASTM D5373-08. Sulphur content was measured with a LECO SC-32 and S-144DR analyzer based on ASTM D4239-08; afterwards, the oxygen content was established within the results of hydrogen, nitrogen, sulphur, carbon and ash contents. The samples were analyzed in a bomb calorimeter in accordance with ASTM D5865-04 and compared against two equations found in the literature. Obernberger [15] referenced the eq. 1, which corresponds to an empirical equation for calculation of high heating value of biomass; whereas, the Leather Technology Center [13] presented the eq. 2 for leather residues. These equations relate the ultimate analysis with higher heating value (HHV) and permit to evaluate this value on a practical manner when the experimental test cannot be performed.

$$HHV(MJ\ kg^{-1}) = 0,3491X_C + 1,1783X_H + 0,1005X_S - 0,0151X_N - 0,1034X_O - 0,0211X_{ash} \quad (1)$$

$$HHV\ (MJkg^{-1}) = \left(\frac{2,3326}{1000}\right) * [146,58X_C + 568,78X_H - 29,45 - 6,58X_{ash} - 51,53(X_O + X_N)] \quad (2)$$

Where HHV (MJ kg⁻¹) is the higher heating value, X_C (% weight) is the carbon content, X_H (% wt) is the hydrogen, X_O (% wt) is the oxygen content, X_N (% wt) nitrogen, and X_{ash} (% wt) the ash content. Thermal decomposition tests were performed at the laboratory of Thermal Plants and Renewable Energy, Bogotá Colombia (4.638°N-74.084°W, 2630m above mean sea level). For thermal treatment, a small reactor was designed and constructed; it was heated by electrical resistances and controlled based on the internal temperature inside the chamber. With regard to the temperature of the process, past research identified, that several changes in the material occurred between 200°C and 300°C [11],[16]; throughout this range, the derivative of the mass loss reached its highest value at 0,4% weight °C⁻¹. Therefore, three set-points were defined, 180°C, 230°C and 280°C. The tanned-wastes were fed in the reactor, it was closed, and heated until reaching the defined temperature; afterwards, the control constantly maintained the same parameter during three hours. Within this time, a complete thermal degradation of the material was expected. In comparison with most of the works performed, this procedure is innovative because they often analyzed the mass loss and the

derivative mass loss rate varying the heating rates by thermogravimetry, but did not evaluate how the change of the chemical composition was at different points at low temperature ranges. Resulting samples were gathered (Figure 2); the ultimate analysis was executed, and heating value was determined again. Based on them, the mass balance and the carbonaceous solid yield were evaluated at each temperature; meanwhile, the dependence of the decomposition for each compound within the temperature was calculated as the difference of the remaining mass in the char before and after each thermal treatment.

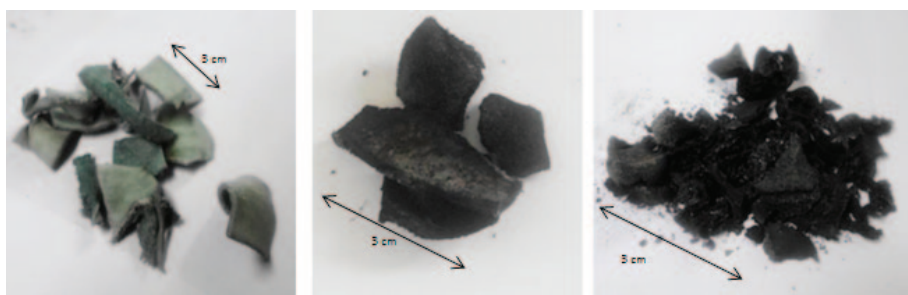


Figure 2. Tanned solid wastes before and after thermal treatment a) at ambient temperature, b) at 180°C, c) at 280°C.

RESULTS

Proximate analysis shows the relationship between moisture content, volatile matter, fixed carbon and ash content. Table 2 summarizes these results in a wet basis (% wt); the sample of tanned wastes has more intrinsic moisture 14% than sawdust (9,67%) or tanned wastes reported in the literature. During pyrolysis, more humidity in the sample will consume higher energy levels due to the drying phenomena. Regarding the volatile matter, the results are in accordance with previous studies, since increasing the decomposition temperature more volatiles burn off and leave the system in the gas current. At ambient temperature, the volatiles in the sample (68,6%) are almost the same in this study as in reference. Nevertheless, they are less than volatiles contained in a typical lignocellulosic material such as sawdust (76,82%). More volatiles affect the thermal decomposition process and char yield because the mass losses are greater at a lower temperature range. The ash content in the sample is greater than the values reported by other authors

[3],[16],[17]. Generally, tanned wastes have more ashes than sawdust or other biomass, such as wood and woody biomass, or herbaceous and agricultural biomass, in which the ash content varies in the 2- 4,5% range [18]. High ash levels lead to corrosion, fouling, slagging and ash deposit formation in boilers and furnaces.

On the other hand, the fixed carbon in the tanned wastes is clearly similar within the sawdust, making this solid waste potentially useful in terms of the energy stored, based on the fact that materials with high fixed carbon exhibit higher heating values. With regard to the proximate analysis of thermal treated tanned wastes, results indicate a strong concentration of fixed carbon and ashes at higher temperatures. Volatile matter drops from 68,6 to 55,21% within a temperature of 280°C, while fixed carbon is almost the double and ash content the triple. There is a remarkable change in the volatile matter content between the initial wastes and the treated wastes at 180°C. Hence, the volatile content in the latter sample is greater, due to the drying stage which occurs approximately at 100°C. The humidity in the samples boils out making a bigger share of volatile matter, fixed carbon and ash content.

Table 2. Proximate analysis of as-received and pyrolyzed tanned wastes in comparison with sawdust and literature results

| Parameter (% wt) | Tanned wastes | Wastes at 180°C | Wastes at 230°C | Wastes at 280°C | Sawdust [14] | Tanned wastes [13] |
|------------------|---------------|-----------------|-----------------|-----------------|--------------|--------------------|
| Moisture content | 14,08 | 0 | 0 | 0 | 9,67 | 11,29 |
| Volatile matter | 68,6 | 69,34 | 61,37 | 55,21 | 76,82 | 67,51 |
| Fixed Carbon | 10,71 | 15,46 | 19,01 | 20,90 | 11,71 | 16,24 |
| Ash | 6,61 | 15,20 | 19,62 | 23,89 | 1,80 | 4,96 |
| Total | 100 | 100 | 100 | 100 | 100 | 100 |

The examination of the thermal decomposition in terms of the change on the ultimate analysis identifies some characteristics of the compounds embedded in the volatile stream and those remaining in the char. The tanned wastes have higher levels of nitrogen and sulphur than traditional biomass like sawdust, mainly due to the structure of the hide and the use of tanning agents. The raw hides are essentially a mixture of natural proteins; the most valuable in the leather process is the collagen, which represents the structural protein of the extracellular matrix [19]. This structure reacts

with the chrome-tanning agent, typically a basic chromium salt, $\text{Cr}(\text{OH})\text{SO}_4$, and converts the protein of raw hides into a stable fiber structure. The high sulphur content appears as a consequence of agent added in the tanning stage. Nashy [20] summarizes the typical composition of native hides after analyzing them by Horizontal Attenuated Total Reflection (HTAR) and Diffuse Reflectance (DR) FT-IR spectroscopy. They state the strong vibration of $-\text{NH}$, CH_2 , $\text{C}=\text{O}$, COO^- and CN groups, which corresponds to the results of the nitrogen content of the ultimate analysis. Defining the chemical structure of tanned leather is not a simple task, because of the alternative paths that chrome atoms follow for reacting with proteins in the hides; most of them based on the interaction between the chrome atoms with either amino, COOH or amide groups, as shown in Figure 3.

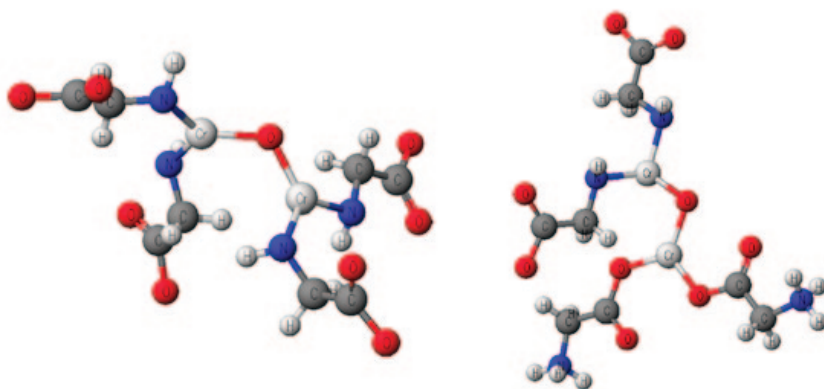


Figure 3. Interaction of chrome with amino groups through 4 protein chains (3a), and interaction of Cr with two COOH and two amides through 4 protein chains (3b) [20].

Table 3 exhibits the results of ultimate analysis of as-received and tanned wastes in a dry basis (%wt d.b.). The tanned wastes collected from leather process industries in Bogotá have more Hydrogen, Oxygen, Sulfur and Ashes than those reported in the literature [13],[16]; their Nitrogen content is in the same range, but their Carbon content is lower, which could negatively affect the heating value. Nevertheless, the differences between these results demonstrate the importance of making detailed ultimate analysis for each sample prior to use them on any thermal system.

Table 3. Ultimate analysis of as-received and pyrolyzed tanned wastes in comparison with references and sawdust

| Parameter (%wt d.b) | Tanned wastes | Wastes at 180°C | Wastes at 230°C | Wastes at 280°C | Sawdust [14] | Tanned wastes [13] | Tanned wastes [16] |
|---------------------|---------------|-----------------|-----------------|-----------------|--------------|--------------------|--------------------|
| Carbon | 35,86 | 40,79 | 45,15 | 47,83 | 42,14 | 47,80 | 48,2 |
| Hydrogen | 9,07 | 4,88 | 4,8 | 4,48 | 9,07 | 6,40 | 5,8 |
| Oxygen | 34,84 | 20,33 | 13,75 | 8,78 | 45,82 | 28,71 | 33,2 |
| Nitrogen | 10,08 | 16,14 | 14,15 | 12,96 | 0,98 | 10,70 | 7,5 |
| Sulfur | 2,46 | 2,66 | 2,53 | 2,06 | 0,00 | 1,43 | 1,9 |
| Ash | 7,69 | 15,20 | 19,62 | 23,89 | 1,99 | 4,96 | 3,4 |
| Total | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

The pyrolysis often pursues either the production of energy from the char, tar and gas fraction or the preparation of activated carbons from the carbonaceous material. The ultimate analysis of the thermal treated materials in this preliminary study indicates that carbon enrichment of the solid is possible. By comparing the results of initial material within treated material at 180°C, it is possible to identify the incidence of the drying stage; both Hydrogen and Oxygen content decrease, the first one reduces from 9,07 to 4,88% and the second from 34,84 to 20,33%. This change results on the rise of the additional components; Carbon rises to 40,79%, Nitrogen to 16,14%, and so on. Samples treated at higher temperatures contain even more carbon and ashes, whereas the other components tend to release the solid. A comparison between samples treated at 180 and 280°C indicates the formation of substances mainly made of Hydrogen, Nitrogen, Oxygen and Sulphur while carbon due to its high thermal resistance remains in the solid. In fact, several studies have pyrolyzed tanned wastes till 600°C [10],[11],[16],[19] and state that the substances, which release the solid, are mainly nitriles, nitro-ketones, alkanes, alkenes, phenols and their derivatives.

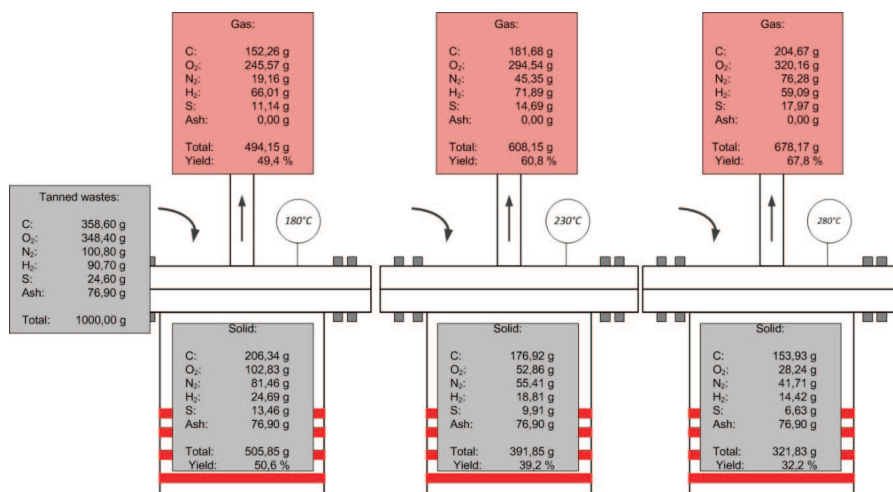


Figure 4. Mass balance, and resulting char and gas yields.

Figure 4 clearly exhibits the distribution of each component between the solid and gas phases at different temperatures. As supposed, the ashes remain constant in the solid phase despite the operational conditions. The yields of solid decreased from 50,6 to 32,2%, while the gas phase achieves 67,8%. The gas stream, denoted here, includes both the condensate and the gas of typical pyrolysis products, which have been broadly studied and are not the scope of this preliminary analysis. This thermal treatment allows the stabilization of these residues and the concentration of heavy metals and carbon. Table 4 presents the mass losses of each component. As stated before, on the initial range (ambient – 180°C) mostly Hydrogen and Oxygen evaporates with mass losses around 70%, followed by Sulfur and Carbon at 45,3 and 42,5% respectively. After 280°C, the solid loses about 91,9% of Oxygen content, 84,1% Hydrogen, 73,1% Sulfur, 58,6% Nitrogen and 57,1% Carbon.

Table 4. Mass loss of each component after thermal decomposition

| Temperature | Carbon | Oxygen | Hydrogen | Nitrogen | Sulfur | Ash |
|-------------|--------|--------|----------|----------|--------|------|
| 180°C | 42,5% | 70,5% | 72,8% | 19,0% | 45,3% | 0,0% |
| 230°C | 50,7% | 84,5% | 79,3% | 45,0% | 59,7% | 0,0% |
| 280°C | 57,1% | 91,9% | 84,1% | 58,6% | 73,1% | 0,0% |

Moreover, these results permit to identify the propensity of each chemical component to release the solid due to changes in temperature. Therefore, the thermal decomposition ratio of each component is calculated with the data of Figure 4. Despite the higher mass loss dependence of Oxygen, Carbon or Nitrogen ($0,746$, $0,524$, and $0,399$ $\text{gr}^\circ\text{C}^{-1}$ respectively), Hydrogen is most affected by temperature and, therefore, most active. The analysis is not totally accurate if we only consider the mass loss ratio; it is often vital to identify the mole loss ratio of every chemical component because each one reacts in quantities defined by its molecular weight. Hence, Figure 5 presents the variation of the moles remaining in the solid after thermal decomposition at different temperatures. The most reactive chemical component is Hydrogen with a decomposition ratio around $0,1027$ $\text{mol } ^\circ\text{C}^{-1}$. Oxygen and Carbon have similar ratios, $0,0466$ and $0,0437$ $\text{mol } ^\circ\text{C}^{-1}$, while Nitrogen and Sulphur are less dependent on temperature ($0,0285$ and $0,0021$ $\text{mol } ^\circ\text{C}^{-1}$).

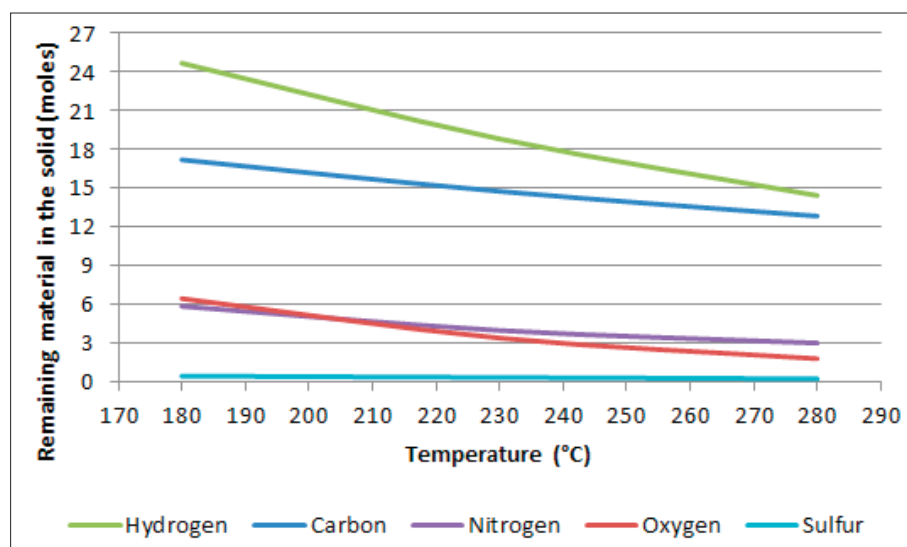


Figure 5. Variation of the remaining material in the tanned wastes after thermal treatment in the 180°C - 280°C range.

In regard to the heating value, the thermal treatment and the concentration of the carbon content in the carbonaceous solid results on higher heating values, which is valuable for its subsequent use in energy systems. Table 5 exhibits the experimental and calculated heating values of the carbonaceous

material after thermal treatment. Empirical correlations show adequate results; the second equation has an average error around 7,5% while the first one is more precise with error less than 3%. Wastes treated at higher temperatures have heating values with an increase of their energy content of about 16%; the valued raised up from 17 to 19,47 and 20,49 MJkg⁻¹, at 230 and 280°C respectively.

Table 5. Experimental and calculated higher heating values for leather wastes after thermal treatment

| Parameter (MJ kg ⁻¹) | Tanned wastes | Wastes at 180°C | Wastes at 230°C | Wastes at 280°C |
|----------------------------------|---------------|-----------------|-----------------|-----------------|
| HHV _{exp} | 17,59 | 17,56 | 19,47 | 20,49 |
| HHV _{eq1} | 19,54 | 17,59 | 19,62 | 20,58 |
| HHV _{eq2} | 18,71 | 15,74 | 18,08 | 19,25 |

CONCLUSIONS

Upgrading the energy content of solid tanned wastes is possible by means of thermal treatment. The resulting heating values of the carbonaceous solid decomposed in the 180 – 280°C range are even higher, about 20,49 MJ kg⁻¹, and an increase of 16% is achievable due to the concentration of the carbon content in the carbonaceous matrix of the remaining solid. Moreover, the results of the ultimate analysis exhibit the effect of temperature on the detachment of other elemental compounds such as oxygen, hydrogen, nitrogen or sulfur. After thermal treatment at 180°C, mostly hydrogen and oxygen release the solid due to the influence of the drying stage while sulfur, carbon and nitrogen remain in the solid. Hydrogen and oxygen are the most active components in the thermal treatment mechanisms; these compounds have decomposition ratios about 0,1027 and 0,0466 mol °C⁻¹ respectively, while temperature lower than 280°C does not affect either the sulfur or the nitrogen decomposition.

The temperature decreases the char yield considerably from 50,6 to 32,2% and boosts up the gas production. The remaining solid can be employed onto energy systems or as a precursor in the activated carbon production process. Colombian tannery industries cause a severe environmental impact because of the wrong disposal of the resulting tanned solid wastes. Some

alternatives are based on the thermal treatment of these solid residues. This preliminary study identifies the behavior of some Colombian tanned wastes during thermal treatment at low temperatures, and how it upgrades the energy content of the carbonaceous material. Nevertheless, in order to promote cleaner environmental practices among tanners in this country, further research should focus on characterizing the produced gas and analyzing the technical features of appliances capable of harnessing the solids.

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REFERENCES

- [1] International Energy Agency, "2011 Key World Energy Statistics". Paris, France, pp. 5-20.
- [2] REN21, "Renewables 2012 Global Status Report". Paris., REN21 Secretariat, Final Rep., 2012
- [3] I. C. Kantarli and J. Yanik, "Activated carbon from leather shaving wastes and its application in removal of toxic materials". *Journal of Hazardous Materials*, vol. 179., pp. 348-356, 2010. Doi: 10.1016/j.jhazmat.2010.03.012
- [4] K. Dhayalan *et al.*, "Biodegradability of leathers through anaerobic pathway". *Waste Management*, vol. 27., pp. 760-767, 2007. Doi:10.1016/j.wasman.2006.03.019
- [5] L. C. A. Oliveira, *et al.*, "Preparation of activated carbon from leather waste: A new material containing small particle of chromium oxide". *Materials Letters*, vol 62., pp. 3710-3712, 2008. Doi: 10.1016/j.matlet.2008.04.064
- [6] Centro Nacional de Producción más Limpia y Tecnologías Ambientales, "Diagnósticos y estrategias, proyecto gestión ambiental en la industria de curtiembre en Colombia", Final Rep., Feb. 2004. [Online]. Available: <http://www.sirac.info/Curtiembres/html/Archivos/Publicaciones/EstrategiasDiagnostico.pdf>
- [7] Cámara de Comercio de Bogotá, "Producción de pellets de materiales de curtiembres para la generación de gas combustible y su posterior uso energético", Mid Report., March. 2012. Contract No. 4600003136
- [8] M. Kolomaznik *et al.*, "Leather waste - Potential threat to human health, and a new technology of its treatment". *Journal of Hazardous Materials*, vol. 160., pp. 514-520, 2008.

- [9] L. K. Ong *et al.*, "Transesterification of leather tanning waste to biodiesel at supercritical condition: Kinetics and thermodynamics studies". *Journal of Supercritical Fluids*, vol. 75., pp. 11-20, 2013. doi:10.1016/j.supflu.2012.12.01
- [10] J. A. Caballero, R. Font, and M. M. Esperanza, "Kinetics of the thermal decomposition of tannery waste". *Journal of Analytical and Applied Pyrolysis*, vol. 47., pp. 165-181, 1998. doi:10.1016/S0165-2370(98)00081-3
- [11] R. R. Gil *et al.*, "Valorization of solid wastes from the leather industry: preparation of activated carbon by thermochemical processes", in *1st Spanish National Conference on Advances in Materials Recycling and Eco-Energy*, Madrid, 2009. [Online] Available: http://digital.csic.es/bitstream/10261/18420/1/S01_7.pdf. Doi:10.1016/j.jaap.2012.08.010
- [12] C. R. Alves *et al.*, "Utilization of ashes obtained from leather shaving incineration as a source of chromium for the production of HC-FeCr alloy". *Mineral Engineering*, vol. 29., pp. 124-126, 2012. doi:10.1016/j.mineng.2011.12.009
- [13] BLC Leather Technology Center, "The development of downdraft gasification for leather industry wastes", Laboratory Rep., Nov, 2003. LR-309. [Online] Available: <http://www.blcleathertech.com/images/leather-reports/LR309.pdf>
- [14] C. A. Forero-Núñez, J. Jochum, and F. E. Sierra-Vargas, "Characterization and feasibility of biomass fuel pellets made of Colombian timber, coconut and oil palm residues regarding European standards", *Environmental Biotechnology* [Online], vol 8(2), pp. 67-76, 2012. Available: http://www.environmentalbiotechnology.pl/eb_dzialy/eb_online/2012/vol8_2/ms179.pdf
- [15] I. Obernberger, and G. Thek, "Physical characterization and chemical composition of densified biomass fuels with regard to their combustion behaviour". *Biomass and Bioenergy*, vol. 27, pp. 653-669, 2004.
- [16] R. R. Gil, *et al.*, "Pyrolysis of biocollagenic wastes of vegetable tanning. Optimization and kinetic study". *Journal of Analytical and Applied Pyrolysis*, vol. 98, pp. 129-136, 2012.
- [17] O. Yilmaz, *et al.*, "Conversion of leather wastes to useful products". *Resources, Conservation and Recycling*, vol. 49, pp. 436-448, 2007. Doi: 10.1016/j.resconrec.2006.05.006
- [18] S. V. Vassilev, *et al.*, "An overview of the chemical composition of biomass". *Fuel*, vol. 89, pp. 913-933, 2010.
- [19] A. Marcilla, *et al.*, "Study of the influence of NaOH treatment on the pyrolysis of different leather tanned using thermogravimetric analysis and Py/GC-MS system". *Journal of Analytical and Applied Pyrolysis*, vol. 92, pp. 194-201, 2011.
- [20] E. H. A. Nashy, *et al.*, "Molecular spectroscopic study for suggested mechanism of chrome tanned leather". *Spectrochimica Acta Part A*, vol. 88, pp. 171-176, 2012.