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OBTENTION OF ETHANOL FROM AGRICULTURAL WASTES

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Operational parameters suitable for the obtention of sweet juices from different agricultural products of great importance in Spain and their use for the production of ethanol or intermediary compounds for the organic chemical industry are studied.

We have studied 8 different materials (stalks and corncobs of sacarine corn; FUNK'S corn; sweet sorghum; rice straw; and vine shoots) and a process of maximum use or its hidrocarbonate potential, developed by ourselves, has been applied. This general process is based on the idea of the obtention in sequential stages, first, soluble sugars in water; second, the pentoses from hydrolysis of pentosans and third, the glucose proceeding from cellulose, in order to get a more complete use of wastes. Likewise, we have established the most suitable objective at which each waste must be aimed.

In the stage of watery extraction, the obtained results with stalks of sweet sorghum, var. WRAY, (for each ton., 330 kg of fermentable sugars and about 180 l of ethanol are obtained) and with stalks of sacarine corn (for each ton., 270 kg of fermentable sugars and about 145 l of ethanol are obtained) are very interesting.

In the selected conditions for the stage of prehydrolysis, stalks and corncobs from both varieties have shown yields in the hydrolysis of pentosans higher to 80% (for each ton., about 230 kg of xylose, in the corncobs FUNK'S, and about 200 kg in the sacarine corncobs are obtained). However, in the stalks the degradation to furfural is over 40% hydrolyzed pentoses and doesn't reach 25% in the corncobs. In the other materials, the hydrolysis is similar, between 60 and 70% initial pentosans, ranging the degradation from 26% (sweet sorghum) to 70% (rice straw) of hydrolyzed pentoses.

The facility of hydrolysis of cellulose is also different according to the waste. It's outstanding the corncobs from both varieties with more than 80% of their cellulose hydrolyzed (for each ton., 340 kg of fermentable sugars in FUNK'S corn and 360 kg in sacarine corn are obtained). The rest of wastes have yields between 43% (rice straw) and 75% (stalks of FUNK'S corn).

OBTENTION OF ETHANOL FROM AGRICULTURAL WASTES

Obtention of liquid fuels from biomass is beeing of great interest in the last years. Although the petroleum crisis has temporally given in, the need of finding fuels for explosion motors that doesn't depend on petroleum is evident. Moreover, the trend to eliminate TEP, for raising the octane number, arise the interest in oxigenated fuels.

In a world with food deficit, the obtention of ethanol-fuel from cereal-grains fermentation, has got encountered positions because of social reasons. A more attractive solution is to make use of the residual biomass like raw material. These agricultural wastes are composed of 3 different kinds of carbohydrates: a) water soluble monosaccharides and olygosaccharides, fermentable by yeasts in a large amount; b) easy hydrolyzable pentosans; and c) lignocellulose which is very resistant to hydrolyze. In a process of maximum use of hydrocarbonate potential, we try to obtain apart each one of these carbohydrates. This process admits a little degradation and a good use of materials. On the other hand each one of the fractions have a different use.

Agricultural residues and agroenergetic harvests, with present or potential importance in Spain, have been studied. With this aim, a general process, designed to obtain the maximum use of hydrocarbonate potential, has been applied to them. This process, has been developed in laboratory-scale in our Department from 1981 to 1984, and has been selected between other studied processes. This process has three stages: a) watery extraction of soluble sugars; b) easy hydrolysis of hemicellulose (prehydrolysis); and c) strong hydrolysis of lignocellulosic residue. Finally, the fermentation capacity of broths from each stage is studied.

A pilot plant is being built nowadays as a result of the laboratory work. In it a industrial process, in which unvaluable materials from several origins could be used as raw materials, will be developed.

According to the former point of view there are two groups of raw materials: a) "sweet" group, rich in soluble sugars (composed by stalks of sacarine corn, var. E-41; stalks of FUNK'S corn, var. G-5050; and stalks of sweet sorghum, of 5 var.: RIO, WILEY, DALE, KELLER and WRAY); and b) "pentosanecellulosic" group, which consist in the rest of studied residues (cobs of sacarine corn, var. E-41; cobs of FUNK'S corn, var. G-5050; rice straw, var. BAHIA; and vine shoots, var. BOBAL).

WORK PLANNING

1) Extraction of soluble sugars:

Sugar composition, yields and alcoholic fermentation capacity of obtained broths have been studied.

2) Hydrolysis of hemicelluloses (prehydrolysis):

Different conditions of prehydrolysis (varying time between 1 and 4 hours and acid concentration between 2 and 9%) have been tested, confronting yields, broth composition and sugar degradation in every one of the processes.

3) Strong hydrolysis of lignocellulosic residue:

2 different processes of hydrolysis have been tested. Yields, composition of broths and degradation have been studied. There is two phases for each process. In the first phase, lignocellulosic residue is attacked with concentrated sulfuric acid (at a suitable ratio for each one of the two processes) between 30-50 °C of temperature (it depends on the process). This phase destroys the crystalline structure of cellulose. In the second phase there is a posthydrolysis. In it the acid is diluted to an adequate concentration (8 or 4 %) at a fixed temperature (100 °C) in 1 or 2 hours time, until the hydrolysis of the oligomers from the first phase was completed.

4) Composition of solid residues in each acid extraction and, specially, the amount of potential reductors of lignocellulosic residue, have been studied to work out yields in each process.

5) Using different yeasts and testing alcohol yield for every yeast-extract combination, fermentation assays with the extracts have been carried out.

RESULTS

Sweet sorghum (var. WRAY) collected with energetic aims, contains the greatest proportion of soluble and fermentable sugars (330 kg/ton). But in corn stalks, residue with a low profit from the grain production, contains amounts that allow its industrial use (270 kg/ton, in sacarine corn; and, about, 110 kg/ton, in FUNK'S corn). (See fig. 1).

Prehydrolysis treatment is of great interest in hemicellulose rich materials (pentosans mainly) since, not only allows the pentose extraction in a great deal, but also make it easy to attack the cellulose (see fig. 2).

Hydrolysis of pentosanic fraction from residues produces xylose rich broths. Utilization of xylose through chemical ways could be of much benefit than alcoholic fermentation in order to obtain chemical by-products.

Corncobs are the pentosan richest residues studied (amounts higher than 300 kg/ton); the rest contain between 140 kg/ton (sorghum) and 230 kg/ton (vine shoot). (See fig. 2).

Depending on the residue, these pentosans are easily hydrolyzed. For that, the amount of residual pentosan is a measure of its resistence index. In corn stalks of both varieties this amount is under 3% of initial pentosans in the strongest conditions. In the corncobs, pentosans are a little more resistant. In the strongest conditions about 12% of initial pentosans still remain in residue. In the sorghum and rice straw pentosanes are even much more resistants; about 30% of initial pentosanes resist the strongest conditions.

There is a relationship between the heterogeneability of pentosanic fractions and degradation to furfural of some hydrolyzed pentoses. In some residues (corn stalks and vine shoot), part of the pentosans is hydrolyzed with smoother conditions whereas the rest needed stronger treatments and therefore have an important degradation to furfural of extracted pentoses.

Pentosans of other residues (sweet sorghum and rice straw) are hydrolyzed together when suitable conditions are reached. In this residues, degradation to furfural of hydrolyzed pentoses is not very high, although there is a pentosanic much more resistant fraction that remains in residue after treatment. This fraction is more than 30% of initial pentosans.

In corncobs there are some pentosans low-resistant which extract easily about 60% in smooth conditions. The rest is hydrolyzed gradually being his degradation to furfural about 25% of initial pentosans in stronger conditions.

Corncobs, vine shoots and stalks of sweet sorghum are, relatively, rich in easy-hydrolyzed hexosans (more than 60 kg/ton). Hexoses appear to join pentoses in broths of prehydrolysis. So that the use of these fractions is complicated. A mixed fermentation with <u>Pachysolen</u> and yeasts or a process with a first stage of chemical recovery of pentoses may be easy-extracted in smooth conditions. Degradation to HMF of these hydrolyzed hexoses will depend on conditions employed to hydrolyze pentosans.

There is a great deal of lignocellulosic fraction in all of the studied residues. Materials with high amounts of soluble and fermentable sugars have, relatively, little amount of cellulose, although this value is over 200 kg/ton in all the studied residues. (See fig. 3).

Materials named "pentosane-cellulosic" are more rich. Corncobs have over 400 kg/ton amount. The availability of hydrolysis is different in each material. This has to do with its lignine content. In general terms, the lignocellulose with lignine content lower than 10% is easier to hydrolyze (usually, over 80%).

The rest of materials have lower yield, having a higher content in lignine (rice straw and vine shoots have over 200 kg/ton amount).

A part of hydrolyzed hexoses is dehydrated to HMF although this degradation don't exceed to 10% of hydrolyzed hexoses.

Use or recuperation of these amounts of HMF is one of the main problems to resolv in the next pilot-plant studies. Moreover, the fermentation by yeasts is partially inhibited when HMF is present in the broths.

Major amounts of fermentable sugars got from hydrolysis of cellulose are obtained in corncobs of both varieties (over 340 kg/ton amount). The rest give amounts between 140 kg/ton (sweet sorghum) and 226 kg/ton (vine shoot).

All broths of hydrolysis contain pentoses that come from more resistant pentosans which didn't hydrolyze through prehydrolysis; for many applications these pentoses are, really, a contaminant. These real pentoses in the broths are more abundant in materials as corncobs and vine shoots (which fractions of residual pentosans are of importance). A important amount of pentoses is degradated to furfural which evaporates and remains in broths in little amount.

Final residue of lignine, with more or less resistant cellulose, varies between 6% (corncobs FUNK'S) and 33% (rice straw).

Broths obtained from each one of the 3 stages have different fermentation yields. During watery extraction, broths obtained from rich in soluble sugars materials yield between 85 and 90% of theoric alcohol, when fermented with adecuate yeast. In broths of prehydrolysis, alcohol yielding, hardly exceed 50% of the theoric one (respect to the hexoses), This is due to pentoses, furfural and HMF in broths that partially inhibit the fermentation. With broths from hydrolysis, yields are between 60 and 65% of the theoric one.

Moreover, yields are different for each residue and for each stage.

Obtained results from this work and agronomic data of these varieties allow to work out an estimation of the amounts in absolute ethanol, xylose, furfural and HMF, produced for hectare in each one of the studied materials (see fig. 4).

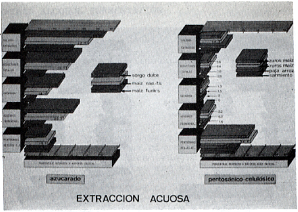

Figure 1: Obtained results from watery extraction.

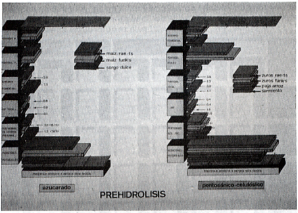

Figure 2: Obtained results from prehydrolysis.

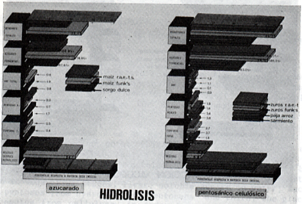

Figure 3: Obtained results from hydrolysis.

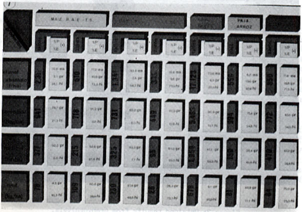

Figure 4: Estimation of the amounts in absolute ethanol, xylose, furfural and HMF, produced for hectare in each one of the studied materials.