CHEMICAL ENGINEERING TRANSACTIONS Volume 21, 2010
Editor J. J. Klemeš, H. L. Lam, P. S. Varbanov
 ISBN 978-88-95608-05-1 ISSN 1974-9791
DOI: 10.3303/CET1021210

# Fuel Ethanol Production from Carob Pod

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There is a growing interest worldwide to find out new and cheap carbohydrate sources for production of bioethanol. In this work, carob pod (*Ceratonia Siliqua*) is proposed as an economical source for ethanol production, especially, in arid regions. The carob tree is an evergreen shrub native to the Mediterranean region, cultivated for its edible seed pods and it is currently being reemphasised as an alternative in dryland areas, because no carbon-enriched lands are necessary. The global process of bioethanol production from carob pod by *Saccharomyces Cerevisiae* yeast cells was analyzed. In a first stage, the aqueous extraction of sugars from the pod was conducted, achieving almost complete extraction of sugars (>99 %) in a short period of time. After that, fermentation of hydrolysates were carried out at 30ºC, 125 rpm, 200 g/L of sugars and 15 g/L of *Saccharomyces Cerevisiae* yeast cells. In these conditions, a maximum of 95 g/L of ethanol was obtained after 24 h.

## 1. Introduction

The demand of energy in developed societies join to the development process of other counties like China and India is accelerating a decrease in fossil energy stocks and an increase in enviromental degradation. For thease reasons government policies are doing big efforts in work out sustainable energy models.

Ethanol has long been considered as a sustainable alternative to fossil fuels in transport sector (Talenbia et al., 2010). Worldwide ethanol production capacity in 2005 and 2006 were about 45 and 49 billion L/y, respectively and total output in 2015 is forecast to reach over 115 billion L (Licht, 2006).

The main types of feedstocks for the production of bioethanol are: (i) raw materials containing fermentable sugars (sugar cane, beet and sweet shorgum), (ii) polysaccharides that can be hydrolyzed for obtaining fermentable sugars (starch contained in several grains, like maize and wheat) and (iii) lignocellulosic biomass. However, several technical difficulties have been identified in the use of biofuels associated with the production costs that are uncertain and vary with the feedstock, (Demirbas, 2009; Börjesson, 2009).

Carob has drought resistance, requires little maintenance and produces a range of products from the seed and the pod. The carob pod is used actually as animal feed or is

Please cite this article as: Sanchez Segado S., de Juan García D., Lozano L. J., Godinez Seoane C., de los Ríos A. P. and Hernandez Fernandez F. J, (2010), Fuel ethanol production from carob pod, Chemical Engineering Transactions, 21, 1255-1260 DOI: 10.3303/CET1021210

grinded to obtain carob powder, which can be used for human consumption although high tannin content limits this application (Batlle and Tous, 1997).
The aim of the present investigation was to analyze the global process of bioethanol production from carob pod by different *Saccharomyces Cerevisiae* yeast cells, including sugar extraction and fermentation of aqueous extracts.

## 2. Materials and Methods

### 2.1. Materials

The study was carried out using grinded carob pod (without seeds) supplied by Mondial Carob Group (Cartagena, Spain). Chemical composition of carob pod (expressed in g/100 g dry weight basis) was the following: moisture, 10–12; starch, 0.94–0.95; total sugar (glucose, fructose, sucrose and maltose), 46–48; crude protein, 6.0–6.5; crude fibre, 10.0–11.5; total ash, 1.2–1.8; pH 4.5–4.8.
The monosaccharides and oligosaccharides content were 70.60% of sucrose, 8.93% of glucose and 18.30% of fructose, with respect to the total amount of sugars in the pod (46 – 48%). The mean size of the fraction selected was 0.57 mm. *Saccharomyces Cerevisiae* yeast A was supplied by S.I. Lessafre, B and C were supplied by local market.

### 2.2. Sugars Extraction

Sugar extraction from carob pods (S) were carried out with water (L) at different L/S ratio. 50 g of grinded carob pod were immersed in the adequate amount of water and mechanically shook in open flasks at ambient temperature (20-25 ºC) until attain extraction equilibrium. Then the mixture was filtered and the extract was analysed for its content of total sugars. Eq. (1) was used to calculate the yield of total sugar in the extract.

$$\text{T.S.}(\%\,\text{w/w}) = \frac{\text{total sugars in the solution}}{\text{total sugars amount of grinded carob pod}} \cdot 100 \qquad (1)$$

### 2.3. Fermentation

The anaerobic fermentation stage was carried out in a 3 L fermentation tank with several sample taking facilities, temperature controls and rpm-regulated agitator. As feedstock, the aqueous extract from the extraction test were used in each batch. Prior to the addition of this aqueous extract to the fermentation tank, solid residues were removed using a vibrating screen with a mesh size of 0.5 mm.
After that, ammonium phosphate (3.2 g/L), potassium sulphate (1 g/L) and magnesium sulphate (1.8 g/L) were added as inorganic nutrients over the previous aqueous solution. Then, the pH was adjusted to 3.5-4, using diluted sulphuric acid. The resulting solution was sterilized by heating until its boiling point and then cooled at 35 ºC.
This solution was fed to the fermentation reactor thermostatized at 35 ºC and the mixture of reaction was stirred 125 r.p.m. Free cells of *Saccharomyces Cerevisiae* (15 g/L) were used as yeast for the sugar to ethanol conversion .
The evolution of fermentation process was determined by measurement of density of hydro-alcoholic solutions obtained and by gas chromatography using a HP-INNOWAX

column (30m × 0.53mm × 0.25µm, Agilent). The monosaccharides and oligosaccharides in the fermentation broth were semiquantitatively analyzed by HPLC using a CarboPac PAl-PG1 column, a PED, Dionex 2010I, 6.0 g/l NaOH**.** Microbial growth using population measurements with a Neubauer chamber was used as complementary analytical methods.

## 3. Results and Discussion

### 3.1. Sugars Extraction

In order to analyze the effect of the ratio of carob pod (S) to water (L) on the efficiency of the extraction of sugars, the extraction process were carried with five different ratios S/L ranging from 4.67 to 38.5 at room temperature.

As can be seen in Figure 1, almost complete aqueous extraction of sugars from carob pods was achieved in a short period of time (less than 30 min.), so this process can be considered easy for industrial application.

Since solutions with a sugar content of 20 % w/w are needed for practical industrial application, the following conditions were established for preparing aqueous extractors for the fermentation process: L/S ratio of 2.5 for 20 min.

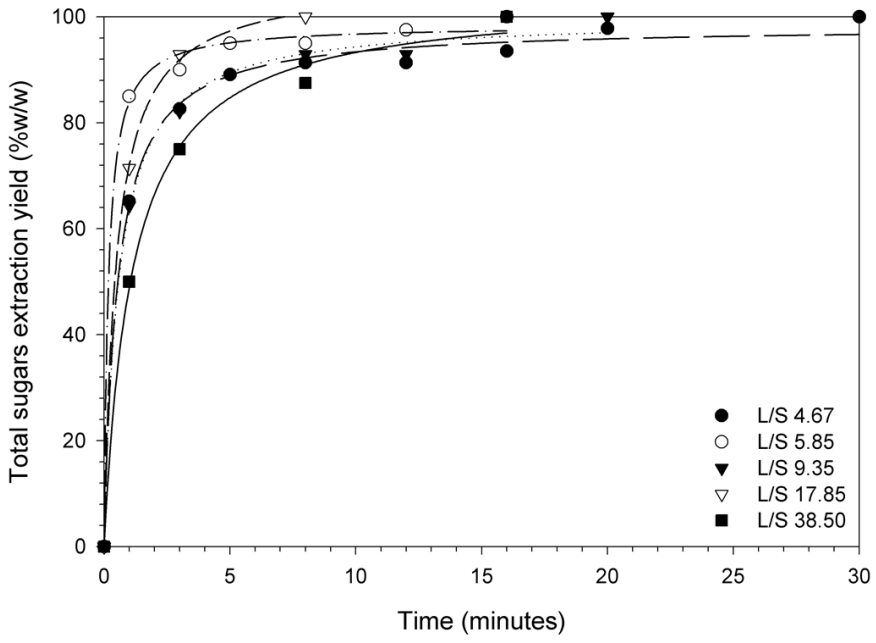


*Figure 1: Sugar extraction yield of sugars contained in carob pod samples using water at room temperature.*

**3.2. Fermentation**

Anaerobic fermentation tests were carried out with sterilized carob pod extracts. These extracts were analyzed with the following average composition: 197.5 g/L for total sugars and 61.36 g/L for reducing sugars.

Three different kinds of *Saccharomyces Cerevisiae* yeast cells from several commercial suppliers were tested. Figure 2 shows the time evolution of ethanol in the fermentation process of aqueous extracts according to the method described in 2.2.

The ethanol concentration increased rapidly during the first hours of fermentation until reach a maximum ethanol level (95 g/L) after 30 h of incubation using yeast A and B. With yeast C a maximum of 70 g/L was achieved after 60 h**.** These results were similar than those reported by for sugarcane-based processes (Cardona and Sánchez, 2007)and better than those reported for carob pods processes (Roukas, 1994) with the same initial sugar concentrations (200 g/L) in the aqueous extracts. This value was the maximum concentration that ensures correct metabolization of the sugars in the culture. Possible reasons for these different ethanol levels are the strain of organisms used, the sterilization pretreatment of the solution and the removal of dissolved solids prior to the fermentation stage.

Measurement of residual sugars confirms a decrease during fermentation.It is worthy of noting that when incubation times were greater than 30 h, concentration of ethanol was kept constant and no degradation products were observed in the solution.

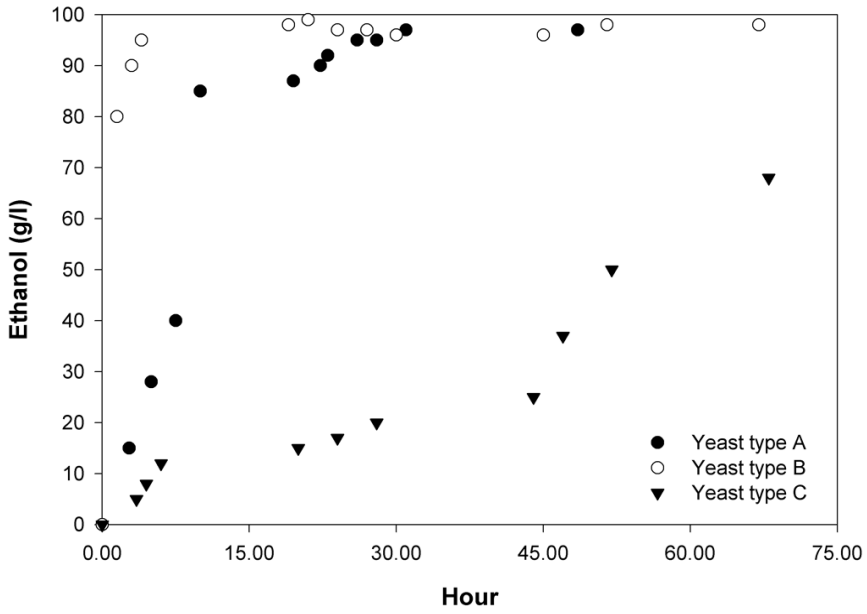


*Figure 2: Kinetics of fermentation of aqueous extracts with free cells of Saccharomyces Cerevisiae. Experimental conditions: pH 3.5-4, 35ºC, 125 r.p.m. and yeast concentration of 15 g/L.*

### 3.3. Advantages derived from the use of carob pod for ethanol production.

For normal harvesting conditions, annual carob pod production in Spain is 60,000 to 65,000 Tn/y. Taking into account average total sugar contents, the global "carob to ethanol" process yield (extraction, fermentation, distillation and dehydration stages) ranges between 19200 and 20800 cubic meters of fuel ethanol (>99.95%) per year.
Figure 3 shows a process production scheme for carob pod.

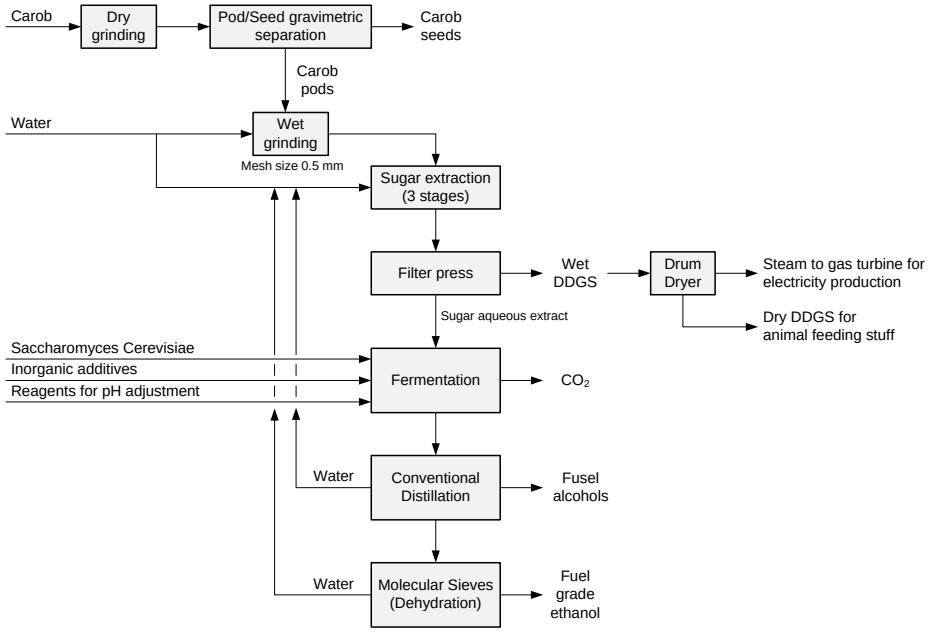


*Figure 3: Bioethanol production process from carob pod.*

With the use of carob pod as an energy crop, part of the energy radiated by the sun can be recovered.
The average solar irradiation in the Southeastern Spanish is about 17.52 MWh $ha^{-1}y^{-1}$ (APPA, 2005). If we consider an average production of 2750 kg $ha^{-1}y^{-1}$ of carob pod with a bioethanol productivity equivalent to 777 kg $ha^{-1}y^{-1}$, the energy stored in this bioethanol would be 6.62 MWh $ha^{-1}y^{1}$.
According to the figures mencioned above, 37.81 % of solar irradiation could be recovered as bioethanol. These reasons emphasize the use of carob pod as a viable alternative for the production of fuel ethanol.

## 4. Conclusions

The results showed that carob pod is a suitable feedstock to produce fuel – grade ethanol because its high sugar content round 50 %. The recovery of these sugars is easy

using water as a solvent with agitation times less than 30 min. The fermentation of the aqueous extracts was carried out achieving yields of 47.5% in ethanol.

## Acknowledgements

The authors wish to thank the Young Researchers Training Programme sponsored by Caja de Ahorros del Mediterráneo (CAM) and Mondial Carob Group for their economic support.

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