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Interaction Effect of Pulping Variables and Storage Time on Pitch Deposit During Kraft Pulping of Mixed Hardwoods

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Abstract
The effects of pulping variable, wood classification and storage time on pitch deposition during kraft pulping of mixed tropical hardwood species growing in Nigeria were investigated. Storage time have effect on pitch deposition in all the groups. Pulp resin decreased from 0.535% in control experiment to 0.235% after the sixth month in group A. In group B, pulp resin decreased from 0.560% for the control experiment to 0.243% after the sixth month while in group C, pulp resin decreased from 0.529% to 0.277% after the sixth month. Pulp resin is also influenced by effective alkali concentration of the pulping medium. With increase in effective alkali concentration from 13% to 15%, pulp pitch was reduced. The interaction effect of storage and effective alkali concentration was not significant indicating that reduction in pulp pitch caused by effective alkali concentration in the different group occurs at about the same rate. However, interaction effect of maximum temperature and effective alkali concentration was significant. This occurs as the combination of high temperature and high effective alkali concentration causes saponification of triglycerides and esters of wood resin to fatty acids which tend to form liquid crystals. On cooling the cook below 100^{o}C during washing, the crystals form micelles which dispersed and which are washed out of the pulp.
Keywords: *pitch, resin, effective alkali concentration, storage, hardwoods, pulping.*

Introduction

One of the major problems militating against optimal utilization of mixed hardwoods for pulp and paper production is the variability in their properties. In tropical countries, hardwoods occur in mixed stands in natural forests, making commercial pulping of single species from natural stands unprofitable. The problem is compounded by the high variation in the extractive contents of tropical hardwoods.

The wood extractives or resins are cell wall components which can be removed using solvents, such as acetones, ether and water. They have relatively small molecules <C40 and are under genetic control in wood species. In hardwoods, the most predominant extractives are fatty acids which make up 60-90% of the total extractive contents. During pulping, the extractives are librated from the parenchyma cells, agglomerate and deposit as pitch on process equipment, causing considerable downtime, reduction in mill efficiency and in the quality of the pulp and paper produced. The deposited pitch also reduces the pulp yield and strength properties of paper. The pitch deposit problem was encountered at the Nigeria Paper Mill, Jebba in the mid 1980's before the mill stopped production in the early part of 1990. The effect of wood storage on pitch deposit during pulping of the mixed hardwood species was reported by Ogunwusi (2012). Also, the influence of the wood extractives on pitch deposit during pulping of the mixed hardwood has been reported by Ogunwusi and Onilude (2009). Likewise, the effect of effective alkali concentration on pitch deposit has also been reported (Ogunwusi, 2009). However, information on the interaction effects of pulping time, temperature and effective alkali concentration, wood extractives, chips storage time on pitch deposit during kraft pulping of the mixed tropical hardwood species is scarce in literature. The present study is carried out to determine the interaction effects of these variables on pitch deposition during kraft pulping of fifteen selected mixed tropical hardwood species.

Materials and Methods

Materials for wood quality studies

The fifteen hardwood species utilized in the study comprised of *Acacia nilotica* wild ex linn Deivar nilotica*;* *Afzelia africana* Smith*;* *Albizia zygia* (D. C), J. F. Macbr; *Anogeissus leiocarpus* (D. C), Guel and Perr; *Butyrospermum* *paradoxum* Geartn F. (Aepper); *Daniellia oliveri* (Rolfe) Hustch; *Detarium senegalense* J. F. Gmel; *Isoberlina doka* Graib et. Stapf; *Lannea acida,* A. Rich; *Mitragyna inermis, Parinarium kerstingii* Engl; *Parkia felicoida* keay; *Prosopis africana* Taub; *Pterocarpus erinaceus* Poir; and *Sterculia setigera.* All the samples were collected from the derived savanna forest at Oke Awon near Jebba (Latitude 9.3°N, Longitute 4.46°E). For wood quality studies, five trees of each species selected at random were felled and wood discs about 7.5cm thick were taken at breast height. The sample discs from each tree were immediately wrapped in plastic bags to prevent loss of moisture during transportation. The discs were stored in a cold room until required for test analysis.

For pulping studies, the fifteen samples were classified into three homogeneous groups A, B and C by the application of the Scheffe (1985) Test Method. The first Group (Group A) was made up of ten species, second group (Group B) three species and the third Group (Group C) two species. Samples of tree species from each group were felled, delimbed, crosscut into pulpwood sizes and properly marked for proper identification. The trees were free of decay. The cross cut samples were transported to the Nigeria Paper Mill, Jebba where they were arranged on species basis. Each species was debarked with a drum barker, chipped with the commercial chipper and screened through an industrial sieve accepting 5mm x 30mm chips. The chips were bagged, weighed and thoroughly mixed together in proportions of 67kg per species in Group 1, 223 kilogrammes per species in Group 2 and 335kg per species in Group 3. The ratios were used based on the number of the species that made up each group. The thoroughly mixed species were conveyed to the open chip storage yard and store in the three groups for a period of six months. Samples were collected for control study, and subsequently, once, in two months for determination of alcohol benzene solubility of the stored wood chips, caustic soda solubility of the wood species and for pulping studies.

Determination of Alcohol-Benzene Soluble Extractive Content and 1% Caustic Soda Solubility of wood samples

Two out of the five test specimens belonging to each species were debarked and 5cm thick strips were removed from the middle of each disc. The strips were pulverized and used for alcohol benzene soluble extractive content and 1% caustic soda solubility determination. The alcohol benzene extractive content was determined by using the procedures outlined in American Standard of Testing Methods (2007)-D-1107 while the 1% caustic soda solubility of wood chips was determined in accordance with American Standard of Testing Methods (2007)-D-1109.

Classification of the Wood Species into Extractive Content Groups

The results of the wood extractive contents of the species were subjected to analysis of variance test to determine if the variation observed were due to chance or were significant at 0.05 test level. After this, the results were classified into wood extractive content homogeneous groups using Scheffe's (1985) Method. The result obtained was used for subsequent studies.

Preparation of Materials for Pulping Studies

Kraft pulping studies were carried out using the laboratory facilities of the Nigeria Paper Mill, Jebba. The batch rotary laboratory digester was used. For each cook, the moisture content of representative sample of wood chips was first determined. The result obtained was used to calculate the actual amount of wood chips whose bone dry quantity will amount to Wta which is equivalent to 1000g using the following equation $Wta = ODwt\ x(1+\%mc/_{100})$ where

Wta = Weight of chips required, ODwt = Bone dry weight of chips required and mc = moisture content percent.

Two cooks were performed on the composite mixture of chips using the following pulping parameters:

Effective alkali	13%, 15% and 17%
Temperature	160°C and 170°C
Time at maximum temperature	60mins. and 90 mins.
Sulfidity	25%
Liquor to wood ratio	4:1

During each cook, temperature and pressure changes were recorded at 5 minutes intervals until the digester temperature attained 130°C. The temperature was held constant at this level for 3 minutes after which the digester was relieved of accumulated gases and the temperature allowed to increase to the predetermined level and held there till the expiration of the time at the maximum temperature. After each cook, the pulp was thoroughly washed, screened, weighed and dried after removing samples for moisture content and yield determinations.

Pulp Property Characterization

The total pulp yield was determined as a percentage ratio of the bone dry weight of pulp and rejects to the bone dry weight of chips charged into the digester. The screened pulp yield was calculated as a percentage ratio of bone dry weight of pulp minus bone dry weight of rejects to the bone dry weight of chips charged into the digester. The percent screen was obtained by deduction of screened yield from total yield. The result was then divided by the bone dry weight of chips charged into the digester. The pulp resin was determined in accordance with American Standard of Testing Methods (2007)-D-1107, while the pulp permanganate number was determined in line with procedures outlined in TAPPI Standard T214 (2007). The black liquor specific gravity was determined using the method and procedures outlined in TAPPI Standard T625 (2007).

Pulp Property Test

Laboratory beating experiments were carried out in accordance with TAPPI Standards – T200 (2007). Pulp samples were beaten to 10, 20, 30, 40, and 50°SR levels and pulp freeness tested in accordance with procedures outlined in TAPPI Standard – T227 (2007).

Results and Discussions

The alcohol benzene soluble extractive content varies considerably between species (Table 1). The values obtained in the study ranged from 1.82 percent in *A. leiocarpus* to 14.30% in *P. felicoida.* These values were higher than 1.0 to 5.0% reported for temperate hardwood species by Yew (2010). Analysis of variance test showed the differences in the alcohol benzene soluble extractive contents of the wood species to be significant (Table 2).

Table 1:Mean, Ranges, Coefficient of Variation for Alcohol Benzene Extractive Contents of the Fifteen Sampled Hardwood Species

S/N	Species	Statistical parameters		Coefficient of
		Mean	Range	variation (%)
1.	*Daniella oliveri*	6.10	4.40 – 6.20	23.00
2.	*Annogeissus leiocarpus*	1.82	1.74 – 1.88	3.00
3.	*Butyrospermum paradoxum*	5.90	5.30 – 7.30	16.00
4.	*Detarium senegalense*	2.67	2.60 – 2.70	18.00
5.	*Isoberlina doka*	2.67	3.40 – 4.20	10.00
6.	*Lannea acida*	4.56	4.50 – 4.60	10.00
7.	*Petrocarpus erinaceus*	11.07	7.60 – 11.83	23.00
8.	*Parkia felicoida*	14.03	13.60– 15.01	3.90
9.	*Parinarium kerstingii*	2.29	2.56 – 2.68	16.00
10.	*Prosopis africana*	4.07	3.74 – 4.50	8.50
11.	*Afzelia africana*	2.64	2.60 – 2.70	1.60
12.	*Mitragyna inermis*	2.50	2.30 – 2.60	6.00
13.	*Sterculia setigera*	3.50	3.50 – 3.60	1.30
14.	*Albizia zygia*	3.87	3.52 – 4.55	12.00
15.	*Acacia nilotica*	53.20	2.64 – 3.51	13.00

The sampled species were classified into three major distinct groups based on their extractive contents (Table 3). Group A consisted of *A. nilotica, A. zygia, A. leiocarpus, A. africana, D. senegalense, I. doka, M. inermis, P. kerstingii, P. africana, S. setigera while* Group B species were made up of *B. paradoxum, D oliveri,* and *L. acida*. The species in Group C were *P. erinaceous* and *P. felicoida*. This finding is in agreement with previous studies by Uprichard (2000) who reported wood extractive to be the most suitable indicator for classification of beeches into pulping groups. It is also in agreement with the species elimination method for pitch control reported by many workers including Doueck and Allen (1991) and Allen *et al*, (1991) for temperate wood species.

Table 2: Analysis of Variance for Comparing Alcohol-Benzene Soluble Extractive Content of the Fifteen Hardwood Species

Sources of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	F Ratio	F Probability	Test of Significance
Between species	14	463.24	33.09	28.36	0.0	*
Within species	30	30.99	1.16	-	-	-
Total	44					

* Statistically significant at 0.05 test level.

The effect of storage time on species classification, alcohol benzene soluble extractable content of wood chips and one percent caustic soda solubility are shown in Table 4. Alcohol benzene soluble extractive content decreased with increase storage time. It decreased from 3.23% for control experiment to 3.20 in the second month of storage. It further decreased to 2.34% and 1.96% after the fourth and sixth months of storage respectively. The same pattern was observed in groups B and C. This indicated that the extractive contents of the wood chip are oxidized with increase in storage time.

Table 3:Result of Wood Extractive Classification of the Fifteen Hardwood Species using Scheffe's (1985) Method

S/N	Species	Group 1	2	3
1.	*S. setigera*	3.5		
2.	*A. leiocarpus*	1.83		
3.	*B. paradoxum*		5.9	
4.	*I. doka*	3.60		
5.	*D. senegalense*	2.67		
6.	*L. acida*		4.50	
7.	*P. einaceus*			11.07
8.	*M. inermins*	2.50		
9.	*A. zygia*	3.87		
10.	*D. oliveri*		6.1	
11.	*P. felicoida*			14.3
12.	*P. kerstingii*	2.29		
13.	*A. Africana*	2.64		
14.	*A. nilotica*	3.20		
15.	*P. Africana*	4.02		

However, in all the groups, one percent caustic soda solubility increased with storage duration (Table 4) indicating microbial attack and degradation of the wood chips. In Group A, it increased from 20.92% in the control experiment to 20.92% in the 2nd month. This further increased from 21.72% to 26.90% in the 3rd and 4th months of storage respectively.

Storage time also influence the pulp pitch content (Table 5). The pulp resin decreased from 0.535% in control experiment to 0.235% after the sixth month in group A. In group B, pulp resin decreased from 0.560% for the control experiment to 0.243% after the sixth month while in group C, pulp resin decreased from 0.592%. to 0.277% after the sixth month of storage.

The effect of chips classification (grouping) and effective alkali concentration on pulp properties are shown in Table 6. In all the groups, increasing effective alkali concentration decreases total and screened pulp yield. The pulp resins also decreased with increasing effective alkali concentration. In group A, pulp resin decreased from 0.48% to 0.18% when effective alkali concentration was increased from 13% to 17%. Also in groups B and C, pulp resin decreased from 0.48% to 0.25% and from 0.52% to 0.25% respectively when the EA concentration increased from 13% to 17%.

The effects of storage time on total and screened yield and on pulp pitch content were significant (Table 7). This indicated that with increasing storage period, the wood extractive content is reduced and this may have led to decrease observe in pulp yield. Also it is possible that with increase in storage time, cellulose depolymerisation may take place as a result of attack by microorganisms. The effect of grouping on total yield was significant (Table 7). Also the effect of effective alkali concentration on pulp pitch, screened yield and % screens are significant. The interaction effects of storage and effective alkali concentration on pulp pitch content is not significant indicating that the rate of reduction in wood extractives in all the groups occurs at about the same rate during storage. The maximum pulping temperature influences pulp pitch content (Table 7). This may be explained by the fact that in the kraft digester, the conditions of high temperature and high alkali concentration causes saponification of glycerides and esters of the wood resin to yield fatty acids. The latter tend to form liquid crystals which are probably lamella in shape and form separate droplets (Allen and Laponite, 2003). On cooling the cook below 100°c, because of the high ionic strength, the droplets have a tendency to coagulate or salt out onto the fibres. During washing the liquid crystalline phase form micelles (Lindstrom *et al.* 1988; Back ,2000; Allen and Lapointe, 2003 and Bjorklund Jasson *et. al.*, 1985) which aids in deresination because some of the unsaponifiable portion of the wood resin dissolves in the middle of the micelles through solubilisation. Once dispersed, the micelles can be washed out. Hence the formation of micelles upon re-dispersion of liquid crystals is highly temperature dependent.

Table 4:Effect of storage time on alcohol benzene soluble extractable contents and on caustic soda solubility of wood species from the three groups

Storage Duration (months)	Species classification (groups)	Alcohol benzene extractable content	One percent caustic soda solubility
0	A	3.23	20.92
	B	4.10	27.62
	C	10.69	25.14
2	A	3.20	20.95
	B	3.73	28.10
	C	9.19	26.27
4	A	2.34	21.72
	B	2.60	29.06
	C	7.22	26.90
6	A	1.96	22.76
	B	2.10	29.61
	C	6.84	27.41

Table 5: Effects of chip storage duration on the Properties of pulp and the specific gravity of black liquor produced from pulping chips from the three species groupings.

Storage Duration (months)	Species classification (groups)	Total pulp yield (%B.D. wood)	Scrreened yield (%B.D. wood)	Screens (%)	Pulp resin (%)	Black liquor specific gravity	Pulp permanganate number
0	A	59.68	46.58	1.29	0.535	1.11	23.01
	B	51.85	44.86	1.49	0.560	1.10	22.10
	C	54.92	45.88	1.15	0.592	1.14	22.30
2	A	54.72	41.87	0.97	0.293	1.17	23.04
	B	49.19	38.19	0.75	0.382	1.13	22.88
	C	49.34	36.28	0.97	0.347	1.14	22.60
4	A	48.14	37.38	1.04	0.296	1.11	24.07
	B	49.67	38.37	1.04	0.271	1.09	23.04
	C	44.34	33.16	0.92	0.309	1.07	23.97
6	A	45.23	36.16	1.58	0.235	1.10	25.75
	B	45.84	38.18	1.31	0.243	1.14	26.44
	C	44.19	33.10	1.88	0.277	1.03	28.28

Table 6:Effect of species classification and effective alkali concentrations on the properties of paper produced from chips from the three groups

Chip classification	Effective alkali concentration (% B.D. wood)	Total pulp yield (% B.D. wood)	Pulp resin (% B.D. wood)	Screened yield	% Screens	Specific gravity	Permanganate
A	13	53.70	0.48	37.66	1.80	1.10	7.99
	15	52.68	0.34	42.67	1.14	1.12	23.37
	17	49.27	0.18	42.64	0.75	1.12	22.89
B	13	49.41	0.48	39.31	1.35	1.10	25.52
	15	48.10	0.31	40.40	1.24	1.13	24.28
	17	46.16	0.25	41.36	0.94	1.14	20.54
C	13	47.68	0.52	35.89	1.67	1.11	24.93
	15	46.12	0.32	39.58	1.22	1.11	23.76
	17	44.13	0.25	41.42	1.00	1.15	22.74

Table 7: Analysis of variance for comparing the effects of pulping variables, grouping and storage time on pulp properties.

Source of variation	Total yield	Screened yield	% screens	Pulp pitch content
M	*	*	*	*
G	*	NS	NS	NS
EA	NS	*	*	*
Te	*	NS	*	*
Ti	NS	NS	NS	NS
MxG	NS	NS	NS	NS
MxTe	*	NS	*	NS
MxEA	*	*	*	NS
GxEA	NS	*	NS	NS
EAxT	NS	NS	NS	NS
MxTi	NS	NS	NS	NS
GxTi	NS	NS	NS	NS
GxTe	NS	NS	NS	NS
EAxTe	NS	*	NS	NS
TixTe	NS	NS	NS	NS
MxGxEA	NS	NS	NS	NS
MxGxTi	NS	NS	NS	NS
MxEAxTi	NS	NS	NS	NS
GxEAxTi	NS	NS	NS	NS
MxGxTe	NS	NS	NS	NS
MxEaxTe	NS	NS	NS	NS

M - Month G - Groups EA - Effective Alkali Concentration T_1 - Time T_e - Temperature
* - Statistically significant at 0.05 level NS - Not Stastically significant at 0.05 level

Conclusion

Pitch deposit problems in kraft pulp mills utilizing mixed hardwood species can be combated by a number of variables. Pulp pitch can be reduced by grouping the wood species into homogenous extractive classes to enable predictability of pulp pitch content. This paper has shown the possibility of controlling pitch deposition in kraft pulp mills by adjusting the pulping variables. Application of high effective alkali concentration will reduce pulp pitch content. However, this does not depend on storage period, as effective alkali operate independently in the pulping medium. Increase in storage time also lead to reduction in pulp pitch content. However, a two months storage period is always advocated to prevent attack of fungi on stored chips which may lead to reduction in yield as observed in this study. The interaction effect of high temperature at 170°C and 17% effective alkali concentration leads to formation of micelles which later goes out of the system during washing thereby reducing pitch problems in mixed pulping. Thus for effective pitch control with the aid pulping variables, high temperature and high effective alkali charge are required.

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