

SOFTWOOD EXTRACTIVES : RECOVERY AND CHARACTERIZATION

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TASK 5 : FINAL REPORT

Deliverable 6

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I. Introduction

Forest thinnings in the western U.S. are mainly composed of small-diameter trees and underbrush. Their recovery is of low economic value to current forest-product industry but it could generate a large, sustainable quantity of softwood residues which represent available low-cost feedstock for ethanol production by fermentation. The constitutive chemical groups of these thinnings are: extractives, holocellulose (cellulose and hemicellulose) and lignin.

Objective

The key objective of this project is to investigate methods for recovery of extractives present in softwood forest thinnings which may be toxic to fermentative organisms, in order to obtain a "cleaner" feedstock for fermentation. Once the extractives from the residual solids, the holocellulose could be further hydrolyzed to a "clean" and fermentable streams of sugars. An added advantage to this strategy is the potential recovery of valuable products from the extractives.

Targets

Main targets of the project are :

- Evaluation of methods for the recovery of extractives from softwood forest thinnings,
- Characterization of the recovered extractives and evaluation of their potential applications.
- Selection of the best method of extraction and evaluation of its effect on aqueous / steam pretreatment.

Strategy

In order to fractionate selectively and efficiently we must :

- a) Remove the extractives present in the raw material. This operation consists of two steps:
 - a.1.) Impregnation to remove occluded and adsorbed oxygen and to introduce the solvent for extraction ;
 - a.2.) Removal of the extractives performed by different solvent combinations ;
- b) Hydrolysis of the residual extracted solids. This operation also consists of two steps:
 - b.1.) Aqueous Treatment : impregnation of the raw material with an aqueous solution to remove occluded and adsorbed oxygen and to introduce an acid catalyst for hydrolysis.
 - b.2.) Steam Treatment. ; a rapid introduction of saturated steam at a desired temperature to induce the acid-catalyzed reaction.

II. Experimental & Results

II.1. Evaluation of Extractives Removal

II.1.1. Raw Material

The raw material consists of softwood forest thinnings of approximated composition 70% White fir (*Pseudotsuga concolore*) and 30% Ponderosa pin (*Pinus ponderosa*).

The samples were air-defrozen, screened for granulometric determination and analyzed for moisture and density. Results were shown in Table 1.

Table 1 : Granulometric composition of material "as received"

Granulometry (Mesh / mm)	Weight (gr)	Percentage (%)
¼" - coarse / 6.35 - coarse	38.5	3
5 - ¼" / 4.00 - 6.35	458.5	39
10 - 5 / 1.68 - 4.00	530.3	45
16 - 10 / 1.00 - 1.68	91.8	8
28 - 16 / 0.595 - 1.00	27.8	2
finer - 28 / finer - 0.595	37.2	3
TOTAL	1184.1	100
Moisture content (98 min @ 105 °C) :		55.12 %
Density (uncompacted): 0.22 gr/mL	Density (compacted) : 0.26 gr/mL	
Uncompacted : adding material (50 gr) to a calibrated cylinder (2.5 cm diameter) and measuring its volume.	Compacted : adding material (50 gr) to a calibrated cylinder (2.5 cm diameter), compacting it by shaking until level is unchanged and measuring its volume.	

We can conclude that the raw material is principally constituted (84%) by thinnings having a size of 2 - 6 mm. In order to obtain a homogenous and stabilized material it was grounded in a mill (Thomas-Wiley - model 4) and analyzed for moisture, density and granulometric composition. Results are shown in Table 2.

Table 2 : Granulometric composition of material "after milling"

Granulometry (Mesh / mm)	Weight (gr)	Percentage
28 - 16 / 0.595 - 1.00	5.14	5
60 - 28 / 0.250 - 0.595	70.4	70
100 - 60 / 0.149 - 0.250	13.83	14
finer - 100 / finer - 0.149	10.63	11
TOTAL	100	100
Moisture content (38 h @ 105 °C) : 5.6 %		
Density (uncompacted): 0.19 gr/mL	Density (compacted) : 0.74 gr/mL	

We can observe that milling reduces the size of thinnings approximately 10 times : 0.2 - 0.6 mm (84%). This operation is important because it facilitates the extraction and as a result we can have a better idea of the potential of extractives in the raw material. As our choice will be done by comparison with raw material contents, it is essential that this value (the extractives contents) be as realistic as possible.

The raw material after milling was analyzed for : total solids (LAP-001), carbohydrates content (LAP-002), lignin insoluble (LAP-003), lignin soluble (LAP-004), ash (LAP-005), and extractives (LAP-010). Results are shown in Table 3.

Table 3 : Raw material composition after milling.

#	ANALYSIS		Recovery Factor for Sugars	Raw Material	Method
			(%)	(%)	NREL
1	Carbohydrates	Glucose	93.75	37.01	LAP-002
		Xylose	84.78	5.62	LAP-002
		Galactose	90.40	4.39	LAP-002
		Arabinose	90.88	2.78	LAP-002
		Mannose	88.09	12.30	LAP-002
		C5		8.4	Calculated
		C6		53.7	Calculated
2	Lignin (acid solubility)	Insoluble (%AIL)		29.58	LAP-003
		Soluble (%ASL)		0.43	LAP-004
3	Ash, %			0.79	LAP-005
4	Others (by diff.)			2.50	Calculated
5	Extractives	Ethanol		4.52	LAP-010

Hydrolysis of standard sugars (determination of Recovery Factors) and milled raw material were carried out under the same conditions (LAP-002):

First Hydrolysis : 2 hours at 30°C with 72% H₂SO₄.

Second Hydrolysis : 1 hour at 121°C with 4% H₂SO₄.

II.1.2. Extraction

The experimental plan for extraction focused in two important aspects which could affect the scale up of the technology :

- 1) The use of a minimal quantity of solvent, and
- 2) The simplest equipment required.

In this context, only three solvents were tested : water, ethanol 50% and ethanol 95%.

Equipment involved was associated with two principal operations : impregnation and extraction.

Impregnations parameters were the following :

- Liquid / solid ratio 10.
- Temperature : ambient (25°C)
- Pressure : 30 Psig
- Time : 10 min.

Extractions parameters were the following :

- Liquid / solid ratio 10.
- Temperature : 80°C (all experiments : 1-7) or 100°C (only 1b)
- Pression : barometric
- Time : 1 hour.

Summarized tested treatments are presented in Table 4 (as addendum).

At laboratory scale (75 gr of raw material) the following equipments were used :

- For impregnations : a batch reactor with the characteristics show in Table 5.

Table 5 : Laboratory impregnation equipment.

Reactor	Impregnator 1
Configuration	Batch
Material	SS-304
Operating Temperature	- 20°C / + 100°C
Operating Pressure	FV - 200 Psig (Piston)
Diameter	4"
Height	6.5"
Total volume	1.2 L
Operating volume	1 L
Operating weight of sample	100 gr
Agitation	None
Heat transfer	Jacket + Steam injection

- For extractions : a rotary evaporator (rotavapor), in which the temperature was carefully controlled.

The method used for the material balances is shown in Figure 1.

After each extraction treatment a solid residue and a liquid are obtained. Solid residue was analyzed for carbohydrate contents, lignin and ash. The extracted material in the liquid was calculated by weight difference between the initial dry weight of the sample used and the dry weight of solid residue recovered at the end of each treatment (impregnation, extraction or impregnation + extraction). Finally "others" present in the residual solid (not accounted as carbohydrates, lignin or ash) are evaluated by difference to 100%.

Material balances following the different treatments are shown in Tables 6 and 7 (in addendum).

Material balances during the impregnations with acid or base were difficult to do by weight difference because it is not possible to determine how much material is added to or removed from the matrix during the impregnation. To avoid problems the material balance was calculated at the end of the combined treatment (impregnation + extraction).

The criteria used for the determination of the best conditions of extraction were : i) the yield of extractives and ii) the content of C6 carbohydrate. In this way, the most selective treatments were those which have a high rate of extractives (more than 90% of extractives present in raw material) and a weak loss of C6 carbohydrate in the solid residue (recovery of 85% of C6 the carbohydrates initially present in the raw material).

These criteria are summarized in Tables 8 and 9.

Table 8 : Criteria for the determination of "Standard Conditions" for extractions.

CRITERIA →		> 90 % Extractives Recovery	> 85% C6 Carbohydrates Recovery
Extraction Treatment			
1a	Extraction water (80 °C)	Failed	Passed
1b	Extraction water (100 °C)	Failed	Passed
2	Imp. + Ext. water (80 °C)	Passed	Passed
3	Ext. EtOH 50% (80 °C)	Passed	Passed
4	Imp.H ⁺ + Ext. EtOH 50% (80 °C)	Passed	Passed
5	Imp. + Ext. EtOH 50% (80 °C)	Passed	Passed
6	Imp. OH ⁻ + Ext. EtOH 50% (80 °C)	Passed	Failed
7	Ext. EtOH 95% (80 °C)	Passed	Passed

Table 9 : Comparison of results among treatments that fulfill the criteria.

% Extractives (>90%)		% Carbohydrates (C6>85%)	
Impreg. Vs. NO Impreg.	EtOH Vs. NO EtOH	Impreg. Vs. NO Impreg.	EtOH Vs. NO EtOH.
2, 4 and 5 Vs 3 and 7	3, 4, 5 and 7 Vs 2	2, 4 and 5 Vs 3 and 7	3, 4, 5 and 7 Vs 2
(3.99) (5.47) (6.05) Vs (4.13) (4.33)	(4.13) (5.47) (6.05) (4.33) Vs (3.99)	(47.96) (50.79) (51.46) Vs (53.46) (50.78)	(53.46) (50.79) (51.46) (50.78) Vs (47.96)
Impreg. : 5	EtOH : 5	NO Impreg : 3	EtOH : 3
Treatment 5 : Extractives = 6.05% C6 carbohydrates = 51.46%		Treatment 3 : Extractives = 4.13% C6 carbohydrates = 53.46%	
Most selective treatment : 5			

As far as extractives yields, treatment 5 shows a higher yield than treatment 3 (x 1.46), and C6 carbohydrate content in treatment 3 is higher than in treatment 5 although at a lesser factor (x 1.04). We thus think that treatment 5 should be the best choice for extraction.

We can also observe from Table 7, that results for treatment 3 are very close to those of treatment 7. This permits to conclude that practically any ethanol concentration between 50% and 95% could be used for a comparable recovery of extractives.

Impregnation seems to play an important role in the extraction process. Treatment 2 (impregnation + extraction 80°C) which uses only water as solvent could also be considered as having (economic) potential.

Impregnation catalyzed by sodium hydroxide (treatment 6), results in extraction of compounds other than "extractives". This can be easily confirmed in Table 7 by the significant reduction of the C6 carbohydrate content. The liquid extract was "contaminated" by sugar derivatives or oxidized tannins and the solid residue reduced in carbohydrate content. It is somewhat expected because alkali media favors oxidative decomposition of sugars and condensed tannins.

Even though impregnation catalyzed by acid (treatment 4) gives goods results, they are comparable to those obtained without catalysts (treatment 5). The "most economical decision" was thus clear to us : treatment 5 which becomes the "selected standard conditions".

The "selected standard conditions" (treatment 5) were applied to the raw material "as received" using a large sample (2Kg). This time, impregnation and extraction were carried out in the same vessel in order to facilitate subsequent scale up. Impregnations were carried under nitrogen (up to 30 Psig) for 10 minutes at ambient temperature. After impregnation nitrogen was released and heating was started (steam in jacket) until the targeted temperature was obtained. No filtration or washing were made between impregnation and extraction. Liquid / solid ratio was fixed at 10 and only when the entire treatment was completed filtration and washing were done.

Main characteristics of the equipment used are summarized in Table 10. Figure 2 shows a schematic of the impregnation and extraction equipment.

Table 10 : Equipment for Impregnations and Extractions

Reactor	IE - 3
Configuration	Batch
Material	SS-304
Operating Temperature	- 20°C / + 195°C
Operating Pressure	FV - 200 psig
Diameter	10"
Height	23"
Total volume	30 L
Operating volume	20 L
Operating weight	1000 g
Agitation	Vessel Axial Rotation
Heat transfer	Jacket + Steam Injection

The treated material provide a Solid Residue and a Liquid filtrate. The latter contains the "extracted products".

II.2. Characterization & Market

The experiments, carried out with the raw material as received, were done with relatively large scale samples (2 Kg) and we will refer to them as "pilot experiments". They were done by duplicate and results are the mean of the values.

A typical experiment consists in a two step extraction : impregnation and extraction. Both operations are carried out in the same vessel. Even though at lab scale this operation was done separately (filtration after impregnation and new solvent for extraction) we assumed that the change will not affect the final yield while facilitating the operations for further scale up. Impregnations were carried under nitrogen (up to 30 Psig) for 10 minutes at ambient temperature. After impregnation nitrogen was released and heating was started (steam in jacket) until the targeted temperature for extraction was obtained. No filtration or washing were made between impregnation and extraction. Liquid / solid ratio was fixed at 10 (wt/wt) and only when the entire treatment was completed filtration and washings were done. The first washing was made with the same solvent (Ethanol 50%) and the second only with Water.

At the same time an experiment suggested by NREL was carried out in the same vessel but with the different conditions. It will be referred to as "Aqueous Treatment" and was conducted as follows :

- A pre-steaming stage to drive out the oxygen and to open up the wood structure. A low pressure steam was introduced by the bottom of the reactor until an regular flow of steam is established. Thermocouples at bottom and top of the reactor monitor the temperature of extraction (90°C).
- An extraction stage where hot water (90°C) was added to the vessel (Liquid/Solid ratio 10) and the temperature was maintained during 10 minutes before centrifugation and washing with water.

Results obtained at laboratory scale [Table 6 in II.1.2] showed that extracted material in liquid was 6.05% (2.11% coming from impregnation and 3.94% from extraction). These values were calculated by weight difference between "initial dry weight" and "final dry weight of the solid residue". As the main objective was to determine which conditions gave the highest extractives removal, we used these percentages for comparison rather than as absolute values.

In the "pilot experiments" the yield of extractives recovered was calculated by determining the weight of the powder obtained after concentration and lyophilization. This value is more representative because it considers the weight loss of volatiles during the concentration step. Table 11 shows the composition of the residual solids and extractives recovered for both experiments : Ethanolic treatment (EtOH 50%) and Aqueous treatment (Steam and H₂O).

In order to evaluate cost/profit of each operation (for a given temperature, time treatment) cumulative yields of recovered extractives were shown. In the case of Ethanolic Treatment : after extraction (2.89%), after washings (3.48%) and after a second extraction (3.89%). It is not

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In order to evaluate cost/profit of each operation (for a given temperature, time treatment) cumulative yields of recovered extractives were shown. In the case of Ethanolic Treatment : after extraction (2.89%), after washings (3.48%) and after a second extraction (3.89%). It is not evident that a second extraction could enhance the yields considerably $3.89 - 3.48 = 0.41$ %. Instead the possibility of grinding the raw material must be considered and studied. The extractives recovered and analyzed are those obtained after washings. Thus, the liquors obtained during extraction and washings were mixed, concentrated and lyophilized.

In the case of Ethanolic Treatment the yield of 3.48 % obtained suggested that aprox. 2.5 % were lost as volatiles in the concentration step via evaporation and lyophilization since 6.05% were obtained at lab. scale.

The major component found in the extractives is "lignin" (85%), which can be explained considering its significant solubility in ethanol. This value was obtained by a typical pulp and paper determination (Klason Lignin). We consider this to be an overestimate since polyphenols, with similar structure as lignin, could also be wrongly accounted as "lignin".

Special efforts were made in order to identify products of commercial interest in the remaining extractives (15%). After preliminary tests for polyphenol content we decided to analyze one particular family of tannins: proanthocyanidins. This family has interesting anti-oxidant properties (Andry 1998, Dauer 1998) which recently, have been successfully commercialized in the OTC (Over The Counter) Market. The percentage of proanthocyanidins, 7.8%, in the extract is indeed significant.

It is also clear from the analysis that there are not many sugars present in the extractives (2.56%) under these conditions. This is a good point because it means that the carbohydrates remain in the residual solid to be subsequently converted in ethanol. No fatty acids neither sterols were detected in significant amounts to warrant further investigations.

In the case of Aqueous Treatment the yield of recovered extractives was only of 1.29%. In this case, the second extraction could be considered as a necessity since the yield doubles (2.4%). "Lignin" content in the extractives is 48.3% while the sugar content is significant, 21.49%. Proanthocyanidins content was almost half, 4.1%, of the one found in the Ethanolic Treatment. It thus seems clear that the Ethanolic Treatment represents a most interesting option for removal / recovery of proanthocyanidins.

Concerning the "standard extracted residue" it must be noted that the carbohydrate contents in Table 6 [II.1.2] are expressed as a function of the initial weight of the milled thinnings. This is equivalent to the maximum potential of sugars to be obtained from the starting material. In the case of pilot experiments (Table 11) the composition is expressed as a function of the "standard extracted residue" itself, in other words the true composition of the solid residue obtained.

Also to evaluate cost/profit of each operation (for a given temperature, time treatment), the composition of residual solids obtained were shown at different stages: just after extraction, after washings and after a second extraction.

In so far the extractives recovered, a second extraction of the residual solids seems to be not very significant in the Ethanolic Treatment. Sugars contents are practically the same (69 % vs. 67.7 %) as well as lignin content (31 % vs. 31.5 %). If we consider to grind the raw material this operation could facilitate the impregnation. In contrast, in the Aqueous Treatment, the second extraction is significant and it represents a reduction of 5% in the sugars (64.4% vs. 70.4%), more precisely C6 sugars.

The ethanolic treatment thus seems to be a successful method to remove valuable extractives (proanthocyanidins in these experiments) present in the thinnings provided by NREL giving furthermore a "purified" sugar-rich substrate for conversion to ethanol.

Economic Considerations.

Two aspects must be considered in the evaluation of the treatments : a) quality of residual solid and b) quality of extractives recovered.

Residual solids (substrate) recovered

Considering a 94% substrate yield and initial dry thinning having 69% carbohydrate content we recover as total carbohydrate (expressed as sugars) : $0.94 * 69\% = 65\%$ (of the initial dry thinnings basis) for further conversion to ethanol.

This means that 1 tonne of thinnings (dry basis) will lead to a theoretical maximum of $1 * 0.65 * 0.5 * 0.8 = 260$ Kg of ethanol assuming 80% fermentation yield of the carbohydrates after total saccharification. This translates into 325 liters (density approx. 0.8) of ethanol per dry tonne of thinnings with a total value of with a total value of 104 US \$ considering US \$1.20/ gal ethanol).

Extractives recovered

Further work must be done to determine the quality of the lignin obtained which was the major constituent of the extract. For the moment we do not attribute any value to it.

Proanthocyanidins extracted from Maritime French Pin are actually commercialized by Henkel as pills (tablets) using microcrystalline cellulose and magnesium stearate as fillers. One box containing 90 pills having 250 mg each of active ingredient has a market price of 20 US \$. The proanthocyanidins contents in the pill are 85 wt %, thus the final content in the box is less than 20 gr of proanthocyanidins. This represents 1 US \$ per gr or 1 000 US \$ per kilo. If the "producer" cost is 1/3 of the market price this means 333 US \$ /Kg.

Proanthocyanidins contents (7.8 wt %) in the extract (3.48 wt %) represents 0.27 wt % of the thinnings used as raw material. Considering one ton of thinnings we have measured 2.7 Kg of proanthocyanidins. This represents US \$ 900 for an eventual "producer". Even considering a yield of 30% recuperation from a final purified product, we could still obtain US \$ 270 by tonne of thinnings. This is quite significant compared to the "value" of the ethanol.

II.3. Aqueous / Steam Treatment

Experiments were done via an aqueous treatment (impregnation) of the standard extracted residue (100 gr dry) obtained after extractives removal. Thus the fiber material is saturated through complete capillary penetration removing occluded air in the capillaries.

Impregnations conditions were 25°C, 10 min. and 30 Psig at a liquid/solid weight ratio of 10. Acid catalysis experimented was set at 2% and 4% H₂SO₄ (wt % in liquid).

The equipment used for the impregnation was similar to one described in Figure 2 (as addendum) and Table 5.

After impregnation, the excess solvent is separated by pressing and the resulting impregnated material cake is desegregated by hand and subjected to steam treatment.

The steam treatment is carried out in a jacketed vessel whose walls have been previously preheated at the desired temperature. The equipment used for the steam treatment (Fig. 3) has the following characteristics :

Table 12 : Equipment for steam treatment.

Reactor	MVC
Configuration	Batch
Material	SS-304
Operating Temperature	- 20°C / + 230°C
Operating Pressure	FV - 400 Psig
Diameter	3 "
Height	14 "
Total volume	1.5 L
Operating volume	1 L
Operating weight	variable
Agitation	---
Heat transfer	Jacket + Steam Injection

Live saturated or slightly superheated steam is admitted to the vessel and the jacket for two sets of conditions:

- 1) Temperature = 190°C and time = 3 min.
- 2) Temperature = 160°C and time = 10 min.

The temperature is monitored by two thermocouples located within the sample. After the desired reaction time has elapsed the blowdown valve is opened and the material is expelled out of the vessel. A receiver vessel (ice-salt cooled) captures the slurry obtained. This product (approx. 10% sugars contents) can be used as such or can undergo a second aqueous / steam treatment.

For analytical purposes, the slurry is filtered (Büchner) and the solid cake (mainly composed of lignin and cellulose or "wet lignocellulose") is thoroughly washed with water. Liquors are mixed for analysis and concentrated to a 10% wt dissolved solids ("Hemicellulose-rich solution").

Experiments at 160°C results in a "pasty mixture" of uncompleted hydrolysis products. Thus, only treatments at 190°C (2% and 4% H₂SO₄) were completed for the material balances.

Two different starting materials were used:

- 1) Standard extracted residue coming from EtOH 50% extraction (Ethanol 50% option), and
- 2) Standard extracted residue coming from aqueous extraction (Aqueous option).

After extraction treatments (EtOH 50% or Aqueous) separation of liquid and solids was made and each fraction was analyzed (Table 11).

Values considered for further downstream material balances were as follows:

Yield of residual solids :

93.59% for EtOH 50% extraction and 89.56% for Aqueous extraction.

Yield of recovered extractives :

3.48% for EtOH 50% extraction and 1.29 % for Aqueous extraction.

Note that carbohydrate contents in the material balance are expressed in terms of hexoses (C6) and pentoses (C5), the products of hydrolysis following HPLC analysis. There was no analysis after the aqueous treatment (impregnation). A solid / liquid separation was carried out by a filter press (P < 200 Psig) and the "Impregnated Extracted Residue" after desegregation was submitted to steam treatment. Liquor obtain from the filter press could be treated and / or recycled.

After aqueous / steam treatment a new separation of liquid and solids was made, this time only by filtration (Büchner). The compositions of residual solid and hemicelluloses-rich liquor (washings included) are shown in Table 13 (as addendum).

As an example of how the material balances are calculated, Table 14 summarizes all analytical values involved in the case of EtOH 50% extraction followed by an aqueous / steam treatment catalyzed by 2 % H₂SO₄ (corresponding to Table 15). Yields are referred to the different fractions pointed by the arrows.

Material balances for the entire treatments are presented in Tables 15, 16, 17 and 18 (as addendum) : Fractionation / Hydrolysis of Thinnings to fermentable sugars :

	EtOH 50%		Aqueous	
	2 % H ₂ SO ₄	4 % H ₂ SO ₄	2 % H ₂ SO ₄	4 % H ₂ SO ₄
Table	15	16	17	18

Tables 19 and 20 (as addendum) show a graphical representation of the hexoses (C6) and pentoses (C5) recuperation with different treatments.

The "Standard Extracted Residue" obtained after EtOH 50% extraction has potentially more hexoses (C6) and pentoses (C5) than the "Standard Extracted Residue" obtained after Aqueous extraction [C6 : 55.3% vs. 49.54 % and C5 : 9.3% vs. 8.1 %]

In both cases (EtOH 50% and Aqueous) increasing the concentration of the catalyst in the aqueous treatment (2% to 4% H₂SO₄) involves an increased recovery of C6 in the "Hemicellulose Rich-Solution" but a decreasing recovery of C5.

Yield	Hemicellulose Rich Solution			
	EtOH 50% Extraction		Aqueous Extraction	
	2% H ₂ SO ₄	4% H ₂ SO ₄	2% H ₂ SO ₄	4% H ₂ SO ₄
C6	31.14	37.23	29.71	32.56
C5	44.41	34.19	64.19	48.88

That means that the 4% H₂SO₄ severity is too high and decomposition occurs at significant extent.

In accordance with these results the potential yield of C6 in "Wet Lignocellulose" is higher when using 2% H₂SO₄ than with 4% H₂SO₄.

Potential Yield	Wet Lignocellulose			
	EtOH 50% Extraction		Aqueous Extraction	
	2% H ₂ SO ₄	4% H ₂ SO ₄	2% H ₂ SO ₄	4% H ₂ SO ₄
C 6	49.91	40.7	55.65	42.79

It is important to note the "Wet Lignocellulose" is already free of pentosans as a result of the steam treatment but the recovery yield of pentosans in the Hemicellulose Rich-solution is low (< 50%). For this reason we tested lower severities (0.4 %, 0.5% and 1% catalyst).

These experiments were carried out similarly to the previous experiences and results are reported in Tables 21, 21 and 23. Tables 24, 25, 26 and 27 (as addendum) show a graphical representation of the hexoses (C6) and pentoses (C5) recuperation with different treatments.

The results of these experiments show that increasing the concentration of the catalyst in the aqueous treatment (0.5%, 1%, 2% to 4% H₂SO₄) leads to a decrease in the recovery of C5 in the "Hemicellulose Rich Solution". The same tendency was observed in the potential yield of C6 in "Wet Lignocellulose".

IV. Conclusion & Recommendations

- The set of extraction conditions (standard conditions) that gave the highest extractives removal and minimal degradation of carbohydrates present in thinnings were obtained by an impregnation followed by an extraction with ethanol 50% .
- Extractives ("standard extract") obtained under the "laboratory conditions" (75 gr) reach a yield of 6.05 % (obtained by weight difference between dry raw material and solid residue).
- Solid residue ("standard extracted residue") obtained under the "laboratory conditions" contains 9.54 % of pentoses and 51.46 % of hexoses (reference to 100 wt units of dry raw material).
- Two treatments were considered at pilot scale (2 kg) :
 - a) Ethanolic Treatment (EtOH 50%):
 - a.1) Impregnation conditions : Liquid / solid ratio 10 ; Temperature 25°C ; Pressure 30 Psig and time 10 min.
 - a.2) Extraction conditions : Liquid / solid ratio 10 ; Temperature 80°C and time 10 min.
 - b) Aqueous Treatment (Steam & H₂O):
 - b.1) Pre-steaming conditions : Temperature 90°C ; Pressure atmosphere and time 10 min.
 - b.2) Extraction conditions : Liquid / solid ratio 10 ; Temperature 90°C and time 10 min.
- Yields for extractives recovered change from lab (6.05%) to pilot scale (3.48%). This difference is associated with two major factors :
 - a) At laboratory scale the yield of extractives recovered was obtained by weight difference between "initial dry weight" and "final dry weight of the solid residue". At pilot scale the yield was calculated by the true weight of the powder obtained after concentration and lyophilization. This value is more representative of an industrial operation because it considers the weight loss of volatiles during the concentration step.
 - b) At laboratory scale the starting material was ground while at pilot scale the feedstock was the starting material.
- To compensate for the effect of grinding, a second extraction was carried out over the residual solid obtained. This second extraction seems to be not very significant in the case of ethanolic treatment but necessary for the aqueous treatment.
- Solid residue obtained after ethanolic treatment at pilot scale (Table 11) has essentially all the carbohydrate initially present in the raw material for further conversion to ethanol. The remaining component in the solid residue has been determined to be acid insoluble lignin.
- The value of the ethanol produced at an 80% fermentation efficiency of the total carbohydrate is 104 US \$ / tonne of dry thinnings.

- Extractives were recovered as a powder (3.48%) after concentration and lyophilization of liquors obtained during the extraction and washings. The major component identified was lignin (85%) but its value seems overestimated by the analytical method used (Klason Lignin). Further work must be done to determine the purity of the lignin obtained.
- Proanthocyanidins contents (7.8%) in the extract represents $(7.8 \times 3.48 = 0.27 \%)$ in the raw material. At 333 US \$ per kilo it represents 900 US \$ by tonne of thinnings. Even with a yield of 30% for a purified product it represents US 270\$ by ton, which is much higher than the ethanol value, hence its interest.
- Aqueous / steam treatments were carried out over the standard extracted residues obtained after removal of extractives (EtOH 50% extraction and Aqueous Extraction).
- Aqueous treatment conditions were 25°C, 10 min and 30 Psig at a L/S weight ratio of 10. Concentration of catalyst (H₂SO₄) used were 2% and 4%.
- Steam treatment conditions were 190°C for 3 minutes and 160°C for 10 minutes. Only the first conditions were retained for further analysis. The severity of the second condition is insufficient to achieve the desired hydrolysis.
- Increasing the concentration of the catalyst in the aqueous treatment (0.5%, 1%, 2% to 4% H₂SO₄) leads to a decrease in the recovery of C5 in the "Hemicellulose Rich Solution". The same tendency was observed in the potential yield of C6 in "Wet Lignocellulose". We can conclude that low severities are required in aqueous / steam treatment if a selective fractionation is desired.
- Lower catalytic concentrations (0.4% H₂SO₄) lead to a decrease in the recovery of pentoses.
- Considering the complexity in the separation of monomeric sugars in all the analysis (overlap of pics, small concentrations, etc.) we strongly recommend to assay an anion exchange column coupled to a pulsed amperometric detection (PAD). The chromatographic system consists of an autosampler, a Quaternary Gradient High Pressure Pump (Dionex), and a Pulsed Amperometric Detector (Dionex). Separation of the sample into individual sugars are achieved with a Carbo-Pak PA1 analytical column (Dionex). The method is well described by Pettersen (1991).
- The treated biomass solids could eventually be destined to two different approaches :
 - 1) A second aqueous/steam treatment to produce a final hydrolysis of the lignocellulosic material followed by fermentation to ethanol. This hydrolysis step can be also achieved by enzymatic methods ; and
 - 2) A base-catalyzed delignification to produce a black liquor, containing most of the lignin, and a crude solid cellulose residue (fiber + fines). The black liquor could be catalytically upgraded and the caustic recovered while the crude cellulose is separated into fiber (to be bleached) and fines (for ethanol production).

VI. References

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2. Dauer, A. ; Metzner P. and O. Schimmer, 1998. Proanthocyanidins from the Bark of *Hamamelis virginiana* Exhibit Antimutagenic Properties against Nitroaromatic Compounds. *Planta Medica* 64, 324 - 327.
3. Pettersen, R.C. and V.H. Schwandst, 1991. Wood sugar analysis by anion chromatography. *J. Wood Chem. Technol.* 11 (4), 495-501.

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Figure 1 : Material Balance Considerations

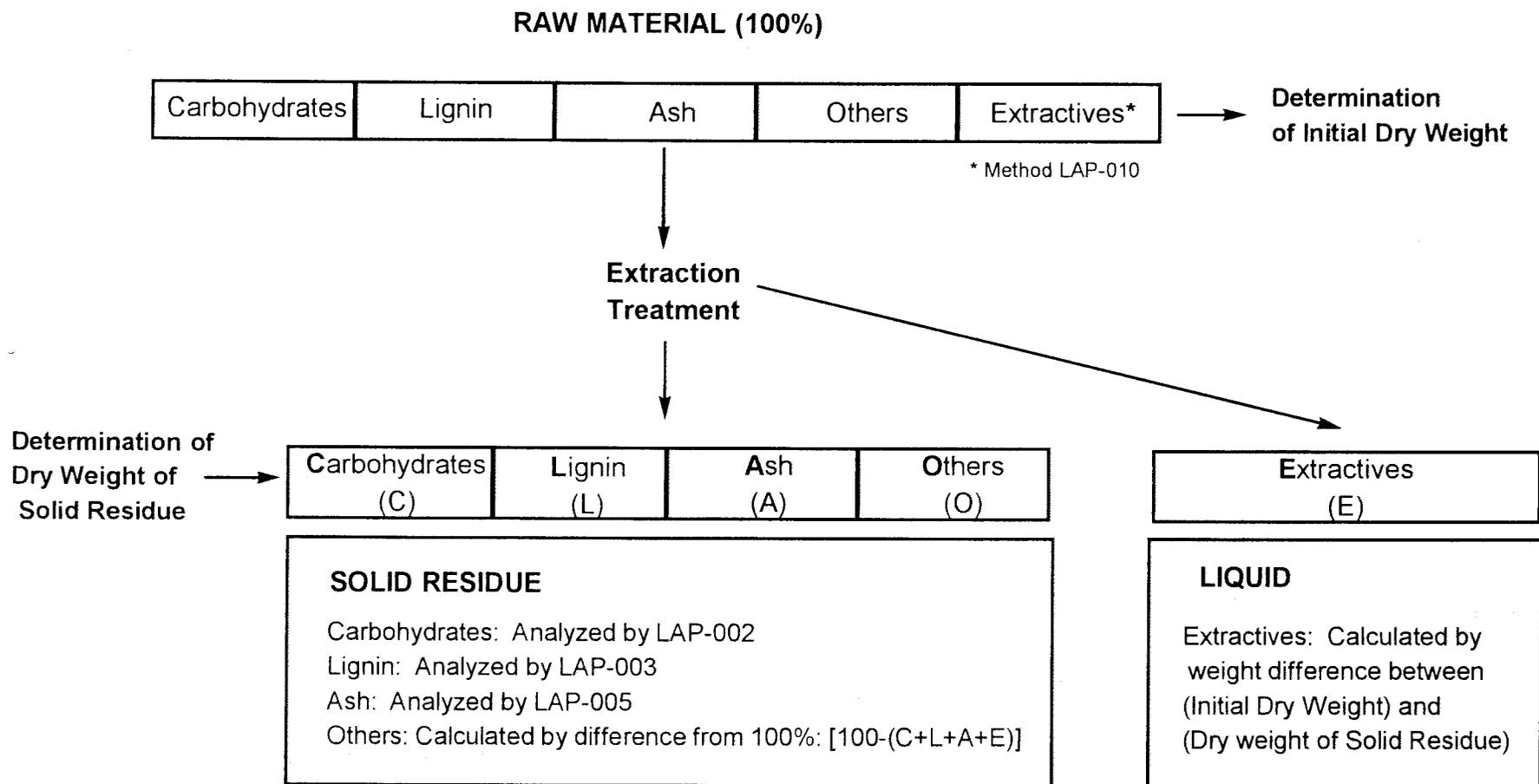


Figure 2. Schematic of Impregnation and Extraction Equipment

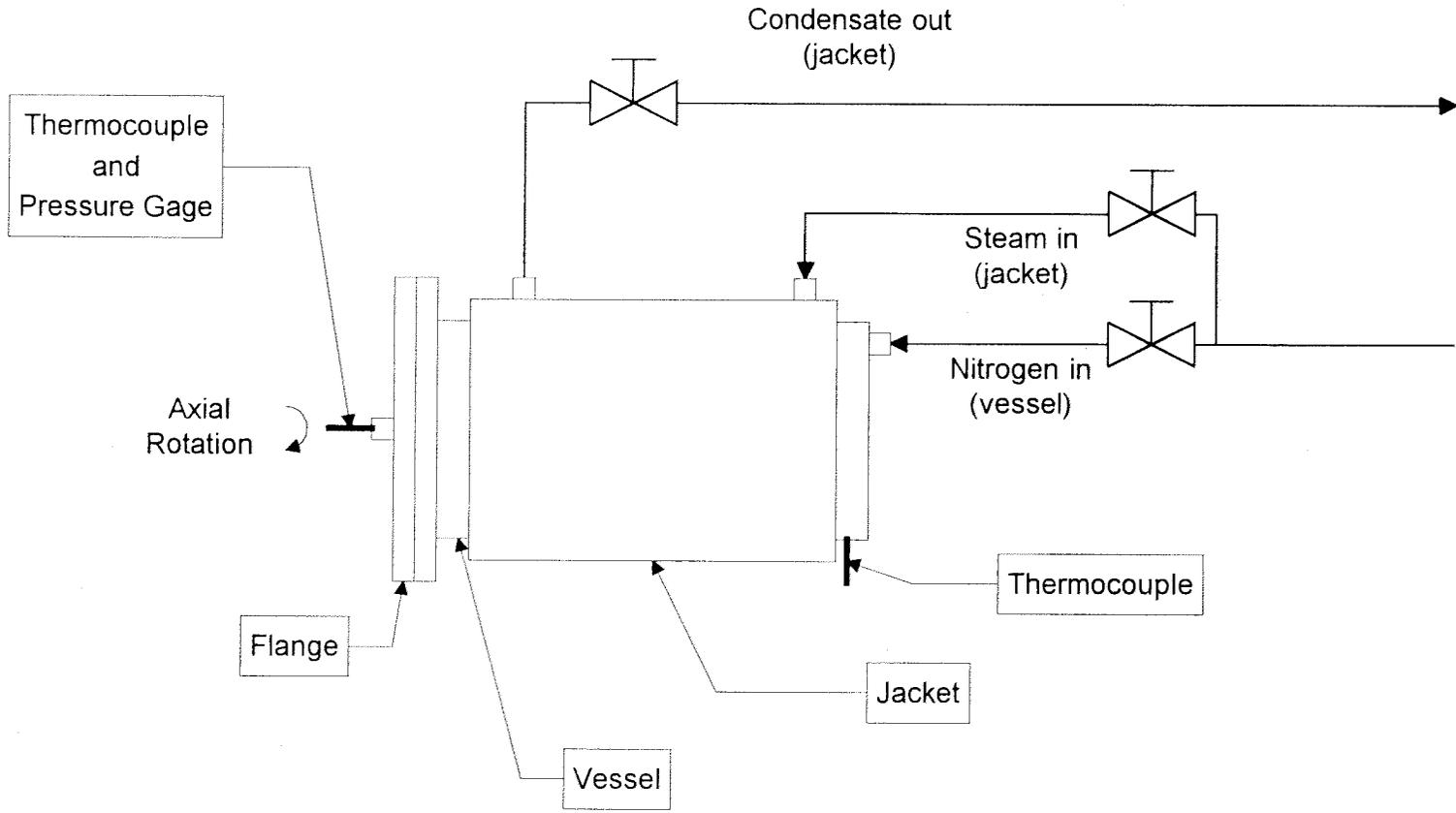


Figure 3: Equipment for Steam Treatment

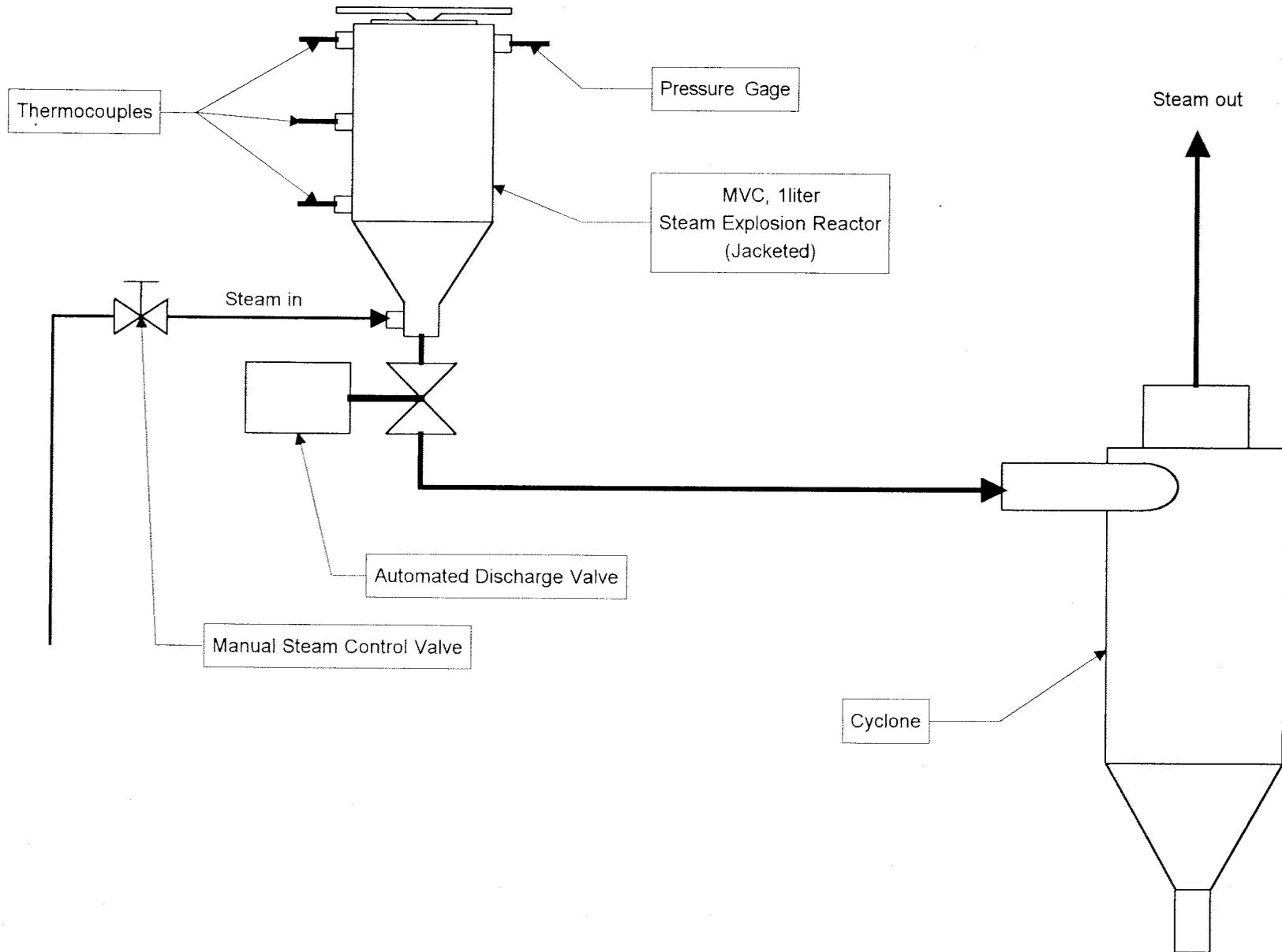


Table 4: Summary of Treatments

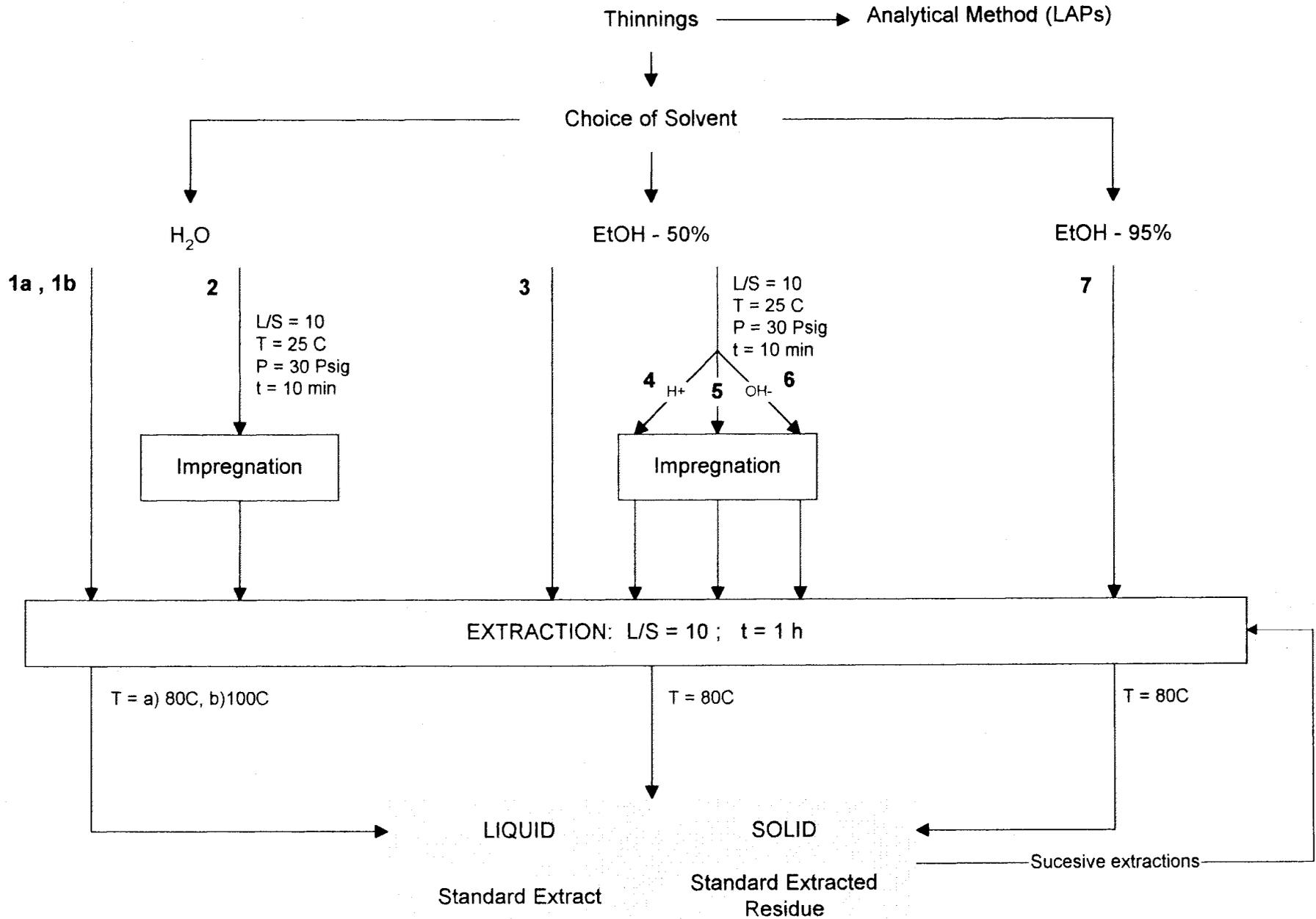


Table 6: Material Balances Following Extraction

ANALYSIS	Raw Material (%)	SOLVENT												Method			
		H ₂ O				EtOH 50%						EtOH 95%					
		1		2		3	4		5		6		7				
		a) Ext.80 (%)	b) Ext.100 (%)	Imp. (%)	Ext.80 (%)	Ext.80 (%)	Imp. H ⁺ (%)	Ext.80 (%)	Imp. (%)	Ext.80 (%)	Imp. OH ⁻ (%)	Ext.80 (%)	Ext.80 (%)				
SOLID	Carbohydrates	Glucose	37,01	36,58	32,73		36,08	39,15		38,65		38,99	28,42	39,32	LAP-002		
		Xylose	5,62	6,59	6,43		6,57	7,9		7,18		7,47	4,7	7,59	LAP-002		
		Galactose	4,39	2,3	2,8		2,25	3,61		2,57		2,77	1,93	2,29	LAP-002		
		Arabinose	2,78	1,88	2,18		1,95	2,6		1,67		2,07	1,95	2,05	LAP-002		
		Mannose	12,3	9,88	9,57		9,63	10,7		9,57		9,7	9,37	9,17	LAP-002		
		C5	8,4	8,47	8,61		8,52	10,5		8,85		9,54	6,65	9,64	Calculation		
		C6	53,7	48,76	45,1		47,96	53,46		50,79		51,46	39,72	50,78	Calculation		
	Total	62,1	57,23	53,71		56,48	63,96		59,64		61	46,37	60,42	LAP-002			
	Lignin in acid	Insoluble (%AIL)	29,58	31,92	32,68		31,01	29,8		29,2		28,95	26,91	29,46	LAP-003		
		Soluble (%ASL)	0,43	n.d.	n.d.		n.d.	n.d.		n.d.		n.d.	n.d.	n.d.	LAP-004		
	Ash, %		0,79	0,52	0,75		0,57	0,8		0,77		0,69	0,46	0,68	LAP-005		
	Other		2,50	7,47	11,04		7,95	5,47		4,92		3,31	17,38	5,11	Obtained by difference from 100%		
LIQUID	Extracted material in liquid		4,52*	2,86	1,82		1,17	2,82		4,13		5,47	2,11	3,94	8,88	4,33	Obtained by weight difference
							(3.99)						(6.05)				

Hydrolysis conditions: 1) 72% H₂SO₄; 2h @ 30C (HPLC)
2) 4% H₂SO₄; 1h @ 121C

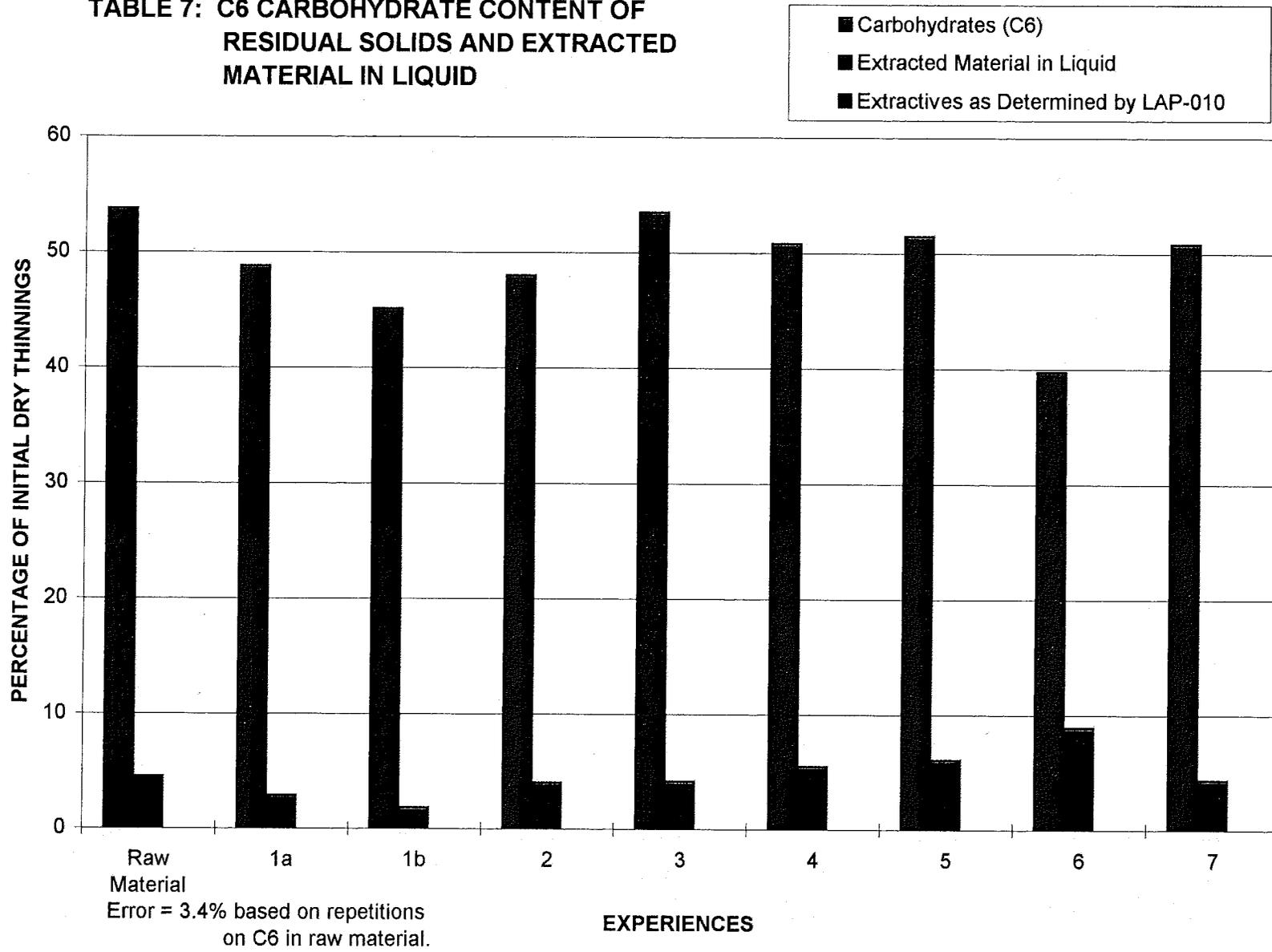
Impregnations conditions: L/S = 10
T = 25 C
P = 30 psig
t = 10 min.
[H⁺] = 1%
[OH⁻] = 1%

Extractions conditions: L/S = 10
T = 80 C (100C only for H₂O)
t = 1 h.

n.d. : not determined due to its low value which is within the error margin

* : EtOH extract (as per LAP-010)

TABLE 7: C6 CARBOHYDRATE CONTENT OF RESIDUAL SOLIDS AND EXTRACTED MATERIAL IN LIQUID



	ANALYSIS		Ethanol Treatment			Aqueous Treatment		Method
			EtOH 50%			Steam & H ₂ O		
			Pilot: 2000 g			Pilot: 2000 g		
			After extraction	After washings	After Re-extraction	After Ext. & washing	After Re-extraction	
RESIDUAL SOLIDS	Carbohydrates (W% Total)	Glucose	42,01	44,31	42,78	40,85	45,33	LAP-002
		Xylose	7,49	7,87	7,67	7,16	8,00	LAP-002
		Galactose	2,99	3,03	3,1	2,93	2,88	LAP-002
		Arabinose	2,13	2,06	2,48	2,54	2,01	LAP-002
		Mannose	10,7	11,7	11,74	10,86	12,23	LAP-002
		C5	9,62	9,93	10,15	9,04	10,01	Calculation
		C6	55,7	59,11	57,62	55,3	60,44	Calculation
	Total C5 + C6	65,32	69,04	67,77	64,34	70,45	Calculation	
	Acid Insoluble Lignin (W% Total)	30,56	31,08	31,59	34,25	31,79	LAP-003	
	Ash (W% Total)	0,68	0,78	0,75	0,97	0,67	LAP-005	
TOTAL	96,56	100,9	100,11	99,56	102,91			
Yield of residual solids (Weight % of initial dry material)				93,59		89,58		Weight of dry residue

EXTRACTIVES RECOVERED AS A POWDER FOLLOWING CONCENTRATION OF LIQUID	Carbohydrates (W% Total)	Glucose		1,28		6,98		LAP-002
		Xylose		0,00		0		LAP-002
		Galactose		0,62		7,08		LAP-002
		Arabinose		0,66		3,37		LAP-002
		Mannose		0,00		4,06		LAP-002
		C5		0,66		3,37		Calculation
		C6		1,9		18,12		Calculation
	Total		2,56		21,49		Calculation	
	Acid Insoluble Lignin (W% Total)		85,23		48,3		LAP-003	
	Ash (W% Total)		2,7		1,7		LAP-005	
	Pro-anthocyanidins (W% Total)		7,8		4,1		Vanillin in H ₂ SO ₄ *	
	Sterols (W% Total)		0,08		n.d.		GC-MS	
	Fatty Acids (W% Total)		n.d.		n.d.		GC-MS	
Others not identified (W% Total)		1,36		24,41		Difference from 100		
TOTAL		100		100				
Yield of recovered extractives (Weight % of initial dry material)			2,89	3,48	3,89	1,29	2,39	Weight of dry extract con. & lyoph.

* Broadhurst, R.B. and W. T. Jones. 1978 J. Sci. Fd. Agric. 29: 788-794.

EtOH 50%	
Impregnations conditions:	L/S = 10 T = 25 C P = 30 psig t = 10 min.
Extractions conditions:	L/S = 10 T = 80 C t = 1 h.

Steam & H ₂ O	
Pre-steaming conditions	Life steam T = 90 C P = atm t = 10 min.
Extraction Conditions	L/S = 10 T = 90 C t = 10 min

Hydrolysis conditions: (HPLC)	1) 72% H ₂ SO ₄ : 2h @ 30C 2) 4% H ₂ SO ₄ : 1h @ 121C
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Table 13: Composition of the residual solid and the hemicelluloses-rich liquor after aqueous and steam treatment

	ANALYSIS		981007	981009	981008	981010	Method
			EtOH 50%		Steam & H ₂ O		
			T = 190 C t = 3 min		T = 190 C t = 3 min		
			2% H ₂ SO ₄	4% H ₂ SO ₄	2% H ₂ SO ₄	4% H ₂ SO ₄	
Residual SOLID	Carbohydrates (W% Total)	Glucose	45,45	41,69	47,99	40,87	LAP-002
		Xylose	0	0	0	0	LAP-002
		Galactose	0	0	0	0	LAP-002
		Arabinose	0	0	0	0	LAP-002
		Mannose	0	0	0	0	LAP-002
		C5	0	0	0	0	Calculation
		C6	45,45	41,69	47,99	40,87	Calculation
		Total C5 + C6	45,45	41,69	47,99	40,87	Calculation
	Acid Insoluble Lignin (W% Total)	48,26	57,47	49,36	57,7	LAP-003	
	Ash (W% Total)					LAP-005	
TOTAL							
Yield of residual solids (Weight % of initial dry material)			64,82	57,84	64,14	57,91	Weight of dry residue
Hemicelluloses-rich LIQUOR (weight % of initial dry material)	Carbohydrates	Glucose	7,77	12,25	8,16	11,31	LAP-002
		Xylose	4,41	2,40	4,28	2,38	LAP-002
		Galactose	2,05	2,19	2,33	2,54	LAP-002
		Arabinose	0	1,00	1,53	2,04	LAP-002
		Mannose	8	7,56	5,94	4,16	LAP-002
		Cellobiose	0,4	1,88	0,49	4,92	
		C5	4,41	3,4	5,81	4,42	Calculation
		C6	17,82	22,0	16,43	18,01	Calculation
		Total	22,23	25,4	22,24	22,43	Calculation

Impregnations conditions:	L/S = 10	Steam Explotion conditions:	L/S = 10
	T = 25 C		T = 190 C
	P = 30 psig		t = 3 min.
	H ⁺ = 2% & 4%		
	t = 10 min.		

Hydrolysis conditions: (HPLC)	1) 72% H ₂ SO ₄ : 2h @ 30C
	2) 2% or 4% H ₂ SO ₄ : 1h @ 121C

Table 14: Analytical values involved in EtOH 50% extraction followed of aqueous / steam treatment (catalyst 2% H2SO4)

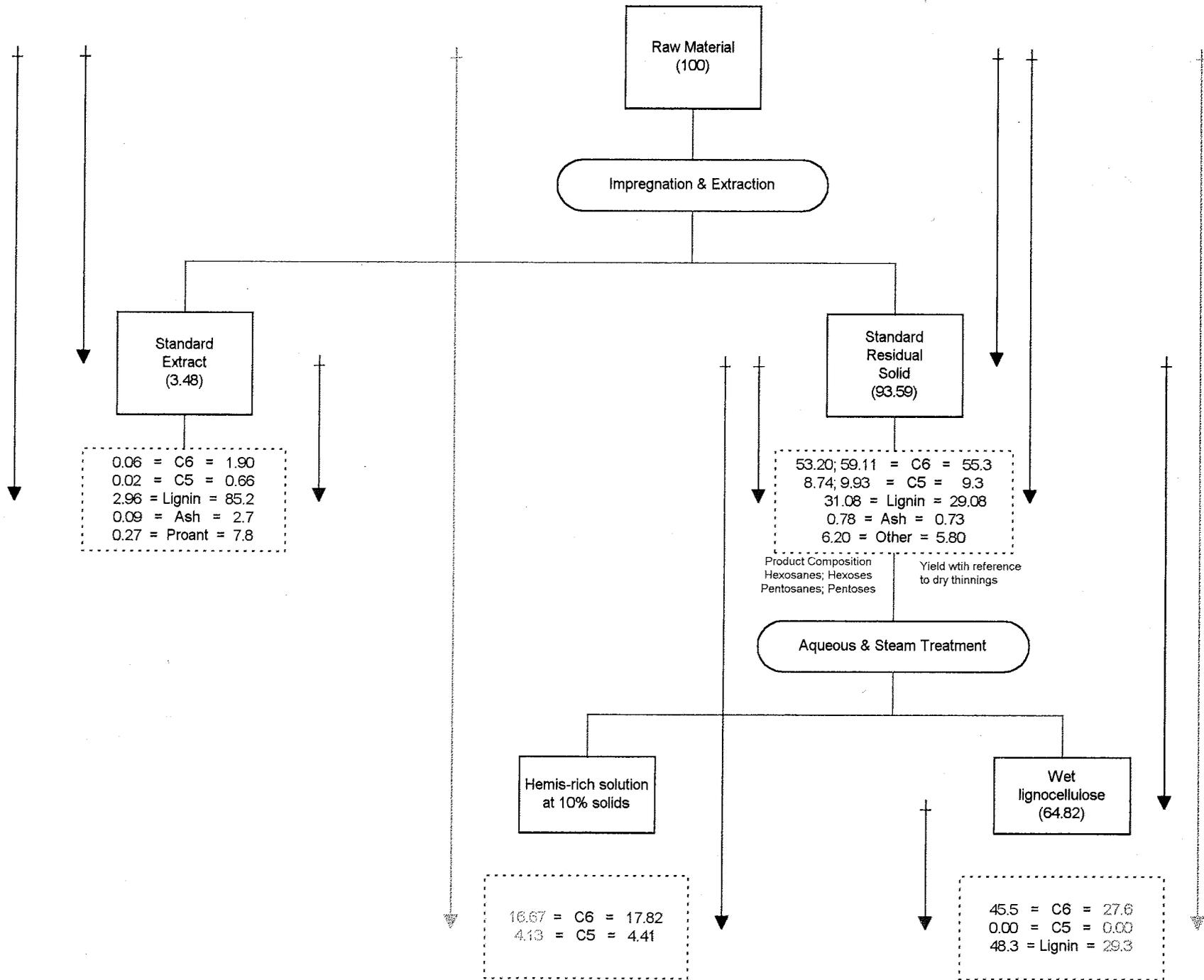
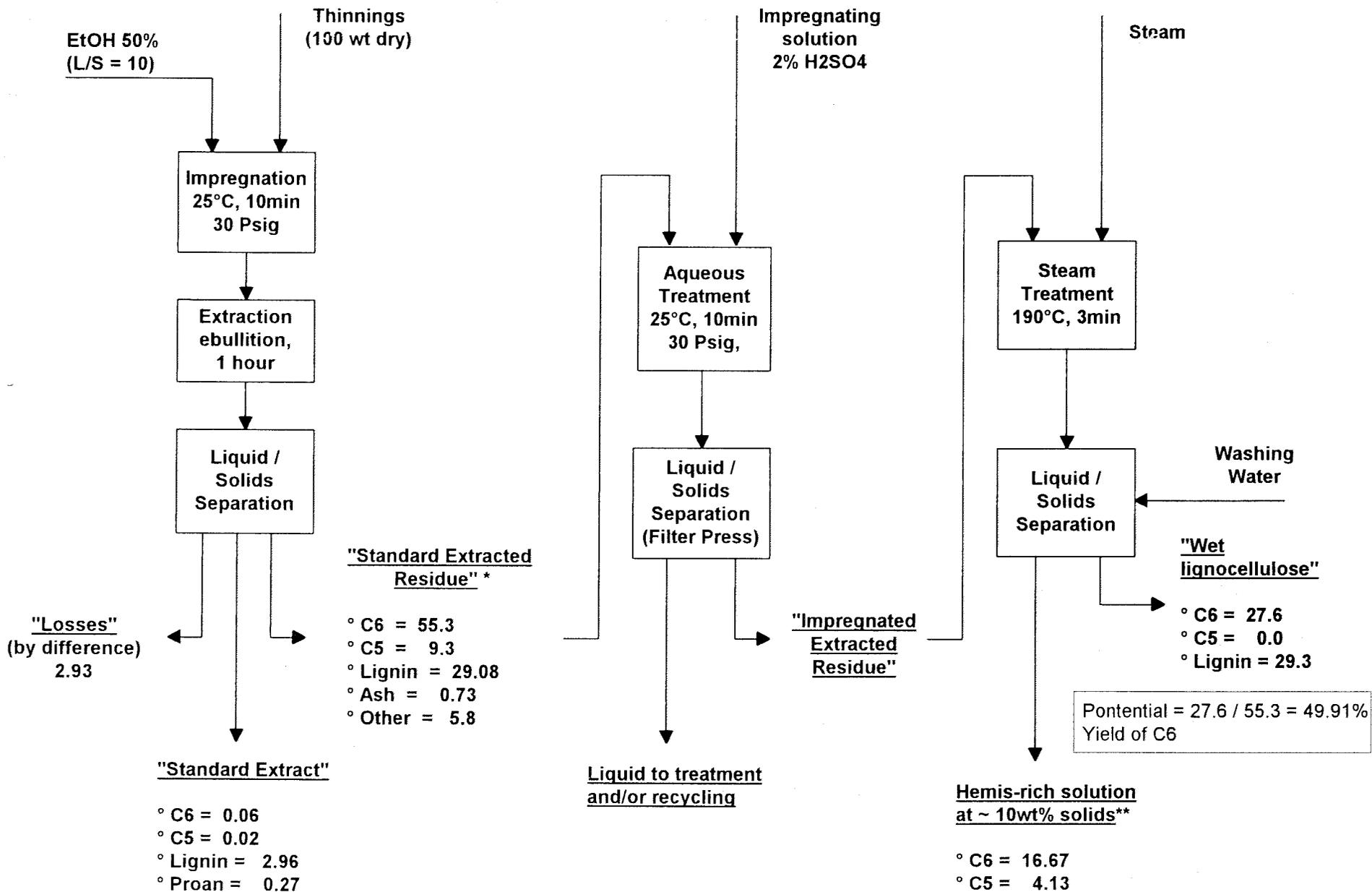


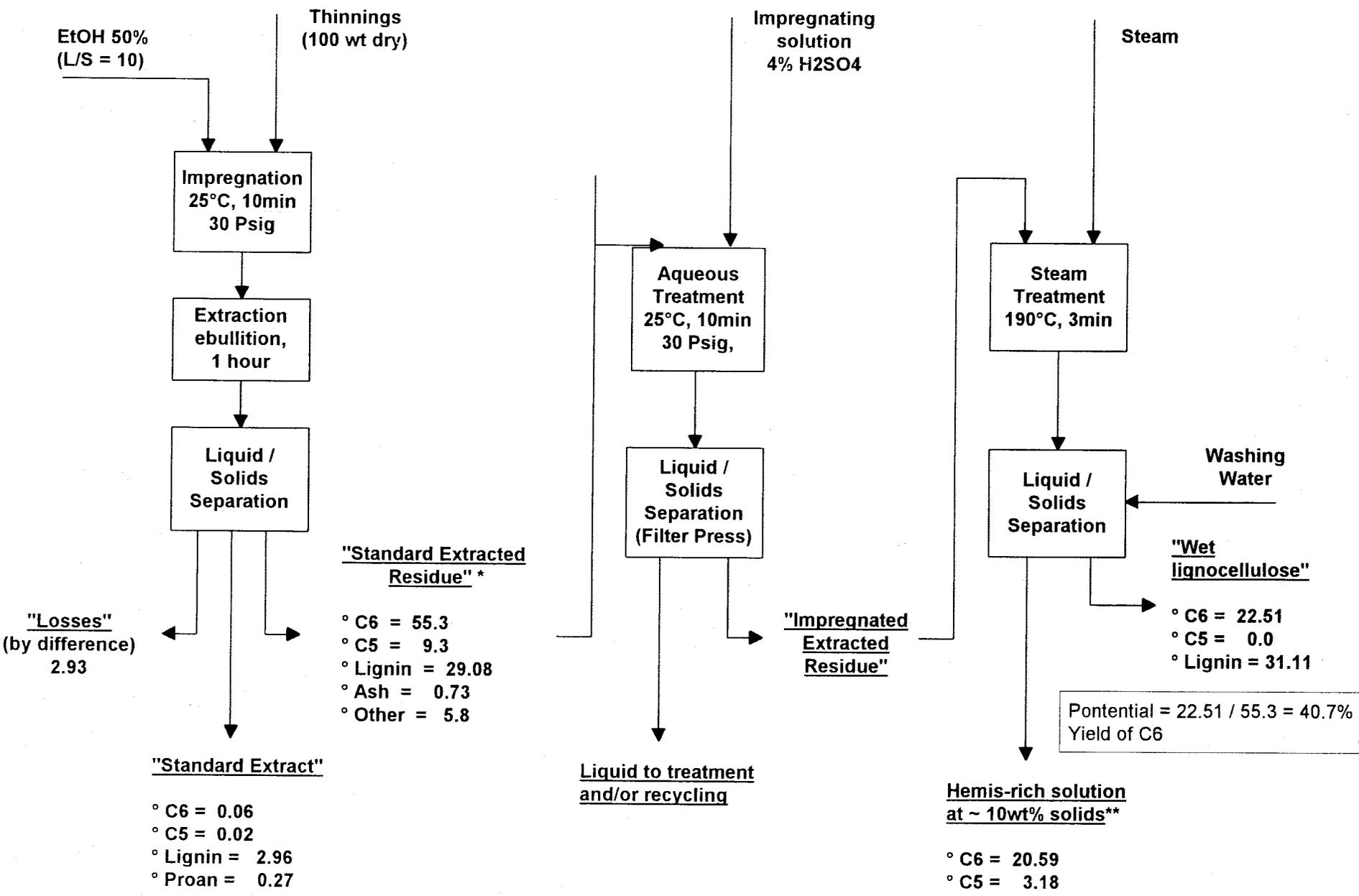
Table 15: Fractionation / Hydrolysis of Thinnings to fermentable sugars: Extraction EtOH 50% & Aqueous / Steam treatment catalyzed 2% H2SO4



* Hexosanes = 0.90 Hexoses (C6)
Pentosanes = 0.88 Pentoses (C5)

Yield of C6 = 16.67 / 55.3 = 30.14 %
Yield of C5 = 4.13 / 9.3 = 44.41 %

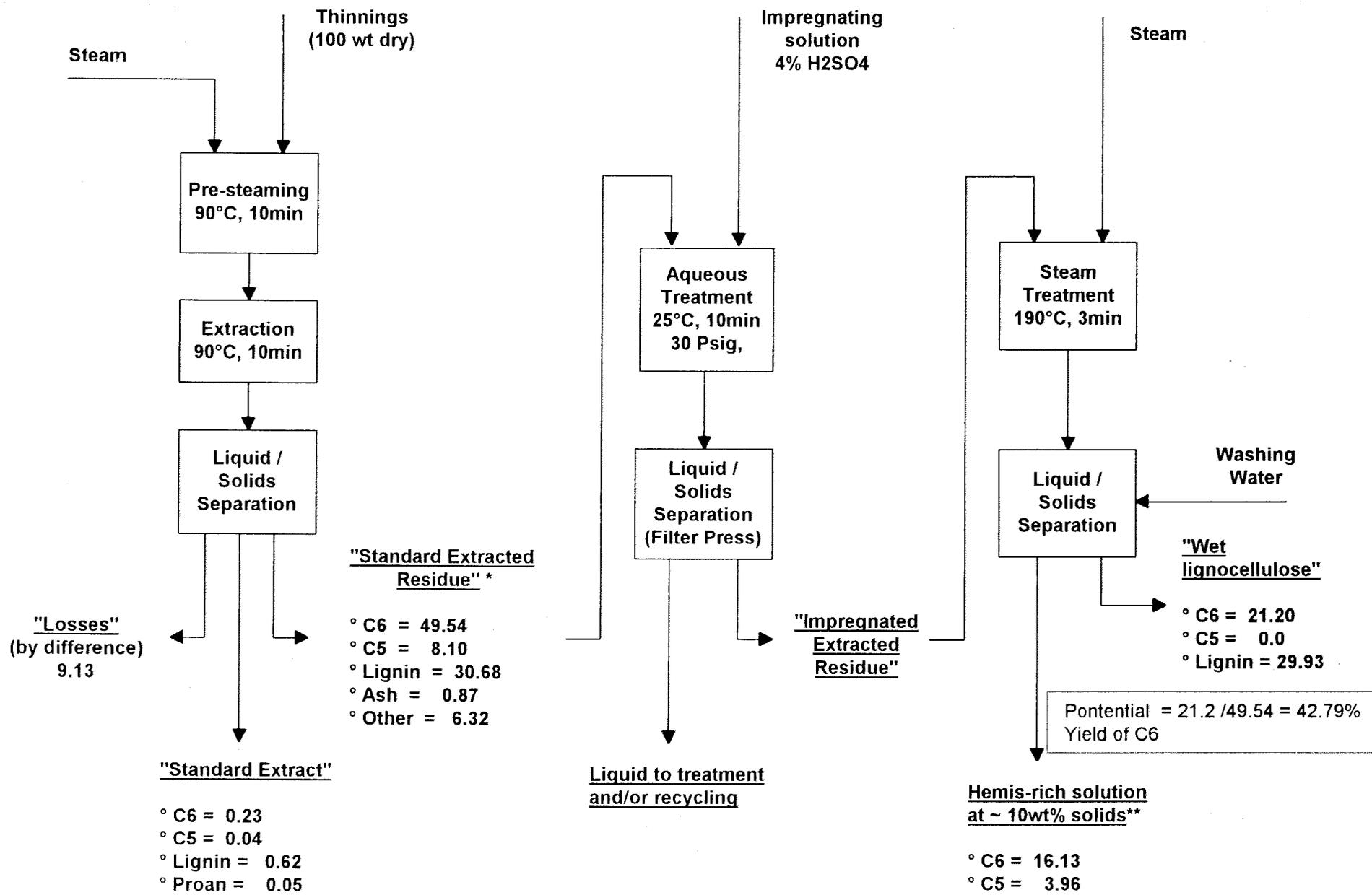
**Table 16: Fractionation / Hydrolysis of Thinnings to fermentable sugars:
Extraction EtOH 50% & Aqueous / Steam Treatment catalyzed 4% H2SO4**



* Hexosanes = 0.90 Hexoses (C6)
 Pentosanes = 0.88 Pentoses (C5)
 ** It requires concentration to reach ~10% wt% dissolved solids

Yield of C6 = 20.59 / 55.3 = 37.23 %
 Yield of C5 = 3.18 / 9.3 = 34.19 %

Table 18: Fractionation / Hydrolysis of Thinnings to fermentable sugars: Aqueous Extraction & Steam treatment catalyzed 4% H2SO4



* Hexosanes = 0.90 Hexoses (C6)
Pentosanes = 0.88 Pentoses (C5)
** It requires concentration to reach ~10% wt% dissolved solids

Yield of C6 = $16.13 / 49.54 = 32.56\%$
Yield of C5 = $3.96 / 8.1 = 48.88\%$

Table 19: Aqueous / Steam Treatment after EtOH 50% Extraction

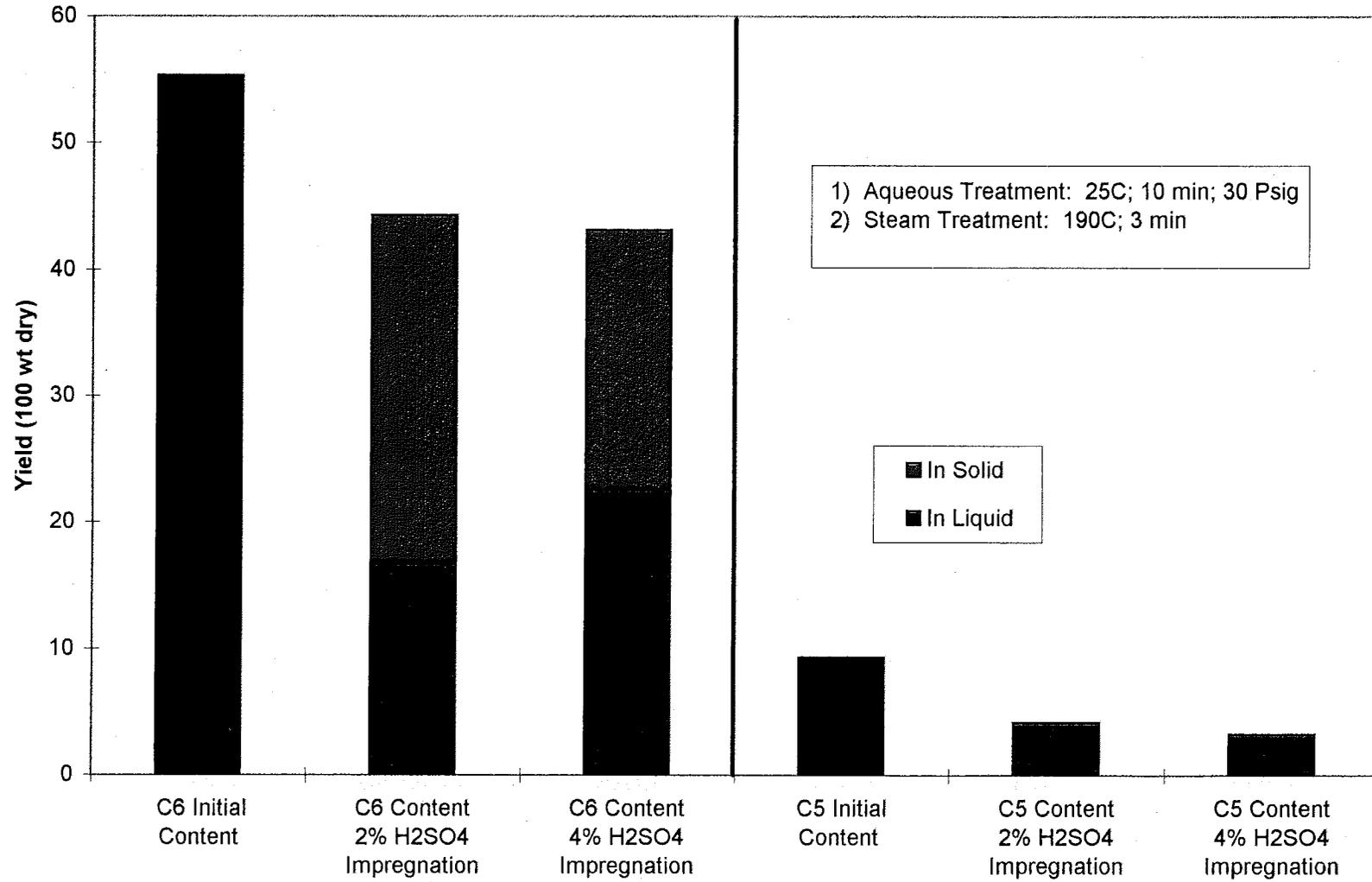


Table 20: Aqueous / Steam Treatment after Aqueous Extraction

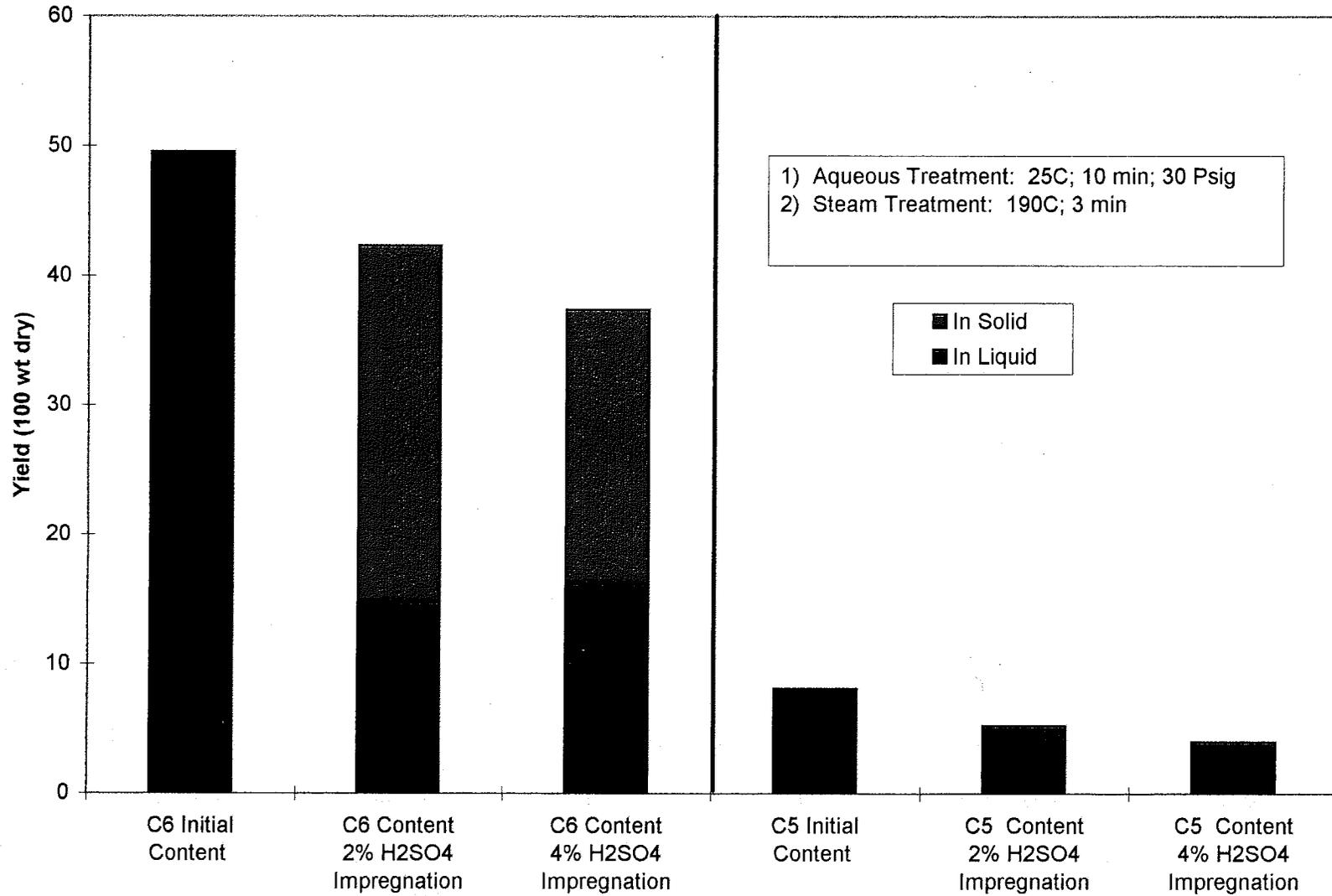
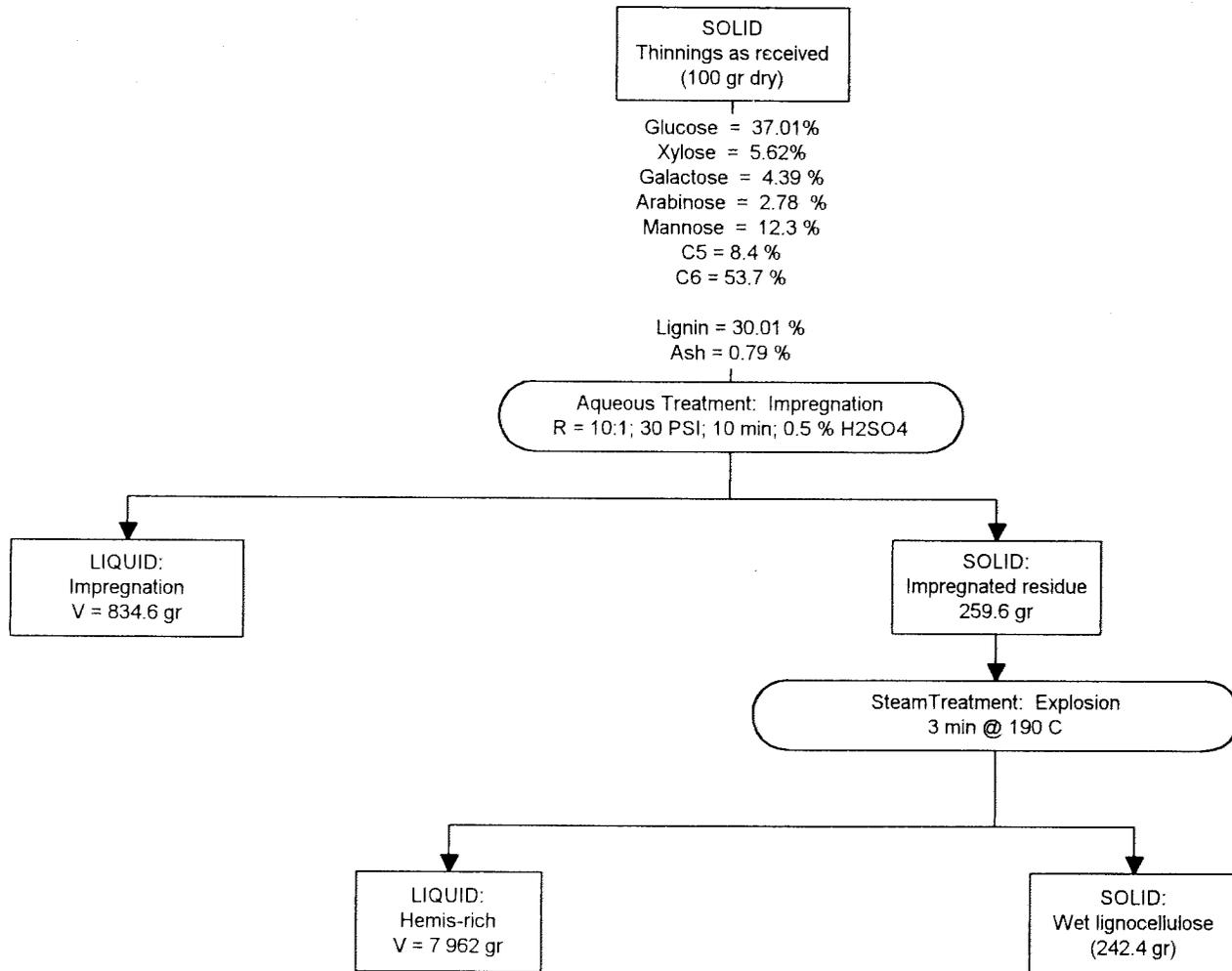


Table 21: Material Balance for Aqueous / Steam Treatment of NREL Thinnings impregnated at 0.4 % H2SO4



SOLID
Thinnings as received
(100 gr dry)

Glucose = 37.01%
Xylose = 5.62%
Galactose = 4.39 %
Arabinose = 2.78 %
Mannose = 12.3 %
C5 = 8.4 %
C6 = 53.7 %

Lignin = 30.01 %
Ash = 0.79 %

Aqueous Treatment: Impregnation
R = 10:1; 30 PSI; 10 min; 0.5 % H2SO4

LIQUID:
Impregnation
V = 834.6 gr

SOLID:
Impregnated residue
259.6 gr

Steam Treatment: Explosion
3 min @ 190 C

LIQUID:
Hemis-rich
V = 7.962 gr

SOLID:
Wet lignocellulose
(242.4 gr)

YIELD

Glucose = 3.05 / 37.01 = 8.24 %
Xylose = 4.82 / 5.62 = 85.77 %
Galactose = 2.05 / 4.39 = 46.7 %
Arabinose =
Mannose = 10.22 / 12.3 = 83.09 %

C5 = 4.82 / 8.4 = 57.38 %
C6 = 15.32 / 53.7 = 28.53 %

Conversion = 26.78 %

HPLC (PH = Post Hydrolyse):

	S.P.H.	PH(1%0)	PH(2%0)	PH(3%0)
Glucose =	3.90 %	3.05 %	3.19 %	3.78 %
Xylose =	5.23 %	4.82 %	4.70 %	4.50 %
Galactose =	2.03 %	2.05 %	1.99 %	1.93 %
Arabinose =	traces	traces	traces	traces
Mannose =	7.85 %	10.22 %	9.98 %	10.5 %

C5 = 4.82 %
C6 = 15.32 %

Yield = 73.22 %
Water = 169.18 gr

HPLC:
Glucose = 38.95 %
Mannose = 1.16 %

C5 = 0.00 %
C6 = 40.11 %

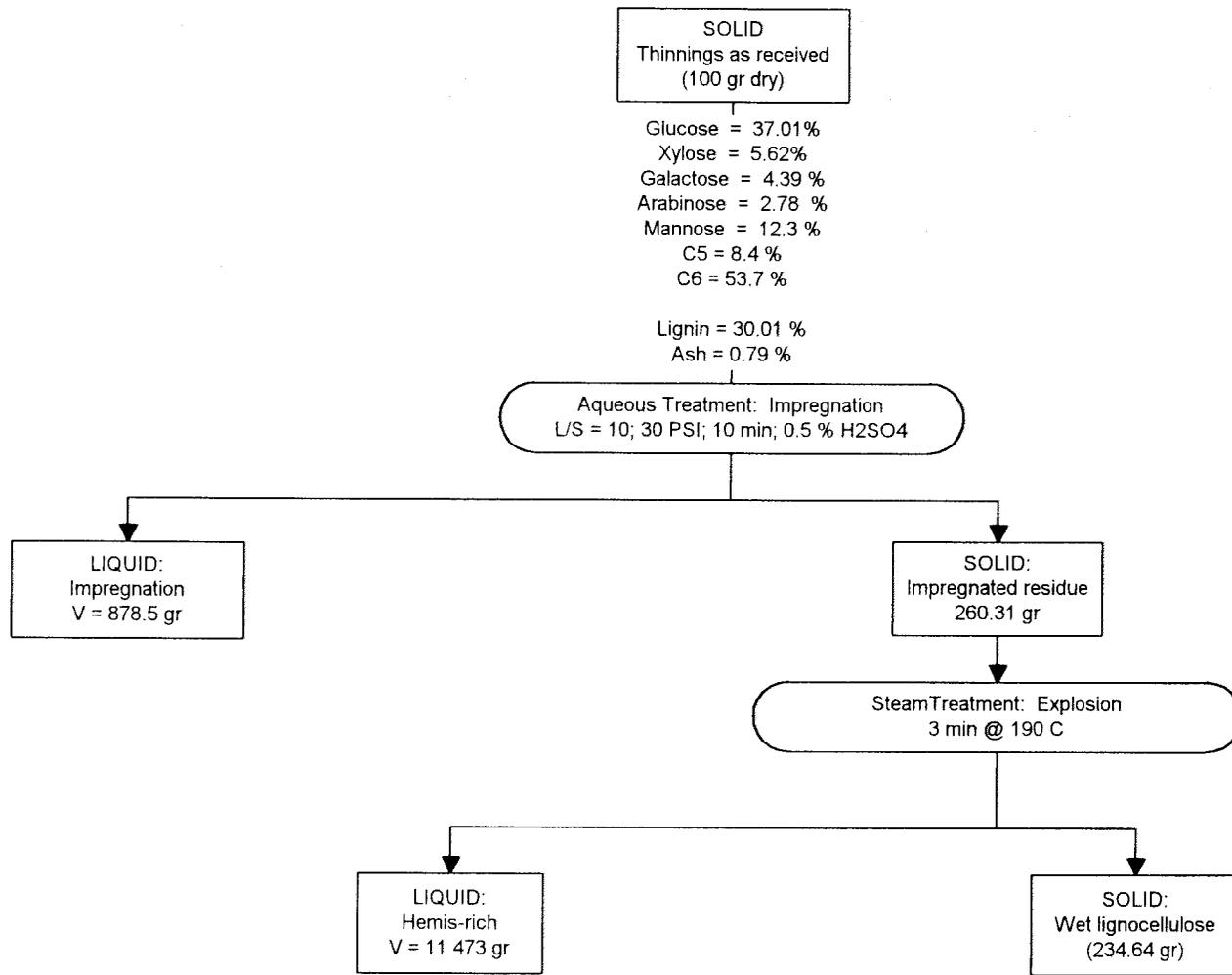
Lignin Klason = 31.59 %

YIELD

Glucose = 38.95 / 37.01 = 105 %
Mannose = 1.16 / 12.3 = 9.41 %

C5 = 0.00 %
C6 = 40.11 / 53.7 = 74.69 %

Table 22: Material Balance for Aqueous / Steam Treatment of NREL thinnings impregnated at 0.5 % H2SO4



SOLID
Thinnings as received
(100 gr dry)

Glucose = 37.01%
Xylose = 5.62%
Galactose = 4.39 %
Arabinose = 2.78 %
Mannose = 12.3 %
C5 = 8.4 %
C6 = 53.7 %

Lignin = 30.01 %
Ash = 0.79 %

Aqueous Treatment: Impregnation
L/S = 10; 30 PSI; 10 min; 0.5 % H2SO4

LIQUID:
Impregnation
V = 878.5 gr

SOLID:
Impregnated residue
260.31 gr

Steam Treatment: Explosion
3 min @ 190 C

LIQUID:
Hemis-rich
V = 11 473 gr

SOLID:
Wet lignocellulose
(234.64 gr)

YIELD

Glucose = 3.75 / 37.01 = 10.13 %
Xylose = 4.93 / 5.62 = 87.62 %
Galactose = 2.06 / 4.39 = 46.93 %
Arabinose = 1.47 / 2.78 = 52.87 %
Mannose = 7.29 / 12.3 = 59.3 %

C5 = 6.4 / 8.4 = 76.19 %
C6 = 13.1 / 53.7 = 24.39 %

Solubilization (by diff.) = 29.25 %

HPLC (Post Hydrolyse 1%):
Glucose = 3.75 %
Xylose = 4.93 %
Galactose = 2.06 %
Arabinose = 1.47 %
Mannose = 7.29 %

C5 = 6.4 %
C6 = 13.1 %

Solids Yield = 70.75 %

Water = 163.89 gr

HPLC:
Glucose = 37.15 %
Mannose = 0.44 %

C5 = 0.00 %
C6 = 37.59 %

Lignin Klason = 31.03 %

YIELD

Glucose = 37.15 / 37.01 = 100 %
Mannose = 0.44 / 12.3 = 3.58 %

C5 = 0.00 %
C6 = 37.59 / 53.7 = 70.0 %

Table 23: Material Balance for Aqueous / Steam Treatment of NREL thinnings impregnated at 1.0 % H2SO4

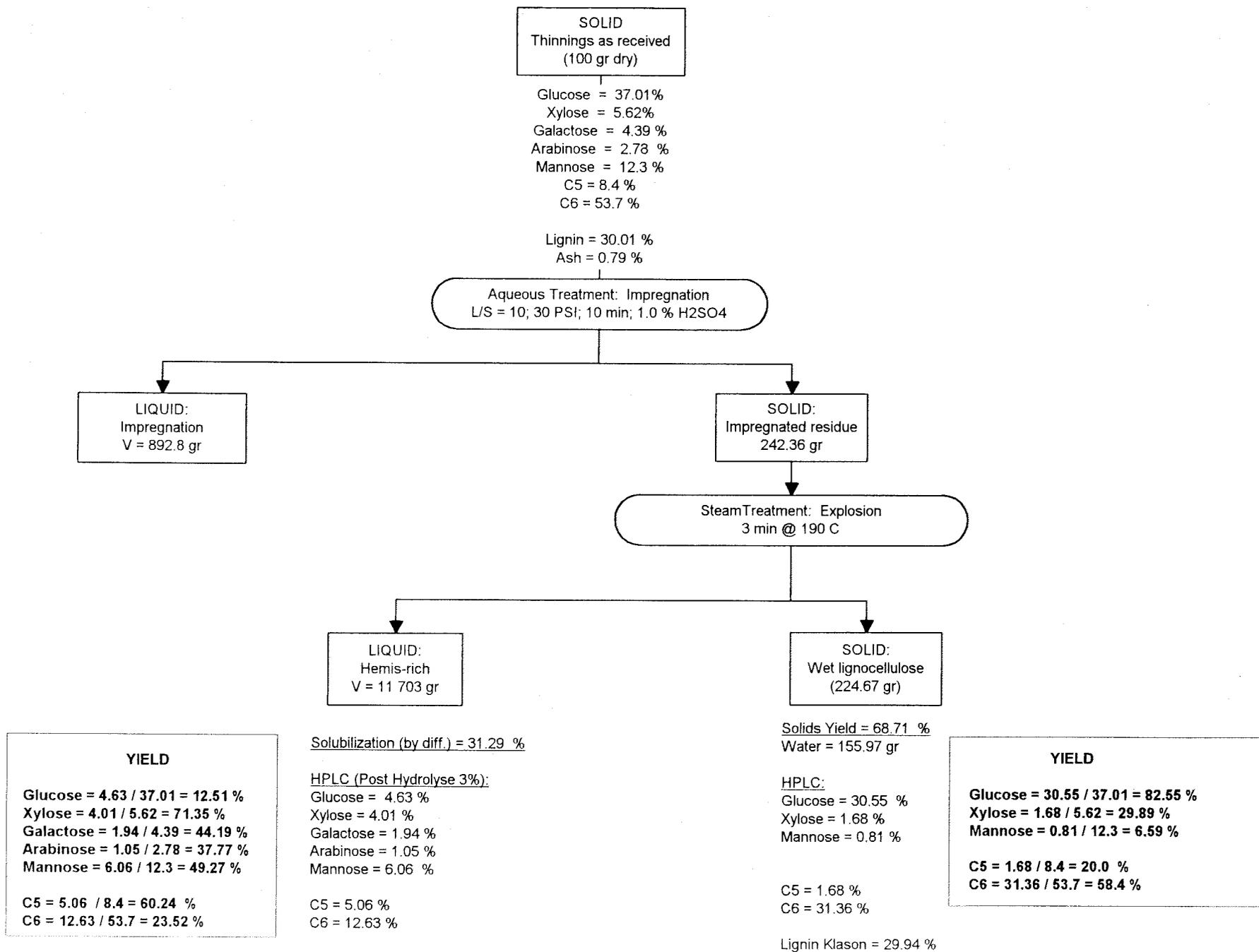


Table 24: Yield of C5 and C6 in Hemis-rich liquor after Aqueous / Steam Treatment at different impregnation conditions (2% and 4% were previously extracted with EtOH 50%)

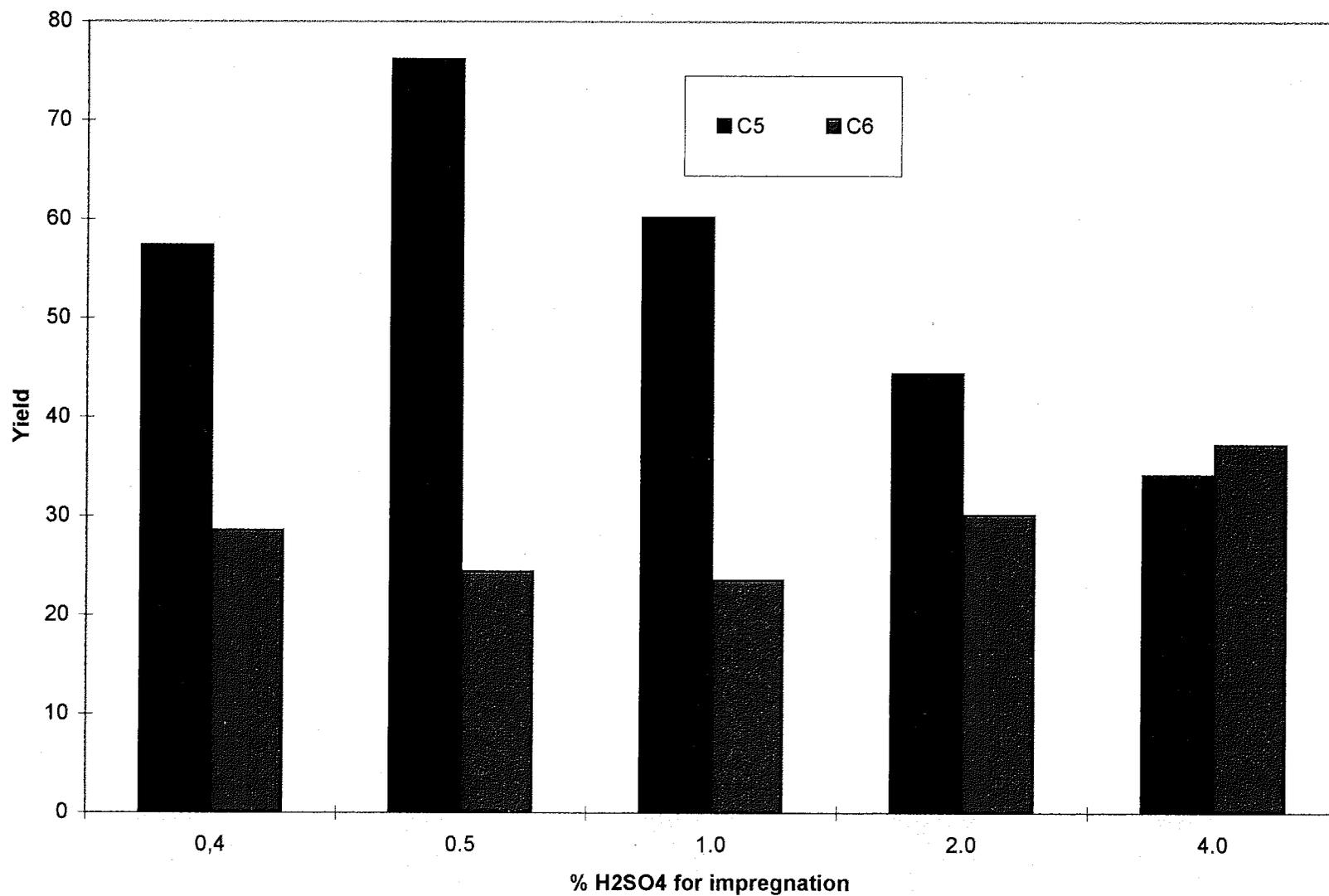


Table 25: Yield of C5 and C6 in Wet Lignocellulose after Aqueous / Steam Treatment at different impregnation conditions (2% and 4% were previously extracted with EtOH 50%)

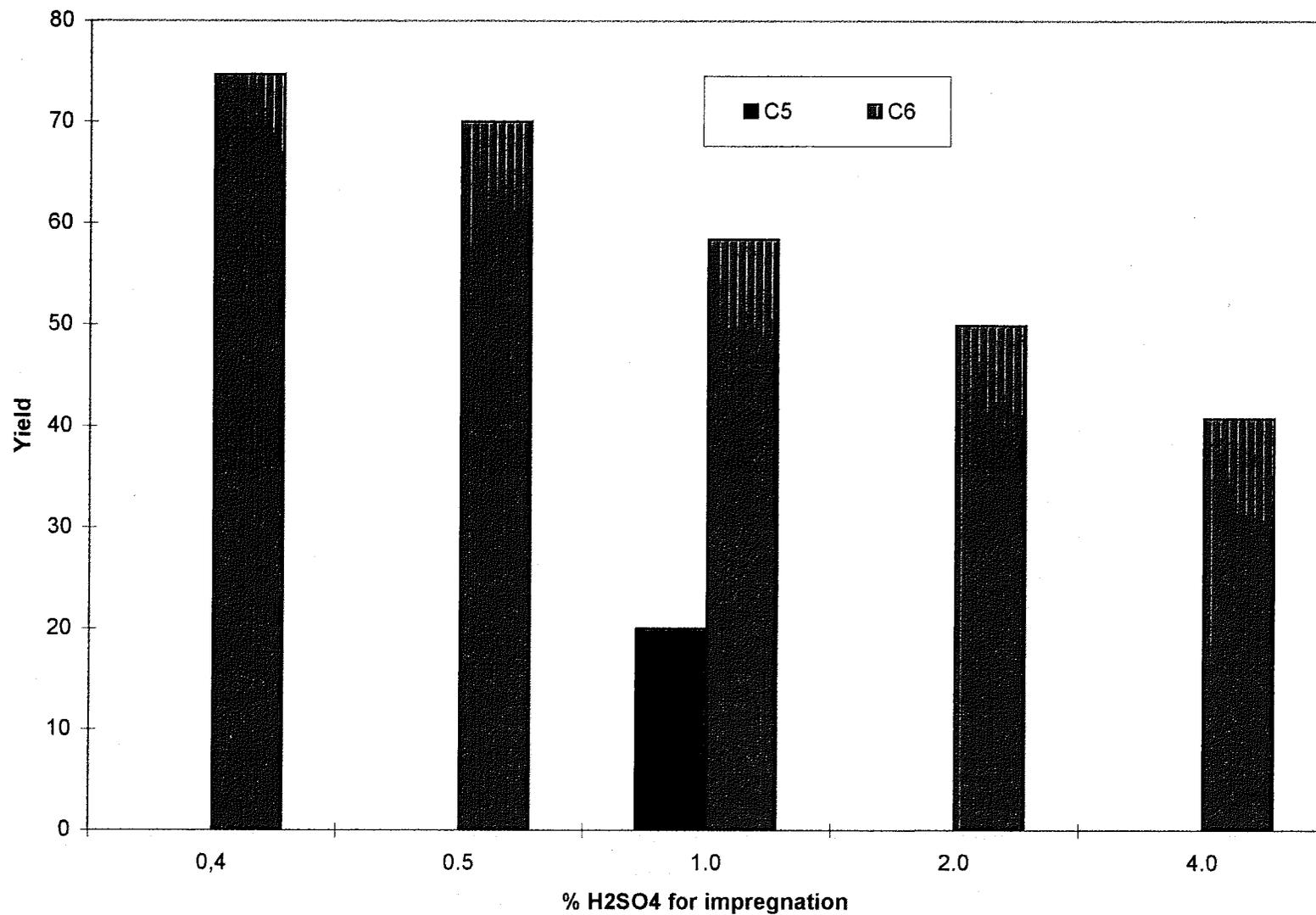


Table 26: Yield of C5 and C6 in Hemis-rich liquor after Aqueous / Steam Treatment at different impregnation conditions (2% and 4% were previously pretreated with steam)

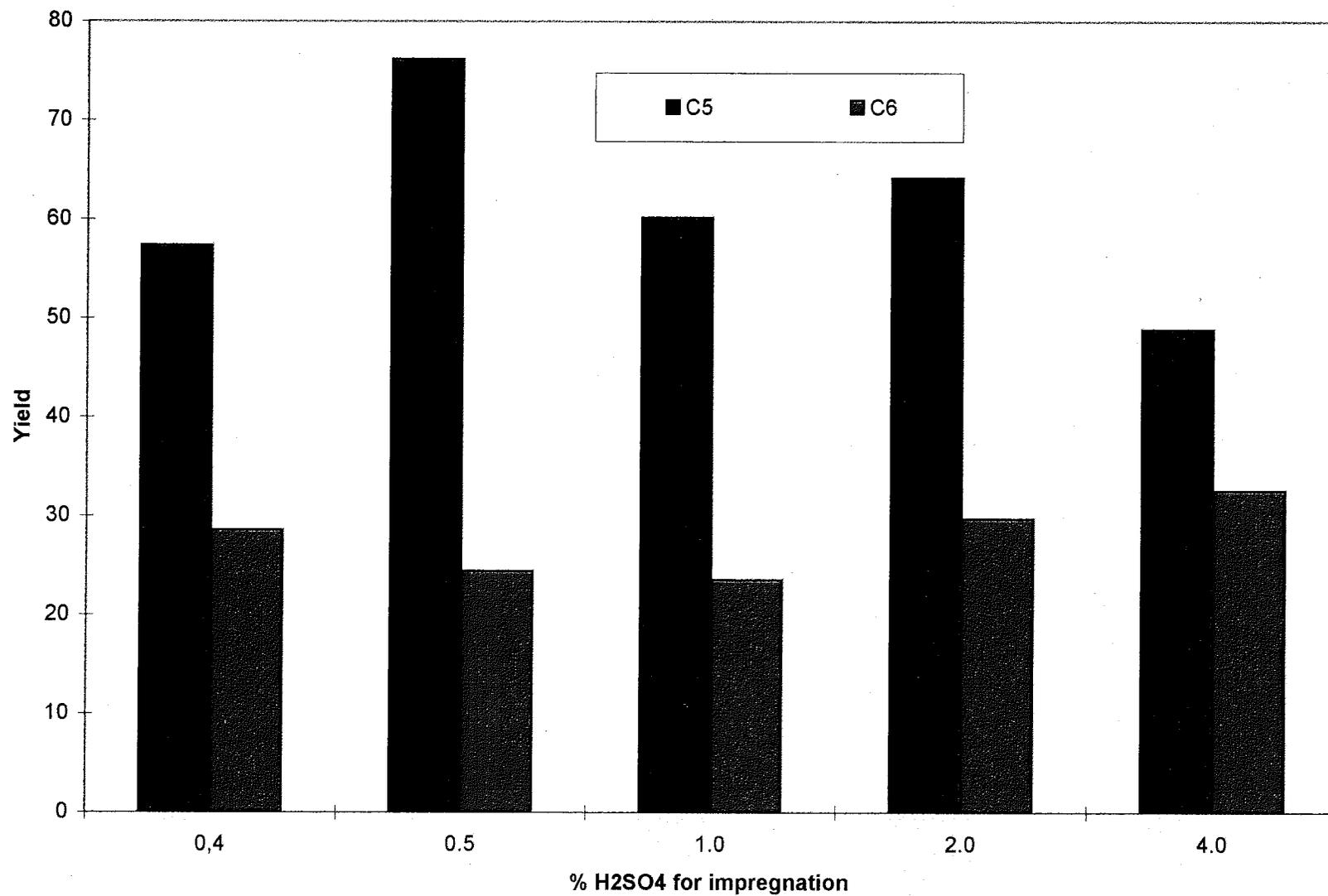


Table 27: Yield of C5 and C6 in Wet Lignocellulose after Aqueous / Steam Treatment at different impregnation conditions (2% and 4% were previously pretreated with steam)

