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Development of products from Acacia mearnsii: a case of sustainability in the leather industry

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Abstract

The development of products from renewable raw materials is a promising alternative to synthetic products obtained from the traditional petrochemical route. The Acacia mearnsii, popularly known as black wattle, is a leguminous tree originate from Australia and cultivated in Rio Grande do Sul since 1918 with a short cycle growth of 7 years, intended to be a important recuperative of poor soils usually depleted by intensive agriculture and it is in the context of Green Chemistry. The wood is used in the production of chips for the paper and cellulose industry, charcoal, wood paneling and pellets to be applied as biofuel. From the bark of black wattle is obtained an extract rich in tannin employed at the synthesis of inputs for various applications such as leather tanning and retanning, coagulant for water treatment, adhesives for wood panels and other. The aim of this study is to present the aspects of sustainability of TANAC S/A along two dimensions: the production chain, from the seed of black wattle until obtaining the vegetable extract, and the final products. The genetic improvement of the specie, forest management and the production chain that follows the FSC® certification, the industrial process with the use of water in closed circuit, energy generation from biomass burning (exhausted bark) and the positive Carbon Footprint are evidences of the sustainability of this industry. The products, free from restricted substances, with lower period of productive cycle than other species and able to replace fully or partially synthetic products exemplify the practice of sustainability management.

Keywords: sustainability, Acacia mearnsii, leather.

Introduction.

The Acacia mearnsii De Wild trees, popularly known as Black Wattle is a medium sized tree belongs Fabaceae (Leguminous), subfamily Mimosoideae (Menezes et al. 2014; Santos et al. 2011; Higa et al. 2009; Mochiutti et al. 2007). This tree offers an important economic advantage for pulp production because it was higher wood density and pulp yield, which translate into higher digester productivity and factory output, and is highly suitable for hardwood bleached craft pulping, dissolving and semi- chemical pulps. These factors make A. mearnsii a sought-after species and have ensured a sustained demand for wattle woodchips in the japanese market, and today continue to attract new customers in emerging markets as China and India. At present the only significant secondary products are charcoal and firewood. This tree is the only temperate Acacia species grown commercially on a significant international scale (Chain et al. 2015).

1.1 – Industrial production of Black Wattle in the world

The Black Wattle tree is originated from Australia and it was introduced in other regions of the world due to its rapid adaptation to different environmental conditions and high productivity (Menezes et al. 2014; Mochiutti et al. 2007). The species is mainly planted in South Africa and Brazil for tannin production and woodchip exports (Griffin et al. 2011). In both countries the Black Wattle is mainly cultivated by farmers (76–78% of the total area). Due to the high prices fetched by the wattle woodchips in the international market, Black Wattle is a profitable crop. In Brazil, the first Black Wattle plantation was carried out in 1918, in the country of Rio Grande do Sul (Caldeira et al. 2011) and in 1928 to commercial purposes (Oliveira, 1960 and 1968; Viera and Schumacher, 2010). Currently, Brazil is the largest producer of this tree in the world, followed by South Africa with 170,000 and 110,000 hectares planted, respectively. It is the third most planted tree species in Brazil, surpassed by eucalyptus and pine. (Chain et al., 2015).

1.2 – Properties and chemical structure

The bark of the black wattle is well known for its high concentration of tannins (proanthocyanidins) with properties of great economic interest mainly used for application as leather tanning, wood adhesives and obtaining natural coagulant agents. The so-called ‘condensed’ or ‘catechol’ tannins have the flavonoid ring structure, as shown in Figure 1, and the more common structures have a catechol group (3,4-dihydroxy benzene) as the B-ring. Rings A and B are aromatic and ring C is alicyclic (Covington 2009). These proanthocyanidins are constituted by the basic structure of flavan-3- ol polymerized in the sense C4-C6 and C4-C8 (Pasch et al, 2001; Venter et al. 2012), as shown in Figure 2. Pasch et al. (2001) developed a method for determining the chemical structure of tannins by MALDI-TOF-MS. The authors concluded that the polymeric chains of black wattle tannins can exist as monomers to octamers. In another study to determine the chemical composition of black wattle extracts, Venter et al. (2012) used the ESI-MS technique. The authors concluded that the black wattle extracts are mainly composed of dimers of catechin or gallocatechin and robinetinidol, as well as trimers having two of the last monomers instead of one in their composition.

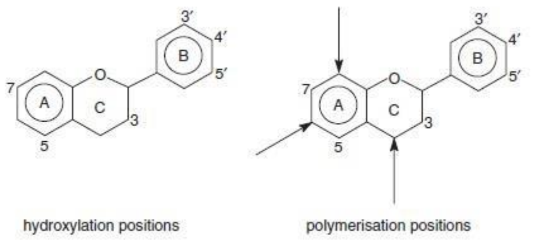
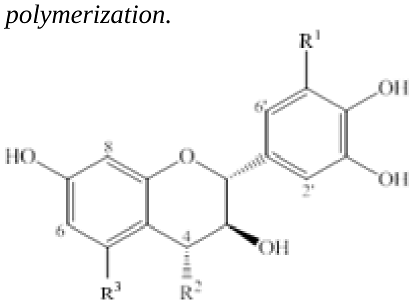


Figure 1: Flavonoid ring system, showing the positions for hydroxyls and the positions for polymerization.



1 R[1] = R[3] = OH, R[2] = H: gallocatechin
2 R[1] = R[2] = H, R[3] = OH: catechin
3 R[1] = OH, R[2] = R[3] = H: robonetinidol
4 R[1] = R[2] = OH, R[3] = H: robinetinidol-4α-ol
5 R[1] = R[2] = R[3] = H: fisetinidol
6 R[1] = R[3] = H, R[2] = OH: fisetinidol-4α-ol

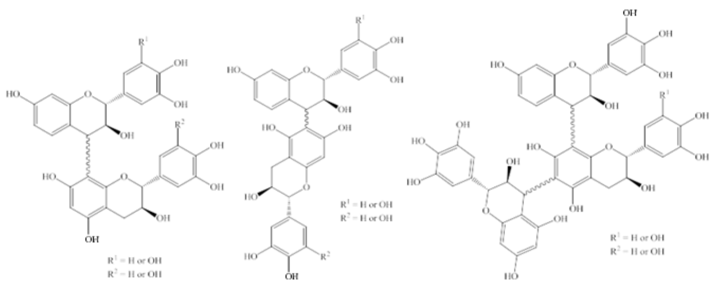


Figure 2: General structure of condensed tannins: polymerization of flavan-3-ol

The acacia tree is very resistant to pests attack and does not need to be protected by pesticides or agrochemical inputs as, for example, pentachlorine-phenol, organo-chlorinated and organo- phosphorated. As a result, the products elaborated with these tannin extract are not pollutants to the environmental and they will not contain hazardous substances. The only pest which attacks acacia plantations, a coleopteran insect called “cascudo serrador” in Brazil, is controlled through removal and burn of the branches where the insect has put its ova. The extract of the bark of Black Wattle (Acacia mearnsii) is produced by water extraction without the use of any organic solvents. Also it is easily biodegradable and does not cause toxicological and carcinogenic disease. In the development of new products TANAC S/A use mainly this natural extract, avoiding the use of restricted substances. Besides technological applications, the tannin extract also exhibit interesting biological properties, such as antioxidant, antitumor, antimicrobial, bacteriostatic and anti-inflammatory (Yoshihara et al. 2014).

The vegetable retanning agent mimosa inhibits the formation of free radicals and the oxidation of unsaturated fatliquoring agents as well as detanning of the leather and formation of hexavalent chromium is avoided (Palop et al., 2010; Fuck et al., 2011). Hexavalent chromium is ranked as 17th on the Priority List of Hazardous Substances based on a combination of the frequency, toxicity, and potential for human exposure made by Agency for Toxic Substances and Disease Registry and the Environmental Protection Agency (ATSDR 2015). It has been reported to cause various forms of genetic damage in short-term mutagenicity tests, including damage to DNA, and misincoporation of nucleotides in DNA transcription (IPCS-INCHEM 2015). Also, there is sufficient evidence in experimental animals for the carcinogenicity of hexavalent chromium compounds, as cancer of the lung (IARC, 2015).

1.3 – Industrial applications of the black wattle tannin

One of the oldest and best known industrial applications of Black Wattle tannin is the transformation of hides into leather. The model of the interaction between polyphenol and collagen is shown in Figure 3 (Covington 2009).

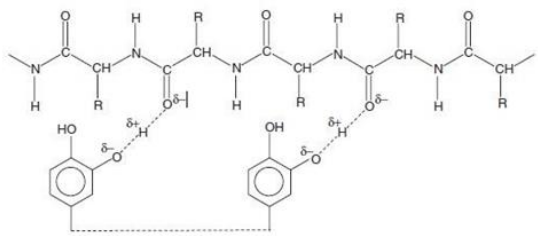


Figure 3: Model of the interaction between plant polyphenol and collagen.

The most widely used reactions to obtain lighter tannin is the sulfitation usually with sodium sulfite or sodium metabisulfite in acid medium (Tambi et al. 2008; Venter et al. 2014), as follows in Figure 4

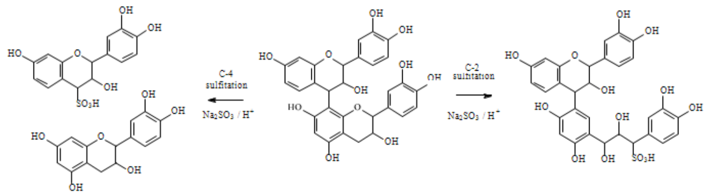
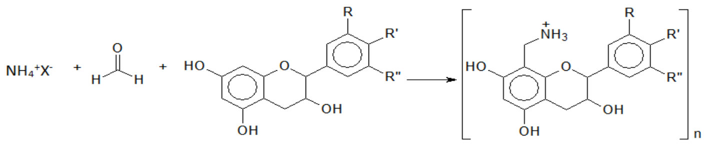


Figure 4: Sulfitation reaction of condensed tannin

The position of sulfite can result in lower proanthocyanidins structures that normally penetrate faster in the skin.

Another very important application is the Mannich reaction of proanthocyanidin with an amino group in acidic medium, as shown in as Figure 5.

Figura 5: Representación esquemática de la reacción de Mannich en las proantocianidinas.



This reaction is widely used mainly for obtaining cationic flocculants for water and wastewater treatment, where the group amine remains protonated in acid medium. Instead of metal salts, these flocculants are biodegradable and do not add metal to the generated residue.

The adhesives industry employs the polymerization reaction with formaldehyde for the production of plywood and particleboard, shown in Figure 6.

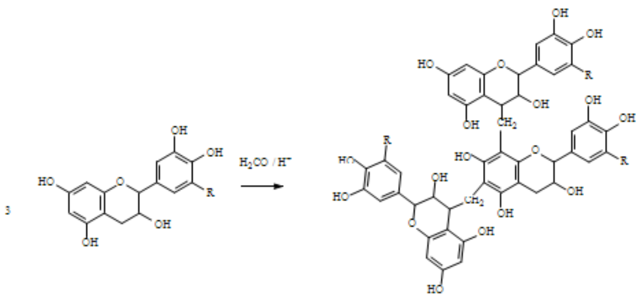


Figure 6: Reaction of proanthocyanidins crosslinking with formaldehyde.

Plywood and agglomerates produced by tannin based adhesives offer typically higher mechanical properties than other commercial products derived from petrochemical synthetic route.

2 – Sustainability management

TANAC S/A is a company based at south part of Brazil, and dedicates its activities since 1948 of producing vegetable tannin extracts (modified or natural ones) and woodchips, obtained from the Black Wattle tree. The company export to more than 70 countries and it is the worldwide market leader with total producing capacity of 36,000 tons of tannin extract and 700,000 tons of woodchip per year. The company is structured into three business units, employing approximately 1,000 employees, as follows: Tannins Unit located in Montenegro where are produced the extracts of Black Wattle bark and products from these; Woodchips Unit in Rio Grande where the raw material to the pulp industry is produced; Forestry Unit (Tanagro), which supplies the renewable raw material employed in the production chain. The company has the ISO 9001 quality system certification since 1996 and the ISO 14001 Environmental Management System certification since 2000. Also, the forest management is certified by the Forest Stewardship Council® (FSC®), which guarantees the quality of the raw material since its origins. The production process of tannin extracts and derivatives is based on principles aimed at the environment preservation.

2.1 – Forest improvement

TANAC S/A has your own reforestation system of Acacia trees and is the greatest individual planter of mimosa in the world with an agroindustrial structure of about 800 employees involved in forest management activities. It is planted up to seven million trees each year that stay growing during a cycle of seven year and covering almost 25,000 hectares. In addition, there are more than 12,600 hectares of preserved native forests adjacent to its reforestation areas and 9,000 hectares fields. These structures are capable to provide the major part of the raw material (wattle extract) and ensure a very stable and constant quality to the products. The other part is supplied by working together with independent farmers: the company supplies seeds and technical advice to them and they provide to the company the trees to make up the production volume required. The ongoing work of advanced technologies in the production of seedlings and breeding research generate a significant increase in industrial productivity, a formation of quality forests and an appropriate environmental management. In the Forestry Unit planting areas there are a consortium of Black Wattle trees with livestock, taking advantage of the availability of areas and native pastures. About 4,500 cattle coexist with acacia forests. The monitoring of fauna and flora is conducted permanently by professionals in order to ensure the maintenance and reproduction of the various species existing in the areas of the company.

The company purchase only certified or controlled forest raw material in accordance to the standards of the Forest Stewardship Council® (FSC®): Preserve the indigenous and civil rights; not to be originated from forests of high conservation value; not to be from genetically modified material; not to be illegally harvested; not to be from converted native forests. Contrary to other species used for tannin extraction (quebracho and chestnut), which are not reforested trees, the Mimosa is totally derived from renewable sources, thus assuring its continuity indefinitely. The mimosa is a tree of legume family, with a vegetative cycle extremely short: in average, it is ready to be industrialized after only seven years. The reforestation with acacia is intended to preserve the environment and occurs in grassland areas where usually don’t have native forests, thus with no cutting of virgin forest and no native forest replacement by mimosa. The mimosa, besides providing the bark for tannin extraction, is nowadays the biggest source of vegetal fuel (firewood and coal) preserving a significant portion of native forests, which otherwise would be used for that purpose. The acacia plantation is also used to save debilitated soils by fixing nitrogen (N2).

2.2 – Industrial process

The production process begins in the Forestal Unit where the trees are cultivated for seven years and then harvested by mechanical or manual process. At the Industrial Unit in Montenegro the bark is classified according to the company quality standards and sent to the grinding central to decrease the grain size.

After that, the ground bark follows through belts to the autoclaves for aqueous extraction of tannins, without using any organic solvent during the whole process. The exhausted bark that passed through autoclaving process is sent to the pressing sector and the resulting liquid returns to be used again to the next extraction. The exhausted pressed bark and the second quality woods are used as biofuel to the own energy generation in the steam boilers to all Industrial Unit without the need of external sources. The excess bark (< 1%) is destined to organic compost. So, the entire black wattle tree is used, avoiding the waste generation.

The extracted liquid is submitted to an evaporation process in order to be concentrated and this will be chemically modified, or not, according to the final product specification. The product can be traded in liquid form, atomized by spray drier (powder) or concentrated in the low pressure evaporator (solid block) and the water separated in the evaporation steps are also reused in the next extractions. Finally, the products are properly packaged and stored until the final distribution.

Flowchart 1: industrial processes with water treatment / recycle and energy generation

In the last 10 years it has been implemented a wastewater treatment system in the company, promoting 90% of water recycle. The only water loss from the factory are due to the human consumption, evaporation in flue gas scrubbers and water content present in the final product. Therefore, the use of water is considered to be in a closed circuit, because there is no effluent disposal into the sewer system. Currently, the total water consumption is 100m3/h, in which 96 m^3/h is destined to the industrial activities and 4 m^3/h for human consumption.

The company has a water treatment station capable of clarifying water to the whole process, and treatment for human consumption according to the Ordinance 2914 from Ministry of Health (2011) that sets the procedures of control and surveillance of water quality for human consumption and its potability standards. All the harvesting water is treated with flocculants produced from the black wattle extract by the company according to the NBR 15784 (2014), chemicals used to treat water for human consumption and its health effects. In addition, these products are in accordance to National Sanitation Foundation (NSF), Halal and, Kosher certification. The water intended for the industrial processes are used in the cooling factory process and in the tannin extractions. All water removed during the pressing of the exhausted bark, evaporation and atomization steps are reused in the subsequent extractions. The cooling water after used is directed to the cooling towers for treatment and subsequent reuse in a closed circuit.

All the water resulting from the cleaning of the factory is directed to the effluent treatment station, where it is treated and reused in the system of flue gas scrubbers. In the burning of the exhausted bark and wood occurs the release of carbon blacks and ash, which are collected in the flue by the action of the gas scrubbers and directed to the wastewater treatment station. The ash and carbon blacks waste after separated from the water are directed to composting together with the remaining 40% of the exhausted bark.

So, these results shows that the production of tannin extract from black wattle bark is an environmental friendly process due to the energy generation from renewable source, water treatment and reuse in a close cycle, low waste generation (solid and liquid).

2.3 – Carbon Footprint

TANAC S/A conducts since 2008 the inventory of greenhouse gas emissions (GGE) from its operations in Rio Grande do Sul, covering the forestry activities, industrial, transportation and logistics (wood and bark transport), administrative processes and disposal of solid waste. The measurement unit is expressed in tons of carbon dioxide equivalent (tCO_2e) per product and reflects the negative impact of companies on the environment and climate change. By means of this study the company gets to know the extent of their emissions, enabling a planning for future actions to reduce the emissions and minimizing the negative impacts to the environmental. The inventory also serves as a management tool in order to ensure an economic, energy and operating efficiency to the company. This inventory consider all operations of TANAC S/A divided into three scopes: Scope 1: Direct emissions of greenhouse gases from sources that are owned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or controlled by the company as emissions from industrial processes, vehicles and production of chemical in equipment. In this scope are not included direct CO2 emissions from the combustion of biomass; Scope 2: Indirect emissions of greenhouse gases from electricity generation acquired and consumed by the company. In this scope emissions occur physically at the place where electricity is generated; Scope 3: emissions of greenhouse gases from sources that do not belong or are not controlled by the company as transport of finished product, business travel, waste treatment and suppliers emissions.

The emissions from the combustion of vegetable biomass or renewable fuel sources are considered as neutral sources, because the CO2 released on its combustion is the same CO2 removed from the atmosphere during the process of photosynthesis, namely, considered as the natural carbon cycle. Each gas has a Global Warming Potential (GWP), which means how much a certain kind of gas contributes to the global warming in relation to the necessary amount of CO2, causing an similar impact. Through GWP the conversion is performed for CO2 equivalent (CO2e). In this study were used the recommended factors by the Intergovernmental Panel on Climate Change (IPCC), GHG Protocol, United State Environmental Protection Agency (US EPA), Department of Energy & Climate Change (DEFRA) e Ministry of Science and Technology from Brazil.

The Table 2 shows the emissions distribution of the TANAC S/A Production Chain for all scopes from 2014 inventory.

Scope	**Emissions**
1 - Direct emissions	
Stationary and mobile	26,063 tCO2e
2 - Indirect emissions	
Electric power consumption	457 tCO2e
3 - Indirect emissions	
Suppliers, air Travel,	25,159 tCO2e
TOTAL	51,679 **tCO2e**

Table 2: Summary of emissions of greenhouse gases in the three scopes

The main emissions source of Scope 1 are the direct mobile sources accounting for 62.2%, followed by cattle management issued 27.4% and the direct emissions from stationary sources (6.7%). In the scope 3 emissions, raw material providers represent 98.6%, 1% air travel and 0.4% waste.

The neutral emissions from TANAC S/A come from the burning of biomass and vegetable residues for energy purposes and fuel consumption as diesel and gasoline, which in its composition contains biodiesel and ethanol. Part of the emissions from these sources is considered neutral and does not appear in any of the three scopes of emissions inventory, thus being presented separately as shown in Table 3.

Table 3: Neutral CO2e emissions per Unit

Unit	**tCO2e**
Management Unit - UM	34,701
Industrial Unit of	79,458
Industrial Unit of Rio Grande	49
TOTAL	**114,208**

The Table 4 shows the values of tCO2e stock by planting area (ha) in the year of 2014 by TANAC S/A

Table 4: values of tCO2e stock by planting area (ha)

Unit	**Plantation**	**tCO2e**
Planted forests on	25,403	360,288
Planted forests in	8,722	112,441
TOTAL	**34,125**	**472,729**

So for every 1 tCO2e emitted, the company kidnapped 9 tCO2e in its forests of black wattle in 2014. However, the current study of greenhouse gases from company operations reveals a sequestration capacity higher than the amount emitted to the environment representing extremely positive carbon footprint (9:1).

The Table 5 shows the type of greenhouse gas emissions by scope in tons of CO2 equivalent (tCO2e) Table 5: emissions by scope and greenhouse gas in tons of CO2 equivalent (tCO2e)

Greenhouse gas	**Scope 1**	**Scope 2**	**Scope 3**
CO_2	14,581	457	25,034
CH_4	9,669	-	122
N_2O	1,786	-	3
$HCFC_s$	27	-	-
Total	**26,063**	**457**	**25,159**

3 – Final considerations

According to the facts discussed in this work it can be concluded that the TANAC S/A employs its industrial operations sustainably since the forest management to final product, looking for new technologies to combine its production capacity to the environment which will allow the continuation of this industry.

The forest structure guarantees the black wattle cultivation as a renewable source of raw material, with capacity to meet current and future demand without compromising the environment (flora and fauna).

The products are obtained mainly from the aqueous extract of the black wattle (Acacia mearnsii) bark with no use of organic solvents in any production step. Maintenance and development of new products with only inputs that do not exhibit hazard properties according to reliable data bank, environmental seals and international legislations.

The factory production process with power generation from the exhausted bark (biofuel), treatment and reuse of water minimizes the negative impact on the environment, reusing and generating less waste.

Still, the current study of greenhouse gases emissions from the industrial activities reveals a higher carbon footprint sequestration capacity than the amount emitted to the environment in the proportion of 9:1. This inventory helps TANAC S/A in the planning future actions of continuous reduction of the

environmental impact, differentiating the company in the global market and strengthening its social and environmental responsibility.

Black wattle extracts are the only tanning agent used in leather industry from organized and sustainable reforestation. Furthermore TANAC S/A is related to new search for products more sustainable for the leather industry; the needed from it will be more and more for products which come from a sustainable source. Pure vegetable tanning articles (sole leathers, leather for belts, leather for artifact, metal-free) as well in retanning process (napas, semi vegetables, automotive and furniture upholstery), for all these articles TANAC S/A will find now and in the future a sustainable product made from Acacia mearnsii.

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