MANUFACTURE OF FORMALDEHYDE FROM ETHYL ALCOHOL.

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Before the technical production of synthetic resins, the use of formaldehyde was restricted mainly to the preparation of synthetic organic medicinal compounds like hexamethylene-tetramine and of certain synthetic dyestuffs, for example, of the acridine series. But with the advent of phenol-formaldehyde and urea-formaldehyde resins in large quantities in the market, formaldehyde has become one of the important heavy chemicals in modern chemical industries. The starting point for formaldehyde manufacture is as yet methanol, but numerous investigations have been directed towards obtaining the same (formaldehyde) from other raw materials as ethyl alcohol, glycerine, glycol, methane, coalgas, ethylene, carbon monoxide and hydrogen. The use of gaseous catalysts and high frequency electric discharge has also been attempted as means of producing formaldehyde, but as yet these processes are in an experimental stage. The importance of manufacturing formaldehyde from sources other than methyl alcohol would be realised when one takes into consideration the unavailability as yet of cheap methanol in this country. Wood spirit of high and suitable purity is manufactured by the Mysore Iron and Steel Works at Bhadravati, but its price on the spot is of the order of Rs.3-8-0 per gallon. Under best possible conditions, with Rs.3-8-0 per gallon of methyl alcohol, the cost of production of a pound of formalin would be about 7½ annas at Bhadravati, whereas from synthetic methanol (at 8*d.* to 11*d.* per gallon), the cost would not exceed 2 annas per pound. As a matter of fact, formalin is *sold* in America at 6 cents = 3 annas per pound, showing thereby that the actual cost of production is somewhat lower than 3 annas per pound. The use of formalin in the manufacture of shellac moulding powders, which has assumed a stage of considerable importance, would require it to be produced at very much lower rates than 7½ annas a pound, and hence a systematic study of processes for the manufacture of formalin from other sources has been initiated at the laboratories of the Indian Lac Research Institute. The present communication is only one of a series to be published shortly, with ethyl alcohol as the starting material in the first instance, as the latter is readily available throughout India. Under very good working conditions, the cost of production of a gallon of 96% ethyl alcohol would be 5 annas, and the sale price would not exceed 8 annas. This figure of 8 annas per gallon of ethyl alcohol has been taken for the calculation of cost of production of formalin with the result that 1 lb. of formalin costs only 1½ annas.

The conversion of ethyl alcohol into formaldehyde *via* acetaldehyde, though not unfamiliar, is as yet very little explored. The experimental procedure followed at the Indian Lac Research Institute was as below:—

The lay out of the laboratory apparatus:—

A 500 c.c. round bottomed flask (*A*) was provided with a triple bored cork through the holes of which are introduced a thermometer, a tube conveying compressed air and another leading in the vapour of ethyl alcohol and air into the reaction tube (*B*) containing a roll of copper gauze of 40 mesh and 12 cm. length. The diameter of the roll was 16 mm. which just fitted into the reaction glass tube. The flask (*A*) containing 200 c.c. rectified spirit was dipped in a water bath so heated that the temperature shown by the thermometer was between 50°–56°C. The compressed air was bubbled at a rate so that five volumes of air corresponded to one volume of ethyl alcohol vapour. This was adjusted by previous calibration. The copper gauze had in its core the thermocouple junction (copper-constantan) the leads of which came out through that end of the reaction tube through which the vapour-air mixture was introduced. The other end of the reaction tube was connected with the absorption system (*C*, *D*, *E*) containing water as shown in the figure. A round bottomed flask and condenser set up between *B* and *C* serves as a catch for unconverted alcohol. The exit gases which contained invariably some CO and H_2 together with a large excess of nitrogen were led out into the air.

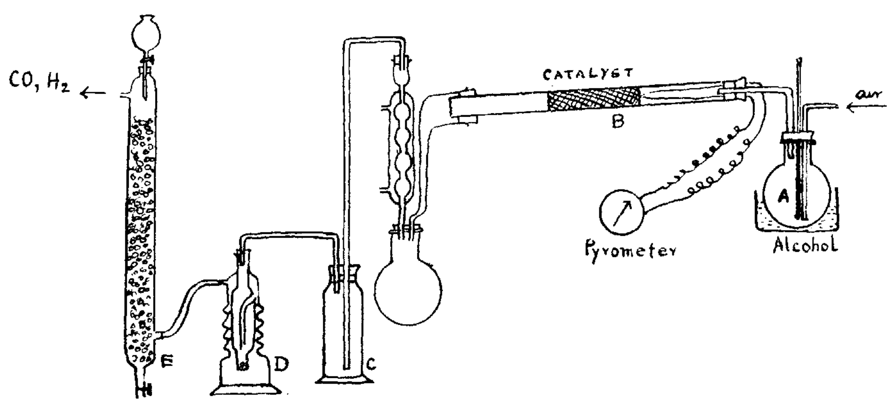

FIG. 1.

The copper roll was at first heated to 300°C. and the alcohol vapour and air mixture was passed over it. The heating was so regulated by a Bunsen burner or electrically that the temperature did not exceed 350°C. With such a single system, 35 to 40 c.c. of ethyl alcohol could be passed hourly with a conversion into acetaldehyde of as high as 80% of the alcohol passed. By more rapid passage, the percentage of alcohol converted into acetaldehyde decreased considerably, but the total quantity of aldehyde produced per hour could be substantially increased. For example, 106 c.c. of ethyl alcohol passed over the copper catalyst in 60 minutes gave 43·4 grams of acetaldehyde, corresponding to 54% conversion, whereas 44 c.c. of alcohol passed in the same period yielded 26·88 grams of acetaldehyde, corresponding to 80% conversion. The contents of *C*, *D*, and the round bottomed flask are distilled up to 60°C. to separate the aldehyde, whilst the water of the scrubber, *E*, is returned to the preceding series. The concentrated aldehyde is then passed through a similar system as described above, but the copper gauze is maintained at a temperature of 450–500°C. A mixture of formaldehyde and acetaldehyde is now obtained which can be separated by fractionation. To illustrate the process, 70 c.c. of alcohol gave rise to 34 gm. of acetaldehyde, which finally on further oxidation gave 6·6 gm. of formaldehyde and 14·2 gm. of acetaldehyde together with a recovery of 21·2 c.c. of ethyl alcohol. For the estimation of formaldehyde in the presence of acetaldehyde and ethyl alcohol, the method proposed by Romijin (Z. Anal. Ch., *36*, 18, 1897) was followed. In brief, this method consists in estimating total aldehyde by the $NaHSO_3$ method and formaldehyde by KCN method. It should be noted here that the method has not been found to be very accurate in our hands. Calculating the yield figures on the basis of the above experiment, 5·75 lb. of formalin (40% formaldehyde) are produced per gallon of ethyl alcohol. Taking alcohol at 8 annas per gallon, the raw material cost for 5·75 lb. of formalin is only 8 annas. Assuming 20 lb. of steam for the fractionation of 5·75 lb. of formalin, the cost of the necessary coal is only three pies when coal is taken at Rs.10 per ton. Adding another 6 pies for depreciation, etc. the cost of 5·75 lb. of formalin works out at 8¾ annas or 1·52 annas per lb. of formalin, a figure attainable only from very cheap synthetic methanol.

As a comparison, the cost of manufacture of formalin from wood spirit of Mysore Iron and Steel Works, Bhadravati, is detailed below:—

	Rs.	as.	p.
One gallon of C.P. methyl alcohol	3	8	0
Process charges including depreciation, interest and overhead charges	0	0	9
Cost of 7·5 lb. of formalin ..	3	8	9

or, 7½ annas per lb.

It would appear that formaldehyde from ethyl alcohol is very much cheaper than that from wood spirit and is practically at the same level of costs as with synthetic methanol.

The separation of formaldehyde from acetaldehyde doubtless brings in complications, but the low cost of ethyl alcohol would appear to justify the introduction of such a process in India, where the disposal of molasses remains as yet an unsolved problem.

The commercial production of formalin in this country would thus appear to be more economical if produced from ethyl alcohol not only now when the only available source of methyl alcohol is from wood distillation, but even at a future date when synthetic methanol might be manufactured in this country. The reason for this is quite obvious when one considers the availability of molasses in very large quantities and at practically no cost in this country. As a matter of fact, the sugar factories with auxiliary plants for the fermentation of molasses could very profitably be manufacturers of formalin, acetaldehyde, ether, acetic acid and ethyl acetate.