

THE FERMENTATION OF RYE<sup>1</sup>

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## Introduction

Rye has long been known as an excellent raw product in alcoholic fermentations. The average starch content of rye is only a little below that of rice, and about the same as that of corn and wheat. The aroma and flavor of distilled alcoholic beverages made from rye are such that rye liquors are favorites with many people.

This investigation was undertaken in an effort to evaluate rye as a possible source of carbohydrates in the manufacture of industrial alcohol. The quality of rye whiskey is therefore of no concern, and only the cost of a gallon of alcohol made from rye starch—as compared to the cost of producing a gallon from other starches—is of importance in this paper.

In such an investigation there are many considerations to be taken into account, for the problem is not simply one of determining whether a pound of corn starch costs less than a pound of rye starch. For example, it is altogether possible that a pound of rye starch will produce, under optimum conditions, 10 per cent more alcohol than will a pound of corn starch. Again, perhaps the amount of malt needed to saccharify a given amount of rye starch is less than that required for the same amount of wheat starch, thus making the cost of producing alcohol from rye less by so much than when producing it from wheat. Other things to be considered in determining the relative efficiency of grains in the manufacture of alcohol are: the thickness of mash allowable, cooking requirements, time required for complete fermentation, possibility of self-saccharification and the ease with which the grain can be worked up.

One of the earliest attempts at working out these factors in a systematic manner is reported by Windisch and Jetter<sup>2</sup>. Their tabulated results are given below:

<sup>1</sup> From the Chemistry Laboratories of Iowa State College.

<sup>2</sup> Karl Windisch and Wilhelm Jetter. *Z. Spiritusind.*, 30, 552 (1907).

Kind of Mash (Rye)	Weight of Mash	Liters of alcohol per 100 kg. of meal
300 g. coarse meal, raw, without malt . . . . .	1857	31.0
300 g. fine meal, raw, without malt . . . . .	1800	32.1
300 g. coarse meal, raw, with 36 g. green malt 1898		33.0
300 g. coarse meal, raw, with 36 g. dry malt .1900		33.0
300 g. coarse meal, steam cooked, with 36 g. green malt . . . . .	2020	27.4
300 g. coarse meal, steam cooked, with 36 g. green malt . . . . .	1800	27.0
300 g. whole grains, 3 atm. steam, with 36 g. green malt . . . . .	1850	22.3
300 g. whole grains, 3 atm. steam, with 36 g. green malt . . . . .	1800	25.7

From these results, it appears that the use of malt does not give significantly higher yields of alcohol (when using uncooked grain); that cooking causes lower yields; and that coarsely ground meal is as good as finely ground meal.

The highest yield reported by Windisch and Jetter above (33.0 liters per kilogram of meal) is lower than the average yield of 20 samples of rye fermented by Staiger<sup>3</sup>, and reported as 34.4 cc. per 100 g. of rye. Staiger's average yield from 12 samples of wheat was 34.0 cc. of alcohol per 100 gm. of wheat. Staiger<sup>4</sup> also found that the optimum temperature for self-saccharification of rye is 55° C. and that the addition of 10 per cent malt to rye mashes increased the alcohol yield usually less than one per cent over the unmalted mash.

Pronin<sup>5</sup> concluded that there is a zone between 55° C. and 64° C. that is a definite optimum for self-saccharification of rye, the actual peak being at 61° C. He attributes the sharp rise at 55° C. to the fact that at this temperature the starch begins to gelatinize.

The above reports are very inadequate for the purposes of this investigation, so that a systematic study of the effect of varying the several factors involved was imperative. Before considering the experimental results of this study, however, it will be well to review the relative properties and

<sup>3</sup> G. Staiger. *Brennerei-Ztg.* 46, 88 (1929).

<sup>4</sup> G. Staiger. *Brennerei-Ztg.* 46, 8 (1929).

<sup>5</sup> S. Pronin, *Biochem. Z.* 240, 94 (1931).

costs of the various grains in the tables given below (approximate values):

Table I  
Average Composition of Various Grains<sup>6</sup>

Grain	H <sub>2</sub> O	Protein	Fat	Carbohydrates
Barley	11.0	12.0	2.5	62.0
Rye	10.6	12.4	1.6	71.3
Corn	10.8	10.0	4.2	71.9
Oats	10.0	12.1	4.4	58.0
Wheat	10.6	12.7	1.7	71.2
Rice	12.2	8.0	0.7	77.0

Table II  
Average Pounds of Starch per Bushel of Grain  
(Calculated on basis of Table I)

Grain	Ave. Weight of 1 Bushel (Lbs.)	Lbs. Starch per Bushel
Barley	48	29.8
Rye	57	40.7
Corn	58	41.7
Oats	40	23.2
Wheat	60	42.7
Rice (polished)	(estimate) 65	50.0

Table III  
Cost of Various Grains on Starch Basis (Approximate)

Grain	Wholesale Price per Bu.*	Lbs. Starch per Bu.	Cost per 100 lbs. starch
Barley	\$0.40	29.8	\$1.34
Rye	0.52	40.7	1.28
Corn	0.41	41.7	0.99
Oats	0.23	23.2	1.00
Wheat	0.80	42.7	1.88
Rice	2.60**	50.0	5.20

\* Prices quoted in Mitchell, S. Dak., on March 23, 1938 and variable.

\*\* Wholesale price not available. Estimated retail price.

From the above tables it appears that rye is one of the least expensive of our carbohydrate materials.

<sup>6</sup> Wahl-Henius Handbook of Brewing and Malting, Vol. II, 3rd edition, Wahl-Henius Institute, Chicago, Illinois.

The diastatic power of malt made from various grains is estimated by Brachvogel<sup>7</sup> as follows:

Table IV

Source of Malt	Diastatic Power
Wheat	108
Barley	100
Rye	93
Oats	30
Corn	28

Table IV indicates that rye malt has very nearly the diastatic power of barley malt and is much superior to oats and corn.

The temperature required to gelatinize various starches is given in Table V below:

Table V

Starch	Temp. according to Lippmann <sup>8</sup>	Temp. according to Lintner <sup>8</sup>	Average
Potato	63°C.	65.5°C.	64
Corn	63	75.5	69
Rye	56	81	63
Wheat	68	81	75
Rice	62	81	72
Barley	63	81	73
Oats	---	85.5	80 (?)
Buckwheat	72	-----	80 (?)

### Experimental

#### Effect of Varying the Mash Concentration

Twelve hundred gm. of rye was mixed thoroughly with 12 gm. of malt. The indicated amount (Table VI) was weighed into each of 14 500-cc. Erlenmeyer flasks. Then 300 cc. of tap water, pre-heated to 65° C. was added to each flask, stirred thoroughly, and allowed to stand for one-half hour. All flasks were then steamed at one atmosphere for one hour, allowed to cool to 65° C., and then had added to

<sup>7</sup> J. K. Brachvogel. *Industrial Alcohol*. 1907. Munn and Company, New York.

<sup>8</sup> W. T. Brannt. *Distillation and Rectification of Alcohol*. 1904. Henry Carey Baird and Co., Philadelphia.

each 5 per cent of malt (i.e. 5 per cent by weight of the total rye). The flasks were then plugged and after cooling to 30° C. were each inoculated with 10 cc. of a 24 hour culture of yeast No. 16. Analysis was made after 4 days incubation at 30° C.

Table VI  
Effect of Varying the Mash Concentration

Flask	Gms. Rye	Final Volume	Gms. Alcohol per 100 gms. Rye*
1	30	315	22.7
2	30	320	
3	45	330	22.2
4	45	330	
5	60	335	25.0
6	60	335	
7	75	342	25.2
8	75	344	
9	90	352	22.4
10	90	352	
11	105	360	22.8
12	105	360	
13	120	365	21.5
14	120	365	

\* Corrected for malt added to the mash.

It is evident that the optimum mash concentration for rye is between 60 and 75 gm. rye per 300 cc. of water. Since the 60 gm. mash handled easier than the 75, this concentration was used in all succeeding experiments.

#### Sour Mash—Effect of Lactic Acid Concentration

Twelve hundred gm. of rye was weighed up and mixed thoroughly with 12 gm. of malt. 60.6 gm. of this mixture was put into each of 19 500-cc. Erlenmeyer flasks. Then 300 cc. of water, preheated to 65° C., was added to each flask, stirred, and the mixtures allowed to stand for one-half hour. The flasks were steamed for one hour. After cooling to 55° C., another 5 per cent of malt was added to each flask and the mixtures stirred thoroughly. When the temperature dropped to 30° C., the indicated amount (Table VII) of lactic acid was added to each flask along with 10 cc.

of a 24 hour culture of yeast No. 16. After incubating at 30° C. for 4 days, analysis was made of the mashes.

Table VII  
Sour Mash—Effect of Varying Lactic Acid Concentration

Flask	cc. of 85% Lactic Acid added	"Degree of Acidity" Lowering	Final Volume cc.	Gms. Alcohol per 100 gms. Rye*
1	0	0	344	25.4
2	0	0	344	
3	0.371	0.25	347	27.2
4	0.371	0.25	346	
5	0.742	0.5	350	27.0
6	0.742	0.5	350	
7	1.113	0.75	355	27.0
8	1.113	0.75	355	
9	1.485	1.0	360	26.0
10	1.485	1.0	360	
11	2.227	1.5	365	20.8
12	2.227	1.5	365	
13	2.970	2.0	375	18.7
14	2.970	2.0	375	
15	3.712	2.5	380	17.0
16	3.712	2.5	380	
17	4.455	3.0	385	16.4
18	4.455	3.0	385	
19	5.940	4.0	405	16.9

\* Corrected for malt added to the mash.

A small amount of lactic acid, i.e. about 0.556 cc. of 85 per cent acid or enough to lower the degrees of acidity by three-eighths degrees, gives maximum yields of alcohol. The increase over sweet mash is about 2 gms. alcohol per 100 gms. of rye. Sour mashes also have the advantage that they are less liable to contamination. Figuring on a basis of lactic acid costing \$3.00 a kilogram and alcohol being worth 30 cents per gallon, it would not be economically feasible to use sour mashes since it would cost about 3.1 cents per kilogram of rye to sour the mash and the return in increased yield of alcohol would amount to only about 0.2 cents. Sour mashes would not pay except to help avoid contamination or if the lactic acid were produced by a preliminary lactic fermentation.

Since, however, the small added expense of using sour mashes is not significant as far as experimental work is concerned, lactic acid was added to all succeeding experiments except where so stated.

#### Effect of Varying Malt Concentration

Twelve hundred gms. of rye was thoroughly mixed with 12 gms. of malt and 60.6 gms. of this mixture was weighed into each of 19 500-cc. Erlenmeyer flasks. Then 300 cc. of tap water, pre-heated to 65° C., was added to each flask, the contents stirred thoroughly, and allowed to stand for one-half hour. The mash was steamed for one hour, allowed to cool to 65° C. and then mixed with the indicated amount (Table VIII) of malt. After attaining a temperature of 30° C., 0.56 cc. of 85 per cent lactic acid and 10 cc. of inoculum No. 16 was added to each flask. Fermentation proceeded for 4 days and then was stopped for analysis. The results are given in Table VIII.

Table VIII  
Effect of Varying Malt Concentration

Flask	Total % Malt	Final Volume	Gms. Alcohol per 100 gms. Rye*
1	2	345	22.6
2	2	345	
3	4	345	26.1
4	4	345	
5	6	345	26.6
6	6	345	
7	8	347	27.2
8	8	347	
9	10	347	27.5
10	10	347	
11	12	347	28.1
12	12	347	
13	14	348	28.6
14	14	348	
15	16	348	29.1
16	16	348	
17	18	350	29.5
18	18	350	
19	22	353	30.5

\* Corrected for malt added.

As could be expected, there is no optimum concentration of malt, the yield of alcohol, after a concentration of 4 per cent is reached, being practically a linear function of the per cent malt. The correct amount of malt to use would depend on the relative cost of malt and of rye and the price of alcohol. In succeeding experiments, it was arbitrarily decided to use a malt concentration equivalent to 6 per cent of the rye used.

#### Effect of Self-saccharification and of Time and Temperature of Cooking Rye Mash

Twelve hundred gms. of rye and 12 gms. of malt were mixed thoroughly and 60.6 gms. of this mixture was added to each of 13 500-cc. Erlenmeyer flasks. Sixty gms. of rye, without malt, was added to two other flasks. Then each flask had added to it 300 cc. of tap water, preheated to 65°C. After standing for one-half hour, each flask of mash was heated at the temperature and for the time indicated (Table IX). Then each flask of mash was brought to 65° C. and the indicated amount of malt was mixed with each. After reaching 30° C., each flask had added to it 0.56 cc. of 85 per cent lactic acid and 10 cc. of culture No. 16. Analysis was run on all flasks after incubating 4 days at 30° C.

Table IX  
Effect of Self-saccharification and of Time and Temperature of Cooking Rye Mash

Flask	% Malt	Temperature	Time (Hrs.)	Gms. Alcohol per 100 gms. Rye
1	6	65	¾	17.6
2	6	65	¾	
3	6	65	1¼	21.1
4	6	65	1¼	
5	6	100	¾	25.4
6	6	100	¾	
7	6	100	1¼	26.0
8	6	100	1¼	
9	6	135	¾	28.0*
10	6	135	¾	
11	6	135	¾	28.0*
12	6	135	¾	
13	6	135	¾	
14	0	65	3½	18.0
15	0	65	3½	

\* Approximate values due to some of the mash boiling over during autoclaving and loss estimated.

Table IX indicates that maximum yields of alcohol cannot be obtained from rye unless the mash is cooked and also that cooking for  $1\frac{1}{4}$  hours is better than cooking for three-fourths of an hour. Moreover, it was found that cooked rye had much less tendency to foam both during fermentation and during distillation than did un-cooked mashes. Table IX also indicates that rye contains enough diastase to give practically complete self-saccharification.

#### Effect of Varying Yeast Cultures and Time of Fermentation

Twelve hundred and sixty gms. of rye were mixed with 12.6 gms. of malt and 60.6 gms. of this mixture was weighed into each of 20 500-cc. Erlenmeyer flasks. Three hundred cc. of tap water, pre-heated to 65° C., was stirred into each flask and the mash allowed to stand for one-half hour. After steaming for 1 hour, the mash was brought to a temperature of 65° C. and mixed with another 5 per cent of malt. Then, after cooling to 30° C., to each flask was added 0.56 cc. of 85 per cent lactic acid and 10 cc. of inoculum of the indicated cultures (Table X). Incubation was carried at a temperature of 30° C. and analysis run at the time intervals indicated.

Table X

Flask	Culture	Time of Fermentation	Gms. Alcohol per 100 gm. Rye*
1	35	24 hours	11.3
2	35	48	24.5
3	35	72	25.8
4	35	95	25.1
5	35a**	24	12.9
6	35a	48	24.5
7	35a	72	26.1
8	35a	95	25.3
9	16	24	20.5
10	16	48	25.3
11	16	72	26.5
12	16	95	26.6
13	16a***	24	20.5
14	16a	48	25.4
15	16a	72	26.4
16	16a	95	26.6
17	2	24	22.6
18	2	48	26.3
19	2	72	26.5
20	2	95	26.8

\* Corrected for malt.

\*\* Culture No. 35 carried through 11 transfers of corn mash.

\*\*\* Culture No. 16 carried through 15 transfers of corn mash.

It is evident from Table X that culture No. 2 is practically finished fermenting in 48 hours while cultures No. 35, 35a, 16 and 16a are finished in 72 hours. There is no appreciable difference between No. 35 and 35a, or between No. 16 and 16a. At the end of 72 hours, there is no significant difference in the amount of alcohol produced by cultures No. 16, 16a and 2. Cultures No. 35 and 35a are slightly inferior to the others. It was noticed that foaming during distillation became less with increased time of fermentation.

#### Analysis of the Rye and Spent Mash

The methods of analysis used were the standard methods described in A.O.A.C. and in Mahin and Carr. Sample A is the original ground rye used in these experiments. Sample B is the evaporated and dried spent mash from a fermentation carried through under optimum conditions. Sample C is the evaporated and dried filtrate from a spent mash.

Table XI

Sample	A	B	C
Moisture	8.24	-----	-----
Sugar	.80	2.60	7.40
Starch	56.30	21.60	-----
Protein	16.00	35.25	29.25
Crude fiber	1.60	7.10	-----
Oil	1.75	6.64	0.21
Ash	1.78	3.95	8.48
N-free extract	13.53	22.86	54.66

#### Summary

This investigation has shown how to control the various factors to obtain the maximum yield of alcohol from rye. The best conditions may be summarized as follows:

- (1) A mash concentration of 60 to 75 gms. of rye to 300 cc. of water.
- (2) A slightly acid mash, equivalent to 0.56 gms. of 85 per cent lactic acid per 60 gm. rye meal.
- (3) The use of 4 per cent or more of malt; the alcohol yield being a linear function of the amount of malt, up to at least 22 per cent malt.

- (4) Rye should be cooked, either with or without pressure.
- (5) Rye should be cooked for one hour or longer.
- (6) Culture No. 2 should be used, but is only slightly better than No. 16.

Several other points have been brought out during the course of this investigation and may be summarized as below:

- (1) Rye, amongst grains, is one of our cheaper sources of starch.
- (2) Rye ranks close to wheat and barley in the diastatic power of its malt.
- (3) Rye will self-saccharify satisfactorily.
- (4) Rye starch is one of the easiest to gelatinize.
- (5) Yields of 27.0 gms. of alcohol per 100 gms. of rye, with low malt concentration (6 per cent), have been obtained. This is equivalent to 47.3 gms. alcohol per 100 gms. of starch and sugar present in the rye.
- (6) Yields of 30.5 gms. of alcohol per 100 gms. of rye have been obtained with high malt concentration (22 per cent). This is equivalent to 53.4 gms. of alcohol per 100 gms. of starch and sugar present in the rye. (The theoretical yield is 56.75 gms. of alcohol per 100 gms. of starch).
- (7) Rye mash, with a good yeast, can be completely fermented in 48 hours.

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