Value Added Leather Auxiliaries from Paper and Pulp Industry Waste

by

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Abstract

The present work involves the preparation of a retanning agent from the organics present in the black liquor generated by paper and pulp industry. Black liquor organics was extracted by using solvent extraction method and subsequently separated as acidic, non-acidic and organic compounds that were not degraded. Acidic and non-acidic organics were sulfonated and further condensed with formaldehyde to obtain a product ideal for application. Sulfonation – condensation reactions were modulated to achieve particle size on par with that of commercial syntans. Condensed products from both acidic and non-acidic components were used in lieu of synthetic tanning agents in retanning. The final leathers exhibit off-white color with good mechanical strength as compared to leathers from commercial phenolic syntan. This work reveals that the black liquor, which is a by-product of paper and pulp industry could through an innovative process, be turned into a retanning agent for leather processing. The product has the advantage of being able to replace phenol – a product with high market fluctuation.

Introduction

The conversion of chrome-tanned hides/skins into usable value added leather is strongly dependent on the use of a wide range of synthetic tanning agents. These classes of compounds consist predominantly of phenolic derivatives, acrylics, melamine, protein hydrolysates etc. Phenol based syntans are used to a greater extent to improve the fullness property of the final leather.[1]

Phenolic syntans are generally prepared from petroleum byproducts such as phenol, naphthalene, cresol etc.[2] These low molecular weight compounds are sulfonated and condensed to yield water-soluble high molecular weight products for retanning. Developing retanning agents without using high priced phenol thus reducing the overall price of the product without affecting its quality is likely to have a great interest amongst researchers and thus the tanners. The opportunity could lie in the use of natural products, wastes of other industries etc. Amongst the natural products, biopolymers like polysaccharides and lignin have been employed as synthetic tanning agents.[3]

Lignin is one of the most abundant renewable organic materials on earth found in higher plants.[4] Lignin is a phenolic polymer present in large amounts in the cell wall of plants (**Figure 1**). Woody tissues especially contain 20-30% lignin. In contrast to other biopolymers, lignin is a network polymer that results from the dehydrogenative radical polymerization of monolignols (e.g. p-coumaryl-, coniferyl-, and sinapyl-alcohols), which are connected via carbon-carbon and ether linkages.[5] This compound also has a large number of functional groups such as methoxy, aldehyde, carboxylic and ester groups. Paper and pulp industry employs the Kraft process resulting in black liquor as a by-product. This black liquor contains water, organic residue such as lignin, degraded lignin, carboxylic acids, and inorganic chemicals such as Na_2CO_3, Na_2SO_4, Na_2S, $Na_2S_2O_3$, NaOH and NaCl. Normally lignin is obtained from black liquor by precipitation with sulfuric acid.[6]

It has been reported that over 1.3 billion tons of weak black liquor are processed into 200 million tons of black liquor dry solids every year.[7] The current application of these solids includes burning in recovery boilers, to produce high-pressure steam through an investment intensive process. Based on the large and easy availability at a relatively low cost, black liquor could have economical advantages when employed in the preparation of retanning agents. The presence of large number of sulfonated groups in black liquor organics would enhance the solubility and dispersion of the developed product in water. Retanning agents from Kraft lignin have been reported; such as that in US patent US2891020A, which details a process for

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degradation of lignin and its use in the preparation of retanning agents. There are no significant reports on the utilization of modified black liquor in the preparation of such products, though US patent US2597809A reports a process by which water insoluble components of black liquor is treated with acid to precipitate lignin and dissolving the same in the presence of sulfonated phenol. In this work, the degraded lignin derivative present in the black liquor, such as acidic and non-acidic organic parts were separated and sulfonated followed by condensation with formaldehyde to produce a tanning agent.

EXPERIMENTAL

Materials and Methods

Black liquor was sourced from a commercial paper and pulp industry in India. All chemicals and reagents used for extraction of lignin, preparation and characterization of syntan etc. were of analytical grade. Wet-blue goat skins were used for evaluating the performance properties of the developed syntan on the final leather. All leather processing chemical were of commercial grade.

Extraction of Acidic and Non-acidic Organics from Black Liquor

The commercial black liquor containing 60% organics (degraded lignin) and 40% inorganics was employed for this study. The degradation of lignin results in the production of acidic and non-acidic organic components as shown in **Figure 1**. The acidic and non-acidic component of the organics present in the black liquor was extracted using ethyl acetate as shown in **Figure 2**. pH of as obtained black liquor was around 14. The same was acidified to a pH of 7.0 using sulfuric acid and the aqueous part that contained both non-acidic and acidic organic components was further extracted with ethyl acetate. After the removal of residue through filtration, the organic part was

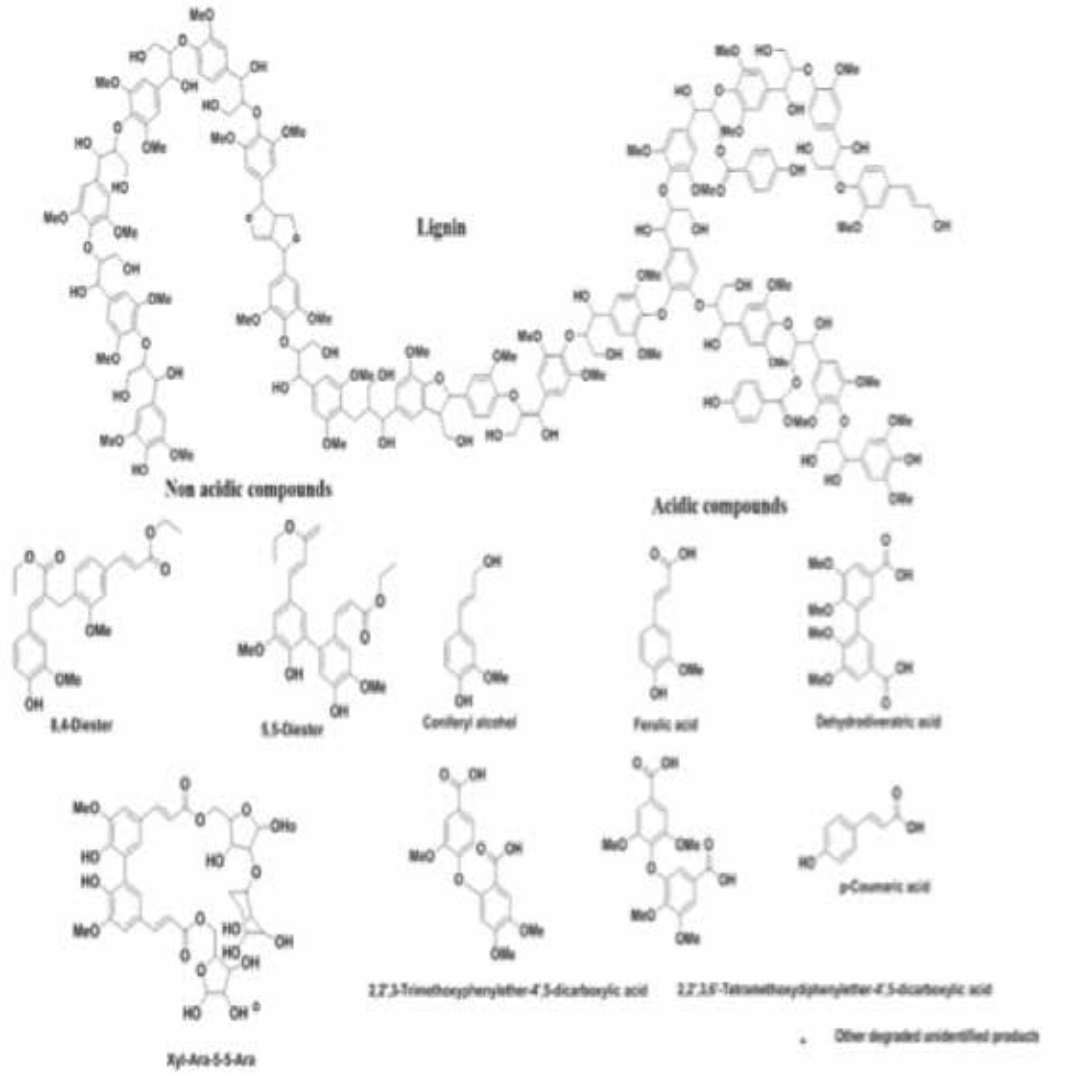

Figure 1. Possible compounds present in the degraded lignin.

extracted from the aqueous solution using ethyl acetate. The extract thus obtained was transferred to the separating funnel and the organic part was again separated. This extraction was repeated several times using ethyl acetate as a solvent. The organic part was subsequently neutralized with sodium bicarbonate solution and the obtained organic part was dried over sodium sulfate. After the removal of organic solvent, the material was dried at 60°C in a hot air oven to get a pure non-acidic organic compound (**Sample 8**). The sodium salt of acidic part of the organics present in the aqueous solution was acidified with hydrochloric acid and further extracted with ethyl acetate. The ethyl acetate organic layer was washed with water until the neutral salt was removed to get a precursor to **Sample 12**. After the removal of organic solvent, the material was dried at 60°C in a hot air oven to get an acidic organic compound with 58% yield (**Sample 12**).

Preparation of Syntan from Non-acidic Organics of Black Liquor (Syntan A)

Naphthalene sulfonic acid was prepared by sulfonation of naphthalene using concentrated sulfuric acid in the mole ratio of 1:3 at a temperature of 80-85°C for a period of 3 to 3.5 hrs. Sulfonation reaction was considered complete when the obtained product was free of naphthalene and sufficiently soluble to yield a clear solution. The non-acidic organic component of the black liquor (Sample 8 of Figure 2) was taken for the manufacture of Syntan A. For this, the organic compound was mixed with the prepared naphthalene sulfonic acid in 1:3 wt % ratios. The mixture after sufficient homogenization was further condensed with formaldehyde in the mole ratio of 1:2 at a temperature of 50-55°C for a period of 5 hrs. The pH of the product was adjusted to 7.5 as against conventional 4.5 due to insolubility at pH <5.0. The sample was air dried at 60°C in hot air oven to get a dried product for further application.

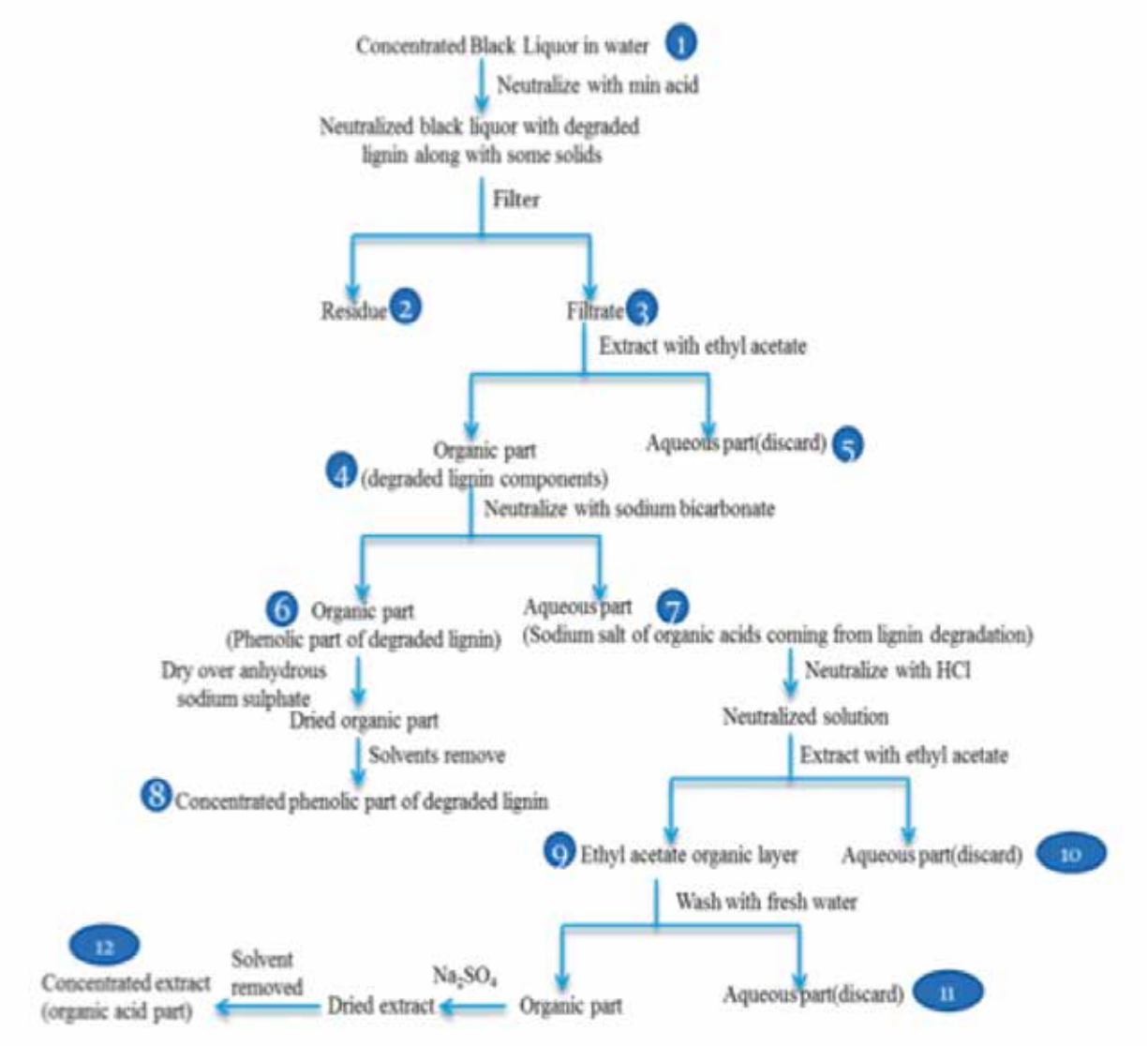

Figure 2. Extraction of organic components from black liquor.

Preparation of Syntan from Acidic Organics (Syntan B)
The acidic component separated from black liquor through ethyl acetate extraction (Sample 12 of Figure 2) was subjected to sulfonation with a mixture of sodium meta bisulfate and sulfuric acid in the ratio 1:1 at a temperature of 80-85°C for a period of 3 to 3.5 h to get a soluble product. The resultant product was cooled to 50°C and condensed with formaldehyde employing a mole ratio of HCHO to organics of 1:2. The product was neutralized with sodium hydroxide to a pH of 7.2. The product was soluble in water. The final product was dried in hot air oven at 60°C.

FT-IR Spectroscopy
FT-IR spectra of both acidic and non-acidic components of the black liquor were obtained using an ABB MB 3000 spectrometer at room temperature. All spectra were taken at 4 cm^{-1} resolution, averaged over 31 scans in the range of 500 to 4000 cm^{-1}. Before taking the spectrum, the samples were mixed with potassium bromide in the ratio of 2:100 (IR grade KBr was used as scanning matrix) to make nearly transparent and homogeneous pellets. The final spectra were collected after subtracting background spectra of KBr

Dynamic Light Scattering (DLS)
The hydrodynamic size of a commercial syntan based on phenol-formaldehyde condensate, and the prepared compounds (Syntan A and Syntan B) were determined using dynamic light scattering (Zetasizer nano, Malvern instruments UK) at 25°C. Initially, the prepared products were dissolved in Milli-Q water and then sonicated for 10 min before the experiments. All the experiments were performed in triplicate and an average was taken.

Performance Evaluation on Leather
Wet blue goat skins of 4 sq. ft. with 1.2 mm thickness were taken for application studies. Commercial syntan based on phenol-formaldehyde condensate was also taken for comparison. The leathers were shaved, washed and neutralized to a pH of 5-5.2. Post tanning was carried out using 10% Syntan A or Syntan B or Commercial syntan (control) with 4% fatliquor and finally fixed with formic acid. The leather was rinsed, piled overnight. Next day it was set, hooked for drying, staked, buffed and trimmed. The final leathers were evaluated for color, organoleptic, and strength properties.

Determination of Color Difference of Crust Leathers
The control and experimental crust leathers processed in this study have been subjected to the reflectance measurements using a premier color scan SS5100A instrument. The color coordinates (L, a*, b*, h and c*) were recorded, where L represents lightness, a* denotes the red and green axis and b* signifies to the yellow and blue axis, h denotes hue, c* represents chromaticity.[7]

TABLE I
L, a, b values of Crust Leather made from Different Syntans.

S .No	Name	L*	a*	b*	c*	H*
1.	Phenolic syntan (control)	84.075	1.274	4.558	4.733	105.646
2.	Syntan A	75.777	2.327	11.414	11.649	78.445
3.	Syntan B	81.987	1.832	8.646	8.657	92.895

TABLE II
Organoleptic Properties of final Leather made from Different Syntans.

Parameter	Phenolic Syntan	Syntan A	Syntan B
		Non acidic organics	Acidic organics
Fullness	7	7	8
Uniformity	8	8	8
Grain Tightness	8	7	7
Softness	7	8	8
Grain Smoothness	6	7	6
Overall appearance	8	8	7

Physical Testing of Crust Leathers

The sampling location for physical testing was chosen according to IUP 2, followed by sample preparation and conditioning as per IUP 1 & 3. Measurement of thickness, tensile strength and percentage elongation at break was performed as per IUP 4 and IUP 6. Measurement of tear load – double edge tear was carried out as per IUP 8. Each value reported is an average of four (2 along and 2 across the backbone) measurements.

Evaluation of Organoleptic Properties

Crust leathers were assessed for softness, grain smoothness, fullness and general appearance by tactile evaluation. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property.

Optical Microscopic Analysis

The final crust leather made from phenolic syntan as well as Syntan A and Syntan B were subjected to microscopic analysis using optical microscope (Aven Inc., Digital Mighty scope, 1.3M. The optical micrograph resolution was fixed to 10X to visualize the surface of leathers. To understand the surface and cross section morphology of leather samples, the brightness and contrast were fixed independently according to the dimensions of various leathers when compared to control leather.

Formaldehyde Content in the Leather

Free formaldehyde content in the leathers treated with commercial phenolic syntan, syntan A and syntan B was determined as per ISO 17226-1: 2008/Analysis using HPLC-DAD.

Gas-permeability Analysis

The gas permeability of phenolic syntan and experimental syntan A and B were performed from advanced automated Humid Air Porometer (HCFP-1100AE, USA)**.** The leather sample was placed between the two metal disks and tightly closed. The air gas was passed through air compressor at room temperature. Gas flow rate was measured through dry sample and yield gas permeability. Permeability can be expressed in terms of m^2.

RESULT AND DISCUSSION

Extraction of Degraded Lignin

The black liquor was sourced from a commercial paper and pulp industry from Tamil Nadu, India. It contained 50-60% total solids with 60-65% organics and 35-40% inorganics. The pH of the black liquor was 14. Black liquor was modified by acidifying to pH 7 using sulfuric acid and the modified black liquor was subjected to ethyl acetate extraction process to separate both acidic and non-acidic organic components. The possible degradation of lignin to acidic and non-acidic components is shown in **Figure 1**. These components were taken for syntan preparation.

FT-IR Spectrum of Organic and Non-acidic Organic Components

Fourier transform infrared spectroscopy is a versatile and rapid technique for identification and determining of an organic compound. The FT-IR spectrum of acidic and non-acidic organic component of the black liquor is shown in **Figure 3**. The peak position at 3387 cm^{-1}, 2996 cm^{-1}, 2824 cm^{-1} and 3324 cm^{-1}, 2986 cm^{-1}, 2887 cm^{-1} corresponds to –OH and -CH_2 symmetric and asymmetric stretching frequency of acidic and non-acidic organic part of degraded lignin respectively. The peak observed at 1739 cm^{-1} that corresponds to carboxyl group

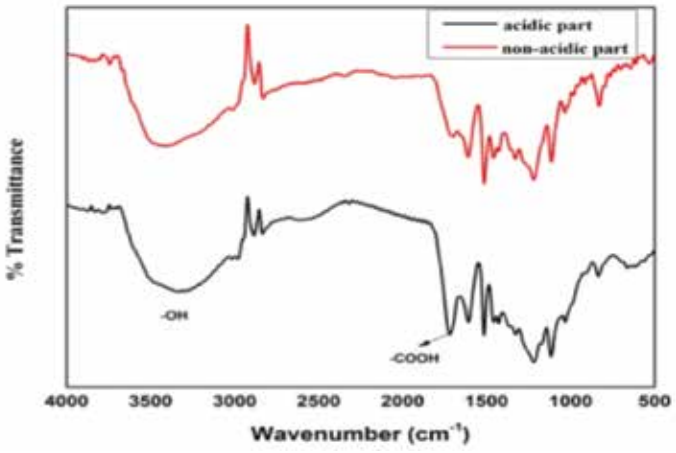

Figure 3. IR spectra of the acidic and non-acidic organics of black liquor.

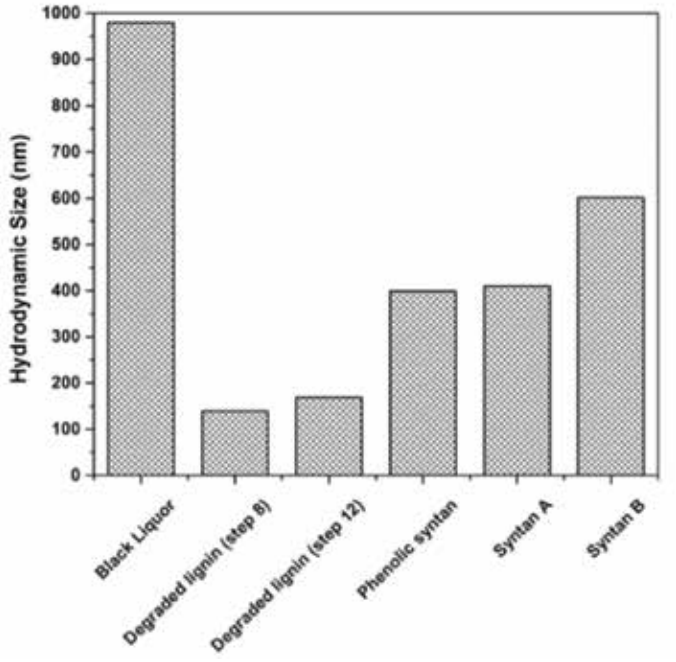

Figure 4. Hydrodynamic size of commercial syntan and experimental Syntan A and B.

of acidic organic part was not present in the non-acidic part. The peak observed at 1630 cm^{-1} and 1624 cm^{-1} corresponds to aliphatic (C=C) of acidic and non-acidic organic part. Both acidic and non-acidic organic parts have other peaks appearing at around 1600 - 1400 cm^{-1} and 1200 – 1000 cm^{-1} attributed to the aromatic olefin (C=C) and ether linkage.[8] This observation clearly indicates that both acidic and non-acidic organic part of degraded lignin were successfully separated and identified.

Particle Size of Condensed Product

The particle size of commercial syntan as well as Syntan A and Syntan B was analyzed using Dynamic light scattering (DLS) technique and thus observed size distribution is shown in **Figure 4**. The size of the condensed products was compared with standard commercial phenolic syntan as well as the degraded lignin obtained at sample and 12. The condensed products were dispersed in water and used for this technique. The developed products have a hydrodynamic diameter in the range of 400 – 600 nm as against the degraded lignin at around 100 – 200 nm, indicating that the formaldehyde condensation was successful in enhancing the molecular weight of the product. It is interesting to note that the size of Syntan A was similar to that of commercial phenolic syntan.

Color Measurements

The acidic and non-acidic products were applied on the leather surface and leather images are shown in **Figure 5**. The color coordinate values of experimental leathers were compared with control leathers and are presented in **Table I**. From the L^*, a^* and b^* values in the table, it is observed that, for control leather L^* value of 84 indicates whitish tinge of the leather sample. Whereas the 'L*' value of syntan A and B are closer and comparable to the phenolic syntan. The 'a*' value of syntan A and B is higher than the control leather which is clearly indicate the higher redness than the control leather. Both syntans had higher b* value than the control leather thus clearly indicating that they had a higher yellow tinge than the control leather. The results reveal that syntan A and syntan B exhibit off-white color comparable to the phenolic syntan.

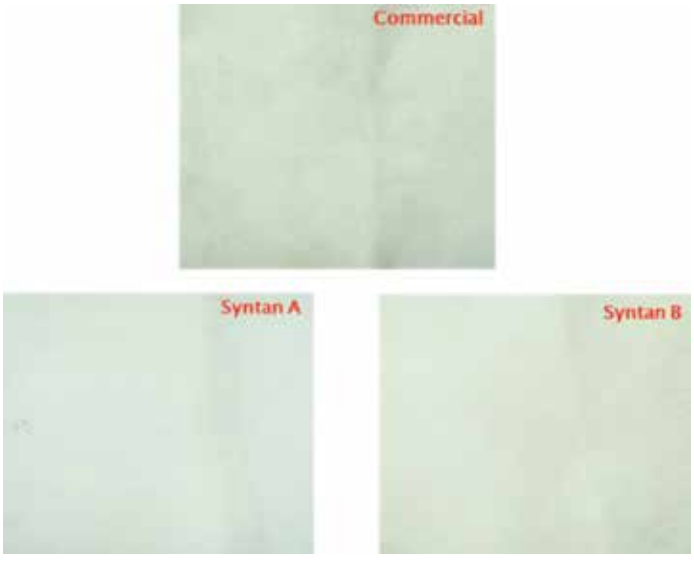

Figure 5. Color of the crust leathers made from commercial phenolic syntan and experimental Syntan A and Syntan B.

Performance Evaluation of Developed Syntans

I. Evaluation of organoleptic properties

Crust leathers made from commercial phenolic syntan and the developed syntans, Syntan A and Syntan B were analyzed for the organoleptic properties with 10 point scale by three experienced leather expert. Scale 10 indicates the property is better and scale 1 indicates low value. The details of the organoleptic properties of the crust leathers are given in **Table II**. It is seen from the data that the leathers made from the study matched that of control (insignificant deviation of ± 1 unit).

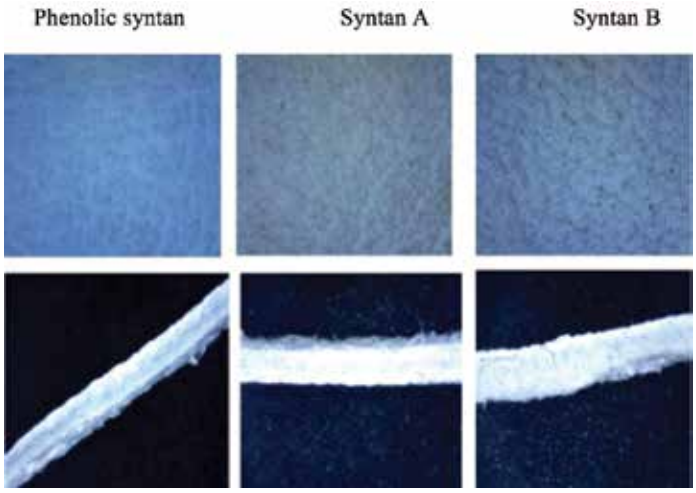

Figure 6. Morphological characteristics of the Crust Leather.

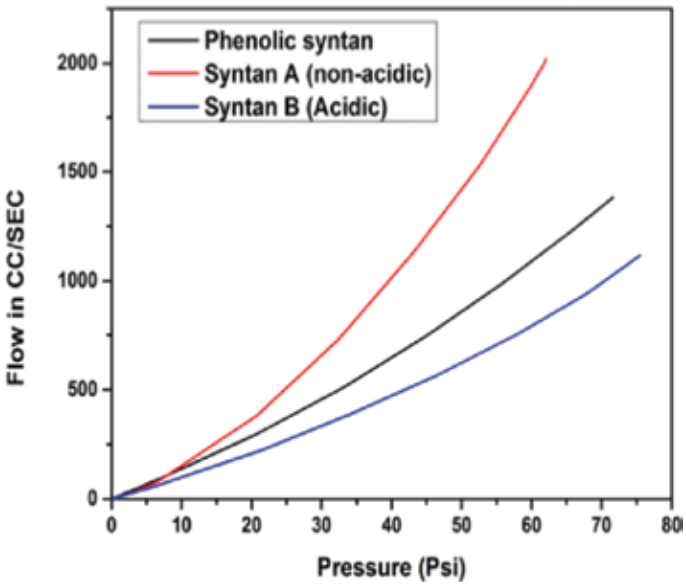

Figure 7. Gas permeability of a) phenolic syntan tanned leather b) Syntan A tanned leather and c) Syntan B tanned leather.

The optical images of the surface and cross sections of the crust leathers made from commercial phenolic syntan as well as Syntan A and Syntan B are given in **Figure 6**. The surface morphology of the crust leather indicates a similar grain pattern. Cross-sectional view indicates that the fibre compactness achieved with syntan A and B was similar to those from conventional phenolic syntan.

Evaluation of Crust Leather

The tensile strength of leathers prepared from Syntan A and Syntan B was 25 and 34 N/mm^2 respectively as against 20 N/mm^2 observed for control leathers. Tear strength values of 46 and 51 N/mm have been found to be comparable with control leathers (40 N/mm). For leathers treated with commercial phenolic syntan, the free formaldehyde content was determined as 12.3 mg/kg, while for that treated with syntan A, no free formaldehyde was detected. In the case of syntan B treated leathers, the free formaldehyde content was 11.3 mg/kg. All values met the standards.[9]

II. Gas Permeability Analysis

The permeability of gas through the syntan treated leathers is shown in **Figure 7**. The permeability of the retanned leathers was examined by the difference in the rate of pressure flow. From the result it is revealed that syntan A and phenolic syntan treated leathers show comparable change in the pressure flow when compared to syntan B treated leather. Similarly the syntan B treated leather shows less pressure flow rate due to its more filling nature arising from the acidic organics present in the system. Finally, the results indicate that syntan B treated leathers exhibit better filling property than commercial phenolic syntan and syntan A treated leathers. This is in accordance with the organoleptic properties shown in the **Table II**.

Overall Considerations

The development of two synthetic tanning agents from wastewater of a paper and pulp processing industry through simple extraction technique paves way for the development of a new range of auxiliaries where value addition to wastes from other industry could be the norm. From the environmental point of view, the process has the following advantages – a) a solution to the problem of black liquor generated by the paper industry as the waste could be turned into a value added product for leather sector; b) a generic product for the leather sector, that could be prepared through simple sulfonation – condensation reaction, providing for properties on par with commercial products and yet not dependent on fluctuations of phenol trade; c) a process wherein the solvent used for extraction of organics is ethyl acetate, which could be easily recovered and reused for subsequent extraction processes.

CONCLUSION

The study provides a methodology for the extraction of the non-acidic and acidic organics present in the black liquor for the manufacture of two syntans namely Syntan A and Syntan B. The syntans had particle size distribution similar to that of commercial phenolic syntan. Both the experimental leathers (Syntan A and B) exhibited lighter shade with similar properties as those prepared from commercial phenolic syntan. This work provides an opportunity to use the by-product of paper and pulp industry waste that is black liquor for the development of syntans for leather application to replace the filling syntans made from phenolic compound.

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