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EFFECT OF LIGNIN ON THE IN VITRO DIGESTIBILITY OF WOOD PULP

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Summary

IN vitro dry matter digestion and chemical analyses are shown for wood pulps with varying lignin contents made by the kraft, or sulfate, process from paper birch, red oak, red pine and Douglas-fir wood.

At high lignin contents, the pulps from the hardwood species are more digestible than pulps from softwood species. At lignin contents below 7%, the pulps have about equal digestibility.

A curve of digestibility *vs.* extent of delignification shows that digestibility depends upon how much of the original lignin has been removed. Also it indicates that, in general, softwoods increase more slowly in digestibility as lignin is removed than do hardwoods.

Calculations from published *in vivo* data on 40 wood pulps made by 10 different pulping methods are given to show that digestibility of a pulp depends upon the quantity of lignin removed but not upon the method of removal.

Introduction

Several investigators have shown the feeding value and digestibility of wood pulp and paper (Saarinen, Jensen and Alhojärvi, 1959; Mertens and Van Soest, 1971; Mertens *et al.*, 1971; Clark, Iqbal and Dyer, 1971). In general, the results have shown that wood pulp has a high digestibility when the lignin content is below about 5%. Few data are available, however, on the digestibility of wood pulps containing 5 to 25% lignin. The purpose of this study was to show how *in vitro* digestibility increased as lignin was removed from wood by pulping chemicals and to relate the digestibility to some property of the wood, extent of delignification, or the pulping process.

Materials and Methods

Fresh wood from the following species was cut into chips: paper birch, *Betula papyrifera* Marsh; red pine, *Pinus resinosa* Ait.; Douglas-fir, *Pseudotsuga menziesii* (Mirb.) Franko, and red oak, *Quercus* sp., red oak group.

Samples of 7.5 g of air dry chips were vacuum impregnated with cooking liquor and pulped in 0.1 liter capacity stainless steel reaction vessels rotated in a heated oil bath. Pulps of various yields and lignin contents were produced by varying time, temperature, effective alkali, and sulfidity (table 1). Cooking time is measured as time at temperature. Twenty minutes were required to heat the reaction vessel to 110 C.; 35 min. were required to reach 170 C. In the kraft process, sodium hydroxide and sodium sulfide concentrations are measured in terms of effective alkali and sulfidity. Effective alkali is defined as the percentage of $NaOH+\frac{1}{2}\ Na_2S$, each expressed as Na_2O, based on the weight of moisture-free wood. Sulfidity is defined as a percentage found by dividing the Na_2S by the total $NaOH+Na_2S$, each expressed as Na_2O. The pulping liquor to wood ratio was 5:1. After pulping, the wood chips were beaten for 1 min. in a blender in 90C. water to break the chips into fibers. The fibers were then collected on a fritted glass filter and washed with 90 C. water to remove pulping chemicals. The pulp was ovendried at 105 C. for 16 hr. and weighed to determine pulp yield.

The pulps were analyzed for 72% sulfuric acid lignin (Klason lignin), total carbohydrate, and in vitro rumen dry matter digestibility. Klason lignin was determined according to procedure of Saeman *et al.*, (1954). The filtrate from the lignin analysis was neutralized and analyzed for reducing substances by Nelson's modification of the Somogyi

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TABLE 1. PREPARATION, COMPOSITION AND *IN VITRO* DIGESTIBILITY OF KRAFT PULPS

Time	Temperature	Effective alkali[a]	Yield	Klason lignin	Total carbohydrate	Delignification	*In vitro* digestibility
Min.	°C	%	%	%	%	%	%
				Red oak			
..	...	....	100	22.8	65.5	0	12
0	140	8.8	79.7	22.4	73.1	21.6	45
0	140	20	73.1	22.2	73.6	28.9	48
0	160	10.5	74.0	20.2	77.0	34.5	61
30	140	20	65.6	15.7	80.6	54.7	77
0	170	13.1	62.2	13.4	87.2	63.4	78
60	140	20	60.2	12.5	87.0	68.6	82
90	140	20	56.1	9.5	91.8	76.7	80
30	170	13.1	51.2	1.6	96.5	96.5	90
				Douglas-fir			
..	...	....	100	31.5	64.9	0	0
0	140	16.0	78.2	29.8	66.5	25.9	0
15	140	16.0	71.8	29.1	68.6	33.4	0
30	140	16.0	69.4	28.1	70.5	37.9	1
0	160	16.0	68.4	27.4	70.4	40.4	1
0	165	16.0	67.7	26.4	73.3	43.3	1.5
60	140	16.0	65.9	25.9	73.5	45.7	3
20	165	16.0	60.2	20.7	79.6	60.5	29
60	165	16.0	51.4	11.6	90.1	81.1	73
130	165	16.0	44.9	6.3	95.7	91.0	84
				Red pine			
..	...	....	100	27.3	68.3	0	0
0	140	25	79.3	27.4	71.7	20.3	3
0	165	25	73.1	24.4	75.1	34.6	15
10	165	25	66.8	20.4	80.4	50.3	40
20	165	25	64.9	19.2	81.8	54.4	45
60	165	25	55.7	11.3	91.6	77.0	68
90	165	25	52.6	6.5	96.1	87.4	80
110	165	25	50.0	5.7	97.1	89.6	90
130	16.5	25	48.5	3.9	98.8	93.0	88
				Paper Birch			
..	...	....	100	19.8	68.0	0	15
0	110	20	80.7	21.7	71.5	11.6	56
0	140	25	79.1	20.4	73.1	18.5	48
120	110	20	68.5	22.4	73.0	22.5	56
120	110	25	71.1	21.4	73.9	23.1	59
600	110	20	68.3	20.1	74.5	30.7	80
10	170	20	64.3	12.2	88.1	60.4	76
22	170	20	51.8	6.2	94.4	83.8	80
30	170	20	52.7	5.6	96.2	85.1	83
70	170	20	46.7	1.2	101.8	97.1	90
30	170	25	44.7	1.1	101.3	97.5	88
60	170	25	42.4	0.7	102.1	98.6	89
120	170	25	39.5	0.9	102.1	98.3	88

[a] Sulfidity was 20.8% for Douglas-fir and 25% for other species.

method (Nelson, 1944). The results are in terms of reducing substances calculated as weight percent glucose and reported as total carbohydrate. The *in vitro* rumen digestion was determined by a method spicifically developed to estabilish the dry matter digestibility of wood-based products (Mellenberger *et al.*, 1970).

Results and Discussion

lignin, total carbyhydrate analysis, and *in vitro* dry matter digestibility of the wood and kraft pulps are presented in table 1 with pulp yield and percent delignification. Pulp yield is the percentage of the original wood recovered as pulp on a moisture free basis. Percent delignification is the percentage of the lignin removed from the original wood. It is calculated from pulp yield and lignin content of the original wood and the pulp. At the high yields it should be noted that some of the pulps have a higher lignin content than the original wood. This is a result of more hemicelluloses than lignin being removed in the

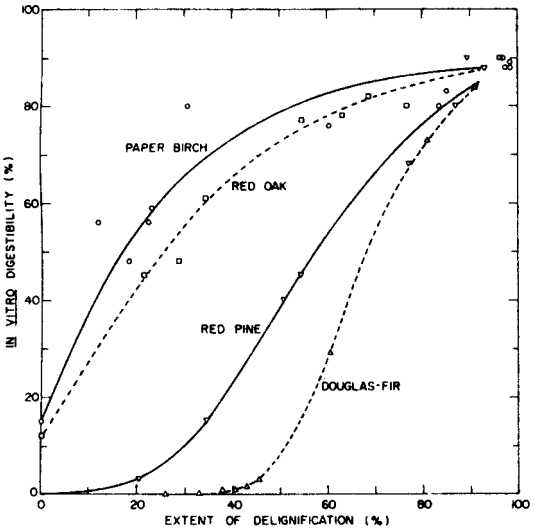

Figure 1. Relationship between in vitro digestibility and extent of delignification for kraft pulps made from four wood species.
(M 140 060)

relatively mild pulping conditions and leaving a pulp which has a lignin content greater than the wood.

The *in vitro* digestibility data for red oak and Douglas-fir samples were determined in duplicate on each of the 2 days, and for paper birch and red pine it was determined in duplicate on 1 day. The greatest difference between duplicates was 7.7 percentage points, and the average difference was 1.6 percentage points. The greatest difference between averages of each day was 6.4 percentage points, and the average was 2.5 percentage points.

A comparison of the *in vitro* digestibility and lignin content data in table 1 shows that at the higher lignin contents, the oak and birch pulps are more digestible than the pine and Douglas-fir. At lignin contents of less than about 7%, however, the pulps have about equal digestibility. The data also show that digestibility increases as the lignin content decreases. Saarinen *et al.* (1959), Feist, Baker and Tarkow (1970) and Mertens and Van Soest (1971) have also shown that digestibility is generally inversely related to lignin content for wood pulps, chemically treated wood, and paper.

The differences between hardwood and softwood in terms of increased digestibility due to delignification is emphasized in figure 1. For the hardwood (birch and oak) pulps, the digestibility increases rapidly as lignin is removed, whereas, for the softwood (pine and Douglas-fir) pulps, considerable amounts of lignin must be removed before digestibility is appreciably affected. Figure 1 indicates that a smaller percentage of the lignin needs to be removed from hardwood species than from softwood species to obtain equal digestibilities. For example, to obtain 60% digestibility, only 25 to 35% of the lignin must be removed from hardwoods, whereas, 60 to 70% of the lignin must be removed from the softwoods.

This difference in response of digestibility to delignification between hardwoods and softwoods is probably true for other hardwood and softwood species. Great differences in response of digestibility between hardwoods and softwoods to other treatments have been noted (Bender, Heaney and Bowden, 1970; Millett *et al.*, 1970). This difference cannot be readily explained, however. It could be related to the fact that softwoods contain 25 to 50% more lignin than hardwoods. It could also be due to the differences in the lignin-carbohydrate association, the lignin distribution or the lignin structure in hardwoods and softwoods. For instance, hardwood lignin differs appreciably from softwood lignin. The basic building units for hardwood lignin appear to be phenolic nuclei of both propyl guaiacyl and propyl syringyl, whereas for softwood lignin it appears to be almost all propyl guaiacyl type.

Saarinen *et al.* (1959), using rams, determined *in vivo* digestibility of 40 birch (probably *Betula pubescens*) and spruce (*Picea excelsa*) pulps made by 10 different pulping

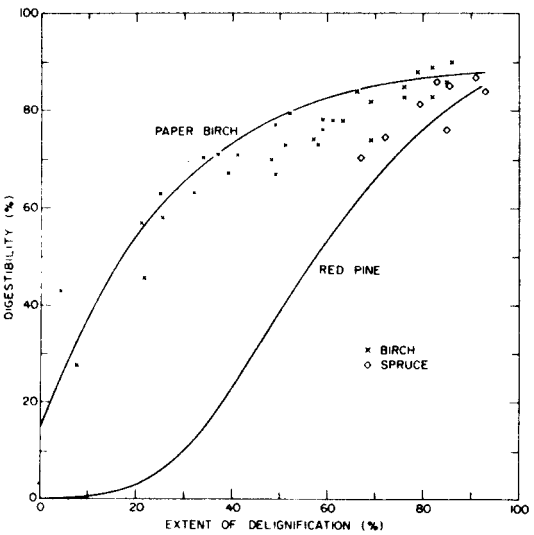

Figure 2. Relationship between digestibility and extent of delignification for wood pulps. Data from Saarinen et al. (1959). Curves from figure 1.
(M 140 059)

methods involving acid, acid-oxidizing, oxidizing, neutral, and alkaline procedures. The extents of delignification, which were calculated from the published data, and the *in vivo* crude carbohydrate digestion coefficients are shown in figure 2. The curves from figure 1 for paper birch and red pine are included for comparison because these woods had lignin contents identical to those of the birch and spruce.

Figure 2 shows that the digestibility of the pulps seems to depend upon how much of the original lignin was removed regardless of the pulping method.

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