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UNIVERSITY OF LOUISVILLE

The Effect of Varying the Malt Concentration
and
The pH on the Conversion of Starch in Corn

A Thesis

Submitted to the Faculty of
The Graduate School in Partial
Fulfillment of the Requirements
For the Degree of
Master of Chemical Engineering

Department of Chemical Engineering

By

Gerald L. Veeneman

July 1938

The Effect of Varying the Malt Concentration
and
The pH on the Conversion of Starch in Corn

Director: Dr. R. C. Ernst.

Approved by Reading Committee.

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Chairman

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INTRODUCTION

This work was an investigation of the conversion of the starch in corn into sugar using varying conditions of pH and different percentages of malt.

This process, commonly called mashing, consists of first cooking the corn in the form of meal, then lowering the temperature and adding malt. Enzymes in the malt act on the starch in the corn converting it to soluble sugars. The greater the yield of the sugars, the greater will be the possible yield of alcohol produced later by fermentation.

In this investigation only the pH of the water used in mashing was determined. Brown (1) in a similar investigation, determined the pH at various stages in the mashing operation and reported that the pH did not vary appreciably throughout the run.

The fermentation industry has found that greater yields of fermentable sugars are obtained when the temperature of the mash during malting is approximately 63°C . For this reason all the malting periods were carried on at approximately this temperature.

It is believed that the amount of sugars formed is dependent on the concentration of malt. It is known that all the enzymes show optimum activity at certain pH values. The object of this investigation was to determine whether the optimum percentage of malt changed with different values of pH. The range in malt concentration was from two to ten per cent of the total grain in the mash. The pH of the water used in mashing was varied from three to nine.

THEORY

The conversion of the starch present in corn and other grains into sugar is one step in the manufacture of whiskey. This conversion is called hydrolysis. That is, the starch molecules are split into more soluble materials by the addition of water. Conversion of starch can be accomplished either by the action of specific enzymes or by acid hydrolysis. Enzymic action is used almost entirely in the fermentation industry.

Prior to actual conversion, corn is given a preliminary treatment in order that conversion may take place easily. This treatment includes cleaning, grinding, and cooking. Cleaning consists of merely screening the corn to remove impurities such as seeds and husks. Grinding the corn breaks the hard shell and makes available the starch in the interior of the grain. Too coarse grinding produces large particles that, in the cooking operation, will not be wet thoroughly. Fine grinding causes the formation of lumps that remain undispersed and thus may not be easily wetted.

Cooking the grain causes the starch granules to swell, and makes the starch available to the subsequent enzymic action of the malt. Starch gelatinizes when heated in the presence of water and Alsberg (2) has reported three factors responsible for gelatinization:

1. The ease with which the anatomical structure is softened by moist heat.
2. The inherent swelling power of the granule.
3. The relation of the mass of swelling substance to the surface area of the granule.

He further stated that a large granule will swell more rapidly than a small granule because of the greater mass of swelling substance exerting pressure per unit area of the granule surface. However, the effect of too large a granule has already been shown. A range in the gelatinization temperature from 64° to 71°C , was reported by Dox & Roark (3) in a study of thirteen different varieties of maize. Alsberg (2) stated there is no such physical constant as a gelatinization temperature, but instead only a gelatinization range.

Several investigators have made studies of starch and of the products obtained by cooking starch. It is claimed by Maquenne and Roux (4) that starch is a mixture of two substances, amylose and amylopectin, the former in the interior portion of the granule, the latter in the envelope. No mention was made of α or β amylose. It is possible that amylopectin is α amylose. Schryver and Thomas (5) have found that certain starches contain small amounts of hemicelluloses, and Ling and Nanji (6) state the ratio of amylose to amylopectin is constant and is equal to 2:1, although their absolute percentage varies according to the proportion of hemicellulose in the starch.

When starch is gelatinized by heat in the presence of water, two products are formed (1) α amylose, which is insoluble in water and (2) β amylose, which is water soluble (7). Taylor and Iddles (8) reported that corn starch contains from 84.4 to 88.5 per cent of β amylose and from 15.6 to 11.5% of α amylose. Other workers expressed the belief that starch granules are more or less uniform throughout and

that the distinction that has been made between α and β amyloses is caused by the outer layers of the granules being more or less resistant to chemical action, on the hypothesis that the outer layers are somewhat dehydrated.

The conversion of starch into sugar by the action of malt is represented by the following scheme:

C. O'Sullivan (9) showed that the products of diastatic action are maltose and dextrin and that the proportion of maltose in the product decreases as the temperature of conversion is raised above 63°C . This is the temperature at which malting is carried on in industry.

Daish (10) stated that prolonged treatment with mineral acid converts starch into dextrin, maltose, and d-glucose or dextrose. As previously stated the enzyme diastase or amylase converts starch into maltose and dextrin. Takadiastase, however, which contains the enzyme maltase yields d-glucose as the final product. (11)

The amounts of maltose and dextrin formed by the action of malt extract on starch paste were found by Brown, Heron, and Morris (12) to be 80.9 parts of maltose and 19.1 parts of dextrin.

According to the scheme shown, it is seen that some dextrin always remain in the product. Dextrin is a collective term for a number of intermediate products formed by the partial

hydrolysis of starch. Part of the dextrin formed during hydrolysis is converted to maltose by the enzyme diastase according to the equation:

Maltose is hydrolyzed by maltase, another enzyme present in malt, to two molecules of dextrose, as shown in the equation:

The importance of enzymes to the process of hydrolysis has been shown. In order to obtain the best results, enzymes must not only be present but their activity should also be at an optimum.

Three factors governing enzyme activity are time, temperature, and hydrogen ion concentration. Every enzyme reaction is a balanced reaction between enzyme action and enzyme destruction. (7). No relationship is known between the rate of increase of enzyme activity and enzyme destruction; therefore any optimum condition should be stated for a definite time of treatment.

That temperature is an important factor is well illustrated in the studies of Rumsey (14) of the effect of temperature on maltose production from wheat flour. His results show the optimum temperature approximates 60° C.

with the time of treatment lasting one hour.

The effect of hydrogen ion concentration has been demonstrated by numerous investigators. Walschmidt-Leitz, E (15) reports that the optimum pH for malt amylase or diastase lies between 4.6 and 5.2 and the optimum pH for maltase, between 6.1 and 6.8. The time of treatment was not stated.

Enzymes are defined by Walschmidt-Leitz, E (15) to be "definite material catalyzers of organic nature with specific powers of reaction, formed by living cells, but independent of the presence of the latter in their operation."

Since enzymes are present in malt, it is seen that the malt has a catalytic effect in the conversion of starch to sugar.

Ordinarily catalysts are employed to increase the rate of a chemical reaction. If this be true, it follows that the time required to produce a definite equilibrium is dependent on the amount of catalyst present. However, the final equilibrium appears to be independent of the amount of catalyst (7). Now, if the time were held constant, the rate of acceleration of a chemical reaction should be dependent on the amount of catalyst present, within certain limits. Therefore, since malt contains enzymes and enzymes are catalytic, the amount of sugar formed from starch, should, within certain limits, be dependent on the concentration of the malt.

PROCEDURE

The experimental work of this investigation was performed in laboratory size equipment. A water bath capable of holding five liter beakers was constructed and used for the malting.

The pH of the water used in these experiments was determined potentiometrically using saturated calomel as a reference and quinhydrone as an indicator electrode.

Corn and malt were the grains used in these experiments. The malt had been previously ground when received. The corn, however, was ground in a laboratory hammer mill.

The weight of the materials in all experiments totaled 875 grams. Of this, 175 grams were grain, and 700 grams were water. The percentage of malt in the experiments was varied from two to ten percent of the total grain in the charge. The pH of the water used was varied from 3 to 9.

The procedure was as follows. Approximately four liters of freshly boiled, distilled water were prepared, and sufficient acid or base was added to obtain the desired pH. This was checked by means of the quinhydrone electrode. Seven hundred milliliters of the water were then poured into a liter beaker and placed on a water bath and heated. At a temperature of about 65°C the corn was added, while it was being stirred constantly. The water in the bath was brought to boiling and held there for fifteen minutes. The mash was then cooled to 65°C and placed in another water bath. The malt was added and the temperature was maintained at 62°-64° C. for thirty minutes. At the end of that time

the temperature of the mash was raised and the mash was made alkaline to stop the action of the malt. The mash was cooled to room temperature and diluted to one thousand milliliters with distilled water. After dilution the mash was shaken well and a sample was taken for filtration. The filtrate was analyzed for dextrose by diluting 25 cc to 250 cc and titrated against 25 cc of a standard Benedict's solution. Dextrin analysis was made by diluting 25 cc of the filtrate to 100 cc and adding 2.5 cc of hydrochloric acid (specific gravity 1.125) and boiling for thirty minutes, keeping the volume constant by adding water from time to time. After boiling the solution, it was cooled and diluted to 500 cc and the solution titrated against 25 cc of a standard Benedict's solution. This indicated the total carbohydrates present. Dextrin was determined by subtracting the amount of dextrose obtained.

Benedict's solution is prepared from the following:

18 gms $\text{Cu SO}_4 \cdot 5\text{H}_2\text{O}$	(1)
200 gms Sodium Citrate	(2)
125 gms KSCN	(3)
100 gms Sodium carbonate (dehydrated)	(4)
0.025 gms $\text{K}_4\text{Fe (CN)}_6$	(5)

Items (2), (3), and (4) are dissolved in warm water. The copper sulfate is dissolved in 100 cc water and this solution is added slowly to the first while it is being stirred. Item (5) is then added, and the entire solution is cooled and diluted to 1000 ml. To standardize this

solution a standard dextrose solution was titrated against 25 cc of the Benedict's solution.

In making the titrations, the procedure was as follows. Twenty-five cc of Benedict's solution were pipetted into an evaporating dish and about 5 gms of sodium carbonate was added. The solution was brought to boiling and the sugar solution added while it was being stirred. The sugar solution was added in two cc portions, until within about two cc of the end point, when the following portions decreased successively until the end point was reached as determined by the last trace of blue in the solution.

The corn and malt were analyzed for total carbohydrates by acid hydrolysis according to the following method. One hundred cc of distilled water and 20 cc HCl (sp. g 1.125) were added to a 1000 gm sample of ground grain and refluxed for two hours. This was then cooled, filtered, and washed with distilled water. The filtrate was made up to 250 cc and titrated against 25 cc of Benedict's solution.

DATA AND RESULTS

The analyses of the corn and malt showed them to contain 61.0% and 50.5% total carbohydrates respectively. Since the percentage of malt was varied, the percentage of corn and the total carbohydrates in the samples varied likewise. Table 1 shows the amount of the corn and malt used, and the total carbohydrates present in the various samples.

TABLE 1
Composition of Mashies

Percentage of Malt	Grams of Malt	Grams of Corn	Grams of Carbohydrates
10	17.5	157.5	105.1
8	14.0	161.0	105.4
6	10.5	164.5	105.8
4	7.0	168.0	106.2
2	3.5	171.5	106.6

The yields of dextrose and dextrin obtained in the various mashies are shown in Tables 2 and 3 respectively.

Variations in the yields, obtained by using different percentages of malt are shown in the curves of constant pH values, Figures I-VI.

Curves of constant malt concentration where the yield is plotted against values of pH, are shown in Figures VII-XI.

On Figures I-VII, the ordinate should contain the word "original", in place of "total."

TABLE 2

Yields of Dextrose in Various Mashers

		pH					
Malt		3	4	5	6	8	9
10%	A	13.2	14.3	14.3	14.4	14.8	16.0
	B	0.365	0.336	0.336	0.336	0.334	0.309
8%	A	14.4	14.3	14.4	14.7	14.7	16.3
	B	0.335	0.335	0.335	0.326	0.335	0.302
6%	A	14.2	14.8	15.0	15.2	16.1	17.0
	B	0.339	0.325	0.320	0.316	0.306	0.290
4%	A	15.6	16.7	16.4	16.3	17.4	18.0
	B	0.306	0.285	0.292	0.293	0.281	0.272
2%	A	17.7	17.9	18.5	18.4	17.8	19.5
	B	0.269	0.265	0.256	0.259	0.274	0.250

C 0.0507 0.0507 0.0507 0.0507 0.0520 0.0520

A = cc of solution $\cong$ 25cc Benedict's solution

B = gms dextrose per gm of original carbohydrates

C = gms dextrose $\cong$ 25 cc Benedict's solution

TABLE 3
Yields of Dextrin in Various Mashcs

Malt		pH					
		3	4	5	6	8	9
10%	A	18.5	18.7	17.9	19.0	19.1	20.6
	B	0.155	0.180	0.204	0.172	0.184	0.171
	C	0.520	0.516	0.540	0.508	0.518	0.480
8%	A	20.1	17.9	17.8	19.5	19.5	21.3
	B	0.144	0.202	0.205	0.168	0.171	0.161
	C	0.479	0.537	0.540	0.494	0.506	0.463
6%	A	19.5	18.5	18.7	19.6	20.9	21.6
	B	0.146	0.194	0.194	0.174	0.164	0.166
	C	0.485	0.519	0.514	0.494	0.470	0.456
4%	A	21.7	22.2	19.8	20.4	22.8	
	B	0.156	0.145	0.189	0.175	0.148	
	C	0.460	0.430	0.481	0.468	0.429	
2%	A	24.8	21.3	21.5	22.8	22.5	23.5
	B	0.115	0.160	0.187	0.159	0.159	0.165
	C	0.384	0.425	0.443	0.418	0.433	0.415
	D	0.0507	0.0507	0.0507	0.0507	0.0520	0.0520

A = cc solution $\cong$ 25 cc Benedict's solution

B = gms dextrin per gm original carbohydrates

C = total soluble Carbohydrates

D = gms dextrose $\cong$ 25cc Benedict's solution

FIG I YIELD OF DEXTROSE AND DEXTRIN AT pH = 9

FIG. II YIELD OF DEXTROSE AND DEXTRIN AT pH = 8

FIG III YIELD OF DEXTROSE AND DEXTRIN AT pH=6

FIG. IV YIELD OF DEXTROSE AND DEXTRIN AT $pH=5$

FIG. V YIELD OF DEXTROSE AND DEXTRIN AT pH=4

FIG. VI YIELD OF DEXTROSE AND DEXTRIN AT pH=3

FIG VII YIELD OF DEXTROSE AND DEXTRIN - MALT CONCENTRATION = 10 PERCENT

FIG TX YIELD OF DEXTROSE AND DEXTRIN - MALT CONCENTRATION = 6 PERCENT

FIG. I YIELD OF DEXTROSE AND DEXTRIN — MALT CONCENTRATION = 4 PERCENT

GRAMS PER GRAM OF ORIGINAL CARBOHYDRATES

0.35
0.30
0.25
0.20
0.15
0.10

DEXTROSE

DEXTRIN

pH

FIG. XI YIELD OF DEXTROSE AND DEXTRIN - MALT CONCENTRATION = 2 PERCENT

SAMPLE CALCULATIONS

Total carbohydrates, as starch in grain sample

$$\frac{\text{str. of Benedict's soln.}}{\text{cc of solution}} \times \frac{250}{\text{wt of sample}} \times 0.9 \times 100 = \% \text{ starch}$$

where 0.9 is the conversion factor from dextrose to starch.

$$\frac{0.0482}{17.8} \times \frac{250}{1.0002} \times 0.9 \times 100 = 61\% \text{ starch in corn}$$

Total carbohydrates in charge.

wt of corn $\times$ % starch + wt of malt $\times$ % starch = total starch

$$157.5 \times 61\% + 17.5 \times 50.5\% = 96.2 + 8.9 = 105.1 \text{ gms}$$

Grams dextrose per gram of original carbohydrates

$$\frac{\text{str. of Benedict's soln.}}{\text{cc of solution}} \times \frac{\text{dilution ratio} \times \text{final volume}}{\text{total original carbohydrates}} = \frac{\text{gms dextrose}}{\text{gm original carbohydrates}}$$

$$\frac{.0507}{14.4} \times \frac{250}{25} \times \frac{1000}{105.4} = 0.334 \frac{\text{gms dextrose}}{\text{gm of original carbohydrates}}$$

(pH 3 - 8% malt)

The same formula is used to calculate total soluble carbohydrates

$$\frac{.0507}{20.15} \times \frac{500}{25} \times \frac{1000}{105.4} = 0.478 \frac{\text{gms sol. carb.}}{\text{gms original carb.}}$$

Grams dextrin per gram original carbohydrates

$$\frac{\text{gms soluble carbohydrates}}{\text{gm of original carbohydrates}} - \frac{\text{gms dextrose}}{\text{gm of orig. carbohydrates}} = \frac{\text{gms dextrin}}{\text{gm original carbohydrates}}$$

$$0.479 - 0.335 = 0.143 \frac{\text{gms dextrin}}{\text{gm original carbohydrates}}$$

Referring to Figures I - VI, it is seen that by increasing the malt concentration from 2 to 8% a gradual increase occurs in the amount of dextrose formed at all values of pH between 3 and 9. Little effect was noticed on the amount of dextrin formed, as it remained virtually constant over the entire range of malt concentration. The ratio of dextrin to dextrose, would therefore decrease as the percentage malt was increased, the decrease being due to change in amount of dextrose formed and not to any change in dextrin. On the same basis, the total carbohydrates formed during mashing, would show an increase with increase in malt concentration.

The yield of dextrose, as shown in Figures VII-XI, remained virtually constant over the range of pH from 3 to 8, but showed a decrease at a pH of 9. The dextrin curves on Figures VII to XI exhibit a maximum at a pH of 5 over the entire range of malt concentration.

CONCLUSIONS

On the basis of the foregoing results, it is concluded that the optimum percentage malt does not vary as the pH is varied. Although the actual yields at various pH values were different, the plot of yield against percentage malt showed that for any pH within the range investigated, the maximum conversion was obtained when the malt amounted to eight to ten percent of the total grain charge. Below eight percent, conversion decreased. The economic optimum percentage of malt would therefore be at a malt concentration of eight percent when the time of treatment is thirty minutes.

The increase in the yield of dextrin obtained at a pH of 5 over the entire range of malt concentration indicated that the enzyme diastase exhibited maximum activity at that point. This is in agreement with Walschmidt-Leitz, E (15) who stated that the optimum pH for the activity of diastase lies between values of 4.6 and 5.2.

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