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# Efforts for the production of liquid biofuels in Crete: Bioethanol and biodiesel

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**Abstract:** The production of liquid biofuels in Greece has not been developed yet. Some efforts have been made for the production of bioethanol from sweet sorghum, but there is no industrial production at this moment in the country. Also, very few studies exist on the production of biodiesel today in Greece where the rape seed has not been cultivated yet. In this paper, the results of two research projects, which are taking place in Crete and are related to the production of bioethanol from carob and of biodiesel from waste cooking oils, are presented. These research projects have been funded by the E.C. through the ALTENER programme.

**Keywords:** Biofuels, Bioethanol, Biodiesel.

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## Introduction

The production of liquid biofuels is being developed in the E.C. and on a world-wide scale today, offering an alternative orientation of the agricultural resources that have a positive impact on the greenhouse effect. Their production and use minimizes the oil dependence of a country as well. The production of bioethanol from carob has not been studied before on a pilot scale and there are no published data on the production cost of ethanol from carob. As far as biodiesel is concerned, there are very few studies in Greece related to the production of diesel from agricultural resources. The reason for this is that the rape seed is not cultivated in Greece and the other vegetable oils are rather expensive raw materials for biodiesel production.

It should be noted that there is a large number of tourists who visit the Greek islands every year and thus consume vegetable oils. Therefore, in Crete, which is a major tourist area, the used fried vegetable oils could become the raw material for the production of biodiesel on this island. It has been estimated that the existing used fried vegetable oils in Crete could feed a small processing plant with a capacity of 2000 tn/year for the production of biodiesel.

## The carob tree in Crete

The carob tree (*Ceratonia Siliqua*) is grown in poor soils and does not need irrigation, fertilization or any cultivation care. Its fruit consists of seeds (8% p.w.) and a fruit mass (92% p.w.), that is rich in sugars (30%-50% p.w.). The seeds are being used at the moment in the food and cosmetic industries while the fruit mass is used as animal feed. A typical analysis of the carob fruit is presented in table 3a.

The advantages that the carob fruit has as an agricultural source for ethanol production are the following:

- a) The tree is grown in poor soils, which are not suitable for other cultivation. It does not need water, something that is important today with the lack of water resources in the East Mediterranean. Also, it does not need any special cultivation care or fertilizers.
- b) It is rich in sugars and therefore the expected yields in ethanol are high.

The production of carob in Crete today varies between 5.000-10.000 tn/ year and the fruit has a current price of 0,2 Euro/ kg. The production of carob decreases every year in Crete since the farmers are not keen on cultivating it, although there are some subsidies for its cultivation from the Greek Government. The only industrial processing of carob fruit today in Crete includes the grinding of the fruit and the separation of the seeds from the fruit mass.

Carob is collected during late August and September, and its collection presents various difficulties, such as:

- In tourist areas (Crete, Cyprus, etc.) the majority of the people who could collect the carob, work in the field of tourism during this particular time of the year.
- Many of these areas, in which the soil for growing carob trees is found, are not easily accessible.
- The mechanical collection of the carob fruit has not been well developed yet.

**Table 3a.** Chemical composition of carob

% Dry matter	Total fruit	Fruit mass	Seed
Crude protein	5	4	17
Crude fiber	6	6	9
Fat	0,5	0,5	2
Ash	3	3	4
N-free extract	86	87	68
Total sugars	52	55	4
Glucose	9	9	---

Source (8)

**Table 3b.** % Sugar content of the carob kibbles

	A	B	C
Sucrose	60,12	76,09	66,66
Glucose	11,21	10,87	}33,34
Fructose	28,66	13,04	

Sources (8, 11)

## Production of bioethanol from carob

The production of ethanol from carob can be obtained in the following stages:

- a) Grinding of the fruit and separation of the seeds from the fruit mass
- b) Extraction of the sugars from the fruit mass with hot water
- c) Fermentation of the water-sugars solution with the yeast *Saccharomyces cerevisiae*
- d) Separation, by distillation, of the produced ethanol from the water solution

These stages are presented in figure 4a.

In tables 4a and 4b the results from the chemical analysis of the residues after the extraction of the sugars as well as the liquid wastes after the distillation of the fermented solution are presented.

## Kinetics and yields

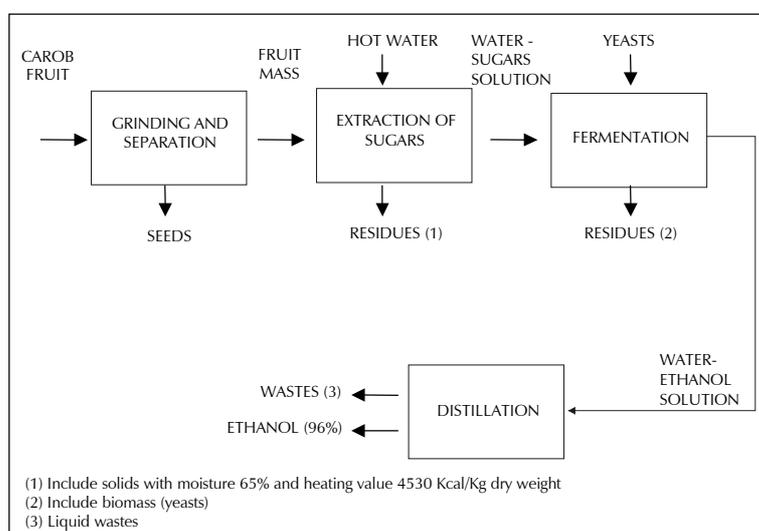
Carob pods in Chania, Crete were found to contain only 32.1% total sugars (fructose, glucose, sucrose). Chopped carob pods (kibbles) could be extracted very efficiently with hot water (65°C - 70°C), yielding solutions with sugar concentration varying from 170-220 g/l. Preliminary fermentation in flasks of sugar-containing solutions obtained after kibble extraction with baker's yeast, afforded an overall yield of 6 - 12g ethanol per 100g of kibbles.

**Table 4a.** Analysis of the solid residues after the extraction of the sugars from the carob (per dry weight)

Higher Heating Value	4530 Kcal/Kg
C	77,18%
H	9,27%
N	2,09%
S	0,05%
O	8,41%
Ash	3,00%

**Table 4b.** Analysis of the liquid wastes after the distillation of the fermented broth (ppm)

BOD <sub>5</sub>	10000
COD	52350
P	40
TOTAL N ((Kjehdal)	69



**Figure 4a.** Production of ethanol from carob

In table 5a the yields in ethanol from various agricultural resources are presented.

In table 5b the production of ethanol from carob on a lab scale with batch and continuous fermentation is presented.

**Table 5a.** Production of ethanol from various agricultural crops

Crop	Productivity	Content of sugars	Ethanol production	
	Tn / hectare		%	lt/tn
sugar beet	40 - 50	16	90-100	3800 - 4800
sugar cane	50 - 100	13	60-80	3500 - 7000
corn	4.0 - 8.0	60	360 - 400	1500 - 3000
wheat	2.0 - 9.0	62	370 - 420	740 - 3800
sorghum	4.0 - 15.0	70	330 - 370	1480 - 6300
carob*	8.0-10.0	45	150	1380

Source (9), \*Source (11)

**Table 5b.** Production of ethanol from carob in lab scale from batch and continuous fermentation

Parameter	Type of fermentation	
	Batch	continuous
Initial sugars concentration (g/l)	200	150
Max. ethanol concentration in 48h (g/l)	75	---
PH	4,5	3,5 – 5,5
T (°C)	30	30 – 35
% of sugars that have been transformed to ethanol	40	62,3
% of sugars which have been utilized	92,5	83,6
Dilution rate ( $-h^{-1}$ )	---	0,4

Sources (5, 6)

**Table 5c.** Production of ethanol from carob in small pilot scale batch fermentations

Parameter	Value
Initial sugars concentration	170-210 gr/l
Temperature	25-30°C
Ethanol yields	32,7 – 36,4 gr ethanol/gr sugars
Sugars Utilization	98,2%

Source (14)

## Production of biodiesel from used fried vegetable oils in Crete

The production of biodiesel from used fried vegetable oils can be obtained using simple technologies. This includes the reaction of the oils with methanol or ethanol in mild conditions in the presence of a catalyst. The co-produced with the ester glycerol is separated easily and removed.

Waste vegetable oils and fats are produced today in Crete from:

- a) Restaurants and assimilated establishments
- b) Various types of hotels
- c) Other large sources of processed vegetable oils and fats such as hospitals, military camps, etc,

It has been estimated that the final cost of produced biodiesel is significantly affected by the collection and storage procedure of waste cooking oils. This produced biodiesel can be used in various market segments in Crete. The total consumption of diesel from various vehicles in Crete has been estimated at 110,440,800 lt/year (2000).

In a recent study (1) the quantities of the waste cooking oils in Crete, which can be collected, were estimated. These waste cooking oils can be used for biodiesel production which however can cover only a rather small percentage of the diesel market in Crete. Various scenarios were examined for the collection and the transport scheme.

According to the scenarios related to the quantities of the waste cooking oils that can be collected in Crete, these quantities vary from 1370 tn/year to 3220 tn/year, with the most probable value being 1990 tn/year.

In table 6a estimates of recoverable and recovered oils/fats in various E.U. countries are presented.

**Table 6a.** Estimates of yearly recoverable and recovered oils / fats in seven E.U. countries

Country	Recoverable oil (kg /head)	Recovered oil (kg / head)
Austria	4,6	1,6
France	0,9	0,3
Germany	2,4 - 4,6	1,3
Ireland	3,3	1,4
Portugal	1,5 - 2	---
Spain	1,2	0,7
U.K.	---	1,7

Source (1)

In table 6b the cost analysis of the produced ester from waste cooking oils in Crete is presented.

**Table 6b.** Cost analysis of the produced ester from processed cooking oils in Crete (€ / lt. of Ester)

a) Transport cost	0,019
b) Labour cost	0,034
c) Depreciation of storing equipment	0,006
d) Raw material cost	0,115
e) Total cost of the collected oils	
e = (a + b + c + d)	0,174
f) Selling price of glycerol	0,044
g) Capital cost	0,103
h) Operating cost	0,147
i) Total cost of the produced ester	
i = (e - f + g + h)	0,380

Source (1)

Finally, in table 6c the costs of producing biodiesel in Europe are presented.

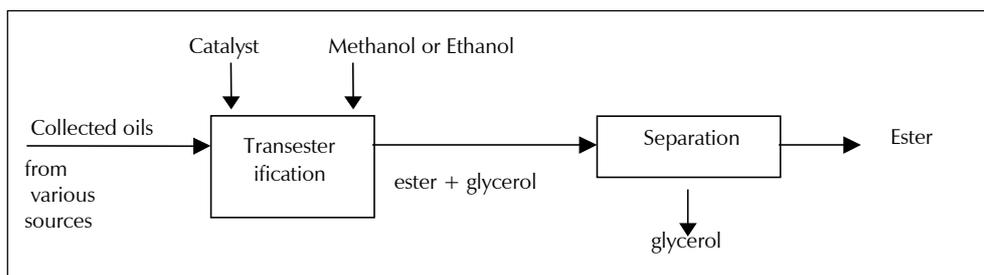
**Table 6c.** Production cost of biodiesel in europe (€ / lt. Ester)

Study in Kilkis, Greece *	0,28
Ireland *	0,53
Austria *	0,58
France (from rape seed)	0,4
Study in Crete *	0,380
Ireland (from tallow)	0,45

\*from waste cooking oil

Source (1)

In Figure 6a the flow diagram for the production of biodiesel from cooking oils is presented.



**Figure 6a.** Production of biodiesel from waste cooking oils

The cost of produced biodiesel is not competitive with the cost of conventional fuel yet; however, with tax reductions biofuel cost can be made competitive. Today, the Greek government offers subsidies for the construction of plants, producing biofuels; therefore, a legal frame does exist now for the promotion of liquid biofuels in Greece.

In the case of Crete, the cost of disposing the waste cooking oils must be taken into account. Their transformation into biofuels offers an environmentally friendly solution to this problem.

## Conclusions

The use of Carob for Bioethanol production can be promoted in the future, although the production of the fruit today in Crete is low and decreasing. There are no published data for large-scale fermentations at the moment. Further experimental and demonstration work is required before the commercialization of such a process.

The increase of the cultivation of this tree in poor soils is an answer to the problem of soil desertification, something that is happening now in Crete.

Although a series of pilot experiments are necessary to determine the exact yields of ethanol production from Carob, from preliminary data it seems that the yields of ethanol production are satisfactory.

Waste cooking oils can be used for biodiesel production. Since Crete is a tourist area and therefore has an increased use in cooking oils, this is a good reason for creating a small plant there for the processing of these oils. The cost of the produced biodiesel is affected by the logistics of the collection scheme, although the final produced biodiesel cost appears to be in the same range as in other European countries.

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