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Utilizing Calcium Carbide for Aqueous Ethanol Dehydration

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Abstract:
Growing requirements for anhydrous ethanol require systems that operate with a minimum of energy and that are also reliable in continuous operation. Also the use of absolute ethanol in many ways has been limited because of the relatively high costs of production. The present work provides a different approach for dehydration of ethanol from an ethanol-water mixture utilizing calcium carbide as dehydration agent. This method has been investigated among some other dehydration techniques. Results show that it is as good as becoming a promising method.

Introduction:
Ethanol can be produced in two forms – hydrated and anhydrous. Hydrated ethanol has a purity of 95% suitable for blending with an ignition improver, or as a 15% emulsion in diesel that is known as Diesohol. Alcohol has a lot of power, and it burns cooler, which is really great for car motors, since heat is a big enemy of engines, along with friction.
A second stage refining process is required to produce anhydrous ethanol (100% purity) for use in ethanol blends in petrol. Growing requirements for anhydrous ethanol for use in motor fuel gasoline blends require systems that operate with a minimum of energy. Also absolute alcohol is an important product required by industry. As per international standards specification it is nearly 100% pure (water free) alcohol. After fermentation and distillation are complete, the next stage of ethanol purification is dehydration. Dehydration is necessary because traditional distillation leaves approximately 3 to 5 percent water in the finished ethanol. There are two main dehydration techniques in the industry, azeotropic distillation and molecular sieve dehydration (1).
While the molecular sieve system is much superior to the azeotropic distillation method, it is still has some areas of concern. The process is very energy intensive, where the energy spent on the anhydride ethanol production exceeds the energy obtained from its combustion. The high vapor pressure ethanol is highly flammable and catastrophic tank rupture or even minor leaks are legitimate safety concerns. An alternative to this process is the use of preferential adsorption of water, using specific adsorbents for this purpose, such as cellulose and starch, first studied by Ladisch and Dick(2). Since then, numerous studies have proven that it is possible to use biomaterials for the dehydration of ethanol (3, 4, 5). The advantages of their use include efficiency, relatively low cost, reuse of the material in fermentation and/or animal feedstock, in addition to the fact that these adsorbents are nontoxic, biodegradable and derived from renewable sources.
A thermodynamic and kinetic study has been undertaken on the liquid phase adsorption of water from an ethanol-water mixture using manioc starch pellets as the adsorbent (6).
Ladisch and Tsao (7) studied the vapor phase dehydration of aqueous alcohol mixtures, through the drying of aqueous ethanol by passing the carrier gas stream (air, nitrogen and carbon dioxide) containing aqueous alcohol vapor through a heated dehydration zone which contains a dehydration agent by materials such as cellulose, cornstarch, shelled corn, or corn (cellulosic) residue, results in a product that is up to 99.8 percent water-free.
Although the water-adsorbing properties of cellulose and starch are known, preferential adsorption of water in the presence of ethanol was unexpected. Furthermore, the energy balance is more favorable than that obtained with CaO. For example, the heat of wetting of cellulose, in the order of 116 kJ/kg, is less than the heat of reaction of CaO. The total energy requirement with cellulose as the dehydrating agent is 2873 kJ/kg of alcohol: 2442 kJ/kg for distillation (from 12 to 84.8 percent), and 430 kJ/kg for cellulose dehydration. Hence, ten times more (combustible) energy is obtained than is used in obtaining the product (8).
The aim of this research is to study the feasibility of using calcium carbide as a drying agent to remove most of the water to yield a product that is close enough to absolute ethanol.

Experimental:
The present work relates to a process and an apparatus system for dehydration of ethanol which comprises desiccant bed followed by a simple filtration. Liquid phase ethanol is passed through the bed (Calcium carbide), which reacts with water content of the ethanol so that an essentially anhydrous stream of ethanol leaves the bed downstream and acetylene gas leaves the bed upstream.

$$2\,H_2O + CaC_2 \rightarrow Ca(OH)_2 \downarrow + C_2H_2 \uparrow$$

Precipitate Acetylene gas

The amounts of CaC_2 used for each experiment were calculated according to material balance for the above equation and the results are shown in Table (1). The amounts of carboxy methyl cellulose (CMC) and calcium oxide were calculated with the same manner.
The ethanol-water solutions were prepared at the required mass concentrations from absolute ethanol and distilled water, using a scale with an accuracy of 0.001g. Dehydration time was (24 hours), and dehydration temperature was (25ºC). Ethanol left the bed was filtered and it's concentration was measured by, a Carel Fisher refractometer with automatic calibration was used and data reproducibility on the order of 0.5% was obtained in this experimental concentration range.

Dehydration of aqueous ethanol by carboxy methyl cellulose (CMC) and calcium oxide for comparison were made according to Ladisch and Tsao (7). Another simple distillation was made after treating with different reagents.
Materials used are:
Absolute ethanol, calcium oxide, and CMC were supplied by Riedel-De-Haenag, while calcium carbide is of commercial grade.

Table (1): Amounts of dehydration agents used according to water concentrations.

Water concentration %	Weight of CaC_2 (gm)	Weight of CMC (gm)	Weight of CaO (gm)
2.2	3.4	0.16	6.4
4.2	6.8	0.33	12.8
6.2	10.2	0.48	19.2
8.2	13.6	0.64	25.6
10.2	17	0.8	32

Results and discussion:

The dehydration results after treating aqueous ethanol with CaO, CMC, simple distillation and CaC_2 are listed in Table (2). These results also shown on Figure (1). Results after simple distillation made after treating with different reagents, are listed in Table (٣), and shown in Figure (2).

Table (2): Results of different dehydration methods

Initialwater concentration %	Concentration % after treating with CaO	Concentration % after treating with CMC	Concentration % after simple distillation	Concentration % after treating with CaC_2
2.2	2.2	2.01	2.2	1.7
4.2	4.02	3.94	3.3	2.84
6.2	5.78	5.04	4.09	3.2
8.2	7.92	5.5	5.9	4.1
10.2	9.96	6.3	6.7	4.59

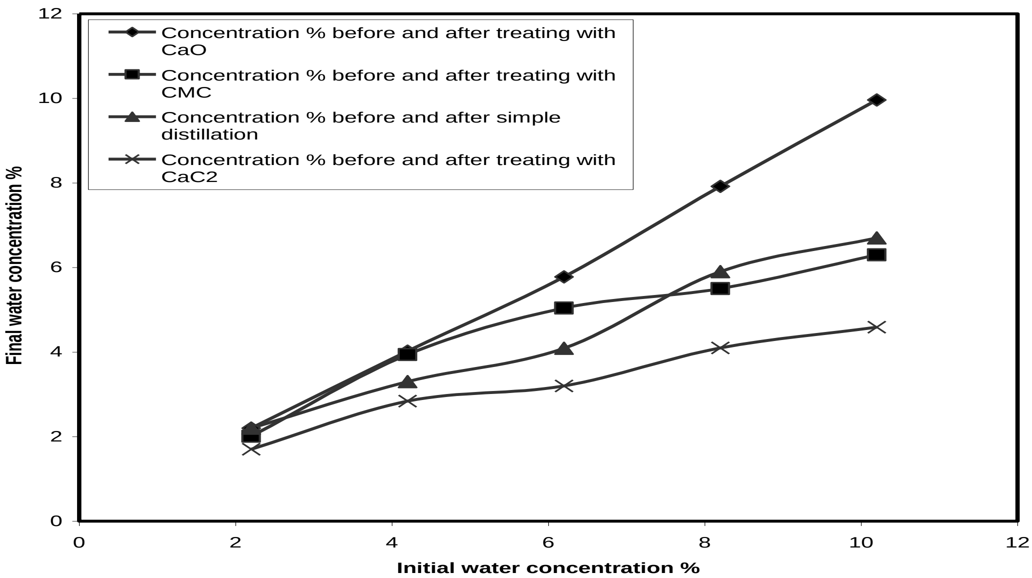

Figure (1): Results of different dehydration methods

Table (٣): Results of different dehydration methods after simple distillation

Initial water concentration %	Concentration % after treating with CaO	Concentration % after treating with CMC	Concentration % after treating with CaC_2
2.2	2.2	2.01	1.7
4.2	3.93	3.27	2.80
6.2	5.16	3.9	3.2
8.2	6.8	4.1	3.8
10.2	7.95	5.31	4.08

Figure (2): Results of different dehydration methods after simple distillation

From these results it is obvious that treating with CaC_2 is the best method against the other methods from the quantity of water removed from the original aqueous ethanol solution.

As well as, this method is the more economic one as it saves more energy. Any project utilizing this method can be installed in association with acetylene gas factory without additional units. In other enrichment schemes an inert carrier gas which will not react with either the mixture or dehydration agent must be used. Suitable gases include for example, air, nitrogen and carbon dioxide. Also the dehydration bed must be heated to a temperature sufficient to volatilize the alcohol (i.e., greater than its dew point) and generally a temperature of about 90ºC is suitable.

In the dehydration process for ethanol by adsorption technique, in order to accomplish the desorption step it must also be heated to about 100ºC which consumes energy.

Another feature of this technique is that it can be executed or constructed in any acetylene gas project with simple accessories. The advantages of the system are:

- Minimal Labor
- Stable operation
- Energy consumption minimized.
- An advanced control system, developed through years of experience, to provide sustained, stable, automatic operation.

References:

1. Kohl, S., Ethanol dehydration, Ethanol today, March 40-41, (2004).
2. Ladisch, M.R. and Dick, K., Dehydration of Ethanol: New Approach Gives Positive Energy Balance, Science, 24, 725 (1979).
3. Hong, J., Voloch, M., Ladisch, M.R. and Tsao, G.T., Adsorption of Ethanol-Water Mixtures by Biomass Materials, Biotechnol. Bioeng, 24, 725 (1982).
4. Robertson, G.H., Doyle, L.R., and Pavlath, A.E., Intensive Use of Biomass Feedstock in Ethanol Conversion: The Alcohol-Water Vapor Phase Separation, Biotechnol. Bioeng, 25, 3133 (1983).
5. Hills, J.H. and Pirzada, I.M., Analysis and Prediction of Breakthrough Curves for Packed Bed Adsorption of Water Vapour on Corn-Meal, Chem. Eng. Res. Des, 67 (1989).
6. M.J. Carmo and J.C. Gubulin, Kinetic and Thermodynamic Study on Adsorption by Starchy Materials in the Ethanol-Water System, Braz. J. Chem. Eng. vol. 14 no. 3 São Paulo Sept. 1997
7. Ladisch, Michael R.; Tsao, George T.; Vapor phase dehydration of aqueous alcohol mixtures, United States Patent 4345973, 1982.
8. Crawshaw, J.P and Hills, J.H., Sorption of Ethanol and Water by Starchy Materials, Ind. Eng. Chem. Res, 29, 307 (1990).

تجفيف الكحول الاثيلي باستخدام كاربيد الكالسيوم

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الملخص:

الطلب المتزايد على الكحول الجاف يتطلب أنظمة تعمل بشكل مستمر وبمتطلبات واطئة من الطاقة. إن استخدام الكحول المطلق في العديد من المجالات قد أصبح محدودا بسبب كلف إنتاجه العالية. هذه الدراسة تقدم طريقة مختلفة لتجفيف الكحول الاثيلي من محاليله المائية باستخدام كاربيد الكالسيوم كعامل للتجفيف. قورنت هذه الطريقة مع بعض الطرق والتقنيات الأخرى المستخدمة في هذا المجال. بينت النتائج أن هذه الطريقة جيدة بحيث أنها قد تصبح طريقة واعدة.