ANNEXOS

ANNEXOS

ANNEX A: CÀLCULS

A1. CÀLCUL DE LA REACCIÓ DE TRANSESTERIFICACIÓ

Cada cultiu estudiat en el present projecte presenta un perfil d'àcids grassos diferent, cosa que donarà lloc a diferents composicions químiques del biodièsel. Segons els resultats obtinguts pel Dr. Fernández de la Escuela Técnica Superior de Ingenieros Agrónomos de Madrid, el contingut en àcids grassos lliures dels olis de gira-sol i Cynara Cardunculus són els següents:

Àcid	Gira-Sol	Cynara
Mirístic	0	0.11
Palmític	6.38	10.62
Palmitoleic	0	0.14
Esteàric	4.09	3.7
Oleic	23.68	24.95
Linoleic	63.79	59.87
Aràquic	0.3	0.36
Gadoleic	0.27	0.15
Behenic	0.83	0
Lignocèric	0.3	0

Taula A.1 Perfil dels àcids grassos dels olis de Gira-sol i Cynara Card. [11]

En el full de càlcul, per tal de simplificar, només s'han estimat els quatre àcids grassos lliures més importants: àcid palmíric, àcid esteàric, àcid oleic i àcid linoleic.

La composició de la barreja de metilèsters es determina amb el percentatge de composició del àcids grassos de l'oli, ponderant la presència de cadascun d'aquests i afegint-hi l'oxigen, els dos hidrògens i el carboni de més que tenen els metilèsters.

$$C = \%_{À.Palmíric} \cdot N^o C_{À.Palmíric} + \%_{À.Estèric} \cdot N^o C_{À.Estèric} + \%_{À.Oleic} \cdot N^o C_{À.Oleic} + \%_{À.Linoleic} \cdot N^o C_{À.Linoleic} + 1$$

$$O = \%_{À.Palmíric} \cdot N^o O_{À.Palmíric} + \%_{À.Estèric} \cdot N^o O_{À.Estèric} + \%_{À.Oleic} \cdot N^o O_{À.Oleic} + \%_{À.Linoleic} \cdot N^o O_{À.Linoleic} + 1$$

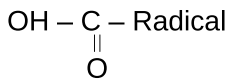
$$H = \%_{À.Palmíric} \cdot N^o H_{À.Palmíric} + \%_{À.Estèric} \cdot N^o H_{À.Estèric} + \%_{À.Oleic} \cdot N^o H_{À.Oleic} + \%_{À.Linoleic} \cdot N^o H_{À.Linoleic} + 2$$

Pel que fa a la reacció de transesterificació, la determinació dels litres de biodièsel obtinguts per a cada quilogram d'oli es realitza:

$$1000\ gr\ oli \cdot \frac{1\,mol\ oli}{PM_{oli}} \cdot \frac{3\,mols\ biodièsel}{1\,mol\ oli} \cdot \frac{PM_{biodièsel}}{1\,mol\ biodièsel} \cdot \frac{1\,l\ biodièsel}{densitat\ \ biodièsel}$$

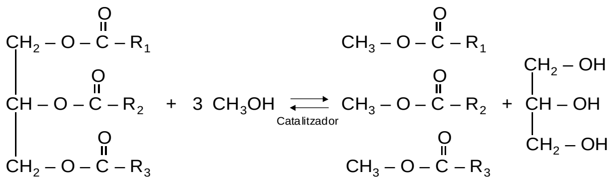
1. Contingut en Àcids Grassos dels diferents olis

	Oli Gira-sol	Oli Cyn. Card.	Fórmula quím.	Pes (g/mol)	C	H	O
Àcid Palmíric	6,40%	10,62%	$C_{16}H_{32}O_2$	256,4308	16	32	2
Àcid Estèric	4,10%	3,70%	$C_{18}H_{36}O_2$	284,4848	18	36	2
Àcid Oleic	25,40%	25,08%	$C_{18}H_{34}O_2$	282,4688	18	34	2
Àcid Linoleic	64,10%	60,60%	$C_{18}H_{32}O_2$	280,4528	18	32	2
	100,00%	100,00%					



2. Reacció de transesterificació

Pes Molecular	C	H	O
g/mol	12,011	1,008	16



Triglicèrid   Metanol   Barreja de metil èsters   Glicerol

Amb el percentatge de composició dels àcids grassos dels olis, es pot quantificar la barreja de metilèsters que en sortirà, ponderant la presència de cadascun dels elements.

Metilèster ⟹ **Àcid Gras + CH_2**

2.1 Composició de la barreja de metilèsters

Procedent de	Gira-Sol	Cynara Card.
C	18,872	18,7876
H	34,672	34,6496
O	2	2
Pes molecular (g/mol)	**293,6198**	**292,5835**
Densitat (kg/l)	**0,8854**	**0,8870**

Fórmula Química del Biodièsel	
Gira-sol	$C_{18,872}H_{34,672}O_2$
Cynara Card	$C_{18,7876}H_{34,6496}O_2$

2.2 Pes molecular dels triglicèrids

Triglicèrid d'Àcid	Palmíric	Esteàric	Oleic	Linoleic
C	51	57	57	57
H	98	110	104	98
O	6	6	6	6
Pes molecular (g/mol)	**807,3414**	**891,5034**	**885,4554**	**879,4074**

	Glicerina	Metanol
C	3	1
H	8	4
O	3	1
Pes molecular (g/mol)	**92,0952**	**32,0424**

Pes molecular promig dels olis	
Oli de Gira-sol	876,827304 g/mol
Oli de Cynara Card.	873,7183812 g/mol

2.3 Reacció de transesterificació

1 kg $oli_{Gira-sol}$ ⟹ 1,0046 kg $biodièsel_{GS}$ ⟹ **1,135 l $biodièsel_{GS}$**
0,10503 kg glicerina

1 kg $oli_{Cynara\ Card.}$ ⟹ 1,0046 kg $biodièsel_{CC}$ ⟹ **1,133 l $biodièsel_{CC}$**
0,10541 kg glicerina

Reacció de transesterificació	
Oli de Gira-sol	1,135 l $biodièsel_{GS}$ 0,10503 kg glicerina
Oli de Cynara Card.	1,133 l $biodièsel_{CC}$ 0,10541 kg glicerina

Consum estequiomètric metanol	
Gira-sol	0,1096 kg
Cynara Card.	0,1100 kg

A2. CÀLCUL CONSUM DE BIODIÈSEL VS DIÈSEL FÒSSIL

Degut a la diferència de PCI, menor en el biodièsel, el consum de dièsel i biodièsel serà diferent.

Per tal de calcular l'augment de consum en cadascuna de les respectives mescles de combustibles s'utilitza la fórmula següent:

$$\%\ Augment\ de\ Consum = \frac{PCI_{Dièsel}}{\%_{Dièsel} \cdot PCI_{Dièsel} + \%_{Biodièsel} \cdot PCI_{Biodièsel}} - 1$$

S'ha de tenir sempre present que, per exemple el B20, significa un 20 % en volum de biodièsel i un 80% en volum de dièsel covencional.

Augment del consum de combustible

1. Augment del biodièsel de Gira-Sol respecte el dièsel convencional

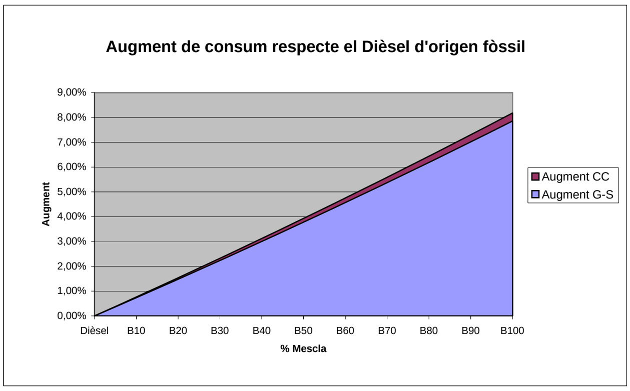
PCI Dièsel 35,7 MJ/l
PCI Gira-Sol 33,1 MJ/l

	Dièsel	B10	B20	B30	B40	B50	B60	B70	B80	B90	B100
% Dièsel	100	90	80	70	60	50	40	30	20	10	0
% Gira-Sol	0	10	20	30	40	50	60	70	80	90	100
Augment de consum	0,00%	0,73%	1,48%	2,23%	3,00%	3,78%	4,57%	5,37%	6,19%	7,01%	7,85%

2. Augment del biodièsel de Cynara-Cardunculus respecte el dièsel convencional

PCI Dièsel 35,7 MJ/l
PCI Cynara Cardunculus 33 MJ/l

	Dièsel	B10	B20	B30	B40	B50	B60	B70	B80	B90	B100
% Dièsel	100	90	80	70	60	50	40	30	20	10	0
% Cynara Cardunculus	0	10	20	30	40	50	60	70	80	90	100
Augment de consum	0,00%	0,76%	1,54%	2,32%	3,12%	3,93%	4,75%	5,59%	6,44%	7,30%	8,18%



A3. CÀLCUL D'EMISSIÓ DE CO_2 DURANT LA COMBUSTIÓ

En aquest apartat, s'usa la fórmula del biodièsel proporcionada pel Dr.Laporta i no la calculada en l'Annex A ja que en aquesta s'ha usat el perfil complet d'àcids grassos dels olis en el moment de calcular-la. Encara que, si s'observa la fórmula d'aquest apartat i la obtinguda en l'Annex A, les diferències són mínimes (fet esperable ja que s'havien menyspreat els percentatges dels àcids grassos no utilitzats en els càlculs per ser molt petits).

La reacció de combustió és la següent:

$$C_xH_yO_z \quad + \quad (\quad x \quad + \quad \frac{y}{4} \quad - \quad \frac{z}{2} \quad) \quad O_2 \quad \rightarrow \quad x \quad CO_2 \quad + \quad \frac{y}{2} \quad H_2O$$

Es considera que la combustió és completa ja que un motor dièsel funciona amb barreja pobre (massa poc combustible per a l'aire introduït) i sempre hi haurà excés d'aire, per la qual cosa no existeix la combustió incompleta (a més a més, els percentatges d'incremats i partícules són menyspreables respecte el percentatge final de CO_2 de la reacció). Les emissions d'aquests últims es determinen en el present projecte de forma experimental.

De la reacció de combustió se n'extreu que per un mol de combustible, s'obté *x* mols de CO_2:

$$kg\ CO_2 / kg_{Combustible} = 1\ kg_{Combustible} \cdot \frac{1\ mol\ Combustible}{PM_{Combustible}} \cdot \frac{x\ mols\ C}{1\ mol\ combustible} \cdot \frac{1\ mol\ CO_2}{1\ mol\ C} \cdot \frac{0{,}044\ kg\ CO_2}{1\ mol\ CO_2}$$

CÀLCUL EMISSIONS DE CO_2

DIÈSEL

Densitat D_{CONV} = 0,830 kg/l

Fórmula D_{CONV} = $C_{15'27}\ H_{27'33}$

PCI_{DCONV} = 35'7 MJ/l

GIRA-SOL

Densitat BD_{GS} = 0,8854 kg/l

Fórmula BD_{GS} = $C_{18'94}\ H_{34'82}\ O_2$

PCI_{GS} = 33'1 MJ/l

$$1\, l_{D_{CONV}} = 1{,}079\, l_{BD_{GS}}$$

CYNARA CARDUNCULUS

Densitat BD_{CC} = 0,887 kg/l

Fórmula BD_{CC} = $C_{18'79}\ H_{34'68}\ O_2$

PCI_{CC} = 33 MJ/l

$$1\, l_{D_{CONV}} = 1{,}082\, l_{BD_{CC}}$$

Combustió Dièsel convencional:

$$C_{15'27}H_{27'33} \quad + \quad 22'1 \quad O_2 \quad \rightarrow \quad 15'27 \quad CO_2 \quad + \quad 13'665 \quad H_2O$$

$$1\,kg\ Dièsel \cdot \frac{1\,kmol\ Dièsel}{210'57\ kg\ Dièsel} \cdot \frac{15'27\ kmol\ CO_2}{1\,kmol\ Dièsel} \cdot \frac{44\ kg\ CO_2}{1\,kmol\ CO_2} = 3'119077 \quad kgCO_2 \big/ kgDièsel$$

$$1\,l\ Dièsel \cdot \frac{0'83\,kg\ Diesel}{1\,l\ Dièsel} \cdot \frac{3'19077\ kg\ CO_2}{1\,kg\ Dièsel} = 2'64834\ kg\ CO_2$$

Combustió Biodièsel de Gira-sol

$$C_{18'94}H_{34'82}O_2 \quad + \quad 27'645 \quad O_2 \quad \rightarrow \quad 18'94 \quad CO_2 \quad + \quad 17'41 \quad H_2O$$

$$1\,kg\ BD_{GS} \cdot \frac{1\,kmol\ BD_{GS}}{294'58\ kg\ BD_{GS}} \cdot \frac{18'94\ kmol\ CO_2}{1\,kmol\ BD_{GS}} \cdot \frac{44\ kg\ CO_2}{1\,kmol\ CO_2} = 2'829 \quad kgCO_2 \big/ kgBD_{GS}$$

$$1\,l\ BD_{GS} \cdot \frac{0'8854\ kg\ BD_{GS}}{1\,l\ BD_{GS}} \cdot \frac{2'829\ kg\ CO_2}{1\,kg\ BD_{GS}} = 2'50478\ kg\ CO_2$$

Combustió Biodièsel de Cynara Cardunculus

$$C_{18'79}H_{34'68}O_2 \quad + \quad 27'46 \quad O_2 \quad \rightarrow \quad 18'79 \quad CO_2 \quad + \quad 17'34 \quad H_2O$$

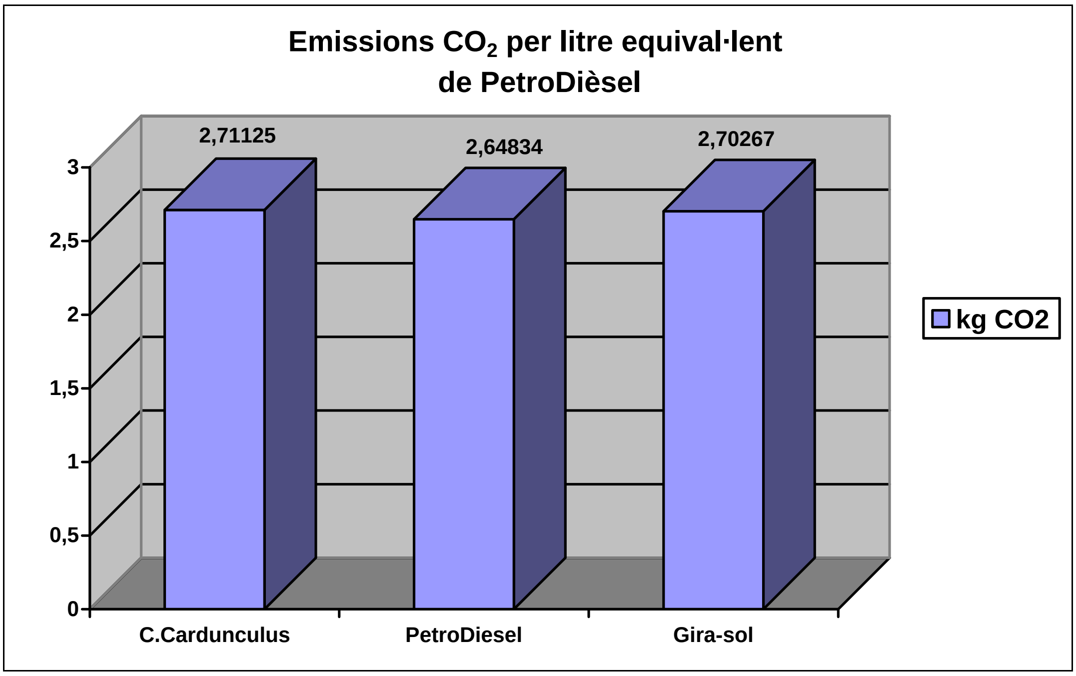
$$1\,kg\ BD_{CC} \cdot \frac{1\,kmol\ BD_{CC}}{292'64\ kg\ BD_{CC}} \cdot \frac{18'79\ kmol\ CO_2}{1\,kmol\ BD_{CC}} \cdot \frac{44\ kg\ CO_2}{1\,kmol\ CO_2} = 2'825 \quad kg\ CO_2 \big/ kg\ BD_{CC}$$

$$1\,l\ BD_{CC} \cdot \frac{0'887\ kg\ BD_{CC}}{1\,l\ BD_{CC}} \cdot \frac{2{,}825\ kg\ CO_2}{1\,kg\ BD_{CC}} = 2'50578\ kg\ CO_2$$

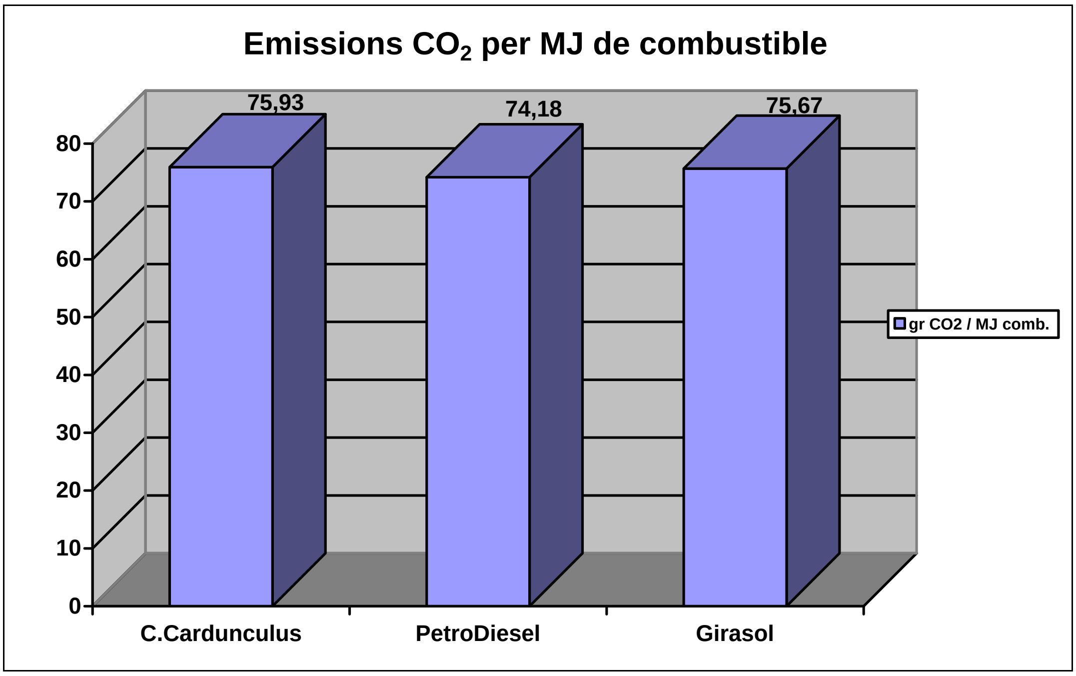
Tenint en compte que, degut a la diferència de PCI, es consumirà aproximadament un 8% més de biodièsel que de petrodièsel, les emissions de CO_2 augmentaran.

$$1\,l\ Diesel \quad \approx \quad 1'079\ l\ BD_{GS} \quad \rightarrow \quad 2'70267\ kg\ CO_2$$

$$1\,l\ Diesel \quad \approx \quad 1'082\ l\ BD_{CC} \quad \rightarrow \quad 2'71125\ kg\ CO_2$$



Una altra forma d'expressar els càlculs anteriors és utilitzar les emissions específiques, és a dir, els grams de CO_2 per MJ de combustible.



Combustió Dièsel

1. Propietats:

	Dièsel	Gira-Sol	Cynara Card.
Densitat (kg/l)	0,83	0,8854	0,887
Fórmula	$C_{15,27}H_{27,33}$	$C_{18,94}H_{34,82}O_2$	$C_{18,79}H_{34,68}O_2$
PCI (MJ/l)	35,7	33,1	33
Pes molecular	210,57	294,1	292,16
Equi. litre dièsel	1	1,079	1,082

	C	H	O	CO_2
Pes Molecular	12	1	16	44

2. Combustió:

$$C_xH_yO_z + \left(x + \frac{y}{4} - 1\right) O_2 \rightarrow x\,CO_2 + \frac{y}{2} H_2O$$

Dièsel convencional

C	15,27 mols	CO_2	15,27 mols	Emissions kg CO_2 per kg: 3,19076792
H	27,33 mols	H_2O	13,665 mols	
O	0 mols			Emissions kg CO_2 per litre: 2,64833737
O_2	22,1025 mols			

CO_2 comparatiu: 2,64833737 kg CO_2/$l_{eq\ Dièsel}$

Biodièsel Gira-Sol

C	18,94 mols	CO_2	18,94 mols	Emissions kg CO_2 per kg: 2,83359402
H	34,82 mols	H_2O	17,41 mols	
O	2 mols			Emissions kg CO_2 per litre: 2,50886414
O_2	26,645 mols			

CO_2 comparatiu: 2,70706441 kg CO_2/$l_{eq\ Dièsel}$

Biodièsel Cynara Card.

C	18,79 mols	CO_2	18,79 mols	Emissions kg CO_2 per kg: 2,82981928
H	34,68 mols	H_2O	17,34 mols	
O	2 mols			Emissions kg CO_2 per litre: 2,5100497
O_2	26,46 mols			

CO_2 comparatiu: 2,71587377 kg CO_2/$l_{eq\ Dièsel}$

Emissions de CO_2 per MJ de combustible	
Dièsel	0,07418 kg CO_2/MJ
Biodièsel GS	0,07580 kg CO_2/MJ
Biodièsel CC	0,07606 kg CO_2/MJ

3. Mescles BD

Biodièsel Gira-Sol

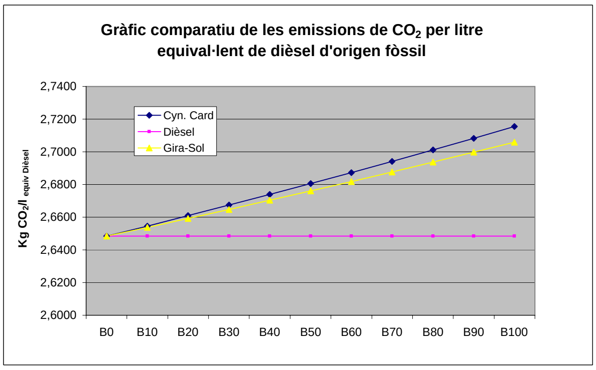
	B0	B10	B20	B30	B40	B50	B60	B70	B80	B90	B100
Dièsel	100	90	80	70	60	50	40	30	20	10	0
Biodièsel	0	10	20	30	40	50	60	70	80	90	100
PCI (MJ/l)	35,7	35,44	35,18	34,92	34,66	34,4	34,14	33,88	33,62	33,36	33,1
Densitat (kg/l)	0,83	0,8355	0,8411	0,8466	0,8522	0,8577	0,8632	0,8688	0,8743	0,8799	0,8854
Equi. Litre dièsel	1	1,0073	1,0148	1,0223	1,0300	1,0378	1,0457	1,0537	1,0619	1,0701	1,0785

Emissions kg CO_2 per litre	2,6483	2,6344	2,6204	2,6065	2,5925	2,5786	2,5647	2,5507	2,5368	2,5228	2,5089
CO_2 equival·lent	2,6483	2,6537	2,6592	2,6647	2,6703	2,6760	2,6818	2,6877	2,6937	2,6998	2,7059

Biodièsel Cynara-Card.

	B0	B10	B20	B30	B40	B50	B60	B70	B80	B90	B100
Dièsel	100	90	80	70	60	50	40	30	20	10	0
Biodièsel	0	10	20	30	40	50	60	70	80	90	100
PCI (MJ/l)	35,7	35,43	35,16	34,89	34,62	34,35	34,08	33,81	33,54	33,27	33
Densitat (kg/l)	0,83	0,8357	0,8414	0,8471	0,8528	0,8585	0,8642	0,8699	0,8756	0,8813	0,887
Equi. Litre dièsel	1	1,0076	1,0154	1,0232	1,0312	1,0393	1,0475	1,0559	1,0644	1,0730	1,0818

Emissions kg CO_2 per litre	2,6483	2,6345	2,6207	2,6069	2,5930	2,5792	2,5654	2,5515	2,5377	2,5239	2,5100
CO_2 equival·lent	2,6483	2,6546	2,6609	2,6674	2,6739	2,6806	2,6873	2,6942	2,7011	2,7082	2,7154



A4. BALANÇ DE CO_2 EN EL CICLE DE VIDA DEL BIODIÈSEL SEGONS L'ORIGEN DE L'OLI

En aquests fulls s'avaluen les emissions totals emeses durant el cicle de vida del biodièsel, des de la plantació fins a la combustió d'aquests en el motor dièsel, passant per les emissions degudes al procés de transformació i transport de les llavors des de la plantació fins a la fàbrica i del biodièsel fins a les estacions de servei.

Les dades base presentades en els fulls excel següents han estat suministrades pel Dr. Fernández de la Escuela Técnica Superior de Ingenieros Agrónomos de Madrid.

Es tindrà com a inputs de CO_2 el carboni absorbit per la planta durant la fotosíntesis. La manera de comptabilitzar aquest carboni absorbit es fa a través de l'anàlisi del contingut de carboni de cadascuna de les parts de la planta ja que és menyspreable la part de carboni que pugui absorbir aquesta a través de les arrels (per aquí absorbeix majoritàriament aigua i altres elements com ara el fòsfor, nitrogen, potassi...)

Els outputs seran les emissions de CO_2 degudes al funcionament de maquinària agrícola, a la producció d'adobs i altres productes per al cultiu, al procés productiu de biodièsel i a les diferents fases de transport de materials.

A més a més, en el cas de l'oli de Cynara Cardunculus, com es tracta d'un cultiu amb doble finalitat (biomassa per a la combustió i oli per a la producció de biodièsel) també es comptabilitzen les emissions degudes a aquesta combustió de la seva biomassa en una central tèrmica de biomassa.

Balanc CO_2 fixat per hectàrea de cultiu

1. Balanc de CO_2 fixat en el cultiu de Gira-Sol

CO_2 fixat pel cultiu	5.045,00	kg CO_2/ha
CO_2 generat pel cultiu		
Maquinària agrícola	211,20	kg CO_2/ha
Matèries primeres	479,60	kg CO_2/ha
Transport del fruit a la fàbrica	26,40	kg CO_2/ha
Fabricació de biodièsel	66,00	kg CO_2/ha
Combustió biodièsel produït en motor dièsel	1.244,26	kg CO_2/ha

CO_2 fixat per hectàrea	**3.017,54**	kg CO_2/ha

Els 3.017,54 kg de CO_2 fixats seràn retornats lentament a l'atmosfera en un període de temps indeterminat

2. Balanc de CO_2 fixat en el cultiu de Cynara Cardunculus

CO_2 fixat pel cultiu	32.512,50	kg CO_2/ha
CO_2 generat pel cultiu		
Maquinària agrícola	250,00	kg CO_2/ha
Matèries primeres	460,00	kg CO_2/ha
Transport del fruit a la fàbrica	60,00	kg CO_2/ha
Fabricació de biodièsel	38,25	kg CO_2/ha
Combustió biomassa restant en una central tèrmica de biomassa	25.039,85	kg CO_2/ha
Combustió biodièsel produït en motor dièsel	721,44	kg CO_2/ha

CO_2 fixat per hectàrea	**5.942,96**	**kg CO_2/ha**

Els 5.942,96 kg de CO_2 fixats seràn retornats lentament a l'atmosfera en un període de temps indeterminat

Balanç CO_2

Plantació de Gira-Sol:

1. Producció de biodièsel per hectàrea

Producció mitjana per hectàrea: 1000 kg/ha

Contingut en oli: 44 %
Rendiment extracc 75 %

Producció total d'oli: 330 kg oli/ha

Transesterificació

Biodièsel: 374,43 l biodièsel/ha

2. Balanç CO_2 en B100

CO_2 fixat pel cultiu		5045 kg CO_2/ha
CO_2 generat pel cultiu		
Maquinària agrícola	0,48 kg CO_2/kg oli	158,40 kg CO_2/ha
Matèries primes	1,09 kg CO_2/kg oli	359,70 kg CO_2/ha
Transport del fruit a la planta	0,06 kg CO_2/kg oli	19,80 kg CO_2/ha
Fabricació de biodièsel	0,15 kg CO_2/kg oli	49,50 kg CO_2/ha
Combustió en motor dièsel	2,5089 kg CO_2/l biodièsel	939,39 kg CO_2/ha

CO_2 fixat per hectàrea **3518,21 kg CO_2/ha**

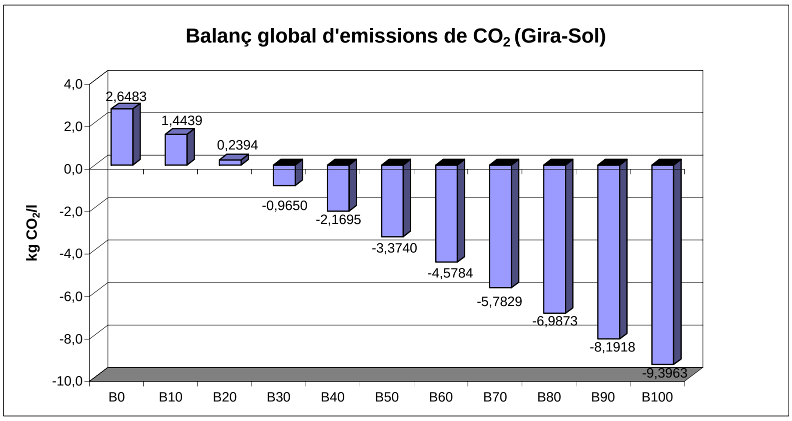
CO_2 fixat per litre de biodièsel **9,3963 kg CO_2/l_{BD}**

3. Balanç CO_2 en mescles

Emissió 1 l dièsel 2,6483 kg CO_2/litre

Per 1 litre de combustible

	B0	B10	B20	B30	B40	B50	B60	B70	B80	B90	B100
Dièsel	100	90	80	70	60	50	40	30	20	10	0
Biodièsel	0	10	20	30	40	50	60	70	80	90	100
Emissió Dièsel	2,6483	2,3835	2,1187	1,8538	1,5890	1,3242	1,0593	0,7945	0,5297	0,2648	0
Emissió Biodièsel	0	-1	-1,8793	-2,8189	-3,7585	-4,6981	-5,6378	-6,5774	-7,5170	-8,4566	-9,3963
Emissió total CO_2	**2,6483**	**1,4439**	**0,2394**	**-0,9650**	**-2,1695**	**-3,3740**	**-4,5784**	**-5,7829**	**-6,9873**	**-8,1918**	**-9,3963**



Balanç CO_2

Plantació de Cynara Cardunculus:

1. Producció de biodièsel per hectàrea

(biomassa aèrea)

Producció mitjana per hectàrea: 17000 kg $_{massa\ humida}$/ha
Producció mitjana per hectàrea: 15640 kg $_{biomassa}$/ha (humitat 12%)
Producció mitjana per hectàrea: 1360 kg $_{llavors}$/ha

$PCI_{biomassa}$ 13,55 kJ/kg $_{biomassa}$

Producció total d'oli: 255 kg oli/ha

Contingut en llavors	8 %
Contingut en biomassa:	92 %
Contingut en oli de les llavors:	25 %
Rendiment en l'exrracció d'oli	75 %

Transesterificació

Biodièsel: 288,81 l biodièsel/ha

2. Balanç CO_2 en B100

(1) biomassa aèrea	1,53	kg CO_2/kg$_{biomas}$
% biomassa sota terra	25	%
	1,9125	kg CO_2/kg$_{biomas}$

CO_2 fixat pel cultiu	1,9125 kg CO_2/kg$_{biomass}$ (1)	32512,5 kg CO_2/ha	
CO_2 generat pel cultiu			
Maquinària agrícola	0,48 kg CO_2/kg oli	250,00 kg CO_2/ha	
Matèries primes	1,09 kg CO_2/kg oli	460,00 kg CO_2/ha	
Transport del fruit a la planta	0,06 kg CO_2/kg oli	60,00 kg CO_2/ha	
Fabricació de biodièsel	0,15 kg CO_2/kg oli	38,25 kg CO_2/ha	
Combustió massa seca restant	1,819333 kg CO_2/kg$_{bmseca}$	25039,85 kg CO_2/ha	En una central de combustió de biomassa
Combustió en motor dièsel	2,5100 kg CO_2/l biodièsel	724,93 kg CO_2/ha	

CO_2 fixat per hectàrea 5939,47 kg CO_2/ha

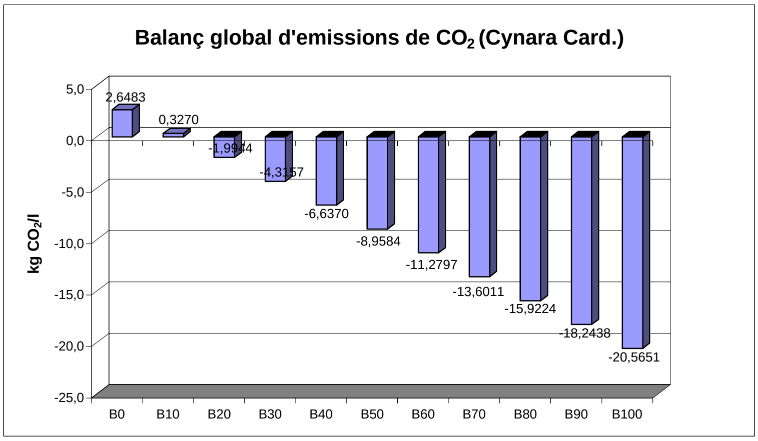
CO_2 fixat per litre de biodièsel 20,5651 kg CO_2/l $_{BD}$

3. Balanç CO_2 en mescles

Emissió 1 l dièsel 2,6483 kg CO_2/litre

Per 1 litre de combustible

	B0	B10	B20	B30	B40	B50	B60	B70	B80	B90	B100
Dièsel	100	90	80	70	60	50	40	30	20	10	0
Biodièsel	0	10	20	30	40	50	60	70	80	90	100
Emissió Dièsel	2,6483	2,3835	2,1187	1,8538	1,5890	1,3242	1,0593	0,7945	0,5297	0,2648	0
Emissió Biodièsel	0	-2	-4,1130	-6,1695	-8,2261	-10,2826	-12,3391	-14,3956	-16,4521	-18,5086	-20,5651
Emissió total CO_2	**2,6483**	**0,3270**	**-1,9944**	**-4,3157**	**-6,6370**	**-8,9584**	**-11,2797**	**-13,6011**	**-15,9224**	**-18,2438**	**-20,5651**



A5. BALANÇ ENERGÈTIC DEL BIODIÈSEL

Les dades utilitzades provenen d'un estudi realitzat pel NREL Laboratori Nacional d'Energia Renovable dels Estats Units.

S'avaluen el rendiment d'eficiència energètica i el rati de consum d'energia fòssil, les fórmules dels quals són les següents:

$$Eficiència\ \ Energètica\ \ del\ \ cicle\ \ de\ \ vida\ \ del\ \ combustible = \frac{Energia\ \ continguda\ \ en\ \ el\ \ combustible\ \ final}{Energia\ \ primària\ \ introduïda\ \ en\ \ el\ \ cicle}$$

$$Rati\ \ d'Energia\ \ Fòssil\ = \frac{Energia\ \ continguda\ \ en\ \ el\ \ combustible}{Energia\ \ Fòssil\ \ introduïda\ \ en\ \ el\ \ cicle}$$

Eficiències energètiques del cicle de vida del biodièsel vs dièsel d'origen fòssil

1. Eficiència energètica del cicle de vida

1.1 Dièsel:

Etapa	Energia primària (MJ per MJ de combustible)	Percentatge %
Obtenció del cru	1,1131	92,70%
Transport del cru	0,0164	1,37%
Refinament del cru	0,065	5,41%
Transport combustible dièsel	0,0063	0,52%
TOTAL	**1,2008**	**100,00%**

Eficiència energètica: 83,28%

1.2 Biodièsel:

Etapa	Energia primària (MJ per MJ de combustible)	Percentatge %
Agricultura del cultiu	0,066	5,32%
Transport de la llavor	0,0034	0,27%
Extracció de l'oli	0,0803	6,47%
Transport de l'oli	0,0072	0,58%
Conversió oli-Biodièsel	1,0801	87,01%
Transport biodièsel	0,0044	0,35%
TOTAL	**1,2414**	**100,00%**

Eficiència energètica: 80,55%

2. Rati d'energia fòssil

2.1 Dièsel:

Etapa	Energia fòssil (MJ per MJ de combustible)	Percentatge %
Obtenció del cru	1,112593	92,75%
Transport del cru	0,016256	1,36%
Refinament del cru	0,064499	5,38%
Transport combustible dièsel	0,006174	0,51%
TOTAL	**1,199522**	**100,00%**

Rati d'energia fòssil: 83,37%

2.2 Biodièsel:

Etapa	Energia fòssil (MJ per MJ de combustible)	Percentatge %
Agricultura del cultiu	0,0656	21,09%
Transport de la llavor	0,0034	1,09%
Extracció de l'oli	0,0796	25,59%
Transport de l'oli	0,0072	2,32%
Conversió oli-Biodièsel	0,1508	48,49%
Transport biodièsel	0,0044	1,41%
TOTAL	**0,311**	**100,00%**

Rati d'energia fòssil: 321,54%

A6. BALANÇ ECONÒMIC DEL BIODIÈSEL

En els fulls següents es realitza el balanç de costos de producció del biodièsel tenint en compte dos factors:

- La combinació o no de més d'una activitat econòmica en el cultiu, cas del Cynara Cardunculus en què s'avaluen tres escenaris:
    - Escenari (i): cultiu per a biomassa.
    - Escenari (ii): cultiu per a biodièsel.
    - Escenari (iii): cultiu per a biomassa i biodièsel.
- La propietat del cultiu, és a dir, si l'empresa de productora compra les llavors o si és ella mateixa la propietària de l'explotació agrícola.

Resum dels costos totals del Biodièsel

1. Balanç econòmic de l'agricultor

€/ha	Gira-Sol	Cynara Card. (i)	Cynara Card. (ii)	Cynara Card. (iii)
Costos				
Cost general de cultiu	229,98	476,05	476,05	476,05
Costos recollida llavors Cynara Card.			60	60
Costos totals de cultiu	*229,98*	*476,05*	*536,05*	*536,05*
Ingressos				
Llavors de girasol	210			
Biomassa Cynara Card. (i)		512,61		
Biomassa Cynara Card. (iii)				457,75
Llavors Cynara Card. (ii)			136	
Llavors Cynara Card. (iii)				136
Total ingressos	*210*	*512,61*	*136*	*593,75*
Subsidi Europeu (CAP)	45	45	45	45
Ajuda per hectàrea	126	126	126	126
BENEFICIS	**151,02**	**207,56**	**-229,05**	**228,7**
PRODUCCIÓ (kg llavors/ha)	1000	0	1360	1360

(i) Cultiu per a biomassa
(ii) Cultiu per a biodièsel
(iii) Combinació d'ambdues possibilitats

2. Costos per litre de biodièsel si l'empresa productora també conrea

€/ litre biodièsel	Gira-Sol	Cynara Card. (ii)	Cynara Card. (iii)
Rendiments			
Producció d'oli per ha (kg oli/ha)	330	255	255
Transesterificació (l biodièsel/kg oli)	1,13463	1,13260	1,13260
Glicerina (kg glicerina/kg oli)	0,10503	0,10541	0,10541
Pasta de llavors per alimentació (kg seedcake/kg oli)	2,030	4,333	4,333
Costos cultiu per litre de biodièsel	*0,15752*	*1,26397*	*1,26397*
Costos de producció			
Costos d'extracció i refinament de l'oli	0,05288	0,05298	0,05298
Cost transesterificació	0,11	0,11	0,11
Total Costos producció	0,16288	0,16298	0,16298
Ingressos addicionals			
Venta glicerina	0,01944	0,01954	0,01954
Pasta de llavors per alimentació	0,16105	0,34434	0,34434
Venta biomassa Cynara Card.	0	0	1,58494
Total Ingressos addicionals	0,18049	0,36388	1,94882
COST TOTAL LITRE DE BIODIÈSEL	**0,13992**	**1,46488**	**-0,52188**

3. Costos per litre de biodièsel si l'empresa productora no conrea

€/ litre biodièsel	Gira-Sol	Cynara Card. (ii)
Rendiments		
Extracció (kg llavors/kg oli)	3,0303	5,3333
Transesterificació (l biodièsel/kg oli)	1,13463	1,13260
Glicerina (kg glicerina/kg oli)	0,10503	0,10541
Pasta de llavors per alimentació (kg seedcake/kg oli)	2,030	4,333
Costos compra llavorsa l'agricultor	*0,56086*	*0,47089*
Costos de producció		
Costos d'extracció i refinament de l'oli	0,05288	0,05298
Cost transesterificació	0,11	0,11
Total Costos producció	0,16288	0,16298
Ingressos addicionals		
Venta glicerina	0,01944	0,01954
Pasta de llavors per alimentació	0,16105	0,34434
Total Ingressos addicionals	0,18049	0,36388
COST TOTAL LITRE DE BIODIÈSEL	**0,54325**	**0,26998**

	Gira-sol	**Cynara**	**Dièsel**	
Preu el m^3	543,252	269,984	300	**€/m^3**
Impostos especials	0	0	269	**€/m^3**
Impostos de Sanitat	24	24	24	**€/m^3**
Preu de venta al distribuïdor	567,252	293,984	593,000	**€/m^3**

COSTOS FINALS DE BIODIÈSEL

1.1 Biodièsel de Gira-Sol

1.1.1 Rendiment del cultiu per hectàrea

1000 kg llavors/ha
44 % contingut en oli
75 % rendiment extracció

330 kg oli/ha → Transesterificació → 374,43 l Biodièsel$_{GS}$ / ha

3,0303 kg llavors/kg oli

1.1.2 Costos del cultiu:

Costos de cultiu (€ per ha)	Treball	Materials	TOTAL
Fertilitzants (200 kg/ha)	6,05	32,8	**38,85**
Llaurar	48,08		**48,08**
Escarificar	25,5		**25,5**
Sembrar (3,75 kg llavors/ha)	24,04	25,24	**49,28**
Control d'humitat	9,02	13,52	**22,54**
Recol·lectar	36,11		**36,11**
Transport de les llavors fins al magatzem	9,62		**9,62**
TOTAL COSTOS CULTIU	**158,42**	**71,56**	**229,98**

Cost llavors 0,61422 €/l biodièsel

Preu de mercat de les llavors 210 €/tonelada llavor
Cost de les llavors 0,21 €/kg llavor 0,56080 €/l biodièsel
3,03 kg llavor/ kg oli

1.1.3 Costos del procés de producció:

Cost d'extracció i refinament de l'oli 0,06 €/kg oli 0,05288 €/l biodièsel
Cost de producció 0,11 €/l biodièsel

1.1.4 Costos final per litre de biodièsel:

Ajudes al cultiu 171 €/ha
0,456698103 €/l biodièsel

Cost de les llavors	0,56080 €/l biodièsel	Cost de les llavors	0,15752 €/l biodièsel
Cost d'extracció i refinament	0,05288 €/l biodièsel	Cost d'extracció i refinament	0,05288 €/l biodièsel
Cost de producció	0,11 €/l biodièsel	Cost de producció	0,11 €/l biodièsel
TOTAL COSTOS sense explotació	**0,72368 €/l biodièsel**	**TOTAL COSTOS amb cultiu propi**	**0,32040 €/l biodièsel**

1.1.5 Ingressos per litre de biodièsel

1 l biodièsel 0,09257 kg glicerina
1,78913 kg de pasta

Venta glicerina	0,21 €/kg glicerina	0,019 €/l biodièsel
Venta pasta del premsat	0,09 €/kg glicerina	0,161 €/l biodièsel
	TOTAL INGRESSOS	**0,1805 €/l biodièsel**

1.1.6 Balanç de Costos del biodièsel de Gira-Sol

COSTOS FINALS PER LITRE	0,72368 €/l biodièsel	**COSTOS FINALS PER LITRE**	0,32040 €/l biodièsel
INGRESSOS TOTALS PER LITRE	0,180 €/l biodièsel	**INGRESSOS TOTALS PER LITRE**	0,1805 €/l biodièsel
BALANÇ costos sense explotació	**0,543 €/l biodièsel**	**BALANÇ costos amb cultiu propi**	**0,13994 €/l biodièsel**

COSTOS FINALS DE BIODIÈSEL

1.1 Biodièsel de Cynara Cardunculus

Només s'avalua l'escenari (iii) en què es combinen producció de biomassa i de biodièsel

1.1.1 Rendiment del cultiu per hectàrea

Producció mitjana per hectàrea:	17000	kg $_{massa\ humida}$/ha	
Producció mitjana per hectàrea:	15640	kg $_{biomassa}$/ha	(humitat 12%)
Producció mitjana per hectàrea:	1360	kg $_{llavors}$/ha	

5,3333 kg $_{llavors}$/kg oli

Producció total d'oli: 255 kg oli/ha

Transesterificació

288,813 l Biodièsel$_{GS}$ / ha

Contingut en llavors	8	%
Contingut en biomassa:	92	%
Contingut en oli de les llavors:	25	%
Rendiment en l'exrracció d'oli	75	%

1.1.2 Costos del cultiu:

Costos de cultiu (€ per ha)	Treball	Materials	TOTAL
Fertilitzants (530 kg/ha)	6,5	100,7	**107,2**
Establiment del cultiu			**47,75**
Escarificar	25,5		**25,5**
Control de plagues	24,6	36	**60,6**
Recol·lectar i embalar biomassa	161,9		**161,9**
Recol·lectar llavors	60		**60**
Transport de bales/llavors fins a la planta	73,1		**73,1**
TOTAL COSTOS CULTIU	**351,6**	**136,7**	**536,05**
		Cost llavors	1,85605 €/l biodièsel

Preu de mercat de les llavors	136	€/ha
Cost de les llavors	0,1	€/kg llavor
	5,3333	kg llavor/ kg oli

0,47089 €/l biodièsel

1.1.3 Costos del procés de producció:

Cost d'extracció i refinament de l'oli	0,06 €/kg oli	0,05298 €/l biodièsel
Cost de producció		0,11 €/l biodièsel

1.1.4 Costos final per litre de biodièsel:

Ajudes al cultiu 171 €/ha

0,592079461 €/l biodièsel

Cost de les llavors	0,47089 €/l biodièsel	Cost de les llavors	1,26397 €/l biodièsel
Cost d'extracció i refinament	0,05298 €/l biodièsel	Cost d'extracció i refinament	0,05298 €/l biodièsel
Cost de producció	0,11 €/l biodièsel	Cost de producció	0,11 €/l biodièsel
TOTAL COSTOS sense explotació	**0,63387 €/l biodièsel**	**TOTAL COSTOS amb cultiu propi**	**1,42694 €/l biodièsel**

1.1.5 Ingressos per litre de biodièsel

1 l biodièsel 0,09307 kg glicerina

3,82601 kg de pasta

Venta glicerina	0,21 €/kg glicerina	0,020 €/l biodièsel
Venta pasta del premsat	0,09 €/kg glicerina	0,344 €/l biodièsel
Venta de Biomassa (només amb cultiu propi)	457,75 €/ha	1,585 €/l biodièsel

TOTAL INGRESSOS sense explotació	**0,364 €/l biodièsel**	**TOTAL INGRESSOS sense explotació**	**1,949 €/l biodièsel**

1.1.6 Balanç de Costos del biodièsel de Gira-Sol

COSTOS FINALS PER LITRE	0,63387 €/l biodièsel	**COSTOS FINALS PER LITRE**	1,42694 €/l biodièsel
INGRESSOS TOTALS PER LITRE	0,364 €/l biodièsel	**INGRESSOS TOTALS PER LITRE**	1,949 €/l biodièsel
BALANÇ costos sense explotació	**0,270 €/l biodièsel**	**BALANÇ costos amb cultiu propi**	**-0,52188 €/l biodièsel**

A7. VIABILITAT ESTRUCTURAL DEL BIODIÈSEL

Les dades de consums de dièsel han estat obtingudes de l'Enciclopèdia Nacional del Petroli, Petroquímica i Gas 2004 i les de superfícies agrícoles del Ministeri d'Agricultura, Pesca i Alimentació.

S'estudien dos possibles escenaris:

- Escenari A: en què el biodièsel es produeix sense aportació d'energia fòssil, és a dir, una part de la pròpia producció de biodièsel es destina a cobrir les necessitats energètiques del seu cicle de vida, autoabastiment.
- Escenari B: en què la totalitat de producció de biodièsel es ven.

Viabilitat del Biodièsel

1. Consum espanyol i català de dièsel en els últims anys

1.1 Consum espanyol de gasoils

(en tones mètriques)

Espanya	2002	2003
Gasoil A	19.234.492,0	20.762.315,0
Gasoil B	4.799.346,0	5.445.189,0
Gasoil C	2.878.679,0	2.958.951,0
TOTAL	**26.912.517,0**	**29.166.455,0**

8,38% d'augment respecte el consum de l'any 2002

1.2 Consum català de gasoils

(en tones mètriques)

Catalunya	2002	2003
Gasoil A	3.187.678,0	3.388.525,0
Gasoil B	641.115,0	726.762,0
Gasoil C	418.632,0	396.149,0
TOTAL	**4.247.425,0**	**4.511.436,0**

6,22% d'augment respecte el consum de l'any 2002

2002	Barcelona	Girona	Lleida	Tarragona
Gasoil A	1.712.196,0	745.842,0	302.772,0	426.868,0
Gasoil B	303.319,0	98.482,0	126.254,0	113.060,0
Gasoil C	231.123,0	106.772,0	48.482,0	32.255,0
TOTAL	**2.246.638,0**	**951.096,0**	**477.508,0**	**572.183,0**

2003	Barcelona	Girona	Lleida	Tarragona
Gasoil A	1.828.953,0	801.306,0	315.018,0	443.247,0
Gasoil B	368.743,0	111.004,0	131.527,0	115.488,0
Gasoil C	209.532,0	101.121,0	46.794,0	38.701,0
TOTAL	**2.407.228,0**	**1.013.431,0**	**493.339,0**	**597.436,0**

2. Producció de biodièsel per tal de produir la demanda total de dièsels

BASES DE CÀLCUL EMPRADES:

Dels balaços energètics anteriors, es determina que es necessiten: 0,311 MJ/MJ $_{Combustible}$ al moment de produir-lo

Es considera que el biodièsel té, en promig, les següents propietats:

PCI	33	MJ/l
Densitat	0,8862	kg/l

Es considera que el dièsel té, en promig, les següents propietats:

PCI	35,7	MJ/l
Densitat	0,83	kg/l

Espanya	Catalunya	
38.015.423,27	5.880.184,929	**m^3 $_{biodièsel}$**
33.689.268,11	5.211.019,884	**Tones biodièsel**

2.1 Consum de biodièsel per a substituir el suministre de dièsel d'origen fòssil a Espanya:

En aquest apartat es consideraran dos escenaris:

A) El biodièsel s'utilitza a ell mateix com a font d'energia per a produir-se:

Gasoil a substituir: 29.166.455.000 kg
Energia continguda en el combustible: 1,25451E+12 MJ

Rati d'autoabastiment: 1,311 MJ/MJ$_{combustible}$

Energia total a subministrar per la producció de BD: 1,64466E+12 MJ

Biodièsel necessari: 49.838.219,91 m^3 $_{biodièsel}$
44.166.630,49 Tones biodièsel

B) S'usa energia no renovable per a produir el biodièsel:

Gasoil a substituir: 29.166.455.000 kg

Rati 1,3033954 l $_{biod}$ / kg $_{dièsel}$

Biodièsel necessari: 38.015.423,275 m^3 $_{biodièsel}$
33.689.268,106 Tones biodièsel

2.2 Consum de biodièsel per a substituir el suministre de dièsel d'origen fòssil a Catalunya:

En aquest apartat es consideraran dos escenaris:

A) El biodièsel s'utilitza a ell mateix com a font d'energia per a produir-se:

Gasoil a substituir: 4.511.436.000 kg
Energia continguda en el combustible: 1,94046E+11 MJ

Rati d'autoabastiment: 1,311 MJ/MJ$_{combustible}$

Energia total a subministrar per la producció de BD: 2,54394E+11 MJ

Biodièsel necessari: 7.708.922,44 m^3 $_{biodièsel}$
6.831.647,07 Tones biodièsel

B) S'usa energia no renovable per a produir el biodièsel:

Gasoil a substituir: 4.511.436.000 kg

Rati 1,3033954 l $_{biod}$ / kg $_{dièsel}$

Biodièsel necessari: 5.880.184,929 m^3 $_{biodièsel}$
5.211.019,884 Tones biodièsel

3. Superfícies de cultiu necessàries per tal de produir el biodièsel requerit:

BASES DE CÀLCUL EMPRADES:

De fulls de càlcul anteriors, es determina que:

1 ha de cultiu de GS	374,43	$l_{biodièsel}$
1 ha de cultiu de CC	288,81	$l_{biodièsel}$

3.1.1 Superfície necessària pel consum total espanyol:

Superfície necessària (ha)	Gira-Sol	Cynara Carduncululs
Escenari A	**133.105.382,89**	**172.562.493,33**
Escenari B	**101.529.658,96**	**131.626.615,81**

Tenint en compte que la superfície total d'Espanya és de: 50.502.171 ha

3.2.1 Superfície necessària pel consum total català:

Superfície necessària (ha)	Gira-Sol	Cynara Carduncululs
Escenari A	**20.588.597,97**	**26.691.781,52**
Escenari B	**15.704.498,83**	**20.359.863,86**

Tenint en compte que la superfície total de Catalunya és de: 3.194.728 ha

3.1.2 Nombre de vegades la superfície espanyola:

	Gira-Sol	Cynara Carduncululs
Escenari A	**2,64**	**3,42**
Escenari B	**2,01**	**2,61**

3.2.2 Nombre de vegades la superfície catalana:

Super. Catalana	Gira-Sol	Cynara Carduncululs
Escenari A	**6,44**	**8,35**
Escenari B	**4,92**	**6,37**

Super. Espanyola	Gira-Sol	Cynara Carduncululs
Escenari A	**0,41**	**0,53**
Escenari B	**0,31**	**0,40**

4. Producció màxima de biodièsel emprant la totalitat de terres cultivables:

BASES DE CÀLCUL EMPRADES:

Segons l'anuari d'estadística agroallimentaria 2002 publicat pel Ministeri d'Agricultura, Pesca i Alimentació:

Total superfície cultivable a Espanya 18.043.700 ha

Total superfície cultivable a Catalunya 899.900 ha

4.1 Producció màxima de biodièsel a Espanya:

No s'evalua l'escenari A ja que, a la vista dels resultats anteriors, no té sentit.

	Gira-Sol	Cynara Card.
Rendiment (l_{BD}/ha)	374,43	288,81
Producció total de Biodièsel (m^3)	6.756.044	5.211.248
% sobre necessitats totals	17,77%	13,71%

4.2 Producció màxima de biodièsel a Catalunya:

No s'evalua l'escenari A ja que, a la vista dels resultats anteriors, no té sentit.

	Gira-Sol	Cynara Card.
Rendiment (l_{BD}/ha)	374,43	288,81
Producció total de Biodièsel (m^3)	336.947	259.902
% sobre necessitats totals	5,73%	4,42%

Com ja es comprèn, no es pot utilitzar tota la superfície conreable amb fins energètics, obviant la vessant alimentícia.
Amb aquesta dada només es pretén marcar un límit superior de producció possible.

5. Superfície necessària per a assolir les 500 ktep per l'Administració l'any 2010:

Equival·lències

1 ktep	41,868	TJ
1 litre dièsel	33	MJ
1 litre dièsel	1,1	litres biodièsel

500 ktep ⟹ 634.363.636 litres dièsel ⟹ **697800 m^3 biodièsel**

	Superfície necessària (ha)	**% respecte la superfície cultivable espanyola**
Gira-Sol	**1.863.648,75**	**10,33%**
Cynara Carduncululs	**2.416.099,69**	**13,39%**

A8. PRESSUPOST

El pressupost pel present projecte és el següent:

Dedicació		Preu	Total
Enginyer Industrial junior:	120 hores	60 €/h	7.200 €
Mecanografia:	32 hores	25 €/h	800 €
TOTAL			**8.000 €**

ANNEX B: ESTUDIS COMPLEMENTARIS

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Diesel emissions from biofuels derived from Spanish potential vegetable oils

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Abstract

Methyl esters obtained from the most interesting Spanish oleaginous crops for energy use—sunflower and *Cynara cardunculus*—were both used as diesel fuels, pure and in 25% blends with a commercial fuel which was also used pure. A stationary engine test bed, together with the instrumentation for chemical and morphological analysis, allowed to study the effect of these fuels on the engine emissions, soluble organic fraction of the particulate matter, origin of adsorbed hydrocarbons, sulphate content, particle number per unit filter surface, and mean particle diameter. Both the consideration of the thermochemical properties of the tested fuels and the computations of a chemical equilibrium model were helpful for the results analysis. These results proved that the use of these vegetable esters provides a significant reduction on particulate emissions, mainly due to reduced soot and sulphate formation. On the contrary, no increases in NO_x emissions nor reductions on mean particle size were found.

Keywords: Emissions; Diesel engines; Combustion; Biofuels; Vegetable oils

1. Introduction

Biodiesel, obtained from methyl/ethyl esterification of fatty acids from vegetable oils, has received significant attention since the last decade. It has become a fuel of growing interest because it is made from renewable resources in local agro-industries. Hence, the production and use of biodiesel implies social and environmental benefits as compared to fossil fuels. The European Commission has been fully aware of this fact and is a directive being elaborated to make compulsory the use of blends that include a certain proportion of biofuels. Besides, the production of vegetable oils for biodiesel in set-aside lands make possible a new earning for the farmers, additionally to subsidies considered by the Common Agriculture Policy (CAP).

The oil of choice for the production of biodiesel in the Mediterranean area is presently the sunflower oil. However, the relative high cost of this oil is a constraint because of its great share in the price of biodiesel. Around 1 l oil is required for the production of 1 l biodiesel. Therefore, if an economic production of biodiesel is wanted, other oils of lower costs should be promoted, regardless of subsidies. The reason for the relative high cost of sunflower oil—the same as for other edible seed oils-lies in that nearly the full crop cost has to be paid back by the seeds production. Better oil prices means lower crop costs and, at present, this is extremely difficult in the European context.

In the search of alternative oils for biodiesel production, the used cooking oils have been envisaged as an option but, as a residual product, difficulties may arise in the process of oil gathering, this resulting in price variation. Hence, used cooking oils cannot be regarded as a massive raw material for biodiesel production on a large scale. New low-cost oil crops are needed to produce economical oils suitable for biodiesel production. One of the possible alternative oil crops for the Mediterranean area is the cardoon (*Cynara cardunculus* L.), also known as 'cynara' in the field of energy crops. First studies of cynara as an energy crop

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started in the 1980s [1]. Activities of research and development on cynara have continued since then by means of several R+D projects supported by the EC [2–4].

The profile of cynara oil is similar to common sunflower oil [5] and it has been successfully used for biodiesel production [6,7]. The advantage of cynara over sunflower would lie in the oil price. The cost of cynara oil would be rather low if the rest of the plant biomass were used as a raw material for energy purposes or for paper-pulp making [8]. Cynara fruits contain 25% oil average (dry weight basis) and represent about 7.5% of the above-ground biomass (dry matter) harvested at the end of the annual plant growth cycle, when the plant is grown in a perennial cultivation system on rainfed conditions. Above-ground biomass production of cynara ranges between 10 and 20 t dry matter per hectare and year, depending on the rainfall. On this assumption, and with the limits imposed by the fact that the cynara oil has not yet been launched out into the market, the cost of cynara oil would be estimated at 0.25–0.30 €/l, half the price of sunflower oil [9]. Although these figures are favourable estimates, detaxation of biodiesel, recently published by the Spanish Parliament [10], has become essential to promote the use of biofuels and the setting-up of the associated industries.

Methyl esters from sunflower (SME) and cynara (CME) were both used as diesel fuels in this work, pure and in 25% blends with a reference fuel which was also used pure. The reference fuel is a typical diesel fuel available in Spanish petrol stations, attaining the present fuel quality requirements for diesel vehicles (EN590-Directive 98/70/CE). It was supplied by Repsol-YPF. A stationary engine test bed, equipped with the appropriate instrumentation for chemical and morphological analysis, allowed evaluation of the effect of these fuels on the engine emissions, and particularly in the main particulate matter characteristics.

2. Production and characterization of vegetable esters as diesel fuels

2.1. Characteristics of vegetable oils

The fatty acid oil content of each of the vegetable oils used in the engine tests is shown in Table 1. It can be noticed that there are only small differences between them. The proportion of unsaturates is 88.1% for sunflower oil and 85.1% for cynara oil.

Table 1
Fatty acid oil content of vegetal oils

Acid	Sunflower	Cynara
Myristic	0	0.11
Palmitic	6.38	10.62
Palmitoleic	0	0.14
Stearic	4.09	3.7
Oleic	23.68	24.95
Linoleic	63.79	59.87
Linolenic	0.36	0
Araquic	0.3	0.36
Gadoleico	0.27	0.15
Behenic	0.83	0
Lignoceric	0.3	0

2.2. Production of vegetable esters

Both vegetable oils were subjected to a transesterification reaction with methanol, using NaOH as catalyst. The reaction conditions were similar in both cases. The transesterification procedure was developed and carried out in CIDAUT (Centro de Investigación y Desarrollo en Automoción) and reached 95% efficiency after 1 day decantation and double washing with water and acidified water. The reaction lasted 1 h at a temperature between 60 and 70 °C. The obtained biofuels were sunflower methyl ester (SME) and cynara methyl ester (CME), and in both cases an acidity below 0.5 mg KOH was reached.

2.3. Thermochemical properties

In order to estimate the main thermochemical properties, the group contributions Joback method [11] was used for the calculation of the specific heat at constant pressure and the standard enthalpy of formation:

$$\frac{C_p}{R}(\text{SME}) = -1.26159 + 0.21362T - 1.2484E-4T^2 + 2.7534E-8T^3$$

$$\frac{C_p}{R}(\text{CME}) = -1.10152 + 0.21159T - 1.2295E-4T^2 + 2.6825E-8T^3$$

$$h_f^0(\text{SME}) = -68851.88\ \text{K}^{-1}$$

$$h_f^0(\text{CME}) = -69615.53\ \text{K}^{-1}$$

These data were used in a chemical equilibrium model [12] which considers 29 chemical species (N_2, O_2, CO_2, H_2O, CO, H_2, NO, OH, N, H, O, Ar, N_2O, NO_2, HO_2, NH_3, NH_2, NH, CN, HCN, NCO, S, S_2, SO, SO_2, SO_3, HS, H_2S, COS) to calculate the adiabatic flame temperature at constant pressure. Initial conditions of 80 bar and 900 K and stoichiometric fuel/air ratio were taken as typical diesel in-cylinder local conditions at the start of combustion. This parameter, together with other chemical characteristics of the tested fuels are listed in Table 2.

2.4. Fuel properties

The obtained esters were tested as automotive fuels together with the commercial fuels, following the European standard methods, established in the European Norm EN590

Table 2
Chemical characteristics of sunflower ester and cynara ester, compared to commercial diesel fuel

Fuel	Commercial diesel	SME	CME
Summarized formula	$C_{15.27}H_{27.33}$	$C_{18.94}H_{34.82}O_2$	$C_{18.79}H_{34.68}O_2$
Molecular weight (g/mol)	210.7	294.58	292.64
Oxygen content (wt%)	0	10.86	10.93
H/C ratio	1.807	1.838	1.846
Average number of double bonds	0	1.53	1.45
Aromatic content (wt%)	37.23	0	0
Adiabatic flame temperature (K)[a]	2730.9	2733.3	2734.3
Stoichiometric fuel/air ratio	1/15.5	1/12.423	1/12.421
Stoich. fuel/oxygen ratio	1/3.58	1/2.814	1/2.816

[a] Calculated at constant pressure, with initial conditions of 80 bar, 900 K and stoichiometric A/F ratio.

(directive 98/70/CE). The main fuel specifications are listed in Table 3. The lower heating values of esters are nearly compensated by their higher density in the volumetric injection system leading to heating values of the same order when expressed in MJ/l. Differences in viscosity and cetane number slightly are significant as they could affect the timing of injection and combustion, respectively. As esters' composition are much more homogeneous than that of diesel fuel, their distillation curves are much more flat, leading to lower final point despite the higher general level of boiling temperature. Finally, higher sulphur content was found in CME than in SME, both being much lower than that of diesel fuel.

3. Experimental set-up for testing and analysis

3.1. Engine test bed and instrumentation

A turbocharged intercooler IDI diesel Renault engine, model F8Q, similar to those commonly used in European passenger car, was tested. The engine was coupled to a hydraulic brake and equipped with the instrumentation for its control and for the measurement of all the parameters affecting emissions [13]. The cylinder engine was instrumented with a water-cooled piezoelectric pressure transducer Kistler 6061B and the injector needle was equipped with a displacement sensor. In all cases the engine was fully warmed up, which avoided the possible disadvantage of biodiesel blends in cold conditions due to their lower volatility at low temperature.

Table 3
Fuel properties of SME and CME, compared to commercial diesel fuel

Fuel	Commercial diesel	SME	CME
Density (kg/m^3)	830	885.4	887
Lower heating value (MJ/kg)	43.0	37.4	37.2
Lower heating value (MJ/l)	35.7	33.1	33.0
Cetane number	49.6	56.4	59
Viscosity (cSt) (40 °C)	3.16	4.13	4.88
Distillation T50 (°C)	277.7	340.0	–
Final boiling point (°C)	376.7	345.0	345.0
POFF (°C)	−15	–	−10
Sulphur content (ppm w)	312	40	160

Table 4
Engine operating conditions

Operation mode	Mean speed (km/h)	Engine speed (rpm)	Torque (N m)
E	32	2087	11.2
E′	50	2311	20.7
F	70	2378	38.9
H	85	3139	70.0
J	120	3175	104.9

This engine was tested in five different operating conditions (see Table 4), selected among the collection of steady stages [14] which reproduce the sequence of operating conditions that the vehicles equipped with this type of engines must follow during the transient cycle established in the European Emission Directive 70/220, amendment 2001/C 240 E/01. Tests with CME were carried out only in the extreme modes E and J, as the available quantity of cynara oil was limited. In all tests the lubricant oil was a SAE 15W40 supplied by Repsol-YPF.

Particulate matter was collected in a partial dilution mini-tunnel (Nova Microtroll) through glass fiber filters covered by Teflon, as stated by regulations. The filters were conditioned in a climatic chamber (Minitest CCM-0/81), before and after the collection, in order to maintain constant temperature and humidity. An analytical balance was employed inside the chamber. The collection and conditioning procedure was optimised as described in Ref. [13].

Further insight into the exhaust composition was gained with the measurement of hydrocarbon and nitrogen oxides, which were detected, respectively, by flame ionisation (Amluk 2010uP) and gas-phase chemioluminiscence (Beckman 951A). The smoke opacity of the exhaust gas was measured by a smokemeter (AVL 415).

All the results presented below were obtained as the average of four measurements in each operating mode, and values with discrepancies above 2% were neglected.

3.2. Instrumentation and software for chemical and morphologycal analysis

After weighing, the filters with particles were subjected to an optimised Soxhlet extraction method [15]. In this process, two particulate fractions were obtained: the soluble organic fraction (SOF), analysed by gas chromatography (Hewlett Packard 6890), and the insoluble fraction (ISF), which was measured by high performance liquid chromatography (Gibson 802C with a ionic conductivity detector 732 Ω Methrom). The SOF chromatograms allowed distinguishing the origin of SOF hydrocarbons by comparison with those from lubricant oil and fuel [16].

Filters similar to those used in the chemical analysis were imaged by scanning electron microscope (SEM). Although these glass fiber filters have a rough surface, such support was selected over a flat glass surface in order to easily integrate the size characterisation method into the particulate certification procedure. The images obtained by SEM (500 magnification) were subjected to a digital treatment developed in Matlab. This algorithm modifies the contrast in order to make the texture more uniform [17], removes the fibers, and finally, binarizes into black/white images. The nanoparticles, smaller than the pixel size, were subjected to a similar procedure from SEM images with 8000 magnification. The last step consist of a weighted counting. The final outputs are the particle size distribution, the standard deviation and several characteristic mean diameters, such as arithmetic or Sauter mean ones. Although these results do not represent the real flowing particle concentration and size distribution, the algorithm gives a fair reproduction of the trends observed with on-line techniques (scanning mobility particle sizer and optical counter), as reported in Ref. [18].

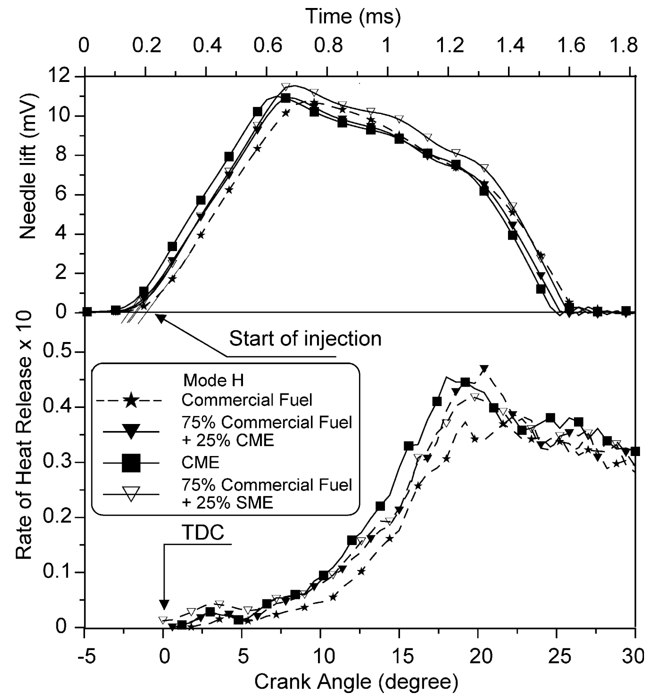


Fig. 1. Effect of the fuel on the injection timing and heat release rate.

4. Effect of biofuels on injection and combustion timing

From comparing the cylinder pressure signal under firing conditions with that under motored ones, and using a diagnostic model described in Ref. [19], the heat release rate was obtained. This rate is compared in Fig. 1 with that of the injection process, obtained from the needle lift signal. Both signals are presented for mode H as an example. No clear conclusions can be obtained about delay time, because combustion starts in the pre-chamber, where no pressure transducer was located. However, as the biodiesel concentration is increased in the blend, an advancing effect can be observed on the injection timing, which is explained in literature either by the increase in the bulk modulus of compressibility of the fuel [20] or also by the increase in its viscosity [21]. As a consequence of such advanced injection process, a similar advancing effect can also be observed on the initial stages of combustion, leading to slightly higher pressure and temperature peaks. Some authors use this observation in literature to justify increases in NO_x emissions [20], while others use it to enlarge the list of arguments justifying the decrease in soot emissions [22], as higher temperature levels are supposed to favour soot oxidation.

5. Effect of biofuels on engine emissions

Particulate emissions were reduced for every mode as the concentration of any of the tested biodiesel fuels were increased in the blend (Fig. 2), despite the higher fuel/air ratio required in each mode necessary to compensate the lower heating value. These reductions are explained by the increase in oxygen content in the fuel which contributes to complete fuel oxidation even in locally rich zones, and by the lower final boiling point which guaranties a complete evaporation of the liquid fuel. This effect can also be observed in the hydrocarbons emissions and the smoke opacity (Figs. 3 and 4) which, unlike the particulate matter, were measured in hot and undiluted conditions. The particulate emission reduction is more significant at low load, because the cylinder temperature is relatively low, which in the case of a multi-component fuel such as the reference, could lead to some difficulties in evaporation

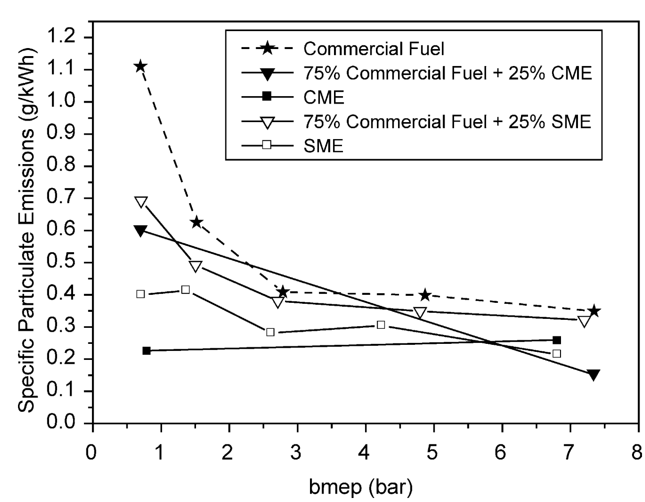


Fig. 2. Specific particulate emissions vs bmep for different tested fuels.

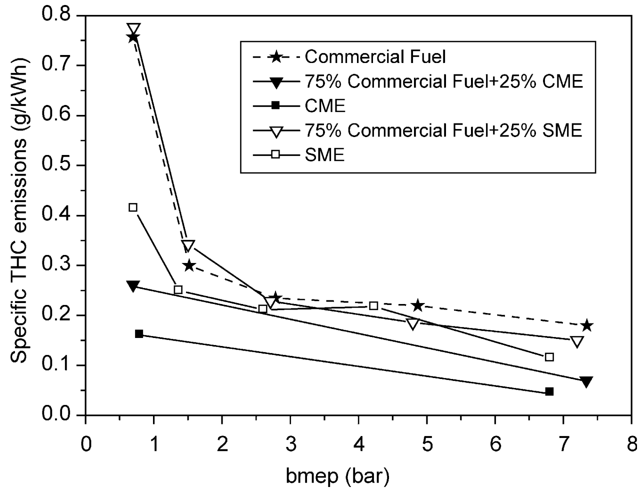


Fig. 3. Specific hydrocarbons emissions vs bmep for different tested fuels.

and burning of heaviest hydrocarbons. The relative reductions in particulate emissions are more drastic from 0% biodiesel to 25% than from this concentration to pure biodiesel.

The comparison between particulate emissions with SME and CME could lead to the conclusion that CME provide slightly higher reductions than SME. Such differences might be due to the lower carbon concentration of CME, and consequently its higher oxygen concentration, although these differences are within the range of accuracy of the measurements. At least it is proved that CME is no worse than SME as a particulate-reducing fuel.

Another significant diesel engine emissions are nitric oxides. Fig. 5 shows that the presence of oxygen on the ester molecule does not lead to increases in NO_x formation. In fact, a certain decrease is observed at high load for all the tested fuels. Increases in NO_x emissions have often been attributed to the oxygen content of the fuel molecule [23,24], either through the thermal or though the prompt mechanisms [25]. However, a simple balance on oxygen availability, assuming local stoichiometric combustion, reveals (Table 2) that, even by including the oxygen of the ester molecule, the oxygen/fuel mass ratio remains below that of the conventional fuel (2.92 in front of 3.58 in the case of sunflower ester). On the other side, the extremely similar values obtained for the adiabatic flame temperature of the tested fuels (Table 2) preclude differences in combustion temperature causing NO_x formation differences.

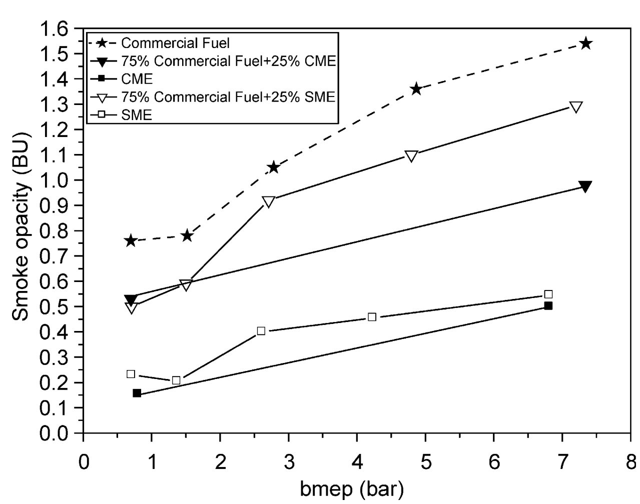


Fig. 4. Smoke opacity vs bmep for different tested fuels.

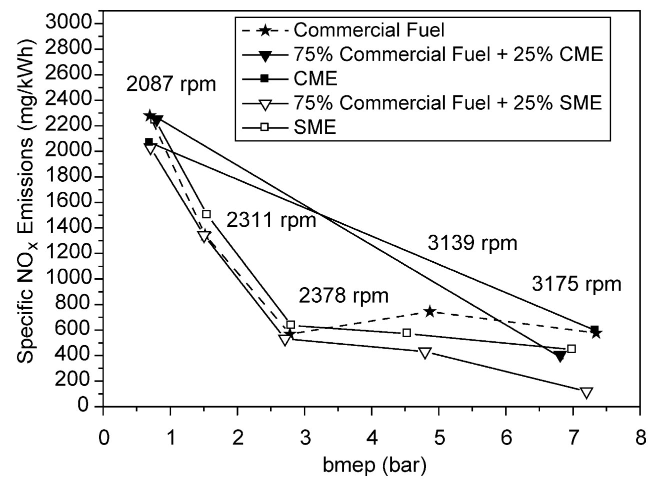


Fig. 5. NO_x emissions vs bmep for different tested fuels.

6. Effect of biofuels on particulate composition and origin

Although the total mass of hydrocarbons adsorbed on the surface of the carbon nuclei increased with load, its proportion with respect the total particulate mass (SOF) decreased as a consequence of the more sloped increase of soot formation. With respect to reference commercial fuel, the soot mass contained in the collected particulate matter was observed to strongly decrease as the concentration of biodiesel was increased, while the mass of adsorbed hydrocarbons remained approximately unchanged leading to increased SOF at any engine load (Fig. 6).

In case that the surface of the soot particles was saturated, the soluble organic fraction would be limited by the adsorption capacity of the soot particles, which depends on the particle size distribution and on the particle surface [22]. Fig. 6 shows that the adsorbed fraction decreases with load and increases with the biodiesel concentration. As such trends are not accompanied by any increase of particle mean diameter with load nor by any decrease of particle mean diameter with ester composition (Fig. 13 presented below), it can be concluded that particles remain unsaturated, and consequently, a decrease on the soot formation does not lead to any restriction on hydrocarbon adsorption.

The effect of fuel on the particulate matter composition is minimized because not all the adsorbed hydrocarbons come from fuel. Many others come from lube oil, which in this

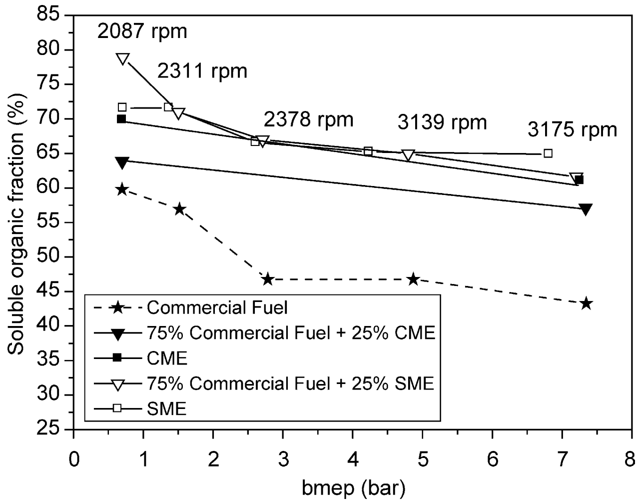


Fig. 6. Soluble organic fraction of the collected particulate filters.

work remained the same. Fig. 7 shows that the major contribution to SOF came from lube oil for all the tested modes and fuels, and that this proportion became even higher as the biodiesel concentration was increased, in accordance with the mentioned effect of oxygenated fuels to reduce not only soot but also hydrocarbons emissions.

The sulphate content in the particulate matter (Fig. 8) was also reduced as the biodiesel concentration was increased, consistently with the sulphur reduction in the fuel (Fig. 9). Note that the residual sulphur content detected in CME was much higher than in SME (Table 3). However, the mentioned reduction was lower than proportional, which could be justified by two reasons: the absence of oxydizing catalyst which did not guaranty a complete sulphur oxidation [26], and the possibility that some of sulphates come from the lubricant oil sulphur content (around 6000 ppm).

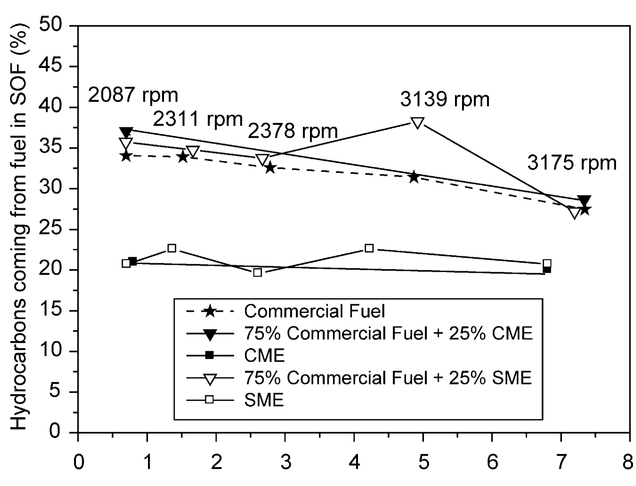


Fig. 7. Origin of the adsorbed hydrocarbons in the particulate matter.

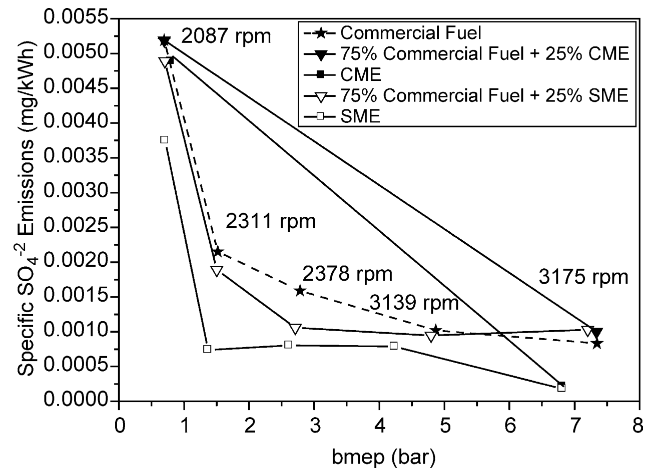


Fig. 8. Sulphate content of particulate matter.

7. Effect of biofuels on particulate morphology

Figs. 10 and 11 are SEM images taken from filters obtained at high load mode from tests with commercial fuel and with pure esters. Although these images show visible differences (the cloak of particulate matter lying on the fiber mesh is noticeably thicker in the case of the commercial fuel), the particulate morphology was quantified through the number of particles per filter surface unit and the Sauter mean particle diameter. Both parameters resulted from the digital analysis of SEM images, as above described.

As Figs. 12 and 13 show, the number of particles strongly increased with load while the mean size remained around a constant value. The presence of vegetable esters in the fuel led to dramatic decreases on the number of particles, accordingly with the reduction in emitted particulate mass, and to slight increases in particle size. The last observation, which could constitute an important additional benefit of biodiesel fuels can hardly be considered significant because the reliability of the averaging process is reduced when the particle population becomes too small.

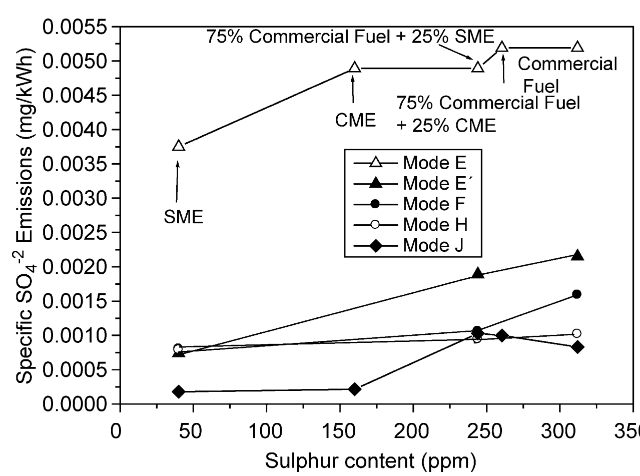
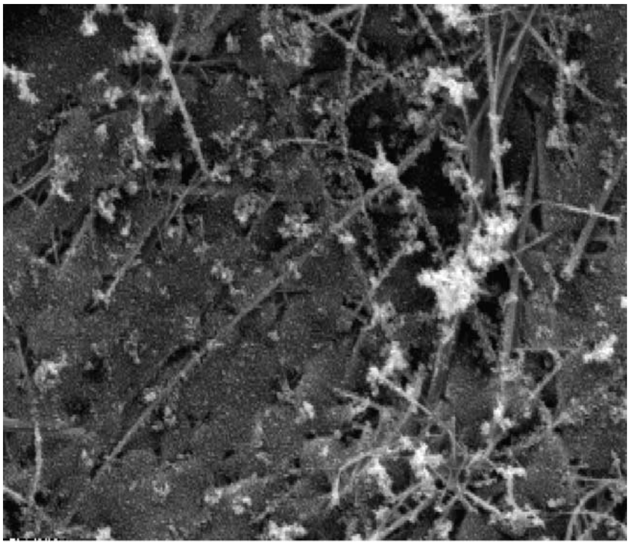
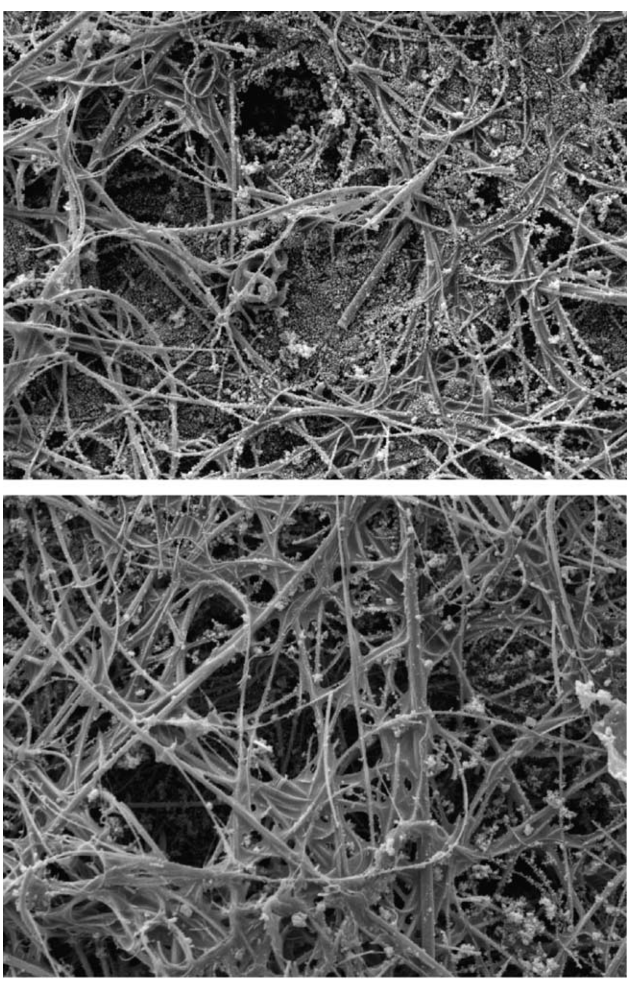


Fig. 9. Sulphate content of particulate matter vs sulphur content of fuels.



50 microns

Fig. 10. SEM image of particulate filter (500×) from engine operating mode J with commercial diesel fuel.



50 microns

Fig. 11. SEM images of particulate filters (500×) from mode J, with pure SME (left) and pure CME (right).

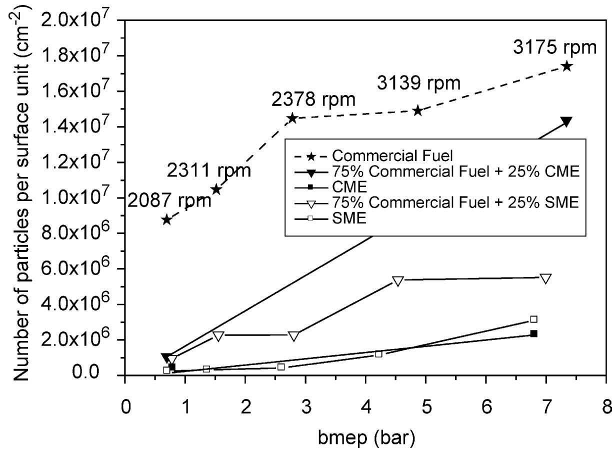


Fig. 12. Number of particles per unit filter surface vs bmep for different tested fuels.

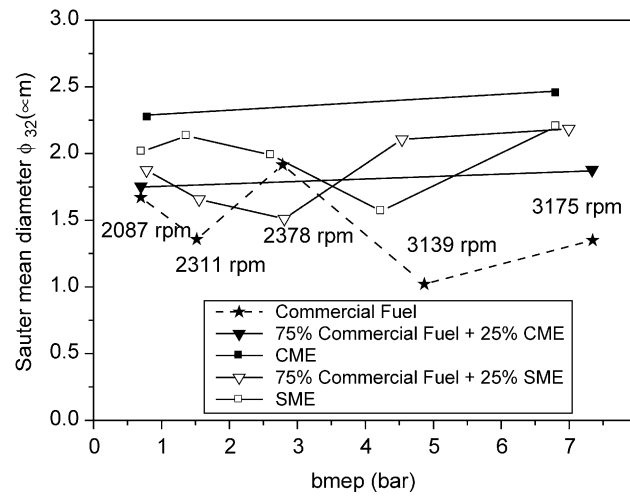


Fig. 13. Particle Sauter mean diameter vs bmep for different tested fuels.

8. Conclusions

- ☐ Methyl esters from sunflower and cynara oils were tested as biofuels in a Diesel engine. These energy sources were chosen because they are the most presently used autochthonous crop for biodiesel production and the most promising one, due to its potential to reduce the oil cost.
- ☐ Particulate emissions were reduced for every mode tested as the concentration of any of the tested biodiesel fuels were increased in the blend. These reductions are mainly justified by the increase in oxygen content in the fuel which contributes to a complete fuel oxidation even in locally rich zones, and by the lower final boiling point which guarantees complete evaporation of the liquid fuel.
- ☐ The presence of oxygen on the ester molecules did not lead to increases in NO_x formation. On the contrary a certain decrease was observed at high load. Although increases in NO_x emissions have often been attributed to

the oxygen content of the fuel molecule, a balance on oxygen availability, reveals that, even by including the oxygen of the ester molecule, the oxygen/fuel mass ratio remains below that of the conventional fuel.

- With respect to reference commercial fuel, the soot mass contained in the collected particulate matter was observed to strongly decrease as the concentration of biodiesel was increased, while the mass of adsorbed hydrocarbons remained approximately unchanged leading to increased soluble organic fraction (SOF) at any engine load.
- The proportion of adsorbed hydrocarbons on the particles surface (SOF) increased with the biodiesel concentration. As such trends are not accompanied by any decrease of particle mean diameter with ester composition, it was concluded that particles remain unsaturated, and consequently, a decrease in the soot formation does not lead to any restriction on hydrocarbon adsorption.
- The major contribution to SOF came from lube oil for all the tested modes and fuels, and this proportion became even higher as the biodiesel concentration was increased, in accordance with the effect of oxygenated fuels to reduce not only soot but also unburned hydrocarbons.
- The sulphate content in the particulate matter was also reduced, consistently with the sulphur reduction in the fuel. Highest reductions were found with sunflower methyl ester.
- The presence of vegetable esters in the fuel led to dramatic decreases in the number of particles, along with the reduction on emitted particulate mass, and to slight increases on the mean particle size.
- The observed emissions reductions using SME and CME in different concentrations, together with the high production potential of their original oils and their low production cost (mainly in the case of cardoon oil), confirm the high interest of these biofuels as substitutes of conventional diesel fuel in Spain.

Acknowledgements

The Government of Castilla-La Mancha is gratefully acknowledged for their financial support (COMBALT research project). CIDAUT (Valladolid) and REPSOL-YPF are also acknowledged for the supply of cynara and sunflower esters, and commercial fuel, respectively.

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Diesel particulate emissions from biofuels derived from Spanish vegetable oils

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ABSTRACT

Methyl esters obtained from the most interesting Spanish oleaginous crops for energy use -sunflower and cynara cardunculus- were both used as diesel fuels in this work, pure and in 25% blends with a reference commercial fuel which was also used pure. A stationary engine test bed, together with the appropriate instrumentation for chemical and morphological analysis, allowed to evaluate the effect of these fuels on the engine emissions, particularly in the main particulate matter characteristics, such as soluble organic fraction, origin of adsorbed hydrocarbons, sulphate content, particle number per unit filter surface, and mean particle diameter. Both the consideration of the main thermochemical properties of the tested fuels and the computations of a chemical equilibrium model were helpful for the analysis of the experimental results. These results proved that the use of these vegetable esters provides a significant reduction on particulate emissions, mainly due to reduced soot and sulphate formation. On the contrary, no increases on NOx emissions nor reductions on mean particle size were found.

INTRODUCTION

The production of biofuels for diesel applications from traditional laboring is an energy alternative of increasing interest, as it enables surplus agricultural production, reduction both the global and local environmental impact of diesel engines, and relief from energy dependency on imports. The recent increases of the petroleum barrel price and the development of industrial technologies for biodiesel production makes this biofuels option more competitive against conventional diesel fuel for the future.

The most interesting crops in Spain for seed oil production for fuel use are sunflower and an autochthonous cardoon named cynara cardunculus (1), both belonging to the same botanical family. The seed oil content is around 25% in both cases. However, the production cost is still too high to compete with fossil diesel, unless the special taxes presently applied to petroleum-derived fuels were reduced or eliminated. Other experiences with rapeseed oil (2)(3), soybean oil (4)(5) and palm oil (6) have been successful in different countries, and have demonstrated advantages on particulate emissions.

Methyl esters from sunflower (SME) and cynara (CME) were both used as diesel fuels in this work, pure and in 25% blends with a reference fuel which was also used pure. The reference fuel is a typical diesel fuel available in Spanish petrol stations, attaining the present fuel quality requirements for diesel vehicles. It was supplied by Repsol-YPF. A stationary engine test bed, equipped with the appropriate instrumentation for chemical and morphological analysis, allowed evaluation of the effect of these fuels on the engine emissions, and particularly in the main particulate matter characteristics.

PRODUCTION AND CHARACTERIZATION OF VEGETABLE ESTERS AS DIESEL FUELS

CHARACTERISTICS OF VEGETABLE OILS

Table 1. Fatty acid oil content of vegetal oils.

Acid	Sunflower	Cynara
Myristic	0	0.11
Palmitic	6.38	10.62
Palmitoleic	0	0.14
Stearic	4.09	3.7
Oleic	23.68	24.95
Linoleic	63.79	59.87
Linolenic	0.36	0
Araquic	0.3	0.36
Gadoleico	0.27	0.15
Behenic	0.83	0
Lignoceric	0.3	0

The fatty acid oil content of each of the vegetable oils used in the engine tests is shown in Table 1. It can be noticed that there are only small differences between them. The proportion of unsaturates is 88.1% for sunflower oil and 85.1% for cynara oil.

OBTAINMENT OF VEGETABLE ESTERS

Both vegetable oils were subjected to a transesterification reaction with methanol, using NaOH as catalyst. The reaction conditions were similar in both cases. The transesterification procedure was developed and carried out in CIDAUT (Centro de Investigación y Desarrollo en Automoción) and reached 95% efficiency after 1 day decantation and double washing with water and acidified water. The reaction lasted 1 hour at a temperature between 60ºC and 70ºC. The obtained biofuels were sunflower methyl ester (SME) and cynara methyl ester (CME), and in both cases an acidity below 0.5 mg KOH was reached.

THERMOCHEMICAL PROPERTIES

In order to estimate the main thermochemical properties, the group contributions Joback method (7) was used for the calculation of the specific heat at constant pressure and the standard enthalpy of formation:

$$\frac{Cp}{R}(\text{SME}) = -1.26159 + 0.21362 \cdot T - 1.2484\text{E-}4\, T^2 + 2.7534\text{E-}8 \cdot T^3$$

$$\frac{Cp}{R}(\text{CME}) = -1.10152 + 0.21159 \cdot T - 1.2295\text{E-}4\, T^2 + 2.6825\text{E-}8 \cdot T^3$$

$$h_f^0 \text{ (SME)= -68851.88 K}^{-1}$$

$$h_f^0 \text{ (CME)= -69615.53 K}^{-1}$$

These data were used in a chemical equilibrium model (8) which considers 29 chemical species (N_2, O_2, CO_2, H_2O, CO, H_2, NO, OH, N, H, O, Ar, N_2O, NO_2, HO_2, NH_3, NH_2, NH, CN, HCN, NCO, S, S_2, SO, SO_2, SO_3, HS, H_2S, COS) to calculate the adiabatic flame temperature at constant pressure. Initial conditions of 80 bar and 900 K were taken as typical diesel in-cylinder conditions at the start of combustion. Other chemical characteristics of the fuel molecules are listed in Table 2.

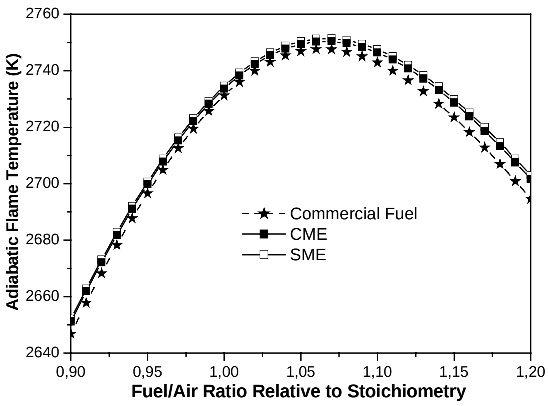

Figure 1. Adiabatic flame temperature vs fuel/air ratio at constant pressure (Initial conditions: p=80 bar and 900K)

Table 2. Chemical characteristics of sunflower ester and cynara ester, compared to commercial diesel fuel.

Fuel	Diesel	SME	CME
Summarized formula	$C_{15.27}H_{27.33}$	$C_{18.94}H_{34.82}O_2$	$C_{18.79}H_{34.68}O_2$
Molecular weight (g/mol)	210.7	294.58	292.64
Oxygen content (% w)	0	10.86	10.93
H/C ratio	1.807	1.838	1.846
Average No. double bonds	0	1.53	1.45
Aromatic content (% w)	37.23	0	0
Stoichiometric fuel/air ratio	1/15.5	1/12.423	1/12.421
Stoich. fuel/oxygen ratio	1/3.58	1/2.814	1/2.816

FUEL PROPERTIES

The obtained esters were tested as automotive fuels together with the commercial fuels, following the European standard methods, established in the European Norm EN590 (directive 98/70/CE). The main fuel specifications are listed in table 3. The lower heating values of esters are nearly compensated by their higher density in the volumetric injection system leading to heating values of the same order when expressed in MJ/l. Differences in viscosity and cetane number slightly affect the timing of injection (9) and combustion, respectively. As esters' composition are much more homogeneous than that of diesel fuel, their distillation curves are much more flat, leading to lower final point despite the higher general level of boiling temperature. Finally, higher sulphur content was found in CME than in SME, both being much lower than that of diesel fuel.

Table 3. Fuel properties of SME and CME, compared to commercial diesel fuel (* Cetane Index)

Fuel	Diesel	SME	CME
Density (kg/m^3)	830	885.4	887
Lower heating value (MJ/kg)	43.0	37.4	37.2
Lower heating value (MJ/l)	35.7	33.1	33.0
Cetane number	49.6	56.4	54.4*
Viscosity (cSt) (40ºC)	3.16	4.13	4.88
Distillation T50 (ºC)	277.7	340.0	-
Final Boiling Point (ºC)	376.7	345.0	345.0
POFF (ºC)	-15	-	-10
Sulphur content (ppm w)	312	40	160

EXPERIMENTAL SET-UP FOR TESTING AND ANALYSIS

ENGINE TEST BED AND INSTRUMENTATION

A turbocharged intercooler IDI diesel Renault engine, model F8Q, similar to those commonly used in European passenger car, was tested. The engine was coupled to a hydraulic brake and equipped with the instrumentation for its control and for the measurement of all the parameters affecting emissions (10). In all cases the engine was fully warmed up, which avoided the possible disadvantage of biodiesel blends in cold conditions due to their lower volatility at low temperature.

This engine was tested in five different operating conditions (see Table 4), selected among the collection of steady stages (11) which reproduce the sequence of operating conditions that the vehicles equipped with this type of engines must follow during the transient cycle established in the European Emission Directive 70/220, amendment 2001/C 240 E/01. Tests with CME were carried out only in the extreme modes E and J, as the available quantity of cynara oil was limited. In all tests the lubricant oil was a SAE 15W40 supplied by Repsol-YPF.

Table 4. Engine operating conditions

Operation mode	Mean speed (km/h)	Engine speed (rpm)	Torque (N.m)
E	32	2087	11.2
E'	50	2311	20.7
F	70	2378	38.9
H	85	3139	70.0
J	120	3175	104.9

Particulate matter was collected in a partial dilution mini-tunnel (Nova Microtroll) through glass fiber filters covered by Teflon, as stated by regulations. The filters were conditioned in a climatic chamber (Minitest CCM-0/81), before and after the collection, in order to maintain constant temperature and humidity. An analytical balance was employed inside the chamber. The collection and conditioning procedure was optimised as described in reference (10).

Further insight into the exhaust composition was gained with the measurement of hydrocarbon and nitrogen oxides, which were detected, respectively, by flame ionisation (Amluk 2010uP) and gas-phase chemioluminiscence (Beckman 951A). The smoke opacity of the exhaust gas was measured by a smokemeter (AVL 415).

INSTRUMENTATION AND SOFTWARE FOR CHEMICAL AND MORPHOLOGYCAL ANALYSIS

After weighing, the filters with particles were subjected to an optimised Soxhlet extraction method (12). In this process, two particulate fractions were obtained: the soluble organic fraction (SOF), analysed by gas chromatography (Hewlett Packard 6890), and the insoluble fraction (ISF), which was measured by high performance liquid chromatography (Gibson 802C with a ionic conductivity detector 732 Ω Methrom). The SOF chromatograms allowed distinguishing the origin of SOF hydrocarbons by comparison with those from lubricant oil and fuel (13).

Filters similar to those used in the chemical analysis were imaged by Scanning Electron Microscope (SEM). Although these glass fiber filters have a rough surface, such support was selected over a flat glass surface in order to easily integrate the size characterisation method into the particulate certification procedure. The images obtained by SEM (500 magnification) were subjected to a digital treatment developed in Matlab. This program modifies the contrast in order to make the texture more uniform (14), detracts the fibers, and finally, binarizes into black/white images. The nanoparticles, smaller than the pixel size, were subjected to a similar procedure from SEM images with 8000 magnification. The last step consist of a weighted counting. The final outputs are the particle size distribution, the standard deviation and several characteristic mean diameters, such as arithmetic or Sauter mean ones.

EFFECT OF BIOFUELS ON ENGINE EMISSIONS

Particulate emissions were reduced for every mode as the concentration of any of the tested biodiesel fuels were increased in the blend (Figure 2), despite the higher fuel/air ratio required in each mode necessary to compensate the lower heating value. These reductions are explained by the increase in oxygen content in the fuel which contributes to complete fuel oxidation even in locally rich zones, and by the lower final boiling point which guaranties a complete evaporation of the liquid fuel. This effect can also be observed in the hydrocarbons emissions and the smoke opacity (Figures 3 and 4) which, unlike the particulate matter, were measured in hot and undiluted conditions. The particulate emission reduction is more significant at low load, because the cylinder temperature is relatively low, which in the case of a multi-component fuel such as the reference, could lead to some difficulties in evaporation and burning of heaviest hydrocarbons. The relative reductions in particulate emissions are more drastic from 0% biodiesel to 25 % than from this concentration to pure biodiesel.

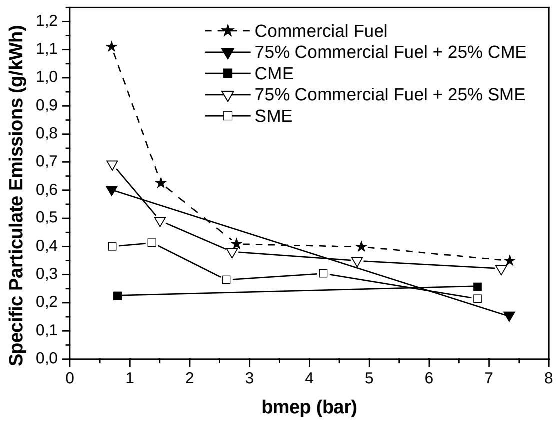

Figure 2. Specific particulate emissions vs bmep for different tested fuels

The comparison between particulate emissions with SME and CME could lead to the conclusion that CME provide slightly higher reductions than SME. Such differences might be due to the lower carbon concentration of CME, and consequently its higher oxygen concentration, although these differences are within the range of accuracy of the measurements. At least it is proved that CME is no worse than SME as a particulate-reducing fuel.

Another significant diesel engine emissions are nitric oxides. Figure 5 shows that the presence of oxygen on the ester molecule does not lead to increases on NOx formation. In fact, a certain decrease is observed at high load for all the tested fuels. Increases on NOx emissions have often been attributed to the oxygen content of the fuel molecule (15)(16). However, a simple balance on oxygen availability, assuming local stoichiometric combustion, reveals (Table 2) that, even by including the oxygen of the ester molecule, the oxygen/fuel mass ratio remains below that of the conventional fuel (2.92 in front of 3.58 in the case of sunflower ester). The extremely similar values obtained for the adiabatic flame temperature of the tested fuels (Figure 1) preclude difference in combustion temperature causing NOx formation differences.

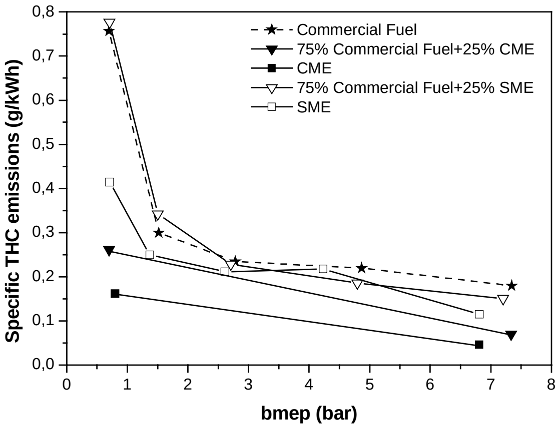

Figure 3. Specific hydrocarbons emissions vs bmep for different tested fuels

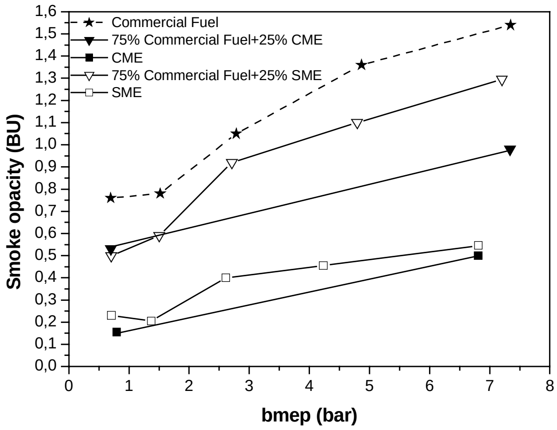

Figure 4. Smoke opacity vs bmep for different tested fuels

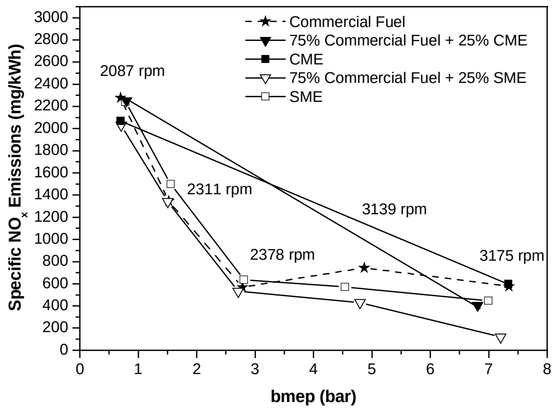

Figure 5. NOx emissions vs bmep for different tested fuels

EFFECT OF BIOFUELS ON PARTICULATE COMPOSITION AND ORIGIN

Although the total mass of hydrocarbons adsorbed on the surface of the carbon nuclei increased with load, its proportion with respect the total particulate mass (SOF) decreased as a consequence of the more sudden increase of soot formation. With respect to reference commercial fuel, the soot mass contained in the collected particulate matter was observed to strongly decrease as the concentration of biodiesel was increased, while the mass of adsorbed hydrocarbons remained approximately unchanged leading to increased SOF at any engine load (Figure 6).

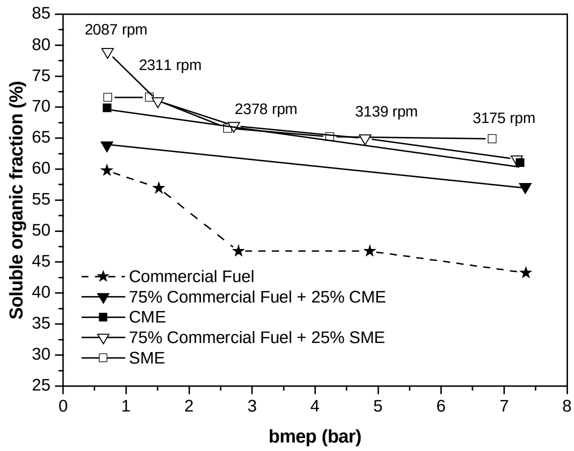

Figure 6. Soluble organic fraction of the collected particulate filters

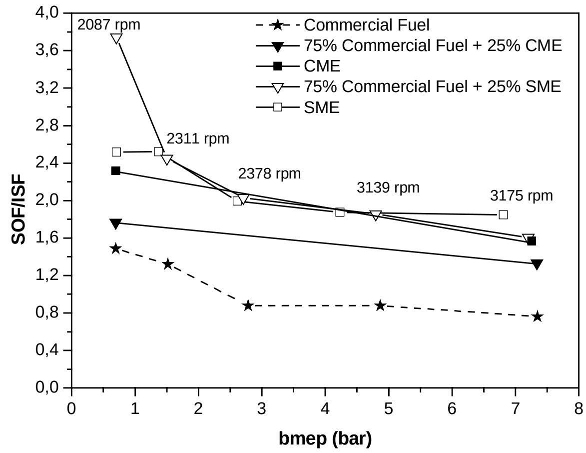

Figure 7. Relative adsorption of the collected particulate matter

In order to interpret this trend, the ratio between the soluble and the insoluble fractions (SOF/ISF) was plotted against bmep for all the tested fuels (Figure 7). This parameter is named here as relative adsorption. In case that the surface of the soot particles was saturated, the relative adsorption would be limited by the adsorption capacity of the soot particles, which depends on the particle size distribution and on the particle porosity. Figure 7 shows that the relative adsorption decreases with load and increases with the biodiesel concentration. As such trends are not accompanied by any increase of particle mean diameter with load nor by any decrease of particle mean diameter with ester composition (Figure 14 presented below), it can be concluded that particles remain unsaturated, and consequently, a decrease on the soot formation does not lead to any restriction on hydrocarbon adsorption.

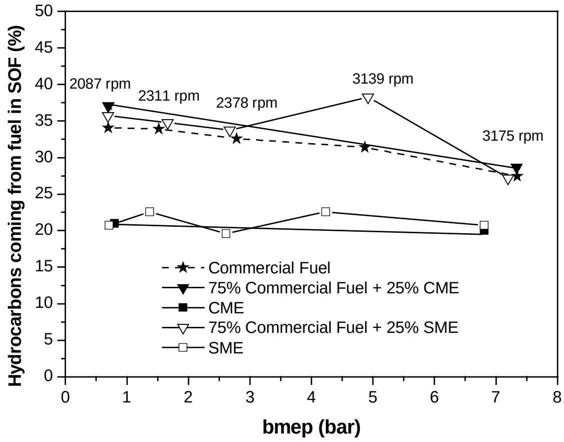

Figure 8. Origin of the adsorbed hydrocarbons in the particulate matter

The effect of fuel on the particulate matter composition is minimized because not all the adsorbed hydrocarbons come from fuel. Many others come from lube oil, which in this work remained the same. Figure 8 shows that the major contribution to SOF came from lube oil for all the tested modes and fuels, and that this proportion became even higher as the biodiesel concentration was increased, in accordance with the mentioned effect of oxygenated fuels to reduce not only soot but also hydrocarbons emissions.

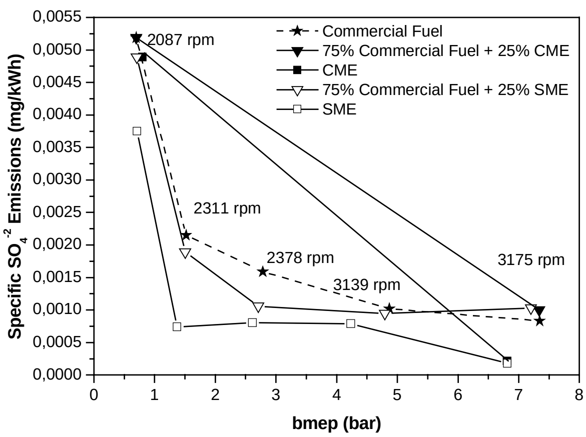

Figure 9. Sulphate content of particulate matter

The sulphate content in the particulate matter (Figure 9) was also reduced as the biodiesel concentration was increased, consistently with the sulphur reduction in the fuel (Figure 10). Note that the residual sulphur content detected in CME was much higher than in SME (Table 3). However, the mentioned reduction was lower than proportional, which could be justified by two reasons: The absence of oxydizing cataliser which did not guaranty a complete sulphur oxidation (17), and the possibility that some of sulphates come from the lubricant oil sulphur content (around 6000 ppm).

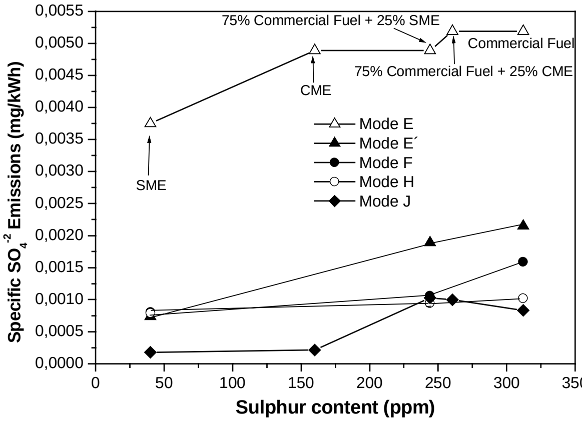

Figure 10. Sulphate content of particulate matter vs sulphur content of fuels

EFFECT OF BIOFUELS ON PARTICULATE MORPHOLOGY

Figures 11 and 12 are SEM images taken from filters obtained at high load mode from tests with commercial fuel and with pure esters. Although these images show visible differences, the particulate morphology was quantified through the number of particles per filter surface unit and the Sauter mean particle diameter. Both parameters resulted from the digital analysis of SEM images, as above described.

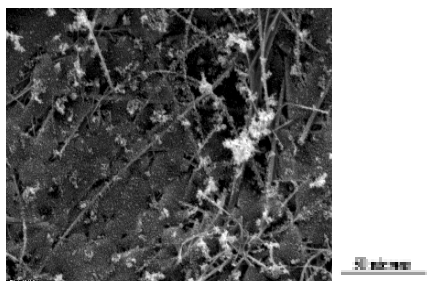

Figure 11. SEM image of particulate filter (500x) from engine operating mode J with commercial diesel fuel.

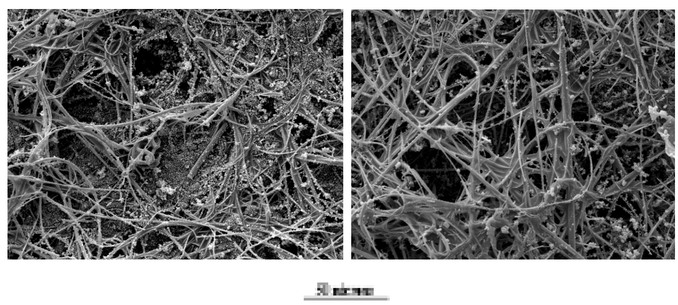

Figure 12. SEM images of particulate filters (500x) from mode J, with pure SME (left) and pure CME (right)

As Figures 13 and 14 show, the number of particles strongly increased with load while the mean size remained around a constant value. The presence of vegetable esters in the fuel led to dramatic decreases on the number of particles, accordingly with the reduction in emitted particulate mass, and to slight increases in particle size. The last observation, which could constitute an important additional benefit of biodiesel fuels can hardly be considered significant because the reliability of the averaging process is reduced when the particle population becomes too small.

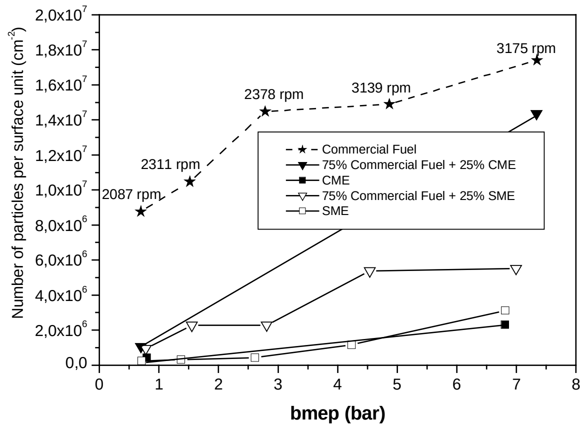

Figure 13. Number of particles per unit filter surface vs bmep for different tested fuels

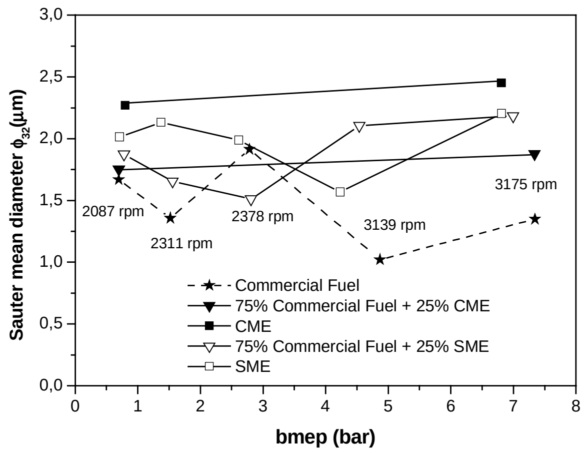

Figure 14. Particle Sauter mean diameter vs bmep for different tested fuels

CONCLUSIONS

- Particulate emissions were reduced for every mode tested as the concentration of any of the tested biodiesel fuels were increased in the blend. These reductions are justified by the increase in oxygen content in the fuel which contributes to a complete fuel oxidation even in locally rich zones, and by the lower final boiling point which guarantees complete evaporation of the liquid fuel.

- The presence of oxygen on the ester molecules did not lead to increases in NOx formation. On the contrary a certain decrease was observed at high load. Although increases on NOx emissions have often been attributed to the oxygen content of the fuel molecule, a balance on oxygen availability, reveals that, even by including the oxygen of the ester molecule, the oxygen/fuel mass ratio remains below that of the conventional fuel.

- With respect to reference commercial fuel, the soot mass contained in the collected particulate matter was observed to strongly decrease as the concentration of biodiesel was increased, while the mass of adsorbed hydrocarbons remained approximately unchanged leading to increased soluble organic fraction (SOF) at any engine load.

- The relative adsorption (SOF/ISF) increased with the biodiesel concentration. As such trends are not accompanied by any decrease of particle mean diameter with ester composition, it was concluded that particles remain unsaturated, and consequently, a decrease in the soot formation does not lead to any restriction on hydrocarbon adsorption.

- The major contribution to SOF came from lube oil for all the tested modes and fuels, and this proportion became even higher as the biodiesel concentration was increased, in accordance with the effect of oxygenated fuels to reduce not only soot but also unburned hydrocarbons.

- The sulphate content in the particulate matter was also reduced, consistently with the sulphur reduction in the fuel. Highest reductions were found with sunflower methyl ester.

- The presence of vegetable esters in the fuel led to dramatic decreases in the number of particles, along with the reduction on emitted particulate mass, and to slight increases on the mean particle size.

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LOW-COST BIODIESEL FROM CYNARA OIL

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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.

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}.

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]

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 cardunculus* 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 cardunculus* 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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L'ús de biodièsel a Catalunya i la satisfacció dels usuaris

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Estudi encarregat per l’Associació Catalana del Biodièsel en col.laboració amb l’ICAEN.

1. Anàlisi de volum de vendes i nombre de sortidors a les benzineres.
2. Anàlisi de enquestes als usuaris de dièsel i biodièsel, enquestes realitzades per Opinometre.
3. Anàlisi global.

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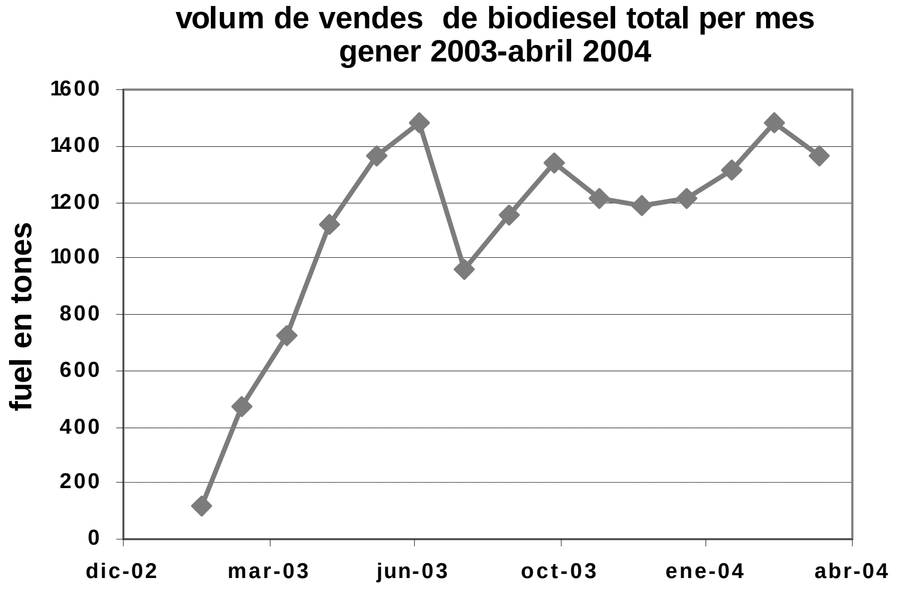
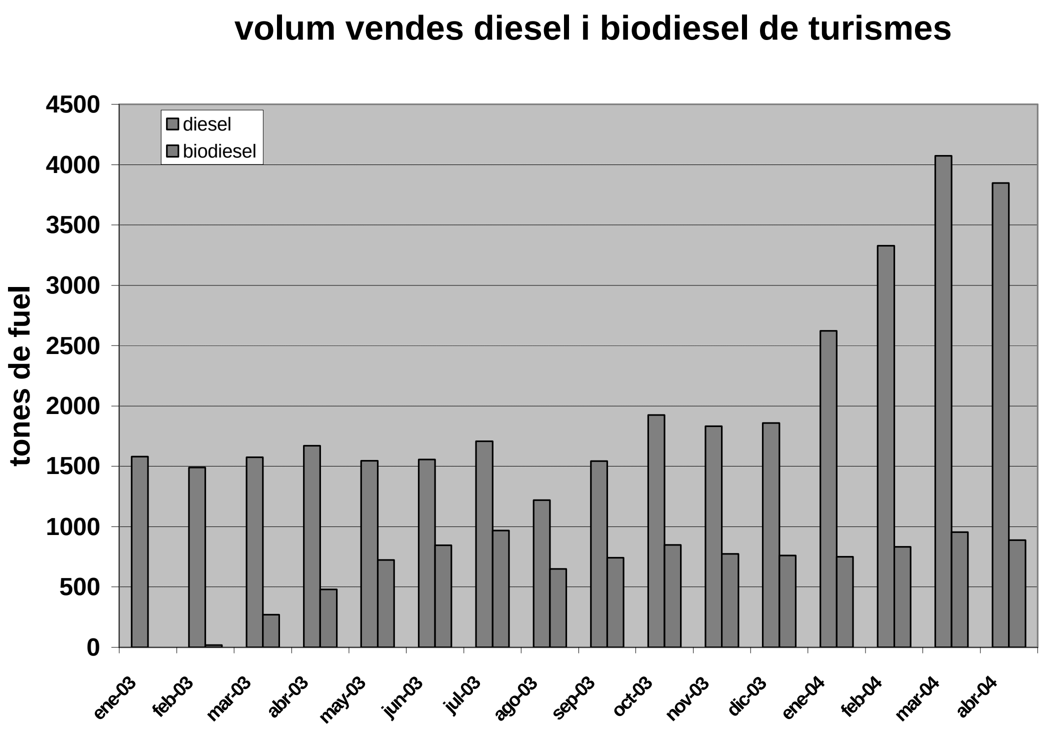
L’ús del biosièsel, augmenta o dismineueix?



El biodièsel afecta les vendes del dièsel?



Dr Xavier Gabarrell, Dra Gara Villalba, Dr J. David Tàbara. Institut de Ciència i Tecnologia Ambientals. UAB. Octubre2004

Anàlisi d'enquestes als usuaris de dièsel i biodièsel.

Tots els usuaris: Manca d'informació sobre el biodièsel (fulletons, institució.

No-usuaris de biodièsel: 37% no coneixen el biodièsel

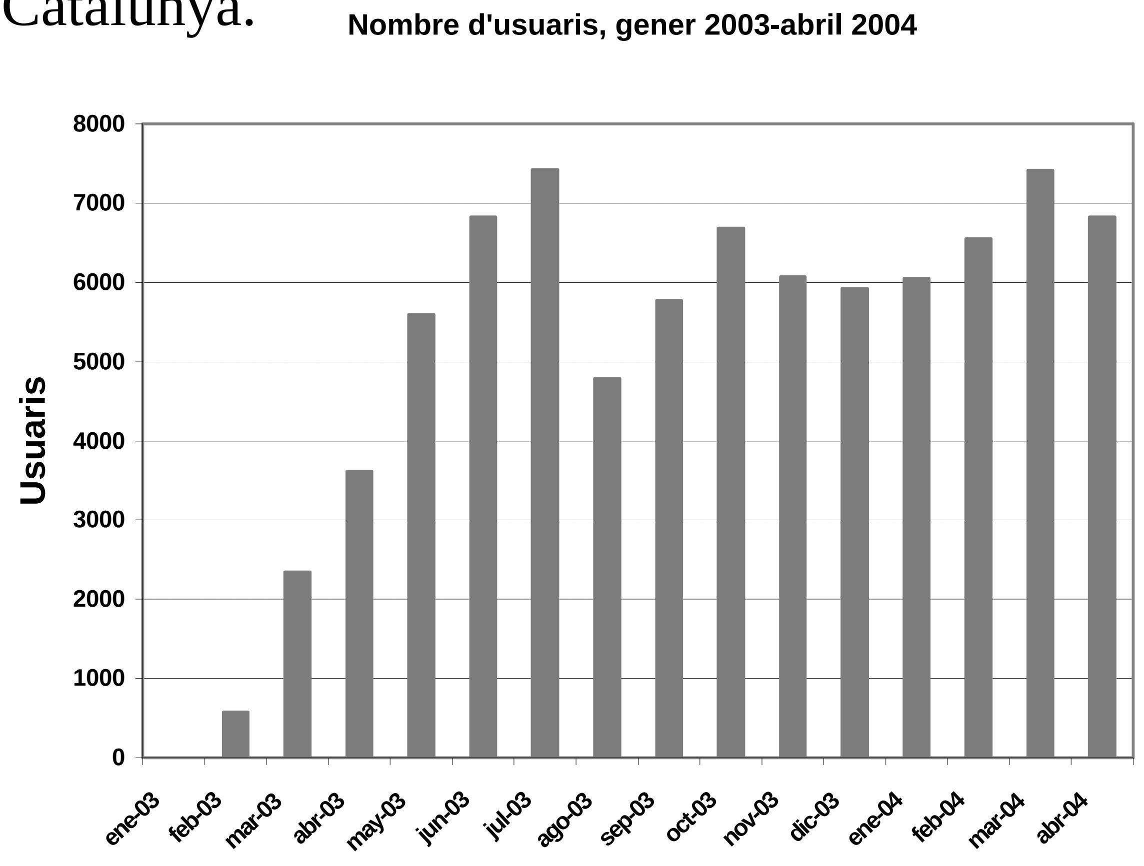
Usuaris de biodièsel:

-Mitjana avaluació: 7,58 (d' 1 a 9) grau de satisfacció.

-72% van expressament a aquesta benzinera per omplir biodièsel i li queda a prop.

-35% dels usuaris només utilitzen biodièsel.

Nombre aproximat d'usuaris/es en actiu de biodièsel a Catalunya.



Anàlisi global

1. Molt desconeixement i desconfiança
2. Es desconeixen els beneficis ambientals
3. Mitjana per sortidor-cotxe: 9000-1000 l mensuals
4. Uns 6000 – 9000 usuaris a tot Catalunya
5. L'usuari del biodièsel és molt fiel.
6. Error de la mostra: 6,9 % (per una població superior a 10.000)

Conclusions

1. Necessitem un punt d'informació.
2. L'usuari del biodièsel és molt fiel i està satisfet amb el seu ús.
3. Les vendes de biodièsel no afecten les vendes d'altres fuels.
4. Les vendes de biodièsel s'han estabilitzat.
5. Futurs treballs.

ANNEX C: FOTOGRAFIES VISITA

“Stocks del Vallès, S.A.”

Vista general de la Planta de Biodièsel de "Stocks del Vallès, S.A"

Vista procés productiu de transesterificació

Vista canonades de transport de biodièsel i olis.