"The affecting factors during acidifying kraft wheat straw black liquor for precipitating lignin"

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INTRODUCTION :

In the Chemical recovery operation process, two of the most troublesome problems are Silica disturbance and black liquor instability during storing. One of the methods to eliminate silicon disturbance is desilication by reducing pH value of weak black liquor. In order to maintain the heating value of black liquor solids, the precipitation of lignin in black liquor must be avoided during the desilication. To achieve this goal, the optimum separating point (pH value) of Silica from lignin during acidifying weak black liquor should be determined. Many researchers (1, 2, 3) have investigated he relations between silicon content and pH value of black liquor. The key is to find out the relation between pH-value and residual lignin content during acidifying black liquor, which is represented by the acidifying residual lignin curve or ARLC, and its affecting factors. On the other hand, the precipitation regularity of lignin during acidifying black liquor can be used to explain and solve the difficult problem of black liquor storing and provide some theoritical basis for precipitaing lignin from black liquor for utilizing lignin or reducing pollution. Due to above reasons, this paper deals with lignin acidifying precipitation regularity of sulphate wheat straw black liquor and its affecting factors by means of study on relations of residual lignin content and pH-value during acidifying black liquor, that is, acidifying residual lignin curve for short ARLC.

EXPERIMENTAL METHODS :

1. Black liquor Preparation :

Except the test of changing cooking condition, the experimental black liquors are prepared as following : Cook in a 15-l electrically heated digester, alkaline demand 16.0% (on bone dry raw material), sulfidity 9.6%, ratio of raw material to liquor 1 : 6, cooking temperature 155°C, "to the temperature period" 1 hour 30 minutes, "at the temperature" 30 minutes, pulp hardness 9-11 ($KMnO_4$ value), residual alkali 8-10 g/l.

2. Acidifying residual lignin curve or ARLC.

Divert 4 ml black liquor into 70 ml centrifugal tube, adjust the amounts of the water and the acid added (7.6 NH_2SO_4) and make their total volume as 8 ml. After stirring, centrifuge the sample for 20 min under the speed of 4000 rpm and centrifugal coefficient Fc 1968. Take out 0.5 ml supernatant and dilute 2000 times with 0.01N sodium hydroxide. Measure the absorbance (A_{208}) of diluted solutions (the experiential coefficient of absorbence : ϵ 208 = 97.1 l/g cm) and pH-value of the centrifuged superr atant. Plot A_{208} against pH-value, i.e. the acidifying residual lignin curve.

Results and Discussion

1. The acidifying residual lignin curve of sulfate wheat straw black liquor or ARLC.

Fig. 1. is ARLC of sulfate wheat straw black liquor, in which the black liquor density at 20°C is 1.050 g/l and the acidifying temperature is 21°C. Obviously, characteristic points (pH value) of lignin precipitation respectively are : starting precipitation point (SPP) pH8.1, maximum precipitation point (MPP) pH 6.2 and ending precipitation point (EPP) pH 3.0. According to precipitation points, the lignin precipitation process could be divided into four stages : Lignin

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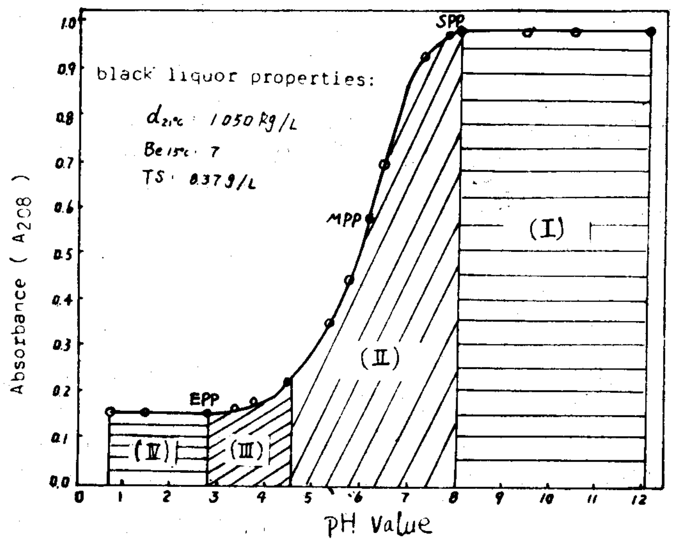

Fig.1: ARLC of sulfate wheat straw black liquor

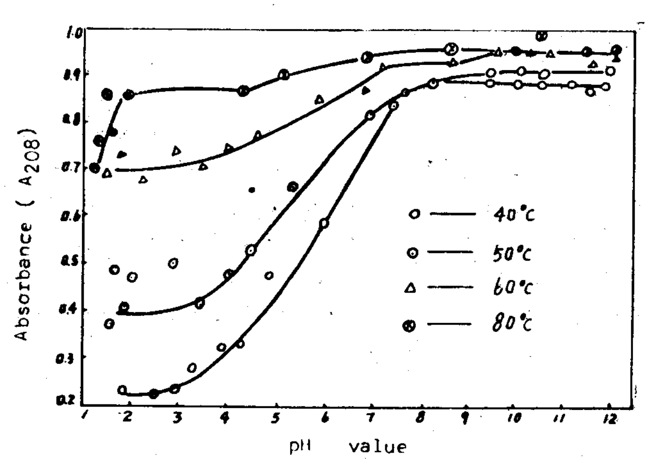

Fig.2: Effect of acidifying temperature upon ARLC

stable (I), rapid precipitating (II), stagnant precipitating (III) and residual stage (IV) (Fig. 1). The optimum point for separating silicon from lignin should be the point where maximum amount of silicon in black liquor has precipitated before the lignin precipitation starts, i.e. the pH value just higher than SPP (pH8.1 here). On the other hand, in order to precipitate almost all the acid insoluble lignin from black liquor, the acidifying end pH-value should be controlled lower than EPP (pH 3.0 here). The residual lignin when the EPP has reached is called unprecipitable lignin or the residual lignin.

Black Liquor is colloidal in nature. According to the principle of the colloid chemistry, the black liquor properties such as temperature, density, ionic strength and lignin structure etc would affect the lignin stability, hence in turn affect the ARLC. Above factors will be discussed respectively.

2. Factors affecting the ARLC.

a) : Acidifying temperature

The test of the effect of acidifying temperature on ARLC was conducted under the condition keeping the Black liquor temperature basically equal to that of the acid used. Fig. 2 is the result. It seems that the influence of temperature of the black liquor or the used acid upon ARLC and precipitation characteristic points is prominent. Under the various acidifying temperatures different ARLC is obtained. With the increase of the acidifying temperature, the SPP moves up to higher pH value and the residual lignin after EPP is increased rapidly. Temperatures are 21, 40, 50, 60 and 80°C, the residual lignin contents are respectively about 3.2, 4.7, 8.4, 15.2 and 17.7 g/l. It may be due to the reaction rate between acid and lignin. It increases as temperature increases and smaller granul is produced.

b) : Black liquor density.

In order to avoid the change of black liquor properties, the black liquor is concentarated under vacuum at room temperature (24—25°C, Vacuum 600mm Hg), the longest concentrating time is limited in 5—6hr. At different density of black liquor, ARLCs are shown in Fig 3, 4. (Appendix 3).

From Fig 3, it can be seen that the influence of black liquor density upon the ARLC is significant. The higher lignin content and total solid content, the more easily the lignin is precipitated and longer is the lignin stable existing range. When black liquor densities are 1.020, 1.084, 1.100, and 1.150 kg/l, the lignin stable existing range are respectively pH 5.75, 8.8, 9.5 and 11.25, and MPPs are about pH 4.6, 5.4, 8.5, and 9.7.

The results show that the more concentrated is the black liquor, the more unstable is the lignin. It can be infered that when the black liquor density is larger than an critical value d_c, the lignin in the black liquor

Appendix I (1) Fffect of Cooking Condition upon ARLC

No.	No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Used Acid		0.00	0.75	1.00	1.15	1.30	1.45	1.75	2.00	3.30	2.40	2.50	2.55	2.60	2.70	4.00	5.00
	pH	13 00	12 40	12.10	11.80	11.50	11.10	10.60	9.70	9.10	8.00	7.50	7.10	6.50	5.55	3.60	1.35
	A208	1.010	0 995	0 994	1.023	1.012	1.022	1 014	1.014	1.033	0.950	0.843	0.686	0.358	0.204	0.163	0.138
	1A208	0.988	0 974	0.973	1.001	0.990	1.000	1.992	0.992	1.011	0.930	0.825	0.671	0.350	0.200	0.159	0.135
	Note				B1 Cooking Condition												
Used Acid		0.00	1.00	1.50	1.75	2.00	2.15	2.30	2.45	2.60	2.75	2.90	3.05	3.25	3.75	4.50	5.00
	pH	12.80	11.50	10.60	9.70	9.10	8.10	7.10	6.60	6.20	5.60	5.40	5.10	4.40	3.60	2.50	2.30
	A208	1.060	1.059	1.060	1.063	1.055	1.042	0.903	0.971	0.572	0.267	0.250	0.230	0.208	0.177	0.169	0.171
	1A208	1.000	0.999	1.000	1 003	0.995	0.983	0.852	0.822	0 540	0.252	0.236	0.217	0.196	0.167	0.158	0 161
	Note				B2 Cooking Condition												

Appendix I (2) Effect of Cooking Condition upon ARLC

	No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Used Acid		0.00	0.25	0.40	0 50	0.75	0.90	1.05	1.15	1.25	1.35	1.50	1.65	1.80	2 00	3 00	4.50
	pH	12.80	11.50	11.00	10.50	10.00	9.30	8.30	8.00	7.50	7.00	6.00	5.50	5.00	4.10	2.40	1.50
	A208	0.953	0.951	0.954	0.952	0 955	0.957	0 957	0 948	0.939	0 896	0.477	0 276	0 238	0.192	0 153	0 152
	1A208	1.000	0.998	1.001	0.999	1 002	1.004	1.004	0.995	0.985	0.940	0 500	0.290	0.251	0 201	0 165	0 160
	Notes	A0 Cooking Condition															
Used Acid		0.00	0.25	0 40	0.55	0.70	0.90	1 00	1 15	1.30	1.45	1 60	1.75	2 00	2 50	3 00	4 00
	pH	12 00	11.10	10.85	10 70	9.85	9.40	8.60	7.60	6.50	5.70	5.00	4 40	3.60	2.90	2.50	2 00
	A208	0.921	0.906	0.918	0.919	0.916	0.924	0.920	0.905	0.805	0.236	0.206	0.178	0.155	0.135	0.133	0 128
	1A208	1.000	0 984	0.997	0.998	0.995	1.007	0.999	0.983	0.874	0.256	0.224	0.193	0.168	0.147	0.144	0 139
	Note	A1 Cooking Condition															
Used Acid		0.00	0 50	0.75	1.00	1.25	1.50	1.75	2.00	2.25	2.50	2.75	3.00	3.25	3 50	4.00	5 00
	pH	13.45	12.85	12.70	12.40	11.40	10.80	10.20	9.60	7.60	6.00	5.10	4.40	3.80	3.20	2.20	1.50
	A208	0.886	0.872	0.880	0.896	0.886	0.884	0.906	0.898	0.881	0.603	0.332	0.214	0.197	0.182	0.173	0.164
	1A208	1.000	0.984	0.993	1.011	1.000	0.998	1.023	1.014	0.994	0.681	0.375	0.242	0.222	0.205	0 195	0.185
	Note	A2 Cooking Condition															

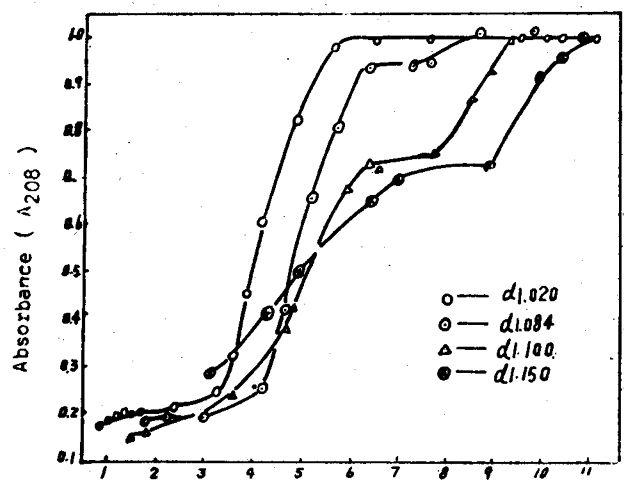

Fig.3: Effect of black liquor density on ARLC

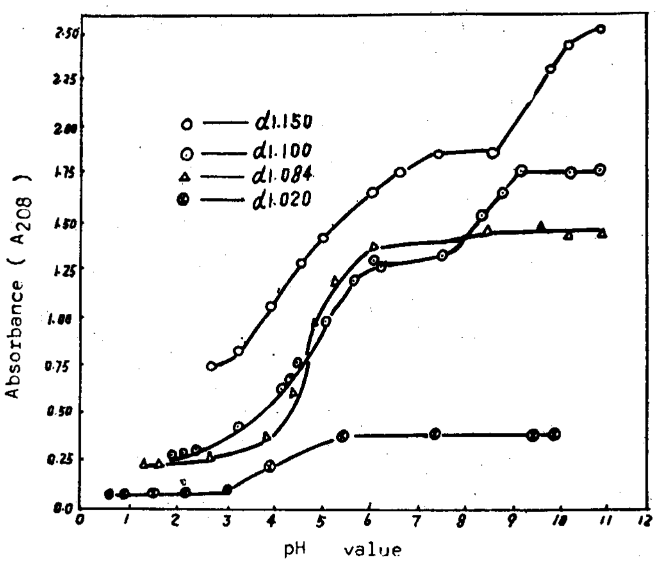

Fig.4: Effect of black liquor density upon ARLC

would be precipitated and seperated by centrigugal force or even by gravity settling without adding any acid.

It is interesting to note that at higher black liquor density, the acute precipitating stage will divide into two Meanwhile, the influence of black liquor density up on the first acute precipitating stage is much stronger than the second one.

Fig 4 is the ARLC, in which the absorbance are normalized to one against A_0. It is shown that though lignin content in black liquor varies, the ratio of residual lignin to the original lignin are nearly same, about 15% by Epp, while the residual lignin concentration increase with elevation of black liquor density (refer to Fig. 3) because there are no drastic impacts (heat, mechanical and chemical treatment) on black liquor.

Thus, the stability of lignin in the black liguor is affectad by the lignin concentration of black liqaor. The higher the black liquor density and lignin content in it, the more the characteristic precipitated points (SPP, MPP) moves up. In the view of extracting lignin, the high concentration of black liquor is favourable, while it will not be desirable in the process of desilification of black liquor where silica precipitation should be completed with lose of lignin.

(c) Salting out effected (or salt concentration).

To investigate the effect of sodium salt (Na_2SO_4 used as salting-out agent) on the ARLC, take 700 ml same black liquor and add various amounts of sodium sulphate, stir untill the solid is completely dissolved and then measure the ARLC as above tests.

The results show us that the salt addition could reduce stability of lignin colloid. The larger the amount of sodium sulfate, the more narrow is the stable existing range of lignin i.e. the SPPs moved towards higher pH-value. When the amounts of sodium culfate added are 0.00, 10 00, 28.57, 40.00, 80 C0 and 12.00 g/l, the SPP of lignin respectively are about pH 7.8, 8.3, 9 2, 9.6, 10.1 and 10.5. With the addition of the salt, the MPP also moves up and residual lignin content reduces.

Comparing the ARLC of black liquor adding the Na_2SO_4 with that of high density black liquor it is easily found that they are very similar. It could be deemed that the enhancement of salting-cut effect is one the causes that the ARLC of strong black liquor has two acute precipitation range.

(d) Ageing effect.

In order to investigate lignin stability during black liquor storage, put 700 ml original black liquor (d 1.050 g/l, pH 12.25) into every 1000 ml beakers, them divide them into two groups. One group is stored open at 10°C and other in 60°C water bath, stir then twice every day with stirring glass rod. After storage for different periods, take them out and measure the ARLC under room temperature.

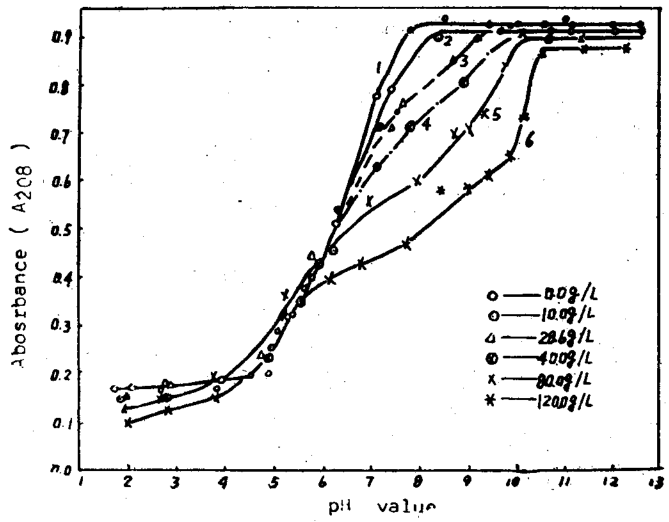

Fig.5: Effect of salt conc, on ARLC

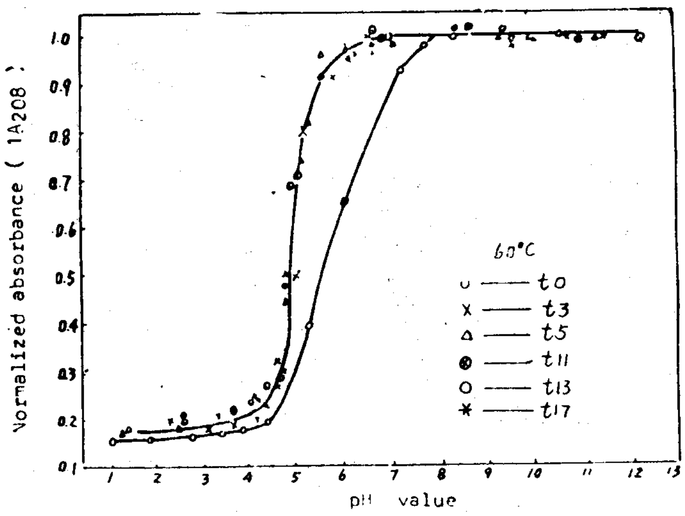

Fig.7: Effect of black liquor ageing at 60°C on ARLC

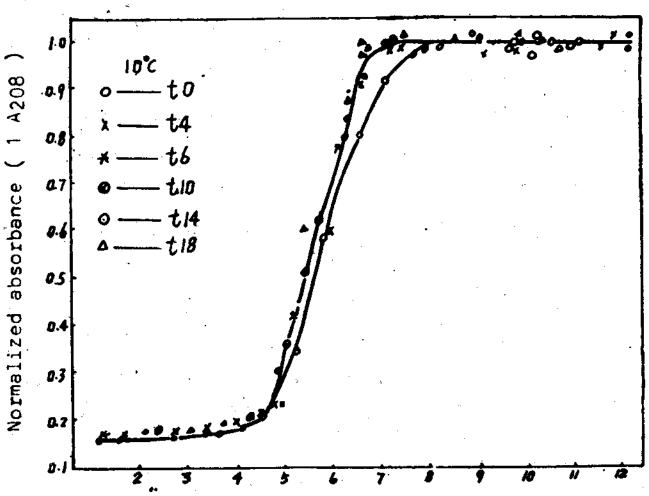

Fig.6: Effect of black liquor ageing at 10°C on ARLC

The results show that either under 60°C or 10°C storage the pH values of black liquor have some reduction. After ageing, the lignin stability not only has no reduction but shows some trend of increase (Fig. 6).

It is not difficult to find out that under 10°C storage, SPP of lignin moves from pH 8 1 to pH 6.7, and MPP moves from pH 6.0 to 5.7. Comparing results under 10°C and 60°C ageing, it can be seen that the higher temperature ageing makes characteristic precipitation point move back much more. However, after ageing under 60°C, the residual lignin ratio has a small increase, from 16% to 18%, while ageing under 10°C, the residual lignin ratio has no obvious change. The increase of lignin stability may be contributed to the degrading or splitting of lignin-carbohydrate complex in the black liquor.

In the experimental it is also found that the black liquor storing for about 6 days under 10°C or about 5 days under 60°C, there would be silicon compounds precipitated.

In all, the effect of black liquor ageing, demonstrotes that ageing is unfavourable and uneconomical for extracting lignin from black liquor but is beneficial for the weak black liquor desilification.

(e) **The influence of cooking condition.**

Above tests are under same cooking conditions (AO). In order to find out the effect of cooking condition on ARLC, the following series of tests have been made. The results are presented in Table 1, Fig. 8, 9.

Table 1 : Cooking conditions

	AO	A_1	A_2	B_1	B_2
NaOH% (as ODRM)	14.5	12.0	16.0	14.5	14.5
Na_2S% (as ODRM)	1.5	1.5	1.5	1.5	1.5
T max : °C	155	155	155	115	140
To Temp. Hr:Min.	1.30	1.30	1.30	1.30	1.30
At Temp. Hr:Min.	0.30	0.30	0.30	0.30	0 30
Ratio of Raw Material to Liquor	1·6	1.6	1 6	1.6	1.6

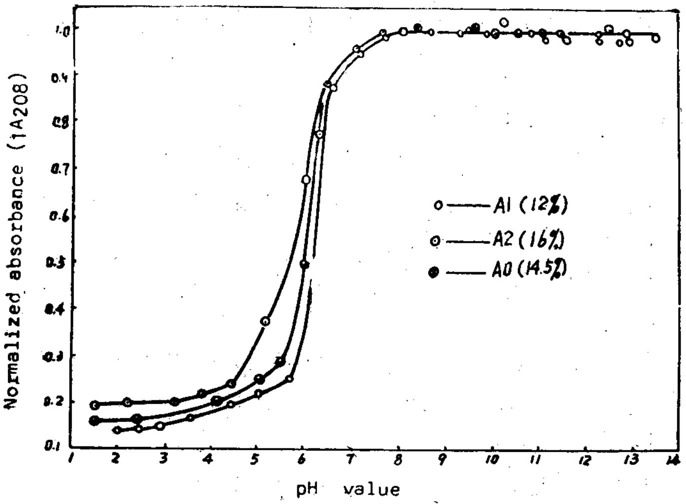

Fig.8: Effect of alkaline demand upon ARLC

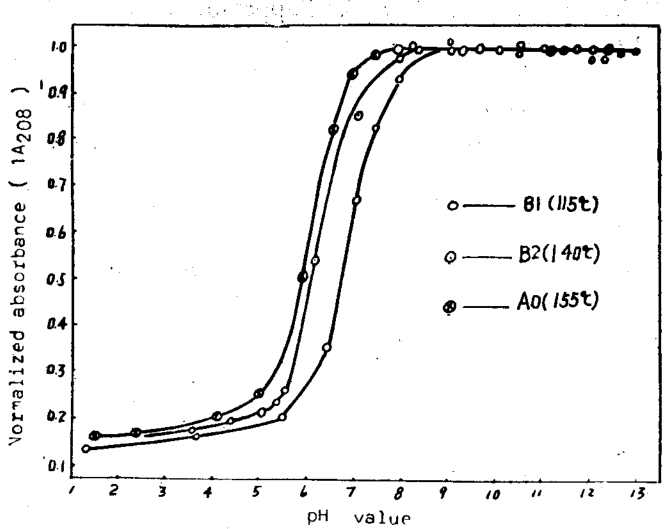

Fig.9: Effect of cooking temp. upon ARLC

At different alkaline charge, ARLCs present their differences. Varying alkaline charge from 12% (as bone dry raw materials) to 16%, there is no appreciable change for the SPP and EPP, whereas in the acute and stagnent precipitating stage, the precipitated lignin per pH value unit reduces with increasing of alkaline charge. At alkaline demand 12%, 14.5% and 16% the stagnent stages are pH 3 0 5.8, pH 3.8—5.5 and pH 3.0—4.5 respectively Obviously, the stagnent lignin stages have a trend to become shorter. Meanwhile, the residua lignin trend to increase with alkaline demand, at alkaline demand 12%, 14.5% and 16%, the residual lignin are about 14%, 16% and 19% (Fig. 8).

Maximum temperature of cooking also has a significant influence on the ARLC (Fig. 9). The higher the cooking temperature, the lower the SPP (pH value). When the cooking temperatures are 115°C, 140°C and 155°C, the SPP are about pH 9.0, 8 5 and 8.1, respec tively. Further more, the residual lignin rate have a trend to rise with the cooking temperature: The temperatures : 115, 140 and 155°C, the residual lignins are 15, 16 and 17%.

Though cooking condition has great influence, the ARLCs at different cooking conditions have their similarities They remain their fundamental shape and dividing precipitation characteristics

According to the author's previous work[4], above results may be caused by the strength of cooking condition. Drastic cooking condition leads to severe damage of dissolved lignin and hence has higher content of lower molecular weight lignin fractions, in black liquor and higher charge density of lignin fractions. So the lignin in black liquor is more stable against acid and has higher residual ratio when acidification. On the other hand, because the raw material is same in above tests, the original lignin has some structure and components. Even under different cooking condition the dissolved lignin has many similar components and properties. So their ARLCs have lots of similarities.

CONCLUSION :

(1) : During acidifying kraft wheat straw black liquor the precipitation of lignin is carried out stage by stage. The precipitation process can be divided into four stages : i.e. lignin stable, acute precipitating, stagnent and residual stage.

(2) The acidifying precipitation characteristics of lignin in wheat straw black liquor are influenced by the factors such as acidifying temperature, black liquor density, salt concentration and black liquor's storage as well as cooking eondition etc.

(a) The higher the black liquor temperature or acidifying temperature, the higher is the pH value of SPP and lignin residual ratio.

(b) The higher the black liquor density, the higher are the pH valu.s of SPP and MPP, but the lignin residual ratio doesn't change with the black liquor density.

(c) The ageing of black liquor results in the increase of the lignin stability. It means that ageing makes SPP and MPP move to lower pH range. The higher the temperature, the more obvious the ageing effect.

d) : For same raw material, wheat straw, ARLCs exhibit differences under various cooking conditions. Drastic cooking condition leads to the higher stability of lignin against acid, and the higher is the lignin residual ratio.

ACKNOWLEDGEMENT :

The advice of the prof. and senior engineer Hua Ning-xi, Zhou Sheng-Guang is greatly appreciated. The author also thanks the senior engineer Chen Zu-Dian and the engineer Xu Wen-Min for use of their equipment in this study.

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