preferred to 125 per cent added water when steam consumption is taken into account, it was felt that the better mixture of acid and wood obtained with the 125 per cent water outweighed the small increased steam consumption and justified its adoption as a standard in our work.

Table III shows no great differences in yields resulting in the reduction of the added water from 400 to 125 per cent, which is of exceeding importance commercially.

TABLE III

1.80 to 1.85 Per Cent H_2SO_4	0 Minute Time	7.5 Atmos. Pressure
WATER Per cent of dry wood	TOTAL SUGARS	PER CENT OF TOTAL SUGARS FERMENTABLE
100	21.09	60.68
125	21.96	59.29
250	23.75	55.31
300	23.16	54.87
400	22.24	56.19
		PER CENT ALCOHOL
		6.440
		6.805
		6.648
		{ 6.096(a)
		{ 6.645(b)
		6.154

(a) Actual average, containing one poor fermentation.

(b) Result recalculating poor fermentation to a normal efficiency.

Sulfuric acid was used as a catalytic agent in amounts varying from 0.5 per cent to 4 per cent of the dry weight of the wood. The results obtained with a zero minute cooking period and 125 per cent water cooked at 7.5 atmospheres pressure are given in Table IV, which shows that not only total sugars increase with increasing acidity, but especially that the portion which is fermentable increases so that the alcohol yields increase proportionally.

TABLE IV

CONCENTRATION H_2SO_4	TOTAL SUGAR Per Cent	PER CENT OF TOTAL SUGARS FERMENTABLE	PER CENT ALCOHOL
0.5	17.42	43.13	4.172
0.75	21.83	56.03	6.085
1.00	21.68	56.43	6.506
1.40	23.09	53.93	6.502
1.83	21.53	54.98	6.623
2.50	22.11	63.16	6.927
4.00	21.10	66.63	7.000

A consideration of the above two variables will show that the concentration of the catalytic agent expressed in terms of dry wood is the single and great determining factor and this is especially true when the following work on the effect of time of cooking is studied. The concentration of acid expressed in terms of the added solution is without effect (contrary to a number of patents that have been granted) except where such variation also varies the ratio of acid to dry wood. In the paper referred to in the beginning of this communication, the conclusion was reached that "a cooking period of 0 minute, that is, blowing off from $7\frac{1}{2}$ atmospheres as soon as that pressure was obtained, was advantageous." This was the result of a study of total sugars only, as shown in Figure 3 of that paper where the total sugar obtained from a series of cooks varying from 0 to 30 minutes varied less than a few tenths of 1 per cent. A repetition of that work has shown practically the same results

TABLE V

TIME OF COOK Minutes	TOTAL SUGAR Per cent	Per cent of Total Sugar Fermentable	ALCOHOL Per Cent of Dry Wood
7.5 Atmos. Pressure and 125 Per Cent Water			
With 1.40 Per cent H_2SO_4			
0	23.09	53.93	6.502
10	23.45	55.08	6.456
30	22.34	63.22	6.862
With 2.50 Per cent H_2SO_4			
0	22.11	63.16	6.927
10	22.36	68.53	7.662
20	23.61	71.44	8.537
45	21.56	77.15	8.295
90	18.06	81.40	7.387

so far as the total sugar is concerned, but careful fermentations have shown a decided difference in composition of that sugar under different conditions. This difference is shown particularly when the acid concentration is fairly high, as in the case of the 2.5 per cent acid, although the rise in fermentable sugars is noticeable even in 1.4 per cent acidity.

Table V shows these variations and fermentable sugar and alcohol yields. In addition it will be noticed that with 2.5 per cent

acid there is a gradual decrease in total sugar as the length of the cook is largely increased (beyond 20-minute cooking periods), even though the portion that is fermentable increases quite decidedly. The causes and explanations of these differences have not been fully worked out, although a number of lines of attack suggest themselves, and we hope to take up this phase of the problem in detail in a subsequent publication. This brief summary of results is given purely for its technical value for the assistance that it may give in the proper choice of operating conditions as determining those prime variables which affect the total and fermentable sugar yields.

CONCLUSION

From an operating standpoint, and taking into consideration, (1) economic operation, which includes acid cost, lime or other neutralizing cost, and steam consumption; and (2) plant depreciation, we feel that the following cooking conditions give the greatest yields of alcohol:

I—Pressure of cook, $7\frac{1}{2}$ atmospheres.

II—Time of cook, about 20 minutes.

III—Water to dry wood ratio, 125 to 100.

IV—Acid to dry wood ratio, $2\frac{1}{2}$ to 100.

The writer wishes to thank the E. I. du Pont de Nemours Powder Company, and Mr. John Boyt and Mr. J. S. Groves, Superintendent and Chemist, respectively, of the alcohol plant of the du Pont Company at Georgetown, S. C., for the many courtesies and suggestions rendered in the yeasting and fermentation work. The writer further wishes to thank Mr. Homer Cloukey, of the Forest Products Laboratory, for the patience and skill exercised in the many hundred analyses required in the study of this problem.

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THE MANUFACTURE OF ETHYL ALCOHOL FROM WOOD WASTE—III. WESTERN LARCH AS A RAW MATERIAL

By F. W. KRESSMANN

The logging of western larch (*Larix occidentalis*) shows a woods loss of 8 per cent due to butting off the lower portion of the tree.¹ This practice is due chiefly to the presence of shakes in the butt. In addition, the base of the tree is usually swelled. The swelled portion is denser than the rest of the trunk and usually sinks, thus preventing rafting. The lengths of the "butts" left in the woods vary from 4 to 8 feet, although occasionally a 16-foot piece is rejected.

The utilization of this waste material up to the present time has not met with success and it was hoped that it might be profitably employed as a raw material in the production of ethyl alcohol.

A sample of sawdust from a butt log was cooked with 1.8 per cent sulfuric acid, 125 per cent of water, at 7.5 atmospheres pressure for 10 minutes. A yield of sugar equal to 29.72 per cent, and of total solids equivalent to 35.18 per cent, of the dry weight of the wood was obtained. Under the same conditions, white spruce would yield about 22 per cent of sugar, of which from 60 to 65 per cent would be fermentable, making an alcohol yield of 6.8 to 7 per cent of the dry weight of the wood, or from 20 to 21 gallons of absolute alcohol per dry ton. The extracts obtained from the hydrolysis of the larch were fermented under standard conditions, the fermentation records and alcohol yields being given in Tables I and II.

The larch yielded about 35 per cent total sugar more than spruce and yet only 37.9 per cent of that sugar fermented compared with 60 or 65 per cent from spruce. Mr. A. W.

¹ U. S. Department of Agriculture, Forest Service Bulletin 122, "The Mechanical Properties of Western Larch," O. P. M. Goss.

TABLE I—FERMENTATION RECORD—WESTERN LARCH

Fermentation No.	Yeast					Mash before fermentation													Beer									
	Cook No.	Seed yeast	96 Hours yeast			Fermenter set. Date	Hours filling fermenter	Hours fermenting, including time of filling	Sp. grav. at 15° C.	Reducing sugar Grams per liter	Acidity	Total solids Per cent	Brix record					Attenuation Degrees	Brix, 4th day	Distillation Date	Reducing sugar Grams per liter	Sp. gr. at 15° C.	Acidity	Total solids % by weight	Alcohol. % by weight			
			Brix.	Acidity.	Alcohol. % by weight								Decrease in Brix															
													1st day	2nd day	3rd day	4th day	5th day											
10 50			1.0243	6.170	18.6	1/21/15	32.5	128.5	1.0495	94.92	3.2	10.301	12.1	3.1	0.3	+0.1	-0.2	0.0	3.5	8.6	1/26/15	56.28	1.0341	7.0	7.207	1.4707		
11 50		22.0	1.0262	5.398	26.4	2/11/15	32.5	128.5	1.0543	97.936	2.4	12.325	13.3	3.0	0.5	0.2	0.2	0.0	3.9	9.4	2/16/15	61.744	1.0392	7.2	9.490	1.598		
14 50		22.5	1.0235	5.784	24.5	3/18/15	32.5	128.5	1.0440	83.38	2.8	9.190	11.0	2.9	0.4	0.3	+0.2	0.0	3.4	7.6	3/23/15	51.264	1.0302	5.6	6.438	1.320		

TABLE II—SUGAR AND ALCOHOL YIELDS FROM WESTERN LARCH

TABLE 11. SUGAR AND ALCOHOL YIELDS FROM WESTERN LARCH											
Species of wood	Cook number	Total reducing sugar in per cent of dry original wood	Per cent of total reducing sugars fermentable	Per cent of total reducing sugars non-fermentable	Fermentation efficiency	ALCOHOL IN BEER			ALCOHOL YIELDS		
						Actual alcohol yield	Theoretical alcohol yield	Per cent of total sugar obtained as alcohol	Per cent of original dry wood	Gallons of absolute per dry ton	Gallons of 190 proof per dry ton allowing 5% distillation loss
Western larch....	50	29.72	37.70	62.30	85.77	1.320	1.539	32.34	4.970	15.033	15.004
Western larch....	50	29.72	39.83	60.17	79.85	1.470	1.841	31.80	5.048	15.269	15.240
Western larch....	50	29.72	36.04	63.96	92.23	1.578	1.711	33.24	4.912	14.857	14.829
AVERAGE.....			37.89	62.11					4.977	15.05	15.03

Schorger, of this laboratory, has analyzed both of these woods with the following results:

	WESTERN LARCH (Base)		WHITE SPRUCE (4 Samples)	
	Per cent		Per cent	Average
Soluble in ether.....	9.75	0.90 to 1.95	1.36	
Soluble in cold water.....	14.47	0.82 to 1.45	1.12	
Soluble in hot water.....	16.52	1.88 to 2.52	2.14	
Soluble in 1 per cent NaOH, 10 min. heating.....	32.72	6.72 to 8.84	7.70	
Soluble in 1 per cent NaOH, 60 min. heating.....	38.58	11.18 to 13.87	12.21	
Pentosan.....	6.99	10.04 to 10.78	10.39	
Methyl pentosan.....	3.42	3.08 to 3.95	3.55	
Cellulose.....	42.57	51.95 to 58.47	56.17	
Volatile oil.....	0.84			
Ash.....	0.36	0.285 to 0.326	0.307	

It will be noticed that the larch contains a large amount of water-soluble material and a proportionally small amount of cellulose. In all cases, the above analyses were made on a fresh sample taken from the same lot. In a subsequent paper, Mr. Schorger will take up the composition of this water-soluble material, the chief constituent of which is a galactan which yielded approximately 10 to 12 per cent of the dry weight of the wood of galactose, which in turn accounts for the high sugar yields obtained from the larch.

It has been suggested by Körner,¹ although disputed by Gallagher and Pearl,² that in the acid hydrolysis of cellulose-containing material, the source of the fermentable sugars and, therefore, the alcohol, is the cellulose itself.

If the sugar yield for the larch is recalculated so that it is proportional to the cellulose content, assuming 22 per cent of sugar from the spruce, we would have then 16.7 per cent of sugar instead of 29.7 per cent, as actually obtained. However, as noted above, about 10 or 12 per cent of galactose was obtained, which subtracted from the total sugar yield of 29.7 per cent, would leave from 17.7 to 19.7 per cent of sugar comparable to that obtained from spruce. Under normal conditions, with a 94 per cent efficiency and a yield of that per cent of the theoretic amount of alcohol formed, which is 51.1 per cent, we get for 60 or 65 per cent of total sugar fermentable the following alcohol yields:

$$16.7 \times 0.511 \times 0.94 \times 0.60 = 4.83 \text{ per cent alcohol}$$

$$16.7 \times 0.511 \times 0.94 \times 0.65 = 5.23 \text{ per cent alcohol}$$

The actual alcohol yield is 4.977 per cent, which corresponds to about 62 per cent of total sugar fermentable, which is the average of the above figures chosen for spruce. It appears, therefore, that the yield of fermentable sugar and alcohol is proportional to the cellulose content of the wood, irrespective of other materials that may be contained therein. In addition, western larch butts will be a good raw material for the production

of ethyl alcohol if a yeast is found which will ferment the galactose as well as the dextrose within the time limit and other limitations as prescribed by the Bureau of Internal Revenue. This phase of the subject has been reserved and will be taken up in the near future.

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THE APPLICATION OF THE DAVIS SPOT TEST IN THE PRELIMINARY EXAMINATION OF CREOSOTES

By HOMER CLOUKEY

The tests undertaken and included in this report were run for the purpose of verifying the "absorption spot test" given in an article by T. H. Davis on "The Examination of Creosote,"¹ and described in this article as follows:

"Absorption Spot—Allow six drops of the sample to fall from a burette upon the surface of clean, white blotting paper. If tar, carbon, or dirt is present, it is very easily observed, as it quickly segregates at the center. The paper should be laid away, in a flat position, for several hours, in a place free from dust. If then examined, foreign matter will be observed in a distinct zone at the center of the spot; the outer zone very readily indicates the character of the oil."

In order to establish some idea of the sensitiveness of this test for carbon and dirt in creosote and make it fairly quantitative a series of spots was made from a carbon-free creosote with definite graduated amounts of carbon in the form of lampblack added.

This series comprises six mixtures of creosote and lampblack as follows:

Per cent lampblack added..... 0.0 0.005 0.01 0.05 0.10 0.50

This series is shown in Fig. I. The results obtained show an increasing gradation in the density of the free carbon ring at the center and indicate that 0.005 per cent is easily shown by this test. In heavier percentages than 0.5 per cent, the amount in an unknown sample would be difficult to estimate by comparison.

The appearance of several authentic samples of various creosotes and oils used for wood-preserving purposes is shown in Fig. II. No. 1 shows coal tar creosote with the characteristic brown gradually shading on the edges to a lighter zone; if carbon and dirt are present, these are segregated in an inner circle which is the size of the original spot before diffusion. No. 2 is a characteristic water gas tar creosote with the large spot and outer yellow zone characteristic of this oil. No. 3 illustrates the character of the spot afforded by a paraffin base crude oil used for wood-preserving purposes: this is almost colorless

¹ Zeitschrift für angewandte Chemie, 1908, 2353.

² Proc. Eighth Intern. Cong. Appl. Chem., 13, p. 147.

¹ Oil, Paint, and Drug Reporter, February 14, 1910.