This photo shows Dedini´s delegation receiving the Best Paper Award – Factory Commission at the XXVII ISSCT Congress

ETHANOL DEHYDRATION SYSTEM BY SIFTEK^{TM} POLYMERIC MEMBRANE

By

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Abstract

ETHANOL is very important renewable energy to Brazil and several companies are improving their technologies by developing processes to increase the benefits of ethanol compared to fossil sources. The Siftek^{TM} polymeric membrane is a technology that can save between 35 and 70% of energy when compared with conventional processes. The first pilot plant (Tiverton, Canada) operated dehydrating grain-based ethanol from 80–90 wt% ethanol to 99.2 wt%, showing the good performance of the membrane system. With the goal of testing the system in a commercial capacity, a second plant (Chatham, Canada) was built and operated with success, drying grain-based ethanol from 40–60 wt% ethanol to 99.5 wt%. To demonstrate this technology to Brazilian ethanol producers, a third demonstration unit was built and operated in ethanol plants from sugarcane. The results confirmed the excellent selectivity of the membrane system to water, dehydrating ethanol from 85–93 wt% to higher then 99.5 wt%, with lower energy consumption and preserving product quality.

Introduction

Ethanol is becoming every day a more popular and important bio-energy source for liquid fuels. In Brazil, its production from sugarcane has reached 22 billion litres in 2007/08, with anhydrous ethanol corresponding to 35% of the total (Unica, 2009).

This result has been achieved by the popularity of the flexible fuel cars and the mixture of ethanol with gasoline that currently represents 25% of the Brazilian ethanol market.

However, it is even more important to have an alternative energy source that has a positive energy balance and the membrane technology can contribute very well to reach this goal.

Recently, polymeric membranes have received much attention because of their excellent performance in gas and vapour separation, especially in separation of water from organic vapour mixtures in industrial processes, which include water-ethanol systems (Huang *et al*., 2003a).

Considering that there are several kinds of polymeric membranes in existence, the one to be used in the industrial process should be solvent resistant and have high permeability (Huang *et al*., 2003b).

The Siftek^{TM} polymeric membrane has these properties and was designed specifically for ethanol-water separation with a higher selectivity for water over ethanol.

Distillation and dehydration are responsible for the largest fraction of energy use in ethanol production.

The technology discussed in this paper has the potential to reduce this energy consumption between 35 and 70% when compared with conventional technology, like molecular sieve or extractive dehydration with cyclohexane (Côté *et al*., 2007).

Siftek™ membrane and system

Siftek™ is a hydrophilic polymer membrane that can be used to dehydrate ethanol in the vapour phase in a continuous process illustrated in Figure 1. The ethanol-water vapour mixture is fed in one side of the module containing thousands of fine polymeric hollow fibre membranes.

The mixture travels in the parallel channels and the water vapour is drawn through the dense polymer membrane (while the ethanol is rejected) under a driving force established by a vacuum on the shell side of the module. The hollow fibre membranes are assembled into a shell to form a module. These modules are arranged in series-parallel in a system (Côté *et al*., 2007).

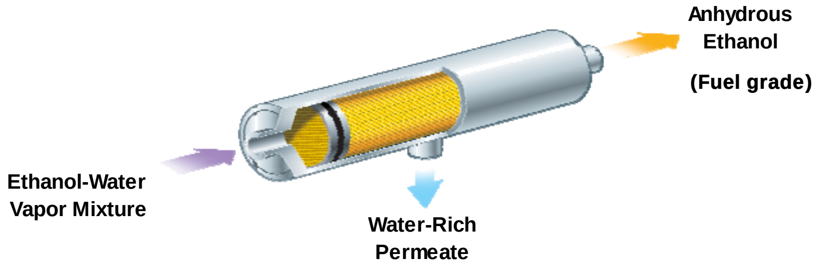

Fig. 1—Conceptual operation of membrane.

The membrane is used under rigorous conditions and has exceptional thermal, mechanical and solvent resistance properties. It is a proprietary polymer formulation based on polyimide that provides a high flux and water/ethanol selectivity.

The main components of the system are shown in Figure 2. The dehydration system is an integrated solution of the membrane with conventional technology. The pre-treatment heats the ethanol-water vapour mixture about 5°C above the dew point. Typically, the operating temperature and pressure is between 100–110°C and 125–170 kPa absolute.

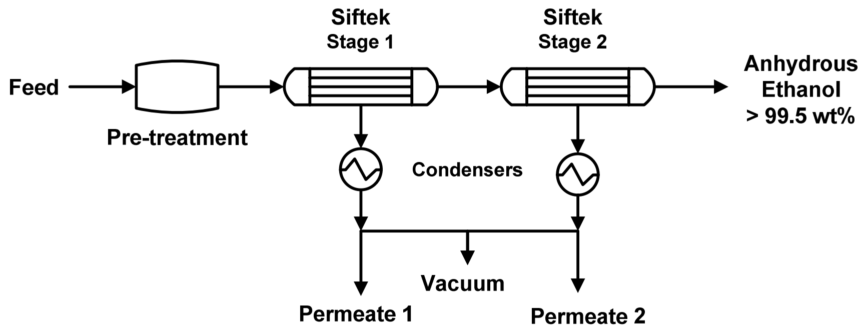

Fig. 2—Components of the Siftek™ membrane system.

In both stages a vacuum is applied on the permeate side of the membrane to create a driving force for water permeation. A lower vacuum is required in Stage 2 because of the lower water concentration after Stage 1 (less then 5%). Typical values for vacuum are 10–30 kPa for Stage 1 and 2–10 kPa for Stage 2. A vacuum pump is normally used to reach a lower vacuum and to evacuate non-condensable gases.

The membrane system is fully integrated with the ethanol plant from a mass and energy point of view. There are many installation options available to maximise the benefits of a membrane.

Tiverton Field pilot unit

The first polymeric membrane technology demonstration was done at the Greenfield Ethanol plant in Tiverton, Ontario, Canada from August 2006. The goal of the field pilot unit was to test the membrane under field conditions. The pilot unit was equipped with a single module (the first generation of commercial modules).

The pilot plant was fed with an ethanol-water mixture from a rectification column with concentration varying between 80 and 90 wt% ethanol. The unit, with capacity of 1.0 m^3/day, operated at an absolute pressure of 120–140 kPa and temperature of 105 to 115°C producing fuel-grade ethanol. Figure 3 shows the results of a continuous operation over 200 days producing ethanol to an average of 99.2 wt%.

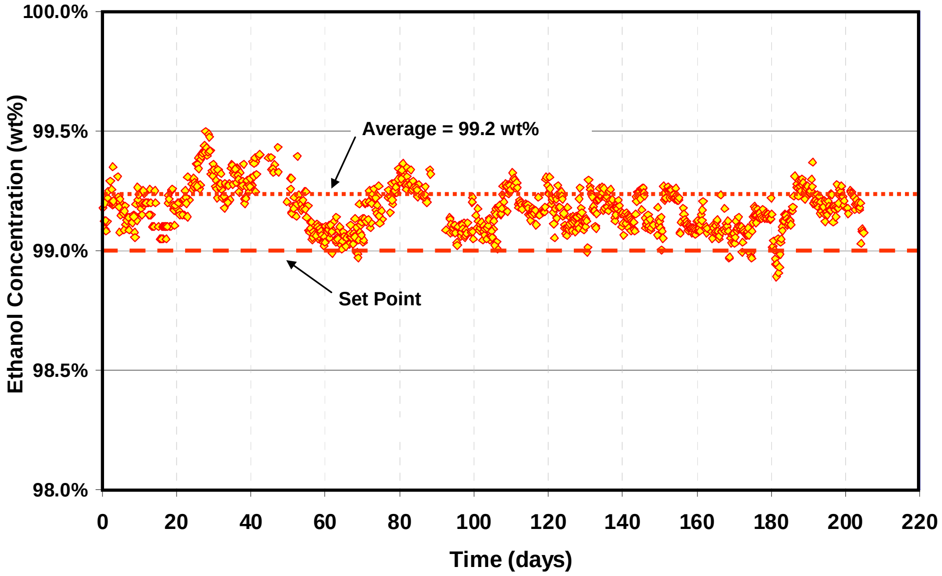

Fig. 3—Result in Tiverton field unit.

Chatham Field demonstration unit

The second demonstration was conducted in a bigger capacity plant (8 m^3/day) with two membrane stages, which was installed at Greenfield Ethanol plant in Chatham, Ontario, Canada, with start up in October 2008. The objective of this field demonstration unit was to test a two-stage commercial scale membrane system fully integrated with an industrial grain-based ethanol plant.

A simplified process flow diagram is shown in Figure 4. The demonstration unit was fed with an ethanol-water vapour mixture from the beer column with concentration between 40–60 wt% ethanol.

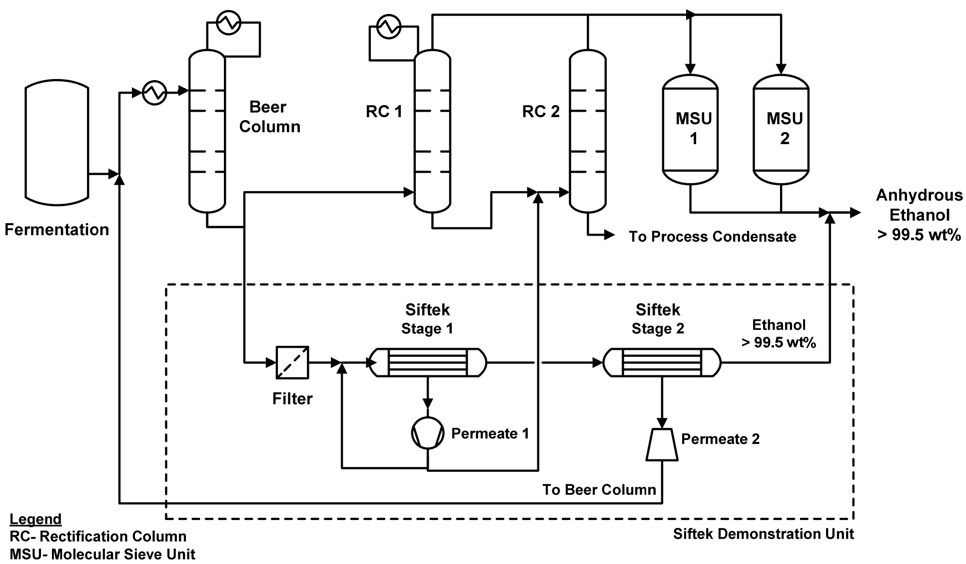

Fig. 4—Process flow diagram of Chatham demonstration unit.

The plant operated with vapour fed at an absolute pressure of 170–175 kPa, and temperature of 105–110°C. Before feeding the membrane, the flow passed though a filter to avoid any liquid or solid in the membrane.

The ethanol concentration was increased to around 90 wt% through the first stage membranes and further to the final concentration through the second stage membranes.

Figure 5 shows the results of a continuous operation, producing ethanol with concentration between 99.2 and 99.8 wt%.

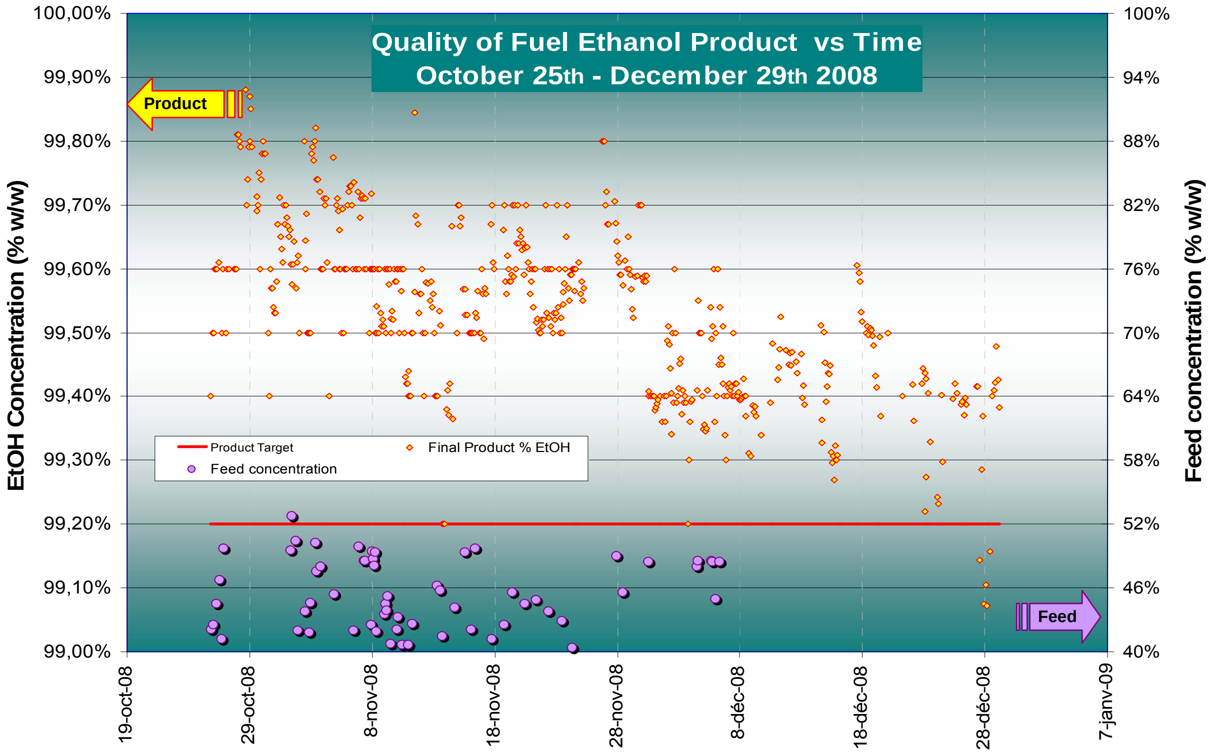

Fig. 5—Result in Chatham demonstration unit.

This demonstration unit was integrated with the industrial plant and involved recompression of the first stage permeate from an absolute pressure of 40 kPa to an absolute pressure of 250 kPa that was re-injected in the rectification column, reducing the fresh steam load.

The permeate from the second stage with a low concentration of ethanol was recycled to the beer column for ethanol recovery.

Dedini demonstration unit

The third demonstration unit was built in Brazil with the objective to demonstrate the Siftek™ technology for ethanol production from sugarcane.

The plant was designed with flexibility to process three types of feed: 45 wt% ethanol from the beer column, 93 wt% from the rectification column, and 85 wt% from molecular sieve recycle (Figure 6).

This last condition is a very interesting application because it allows an increase of the anhydrous ethanol production in the distillery (this alternative is described further in this paper).

The Dedini demonstration unit (Figure 7) operates with two membrane stages (one membrane in each stage) and has a capacity of 5 m^3/day.

The industrial performance tests were carried out at Costa Pinto Sugar Mill in Piracicaba-SP (2008) and São Martinho Sugar Mill in Pradópolis-SP (2009) (Gabardo Filho, 2008, 2009).

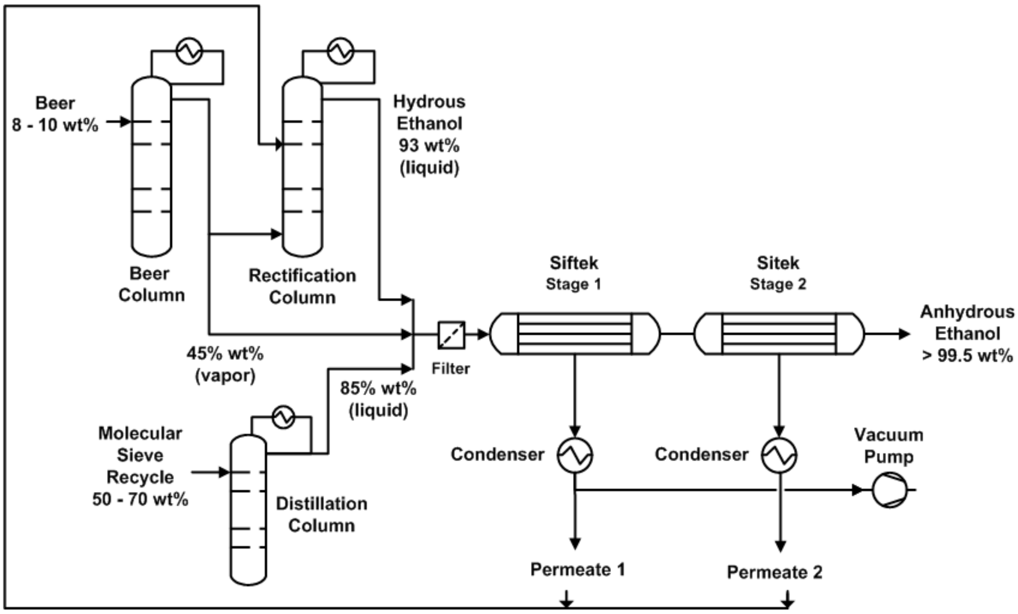

Fig. 6—Process flow diagram of Dedini demonstration unit.

Fig. 7—Dedini demonstration unit.

The plant operated with vapour fed at an absolute pressure around 160 kPa, and temperature of 115^{o}C. Before feeding the membrane, the flow passed though a knock pot to avoid any liquid or solid in the membrane and in the super-heated system.

A molecular sieve unit (MSU) produces a recycle flow with ethanol concentration between 50 and 70% during its operation and this flow needs to be reprocessed in the distillation (the lower value is the result of the dilution in the liquid ring vacuum pump used). One alternative to the membrane system is to dehydrate this recycle flow to increase the anhydrous production, avoiding the re-processing step. The first operating condition was to process the MSU recycle in a distillation process to increase the concentration to around 85% and then dehydrate it in the membrane system. The second operating condition was dehydration of the hydrous ethanol (93 wt%) from the rectification column producing anhydrous ethanol.

The third operating condition was to process the ethanol-water flow from the beer column with concentration around 45 wt% producing ethanol 99.5 wt% (to be done in November 2009).

Figure 8 shows the results of the dehydration process from the MSU recycle by membrane system (operating condition 1).

The feed concentration oscillated between 76 and 93 wt% ethanol, according to the operation of the industrial distillation column.

The system assimilated this variation very well, providing a flexibility feature for the Siftek^{TM} membrane that is not found in other, conventional technology.

The two black bars in Figure 8 represent the leak of feed from the distillery during rain periods.

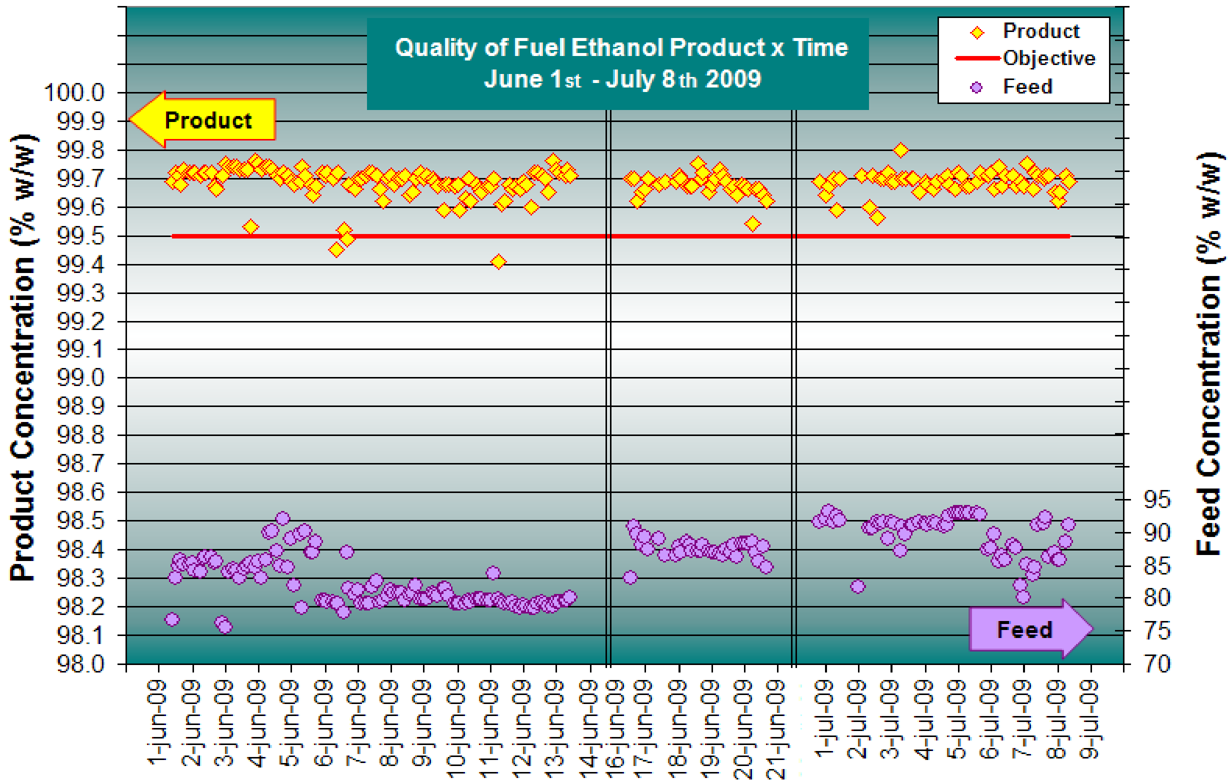

Fig. 8—Quality of ethanol product from the system (85 to 99.5 wt%).

The permeate flow, with low ethanol concentration, was sent to be recovered in the distillation process. It represented a recycle between 2 and 2.5% of the feed ethanol, compared with around 15 – 30% from molecular sieve.

Other parameters measured were the acetic acidity and conductivity. Figure 9 shows the behaviour of the acidity during operation.

It shows a small increase of around 2 mg/L in the acidity of the product. This increase is the result of the water reduction in the product and consequent concentration of the organic compounds.

It is more an indicative parameter that confirms the higher selectivity of the membrane to water compared to organics. Although the acidity is increasing, it remains lower then the specification (30 mg/L).

Figure 10 shows the conductivity in the feed and in the product, resulting in an average reduction of 55%, helping to meet the product quality specification value (500 μS/m).

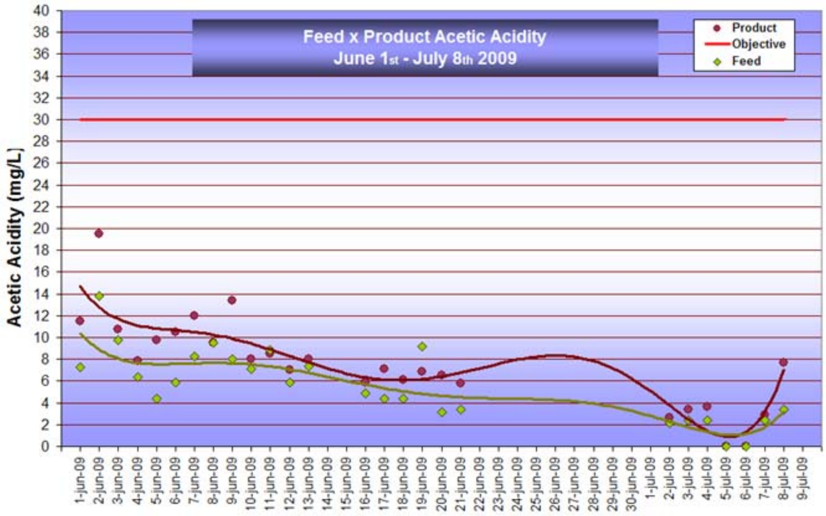

Fig. 9—Acetic acidity (Feed × Product).

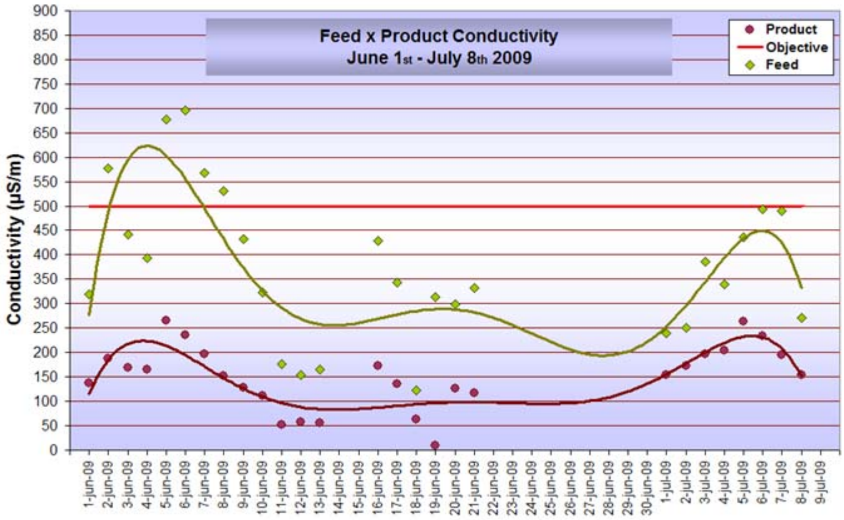

Fig. 10—Conductivity (feed × product).

In the second operating condition, the system was fed with 93.0 wt% hydrous ethanol in liquid phase. Figure 11 shows the results where it is possible to see again the stability in product quality, with average of 99.65% wt% ethanol.

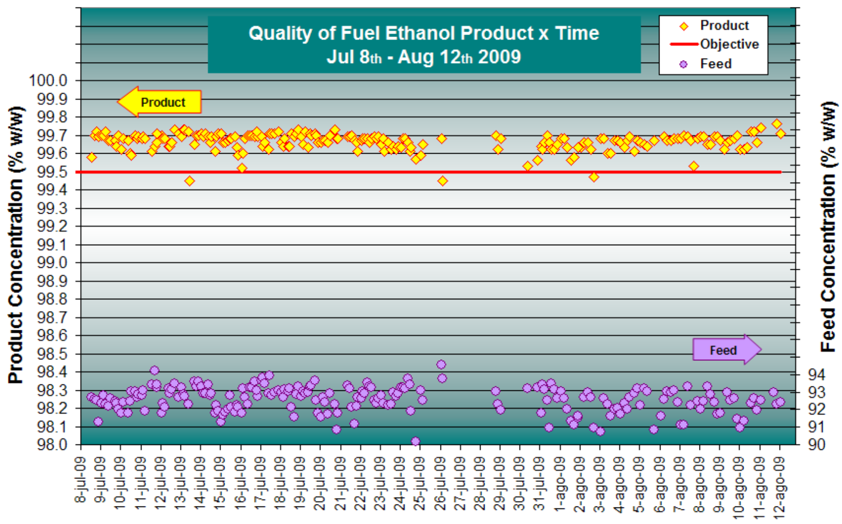

Fig. 11—Quality of ethanol product from the system (93 to 99.5 wt%).

Application of the membrane technology

There are some industrial applications where the Siftek™ Technology can be integrated in a bio-ethanol plant. Figure 12 shows the membrane application like a dehydration plant, replacing conventional technology like molecular sieve or dehydration via extractive distillation with cyclohexane in greenfield plants. The Siftek™ membrane is a product that has the advantage of no chemical contamination and high energy saving. The membrane steam consumption is around 0.41 kg steam/L of product, resulting in an energy saving around 35% when compared with MSU (consumption of 0.65 kg steam/L) and around 70% when compared with a cyclohexane dehydration process (1.55 kg steam/L).

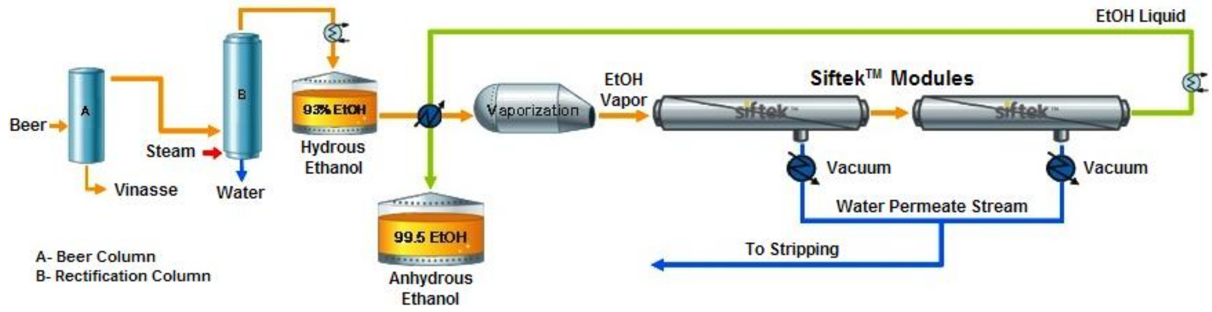

Fig. 12—Membrane in dehydration process.

Another industrial application of the Siftek™ technology is the treatment of the MSU recycle stream. In a conventional plant, a MSU is regenerated by applying vacuum sweeping with purified ethanol. This stream, containing 50–70 wt% ethanol, is recycled to the rectification column, representing a recycling of about 15–30% of the purified ethanol produced by the plant, resulting in an additional energy consumption for re-purification.

The use of a membrane system for dehydration of the MSU recycle stream can save around 15% energy, with a consumption of 0.55 kg steam/L, and debottlenecking the plant by freeing up capacity in the rectification column and MSU. If these processes are limiting, plant production could be increased by around 20%. This process flow diagram is shown in Figure 13.

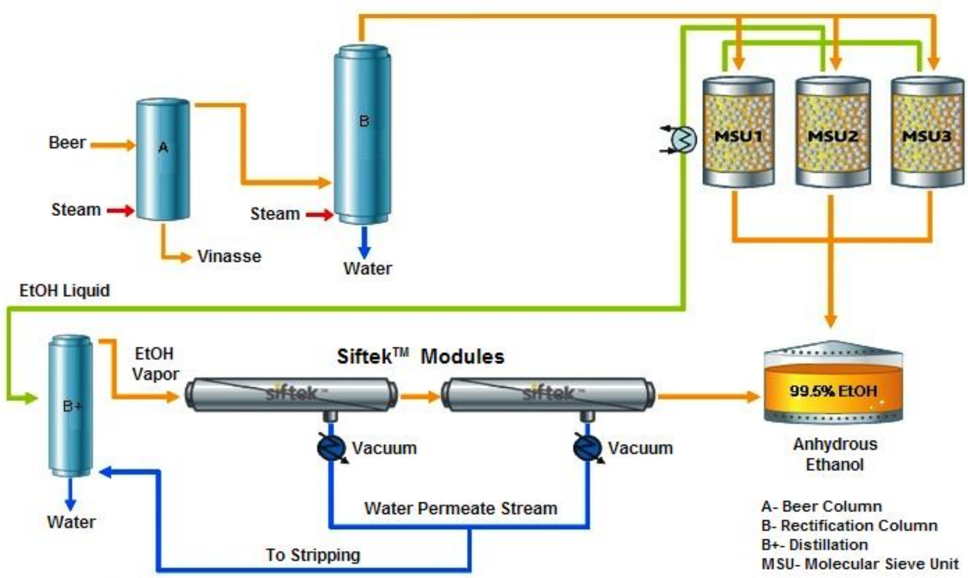

Fig. 13—Membrane in the treatment of MSU recycle.

Conclusions

Considering the excellent results obtained in the demonstration plants and in the industrial design, the conclusions are:

- The Siftek^{TM} system is a polymeric membrane that can be used to dehydrate ethanol in vapour phase because of its high selectivity of water over ethanol, with benefits of no contamination in the product and lower energy consumption.
- The three demonstration plants showed a high membrane performance in water removal, producing ethanol in a continuous process with concentration higher than 99.5 wt% ethanol.
- The Dedini system showed a high stability in quality product with an average of 99.65 wt% ethanol, with a system flexibility to assimilate variation in the feed concentration.
- Recirculation of ethanol is minimised.
- The membrane technology can be installed in new plants with lower energy consumption, saving around 35% of energy when compared with molecular sieve technology and around 70% when compared with extractive distillation by cyclohexane.
- When used to treat the MSU recycle stream, the membrane results in a reduction of around 15% in energy consumption with increased production capacity of 20%.

Acknowledgments

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SYSTÈME DE DÉSHYDRATATION D'ÉTHANOL PAR DES MEMBRANES POLYMÉRIQUES SIFTEK™

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MOTS-CLEFS: Éthanol, Déshydratation, Membranes Polymériques, Vapeur Imprégnation, Pervaporation.

Résumé

L'ETHANOL est une énergie renouvelable importante au Brésil et plusieurs sociétés améliorent leurs technologies afin d'accroître les avantages de l'éthanol par rapport aux combustibles fossiles. Les membranes polymériques Siftek™ donnent une technologie qui peut économiser entre 35 et 70% d'énergie par rapport aux processus classiques. La première usine pilote (Tiverton, Canada) a exploité une déshydratation d'éthanol de grain de 80–90% d'éthanol à 99.2 % (masse), démontrant la bonne performance des membranes. Dans le but de tester le système à titre commercial, une deuxième usine (Chatham, Canada) a été construite et exploitée avec succès, utilisant l'éthanol de grain de 40 à 60% d'éthanol à 99.5% (masse). Pour démontrer cette technologie aux producteurs d'éthanol brésiliens, un troisième appareil de démonstration a été construit et exploité dans les usines d'éthanol a partir de la canne. Les résultats ont confirmés l'excellente sélectivité du système de membrane pour l'eau; une déshydratation de 85–93% d'éthanol a été augmentée a 99.5%, avec une faible consommation d'énergie et en préservant la qualité du produit.

SISTEMA DE DESHIDRATACIÓN DE ETANOL CON MEMBRANA POLIMÉRICA SIFTEK™

Por

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PALABRAS CLAVE: Deshidratación de Etanol, Membrana Polimérica, Permeabilidad al Vapor, Pervaporación.

Resumen

EL ETANOL es energía renovable muy importante para Brasil y varias compañías están mejorando sus tecnologías desarrollando procesos para incrementar los beneficios del etanol comparado con las fuentes fósiles. La membrana polimérica Siftek™ es una tecnología que puede ahorrar entre 35 y 70% de la energía cuando se la compara con procesos convencionales. La primera planta piloto (Tiverton, Canadá) operó deshidratando etanol de granos desde 80–90% en peso hasta 99.2% en peso, evidenciando el buen desempeño del sistema de membrana. Con la meta de probar el sistema a capacidades comerciales, una segunda planta(Chatham, Canadá) fue construida y probada exitosamente, deshidratando etanol de granos desde 40–60 % en peso hasta 99.5% en peso. Para demostrar esta tecnología a los productores de etanol brasileros se construyó una tercera planta piloto y se operó en las plantas de alcohol a partir de caña. Los resultados confirmaron la excelente selectividad del sistema de membrana al agua, deshidratando desde 85–93% en peso a 99.5%, con un menor consumo de energía y preservando la calidad del producto.