DEHYDRATION OF RECTIFIED SPIRIT BY MEANS OF ANHYDROUS CALCIUM CHLORIDE.

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The rectified spirit usually met with in India contains about 88 per cent. of ethyl alcohol, and by fractional distillation the highest percentage theoretically obtainable is 95·6 but in actual practice the highest concentration is usually 92 per cent. (Wade and Merriman[1]).

For many purposes alcohol of higher concentration is required, and various methods of treatment have been suggested to obtain alcohols containing 95 to 100 per cent. of ethyl alcohol. Such methods include:—

1. Treatment with dry potassium carbonate and subsequent slow distillation. (Lowitz).

2. Treatment with anhydrous calcium chloride and subsequent distillation. (Richter).

3. Digestion first with dry potassium carbonate and subsequently with freshly burnt quicklime and distilling at 82·2°. (Drinkwater, Squibb).

4. Digestion with quicklime at 40° and repeating the operation. (Mendeleeff,[2] Erlenmeyer [3]).

5. Digestion with metallic calcium free from nitride. (Klason and Norlin[4]).

6. Treatment with glycerol (Knecht and Miller [5]).

7. By adding benzene and distilling, when a ternary mixture passes over first (b. p. 64·85°), then the binary mixture of benzene and alcohol (b. p. 68·25) and finally pure alcohol (b. p. 78·3°)[6].

Recently W. A. Noyes [7] has published the results of experiments on the dehydrating action of anhydrous calcium chloride on rectified spirit. The following Table I gives the results obtained by adding 80 grams of calcium chloride per litre of alcohol.

TABLE I.

Original percentage...	83·0	90·0	93·0	95·0	96·0	97·0	98·0	98·5	99·0	99·3
After treatment ...	91·5	94·5	96·3	97·3	98·0	98·4	98·8	99·0	99·4	99·5
Change per cent. ...	8·5	4·3	3·3	2·3	2·0	1·4	0·8	0·5	0·4	0·2

[1] *J. Chem. Soc.*, 1911, **99**, 1002.
[2] *Ann. Phys. Chem.*, 1869, [II], 138, 230.
[3] *Annalen*, 1871, **160**, 249. Cf. Squibb, *J. Amer. Chem. Soc.*, 1893, **15**, 126.
[4] *Arkiv. Kem. Min. Geol.*, 1906, **2**, No. 24. Small amounts of ammonia are formed and can be removed by adding a few centigrams of alizarin and a 5 per cent. solution of dry tartaric acid in the alcohol until the reddish blue colour changes to yellow when the whole is distilled. Metallic sodium is of very little use, Noyes, *J. Amer. Chem. Soc.*, 1923, **45**, 861.
[5] *J. Soc. Chem. Ind.*, 1924, **43**, 177 T.
[6] Young, *J. Chem. Soc.*, 1902, **81**, 707.
[7] *J. Amer. Chem. Soc.*, 1923, **45**, 857.

The author draws the following general conclusions from the results of his experiments :—

1. From concentrated alcohol containing rather more than 1 molecule of calcium chloride per molecule of water, alcohol of 99·5 or more per cent. concentration, may be distilled.

2. On concentrating such a solution, an alcoholate and not a hydrate of calcium chloride begins to separate when the temperature reaches 95 – 100°, and there is an equilibrium between the alcoholate and hydrate present. A high temperature is required to expel the alcohol from the solid alcoholate.

3. The solution containing calcium chloride and water in the molecular ratio 1 : 4·5 boils at 140°, and from such a solution the alcohol may be distilled completely with a concentration of 90 per cent. or more. The solution of calcium chloride of this composition is liquid at 140°, but solidifies on cooling.

Based on these principles, an apparatus of galvanised iron has been designed for preparing alcohol of 99·0–99·6 per cent. by weight of alcohol, as a more or less continuous reaction. The calcium chloride is removed after 10 litres of 99 per cent. alcohol have been obtained and the operations restarted.

This apparatus is convenient when a more or less continuous working is required, but is tedious for intermittent preparation of high grade alcohol.

We have carried out two series of experiments, one on the small scale in glass vessels, and the other on a semi-commercial scale in jacketted pans in order to study the effects of distilling 88 per cent. alcohol with different quantities of anhydrous calcium chloride. The two points to which attention was paid were : (*a*) the concentration of the alcohol obtained and (*b*) the loss of alcohol during the operation, i.e., the percentage of the total alcohol retained by the calcium chloride.

Finally we carried out experiments to determine the minimum number of distillations required to obtain a good yield of 98–99 per cent. alcohol from the commercial rectified spirit containing 88 per cent. of alcohol.

EXPERIMENTAL.

Alcohol.—The alcohol used as starting-material was commercial rectified spirit manufactured in India. This had a density 0·8185 at 25·4° and contained 88·0 per cent. of ethyl alcohol by weight.

Calcium Chloride.—The chloride used was the commercial anhydrous, but as this contained as much as 30·0 per cent. of water, it was always heated before use. This was done in large, shallow, iron dishes heated over a charcoal fire, and the product added to the alcohol as soon as it was sufficiently cool.

Small-Scale Experiments.—For these experiments a round-bottom flask (1 litre) was used, the alcohol and dry calcium chloride added and the mixture well shaken and left overnight or refluxed for 3 hours by heating in an oil-bath at 130°. The alcohol was then distilled, while the oil-bath was maintained at 130°, into a receiver provided with a tube containing anhydrous calcium chloride. About 90 per cent. of the total distillate passes over during the first hour, but the rate falls rapidly until at the end of three hours no drops of distillate can be observed. The flask was so arranged that the solid residue was below the level of the hot oil outside.

With this apparatus experiments have been made with alcohols of the following initial concentrations, using different quantities of calcium chloride:—88, 91–93, 95, 97–98 per cent. The results are summarised in Table II.

TABLE II.

Small-Scale Experiments.

No. of Expt.	Grams of Alcohol	Concentration of Alcohol	Grams of Ca Cl_2	Molec. ratio of Ca Cl_2 to H_2O	Grams of distillate	Concentration of distillate	Per cent. yield of alcohol
41	514	88·0	85	1 : 4·50	461	95·3	97
42	583	88·0	95	1 : 4·50	537	95·0	99
20	300	88·4	222	1 : 1·00	213	97·8	80
40	380	88·0	269	1 : 1·00	303	97·3	88
38	350	88·0	243	1 : 1·00	283	96·7	90
39	472	88·0	333	1 : 1·00	385	97·1	90
21	300	88·4	280	1 : 0·80	173	97·8	64
22	200	88·4	180	1 : 0·80	112	97·5	61
43	484	91·5	56	1 : 4·50	450	95·5	97
44	489	91·5	57	1 : 4·50	458	95·7	98
45	461	91·5	240	1 : 1·00	376	97·3	87
14	407	92·1	200	1 : 1·00	340	97·5	89
15	407	92·1	200	1 : 1·00	335	97·8	88
16	407	92·1	300	1 : 0·67	280	98·2	73
17	407	92·1	300	1 : 0·67	300	98·0	78
18	407	92·1	400	1 : 0·50	280	98·0.	73
48	480	95·0	33	1 : 4·50	453	97·1	97
49	960	95·0	298	1 : 1·00	750	98·3	81
46	392	95·0	122	1 : 1·00	310	98·3	82
47	403	95·0	124	1 : 1·00	336	98·3	88
5	316	96·8	200	1 : 0·30	225	99·0	73
31	1590	97·6	270	1 : 0·83	1300	99·0	82
33	1480	97·7	270	1 : 0·77	1180	99·0	81
23	400	97·7	125	1 : 0·56	302	99·5	76
25	3070	97·8	450	1 : 1·00	2540	99·0	82

Large-Scale Experiments.—The vessel used in these experiments was a steam-jacketted cast-iron pan. The jacket covered the lower half of the pan and was lagged with asbestos powder. The heating was by means of steam under a pressure of 40 lbs. and the outlet from the jacket was provided with a steam-trap. The level of the alcoholic solution of calcium chloride in the pan was below the level of the steam-jacket, so that the whole solution was surrounded by a jacket at about 135°. The usual amount of alcohol taken for these experiments was 5 gallons or 22 litres.

The results of the experiments are given in Table III.

TABLE III.

Large-Scale Experiments.

No. of Expt.	Pounds of Alcohol	Concentration of alcohol	Pounds of $CaCl_2$	Molec. ratio of $Ca\ Cl_2$ to H_2O	Pounds of distillate	Concentration of distillate	Per cent. yield of alcohol
53	40·5	88·0	8·3	1 : 4·50	33·0	95·5	90
59	37·0	88·0	7·8	1 : 4·50	32·0	95·0	93
60	57·0	88·0	9·0	1 : 4·50	51·0	95·0	97
52	39·8	88·0	8·0	1 : 4·50	33·5	95·2	91
56	56·0	88·0	9·8	1 : 4·25	49·3	94·3	95
30	40·5	88·0	8·5	1 : 3·50	30·3	95·0	80[1]
32	40·5	88·0	8·5	1 : 3·50	30·0	95·0	80[1]
69	122·8	88·0	25·0	1 : 3·50	100·5	96·2	90
62	76·5	88·0	18·0	1 : 3·00	65·5	94·7	93
63	39·0	95·0	11·0	1 : 1·10	33·5	97·0	88
54	39·0	95·2	11·8	1 : 1·10	32·0	98·0	84
57	39·8	95·0	13·0	1 : 1·10	32·5	98·0	85
70	98·5	96·2	31·0	1 : 0·71	79·8	98·0	83
66	20·0	97·0	10·5	1 : 0·35	15·0	98·0	76
55	40·5	97·7	7·0	1 : 0·83	35·5	98·5	89
58	32·3	98·0	8·3	1 : 0·50	28·0	98·3	88

The concentration of the distillate was calculated from the density determined in all cases by means of a 25 cc. sp. gr. bottle with thermometer attached. The tables used for the calculation were those of the Bureau of Standards, Washington,[2] and all concentrations are expressed in per cent. by weight.

The density varied during the distillation and was invariably lower during the earlier stages as shown by the following figures (Table IV). So that as a rule if the yield is poor the concentration is high.

[1] The experiments were conducted with a fractionating column.
[2] *Bull. Bur. Stand.*, 1913, 9, 424.

TABLE IV.

Distillation No.	Weight of first fraction in lbs.	Percentage of alcohol	Weight of second fraction in lbs.	Percentage of alcohol	Weight of third fraction in lbs.	Percentage of alcohol
62	40·0	95·0	25·5	94·0	...	...
69	43·8	96·5	32·2	96·3	23·5	95·5
70	38·5	98·7	37·0	97·3	4·3	95·1

Table V gives the results of a few experiments in which water was added to the residues from the experiments in which a relatively large quantity of calcium chloride was used.

TABLE V.

Addition of Water to Calcium Chloride Residues.

Residue from Exp. No.	Alcohol originally taken	Calcium chloride originally taken	Ratio $CaCl_2$: H_2O	Water added to residue	Weight of alcohol recovered	Concentration of alcohol recovered per cent.	Percentage of the original total alcohol recovered
30	40·5 lbs.	8·5 lbs.	1 : 3·5	2 lbs.	4·25 lbs.	91·5	11
32	40·5 lbs.	8·5 lbs.	1 : 3·5	1·25 lbs.	3·75 lbs.	92·0	10
38	350 grams	243 grams	1 : 1	137 grams	27 grams	88·0	8

SUMMARY.

1. Starting with an 88 per cent. rectified spirit, it is possible by distilling with anhydrous calcium chloride in the molecular ratio $CaCl_2 : H_2O = 1 : 4{\cdot}5$, i.e., anhydrous calcium chloride equal to one-sixth of the weight of the spirit taken, to obtain 95 per cent. of the total alcohol taken in the form of a 95 per cent. spirit.

2. By increasing the proportion of calcium chloride it is possible to obtain a slightly stronger alcohol, but the yield is always diminished, owing to the retention of a portion of the alcohol as calcium chloride alcoholate. With calcium chloride in the molecular ratio, $CaCl_2 : H_2O = 1 : 1$, the concentration of the distillate is 97 per cent., but less than 90 per cent. of the total alcohol taken is present in the distillate.

3. When the initial concentration of the alcohol is 91·5 per cent. and the calcium chloride used is in the molecular ratio $CaCl_2 : H_2O = 1 : 4·5$, 98 per cent. of the alcohol can be obtained in the form of 95·6 per cent. spirit.

4. When the 95 per cent. alcohol obtained from the first distillation is again distilled with calcium chloride (ratio, $CaCl_2 : H_2O = 1 : 1·1$), an 86 per cent. yield of spirit containing 98 per cent. of alcohol can be obtained. Thus from an 88 per cent. spirit it is possible, after the two distillations, to recover 82 per cent. of the total alcohol in the form of 98 per cent. spirit.

5. The further concentration of the 98 per cent. alcohol by distillation with calcium chloride is tedious, and the most efficient method of obtaining 99·5 or 100 per cent. alcohol from the 98 per cent. material appears to be treatment with metallic calcium in the form of fresh turnings (5 per cent. on the weight of the alcohol).

6. During the first distillation the yield is good, viz., 98 per cent. of the theoretical and practically no alcohol is retained by the calcium chloride remaining in the still. At the end of the second distillation in which the molecular ratio of $CaCl_2$ to H_2O is 1 : 1·1, only 90 per cent. of the total alcohol is found in the distillate; and the residue in the still, when treated with a suitable [1] quantity of water, yields an additional 8 per cent. of alcohol in the form of 88–90 per cent. spirit.

7. As a rule it does not pay to recover the calcium chloride.

[1] Sufficient to bring the ratio $CaCl_2 : H_2O$ to 1 : 4·5.

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