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THE SPONTANEOUS HEATING AND IGNITION OF HAY AND OTHER AGRICULTURAL PRODUCTS¹

By Dr. C. A. BROWNE

U. S. BUREAU OF CHEMISTRY AND SOILS

THE production of heat, as a manifestation of vital activities, was associated at first almost entirely with the processes of animal life. This is not surprising when we consider the effect of the transpiration of large quantities of water from the immense leaf surfaces of growing plants which tends to keep their temperatures below that of the surrounding air.

The original observation of Lamarek² in 1777 that the fleshy spike or spadix of the flowers of *Arum maculatum* at a certain stage of growth was perceptibly warm to the touch first called the attention of scientific men to the heat-producing power of growing plants. Senebier³ in 1800 confirmed this observation

¹ Address of the vice-president and retiring chairman of Section C—Chemistry, American Association for the Advancement of Science, Atlantic City, December, 1932.

² Lamarek, "Flora française," 1777.

³ Senebier, "Physiol. végétale," III, 314. 1800.

of Lamarek and at the same time noted the additional fact that this production of heat was especially pronounced in the presence of oxygen. The connection of this observation with the familiar oxygen respiration of animals was indicated later by the experiments of Saussure⁴ in 1822, since which time the validity of a true respiration process by plants, in which oxygen is consumed and carbon dioxide evolved, has been universally recognized.

The intensity of this heat production by plants and its relation to oxygen consumption were examined by other investigators in succeeding years. In experiments by Kraus⁵ in 1882 upon the spadix of flowers of *Arum italicum* a maximum temperature of 44.7° C.

⁴ Saussure, *Ann. Sci. Nat.*, 21, 285, 1822; *Ann. Chim. et Phys.* (2), 21, 279, 1822.

⁵ Kraus, *Abhandl. Naturf. Gesell. Halle*, 16, 1882.

was observed. During the production of this heat large quantities of carbon dioxide were evolved, and in a few hours a third or more of the dry substance of the spike (consisting of reserves of starch and sugar) was consumed.

If transpiration and the radiation of heat are retarded, as when the organs of plants are heaped together in large piles, the production of heat by vegetable cells becomes very apparent. The production of heat in piles of grain and in heaps of grass was probably observed by man in prehistoric times. It was also observed at a very early period that under certain conditions some plant materials, as hay or straw, might undergo so great an increase of temperature during spontaneous heating as to burst into flames. In later times, when men began to speculate as to the cause of things, the phenomenon of the spontaneous heating and ignition of plant materials was ascribed to the presence of an occluded fire or heat, and this explanation was retained by Bacon,⁶ Boerhaave⁷ and other philosophers until comparatively modern times.

The German botanist Goeppert⁸ showed in 1830 that when a mass of barley grains was allowed to germinate in a wooden box, temperatures as high as 50° C. might be obtained. He did not differentiate, however, between the heat evolved by the respiration of the sprouting grain and that developed by the vital processes of adhering micro-organisms. This distinction was first clearly demonstrated by Cohn,⁹ a plant physiologist of Breslau, who showed in 1890 that the first production of heat by the respiration of germinating seeds came to an end at about 40° C., which coincided with the thermal death point of the young plants. Cohn then observed after a short pause a second rise of temperature to about 65° C., which he attributed to the vital processes of thermogenic micro-organisms.

The maximum temperature observed in the most carefully controlled experiments upon the heating of plant materials by biological agencies does not usually exceed 70° C., which is about the thermal death point of most vegetating micro-organisms. This is some 160° C. lower than the temperature necessary for the ignition of hay, and the problem which has perplexed scientific men for so long is how to explain the great increase in temperature between the death point of the thermogenic micro-organisms and the point of spontaneous ignition.

⁶ Bacon, "Novum Organum." Translated by P. Shaw, 2 v. London. 1802.

⁷ Boerhaave, "A New Method of Chemistry." Translated from the printed edition by P. Shaw and E. Chambers. London. 1727.

⁸ Goeppert, "Ueber die Wärme-Entwicklung in den Pflanzen." 272 pp. Breslau. 1830.

⁹ Cohn, "Ueber Wärme-Erzeugung durch Schimmelpilze und Bakterien." Jahrg. Schles. Gesell., 68: 23-29. Breslau. 1890.

There have accumulated during the past fifty years many detailed accounts, by careful observers, of the visible phenomena of the spontaneous ignition of hay. These accounts all largely agree as to the main facts, so that the one specific instance which we have selected will be sufficient for general purposes of illustration. This typical case, related in *Liebig's Annalen* in 1873 by the German agricultural chemist Ranke,¹⁰ is of classic interest, for its publication acted as a stimulus in drawing the attention of scientific men for the first time to a careful study of the complicated problem of the spontaneous ignition of hay.

A partial translation (by the author) of Ranke's original article is as follows:

On my estate Laufzorn, which is situated south of Munich about four hours by post near the Grünwald forest, a burning odor was observed on the morning of October 19, 1872, in the west corner of a large massively constructed barn.

In this section of the barn was stored a part of a crop of rowen that had been harvested upon the estate and unloaded in two adjacent piles, one of which contained about 22½ tons and the other about 15 tons.

This rowen had all been harvested in apparently well dried condition during excellent weather between the 5th and 10th of August. During the whole of September there was noticeable only the customary strongly aromatic odor of hay which increased in intensity until finally on the 17th and 18th of October a perceptible burnt odor began to be noticed. This empyreumatic burnt odor had become so strong on Saturday morning, October 19, that my manager was convinced the interior of the mow had caught fire. He determined at once to remove the hay as carefully as possible and in case fire should be discovered to extinguish it with a large quantity of water.

All available buckets, casks and other containers were accordingly filled with water upon the scaffold of the barn above the rowen and at 10:30 A. M. the removal of the hay was very carefully commenced. . . .

As the removal now began to be pushed more vigorously from the top there were suddenly observed at a depth of about 5 feet several sparks. At the same time smoke and flashes of sparks were suddenly observed on one of the wagons, upon which the latest removed portions of rowen were being hauled from the barn. This was about 1:30 P. M.

The entire mow and the loaded wagon were now drenched with water. The rowen that was now being hauled out was of a deep brown color and was spread out upon the grass near a pond situated behind the barn.

From now on the removal of rowen could be performed only with constant drenching with water, since almost every forkful as soon as it was taken out began to glow. It was also frequently necessary to pour water again upon the material which had been loaded since even the boards of the wagon repeatedly broke into flames. Even the rowen that had been spread out on the grass near

¹⁰ Ranke, "Experimenteller Beweis der Möglichkeit der Selbstentzündung des Heues." *Liebig's Ann. Chem. und Pharm.*, 167: 361-8. 1873.

the pond reignited repeatedly, so that it had to be extinguished three times. The material outside in the open broke out into actual flames, which was prevented inside the barn by the constant energetic drenching with water. It might be mentioned in this connection that on the following day the grass sod, upon which the removed rowen had been spread, was found to be completely burned. . . .

Finally after it had become dark the work of removing the burning material from the barn was completed. The burnt mass formed, as it were, the core of the pile and was estimated to have a diameter of about 11 feet at the top; it extended downwards to about $1\frac{1}{2}$ feet from the floor where the diameter of the hot portion, however, had narrowed down to about 4 to 5 feet. The burned area extended backwards to within about $1\frac{1}{2}$ feet from the rear wall of the barn.

The condition of the burnt mass was that of an actual carbon with a retention, however, of its original structure. The form of every spear of grass and of every flower could be plainly recognized. If this grass carbon was rubbed upon paper, the latter was colored black.

Ranke, acting upon a suggestion by Professor Buchner,¹¹ of the University of Munich, attributed the repeated spontaneous ignition of his hay to the strong absorptive power of the hay charcoal for atmospheric oxygen.

The pyrophoric carbon theory of Ranke was at once confronted with a serious objection, which was the difficulty of explaining the origin of the heat that is necessary to raise the temperature of the hay to the point of carbonization. When a pile of green grass begins to heat, the incipient elevation of temperature is commonly attributed to the oxidation of sugars by the action of enzymes in the plant cells and in the adhering micro-organisms that produce fermentation. The life of the plant cells and of the micro-organisms is, however, destroyed before the temperature reaches 80°C ., and the activity of the oxidizing enzymes can hardly be supposed to exceed 100°C ., which is some 50°C . below the temperature at which hay begins to carbonize and some 130°C . below the temperature at which hay ordinarily ignites. It is the bridging over of these large unexplained gaps in the increase of temperature in a heating haystack that constitutes the real problem of its spontaneous ignition.

It is not possible in the limits of space at our disposal to describe all the theories which have been proposed to explain this difficulty. Laupper,¹² the well-known Swiss authority upon the spontaneous ignition of hay, supposes pyrophoric iron, and not pyrophoric carbon, to be the causative factor. Others

have supposed spontaneously inflammable gases, such as phosphine, to be responsible for the ignition. It has been also supposed by some that there are two kinds of heat production, one due to vital causes at low temperatures and one due to chemical causes at high temperatures. This conception, however, is baseless, for the entire production of heat, from the first rise in temperature to the point of ignition, is due to the effects of chemical reactions; therefore scientifically no differentiation can be made between vital heat and chemical heat.

In order to explain how a heating haystack can catch fire the German bacteriologist Mische¹³ assumed that pyrophoric carbon can be formed at the comparatively low temperature of 70° or 80°C . The following passage is translated from his original article upon the subject:

I believe that carbonization may indeed take place even at this temperature, for it must be considered that the action continues for a considerable time, even for months. The hay undergoes so to speak a dry distillation, in which the elements of the organic compounds are rearranged; new volatile compounds of simpler composition are set free and the material remaining behind approaches more and more the composition of pure carbon. That oxidations still take place above 75° and 80° has already been indicated by the experiments of Schlösing and of Boekhout and DeVries. The carbon is of an extremely fine porous character, each cell retaining its structure. It is plausible to suppose that such carbon may condense oxygen in a manner similar to finely divided platinum (platinum sponge). It would then, perhaps similar to platinum sponge, acquire a strong oxidizing power and perform oxidations that would be possible normally only at a much higher temperature. It could exercise this oxidizing effect either upon itself or upon the absorbed easily oxidizable gases, such as hydrogen, phosphine, volatile hydrocarbons (methane, ethylene, etc.), that are produced by the slow distillation or decomposition of the organic constituents of the hay. Such oxidations might perhaps take place even in undisturbed piles of hay after a certain interval of time when the ingress of oxygen was limited. The temperature would then slowly increase. Or, as seems more probable, the oxidations would develop only when an abundance of oxygen can enter, or in other words when the pile is torn open or when air passages are created intentionally or unintentionally. In fact, it is the general consensus of opinion (see Medem and other writers) that ignition is only produced when free entrance is given to the air by the insertion of poles, construction of air pits, opening up of the stack, etc.

The assumption of Mische that pyrophoric carbon is produced at low temperatures has been adopted by other students of the problem. The supposition, however, is hardly tenable, for there are many cases

¹¹ Buchner, *Liebig's Ann. Chem. und Pharm.*, 167: 361. 1873.

¹² Laupper, "Die Neuesten Ergebnisse der Heubrandforschung," *Landw. Jahrb. Schweiz Jahrg.*, 34: 1-54. 1924.

¹³ Mische, "Die Selbsterhitzung des Heues. Eine biologische Studie." 127 pp. Jena. 1907.

recorded where spontaneous ignition of hay has taken place without any evidence of carbonization and indeed within only a few days after it has been stored away, whereas Mische supposes that the action continues "for a considerable time, even for months."

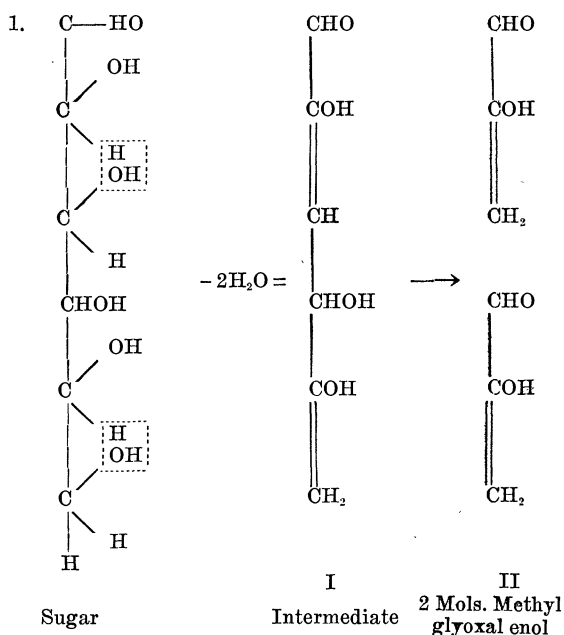
In 1929 the author¹⁴ suggested as a possible solution of the problem of spontaneous ignition the formation, by micro-organisms under anaerobic conditions, of unsaturated unstable intermediary compounds which, in the sudden exposure of the interior of the fermenting mass of hay to the air, absorb atmospheric oxygen with so much avidity that the temperature is rapidly raised not only above the death point of the micro-organisms but even to the point of ignition of the hay. This spontaneous ignition may take place almost instantly, as James, Bidwell and McKinney,¹⁵ of the Department of Agriculture, have observed in the case of heating horse manure, or it may take place more slowly, according to the rapidity with which the outside air gains access to the hot pocket in the interior of the hay. In other words, the micro-organisms that produce the incipient fermentation of the hay by enzyme action or otherwise are responsible for the preparation of the mine that may, or may not, later be sprung with the spontaneous ignition of the mow or stack.

The splitting-off of water from the organic constituents of plants is one of the most common reactions attending the deterioration of agricultural products, and one effect of this change, of great importance in the study of the problem of spontaneous ignition, is the accumulation of residues of greater and greater calorific energy. The significance of this reaction in plant life and in fermentation was pointed out as far back as 1870 by the German chemist, Adolph Baeyer,¹⁶ who in a very suggestive article published in the *Berichte* of the German Chemical Society may be said to have blazed the way to an understanding of some of the reactions that take place in the decomposition of plant materials by micro-organisms.

Baeyer supposed that as a first step in this decomposition the elements of water are stripped off from the sugar molecule with the formation of unstable intermediary products, which, by the readdition of water and in other ways, finally give rise to lactic acid, alcohol, carbon dioxide and the other end-products of fermentation. The splitting-off of water

from the carbohydrate molecules results in the removal of H and OH groups from the carbon chains and in the formation of unsaturated intermediary compounds with carbon atoms that are united by double bonds. These compounds are of a very labile reactive character and by the subsequent readdition and reelimination of water pass through various modifications before the final end-products of the fermentation are reached.

Since the time of Baeyer's classical paper there have been almost innumerable speculations as to the nature of the intermediary compounds which are produced in the fermentation of sugars. Among the most plausible of the theories which have been proposed is the one of Wohl¹⁷ and Neuberg¹⁸ that the first compound produced by the stripping-off of water from the sugar molecule is an unsaturated intermediary substance that breaks down immediately into two molecules of an enolic form of methyl glyoxal as shown by the following equation:



The unsaturated enolic form of methyl-glyoxal has not been isolated from fermentation mixtures, and it probably only exists momentarily. Methyl glyoxal itself ($\text{CHO}-\text{CO}-\text{CH}_3$) has, however, been detected in fermentation products, and this fact is a strong argument in favor of the Wohl-Neuberg theory of fermentation.

¹⁴ Browne, "The Spontaneous Combustion of Hay." Tech. Bulletin No. 141, U. S. Dept. of Agriculture. September, 1929.

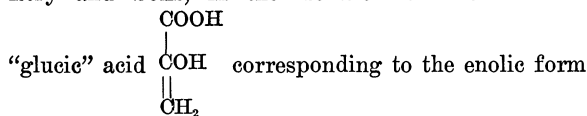
¹⁵ James, Bidwell and McKinney, "An Observed Case of Spontaneous Ignition in Stable Manure." *Jour. Agr. Research*, 36: 481-5. 1928.

¹⁶ Baeyer, "Ueber die Wasserentziehung und ihre Bedeutung für das Pflanzenleben und die Gährung." *Ber. Deutsch. Chemisch. Gesell.*, 3: 63-75. 1870.

¹⁷ Wohl, "Die neue Anschauung über den chemischen Verlauf der alkoholischen Gärung." *Biochem. Zeits.*, 5, p. 45. 1907.

¹⁸ Neuberg, "Zuckerumsatz der Pflanzenzelle." *Handbuch der Biochemie*, II Aufl. Bd. 2, Jena. 1925. For a full discussion of the Wohl-Neuberg and other theories regarding the fermentation of sugars see Oppenheimer's "Die Fermente," Bd. II, p. 1450, V Aufl. 1925.

A direct proof of the formation of unsaturated highly reactive enolic compounds in the decomposition of sugars has recently been furnished by Nelson and Browne,¹⁹ of the Bureau of Chemistry and Soils, in the isolation of the so-called



of methyl glyoxal. This acid is produced by the action of weak calcium hydroxide upon a dilute solution of glucose at 70° C. in the absence of air. The calcium salt of the acid deposits almost immediately; it absorbs oxygen from the air with the greatest avidity and with an intense evolution of heat. It is perhaps by the rapid oxidation of unsaturated highly reactive intermediary substances similar to this that the heat of a fermenting haystack is produced. In this connection it might be noted that Lange²⁰ has recently obtained evidence of the production by *B. coli* of an unsaturated very unstable highly oxidizable intermediary product, which is similar in some of its reactions to propiolic acid $\text{CH}_2\text{C}\cdot\text{COOH}$. It is possible that the acid detected by Lange is closely related to the glucic acid of Nelson and Browne.

The oxygen which is needed for the transformation of the intermediate unsaturated compound may come in part from the air; but it may also be supplied by the decomposition of water, in accordance with the simultaneous reduction-oxidation reactions which have been especially studied in Germany by Wieland.²¹

Tschirch²² has proposed a modification of this reduction-oxidation theory to explain the spontaneous ignition of hay. He criticizes the hypothesis of the formation of pyrophoric carbon at 70° C., as suggested by Miehe, and as a substitute for this supposes that the ignition is due to the rapid evolution of oxygen from the organic constituents of the hay as a result of the action of reducing enzymes under anaerobic conditions. To quote from Tschirch's original article (author's translation):

If half-dried hay is packed tightly together in a thick layer, the most easily reacting oxydases are the first to become active. This first phase of the reaction is the first nondangerous stage that is associated with only a

¹⁹ Nelson and Browne, "The Properties and Chemical Constitution of Glucic Acid," *Jour. Am. Chem. Soc.*, 51, pp. 830-6. 1929.

²⁰ Lange, "Production of an Unsaturated Compound by *B. coli* in a Synthetic Medium," *Proceedings for the Soc. of Experimental Biology and Medicine*, p. 1134. June, 1932.

²¹ Wieland, "Ueber den Mechanismus der Oxydations-Vorgänge," *Ber. Deut. Chem. Gesell.*, 45 (2606); 46 (3327); 47 (2085); etc. 1914, etc. For a full review of Wieland's theory see Oppenheimer's "Die Fermente," Bd. II, pp. 1283-95. 1925.

²² Tschirch, "Die Entzündung der Heustöcke," *Mitt. Naturf. Gesell. Bern*, pp. 133-137. 1917.

slight increase of temperature. It is an oxidation or combustion process that involves a consumption of oxygen. As soon as the oxygen is used up, however, the activity of the reductases sets in. They find points of attack in all the oxygen-containing constituents of the cell contents and cell membrane. . . . Cellulose, for example, contains 51 per cent. and aspartic acid 48 per cent. oxygen. The reduction process which advances rapidly with rising temperature is the second dangerous stage which sets in about 50°-70°. At these ranges of temperature the reductases apparently attain their optimum of activity. Very favorable conditions for their action exist especially in the interior of a haystack where all the oxygen is consumed by oxydases. The disintegration process reaches its maximum, therefore, in the interior of the haystack and can proceed here to complete carbonization, preceding which in a preliminary stage, there are first produced brown colored intermediary products, that still contain H and O, and which also constitute the basis for the color of "brown hay." The abundant supply of oxygen, that is suddenly made available in the reduction process within the firmly packed haystack, where no outlet is possible for the generated gas, leads finally as in so many other cases to an explosion, that is to say to a rapid combustion of the available carbon compounds, both those reduced as well as those still unreduced. The heat that is generated in the reduction process can not alone explain the ignition since this never mounts to the ignition temperature of cellulose. It is only the generation of oxygen and the occurrence of an explosion that explains satisfactorily the ignition.

The hypothesis of Tschirch has not met with general acceptance, principally for the reason pointed out by Hildebrandt²³ that the development of high temperatures in heating hay does not take place under the complete exclusion of the air, as would be expected if his explanation were correct, but only after atmospheric oxygen has gained access to the fermenting material.

There is not time, nor would it be altogether profitable in this connection, to discuss the possible rôle of the reductases, oxydases, peroxydases, catalases and other enzymes that are supposed to take part in the fermentation of plant materials. They play unquestionably a very important part in the chemical reactions which are involved in the spontaneous heating of plant materials, although not necessarily an indispensable part. The writer²⁴ described in 1929 a peculiar spontaneous decomposition of sugar cane molasses that was perfectly free from micro-organisms and enzymes, in which the sugars were gradually converted into dark-colored organic compounds of higher and higher carbon content. These changes, which are the result of obscure internal chemical reactions, can

²³ Hildebrandt, "Beiträge zur Frage der Selbsterwärmung des Heues," *Zentbl. Bakt.*, (II) 71: 440-90. 1927.

²⁴ Browne, "The Spontaneous Decomposition of Sugar Cane Molasses," *Ind. Eng. Chem.*, 21: 600-6. 1929.

be explained only upon the basis of a progressive splitting-off of water from the sugar molecules, similar to those which have been previously described. As a result of this continual stripping-off of hydrogen and hydroxyl groups, residues are left which under certain conditions release their energy almost explosively in the "hot room" of sugar factories with the evolution of acid vapors, carbon dioxide and other gaseous decomposition products. A very high temperature is developed, with the result that the molasses froths and boils over, being finally converted into a porous carbonaceous residue.

We have so far considered only the heat evolution which results from the rapid oxidation of the unsaturated compounds that are produced by the splitting-off of water from sugar molecules. A certain part of the celluloses and hemi-celluloses of hay is hydrolyzed into sugar in the initial stages of the fermentation process, and the sugar thus formed must be considered as sources of heat production in addition to the sugar originally in the hay.

There are in the hay, however, large quantities of insoluble cellular materials, such as cellulose, lignin and pentosans, which are not hydrolyzed in this way, but which nevertheless undergo decomposition in the anaerobic fermentation of hay by the same process of splitting-off of water. Analytical determinations show that these cellular components of the hay undergo in the process of sweating a continual loss of oxygen and hydrogen in the form of water, with the accumulation of unsaturated residues that become richer and richer in carbon. As this decomposition progresses, the hay changes in color first to yellow, then to light brown (the color of the so-called brown hay), then to dark brown and finally to black, the product in the last state approaching the composition of the so-called hay carbon. It is not pure carbon, however, and contains only from 50 to 70 per cent. of carbon, according to the degree of alteration which the cellular substance of the hay has undergone.

It can now be readily seen that with the formation and accumulation of unsaturated residues under anaerobic conditions in the porous cellular materials of hay the accidental entrance of air into the interior of the stack may bring about such a rapid absorption of oxygen at the points of unsaturation that the temperature may be quickly raised to the point of ignition. The reaction is perfectly similar to the familiar spontaneous ignition of cotton whose fibers have been coated with thin layers of an unsaturated vegetable oil, such as that of linseed. It is not necessary, therefore, to assume with Mische, and other students of the subject, that ignition takes place only as a result of the formation of pyrophoric carbon or, according to Laupper, with the formation of pyrophoric iron. The unsaturated highly reactive de-

composition products in a fermenting haystack are produced at comparatively low temperatures far below those necessary for the production of pyrophoric carbon or pyrophoric iron. Many spontaneous ignitions of hay have occurred when there was no blackening of the material, such as would be produced as a result of carbonization. The traces of iron compounds in hay no doubt act as catalysts in the process of spontaneous ignition, similar to the action of traces of iron and cobalt compounds in the spontaneous ignition of an oily piece of cotton, but such iron can not be regarded as the fundamental cause of the ignition.

The exact coincidence of all the conditions necessary for the spontaneous ignition of hay is fortunately of infrequent occurrence. If the hay is too wet it will not ignite; if the hay is too dry it will not ferment. If there is a constant unimpeded circulation of air through the interstices of the hay, the unsaturated intermediate substances are oxidized as fast as they are formed and there is no accumulation of those easily decomposable residues which by their final almost instantaneous oxidation raise the temperature in a few minutes from 80° or 90° to the point of ignition of the hay. The opening up of a hot haystack is, therefore, a hazardous operation and should only be done when every precaution has been taken to extinguish the conflagration that may immediately break out, such as happened in the case narrated by Ranke and such as has happened in so many of the other cases that have come under observation. The first quenching of the outbreak of fire with water does not remove the danger. The unstable rapidly oxidizable residues are still there and, with the evaporation of the water from the hot hay, may ignite spontaneously again and again, as indicated by Ranke, whose description of the phenomenon has been repeatedly confirmed by other observers.

Statistics show that spontaneous ignition of hay occurs almost exclusively in large mows and stacks. The large stack not only creates a better insulation against radiation of heat from the inside and a slower penetration of atmospheric oxygen from the outside during the precursory period of anaerobic fermentation, but it also offers a more favorable opportunity for creating somewhere in the mass of material the exact conditions of moisture, temperature and oxygen penetration that are necessary for spontaneous ignition. When fermentation begins there is an immediate migration of moisture from the warmer to the cooler zones of the stack; a cool section that was previously dry enough to withstand fermentation may acquire by condensation sufficient moisture from a contiguous hot fermenting zone to become a good medium for the rapid development of micro-organisms. In this way a single load of undereured hay in

the center of a large mass of well-cured hay may start fermentations throughout the whole mass of material. With the migration of these fermenting zones from point to point there may finally be found somewhere a zone having the optimum conditions of moisture, temperature and air supply that lead finally to ignition. If this necessary coincidence of optimum conditions does not obtain, the stack, after several months of fluctuating changes of temperature, begins to cool down, with perhaps an occasional sporadic elevation of temperature at isolated points. The impeded penetration of air prevents the accelerated oxidation of the unstable organic residues; these are only very slowly oxidized and when the stack has finally approached the temperature of the outside air, these once highly oxidizable complexes are so sufficiently stabilized that the stack may be opened up without danger.

While this sketch of the chemical processes involved in the spontaneous heating and spontaneous ignition of hay is probably in general correct, there are many details of the problem that must be worked out under carefully controlled quantitative conditions. We need observations upon the production of heat, consumption of oxygen and evolution of carbon

dioxide, water, etc., by large masses of fermenting hay in a respiration calorimeter, for it is only in this way that we can determine how much of the heat is produced as a result of anaerobic reduction-oxidation reactions and how much is produced by atmospheric oxidation. We need more observations upon the elementary analysis and heats of combustion of hay at various stages of spontaneous heating. We need further research on the nature of the solid, liquid and gaseous organic compounds that are produced in both the anaerobic and aerobic fermentations of hay, particularly of those elusive intermediate compounds which are the most difficult of all to detect. We need more knowledge of the phenomena of moisture migration and heat transference in large masses of hay. We need also more exact information as to the temperatures of ignition of hay at different stages of the fermentation process. When fundamental knowledge upon these and other points has been acquired we shall be able to visualize more clearly the details of the complicated reactions that take place in the spontaneous heating and spontaneous ignition of hay and other agricultural products and to arrive at the best practical means for reducing the enormous economic losses from this cause.

BREAD QUALITY OF WHEAT PRODUCED IN AQUEOUS CULTURE MEDIA

By Dr. W. F. GERICKE

LABORATORY OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA

AMONG the causes of differences in the bread properties of wheats, those related to the quality of their proteins are of much interest to cereal chemists. Quality in flour as affected by the character of protein appears to be a very definite entity when expressed by baker's marks, and while the loaf of bread is and perchance always will remain the ultimate criteria of quality, nevertheless the concept "quality of protein" is still an intangible term, lacking a precise chemical definition. The interested trades feel a real need for simple and reliable tests of protein quality, which apparently may vary from season to season in accordance with the vagaries of climate; consequently experiments were designed to attack the problem from another angle, namely, by the water culture method, whereby specific treatment could be accorded the material selected for milling and baking operations.

Wheat protein is supposed to be identical in chemical composition among varieties. The fact of differences in the character of bread due to protein would, in lieu of differences in quantity thereof, be accounted for by differences in its physical character. It is

known that the physical state of colloid particles varies with the nature of the medium surrounding them, and as plant sap is a more or less concentrated salt solution, it appeared as not improbable that variation in the quality of wheat protein might reflect certain features of plant sap. The fact of variation in the concentration and composition of plant sap with cultural treatment and also the differences in physical character of starches derived from the same source also were suggestive as to the type of experiment required to throw more light on the protein problem.

To obtain such data, the writer grew wheat in aqueous culture media on a scale large enough to provide samples for milling and baking operations. The plants were grown in a series of tanks filled with water, over which a seed bed was mounted, and which permitted production of a crop in culture media that could be altered at will.

Full description of the technique of crop production in a water medium by mass planting will appear in due season. As a preliminary note, however, it may