PURIFICATION OF HYDRATED ETHANOL THROUGH ION EXCHANGE RESINS

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Keywords: Ethanol, corrosion, ion exchange.

ABSTRACT

Ethanol (using sugar cane as raw material) was first introduced as fuel in Brazil in 1979. The process of ion exchange resins was developed to purify this ethanol, which contains six percent water, leading to corrosion problems in fuel tanks, carburettors, fuel pumps and engines of ethanol-powered vehicles. Ion exchange resins provide an efficient means of fuel purification at a competitive cost and with ease of operation when compared to other corrosion and scale prevention alternatives. Demineralized alcohol can be produced through one simple passage of the ethanol through cationic and anionic columns, this being sufficient to neutralise the acidity and remove the inorganic ions present. Laboratory and vehicle tests with demineralized alcohol showed a significant reduction in the corrosiveness of ethanol fuel. A standard quality of alcohol could also be obtained from material obtained from different sources and different regions within the country.

INTRODUCTION

Hydrated ethanol fuel is highly corrosive (Colding¹, Tanaka and Wolynec²) despite its low impurity content (< 50 mg/l). This corrosiveness is due to the presence of contaminants such as chlorides, sulphates and other ions (Tanaka et al.³). Since 1979, when the use of hydrated alcohol as a vehicle fuel was intensified, problems such as corrosion and scale have been detected, mainly in fuel tanks, fuel pumps and carburettors. Several methods, such as the application of a metallic coating or the use of chemicals inhibitors, have been tried in order to avoid or minimise corrosion of metallic components in contact with ethanol fuel (Pinto², Wolynec and Tanaka³), but none of them has been effective.

The elimination of corrosive and scaling agents seemed to be a logical solution. The ion exchange technique has been used for a long time to eliminate the cations and anions present in boiler feedwater for protection against scale and corrosion.

EXPERIMENTAL PROCEDURE

The ion exchange treatment is a process whereby all cations present in a liquid medium are exchanged for hydrogen ions, and all anions are exchanged for hydroxyl ions. The chemical reactions that occur during the process are:

CATIONS

\[
\begin{align*}
(CER) - H & \rightarrow Na \\
(CER) - Ca & \rightarrow Na + HCl \\
(CER) - Mg & \rightarrow Na + H_2SO_4 \\
& \rightarrow Acetic Acid
\end{align*}
\]
After the exhaustion of the exchange capacity of the CER, it is regenerated by the passage of diluted sulphuric or hydrochloric acids:

\[
\text{DILUTE} \\
\begin{array}{llll}
\text{(CER)} & \text{Na} & + & \text{H}_2\text{SO}_4 & \rightarrow & \text{(CER)} - \text{H} & + & \text{Salts} \\
\text{Ca} & \text{or} & & & & \\
\text{Mg} & \text{HCl} & & & & \downarrow \\
\text{Zn} & & & & & \text{Waste} \\
\text{Others} & & & & & \\
\end{array}
\]

The action of the anionic exchange resin (AER) is:

\[
\text{ANIONS} \\
\begin{array}{llll}
\text{(AER)} & - & \text{OH} & + & \text{SO}_4^- & \rightarrow & \text{(AER)} & \text{SO}_4^- & + & \text{H}_2\text{O} \\
\text{Cl} & & & & \text{Cl} & & & & \\
\text{Acetate} & & & & \text{Acetate} & & & & \\
\end{array}
\]

After the exhaustion of the exchangeable capacity of the AER, it is regenerated by the passage of a dilute solution of sodium hydroxide:

\[
\text{DILUTE} \\
\begin{array}{llll}
\text{(AER)} & - & \text{SO}_4^- & + & \text{NaOH} & \rightarrow & \text{(AER)} & - & \text{OH} & + & \text{Salts} \\
\text{Cl} & & & & \text{Cl} & & & & \downarrow \\
\text{Acetate} & & & & \text{Acetate} & & & & \text{Waste} \\
\end{array}
\]

In general, the total amount of cations present in a liquid medium is equal to the total amount of anions. Hence, when cations and anions have been exchanged by hydrogen and hydroxyl ions, the treated liquid will be neutral. The resins used for the ethanol treatment are: cationic exchange resin AMBERLITE ALC-50 and anionic exchange resin AMBERLITE ALA-20. The equipment for this process consists of two columns; the first contains the CER and the second contains the AER. The ease of operation of the ion exchange process is such that fluctuations in the quality of the raw material do not affect the quality of the demineralised ethanol. A unique feature is that there is a shorter operation cycle when the concentration of influent salts is higher, and when the concentration is lower, the operation cycle is longer. The equipment is illustrated in Fig. 1.
RESULTS

The first demineralised ethanol was produced in União São Paulo distillery in 1983, using a pilot plant having 20 litres of CER and 30 litres of AER. The flow rate in the pilot plant was 300 l/h. More than 20 complete cycles were run. The effects of demineralization are shown in Fig 2 a, b and c. The results showed that the pH range of the influent was from 2.8 to 4.3, 70% of the samples in the range 3.7.
to 4.0. The effluent pH varied from 6.5 to 8.6, and for most of the samples it was between 7.1 and 8.0. The acidity range was from 17 to 40 mg/l as acetic acid in the influent, and in the effluent it ranged from 2.5 to 5.5 mg/l. The acidity was determined by titration using alfa naphthalein as an indicator.

![Histograms showing pH, acidity, and conductivity](image)

Figure 2 a, b, c. Results of pH, acidity and conductivity obtained at pilot plant.

The range of conductivity in the influent was from 1.0 to 3.5 micromho/cm, and in the effluent from 0.01 to 0.06 micromho/cm. The demineralized ethanol was used by the Instituto de Pesquisas Tecnológicas do Estado de São Paulo to carry out two tests, one
on a laboratory scale using loop tests, and the other a fleet test using regular vehicles. The scale and corrosion caused to normal gasoline-powered car components when using ethanol fuel were determined using the loop test shown in Fig 3 to simulate normal flow. Tests were performed for six weeks according to the following programme: eight hours of fuel flow and 16 hours of stagnant conditions for the five week days, followed by 48 hours of stagnant conditions (weekends). The flow rate was adjusted to 20 l/h. The ethanol fuel was changed at the beginning of each week. Two complete tests were performed simultaneously using regular and demineralised ethanol.

Figure 3. Loop test diagram.

All metallic components in contact with regular ethanol fuel showed scale or corrosion after six weeks, while the components in contact with the demineralized ethanol showed no corrosion or scale after the same period, as can be seen in Fig 4 a, b, c and d. These tests demonstrated that the ion exchange resin treatment effectively eliminated the scaling and corrosive properties of hydrated ethanol fuel used in Brazil for passenger cars. The results of analyses of the demineralized and regular ethanol used in the test are reported in Table 1. The past and present specifications for ethanol fuel are given in Table 2.

In order to evaluate the performance of demineralized ethanol fuel in vehicles, three cars were specially assembled by car manufacturers, in the conventional manner of gasoline-powered cars, with respect to materials. (Ethanol-powered cars have specially treated internal surfaces which would resist corrosion during this test).

One of the cars was run with regular ethanol as a reference and the two others with demineralized ethanol. The tests were performed for 30,000 km, 70% city driving and 30% highway driving, with a minimum of 1,500 km a month and a maximum of 3,000 km a month, in order to simulate normal driving patterns of passenger cars. The carburettors were visually inspected every 5,000 km. Chemical analysis and visual and metallographic examinations of all components were done at the end of the tests.
Figure 4a, Fuel tank - untreated ethanolic corrosion with white corrosion product.

Figure 4b, Fuel tank - treated ethanolic - no corrosion.
Figure 4c. Carburettor - untreated ethanol - corrosion below the liquid line.

Figure 4d. Carburettor - untreated ethanol - intense corrosion below liquid line.
Table 1 - Chemical analysis of ethanol.

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Regular ethanol</th>
<th>Demineralized ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>5.5</td>
<td>7.9</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>0.8045</td>
<td>0.8056</td>
</tr>
<tr>
<td>Ethanol content</td>
<td>% mass</td>
<td>94.4</td>
<td>94.5</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>µS/m</td>
<td>300</td>
<td>35</td>
</tr>
<tr>
<td>Acidity as acetic acid</td>
<td>mg/l</td>
<td>28</td>
<td>3</td>
</tr>
<tr>
<td>Sodium as Na</td>
<td>mg/l</td>
<td>2.5</td>
<td>Not detected</td>
</tr>
<tr>
<td>Magnesium as Mg</td>
<td>mg/l</td>
<td>0.008</td>
<td>0.003</td>
</tr>
<tr>
<td>Iron as Fe</td>
<td>mg/l</td>
<td>0.012</td>
<td>0.003</td>
</tr>
<tr>
<td>Copper as Cu</td>
<td>mg/l</td>
<td>0.013</td>
<td>0.008</td>
</tr>
<tr>
<td>Zinc as Zn</td>
<td>mg/l</td>
<td>0.029</td>
<td>0.010</td>
</tr>
<tr>
<td>Chloride as Cl</td>
<td>mg/l</td>
<td>2.0</td>
<td>0.220</td>
</tr>
<tr>
<td>Sulphate as SO₄</td>
<td>mg/l</td>
<td>1.76</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

Table 2 - Specifications for ethanol fuel.

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Past specifications</th>
<th>Present specifications (May 1988)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td>7.0 + 1.0</td>
</tr>
<tr>
<td>Density at 20°C</td>
<td>kg/cm³</td>
<td>809.3 + 1.7</td>
<td>809.3 + 1.7</td>
</tr>
<tr>
<td>Ethanol content</td>
<td>% mass</td>
<td>93.2 + 0.6</td>
<td>500 max</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>µS/m</td>
<td>—</td>
<td>30 max</td>
</tr>
<tr>
<td>Acidity as acetic acid</td>
<td>mg/l</td>
<td>30 max</td>
<td>30 max</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>—</td>
<td>Negative</td>
<td>—</td>
</tr>
<tr>
<td>Iron as Fe</td>
<td>mg/l</td>
<td>—</td>
<td>5 max</td>
</tr>
<tr>
<td>Sodium as Na</td>
<td>mg/l</td>
<td>—</td>
<td>2 max</td>
</tr>
<tr>
<td>Sulphate as SO₄</td>
<td>mg/l</td>
<td>—</td>
<td>1 max</td>
</tr>
<tr>
<td>Chloride as Cl</td>
<td>mg/l</td>
<td>—</td>
<td>1 max</td>
</tr>
<tr>
<td>Gasoline content 30</td>
<td>mg/l</td>
<td>30 max</td>
<td>30 max</td>
</tr>
<tr>
<td>Density at 20°C with 30 mg/l of gasoline</td>
<td>kg/m³</td>
<td>—</td>
<td>808.0 + 3.0</td>
</tr>
<tr>
<td>Evaporation residue</td>
<td>mg/l</td>
<td>50 max</td>
<td>50 max</td>
</tr>
<tr>
<td>Non-volatile material at 105°C</td>
<td>mg/l</td>
<td>50 max</td>
<td>30 max</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>mg/l</td>
<td>60 max</td>
<td>—</td>
</tr>
<tr>
<td>Esters</td>
<td>mg/l</td>
<td>80 max</td>
<td>—</td>
</tr>
<tr>
<td>Superior alcohol</td>
<td>mg/l</td>
<td>60 max</td>
<td>—</td>
</tr>
<tr>
<td>Aspect</td>
<td></td>
<td>clear and without</td>
<td>clear and without</td>
</tr>
<tr>
<td></td>
<td></td>
<td>suspension material</td>
<td>suspension material</td>
</tr>
</tbody>
</table>

No corrosion was observed on any metallic component of the demineralized ethanol-powered cars, but regular ethanol-powered car components showed corrosion. The car-
burettor of the car using regular ethanol began corroding at 5,632 km (about two months). Fig 4c and d shows the results obtained with the carburettors after 30,000 km. Chemical analysis of corrosion products of regular ethanol-powered car components showed the presence of oxides, carbonates and sulphates (zinc carbonate hydroxide; zinc hydroxide hydrate; zinc oxide; lead sulphate).

During the 1988 season an industrial plant started to operate at Destilaria São João. The system was designed to operate at 10 m³/h, so the capacity of the cationic exchange column was 300 litres of CER and that of the anionic exchange columns was 1,000 litres AER. The large differences in volume of resins between cationic and anionic resins was due to the low level of cations in the ethanol, while the level of anions was higher due to the acetic acid content. The system operated for 7 months and 45 regenerations were conducted. The average cycle time was 109 hours. During 1988 49 million litres of ethanol were demineralized. The results of the first 30 cycles are presented in Fig 5 a, b and c where pH, acidity and conductivity of influent and effluent ethanol are compared.

**Figure 5 a, b and c. Average of demineralized alcohol at industrial plant**
DISCUSSION AND CONCLUSIONS

The ion exchange treatment of ethanol fuel reduces the hydrated ethanol corrosiveness almost to zero level. This reduction is due to the elimination of corrosive impurities at little additional cost to the ethanol production. In addition, this treatment is able to produce uniform ethanol quality everywhere, independent of local manufacturing conditions. The ion exchange treatment has an advantage when compared to neutralization or the use of inhibitors because there is no addition of chemicals to the ethanol. The same alcohol can therefore be used also by the chemical industries.

REFERENCES


PURIFICATION DE L’ÉTHANOL HYDRATÉ PAR DES RÉSINES ÉCHANGEUSES DE IONS.

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EXtrait

- L’éthanol (quand on utilise la canne à sucre comme matière première)) a d’abord été introduit comme combustible au Brésil en 1979.
- Le processus d’échange d’ions par résines a été développé pour purifier cet éthanol, lequel contient dans sa composition 6% d’eau, évitant des problèmes de corrosion dans le réservoir du combustible, dans le carburateur, dans la pompe et dans les véhicules mus à l’éthanol.
- L’échange d’ions par résines est un procédé de purification du combustible hautement efficace, offrant un coût compétitif et une facilité d’opération quand on le compare avec d’autres corrosion et échelle de prévention alternatives.
- Le processus pour produire de l’alcool demineralisé consiste en un simple passage d’éthanol à travers des colonnes de résines cationique et anionique, cela étant suffisant pour neutraliser l’acidité et ôter les ions inorganiques présents.
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- Des tests en laboratoire et surdes instruments effectués avec déminéralisé ont montré une réduction significative de corrosion d'éthanol combustible, ainsi que la possibilité d'obtenir des propriétés physiques et chimiques adéquates pour les produits finals, grâce à l'habilité à standardiser l'alcool provenant de sources et régions diverses à l'intérieur du pays.

PURIFICACION DEL ETANOL HIDRATADO POR RESINAS TROCADORAS DE IONES.
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RESUMEN

El etanol (utilizando caña de azúcar como materia prima) como combustible fue introducido inicialmente en Brasil en 1979. El proceso de resinas de intercambio iónico para purificar este etanol fue desarrollado, con una composición del 6% de agua, creando problemas de corrosión en el tanque de combustible, carburador, bomba de gasolina y motor de vehículos accionado por etanol.

Las resinas de intercambio iónico representan un proceso de purificación de combustible altamente eficiente que ofrece costos competitivos y fácil operación cuando se compara con otras alternativas de prevención de corrosión. El proceso para producir alcohol desmineralizado consiste en un paso simple del etanol a través de resinas catiónicas y de columnas de resinas aniónicas siendo suficiente para neutralizar la acidez y remover los iones inorgánicos presentes.

Las pruebas con alcohol desmineralizado en laboratorio y en vehículos mostraron no sólo una reducción significativa de la corrosividad del combustible etanol sino también la posibilidad de obtener propiedades físicas y químicas adecuadas de los productos finales debido a la factibilidad de estandarizar el alcohol suministrado a partir de diferentes fuentes o regiones dentro del país.