

Utilisation of waste products is not overlooked in the canning industry. The small fruits, trimmings, etc., are sometimes extracted for their juice for fountain syrups.

The apple wastes such as peelings and cores are either dried and sold for wine and vinegar purposes, or else the juice is pressed out and sold as cider, or made into cider vinegar. Unfortunately the demand for cider vinegar in Canada is not sufficient to allow of the profitable treatment of apple waste for this purpose. However, it is very profitably turned into apple jelly to be used as the base for compound jams. When these wastes are properly handled, no objection whatever can be taken to their use.

In pea canning large quantities of pea vines are left over, which make very good ensilage. Some factories have their own silos, and sell the ensilage in the winter, while others allow the farmers to take the vines away free of charge; in other places it is necessary to pay to have them carted away.

In corn canning there are large quantities of corn silk, a small part of which is used to make extract of corn silk for medicinal purposes. The use is limited, however, but we hope some day to find a large and profitable outlet for corn silk. The corn stalks, corn cobs, and husks, make good ensilage. The question of production of alcohol has been investigated, but it was found that the recovery of alcohol would hardly pay for the cost of installing a plant.

Large quantities of seeds from tomatoes and pumpkins, as well as the stones, etc., from cherries, plums, and peaches, are now being utilised for their oil.

Many companies now have experimental farms, including several in Canada carried on by the Dominion Canners, the largest of which, situated near Brantford, is about 1000 acres, and is devoted entirely to seed production.

In the modern factory equipments the effect of the laboratory can be seen. The old retorts are being supplemented by ones in which the cans are agitated, thus shaking the contents and lessening the time of penetration of the heat, cutting down the time of sterilisation, and giving improved flavour and appearance.

No doubt the future will see the more general adoption of the intermittent system of sterilisation, that is, instead of sterilising in one operation at a high heat to kill the spores, the sterilising will be accomplished in two operations at lower temperatures: the first will kill all organisms except the spores, then in two or three days these spores will have developed, and a second heating will kill these developed organisms. This of course entails handling the product twice, and hence would be costly, but no doubt can be worked on a small scale, and the increased quality and appearance of the goods will bring a higher price.

In place of the old iron pipes and iron parts on cookers, filling machines, etc., there are now copper, brass, enamel, or silver. In place of the old wooden floors is concrete, and in place of the old wooden top tables, enamel or even glass tops; in fact, everything is arranged so that a hose can be turned on and the factory washed out very rapidly.

In Germany the canners subscribe to a large laboratory and experimental factory; in the United States there are many private laboratories, and now a laboratory under the Canners' Association is to be started. In Canada, the Dominion Canners are the largest corporation, and they have their own laboratory and experimental departments.

The canning industry makes it a practice to investigate all the reports as to alleged ptomaine poisoning due to canned foods, and in practically every case gets a denial of the charge. A ptomaine is described by Vaughan and Novy as "an organic chemical compound, basic in character, and formed by the action of bacteria on nitrogenous matter," or in other words it is a putrefactive alkaloid, a product of decomposition. There are many known ptomaines, but very few of them are really poisonous. The poisonous ptomaines may be formed by pathogenic organisms, by a few yeasts and moulds, and a few anaerobic spore-bearing organisms, all putrefactive in their action. There must be putrefaction to get poisonous

ptomaines, and no packer would think of packing putrefactive products, so the only possibility arises where a can has leaked or swelled. Of the hundreds of reported cases of poisoning from canned foods, I only know of one where the charge was proved, and that was from a can of salmon that had a pin-hole leak, and the consumer should not have eaten the contents, which were abnormal. Physicians and others should be very careful before diagnosing a sickness as due to ptomaine poisoning caused by eating canned foods: an injury is being done to a large industry, and the public are needlessly scared.

Canned foods are generally regarded as non-perishable products, and are consequently put into a shed or damp cellar which is not fit for anything else. The result is that the labels are discoloured, the cans rust, and pin-hole leaks result. Although freezing does not materially alter the flavour of canned foods, it is not advisable to allow them to be frozen, for when they thaw out the cans sweat and rust very easily. All canned foods should be stored in a dry place, of even temperature, with good air circulation around and underneath the pile.

London Section.

Meeting held at Burlington House on Monday, 3rd February, 1913.

DR. W. R. HODGKINSON IN THE CHAIR.

THE TECHNICAL PRODUCTION OF ETHANE.

BY DR. C. SPRENT.

On account of the growing importance of Sabatier's method of "hydrogenation" in chemical industry, the following description of another successful technical application of this method, namely, the production of pure ethane by the combination of hydrogen and ethylene in the presence of finely divided nickel, will no doubt be of interest.

The investigations here outlined are the results of experiments carried out by the author at the "Elektro-chemische Werke G.m.b.H." in Bitterfeld. The ethane, on account of its low boiling point ($-93^{\circ}\text{C}.$), was required in the place of carbon dioxide for a refrigerating machine, which required a filling of about 600 kilos. of ethane, and was especially constructed for this purpose.

All other known methods for the production of ethane were first tried, but were found to be unsuitable. To make ethane, Sabatier* passed a mixture of 2 vol. of ethylene and one vol. of hydrogen through a tube one metre in length, containing freshly reduced and finely divided nickel: the gas on leaving the tube was passed through fuming sulphuric acid in order to absorb the excess ethylene. The resulting gas was then found to be pure ethane.

By means of the theorem of Nernst applied to the equilibrium, $\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$, it may be shown that one vol. of hydrogen can be added to an equal vol. of ethylene in such a way as to leave practically no remainder of either of the gases of the left side of the equation. It is merely necessary to find the right catalyst and conditions for the desired result. Simple though this reaction appears, the production of ethane in quantity was found to be a difficult matter, requiring for its completion as a rational process a thorough investigation and the application of very different methods than would have been supposed necessary.

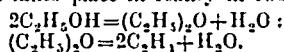
The chief difficulties encountered can be placed under two heads, firstly the production of pure ethylene, and secondly the quantitative saturation of one vol. of ethylene by one vol. of hydrogen.

* Chem. Zeit., 1907, 1096.

First, as regards the former of these. The method used was fundamentally that of Mailhe, by the passing of the vapour of alcohol over aluminium oxide according to the reaction, $C_2H_5 \cdot OH = C_2H_4 + H_2O$. Mailhe* showed that the catalytic action of the aluminium oxide was not only dependent on the temperature, but also on the physical structure of the catalyst, an amorphous oxide giving a good yield of ethylene, and the crystalline oxide a poorer one. In these experiments the same phenomena were very often observed; many samples of alumina gave no ethylene whatever, but converted the alcohol into an oily substance. The catalytic value of any sample of alumina can be tested to some extent by shaking the oxide with distilled water. The active samples treated thus are converted partially into a colloid, the particles of which move towards the cathode when subjected to an electric current. The particles of inactive samples immediately fall to the bottom of the vessel. Kahlbaum's aluminium oxide, "gereinigt," gave better results than any oxide prepared by myself.

Great care must be taken to keep the reaction at the temperature at which the yield of ethylene is at a maximum, namely, $360^\circ C$. If the temperature be raised the ethylene commences to decompose, forming hydrogen, methane, and carbon, and, moreover, the yield of gas decreases, on account of the amorphous oxide being slowly converted into the crystalline state. The high temperature also affects the catalyst in such a way as to alter the nature of its reaction with the alcohol, and thus aldehyde and hydrogen can be evolved by the decomposition of the alcohol.

On the other hand, the temperature should not be allowed to fall below $360^\circ C$; because not only does the amount of ethylene then decrease, but a considerable amount of ether may in this way pass into the ethylene. The ether is formed by a primary decomposition of the alcohol, which takes place at a temperature of about $230^\circ C$. The ether itself, however, is also decomposed, forming ethylene and water at a temperature of 300° . Unless the temperature of the whole apparatus where the gas is generated is kept at 360° , a portion of ether may pass through with the ethylene without forming ethylene. The reaction takes place in reality in two phases,



Especially in an apparatus on a large scale it was found that the ethylene always contained some ether, sometimes as much as 10 per cent. This fact is lost sight of in the laboratory if the gas is collected over water, or the usual solutions used for the determination of the gases by absorption.

The formation of the ether can be reduced to a small percentage, if the oven in which the reaction takes place be placed in a lead bath and the alcohol vapour heated to a temperature of 360° before being passed through.

For the production of ethylene in quantity, iron tubes 3 inches in diameter and $1\frac{1}{2}$ metres in length were employed; these were fitted inside with suitable contrivances to hold the catalyte. The tubes were connected with the vessel in which the methylated spirit was evaporated.

Ethylene produced in this way is not, however, yet able to be used for the synthesis with hydrogen to form ethane, as it contains impurities which on coming in contact with the finely divided nickel bring about a decrease of the catalytic activity of the nickel, and, if the process is continued, eventually cause it to become entirely inactive. The elimination of these disturbing impurities formed the chief difficulty in the beginning of these experiments. Firstly it was found indispensable to eliminate the ether and other traces of impurities such as aldehyde, isoprene, etc., by compressing the ethylene up to about 50 atmospheres. In this way the impurities were condensed and could be removed by a suitable contrivance in the apparatus. If these impurities were allowed to pass into the nickel oven not only was the catalytic action impaired, but the gas was made impure by the products of decomposition of these substances. The ethylene thus

treated was also found to contain traces of sulphuretted hydrogen arising from the presence of sulphates in the alumina. This impurity was removed by passing the gas through a solution of lead acetate. A further washing of the gas with concentrated sulphuric acid was found essential; certain impurities, the nature of which was not determined, and which acted as poisons to the contact substance, were eliminated by this treatment.

The ethylene purified in this way was entirely free from any impurity, having a weakening effect on the catalyte. The hydrogen used was a product of the alkali works of "Griesheim-Elektron" in Bitterfeld, and was so pure as to require no further treatment.

The two gases, ethylene and hydrogen, were mixed in equal volumes, the adjustment being made with the aid of the gas-mixing and measuring apparatus known as the "Rotamesser," and then allowed to pass into the oven containing the finely divided and freshly reduced nickel. This oven was constructed similarly to the oven used for ethylene, only here the tubes were only one meter in length and four in number. The first two were coupled parallel with one another, the gas leaving each of these combining and passing into two more similar tubes coupled one behind the other. The dimensions of the tubes were determined by experiment, so that by the gas-velocity used (2 cbm. per hour) the temperature arising from the formation of the ethane (the reaction is exothermic) was unable to reach the point at which ethane decomposes, on account of the radiation of the heat. Working with the same gas velocity and a greater diameter of the oven, it was necessary to cool the interior by means of waterpipes.

The necessary temperature of $200^\circ C$. can be kept up with very little external heating. The difficulty, however, was that under no conditions of temperature, or by means of any arrangement of the contact substance in the oven, could the reacting gases be made to unite quantitatively, the best result obtained being a percentage of 10 per cent. ethane in the gas formed. This became a very acute difficulty, as chemical methods of removing the hydrogen and ethylene proved impracticable.

The next step was to employ an air-condensing apparatus (Linde's system), used for the production of oxygen, and attempt to separate the ethylene and hydrogen from the ethane by means of rectification. This proved only a partial success, as only hydrogen could be eliminated, the ethylene remaining with the ethane. The rectifying column of the machine worked under a pressure from 3—5 atmospheres, and no doubt it would have been possible to get a better result had there been another column where the liquid gases had been under a pressure of only a little more than that of the atmosphere. In fact it was shown that the liquid gas mixture, after standing some time in a Dewar flask, contained only 1 per cent. of ethylene. However, the loss of ethane carried off with the other gases would mean a very considerable one.

The solution of the problem was only arrived at when it was decided to effect the combination of the two gases under pressure. According to the law of Le Chatelier, it was clear that pressure must have a beneficial effect, but in consideration of the sudden rise of temperature occasioned by the combination of so much gas in the small oven, it seemed unavoidable that the temperature should rise above the temperature of decomposition of ethane. Moreover, a polymerisation of the ethylene seemed possible.

Experiments showed that the combination of equal vols. of ethylene and hydrogen under pressure in this way was impracticable, owing to the sudden rise of temperature making a proper control of the apparatus uncertain and precarious. However, by passing the gas mixture containing 80% ethane, 10 per cent. ethylene, and 10 per cent. hydrogen at a pressure from 30—40 atmos. through an iron autoclave filled with nickel pumice stone, a complete success was attained, the resulting gas being pure ethane.

The 80 per cent. ethane gas mixture, produced in the way mentioned above, which was collected in a gasometer, needed only to be drawn off by means of a gas-compressor, which then pressed the gas through a second nickel oven which, as already stated, was held under a pressure of

* Chem. Zeit., 1909, pp. 18, 20, 242, 253.

from 30 to 40 atm. From thence the gas passed through the condenser straight into the steel cylinder, where the ethane was liquefied and weighed off.

A careful adjustment of the "Rotamesser" measuring the volumes of the two gases at the commencement of the process is necessary to the success of the reaction, as an excess of one or the other of these gases naturally detracts from the purity of the ethane. The error must be in this case corrected by an addition of the required amount of one of the gases to the gasometer containing the ethane gas mixture.

It is advisable to work with a slight excess of hydrogen in order to avoid disturbances of this kind, as the hydrogen can always be "blown off" by opening the valve of the cylinder containing the liquid ethane. In the case of ethylene this is not possible.

The process here described runs continuously, and, with the little trial plant set up in Bitterfeld, 25 kilos. of liquid ethane were made daily. The plant is to be employed to produce 100 kilos. per diem.

During these experiments several interesting secondary reactions were observed, a description of which will be given at a later date.

THE FEEDING VALUE OF THE HORSE-CHESTNUT.

BY S. J. M. AULD, D.Sc. (LOND.),

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During the year 1911, particularly abundant crops of acorns and of horse-chestnuts caused farmers and stock breeders throughout the country to turn their attention seriously to the possibility of using these substances for feeding purposes. The value and use of acorns as a stock feed has been much discussed, and many owners are well acquainted with their use, but the horse-chestnut has not been so seriously considered, although one or two cases are known to the writer where they have been used as a feeding stuff. Many inquiries on the subject were received at Wye College during the past year, and as very little information was available in the literature, it was decided to investigate the value and suitability of horse chestnuts as a constituent of regular rations for various animals.

The horse-chestnut, *Aesculus Hippocastanum*, grows in large quantities throughout the United Kingdom and the nuts, which have a very bitter taste, are popularly supposed to be poisonous. Little is known, or at any rate recorded, with regard to their chemical composition. They contain a saponaceous substance, the exact nature of which is undetermined, but the presence of which can easily be demonstrated by the froth produced when the ground-up nuts are shaken with water.

Preliminary examination.—A preliminary chemical examination showed the presence in the horse-chestnuts of an appreciable quantity of a non-drying oil, a small amount of tannin, the saponin, and certain uncharacterised glucosides. Whether the latter are identical with the aescoulin and aesculetin which have been separated from the bark of the tree, and aphrodisin which is stated to exist in the seeds, is not certain. The bitterness of the nut is, however, probably due to glucoside-like substances, and not to tannin, since it persists after the removal of the latter and is destroyed by digestion with dilute acid. The bitter substance is extracted with alcohol and is not precipitated with the saponin by means of lead acetate.

Analysis of horse-chestnuts.—About half a ton of chestnuts were procured for the experiments and samples were drawn from these for analysis. The relative proportions of husk and kernel were determined on the material as received and also after drying at 50°–60° C., and at 100° C. The proportions are:—

As received—			
85.5 per cent.	kernel	containing	41.17 per cent. water.
14.5 "	husk	"	19.44 "
Air dried—			
82.0 "	kernel	"	2.22 "
18.0 "	husk	"	7.06 "
Dried at 100° C.—			
83.1 per cent.	kernel		
16.9 "	husk		

The kernel consequently loses its moisture more readily than the husk, and, in so doing, it shrinks away from the latter, thus facilitating decortication.

Analyses of the ground air-dried kernel and husk carried out by Mr. E. A. Fisher, of the Wye College Chemical Department, gave the following results:—

	Kernel per cent.	Husk per cent.	Total nut per cent.
Water.....	2.22	7.06	3.04
Ash.....	2.86	1.60	2.66
containing phosphoric acid (P ₂ O ₅)	20.11	12.10	—
Crude protein	12.03	5.66	10.99
True protein	8.77	4.37	—
Crude fibre	2.13	13.15	5.34
Oil (ether extract)	0.26	0.89	—
Carbohydrates (non-nitrogenous extractive matter) containing sugar	71.45	71.58	73.07
	2.51	—	—
	100.00	100.00	—

It is obvious, therefore, that the horse-chestnuts should form a very nutritious feeding-stuff. The amount of crude fibre is greatest in the husk, but in the complete nut it is not excessively high. The amount of crude protein is considerable and very important, despite the fact that about 3 per cent. consists of amides, amino-acids, etc. The oily material, also, is higher than generally supposed.

Feeding experiments with horse-chestnuts.—The feeding trials were largely carried out by Mr. G. O. Searle of Wye College, to whom the writer wishes to express thanks for his painstaking assistance. The experiments throughout were regarded as of a preliminary nature, and though many animals were given the nuts in small quantities to test their palatability, four only were set aside for a protracted trial, *viz.*, a calf, a sheep, and two pigs.

Preparation of the nuts.—Given whole, or only roughly crushed, most animals refused the nuts or ate them sparingly. It was decided that they should be dried and ground. Air-drying at ordinary temperatures is too slow and incomplete, and recourse was had to drying with artificial heat. Experiment showed that this could be done in a hop-oast by using a good fire, but any oven in which the temperature can be raised to about 70° C. could no doubt be used. After drying and partial crushing, the greater portion of the outer husk may readily be removed; the residue is then ground to a meal of any desired fineness. For these trials the grinding was done in a hand mill in the laboratory.

Grinding after boiling with water.—The ordinary chestnut meal prepared as above retains the bitter taste of the original nuts, and attempts were made to remove or reduce the quantity of the bitter principles present in order to make the feed more palatable. Boiling the meal with water produces a thick porridge-like mass which is impossible to strain, and soaking in cold water alone has practically no effect. Extraction with alcohol is useful, but does not wholly remove the bitterness; indeed, the extracted material when mixed with milk was refused by some young pigs.

Eventually the partly crushed chestnuts were allowed to soak in cold water over-night, then boiled for half an hour or so and the water rejected. The residual material was dried, partially husked and reduced to a meal as before. This material is still bitter, but less so than the ordinary meal, and has a pleasant smell and appearance. An analysis of this mixture showed the following composition:—

	Per cent.
Water	8.2
Ash	2.5
Crude protein	9.1
Oil (ether extract).....	6.3
Crude fibre	9.5
Carbohydrates	64.2
	100.0