LOW-COST BIODIESEL FROM CYNARA OIL

Jesús Fernández and Mª Dolores Curt
Dpto. de Producción Vegetal: Botánica y Protección Vegetal
E.T.S. Ingenieros Agrónomos. Ciudad Universitaria. 28040 Madrid (Spain)
Phone: +34915492692. Fax: +34915498482. E-mail: jfernandez@pvb.etsia.upm.es

ABSTRACT: This work deals with the feasibility of producing biodiesel from cynara oil on the assumption that the whole crop produce is used for energy purposes. Crop production costs are shared between the lignocellulosic biomass and the oil seeds of cynara grown in the rainfed conditions of Central Spain. The state-of-the-art is analysed in relation to traditional oilseed crops. Estimates of the cost of cynara oil and cynara biodiesel in the Spanish context are advanced, assuming the selective application of the crop produce. Properties of the cynara biodiesel obtained by ethanolysis and methanolysis are presented with reference to biodiesel standards.

Keywords: cynara cardunculus, bio-oil, biodiesel, combined application biomass, economic aspects, energy crops, liquid biofuels, solid biofuels.

1 TRADITIONAL RAW MATERIALS OF BIODIESEL

1.1 Rapeseed

Most of the biodiesel presently produced in Europe comes from rapeseed oil on the grounds that the rape crop yields high productions in Central Europe. Set-aside lands put in production for energy purposes may yield 2.75 t rapeseed ha^{-1}, with an average of 36% oil content. As an average, 1 ha rape yields about 990 kg oil, equivalent to 1090 litres biodiesel. The production cost of the rapeseed biodiesel was estimated by the Institute for Prospective Technological Studies (IPTS) at 0.557 € litre^{-1} [1]. The most important component of this cost is the rapeseeds price -0.214 € kg^{-1} as a reference price-, that represents 85.6% of the production cost of the rapeseed biodiesel (2.23 kg rapeseeds per litre biodiesel). Table I shows a summary of the rapeseed study by IPTS.

Table I: Production cost of rapeseed biodiesel after IPTS [1]

Fixed costs	
• Manufacturing costs	0.147 €
• Capital costs (annualised)	0.012 €
• Staff and overhead costs	0.005 €
⇒ Total fixed costs	0.164 €
By-products income	-0.084 €
Variable costs	
• 2.23 kg of rape-seed (0.214 €/kg) for 1 litre of biodiesel	0.477 €
TOTAL PRODUCTION COSTS	0.557 € L^{-1}

1.2 Sunflower

The relative high water needs of the rape crop are a limiting factor for growing this crop in the rainfed conditions of the Mediterranean region. This is the reason for that another traditional oil crop, the sunflower (*Helianthus annuus* L.), is preferred for the production of biodiesel in this area. There, the sunflower crop may yield about 1000 kg fruits –henceforth, 'seeds'- per hectare in rainfed conditions and the seed oil content is nearly 44%. On the whole, one hectare of sunflower yields about 440 kg oil on average, from which ~513 litres biodiesel may be produced.

The crop cost of sunflower, grown in rainfed conditions in Spain, is estimated at 229.98 € ha^{-1} (land rental not included) (see Table II). Assuming 1000 kg ha^{-1} as the average crop yield and 210 € t^{-1} as the seeds selling price (2003 season), the economic crop balance is negative -regardless of CAP subsidies- since the difference between the gross income (210 € ha^{-1}) and the crop cost (229.98 € ha^{-1}) is -19.98 € ha^{-1}. However, the farmer is interested in growing sunflower because of the CAP subsidies. The aid per hectare is ~126 € as an average in Spain; 45 € ha^{-1} could be added to this figure as soon as the energy crops regulation comes into force.

Table II: Crop cost of sunflower (€ ha^{-1})

Task	Labour	Materials	Sum
Fertilisation (200 kg ha^{-1} 8:15:15)	6.05	32.80	38.85
Ploughing	48.08		48.08
Harrowing	25.50		25.50
Sowing (3.75 kg seed ha^{-1})	24.04	25.24	49.28
Weed control (1.5 l trifluraline ha^{-1})	9.02	13.52	22.54
Harvesting	36.11		36.11
Seeds transport to store (1000 kg ha^{-1})	9.62		9.62
TOTAL	158.42	71.56	229.98

The cost of the biodiesel produced in Spain from sunflower oil can be estimated from the following data:

- Seed market price: ~0.24 € kg^{-1} seed (3.03 kg seeds kg^{-1} oil, 75% extraction efficiency).
- Cost of the oil extraction and refining: 0.06 € kg^{-1} oil
- Biodiesel yield:~1 kg oil to produce 1 litre biodiesel
- Production cost: ~0.11 € per litre biodiesel
- Incomes: 0.04 € from glicerine (~0.21 € kg^{-1}, 0.18 kg glicerine kg^{-1} oil) and 0.18 € from the seedcake (0.09 € kg^{-1} cake, 1.12 kg cake kg^{-}1 oil).

On the whole, the cost of the final product -sunflower biodiesel- would amount to 0.67 € litre^{-1}. Comparing to the rapeseed biodiesel (IPTS estimate), the sunflower biodiesel results in a higher cost in Spain. It can be infered that other oil raw materials with lower costs have to be found so that the biodiesel sector is sustainable, regardless of CAP subsidies, if the biodiesel promotion is wanted for Mediterranean areas.

According to the figures given before, the main component of the biodiesel price is the cost of the raw material. The cost of the traditional seed oils is too high for biodiesel production in the present conditions. The main reason for this is that nearly the whole crop costs have to be compensated with only the seeds production and the crop costs are really difficult to decrease by now.

2 CYNARA OIL AS AN ALTERNATIVE RAW MATERIAL FOR BIODIESEL

2.1 Cynara oil production and oil properties

In the search of low-cost raw materials for biodiesel the used cooking oils have been proposed as an alternative to raw oils from traditional crops. However, as residual products, difficulties in gathering and pricing may arise; hence, the used cooking oils can not be regarded as a main raw material for biodiesel on a large scale. New oil crops should be found that produce oils at low cost and apt to the production of biodiesel.

The cardoon (*Cynara cardunculus* L.), also known as cynara in the field of the energy crops, could be an alternative crop for the production of biodiesel. Studies of the potential of this species for biomass production started in the 1980's [2] and since then, several R+D projects have been carried out with the support of the EU [3,4,5]. Results have shown the feasibility of cynara, grown as an energy crop in several Mediterranean countries [6,7,8,9]. As a member of the *Compositae*, the cynara plant produces heads, where many oil fruits ('seeds') are hold, the same as the sunflower plant.

The cynara oil exhibits a similar fatty acid profile to the common sunflower oil [10] and thus, it has been successfully experimented for the production of biodiesel [11]. This application would have the advantage that it is compatible with the use of the aerial biomass for energy production or as a raw material for paper pulp. In this way the crop costs would be shared between the different applications of the crop produce and so, the oil produced from the cynara seeds would result in a lower cost. Table III shows the oil properties of cynara as compared to sunflower.

Regarding the crop yields, they are closely related to the rainfall received by the crop during the growth cycle. In Mediterranean rainfed conditions (~450 mm rainfall year^{-1}) cynara grown in a perennial cultivation system with annual harvests of the aerial biomass yields about 17 t fresh matter ha^{-1} year^{-1} with ~12% moisture (⇔ 15 t dry matter ha^{-1} year^{-1}) on average. The fruits (known as 'seeds') represent nearly 8% of the biomass (⇔ 1.36 t seeds ha^{-1} year^{-1}) at the end of the development cycle, as average. They contain about 25% oil (dry matter basis). The hull represents 45% of the fruit (w/w) and the kernel, 55%; the latter contains ~20% protein.

2.2 The cultivation of cynara for biomass

Cynara is a perennial herb native to the Mediterranean region. Its growth cycle is well adapted to the particular rainfall regime of this region: rainfalls are mostly concentrated on autumn and spring, and there is a long drought period in summertime. Cynara overcomes the drought period by drying up its aboveground biomass. The natural life form of the plant is as follows: it sprouts from stump in autumn giving rise to a leaf rosette that grows steadily during winter and early spring; in mild weather conditions, the plant develops a floral scape that holds several heads of flowers. While the fruits ripen –about July- the aboveground biomass dries up; however, the roots remain alive. Then, in summertime, it is time to harvest. Afterwards, as soon as the first rains fall –September or October- the latent buds in the plant stump sprout and a new growth cycle starts. The life span of cynara, grown as an energy crop with annual harvests of its aboveground biomass, is still unknown. So far, it has been revealed longer than 12 years.

Table III: Oil properties of cynara as compared to common sunflower oil.

	Cynara	Sunflower
Fatty properties:		
Refractive index	1.47 [12]	1.47 [15]
Iodine index	125 [14]	119-138 [15]
Saponification index	186.6 [12]	187-195[15]
Peroxide value (meq O_2/kg)	4.77 [12]	<10 [15]
Unsaponificable matter (%)	1.87 [12]	<1.0 [15]
Fatty acids composition (%):		
Palmitic acid, $C_{16:0}$	10.7 [10]	6.1 [13]
Steric acid, $C_{18:0}$	3.7 [10]	3.3 [13]
Oleic acid, $C_{18:1}$	25.0 [10]	15-38 [15]
Linoleic acid $C_{18:2}$	59.7[10]	50-72 [15]
Fuel properties:		
Density	0.924 [14]	0.925 [14]
HCV (MJ/kg)	32.99 [14]	37.1 [14]
Viscosity 40º (mm/s)	31.3 [16]	34.9 [17]
Cetane number	51.4 [14]	35.5 [14]
Flash point (ºC)	350 [14]	316 [14]

In order to estimate the annual crop cost of cynara grown in a perennial cultivation system, the costs of the first year of cultivation (crop establishment) have to be input to the following crop years (productive years). Table IV shows that the costs of the 1st crop cycle amount to 368.74 €. In Table V, the annual costs of a standard productive cycle are given; they amount to 476.05 €, including the annuity of the crop establishment. According to these estimates, the unitary cost of the cynara biomass, assuming 17 t fm (12% moisture) ha^{-1} year^{-1} as an average yield, would be 28.00 € t^{-1}.

2.3 Economic value of the crop produce

Two scenarios are considered for the crop produce, regardless of CAP aids:

i) Non-separative scenario: The crop produce is used as a whole for energy production. Assuming 2.16 € GJ^{-1} primary energy as the market price for biomass (power production), the economic value of the whole crop produce (17 t ha^{-1} year^{-1}, 12% moisture, 13.96 GJ t^{-1} as lower heating value) is 512.61€ ha^{-1} year^{-1}(⇔30.15 € t^{-1}). Therefore, the benefit for the farmer (gross income minus crop cost) would be 36.56 € ha^{-1} year^{-1}.

Table IV: Costs of the establishment of the cynara crop, in € ha^{-1}. (First growth cycle).

Task	Labour	Materials	Total
Fertilisation (700 kg ha^{-1} 9:18:27)	7.5	133.8	141.3
Ploughing	48.08	----	48.08
Harrowing	25.5	----	25.5
Sowing (5 kg ha^{-1})	24.04	30	54.04
Chemical weeding (alachlor+linuron)	9.02	35	44.02
Mechanical weeding	25.5	----	25.50
Pest control (dimethoate)	12.3	18	30.30
TOTAL	151.94	216.8	368.74
Annuity (10 years at 5%)			**47.75**

Table V: Annual production cost of cynara in an average productive cycle. Values in € ha^{-1}. Average production: 17 t ha^{-1} year^{-1}, ~12% moisture.

Task	Labour	Materials	Total
Fertilisation (400 kg ha^{-1} 15:15:15 + 130 kg ha^{-1} urea)	6.5	100.7	107.2
Harrowing	25.5	----	25.5
Pest control (dimethoate)	24.6	36.0	60.6
Harvesting & baling	161.9	----	161.9
Bales transport to plant (10 km distance)	73.1	----	73.1
Establishment annuity	----	----	47.75
TOTAL	291.6	169.8	**476.05**

Table VI: Economic balance of cynara versus sunflower when grown for energy applications. Values in € ha^{-1}. (i)Non-separative scenario; (ii) Separative scenario.

	Sunflower	Cynara (i)	Cynara (ii)
Costs:			
General crop costs	229.98	476.05	476.05
Cynara seeds harvesting	-----	-----	60.00
Total crop costs	*229.98*	*476.05*	*536.05*
Incomes:			
Sunflower seeds	210.00	-----	-----
Cynara biomass (i)	-----	512.61	-----
Cynara biomass (ii)	-----	-----	457.75
Cynara seeds	-----	-----	136.00
Total gross income	*210.00*	*512.61*	*593.75*
Energy crops subsidy (CAP)	45	45	45
Aid by hectare*	126	126	126
Benefit	*151.02*	*207.56*	*228.70*

* 63 € t^{-1} ha x 2 t ha^{-1} (average regional index) = 126 €

ii) Separative scenario: The selective application of the crop produce is aimed. The lignocellulosic biomass (15.64 t ha^{-1} year^{-1}) would be used for energy production (13.55 GJ t^{-1} biomass with 12% moisture), and the seeds (1.36 t ha^{-1} year^{-1}) for oil production, and subsequently for biodiesel production. On the one hand, the crop cost would be increased in about 60 € ha^{-1} to pick up the seeds from the aboveground biomass. On the other hand, the seeds represent an added value and could be sold for oil production at approximately 100 € t^{-1}. On the whole, the benefit for the farmer would be 57.70 € ha^{-1} year^{-1}. This figure is much higher than the one estimated for the sunflower (-19.98 € ha^{-1}), regardless of subsidies. Table VI shows the economic balance of cynara vs. sunflower.

The economic balance would be improved if the biomass were sold for heating instead of power production. A realistic selling price of the biomass for that purpose (solid biofuel) could be 54 € t^{-1} pellets, although the pelletisation cost (18 € t^{-1}) would have to be discounted.

2.4 Costs of the cynara oil and cynara biodiesel

Assuming 25% seed oil content and 75% extraction efficiency, 5.3 kg seeds are needed to produce 1 kg oil. The cost of oil extraction and refining is estimated at 0.11 € kg^{-1} L oil (0.02 € kg^{-1} seed). The by-product of the extraction process is a seed cake (4.3 kg cake kg^{-1} oil) with ~24% protein [10] and hence, useful as animal feedstuff; it would be sold at about 90 € t^{-1}. On the assumption that the seeds price is 100 € t^{-1}, the production cost of the oil would be 0.25 € kg^{-1} oil, which is less than 50% of the sunflower oil cost (0.61 € kg^{-1}). This is a really competitive cost in the present conditions, which could contribute to increase the benefits of the farmer and of the biodiesel industry. Moreover, cynara as an energy crop could be subsidied –the same as the sunflower-, because of the CAP. On the assumption that the cost of producing biodiesel (industry cost) is the same for any of the vegetable oils aforementioned (0.11 € L^{-1}), the estimates of the total cost of the biodiesel produced from rapeseed (IPTS), sunflower and cynara would be 0.56, 0.67 and 0.32 € kg^{-1}, respectively.

2.4 Properties of the cynara biodiesel

Transesterification (alcoholysis) of the cynara oil was carried out with methanol and ethanol, in order to determine the properties of the respective cynara oil esters. Catalyst, operating ratios and reacting conditions depended on the reacting alcohol. For the ethanolysis, the conditions were the following: 1.5% sodium ethylate (=catalyst):oil ratio, 30% ethanol:oil ratio, 80ºC, 1 h. The value of the same parameters for the metholysis were: 0.5% sodium methylate (= catalyst) : oil ratio, 20% methanol:oil ratio, 65ºC, 1 h (ratios in % oil weight). From the mixture obtained, the glycerol (co-product) was separated by gravitational settling and a laboratory purification process (water-washes, filtration, centrifugation) was followed to obtained a clean mixture of esters.

The two mixtures of esters –by methanolysis and by ethanolysis- were analysed by Repsol YPF and Cepsa (see Table VII). The results showed that both products were potentially suitable to biofuels. However, the ethyl esters mixture fitted better than the methyl esters mixture to the future applicable requirements for biofuels (EN-

14214). Specific requirements for ethyl esters biodiesel are not referred in that future regulation.

Table VII: Properties of the ethyl esters and methyl esters obtained from cynara oil. Samples analysed by Repsol-YPF [18] and Cepsa [19].
Requirements in EN-14214 are also given.

Properties	Ethyl esters	Methyl esters	EN-14214
Density 15ºC (g cm^{-3})	0.8794	0.8890	0.86-0.90
Viscosity 40º (mm^2 s^{-1})	4.479	5.101	3.5–5
Flash point (ºC)	184	182	> 101
Cloud point (ºC)	- 5	- 4	--
Cold filter plugging point (CFPP) (ºC)	-10	-10	≤ -10**
Cetane number	66	59	> 51
Carbon residue (% m/m) (10% distillation residue)	0.28	0.36	< 0.3
Iodine index	109	117	<120(140*)
Phosphorus (mg kg^{-1})	< 5	< 5	< 10
Sulphur (% m/m)	< 0.02	< 0.02	< 0.02

(*) 140 is the maximum Iodine Index allowed in Spain
(**) Spain climate conditions

3 CONCLUSIONS

The main component of the cost of biodiesel is the cost of the raw material, the oil. Hence, the need of finding other raw materials less expensive than traditional vegetable oils is clear. This is extremely important in Mediterranean regions because the low rainfall limits the yields of the traditional oilseed crops. *Cynara carduncu1us* is an energy crop adapted to the climate of that regions, botanically related to sunflower and, like the sunflower, it produces oilseeds. The use of *Cynara carduncu1us* seeds for oil production would have the advantage over sunflower that the crop costs would be shared between two economic products of the crop: the lignocellulosic biomass for energy production, as a solid biofuel, and the seeds for oil production, to be used as a raw material of biodiesel. Assuming a double application of the crop produce, the production of biodiesel from cynara oil is revealed as technic and economic feasible.

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