SUBSTITUTION OF NITRIC FOR SULPHURIC ACID IN THE PRODUCTION OF PHOSPHATE FERTILIZERS

By Dr. G. R. DAVIES
Chemical Research Laboratory, Teddington

SULPHURIC acid is, perhaps, the most important of all chemicals, and the amount consumed usually provides a reliable index to the industrial virility of a country. In the United Kingdom the annual production of the acid has increased steadily over the years, rising in the past decade from about 1,200,000 tons to more than 1,800,000 tons in 1950. More than fifty per cent of the recent production has been made from sulphur, the remainder being manufactured from pyrites, spent oxide, zinc concentrates and anhydrite. Native sulphur is the preferred raw material because of its high purity, low shipping costs and because of the lesser operating costs of plants burning sulphur as compared with those using pyrites. Considerable concern has therefore been caused in recent months by the statements which have been issued regarding the limited extent of the reserves of brimstone in the United States, which is the major producer of native sulphur. At the present rates of consumption these reserves may last only ten or eleven years. This has led the United States to reduce its exports, and British imports of sulphur have therefore been decreased by some thirty per cent. Although the reserve position in regard to pyrites is much more secure, yet any conversion of sulphur-burning plants to enable them to use pyrites must cause serious dislocation and must require some years to complete. The present position therefore calls for strict economy in the use of sulphuric acid.

The largest consumer of the acid in Britain is the fertilizer industry, which last year used 435,500 tons in the manufacture of superphosphate, while a further 260,000 tons was employed in the manufacture of ammonium sulphate. A reduced production of sulphuric acid must lead to a decrease in the manufacture of artificial fertilizer and to a lowered productivity of British farm lands. Of course, there are numerous other users of sulphuric acid, such as the rayon industry, of which much has been heard recently and which itself consumes more than 200,000 tons of acid annually.

Because of the difficulties that might arise in maintaining adequate supplies of sulphuric acid to the fertilizer industry, the Chemical Research Laboratory, Teddington, has been studying for the past two years the possibility of making phosphate fertilizers by methods which might effect a saving in the amount of sulphuric acid used. The most obvious alternative to sulphuric acid is nitric acid, for its production does not call for the use of imported raw materials, while the nitrogen value of the acid is recoverable in the form of a nitrogenous fertilizer, and this offsets to some extent the greater cost of the acid as compared with sulphuric acid. Unfortunately, the action of nitric acid on phosphate rock leads to the production of a fertilizer containing much calcium nitrate, which is a highly hygroscopic substance and causes the fertilizer to become damp and difficult to use. Consequently, the work at the Chemical Research Laboratory has largely been confined to the use of mixtures of nitric and sulphuric acids. The action of these acids on phosphate rock leads to the formation of monocalcium phosphate, calcium sulphate and calcium nitrate, and there seemed the possibility that the inert calcium sulphate might so coat and protect the calcium nitrate as to prevent it absorbing moisture or, at least, that it would so slow down the rate of adsorption of moisture as to render the product usable without further treatment. Actually, it has been found that products made in this way are more stable to atmospheric conditions than when nitric acid is used alone. The maximum amount of nitric acid which can be tolerated in order to give a product having a low absorption of moisture is when the mixture of acids contains about 2 mol. of nitric acid to one of sulphuric. Even with this mixture of acids the fertilizer made from it is somewhat hygroscopic if the theoretical amount of acid is used to decompose the rock completely, but when only eighty per cent of this amount is used the material does not pick up any appreciable amount of moisture at relative humidities below seventy per cent. The reaction between the phosphate rock and nitric–sulphuric acid mixtures is quite vigorous and goes to completion much more rapidly than when sulphuric acid is used alone as in ordinary superphosphate manufacture. The product also sets quickly to a dry, crumbly product, although it will dry out a little further in the course of a day or two. The fertilizer made in this way contains about 18 per cent of phosphate (reckoned as P_2O_5), of which 86 per cent is water-soluble, while 96 per cent is dissolved by 2 per cent nitric acid. The nitrogen content is about 4 per cent. There is very little evolution of hydrofluoric acid during the reaction and virtually no loss of nitric acid as nitrous fumes.

Attempts have been made to include potassium chloride in order to provide a complete fertilizer ; but with any substantial addition of this substance the products are more sensitive to atmosphere moisture.

A report on the work has been presented to the Fertilizer Manufacturers' Association.

SCIENCE AND BREWING

WHETHER brewing is an art or a science continues to be a question for debate ; but it cannot be doubted that the impact of science on the brewing industry is becoming ever more insistent. Economic conditions are enforcing a more considered use of raw materials and plant ; on the other hand, the selection of new barleys suited to changing agricultural conditions, malting for brewing, the selection and conservation of desirable yeasts, the development of acceptable disease-resistant hops and a better understanding of the many processes of mashing, fermentation, maturation and others making up what is colloquially known as brewing, are only a few of the numerous questions calling for scientific investigation. It was timely, therefore, when the Microbiological Group of the Society of Chemical Industry, the Incorporated Brewers' Guild and the Royal Microscopical Society held a symposium on brewing on March 14 in the Chemistry Department, King's College, Newcastle upon Tyne.

In an opening contribution on "Beer and the Biochemist", M. H. Van Gruisen (Newcastle Breweries, Ltd.) paid tribute to the help which science has given and is giving to the brewer in enabling him to produce a stable and uniform product from unstable and variable raw materials. Thus, malting barley has received much attention from agriculturists and plant breeders, with the result that, through selection and breeding within the past fifty years, the brewers' extract of normal malts has risen by four or five pounds per quarter, while at the same time the farmers' yield per acre has also increased.

In the hop garden the main task has been the continued warfare against various pests and diseases to which the plant is prone. Wilt-resistant varieties have been bred, and these are at present undergoing large-scale brewing trials. Hops with a high resin content have also been reared to replace American hops which are no longer available.

Finally, of the ingredients of the brew, the water or 'liquor', the composition of which is often thought to account for the pre-eminence in brewing of certain areas, such as that of Burton-on-Trent, must not be overlooked. Now, with analytical methods available and the effects of minor constituents on various reactions in the brewing process better understood, breweries with less-favourable water supplies are able to make the necessary adjustments.

From the biochemical point of view, the brewing process is in effect the production of a culture medium for yeast. The need for a thorough understanding of wort constituents and yeast nutrition has led to a considerable volume of research on starch and plant proteins.

During malting, enzyme systems develop which in the mash tun break down the starch of the original barley corn into maltose and dextrins of various degrees of complexity. The ratio of these fermentable to non-fermentable products may be controlled by mashing conditions and are of importance to the brewer. Maltose, by its breakdown to alcohol and carbon dioxide, yields to the yeast the energy required for reproduction, while the unfermentable dextrins give character to the finished beer.

The protein breakdown largely occurs during malting. The amino-acids and some of the very simple di- and tri-peptides are potentially utilizable by the yeast as nitrogen sources for building new cells. These amino-acids may be used directly or may supply nitrogen by transamination or deamination, by the Ehrlich mechanism, to give the alcohol corresponding to the amino-acid. This factor is of some importance, as the resulting higher alcohols contribute to the aroma of the beer. Of the more complex nitrogenous products, most are removed during the brewing process, but the β-globulin fraction survives in combined form with hop tannin. Albumen degradation products are probably responsible for the head-retaining properties of the beer, but globulin tannate is the cause of chill and oxygen hazes which are particularly detrimental to bottled beers.

In a second contribution, "Enzymes and their Significance in Brewing" were discussed by Prof. I. A. Preece (Heriot-Watt College, Edinburgh). He said that, if the term brewing be restricted to mean the preparation of a specialized medium for yeast growth and fermentation, the enzymes to be considered weie those of barley and malt, and the reactions those concerned in malting and mashing; the subsequent boiling of the wort with hops inactivates residual enzymes and stabilizes the composition of the fermentable medium.

The enzymes concerned may be considered to form two groups, of which the first contains the general metabolic enzymes already present in the raw barley. Particular significance here is attached to the dehydrogenase system, the activity of which in living corns permits determination of the germinative capacity of a barley sample, so giving rapid distinction between dead corns and those which are merely dormant. However, since the power to germinate is not accurately paralleled by retention of dehydrogenase activity, samples which have suffered a moderate degree of heat damage may give misleading results in the test. Other enzyme systems in this general group include: catalase, which again shows differences of behaviour in living and dead corns; phosphorylase, associated with starch synthesis; and the interlinked systems concerned in aerobic and anaerobic energy release.

The second group of special metabolic enzymes includes many where reversibility of action has not been demonstrated; to some extent, these enzymes resemble those of the animal digestive tract. It is a main purpose of malting to allow development of these enzymes, or—if they are already present in the raw grain—to facilitate their extraction in the subsequent mashing. A second main purpose is the modification of the hard barley grain, the intense enzymic activity during germination causing hydrolysis of cell-wall and related materials, so permitting adequate crushing of the grain and reducing the viscosity of the extract obtainable; at the same time, a proportion of the nitrogenous material is hydrolysed to provide yeast-feeding compounds, and α-amylase is produced in amounts which permit speedy saccharification of starch to be achieved in the mashing process. The kiln treatment of the germinated grain produces a malt dry enough for safe storage, stabilizes its composition, allows control of the proportions of the various enzymes present, and adds colour and flavour.

Little cytolysis or proteolysis occurs during the British infusion system of mashing, and quantitatively the main enzymic reaction is starch hydrolysis. This produces fermentable sugars (glucose, maltose, maltotriose) and unfermentable dextrins (branched and unbranched α-dextrins) as a result of the joint activity of α- and β-amylases. The heat instability of the latter near the temperature of an infusion mash (for example, 65° C.) permits a high measure of control of the proportions of fermentable and unfermentable materials formed, since the production of maltose by β-amylase in mashing decreases sharply as the temperature is raised, while the α-amylase activity is but little affected in the range 63–67° C.

In the final session, Dr. A. H. Cook (Brewing Industry Research Foundation) spoke on "The Significance of Microbiological Research in Brewing". This significance does not so much extend into the past as reach out into the future; despite three centuries of microbiological history, this science has only acquired any coherent form as a result of a few epoch-making advances, such as that of the antibiotic field, of the comparatively recent past.

Consideration shows that antibiotics may have some, if limited, use in the brewery. Subtilin is receiving attention as a preservative of foodstuffs, while antibiotics in a more limited sense may play a part in the orderly development of the individual organisms comprising a normal brewers' yeast; a prominent example is the development of *Brettanomyces* species in maturing cultures of *Saccharomyces cerevisiæ*. Although not of microbial origin, humulone and lupulone have an antimicrobial action, and the suggestion has been made that lupulone may offer a means of ingress to the antitubercular field. In adding to such approaches, many physical methods of controlling yeast and bacterial growth in the brewery have still to be explored. Ultra-violet sterilization has not been without success ; ultrasonic treatment may be of value in this way as well as in rapid 'conditioning' (so far as protein precipitation is concerned), and cathode-ray treatment, now receiving intensive examination in processing foods, may provide another sterilization treatment lacking the disadvantages of pasteurization.

Turning more particularly to some aspects of brewery fermentation, only very recently has there become available even a partial view of the carbohydrates and of the amino-acids and other nitrogenous constituents of brewers' wort, as well as of their value as yeast nutrients and substrates. A brewery yeast, however, must obviously effect a composite fermentation, and in studying the component parts the National Collection of Yeast Cultures, which will be a responsibility of the Brewing Industry Research Foundation, seems likely in many instances to play an important part. Subsidiary collections of brewers' yeasts and of genetically pure and hybrid yeasts should have a peculiar research interest. The hybridization of yeast has only recently been intensively studied, mainly by Winge and his associates, who have provided much of the available data on the sporing and on the haplo- and diplo-phases of certain species of *Saccharomyces*. This work has proved valuable in the selection of hybrids for simple fermentation yeasts, but its exploitation in the brewery has hitherto been less marked. Such exploitation is, however, brought nearer by recent work of Thorne, who has succeeded in hybridizing several British top-fermentation brewery yeasts. Selection of the hybrids reveals that flocculence is a genetically controlled character. The observed segregation of the readily mutating hybrids makes it appear that not less than three genes are concerned with the appearance of flocculence, while still another seems concerned with inhibiting the expression of flocculence.

There are innumerable other points at which microbiology touches brewing. These range from the use of insecticidal washes in hop culture to the importance of wild yeasts in brewery casks, from the disposal of potentially toxic materials by yeasts to the formation of valuable vitamins. These are but a few of the problems which research in the not too distant future should do much to answer.

OBITUARIES

Mr. J. W. Tutcher

By the death, on April 11, of John William Tutcher, in his ninety-third year, geology has lost one of its outstanding amateur workers. He will be remembered particularly for his many contributions to the study of the palæontology and stratigraphy of the Jurassic rocks of the Bristol district, and for his pioneer work in scientific photography.

Until recent years Mr. Tutcher carried on business as a bootmaker in Bristol; but most of his leisure was devoted to geology. In his younger days this frequently involved cycling out before business hours to the quarries of Dundry Hill and, when some particularly interesting bed was being uncovered, walking back with his cycle loaded with specimens. When his own lameness is borne in mind, one could only marvel at his success in bringing together and preparing the collections which overflowed into all parts of his home. Apart from numerous specimens which found their way into other museums, the Bristol City Museum has more than 20,000 fossils from the Tutcher Collection, all with details of locality and precise horizon. At all times his specimens were placed at the disposal of other geologists, and many younger geologists owe much to his ready help. He wrote comparatively little himself, unless very strongly persuaded ; but he contributed several papers to the *Proceedings of the Bristol Naturalists' Society* and to the *Quarterly Journal of the Geological Society*. For many years he worked with the late S. S. Buckman, and his name appears on the title-pages of the seven volumes of "Yorkshire Type Ammonites" and "Type Ammonites", for which he provided most of the photographs. But his contribution, as Buckman always freely admitted, was not confined to the preparation of plates ; his great knowledge of the detailed stratigraphy of the Lias in particular was of great service to his collaborator.

Mr. Tutcher was probably the first person in Britain to build a piece of equipment for the lighting and photography of fossils, a work in which he acquired such skill that, twenty years ago, it was nearly always possible, on skimming a volume of geological papers, to pick out by their high quality the illustrations prepared by Tutcher ; for in this field he was always ready to help others, and it has been estimated that he provided for reproduction photographs of several thousand fossils.

Mr. Tutcher was awarded the Lyell Fund by the Geological Society in 1924, and received the honorary degree of master of science from the University of Bristol in 1927. He was for many years a prominent member of the Bristol Naturalists' Society, of which he became president. He was also president of the South-Western Naturalists' Union. His modesty and kindness will long be remembered by those who were privileged to work with him. A. E. TRUEMAN

Prof. F. K. Kleine

PROF. FRIEDRICH KARL KLEINE, a distinguished pioneer and leader in the field of research into tropical diseases of man and animals in Africa, died in Johannesburg on March 22 at the age of eighty-one.

Kleine was born on May 14, 1869, at Stralsund, a Baltic port of Germany. He was the son of a medical practitioner, and early decided to follow his father's profession, entering the University of Halle as a medical student. After qualifying, he worked at the Pharmacological Institute in Halle, and at the University Clinic in Kiel, and served also for a time in the Army Sanitary Service. In 1900 he was appointed to the staff of the Institute for Infectious Diseases in Berlin, and there became personal assistant to Prof. Robert Koch, the discoverer of the tubercle bacillus and of the cholera vibrio. In 1903 Kleine went with Koch to Southern Rhodesia to investigate a disease, thought to be redwater, in cattle, which was causing great economic losses. Their investigations showed the disease to be tick-borne and distinct from redwater, and they named it 'African coast fever'. This finding led Kleine to become one of the first to work on the developmental stages of the parasite of tick fever in dogs—a story which is still not properly elucidated. During 1906–7