hours. On the basis of 10 per cent fiber, this represents 5.0 kilowatt per ton of fiber per 24 hours, leaving a power consumption chargeable against pulp production of 13.3 kilowatts per ton fiber per 24 hours. This figure, however, should be further reduced, as the energy expended in grinding is not dissipated but is recovered as heat, as the mixture of pulp and juice becomes heated in the grinding operation. Since the juice must be heated in any case, the heat absorbed by the juice represents useful work, so that the new power chargeable against board is only the energy lost in transforming the electrical energy through mechanical energy into heat plus the subsequent loss by radiation. Even without taking the saving in steam for heating into consideration, the figure of 13.3 kilowatts per ton of fiber per 24 hours compares very favorably with the 37 to 45 kilowatts per ton of pulp per 24 hours in grinding wood for similar grades of wallboard.

Since the refining and beating costs are practically the same, these power consumptions in grinding form a good index for the comparison of cost in the use of wood and Vazcane pulp for board manufacture.

Figure 5—Cabaret Tokio, Havana. Vazcane Semi-Pressed Board Used as Interior Finish

Properties of Board

The insulating board produced from Vazcane pulp has proved to be equal to the best, and superior to most of the insulating boards on the market. In appearance the board is very uniform, with a fine mat surface. Strength equal to that of current boards is attained with a less dense board. The decreased density gives a board of decreased thermal conductivity over current boards.

The semi-commercial plant has proved so well the merit of the Vazcane process that plans are under way for the erection of commercial-size plants in several sugar-producing countries.

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Studies in the Drying Oils

XIII—Changes in Linseed Oil, Lipase, and Other Constituents of the Flaxseed as It Matures (1929)[1]

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Rapid formation of oil in the early stages of growth of flaxseed is accompanied by marked decrease in the activity of the enzymes present and by desaturation of the first formed glycerides. Analysis of the oil in terms of the four groups of fundamental acids shows a higher percentage of oleic acid in oil from the 1929 northwest crop than is normal for northwest oil.

IN A previous paper (*3*) data were given showing some progressive changes in the constituents of flaxseed during the growing season. The presence of the enzyme lipase in flaxseed was proved. The flax plant flowers over a period of 10 or 12 days. The samples collected in 1928, at definite intervals, represented an average of ages within this variation. The writers did not, therefore, feel justified in making complete analysis of these extracted oils.

In the case of the 1929 St. Paul samples herein described, each individual flower was tagged with pieces of colored string. Each seed in every sample is therefore the age specified. The writers felt justified in making analyses of the oil samples extracted by means of ether from the seeds. Even with the elaborate scheme of tagging each flower there are some slight fluctuations in the figures. This probably comes from variations in soil and depth of planting.

Also the weather of the past year was abnormal. The early part was favorable and the fields both at St. Paul, Minn., and at Bethlehem, Pa., got an early start. At St. Paul, however, and throughout the Northwest in general, the latter half of the season was abnormally hot and dry and undoubtedly checked the normal growth of the plant, which was distinctly not the case at Bethlehem. At Bethle-

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Table I—Changes in Constituents of Oil during Maturation of Flaxseed

Time after Flowering	Oil	Iodine No. Oil	Thiocyanate No. Oil	Satd. Acids	Oleic Acid	Linoleic Acid	Linolenic Acid	Unsaponifiable	Neutralization No. Satd. Acids	Stearic Acid	Palmitic Acid	Saponification Value	Hexabromide No.
Days	*Per cent*			*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*		*Per cent*	*Per cent*		
						NORTHWEST OILS							
10	...	138.3	90.8	12.5	32.6	37.4	17.5	2.52	...	..	..	...	
12	...	149.5	97.9	10.4	30.0	36.1	23.5	2.32	...	..	..	196.5	
13	24.97	159.6	101.5	10.1	22.9	39.7	27.3	3.52	202.5	7.4	2.7	205.8	
14	28.51	169.6	104.4	10.0	14.5	44.8	30.7	2.86	201.0	8.0	2.0	199.9	
15	28.44	163.8	101.0	10.0[a]	17.4	45.8	26.8	...	...	..	..	...	
16	28.55	158.8	99.7	10.5	21.2	42.7	25.6	1.3	...	..	..	196.5	
17	30.55	161.0	100.4	10.1	19.9	43.9	26.1	1.57	...	...	...	198.6	
18	37.77	169.1	108.0	8.8	20.6	37.0	33.6	..	205.1	5.71	3.07	204.4	
20	37.94	169.4	107.6	8.8	19.7	38.3	33.2	1.02	...	...	...	...	
22	37.50	176.2	108.3	7.1	14.5	46.2	32.2	..	198.0	6.9	0.2	204.2	
23	37.07	170.5	109.2	9.0	20.2	35.6	35.2	1.08	204.7	5.97	2.98	...	
24	37.46	174.2	109.5	7.8	17.5	40.4	34.3	1.76	...	...	...	201.0	
25	37.67	175.0	109.3	9.1	15.1	40.5	35.3	..	204.9	6.02	3.10	205.6	
27	37.33	171.2	106.6	6.7	18.7	44.8	29.8	2.4	201.7	5.3	1.4	205.1	
28	37.72	175.7	107.3	7.5	13.5	47.5	31.5	1.69	203.0	5.3	2.2	205.3	
29	36.04	162.3	103.5	8.1	23.9	40.3	27.7	2.3	202.0	6.2	1.9	201.3	
33	36.17	176.8	111.2	6.3	18.0	41.1	34.6	..	197.5	6.3	0	204.1	
34	37.40	174.0	107.1	7.8	14.9	45.7	31.6	0.94	201.7	6.28	1.51	...	
37	37.85	175.6	108.9	7.0	15.9	44.3	32.8	1.39	205.0	4.3	2.7	203.2	
39	37.31	170.3	108.3	7.5	20.8	39.0	32.7	..	206.1	4.45	3.00	206.2	
40	35.30	163.9	104.5	7.0	24.4	40.9	27.7	..	202.7	5.1	1.9	205.5	
												Acid Value	
						PENNSYLVANIA OIL							
23	33.89	173.9	109.8	4.75	21.1	42.5	31.6	1.23	197.8	4.75	0	1.64	32.4
23[b]	31.18	188.7	116.3	5.34	11.0	44.0	39.7	1.6	200.1	4.5	0.8	1.71	41.4
30	34.33	178.5	114.9	5.65	20.7	35.1	38.5	1.84	199.1	5.1	0.6	1.70	36.8
37	34.89	182.9	114.4	5.45	15.5	41.5	37.6	..	198.2	5.2	0.3	1.22	35.2
44	36.83	190.7	117.8	5.40	10.4	42.8	41.4	1.31	198.1	5.1	0.3	1.96	47.8
49	37.53	189.0	114.9	5.58	9.0	47.4	38.0	1.43	198.5	5.3	0.3	2.06	41.3

[a] Estimated; sample too small for determination. [b] Picked from prematurely ripe spot in field.

not generally the case. In the previous paper (*3*) it was mentioned that in the laboratory the enzymes worked best at moderate temperatures and with ample moisture. The hot, dry conditions at St. Paul are manifested by lack of further increase in unsaturation after 22 days and by a low degree of unsaturation of the oil from even the last seed samples.

The iodine numbers are very low for North American seed. As shown by Table I, the percentage of oleic acid is much higher than normal. The data on the St. Paul samples serve, therefore, as criteria for an abnormal year and explain many of the abnormalities which are at present being encountered with the 1929 crop of northwest oil. The Bethlehem samples, on the other hand, matured more slowly and the iodine number rose to 190.7, with a corresponding low content of saturated acids and oleic acid. Protective coating films made from 1929 crop North American oil are likely to be soft, unless steps are taken to compensate for the higher content of oleic acid in the oil glycerides.

Method

The seed samples taken at frequent intervals at the Farm School of the University of Minnesota, and at weekly intervals at Bethlehem, were treated as previously described (*3*). The following method was used to separate the constituents of the lipid material from the flaxseed samples and to get the data given in Table I, from which the percentages of the various constituent acids were calculated.

After the determination of the iodine and thiocyanate (*2*) numbers, the oil was saponified with 0.5 *N* alcoholic potassium hydroxide and the resulting solution titrated to determine the saponification number. The alcohol was then evaporated and the resulting soap solution extracted with ether in order to determine the percentage of unsaponifiable matter. Hydrochloric acid (12 *N*) was added to liberate the fatty acids, which were washed with water until the washings were neutral to methyl orange. The ether solution of the fatty acids was filtered through a dry filter to remove traces of water and the ether then evaporated. The saturated acids were next precipitated by the Twitchell (*4*) method on one portion of these. The hexabromide number was determined on another portion. The saturated acids obtained from the Twitchell method were dissolved in alcohol and titrated with 0.1 *N* potassium hydroxide with phenolphthalein as indicator and the neutralization value thus determined. From this number the percentage stearic and palmitic acids was obtained.

In many cases the original sample weighed only 2 or 3 grams.

As before stated, the percentage of stearic acid (designated S) was directly determined. The percentages of oleic acid (O), linoleic acid (L), and linolenic acid (Le) were calculated from the iodine number (I.N.) and thiocyanate number (T.N.) with the aid of the following relationships:

$$O + L + Le = 100 - S$$

$$O + 2L + 3Le = \frac{100\ I.N.}{86.65} = 1.154\ I.N.$$

$$O + L + 2Le = \frac{100\ T.N.}{86.65} = 1.154\ T.N.$$

Table II—Composition of Linseed Oil

Linseed Oil	Iodine No. Oil	Thiocyanate No. Oil	Satd. Acids	Oleic Acid	Linoleic Acid	Linolenic Acid	Unsaponifiable	Neutralization No. Satd. Acids	Stearic Acid	Palmitic Acid	Acid Value	Hexabromide No.
			Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*		*Per cent*	*Per cent*		
N. W. Raw												
1924	188.0	117.2	4.8	13.3	41.6	40.3	..	198.2	4.5	0.3	..	..
1927	184.1	113.5	5.4	13.2	45.0	36.4	..	197.5	5.4	0	..	..
1928	185.0	117.7	5.9	16.4	35.9	41.8	1.36	199.2	5.3	0.6	2.86	40.8
1929	180.5	112.8	7.6	14.2	40.4	37.8	1.83	198.7	7.2	0.4	1.89	37.2
1929	179.9	113.1	6.8	16.0	39.7	37.5	1.44	201.4	5.4	1.4	2.28	37.0
S. A. Alkali-refined	182.9	113.5	9.0	10.8	40.1	40.1	0.96	202.0	6.9	2.1	0.36	40.3
N. W. Alkali-refined	185.2	115.2	6.5	12.7	41.3	39.5	1.22	201.8	5.1	1.4	0.32	37.4
Calcutta raw	181.4	113.8	9.3	12.7	37.4	40.6	1.17	201.2	7.5	1.8	2.02	41.2
1929 S. A. raw	178.2	112.1	9.0	14.5	37.9	38.6	1.43	203.2	6.5	2.5	..	40.0

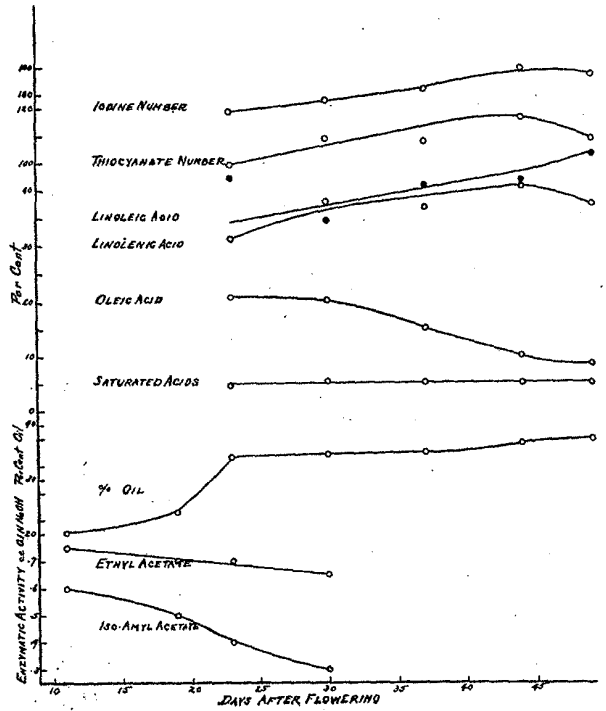

Figure 1—Progressive Changes in Enzymatic Activity of the Seeds, Oil Formation, and Constituents of the Oil Samples from Bethlehem, Pa. (1929)

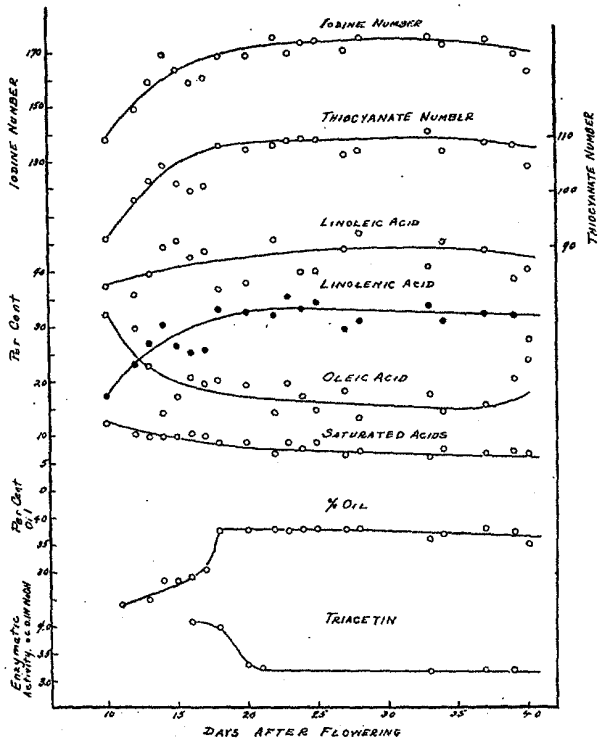

Figure 2—Progressive Changes in Enzymatic Activity of the Seeds, Oil Formation, and Constituents of the Oil Samples from St. Paul, Minn. (1929)

These relationships are based on data obtained by Kaufmann and Keller (*2*), that each molecule of oleic acid adds 1 molecule of $(SCN)_2$, 1 molecule of linoleic acid adds $1(SCN)_2$, and 1 molecule of linolenic acid adds $2(SCN)_2$. The figure 86.65 is the average of the three factors 86.06, 86.66, and 87.20, which, when multiplied across by 1, 2, and 3, respectively, give the iodine numbers of the individual glycerides which add up to the iodine number of the oil. Thiocyanate numbers are also expressed as milligrams of iodine per gram of oil. Kaufmann and Keller also show more exact and complicated forms of these equations, but point out that the errors involved in the methods are greater than those entailed in using the equations with the average factor 86.65.

The presence of lipase in the flaxseed and its progressive change during the growing season were confirmed for nineteen samples by determining the rate of hydrolysis of eight different esters.

Table III—Decrease in Enzymatic Activity during Maturation

Bethlehem Samples [a]			St. Paul Samples [a]		
Time after flowering	Isoamyl acetate	Ethyl acetate	Time after flowering	Tri-acetin	Methyl propionate
Days	*Cc.*	*Cc.*	*Days*	*Cc.*	*Cc.*
10	0.6	0.75	16	4.0	1.8
18	0.5	0.70	18	3.3	1.4
23	0.4	0.70	20	3.25	1.25
30	0.3	0.65	21	3.2	
			33	3.2	1.0
			37	3.2	1.0
			38	3.2	0.9
			39	3.2	0.9
			40	3.2	0.9

[a] 0.1 normal alkali used in both cases.

The change in enzymatic activity during maturation was determined by a study of the hydrolysis of eight esters. The technic followed was precisely that previously described (*3*). The esters used were triacetin, methyl propionate, methyl benzoate, butyl acetate, methyl acetate, ethyl acetate, isoamyl acetate, and isobutyl acetate. In all cases the enzymes in the seed caused hydrolysis of the esters and the enzymatic activity decreased as maturation of the seed progressed. Data for four typical esters are given in Table III. Three of these are plotted in Figures 1 and 2.

Discussion of Results

The enzymatic activity of the seeds decreases during maturation. This is in agreement with the writers' results on the 1928 crop. Further, as indicated by the curves, the enzymatic activity decreases as the percentage of oil increases.

There is marked decrease in enzymatic activity right after the big jump in oil formation 17 days after flowering. Apparently the enzymatic activity is spent in synthesis of fatty acids and glycerol into oil.

When the curves are inspected together, it is observed that as the degree of unsaturation increases the percentages of linoleic and linolenic increase and those of oleic and stearic decrease. This suggests that as the seeds mature desaturation proceeds through the stages stearic, oleic, linoleic, to linolenic. Similar desaturation occurs in animal life.

The percentage of saturated acids agrees with previous data in the literature. It is, however, likely that this is low. Bertram's method (*1*) yields a precipitate with a low iodine number and gives results 2 per cent higher for saturated acids. If this method had been employed, the percentage of oleic would have been decreased by 2 per cent. However, even on this basis the percentage of oleic acid in the St. Paul 1929 samples is higher than in previous years and higher than most of the data reported in the literature.

Acknowledgment

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Vapor Pressure and Heat of Vaporization[1]

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OWING doubtless to its industrial importance in plant design, a number of papers on the vapor pressure and latent heats of liquids have recently appeared in INDUSTRIAL AND ENGINEERING CHEMISTRY (*2*, *3*, *4*). Dühring's rule has found wide application in the calculation of vapor pressures beyond the observed range, and recently Schultz (*5*) has developed a relation of similar form between the molal entropies of two liquids, yielding heats of vaporization and critical temperatures. A great many other empirical relations have been suggested, ranging from Trouton's simple $ML = 21\ T_b$ to the complicated formula of Cederberg. Any new formula must be both simple and exact to be useful.

Thermodynamics leads no further than the exact relation (*1*):

$$\left(\frac{dE/dm}{dW/dm}\right)_T = \frac{d\ \log\ p}{d\ \log\ T} - 1 \qquad (1)$$

between internal thermal energy, E, mechanical work, W, and vapor pressure, p. E is here identified with the internal latent heat, W with external latent heat, and p with pressure of saturated vapor. While Equation 1 cannot be solved in general terms, it is well adapted to the calculation of E when p is known through a range of temperatures. Another advantage is that it is dimensionless and therefore independent of the units employed. dW/dm is known exactly, if concentrations of vapor and liquid are known, from the Clapeyron equation:

$$\frac{dW}{dm} = \frac{RT}{M}\left(\frac{C_v}{C_l} - 1\right)\frac{\text{calories}}{\text{gram}} \qquad (2)$$

A check of the combination of Equations 1 and 2 in the form

$$L = L_i + L_e = \frac{RT}{M}\frac{d\ \log\ p}{d\ \log\ T}\left(\frac{C_v}{C_l} - 1\right)\frac{\text{calories}}{\text{gram}} \qquad (3)$$

with numerical data shows that it does give results as certain as the data, as it should.

In setting up empirical relations between L, p, and T for practical work, the forms of Equations 1 and 3 indicate the paramount importance of a relation between p and T which shall make $d\ \log\ p/d\ \log\ T$ simple. Most such relations previously suggested are parabolic in form, exceedingly cumbersome to use, and afflicted with troublesome dimensions. The approximate energy line obtained by plotting $\log\ p$ against $1/T$ is nearly straight but not so convenient as the more curved line given by the plot of $\log\ p$ against $\log\ T$. This can be very accurately represented by the hyperbola

$$(\log\ T + a)(\log\ p + b) = C \qquad (4)$$

which is dimensionless throughout, since the constant a is the (negative) log of a temperature and b the log of a pressure so that $\log\ T + a = \log\ T/A$, etc. The derivative of Equation 4 is also dimensionless and very simple.

$$\frac{d\ \log\ p}{d\ \log\ T} = -\frac{\log\ p + b}{\log\ T + a} \qquad (5)$$

Values of the constants a, b, and c for water, carbon tetrachloride, and toluene are tabulated below. All three are negative in each case and all are referred to natural logarithms. The pressure units are indicated, as are also the temperatures used in determining the constants.

Constants of $(\log\ T + a)(\log\ p + b) = C$

	T	p	a	b	c
Water	0, 50, 100	mm.	−4.19916	−29.73019	−39.78249
Water	100, 200, 300	atm.	−4.43978	−19.76527	−29.28810
Carbon tetrachloride	100, 180, 260	mm.	−4.19173	−17.39190	−28.95958
Toluene	110, 214, 320	atm.	−4.54285	−15.77465	−22.19930

Pressures calculated from Equation 4 using these constants are in excellent agreement with those observed and will even stand for considerable extrapolation.

Relation between Heat of Vaporization and Temperature

The other new formula is a relation between heat of vaporization and temperature, namely:

$$L = A(T_c - T)^n \qquad (6)$$
$$\text{or } \log\ L = \log\ A + n\ \log\ (T_c - T)$$

latent heat proportional to a power of the temperature measured down from the critical temperature. There is a rational basis for this formula, since internal latent heat represents work done on a liquid by the cohesive force within it and $T_c - T$ represents an energy deficit from a temperature, T_c, at which the cohesive force is zero. The constant n is about $^1/_3$ for latent heats and $^2/_3$ for surface tensions as might be anticipated.

For carbon tetrachloride $L = 6.128\ (T_c - T)^{0.379}$ holds very well from 0° C. to the critical temperature 283.1. For water, $L = 8.2674\ (T_c - T)^{0.38357}$. For ethyl alcohol, $n = 0.36$; for CO_2, $n = 0.424$; for SO_2, $n = 0.64$. The linear relation indicated by Equation 6 is shown to hold very well in all the cases tried. Log surface tension plotted against $\log\ L$ is also a perfectly straight line for water, the only liquid for which a range of data are available. Critical temperatures may be calculated by Equation 6, but probably more easily by the Schultz formula relating differences in molal entropies.

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[1] Received April 16, 1930. Published by permission of the Director, U. S. Geological Survey.