Studies in Engineering and Technology
Vol. 4, No. 1; August 2017
ISSN 2330-2038 E-ISSN 2330-2046
Published by Redfame Publishing
URL: http://set.redfame.com

Possibilities of Upgrading Solid Underutilized Lingo-cellulosic Feedstock (Carob Pods) to Liquid Bio-fuel: Bio-ethanol Production and Electricity Generation in Fuel Cells - A Critical Appraisal of the Required Processes

John Vourdoubas[1], Vasiliki K. Skoulou[2]

[1]Department of Natural Resources and Environmental Engineering, Technological Educational Institute of Crete, 3 Romanou Str., GR73133, Chania, Crete, Greece

[2]Chemical Engineering-School of Engineering and Computer Science, University of Hull, Hull University Campus, HU6 7RX, Kingston Upon Hull, United Kingdom

Correspondence: John Vourdoubas, Department of Natural Resources and Environmental Engineering, Technological Educational Institute of Crete, 3 Romanou Str., GR73133, Chania, Crete, Greece.

Received: December 2, 2016 Accepted: January 17, 2017 Online Published: January 20, 2017

doi:10.11114/set.v4i1.2170 URL: http://dx.doi.org/10.11114/set.v4i1.2170

Abstract

The exploitation of rich in sugars lingo-cellulosic residue of carob pods for bio-ethanol and bio-electricity generation has been investigated. The process could take place in two (2) or three (3) stages including: a) bio-ethanol production originated from carob pods, b) direct exploitation of bio-ethanol to fuel cells for electricity generation, and/or c) steam reforming of ethanol for hydrogen production and exploitation of the produced hydrogen in fuel cells for electricity generation. Surveying the scientific literature it has been found that the production of bio-ethanol from carob pods and electricity fed to the ethanol fuel cells for hydrogen production do not present any technological difficulties. The economic viability of bio-ethanol production from carob pods has not yet been proved and thus commercial plants do not yet exist. The use, however, of direct fed ethanol fuel cells and steam reforming of ethanol for hydrogen production are promising processes which require, however, further research and development (R&D) before reaching demonstration and possibly a commercial scale. Therefore the realization of power generation from carob pods requires initially the investigation and indication of the appropriate solution of various technological problems. This should be done in a way that the whole integrated process would be cost effective. In addition since the carob tree grows in marginal and partly desertified areas mainly around the Mediterranean region, the use of carob's fruit for power generation via upgrading of its waste by biochemical and electrochemical processes will partly replace fossil fuels generated electricity and will promote sustainability.

Keywords: bio-ethanol, carob, direct ethanol fuel cell, electricity, hydrogen

1. Introduction

One of the basic environmental problems appearing in arid and semi- arid areas and ecosystems in countries around the Mediterranean basin is soil degradation. For such areas a well-designed afforestation strategy is crucial for the sustainable development of the corresponding countries. Any afforestation attempt, as well as strategy, should then be based on carefully selected plants. Those plants should in priority be native to the degraded lands and in addition have the ability to adapt well and flourish in poor and degraded soil environments. Such natively grown plants, like the 'forgotten' plantation in Greece, carob trees do not necessitate any cultivation care, irrigation and/or fertilization. Carob trees grow all around the Mediterranean basin and countries such as Portugal, Spain, Italy, Greece, Turkey, as well as Morocco and several regions of North America. It is also known that flourishes in Greece since the antiquity (*Vekiari et al., 2011*). Recently studies indicated the attractive potential of carob pods for its sustainable growth and nutrient status in order to improve afforestation programs based on carob trees plantation in degraded environments *(Manaut et al., 2015).* Moreover *Mahkzoumi, 1997* indicated also the advantages of changing the arid and semi-arid areas landscape to the best by cultivating carob trees along with olive trees. The latest is maybe the most widespread and characteristic cultivation in Mediterranean countries while both trees, carobs and olive, are widely distributed around the Mediterranean basin, be indigenous as well as the knowledge for their cultivation techniques exist for centuries.

In 2010 the worldwide production of carob fruits was 162 911 tons (*Germec at al., 2015*), an at a first sight considerable low amount due to the fact that this is a neglected plantation. According to *Vekiari et al., 2011* though the world production of carob fruit almost doubled at about 310 000 tons in year2011. This amount produced from ~200 000 ha of areas planted with carob trees, with Spain to be the leading carob producer (135 000 tons/yr) followed by Italy, Portugal, Morocco, Greece, Cyprus, Turkey, Algeria and some other countries.

In general carobs have approximately 90% wt of total dry mater (d.m.) content with the rest 10 % wt being the carob beans (fruit). The fruit of carob tree, the carob pod, contains the carob beans which are rich in sugars and even though has a great potential to be used as a bio-refinery candidate feedstock i.e. producing food and fine chemicals, it underestimated and currently used for animal feed. The carob fruit has approximately 65% of total soluble solids and primarily consist of the sugars sucrose, fructose and glucose. The productivity of carob trees in the Mediterranean region is estimated at 2 000-3 500 kg/ha *(Sanchez et al., 2010).* For this reason it was used as an alternative to sugar in the past in Greece, when the country was suffering from economic crisis.

The carobs pods on the other hand, due to their physicochemical characteristics seems to have the potential of being an attractive and inexpensive feedstock for bio-ethanol production. Today carobs are partly exploited (only the beans) by the locust bean gum industry but can be also used as an alternative renewable feedstock for bio-based fine chemicals production i.e. succinic acid (*Carvalho et al., 2016*).

In addition carob plant although has been widely grown in the Mediterranean region for a long time it has been regarded as a forest tree species, thus neglected and for long time left aside any of the economic benefits it could offer. However, in recent years and as the petroleum has been depleted, renewable energy production has started to gain attention including the production of bio-ethanol from underutilized agricultural products and their residues such as carobs. Future exploitation of the carob pods for electricity generation will create new possibilities for using such neglected Mediterranean biomass produced in semi-arid and partly desertified lands which is not preferred for food production in a region where energy generation from benign energy sources is highly desirable.

1.1 Bio-ethanol Production from Carob: A Literature Survey.

Ethanol could be used directly in fuel cells for power generation. It also could be used with steam reforming for hydrogen production which could be fed in a fuel cell generating electricity. *Mussatto et al., 2010* reported the technological trends, global market opportunities and challenges for bio-ethanol production stating that ethanol, as a fuel source, has grown in popularity due to governmental regulations, enhanced in some cases with economic incentives and the desire to reduce oil dependency and reach if possible the self-sustained oil economy. Currently worldwide ethanol production is at its high levels; grains and sugarcane are the main raw materials-feedstock used for this purpose. However current advances and technological improvements in the production of low cost cellulosic ethanol and bio-ethanol production from microalgae may change the current pattern. In order to become a viable alternative, bio-ethanol, must present a high net energy gain, offer ecological benefits, is economically competitive and able to be produced in large scale without affecting the food production chain. The use of various renewable cellulosic waste sources and alternative raw materials e.g. food waste could solve the problem without sacrificing food demands. The renewed also interested in carob (*Ceratonia silique L.*) pods is shown by the latest published research studies in the field, as *Germec at al., 2015* indicates that bio-ethanol yield reached 48.59 % wt in a bio-film reactor, and approximately 40 % wt in a stirred tank bioreactor (*Ercan et al., 2013*)

Mazaheri at al., 2012 studied the bio-ethanol production from carob pods by *Zymomonas mobilis* through the solid fermentation process and by selecting the optimum process conditions they achieved a maximum of 0.30 g ethanol/1t of sugars at process conditions of 31^{o}C and after 43hrs. Carob pod originated bio-ethanol produced in a lab scale fermenter by the researchers *Lima-Costa et al., 2010* using different strains of *Saccharomyces cerevisiae*. They performed experiments in lab scale fermented and achieved the best bio-ethanol production yield of 43% after 60 hrs. The promising thing was that they attained a similar yield when they scaled up the process in a 3 lt reactor and it seemed that there was not any growth inhibition due to high phenolic content of the carob pods extract. Similar procedure has been also reported by *Roukas, 2009* using the *Saccharomyces cerevisiae*. The researcher firstly extracted the sugars from carob pods in water at 70^{o}C for two (2) hours and fermented afterwards the sugars with *Saccharomyces cerevisiae* at 30^{o}C producing an ethanol-water solution of a pH ranging between 3.5 and 5. Under these fermentation conditions a maximum bio-ethanol concentration of 75gr/lt was achieved after 48 hr. The author reported that sterilization of the initial solution was not needed and the addition of nutrients in the initial carob pod extract was not necessary. Bio-ethanol production from carob extract by using *Saccharomyces cerevisiae* has been reported also by *Turhan et al., 2010* who concluded that carob pods can be a good feedstock source for bio-ethanol production using a batch fermentation technique. Carob pod as a feedstock for bio-ethanol in Mediterranean areas has been highligthed by *Sanchez et al., 2010* as a cheap source for bio-fuels production especially in the arid regions. The authors investigated sulphuric acid hydrolyzation of this food waste followed by yeast fermentation in order to increase bio-ethanol yields.

They concluded that carob pod is a suitable feedstock to produce bio-ethanol due to its high sugar content and easiness of recovery by means of water extraction. In addition they highlighted the following advantages of carob pods: a) Carob tree does not compete with food production; b) the expected production costs are similar to those from sugarcane processes; c) its cultivation does not require fertilizers or irrigation, and; d) mild acid hydrolysis could improve the bio-ethanol yield. In addition *Rodrigues et al., 2016* indicated a promising alternative of co-processed carobs with cheese whey, in an attempt to indicate the viability of simultaneous management of different streams of agricultural and agro-industrial waste. They indicated that even though the co-fermentation process might be more complex the co-fermentation process produced 80 g/lt of bio-ethanol indicating a good conversion factor (0.4 gr ethanol/gr sugars)

An economic analysis of a hypothetical bio-ethanol production from carob pods as a 2nd generation bio-fuels production feedstock has been presented by *Sanchez-Segado et al., 2012*. The corresponding plant was assumed to perform an aqueous extraction of sugars from the carob pods followed by fermentation and distillation to produce carob originated bio-ethanol. The total fixed capital investment for a base case process with a capacity to transform 68 000 tons/yr (which is approx. the annual production in Spain) for carob pod was calculated at 39.61 M€, with a minimum bio-ethanol production cost of 0.51 €/lt and an internal rate of return of 7%. The plant was found to be profitable for carob pod prices lower than 0.188 €/kg. *Vourdoubas, 2002* reported also the production of bio-ethanol from carob pods in Crete, Greece, stating that the production of carob pods in Crete Island is low and decreasing continually. This trend happens as it is a forgotten and underestimated cultivation even though the carob tree can grow in poor soils without irrigation and fertilization, like most of the Greek island territories are. Therefore there will be a great bio-fuels and bio-energy production potential if interest in carob trees would be renewed in future due to their minimum cultivation necessities. This will also lead to reversing land desertification which is taking place in Crete and offering at the same time a pleasant aesthetic advantage. Recent trends in global production and utilization of bio-ethanol have been presented by *Balat et al., 2009*, who reported that bio-ethanol is by far the most widely used bio-fuel for transportation worldwide. As in the past the 'first generation' bio-ethanol was produced from different kinds of crop seeds, which being rich in sugars and starch competed with food industries, the scientific and bio businesses interest is focusing today in the second generation bio-ethanol production sources (any underestimated lingo-cellulosic waste either emerging from food processing waste or abandoned in fields but indigenous and water-lack tolerant cultivations), yet promising for an alternative use of their fruits. They concluded, however, that one major problem with bio-ethanol production is the availability of raw feedstock materials which vary depending on the season and geographic location.

1.2 Use of Bio-ethanol in Direct Alcohol Fuel Cells: A Literature Survey.

During the latest decade literature is referring to a relative new fuel cell concept the direct ethanol fuel cells (DEFCs). *Kamarudin et al., 2013* stated that DEFCs is an emerging technology and there are still many challenges to be addressed. This kind of technology is still in R&D stage focusing primarily on suitable catalysts which will increase their efficiency. DEFCs in alkaline medium have better performance compared to the ones working with an acid medium and the possibility of using non-Pt based catalysts results in their lower cost. Several experimental studies have been also implemented on the anion exchange membrane-DEFCs in an attempt to investigate the influence of the type of catalyst, operating temperature, electrolyte solution and other parameters on their performance and efficiency. *Matsuoka et al., 2005* studied the alkaline direct alcohol fuel cells using an anion exchange membrane (AEM). They reported that the alkaline direct ethylene-glycol fuel cells using silver as a cathode presented an excellent performance, comparable to that of a Pt- based catalyst. Similarly *Fujiwara et al., 2008* studied the DEFCs using an AEM instead of a cation exchange membrane (CEM). They found that the performance of the fuel cell was optimized when the CEM was replaced with an AEM. *Li et al., 2009* studied also the performance of a DEFC with an AEM and a non-Pt catalysts. They found that the fuel cell performance was improved when they increased the operating temperature of the fuel cell. *Antolini et al., 2010* stated also that the faster kinetics of the alcohol oxidation and oxygen reduction reactions in the alkaline direct alcohol fuel cells permits in fact the use of less expensive than the Pt metal catalysts, indicating the potential of developing a low cost direct fuel cell technology. It is obvious however that quite a lot research effort is needed before this technology would be able to reach the commercial scale applications. A study on direct ethanol proton exchange membrane fuel cells was published by *Song et al., 2006*. The authors reported that the combination of ethanol and fuel cell will bring both economic and environmental benefits, creating thus a more sustainable technology fuel cell based energy production technology. A study on DEFC for application in vehicles was lately reported by *Berg et al., 2015*. The authors concluded that DEFCs using AEM and free from Pt-catalyst could be an attractive and promising technology due to their high efficiency accompanied with their low cost. In addition, the widespread bio-ethanol production and existing infrastructure supports their future utilization. But again a lot of research effort is required for the commercialization of such an integrated technology.

A review study concerning reforming of bio-ethanol for hydrogen production has been published by *Ni et al., 2007*. The authors stated that bio-ethanol reforming is a promising method for hydrogen production from renewable resources. According to them Rh and Ni seems to be, so far, the best and the most commonly used catalysts for ethanol steam reforming when aiming at hydrogen production. Another study on hydrogen production for fuel cells by reforming of biomass derived ethanol has been published by *Fatsikostas et al., 2002*. The authors stated that the Ni/La_2O_3 catalyst is characterized by high activity and selectivity towards hydrogen for the reaction of steam reforming of ethanol and it could be used in ethanol reforming processors for fuel cells applications. Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts has been reported by *Liguras et al., 2003*. They investigated the catalytic performance of supported noble metal catalysts (Rh, Ru, Pt, Pd) for steam reforming of ethanol in the temperature range of 600-850^{o}C with respect to the nature of the support (Al_2O_3, MgO, TiO_2). They concluded that Rh supported catalysts are significantly more active and selective to ethanol steam reforming for the production of a hydrogen-rich gas, compared to Pt, Ru and Pd. A review of steam reforming of ethanol to produce hydrogen for fuel cells has been presented also by *Vaidya et al., 2006*. They discussed the various process engineering aspects of ethanol steam reforming like high temperatures, low pressures, high water to ethanol ratios and the nature of the catalysts used. Among various other catalysts Ni, Co, Ni/Cu and noble metal supported catalysts were highlighted as promising. They concluded that the process of ethanol steam reforming coupled with selective CO_2 capture technique would enable the production of high-purity hydrogen stream and hence it is very promising for the DEFC concept. A review on the current status of hydrogen production techniques by steam reforming of ethanol has been presented by *Haryanto et al., 2005*, who used different catalysts for the steam reforming of ethanol and they found that the Co/ZnO, ZnO, Rh/Al_2O_3, Rh/CeO_2 and Ni/La_2O_3-Al_2O_3 have shown the best performance. As hydrogen production from ethanol steam reforming is still in the research and development stage, sustainability considerations for electricity generation from biomass residues have been studied by *Evans et al., 2010.* The authors assessed the biomass generated electricity using key indicators such as cost, efficiency, GHG emissions, availability, limitations, land and water use and social impacts. They found that the high land area and water use which affected social impacts were unfavorable. In the case of carob pods bio-ethanol production and use those impacts would be eliminated due to the reasons states above, as sustainable power generation can be achieved by growing native crops on marginal or land which is not used due to soil degradation. An overview on the application of direct methanol fuel cells (DMFC) for portable electronic devices has been reported by *Kamarudin et al., 2009* with the authors concluding that DMFCs are capable of replacing the conventional batteries without recharging from the AC mains. Refueling of the DMFC is fast and the fuel can last several months. The DMFC is cost effective in the long run but the problem of methanol crossover must be solved from the designers-construction engineers of the fuel cells. A performance evaluation of DMFCs for portable applications has been reported by *Rashidi et al., 2009*. A rechargeable Li-ion battery compared with a DMFC to power the portable applications for a period of 4 (four) years. The volume and weight of the DMFC and battery systems were similar. Its cost analysis demonstrated however the advantages of the DMFC system over the battery. The stationary fuel cell program of the US Department of Energy has been presented by *Williams et al., 2005* who reported that by using advanced materials and further R&D, the costs of fuel cells could be reduced to 400 $/$KW_{el}$. Hydrogen also is an appropriate fuel for all fuel cells which can be used in residential and commercial applications provided that a viable distributed generation market will be developed. The way towards a sustainable energy future with the use of hydrogen and fuel cells has been reported by *Edwards et al, 2008*. The authors stated that together, hydrogen and fuel cells, have the potential of possibly leading to a 'green' revolution. These technologies, they report, offer the opportunity to shift our current carbon-based global energy economy to a clean, renewable and sustainable economy based on hydrogen, the fuel of the future.

Based on the findings of the above literature review it seems that the process of generating electricity from carob pods includes various stages which have been studied separately. However, the holistic, integrated study of the process with the pros and cons has not yet been reported, to the best of the authors' knowledge.

The aims then of this study are:

a) To examine the technical and economic viability of various stages of the integrated process.

b) To investigate the current status of the required technologies which could be used for power generation from carob pods.

The approach then followed in order to answer the previous points includes:

a) Investigation of the published work related with bio-ethanol production from carob pods.

b) Investigation of the published work related with direct and indirect bio-ethanol use for power generation in fuel cells.

c) Critical appraisal of the above mentioned work regarding the future commercialization of the process of electricity generation from carob pods.

1.3 Use of Carob Pods for Bio-ethanol Production

The considerable high concentration of sugars in carob pods seems attractive towards its fermentation and production of carob pods originated bio-ethanol. Fermentation of carob pod extract has been proved to be simple, does not need sterilization of the water-sugars solution or any addition of nutrients. As also carob tree grows in marginal lands which is not used for food or animal feed production its cultivation does not compete with food industry, like other first generation energy crops do. This plantation does not need any cultivation care, irrigation or fertilization. Since in many Mediterranean regions lands are slowly being desertified, planting and growing carob trees would mitigate this important soil degradation problem. Therefore its cultivation for energy use will result in many external environmental benefits. At the same time both carob tree cultivation and carob pods utilization will strengthen the local bio-business opportunities, create new job positions and add a bio-based income to the local communities which currently do not have many alternative sources of wealth. A comparison of the cost of bio-ethanol production from various crops including carob pods, is presented in **Table 1**, from where it can be seen that carobs present similar bio-ethanol production cost with corn and sugar beets, the latest being highly desirable crops for food industry.

The cultivation of carob tree and use of carob pods for bio-ethanol production at commercial scale presents however some challenges including the following:

a) In order for the process to be economically viable, the capacity of the plant must be high thus requires large quantities of raw feedstock materials. These quantities are not currently available in many Mediterranean regions while carob pods transport over long distances is expensive due to logistic issues. Provided however that proper governmental subsidies will be offered for bio-ethanol production from carob pods the process could be profitable on a smaller scale implemented locally i.e. small scattered bio-ethanol production units nearby the available feedstock production location.

b) Productivity of carob tree is low compared to other agricultural residues and residues rich in sugars and starch.

Table 1.Cost of bio-ethanol production from various crops[1] (*0.01$/L)

Lignocellulosic Feedstock	**2006 prices**	**long term forecast**
Sugarcane[1]	25-50	25-35
Corn[1]	60-80	35-55
Sugar beet[1]	60-80	40-60
Wheat[1]	70-95	45-65
Lignocellulose[1]	80-110	25-65
Carob pods[2]	57	n.a.

[1]Balat et al., 2009

[2]Sanchez-Segado et al., 2012

Bio-ethanol productivity from various crops and their promising potential of carob pods according to estimations taken from the literature, and estimated for carob pods, is presented in Table 2.

Table 2. Estimation of bio-ethanol productivity from various crops[1]

Crop	**Dry biomass matter yield (tons $_{DM}$/ha)**	**Bio-ethanol yield (M^3/ha)**
Sugarcane	19.2	5.9
Sugar beet	14.5	6.3
Sweet sorgum	21.5	1.4
Maize grain	7.4	3.3
Miscanthus sp.	13.2	5.0
Carob pods	1.8-3.9	n.a.

[1]Hattori et al., 2010

The process of bio-ethanol production from sugar containing feedstock like carob pods is well known and does not present any technical or technological difficulties. In addition from Table 2 it seems that carob pods have similar productivity expressed in tons of dry matter per hectare (ton DM/ha) as conventional sugars containing crops (maize grain). Additionally it is an indigenous to Mediterranean area plantation. The profitability however of such plants depends on its scale and the availability of feedstock, bio-ethanol production process as well as any financial subsidies offered by the governments.

1.4 Use of Bio-ethanol in DEFCs for Electricity Generation

The flow diagram for the new concept of electricity generation from carob pods, either as pure raw feedstock or a co-feed with other agro industrial residues is schematically presented in Figure 1.

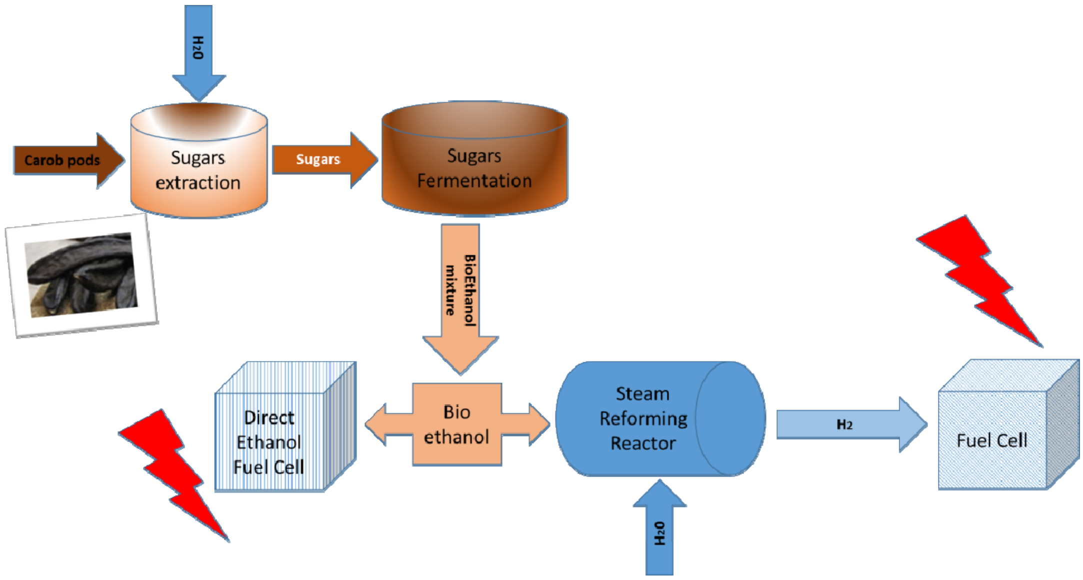

Figure 1. Flow diagram of the conceptual process of carob pods exploitation for electricity generation through DEFCs and bio-ethanol steam reforming

Bio-ethanol can be used directly in fuel cells for electricity generation. Although the technology is still in R&D stage it is quite promising as it has to offer many advantages compared to other types of fuel cells. A comparison of some of the advantages and disadvantages of DEFCs are presented in Table 3. In addition DEFCs can operate in low temperatures but at high efficiency which can even reach 80%. DEFCs can be alkaline or acidic having either an anion exchange membrane (AEM) or a proton exchange membrane (PEM). DEFCs with AEM are very promising technologies since the alcohol crossover is reduced and they overcome the problem of progressive carbonation of the alkaline solution. Even though bio-ethanol constitutes a non-toxic liquid fuel, its use results in direct CO_2 emissions which are however offset with the growth of new biomass through the photosynthetic circle of the plants and or integration of a downstream carbon capture or utilization technology. Alkaline membrane DEFCs can use cheap, non-noble metals as catalysts based on Ag, Ni and Pd instead on Pt, presenting at the same time satisfactory efficiency and operational behavior. The use of low cost catalysts allows a reduction of the DEFCs' construction cost facilitating in that way their use for bioelectricity generation. Studies concerning the expected cost of power generation from DEFCs suggest a cost of approximately 0.04 $/KWh. DEFCs can be used either in electric cars or in either mobile or stationary applications, depending on their size and necessity, for electricity generation.

Table 3.Advantages and disadvantages of direct ethanol fuel cells (DEFCs) use for electricity production

Advantages	**Disadvantages**
-High efficiency and energy content	-Its use results in CO_2 emissions
-Cheap non-noble catalysts can be used	-Cheap non-noble catalysts can be used
-Non-toxic, easy to handle liquid fuel	-The absence of operative fuel cells larger than
-Know-how and existing	micro scale does not allow to draw reliable conclusions
infrastructure for bio-ethanol production	
-Progressive carbonation of alkaline solution	-Reactions in DEFCs are not complete and
can be overcome with AEMs	ethanol must be fed in low concentrations

1.5 Hydrogen Production by Steam Reforming of Bio-ethanol

Steam reforming is the most widely used thermo-chemical technology for hydrogen production. Raw materials like natural gas, coal, methanol or ethanol can be used as precursor for H_2 production. Thermal reforming of natural gas comprises almost 50% of the world feedstock for hydrogen production. Steam reforming of ethanol or bio-ethanol necessitates high temperature and is enhanced by the presence of suitable catalysts. The nature of catalysts affects the cost of the process. It has been found that relatively cheap catalysts like Ni and Ru supported in various oxides like

La_2O_3, MgO and ZnO can be used instead of expensive catalysts based on noble metals such as Pt. This fact is offsetting the hydrogen production cost. The required temperatures are high and the efficiency of the process approaches 90-99%. Part of the required heat for the ethanol steam reforming process can be co-generated during the operation of the fuel cell. During the steam reforming of bio-ethanol, CO is co-produced with the H_2 and it must be separated and removed. The cost of hydrogen production when produced from various raw materials with thermo-chemical and electrochemical processes fluctuates between 2 and 7.5 \$/kg of H_2. Commercial applications of steam reforming of ethanol for hydrogen production have not yet been developed but existing studies support the technical and economic viability of the process with the use of cheap catalysts. In addition bio-ethanol steam reforming for hydrogen production does not result in greenhouse gas emissions like the steam reforming of natural gas which is currently used.

1.6 Use of Hydrogen in Fuel Cells for Electricity Generation

The future use of hydrogen in fuel cells needs to overcome many scientific, technological and socioeconomic barriers in order to become sustainable and our future seems to be driven towards a H_2 energy based society. Various types of fuel cells using hydrogen have been developed as suitable in many applications. Among them, phosphoric acid, molten carbonate and solid oxide fuel cells (SOFC) have been designed for medium and large scale power generation (*Athanasiou at al., 2007*). A comparison also of the specific energy of hydrogen and various fuels containing hydrogen are presented in Table 4, indicating that the specific energy of H_2 is much higher than other widely used fuels.

Table 4. Specific energy of various fuels containing hydrogen[1]

Fuel	**Specific energy (KWh/kg)**
Liquid fuel	33.3
Natural gas	13.9
Methanol	5.5
Ethanol	7.2
Diesel oil	12.6
Petrol	12.8

[1]Edwards et al., 2008

The level of maturity of the required technologies for electricity generation from carob pods as well as their economic viability are presented in Table 5.

Table 5. Maturity and economic viability of various technologies which could be used for power generation from carob pods.

Required technology	**Maturity**	**Economically**
Ethanol production from carob pods	Yes	Proved viable theoretically, but only in large scale plants
Electricity generation with DEFC	No, more research is required	Unknown open to R&D
Steam reformation of ethanol for hydrogen production	More research and development is needed	Possibly yes
Electricity generation with fuel cells and hydrogen	Yes with various types of fuel cells	Proved

2. Social and Environmental Implications

The development of an integrated process for generating power from carob pods and other agricultural and agro-industrial waste has many social and economic advantages. First of all it will give the opportunity to cultivate and re-exploit under a novel bio-energy production technology an indigenous, traditional fruit which is currently underutilized for various reasons in Mediterranean region. Carob tree grows in semi-arid lands which in addition are sometimes partly desertified. Marginal land which is unsuitable for various cultivations could be used for carob tree cultivation and growth which, at the same time, could reverse the land desertification process and offer several advantages from land reclamation to improvements of the landscape aesthetics. Since carob tree growth does not need any cultivation care, the environmental footprint of this plantation during its growth could be very low. In

Mediterranean region its cultivation and the prospects of its industrial utilization, alone or in co-processing with other residues could create additional income for the local agricultural communities with few alternative sources of wealth. It could also create locally new jobs during its harvesting in late summer. New investments in bio-business in rural areas could be required for the fermentation of carob pod sugars and the production of bio-ethanol as well as for electricity generation when bio-ethanol production process is integrated with the appropriate fuel cell technology. The use of bio-ethanol for power generation in fuel cells could promote distributed power generation in small scale, in parallel with the existing small scale photovoltaic cell applications and wind farms, and it could partly decrease the use of fossil fuels for that. This could imply fewer greenhouse gas (GHG) emissions resulting in the mitigation of climate change due to locally applied good practices which simultaneously take advantage of an indigenous plantation, the new bio-business opportunities and the positive social perception.

3. Conclusions

Carob tree grows in the Mediterranean region in unfertile land without requiring a lot of cultivation care including irrigation and fertilization.   Carob pods, a rich in sugars underutilized feedstock, can be fermented with *Saccharomyces cerevisiae strain* to produce bio-ethanol. Such fermentation can be easily implemented without presenting any major technological problems, but commercial fermentation of carob sugars has not been reported yet, probably due to the fact that it is a forgotten cultivation and as it stands today the unfavorable process economics resulting from the lack of large quantities of raw materials. However a future effort of cultivating this indigenous and tolerant for the Mediterranean conditions plantation does not need any special cultivating care as well as it can be co-fermented with other agro industrial waste and give considerable bio-ethanol yields. Such tactics will increase this underutilized rich in sugars feedstock availability and exploitation for bio-energy production. Such a carob-tree derived bio-ethanol can be used directly for electricity generation in direct ethanol fuel cells (DEFCs) but again commercial scale fuel cells utilizing ethanol have not yet been reported although experimental results of the performance of this type of fuel cells are rather promising. Alternatively bio-ethanol can be reformed by steam to hydrogen production and be fed in fuel cells for generating electricity. Various types of fuel cells can be used for flexible energy production either in small or larger scale, depending on the application and future electricity production from bio-ethanol could be sustainably produced from carob pods. Firstly because unfertile land could be used for bio-fuels production and secondly because bio-ethanol could be used for power generation decreasing the use of fossil fuels. The possibility of heat or power generation from carob pods through thermo-chemical processes or with other technologies has not been reported so far. Further work is needed in order to assess the key-points regarding the technical feasibility and the economic viability of the above mentioned processes which could result in the use of carob pods and or co-feeding with other agricultural and agro-industrial waste for the integrated approach of bio-ethanol production and electricity generation combined with the fuel cells technology.

References

Antolini, E., & Gonzalez, E. R. (2010). Alkaline direct alcohol fuel cells. *Journal of Power Sources, 195*(11), 3431–3450. https://doi.org/10.1016/j.jpowsour.2009.11.145

Athanasiou, T. C., Coutelieris, F., Vakouftsi, E., Skoulou, V., Antonakou, E., Marnellos, G., & Zabaniotou, A. (2007). From biomass to electricity through integrated gasification/SOFC system-optimization and energy balance. *International Journal of Hydrogen Energy, 32*(3), 337–342. https://doi.org/10.1016/j.ijhydene.2006.06.048

Balat, M., & Balat, H. (2009). Recent trends in global production and utilization of bio-ethanol fuel. *Applied Energy, 86*(11), 2273–2282. https://doi.org/10.1016/j.apenergy.2009.03.015

Berg, H., Nyman, J., Erlandsson, P., Johansson, P., & Matic, A. (2015). Direct Ethanol Fuel Cells. Ethanol for our future fuel cells? Swedish hybrid Vehicle Center, Report 137/2015

Carvalho, M., Roca, C., & Reis, M. A. M. (2016). Improving succinic acid production by Actinobacillus succino genes from raw industrial carob pods. *Bio-resource Technology, 218,* 491–497.https://doi.org/10.1016/j.biortech.2016.06.140

Edwards, P. P., Kuznetsov, V. L., David, W. I. F., & Brandon, N. P. (2008). Hydrogen and fuel cells: Towards a sustainable energy future. *Energy Policy, 36*(12), 4356–4362. https://doi.org/10.1016/j.enpol.2008.09.036

Ercan, Y., Irfan, T., & Mustafa, K. (2013). Optimization of ethanol production from carob pod extract using immobilized Saccharomyces cerevisiae cells in a stirred tank bioreactor. *Bio-resource Technology, 135,* 365–371.https://doi.org/10.1016/j.biortech.2012.09.006

Evans, A., Strezov, V., & Evans, T. J. (2010). Sustainability considerations for electricity generation from biomass. *Renewable and Sustainable Energy Reviews, 14*(5), 1419–1427. https://doi.org/10.1016/j.rser.2010.01.010

Fatsikostas, A. N., Kondarides, D., & Verykios, X. E. (2002). Production of hydrogen for fuel cells by reformation of biomass-derived ethanol. *Catalysis Today, 75*(1-4), 145–155. https://doi.org/10.1016/S0920-5861(02)00057-3

Fujiwara, N., Siroma, Z., Yamazaki, S., Ioroi, T., Senoh, H., & Yasuda, K. (2008). Direct ethanol fuel cells using an anion exchange membrane. *Journal of Power Sources, 185*(2), 621–626. https://doi.org/10.1016/j.jpowsour.2008.09.024

Germec, M., Turhan, I., Karhan, M., & Demirci, A. (2015). Ethanol production via repeated-batch fermentation from carob pod extract by using Saccharomyces cerevisiae in bio film reactor. *Fuel, 161*, 304–311. https://doi.org/10.1016/j.fuel.2015.08.060

Haryanto, A., Fernanto, S., Murali,N., & Adhikari, S. (2005). Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: A Review. *Energy and fuels, 19*(5), 2098-2106. https://doi.org/10.1021/ef0500538

Hattori, T., & Morita, S. (2010). Energy Crops for Sustainable Bio-ethanol Production; Which, Where and How? *Plant Production Science, 13*(3), 221-234. https://doi.org/10.1626/pps.13.221

Kamarudin, M. Z. F., Kamarudin, S. K., Masdar, M. S., & Daud, W. R. W. (2013). Review: Direct ethanol fuel cells. *International Journal of Hydrogen Energy, 38*(22), 9438–9453. https://doi.org/10.1016/j.ijhydene.2012.07.059

Kamarudin, S. K., Achmad, F., & Daud, W. R. W. (2009). Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices. *International Journal of Hydrogen Energy, 34*(16), 6902–6916. https://doi.org/10.1016/j.ijhydene.2009.06.013

Li, Y. S., Zhao, T. S., & Liang, Z. X. (2009). Performance of alkaline electrolyte-membrane-based direct ethanol fuel cells. *Journal of Power Sources, 187*(2), 387–392. https://doi.org/10.1016/j.jpowsour.2008.10.132

Liguras, D. K., Kondarides, D. I., & Verykios, X. E. (2003). Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts. *Applied Catalysis B: Environmental, 43*(4), 345–354.

Lima-Costa, M. E.,Tavares, C., Rodrigues, B., Quintas, C., & Raposo, S. (2010). Bio-ethanol production using carob pod, as carbon source on submerged fermentation. Special Abstracts / Journal of Biotechnology, 150S(2010), S1–S576.

Makhzoumi, J. M. (1997). The changing role of rural landscapes: olive and carob multi-use tree plantations in the semiarid Mediterranean. *Landscape and Urban Planning*, *37*, 115-122. https://doi.org/10.1016/S0169-2046(96)00376-3

Manaut, N., Sanguin, H., Ouahmane, L.,Bressan, M., Thioulouse, J., Baudoin, E., ..., Duponnois, R. (2015). Potentialities of ecological engineering strategy based on native arbuscular mycorrhizal community for improving afforestation programs with carob trees in degraded environments. *Ecological Engineering, 79*, 113–119. https://doi.org/10.1016/j.ecoleng.2015.03.007

Matsuoka, K., Iriyama, Y., Abe, T., Matsuoka, M., & Ogumi, Z. (2005). Alkaline direct alcohol fuel cells using an anion exchange membrane. *Journal of Power Sources, 150,* 27–31. https://doi.org/10.1016/j.jpowsour.2005.02.020

Mazaheri, D, Shojaosadati, S. A., Mousavi, S. M., Hejazi, P., & Saharkhiz, S. (2012). Bio-ethanol production from carob pods by solid-state fermentation with Zymomonas mobilis. *Applied Energy*, *99*, 372–378. https://doi.org/10.1016/j.apenergy.2012.05.045

Mussatto, S. I., Dragone, G., Guimarães, P. M. R., Silva, J. P. A., Carneiro, L. M., Roberto, I. C., & Teixeira, J. A. (2010). Technological trends, global market, and challenges of bio-ethanol production. *Biotechnology Advances, 28*(6), 817–830. https://doi.org/10.1016/j.biotechadv.2010.07.001

Ni, M., Leung, D. Y. C., & Leung, M. K. H. (2007). A review on reforming bio-ethanol for hydrogen production. *International Journal of Hydrogen Energy, 32*(15), 3238–3247. https://doi.org/10.1016/j.ijhydene.2007.04.038

Rashidi, R., Dincer, I., Naterer, G. F., & Berg, P. (2009). Performance evaluation of direct methanol fuel cells for portable applications. *Journal of Power Sources, 187(2),* 509–516. https://doi.org/10.1016/j.jpowsour.2008.11.044

Rodrigues,B., Lima-Costa, M.E., Constantino, A., Raposo, S., Felizardo, C., Goncalves, D.,... Peinado, J. M. (2016). Growth kinetics and physiological behavior of co-cultures of Saccharomyces cerevisiae and Kluyveromyces lactis, fermenting carob sugars extracted with whey. *Enzyme and Microbial Technology*, *92*, 41–48. https://doi.org/10.1016/j.enzmictec.2016.06.012

Roukas, T. (1993). Ethanol production from carob pods by *Saccharomyces cerevisiae*. *Food Biotechnology, 7*(2), 159-176. https://doi.org/10.1080/08905439309549854

Sánchez, S., Lozano, L. J., Godínez, C., Juan, D., Pérez, A., & Hernández, F. J. (2010). Carob pod as a feedstock for the production of bio-ethanol in Mediterranean areas. *Applied Energy, 87*(11), 3417–3424. https://doi.org/10.1016/j.apenergy.2010.06.004

Sánchez-Segado, S., Lozano, L. J., de los Ríos, A. P., Hernández-Fernández, F. J., Godínez, C., & Juan, D. (2012). Process design and economic analysis of a hypothetical bio-ethanol production plant using carob pod as feedstock. *Bio-resource Technology, 104,* 324–328. https://doi.org/10.1016/j.biortech.2011.10.046

Song, S., & Tsiakaras, P. (2006). Recent progress in direct ethanol proton exchange membrane fuel cells (DE-PEMFCs). *Applied Catalysis B: Environmental, 63(3-4),* 187–193. https://doi.org/10.1016/j.apcatb.2005.09.018

Turhan, I., Bialka, K. L., Demirci, A., & Karhan, M. (2010). Ethanol production from carob extract by using *Saccharomyces cerevisiae*. *Bio-resource Technology, 101*(14), 5290–5296. https://doi.org/10.1016/j.biortech.2010.01.146

Vaidya, P. D., & Rodrigues, A. E. (2006). Insight into steam reforming of ethanol to produce hydrogen for fuel cells. *Chemical Engineering Journal, 117*(1), 39–49. https://doi.org/10.1016/j.cej.2005.12.008

Vekiari, S. A., Ouzounidou, G., Ozturk, M., & Görk, G. (2011). Variation of quality characteristics in Greek and Turkish carob pods during fruit development, The 2nd International Geography Symposium GEOMED 2010, *Procedia Social and Behavioral Sciences,19,* 750–755. https://doi.org/10.1016/j.sbspro.2011.05.194

Vourdoubas, J. (2002). Efforts for the production of liquid bio-fuels in Crete: Bio-ethanol and biodiesel. *In Options Mediterraneennes, Serie A-no 48,* 151-158.

Williams, M. C., Strakey, J. P., & Surdoval, W. A. (2005). The U.S. Department of Energy, Office of Fossil Energy Stationary Fuel Cell Program. *Journal of Power Sources, 143*(1-2), 191–196. https://doi.org/10.1016/j.jpowsour.2004.12.003