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## BIOETHANOL – ONE OF THE RENEWABLE ENERGY SOURCES

The problem of using bioethanol as a fuel additive in Poland and in other countries is presented. Dehydration methods, such as pressure swing adsorption (PSA), pervaporation (membrane technique) as well as hybrid method are described.

### 1. INTRODUCTION

Since the 1970s, the world market has been facing massive fluctuations in the availability and prices of conventional motor fuels. Moreover, due to excessive emissions of carbon dioxide and other greenhouse gases, environmental changes associated with global climate warming began to accelerate. Nowadays, different kinds of biofuels are emerging as potential alternatives to fossil fuels [1]. The two most common types of liquid biofuels are ethanol and biodiesel.

### 2. BIOETHANOL USED AS A FUEL

Ethanol is obtained by fermenting any biomass high in carbohydrates (e.g., starches, sugars or celluloses), so its combustion does not increase the greenhouse effect (zero carbon dioxide emission).

Ethanol is well known as an octane number enhancer. Moreover, the addition of ethanol to conventional fuel leads to decreased emissions of gaseous pollutants, such as carbon monoxide (CO) and carcinogenic volatile organic compounds.

The European Union, in an attempt to reduce emissions of greenhouse gases, in line with the obligations of the Kyoto Protocol [2], set a target that fuels for transport should contain 2% of biofuels in 2005 and 5.75% in 2010. The Protocol sets legally binding emission targets for 36 industrialized countries, which should reduce their collective

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emissions of six key greenhouse gases by at least 5% by 2008–2012, compared to the 1990 levels. On the other hand, the developing countries have not been set specific emission targets, but under the 1992 Climate Change Convention are committed to taking measures to limit emissions. The Protocol came into force on 16th February 2005, after ratification by 137 countries (excluding the U.S.A., Australia and Saudi Arabia), which in 1999 emitted 55% of all greenhouse gases to the atmosphere. It must be stressed that during the combustion of biofuels there are no net emissions of greenhouse gases.

Many countries are already blending from 5 to 10% v/v of ethanol in gasoline in order to reduce petroleum dependence and/or to minimize environmental impact of vehicle exhaust emissions. Vehicles in these countries are not specifically adapted for the blending, since the addition of up to 10% of ethanol does not require engine adjustments, calibration or changing of materials. After more than 15 years of blending in the U.S.A., no vehicle problems were reported by the manufacturers due to the use of bioethanol. Brazil is the world leader in using fuel ethanol. The Brazilian bioethanol programme started in 1975. First, it aimed at the introduction into the market gasoline blended with ethanol (i.e., 2.4% v/v) and then at the development of vehicles straight-fuelled by ethanol (FFV – flex fuel vehicles).

### 3. ETHANOL DEHYDRATION TECHNOLOGIES

In Poland, experience with fuel ethanol started in the late 1920s [3]. More recently, bioethanol has been regularly blended with gasoline since 1993. The permitted amount of ethanol in the fuel (i.e., 5% v/v) is specified by Polish and EU standards [4]. In 1996, 100 million litres of bioethanol were produced in Poland, but up to 300 million litres will soon be needed. Crude ethanol (89–95% v/v) is easy to obtain in Poland. The dehydration step is the bottleneck in bioethanol production. According to Polish standards, fuel bioethanol should contain no more than 0.40% (by weight) of water (0.32% v/v) [4].

Bioethanol is produced by the dehydration (removal of water molecules) from rectified spirit or industrial raw alcohol. Commercially available dehydration technologies can be divided into azeotropic distillation [5], molecular sieve technology (pressure swing adsorption – PSA) [6] and pervaporation (membrane technology) [7].

Azeotropic (or entrainer) distillation employs a third component (benzene or cyclohexane) to form a ternary azeotrope, which is then distilled off from the system. This method is now seldom used, as traces of the entrainer remain in the product, the operational costs are very high and the installation needed for the regeneration of entrainer is quite complex.

The main advantages of the two remaining methods are high purity of ethanol, no effect of waste materials on the process performance and no environmental pollution.

#### 4. ETHANOL DEHYDRATION BY MOLECULAR SIEVE TECHNOLOGY

The ethanol dehydration PSA system consists of three sections (figure 1) in which the following processes take place: evaporation, adsorption (in two columns) and ethanol recovery. The raw material is fed into the evaporation section. In this section, the ethanol solution is transformed into superheated vapour, using the heat from other sections.

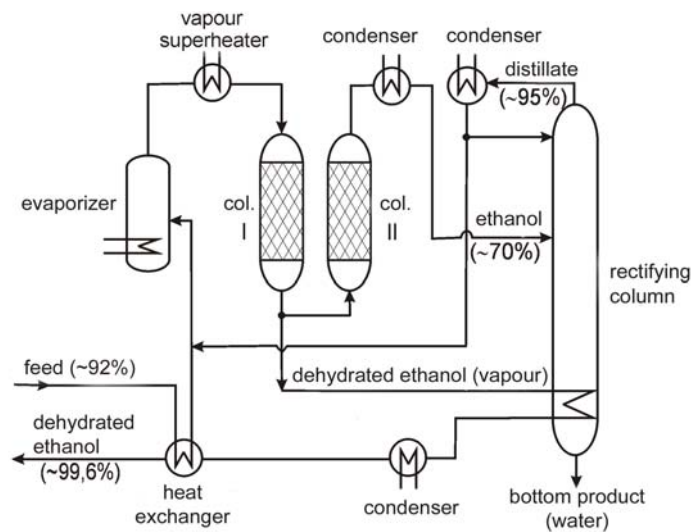


Fig. 1. Ethanol dehydration – hybrid Pressure Swing Adsorption – rectification system

The adsorption section is supplied by the vapours from the evaporation section. Dehydrated ethanol is a product of the adsorption step. A fraction containing about 70% ethanol is the second product of the adsorption section. This fraction is the feed to the ethanol recovery section.

When ethanol–water mixture flows through a 3A zeolite bed [5], water vapour is selectively adsorbed and thus removed from the mixture. While in column I at a higher pressure water vapour is adsorbed, in a column II the regeneration step (desorption, purge) takes place at a lower pressure. A part of the vapour (i.e., dehydrated ethanol) leaving column I is used as the desorbing agent. After a specified period of time, there is a stream switch. Then regeneration takes place in column I, whereas adsorption occurs in column II.

The ethanol recovery section consists of a rectification column in which the poor fraction (from the adsorption section) is rectified. The distillate (the upper product of the rectifying column) is a solution whose composition is close to the azeotropic one. This stream is recycled to the evaporation section (i.e., it is mixed with the raw material stream). The bottom product from the rectifying column contains practically no

ethanol and is discharged as a wastewater.

## 5. ETHANOL DEHYDRATION BY PERVAPORATION

Pervaporation (PV) is defined as a separation process in which a binary or multicomponent liquid mixture is separated by partial vaporization through a dense non-porous membrane [7]. During pervaporation, the feed mixture is circulated in contact with one side of the membrane while the permeate is removed as a vapour from the opposite side into a vacuum (figure 2A) or sweeping gas (figure 2B) and then condensed.

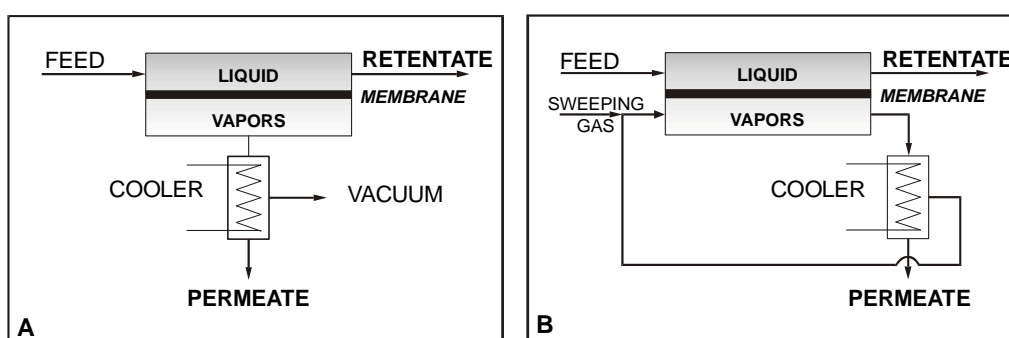


Fig. 2. Schema of pervaporation process: vacuum pervaporation (A), sweeping gas pervaporation (B)

The dehydration of ethanol has become a classic example of successful membrane pervaporation and the largest pervaporation units are employed for this purpose [8]. As mass transport through the membrane determines the permeate composition, the water/ethanol azeotrope can readily be broken, to give the ethanol product of much higher purity than is possible through simple distillation. Since at high water levels, distillation can be shown to be more thermodynamically efficient than pervaporation, it is usual for the pervaporation unit to be incorporated within a hybrid separation process, the first step of which consists in concentrating the ethanol to the azeotropic composition by distillation.

A typical pervaporation plant includes several membrane modules connected in series, separated by reheaters (figure 3) [7], [8]. This multistage operation is required because the latent heat of evaporation of the permeate is drawn out from the feed liquid mixture. The feed is therefore cooled down, and the permeate flux through the membrane decreases. The reheating of the feed optimizes the membrane flux and reduces the membrane area. The membrane modules are placed inside a vacuum vessel where the permeate is collected. A condenser using chilled brine condenses the permeate and a vacuum pump maintains the required vacuum level in the system by removing non-condensable gases. In commercial applications, use is made of a plate and

a frame or spiral wound modules in stainless steel, with solvent compatible gaskets. This is due to the harsh environment, with the concentrated solvents at a high temperature on one side and a vacuum on the other.

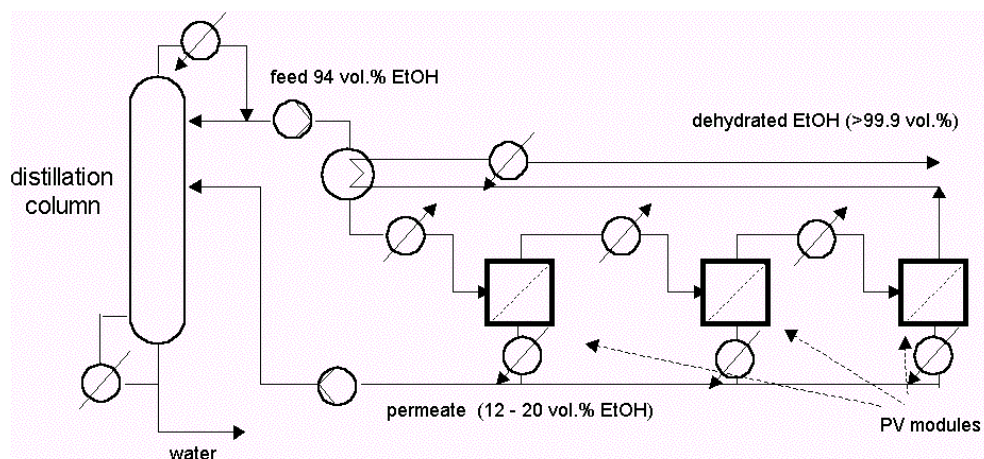


Fig. 3. Schematic of dehydration of ethanol by distillation–pervaporation hybrid process

Table

Flexibility of the ethanol dehydration pervaporation plant

Concentration				
Inlet [wt. %]	85.7%	93.9%	85.7%	93.9%
Outlet [wt. %]	99.8%	99.8%	99.95%	99.95%
Plant capacity	1 195 kg/h	1 500 kg/h	840 kg/h	970 kg/h
Utility requirements				
Steam	195 kg/h	110 kg/h	145 kg/h	83 kg/h
Power	85 kW	85 kW	85 kW	85 kW

Flexibility with respect to part load and to changing concentrations of product and feed is one of the advantages of pervaporation over other separation processes. The table presents the flexibility of the ethanol dehydration pervaporation plant with a membrane area of 480 m<sup>2</sup>. A given pervaporation plant may be used to dehydrate a large number of different solvents. Changing from one solvent to another can be done quickly and without risk of mixing the solvents.

## 6. ETHANOL DEHYDRATION BY HYBRID PV-PSA SYSTEM

In many practical applications it may be more economical to use pervaporation only to increase the ethanol concentration to above that in the azeotrope. The retentate can then be concentrated further by pressure swing adsorption. The flow diagram for such a hybrid PV-PSA process for ethanol dehydration is shown in figure 4. In the hybrid process, water is finally removed from the system at the PSA step. This concept offers special advantages if the capacity of the existing PSA plant has to be increased or, if the final alcohol concentration required is extremely high, with very low residual water content of less than 50 ppm.

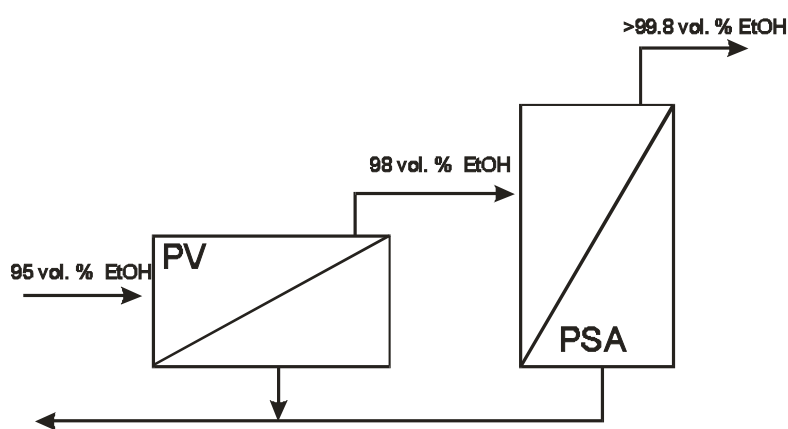


Fig. 4. Schematic of hybrid PV-PSA dehydration process

## 7. CONCLUSIONS

Summing up, the following conclusions can be drawn:

- Biocomponent addition to liquid fuels has a beneficial effect on the environment. The problems that might arise could be eliminated by strictly following the biofuel quality standards.
- Pressure swing adsorption (PSA) or pervaporation (membrane technology) can be employed to dehydrate ethanol in an ecologically acceptable way.
- Hybrid PSA-PV systems can be used to increase the throughput of existing industrial dehydration plants.

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#### BIOETANOL JAKO JEDNO Z ODNAWIALNYCH ŹRÓDEŁ ENERGII

Opisano stosowanie bioetanolu jako dodatku do paliw silnikowych w Polsce i na świecie. Omówiono metody odwadniania etanolu: adsorpcję zmiennociśnieniową (PSA), perwaporację (technikę membranową) oraz technikę hybrydową.