Green Chemistry Approach in Leather Processing: A Case of Chrome Tanning

by

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Abstract

The leather industry, world over, has adopted several new practices as a part of their green initiative. In this study the chrome tanning process, one of the most important steps in leather making, was evaluated for its 'greenness'. The prominent tool employed for assessing greenness for an industrial process, atom economy (the conversion efficiency of a chemical process in terms of all atoms involved) was studied for the first time for four types of chrome tanning processes: direct chrome liquor recycle (DCLR), ethanolamine-assisted, pickleless chrome tanning, and conventional chrome tanning. All chemicals involved in the reaction with skin protein were taken into consideration for the computation of overall atom economy. An atom economy of only 29% was obtained for the conventional chrome tanning system. Among the four improved methods of chrome tanning evaluated, the pickleless chrome tanning method provides the maximum atom economy of about 57% followed by ethanolamine and DCLR, having atom economies of 42 and 32%, respectively.

Resumen

La industria del cuero, en el mundo entero, ha adoptado diversas nuevas prácticas como parte de su iniciativa ecológica. En este estudio el proceso de curtido al cromo, uno de los pasos más importantes en la fabricación de cuero, fue evaluado por su comportamiento ecológico. La herramienta más prominente empleada para evaluar el comportamiento ecológico de un proceso industrial, la economía por átomo ofrecido (la eficiencia de conversión de un proceso químico en términos de todos los átomos implicados) se estudió por primera vez para cuatro tipos de procesos de curtido al cromo: licor de cromo directo por reciclado (DCLR) , etanolamina como auxiliar en un curtido al cromo sin pickelado y curtido al cromo convencional. Todos los productos químicos que participan en la reacción con la proteína de la piel se tuvieron en cuenta para el cómputo de la economía global del átomo. Una economía del átomo de sólo el 29% se obtuvo para el sistema de curtido al cromo convencional. Entre los cuatro métodos mejorados de curtido al cromo evaluados, el método de curtido al cromo sin pickelado ofrece la economía por átomo máxima de alrededor del 57%, seguido por el con etanolamina y DCLR, con economías de átomo de 42 y 32%, respectivamente.

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INTRODUCTION

Green chemistry as a concept provides enormous challenges/ opportunities for those who practice chemistry in industry, education, and research.[1,2] By definition, the concept of green chemistry advocates efficient utilization of raw materials, elimination of waste, and avoiding the use of toxic and/or hazardous reagents and solvents in the manufacture and application during chemical processes.[3] This innovative concept towards the elimination of waste at the source involves putting together tools, techniques, and technologies that can develop into an eco-friendly and efficient process with significant financial benefits.[4-6] The prospective impact of green chemistry concept is diffusing in almost all type of industries.[7] The reason for its recognition is mainly due to the anticipated direction provided by its twelve principles, viz. preventing waste; designing safer chemicals; designing less hazardous chemical synthesis; using renewable feed-stocks; using catalysts; avoiding chemical derivatives; maximizing atom economy; using safer solvents and reaction conditions; increasing energy efficiency; designing chemicals and products to degrade after use; real time analysis for pollution prevention; inherently safer chemistry for accident prevention.[8,9]

One of the most fundamental aspects of green chemistry is atom economy, which introduces methods designed to maximize the incorporation of all materials used in the process into the final product.[10,11] Barry M. Trost is credited with coining of the term ‘atom economy’ and mathematically expressing it as molecular weight of the product divided by the sum of molecular weight of all reactants.[12] The incorporation of more reactants into the desired product reduces waste thereby diminishing exogenous cost associated with cleanup, procurement of starting material etc. The commercial success of studying atom economy reaction is well elucidated by comparison of six step boot synthesis of Ibuprofen to that of three step BHC synthesis developed by BHC company (a joint venture between Boots company and Hoescht Celanese). The former method has an atom economy of 40% whereas the latter reaction method had 77%, resulting in the decrease of pollution load.[13]

Tanneries, world over, have put in considerable effort for ‘greening’ their processes. Currently practiced cleaner leather processing methodologies focus primarily on the waste minimization and treatment. Cleaner technologies are in great demand in tanning sectors, as chrome bearing wastes are classified as hazardous to human habitat. Industrially proven methods for reducing the chrome content in effluents can be categorized as high exhaust tanning process, recycling/reuse and recovery/recycling.[14] High exhaustion of chromium or in other words a better incorporation of chromium into the product leather is generally brought about by incorporation of additives. Ethanolamine, a classic external aid, which works as an organic analogue of aluminium(III) catalysis,[15] is added to reaction bath prior to addition of chromium in a conventional chrome tanning process. By employing this process, a maximum exhaustion of about 90% was reported.[16] The most renowned recycle/reuse method is direct chrome liquor recycle process (DCLR). DCLR involves reuse of spent chrome liquor in the tanning stage or the previous step of pickling without any process intervention. The spent chrome liquor is added to pickling or chrome tanning bath after pre-adjusting the pH using sulfuric acid and NaCl. This DCLR method helps to improve exhaustion of chromium, and also reduces total dissolved solids (TDS) in waste water.[17] Pickleless tanning is yet another promising alternative to enhance chromium uptake by skin and to minimize TDS in waste water. The exhaustion of chromium in pickleless tanning is above 90%.[18] Determining the percentage yield of a product is one of the ways by which the efficiency of a particular reaction is ascertained. Tanners in general calculate the efficiency of chrome tanning process based on the amount of chromium taken up by the skin after the process of tanning. However, this strategy fails to take in to account the uptake of other reactants/raw materials and mass of the co-products such as water, skin protein and salts. The inadequacies in this type of calculations were addressed in this work using the atom economy concept.[12]

In this study the chromium exhaustion or uptake parameter used by tanners was replaced with atom economy. The calculation of atom economy for chrome tanning process is impaired by the fact that no proper method exists for determining molecular weight of skin protein. Hence, being the first attempt to measure the atom economy of leather process and also owing to the complex nature of leather making process, some assumptions/approximations were made. Nitrogen content was determined and taken as a measure of skin protein, where moles of skin protein in raw material and product were assumed to be equivalent to moles of nitrogen. Secondly, moles of chromium were taken in to consideration instead of that of basic chromium sulfate. Other reactants such as chlorides, sulfates were also quantified. Results obtained were then substituted and % atom economy calculated for each component and cumulatively.

EXPERIMENTAL METHODS

Materials and methods

Delimed goat skins were chosen as raw material for pickleless chrome tanning process. For other three chrome tanning processes pickled goatskins were chosen as raw material. All chemicals used for leather processing were of commercial grade and the chemicals used for the analysis of spent liquors were of analytical grade. Well established conventional chrome tanning, ethanolamine-assisted chrome tanning, direct chrome liquor recycle method and pickleless chrome tanning were employed for processing of leathers.[16-18] The details of the recipe are given in appended supporting information.

Analysis of leather and spent liquors
Leather samples from conventional and other chromium tanning systems were taken from the official butt portion[19] and analyzed for moisture content, chromium, nitrogen, chloride and sulfate as per standard procedures.[20, 21] Spent chrome liquor from conventional and other chrome tanning systems were collected, filtered and analyzed for chromium, sulfates and chlorides as per standard procedures.[22, 23] Proper precautions were taken to avoid loss of chemicals and water during tanning trials. All the experiments were done in triplicate.

RESULTS AND DISCUSSION

Atom economy for conventional chrome tanning process
Conventional chrome tanning process involves pickling, chrome tanning and basification followed by piling of chrome tanned leathers.[14] Table 1 provides the mole input and output of various reactants employed in chrome tanning. The total amount of nitrogen (skin protein) before and after chrome tanning was determined to be 795.70 mmol. The input of chromium accounts to 47.28 mmol out of which 28.82 mmol is present in the final leather. Based on these parameters, atom economy can be calculated for conventional tanning using the following Equation 1.

Where, Cr, N_2 and Cr-N_2 denote the amount of chromium, nitrogen (skin protein) and chrome tanned leather (sum of moles of chromium and nitrogen in the final leather), respectively. The Cr-N_2 complex was estimated to be 824.52 mmol. Substituting the values in Equation 1, an atom economy of 97.8% for conventional chrome tanning system was determined. Higher value of atom economy could be attributed to the nitrogen content, which is in larger portion compared to chromium. Including substituent like chlorides, sulfates and water progressively for the calculation of atom economy would suggest the direct relevance and importance of inclusion of all the reactants. The input/output audit of various reactants like chlorides, sulfates and water for the conventional process is provided in Table 1. The progressive substitutions of various reactants for the calculation of atom economy are mathematically represented in the following Equations 2-4.

Where, Cl, SO_4, H_2O, Cr-N_2-Cl, Cr-N_2-Cl-SO_4 and Cr-N_2-Cl-SO_4-H_2O, denote the millimoles of chloride, sulfate, water and the respective chrome-nitrogen complexes formed. Values of atom economy obtained by progressive inclusion of reactants derived are graphically depicted in Fig. 1.

It could be observed that inclusion of all reactants progressively shows a steep decrease in atom economy from 97.8 to 29.75%, which indicates the role played by individual reactants in the calculation of atom economy for chrome tanning process. Inclusion of chloride ion in the calculation results in an atom economy of 77.73% and sulfate inclusion results in 75.09%, which is derived from Equation 2 and 3, respectively. An interesting observation is the steep decrease of atom economy to 29.75% after inclusion of water as derived from Equation 4, suggests that proper quantification and reduction of water usage could improve the atom economy.

Atom economy of various chrome management systems
The input/output parameters and the calculated atom economy for direct chrome liquor recycle method are provided in Table 1 and Fig. 2, respectively. A simple additional assumption is also included in the calculation of atom economy of the various chrome management systems. Atom economy was calculated with and without incorporating nitrogen (skin protein) as a reactant for ethanolamine, DCLR and pickleless methods, respectively. This was carried out to understand the role of nitrogen in the calculation of atom economy.

$$\% Atom\ economy = \frac{Moles of\ (Cr-N_2)}{Moles\ of\ Cr + Moles\ of\ N_2} \times 100 \quad ------------------- 1$$

$$\%\ atom\ economy_{cl} = \frac{mmol\ of\ [Cr-N_2-Cl]}{mmol\ of\ Cr + mmol\ of\ N_2 + mmol\ of\ Cl} \quad ------------ 2$$

$$\%\ atom\ economy_{Cl+SO_4} = \frac{mmol\ of\ [Cr-N_2-Cl-SO_4]}{mmol\ of\ Cr + mmol\ of\ N_2 + mmol\ of\ Cl + mmol\ of\ SO_4} \quad ---------- 3$$

$$\%\ atom\ economy_{Cl+H_2O+SO_4} = \frac{mmol\ of\ [Cr-N_2-Cl-SO_4-H_2O]}{mmol\ of\ Cr + mmol\ of\ N_2 + mmol\ of\ Cl + mmol\ of\ H_2O + mmol\ of\ SO_4} \quad ------ 4$$

TABLE I
Input and output of various tanning systems

Components	Conventional Chrome Tanning		Direct chrome liquor recycle process		Ethanolamine-assisted process		Pickleless chrome tanning	
	Input reactant (mmol)	Output product (mmol)	Input reactant (mmol)	Output product (mmol)	Input reactant (mmol)	Output product (mmol)	Input reactant (mmol)	Output product (mmol)
Chromium	47.28 ± 2.5	28.82 ± 2.5	39.81 ± 2.5	25.4 ± 2.5	20.06 ± 2.5	18.48 ± 2.5	58.08 ± 2.5	55.19 ± 2.5
Nitrogen	795.70 ± 15	795.70 ± 15	364.28 ±15	364.28 ± 15	282.96 ± 5	282.96 ± 5	807 ± 5	807 ± 5
Chlorides	427.18 ± 10	162.82 ± 10	170.98 ± 6	90.42 ± 6	250 ± 5	127.89 ± 5	0	0
Sulfates	59.50 ± 3.0	11.11 ± 3.0	40.00 ± 2.5	13.75 ± 2.5	25.281± 2	11.65 ± 2	73.411 ± 5	32.64 ± 5
Water	33110 ± 120	9247 ± 120	28878±150	8943 ±150	13888 ± 110	5634 ± 110	23100 ± 140	12807 ± 140

From Fig. 2 it is clear that the atom economy of DCLR decreases with increasing input components. The atom economy calculated with chromium component alone has a value of about 63% and with nitrogen inclusion it is 96%. While the first case reflects the exhaustion of chromium, by including nitrogen, the atom economy increased to 96%. This is attributed to the higher fraction of nitrogen present. A steep decrease in the calculated atom economy values from 83 and 80 to 32% were observed by progressive incorporation of chloride, sulfate and water, respectively.

The mole input/output of ethanolamine-assisted chrome tanning is provided in Table 1 and the atom economies thus calculated are depicted in Fig. 3. Chromium exhaustion was calculated as 89%. The atom economy of 99% was obtained after inclusion of nitrogen and chromium. The inclusion of sulfate, chloride and water components results in atom economy of 77, 76 and 42%, respectively. For ethanolamine-assisted chrome tanning an improved atom economy, as compared to DCLR, was mainly due to the higher amount of chromium being reacted with the leather protein due to additional reactive sites created by ethanolamine.

Pickleless chrome tanning is where the pickling process carried out prior to tanning is eliminated. This process thus enables the avoidance of sulfuric acid and sodium chloride employed in pickling and its carry forward to tanning. Mole input/output components of pickleless chrome tanning are listed in Table 1 and the atom economies so obtained are shown in Fig. 4. Higher chrome exhaustion (95%) was observed in this system. This observation was also supported by the atom economy value of 99%. Also, atom economy value obtained after inclusion of all components (sulfates and water) is 57%, which is higher compared to conventional and other chrome management technologies.

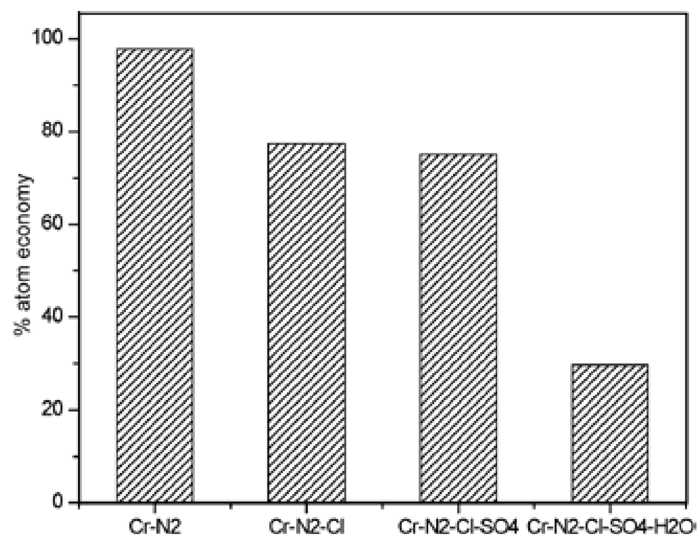

Fig. 1. Atom economy of a conventional chrome tanning process including various individual components

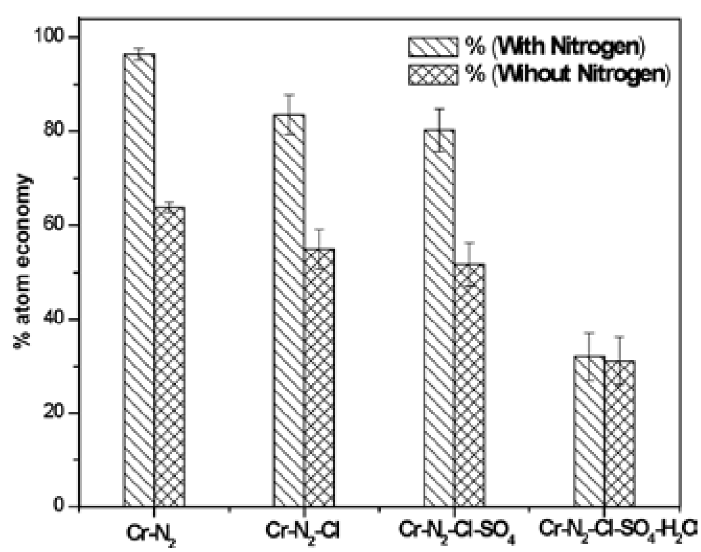

Fig. 2. Atom economy of a DCLR process including various individual components

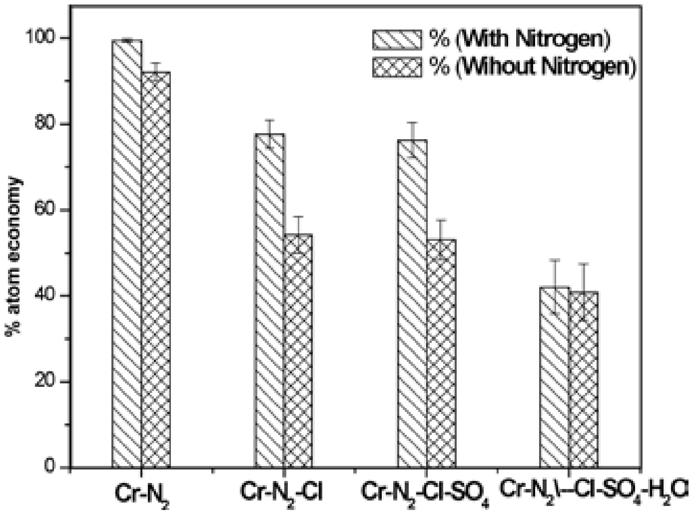

Fig. 3. Atom economy of an ethanolamine-assisted chrome tanning including various individual components

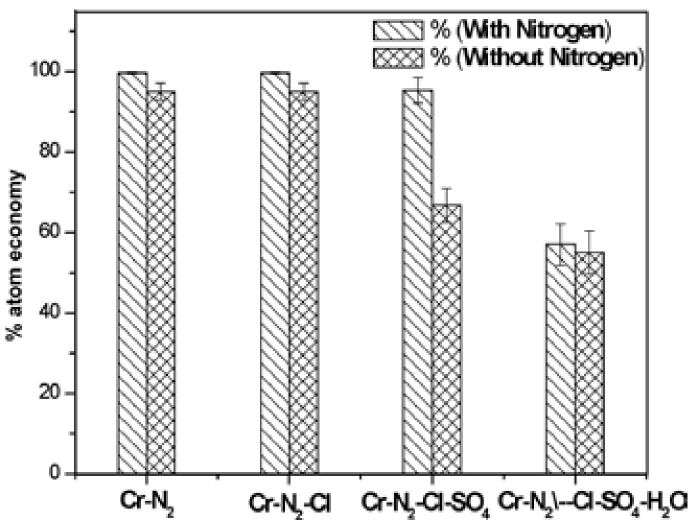

Fig. 4. Atom economy of pickleless chrome tanning including various individual components

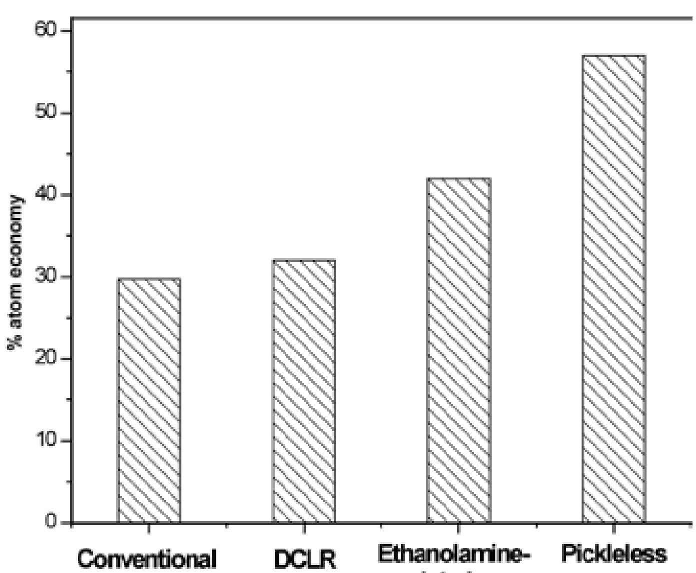

Fig. 5. Comparison of atom economy of various chrome management systems

From the above results, we can infer that the method of tanning plays a vital role in determining the process efficiency. A comparison of atom economy calculated for various chrome management systems is depicted in Fig. 5. The atom economy for various chrome management systems follows the order; pickleless tanning> ethanolamine-assisted chrome tanning > DCLR > conventional chrome tanning. The inputs like chloride, sulfate and water reduce the efficiency of the chrome tanning process indicating their role in determining the process efficiency. In order to improve the efficiency of the chrome tanning process to make it greener, these inputs need to be reduced/optimized. Water has a major role to play when compared to other inputs in determining the atom economy. Proper audit on the use of water for improving the process efficiency is recommended from this study. Although DCLR system gave an atom economy of 32% after the incorporation of various inputs, this could increase in principle on further subsequent recycling steps.

CONCLUSIONS

The concept of atom economy determines the importance of input of reactants and final product formed rather than assessing one component (chromium uptake alone), which is practiced in conventional leather processing. This enables the reduction in inputs for efficient usage, thereby avoiding or minimizing the waste produced. Among the various chrome tanning systems studied in the present investigation, it is seen that pickleless chrome tanning provides an improved atom economy as compared to other chrome tanning systems, predominately due to avoidance of a step in leather making; this reduces water and chloride input. Water usage through reduced float tanning techniques are required to reach atom economy levels of above 90% in chrome tanning. Our study indicates that such efficiencies are achievable as removal of water as an input from the atom economy evaluation increases % atom economy. The present work thus provides an insight on challenges and hurdles to be addressed for implementing green chemistry concepts in leather processing.

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SUPPLEMENTARY INFORMATION:

Procedure for ethanolamine-assisted chrome tanning[15]

Process	Chemicals	%	Duration	Remark
Ethanolamine	Water	75	Drummed for 10 min	
pretreatment	Sodium chloride	10		
	Formic acid	1		
	Water	10	3 feed with 10 min interval	
	Ethanolamine	1		
	Water	10	Run for 30 min	
	Sulfuric acid	1		
	Water	10	2 feed with 15 min interval	Check for pH 2.8-3.0
Chrome tanning	Basic chromium sulfate	6	Drummed for 60 min	Check for penetration
Basification	Sodium formate	1	Drummed for 10 min	
	Sodium carbonate	1	3 feeds with 10 min interval + 60 min	Check for pH 3.8-4.0
	water	10		Piled overnight

Procedure for direct chrome liquor recycle[16]

Process	Chemicals	%	Duration	Remark
Pickling	Preacidified	60		
	Spent liquor*			
	Sodium chloride	3	Drummed for 10	
	Sulfuric acid	0.5	min	
	Water	5	2 feed with 15 min interval	Check for pH 2.8-3.0
Chrome tanning	Basic chromium sulfate	6	Drummed for 60 min	Check for penetration
	Water	10	Drummed for 15 min	
Basification	Sodium formate	1	Drummed for 10 min	
	Sodium carbonate	1	3 feeds with 10 min interval + 60 min	Check for pH 3.8-4.0
	water	10		Piled overnight

* Chrome liquor collected from the conventional trial and acidified with sulfuric acid to pH 1

Procedure for pickleless chrome tanning[17]

Process	Chemicals	%	Duration	Remark
	Water	100	Drummed for 10 min	
	Formic acid	0.1		
	Sulfuric acid	0.3		
	Water	10	4 feed with 10 min interval + 30 min	Check for pH 5.2-5.5 Drain 50% float
Chrome tanning	Basic chromium sulfate	6	Drummed for 60 min	Check for penetration
				Check for pH 3.8-4.0, piled

Procedure for conventional chrome tanning[17]

Process	Chemicals	%	Duration	Remark
Pickling	Water	100	Drummed for 10 min	
	Sodium chloride	10		
	Sulfuric acid	1		
	Water	10	3 feed with 10 min interval + 30 min	Check for pH 2.8-3.0
Chrome tanning	Pickle liquor	50		
	Basic chromium sulfate	8	2 feeds with 15 min interval	Check for penetration
	Water	50	Drummed for 15 min	
Basification	Sodium formate	1	Drummed for 10 min	
	Sodium carbonate	1	3 feeds with 10 min interval + 60 min	Check for pH 3.8-4.0
	water	10		Piled overnight