針葉樹材のアルカリ蒸解における炭水化物収率とヘキセンウロン酸生成の挙動

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Behaviors of Carbohydrate Yield and Hexenuronic Acid Formation during Softwoods Alkaline Cooking

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Abstract

It is required to use more Japanese softwoods, for example, *Larix leptolepis* (Japanese larch), *Pinus densiflora* (Japanese red pine), and *Cryptomeria japonica* (Japanese cedar) for the effective production of pulp and bio-energy. The pulp yield in cooking stage is one of the most important factors at a pulp mill. However, it is difficult to know the yield due to a continuous operation of the mill. In this paper, we proposed on a method for estimating Japanese softwood pulp yields at a continuously operated kraft pulp mill. The behaviors of xylan, mannan, carbohydrate and hexenuronic acid (HexA) contents in various alkaline cooking of Japanese larch were studied. A part of dissolved xylan was re-adsorbed by wood fibers in the cooking, and the result indicates that the pulp yield can not be estimated from ratios of xylose to glucose (X/G ratios) liberated by acid hydrolysis from the pulps. Therefore, we made some equations which could simulate the behaviors of delignification, carbohydrates, ratio of mannose to glucose (M/G ratios), and HexA in the cooking from the results of kraft, kraft-AQ and PS-AQ cooks. From these equations, we clarified the relationship between pulp yields and the M/G ratios, and then, it was shown that a good correlation existed between pulp yields and M/G ratios at kappa number 25. The softwoods pulp yields with kappa number 25 at the mill using the Japanese red pine and Japanese cedar mixed wood chips were estimated by the proposed method. The M/G ratios of mill pulps from kraft-AQ and kraft cooks were

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0.0812 and 0.0704, respectively, and the result means that the pulp yield by kraft-AQ cook was 1.3% higher than that by kraft method. HexA contents of PS-AQ and kraft-AQ pulps with kappa number 25 at a given H-factor from Japanese softwoods were higher than that of kraft pulp. At the mill trial, the HexA content of kraft-AQ pulp was 7 mmol/kg higher than that of kraft pulp.

Keywords : kraft, anthraquinone, polysulfide, pulp yield, carbohydrate, hexenuronic acid

分類 : F₂KP 蒸解, W₁ 蒸解薬品

1. 緒 言

日本の森林率は67%であり、2005年における日本の森林蓄積は約40億m³ (162m³/ha)である。森林の約42%は人工林である。人工林の森林蓄積は約24億m³であり、針葉樹がその98%を占めている¹⁾。針葉樹の人工林齢級別蓄積をみると、9齢級(林齢が40~45年生)の蓄積が全齢級のうち最も多い²⁾。これらは今後主伐期に到達し、国産針葉樹材の供給量が増大することが予測される。しかし、約730万haにおよぶ国有林における針葉樹の成長量(2006年)は1,555万m³/年であり、我が国の木材自給率は20%前後を推移している。

京都議定書では、温室効果ガス排出量について1990年を基準年として2010年までに基準年排出量の6%を削減することを目標とし、その約3分の2にあたる3.9%を森林による吸収量で確保することが定められた。国産材需要の低迷と森林経営における生産性の低さなどの問題があるために、人工林は放置されて荒廃している。京都議定書において温室効果ガス削減の算出を認められた森林は、適切な森林施業が行われているものと限定されている。地球温暖化防止のためにも人工林の間伐等、森林の適切な管理と保全が急務となっている³⁾。

パルプ用材として植林されている広葉樹材と比較すると、国産針葉樹材の蒸解後パルプ収率は低いが、そのため原料1kgから黒液として得られるバイオエネルギーは大きい。したがって、パルプ原料として国産針葉樹材の利用を拡大することは、国内バイオエネルギー生産にとっても大きな意義がある。

以上のことから、木材の工業的利用の過半を占めるパルプ産業においても国産針葉樹材の利用を拡大する意義は大きい。木材資源を有効に利用するために、パルプ製造工程において収率を正確に評価することが重要である。通常、蒸解工程では連続操作を行うため、蒸解におけるパルプ収率の測定が困難である。国産針葉樹材をパルプ原料とする場合、製材工場からの端材などの混合材チップを使用することが多い。そのため、由来が既知の単一樹種の木材チップを使う場合よりも、パルプ品質および収率の予測がより困難となる。これらのことから、特に国産針葉樹材を原料とする場合、蒸解におけるパルプ収率の正確な評価方法の開発が求められている。一方、アルカリ蒸解ではキシラン側鎖に結合する4-O-methyl- α -D-glucuronic acidが4-deoxyhex-4-enouronic acid (HexA)へと変化し、蒸解条件はパルプ中のHexA量に影響を与える⁴⁾。プナクラフト

パルプはアカマツクラフトパルプよりキシラン含有量が2.5倍多く、針葉樹材のキシラン中の4-O-メチルグルクロン酸基の頻度は広葉樹材より2倍多いという報告がある⁵⁾。針葉樹材パルプは広葉樹材パルプよりHexA量が少ないといわれているが、蒸解条件によって針葉樹材でもHexA量は異なり、たとえばpine材クラフトパルプの場合、カップー価25.9でHexA量が54 μ mol/gであるという報告がある⁶⁾。針葉樹に対してもHexA生成について蒸解条件の影響を調べ、蒸解で取り除ける可能性を検討することは意義のあることである。国産針葉樹材をパルプ原料として利用する場合、炭水化物の挙動と合わせてアントラキノン(AQ)などの蒸解助剤を添加したときのHexA酸生成の挙動を検討する必要がある。

そこで本研究では第一に、カラマツ(*Larix leptolepis*)、アカマツ(*Pinus densiflora*)、およびスギ(*Cryptomeria japonica*)材のアルカリ蒸解中における炭水化物の挙動を明らかにし、工場における国産針葉樹材の蒸解パルプ収率の評価法について検討を加えた。第二に、クラフト法(Kraft法)とクラフト・アントラキノン法(Kraft-AQ法)およびポリサルファイド-アントラキノン法(PS-AQ法)による蒸解において、蒸解助剤であるAQとイオウの添加が、国産針葉樹材パルプのHexA量に与える影響を明らかにした。

2. 実験方法

2.1 供与試料

筑波大学八ヶ岳演習林から樹齢30年のカラマツ材(*L. leptolepis*)を伐採し、実験室で辺材部および心材部に分別した後、チップを調製した。辺材部由来チップについて、チップの平均形状が13.2mm×24.8mm×2.4mm(厚さ)のものを蒸解用試料とした。また、三菱製紙八戸工場入手した工場用アカマツ・スギ材混合チップを、実験室でアカマツ材(*P. densiflora*)とスギ材(*C. japonica*)にわけた。アカマツ材およびスギ材の混合重量比は76:24であった。分別したアカマツあるいはスギ材チップを用いて実験室で蒸解を行った。

2.2 実験室におけるカラマツ材の蒸解およびその条件

木材チップ(絶乾重量45g)を精秤し、350ml容オートクレーブに入れ、Kraft法、Kraft-AQ法、ソーダ・アントラキノン法(Soda-AQ法)、および、PS-AQ法によって、蒸解を行った。活性アルカリ添加率(AA添加率)を23~33%、硫化度を0または30%とし、156℃で2.5~8.5時間蒸解を行った。アントラキノン(AQ)系蒸解

助剤として、川崎化成工業製の1,4-dihydro-9,10-dihydroxy-anthracene sodium salt (SAQ)を用い、添加率は0.14%とした。PS-AQ法では、クラフト蒸解液にイオウを加えてPS蒸解液を調製し、イオウ添加率を2.0%とした。また、液比は5.5 L/kgとした。

2.3 実験室におけるアカマツ・スギ材の蒸解条件

アカマツ・スギ材それぞれについて、AA添加率を23または28%、AQ添加率を0または0.14%、硫化度を30%とし、168℃で2.5時間の条件下で、Kraft法、Kraft-AQ法による蒸解を行った。

2.4 工場実験およびその蒸解条件

三菱製紙八戸工場において、2004年10月26,27日にKraftおよびKraft-AQ蒸解による工場実験を行った。前者のAA添加率は19.7%、後者は17.0%およびSAQ添加率0.1%で、硫化度は両者において30~32%であった。KraftおよびKraft-AQ蒸解操業時に、それぞれパルプを10サンプル以上採取し、その中からカップー価が25前後のパルプを選び、分析を行った。

2.5 パルプの構成糖分析とHexAの定量

2.5.1 パルプの収率とカップー価測定および中性糖分析

実験室の蒸解では、パルプから気乾シートを作成し、シートの絶乾重量を測定してパルプ収率を求めた。また、カップー価測定⁷⁾とアルジトールアセテート法⁸⁾による中性糖分析を行った。中性糖分析の結果から、グルコースに対するキシロースの質量比(X/G比)およびグルコースに対するマンノースの質量比(M/G比)を求めた。工場パルプについても中性糖分析を行い、M/G比を求めた。

2.5.2 パルプ中のHexAの定量分析

HexAは酸処理に対して不安定で、分解して5-formyl-2-furancarboxylic acid (FF)と2-furancarboxylic acid (FA)を与える^{9,10)}。パルプ中のHexAの代表的な定量法として、選択的酸加水分解後にUV吸光度を用いて定量するHUT法がある^{9,11)}。本研究では、HUT法に準じて酸加水分解した後、加水分解液のUV吸収を測定するHUT法ではなく、高速液体クロマトグラフィー(HPLC)を用いて加水分解物を分離後にHexAを定量する方法¹²⁾を用いた。すなわち、パルプ絶乾重量0.8 gにpH 2.5のギ酸水溶液80 mlを加え、オートクレーブ中で120℃、3時間処理をした。パルプの酸加水分解溶液を10 μl採取してHPLCで分析し、HexAの酸加水分解生成物であるFFとFAを265 nmで検出して定量することにより、その合計量をHexA量とした。

3. 結果と考察

3.1 カラマツ材のアルカリ蒸解における炭水化物の挙動

アルカリ蒸解におけるパルプ収率を評価する方法については、いくつかの方法が提案されている¹³⁻¹⁶⁾。Kleppe¹³⁾は、蒸解後のパルプ収率を評価する方法として、パルプ収率とカップー価との相関を利用し、カップー価30~90の針葉樹材パルプに対して、下記(1)式を提案した。

$$\text{Pulp yield (\%)} = 0.14 \times \text{kappa number} + \text{定数} \quad \cdots(1)$$

Kleppeの方法はカップー価とパルプ収率の間の直線的

な関係から、未知のパルプ収率を評価する簡便な方法である。しかし、この工場では、針葉樹材の漂白用パルプの目標カップー価は25であるため漂白用パルプの収率の評価法としてKleppeの方法を用いることはできない。さらに、同じカップー価のパルプでも蒸解助剤の添加の有無によって収率が異なることが予想され、蒸解助剤を添加したときに得られる収率向上を評価する場合には、この方法は適切ではないと考えられる。

Marcocciaら¹⁴⁾は、広葉樹材パルプ収率を評価する方法として、パルプのグルカン含有率と粘度を用い、下記(2)式を報告した。

$$\text{Pulp yield (\%)} = \text{定数 a} \times \log(\text{viscosity}) \div \text{Glucan content (\%)} + \text{定数 b} \quad \cdots(2)$$

Marcocciaらの方法は粘度とグルカン量を測定することが必要であり、煩雑で時間を要するのが難点であり、ポリサルファイドやAQを添加することにより得られる収率増加の予測には適していないことが報告されている¹⁵⁾。

Eastyら¹⁶⁾は、パルプ中の炭水化物とリグニンの含有率によってパルプ収率を(3)式により評価する方法(炭水化物・リグニン法)を提案した。これは実験室で木材に対するセルロース(グルカン)収率を求め、一方で工場パルプの炭水化物含有量およびリグニン含有量を定量し、パルプ収率を評価する方法である。

$$\text{Pulp yield (\%)} = Y_{\text{cell}} \times (C+H) \div C + Y_{\text{cell}} \times L \div C \quad \cdots(3)$$

ここで Y_{cell} は絶乾チップに対するセルロース収率、C、HおよびLはそれぞれパルプのセルロース、ヘミセルロースおよびリグニン含有率である。Eastyらの方法はグルカン収率はパルプ収率が異なっても一定の値であること、すなわち Y_{cell} は蒸解段階に依存せず一定であることが前提とされている。 Y_{cell} が一定にならない場合、収率評価の誤差となるため針葉樹材パルプの収率評価には用いることができないと考えられる。

様々の蒸解条件において得られたカラマツ材パルプの構成糖の変化を表1に示した。蒸解中のキシラン量の経時変化をみるとKraft、Kraft-AQとSoda-AQ蒸解において、蒸解時間が大きくなるとキシラン量が増加した。Yokoyamaら^{8,17,18)}は、広葉樹材パルプの糖分析を行い、主要ヘミセルロース構成糖のキシロースとセルロース構成糖のグルコースの質量比(以下X/G比)を求め、蒸解パルプ収率との間に高い相関があることを見出した。広葉樹材は一般に、50%程度のセルロースおよび20~30%のキシランのほかに、数%のグルコマンナンを含有している。しかし、キシラン含有量が少ない針葉樹材についてYokoyamaらの方法を用いることができるか不明であった。図1に示すように、カラマツ材パルプのX/G比とパルプ収率の関係をみるとパルプ収率とX/G比の相関が低いことがわかる。これは蒸解終期に起こるキシランのパルプ繊維への再吸着¹⁹⁾が原因の一つと考えられる。針葉樹材の場合、パルプのX/G比によりパルプ収率を評価することは困難であることが明らかとなった。

Kleppe^{20,21)}は、工場でKraft蒸解にポリサルファイドを

Table 1 Change of xylan, mannan, glucan and HexA contents of Japanese larch pulps given by kraft, kraft-AQ, PS-AQ, and soda-AQ cooks.

Cooking method	AA charge (%)	Cooking time (h)	Xylan content (% on wood)	Mannan content (% on wood)	Glucan content (% on wood)	Pulp yield (%)	Kappa number	HexA content ($\mu\text{mol/g}$)
Kraft-AQ	28	2.5	0.7	1.9	18.2	48.7	39.0	13.6
Kraft-AQ	28	3.5	0.8	1.7	18.7	48.5	29.3	11.1
Kraft-AQ	28	4.5	0.9	1.3	17.3	46.1	23.7	8.1
Kraft-AQ	28	8.5	0.6	1.2	14.3	41.3	11.4	1.3
Kraft-AQ	25	4.5	0.9	1.6	16.6	46.0	27.9	12.3
Kraft-AQ	23	4.5	1.0	1.6	17.2	47.2	34.0	16.1
Kraft-AQ	26.5	4.5	—	—	—	45.5	23.3	9.2
Kraft	28	4.5	0.8	1.5	15.7	44.6	28.0	8.1
Kraft	28	5.5	0.7	1.1	16.1	44.0	20.5	—
Kraft	28	8.5	0.9	1.1	14.2	41.3	11.4	1.1
PS-AQ	28	4.5	1.1	2.2	17.1	47.5	23.9	10.6
PS-AQ	23	4.5	1.0	2.6	19.0	50.5	32.2	20.5
Soda-AQ	33	4.5	0.4	2.0	16.5	47.0	44.5	—
Soda-AQ	33	7.5	0.3	1.5	15.4	43.8	26.8	—
Soda-AQ	33	8.5	0.7	1.3	14.1	41.9	23.3	—

Note : AQ charge and sulfur charge were 0.14% and 2.0%, respectively.

Fig.1 Relationship between pulp yields and X/G ratios for Japanese larch pulps with various kappa numbers given by various alkaline cooks.

添加したときの収率向上効果を把握するために、針葉樹材パルプ中のグルコマンナン量を用いてパルプ収率を評価する方法（グルコマンナン法）を提案した。しかし、評価の対象パルプのカッパー価は40-45であり、カッパー価30以下の漂白用パルプの場合にも、この方法が有効であるのかどうか明らかでない。また、グルコマンナン法はセルロース収率の向上分をパルプ収率評価に考慮していないため、最大で1.5%の収率誤差が生じると報告されている²²⁾。一方、針葉樹材パルプの構成糖に着目した収率評価法として

マンノース法が報告されている¹⁵⁾。これは、パルプに含まれるマンノース残基量とパルプ中の炭水化物の収率との間の相関を利用し、工場におけるパルプ収率を予測する方法である。Luthe ら¹⁵⁾は、ウェスタンヘムロック材(*Tsuga heterophylla*)を用い、AQやイオウのような蒸解助剤が添加された場合であってもパルプ収率の予測が可能であると報告している。

表1に示すように、カラマツ材のさまざまな蒸解法により得られたパルプ中のマンナン量の経時変化をみると、蒸解が進行するにつれて、マンナン量は減少した。しかし、Luthe らの結果に反してマンナン量とパルプ収率の間の相関が低かった。そこで本研究では、M/G比によりパルプ収率を評価する方法を検討した。図2にカラマツ材の様々なカッパー価のパルプの収率とM/G比との関係を示した。期待に反して、カッパー価が異なるパルプの場合、パルプ収率とM/G比の間の相関は低かった。そこで、以下のよう手順でさらに検討を加えた。

3.2 同一カッパー価におけるパルプ収率およびM/G比の関係

同一カッパー価のパルプにおける収率とM/G比の相関を検討するため、図2のデータについて、Kraft, Kraft-AQ, PS-AQおよびSoda-AQ蒸解ごとに、カッパー価が25となる内挿点を求めた。これらの4点を図3に示す。Soda-AQ蒸解は、工場のプロセスを考えると採用できないため、これを除去した。

そこで、Soda-AQ蒸解を除いたKraft, Kraft-AQ, PS-AQ蒸解の結果を用い、多変量解析によりカラマツ材の

Fig. 2 Relationship between pulp yields and M/G ratios for Japanese larch pulps with various kappa numbers given by various alkaline cooks.

Fig. 3 Relationship between pulp yields and M/G ratios for Japanese larch pulps with kappa number 25 given by various alkaline cooks.

アルカリ蒸解における炭水化物収率: [C] (% on wood), マンナン量: [M] (% on wood), グルカン量: [G] (% on wood), およびグニン含有量: [L] (% on wood) を予測する実験式を作成した (表 2)。つぎに, この実験式から, H-ファクター 1155~1605 の範囲で, 異なる AA 添加率, AQ およびイオウ添加率の条件でカップー価 25 のパルプを調製できる条件を選択し, それぞれの条件で 3 回繰り返した。

すなわち, 蒸解時間: t (h), 蒸解液中の水酸化物イオン濃度: [OH] (mol/L), AQ 添加率: AQ (% on wood) およびイオウ添加率: S (% on wood) を説明変数とし, [C], [M], [G] をそれぞれ目的変数にとった。ただし, [L] を目的変数とする場合は t ではなく $1/t$ を説明変数とした (表 2)。表 2 の式から, カップー価 25 となる [C] および [L] を与える蒸解条件 ([OH], AQ, S) を決定した。これらの蒸解条件とカップー価とパルプ収率の関係式(4)お

Table 2 Multiple liner regression for behaviors of carbohydrates and lignin during alkaline cooks.

Multiple liner regression equation	
$\ln[C] = 4.00 - 0.08[OH] + 0.146AQ + 0.03S - 0.03t$	
$\ln[M] = 2.29 - 0.43[OH] + 0.204AQ + 0.19S - 0.12t$	
$\ln[G] = 3.78 - 0.04[OH] + 0.169AQ + 0.01S - 0.02t$	
$\ln[L] = 1.68 + (-0.34[OH] - 0.258AQ + 0.01S + 0.21)t$	

Legend :

[C] : Carbohydrates yield (% on wood)

[L] : Lignin content (% on wood)

[M] : Mannan content (% on wood)

[G] : Glucan content (% on wood)

[OH] : Hydroxide concentration (mol/L)

AQ : AQ charge (% on wood)

S : Sulfur charge (% on wood)

t : cooking time (h)

Kappa number = $[L] \div \text{Pulp yield} \times 100 \div 0.13$ (4)

Pulp yield = $[C] + [L]$ (5)

Fig. 4 Relationship between pulp yields and M/G ratios for Japanese larch pulps with kappa number 25 at H-factor 1155-1605.

よび(5)式よりカップー価 25 における Kraft, Kraft-AQ および PS-AQ 蒸解によるパルプ収率と M/G 比を算出した。これらのパルプの収率と M/G 比の関係を図 4 に示した。

Kappa number = $[L] \div \text{Pulp yield} \times 100 \div 0.13$ (4)

Pulp yield = $[C] + [L]$ (5)

図 4 に示すように, 同一カップー価の場合, パルプ収率と M/G 比の間の相関は高い。このことより, あらかじめ実験室で工場チップを蒸解し, 同一カップー価のパルプ収率とパルプの M/G 比の関係から収率評価のための検量線を作成すれば, 工場で採取したパルプの M/G 比を定量することにより工場パルプの収率の評価が可能となること示された。しかし, H-ファクターが 1155 から 1605 の範囲の場合, 同一 M/G 比であってもパルプ収率が約 0.3%

Fig.5 Relationship between pulp yields and M/G ratios given by laboratory cooks of Japanese red pine and Japanese cedar.

異なる点には注意する必要がある。

3.3 M/G 比による工場のパルプ収率の評価

実験室でカラマツ材を対象に M/G 比と収率の関係を検討し、針葉樹材パルプ収率評価の方法論を確立した。材は異なるが、国産針葉樹材を用いている実際の工場に適用して、蒸解法が異なった場合の、カップパー価 25 における収率の差を評価した。図 5 は実験室の蒸解から得られたアカマツおよびスギパルプの M/G 比とパルプ収率の関係を表している。パルプのカップパー価は 20~30 の範囲にある。ここでは、これらの結果の内挿点として、工場チップ材の混合比（重量比がアカマツ：スギ=76：24）でカップパー価 25 のパルプが得られると仮定した。すなわち、内挿によって Kraft および Kraft-AQ 蒸解の各パルプの収率と M/G 比を得て、この 2 点から検量線を作成した。検量線に用いたパルプの H-ファクターは 1650 である。

一方、表 3 にはカップパー価 25 の工場パルプの M/G 比を分析した結果を示した。Kraft-AQ 法が Kraft 法よりも M/G 比が高い。カップパー価 25 のパルプの M/G 比からパルプ収率を予測した結果、アカマツ・スギ混合材の Kraft-AQ 法のパルプ収率は Kraft 法より 1.3% 高いことが示された。

3.4 蒸解助剤の添加が HexA 量に与える影響

アルカリ蒸解中にキシラン側鎖に結合する 4-O-methyl- α -D-glucuronic acid は、メタノールの β 脱離によって、二重結合を有する HexA へと変化する⁴⁾。パルプ中に含まれる HexA は、カップパー価測定で用いる過マンガン酸カリウムあるいは漂白薬品の塩素、二酸化塩素およびオゾン消費することが報告されている^{4,11,23)}。また、漂白後残存した HexA はパルプ黄変（色戻り）の原因の一つと報告されている^{24,25)}。HexA 量の少ない漂白パルプを得るためには、蒸解後に HexA 量の少ないパルプを得ることが望ましい。

同一 H-ファクターにおいて有効アルカリ添加率が高い条件の場合、パルプ中の HexA が少ないことが報告されている⁴⁾。また、同一カップパー価を得るために必要な水硫化物イオン濃度、および、温度が高いと、HexA 量が高いと報告されている²⁶⁾。しかし、AQ およびポリサルファイドはパルプ収率向上の役割を担うが、これらの添加が蒸解後のパルプ中の HexA 量にどのような影響を与えるかに関する報告は少ない。

カラマツ材パルプの HexA 量：[HexA] ($\mu\text{mol/g}$) と蒸解条件の関係について、多変量解析を行って下記(6)に示す実験式を求めた。

$$\ln [\text{HexA}] = 8.28 - 3.14 [\text{OH}] + 0.247 \text{AQ} + 0.16 \text{S} - 0.44 t \quad \dots\dots(6)$$

つぎにこれを用い、H-ファクター 1200 でカップパー価 25 のパルプを与える蒸解条件を求め、Kraft, Kraft-AQ および PS-AQ 蒸解によるパルプの HexA 量の算出を行った結果を表 4 に示した。各パルプの蒸解条件および HexA 含有量は表 1 に示した。カップパー価 25 におけるパルプの HexA 量は、3 つの蒸解法のうち PS-AQ 蒸解が最も高い結果となった。AQ およびイオウを添加すると HexA 量を増加させることが示された。AQ を添加すると HexA 量が高くなる原因として、同一カップパー価を得るために必要な [OH] が低いことがあげられる。PS-AQ パルプが Kraft パルプと比較して HexA 量が高い原因についても、同一カップパー価を得るために必要な [OH] が低いことが考えられる。Chai ら²⁷⁾は HexA 生成と分解速度に対して AQ は影響を与えないが、AQ を添加すると脱リグニンが促進され

Table 3 Estimation of Japanese red pine and Japanese cedar mixed pulp yields with kappa number 25 given kraft and kraft-AQ cooking at a mill.

Cooking method	Kappa number	M/G ratio	Pulp yield, estimated (%)
Kraft	25.2	0.0696	43.0
Kraft	24.8	0.0713	43.2
Kraft-AQ	25.2	0.0821	44.5
Kraft-AQ	24.8	0.0803	44.3
<hr/>			
Kraft (average)	25.0	0.0705	43.1
Kraft-AQ (average)	25.0	0.0812	44.4

Table 4 Comparison of HexA contents between various alkali Japanese larch pulps with kappa number 25 at H-factor 1200.

Cooking method	HexA content ($\mu\text{mol/g}$)	Pulp yield (%)	[OH] (mol/l)	AQ charge (%)	Sulfur charge (%)
Kraft	6.3	44.7	1.46	0.00	0.0
Kraft-AQ	10.3	46.1	1.34	0.14	0.0
PS-AQ	13.6	48.5	1.36	0.14	2.0

Note : $\ln[\text{HexA}] = 8.28 - 3.14[\text{OH}] + 0.247\text{AQ} + 0.16\text{S} - 0.44t$

Table 5 Estimation of HexA contents in Japanese red pine and Japanese cedar mixed pulp with kappa number 25 given kraft and kraft-AQ cooking at a mill.

Cooking method	Kappa number	HexA content ($\mu\text{mol/g}$)
Kraft	25.2	11.2
Kraft	24.8	10.6
Kraft-AQ	25.2	18.1
Kraft-AQ	24.8	17.2
Kraft (average)	25.0	10.9
Kraft-AQ (average)	25.0	17.7

て蒸解時間が減少するため、同一カップー価で比較した場合には HexA 量が高くなると報告している。

しかし、Kraft-AQ パルプと PS-AQ パルプを比較すると、同一カップー価を得るために必要な [OH] は PS-AQ 蒸解が多いにもかかわらず、パルプの HexA 量が高かった。イオウ添加が HexA 量を大きくする影響もあることが示唆され、この理由の解明は今後の課題である。

3.5 AQ の添加が工場パルプの HexA 量に与える影響

工場実験で得られたカップー価 25 の Kraft および Kraft-AQ パルプの HexA 量を表 5 に示した。AQ を添加することにより HexA 量は $7\mu\text{mol/g}$ 高い値を示した。工場実験の条件では H-ファクターは同一で、Kraft-AQ 蒸解は Kraft 蒸解より AA 添加率を低くしてカップー価 25 のパルプを得ている。蒸解液のアルカリ量が低いと HexA 量が多くなるので、Kraft-AQ 蒸解によるパルプの HexA 量が高くなったと考えられる。

4. 結 論

連続操業を行っている工場で国産針葉樹材パルプ収率を化学的に評価する方法について検討した。カラマツ材の Kraft, Kraft-AQ と Soda-AQ 蒸解の結果、キシランの再吸着などが起こるため、パルプの X/G 比からパルプ収率を評価することはできないことが明らかとなった。様々な

カップー価のパルプ収率と M/G 比の間では相関が低かった。Kraft, Kraft-AQ と PS-AQ 蒸解でカップー価 25 のパルプでは、パルプ収率と M/G 比との相関が高いことが明らかとなった。このことからアカマツ・スギ混合材を原料に用いている工場パルプの M/G 比からカップー価 25 (当工場での目標カップー価) のパルプ収率を評価した。Kraft 法に AQ を添加することで収率が 1.3% 増加することが示された。また、多変量解析により蒸解因子と HexA 量の関係を示す実験式を作成した結果、AQ および S の添加は HexA 量を増加させる影響があることが示された。同一カップー価、同一 H-ファクターでは PS-AQ 蒸解が最も HexA 量が高いパルプを与えた。工場実験では、Kraft-AQ パルプの HexA 量は AQ を添加することで Kraft パルプよりも $7\mu\text{mol/g}$ 高い値となった。

References

- 1) 農林水産省統計部：農林業センサス累年統計書—林業編—(昭和 35 年～平成 17 年)，農林統計協会，2008
- 2) 林野庁編：森林・林業統計要覧 2007，林野弘済会，2007，10-11
- 3) Forestry Agency, The Ministry of Agriculture, Forestry and Fisheries of Japan : Annual Report on Trends in Forests and Forestry Fiscal Year 2005, p 142
- 4) Buchert J., Teleman A., Harjunpää V., Tenkanen M., Viikari L. and Vuorinen T. : Tappi J. 78 (11) 125-130 (1995)
- 5) Ikada T., Tomimura Y., Magara K., Ishihara M. and Hosoya S. : J. Wood Sci. 45 (5), 417-424 (1999)
- 6) Jiang Z. -H., Lierop B. V. and Berry R. : Tappi J. 83 (1) 167-175 (2000)
- 7) TAPPI TEST METHODS : "T 236 cm-85", TAPPI PRESS, 1996
- 8) Yokoyama T., Ohi H. and Nakamata K. : JAPAN TAPPI J. 58 (6) 79-85 (2004)
- 9) Telman A., Harjunpää V., Tenkanen M., Buchert J., Hausalo T., Drakenberg T. and Vuorinen T. : Carbohydrate Res. 272, 55-71 (1995)
- 10) Telman A., Hausalo T., Tenkanen M. and Vuorinen T. : Carbohydrate Res. 280 (2), 197-208 (1996)

- 11) Vuorinen T., Renkanen A., Fagerström P., Buchert J. and Tenkanen M. : 1996 Int. Pulp Bleaching Conf., Conf. Proceedings. TAPPI, Washington, D. C., Apr. 14–18, 1996, p 43–51
- 12) Takahashi S., Nakagawa A., Jin G. and Ohi H. : Proceedings of The 52nd Lignin Symposium, Utsunomiya, Japan, November 14–15, 2007, 110–113
- 13) Kleppe P. J. : Tappi J. 53 (1), 35–47 (1970)
- 14) Marcoccia B., Stromberg B., Progh I.R. and Kawakami C. : Japan Tappi J. 52 (4) 458–468 (1998)
- 15) Luthe C., Berry R. M., Radiotis T. and Nadeau L. : J. Pulp Paper Sci. 29 (11), 371–376 (2003)
- 16) Easty D. B. and Malcolm E. W. : Tappi J. 65 (12) 78–80 (1982)
- 17) Ohi H., Yokoyama T., Nakamata K., Suzumi R. and Sato T. : JAPAN TAPPI J. 58 (10) 1446–1452 (2004)
- 18) Yokoyama T. and Ohi H. : JAPAN TAPPI J. 58 (12) 1742–1751 (2004)
- 19) Meller A. : *Holzforschung* 19 (4) 118–124 (1965)
- 20) Kleppe P. J. : Tappi J. 58 (8) 172–176 (1975)
- 21) Kleppe P. J. : *Paperi Puu*, 63 (4) 204–210 (1981)
- 22) Vaaler D., Eriksen O., Ribe E. and Moe S. : Seventh European Workshop on Lignocellulostics and Pulp, Conf. Proceedings. Turku, Finland, August 26–29, 2002, 265–268
- 23) Li J. and Gellerstedt G. : *Carbohydrate Res.* 302, 213–218 (1997)
- 24) Granström A., Eriksson T. and Gellerstedt G. : *Nord. Pulp Paper Res. J.* 16 (1) 18–23 (2001)
- 25) Kawae A. and Uchida Y. : *Appita J.* 58 (5) 378–381. (2005)
- 26) Gustavsson C. and Wafa AI-Dajani W. : *Nord. Pulp Paper Res. J.* 15 (2) 160–167 (2000)
- 27) Chai X. -S., Yoon S., -H., Zhu J. Y. and Li J. : *J. Pulp Paper Sci.* 27 (12) 407–411 (2001)

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1. Introduction

In Japan, 67% of the area of national land is covered with forests. The growing wood stock in Japan is about 4 billion m³ (162 m³/ha) in 2005. Planted forests constitute about 42% of all the Japanese forests, and the growing wood stock of planted forests reaches about 2.4 billion m³, which are mostly consisted of softwoods (98%)¹⁾. When we focus on age of planted softwood forest, the growing wood stock in the class IX (40–45 years old) is the largest among all the classes²⁾. It is anticipated that the forests classified in the class IX will hereafter reach the final cutting age, involving increase in domestic softwood supply. However, annual increment of softwood in Japanese national forests (7.3 million ha) is 15.55 million m³/year for 2006, and the self-sufficiency rate of industrial wood is maintained at about 20% in Japan.

It was decided as the target of the Kyoto Protocol that the greenhouse gas emission would be reduced by 6% of the base year (1990) by 2010 and about two thirds of this

6% reduction (3.9%) should be secured through the forest carbon sink. Japanese planted forests have not been managed well and devastated because of several problems, such as low domestic wood demand and low productivity of forest management. The Kyoto Protocol permits only appropriately managed forests to contribute to reduction of the greenhouse gas. Therefore, it is the urgent problem that planted forests should be appropriately managed and conserved by thinning of the forests as well as by others to prevent the global warming³⁾.

Pulp yield after cooking of domestic softwoods is lower than that of hardwoods planted as raw materials of pulp, which alternatively accompanies larger bio-energy production from softwoods black liquor that is obtained from 1 kg of original wood. Therefore, it is very important to promote utilization of domestic softwoods as raw materials of pulp, aiming at producing larger bio-energy.

On the basis of these backgrounds, it is significant to expand utilization of domestic softwoods in pulp and paper industry, which occupies the majority of industrial wood

consumption. For efficient utilization of wood resources, it is required to accurately estimate pulp yield during its production process. It is generally difficult to estimate pulp yield in cooking process because of continuous operation of the process. When domestic softwoods are utilized as raw materials of pulp, it is common to use mixed wood chips, parts of which are discharged as residues from sawmills. Because of this, the estimation of pulp yield and quality is more difficult than when raw material woods are constituted only from a wood species whose origin is clearly known. It is necessary to develop a method for the accurate estimation of pulp yield in continuous cooking process especially when domestic softwoods are utilized as raw materials.

During alkaline cooking, 4-*O*-methyl- α -D-glucuronic acid groups linked to xylan are converted into 4-deoxyhex-4-enuronic acid (HexA) groups, and cooking conditions affect HexA content of pulp⁴⁾. It has been reported that the xylan content in beech kraft pulp was 2.5 times higher than that in red pine kraft pulp, and that the amount of 4-*O*-methyl- α -D-glucuronic acid in softwood xylan is about twice of that in hardwood xylan⁵⁾. It is believed that softwood pulp contains smaller amount of HexA than hardwood pulp. However, HexA content of softwood pulp varies depending on cooking conditions, and it has been reported, for example, that the amount of HexA in pine kraft pulp is 54 μ mol/g when the kappa number is 25.9⁶⁾. It is significant to examine the effect of cooking conditions on the HexA formation and the possibility of the HexA removal during cooking of softwoods. When domestic softwoods are used as raw materials of pulp, it is required to examine the formation of HexA as well as the behavior of carbohydrates in cooking with an additive, such as anthraquinone (AQ).

In this study, we clarified the behavior of carbohydrates during alkaline cooking of Japanese softwoods, larch (*Larix leptolepis*), red pine (*Pinus densiflora*), and cedar (*Cryptomeria japonica*), and developed a method for the accurate estimation of domestic softwood pulp yield at a continuous cooking mill. We also evaluated the effect of adding AQ and elemental sulfur as cooking additives on the amount of HexA in domestic softwood pulps obtained by Kraft, Kraft-anthraquinone (Kraft-AQ), and polysulfide-anthraquinone (PS-AQ) methods.

2. Materials and methods

2.1 Materials

Japanese larch (*L. leptolepis*) was obtained from the Agricultural and Forestry Research Center of University of Tsukuba, Yatsugatake forest (Kawakami, Nagano, Japan), which has been grown for thirty years. The larch wood was divided into sapwood and heartwood portions in our

laboratory (at University of Tsukuba), and two kinds of wood chips were prepared from each portion. The average size applied to cooking experiments was 13.2 mm $\times$ 24.8 mm $\times$ 2.4 mm in sapwood chips.

Industrial softwood chips, which were consisted of Japanese red pine (*P. densiflora*) and Japanese cedar (*C. japonica*), were obtained from Hachinohe Mill, Mitsubishi Paper Mills, Ltd. (Aomori, Japan), and divided into each wood species by hand in our laboratory. The weight ratio of red pine to cedar was 76 to 24. Wood chips of each species were individually subjected to cooking experiments in our laboratory.

2.2 Method and conditions for laboratory cooking of Japanese larch

Into a 350 ml stainless steel autoclave, 45 g (oven-dry base) of Japanese larch chips were put, and cooked by Kraft, Kraft-AQ, Soda-AQ, or PS-AQ method. Cooking conditions were as follows: active alkali charge (AA charge) 23–33%, sulfidity 0 or 30%, maximum temperature 156°C, total time 2.5–8.5 h. A cooking additive of AQ type, 1, 4-dihydro-9, 10-dihydroxyanthracene sodium salt (SAQ), was provided by Kawasaki Chemicals Ltd. (Kanagawa, Japan), and used with 0.14% charge. In PS-AQ method, cooking liquor was prepared by the addition of elemental sulfur into white liquor with 2% charge. The ratio of liquor to wood was adjusted to 5.5 l/kg.

2.3 Method and conditions for laboratory cooking of Japanese red pine and cedar

Japanese red pine and cedar chips were individually cooked by Kraft or Kraft-AQ method under following conditions: AA charge 23 or 28%, AQ charge 0 or 0.14%, sulfidity 30%, maximum temperature 168°C, total time 2.5 h.

2.4 Description of mill trial and conditions of mill cooking

A mill trial was conducted at Hachinohe Mill, Mitsubishi Paper Mills, Ltd. on October 26–27 th, 2004. Kraft and Kraft-AQ methods were applied to the mill trial. Conditions were as follows: AA charge 19.7%, sulfidity 30–32% in Kraft method, AA charge 17.0%, SAQ charge 0.1%, sulfidity 30–32% in Kraft-AQ method. More than 10 pulp samples were collected during each cooking method, and pulps with kappa number around 25 were chosen from these samples and subjected to chemical analyses.

2.5 Analysis of carbohydrate composition and determination of HexA content of pulp

2.5.1 Analysis of yield, kappa number, and neutral sugar composition of pulp

Hand sheets were prepared from pulps obtained by the laboratory cookings, and the pulp yields were determined by measuring their oven-dried weights. Kappa numbers of the pulps were determined using the hand sheets, according to TAPPI test method⁷⁾. Neutral sugar composi-

tions of the pulps were analyzed by the alditol acetate method⁸⁾. The weight ratios of xylose to glucose (X/G ratio) and of mannose to glucose (M/G ratio) in the hydrolyzates of the acid hydrolysis of the pulps were determined using the results of the neutral sugar compositions. The M/G ratios were also determined for pulps obtained at the mill trial.

2.5.2 Analysis of HexA content of pulp

HexA is readily hydrolyzed and converted into 5-formyl-2-furancarboxylic acid (FF) or 2-furancarboxylic acid (FA) under acidic conditions^{9),10)}. One of the representative methods for the determination of HexA content of pulp is the HUT method in which HexA is determined by UV absorbance of the hydrolyzate obtained by the selective hydrolysis under the acidic conditions^{9),11)}. We applied an acidic hydrolysis similar to the selective hydrolysis in the HUT method to this study. After the hydrolysis, the hydrolyzate was subjected to high performance liquid chromatography (HPLC), and FF and FA were separately quantified using a UV detector¹²⁾. That is, 0.8 g of oven-dried pulp was quantitatively treated with 80 ml of an aqueous solution of formic acid (pH 2.5) at 120°C for 3 h in an autoclave. Then, 10 μ l of the reaction solution was directly injected to HPLC and the amounts of FF and FA were quantified using the absorbance at 265 nm. The total amount of FF and FA was applied to the amount of HexA.

3. Results and discussion

3.1 Behavior of carbohydrates during alkaline cooking of Japanese larch

Several methods have been proposed for the estimation of pulp yield during alkaline cooking¹³⁻¹⁶⁾. Kleppe has proposed the following formula (1), which is dependent on the linear correlation between pulp yields and kappa numbers of softwood pulps in the kappa number range between 30 and 90¹³⁾.

$$\text{Pulp yield (\%)} = 0.14 \times \text{kappa number} + \text{constant} \quad \dots\dots(1)$$

The utilization of this correlation is a simple method to estimate unknown pulp yield. However, this method cannot be applied to the estimation of pulp yield when the target kappa number is set up to 25 for lowering loads in subsequent bleaching processes. Furthermore, it is considered that the method of Kleppe is not appropriate when the focus of attention is on the gain of pulp yield attained by the addition of cooking additives. This is because it is expected that pulp yields at a given kappa number vary depending on the presence or absence of cooking additives.

Marcoccia and co-workers have proposed the following formula (2) as a method for the estimation of hardwood pulp yield using glucan content and viscosity of pulps¹⁴⁾.

$$\begin{aligned} \text{Pulp yield (\%)} &= a \times \log(\text{viscosity}) \\ &\div \text{Glucan content (\%)} + b \quad (a, b : \text{constants}) \quad \dots\dots(2) \end{aligned}$$

The method of Marcoccia disadvantageously requires complex and time-consuming procedures, which are the determination of viscosity and glucan content of pulp. It has been reported that this method is not appropriate for the estimation of yield gain attained by the addition of AQ and polysulfide¹⁵⁾.

Easty and co-workers have proposed a method (carbohydrate-lignin method) to estimate pulp yield based on carbohydrate (glucan) and lignin contents of pulp using the following formula (3)¹⁶⁾.

$$\text{Pulp yield (\%)} = Y_{\text{cell}} \times (C + H) \div C + Y_{\text{cell}} \times L \div C \quad \dots\dots(3)$$

Y_{cell} represents cellulose yield based on oven-dried wood. C, H and L represent cellulose, hemicellulose and lignin contents of pulp, respectively. It is assumed in this method that glucan contents of cooked pulps are constant even when their yields are different. This indicates that Y_{cell} is constant without depending on progress of cooking process. When Y_{cell} varies with change in pulp yield, this method cannot be applied to the estimation of softwood pulp yield.

Table 1 shows the changes in the carbohydrate compositions of Japanese larch pulps obtained by various cooking conditions. The xylan contents of pulps cooked by Kraft, Kraft-AQ and Soda-AQ increased with the progress of the cooks. Yokoyama and co-workers examined carbohydrate compositions of hardwood pulps to determine the weight ratios of xylose to glucose (X/G ratio)^{8),17),18)}, which are compositions of hemicellulose and cellulose, respectively, and liberated by acid hydrolysis of the pulps. They have found that there is a good linear correlation between pulp yields and X/G ratios. Hardwoods generally consist of a few percent of glucomannan, about 50% of cellulose and 20-30% of xylan. However, it has been unknown whether the method of Yokoyama can also be applied to the yield estimation of pulp obtained from softwood because xylan content is much lower in softwood than in hardwood. As shown in Fig. 1, the correlation between pulp yields and X/G ratios of Japanese larch pulps prepared in this study was low. It is considered as one of the reasons of this low correlation that a part of dissolved xylan is re-adsorbed on wood fiber surface in the final stage of cooking¹⁹⁾. It has been proved that the estimation of pulp yield using X/G ratio of the pulp is difficult when softwood is used as a raw material.

Kleppe has proposed a method to estimate softwood pulp yield using glucomannan content of pulp (Glucomannan method), aiming at examining the effect of adding polysulfide to mill kraft cooking on the yield gain^{20),21)}. However, it is unclear whether the Glucomannan method is

also effective for pulps with kappa number below 30 because the target kappa number is 40–45 in this method. Moreover, it has been reported that the yield estimation by the Glucomannan method includes errors as the maximum value to be 1.5% since this method does not take a part of the yield gain of cellulose into consideration²²⁾. On the other hand, the Mannose method has been proposed for the estimation of pulp yield based on carbohydrate composition of softwood pulp¹⁵⁾. This method estimates yields of softwood pulps prepared at a mill, using a correlation between carbohydrate yields and contents of mannose residues of pulps. Luthe and co-workers have reported that the Mannose method can also estimate yield of pulps obtained by cookings with addition of AQ and elemental sulfur, using Western hemlock (*Tsuga heterophylla*) wood¹⁵⁾.

As shown in Table 1, mannan content of pulps obtained by various alkaline cooks of Japanese larch wood decreased with the progress of the cooking processes. Contrary to the results of Luthe and co-workers, the correlation between yields and mannan contents of pulps was low. Thus in this study, we evaluated a method for the estimation of pulp yield using weight ratio of mannose to glucose (M/G ratio), which are obtained by acid hydrolysis of pulp. Fig. 2 shows the correlation between yields and M/G ratios of Japanese larch pulps with various kappa numbers. Contrary to our expectation, the correlation was low when kappa numbers of the pulps were different. We evaluated this method further according to the procedures described in the next section.

3.2 Correlation between yields and M/G ratios of pulps with a given kappa number

In order to examine the correlation between yields and M/G ratios of pulps with a given kappa number, the pulp yields and M/G ratios at kappa number 25 were calculated for each cooking method, Kraft, Kraft-AQ, PS-AQ and Soda-AQ, by the interpolation using the data shown in Fig. 2. The resulting four points are shown in Fig. 3. The data of Soda-AQ cooking was rejected since this cooking could not be applied to the mill trial due to the mill process.

Thus, we created experimental equations for the estimation of the compositions of pulps during alkaline cooking of Japanese larch wood, utilizing the data points of Kraft, Kraft-AQ and PS-AQ cooks in the multiple classification analysis. The compositions analyzed were as follows: carbohydrate yield [C] (% on wood), mannan content [M] (% on wood), glucan content [G] (% on wood), and lignin content [L] (% on wood) (Table 2). We subsequently selected the cooking parameters, AA charge, and AQ and sulfur charges, by which pulps with kappa number 25 could be prepared at three H-factors, 1155, 1200 and 1605. That is, we conducted the multiple classification

analysis, using each of the following parameters, cooking time: t (h), hydroxide ion concentration in cooking liquor: $[\text{OH}]$ (mol/L), AQ charge: AQ (% on wood) and sulfur charge: S (% on wood), as an explaining variable and each of [C], [M] and [G] as an objective variable. When we used [L] as an objective variable, not t but $1/t$ was used as an explaining variable. The cooking conditions, $[\text{OH}]$, AQ and S , were determined by the equations shown in Table 2, under which pulps with [C], [L] and kappa number 25 could be prepared. These cooking conditions and the following formulas (4) and (5), representing kappa number and pulp yield, respectively, made it possible to estimate pulp yields and M/G ratios of pulps with kappa number 25 obtained by Kraft, Kraft-AQ and PS-AQ methods. The correlation between these pulp yields and M/G ratios is shown in Fig. 4.

$$\text{Kappa number} = [\text{L}] \div \text{Pulp yield} \times 100 \div 0.13 \cdots \cdots (4)$$

$$\text{Pulp yield} = [\text{C}] + [\text{L}] \cdots \cdots (5)$$

The correlation between pulp yields and M/G ratios was high when pulps with the same kappa number were evaluated, as shown in Fig. 4. It was suggested that yield of pulps prepared at a mill can be estimated by the determination of M/G ratios of the pulps when a calibration line is created by utilizing the high correlation between yields and M/G ratios of pulps with a given kappa number. However, it should be noted that the difference in yields of pulps obtained by cooks with the H-factor range between 1155 and 1605 is about 0.3% even if the pulps have the same M/G ratio.

3.3 Estimation of yield of pulp obtained at mill trial using M/G ratio

We have evaluated the correlation between yields and M/G ratios of pulps obtained from Japanese larch wood in our laboratory, and established a method for the estimation of softwood pulp yields. On the basis of this method, we estimated the difference in pulp yields when the pulps were prepared to be kappa number 25 by various cooking methods in the mill (see 2.4 for description) although not Japanese larch but Japanese red pine and cedar were used as mixed chips in the mill. Fig. 5 shows the correlations between yields and M/G ratios of pulps obtained by the cooks of each of Japanese red pine and cedar in our laboratory. The kappa numbers of the pulps were in the range from 20 to 30. The weight ratio of Japanese red pine to cedar in mixed chips was 76 to 24 at the mill. It was presumed that the interpolations of the data shown in Fig. 5, according to this mixed ratio, gave data points which represent pulps prepared from the cookings of wood chips mixed with the same ratio. Thus, yields and M/G ratios of pulps were estimated by the interpolation in each of Kraft and Kraft-AQ method. Two data points obtained by the interpolations in each method (Fig. 5) were used as a cali-

bration line for the estimation of pulp yield at the mill trial. The H-factor 1650 was applied to the creation of the calibration line.

M/G ratios of pulps with kappa number 25 obtained from the mill trial are shown in Table 3. The M/G ratios of the pulps cooked by Kraft-AQ method were higher than those by Kraft method. It was shown that the yield of pulps cooked by Kraft-AQ method is 1.3% higher than that by Kraft method when pulp yields are estimated from M/G ratios of pulps with kappa number 25.

3.4 Effect of addition of cooking additives on HexA content

During alkaline cooking, 4-*O*-methyl- α -D-glucuronic acid groups linked to xylan are converted into HexA, which have a double bond in a molecule, by the β -elimination of methanol⁴⁾. It has been reported that HexA in pulp consumes permanganate, which is used in the determination of kappa number, or some bleaching chemicals such as chlorine, chlorine dioxide and ozone^{4), 11), 23)}. HexA remaining in bleached pulps are considered to be one of the factors for yellowing of pulps (brightness reversion)^{24), 25)}. It is required to obtain unbleached pulp with small content of HexA for preparing bleached pulp with small content of HexA.

It has been reported that high effective alkali charge leads to pulp with low HexA content at the same H-factor⁴⁾. It has also been reported that pulps with a given kappa number but relatively high HexA contents are prepared when high concentration of hydrogen sulfide and high temperature are applied as cooking parameters²⁶⁾. The addition of AQ and polysulfide attains the gain of pulp yield. However, there are few studies as to the effect of cooking additives on HexA content of unbleached pulp.

We determined the following experimental equation (6) for Japanese larch pulps, conducting the multiple classification analysis of the correlation between HexA content : [HexA] (μ mol/g) and cooking conditions.

$$\ln [\text{HexA}] = 8.28 - 3.14 [\text{OH}] + 0.247 \text{AQ} + 0.16 S - 0.44 t \quad \cdots \cdots (6)$$

By utilizing this equation, we subsequently determined cooking conditions, under which pulps with kappa number 25 were prepared at H-factor 1200. Based on these conditions, the HexA contents of the pulps, which were assumed to be prepared by Kraft, Kraft-AQ and PS-AQ cooking methods, could be calculated by the equation (6), and are shown in Table 4. The cooking conditions and the HexA content of each pulp are shown in Table 1.

The HexA content of the pulp obtained by PS-AQ method was the highest among three cooking methods when kappa number of the pulp was 25. It was also shown that the addition of AQ and elemental sulfur increased HexA content. One of the main reasons for high HexA

contents in pulps obtained by cooks with the addition of AQ would be that Kraft-AQ pulps with kappa number 25 are obtained by a lower [OH] than Kraft pulps with the same kappa. The same reason can also be applied to the explanation of the phenomenon that the PS-AQ pulp has higher HexA content than the Kraft pulp. Chai and co-workers have reported that HexA content of a pulp prepared by cooking with AQ is higher than that without AQ at a given kappa number because AQ shortens cooking time due to the acceleration of delignification in spite of the absence of the effect on the formation and degradation of HexA²⁷⁾. However, the PS-AQ pulp had higher HexA content than the Kraft-AQ pulp at a given kappa number although [OH] required was higher for the preparation of the former than for the production of the latter. It was suggested that the addition of elemental sulfur may affect HexA content of pulp. This topic is further investigated in the future.

3.5 Effect of addition of AQ on HexA content at mill trial

The HexA contents of the mill Kraft and Kraft-AQ pulps with kappa number 25 are shown in Table 5. The addition of AQ increased HexA content by 7 μ mol/g. In the mill trial, Kraft-AQ method required lower AA charge than Kraft method when pulps with kappa number 25 were prepared by these methods at the same H-factor. It is considered that the HexA contents of the mill Kraft-AQ pulps are higher than those of the mill Kraft pulps because HexA content increases with the decrease of AA charge in cooking liquor.

4. Conclusions

We tried to develop chemical methods for the estimation of domestic softwood pulp yield at a mill with continuous operation. Pulp yields could not be estimated by X/G ratios of the pulps probably because of the re-adsorption of xylan on pulp surface, when Japanese larch wood was cooked by Kraft, Kraft-AQ and Soda-AQ methods as a raw material. The correlation between yields and M/G ratios of pulps with various kappa numbers was not good. It was proved that there was a good correlation between yields and M/G ratios of pulps with kappa number 25 obtained by Kraft, Kraft-AQ, and PS-AQ cooks. On the basis of this good correlation, pulp yields at the mill, where raw material was mixed chips of Japanese red pine and cedar, were estimated by M/G ratios of the pulps when kappa number of the pulps was 25 (the target number of this mill). The yield gain by the addition of AQ to the Kraft method was shown to be 1.3% in the mill trial. An experimental equation was developed by the multiple classification analysis, which led to establishing the correlation between cooking conditions and HexA contents of pulps. It

was shown that the addition of AQ and elemental sulfur increased HexA content of pulp. The PS-AQ method gave pulps with the highest HexA content among three cooking methods at a given kappa number and H-factor. At the mill trial, the HexA content of the Kraft-AQ pulp was 7 μ mol/g higher than that of the Kraft pulp. The HexA content of pulps was the highest when the pulps were prepared by three cooking methods to show the same kappa number at the same H-factor.

References

- 1) Ministry of Agriculture, Forestry and Fisheries Statistics department : Census of Agriculture and Forestry Ruinen tokei sho —Ringyou hen— (1960~2005), Nourintoukeikyokai, 2008
- 2) Forestry Agency : Shinrin • Ringyou tokei youran 2007, Rinyakousaikai, 2007, 10-11
- 3) Forestry Agency, The Ministry of Agriculture, Forestry and Fisheries of Japan : Annual Report on Trends in Forests and Forestry Fiscal Year 2005, p 142
- 4) Buchert J., Teleman A., Harjunpää V., Tenkanen M., Viikari L. and Vuorinen T. : Tappi J. 78 (11) 125-130 (1995)
- 5) Ikada T., Tomimura Y., Magara K., Ishihara M. and Hosoya S. : J. Wood Sci. 45 (5), 417-424 (1999)
- 6) Jiang Z. -H., Lierop B. V. and Berry R. : Tappi J. 83 (1) 167-175 (2000)
- 7) TAPPI TEST METHODS : "T 236 cm-85", TAPPI PRESS, 1996
- 8) Yokoyama T., Ohi H. and Nakamata K. : JAPAN TAPPI J. 58 (6) 79-85 (2004)
- 9) Telman A., Harjunpää V., Tenkanen M., Buchert J., Hausalo T., Drakenberg T. and Vuorinen T. : Carbohydrate Res. 272, 55-71 (1995)
- 10) Telman A., Hausalo T., Tenkanen M. and Vuorinen T. : Carbohydrate Res. 280 (2), 197-208 (1996)
- 11) Vuorinen T., Renkanen A., Fagerström P., Buchert J. and Tenkanen M. : 1996 Int. Pulp Bleaching Conf., Conf. Proceedings. TAPPI, Washington, D. C., Apr. 14-18, 1996, p 43-51
- 12) Takahashi S., Nakagawa A., Jin G. and Ohi H. : Proceedings of The 52nd Lignin Symposium, Utsunomiya, Japan, November 14-15, 2007, 110-113
- 13) Kleppe P. J. : Tappi J. 53 (1), 35-47 (1970)
- 14) Marcoccia B., Stromberg B., Progh I. R. and Kawakami C. : Japan Tappi J. 52 (4) 458-468 (1998)
- 15) Luthe C., Berry R. M., Radiotis T. and Nadeau L. : J. Pulp Paper Sci. 29 (11), 371-376 (2003)
- 16) Easty D. B. and Malcolm E. W. : Tappi J. 65 (12) 78-80 (1982)
- 17) Ohi H., Yokoyama T., Nakamata K., Suzumi R. and Sato T. : JAPAN TAPPI J. 58 (10) 1446-1452 (2004)
- 18) Yokoyama T. and Ohi H. : JAPAN TAPPI J. 58 (12) 1742-1751 (2004)
- 19) Meller A. : Holzforschung 19 (4) 118-124 (1965)
- 20) Kleppe P. J. : Tappi J. 58 (8) 172-176 (1975)
- 21) Kleppe P. J. : Paperi Puu, 63 (4) 204-210 (1981)
- 22) Vaaler D., Eriksen O., Ribe E. and Moe S. : Seventh European Workshop on Lignocellulostics and Pulp, Conf. Proceedings. Turku, Finland, August 26-29, 2002, 265-268
- 23) Li J. and Gellerstedt G. : Carbohydrate Res. 302, 213-218 (1997)
- 24) Granström A., Eriksson T. and Gellerstedt G. : Nord. Pulp Paper Res. J. 16 (1) 18-23 (2001)
- 25) Kawae A. and Uchida Y. : Appita J. 58 (5) 378-381. (2005)
- 26) Gustavsson C. and Wafa AI-Dajani W. : Nord. Pulp Paper Res. J. 15 (2) 160-167 (2000)
- 27) Chai X. -S., Yoon S., -H., Zhu J. Y. and Li J. : J. Pulp Paper Sci. 27 (12) 407-411 (2001)