

An innovative new application for waste phenolic compounds: Use of Kraft lignin and naphthols in leather tanning

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Abstract

Degradation of Kraft lignin by using hemin and hydrogen peroxide was investigated to produce phenolic compounds. The degradation products were identified using spectroscopic methods and gas chromatography–mass spectrometry (GC–MS). 2-Methoxyphenol, 4-hydroxybenzaldehyde, vanillin, and vanillic acid were produced. Their polymerisation products were used as synthetic tanning agents for tanning collagen. Polymerised 2-methoxyphenol can increase the hydrothermal stability of collagen, like a conventional syntan, through hydrogen bonding interactions between the polymers and the protein. These products have potential to be used as raw materials for tanning of animal skins and other industries, such as chemical, pharmaceutical, food, and perfumery industries. Therefore, this can add value to the industrial byproduct (Kraft lignin), often considered a waste, and reduce its environmental impact. Leather tanning reactions between collagen and dihydroxynaphthalenes (DHNs) and oxazolidine have also been investigated, using hide powder and sheepskin pickled pelt. This investigation showed that some DHNs have a tanning effect on collagen. The measurement of combined and cross-linked DHNs on collagen showed that 30–40% of 1,6- and 2,6-DHNs were fixed through covalent bonding. Shrinkage temperature of the leather changed little after the non combined DHNs had been removed from the leather, indicating that the high stability of the combination tanned leather comes from the covalent bonding formed between DHNs and collagen through oxazolidine. This work indicates that Kraft lignin degradation products could be used as new and innovative agents for leather production in a way that opens up new markets and reduces environmental pollution.

Keywords: Waste phenolic compounds; Kraft lignin; Syntans; Dihydroxynaphthalenes; Cross-links; Tanning; Covalent bond

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1. Introduction

The management of solid waste in the UK has entered a period of unprecedented change, driven mainly by legislation deriving from the European Union (EU). Within the UK, in response to EU legislation, waste strategies have been produced for England and Wales ([DETR, 2000a](#)), Northern Ireland ([DoE, 2000](#)), Scotland ([SEPA, 2003](#)), and since 2000, for Wales ([Welsh Assembly Government, 2002](#)). Waste management is a key component of the UK Sustainable Development Strategy ([DTI, 2000](#)).

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The waste strategies within the UK utilise a wide range of tools to support action to fulfil targets set by EU drivers. The tools are used to tackle not just the quantitative nature of waste arisings but also qualitative issues ([DETR, 2000a](#)). This arises in respect of drivers such as the Landfill Directive, European Hazardous Waste Directive and the Restriction of Hazardous Substances (RoHS) in Waste Electrical and Electronic Equipment (WEEE). Sectors and companies are encouraged to develop risk reduction strategies so as to reduce the levels of certain hazardous substances ([DEFRA, 2004](#)) and report clearly on waste reduction in both quantitative and qualitative terms ([DETR, 2000b](#)) in an attempt to reduce the need for the introduction of economic instruments alone to bring about change ([DEFRA, 2002](#)).

The UK economy is highly dependant upon innovation to drive progress at the high technology end of the spectrum. Resource productivity, making more with less, has been acknowledged to be key to the UK economy ([Cabinet Office, 2001](#)). It is possible in many areas to reduce resource consumption markedly and to increase output per unit of consumption. As industry adopts more innovative approaches to production, arisings reduce for both quantitative and qualitative wastes ([Cabinet Office, 2001](#)). The UK has developed sustainable consumption and production indicators ([DEFRA, 2003a](#)) and a framework for sustainable consumption and production ([DEFRA, 2003b](#)) and is active in developing methods to measure resource productivity ([DTI, 2001](#)).

However, the rate of progress as been perceived as being too slow not just in meeting targets for waste arisings but in developing new attitudes and approaches across all industry sectors ([Strategy Unit, 2002](#)). The Strategy Unit report ([Strategy Unit, 2002](#)) unambiguously proposes a number of very strong recommendations for UK industry. These include: (Recommendation 4) economic instruments to encourage environmentally friendly products and (Recommendation 19) the expansion of best practice programmes to cover a much greater proportion of UK industry, in an attempt to stimulate innovation in respect of consumption and production ([Phillips et al., 2004](#)).

The leather industry is one such area in the UK that could innovate, by using new colorants, from diverse plant sources ([MAFF, 1997](#)) and new tanning materials in an attempt to tackle the problems of chromium in waste ([Lyubchik et al., 2004](#)). This is a major qualitative problem, in respect of waste, that is actively being researched internationally to produce cleaner chrome tanning (e.g. [Suresh et al., 2001](#)), using a range of eco-technologies ([Giannetti et al., 2004](#)) and with a growing use of biotechnology ([Thanikaivelan et al., 2004](#)). It is increasingly likely that future processes will need to demonstrate an eco-friendly methodology so that its products have wide appeal to a diverse consumer market.

2. Leather and lignin

Leather is made by subjecting the protein of animal skin or hide to a process known as tanning, whereby the skin or hide becomes more durable and capable of being used for a wide range of purposes. The leather industry may be regarded as a bridge between production of the hide as a byproduct of the food industry and its manufacture into shoes and apparel, for which it provides basic raw materials ([Thorstensen, 1993](#)).

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The practice of leather manufacture varies considerably from tannery to tannery and from country to country, so that there is no single universally applied process. The main sequences of operations and their aims are the same, but there are wide differences in detailed techniques ([Tuck, 1981](#)). The production of leather can be regarded as taking place in three steps. The first step is to remove unwanted components, hair, fats, etc., leaving the fibrous network of the hide protein. The second step is to react this network with tanning materials to produce a stabilised fibre structure. The third step is to build in the characteristics of fullness, colour, softness, and lubrication, and to finish the surface, to make a practically useful product ([Thorstensen, 1993](#)).

Nowadays, more than 90% of the world's leather is tanned with chromium, which is a consequence of the easy processing, the broad achievability and the excellent properties of such leather. However, it also has considerable potential for environmental pollution and the leather industry is facing a serious challenge.

Lignin is one of the most abundant renewable organic materials on earth, found in higher plants. Wood and other vascular tissues generally contain 20–30% lignin ([Kirk and Farrell, 1987](#) and [Kirk, 1984](#)), which is a complex polymer, made by the oxidative polymerisation of cinnamyl alcohol precursors ([Kirk and Farrell, 1987](#)). Lignin is the material that confers the qualities of rigidity and durability of wood ([Reid, 1995](#)). In this natural composite material, the cellulose fibrils provide tensile strength, and the hemicellulose and lignin provide cross-linking, binding the structure together.

Kraft lignin is a polymer that is readily available as a byproduct of the Kraft pulping process. The conversion of wood chips to pulp for manufacturing paper generates huge quantities of byproduct lignins; the best estimates indicate that more than 26 million tonnes of Kraft lignin are generated as byproducts of such pulping operations every year in the United States only ([Sarkanen, 2002](#)).

Development of lignin bioconversion processes has considerable potential for the future; as such bioconversions might produce a variety of chemicals. One of the uses of lignin with potential value would be in its conversion to low molecular weight chemicals ([Kirk and Chang, 1981](#) and [Suparno et al., 2003](#)). The products have possibility for use in tanning of leather ([Suparno et al., 2004](#)) and other industries.

3. Materials and methods

3.1. Materials

Kraft lignin, hemin, dihydroxynaphthalenes (DHNs), and other chemicals and reagents were purchased from Sigma–Aldrich Company Ltd., Dorset, UK. Hydrogen peroxide was obtained from Beecroft & Partners, Rotherham, UK. Hide powder was supplied by British Leather Confederation (BLC) the Leather Technology Centre, Northampton, UK. Sheepskin pickled pelt were obtained from the British School of Leather Technology, Northampton, UK. Oxazolidine (Neosyn, TX) was obtained from Clariant, Beverly, UK.

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3.2. Methods

3.2.1. Degradation of Kraft lignin

Kraft lignin (0.1 g) was dissolved in 250 ml of 50% 1,4-dioxane-water (v/v). The pH of solution was adjusted to 3.0 with 2 M HCl and then 7.5 ml of hemin solution containing 10 mg of hemin was added. One-milliliter aliquots of hydrogen peroxide were added every 30 min over 2 h, a total of five aliquots. The mixture was boiled at 90 °C, under reflux for 5 h. On completion, the reaction mixture was cooled over crushed ice. Controls included treatments in the absence of hemin, the absence of H₂O₂ and the absence of both.

3.2.2. Isolation of the degradation products

Any residual peroxide was reduced with sodium sulfite, then the reaction mixture was centrifuged at 1900 × *g* for 30 min. The supernatant, containing the degradation products was acidified with 6 M HCl to pH 1.0 and then extracted four times with 200 ml of diethyl ether, which had been previously treated with a saturated aqueous solution of iron(II) ammonium sulfate (Fe(NH₄)₂(SO₄)₂·6H₂O) to remove peroxides ([Hedges and Ertel, 1982](#)). The ether extract was dried over anhydrous sodium sulfate overnight. Solvent was evaporated on a water bath at 35–40 °C and then under reduced pressure, using a rotary evaporator at 40 °C to remove the 1,4-dioxane.

3.2.3. Identification of the degradation products

3.2.3.1. UV spectroscopy

The degraded Kraft lignin and controls were analysed using UV spectroscopy. The absorbance was recorded by a Lambda 2 UV/VIS spectrophotometer (Perkin-Elmer, UK) with a light path of 1 cm; wavelength range was 240–370 nm.

3.2.3.2. FT-IR spectroscopy

The isolated products were analysed using a 1720X FT-IR spectrometer (Perkin-Elmer) under the following conditions: spectral range 4000–400 cm⁻¹ and coated fast response deuterated triglycine sulfate (FR-DTGS) temperature stabilised detector.

3.2.3.3. Gas chromatography–mass spectrometry

The ether extract of the degradation products was dissolved in 0.5 ml of pyridine. The mixture was then silylated by addition of *N,O*-bis-trimethylsilyl trifluoroacetamide and 1% trimethylchlorosilane for GC–MS analysis. The sample solution (2 µl) was injected into a GC–MS system (Varian model CP-3800 GC and Saturn 2000 GC/MS) with a SGA BPX5 bonded phase, fused silica column (30 m × 0.32 mm i.d., 0.1 µm film thickness). The temperature profile for GC operation was isothermal at 80 °C for 2 min, followed by a 5 °C/min temperature gradient to 200 °C, a 15 °C/min gradient to 280 °C, and isothermal period at 280 °C for 10 min

([Crestini and Argyropoulos, 2001](#)). The MS conditions were electron ionisation (EI) mode (70 eV) and scanning rate of 60 scans/min.

3.2.4. Yields

Yields of the lignin degradation products were measured using GC–MS. Pure compounds of the degradation products were used as references or standards. The standards were run through GC–MS using the same procedure as used for samples, as described above and the peak area of each product was calculated.

3.2.5. Preparation of syntans

The degradation products were polymerised using formaldehyde with alkali catalysis. 0.05 mol of each lignin degradation product was dissolved in 50 ml of distilled water and 50 ml of 2 M NaOH. The mixtures were stirred for 15 min at a constant temperature of 40 °C and the pH of the solution was measured. Some 0.05 mol of 37% (w/v) formaldehyde was added gradually at a constant temperature of 40 °C with vigorous stirring, and then the mixtures were stirred for 5 h. The solution was neutralised with 2 M HCl. Due to the difficulty in polymerising 2-methoxyphenol in alkaline conditions, the phenol was sulfonated prior to formaldehyde polymerisation and polymerised by acid catalysis ([Gasser, 1922](#)). This is a commonly used element of syntan synthesis. Sulfonation was carried out by adding 0.055 mol of concentrated sulfuric acid gradually at 90 °C for 30 min with vigorous stirring; constant heating and stirring were continued for 2 h. The sulfonic acid formed was diluted with three volumes of water and then polymerised using the same procedure as above, except after heating at 40 °C for 2 h the product was heated at 105 °C for 15 min to complete reaction of the formaldehyde.

Molecular weight distribution of the products was measured by gel permeation chromatography (GPC) using deionised water at pH 7 as eluent at flow rate of 1.0 ml/min. The GPC analysis was carried out using a PL-DCU data collection unit, LC 1120 HPLC pump, and PL aquagel-OH30 column (polymer 8 µm particle size, 300 mm length, 7.5 mm i.d.) (Polymer Laboratories, UK) and UV detector 132 RI (Gibson Ltd., UK). Polysaccharides were used as references. Functional groups of the polymers were analysed using FT-IR spectroscopy.

3.2.6. Tanning experiments using the polymerisation products and oxazolidine

Combination tanning, using the polymerisation products and oxazolidine was carried out. To 1 g hide powder, soaked in 15 ml of water at 30 °C for 30 min, 1.5 g of NaCl was added. The pH of the hide powder was adjusted to 4.5 with 5% formic acid solution, followed by addition of 0.4 g of each lignin degradation product or their polymerisation products (syntans), which were previously dissolved in 3 ml of acetone. The reaction was run at 35 °C, with shaking for 24 h; then the mixtures were filtered through a fast filter paper. After re-soaking with 10 ml of water, 0.2 g of oxazolidine was added, shaken at 35 °C for 30 min and warmed to 50 °C for 2 h. On completion, the mixtures were filtered through a fast filter paper.

3.2.7. Measurement of hydrothermal stability

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The tanning effects of the products on hide powder were measured by determining the denaturation or shrinkage temperature (T_s) and energy or enthalpy (ΔH) of shrinking. T_s is the temperature at which measurable shrinkage occurs when the hide powder is gradually heated in an aqueous medium. Untreated, wet hide powder was used as a control. A rise in shrinkage temperature (ΔT_s) and the shrinkage temperature difference between treatment and control indicates the tanning ability of the products. T_s and ΔH were measured using a DSC822^e differential scanning calorimeter (DSC) (Mettler Toledo, UK). Ten to fifteen milligrams of wet samples were weighed and placed in a 40 μ l standard aluminium pan and then the pans were transferred to the DSC carousel. Samples were heated at a rate of 5 $^{\circ}$ C/min and measurement range was 35–120 $^{\circ}$ C.

3.2.8. Combination tanning using the DHNs and oxazolidine on hide powder

The same procedure was used as described above. After discarding the float, 10 ml water was added, then the mixture was adjusted to pH 6 with 5% sodium bicarbonate solution; 0.2 g oxazolidine was added, then shaken at 50 $^{\circ}$ C for 2 h. The mixture was adjusted to pH 3.2–3.8 by adding 5% formic acid, then shaken at 35 $^{\circ}$ C for 1 h. On completion, the mixtures were filtered. DSC was used to measure hydrothermal stability of the treated hide powder.

3.2.9. Combination tanning using the DHNs and oxazolidine on sheepskin

The same procedure was used as described above. One hundred and fifty percent of water was added, then the mixture was adjusted to pH 6 with 5% sodium bicarbonate solution. Ten percent of oxazolidine was added, and then shaken at 50 $^{\circ}$ C for 2 h. On completion, the float was discarded. Hydrothermal stability was measured using DSC. Thickness, colour, tensile strength, elongation at break, and tear strength of the leather were measured according to the Official Method of Analysis for physical testing of leather ([SLTC, 1996](#)).

3.2.10. Determination of tannin combination on leather

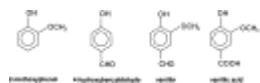
The method described by [Covington and Song \(2003\)](#) was used to determine the DHNs combination on leather. DHN tanned or combination tanned hide powder was soaked in 50 ml of 50% (v/v) aqueous acetone solution at 20 $^{\circ}$ C for 20 min under vigorous shaking and washed with the same solution. The amount of washed out tannin was measured by the gravimetric method. DSC was used to measure the shrinkage temperature of the washed hide powder.

4. Results

4.1. Identification of the lignin degradation products

The mass spectra of the degraded lignin products indicate that the products were: 2-methoxyphenol, 4-hydroxybenzaldehyde, vanillin, and vanillic acid. Structures of the products are given in [Fig. 1](#). The mass spectrometric data were supported by the FT-IR spectrum of the reaction products, containing absorption bands of carbonyl group, hydroxyl group, C–H

stretching vibration of aromatic, and C=C stretching vibration of aromatic rings; and the UV spectrum of the products showing an increase in α -carbonyl groups.



[Full-size image](#) (5K)

Fig. 1. Chemical structures of the biomimetic degradation products of Kraft lignin.

4.2. Yields of the lignin degradation products

Yields of the degradation products are given in [Table 1](#). Total yield of the products was 32%.

Table 1.

Yields of the biomimetic Kraft lignin degradation products

Product	Retention time (min)	Yield (%) ^a
2-Methoxyphenol	15.2	1.7 ± 0.3
4-Hydroxybenzaldehyde	19.5	1.9 ± 0.5
Vanillin	23.6	19.0 ± 0.8
Vanillic acid	29.1	9.3 ± 0.9

^a Means ± standard deviation of triplicate experiments.

4.3. Polymerisation of the lignin degradation products

[Table 2](#) shows the molecular weight distributions from gel permeation chromatography of the polymers of the lignin degradation products.

Table 2.

Molecular weight distributions of the polymers of the lignin degradation products

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Phenolic compound	Monomer (M_w)	Polymerisation product ^a		
		M_w (k)	M_n (k)	PD
2-Methoxyphenol	124	216	188	1.14
4-Hydroxybenzaldehyde	122	122	86	1.41
Vanillin	152	0.65	0.59	1.10
Vanillic acid	168	154	136	1.13

M_w , the weight-average molecular weight; M_n , the number-average molecular weight; PD, polydispersity.

^a Based on the calibration curve with polysaccharide standards.

4.4. Use of the products for leather tanning

The polymerisation products of the lignin degradation products were applied for tanning of hide powder and then retanned with oxazolidine as a cross-linking agent; they exhibited good tanning ability. The hydrothermal stability of hide powder tanned with the polymers and oxazolidine is given in [Table 3](#).

Table 3.

Hydrothermal stability of collagen tanned with the polymers of lignin degradation products and oxazolidine

Tanning method	T_s (°C)	ΔT_s (°C)	ΔH (J/g)	$\Delta T_{s(Oz)}$ (°C) ^a
None	58	–	30	–
Oxazolidine (Oz)	75	17	30	–
Polymer of 2-methoxyphenol + Oz	82	24	33	8
Polymer of 4-hydroxybenzaldehyde + Oz	76	18	28	11
Polymer of vanillin + Oz	74	16	23	20
Polymer of vanillic acid + Oz	78	20	32	10

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^a The effect of oxazolidine cross-linking, ΔT_s [(polymer + Oz) – polymer].

4.5. Combination tanning using dihydroxynaphthalenes and oxazolidine

Hydrothermal stabilities of hide powder and skin tanned using DHNs and oxazolidines are given in Table 4. The highest shrinkage temperatures were achieved using 1,6- and 2,6-DHNs. The combination tanning using 2,6-DHN and oxazolidine produced a leather with shrinkage temperature equivalent to conventional chrome tanned leather.

Table 4.

Hydrothermal stability of collagen treated by dihydroxynaphthalenes and oxazolidine (important results are highlighted in bold)

Tanning method	T_s (°C)	ΔT_s (°C)	ΔH (J/g)	$\Delta T_{s \text{ (synergy)}}$ (°C) ^a
Hide powder				
None	57	–	31	–
Oxazolidine (Oz)	75	17	29	–
1,5-DHN + Oz	85	27	32	12
1,6-DHN + Oz	90	32	29	8
2,6-DHN + Oz	110	53	36	32
2,7-DHN + Oz	79	22	34	0
Sheepskin				
None	55	0	22	–
Oxazolidine (Oz)	78	23	20	–
1,5-DHN + Oz	95	40	20	8
1,6-DHN + Oz	100	45	23	6
2,6-DHN + Oz	110	55	20	16
2,7-DHN + Oz	86	31	27	–8

^a $\Delta T_{s(\text{synergy})} = \Delta T_s [(DHN + Oz) - DHN - Oz]$.

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4.6. Affinity of DHNs on collagen

[Table 5](#) shows the affinity of DHNs on collagen. Fifty to seventy-five percent of DHNs were bound to collagen. Seventy to ninety percent of DHNs were washed out by 50% (v/v) aqueous acetone from DHN tanned hide powder and DHNs (50–80%) were washed out after the cross-linking using oxazolidine. This indicates that 20–50% of DHNs were irreversibly fixed in combination tanning of collagen.

Table 5.

The affinity of some dihydroxynaphthalenes on collagen in hide powder

Tannin	DHN bound to collagen^a (%)	DHN left after acetone washing^b (%)	Cross-linked DHN left after acetone washing (%)
1,5-DHN	57	9	15
1,6-DHN	74	38	50
2,6-DHN	76	35	49
2,7-DHN	69	36	35

^a Calculated by difference between initial DHN used and DHN left in the after tanning liquor.

^b Calculated by difference between DHN bound to collagen and DHN in washing liquor after washing with 50% (v/v) aqueous acetone.

4.7. Differential scanning calorimetry studies

Differential scanning calorimetry analysis ([Table 6](#)) shows that the highest shrinkage temperatures were achieved by oxazolidine combination tanning using 1,6- and 2,6-DHNs. There was some loss of hydrothermal stability after washing with the hydrogen bond breaker, 50% (v/v) acetone–water, but it remained, overall, high.

Table 6.

Shrinkage temperature (°C) of treated collagen (important results are highlighted in bold)

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Tanning method	Tanned collagen	Acetone washed collagen
None	57	56
Oxazolidine	75	71
1,5-DHN	56	56
1,5-DHN + oxazolidine	85	82
1,6-DHN	64	57
1,6-DHN + oxazolidine	90	89
2,6-DHN	62	57
2,6-DHN + oxazolidine	110	97
2,7-DHN	62	58
2,7-DHN + oxazolidine	79	67

5. Discussion

The polymers of lignin degradation products were applied to hide powder and then the treated hide powders were retanned with oxazolidine as a cross-linking agent. The combination tannages increased the shrinkage temperature of hide powder between 10 and 20 °C.

Enthalpies or energies of shrinking of the hide powder treated with the polymers of lignin degradation products and oxazolidine are given in [Table 3](#). Shrinking energy of hide powder treated with the polymer of vanillin and oxazolidine indicates a tanning reaction, causing an increase of stability by the interactions with collagen.

From [Table 3](#), shrinkage temperatures of hide powder tanned with polymers of 4-hydroxybenzaldehyde, vanillin, and vanillic acid and retanned with oxazolidine were around 75 °C, which are the T_s of oxazolidine-tanned hide powder. This shows that the increases in T_s are primarily due to retanning with oxazolidine; therefore, those polymers did not undergo tanning reactions on collagen.

[Table 4](#) shows that tanning, using some DHNs, and retanning using oxazolidine increased the hydrothermal stabilities of hide powder and sheepskin between 20 and 55 °C as shown by ΔT_s . The highest shrinkage temperatures are achieved using 1,6- and 2,6-DHNs. The DHNs, 1,5- 1,6-, and 2,6-produced additive tannages that exhibited positive synergies, as shown by $\Delta T_{s(\text{synergy})}$.

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Combination tanning using 2,6-DHN and oxazolidine produced a leather with a shrinkage temperature equivalent to conventional chrome tanned leather. Therefore, this type of reaction might be useful as a substitute for chrome tanning leather.

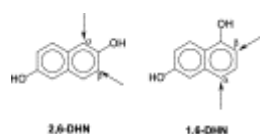
From [Table 5](#), 20–50% of DHNs was irreversibly fixed in combination tanning of collagen. The reason for this phenomenon is that some of the DHN molecules are fixed on collagen chains by covalent bonding, analogous to observations in the combination tanning using condensed plant polyphenols and oxazolidine, reported by [Covington and Song \(2003\)](#).

Covalent bonding has an important role in DHN-oxazolidine combination tanning ([Table 6](#)), which is supported by the affinity of the DHNs on collagen. Combination tanning using 2,6- and 2,7-DHNs with oxazolidine gives a synergistic effect to create high hydrothermal stability.

This result shows the reactivities of the DHNs to produce tanning effects towards collagen depend upon their structures, where 1,6- and 2,6-DHNs are more reactive than the other naphthols. It also indicates that 2,6- and 1,6-DHNs undergo cross-linking with oxazolidine and collagen with different reactivities, as shown by the differences in their ability to raise shrinkage temperature.

On the other hand, there was no marked increase in T_s for collagen treated by the other DHNs. This could be attributed to the limited cross-linking between the DHNs, oxazolidine, and collagen, perhaps due to positions of phenolic hydroxyl groups in their structures giving rise to unfavourable steric hindrance.

The reactivities of 1,6- and 2,6-DHNs can be explained by the electronic nature of naphthalene, which normally undergoes electrophilic substitution at C-1 (α -location) more rapidly than at β -sites, *ortho*-coupling is preferred and its substitution reactions tend to proceed in a manner that maintains one intact benzene ring ([Reusch, 2004](#)). Based on these characteristics, reactive sites of the naphthol compounds, where the substitution reactions most readily occur can be determined ([Suparno, 2005](#)). The reactive sites for 2,6-DHN are at C-1 (α) and C-3 (β) and for 1,6-DHN are C-2 (β) and C-4 (α), as shown in [Fig. 2](#). Both reactive sites for 2,6-DHN are at *ortho* positions to the phenolic hydroxyl group, so the substitution reactions at both sites are preferred. On the other hand, reactive sites for 1,6-DHN are at *ortho* (C-2) and *para* (C-4) positions to the phenolic hydroxyl group; consequently, the coupling reaction at C-4 position will occur after the first coupling at *ortho* (C-2). Therefore, the 2,6-DHN should be more reactive than 1,6-DHN. As a result, 2,6-DHN can create more cross-linking between the naphthol, oxazolidine, and collagen, leading to higher shrinkage temperature.



[Full-size image \(3K\)](#)

Fig. 2. Reactive sites of 2,6- and 1,6-dihydroxynaphthalenes.

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The electronic effect in naphthol is a resonance induced feedback of electrons from the oxygen lone pairs into the ring. This tends to decrease the electron density round oxygen and to decrease the strength of the O–H bond, and therefore encourages proton loss ([Whitfield, 1971](#)), which in turn promotes hydrogen bonding to collagen. In other words, the phenolic hydroxyl group of the DHNs is an electron donor to the aromatic ring.

The resonance forms of the naphthol indicate that electron donation results in negative charges at the *ortho* and *para* positions. Therefore, the naphthols will be prone to electrophilic attack at those positions. Based on the positions of reactive sites in the compounds, cross-linking reactions of 2,6- and 1,6-DHNs with oxazolidine can be predicted, as given in [Fig. 3](#). This accounts for the cross-links between the naphthols with oxazolidine and then the naphthols will cross-link with collagen by hydrogen and covalent bonds leading to high shrinkage temperature.

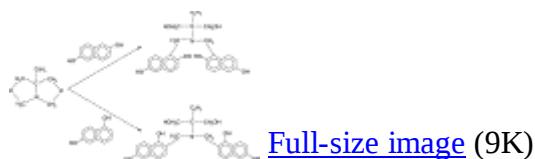


Fig. 3. Cross-linking reactions of 2,6- and 1,6-dihydroxynaphthalenes with oxazolidine.

Degradation of Kraft lignin using the biomimetic system is an acceptable technique to convert the byproduct of the pulp industry to useful products. It produces simple phenolic compounds. The use of the byproduct not only reduces the waste, but also can add value to the waste. By the conversion of the byproduct lignin, new products can be obtained to give new and innovative products to fulfil a niche in a dynamic, consumer led market.

The use of 2,6- and 1,6-DHNs for combination tanning with oxazolidine can produce leather with similar properties to that tanned using conventional chrome tannage ([Suparno, 2005](#)). They produced leathers with high shrinkage temperature, good elasticity, and strength properties. The leathers were also coloured, yellow, and brown, respectively, which can be useful as base colours for the production of either light or dark coloured leather. The physical properties of the leathers are given in [Table 7](#). It is predicted that they will have good lifetime and high public acceptability, because they are produced using materials that are less hazardous than chrome tannage.

Table 7.

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Physical properties of leathers tanned by 2,6- and 1,6-DHNs and retanned by oxazolidine

Physical property	2,6-DHN tanned leather	1,6-DHN tanned leather
Shrinkage temperature (°C)	110	100
Thickness (mm)	2.0	2.1
Colour	Yellow	Brown
Tensile strength (MPa)	7.5	6.2
Tear strength (N/mm)	24.8	31.9
Elongation at break (%)	47.2	52.1

There are a number of future research issues. Firstly, the uses of the lignin degradation products and DHNs for combination tanning with oxazolidine might be able to substitute chrome tannage, so that the environmental impact of the chrome tanning might be reduced. Secondly, the uses of the phenolic lignin degradation products and DHNs in conjunction with laccase, a polyphenol oxidase, can be used for leather dyeing, producing a range of potentially acceptable colours.

6. Conclusions

Kraft lignin biomimetic degradation yields some simple phenolic products. The phenols did not give good tanning effects towards collagen. However, after polymerisation, 2-methoxyphenol can increase the hydrothermal stability of collagen, like a conventional syntan. The degradation products have potential to be used as raw materials for various applications and in manufacturing other compounds for the chemical, pharmaceutical, food, and perfumery industries.

Tanning using 2,6- or 1,6-DHNs and retanning with oxazolidine can produce a high hydrothermal stability of leather, possibly exploitable as a substitute for chrome tanning, although more likely to constitute a new organic tannage. In this way, use of basic chromium(III) sulfate in leather manufacturing might be reduced, so environmental pollution from chrome tanning might be decreased.

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