

PROPERTIES OF SPENT BREWERS GRAINS

by

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B.S. University of Illinois, 1973

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

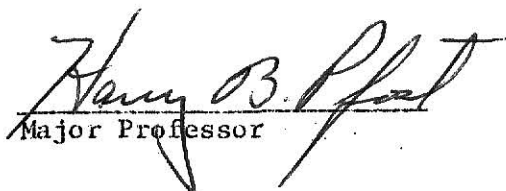
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1977

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1. Introduction

When beer is made essentially four classes of ingredients are needed: flavor ingredients, starch containing ingredients, yeast, and a source of enzyme. Amylase enzyme converts complex carbohydrate starches to simple carbohydrate sugars. Yeasts can only ferment sugars. Flavor ingredients include hops and other ingredients. Starch is usually provided by a grain such as barley, corn or rice. Sprouted barley (malt) may be used to supply the amylase, for when a seed sprouts, amylase is produced to degrade the starchy endosperm into simple sugars. The yeast used is specific to the brewery and pure cultures are maintained to assure quality and constancy.

Other sources of amylase have been used. The American Indian chewed his corn and spat it into a vat, his saliva providing the necessary amylase. To make Saki, a rice wine, mold is used to provide the amylase necessary to degrade the starch in rice. In this country a barley malt is used to provide the amylase. The mixture of malt, grain, hops and other ingredients is steeped in water. The liquid is then strained off, fermented and processed to beer. The resultant solid material-spent brewers grains, is used wet or dry as an animal feed.

The most common form of spent brewers grains is dry. This is due to the problems of storing any wet organic material. Typically, the initial wet spent brewers grains are at about 90% moisture content, wet basis. Mechanical presses reduce the moisture content to about 50%, wet basis, and the resultant grains are then dried in warm air to about 11% moisture content, wet basis. The drying process is done with rotary drum dryers. A few manufacturers then pellet the resultant dried grains.

When dried spent brewers grains are stored in bulk, fires have occurred. C. P. Beistle (1) in 1930 indicated that between 1910 and 1927 there were forty reported instances of spontaneous fires or heating in spent brewers grains being transported on United States railroads. Arms (2) reported and described a fire due to spontaneous heating of spent brewers grains. Moulton (3) recommends storing the grains at between seven and ten percent moisture content, wet basis, and at temperatures not exceeding one-hundred degrees F. The Bureau of Fire Mobilisation and Control, 1952 (4), the Board of Underwriters of New York (Via Thomas (5), 1957), and the Fire Protection Association, 1957, (6), warn against storing dried spent brewers grains at very low moisture contents. A Mill Mutual pamphlet (7) warns that feed ingredients which depend upon a drying process should be handled with special care.

2. Theoretical Aspects and Literature Review

2.1. Composition and Definition:

We will summarize the definition and composition of commercial spent brewers grains. The Feed Manufacturing Technology Handbook (8) defines brewers dried grains as:

Brewers' Dried Grains

(1) Definition: Brewers dried grains is the dried extracted residue of barley malt alone or in mixture with other cereal grain or grains products, resulting from the manufacture of wort or beer and may contain pulverized dried spent hops in an amount not to exceed 3%, evenly distributed (AAFCO 1974 (9)).

(2) Chemical Composition:

Nutrient	Expect %	(Range %)
Moisture	7.0	6.5 - 11.0
Protein	25.0	22.0 - 26.0
Fat	6.0	4.0 - 7.0
Fiber	15.0	14.0 - 17.0
Ash	4.0	2.5 - 4.5
Ca	0.25	0.15- 0.35
P	0.48	0.35- 0.55

(3) Color: Varies but is usually grayish tan

(4) Odor: That of dried fermented grain

(5) Texture: Varies. five to 10% is retained on a No. 16 screen and approximately 75% passes through a No. 10 screen.

(6) Test Weight: Expected -- 15 lbs/cu. ft.

Range -- 12 lbs to 18 lbs/cu. ft.

(7) Microscopy: Refer to AAFM Manual, page 9 (10).

The American Feed Control Officials (11) define Brewers Dried Grains as "the dried extracted residue of barley malt alone or in mixture with other cereal grains or grain products resulting from the manufacture of wort or beer and may contain pulverized dried spent hops in an amount not to exceed 3%, evenly distributed."

The United States Brewers Association (12) lists this data on spent brewers grains:

Proximate Analysis:

Protein	27.1%
Fat	7.5%
Linoleic Acid	3.9%
N-Free Extract	43.4%
Fiber	11.7%
Ash	4.0%
Moisture, w. b.	6.3%

Minerals:

Ca	0.27%
P	0.66%
K	0.08%
Mg	0.19%
Fe	0.029%
Na	0.26%
Cu	21.3 mg/kg
Mn	37.6 mg/kg

Vitamins:

Thiamin	0.7 Mg/kg	Folic Acid	0.22 mg/kg
Riboflavin	1.5 Mg/kg	Biotin	0.08 mg/kg
Niacin	46.4 mg/kg	PABA	4.0 mg/kg
Pantothenic Acid	8.6 mg/kg	Inositol	264 mg/kg
Choline	2110 mg/kg	Vitamin B12	3.7 Mcg/kg
Pyridoxine	1.7 mg/kg	Vitamin E	65.1 IU

Amino Acids:

Arginine	1.3%	Threonine	1.0%
Histidine	0.6%	Tryptophan	0.4%
Isoleucine	2.0%	Tyrosine	1.2%
Leucine	3.2%	Valine	1.7%
Lysine	0.9%	Cysteine	0.4%
Methionine	0.6%	Aspartic Acid	1.9%
Phenylalanine	1.8%	Serine	1.4%
		Glutamic Acid	6.5%
		Glycine	1.2%
		Alanine	1.8%

2.2 Heating: General Considerations

A variety of materials, not all organic, are known to heat spontaneously: coal, linen fabric, soap chips, wool, cardboard, jute, cotton, sewage, sawdust, manure, fish meal, alfalfa, and cereal grains to name just a few.

Exothermic chemical reactions do not proceed vigorously at normal temperatures. A means of raising the temperature to about ninety or one hundred degrees centigrade must be at hand. Typically this "triggering" is accomplished via microbial thermogenesis or through heat released during water adsorption (13).

Fire results when reaction rates become increasingly exothermic in a nonlinear manner with corresponding temperature rise (14). The term "thermal explosion" is given to mechanisms of this type. Thomas (15) combined and extended earlier theories (16, 17, and 18) to give a general mathematical treatment for heating in reacting masses. The theory considers masses of materials with various internal heat distributions and allows for surface cooling. Heat losses are allowed by either heat transfer at the surface of the reacting mass or by thermal conduction within the reacting mass or both. The most useful application is of a uniformly reacting mass (provision is made for the shape of the reacting mass) with known external ambient temperature.

The size, shape, and thermal conductivity of a mass of reacting material greatly affect its potential temperature increase. In general, heat generation varies with the cube of dimension, but heat dissipation varies with the square of dimension. So, hazards increase as larger bulks are stored. Thermal conductivity, if low, can decrease effective heat dissipation. In organic materials, once temperatures of about

180°C are achieved, extremely exothermic reactions can occur.

2.3 Moisture Effects

Baxter (19) and Kumar (20) state the higher the moisture content of a hygroscopic material, the higher its thermal conductivity will be. Thus, wet, porous solids have a very large coefficient of thermal conductivity. Krischer and Esdorm (21) extend this theory to water in any porous solid and Nissam, Hansen, and Walker (22) give the general treatment for an arbitrary volatile liquid in an arbitrary porous solid. In the general case, higher concentrations of a volatile liquid in a porous solid imply higher thermal conductivities.

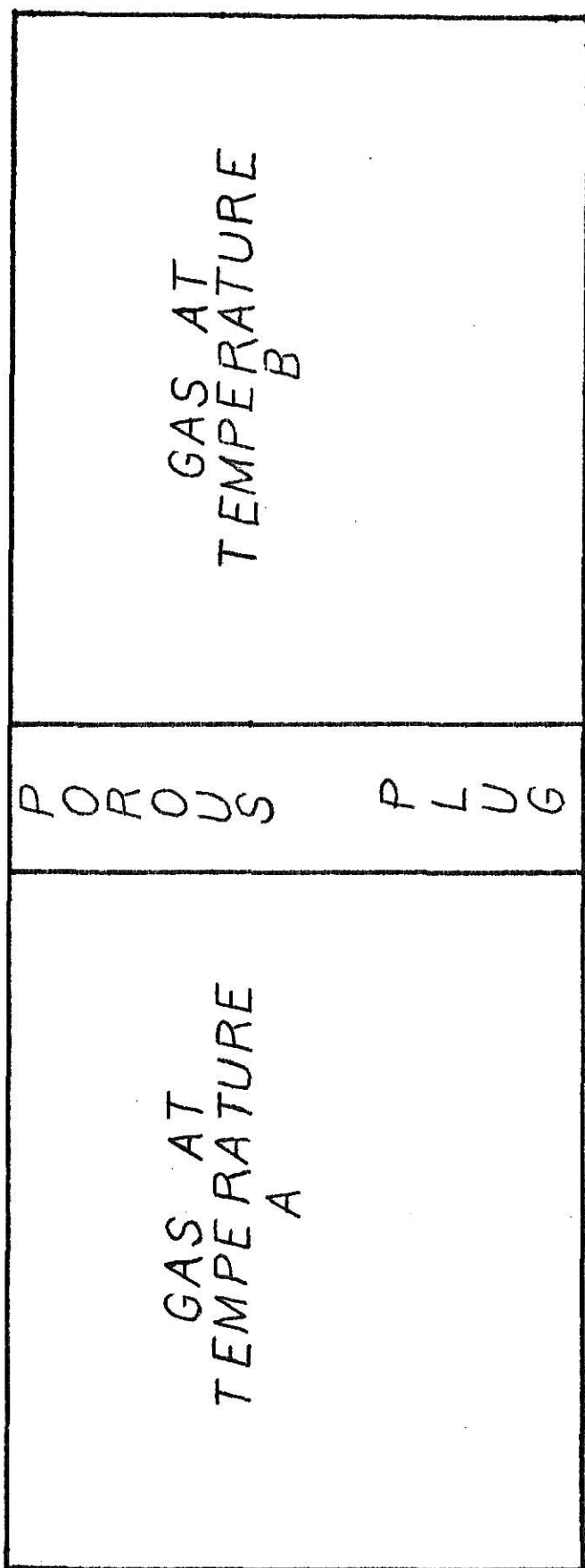
When equilibrium relative humidities are below 100%, a further mechanism can operate. The opposing mechanisms of gaseous and thermal diffusion may reach an equilibrium. Partington (27) showed this more clearly, consider Fig. (1).

According to Neumann (23) gas will tend to pass from the cooler zone to the warmer zone. Eventually a steady state will be reached with the pressure in A and B being different. Feddersen (24) and Reynolds (25) independently observed this experimentally. Reynolds called the phenomenon thermal transpiration. Maxwell (26) described a theory for the phenomenon and called it thermal effusion. Partington (27) says that the pressures in A and B will be related by:

$$\frac{P_A}{P_B} = \frac{A \frac{T_A}{T_B}}{B \frac{T_B}{T_B}} = \frac{T_A}{T_B} \quad (1)$$

**THIS BOOK
CONTAINS
NUMEROUS PAGES
WITH DIAGRAMS
THAT ARE CROOKED
COMPARED TO THE
REST OF THE
INFORMATION ON
THE PAGE.**

**THIS IS AS
RECEIVED FROM
CUSTOMER.**



$A \neq B$

Figure 1. Thermal Diffusion.

An opposite effect to thermal effusion is related to differences in vapor pressure which causes vapor diffusion. Consider a hygroscopic porous solid body of uniform moisture content. If a part of the body is heated the vapor pressure increases. Eventually, the mass transfer of water from the hot zone to the cool zone lowers the interstitial relative humidity of the hot zone and raises the relative humidity of the cool zone until a path of nearly constant water vapor concentration occurs. Water transport then ceases and the effect of this is that thermal conductivity is radically reduced at temperatures above 60°C , although the effect is not quite so serious at lower temperatures. So, in large masses wherein the water concentration is lower than that of total saturation, but high enough to ensure thermophilic bacterial growth, maximum biological temperatures can be attained due to reduced thermal conductivity and heat dissipation. This is why many experiments using very wet hay (more than 100% saturation) have failed to observe excessive temperatures due to microbial thermogenesis. In these over-wet experiments the thermal conductivity remains high.

Water may affect the thermal conductivity of wet porous materials in another way. Heat can diffuse out either as sensible heat or as latent heat contained in evaporated water vapor. Henry (28, 29) has shown that these two diffusion processes can interact within the hygroscopic range to cause "waves" of simultaneous coupled diffusion of temperature and water vapor. He has shown that diffusion coefficients can be calculated for these coupled waves.

Water vapor affects the partial pressure of oxygen also (30). Oxygen exerts a partial pressure of 160 mm Hg at all temperatures in a normal, dry atmosphere. At room temperatures the presence of water

does not drastically effect the partial pressure of oxygen. However, at high temperatures the partial pressure of water causes the partial pressure of the oxygen to fall off. At 100°C it may become 0 mm Hg for saturated air. For less than saturated air, the effect is lessened.

However as the material dries, water vapor migrating from a reacting mass to the external environment carries latent heat with it, cooling the mass. As the material dries further the existing water also enhances aeration of the reacting mass by oxygen as the water vapor pressure falls. Effects of this type are documented in coal (31, 32 and 33).

Almost all solid materials that adsorb water do so with release of heat. The heat released can be considerable when the adsorbing material is at a very low moisture content. When water vapor is involved the phase change must be included also. Davis and Byrne (31) and Hodges and Acherjee (33) found that the temperature of coal rises when aerated by moist oxygen. Extremely large temperature rises due to moisture adsorption have been documented in the textile industry (34 and 35). Many authors believe that the heat of wetting may act as a trigger mechanism raising internal temperatures of a reacting mass of porous material to the threshold temperature of other exothermic reactions (36, 37, 38 39). The authors of (40 and 41) even suggest that the heat of wetting may raise the temperature of a mass of reacting material to the ignition temperature.

All microbial populations have temperature optimums for growth and specific ambient air relative humidity requirements. Most molds grow between relative humidities of 65% and 100% (42). Bacteria require relative humidities above 90%.

Organic compounds undergo some oxidation at ordinary temperatures. At temperatures above 100°C , these reactions take place at increasingly high rates. There is overwhelming evidence that water increases the rates at which certain of these reactions take place. Experimental evidence exists for this on diverse substances: viscose rayon (43), coal (44 and 45), charcoal (46), hay (47), wool (48), asbestos fibers with glucose spread on them (47), and sewage sludge (49 and 50). Of course, water may also carry catalytic metal ions capable of catalyzing oxidation reactions (51, 52). Apparently, the water and metal ions accelerate the uptake rate of gaseous oxygen.

Water produced by microbial thermogenesis or by chemical oxidation reactions can be adsorbed by the heating mass releasing yet more energy. Walker et al. (53) have calculated the heat generated if the hydrogen in wool were oxidized to water and then adsorbed on undamaged wool.

Materials that have been wet and then dried have higher subsequent rates of oxidation than the initial dry material. Walker et al. (13) found that pie wool (See section 2 for definition of pie wool) reacted more vigorously with oxygen at 100°C after prior drying and that the Lea Peroxide value (54) of the fat was lowered by the drying treatment. The theory is occasionally advanced that surfaces prone to exothermic reaction with oxygen can be protected by a layer of carbon dioxide, and that adsorption and subsequent desorption destroy this film. Support is derived from experiments on powdered graphite which became pyrophoric after immersion in liquid argon, followed by desorption (55). Results like these prompted the Fire Protection Association (56) to issue a warning regarding increased spontaneous heating hazards caused by wetting and re-drying of charcoal. So, drying after wetting

may greatly increase the hazard of oxidation reactions.

The production or removal of water from a reacting mass can play yet another role. Once a mass becomes wet that is wet to between 94% and 98% (interstitial relative humidity) may have its thermal conductivity fall off drastically as discussed by Partington (27). For a reacting mass that continues to react as before but suddenly cannot dissipate heat as fast due to loss of conductivity, temperatures may increase rapidly. The range of moisture contents corresponding to the 94-98% (94 is the lower limit because of the lower limit for bacterial growth, and 98 is the upper limit because of rapidly increasing thermal conductivity) is then critical as we may estimate the chances of being within this critical moisture range.

2.4. Heating of Wet Materials, General

The general mechanism in the spontaneous heating of wet materials appears to be (1) a triggering reaction followed by (2) higher levels of exothermic reactions. The primary exothermic reaction can be wet combustion of cellulose, decarboxylation of amino acids or some other similar reaction. Common triggering reactions are adsorption of water vapor and microbial thermogenesis. These reactions can often raise the temperature of organic materials to $70^{\circ} - 100^{\circ}\text{C}$. For the microbial process to do this a very narrow range of relative humidities is required (94%-98%, depending on the organic material). The lower limit is set as the lowest interstitial relative humidity at which thermophilic bacteria can grow actively. The upper limit is set at 98% as above this interstitial relative humidity, the mass will dissipate heat too rapidly due to increased thermal conductivity. To achieve the very high

temperatures via microbial thermogenesis (70°C) a situation of constant vapor pressure must develop (27) so that thermal conductivity drops off markedly.

Wet oxidations occur at low temperatures ($< 80^{\circ}\text{C}$), however near adiabatic heating conditions are needed for the reactions to raise the temperature to 100°C .

Experiments show that it does not matter how the reacting mass reaches the 80°C - 100°C range. However, once these temperatures are attained, if wet oxidative reaction can occur in the mass, the temperature will continue to rise. If the material dries out then at about 170°C other dry reactions can continue unless the excess heat can be dissipated.

The general mechanism described above is advanced by Rothbaum (47) and found consistent for esparto grass (57) and hay (47). It appears likely that this same general mechanism can be applied to a wide class of wet organic materials: wet stable manure (58), wet saw dust (59), wet nutshells (60), wet fish meal (61), wheat (62), wet sheepskins (63), wet wool (under laboratory conditions) (64). Experimentally, ignition can be produced in cloth, wool, paper, etc., however, in practice, baled products have failed to ignite: wet wool (65, 66, 67, 68), large heaps of jute (69, 70), and baled cotton (71, 72). Apparently baling or stacking of sacks decreases ignition hazard. Possibly, pelleting would help also.

2.5 Heating of Air-Dry Materials, General:

The theory of Henry (28, 29) indicates that the coefficient of thermal diffusivity for rapidly dried hygroscopic materials will be lower than

for materials dried more slowly. The effect of this is that rapidly dried materials will lose heat less rapidly than properly dried materials. This effect is documented for wool (73), and further substantiation is provided by the fact that materials usually not susceptible to spontaneous heating at room temperatures will heat when stored in bulk after machine-drying: cardboard (74), and wood fiberboard (75, 76).

This tendency of materials to retain heat more effectively after rapid drying is important when one considers that many oxidative reactions have periods of induction (77). Specifically, if higher temperatures are maintained longer there is more chance of a mass passing through an induction period. Many of these wet oxidative reactions having induction periods are responsible for spontaneous fires in commerce (78, 79). After the induction phase passes, most wet oxidative reactions proceed at a vastly increased rate. So, in actual practice pockets of heat formed could cause temperature rises in nearby air-dry areas that would retain heat long enough to allow the reaction to proceed beyond the induction phase. These pockets of local heat could be due to the effects of non-uniform moisture distribution or other causes, Freitag (37).

2.6. Oxidative Reactions

Walker (30) classifies four types of oxidative reactions:

- A. Oxidation of combustible materials by chemical oxidizers such as nitric acid, peroxides, or perchlorates.
- B. Addition of gaseous oxygen to diene and triene bonds in organic materials such as lipids and rubbers.
- C. Direct reaction of gaseous oxygen with combustible materials at normal storage temperatures (as with coal).

- D. Direct gaseous oxidation of most organic materials at higher temperatures, say $> 80^{\circ}\text{C}$. At any given temperature, these reactions usually proceed faster in wet materials than in dry materials.

Of the mechanisms, A, B, and C are capable of generating enough heat at ordinary temperatures to cause thermal explosion in sufficiently large (adiabatic) piles. Mechanisms D will normally require a prior, triggering mechanism to raise the temperature to a level where strong exothermic reactions occur. Microbial heating or heat of wetting can act as such triggering mechanisms. The role of water is obvious in both.

2.6.1: Keratin Reaction (protein)

Walker and Harrison (80) found that dry oxygen will react exothermically with the keratin of scoured wool. They found that the rate of heat generation due to the reaction between 90°C and 150°C and at times between 1 hour and 200 hours can be given by:

$$Z = 2.4 \times 10^{-6} 2^{0.08T} / \phi^{0.282}$$

where: Z is the rate of heat generation in cal/sec . g

T is the temperature in $^{\circ}\text{C}$

ϕ is the time since inception of the reaction in seconds.

The rate of heat generation was not influenced by wool fibre diameter over the normal commercial range of fibre diameter. The wool was extracted with acetone before experimentation to insure that oil oxidation would not be possible. The heat generating capacity of the scoured wool was found to be less than for non-scoured wool but larger than that of wood fibres, 2×10^{-5} cal/sec . g (81). The temperature rises obtained (80) were very

small, between 1°C and 15°C, with a median rise of about 3°C. Adiabatic heating was used in all experiments. In general, larger experimental volumes experienced larger temperature rises. Further, higher initial ambient temperatures produced larger temperature rises.

It was found that the keratin in wool, while reactive with oxygen, would probably not present an ignition hazard at storage temperatures below about 170°C.

2.6.2: Amino Acid and Similar Reactions

The exothermic reaction between amino acids and oxygen was investigated by Rothbaum (48). In earlier work Schönberg and Monbacher (82) reviewed the "Strecker Degradation" which they define as all non-biological degradations of α -amino acids into substances of one carbon atom less. Wieland and Bergel (83) found that α -amino acids in an aqueous medium under the presence of oxygen and charcoal were decomposed. Bergel and Bolz (84) found that amino acid solutions were decomposed by ionized oxygen, evolving carbon dioxide. Heyns et al. (85) found that glycine completely decomposed under hydrothermal conditions (solutions under pressure at 373°C). Huggins and Moses (86) found that during paper chromatography of glycine, using phenol-water, up to 40% decomposition may occur yielding unidentified compounds.

Similar reactions may be the cause of ignition in the spontaneous combustion of hay (47), and are probably also the reactions occurring in the wet combustion of sewage and sludge (49, 50). This type of relatively low temperature oxidation probably proceeds via free radicals and involves water vapor. It may be general for all organic compounds containing functional groups involving oxygen or nitrogen on carbon

atoms. This reaction, though, has only been studied in detail for solutions of carbohydrates (87, 88) where each molecule of sugar loses one carbon atom as formic acid.

Cellulose is an important complex carbohydrate and weight loss in wood over extended periods is a practical test of the above. Stamm (89) has shown that wood loses about 10% of its weight after five years of storage in room air heated to 90°C, while wood at 90°C in a water saturated atmosphere loses 10% of its weight in one month. This emphasizes that all of these wet combustions proceed via water-vapor related mechanisms.

Finally, Thompson and O'Donnell (90) have shown that wool which has been oxidized with 5% peracetic acid, and then washed with water has approximately 85% of its disulfide bonds broken and oxidized to cysteic acid.

Rothbaum (48) found that amino acids are oxidized by oxygen at relatively low temperatures (90°C) when moisture is present, and that under similar conditions, amino acids degrade much more slowly in nitrogen. The experimental conditions were essentially surface reaction conditions so that the available oxygen was not limited. The reaction requires the presence of water and is greatly reduced when the relative humidity is less than 60%. He used radioactive glycine to determine that the carboxyl carbon is lost first. As the oxidation proceeds, carbon dioxide is derived steadily more from both carbon atoms. Rothbaum observes two heat output peaks that he believes are due to two separate reactions. The slower degradation of glycine by nitrogen is also a decarboxylation reaction. Rothbaum found that

cysteine and tyrosine react exothermically with oxygen also. In all cases, the calculated heat production agreed well with the experimental value. There is probably less decarboxylation of cysteine and tyrosine than of glycine. He investigated sodium acetate, sodium stearate, and glucose, also, and found that the sodium compounds showed no significant reaction with oxygen whereas glucose did (210×10^{-4} cal/sec⁻⁸).

Rothbaum observed that the formation of water-soluble substances by the oxidation of wet wool greatly lowers the thermal conductivity of the wool at 90°C.

2.6.3. Cellulose Reactions

The ignition of wood cellulose was studied by Walker et al. (91). The reaction between solid phase cellulose and oxygen at 80°C was studied by Murphy (92) and found to be exothermic. Murphy theorized that oxygen may form a complex, which slowly breaks down to yield carbon dioxide. Farguhan (93) and Major (94) have stated that cotton undergoes more degradation when heated in air (i.e.: oxygen) than when heated in nitrogen. Many indications of increasing rates of degradation with time have been observed. Czepil (95) found an increasing rate of degradation for alpha-cellulose catalyzed by iron salts in air at 105°C, when measured by the increase in intrinsic fluidity. Walker et al. (91) hypothesized that some mechanism of chain cleavage produced pyrolysed glucose units, perhaps laevoglucosan, which could then react with oxygen more rapidly than the original cellulose. This is confirmed in Gobva (96) and in Broido and Kilzer (97). Walker et al. (91) claim that it is possible that this chain

cleavage proceeds more rapidly in an atmosphere containing oxygen. In this connection, Major (94), it may be significant that cotton linters heated for 96 hours at 170°C in an oxygen atmosphere have been reported to harbor thirty times as much water-soluble material as cotton linters heated in nitrogen. Walker et al. (91) have shown a definite increase in the rate of exothermic aerial oxidation of wood cellulose above 148°C (dry air temperature) after an initial decrease. This increase in the rate of exothermic oxidation can lead to ignition at a lower ambient temperature than is necessary to ignite fresh cellulose. Walker also concludes that below 100°C , small bulks, e.g., several litres, of cellulosic materials offer only a low ignition hazard.

Walker et al. (43) discuss ignition of regenerated cellulose, as viscous rayon. They found similar results, but their proposed equation to describe the rate of this reaction between 128°C and 159°C does not conform to conventional chemical reaction theory for fluid phase reactions.

Ambler and Finney (98) found that oxygen can react directly with cellulose over a broad temperature range (room to ignition). This attack causes the yellowing and loss of strength commonly observed in cellulosic materials, such as in paper. As Alvares (99), among others, have shown, the reaction is exothermic and can lead to ignition. See also Lipska (100), MacKay (101), and Shafigadeh (102).

A reaction concerning us would be the reaction and ignition of solid phase cellulose as suggested by Firth (103) and Matson et al. (104). Nuckolls (105) suggests that long-continued heat below 200°C

can convert cellulose to pyrophoric carbon. This theory is supported in Specht (106), Cameron (107), and Virtala et al. (108).

Returning to Walker et al. (43), they found that the rate of exothermic degradation of cellulose in viscose rayon maintained at 135°C, or higher temperatures, in dry oxygen increases after an initial decrease. This treatment also lowered the ignition temperature as compared to fresh cellulose. This effect appears to be common in all cellulosic materials.

2.6.4: Waste Disposal Reactions

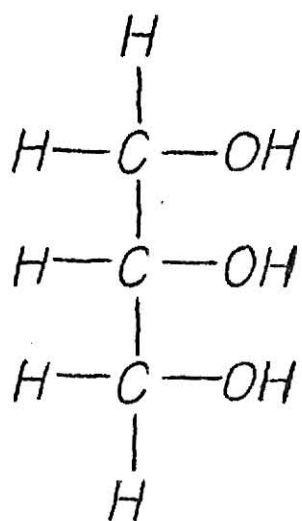
Cederquist (49) and Zimmerman (50) describe a new waste disposal process used in commerce. The details of the reaction are not given, if indeed known, but wet combustion similar to the reaction above can be assumed. The reactions were used to destroy waste and to supply steam to paper mills in (49). The operating temperatures selected were usually about 600°C, although the reaction proceeded at much lower temperatures (200°C), albeit at commercially infeasible levels. The products were listed as the same as for dry combustions (50).

2.6.5: Fat Rancidity

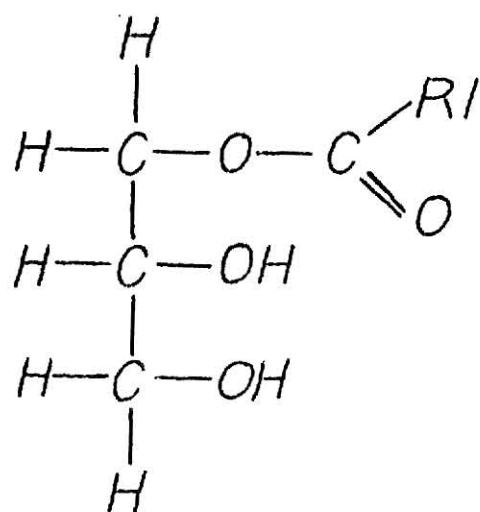
Rancidity in fats may occur in two ways, hydrolytic or oxidative.

The fatty acid esters of glycerol are glycerides. If all of the hydroxyl groups of glycerol are esterified with fatty acids, the fat is called a triacylglycerol (triglyceride). These constitute the bulk of naturally occurring glycerides. Di- and mono-acylglycerols occur also, but not in large quantities. See Fig. (2).

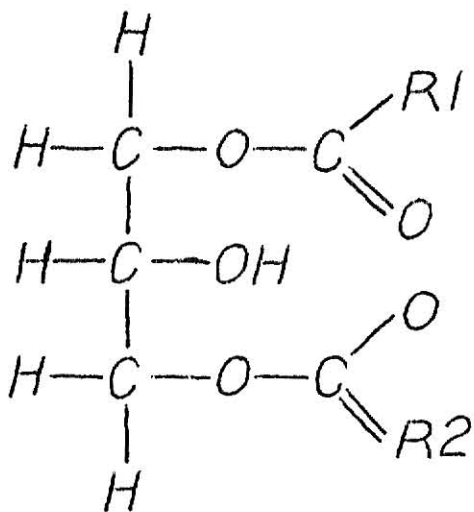
Glycerides undergo hydrolysis when boiled with acids or bases, or when attacked by lipases. See Fig. (3). However, hydrolytic rancidity



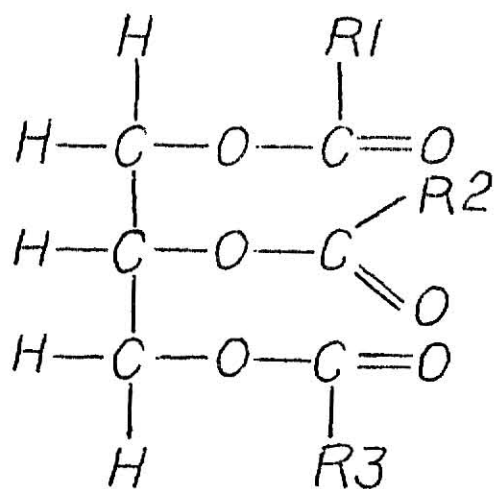
GLYCEROL



1-MONOACYLGLYCEROL



1,3-DIACYLGLYCEROL



TRIACYLGLYCEROL

Figure 2 Glycerol and its Fatty Acid Esters.

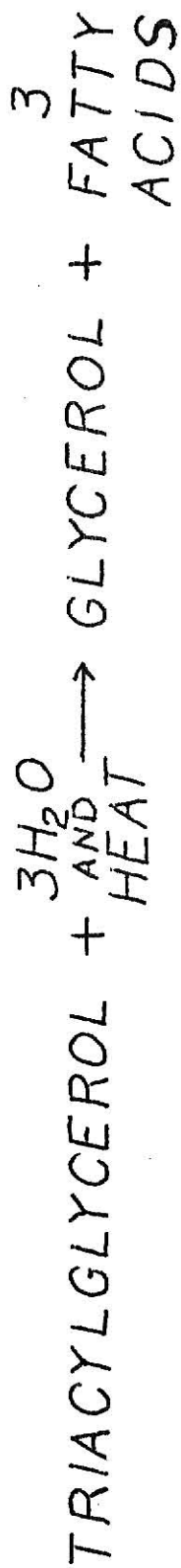
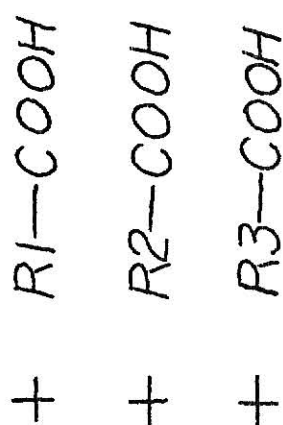
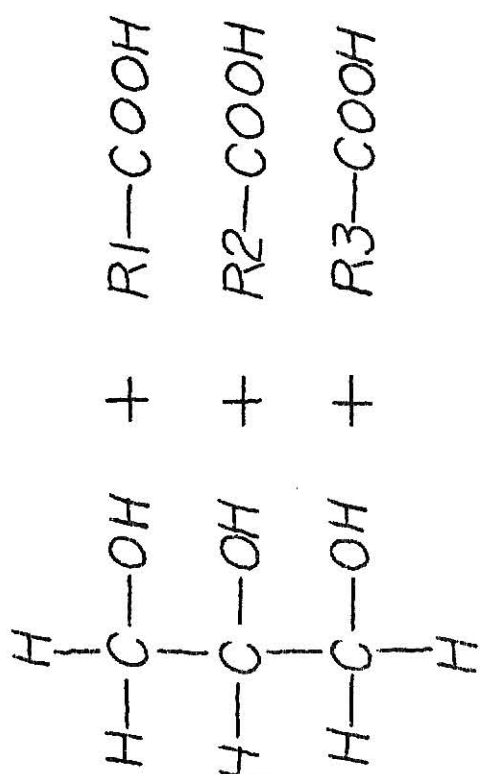
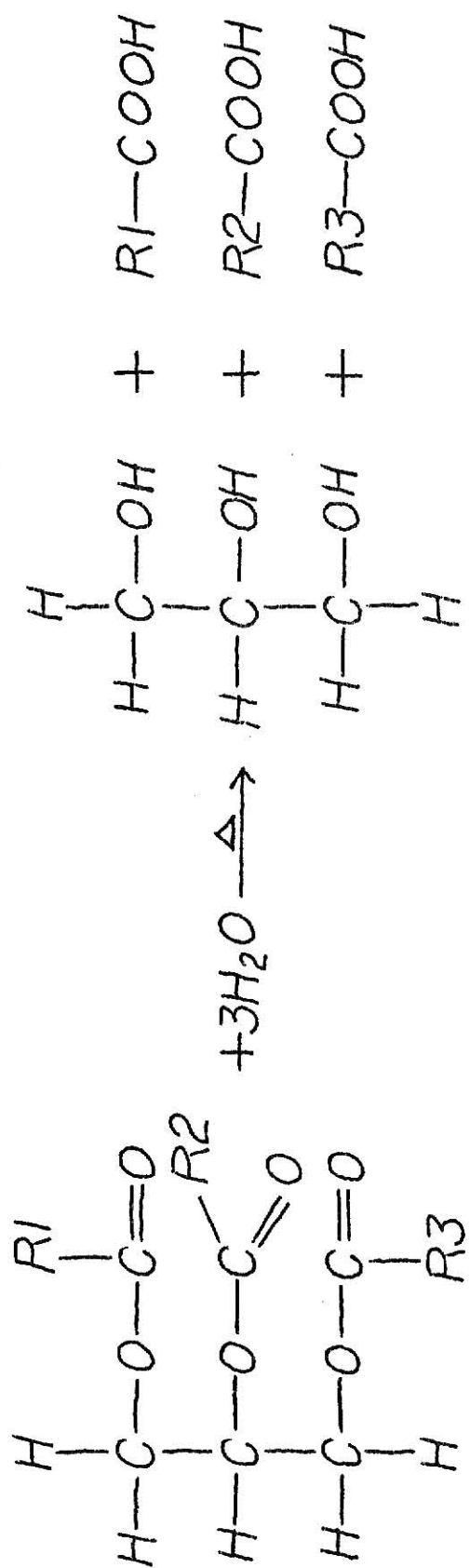


Figure 3 Hydrolytic Rancidity.

is of no real interest in exothermic heating as only relatively small quantities of energy are liberated.

In oxidative rancidity large amounts of energy are available. Current literature indicates that the autoxidation of fatty acids includes formation of a hydroperoxide which contains the unchanged double bond. Autoxidation of all unsaturated organic compounds is then explained by the formation of free radicals at the α -methylenic group. By this mechanism (109) autoxidation proceeds via a chain reaction by detaching a hydrogen atom from the α -methylenic group. See Figure (4) from Braverman (110).

With more double bonds or with triple bonds, the process is similar but more complex as more resonance possibilities exist.

So autoxidation is essentially a chain reaction where during the transfer of energy from one excited molecule to another, oxygen is added as a peroxidic free radical. Farmer et al. (111, 112) have elucidated the sites of oxygen fixation in long chain fatty acids and Lundberg (113) and Saunders (114) have studied subsequent reactions of the peroxides.

However, autoxidation of fats is a very complex phenomenon as can be inferred from the wide range of compounds produced in rancid fats. Fig. 5 shows several reactions that can occur to a hydroperoxide (From Laury (115)).

The autoxidation of all organic unsaturated compounds is preceded by an induction period during which the amount of hydroperoxides is built up. During this period, oxidation is necessarily slow. Previous heating may have formed these hydroperoxides whereupon the induction period is shortened or eliminated. The addition of some already rancid

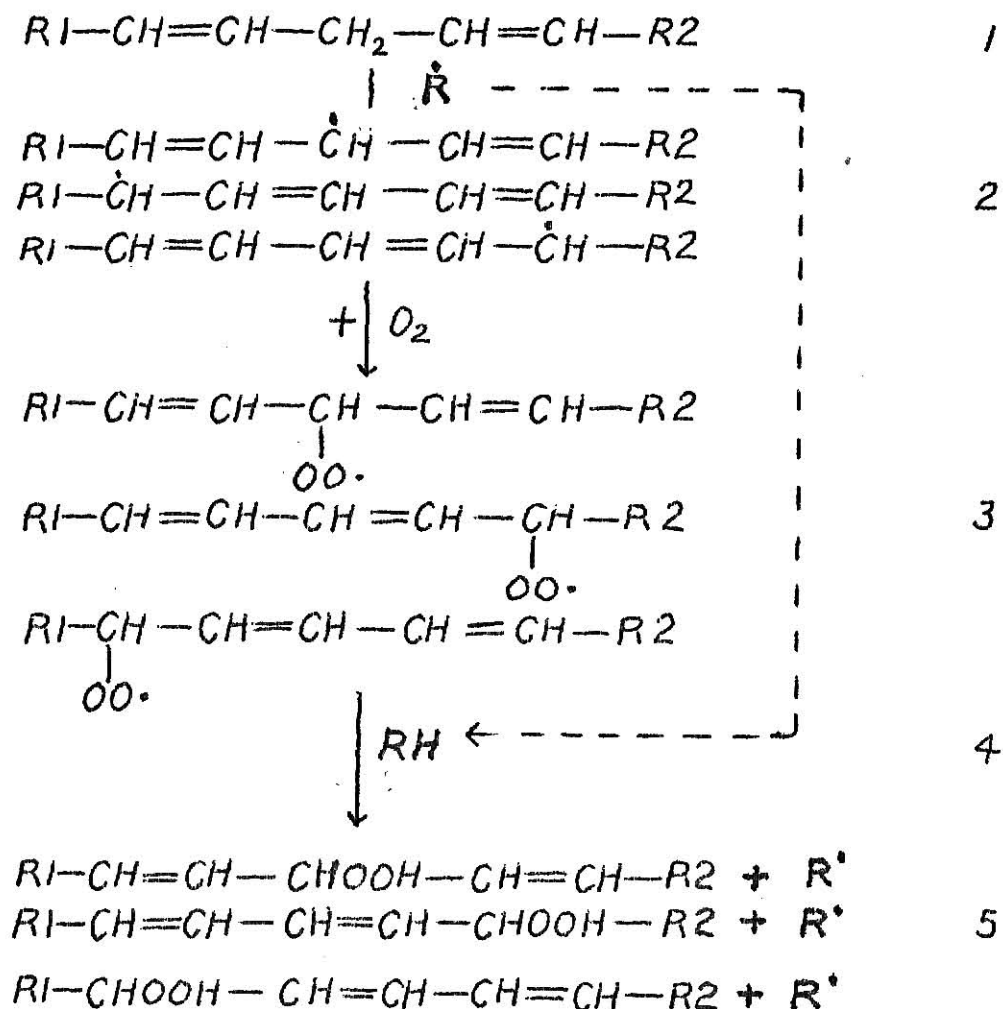


Figure 4 The Free Radical Mechanism of Autoxidation in Fats.

1. is a molecule of linoleic acid. 2. are three resonance possibilities for the free radical formed by the loss of the hydrogen atom. 3. are three possible peroxide radicals after the addition of oxygen. At 4. a hydrogen atom from another molecule of linolenic acid is added, making the reaction cyclic. 5. shows the three possible hydroperoxides, two of them conjugated--the most common form in nature.

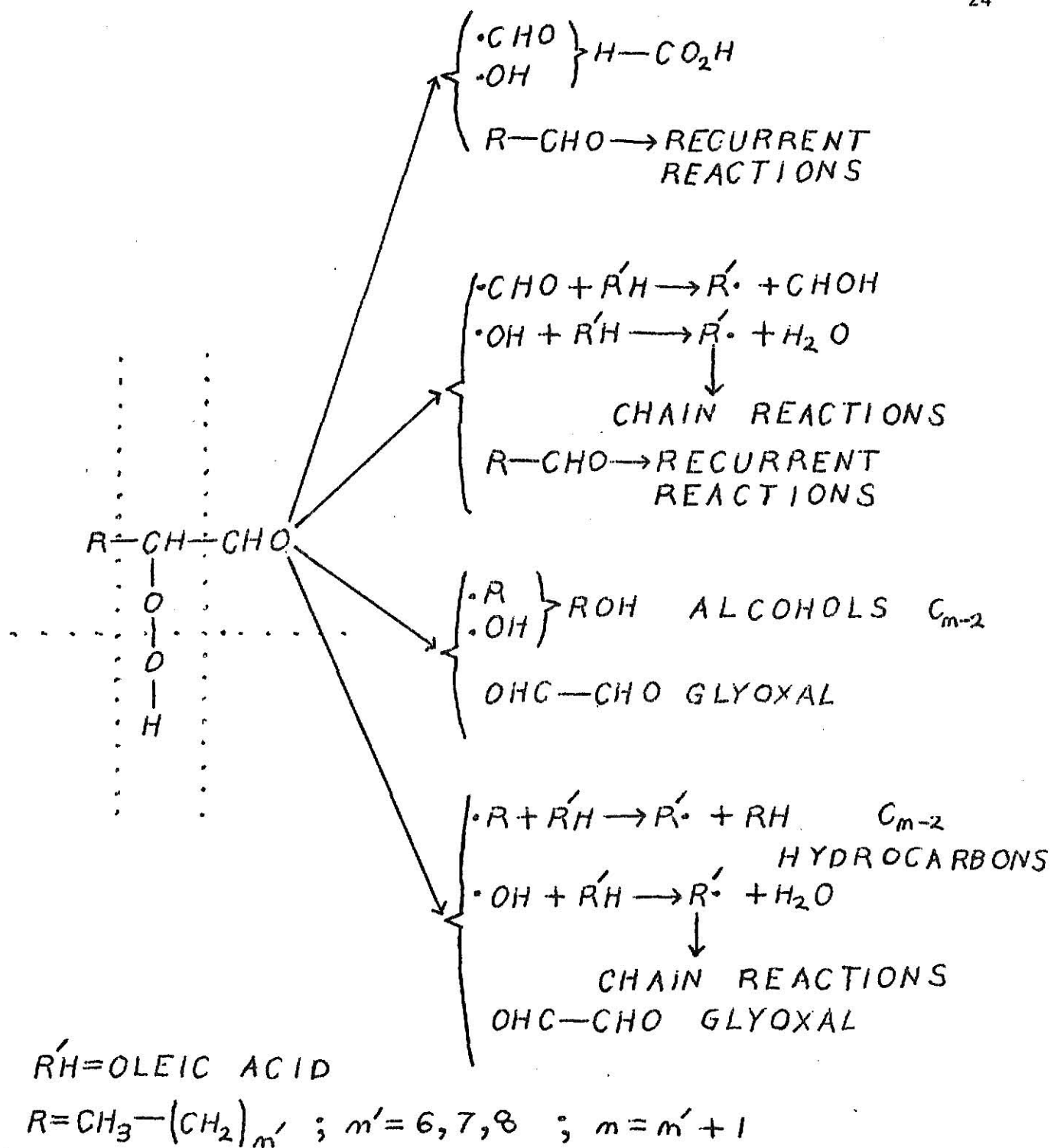
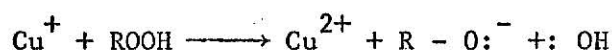


Figure 5 Possible decomposition of the second hydroperoxide resulting from autoxidation of the aldehydic breakdown products of oleic hydroperoxides.

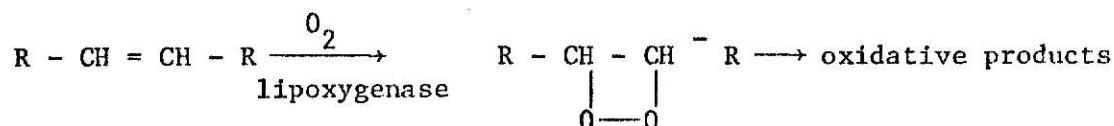
oil to non-rancid oil has this same effect also as the necessary free radicals will be provided in the rancid oil.

Research by Walker and Harrison (52) reveals that unsaturated fatty acids such as oleic acid oxidize much more rapidly than saturated fatty acids such as stearic acid.

Heavy metal ions can disrupt peroxides and create new free radicals. So, heavy metal ions can catalyze fat oxidation. For example:



Oxidation can also occur by the action of the enzyme lipxygenase:



Antioxidants are known which can block or retard autoxidation. Usually commercial antioxidants are merely substances with preferential ability to oxidize. This has the drawback that once the antioxidant is "used up" (preferentially oxidized), the oxidation proceeds as before. Common antioxidants include tocopherols, lecithin, gum gudiac, propyl gallate, butylated hydroxyanisole (BHA), nordihydroquaiaric acid (NDGA), butylated hydroxytoluene (BHT), and 6-ethoxy-1, 2-dihydro-2, 2, 4-trimethylquinoline (Santoquin).

2.7. Microbial Thermogenesis

The maximum reported temperatures by microbial heating have been about 90°C in the field, i.e. haystacks, etc., and somewhat higher under near adiabatic laboratory conditions. Pure cultures have never been reported to raise the substrate temperature above 60°C, even under

adiabatic laboratory conditions (116). Apparently this is because each strain will have different optimum temperatures for growth and several "overlapping" strains are required to achieve truly elevated temperatures. But, Kempner (117) reports that it is very unlikely that life can exist above 80°C. Higher temperatures are only attained between very narrow interstitial relative humidity limits (47). This is essentially due to several factors. Thermophillic bacteria generally require interstitial relative humidities of more than 95% to grow. However, with increasing relative humidity, the thermal conductivity of any porous solid rises rapidly (19, 21, 22). So 97% becomes the upper limit.

Therefore, between 95% and 97% interstitial relative humidity limits, factors favoring heat genesis and retention exist. The heat can be retained even more effectively in masses less than 100% saturated, where paths of nearly constant relative humidities are set up (27). When this happens thermal conductivity can fall off drastically at high temperatures (100°C).

Rothbaum (118) and Imseneski and Solnzeva (119) found that thermophillic populations on wool or other media can be as large as 2×10^9 individual organisms per ml. Carbyle and Norman (120) found that heating straw can contain 1.6×10^6 thermophiles per gram at 60°C. These large concentrations of bacteria are capable of producing large amounts of heat that can in turn raise the temperature of the substrate until the organisms are destroyed (provided there is adequate heat retention).

2.8. Spontaneous Combustion of Hay

We are providing references (121---,139) for historical purposes.

Hay is the material that has been researched the most as related to spontaneous combustion and it is interesting to trace the theory of thermal explosion as related to hay down through the years.

In the preceeding material we have discussed spontaneous combustion in very general terms. We will now examine the current theory on the spontaneous combustion of hay.

The spontaneous ignition of hay is believed to be due to an initial microbial heating which raises the temperature of pockets in a hay stack to about 80°C followed by severe chemical heating leading to ignition. Experiments show that (47) the initial microbial heating is not a necessary precursor to the chemical heating, but merely a triggering mechanism that is "at hand" to raise the temperature of any given pocket in the haystack to about 80°C . At this temperature, the rate of the chemical heating reactions is fast enough to produce further heating. The microbial triggering mechanism was shown by Rothbaum (47) to be able to elevate the temperature of adiabatically heated hay to the biological maximum of about 76°C only over a very narrow range of relative humidities, 95% to 97%. In one experiment the temperature attained by adiabatic microbiological heating with forced oxygen aeration was 98°C . The chemical heating reaction was shown to occur only in the presence of water and was believed to be due to direct oxidation of the cellulose in the hay. It was observed that at 170°C the hay was dried out and further oxidation above this temperature was extremely exothermic, leading to combustion. Rothbaum (47) believes that two chemical oxidations are at work in the spontaneous combustion of hay. One, a dry oxidation, occurs exothermically only at temperatures above 170°C . This is confirmed

(47) as dry hay samples heated at 140° never ignited or charred, whereas dry samples heated at or above 170°C always charred and ignited.

To summarize, the mechanism of spontaneous combustion in hay appears to be

- (1) microbial (or other) heating to 90°C to 100°C
- (2) wet oxidation of cellulose to 170°C
- (3) dry oxidation of organic material to ignition

It is to be stressed that only a very narrow range of relative humidities allowed microbial thermogenesis to pass to chemical heating. Rothbaum (47) hypothesized that this general mechanism is applicable to a variety of organic materials although the critical relative humidity band may vary with material.

Size of haystack also affects tendency towards spontaneous heating. Large size encourages heat retention, simulating adiabatic heating conditions, and also increases the chance of some local pocket within a haystack being within the critical relative humidity band long enough for microbial thermogenesis to elevate the local temperature to about 100°C .

2.9. Spontaneous Combustion of Wool

Published papers read on the spontaneous combustion of wool were all on New Zealand wool. Wright (140) and Crossland (141) provide a good description of the New Zealand wool industry. There are essentially four types of New Zealand wool: sheared, scoured, pie, and slipe. Slipe wool is obtained by using chemical depilatory agents (sodium sulfide and lime) to dissolve the wool roots from sheep skins. The depilatory is applied on the flesh side of the skin, and the wool harvested by hand plucking from the skin. Usually, the slipe process is used on whole skins. The

pie (piece) process is used on smaller pieces, wherein the wetted pieces are allowed to steep (rotted) in hot tanks. The skin rots faster than the wool and the wool is harvested by plucking as before. Pie wool can be very greasy. Sheared wool is sheared from the animal as is common in the United States. Scoured wool is pie or slipe wool that has been dried and defatted.

Scoured wool and sheared wool were found to react exothermically with oxygen under adiabatic heating conditions (80). Presumably the keratin in the wool fibers is reacting with oxygen. However, this is not likely to be related to spontaneous fires observed in wool, as temperature rises of only at most 14°C were observable from a 100°C starting temperature after over 100 hours of exposure to oxygen aeration under essentially adiabatic heating conditions. However, the effects were multiplied at higher temperatures and conceivably at very high temperatures (180°C) the reaction may be exothermic enough to contribute to spontaneous ignition. The reaction rates were not influenced by fiber diameters within the commercial range, and a triggering mechanism would be required to elevate the temperature to about 180°C before scoured wool would represent an ignition hazard.

Walker and Williamson (68) detail the ignition hazards of pie and slipe wool. They found that dumping (the mechanical process of baling wool), microbial thermogenesis in wool, and the reaction between wool and water vapor were not capable of raising wool to ignition temperatures. They did find, however, that these three processes may act as triggering mechanisms to raise the temperature to about 100°C where direct exothermic reaction between the wool and oxygen could occur. This latter reaction is capable of raising the temperature of wool to ignition levels. They

found that when 100 g pie wool samples were exposed to air at 102-105°C under moderate aeration they heated within six hours. Later, a more refined apparatus was used to simulate adiabatic heating. In these experiments it was observed that fat (ether soluble) content showed a rough correlation with tendency to heat. No pie wool sample with a fat content above 16% failed to reach ignition temperature, between 16% and 5% fat content, tendency to reach ignition temperature was erratic, and below 5% fat content, tendency to reach ignition temperature was rare. Typically, between 15 minutes and two hours, with a typical time being 60 minutes were required for a sample to reach ignition temperature (if reached) under adiabatic heating. It was concluded that spontaneous wool fires in New Zealand are due to fat oxidation. The authors were unable to correlate the tendency to ignite with analysis of fat, iodine number, or proportions of trienes and dienes. The proportion of free fatty acids seemed to bear some relationship to heating, and the Lea Peroxide value did also.

Dye and Rothbaum (64) found that microbial heating may be followed by wet oxidative reactions as in Zimmerman (50). The critical relative humidity range for wool was found to be 94-98% (63).

In Carrie et al. (142) it was determined that a new process making slipemaster wool rather than pie wool from sheepskin pieces can reduce greatly the risk of spontaneous fires in wool while in commerce. The process reduces the "greasiness" of the wool obtained by using an improved processing technique.

2.10. The Heat Balance Applied to Exothermic Heating

By using the heat balance we may predict so called critical radii for

a solid porous material reacting at a certain rate in a certain ambient surrounding temperature. See Fig. (6). For masses that have radii above this critical radius ignition will theoretically occur and for masses that have radii less than this critical radius ignition will not occur. The theory of this can be found in Walker (143) and Gross and Robertson (81). We review the results of this theory. For spherical piles we have these critical state equations:

$$\frac{n^2 p ZB}{ky} = 4.79$$

For a cylinder of infinite length

$$\frac{n^2 p ZB}{ky} = 2.89$$

For an infinite plane parallel slab

$$\frac{n^2 p ZB}{ky} = 1.27$$

where: n is the half-thickness of the pile (radius of a sphere or a cylinder, half-thickness of a slab).
(cm)

p is the density of the material g/cm^3

ZB is the reaction rate at T_B , the surface temperature of the pile. (cal/sec-g).

k is the thermal conductivity of the material
(cal/sec-cm $^{\circ}\text{K}$)

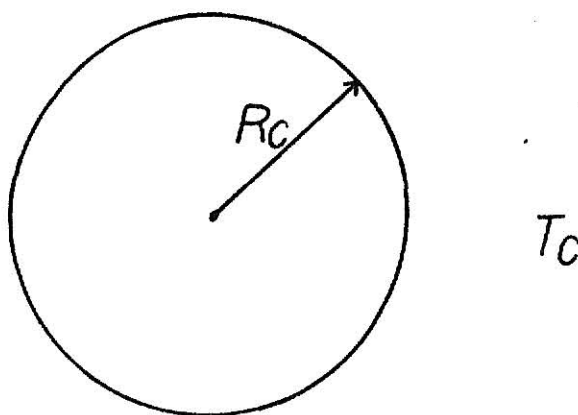


Figure 6 The Critical Radius of a Reacting Sphere of Porous Solid Material. Here we see a sphere of porous solid material reacting at a certain rate. This rate may vary with temperature. Depending on the volume of the sphere, a varying amount of heat will be formed in the sphere per unit time. So the heat formed is related to R_C^3 . The cooling of the sphere depends on the sphere's surface area (R_C^2) and on T_C . A temperature gradient will be formed between the sphere's core and its surface with the highest temperatures near the core. Using kinetic reaction equations and Newtonian cooling equations for a reacting mass with initial ambient temperature T_C , a critical radius, R_C , can be determined. Spheres of radius greater than R_C will theoretically heat to ignition, whereas spheres of radius less than R_C will not spontaneously ignite. Similar calculations can be made for other geometric forms. Adequate ventilation is assumed.

and y is the temperature interval to change the reaction rate by a factor of 2.

Once the above data is known for a material, graphs like Fig. (7), Walker (143), can be prepared.

2.11. Heating of New Zealand Spent Brewing Grains

Walker (79) uses two approaches to the problem: the experimental one (47, 68, 80) and the use of heat balance equations (51, 143) with experimental data from one experiment.

Spent brewers grains in Walker's article (New Zealand) have somewhat higher ether-extract percentages that are generally found in American spent brewers grains (Fig. 8). Possibly, New Zealand beer is made from a malt higher in barley content. The results show clearly that the oil in spent brewers grains is the ignition hazard present in New Zealand since removal of the oil prevented the reaction.

Walker also determined

$$ZB(\text{cal/sec.-g}) = 2.15 \times 10^{-6} \cdot 2^{0.0806T} \quad T = \text{temperature } ^\circ\text{C}$$

between 35° and 90°C

$$k = 1.8 \times 10^{-4} \text{ cal/sec cm}^3 ^\circ\text{C}$$

$$\text{reaction order rate} = \frac{1}{2} \text{ (change the theory of (109) slightly)}$$

$$p = 0.271 \text{ g/ml}$$

experimentally and used the results of Walker (143) to determine the results in Fig. (9).

The role of water is uncertain. The Fire Protection Association (6) recommends not storing spent brewers grain at moisture contents less than 5 to 7%. The Bureau of Fire Mobilisation and Control, 1952 (4) says that

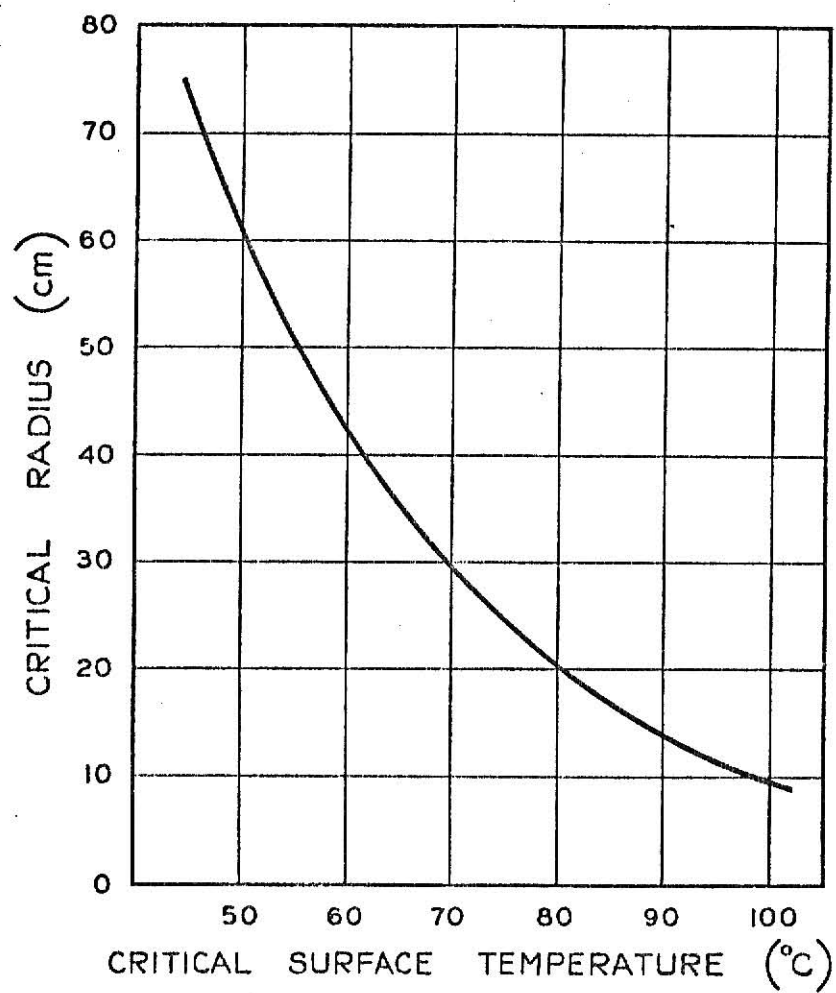


Figure 7 Critical Surface Temperatures for Spheres of Various Radii of Pie Wool.

Sample Designation	Description	Drying Process	Ether Extract (% on Dry Weight)	Dry Bulk Density (g/ml)	Ignition Tests (Oxygen at 100°C)		
					Maximum Temp. Rise (°C)	Time to Reach Max. Temp. (hr)	
A	Whole malted barley	1.9	0.54	1	55.2	
A	Crushed malted barley	1.6	0.43	3	15.8	
A	Spent brewing grain	Laboratory	8.0	0.17	37	5.3	
B	Whole malted barley	1.8	0.59	2	15.5	
B	Spent brewing grain	Laboratory	6.9	0.20	44	5.9	
C	Spent brewing grain	Laboratory	9.4	0.20	128 plus	3.5	
D	Spent brewing grain	Laboratory	7.8	0.20	51	5.7	
E	Spent brewing grain	Laboratory	7.5	0.20	51	5.8	
F	Spent brewing grain	Commercial	9.3	0.24	60	5.7	
G	Spent brewing grain	Commercial	8.3	0.25	69	7.8	
H	Spent brewing grain	Commercial	9.3	0.26	136 plus	5.4	
I	Spent brewing grain	Commercial	9.3	0.26	59	8.8	
J	Spent brewing grain	Commercial	8.8	0.26	105 plus	7.8	
K	SBG standard sample	Commercial	9.3	0.23	77	5.8	
K	SBG standard sample	Commercial	9.3	0.23	63	7.3	
K	SBG standard sample	Commercial	9.3	0.24	124 plus	4.9	
K	SBG standard sample	Commercial	9.3	0.25	157 plus	5.8	
K	SBG standard sample	Commercial	9.3	0.24	70	6.9	
K	SBG, standard sample after extraction with ether	0	0.21	2	6.3	

Figure 8. Ignition Testing and Analysis of Brewing Grains.

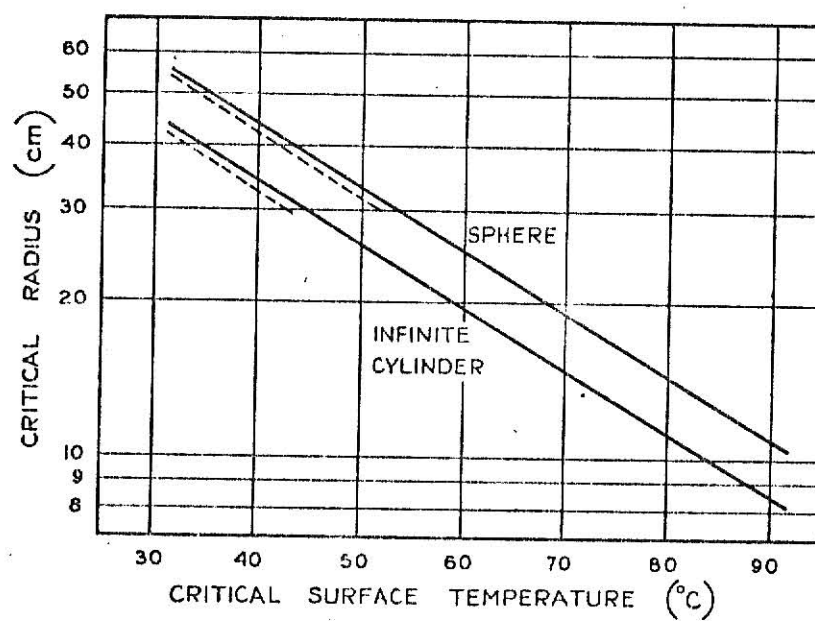


Figure 9 Thermal Instability in Piles of Dry Spent Brewing Grains In Dry Air.

severe drying may cause oxidation of the oil and Van Elteren (78) describes how textile oleines increase as fire hazards after such drying by completing the induction period for the oil. Further, if severe over-drying occurs the material can liberate heat of adsorption of water vapor during subsequent wetting. Further, the absence of water removes one aspect by which grains may resist heating: evaporation of water. Of course, too much water may lead to microbial heating which may trigger a variety of other exothermic reactions leading to thermal instability with consequent ignition.

The calculations in Walker (79) are based on ample of supply of oxygen, and thus represent maximum hazard.

2.12. Differential Thermal Analysis

Differential thermal analysis is an analytical technique used to study the physical and chemical changes occurring when materials undergo heating or cooling. The more sophisticated technique of differential scanning calorimetry or the methods of Walker and Harrison (79, 80, 142) might well be utilized.

The physical and chemical changes occurring during heating or cooling of a substance involve release or absorption of heat; differential thermal analysis measures this. The liberation or absorption of heat can be due to a variety of causes: chemical reaction, crystal transition, change of state or decomposition.

The essence of the analytical technique used in differential thermal analysis is continuous monitoring of the temperature differential between a sample of thermally inert reference material and a test sample while both samples are heated at a uniform and known rate. We used aluminum

oxide, also called alumina or Al_2O_3 , as our thermally inert reference substance.

Provided the heat capacities per sample (not per gram of each material) are nearly the same, a temperature differential will appear between the test sample and the reference material only when a physical or chemical change is taking place in the test sample. Specifically, the temperature of the test sample will lag behind that of the reference sample during any time period when the test sample is reacting endothermically, or absorbing heat. Examples of this type of behavior would be water evaporation, or crystalline transition. Conversely, the temperature of the test sample will precede that of the reference sample when the test sample is reacting exothermically, or releasing heat. Examples of this type of behavior would be water adsorption and many chemical reactions.

In differential thermal analysis, the temperature differential, ΔT , between the test sample and the reference material is plotted against increasing temperature. This curve is called a thermogram, see Fig.

(10). At all temperatures where no thermal changes are occurring in the sample a straight baseline is produced. Peaks or valleys from this baseline represent exothermic and endothermic reactions.

Actually, the temperature axis of Fig. (10) corresponds to a time axis, because since heating is at a constant rate this line has a temperature interpretation. Similarly, the ΔT axis of Fig. (10) is really a millivolt axis. The differential thermistor between the test sample and the reference sample produces current whenever temperature differences occur between the two samples. The absence of current is set at "50", the midline on the chart paper. This gives the ΔT axis its differential temperature interpretation.

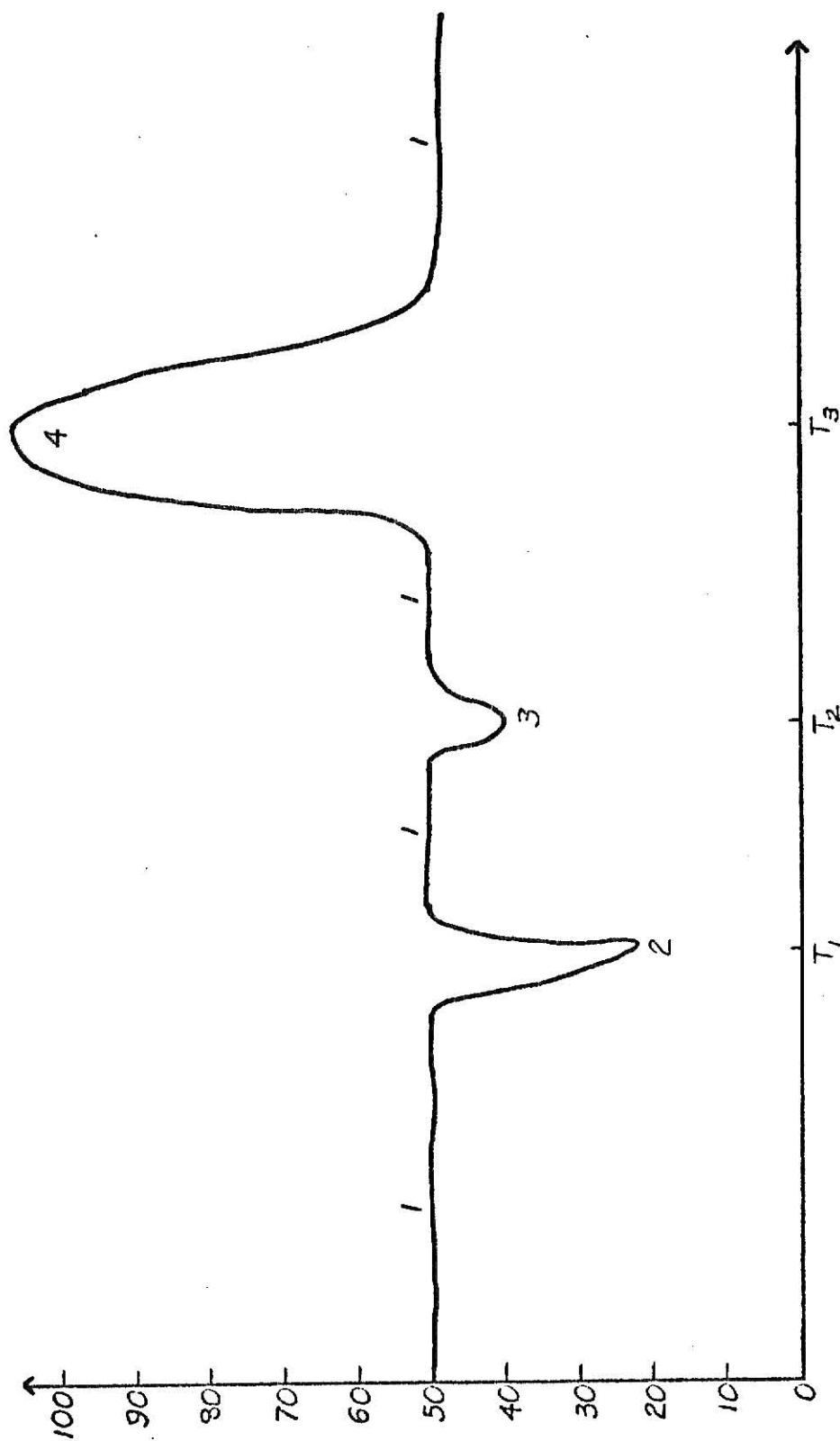


Figure 10. A Thermogram. Here (1) represents the baseline, (2) and (3) represent endothermic reactions in the sample at temperatures T_2 and T_3 respectively, and (4) represents an exothermic reaction of the sample at temperature T_4 .

Therefore, a thermogram represents a record of the temperature changes occurring in the sample over some temperature range of interest. These changes can be related to material decomposition, melting, boiling, vaporization, crystalline transition, dehydration, hydration, polymerization, oxidation, reduction of the sample, etc. To specify the cause of a temperature change requires knowledge of the test material and cannot be done with differential thermal analysis alone. The resultant thermogram is a "fingerprint" of the test material, characterizing it in a unique way.

The area under each peak or valley is theoretically related to the actual quantity of heat exchanged by the test sample and its surroundings. So each thermogram gives some indication as to the heat of reaction for each thermal change occurring in the test sample. It can even give some indication of the concentration of the reacting substance in the test sample.

Lavorsier and Laplace (144), Roberts-Austen (145), O'Neil (146), O'Neil and Gray (147), Brennan (148), Cassel (149), Cater et al. (150), (151), Brennan (152), and Cassel (153) discuss the theory and application of differential thermal analysis.

Figure 11 is a schematic diagram of a differential thermal analyzer.

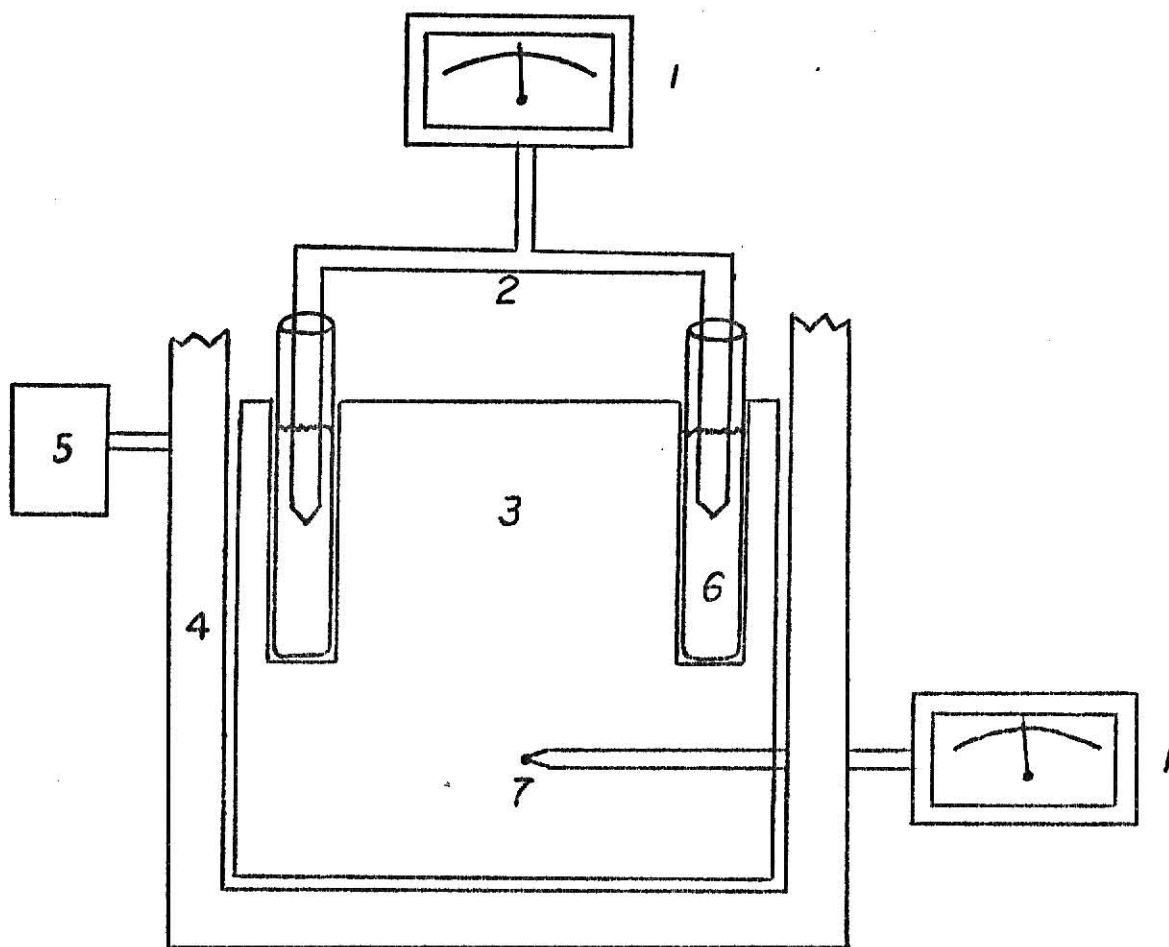


Figure 11 Schematic View of a Differential Thermalyzer. Here:

- (1) Millivoltmeter
- (2) Differential Thermocouple
- (3) Block
- (4) Heater
- (5) Variable, Programmable Transformer
- (6) Quartz Crucible
- (7) Thermocouple

3. Materials and Methods

3.1. Composition

Spent brewers grains were separated into fractions using Tyler Testing Sieves (154) and standard techniques (8). Sieves used were the #10, #14, #20, #28, #35, #48, #65, #100, #150, #200, #270 screens, and the pan. Particle size analyses were done (8) and the overs from the #10, #20, and #150 screens were analyzed for amino acid contents.

Proximate analyses were run on the overs of each of the above screens, and on the unsieved spent grains themselves. Proximate analyses were made on brewers yeast.

3.2. Chemical Reactions

As a result of the literature review we decided to investigate chemical reactions.

3.2.1. Differential Thermal Analyses

We used a Fisher Scientific Model 260 Differential Thermalizer.

Fig. (11) is a schematic representation of this differential thermal analyser. It consists of a metal block containing wells for eight small, quartz crucibles (we show only two crucibles in our diagram). The junctions of a chromal-alumel differential thermocouple are inserted into the crucibles reclining in the sample and reference wells. The output of the differential thermocouple is measured by a sensitive valvanometer or millivolt meter. A heating device powered by a variable, programmable transformer is coupled to the metal block permitting the temperature of the block to be controlled. As additional thermocouple inserted into the block allows monitoring of the block temperature.

The furnace is the top-loading, vertical tube type and can be used to heat the block up to a maximum temperature of 1200°C . Power to the furnace can be varied by changing the amperage input. This is controlled by a solid-state device capable of increasing the block temperature at any of three rates: 5°C , 10°C , or 25°C per minute.

The sample holder assembly consists of a cylindrical Inconel metal block suspended by means of an Inconel tube from a housing containing receptacles for affixing thermocouples. The entire holder assembly is fitted with an insulated handle to facilitate mounting and removal from the furnace. The sample block contains eight wells to permit analysis of one or two test samples simultaneously, as well as positions for reference samples, and temperature control and monitoring.

With the Model 260, test sample and reference materials are held in thin-walled quartz crucibles, each 3.8 cm long and 5 mm in diameter. Typically, sample sizes of 50-200 mg are used, depending on test material density. Generally, the crucibles are filled about one-third full. We deviated from this slightly. Known amounts of the reference material (Al_2O_3) were used. However, due to differing test sample densities and heat capacities, differing test sample amounts were used for each test material. The specific heat of aluminum oxide is about 0.13, whereas the specific heat of most grain materials is between 0.25 and 0.45 depending largely on moisture content. We assumed that the specific heat of dry spent brewers grains is about 0.25 and used only one-half as much spent grains, by weight, in the test samples crucibles as aluminum oxide.

Positioning of the thermocouples in the crucibles is critical. The proper method is shown in Fig. (12). Under no circumstances should the

sample contact the insulator of the thermocouple.

The measuring unit of the Model 260 consists of two thermocouples, a zero suppressor, and an accessory 1-mv strip chart recorder. As long as no differential exists between the temperature of the sample and the reference junctions of the differential thermocouple, the recorder traces an even baseline. The moment a temperature differential manifests itself, the difference signal from the differential thermocouple causes the strip chart recorder to deviate from its baseline causing peaks or valleys on the chart. Besides the chemical and physical factors affecting the temperature differential that we noted earlier, differences of particle size, differences in crucible packing, thermocouple positioning, heating rate, and furnace atmosphere may effect the chart readout.

Fig. (14) is typical thermogram for ammonium nitrate. We ran an analysis on ammonium nitrate to check the working order of the Model 260 as previous thermograms of ammonium nitrate are available for comparison. The thermogram we obtained compared favorably with known standards thermograms for NH_4NO_3 . We shall describe in detail this experiment on NH_4NO_3 :

a. The reference material, aluminum oxide, was placed into seven crucibles. The crucibles were then heated to 500°C for one hour to drive off any complexed water which could detract from the reference qualities of the thermally inert pure Al_2O_3 . The crucibles were placed in holes 1, 2, 4, 5, 6, 7, and 8. See Fig. (12).

b. A sample of pure, finely ground ammonium nitrate was weighed and placed in a crucible. The crucible was placed in hole number three of the Inconel Blocks (see Fig. (12)). All crucibles contained approximately the same weight of material.



Figure 12. Proper Thermocouple Positioning.

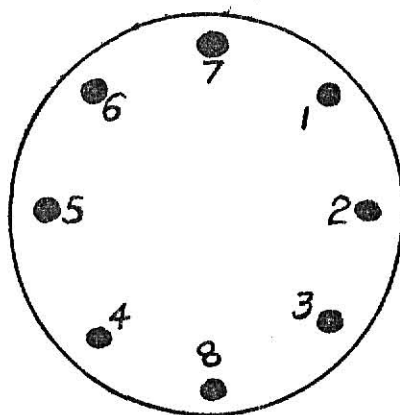


Figure 13. The Inconel Block. Positioning is as follows:

- (1) Control Thermocouple
- (2) Reference Substance # 1
- (3) Sample Substance # 1
- (4) Sample Substance # 2
- (5) Reference Substance # 2
- (6) Remote Block Temperature Monitoring Thermocouple
- (7) & (8) Ballast-- Al_2O_3 .

When holes (4) & (5) are not used for a second sample they are filled as ballast holes (Al_2O_3). The crucibles in (1), (2), (5), (6), (7), & (8) are always filled with a thermally inert substance such as Al_2O_3 .

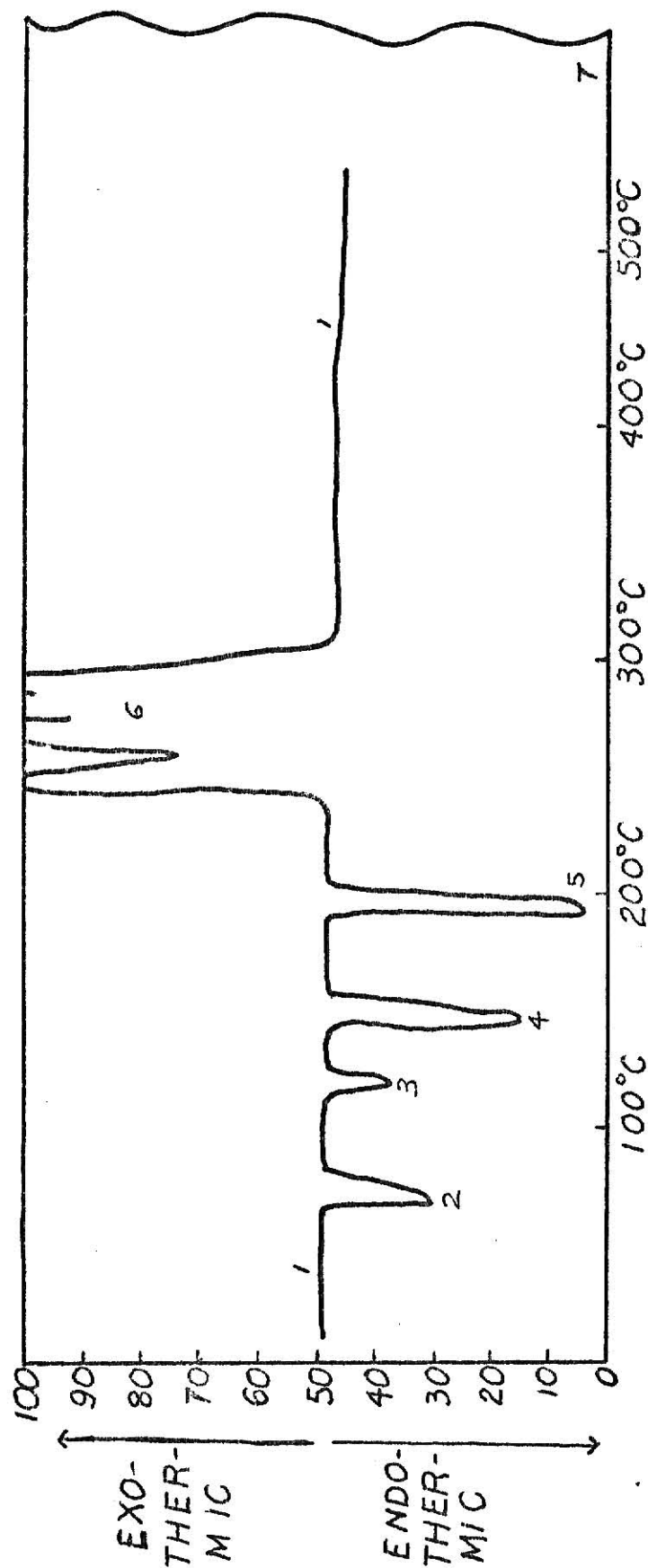


Figure 14. Thermogram for Ammonium Nitrate. Here: (1) represents the baseline, (2) represents the crystalline transition from Rhombic II to Rhombic I, (3) represents the crystalline transition from Rhombic I to Tetragonal, (4) represents the crystalline transition from tetragonal to cubic, (5) represents sample melting, (6) represents sample decomposition, and (7) is the paper output of the strip chart recorder. Additional data: sample used was NH_4NO_3 , sample weight was 120 mg, the reference sample was Al_2O_3 , the heating rate was 10 degrees centigrade per minute, and the differential thermocouple was chromel-alumel.

c. The thermocouple junctions were inserted as shown in Fig. (13). One junction of the differential thermocouple went into hole 3 and the other junction went into hole 2. The thermocouple in hole 6 was attached to a separate millivoltmeter, allowing monitoring of the block temperature at all times.

d. The remaining holes are only "ballast."

e. The sample holding assembly was inserted into the furnace and the appropriate connections and programming settings made. We used a heating rate of 10°C per minute, an upper temperature of interest of 500°C , and an initial programmer temperature setting of 0°C .

f. The strip chart recorder was set to have a baseline at "50," the midline of the chart paper. Time for steady attainment was allowed.

g. The experiment was run, Fig. 14, and the actual and program temperatures were noted on the chart paper about once a minute.

We ran differential thermal analyses on

- (1) Fat-free spent brewers grains
- (2) Commercial spent brewers grains
- (3) Commercial spent brewers grains with added fat
- (4) Soybean meal
- (5) Yellow dent cornmeal
- (6) Wetted spent brewers grains
- (7) Brewers yeast
- (8) Brewers grains with Santoquin added

In all cases only finely ground samples were used. Fat was added by dissolving first in Skelly-F and then mixing the Skelly-F into the grains. Later the Skelly-F was evaporated leaving the fat. A similar process, using mineral oil was used to apply Santoquin.

3.2.2. Soxlet Extraction

A large soxlet extractor was used to separate the oil from approximately fifty pounds of spent brewers grains. Skelly-F solvent was used. The low boiling point was critical to reduce oxidation of the fat during extraction. The defatted spent grains were saved for experimentation.

3.2.3. Heating Ovens

Conventional, commercial air ovens were used for experimentation on heating effects. Another insulated oven, fitted with four 1500 watt strip heaters, a thermostatic control unit connected to the heaters, and thermistors and insulated canisters for six test samples was used. A fan was provided to circulate air in the box and assure homogeneity of temperature within the box. The box was used up to temperatures of 110°C.

The air ovens were used to experiment on spent brewers grains under a variety of conditions; wet, dry, floured, with yeast added, with various chemicals added, steamed, pasturized and rewetted, and so on. Heating conditions varied from using a set box temperature to raising the box temperature at various rates.

3.3. Microbial Experiments

Experiments were made to determine the ability and degree to which spent brewers grains can sustain microbial life. Temperatures of 4°C, 25°C, 38°C, and 50°C were examined in addition to simulated adiabatic heating experiments, where in one instance a temperature of about 65°C was attained. The substrate was varied from normal spent brewers grains by enrichment with yeast or flour, by addition of propionic acid, by adjusting moisture levels, and by pasteurizing the wet, spent grains following in some cases

by subsequent rewetting with distilled water or steam. In all cases the temperature differential between the ambient temperature and the core temperature of the sample was monitored. Where set ambient temperatures were used these differences were recorded, whereas for simulated adiabatic heating experiments these temperature differentials were minimized by adjusting the ambient temperature. All samples were insulated with two inches of fiber glass insulation or were contained in fifty gallon barrels with middlings surrounding the central core. The barrel experiments were protected from the metal of the barrels by plastic sacks to prevent the interference of heavy metal ions.

4. Results and Discussion

4.1. Composition

The particle size distribution of spent brewers grains is shown in Figure (15). Figure (16) lists proximate analyses of unseparated spent brewers grains and of dried brewers yeast. In Figure (17) the overs from each sieve used (Fig. (15)) are analysed for moisture, protein, ash, c-fat, and c-fiber. Figure (18) contains amino acid analyses of the overs of spent brewers grains on a Tyler #10 screen, Figure (19) contains amino acid analyses of the overs of spent brewers grains on a Tyler #20 screen, and Figure (20) contains amino acid analyses of the overs of spent brewers grains on a Tyler #150 screen. Figure (21) contains moisture and protein analyses on another sieve test.

Frozen, wet, spent brewers grains were freeze-dried to determine whether the commercial drying process decreases the fat level of dried spent brewers grains. Figure (22) contains a proximate analysis on these grains and on the defatted grains obtained by Skelly-F soxlet extraction.

Tyler Screen Number	Diameter, μ	% Overs
#10	1680	10.6
#14	1190	8.5
#20	841	10.4
#28	595	9.3
#35	420	8.4
#48	297	7.8
#65	210	9.2
#100	149	6.3
#150	105	6.6
#200	74	9.4
#270	53	10.3
Pan	<53	3.0
		96.3% Recovery

Figure 15. Tyler Sieve Distribution for Sieved Spent Brewers Grains.

	SBG1	SBG2	SBG3	BDY1	BDY2
Moisture	5.7	4.2	6.3	6.3	7.0
Protein	24.7	22.15	23.9	52.9	51.2
Ash	5.2	4.4	4.9	6.9	7.1
Fat	3.5	6.9	7.2	0.2	0.5
Fiber	15.8	13.0	14.1	3.1	2.9

Figure 16. Proximate Analysis of Spent Brewers Grains (three samples) and of Brewers Dried Yeast (two samples).

Amino Acids	% Sample G Per 100 G Sample Moisture Free	G AA Per 100 G KJELD Protein
Lysine	0.390	3.176
Histidine	0.231	1.884
Ammonia	0.150	1.219
Arginine	0.474	3.866
Aspartic Acid	0.813	6.627
Threonine	0.375	3.058
Serine	0.517	4.215
Glutamic Acid	2.223	18.113
Proline	0.880	7.168
Glycine	0.492	4.011
Alanine	0.562	4.583
Half Cysteine	0.305	2.488
Valine	0.628	5.116
Methionine	0.041	0.337
Isoleucine	0.375	3.060
Leucine	0.763	6.218
Tyrosine	0.146	1.189
Phenylalanine	0.405	3.304

Figure 18. Amino Acid Analysis of Spent Brewers Grains Overs for Tyler #10 Screen. Protein on Moisture Free Basis = 12.27.
Moisture Content = 7.1. Recovery Protein = 79.63%.
Recovery Nitrogen = 69.98%.

Amino Acids	% Sample G Per 100 G Sample Moisture Free	G AA Per 100 G KJELD Protein
Lysine	0.338	2.876
Histidine	0.180	1.529
Ammonia	0.144	1.228
Arginine	0.551	4.684
Aspartic Acid	0.780	6.630
Threonine	0.366	3.110
Serine	0.462	3.927
Glutamic Acid	1.866	15.867
Proline	0.852	7.245
Glycine	0.509	4.331
Alanine	0.434	3.687
Half Cysteine	0.149	1.270
Valine	0.446	3.795
Methionine	0.022	0.186
Isoleucine	0.369	3.139
Leucine	0.692	5.887
Tyrosine	0.250	2.123
Phenylalanine	0.499	4.241

Figure 19. Amino Acid Analysis of Spent Brewers Grains Overs for Tyler #20 Screen. Protein on Moisture Free Basis = 11.76. Moisture Content = 7.30. Recovery Protein = 75.76%. Recovery Nitrogen = 67.98%.

Amino Acids	% Sample G Per 100 G Sample Moisture Free	G AA Per 100 G KJELD Protein
Lysine	2.738	6.125
Histidine	1.175	2.628
Ammonia	0.909	2.034
Arginine	5.202	11.636
Aspartic Acid	2.842	6.357
Threonine	1.202	2.687
Serine	1.616	3.615
Glutamic Acid	7.031	15.726
Proline	3.073	6.873
Glycine	1.564	3.499
Alanine	1.915	4.284
Half Cysteine	0.939	2.100
Valine	1.804	4.036
Methionine	0.533	1.192
Isoleucine	1.470	3.289
Leucine	2.722	6.089
Tyrosine	1.013	2.266
Phenylalanine	1.794	4.012

Figure 20. Amino Acid Analysis of Spent Brewers Grains Overs for Tyler #150 Screen. Protein on Moisture Free Basis = 44.71.
Moisture Content = 7.40. Recovery Protein = 88.45%.
Recovery Nitrogen = 91.60%.

Tyler Screen Overs	Moisture Content	Protein
#10	7.1	11.7
#14	7.8	13.4
#20	7.3	10.9
#28	7.1	11.2
#35	7.7	21.1
#48	7.4	31.3
#65	7.4	38.3
#100	7.3	38.4
#150	7.4	41.4
#200	7.7	41.2
#270	7.9	36.8
Pan	8.2	25.2

Figure 21. Analysis of Overs on Various Tyler Sieves.

Material	Moisture Content	Fat
Freeze-dried Grains	8.4	6.2
Extracted Grains	4.2	0.5

Figure 22. Proximate Analysis of Frozen Wet Spent Brewers Grains that were Freeze-dried, and of Skelly-F Defatted Spent Brewers Grains.

Using the data of Figure (15) and the methods of Headly and Pfof (155), a particle size analysis was done for spent brewers grains. Figure (23) contains this analysis, which indicates an average particle size of 342μ .

We must point out that this method has no real theoretical basis for spent brewers grains as the method assumes log normal distribution of particle size as distributed by weight fractions. For most pure grain materials this assumption is nearly valid. However, for materials such as oats the assumption is not valid. In oats, the hulls and the endosperm tend to show up as two separate log normally distributed fractions. Spent brewers grains appear to be a mixture of two or more log normally distributed fractions also. The hulls, the yeast, and the grain endosperm material are three possible separate sources of unique log normally distributed fractions.

In Figure (16) we note that brewers dried yeast has a very low fat content. The spent brewers grains we tested contained six to seven percent fat except for one early shipment. The high protein level of brewers yeast may account for the high protein contents of finer particles.

From Figure (17) we can see that the overs on the middle Tyler sieves contain higher amounts of protein and fat, whereas the overs on the larger Tyler sieves contain higher fiber contents, probably due to the barley hulls and hops.

The fact that fat is concentrated in the smaller particles of spent brewers grains may influence heating of the grains, if separation of the material by particle size occurs during storage.

Fresh, wet grains were freeze-dried, and analyzed for fat to determine if the fat content could be lowered by the processing technique used to dry them. Figure (22) indicates that this is probably not the case.

Screen	d, μ	W _i , gms	P _i , %	ΣP_i , %	$\log d_i$	W _i $\log d_i$	($\log d_i - \log d_{gw}$)	w($\log d_i - \log d_{gw}$) ²
#10	1680	10.2	10.6	91.7	3.301	33.7	0.767	6.0
#14	1190	8.2	8.5	83.2	3.149	25.8	0.615	3.1
#20	841	10.0	10.4	72.8	3.000	3.0	0.466	2.2
#28	595	9.0	9.3	62.5	2.849	25.5	0.315	0.9
#35	420	8.1	8.4	53.2	2.699	21.8	0.165	0.2
#48	297	7.5	7.8	44.8	2.549	19.1	0.015	0.0
#65	210	8.9	9.2	35.6	2.398	21.2	-0.136	0.2
#100	149	6.1	6.3	29.3	2.248	13.6	-0.286	0.5
#150	105	6.4	6.6	22.7	2.097	13.3	-0.437	1.2
#200	74	9.1	9.4	13.3	1.944	17.6	-0.590	3.2
#270	53	9.9	10.3	3.0	1.799	17.8	-0.735	5.3
Pan	<53	2.9	3.0	-	1.643	4.7	-0.900	2.3
Totals		96.3	99.8			244.1		25.1

Figure 23. Particle Size Analysis on Spent Brewers Grains.

$$\log d_{gw} = \Sigma W_i \log d_i / \Sigma W_i = 2.534 \quad d_{gw} = 342 \mu$$

$$(\log S_{gw})^2 = \Sigma W_i (\log d_i - \log d_{gw})^2 / \Sigma W_i = 0.26$$

$$\log S_{gw} = 0.5105 \quad S_{gw} = 3.24$$

Taken in full, our data agrees well with previous data on spent brewers grains (8, 9, 10, 11). The analyses of the overs of the Tyler screens, Fig. (17), are also as would be expected. The coarser material, mainly barley hulls and hops is high in fiber and low in fat and protein. The finer material, presumably containing some yeast, is high in fat and protein.

4.2. Heating Studies With Dry Brewers Grains

A variety of experiments were performed in this section. In some, set ambient temperatures were used, while in others near adiabatic heating was simulated. Finally, the experimental technique of differential thermal analysis (DTA) was applied.

All treatments labeled extra fat were samples of normal, commercial spent brewers grains to which had been added extra fat. The fat added was extracted previously from other spent brewers grains by soxlet extraction with Skelly-F. The treatments labeled normal were commercial spent brewers grains, while the treatments labeled defatted were the grains from which fat had been extracted. Finally, treatments labeled Santoquin (74) were ones which had been treated with the antioxidant Santoquin.

4.2.1. 15°C and 25°C

Samples were placed in 5" by 9" metal containers having friction sealing lids. The cans were surrounded by two inches of insulation and were equipped with an 1/8" hole for thermistor placement. Samples were placed in air ovens with an ambient temperature of 15°C or 25°C. Only very dry spent brewers grains (6 to 8%, wet basis, moisture) were used and no significant heating was observed. We conclude that as long as moisture levels are controlled spent brewers grains may be stored safely

at ambient temperatures at or below 25°C. Figure (24) shows representative examples. As no temperature rises were observed experiments with Santoquin and varying fat levels were not performed at these ambient temperatures.

4.2.2. 40°C

Cans and treatments were as above but an ambient temperature of 40°C was selected. Figure (25) and Figure (26) show representative examples.

Note that heating occurs in the normal and extra fat samples, possibly somewhat more so in the cases of extra fat, but that the defatted and Santoquin treated samples display only negligible heating. Apparently, defatting or Santoquin addition will retard heating in spent brewers grains stored in bulk at an ambient temperature of 40°C. Our Santoquin addition levels were purposely high (0.25% here) to guard against the possibility of preferential oxidation of the antioxidant masking its effects.

4.2.3. 60°C

Can and treatments were as above but an ambient temperature of 60°C was used. Figure (27) and Figure (28) show representative examples.

The trends are similar to those at 40°C, however at this ambient temperature we notice a definite heating over the ambient in Santoquin and defatted samples. However, the antioxidant and defatting again retard the heating displayed by the normal and extra fat samples.

4.2.4. 86°C

Here 8" by 9" cans were used and no insulation was provided. Ambient temperature was 86°C and treatments were as above. Figure (29) details our results.

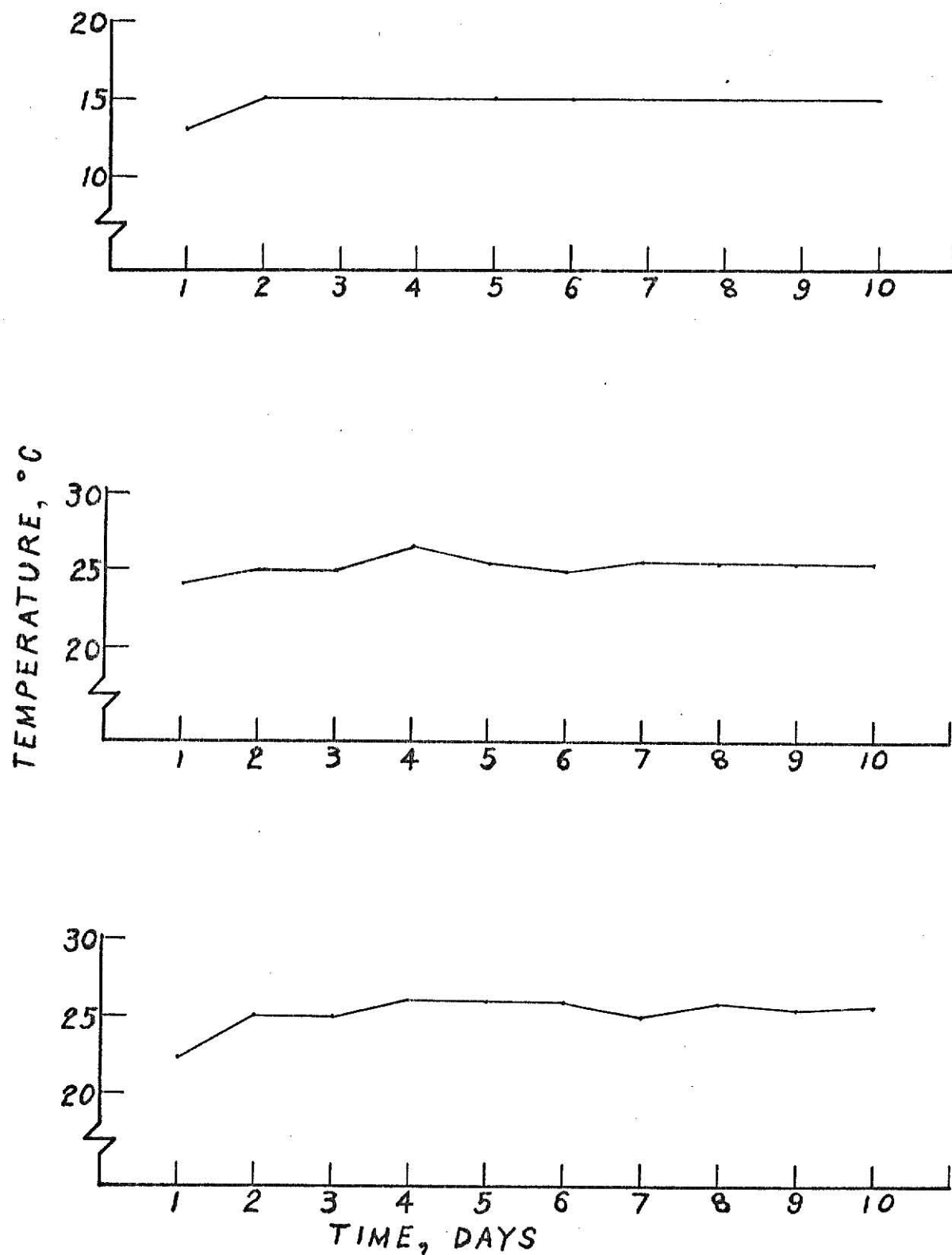


Figure 24. Heating Studies, 15°C and 25°C. All samples are normal. The top graph is for an ambient temperature of 15°C, while the bottom two graphs are for an ambient temperature of 25°C. All vertical axes are temperature°C and all horizontal axes are time, days.

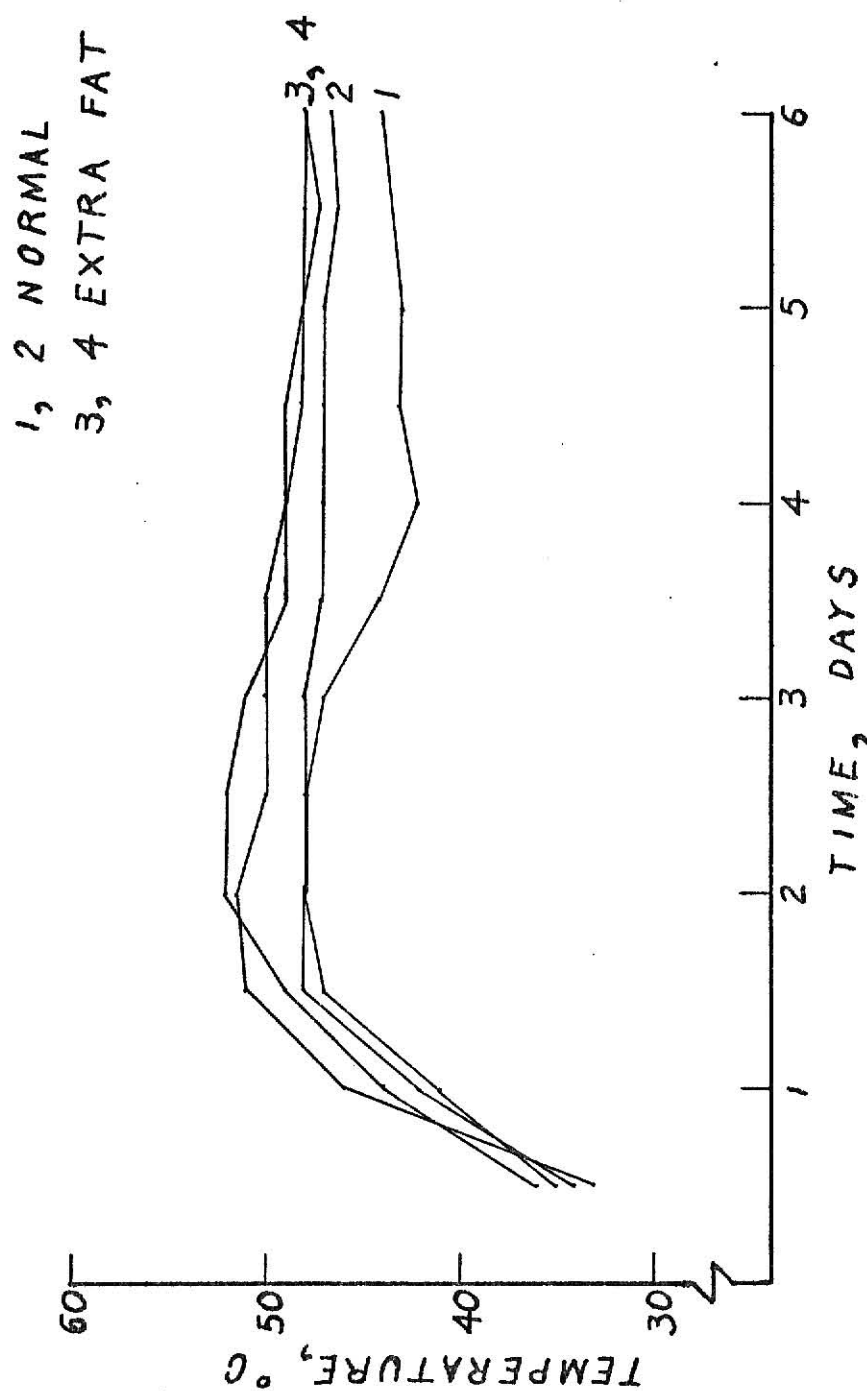


Figure 25. Heating Studies, 40°C

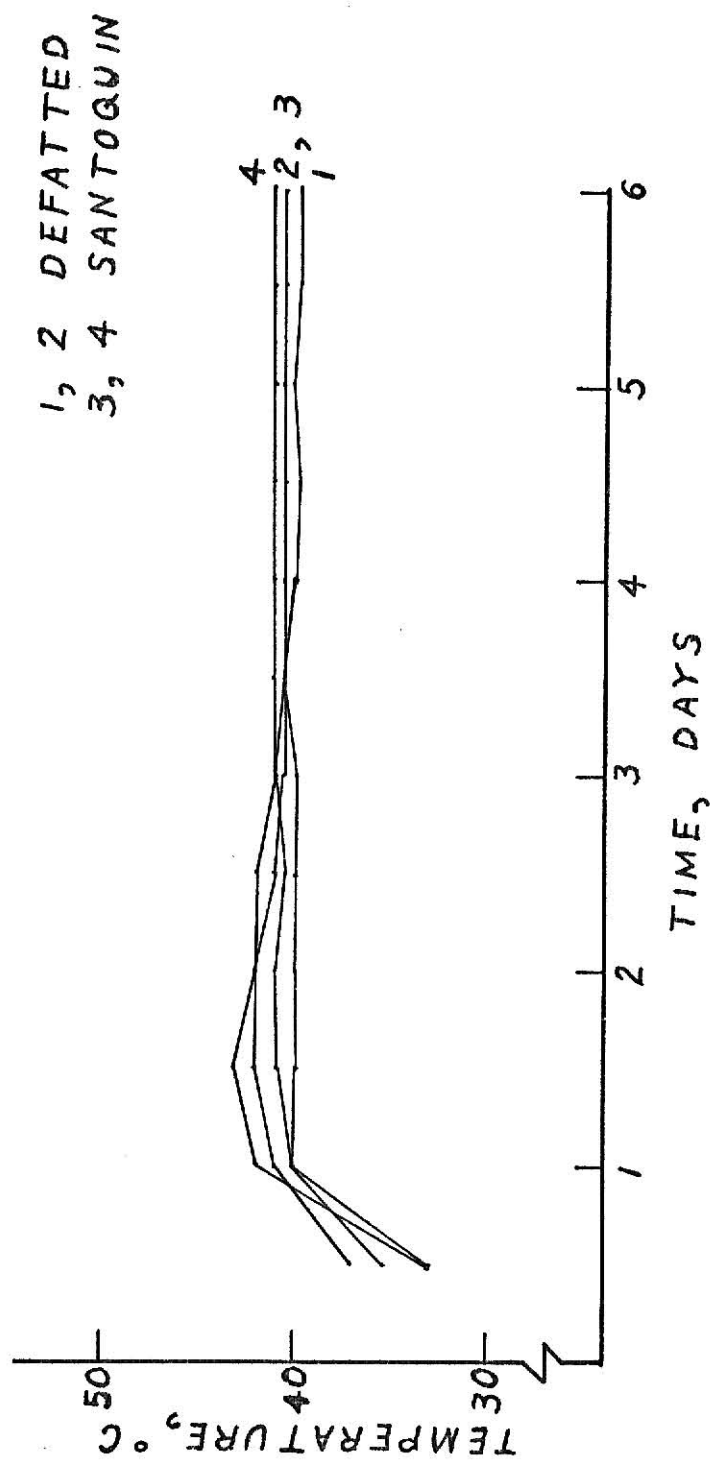


Figure 26. Heating Studies, 40°C

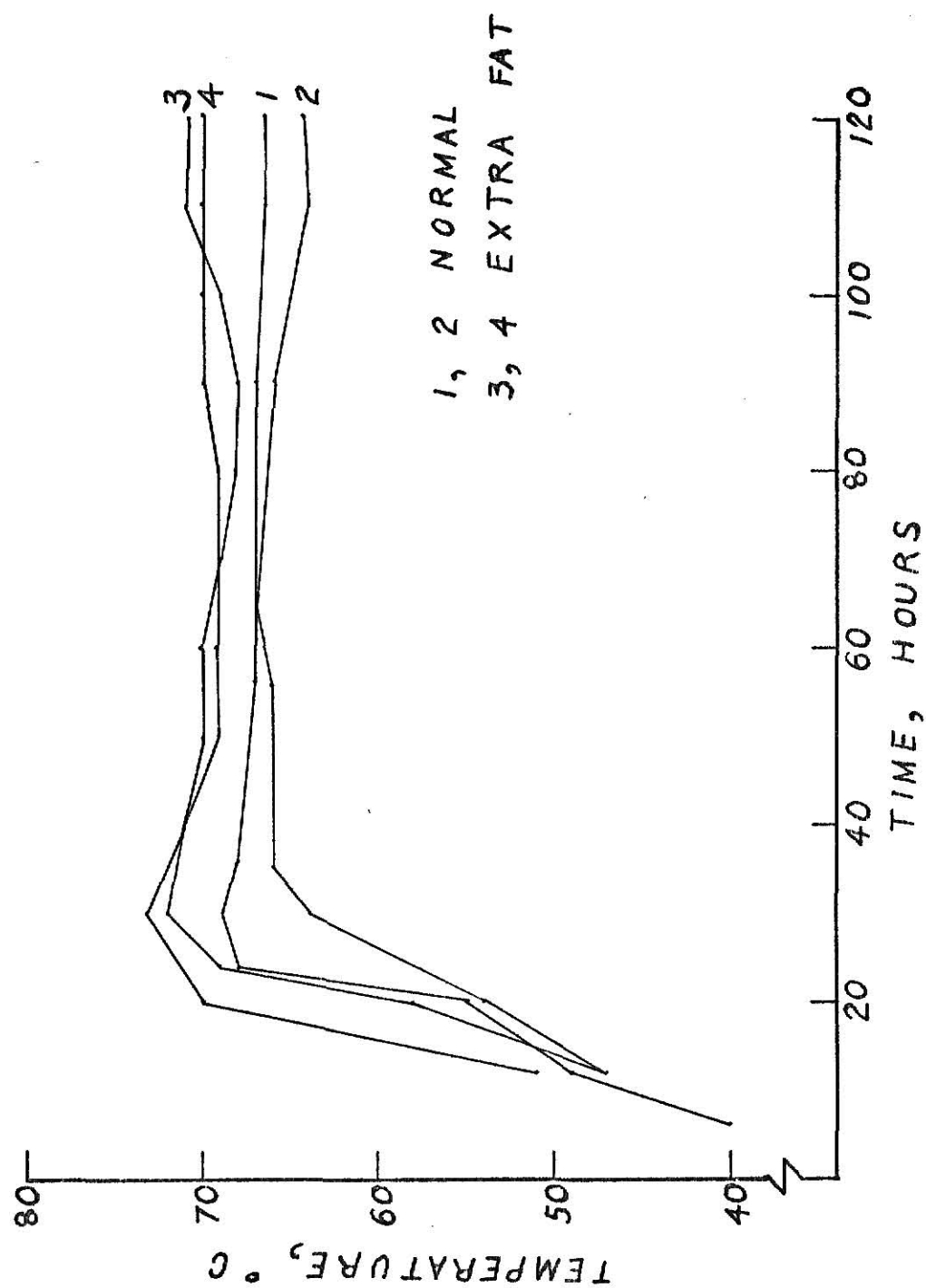


Figure 27. Heating Studies, 60°C

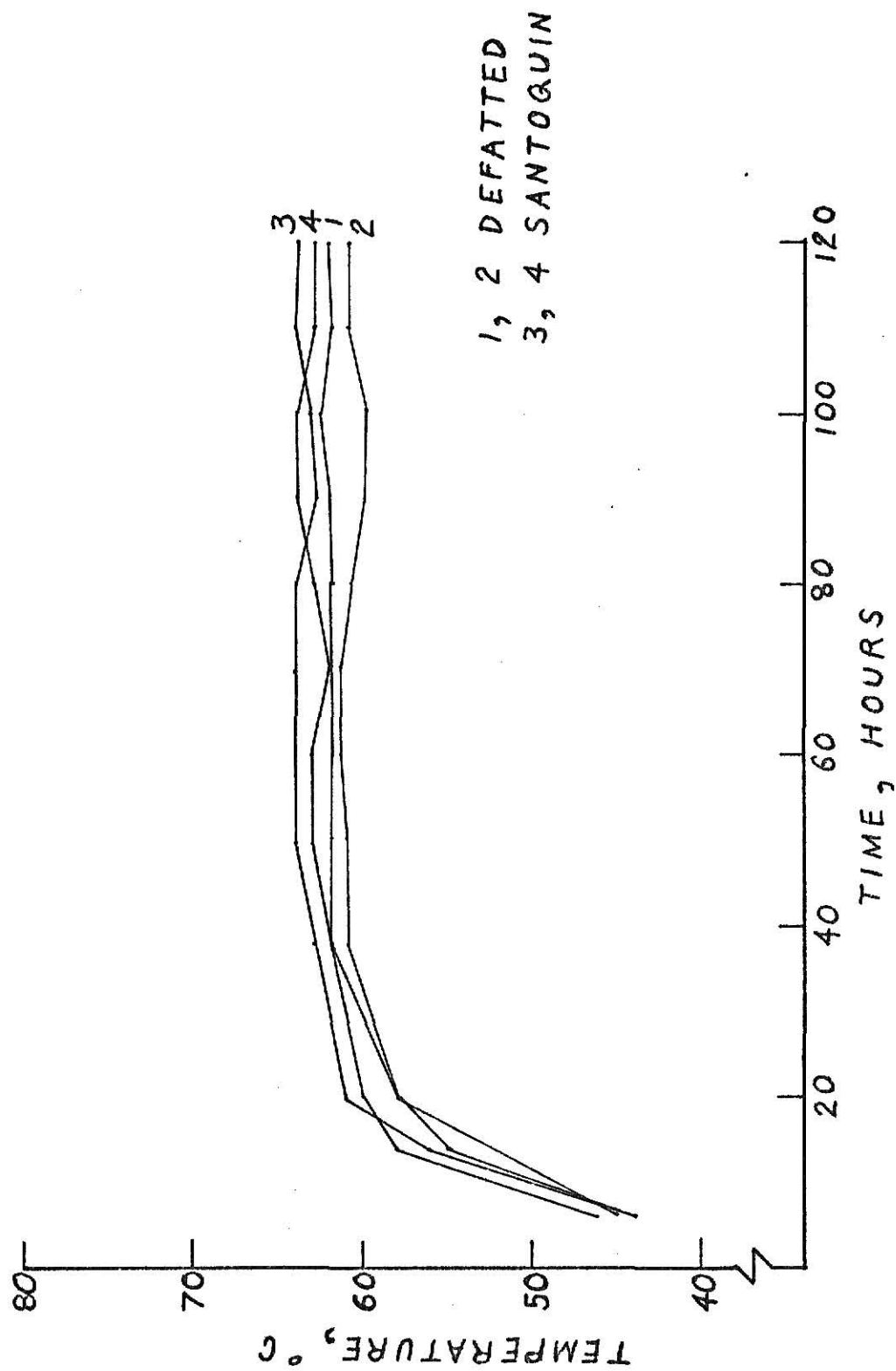


Figure 28. Heating Studies, 60°C

There is considerable heating in the normal sample and definite, though reduced heating in the defatted example. After thirty-one days the core temperature of the normal sample was still $> 110^{\circ}\text{C}$ (our telethermometer only allowed temperature measurement to 110°C), and upon subsequent sample removal, the normal sample was pungent smelling, very brittle, slightly charred, and had lost about 16% of its original weight, where only 6% could be accounted for as moisture loss. The defatted sample was normal in appearance. Clearly, oxidation occurs in spent brewers grains at an ambient temperature of 86°C . While fat oxidation (see Figure 29) appears to be a major component of this oxidation other oxidations are clearly involved (also see Figure 29).

4.2.5. 93°C

Can and treatments were as in 4.2.4 only here extra fat samples and Santoquin samples were tested and an ambient temperature of 93°C was used. Figure (30) shows our results.

The trend is the same as at 86°C . Santoquin addition and defatting retard the oxidation of spent brewers grains. Large levels, 0.5%, of Santoquin were again used as before.

Upon sample removal, the extra fat sample was very charred, very brittle, had a pungent odor, and had lost about 30% of its weight and volume. The Santoquin sample was only slightly charred.

4.2.6. Differential Thermal Analysis

DTA's were done for several treatments of spent brewers grains as described above, and for yellow dent corn, brewers dried yeast, and 44% soybean meal. Figures (31) through (41) show representative DTA's.

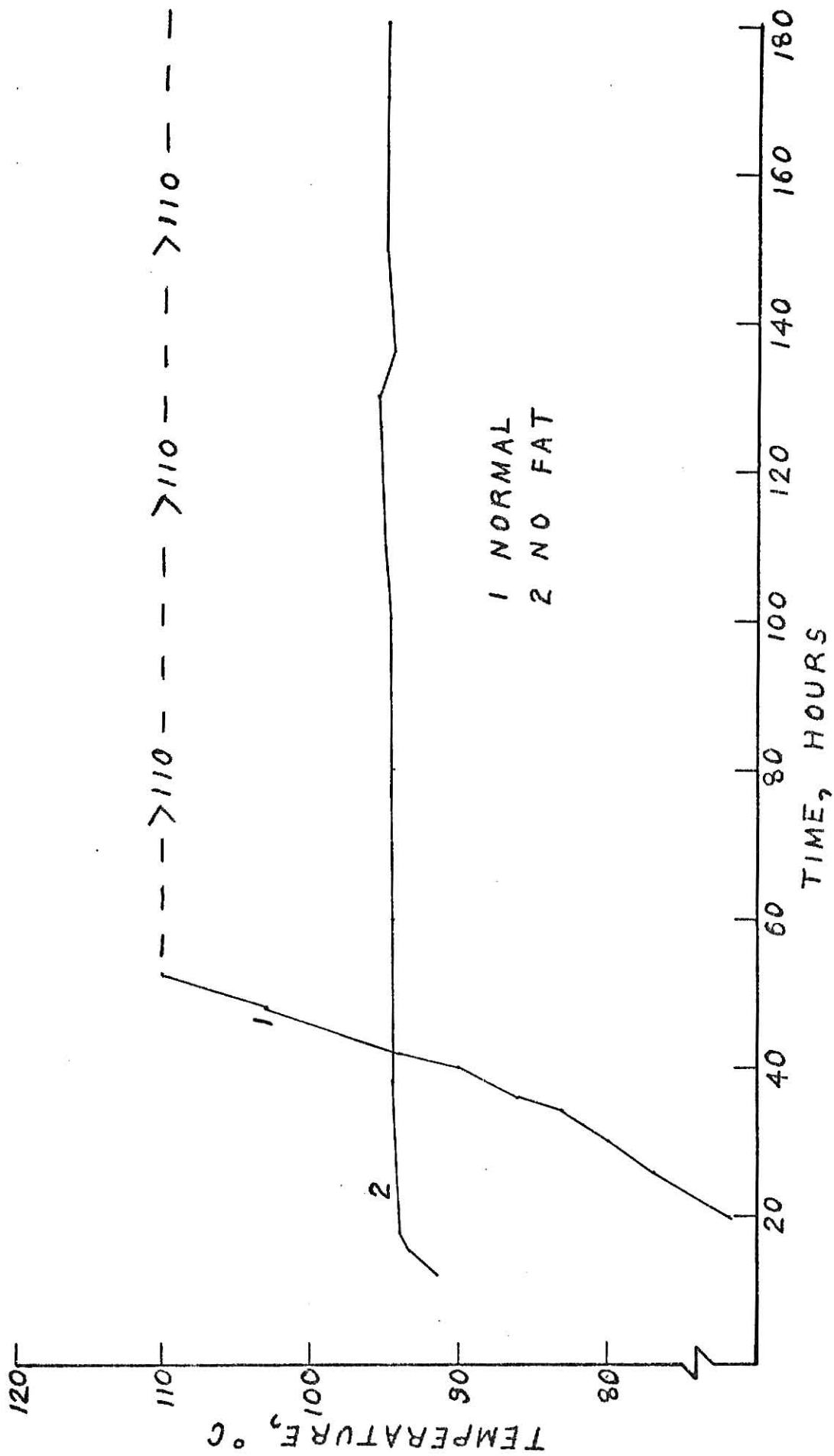


Figure 29. Heating Studies, 86°C

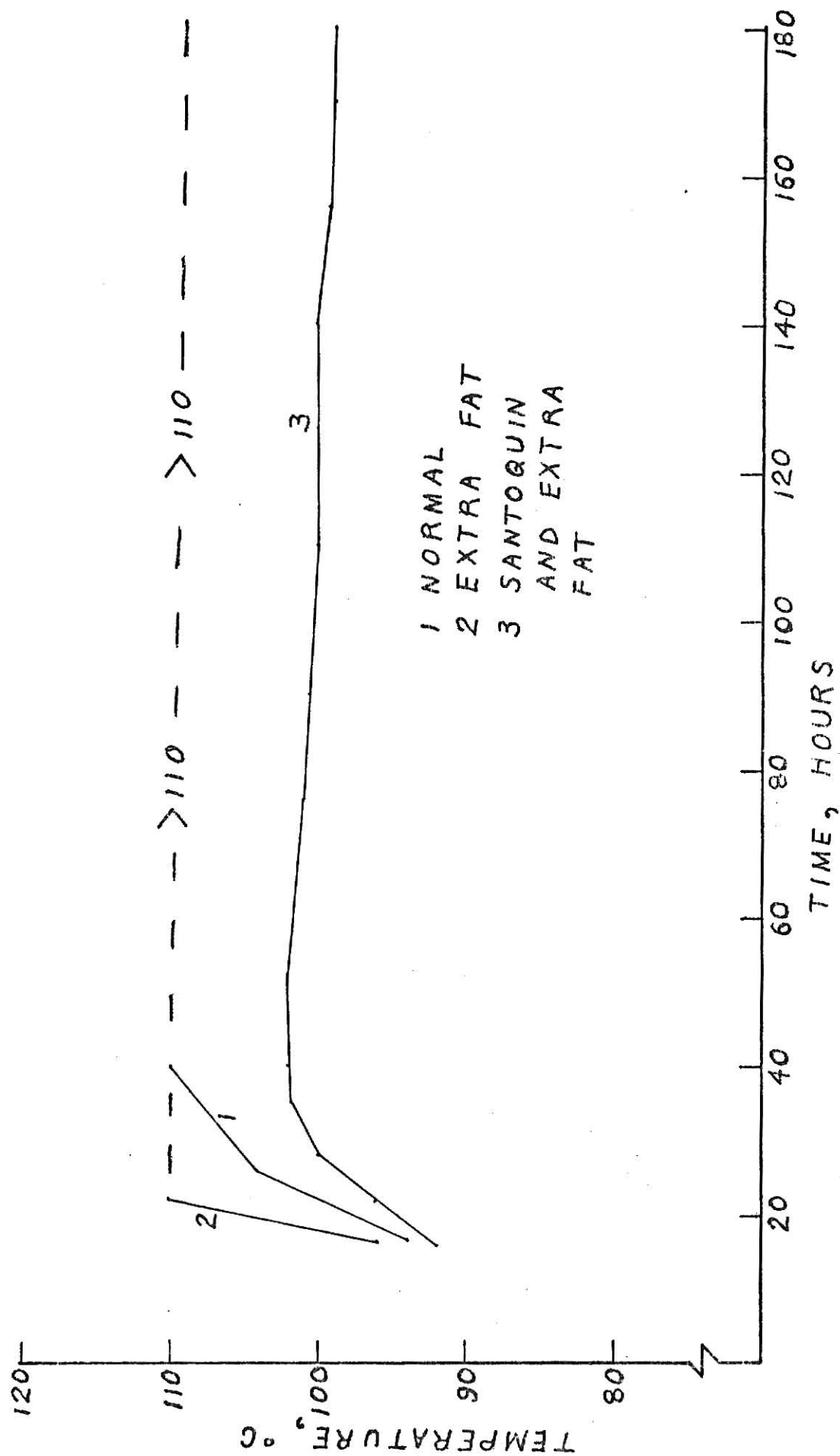


Figure 30. Heating Studies, 93°C

In these figures the baseline is the horizontal "50" line - the midline. On each DTA the directions of endotherms and exotherms are shown as vertical lines near the center of each analysis. Included on all plots are actual block temperature readings as the bottom line of numbers. Where significant differences arose between the actual block temperature and the program setting, the programmed temperatures are shown as the upper line of readings. Any difference between the two is ideally due only to the reacting samples.

For all plots the instrumentation was set as follows:

initial temperature ----- 0°C

initial room temperature ----- about 25°C

heating rate ----- $10^{\circ}\text{C/minute}$

Span ----- 1 mv

Zero Range ----- 0 to -100

From Figure (31), a DTA of brewers dried yeast, we see a thermogram of a material that should present no special heating problems during storage. The fat level of brewers dried yeast is 0.5%, by weight, which would eliminate fat autoxidation as a factor in heating. Note the little exothermic peak at about 130°C . We shall see this little peak in other materials also. As DTA baselines can drift with time, it is difficult to conclude much else about brewers dried yeast except that ignition probably occurred at about 290°C . Apparently, the addition of brewers dried yeast to spent brewers grains will not enhance heating in spent brewers grains.

From Figure (32), a DTA of yellow dent corn, we see a more reactive sample than in Figure (31). The peaks are larger, more erratic and a larger proportion of the curve is on the exothermic half of the plot.

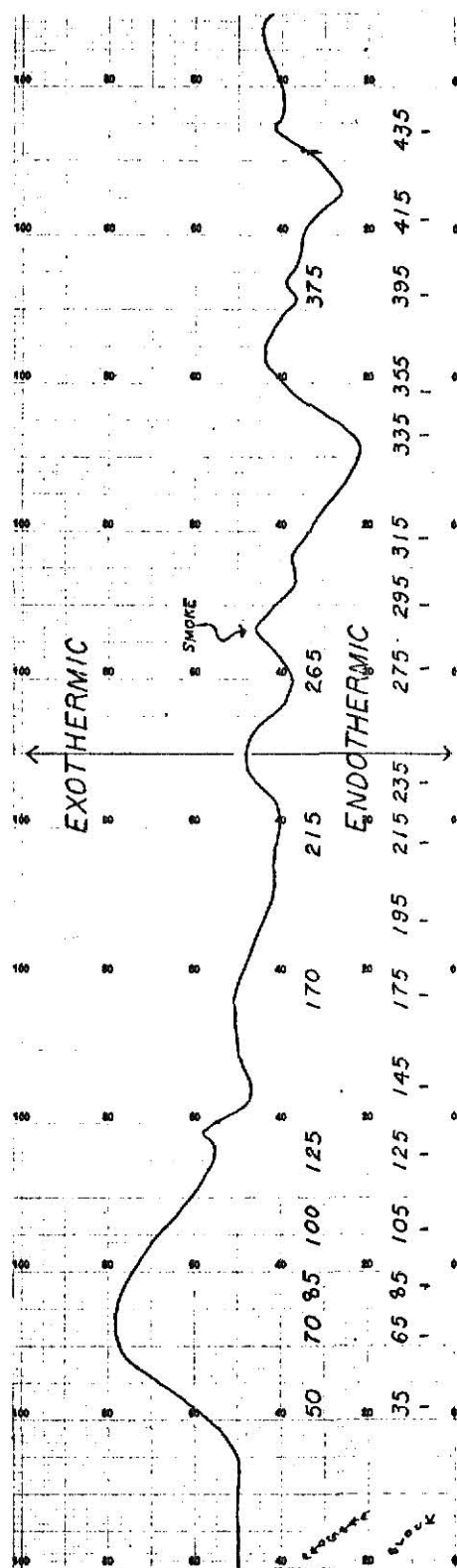


Figure 31. DTA, Brewers dried yeast.

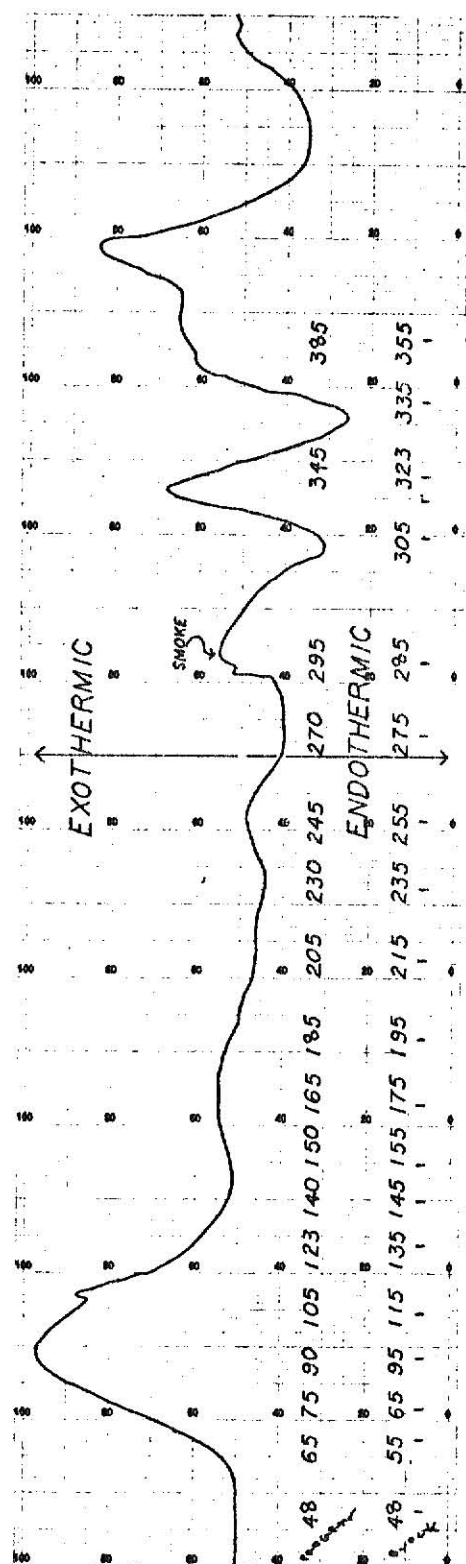


Figure 32. DTA, yellow dent corn.

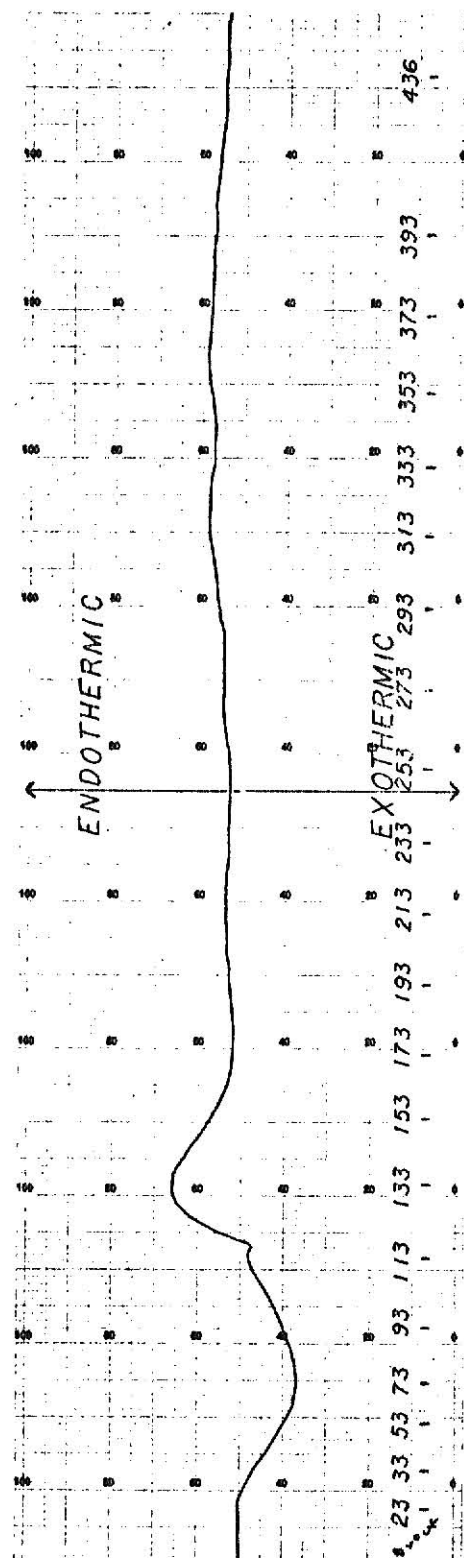


Figure 33. DTA, soybean meal, 44%.

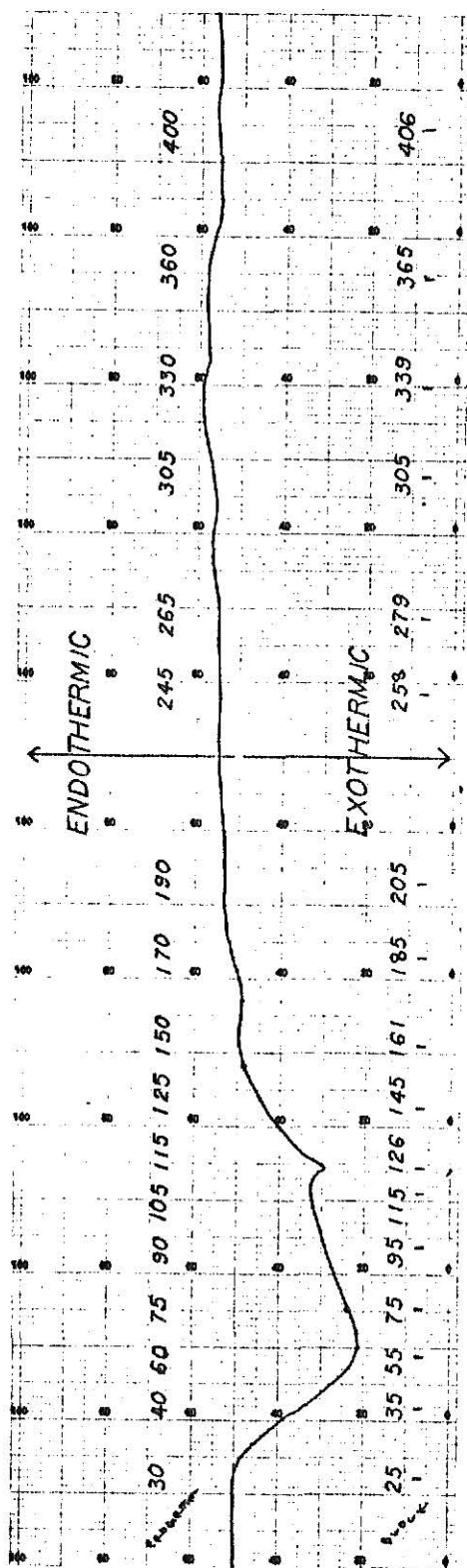


Figure 34. DTA, defatted spent brewers grains.

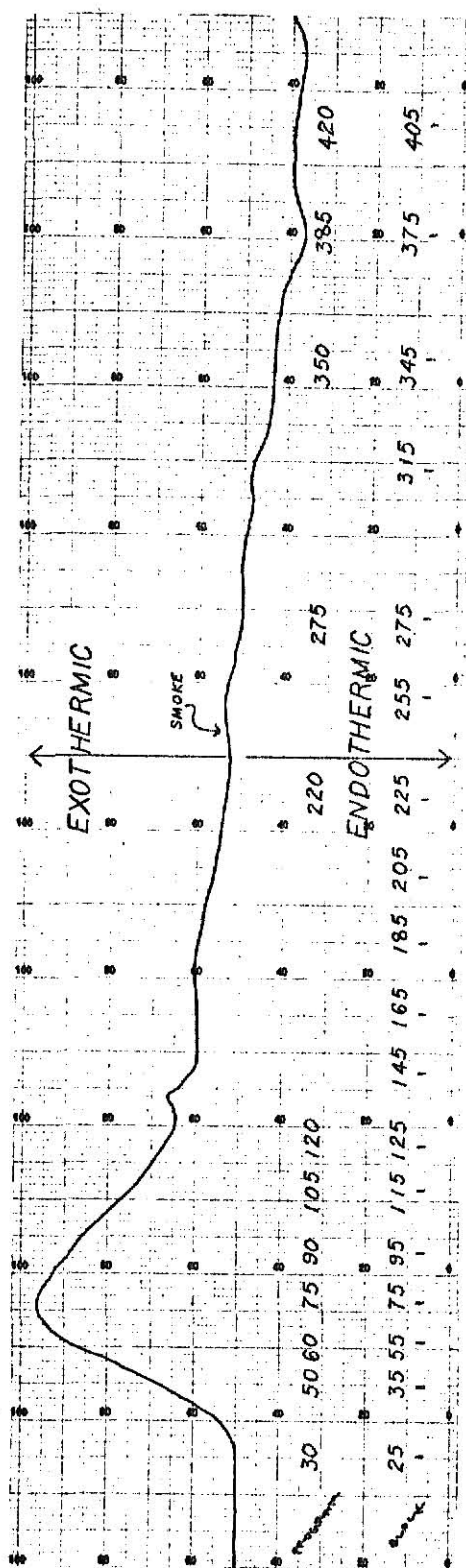


Figure 35. DTA, spent brewers grains.

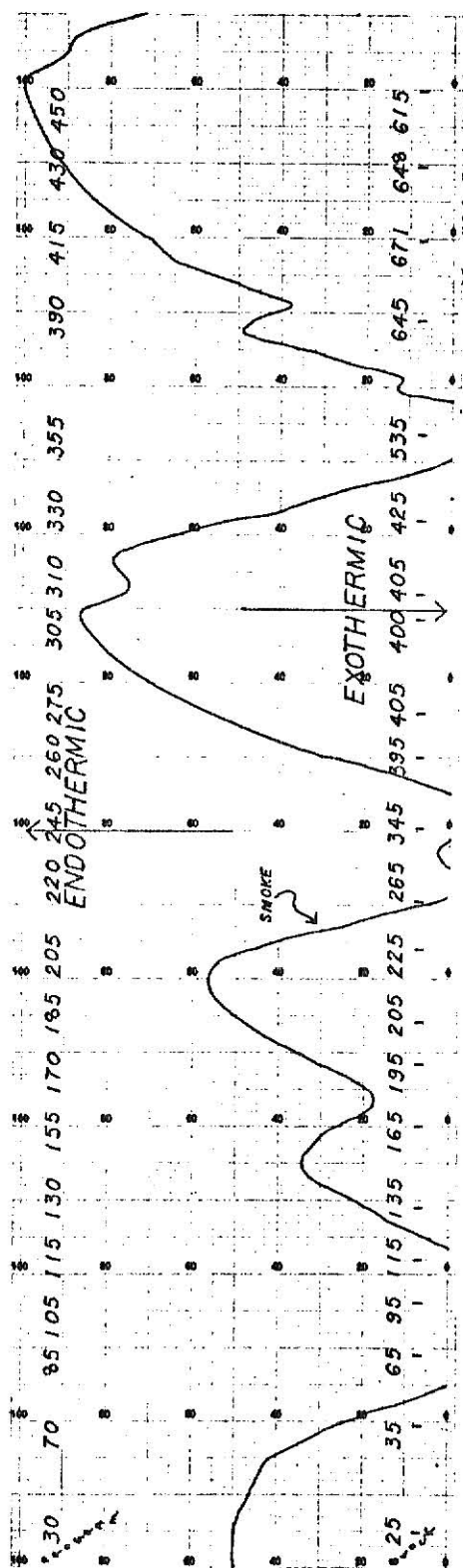


Figure 36. DTA, spent brewers grains.

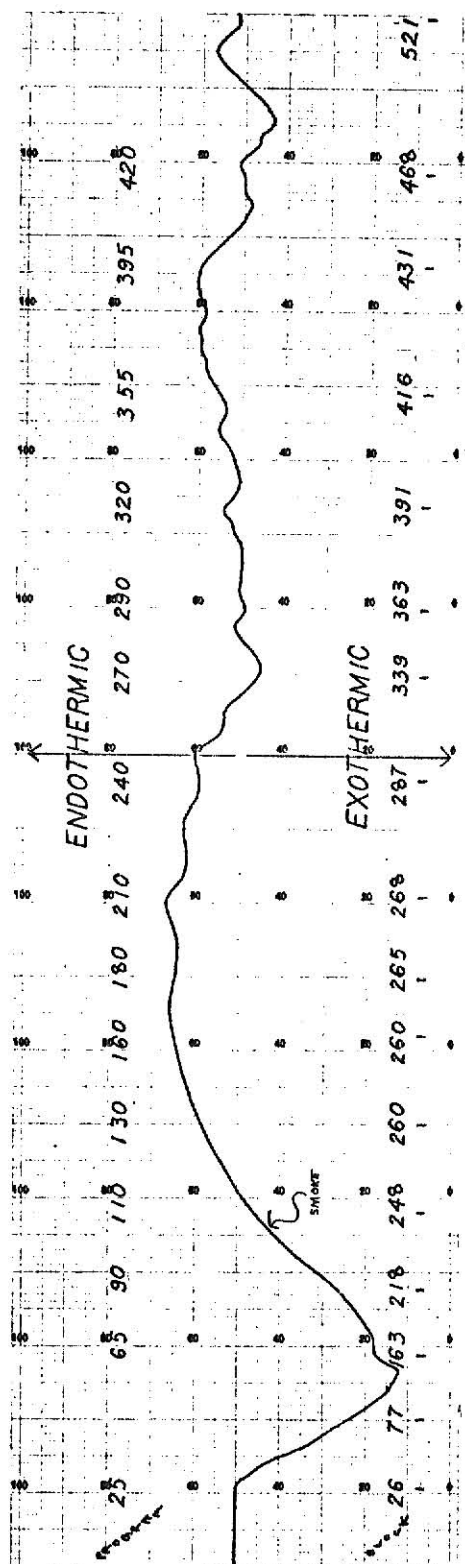


Figure 37. DTA, spent brewers grains, 4X fat.

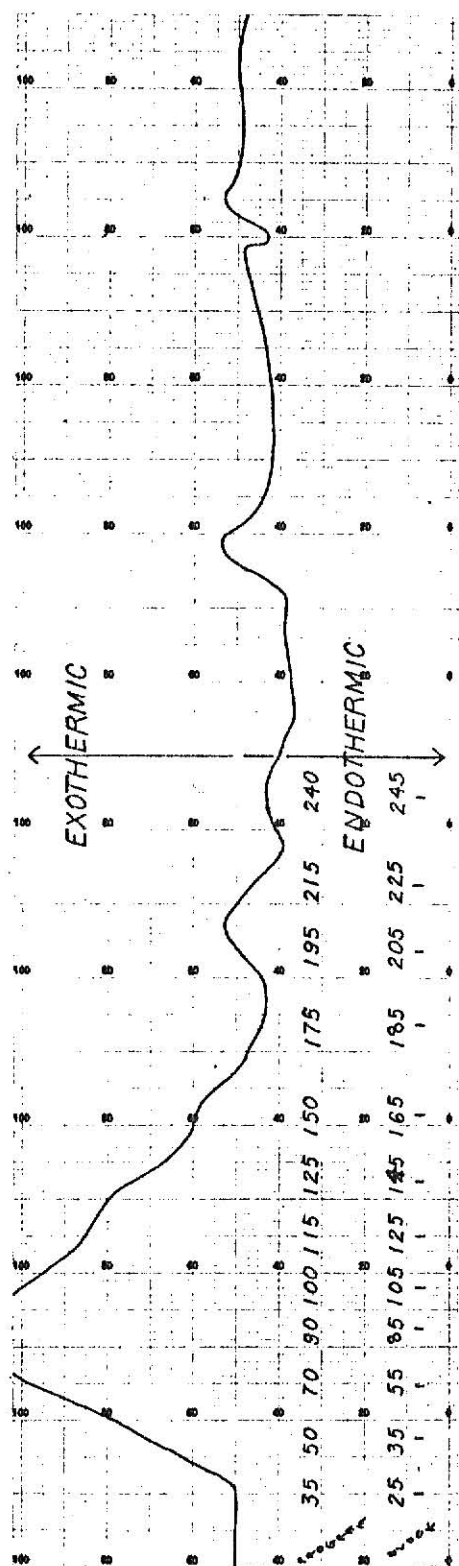


Figure 38. DTA, spent brewers grains, 4X fat.

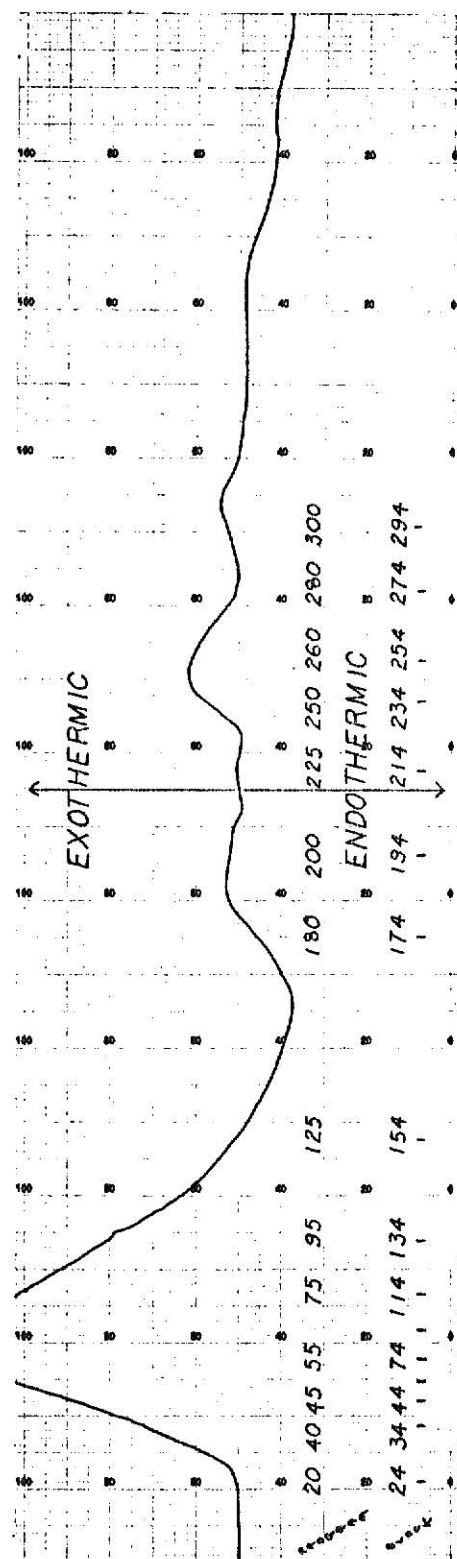


Figure 39. DTA, spent brewers grains, 4X fat, 0.5% Santoquin. Analyzed immediately after treatment.

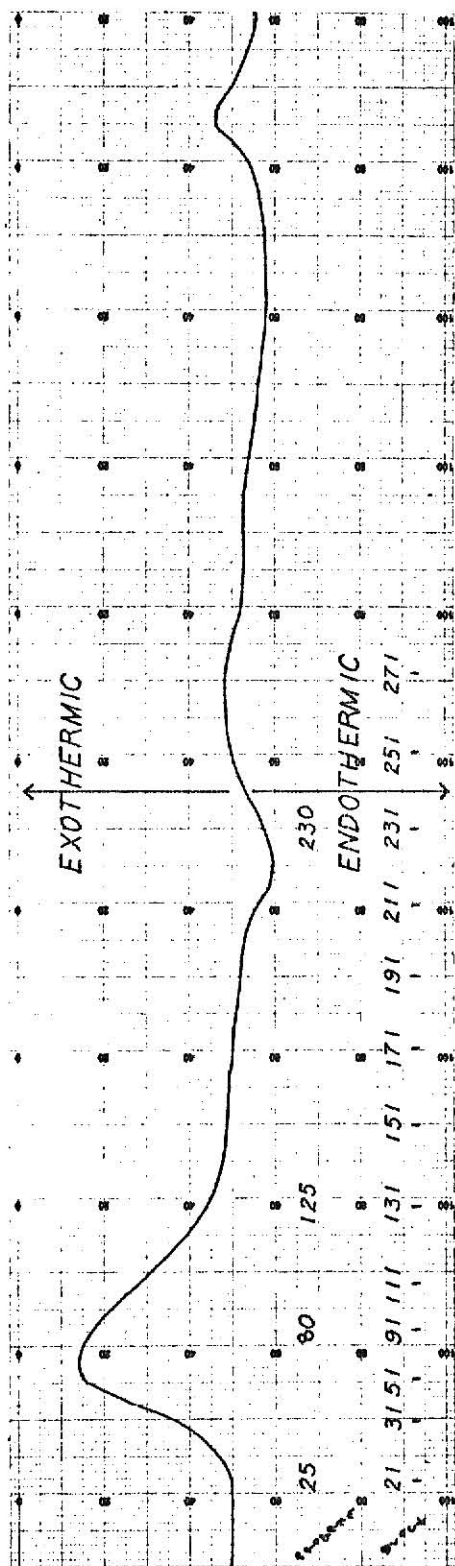


Figure 40. DTA, spent brewers grains, 4X fat, 0.5% Santoquin. Analyzed after 48 hours.

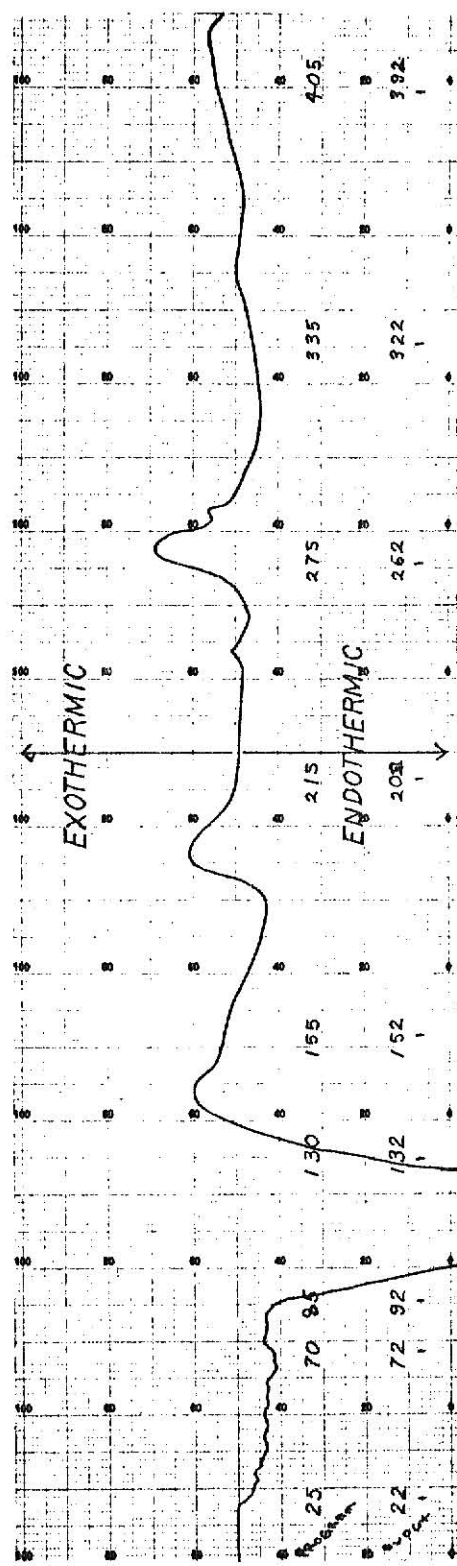


Figure 41. DTA, spent brewers grains with 19% moisture (wet basis).

Note the characteristic peak again at about 115°C . Possibly, the fat level of corn (about 3.5%) is high enough to facilitate some autoxidation of fat in corn. Ignition appeared to occur at about 295°C .

Figure (33) is a DTA for 44% soybean meal. Note the small exotherm area followed by an endotherm that would tend to "stop" any spontaneous heating in soybean meal.

The above materials were analysed to see if our preconceptions of their storability were similar to what we could conclude from their DTA's.

Figure (34) is a DTA for defatted spent brewers grains. All DTA's for defatted spent brewers grains were similar and only one sample produced significant temperature differences between the block and program temperature. Note the little exotherm again at about 125°C . We concluded that defatted spent brewers grains will not heat significantly since the first exotherm is no greater than for corn.

Of the DTA's we ran on commercial spent brewers grains we include two -- Figure (35) and Figure (36). They represent the least and most reactive cases we observed. Typically, these DTA's had larger peaks, more exothermic area per plot, and produced temperature differentials between the block and the program of 30° to 50°C . Figure (36) heated radically above 225°C after not heating significantly at lower temperatures. This was the only sample to display this radical heating above 225°C . Ignition in both cases took place at about 240°C , a lower figure than in the DTA's for Figures (31) through (34).

Figures (37) and (38) are DTA's for extra fat spent brewers grains. The fat was at about four times normal level. In general, the curves were more violent (off the chart more) and produced temperature differentials between the program and block temperatures of between 30 and 75°C .

Behavior was, however, erratic. Ignition again occurred at the somewhat low value of 240°C .

Two DTA's, Figure (39) and Figure (40) are shown for which Santoquin was added to extra fat spent brewers grains. In Figure (39) the DTA was performed immediately after the antioxidant was added, whereas in Figure (40), forty-eight hours had elapsed. Apparently time is required for the Santoquin to penetrate the material and become effective.

In Figure (41) we see the effect of extra moisture (13%) on the DTA of commercial spent brewers grains. Evaporation of the water caused an early endothermic reaction.

Figure (42) contains plots of the temperature differential between program and block temperature vs. program temperature for the most radical DTA's of defatted, normal and 4X extra fat samples of spent brewers grains. Note the trend below 150°C for the samples with more fat to heat more. We included the one normal sample also to display its truly remarkable heating above 200°C .

4.3. Microbial Investigations with Wet Brewers Grains

For these tests, wet brewers grains were collected after pressing and frozen immediately. They were kept frozen until used in tests.

4.3.1. Experiments at 4°C

Samples of wet spent brewers grains at 50% moisture content, wet basis, were prepared for future experimentation by packing the spent grains into insulated cans. The sample containers (metal ones similar to three-pound coffee cans in size and equipped with friction sealing lids with a small hole to permit thermistor or thermocouple passage) were placed in a walk-in cooler at 4°C . After one month of storage the containers showed

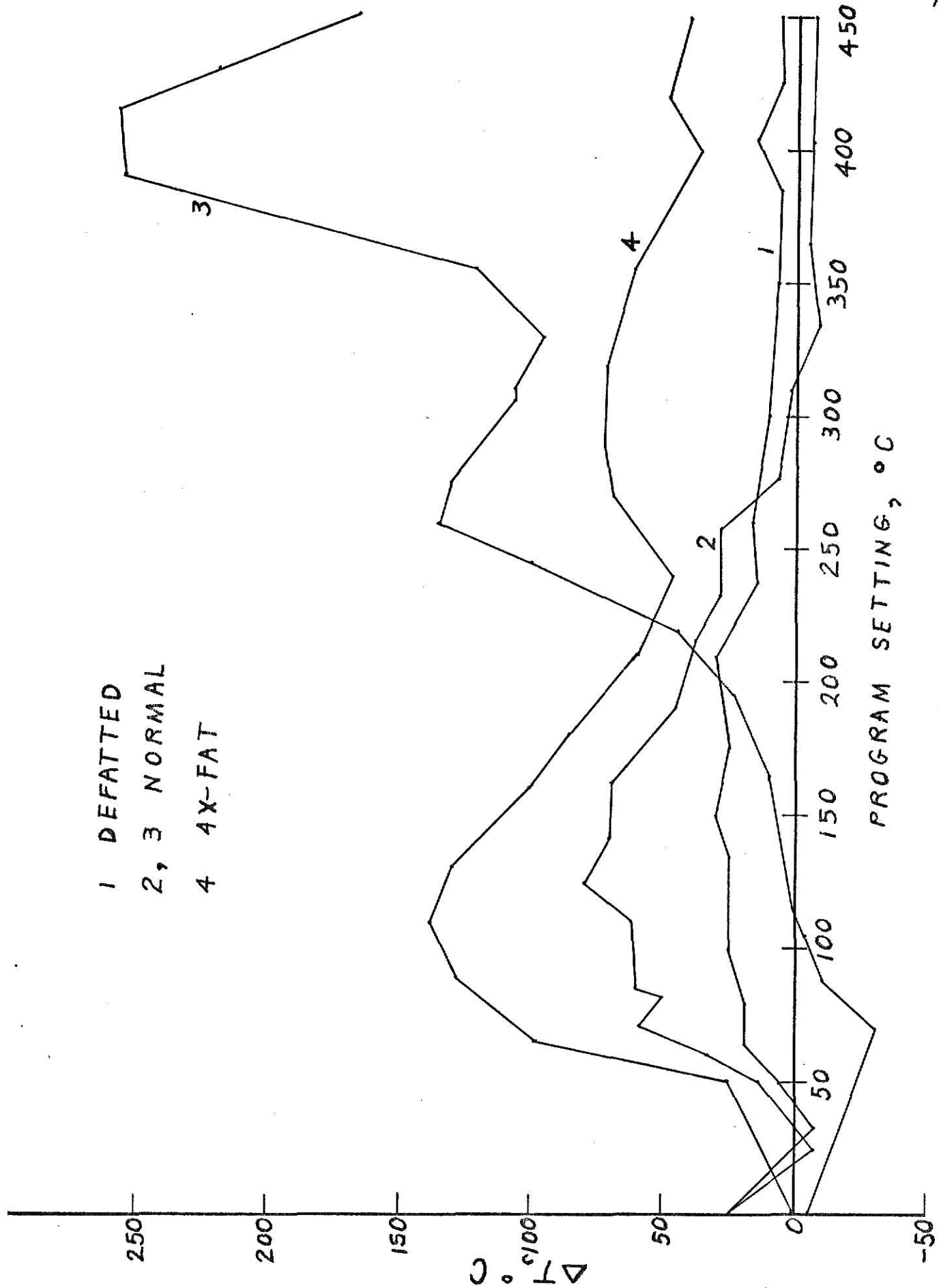


Figure 42. Heating Curves

no adverse affects. After nine months a slight darkening of the material in the upper material of each can was observed with an accompanying ammonia odor. No significant ($<1^{\circ}\text{C}$) temperature differences between the material and the ambient atmosphere were observed. After eighteen months of storage, the containers were removed from storage and examined. The upper $\frac{1}{4}$ " of material in each container was significantly darkened and a very noticeable ammonia odor was present. As before, no temperature differentials were detected between the material and the ambient atmosphere. The material below the top $\frac{1}{4}$ " was progressively more normal in appearance and the ammonia odor disappeared with increasing depth.

4.3.2. Experiments at 25°C

Two types of experiments were done at 25°C ambient temperature. In one type we merely stored wet spent brewers grains at 25°C and noted the changes that occurred over extended storage periods. In the second type containers as in 4.3.1 were used with insulation provided and internal temperatures monitored.

Experiments of the former type revealed that wet spent brewers grains invariably become infested and spoil. The pattern of spoilage followed this typical pattern.

(a) Within 48 hours light colored mold tufts appear on the material mass.

(b) Complete mold infestation occurs within a very short time and lasts up to one month. A distinct musty odor is discernible.

(c) The material gradually blackens releasing ammonia. Mold evidence disappears. One sample stored in a sealed plastic bag blackened and smelled strongly of putrefication.

(d) Often after several months the blackened material can become insect and mite infested, even though the ammonia smell may still be present.

This general spoilage pattern was observed repeatedly.

To determine if indigenous microflora are involved, both wet and dried spent brewers grains were dried, pasturized, rewet to 50% moisture content, wet basis, and stored. The pattern of spoilage was similar to that described above.

In most cases the time period necessary to develop the ammonia odor was three to six weeks. The time required for insect infestation, if it occurred, was usually about a month after this.

In experiments of the second type internal temperatures of cans containing spent grain were monitored. Metal containers with friction-sealing lids and 2 in. of insulation were used. The containers were 5 in. in diameter, 9 in. high and had one 1/8" hole in the top to allow thermistor placement. For the treatments labeled "Prop.", proprionic acid was added to wet grains at level of 1%, by weight. The treatments labeled "yeast" had 10%, by weight, brewers dried yeast added to the wet spent grains and the treatments labeled yeast/Prop. had yeast, 10% by weight, and proprionic acid, 1%, added to wet spent grains. In treatments labeled "Past." wet spent grains were pasturized and then rewetted to 50% moisture content, wet basis. Near sterile conditions were used.

Figures (43) and (44) show representative results.

The results show that pasturization reduced the tendency to heat above the ambient temperature and that proprionic acid was effective in preventing heating. The results indicate that the microbial material which is normally in the wet grains could be a source for heating.

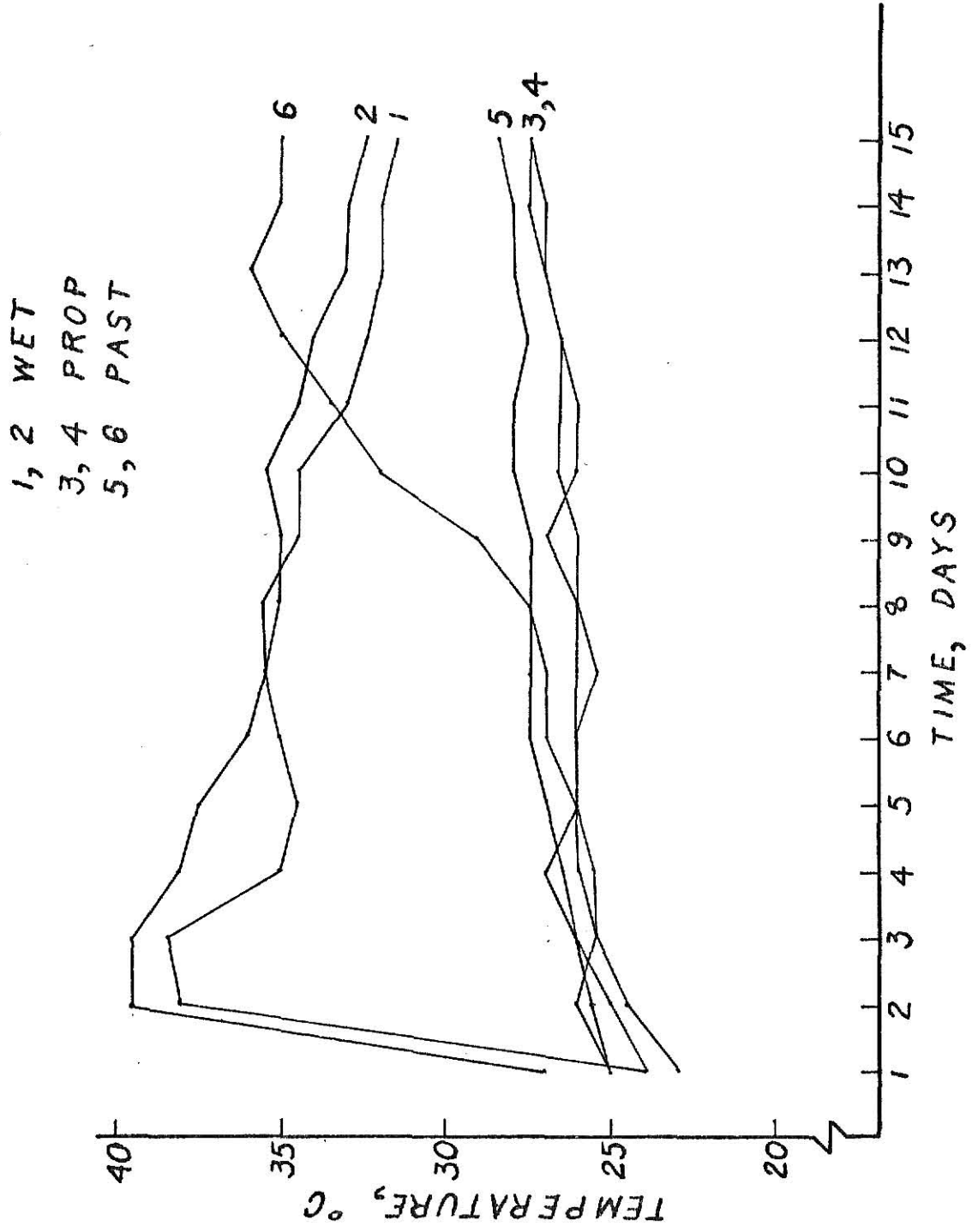


Figure 43. Microbial Studies, 25°C

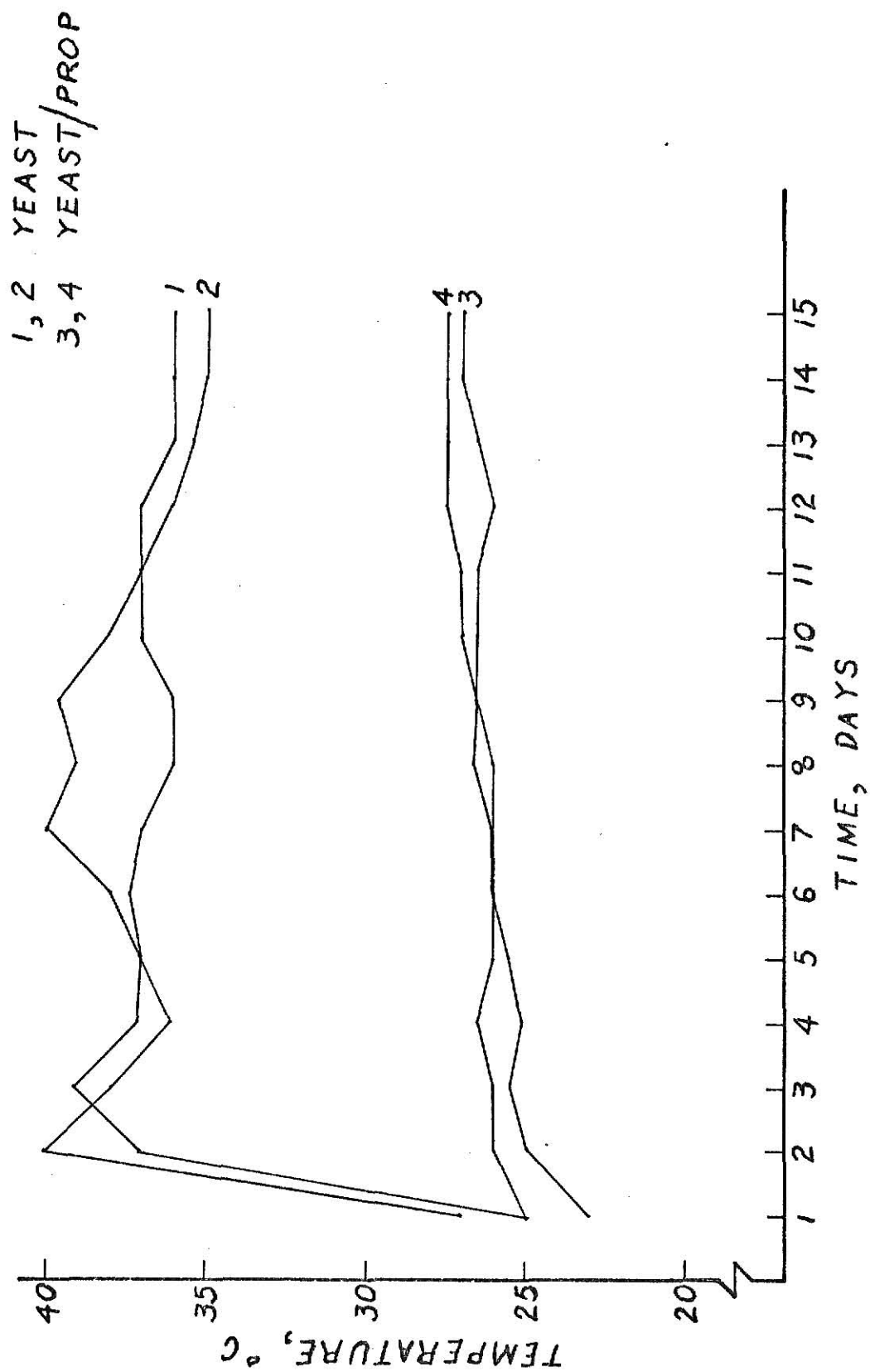


Figure 44. Microbial Studies, 25°C

4.3.3. Experiments at 38°C

An air oven of our own construction was set to an ambient temperature of 38°C. Containers as in 4.3.2. were used and the same experiments were run as in 4.3.2, using wet grains with and without the addition of yeast and proprionic acid. Pasturized spent grains were also tested.

Figures (45) and (46) again show that pasturization and proprionic acid were effective in preventing microbial heating.

4.3.4. Experiments at 50°C

50°C is a rather high temperature for microbial thermogenesis. Indeed molds do not readily grow at this temperature and only thermophilic bacteria can grow actively at this temperature. The same conditions, excluding ambient temperature, were used as in 4.3.2.

The results, Figures (47) and (48), indicate that some microbial heating occurred.

4.3.5. Simulated Near Adiabatic Heating

In these experiments containers were prepared for the air oven as in 4.3.2. However, in these experiments the oven temperature was kept as close as possible to the canister's internal temperature. Oven temperature was allowed to equal but never exceed container internal temperatures. Usually, the oven was 2°C - 5°C cooler than the sample in the container. Settings were checked every two hours with an eight to twelve hour gap during nighttime. No provision was made for container aeration.

The results, Figure (49), show again that proprionic acid treatment is effective in preventing microbial heating.

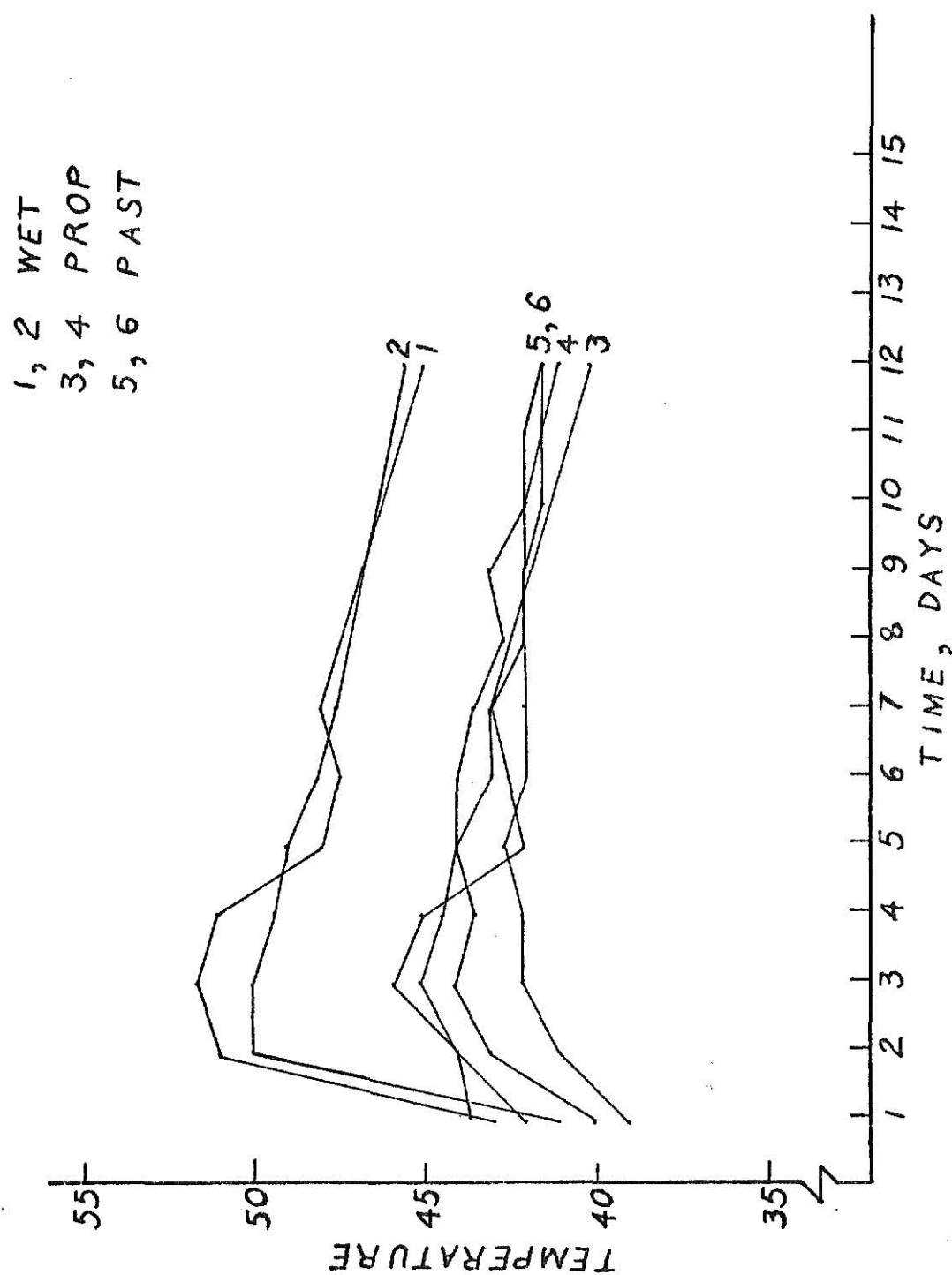


Figure 45. Microbial Studies, 38°C

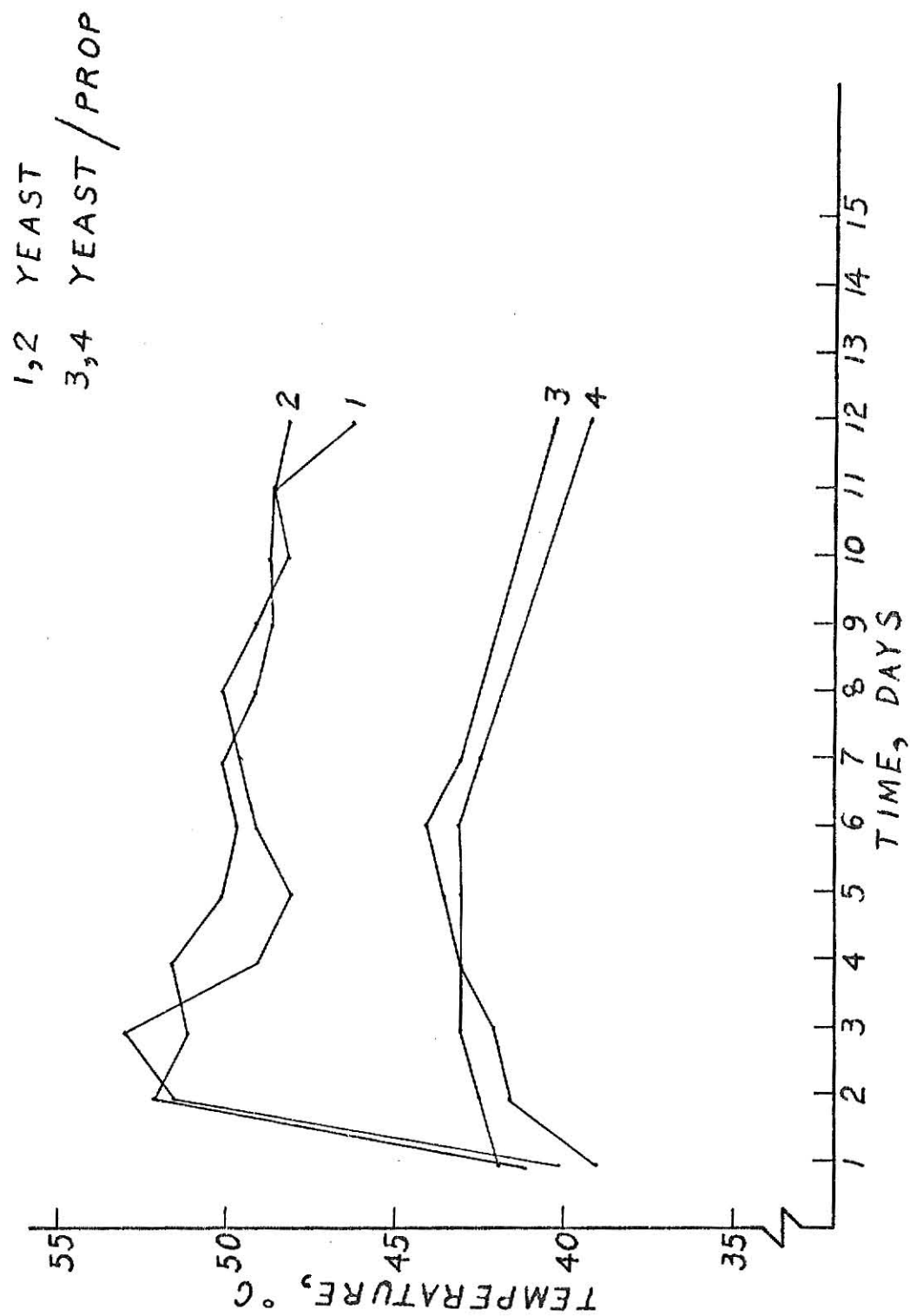


Figure 46. Microbial Studies, 38°C

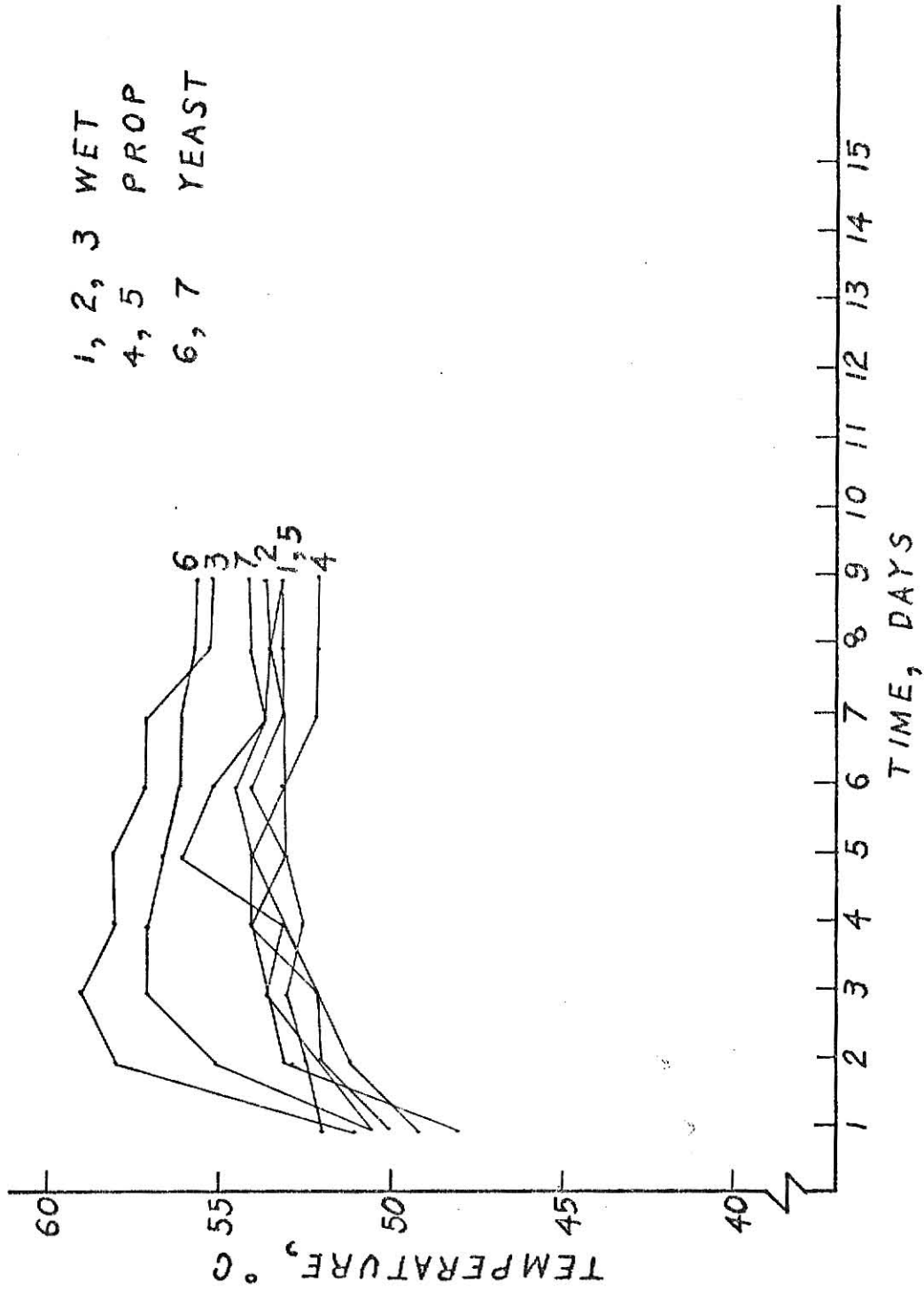
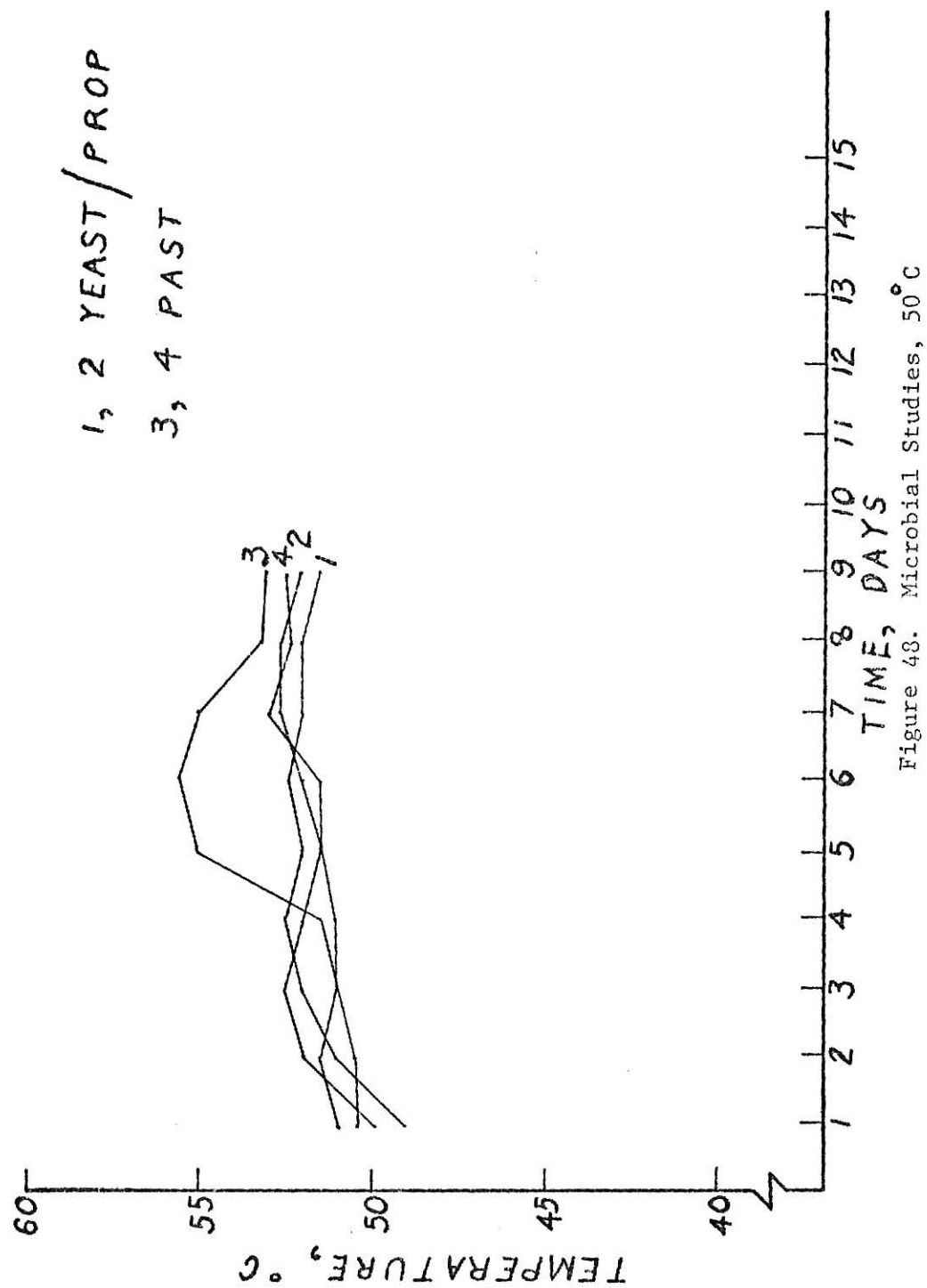


Figure 47. Microbial Studies, 50°C



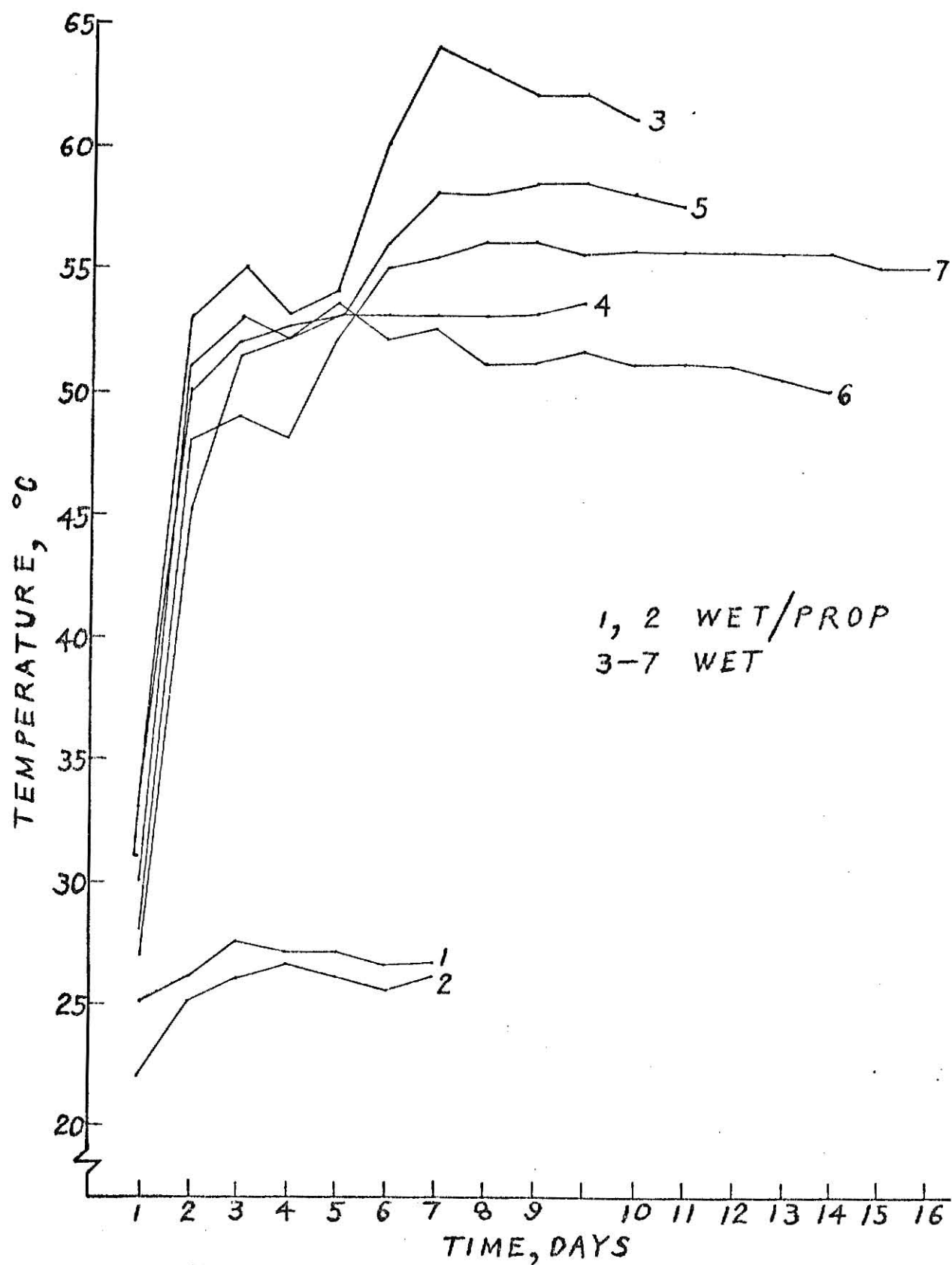


Figure 49. Simulated Near Adiabatic Heating of Spent Brewers Grains

4.3.6. Barrel Experiments

A variety of experiments were run in fifty gallon barrels. A five gallon central core of the test material was implanted in the middle of each barrel and surrounded with wheat middlings of about 16% moisture for insulation. The middlings were surrounded by a plastic sack. A variety of central cores were investigated at two average ambient temperatures. Thermistors were implanted in the central core of each barrel to monitor temperature.

All "wet" samples were about fifty percent moisture content, except where noted, all "Prop." samples were one percent propionic acid, and all "flour" or "yeast" samples were ten percent flour or yeast by weight. The "past." samples were heated to 100°C in forty-five minutes, held at this temperature for one minute, and removed and cooled rapidly under sterile conditions. When the pasturized samples were treated with water (steam) or with propionic acid near sterile conditions were used. The "Normal" cores were at <10% moisture content, wet basis. All fat levels were near 6%.

Figures (50) to (54) show the results.

4.3.7. Discussion of the Microbial Experiments

First of all it is apparent that spent brewers grains constitute a very fertile substrate for the growth of microorganisms and that these growing organisms can create heat. Adiabatic conditions can encourage higher maximum attained temperatures in the heating mass.

From section 4.3.1 we find that there are indigenous organisms on spent brewers grains that can grow at quite low temperatures. It was found that storage of wet spent brewers grains at 4°C was possible for

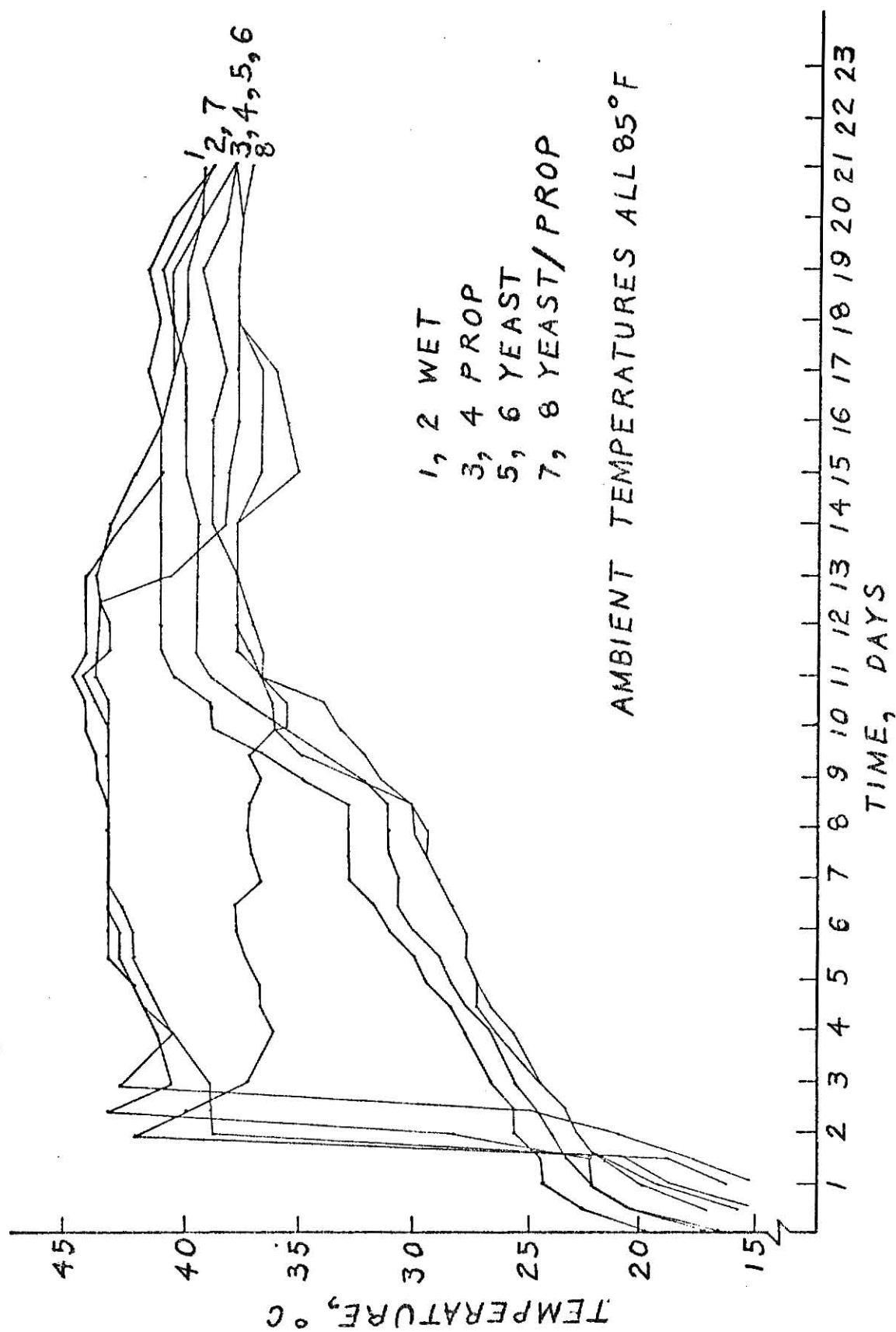


Figure 50. Barrel Experiments Showing Effect of Propionic Acid. When Storing Wet Brewers Grains, 30°C Ambient.

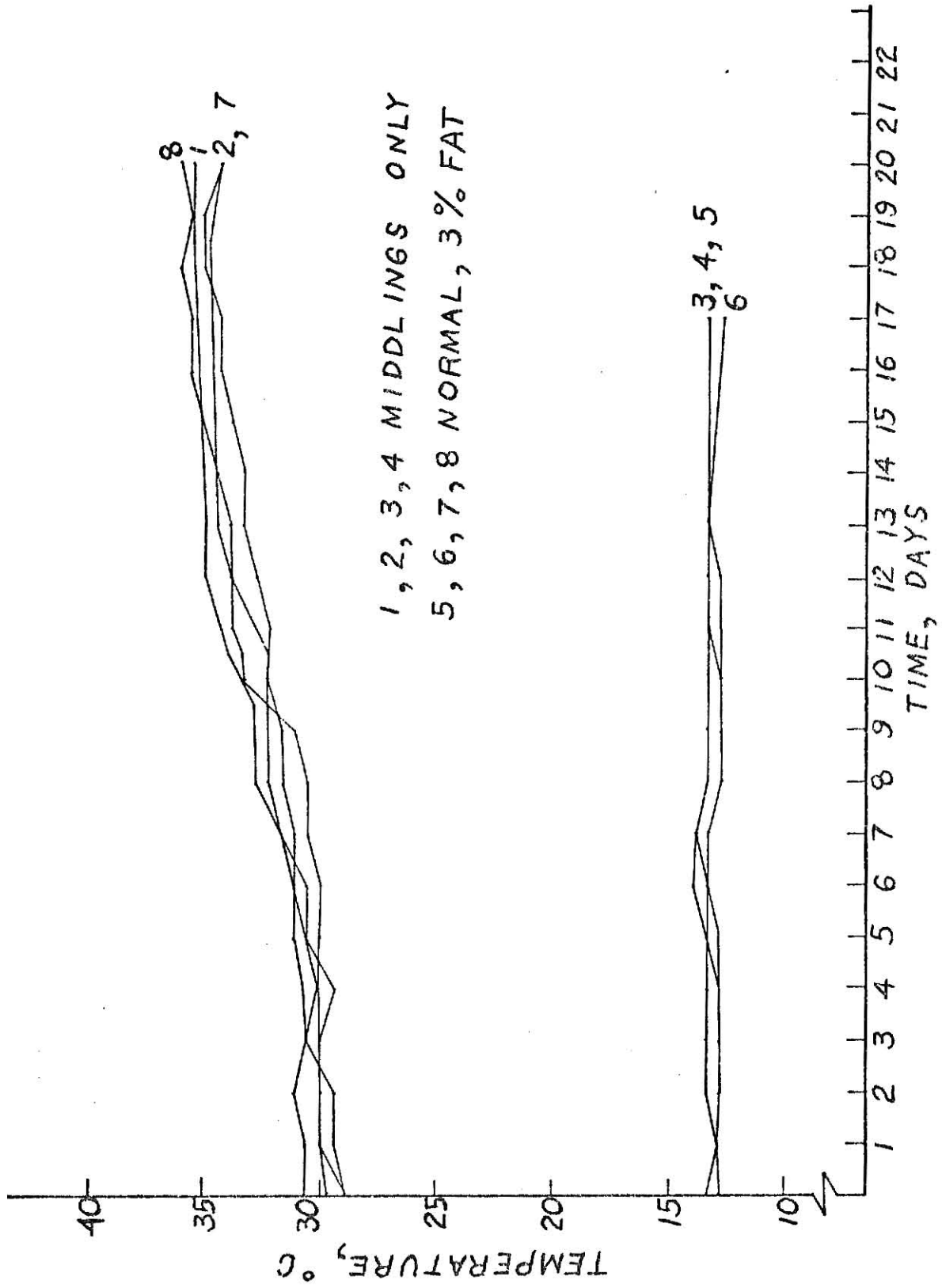


Figure 51. Barrel Experiments Showing Effect of Propionic Acid When Storing Wet Brewers Grains, 30°C Ambient with Added Yeast.

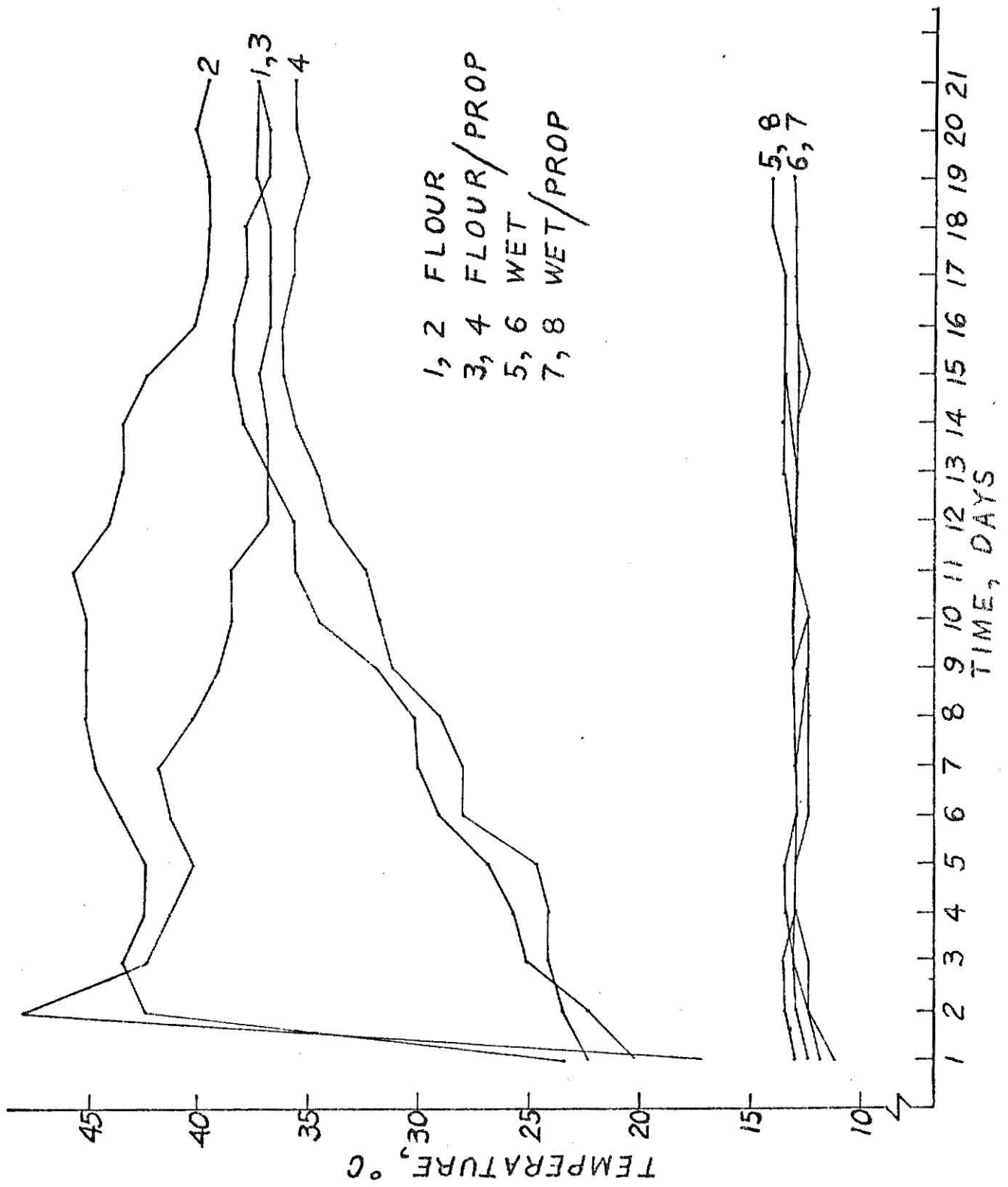


Figure 52. Barrel Experiments

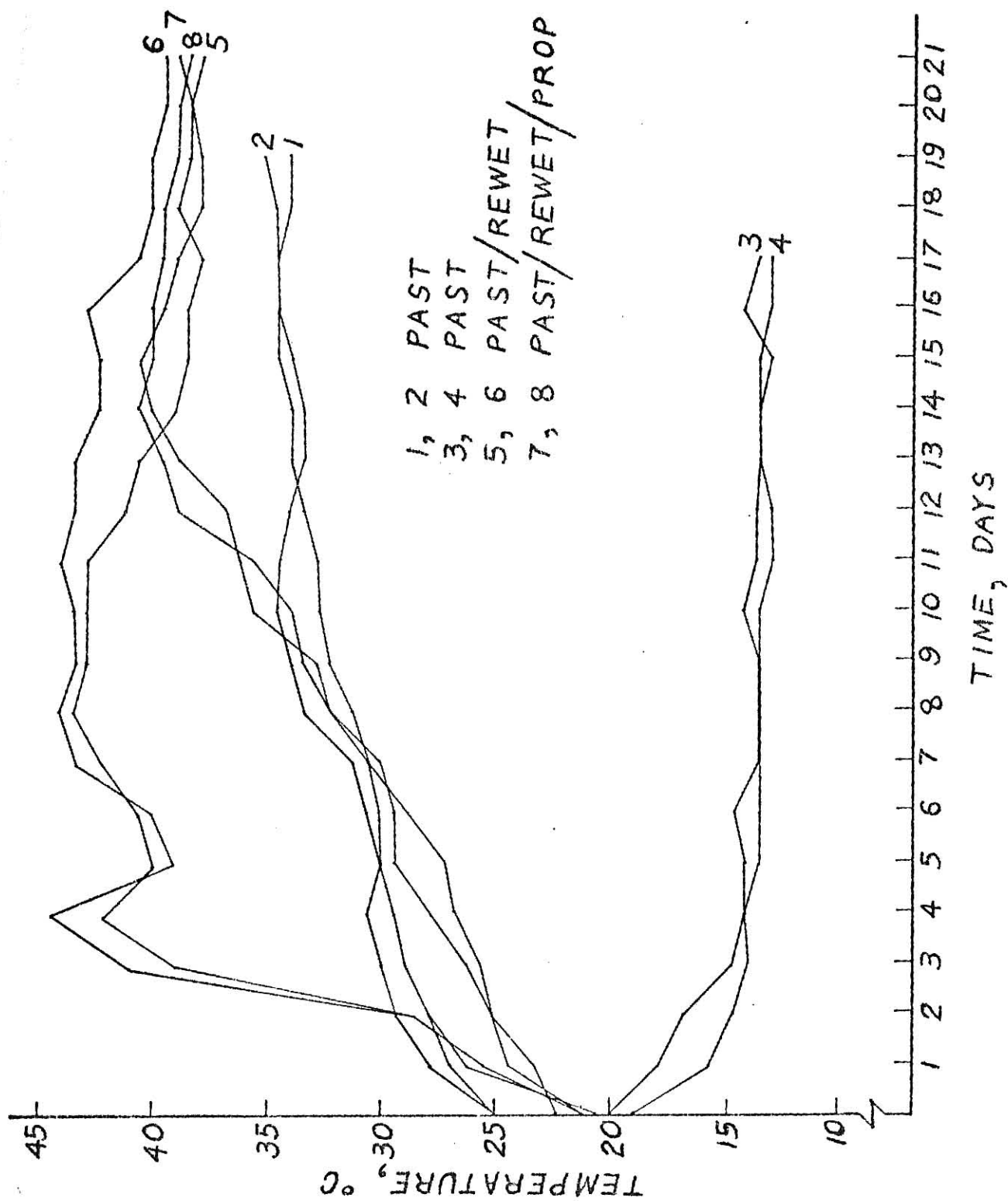


Figure 53. Barrel Experiments

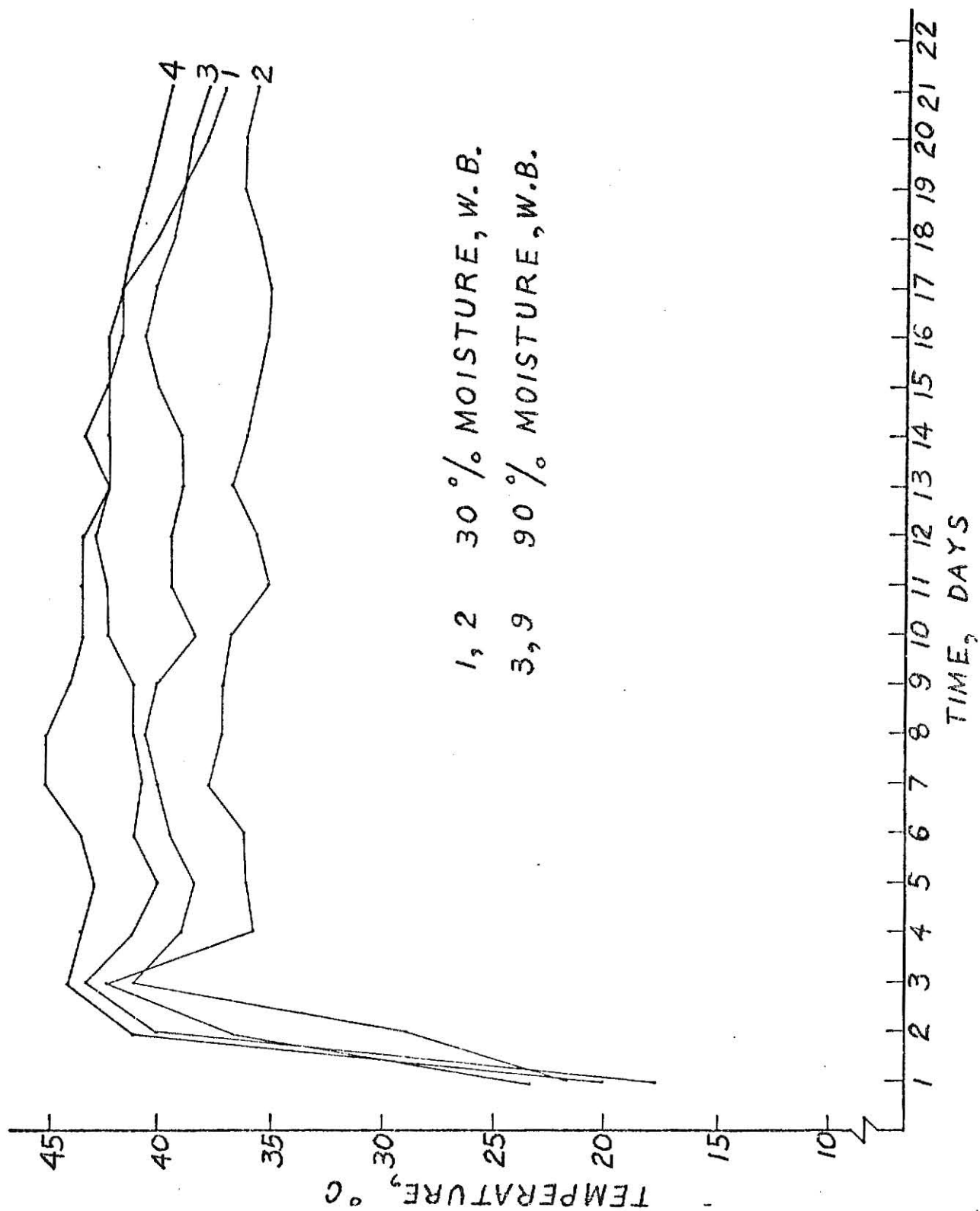


Figure 54. Barrel Experiments

fairly extended time periods while only minor spoiling of the surface layers occurred.

At an ambient temperature of 25°C, Figure (43) and Figure (44), with two inches of insulation heating was observed. Presumably under more nearly adiabatic heating conditions—more insulation, higher temperatures would be possible. Propionic acid clearly curtailed heating due to mold and/or bacteria. However, another form of heating was present or the propionic acid lost its effectiveness with time.

The experiments at 38°C, Figure (45) and Figure (46), show the same trends as the experiments at 25°C with the following difference: the temperature increase in the acid treated cans are more noticeable at 38°C. As shown in section 4.2, autoxidation of fat may account for this. The addition of yeast did not affect the results, again indicating that spent brewers grain constitute a rich growing medium for microorganisms. Visual inspection of the containers after experimentation seemed to indicate mold rather than bacterial invasion. Possibly bacteria follow mold activity on spent brewers grains (See 4.2.3.). Note again how propionic acid discouraged heating.

The situation appears to be more complicated at an ambient temperature of 50°C. See Figure (47) and Figure (48). Again, some heating occurs in all samples, possibly due to fat autoxidation (see 4.2.). Propionic acid seems to inhibit heating here also, but to a much lesser degree than at the lower temperature. Possibly the propionic acid is gradually driven off at lower temperatures because of the temperature limits for most microorganisms. In sample 7 of Figure (47) and sample 3 of Figure (48) we see two apparent heatings. Presumably, the first in each case is due to

mold action and the second due to thermophilic bacteria. Samples 3 and 6 in Figure (47) do not display two separate heating curves but do reach temperatures above which molds are likely to grow. These experiments do not clarify whether bacterial heating requires mold heating to precede it. The second heatings are short lived which is characteristic of most thermophilic bacteria (short but violent activity (118, 119)).

In the near adiabatic heating experiments, 4.3.5, we found that proprionic acid plays a key role. See Figure (49). Its presence at 1% by weight strongly inhibits heating. Note that the ambient temperature was low enough to discourage non-microbial exothermic reactions from proceeding at significant rates. In several of the samples a double heating peak is observable, again, possibly due to mold heating followed by bacterial heating. In no case were temperatures over 65°C produced. Presumably, the more refined techniques of Rothbaum (47) are necessary to achieve conditions adiabatic enough for heating above 65°C. Many experiments of this type were done and the examples in Figure (49) are typical.

Upon removal, samples that had heated to around 55°C or more sometimes had an ammonia smell. However, these experiments indicate that microbial thermogenesis is not itself a direct fire hazard.

The barrel experiments, 4.3.6, and Figures (50) through (54), also revealed some very key information. Note some heating always occurred at 85°F but was very minimal at 55°F. Proprionic acid always reduced the maximum temperature rise, however, in most cases after about three weeks the temperatures of wet samples with and without proprionic acid were roughly the same. It is possible that some of the water from the wet

samples migrated to the surrounding middlings causing them to heat. Note how middlings heated at 85°F anyway, implying that they were wet enough to cause some heating. The addition of yeast or flour in no way enriched the spent brewers grains as a medium for microbiological growth. All microbial heating curves showed a strong initial peak followed by a sustained peak later. This may indicate mold followed by bacterial activity. Often the second peak was higher than the first peak. Dry samples at 55°F displayed no heating, whereas dry samples at 85°F did display some moderate heating. This is consistent with the experiments of section 4.2. At 55°F propionic acid inhibited microbial growth but heating from microbial thermogenesis at 55°F is no hazard. The pasteurized samples heated anyway indicating that microbial heating in spent brewers grains probably does not require indigenous microflora. The varying amounts of water in Figure (54) indicate that there is no distinct trend here. Possibly at lower moisture contents there is a trend. However, it is worth noting that a hygroscopic material cannot exceed the temperature at which its water-vapor pressure is equal to atmospheric pressure. Thus, a very wet sample may spoil due to microbial action but as long as it is very wet, it will never reach critical temperatures until it has dried.

5. Conclusions

Our research indicates that:

1. The nutritive values of various fractions of spent brewers grains are highly variable.
2. Components of spent brewers grains, especially fat, can oxidize exothermically. The addition of an antioxidant retards this reaction at normal ambient temperatures.
3. Microbial thermogenesis can elevate the temperature of spent brewers grains to around 80°C if moisture conditions are proper. Addition of propionic acid coupled with proper moisture control can aid in controlling this heating.
4. Overdried spent brewers grains will adsorb moisture from the ambient atmosphere and this process can result in significant temperature increases. Subjecting very dry grains to water in the liquid phase can lead to heating also, but to a lesser degree.
5. Spent brewers grains fresh from rotary drum dryers should be reduced in temperature before long term storage.

6. Suggestions for Future Work

The following suggestions are made for future work:

1. Investigate, using differential thermal analysis, differential scanning calorimetry, or the methods of Walker (79), the effectiveness of various antioxidants in controlling exothermic heating in spent brewers grains.
2. Determine moisture adsorption isotherms for various samples of spent brewers grains and use these isotherms to predict optimum storage conditions and moisture levels for spent brewers grains at various temperatures.

3. Determine moisture levels of samples of spent brewers grains obtained during startup and shutdown of rotary drum dryers to determine if moisture control is adequate at these times.

4. Investigate the possible effectiveness of pelleting spent brewers grains to control exothermic heating.

ACKNOWLEDGEMENTS

The author wishes to dedicate this work to his father who has awaited eagerly its completion. Without his father's inspiration this work might not have been completed.

The author wishes to express his sincere and deep appreciation to his major professor, Dr. Harry B. Pfoest for his guidance and advice in the course of this research and in the preparation of this thesis; to Dr. Do Sup Chung and to Dr. Paul Seib for their assistance as members of the author's graduate committee; to Dr. James Copeland who unsparingly assisted the author in the work involving differential thermal analysis and in interpreting references 25 and 39; to Dr. David Sauer and Mrs. Rosemary Burroughs at the USDA Grain Marketing Research Center, Agricultural Research Service, in Manhattan for their guidance and for the use of their facilities; and to Dr. Charles W. Deyoe for assistance in reading the amino acid analyser and for his encouragement to me. Finally, the discerning reader will note that a great debt of gratitude must be paid to Dr. Ian K. Walker of New Zealand whose pioneering and thorough research has inspired the author.

The author wishes to express his deep gratitude and appreciation to his family, especially his wife, for their continued support, encouragement, and patience throughout the course of this work; and to his friends who in one way or another helped in the completion of this work.

VITA

David W. Calton was born December 13, 1950 in Peoria, Illinois, the first son of Mr. and Mrs. Marion Roy Calton. He graduated from Metamora Township High School in Metamora, Illinois in 1968 and continued his education at the University of Illinois. He received a Bachelor of Science degree in mathematics in 1973.

David W. Calton has two publications with Dr. Harry Pfost in manuscript form to be published in Feedstuffs in 1977. He will be working for Cargill, Inc., Nutrena Feed Division as of January 24, 1977 as a plant engineer.

David W. Calton married Judy Ann Bamberger on June 10, 1972 in Fort Lauderdale, Florida. They have a three-year old son and a daughter who was born soon after this work was done.

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PROPERTIES OF SPENT BREWERS GRAINS

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B.S. University of Illinois, 1973

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Grain Science and Industry

Kansas State University

Manhattan, Kansas

1977

The purpose of this study was to investigate exothermic heating in spent brewers grains. The heating due to microbial thermogenesis, to wetting of the grains, and to exothermic oxidations were examined. The nutritive qualities of spent brewers grains and its particle size distribution were also examined.

It was found that heating due to wetting spent brewers grains or to microbial thermogenesis could raise bulk temperatures significantly; oxidations occurring in spent brewers grains were found to be capable of raising the temperature even more.

It was found that the use of propionic acid to control microbial growth, the use of an antioxidant to control fat autoxidation, and careful temperature and moisture control of spent brewers grains stored in bulk at normal temperatures reduced heating significantly.