研 究 報 文

高濃度ポリサルファイドを用いた新蒸解システムの開発（第2報）

—蒸解薬液の多段添加を行う修正蒸解への適用—

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Development of a New Cooking System using Highly Concentrated Polysulfide (II)

—Application to Modified Cooking with Multi Charges of Cooking Liquor—

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Abstract

Polysulfide (PS) cooking is one of the most efficient technologies available today to increase pulp yields. The PS has to be produced from Na_2S in the white liquor (WL) to keep Na^+ and S^{2-} balance in the WL recovery cycle. To produce the PS in high efficiency, a WL electrolysis using ion-exchange membranes has been developed by Nippon Paper Industries CO., LTD.

Modified cooking is characterized by sequential charges of WL to the cooking digester. Recently, Iso-thermal cooking (ITC), which is one of the modified cooking, characterized by low temperatures and long-cooking times has been industrialized and installed in a lot of kraft pulping processes. However, not only NaOH concentrations but also Na_2S concentrations at a start of the cooking are decreased, because the initial charge of WL was decreased by the modified cooking.

In this study, the combinatorial use of ITC cooking and PS cooking were evaluated, expecting a process in

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which the mill scale pilot electrolyzers were installed. A yield gain caused by the PS cooking was decreased in cases of the modified cooking conditions. However, when the PS was produced by the electrolyzers, the yield gain was increased contrary to the case by the air oxidation. By the electrolyzers, the PS concentrations became double and a lack of initial Na_2S concentration was minimized.

In addition, the electrolyzers, which have a function of electro dialysis using ion-exchange membranes, enabled sulfide elements in WL to be concentrated as PS and Na_2S . Consequently, much more yield gain was expected by using the new modified cooking.

Keywords : Polysulfide, Sulfidity, Na_2S , Pulp yield, Electrolysis

分類 : F_2KP 蒸解, W_1 蒸解薬品

1. 緒 言

原料の大半を輸入木材チップに依存する日本のパルプ工場にとって、クラフト (KP) 蒸解におけるパルプ収率の向上は経済的に重要な課題である。一方、ポリサルファイド (PS) 蒸解においては、薬品回収工程のナトリウムとイオウ (Na/S) のバランスを崩さないように、白液中の Na_2S から空気酸化により PS を生成する空気酸化法が工業化されている。しかし、空気酸化法では PS 生成時に $\text{Na}_2\text{S}_2\text{O}_3$ を生成する副反応が起こり、また白液中の限られた Na_2S から PS を生成させるため、通常の硫化度 (約 30%) の白液を用いた場合には PS 濃度の上限が制約され、蒸解液中の Na_2S 濃度が低下する。そのため、PS の効果をとらえ難いことが課題であった。

蒸解における脱リグニン反応速度は蒸解液中の薬液濃度の影響を受けるため、蒸解液量の木材絶乾重量に対する比 (液比, l/kg) は、活性アルカリ (AA) 添加率とともに蒸解結果に影響する重要な要因である。広葉樹材の連続蒸解の液比は $2.5 \text{ l}/\text{kg}$ 程度であり、蒸解開始時の AA 濃度は $60 \text{ g}/\text{l}$ 程度である。

第一報では、実験室で回転式蒸解釜を開発し、連続蒸解の液比条件に合わせた任意の初期薬液濃度による蒸解を行った。そして、蒸解初期の PS 濃度が高くなればパルプ収率の向上効果が大きくなるが、PS 生成に伴って Na_2S 濃度が $6\text{--}9 \text{ g}/\text{l}$ (Na_2O 当量) 以下に低下すると、パルプのカッパー価と粕率が上昇する条件があるという問題を明らかにした。

Watanabe ら¹⁾は、白液から高濃度ポリサルファイド蒸解液を製造する電解酸化プロセスを新たに開発した。小規模セルを用いて長期間の実験を行って電解酸化プロセスの利点を確認し、工場での実機蒸解に適用する可能性を示した。このプロセスでは白液が電気化学的に酸化され、陽極にポリサルファイドが生成すると同時に陰極には純粋な NaOH が生成する。 $\text{Na}_2\text{S}_2\text{O}_3$ の生成が抑制されるために、効果的な電氣的制御によって高濃度ポリサルファイドの調製が可能である。同時に白液中の Na_2S 濃度を濃縮することができる。また、KP 蒸解プロセスの Na/S バランスを維持することができる。さらに、小規模セルを用いて調製した PS 蒸解液を想定し、実験室で蒸解薬液の二段添加を行う修正蒸解 (MC 蒸解) の条件を想定した実験を行い、このプロセスを用いる蒸解法がパルプ収率向上とカップ

価低減を実現する新蒸解システム開発に繋がる可能性を示唆した。

現在、通常蒸解 (CK 蒸解) よりも低温で白液を分散添加して長時間の蒸解をすることを基本とする修正蒸解、すなわち全缶等温蒸解 (ITC 蒸解) が実用化され、多くのプロセスに導入されている。既往の修正蒸解は蒸解初期の NaOH 濃度を下げるために、蒸解初期に添加する白液を減らし、その代わりに白液を逐次添加して NaOH 濃度を平準化するものである。しかし、添加する白液の容量そのものを減らすため、蒸解初期の NaOH だけでなく Na_2S の濃度が低下してしまう。蒸解初期の Na_2S 濃度低下は白液中の Na_2S から PS を生成する際にも起る。Watanabe ら¹⁾は、既往の MC 蒸解に PS 蒸解を単に組み合わせると、CK 蒸解より好ましくない結果をもたらすことを報告した。CK 蒸解において低温で長時間の浸透をとれば PS の収率向上効果は増加傾向になるが、ITC 蒸解において蒸解液の逐次添加を行うと、PS と Na_2S 濃度が低い場合には収率向上効果が減少傾向になることが懸念される。

MC 蒸解または ITC 蒸解においても望ましい PS 蒸解を行う方法として、蒸解初期に空気酸化した白液を加え、空気酸化しない白液を後段に用いる方法が報告され^{2,3)}、実用化されている。しかし、この方法では、PS 生成後、初期添加に用いられる酸化白液中の Na_2S 濃度を上げることはできない。また、蒸解初期の Na_2S 濃度を高くする方法として、白液を高硫化度白液と低硫化度白液に分画し、高濃度画分を酸化して蒸解初期に用いる二段硫化度 PS 蒸解法および PS 生成法が研究されている^{4,5,6)}。しかし、白液を高硫化度と低硫化度の白液に分画する技術に関しては、緑液結晶化法、ガス化法⁷⁾や電気透析法⁸⁾などが検討されたが、工業的に実用化された方法は今のところ見られない。また、別途必要になる PS 生成法に関しても、S 分の分離再溶解法や電気化学的方法など種々検討されたが、現在実用化されているのは、活性炭^{9,10)}、 MnO_2 ¹¹⁾、ライムマッド¹²⁾などを触媒に用いた空気酸化法のみである。

そこで本研究では、電解酸化プロセスによる PS 蒸解および ITC 蒸解を想定した低温長時間の蒸解による新規な方法に関して、実験室での蒸解による評価を行った。

2. 実 験

2.1 材料と方法

蒸解には南アフリカ産ユーカリ材を主体とする早生広葉

樹材混合チップを用いた。チップのサイズおよび固形分重量%は、工場の実機で用いられているもの (T 16 wd-74 準拠 3/4 インチおよび固形分 60~80%) と同等である。白液 (WL) および PS 蒸解液 (OL) は市販特級試薬の NaOH, Na_2S および粉末イオウ (S) から調製した。OL 中の PS は S を Na_2S 溶液と反応させることにより、実験室的に調製した。NaOH および Na_2S 重量を Na_2O 当量で表し、合計量を活性アルカリ (AA) とした。

白液から PS を生成する場合は、OL 生成時の酸化率と酸化効率を変化させて OL の組成を計算した。NaOH, Na_2S および PS から計算された処方に従って供試蒸解液を調製した。酸化率と酸化効率の定義を以下に示す。

酸化率：消費される WL 中の Na_2S (S 当量)/WL 中の全 Na_2S (S 当量)

酸化効率：生成 PS 量 (S 当量)/消費される WL 中の Na_2S (S 当量)

広い条件範囲での影響をとらえるために、蒸解時の AA 添加率は 14.0~16.5% とした。チップへの AA 添加率は、OL を用いた蒸解の場合であっても OL を生成する前の WL の組成を基準に決めて表記した。想定した白液の AA 濃度は、空気酸化法で 109 g/l (一部 107 g/l)、電解酸化法で 115 g/l (一部 106 g/l) とした。また、想定した白液硫化度は、空気酸化法で 30% (一部 33%)、電解酸化法で 35% (一部 33%) とした。AQ 添加率は 0.03%、液比は 2.5 l/kg、浸透条件は 120℃ で 30 分間、および蒸解条件は 152℃ で 60 分間とした。

2.2 従来法 PS 蒸解による修正蒸解

PS 蒸解の場合には、実機 MOXY 法の例に従い、酸化率は 49%、酸化効率は 49% として、白液を空気酸化してできる PS 蒸解液中の PS 濃度が 4 g/l as S となるように、蒸解液を調製した。ITC 蒸解の場合には、浸透開始時に全蒸解液の 90% を添加し、その後、蒸解温度が最高温度に到達した時点で残り 10% の蒸解液を添加した。なお、実験室では蒸解最高温度における薬品添加は窒素圧により行ったが、添加操作の影響があるため、通常蒸解 (CK) の場合にも空操作として、全蒸解液の 5% の蒸解液を蒸解温度が最高温度に到達した時点で添加した。

2.3 高濃度ポリサルファイドを用いた修正蒸解

電解酸化法による PS 生成を想定した PS 蒸解 (EPS) に関して、ITC 蒸解と CK 蒸解を模した蒸解実験を行った。EPS 蒸解の場合には、酸化率を 45~54%、酸化効率を 95~100% とし、白液を酸化してできる PS 蒸解液中の PS 濃度が 9 g/l as S となるように、蒸解液を調製した。なお、この PS 濃度は、後述するパイロット電解槽で得た電解槽の性能データに基づいている。

PS 生成に用いる電解槽は陽極室と陰極室に分かれており、PS 生成に伴って、陽極室から陰極室へ PS 生成量の約 2 倍モル等量の Na^+ が若干量の水とともに移動する。実証機による EPS-ITC 蒸解では、パイロット電解槽で得た電解槽のマテリアルバランスに基づいて、陽極液全量を蒸解初期に添加し、陰極液 (10% NaOH 液として) を最高温度到達時点で添加することを計画している。液量として

約 70% が初期添加、30% が後添加となる。

3. 結果と考察

3.1 従来法 PS 蒸解を修正蒸解に適用した場合の制約

本実験では、PS 蒸解液を分散添加した場合の影響を明らかにするために、分散添加を行わない通常 KP 蒸解 (KP-CK) と、同 PS 蒸解 (PS-CK)、そして ITC 条件で分散添加を行う PS 蒸解 (PS-ITC) を比較した。

同一カップー価での比較における総収率 (図 1) は、 $\text{KP-CK} < \text{PS-ITC} < \text{PS-CK}$ の順であった。CK 条件で PS 蒸解をすることで収率が向上したが (KP-CK と PS-CK の比較)、ITC 条件下 PS 蒸解をすると、PS の収率向上効果が減少した (KP-CK と PS-ITC の比較)。なお、KP 蒸解の場合は、通常蒸解、修正蒸解を問わず、収率はほぼ同等であった (KP-CK と KP-ITC の比較)。

同一 AA 添加率での比較におけるカップー価 (図 2) は $\text{KP-CK} \approx \text{PS-CK} < \text{PS-ITC}$ の順であった。CK で PS 蒸解をしても、カップー価は同等であったが (KP-CK と PS-CK の比較)、ITC 条件で PS 蒸解をすると、カップー価が上昇した (KP-CK と PS-ITC の比較)。

Fig.1 Relationships between kappa numbers and total yields

Fig.2 Relationships between AA dosages and kappa numbers

Fig.3 Schematic diagram of WL electrolytic cell for a pilot

Fig.4 Na/S balance of the modified PS cooking by using WL electrolyzer

以上から、PS の効果に関しては、ITC 蒸解条件ではPS による収率向上効果の一部が失われることが明らかとなった。また、同一 AA 添加率での銅価低下が期待されたが、PS 蒸解時には銅価がむしろ上昇することが明らかとなった。

第一報の結果から、PS-ITC 蒸解時の収率低下と銅価上昇は蒸解初期の Na_2S 濃度の不足によるものと考えられる。このような制約を解決するためには、PS-ITC 蒸解時の Na_2S 濃度を高く維持する必要がある。

3.2 新しい高濃度ポリサルファイド生成法

現在工場規模で開発中の方法は膜電解によるもので、白液を原料として陽極室で電気化学的に PS 生成を行いながら、陰極側に電気透析的に若干量の水とともに Na^+ が抜き取られる (図 3)。その結果、白液から効率よく PS を生成するだけでなく、陰極側に Na^+ を抜き取ることによって陽極液中の S 分 (PS と Na_2S に含まれる S の合計) を濃縮できることが明らかとなった。

そこで筆者らは、PS-ITC 蒸解時の Na_2S 濃度を高く維持するための具体的方法として、ITC または MC 蒸解などの修正蒸解の初期添加に陽極液を用い、逐次添加に NaOH を用いることを基本とする新蒸解方法を考案した (図 4)。現在実証設備の電解槽部分に関する性能確認を進めている。

また、実際に工程に設置した電解槽の陰極で得られる NaOH は、S 分や重金属などがよく除かれており (表 1)、酸素脱リグニンに用いることが可能な品質であることが明らかとなったため、陰極 NaOH を酸素脱リグニン工程でも用いることとした (図 5)。

3.3 電解酸化法 PS 蒸解液による修正蒸解の効果

修正蒸解に伴う蒸解初期の Na_2S 濃度の不足を補うために、高効率酸化法を用いることは有益である。しかし、分散添加により初期の Na_2S 濃度と PS 濃度が低下する。白液中の Na_2S 分と PS 分を集め、蒸解初期に集中的に添加することができれば、この問題を解決することができる。

Table 1 Analyses of ions in WL, PS liquor and NaOH from cathode by inductively coupled plasma-atomic emission spectroscopy

	Na	K	Li	Mg	Ca	Ba	Mn	Fe	Ni	S
WL	92500	19500	0.39	0.19	10.7	0.43	1.2	0.6	<1	15500
PS Liquor	86020	14820	0.39	0.13	11.2	0.40	1.2	0.6	<1	7200
Cathode	47150	14040	0.09	0.01	0.33	0.07	<0.1	0.3	<0.1	<3

Unit; ppm

Fig. 5 Cooking process with electrolytic PS system

Fig. 6 Relationships between kappa numbers and total yields

Fig. 7 Relationships between AA dosages on wood and kappa numbers

これらを工業的に実現するために、 Na_2S 濃縮とPS生成を同時に行う電気化学的なシステムとそれを用いた蒸解法を開発することが求められている。それらの効果を確認するために、分散添加を行わない通常KP蒸解（KP-CK）、同EPS蒸解（EPS-CK）蒸解に対して、実証機を用いて現在開発中の電気化学的なPS生成法（電解酸化法）を活用した修正蒸解（EPS-ITC）を想定し、その効果の比較を行った。

図6に銅価と総収率の関係を示す。同一銅価での総収率の序列は、 $\text{KP-CK} < \text{EPS-CK} < \text{EPS-ITC}$ の順であった。すべての点は銅価が高くなれば総収率が高くなる直線状に分布した。

図7にAA添加率と銅価の関係を示す。同一AA添加率における銅価の序列は $\text{KP-CK} > \text{EPS-CK} > \text{EPS-ITC}$ の順であった。すべての点はAA添加率が高くなれば銅価が低くなる線上に分布した。

Table 2 Conditions and results of laboratory cooking

Cooking methods	Sulfidity of WL %	AA on wood %	Oxidation ratio %	Efficiency %	init. PS concentration* g/l	Init. Na ₂ S concentration** g/l	Kappa number	Screened pulp yield %	Screened reject %	EA in BL g/l	pH of BL
KP-CK	30	14.0	0	0	0.0	16.9	26.0	53.4	1.67	2.3	12.7
KP-CK	30	15.0	0	0	0.0	18.2	21.4	54.2	0.56	3.7	13.0
KP-CK	30	16.0	0	0	0.0	19.4	19.7	53.9	0.28	5.8	13.3
KP-CK	35	14.0	0	0	0.0	19.5	22.6	53.5	0.91	4.4	13.2
KP-CK	35	15.0	0	0	0.0	20.9	20.7	53.8	0.37	6.0	13.8
KP-CK	35	16.0	0	0	0.0	22.3	18.6	52.9	0.65	7.9	14.0
KP-CK	33	14.0	0	0	0.0	18.3	24.5	54.2	0.97	3.3	13.1
KP-CK	33	15.0	0	0	0.0	19.6	22.1	53.9	0.50	5.4	13.5
KP-CK	33	16.0	0	0	0.0	20.9	17.9	52.1	0.19	9.3	13.9
KP-ITC	35	14.0	0	0	0.0	19.5	24.5	53.2	1.37	4.9	13.5
KP-ITC	35	15.0	0	0	0.0	20.9	22.2	53.7	0.69	6.4	13.9
KP-ITC	35	16.0	0	0	0.0	22.3	19.5	53.2	0.18	7.9	14.1
KP-ITC	33	14.0	0	0	0.0	18.3	28.0	52.5	3.49	3.3	13.0
KP-ITC	33	15.0	0	0	0.0	19.6	21.6	53.9	0.61	5.4	13.4
KP-ITC	33	16.0	0	0	0.0	20.9	20.5	53.0	0.40	7.3	13.7
KP-ITC	33	14.0	0	0	0.0	18.5	26.9	53.4	2.38	3.6	13.1
KP-ITC	33	15.0	0	0	0.0	19.8	23.1	53.9	0.68	5.2	13.4
KP-ITC	33	16.0	0	0	0.0	21.1	20.9	53.5	0.60	7.5	13.6
PS-CK	30	14.5	49	49	2.3	8.9	23.2	55.0	0.86	3.0	13.0
PS-CK	30	15.5	49	49	2.5	9.5	20.0	54.5	0.26	5.4	13.3
PS-CK	30	16.6	49	49	2.6	10.1	18.9	54.0	0.31	7.0	13.4
PS-ITC	30	14.5	49	49	2.2	8.9	27.6	53.6	2.45	2.3	12.7
PS-ITC	30	15.5	49	49	2.3	9.5	22.8	54.0	0.67	4.0	13.1
PS-ITC	30	16.6	49	49	2.5	10.1	22.0	54.6	0.37	5.3	13.2
EPS-CK	35	14.0	45	100	4.8	11.2	20.6	54.4	0.84	4.8	13.5
EPS-CK	35	15.0	45	100	5.2	12.0	19.7	54.4	0.28	6.7	13.3
EPS-CK	35	16.0	45	100	5.5	12.8	17.4	53.6	0.28	8.2	13.9
EPS-CK	33	14.0	53	98	5.2	9.1	24.0	55.5	1.25	4.0	13.2
EPS-CK	33	15.0	53	98	5.6	9.8	19.5	54.5	0.60	5.6	13.4
EPS-CK	33	16.0	53	98	6.0	10.4	19.5	53.8	0.49	7.3	13.5
EPS-ITC	35	14.0	45	100	6.5	15.2	21.4	57.0	0.67	5.4	13.8
EPS-ITC	35	15.0	45	100	7.0	16.3	21.3	54.9	0.83	4.7	12.8
EPS-ITC	35	16.0	45	100	7.5	17.3	16.8	54.1	0.23	8.6	12.9
EPS-ITC	35	14.0	45	100	6.5	15.2	20.0	55.3	0.58	5.1	13.7
EPS-ITC	35	15.0	45	100	7.0	16.3	17.8	54.7	0.46	6.6	13.9
EPS-ITC	35	16.0	45	100	7.5	17.3	17.4	54.2	0.26	8.4	14.1
EPS-ITC	33	14.0	54	95	6.9	12.1	21.9	55.8	0.87	5.1	13.6
EPS-ITC	33	15.0	54	95	7.4	13.0	19.5	55.0	0.57	6.3	13.6
EPS-ITC	33	16.0	54	95	7.9	13.8	18.5	54.7	0.28	8.2	13.7

* Calculated as initial PS concentrations (as S) in the supposed continuous digester at a mill.

** Calculated as initial Na₂S concentrations (as Na₂O) in the supposed continuous digester at a mill.

また表2から, PS, EPS 蒸解時の銅価や粕率の序列は PS-ITC>PS-CK>EPS-CK>EPS-ITC の順であった。蒸解結果は AA 添加率の影響も受けたが, EPS-ITC 蒸解では Na₂S 濃度の低下が最も抑制されたため, 最も低い銅価と粕率になることが示された。

図7および表2の結果から白液の電解により生成した高濃度 PS 液と NaOH 溶液を混合して蒸解初期に一括添加する EPS-CK 蒸解によって, 空気酸化 PS 蒸解 (PS-CK) の約 1.5 倍の収率向上効果が得られることがわかった。さら

に, 蒸解初期に高濃度 PS 液を添加し, その後の分散添加には 10% NaOH 溶液を用いる EPS-ITC 法では, さらに大きな収率向上が期待できることがわかった。電気化学的な PS 生成法を用いる PS 蒸解を修正蒸解に適用することによって, PS 蒸解に伴う Na₂S 濃度不足の問題点を解決できることが示された。

4. 結 論

空気酸化法による PS 蒸解を ITC 蒸解に適用すると, PS

添加による収率向上効果の一部が失われ、また同一 AA 添加率での銅価低減効果が失われることが明らかとなった。

膜電解法による白液の電解によって、PS 生成時の Na_2S 濃度低下を最低限に抑制し、同時に白液中の S 分を濃縮できることが実証機で明らかとなり、これに基づき、電解酸化法 PS 蒸解によって、空気酸化法 PS 蒸解の約 1.5 倍の収率向上効果が得られた。

さらに電解酸化法では、S 分濃縮の効果を蒸解初期の Na_2S 濃度に反映させ、ITC 蒸解等の蒸解薬液の多段添加を行う修正蒸解においては、大きな収率向上が期待できることがわかった。

電解酸化法 PS 蒸解を修正蒸解に適用することによって、PS 蒸解の問題点、および白液分割添加に伴う蒸解初期 Na_2S 濃度不足の問題点を同時に解決できることが示された。すなわち、電解酸化 PS 蒸解法を修正蒸解に適用した新蒸解システムを実用化することによって、収率向上効率が上げられない従来法 PS 蒸解の課題と初期 Na_2S 濃度を上げられない修正蒸解の課題とを同時に解決できると考える。

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1. Introduction

For pulp mills in Japan which use imported chips as their major wood resource, it is an economically important concern to increase pulp yield in their kraft cooking (abbreviated as KP), and polysulfide (abbreviated as PS) cooking is one of systems for improving pulp yield. To produce polysulfide from conventional chemical recovery system without disturbing its balance between sodium and

sulfur, air oxidation process is in operation, which oxidizes sodium sulfide in white liquor by air. The process, however, produces sodium thiosulfate as a by-product. As PS is converted from sodium sulfide existing in white liquor, resultant PS concentration is limited to a certain value with conventional white liquor whose sulfidity is about 30%. Furthermore, sodium sulfide concentration in cooking liquor is also reduced by the conversion. Therefore, the effect of PS has not been clearly demonstrated.

As the rate of delignification in cooking is affected by concentrations of cooking chemicals in cooking liquor, liquor to wood ratio, which is a ratio of volume of cooking liquor against amount of oven dry wood (l/kg), is very influential along with active alkaline dosage. In normal continuous cooking for hardwood, the liquor to wood ratio is around 2.5 l/kg and AA concentration at the beginning of cooking is about 60 g/l.

In our first report, we developed a rotational autoclave in our lab, which could start cooking at any initial liquor concentration, and simulate cooking with the liquor to wood ratio of continuous cooking. We found that high PS concentration at the beginning of cooking effectively increased pulp yield. However, a problem was also found. When sodium sulfide concentration in cooking liquor was reduced to 6–9 g/l as Na_2O by the conversion to PS, pulp kappa number and screened reject increased.

Watanabe et al.¹⁾ developed a new process, which produced cooking liquor of high PS concentration from white liquor by electrolytic oxidation. They proved the advantage of the electrolyzer by a long run test using a small-scale cell and demonstrated that their process could be applied to mill operation. In this process, white liquor was electrochemically oxidized and polysulfide was produced at an anode and pure sodium hydroxide was generated at a cathode. As formation of sodium thiosulfate was restricted, polysulfide solution of high concentration was prepared effectively by electrical control. At the same time, sodium sulfide in white liquor could be concentrated. The Na/S balance in kraft cooking process was also maintained. Supposed that PS cooking liquor was like one prepared by their experimental small cell and it was fed to modified cooking operation (MC cooking) in which white liquor was sequentially charged, the condition was simulated in a laboratory scale. It was suggested that this cooking trial could be developed to a new cooking system in which pulp yield was improved with lower kappa number.

Modified cooking, which is based on the concept that cooking should be done in longer time at a lower temperature with feeding cooking liquor in more sequence than conventional kraft cooking (CK cooking), i.e. isothermal cooking (ITC cooking), has been introduced in many mills. In the present modified cooking, white liquor is fed at a lesser amount at the beginning of cooking to make sodium hydroxide concentration low enough and is fed, instead, sequentially to maintain constant sodium hydroxide concentration throughout the cooking. When the volume of white liquor at the initial charge is reduced, not only the concentration of sodium hydroxide but also that of sodium sulfide is reduced. Producing PS from sodium sulfide in white liquor also reduces sodium sulfide concentration, which results in less concentration at the initial charge. Watanabe

et.al¹⁾ reported that simply integrating PS cooking to the present modified cooking gave result worse than conventional kraft cooking. Some yield improvement was expected with PS cooking carried out in the condition of CK cooking with long impregnation time at low temperature. However, in ITC cooking where liquor is sequentially fed, there would be a case where concentrations of PS and sodium sulfide were both low and their effect for yield improvement was not fully exploited.

Some papers proposed a method of efficiently integrating PS cooking to MC cooking or ITC cooking^{2,3)}, and the method is in mill operation. The method is to feed air oxidized white liquor at the beginning of cooking and feed un-oxidized white liquor at the late part of cooking. With this method, sodium sulfide concentration in the initial white liquor is low and can not be sufficient enough. As for method of increasing sodium sulfide concentration at the initial feed, two-sulfidity PS cooking was proposed^{4,5,6)}. White liquor was disproportioned to one of higher sulfidity and the other of lower sulfidity. The higher one, after oxidized, was used at the beginning of cooking. Regarding disproportioning of white liquor, several methods like crystallization from green liquor, gasification and electro-dialysis were investigated. But, no process is in mill operation yet. Regarding producing PS, several methods were also studied, like separating and then re-dissolving sulfur and electrochemical method. Only air oxidation process using activated carbon, MnO_2 or lime mud as a catalyst is used.

Therefore, we evaluated, in a laboratory scale, a new process where PS production system by electrolyzer was integrated to PS cooking and ITC cooking which were usually done in long time at a low temperature.

2. Experiment

2.1 Materials and method

Mixed hardwood chips, most of which were fast growth eucalyptus from South Africa, were used for cooking. They were similar to those used in mills in their chip size and oven dry weight, which were 3/4 inches based on T 16 wd-74 and were 60–80% solid respectively. White liquor (abbreviated as WL) and PS cooking liquor (abbreviated as OL) were prepared with sodium hydroxide and sodium sulfide, both of which were reagent grades, and powder sulfur. PS in OL was prepared in a lab by the reaction between sulfur and sodium sulfide. Amounts of sodium hydroxide and sodium sulfide were calculated as Na_2O and their sum was expressed as active alkali (AA).

When PS was produced from white liquor, the composition of OL was calculated by changing the oxidation ratio and the efficiency at the reaction. Their definitions were as follows.

Oxidation ratio : Na_2S consumed in white liquor (calcu-

lated equivalent to S)/total Na_2S in white liquor (equivalent to S)

Efficiency : PS produced (equivalent to S) / Na_2S consumed in white liquor (equivalent to S)

To study effects in a wide range, AA dosage was from 14.0 to 16.5%. In cooking with OL, its AA dosage was expressed with that of white liquor before PS generation. Its AA concentration was 109 g/l with air oxidation method (some trials with 107 g/l) and 115 g/l with electrolytic method (some trials with 107 g/l). White liquor sulfidity was 30% with air oxidation method (some trials with 33%) and 35% with electrolytic method (some trials with 33%). AQ addition rate was 0.03%. Liquor to wood ratio was 2.5 l/kg. Impregnation condition was at 120°C for 30 minutes. Cooking condition was at 152°C for 60 minutes.

2.2 Modified cooking using PS liquor by conventional air oxidation method

In PS cooking, mill operation by MOXY process was modeled, and the oxidation ratio and the efficiency were assumed to be 49% and 49% respectively. Then, cooking liquor was prepared to have PS concentration of 4 g/l as S, which was expected to be produced by air oxidation. In ITC cooking, 90% of total cooking liquor was fed at the start of impregnation, and the rest 10% was added at the time when temperature reached its maximum. As the liquor was fed at the maximum temperature by nitrogen pressure, this operation might be influential. So, the same operation was done in conventional cooking (CK) as a blank procedure, and 5 % of the total liquor was fed when its temperature got to its maximum.

2.3 Modified cooking using polysulfide liquor of high concentration

By assuming that PS was produced by the electrolytic method, its oxidation ratio was 45–54%, and its efficiency was 95–100%, PS concentration in cooking liquor (EPS) was adjusted to be 9 g/l as S. That PS concentration was based on our pilot trial, which would be described later. The PS liquor was used in lab trials simulating ITC cooking and CK cooking.

The electrolytic cell was separated into two compartments, a cathode compartment and an anode compartment. When PS was produced, Na^+ , which was twice in equivalent amount as much as PS produced, moved from the anode compartment to the cathode compartment along with small amount of water. We are planning to have EPS-ITC cooking in a pilot scale. In that trial, whole liquor in the anode compartment will be fed at the initial stage, and that in the cathode compartment (assumed to be 10% sodium hydroxide) will be added at the maximum temperature. In liquor volume basis, 70% will be fed at the initial and 30% will be added later.

3. Result and discussion

3.1 Restrictions when conventional PS cooking was applied to modified cooking

To clarify effects by feeding PS cooking liquor sequentially, conventional kraft cooking (KP-CK) and conventional PS cooking (PS-CK), both of which were operated not by sequential feed and PS cooking with sequential feed simulating ITC (PS-ITC) were compared each other.

Total yields at the same kappa number were in a following order : $\text{KP-CK} < \text{PS-ITC} < \text{PS-CK}$ (Fig. 1). Under the condition of CK cooking, PS cooking increased its yield (comparison between KP-CK and PS-CK). Under the condition of ITC cooking, the effect of PS cooking on yield increase became less (comparison between KP-CK and PS-ITC). In KP cooking, the yield was almost the same whether its condition was conventional or modified (comparison between KP-CK and KP-ITC).

When pulp kappa numbers were compared at the same AA dosage, their order was as follows : $\text{KP-CK} \approx \text{PS-CK} < \text{PS-ITC}$ (Fig. 2). Under the condition of CK cooking, PS cooking gave the same kappa number (comparison between KP-CK and PS-CK). Under the condition of ITC cooking, PS cooking gave a larger kappa number (comparison between KP-CK and PS-ITC).

It was proved that the effect of PS cooking on yield increase was less under the ITC condition. Though it was expected that PS cooking would give lower kappa number at the same AA dosage, PS cooking under the ITC condition rather increased its kappa number.

The reason of lower yield and higher kappa number in PS-ITC cooking was supposedly due to insufficient sodium sulfide concentration at the initial stage of cooking, judging from the result in our first report. To be free from the problem, it was necessary to increase sodium sulfide concentration at the initial stage of PS-ITC cooking.

3.2 New process for producing polysulfide at high concentration

Our process, which was developing in a mill scale, used ion exchange membrane. It produced electrochemically PS from white liquor in an anode compartment, and sodium ion and some water were extracted to a cathode compartment by electro-dialysis (Fig. 3). As the process not only produced PS efficiently but also extracted sodium ion to a cathode compartment, it turned out that sulfur fraction (sum of sulfur in PS and sodium sulfide) in solution in an anode compartment was concentrated.

So, we proposed a new cooking process where the anode liquor was fed at the initial stage of modified cooking like ITC cooking and the sodium hydroxide was added at later stages so that sodium sulfide concentration was maintained in a high level during PS-ITC cooking (Fig. 4).

We are collecting data on the electrolyzer in a pilot scale, which is installed in mill recovery line.

As sodium hydroxide produced in a cathode compartment of our pilot plan was almost free from sulfur and heavy metals, and clean enough (Table 1), it was designed to be used for oxygen delignification (Fig. 5).

3.3 PS cooking liquor by electrolyzer : its effect on modified cooking

Oxidation process, if its efficiency is high, is useful for making up the deficit of sodium sulfide in the initial stage of modified cooking. But, if sequential addition is done, sodium sulfide and PS in the initial stage are forced to be of low concentrations. If sodium sulfide fraction and PS fraction are taken out from white liquor and are fed at the initial stage, the problem would be solved.

To make it possible in mill operation, a process, which could concentrate sodium sulfide and produce PS at the same time, which would be an electrochemical system, had to be developed and it had to be integrated in cooking process. To verify the effects, cooking trials were carried out, simulating modified cooking in which PS produced by electrolytic method was used (EPS-ITC) against conventional KP cooking (KP-CK) and EPS cooking (ESP-CK), both of which were without sequential feed. As mentioned before, the electrolyzer was developing in our pilot plant.

Fig. 6 summarizes relationships between kappa numbers and total yields. If compared at the same kappa number, total yields were in a following order : KP-CK < EPS-CK < EPS-ITC. On each type of cooking, there was a linear relationship between kappa numbers and total yields, a higher kappa number corresponding to a higher total yield.

Fig. 7 summarizes relationships between AA dosages and kappa numbers. If compared at the same AA dosage, kappa numbers were in a following order : KP-CK > ESP-CK > ESP-ITC. On each type of cooking, there was linearity between AA dosages and kappa numbers, a higher dosage corresponding to a lower kappa number.

As seen from Table 2, kappa numbers and screened rejects among PS and EPS cooking trials were in a following order : PS-ITC > PS-CK > EPS-CK > EPS-ITC. Though AA dosage affected cooking result to some extent, EPS-ITC gave the lowest kappa number and the least amount of screened reject. It was because ESP-ITC cooking restricted the declination of sodium sulfide concentration most efficiently.

From Fig. 7 and Table 2, it was demonstrated that EPS-CK cooking, in which PS liquor of high concentration and sodium hydroxide, both of which were produced by electrolysis of white liquor, were charged for once at the initial stage of cooking, could give yield one and a half times as much as that of PS-CK in which PS liquor by air oxidation was used. Further yield increase was expected with ESP-

ITC in which PS liquor of high concentration was fed at the initial stage of cooking and 10% sodium hydroxide solution was added at the later stage in sequence. By using PS liquor by the electrochemical process to modified cooking, the problem in PS cooking that was insufficient sodium sulfide concentration was also removed.

4. Conclusion

PS cooking with PS liquor produced by air oxidation method was carried out in the condition of modified cooking, and beneficial effects by PS addition, higher yield and lower kappa number at the same AA dosage, were lost to some extent.

We found with our pilot plant that PS was produced by electrolysis using membrane, and the reduction of sodium sulfide concentration by PS formation was restricted to the minimum level, and sulfur component in white liquor simultaneously condensed. The PS liquor by that electrolyzer increased pulp yield one and a half times as much as PS liquor by air oxidation.

Sulfur components were concentrated by using electrolytic method. Consequently, Na₂S and PS concentrations at the start of the cooking were able to be increased. That increases pulp yield further in modified cooking like ITC cooking in which cooking liquor was fed sequentially.

Therefore, by using electrolytic method and modified cooking in combination, problems in PS cooking and problems of insufficient sodium sulfide concentration at the initial stage of cooking due to sequential white liquor feeding was able to be solved simultaneously.

In other words, the new cooking system, in which electrolytic PS cooking is carried out in the concept of modified cooking, would be able to solve the problems in conventional PS cooking in which expected pulp yield increase was not fully exploited and the other problem in modified cooking in which initial sodium sulfide concentration was not sufficient enough.

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