Utilization Of Black Liquor Lignin In Detergent Making

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ABSTRACT

Unlike the large scale paper mills which use the black liquor for recovery of chemicals, the small and medium mills usually throw away the black liquor after pulping, leading to pollution problems. It is therefore required for these mills to have a proper management of black liquor. The black liquor is an aqueous solution of lignin residues, hemicellulose, and the inorganic chemicals used in the process. The aim of this study was to utilize lignin from the black liquor for detergent making. Lignin was isolated from black liquor by treating it with dilute hydrochloric acid. About 75% lignin got precipitated which was then filtered. This lignin was used as an active material for making powder detergent. The detergent was tested for its properties like detergency, foaming and surface tension. This detergent gives improved cleaning of cloth, higher brightness. However, it has a slight colour.

Introduction

Approximately 7 tons of black liquor (15% solids by weight of which 10% are inorganic and 5% are organic) are produced in the manufacture of one ton of pulp. Most of the large kraft pulp mills use recovery boilers to recover and burn much of the black liquor they produce, generating steam and recovering the cooking chemicals. This has helped paper mills reduce pollution problems, reduce their use of chemicals by recovery and reuse, and become nearly energy self-sufficient by producing, on an average, 66% of their own electricity needs on-site.

Most small and medium paper mills do not have a recovery system for black liquor. These mills can utilize the lignin of the black liquor for making detergent[1]. Detergents are short-chain alkyl naphthalene sulphonates, made by coupling propyl or butyl alcohols with naphthalene and subsequent sulphonate[2]. Surface active agents or surfactants have distinct molecular structures that give rise to their molecular properties[3]. A surfactant is an organic compound that encompasses in the same molecule two dissimilar structural groups, viz. water soluble and water insoluble moieties[4]. The composition, solubility, properties, location and relative sizes of these dissimilar groups in relation to the overall molecular configuration determine the surface activity of the compound[5]. Making a detergent from waste liquor can be a good management practice.

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Experimental

The black liquor sample was collected from a nearby mill, which was using kraft pulping process and analyzed for its contents. The following observations were made:

pH of black liquor = 12.4
Total Solids = 15.7 %
Na_2CO_3 as Na_2O = 27.4 g/l
NaOH as Na_2O = 3.4 g/l
Na_2S as Na_2O = 5.6 g/l
Na_2SO_4 as Na_2O = 1.1 g/l

Lignin was isolated from black liquor by treating it with dilute hydrochloric acid to reduce the pH to 8.5. The lignin got precipitated which was then filtered and washed with distilled water. It was then treated with dilute sulfuric acid in the temperature range of 45 – 50°C. The yield was found to be 21 g/l, i.e. 2.1 %. This lignin was used to make detergent.

TABLE - 1: Composition of Powder Detergents Based On Lignin

Sr. No.	Ingredient	Samples (% By Weight)			
		P1	P2	P3	P4
1	Lignin	-	10	20	30
2	- Olefin sulphonate	30	20	10	-
3	Sodium Carbonate	45	45	45	45
4	STPP	4	4	4	4
5	EDTA	0.5	0.5	0.5	0.5
6	CMC	1	1	1	1
7	Sorbitol	7	7	7	7
8	1% Perfume and Colour	0.8	0.8	0.8	0.8
9	Water	11.7	11.7	11.7	11.7

TABLE - 2: Analysis of Prepared Detergent Powders

Powder Detergent	Moisture (%)	Concentration (%)	Foam Volume (cc)				pH	Surface Tension (dynes/cm)
			0 min	5 min	10 min	15 min		
P1	16.52	0.1	280	270	270	260	7.5	27.51
		0.25	280	270	270	270	7.5	26.14
		0.5	300	290	280	280	7.5	26.01
		1.0	330	320	320	310	7.5	25.78
P2	15.50	0.1	250	240	230	210	7.0	30.12
		0.25	270	250	240	230	7.5	29.28
		0.5	290	290	270	260	7.5	28.98
		1.0	310	310	300	300	7.5	28.26
P3	14.85	0.1	150	140	130	120	7.5	29.16
		0.25	160	140	140	130	7.5	28.35
		0.5	170	160	150	140	7.5	27.98
		1.0	180	170	170	160	7.5	27.19
P4	12.82	0.1	130	120	110	110	7.0	24.26
		0.25	140	130	130	130	7.0	23.85
		0.5	150	150	150	140	7.5	21.21
		1.0	160	160	150	150	7.5	20.92

TABLE - 3: Percent Detergency Evaluation of Prepared Detergent Powders

Cloth	Medium for Staining	Concentration (%)	% Detergency by Detergent Powders				
			P1	P2	P3	P4	Commercial Samples
POLYESTER	Soil Solution	0.1	90.58	92.35	90.01	91.47	93.18
		0.25	91.76	94.63	90.95	92.86	93.98
		0.5	92.70	96.09	92.17	94.50	95.60
		1.0	94.51	97.32	93.98	95.69	96.16
	Tea Solution	0.1	92.92	93.41	91.38	92.01	92.99
		0.25	97.07	97.32	93.68	94.68	95.63
		0.5	97.07	98.43	95.25	95.79	96.32
		1.0	98.29	98.96	96.99	96.38	97.88
	Coffee Solution	0.1	88.30	90.64	88.36	89.07	89.78
		0.25	91.23	91.52	90.71	91.08	90.15
		0.5	92.98	92.69	91.17	91.85	91.25
		1.0	94.15	97.13	92.98	94.68	91.96
TERRICOT	Soil Solution	0.1	95.17	92.93	93.56	91.51	93.14
		0.25	95.52	94.14	93.79	93.09	94.58
		0.5	96.21	95.68	94.63	94.79	95.86
		1.0	97.41	97.75	96.31	96.05	97.01
	Tea Solution	0.1	90.15	89.99	87.68	88.78	90.12
		0.25	91.63	90.43	89.90	90.12	91.12
		0.5	93.06	91.86	91.56	92.05	93.45
		1.0	94.02	94.26	93.65	93.12	93.96
	Coffee Solution	0.1	92.95	92.68	90.43	90.14	93.21
		0.25	94.52	95.04	91.67	92.39	94.15
		0.5	96.86	97.91	93.11	93.64	95.96
		1.0	98.95	98.90	95.33	94.56	96.69
COTTON	Soil Solution	0.1	80.83	75.56	84.12	75.18	80.12
		0.25	80.01	76.93	85.96	76.52	83.31
		0.5	83.46	80.21	89.15	79.23	85.00
		1.0	87.37	83.85	90.19	80.96	87.77
	Tea Solution	0.1	84.63	81.63	84.44	81.25	80.48
		0.25	85.03	85.03	85.02	84.96	84.61
		0.5	87.07	88.09	87.06	86.91	86.05
		1.0	90.13	90.13	89.97	88.28	89.95
	Coffee Solution	0.1	87.82	83.63	85.20	81.04	84.56
		0.25	88.79	86.95	87.32	83.45	86.99
		0.5	92.49	91.30	90.01	87.95	89.91
		1.0	93.67	91.52	90.99	90.89	90.98

Four types of detergents were made. Their composition is given in Table 1.

– Olefin sulphonate and sorbitol are used 100% based on their actual % solids. The actual percent solids of these raw materials are:

– Olefin sulphonate = 70%
Sorbitol = 70%

The prepared detergent powders P1, P2, P3 and P4 were analysed for foam volume and surface tension for different concentrations and the results are given in Table 2.

The different cloth samples, which were washed, dried and ironed, were used to find out percent detergency. The % detergency was found out using Lambert's and Sander's formula[6].

$$\% \text{ Detergency} = \frac{Rw - Rs}{Ro - Rs} \times 100$$ where;

Rw = Reflectance measured on washed cloth
Rs = Reflectance measured on stained cloth
Ro = Reflectance measured on original cleaned cloth

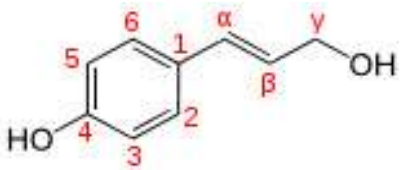
The reflectance of different cloth samples was measured using the Reflectance Meter (Brightness tester for paper / pulp, cat no. UEC-1018 AI, photovolt type, Universal Engineering Corporation, Saharanpur). The readings were noted and percent detergency, as given in Table 3, was calculated by using the above formula.

Results and Discussion

Lignin is a complex polymer, built up of hydroxyl phenyl propane units and is therefore, phenolic in character. In both, soda and kraft liquor, the lignin is degraded by the cooking chemicals and the fragments dissolve in the liquor. The alkali lignin contains two types of acidic groups- phenolic acids and carboxylic acids[7]. The three common monolignols are given below:

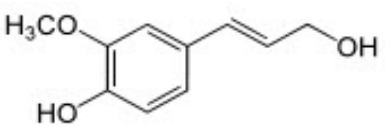
Precursors of Lignin

(1) paracoumaryl alcohol,



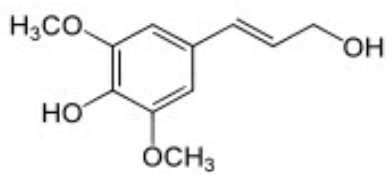
(1)

(2) coniferyl alcohol



(2)

(3) sinapyl alcohol.



(3)

Black liquor from kraft pulping was taken, as it contains lignin in the form of phenyl sulfonates, which is the active chemical in detergent making. From Table 1, it is evident that lignin varied from 10 to 30%. Similarly, alpha olefin sulphonate (AOS) has been used form 30 to 10 %. A slightly higher percentage of sodium carbonate i.e. 45% has been used. The proportion of sodium tri polyphosphate has been restricted to 4% only. A small proportion of sorbitol has been inducted to avoid the dusty feel and behavior of detergent. Sorbitol also reduces the irritating feel due to high proportion of sodium carbonate and gives a well feel to the detergent. Detergent powders P2 and P3 appear to be the best which are a 50:50 combination of lignin and AOS. The special features of these formulations were:

1. Linear alkyl benzene sulphonate was not used.
2. Very small amount of STPP was used- only 45%, and therefore, the problem of pollution was reduced considerably.

From Table 2, it is observed that the foaming gradually decreases from P1 to P4. This is, because in P1, foaming was wholly contributed by AOS whereas in P2 and P3, moderate foaming was obtained due to synergism of lignin and AOS. However, P4 gave very less foaming compared to P1 due to absence of AOS. Though foaming decreases, reduction in surface tension shows excellent results with increase in the lignin percentage which proves its good detergency quality as is obvious from Table 3. The stain removing ability of detergent made from lignin is more than 95% for polyester and terricot while it is about 90% in case of cotton; when compared to the commercially available detergent. The other detergent powders which have been identified to moderate foaming and low foaming could be recommended for special applications, such as for use in washing machine, floor cleaning etc.

Detergent P4 was based on purely lignin and has excellent soil and stain removing capacity which is comparable to commercial detergents and no special additives like enzyme or perborate have been used.

Conclusions

The detergent based on lignin gives appreciable cleaning and higher brightness when compared to the commercially available detergent. It is also more eco-friendly than the commercially available one. However, it has a slight colour. At the same time, it helps in curbing the pollution load to the environment and detergent is expected to cost lower than the Conventional detergent as the expensive active component has been replaced by the low cost lignin.

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