

DEHYDRATION OF ALCOHOL

by

POTASSIUM CARBONATE

THESIS

by

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INTRODUCTION

There has been considerable investigation into the feasibility of concentrating alcohol in fairly dilute solutions up to 95% alcohol, the product ordinarily sold on the market, by means of solid dehydrating agents such as anhydrous salts or metallic sodium. This investigation has been inspired by the hope of eliminating large and expensive fractionating columns and other distilling equipment. The use of calcium oxide as a dehydrating agent is a possibility, but in many cases where a pure product is required, the comparatively high solubility of the calcium compounds prevents the use of this substance. Copper sulphate has also been investigated.

The purpose of this research has been to inquire into the feasibility of, and to study a method for, the use of potassium carbonate in dehydrating alcohol, with a view to putting this process on a commercial basis. No record of previous work on this subject could be found in the literature.

The principles underlying this dehydration process are these: When anhydrous K_2CO_3 is added to a dilute alcohol solution a certain amount dissolves. As more is continually added, two liquid phases are formed, the lower containing

most of the K_2CO_3 and but little alcohol; and the upper containing but little K_2CO_3 , and decreasing amounts of water. When the liquid system will not dissolve any more K_2CO_3 , the alcohol layer has been concentrated to 91% by weight of alcohol, (hereafter all alcohol percentages will be given as percent by weight) and shows but a trace of K_2CO_3 . The aqueous layer has dissolved about its own weight of K_2CO_3 . If further anhydrous salt is now added, a new solid phase appears which is a hydrated K_2CO_3 and probably has the composition, $K_2CO_3 \cdot 2 H_2O$; and the aqueous phase disappears. If, however, the aqueous layer is first removed and anhydrous salt then added, this new phase forms with the removal of water from the alcohol, and much less anhydrous salt is needed than is used when the aqueous layer is not first removed.

EXPERIMENTAL METHODS AND RESULTS

The first problem that arose in the execution of this investigation was to decide on a method of analysis. Since there is no simple chemical method of analysis of alcohol - water - K_2CO_3 systems, physical methods were relied upon. The density has been taken as a measure of the ratio of alcohol to water.

The solutions of interest in this work contained 80% alcohol or above, a very little K_2CO_3 , and the rest, water; or else they are about 50% water and 50% K_2CO_3 with but little alcohol. For the latter case no estimation of the amount of alcohol will be made due to the lack of a convenient method.

A mixture of 92% alcohol saturated with K_2CO_3 showed a density of .8170. It was then distilled, leaving a very slight residue of K_2CO_3 . The distillate showed a density of .8175. In the following work the density has therefore been assumed to measure the per cent of alcohol in concentrated alcohol solutions saturated with K_2CO_3 , and the effect of the K_2CO_3 on it has been neglected.

A sample of the commercial K_2CO_3 used in this work was weighed, heated for two hours in an iron dish and reweighed. A loss of weight of about $3\frac{1}{2}\%$ occurred due to the presence of moisture. All references to "anhydrous K_2CO_3 " will be under-

stood to mean this salt which actually contains $3\frac{1}{2}\%$ water.

A preliminary run was first made to determine qualitatively and semi-quantitatively the effects when anhydrous K_2CO_3 is added to a 50% alcohol solution. 500 c.c. of 51% alcohol were used, and to this was added K_2CO_3 :

10 grams K_2CO_3 gave			2 c.c. water phase		
20	"	"	25	"	"
30	"	"	60	"	"
40	"	"	70	"	"
50	"	"	100	"	"
60	"	"	120	"	"
70	"	"	135	"	"
80	"	"	150	"	"
100	"	"	80	"	"
125	"	"	205	"	"
250	"	required to saturate.			

500 c.c. of 50% alcohol were shaken in a liter separatory funnel with different amounts of anhydrous K_2CO_3 until equilibrium was attained, and the resulting phases were then analyzed.

The following results were obtained:

500 c.c. of 50% Alcohol used						
K ₂ CO ₃	Water Layer			Alcohol Layer		
Grams	c.c.s	%K ₂ CO ₃	%H ₂ O	c.c.s	%Alcohol	%H ₂ O
100	178	40	60	349	75	25
125	205	44	56	339	80.5	19.5
150	224	45	55	329	84.5	15.5
175	242	51	49	318	87	13
200	260	51	49	307	90	10

In the above table the K₂CO₃ in the alcohol is very small and is neglected. An attempt was made to distil the liquid of the aqueous layer off from the K₂CO₃ and then determine the ratio of alcohol to water from the density of the distillate. However this was found to be impracticable because of the large proportion of K₂CO₃ present. In an extensive investigation of this problem some such method would doubtless have to be resorted to, as the losses of alcohol in the aqueous layer are apparently quite appreciable, and might even prove to be an important deciding factor in the usefulness of the whole process.

An investigation was next made of the dehydration of alcohol by contact with the anhydrous K₂CO₃, but one liquid phase being present. Eighty-six percent alcohol was used, as it

was thought that that concentration would probably be attained by the salting out process, in which two liquid phases are present.

200 c.c. of 86% alcohol was shaken with an excess of anhydrous K_2CO_3 , (75 grams were used) in a 500 C.C. bottle. The shaking was carried on vigorously for 3 minutes and a concentration of 94% was attained. The mixture was then shaken 4 more minutes and the alcohol concentration rose to about 94.3%.

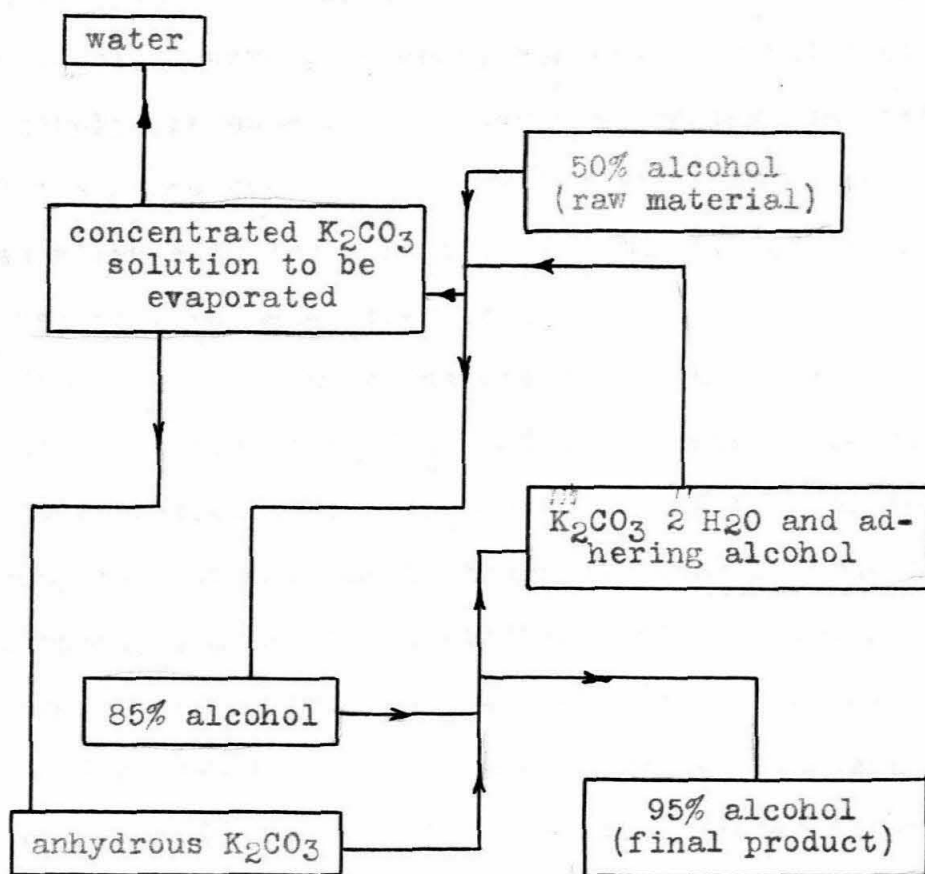
It was thought that some time might be required for this dehydration in a commercial scale process, as much more intimate contact would be attained by hand shaking than is possible in any kind of machine agitator. Accordingly, a 500 c.c. bottle was wired to a wheel geared to an electric motor so that the bottle was made to revolve and cause a tumbling over of the contents. A sample of 200 c.c. of 86% alcohol and 75 grams of anhydrous K_2CO_3 was mixed in this device for 40 minutes and an alcohol of 93% was obtained. After 25 more minutes of shaking, the alcohol attained a concentration of 94%.

Since K_2CO_3 is comparatively expensive, it must be recovered after use. The problem therefore arises of dehydrating the dehydrating agent. To observe the qualitative effects, a concentrated solution of K_2CO_3 was heated in a small iron dish over a bunsen burner. Except for a spattering just

before the free water was all driven off, no difficulty was encountered. The anhydrous material forms a hard cake which adheres to the container, so that it may be expected that precautions will have to be taken to prevent a serious reduction of the heat transfer in this process.

Having learned these things about the process, it was next necessary to devise a procedure for the whole working process. It would obviously be desirable to carry on both the preliminary dehydrations by salting out, and the final dehydration by contact with the anhydrous salt, in the same container, and thus avoid the problem of transportation of the final pasty mass.

The following process was decided upon:



For preliminary work this process was carried out in a glass jar about 5 inches in diameter. Stirring was accomplished by a brass propeller 4 inches long of thin gauge. The propeller was placed almost touching the bottom of the jar in order to prevent the formation of a cake on the bottom and thus reduce the exposure of new surface. In spite of all precautions, however, tendency for cake formation could not be entirely prevented. One dehydration test was made in which the anhydrous salt was wetted with 95% alcohol before it was mixed with the more dilute alcohol, and the cake formation was reduced materially in this way.

The first test made was started with 800 c.c. of 90% alcohol and 200 grams of K_2CO_3 . After stirring, 550 c.c. of 94% alcohol were decanted. 1000 c.c. of 50% alcohol and 200 grams of K_2CO_3 were then added to the pasty mass of hydrated K_2CO_3 and alcohol, and the whole stirred until the solid phase had disappeared and equilibrium was reached. The resulting alcohol solution was 89%. The lower aqueous layer was then siphoned off and 200 grams of K_2CO_3 added. After vigorous stirring the alcohol was concentrated again to 94% and 500 c.c. removed. To be sure that the whole process had come to equilibrium as far as the amounts of substances involved were concerned, the cycle was again repeated and ^{again} 470 c.c. of a 94% alcohol were obtained.

With the object of reducing the amount of K_2CO_3 needed per

given amount of 95% alcohol obtained, additional runs were made in which all K_2CO_3 used in one cycle was added in one batch, instead of two; and the alcohol was not brought up to as high a concentration as 89% in the first step.

The next run was started with 1000 cc of 50% alcohol and 300 grams of K_2CO_3 added to the 89% alcohol remaining. After again stirring, 380 c.c. of 94% alcohol were removed. Another 1000 c.c. of 50% alcohol were then added to the pasty mass and the mixture stirred without the addition here of more anhydrous salt. After the solid phase had disappeared, the aqueous layer was siphoned off and 300 grams of anhydrous K_2CO_3 were added. After stirring, 600 c.c. of 92% alcohol were obtained. On repeating the whole cycle again 500 c.c. of 92% alcohol were obtained. From this was assumed that after the process had settled down to a uniform running condition, the average output would be 500 c.c. of 92% alcohol per 1000 c.c. of 50% alcohol per 300 grams of K_2CO_3 introduced. The small amount of final alcohol (380c.c.) obtained in the first cycle may be accounted for by the large amount which must have adhered to the hydrated K_2CO_3 present.

A run was next made using 350 grams of K_2CO_3 per 1000 c.c. of 50% alcohol. Running conditions settled down after three cycles and it was found that on an average about 470 c.c.

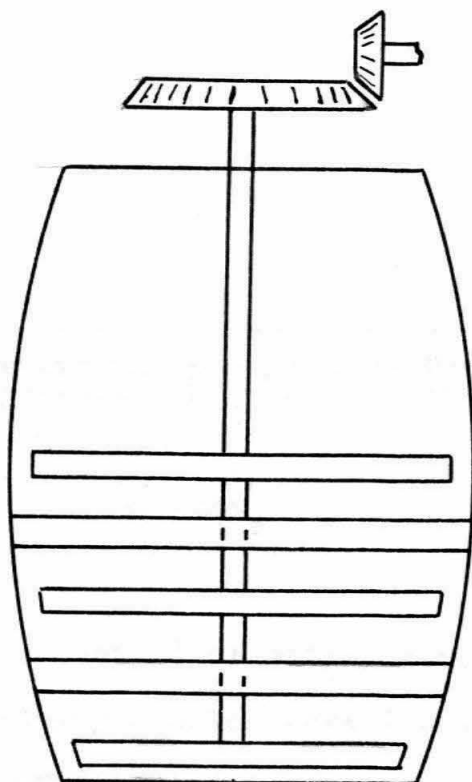
of 94% alcohol were removed per 1000 c.c. of 50% alcohol per 350 grams of K_2CO_3 .

Some difficulty was encountered in the above run before it was successfully finished. The anhydrous K_2CO_3 used for the final dehydration had been pulverized to a fine dust so that after the alcohol had been concentrated to 94%, the K_2CO_3 remained as a finely divided suspension and the alcohol could not be decanted. It is therefore probable that some surface will have to be sacrificed in this step to avoid the necessity of filtering instead of decanting the alcohol. Apparently about 60 mesh particles will give enough surface for the dehydration and still be large enough to prevent the formation of an undesirable suspension.

SEMI--WORKS SCALE OF EXPERIMENTATION

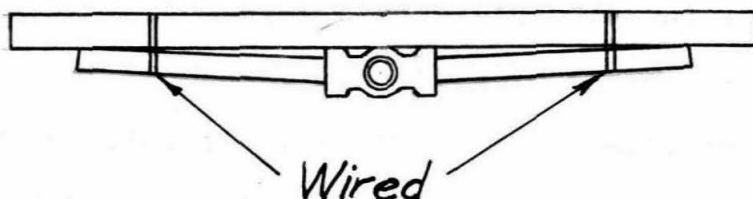
On the basis of the above laboratory experimental work, the transition to a semi-works scale was next attempted. Both time and equipment proved inadequate for a thorough investigation of this phase of the problem. It is believed, however, that some valuable information was obtained, much of which is of a qualitative nature.

The mixing operations were carried on in an oak barrel provided with two stationary horizontal paddles and 3 moving paddles revolving at a speed of 60 R.P.M. This apparatus is shown in Fig. 1.

*Fig. 1*

The stirrer shaft was made of $\frac{1}{2}$ inch iron pipe. The stirring blades were of wood $\frac{3}{4}$ inch thick, and presented a stirring surface $1\frac{3}{4}$ inches wide. These blades were fastened to the shaft by inserting a $\frac{1}{2}$ inch cross in the shaft and wiring to this. It was found in the first test, however, that such a large torque was developed in the final dehydrating step by the large quantity of solid material which must be moved in addition to agitating the liquid, that this type of construction was not sufficiently rugged. Accordingly, a piece of $\frac{1}{2}$ inch pipe - about a foot long - was screwed into each side of the cross and wired to the wooden paddles in the manner of Fig. 2.

Fig. 2.



This bracing proved to be satisfactory.

The two stationary paddles were 2 x 4's drilled $7/8$ inch for the stirrer shaft, and nailed to the side of the barrel.

Solutions were removed from the barrel by siphoning with a rubber hose, as in this way either the upper or lower phase could be removed with ease.

The barrel was provided with a wooden cover to reduce evaporation losses of alcohol.

The most satisfactory apparatus available for drying the concentrated solution of K_2CO_3 to the anhydrous salt was an iron crystallizer which was steam jacketed and closed, except for a vapor line leading from the top, and a door about one foot square in the top. This crystallizer was provided with a heavy two-bladed stirrer revolving slowly and just clearing the bottom and sides. The stirrer was effectual in maintaining the bottom and wall free from cake formation, and therefore

suggests ideas for an agitator for the final dehydration step.

Lack of equipment prevented the removal of the water vapor by the jet condenser connected to the vapor line. To accomplish this function, a blower was therefore trained on the surface of the evaporating liquid through the door in the top of the crystallizer and the air and vapor expelled through the vapor line and two ports in the top of the kettle.

In this apparatus the K_2CO_3 was dried to a moist crystalline mass, which was then removed to a sheet iron plate. It was spread upon this and heated by gas burners until all water had been driven off. The resulting lumps were pulverized to about 60 mesh and the material was then ready for another run.

For the first test on the semi-works scale, 73 pounds of K_2CO_3 and 25 gallons of 50% alcohol were used. These figures correspond to the 350 grams of K_2CO_3 and 1000 c.c. of 50% alcohol found advisable in the work on laboratory scale.

The test was started with 22 gallons of 80% alcohol and 73 pounds of K_2CO_3 . After stirring, an alcohol of 92% was obtained. This was drawn off and 25 gallons of 50% alcohol were added.

The test was made through two cycles. The first cycle produced 15 gallons of 91% alcohol, and the second cycle produced 15 gallons of 90% alcohol. (In the second test there was a shortage of 12 pounds of K_2CO_3 . This might bring the alcohol up to 91%.)

Lack of time prevented the further investigation of this problem.

CONCLUSIONS

On the basis of the semi-works scale experimentation, recommendations will here be made for the design of a plant to operate this process:

The stirring tanks will have to be operated in small units because of the difficulty encountered in securing efficient agitation. The agitator blades should be horizontal rather than vertical. The bottom blade should be of sturdy construction, as it will be heavily loaded. It should barely clear the bottom and sides of the tank. The revolving blades should all widen at their ends to cover the space between the stationary blades almost completely. It is very important that these precautions be taken to prevent cake formation in the second step of the dehydration, as this materially lowers the efficiency of the process.

It is recommended that the recovery of the K_2CO_3 be carried out in two stages.

In the first stage, the concentrated solution is to be evaporated in salting-out evaporators designed for continuous operation. A double seal or "salt catch" is to be used for the removal of crystals. Multiple effect evaporation may be used if the size of the plant seems to warrant it.

It is recommended that the moist crystalline mass be dried in thin layers on a hot plate. The plate may be heated by gas or oil burners, but the mass must be maintained above 135 deg. C. For large quantities the process should be made automatic by moving the plate and providing means for scraping off the dried product.

For pulverizing the dried product a ball mill is recommended.

Many thanks are due to Dr. W. N. Lacey for his valuable aid and suggestions, and to Dr. A. A. Noyes, at whose suggestion the use of K_2CO_3 , was tried for this work.

SUMMARY

1. Investigation was made of the system Alcohol - K_2CO_3 - Water, and a process devised for the dehydration of alcohol on the laboratory scale.
2. This process was carried out on a semi-works scale with the view of designing a commercial plant for the carrying out of this process.
3. Recommendations are made for the design of such a plant.