Recycling of waste leather: a review of experimental studies

Reciclaje de residuso de cuero: una revisión de estudios experimentales

Received: 04- 05 - 2015 Accepted: 05-11-2015

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Abstract

Tanning transforms raw hides in leather, a rot-proof, flexible and durable material. During this complex process significant amounts of waste are generated. Therefore, an appropriate environmental management is required. This work presents a review on the recycling of solid waste from leather processing. Pyrolysis was found as a widely studied way for recycling leather scrap, obtaining alternative solid fuels and carbonaceous materials with multifunctional properties, potentially useful for carbon dioxide capture and dye adsorption in aqueous solutions. Transesterification of leather for biodiesel production, mixing of leather scrap with asphalt for improving the durability of pavements and reinforcement of rubbers appears to be viable processes for wastes of tanning. We conclude that is possible to reduce the environmental pollution from leather industry, not only by effluent treatment, by processing the solid waste for obtaining valuable new products.

Keywords: Leather processing; wet blue; tanning; solid waste recycling.

Introduction

The tanning is a process in which the skin of various animals until making them permanently rot-proof, but preserving its fibrous natural structure and thereby its resistance and flexibility (NPCS, 2005). With the leather, name given to the tanned skin, is manufactured, shoe wear, furniture, tapestry, clothes, gloves, personal accessories and even some industrial pieces (Marshall, 2003).

The leather production is a relevant activity in the economic development of countries like Turkey, China, India, Pakistan, Ethiopia, Italy, Spain, Brazil (Orhon *et al*., 1999; Leta *et al*., 2004; Lefebvre *et al*., 2006; Rajesh and Kaliappan, 2007; Kanagaraj *et al*., 2015) and Colombia

(DNP, 2014). The first Colombian tanneries date from 1920 in Antioquia and of 1950 in the cities of Villapinzón and Chocontá in Cundinamarca. Currently there are tanneries in Nariño, Quindío, Risaralda, Cundinamarca, Antioquia, Atlántico, Valle del Cauca, Tolima, Bolívar, Santander y Huila, that is to say, in the 11 of the country's department with the highest economic activity (Alzate, 2008). It is pertinent to point that the Colombian leather chain has registered commercial surplus since 2003, and is even considered by the National Development Plan as a key producing sector for various regions of the country, specifically in the strategy that points to create technological and competitive platforms to take advantage of human talent in the region, and be source of new and sophisticated employees (DNP, 2014).

However being an economically relevant industry, a lot of concerns must be taken to mitigate the environmental pollution caused by the generated wastes during the leather processing, though in the last years important improvements have been implemented during the leather processing technologies to decrease the impact upon the environment (Dixit *et al*, 2015).

To understand this type of residues that are generated, it's pertinent to point that in the tanning process four sup-groups are present that at the same time imply multiple tasks each one, which are: operation, tanning, retannage and finishing (Beghetto *et al*., 2013) as it's schemed in the Figure 1. During the process great amounts of solid and liquid amounts are generated, that should be treated adequately to avoid high environmental contamination; one of the ways to attenuate the risk of the introduction of clean sustainable technologies (Kanagaraj *et al*, 2015), or the incorporation of added value to these residues (Shabani *et al*., 2009), this last one being one of the main challenges for the tanneries in the world (Cabeza *et al*., 1998; Rao *et al*., 2002), And Colombia is not the exception.

Figure 1. Flow diagram of the tanning process
Source: (Adapted from Beghetto *et al*., 2014; Cooman *et al*., 2003)

Most of the solid residues belong to the defective non-processes skin, processed leather pieces and other, that represent more than 150,000 tons a year in all around the globe (Bermúdez, 2013), which contain metals and chemical products that include titanium, chrome and others (El-Sabbagh and Mohamed, 2011). From here the importance to find alternatives that give added value to these kind of residues, offering a current practical alternative to dispose them in rubbish dumps.

Considering that various methods to obtain different applications for these kind of residues, this revision describes various important goals for the reduction and pollution with the treatment of solid protein coming from the leather operations after the tanning, including possible applications that can give these kind of materials.

It's pertinent to take in account that the tanning process is different for each final product, and the kind and residue quantity that are produced can meaningfully (Islam *et al*. 2014). The used chemicals during the leather processing can be vary a lot: acids, alkali, chrome salts, tannins, solvents, sulfurs, colorants among other compounds that can be used in the transformation of raw skin into commercial goods (Lofrano *et al* 2013). These compounds aren't completely fixated to the skins and can migrate to the water that forwardly dispose in the health network, from here that a great number of researchs in this industries focus in looking for alternatives to decrease the water (Suganthi *et al*. 2013; Fabbricino *et al*. 2013; Mannuci *et al*. 2010;). Nonetheless are few the studies related with the processes and technologies that enhance the solid residues to become them into new products for example, materials, chemical products and energy, which according to some researchers should be the focus of future research projects (Lin *et al*. 2012; El-Sabbagh and Mohamed, 2011). Enhancing the residues, different to the basic management of disposing of them in sanitary landfills, could be an alternative for the organizations to decrease the environmental impact at the same time they obtain sub-products that could generate new incomes (Lofrano *et al*. 2013).

In similar way some studies have been reported that present treatment and alternative uses for these kind of residues, can be taken to specific applications and useful for the industry in general, as described up next.

Main applications for the leather residues

The pyrolysis can be one of the alternative routes for the treatment of solid residues in the tannery (Lua *et. al*, 2004). Consist in heating the organic material widely applied for the treatment of organic residues, which are the agricultural ones, the tires out of use, the purifier plants mud and the plastics. The reaction products are gases that can be used as fuel, oil that can be used as combustible or raw material for chemical products and carbonaceous residues that can be used as combustible or the production of activated coal (Yilmaz *et al*, 2007). Some studies about pyrolysis leather residues are presented for the application in combustibles for the synthesize of carbonaceous materials.

Using of solid residues of the leather industry as a source of combustion

The increase of the petroleum's price, just like the decrease of world reserves of oil, has become one of the main causes for the search and development of alternative combustibles (Silitonga *et al.*, 2013), in particular for the transportation and indrustrial purposes (Koutinas *et al.*, 2012). In a study done by Yilmaz *et al.*, (2007), pyrolysis with leather residues was treated in various presentations as: steel shavings tanned in chrome, and/or with vegetable inks in the form of grinded dust, showing interesting features as source for the combustible productions; the grinded dust presented the highest performance in the oil production (23% in weight), while the other two wastes only produced between 8% and 9%. The performance of the carbonaceous residues was between the 37.5% and 485%, and its caloric value was between the 4300 and 6000 kg^{-1} kcal, adequate values for this application. The solid combustible production from the leather residues is a technically alternative way to be implemented at industrial scale, but the ammoniac, hydrogen cyanide, sulfur dioxide that was generated during the process should be considered, like the economic feasibility given the high required temperatures and the need to use inert gases (Font *et al*, 1999).

Carbonaceous materials synthesize

The activated coals can be produced from carbonaceous materials by chemical activation (Girgis and Ishak, 1999) and by physical activation (Lua *et al*. 2004; San Miguel *et al*., 2003). The method of physical activity implied the pyrolysis of the raw material, and the posterior activation of high temperature in a carbon dioxide or steam atmosphere, that in reality it was a thermic activation. The chemical activation implied the impregnation of leather residues with chemical activating agents like phosphoric acid, zinc chloride, potassium hydroxide or potassium carbonate; these activates degrade the remaining organic material in the carbonaceous type *char*, when developing the dehydration or oxidation reactions in the cellulosic precursor. The mixture was submitted to pyrolysis in a way that the volatile material that is still in the carbonaceous residue type *char* and that generate free pores is removed by pulling. The activation mechanism depends of the used agent type, but in this case these hydroxides only react with coal at temperatures between 630°C and 730°C, to produce finally sodium or metallic potassium, according to the used activator, and the carbon monoxide. Although the mechanisms in which was given the pore formation aren't clearly understood (Afinata *et al*., 2007), it was found that the potassium carbonate was derived in its chemical activation and hence its adsorption capability. (Hayashi *et al*., 2002).

The collection of activated carbon from the tanned leather residues to chrome has become in a useful option for its disposal. After being classified according to particle size, these residues were treated in high temperatures (around 850°C) in CO_2 atmosphere, which encourages the activation and formation process of activated (Oliveira *et al*, 2008). These carbonaceous materials or carbonated materials have a structure partially grafted with a morphology of an onion and are naturally enriched with nitrogen and oxygen, with an approx. superficial area of 800 $m^2.g^{-1}$ (Yilmaz *et al*., 2007) which offers multifunctional properties (Ashokkumar *et al*., 2012). These multifunctional properties of the carbonated materials allow its application in the kidnapping of CO2 (D'Alessandro *et al*., 2010; Ashokkumar *et al*., 2012), electrodes for battery (Ashokkumar *et al*., 2012; Thanikaivelan, 2011), fibers, gels, films, sponges collection through the reticulation mean with various composited for the cosmetic, medicine and veterinary field (Catalina *et al*., 2012; Catalina *et al*., 2013) and as ink absorbent in aqueous solutions (Yilmaz *et al*, 2007).

The potential application of the activated coals from tanned leather shavings with vegetable anilines have also been studied, and have demonstrated being a good option as adsorbent for the removal of phenols, methylene blue and hexavalent chrome of polluted waters (Kantarli and Yanik, 2010).

Other ways to manage the leather residues of different pyrolysis were studied. Up next are described the main reported studies.

Leather residue use for the collection of biodiesel

The biodiesel positioned itself as an alternative for combustibles deriving from oil, nonetheless, as it was obtained from vegetable oil (Barbosa *et al*., 2010; Endalew *et al*., 2011) and animal oil (Alptekin and Canakci 2010; Encinar, 2011), the industry considers the price of these raw materials in some applications to not be competitive (Haas and Foglia, 2005). On another hand, some vegetable oils and animal oils are edibles, which carries to an intense competing between the alimentary companies. Recent studies have been directed to the using of non-edible raw materials, of low cost and in high content of lipids for the production of biodiesel, as the leather tanning residue described up next.

The most used methods for the production of biodiesel are from the tanned leather residue based in the transesterification, well one or two stages, using acid and alkaline catalyzers (Alptekin *et al*., 2012; Kolomazník *et al*., 2009; Özgünay *et al*., 2007). The process was carried using an alkaline catalyzer to directly convert the triglycerides in alkyl esters. However, the transesterification catalyzed by alkali is very sensible to high contents of free fat acids (FFA) and water reducing the biodiesel's performance. Thus, this method was sued for refined raw materials with contents low in FFA and water (Canakci, 2009).

Using leather residues for the modification of asphalts

Currently mechanic studies of modified asphalt with polymers and leathers that are used in the shoe wear elaboration are being done. This research line has been the biggest since its arrival in Colombia, if it's compared with the other studied applications in the literature (Barinas and Manotas, 2012; Aranda and Clavijo, 2014; Viveros and Gonzales, 2012; Reyes and Pinzón, 2013; Menjura, 2014). These researches have been oriented in studying the physical-mechanical behavior of the asphaltic cement modified with these kind of residues, and also to make a chemical analysis of the modified material. The shoe wear wastes used in the industry as shoe wear provision; is reported that the addition of the residues improves the mechanical properties in an asphaltic mixture, showing that this research line can be an alternative can be very reliable to take advantage of the leather residues (Moreno and Calvo, 2014; Gutiérrez *et al*., 2014).

Other recent researches evaluate the behavior of modified asphalt samples with the obtained leather from the shoe wear industries, without considering other polymers like in the previously referred studies. A leather milling was done, to forwardly sieve it using only the N°40 through filter and retained in the N°80 filter. The inked leather was added as a modifying agent in 4%, 8% and 12% proportions in weight. Milled leather was added as a modifying agent in 4%, 8% and 12% proportions in weight. To do the mixing process the oven was heated at a temperature of 150°C, that gave result to a fluent material which was added the leather particles. The authors report that the addition of the leather improved the asphalt's properties (Rodríguez and Téllez, 2013).

Leather as a material for the treatment of colored waste waters

The solid humid residues in the tanning process, that is to say, the fleshing or blue leather, possess a high protein content and an adequate isothermal adsorption pattern to capture the colorant reactive of the different textiles. (Gupta, 2009; Oliveira *et al*., 2007). The other researches have demonstrated that the fleshing or blue leather organically stabilized has been used as an adsorbent material for the removal of color in the polluted waste waters. In this works parameters for values like adsorbent doses, colorant concentration and pH, which are obtained in the higher pollution adsorption for each condition of the study were found (Fannun, 2014; Piccin *et al*., 2012; Fathima *et al*., 2011, Fathima *et al*., 2009). Also it has been studied that the neutral salts like stabilizers in the leather residues, and it has been identified its effect in their capacity to adsorb colorations, it was found that it was managed to remove more than the 99% of water coloring (Fathima *et al*, 2009). Commercial tests affirm that the organically stabilized fleshing can be used for the treatment of color in waste waters; in these studies is informed another advantage of the method after using the fleshing or blue leather for the adsorption of the colorant, can chrome can be drawn by basic hydrolysis (Oliveira *et al*, 2007). For the removal of blue methylene and red of some textiles were also evaluated, but are relatively more expensive that the other adsorbent materials (Oliveira *et al*, 2007).

The fleshing and blue leather residues have been evaluated with glutaraldehyde to stabilize them against degradation, with the study of the effect of pH, the function of salt concentration, the absorbent doses and the initial concentration of ink. Find that around 90% of the ink in colored waters through the dilution of the colorant with fleshing can be removed (Fathima *et al*, 2011). Iron was also used to stabilize the fleshing residues or blue leather, and reached a color removal of more than the 99% (Fanun, 2014). Other research line evaluated the possibility to reuse the colorant charged in the fleshing or blue leather as a reducer in the fabrication of a used salt for the inking during the leather tanning (Fanun, 2014; Fathima *et al*, 2011).

Leather residues with reinforcing materials in the rubber mixtures

Various studies have focused in the incorporation of leather residues to a rubber matrix, to act a as a reinforcing charge. A high compatibility was demonstrated inside these compounds (El-Sabbagh *et al*., 2011), reliable for the specific application. This is because the leather is a fibrous protein with high collagen contents that form reticulated chains in different directions; can favor the intertwining of carbonated chains in elastomers like rubber, which achieved with rheological properties and interesting thermic stability (El-Sabbagh *et al*., 2011). It has also been studied the incorporation of tanned leather shavings as a matrix composed by natural rubber and different synthetic rubber; it was concluded that this is a feasible methodology (Przepiorkowska *et al*., 2004).

The leather fibers have been used as an additive in many elastomeric compounds based in Nitrile Butadiene Rubber (NBR), Chloroprene Rubber (CR), ethylene-propylene-diene monomer (EPDM) copolymers and chlorinated isobutylene-isoprene rubber (CIIR) (Shabani *et al*, 2009). In this studies the effects of the use of leather fibers was evaluated in the vulcanization features like in the physical-mechanic and thermic of the compounds. The results show that the vulcanization features weren't affected by the incorporation of leather fibers, since no meaningful effect was found about the initial viscosity, the processing and the curing time of the compounds, but a reticulation density increase was evidenced. Regarding the evaluations of mechanical properties of the vulcanized compounds, the study showed that the use of leather fibers increases the traction resistance based in the NBR, due to the compatibility between the NBR and the leather. However, with the other elastomers didn't make meaningful changes in the properties, except to the toughness because the use of leather fibers drastically increased this property in all of the compounds.

Other studied application for the leather shavings has been the use as a filling in a styrene-butadiene rubber compound (XNBR) and in the acrylonitrile-butadiene rubber (NBR), that is used as an spreading Limanol PEV agent manufactured by the company Schill+Seilacher. They find that the dust leather shavings improve the mechanical properties such as the traction, the breaking elongation and the increase of the reticulation density with both types of rubber, thanks to the proteins that contain the leather shavings (Przepiorkowska et al., 2007). Another similar study shows that filling with leather shavings improves the properties like resistance to thermic ageing and the electric conductivity in these kind of rubbers (Chronska and Przepiorkowska, 2008).

Other studies with NBR rubber and leather shavings have checked the effect of the neutralized of the leather residues with the sodium and ammoniac residues, and with the hydroxide sodium. Show better vulcanization features and mechanical properties in the mixtures where the leather shavings were neutralized with sodium bicarbonate and ammoniac (Natchimuthu *et al*., 1994).

The leather residues are used as filling with the thermoplastic polymer reinforcement like the acrylonitrile-butadiene-styrene (ABS), was studied by Ramaraj (Ramaraj, 2006). This work with the compounds material of ABS and the leather dust were prepared thought the extrusion of the ABS with 2.5%, 5%, 7.5%, 10%, 12.5%, and 15% in weight of the leather dust in a double co-rotating screw extruder. The extruded filaments were pelletized and molded by injection to obtain test tubes with the goal to evaluate the physical-chemical properties as a resistance to traction, to flexion, Charpy impact, to abrasion, Rockwell toughness, density, Heat deflection temperature (HDT) and the Vicat softening point (VSP), among others. The leather waste dust didn't meaningfully affect the resistance to traction, to flexion, to abrasion, strength, density or HDT temperature- However, the traction module, traction elongation and resistance to Charpy impact were meaningfully reduced. A behavior similar to the increase of traction resistance is observed by the incorporation of leather residues in the recycled material matrixes of polyvinyl butyral (PVB) (Ambrósio *et al*., 2011).

It has been found that the incorporation of leather residues in a compound matrix by natural rubber and natural recycled rubber is feasible, taking advantage in a simultaneous way two residues that constitute an environmental issue, like are the leather residues and vulcanized rubber. During these researches the used leather residues are used as a de linking method between the virgin rubber and the already vulcanized as a reinforcing load, and show that carrying a vulcanization between the 140° and 150°C don't present a meaningful reversion in the reaction, as long as there is a previous neutralization to the leather residues, besides its morphology shows a continuous stage through all the matrix (Ravichandran, and Natchimuthu, 2005). It's important to take in account that most of the reported studies have used leather residues with particle sizes lower than 300 µm, factor that becomes more important at the moment of designing of the mixture, since it is directly related with the distribution of the added loads inside the rubber matrix (Ravichandran and Natchimuthu, 2005).

As it can be observed in the leather residues can apply as filling material or reinforcement both in natural and synthetic materials; this is because with the leather being a fibrous protein with high collagen content that forms reticulated of carbonated elastomers chains, showing rheological properties and interesting thermic stabilities (El-Sabbagh and Mohamed, 2011).

Future orientation for the advantage of leather residues

An strategy to apply a cleaner production method in the leather industry is to look for new applications to the residues that generate their processes, for which this study made diverse methods and applications for the advantaging of o the residues that generate their processes, for which this study made diverse methods and applications for the advantaging of tanned leather solid residues. Having in mind the importance of the residue management and the advantaging of these to generate added value, different uses have been found that can be of feasible application in the Colombian industry. The use of leather residues for the elaboration of biofuels for the modification of asphalts and rubber formulations, and as color absorbent for waters, are some of the applications that have been suggested. With the adoption of these technologies is to reduce the generation of fleshing or blue leather, one of the main protein residues coming from the leather stark.

Conclusions

In this work were identified the tendencies for the treatment of leather industry residues, as well as the developed technologies to obtain innovative products from these. It was detected that these products are being mainly used to obtain composed materials with rubber and pavements, to develop chemical recycling, being especially important the pyrolysis, and as a starting point to obtain biofuels.

The addressed technologies show that it is possible to decrease the environmental of the leather industry, with the treatment of effluents, that has been the most studied tendency, and of the solid residues that are most generated during the leather tanning. If well it's identified in the consulted studies that there are diverse options technically feasible for the reusing of leather residues, it's pertinent to remember the need to evaluate the economic feasibilityand implement them according to the solutions in the environment that is wished to be solved.

Acknowledgements

The authors thank the help of Claudia Patricia Aristizábal, apprentice in Integrated Quality in Technology Systems, for its participation at the beginning of the project as research monitor in the Leather Design and Manufacturing Center.

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