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SUSTDEV-2004-1.2.5**



**“Energy from Crops”
BIOCARD**

**Global Process to Improve Cynara cardunculus Exploitation for
Energy Applications
Contract n° - 019829**

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Definitions and Abbreviations

Abbreviations

AFM: Ash Forming Matter
CFD: Computational Fluid Dynamics
CYN-CRU: Crushed Cynara bales
CYN-PELL: Pelletized Cynara
CYN-SAC: Cynara - South African coal blends
CYN-SPA: Cynara - Spanish coal blends
d.b.: dry basis
DRIFT: Diffuse reflectance infrared Fourier transform
EDX: Energy dispersive X-ray spectroscopy
EGA-MS: Evolved gas analysis coupled to mass spectrometry
en.b.: energy basis
FAME: Fatty Acid Methyl Ester
FB: Fluidized Bed
FFA: Free Fatty Acids
FTIR: Fourier Transformation Infrared Spectroscopy
GHG: Green House Gases
HFO: Heavy Fuel Oil
HHV: High Heating Value
ICP-OES: Inductively Coupled Plasma Spectroscopy
IPR: Intellectual Property Rights
LFR: Laminar Flow Reactor
LHV: Low Heating Value
MDO: Marine Diesel Oil
MGO: Marine Gas Oil
PA: palmitic acid
PF: Pulverized Fuel
SAC: South African coal
SAC-13: silica-supported nafion resin
SEM-EDS: Scanning Electron Microscopy – Energy Dispersive Spectrometer
SM: static mixers
SPA: Spanish coal
TGA: Thermogravimetric analyses
TPD: Temperature programmed desorption
w.b.: wet basis

WP1: Work Package 1

WP2: Work Package 2

XPS: X-ray photoelectron spectroscopy

XRD: X-Ray Diffraction

0 SUMMARY

This report cumulates and summarises the project activities and results over the full duration. It includes a summary description of the project objectives, challenges and expected results, the contractors involved, work performed and end results. It also includes a publishable summary of each exploitable result the project has generated.

1 PROJECT EXECUTION

Global Process to Improve *Cynara Cardunculus* Exploitation for Energy Applications BIOCARD

EC PROGRAMME:	FP6-SUSTDEV-2004-1.2.5
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The use of biomass for energy applications is getting importance year after year in Europe. Countries with higher biomass exploitation are north-European ones, with a high production of wood and crop residues due to more appropriate climate. Mediterranean countries must find a proper dry farming with low cost of exploitation and aiming at the use of the lands set-aside in the last years. In order to carry out this goal, BIOCARD project is focused on 'Cynara Cardunculus' (commonly know as "Cynara" in the area of the energy crops) as an alternative crop for solid and liquid biofuel production.

Challenges:

The proposal aims at demonstrating technical and economical feasibility of a global process for cardoon (*Cynara Cardunculus L.*) exploitation for energy applications. This energy crop is appropriated for Mediterranean Area, where water shortage problems exist. A combined process to produce a low-cost liquid biofuel from seeds and energy from lignocellulosic biomass is proposed. Different technologies for biomass energy conversion have been researched and compared. Additionally, to increase competitiveness and breaking the cost barriers, new heterogeneous catalysis for liquid biofuel production has been tested.

Expected results of the project:

- This project is expected to **promote the use of biomass and liquid biofuels in Mediterranean Areas** where climatic conditions are not advantageous, through the complete exploitation of the Cynara products, giving a global solution that could contribute to European policies of energy supply and CO₂ reduction.
- **Improvements in Cynara crop cultivation**
- **Improvements in Cynara Biomass valorization**
 - × Use as alternative fuel for fossil power plants
 - × Reduce emissions from fossil fuels → CO₂ reduction costs
- **Improvements in Seeds valorization**
 - × Develop a **new heterogeneous catalysis** process to produce biodiesel obtaining several advantages when compared to homogeneous process
 - ✓ A solid catalyst is able to be re-used → reduction of liquid biofuel production costs
 - ✓ The washing steps, reduce large water volumes

- ✓ High quality glycerin
- **New Raw material for energy production**

The main BIOCARD proposal objectives have been covered through several intermediate goals:

- Optimization of crop conditions to yield in biomass production
- Development of new machinery to improve seeds separation from Cynara biomass
- Analyze Biomass combustion alternatives:
 - ✓ Co-combustion in burners
 - ✓ Combustion in grates
 - ✓ Combustion in fluidized beds
- Reduce liquid biofuel production costs:
 - ✓ Use of Cynara seeds to produce biofuel through traditional catalysis process
 - ✓ Use a new heterogeneous catalysis process for biodiesel production
- Analyze Biodiesel combustion alternatives for electricity production:
 - ✓ Use mixes of Cynara biofuel and Cynara oil for being used in big stationary diesel engines

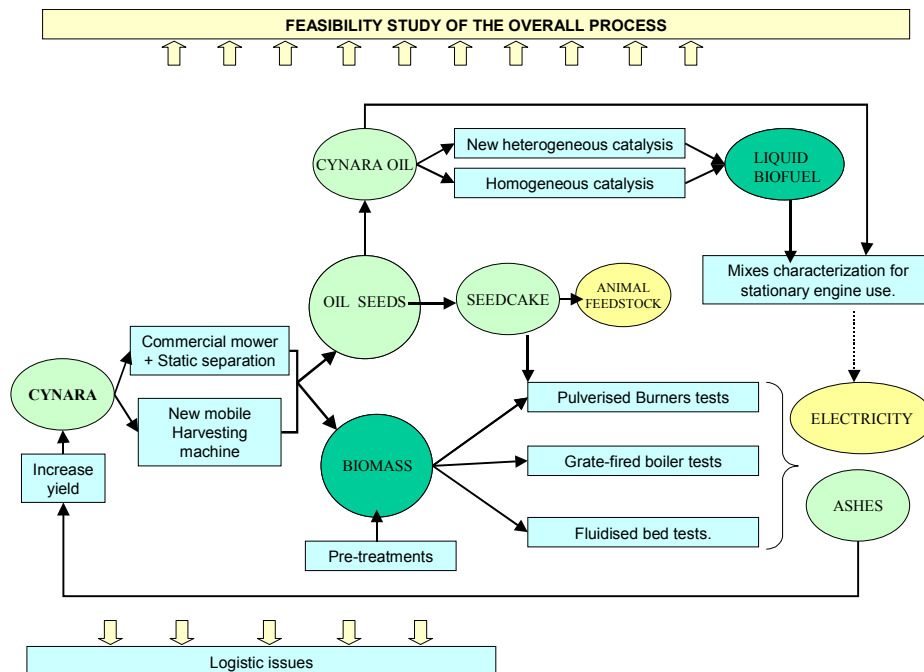


Fig 1. Project Structure

Project Structure:

The project has been split into 6 different Workpackages:

- WP0 Project Co-ordination
- WP1 Energy Crop management and harvesting
- WP2 Biomass valorization for energy conversion
- WP3 Cynara seeds valorization for energy conversion
- WP4 Overall technical and economical evaluation. Feasibility study
- WP5 Dissemination and exploitation activities

The work performed and results obtained under the main workpackages are explained in deeper detail in the following sections.

1.1 ENERGY CROP MANAGEMENT AND HARVESTING ACTIVITIES

1.1.1 Description of project objectives

The Work Package 1 “Energy Crop management and harvesting” focuses on the first step of the bioenergy chain of cynara, namely the production of the feedstock. It involves the agrarian tasks including sowing, harvesting and separation of different energy products and the tasks of biomass pre-treatment and logistics.

More specifically the objectives of WP1 were:

- Implantation of the experimental cynara crop.
- Crop efficiency assessment.
- Cynara oil procurement.
- Development a prototype of static system for bales unpacking and separation of the seeds from the lignocellulosic biomass.
- Development of specific machinery to harvest and separate the economic products of cynara biomass.
- Analysis of low-cost pre-treatments for Cynara biomass.
- Development of a cynara logistic analysis.

1.1.2 Work performed and end results

The work performed for WP1 was organized under seven tasks. Approach and end- results are detailed below.

Task 1.1. Establishment of the experimental cynara crop.

This task represents the first step of the biomass production chain. The aim of this task was essentially to get a large field cynara crop available for the activities involving crop management, harvest mechanization, crop efficiency, biomass supply, biomass pre-treatment, oil procurement, logistics and demonstration.

Three plantations were established from seeds at different sites of Spain: 20 ha in Alcalá de Henares (Lat. 40° 29' 22.54" N, Log 3° 21' 39.48" W), 10 ha in Castellar de la Frontera (Lat. 36° 17' 18.85" N, Log 5° 25' 4.01" W), and 3 ha in Alcala de los Gazules (Lat. 36° 27' 49.31" N, Log 5° 43' 21.28" W). The protocol of establishment was the same for the three sites. The three crops were established and maintained under non-irrigated conditions for the whole Project duration. For logistic reasons, the crop sited in Alcalá de Henares was the base for the majority of the Project activities.



Fig 2. Establishment of the cynara crop. Left: cynara plantlets; Right: cynara rosettes.

Task 1.2 Crop efficiency assessment

This task represented the second step of the biomass production chain. It aimed at the assessment of the management and the productivity of cynara grown in dry conditions at large scale and it used the crop sited in Alcalá de Henares as the reference plantation. Soil survey and climate records compounded the characterization of the abiotic factors. As regards the crop, it was managed according to the recommendations of cynara grown for biomass production, following an annual pattern of development cycle from September to September; agricultural operations were recorded; biomass production was assessed when the aerial biomass was fully dry.



Fig 3. Left: Cynara crop at harvest time. Right: On site evaluation of the productivity

End results of this task were produced at two levels: availability of feedstock and contribution to the knowledge. Within the former, the availability of different types of biomass of cynara produced for the interest of other WPs, like solid biofuel for WP2 and achenes for oil seed production for WP3. Within the latter, the end results of WP1 shaped the Deliverables D 1.2 '*Crop Efficiency Assessment Report*' and D.4.1. '*Crop Management Report*'. Main findings are summarized below.

As a rainfed crop under a Mediterranean climate, the yield of the crop depended on the rainfall regime of the agricultural campaign. It was shown that in average conditions of rainfall (~500 mm/year) and soil (deep soils, loam texture), the crop can yield about 14 t dry matter ha⁻¹ year⁻¹. In the event of a dry year, cynara can overcome long-lasting drought periods

provided it is well established but in this case the biomass production is low in that year. The crop produce is partitioned into 37 % basal leaves, 11 % cauline leaves, 21 % stem (stalk+branches) and 31% heads, on average. Heads weighing > 22 g contained nearly 28% seeds (w/w) containing 25% oil on average. The cultivation design in rows 0.8 cm apart gives more productivity (dry matter per ha) than the design in paired rows (two rows out of four). Soil conditions as narrow soil depth, skeletal particle size class or the presence of limestone have been revealed limiting to cynara. In these conditions the biomass production may be reduced by 60%. It was revealed that the effect of the rainfall on the cynara productivity interacts with the effect of the soil conditions.

The reference for the elaboration of the energy balance and the crop costs was the standard protocol of cynara cultivation with the assumption of: 15 year crop duration, 14.7 t fm/ha (13.8% moisture content) biomass yield and 14.59 GJ/t fm low heating value of the harvestable biomass. Values needed for the energy balance and the estimation of the crop costs as spent coefficients, energy coefficients, manpower and costs of agricultural practices and materials, which are site-dependent, referred the conditions of central Spain and should not be extrapolated. According to the estimations of this work the Net Energy Output (=Total output-Inputs) of the cynara energy crop would be equivalent to 4.77 toe/ha, with an Energy Efficiency (=Output/Input) of 17.0. The cost of the cynara biomass (2008 values) was estimated at 59.7 €/t in terms of harvestable biomass weight; if expressed on energy content, 4.1 €/GJ; both figures for average conditions of Spain.

Task 1.3. Selection of adequate machinery for mowing and baling the whole biomass

The mechanization of the energy crops is a key issue to achieve their penetration into the agricultural sector, particularly in the case of recently-developed energy crops. The options to tackle this problem are basically two: the use/adaptation of machinery already available and the design/manufacture of a harvester ad hoc. The former was the one studied under the Task 1.3 of Biocard.

A screening of machinery available around the reference cynara plantation was performed for mowing and baling the crop produce. Manufacturers of agricultural machinery and farmers were the target.

Results of this task shaped the profile of conventional machinery that could be used for the harvest of cynara when the whole biomass is wanted. Drum mowers and baling with either round-balers or square balers performed reasonably well. Mowing by means of a Kemper-like head is possible but the annexed chopping device is needed to prevent clogging. Involvement of machinery manufacturers and farmers was kept.



Fig 4. Tests of baling of whole biomass with the collaboration of farmers.

Task 1.4. Development of adequate machinery for bales unpacking and separation of the seeds from the lignocellulosic biomass in static conditions

The Technical Annex of the Project stated that the overall objective was to give out different ways of exploitation of cynara for energy purposes. In this respect, Task 1.4 was planned to work out one of the different strategies of exploitation of the cynara biomass. The crop produce is made up of different biomass fractions; the nature of the stalks, branches, leaves and most parts of the heads are lignocellulosic and can be directly used as solid biofuel. Additionally the quality of some of these fractions is compatible with paper pulping. On the other hand the achenes (dry fruits commonly known as 'seeds') are rich in oil and can be picked up for oil and biodiesel. Therefore, a new challenge came out: the development of different mechanization solutions for the harvest.

Two strategies were envisaged: i) Whole biomass harvest and whole biomass use ii) whole biomass harvest followed by a further fractionation in a treatment facility, iii) separate harvest of achenes and lignocellulosic biomass. From the point of view of the machinery, the first one is the cheapest option but it does not mean an improvement in the valorization of the biomass. The other two options imply the development of ad hoc machinery; in one case the development of a facility and in the other the development of a harvester. Task 1.4. faced the former and Task 1.5 the latter.

Specific objective of Task 1.4. was to develop a static prototype for fractioning whole biomass of cynara. The starting point of this Task was that the harvest operation should be a short-time-consuming operation at the field and that the biomass would be harvested in the form of round bales of whole biomass. Then, the bales would be transported to the fractionation facility where they would be unpacked and fractionated into valuable biomass fractions.

The approach used for this Task covered the areas of conceptual design of the prototype, draft development of working units, implementation and adaptation of components, assembling of units, tests of performance and project engineering.

End result of this Task was Deliverable 1.2 & 1.4 '*Project of a separative static plant' prototype*' and the physical development of the prototype. In essence, the prototype consists of four units: i) a round-bale-unpacking unit, i) a feeding system endowed with a conveyor belt unit iii) separation unit of stems and achenes endowed with a set of counter-rotating rollers, brushes, screens, hopper, pulleys, engines and chains, and iv) a separation unit of the

lightest biomass fractions, floral hairs (paleas and pappus) by means of air flow. The system separates first the stalks from the rest of the biomass; then the heads are threshed so that the achenes are separated with the help of motile screens. On the whole, the system permits to gather four different fractions: stems, achenes, hairs, and other biomass remains (pulverized leaves, capitulum bracts, and others) that can be valorized as required and according to their composition. The oil achenes would be directed to a seed screw press to obtain oil and so, to use it for either dietary or energy purposes and the lignocellulosic fraction would be directed to a solid biofuel facility. Additionally this type of fractionation permits the use of several components of the biomass (stems and/or hairs) for paper pulping.

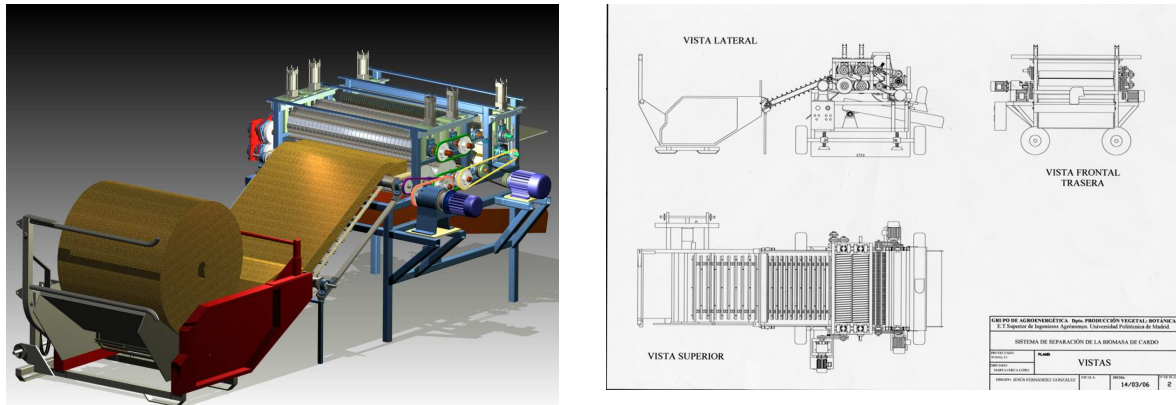


Fig 5. Static prototype for cynara fractionation. Left: Conceptual design. Right: Engineering project.

Task 1.5 Development of specific separative machinery for harvesting: Cynara harvester prototypes

Two prototypes were designed and built. The first machine project aimed at “teasing” the area where the capitula are present. As they are in the same plant at different heights and the plants do have different heights, a harvest system with a fixed mower will provoke the loss of the low capitula and the harvest of the higher ones with a considerable portion of stalk.

The suggested system allowed the introduction of points (teeth of comb) among the heads, the traction towards the soil of the stalk also through a rotating roll, the removal of possible residues of the stalk by a mowing lever, and the conveyance towards a wagon through a belt conveyor.

The points were composed by a series of shaped sheets, about 30 mm away one from each other, under which a mowing lever and a toothed roll acted, and overhung by a pickup reel.

At the back, a belt conveyor, pliable during the transportation, permitted the discharge of the product on a wagon. During the tests the prototype was put on the front lifter of a tractor, equipped with a hydraulic circuit connected to the tractor for the operating parts power needs.

The machine operated the detachments of the capitula by a simple traction (from previous field tests the necessary strength was found to be about 220N). The mower cut those plants on which the detachment had not taken place, helped by the rotating roll that operated the downward traction on the stalk.

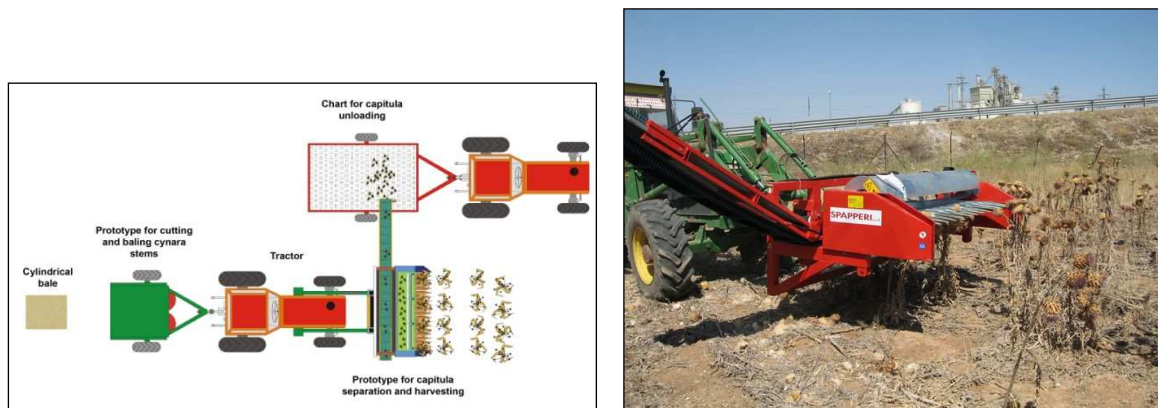


Fig 6. Left: 2006 project concept. Right: 2006 prototype.

The second project concept was a combine head which includes the upper devices of a maize head and a classic wheat head (without the paddle wheel) in the lower part, to obtain capitula detachment and effective threshing and, at the same time, the stalk cut.

The combine harvester fitted with the head prototype is able to separate the seed with good accuracy, cut the stalk in an appropriate height range, collecting the lignocellulosic fraction in the space between the combine wheels, where the discharge system of the threshing device would then provide to drop the remains of the capitula threshing. The biomass fraction will be picked up by a baling machine.

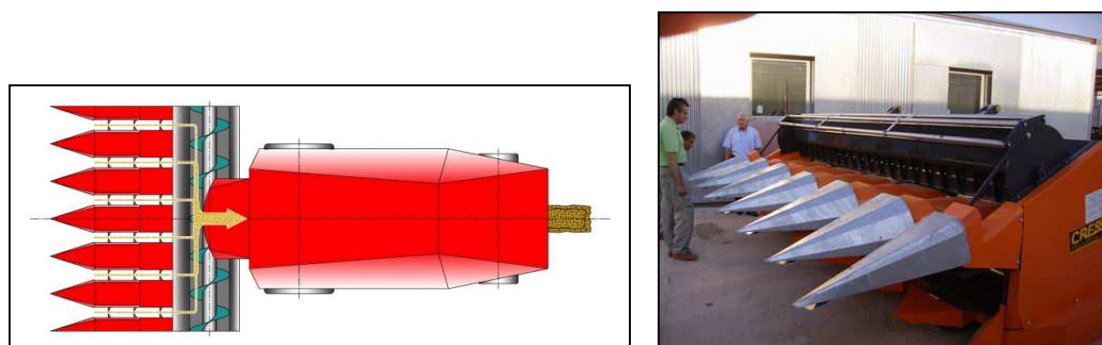


Fig 7. Left: Project concept. Right: View of the Cynara head

Second prototype technical characteristics

- The overall dimensions of the head are:
 - width: 4940 mm
 - height: 1731 mm
 - length: 2770 mm
- The head is built for six rows; the distance between dividers is 800 mm. The gap between dividers is 131 mm.
- To move the capitula towards the threshing device inlet (1280 mm width), there are an Archimedean screw, 4516 mm long, with a diameter of 370 mm, rotating at 144 rpm, and a rotating paddle wheel, 4590 mm long, with a diameter of 600 mm, rotating at 50 rpm.

- The squeezing rolls, two for each row, are slightly tilted forward: the roll has five knives, for a better pre-cut and conditioning. The diameter is 110 mm, the length is 460 mm. The rotation speed is 954 rpm, with a linear tip speed of 5.5 m/s.
- About 115 mm under the front end of the squeezing rolls there are rotating cutting blades, whose overall length is 534 mm. The rotation speed is 2084 rpm.
- The lower part, as well as the upper, is for a six row cultivation; again the distance between dividers is 800 mm.
- Aligned with the gap between dividers, 450 mm below the rotating blades, there is the mowing device, with 644 cut per minute; the gap between lower dividers is 100 mm.
- The biomass is moved towards the dropping slot (1280 mm width) by a second Archimedean screw, 4560 mm long, with a diameter of 445 mm, rotating at 130 rpm.
- Tilting of the head is achieved by means of a double screw mechanical system.
- The mechanical power is supplied by the combine through two Hooke's joints (one per side), the hydraulic power through a hydraulic quick coupler (single location).

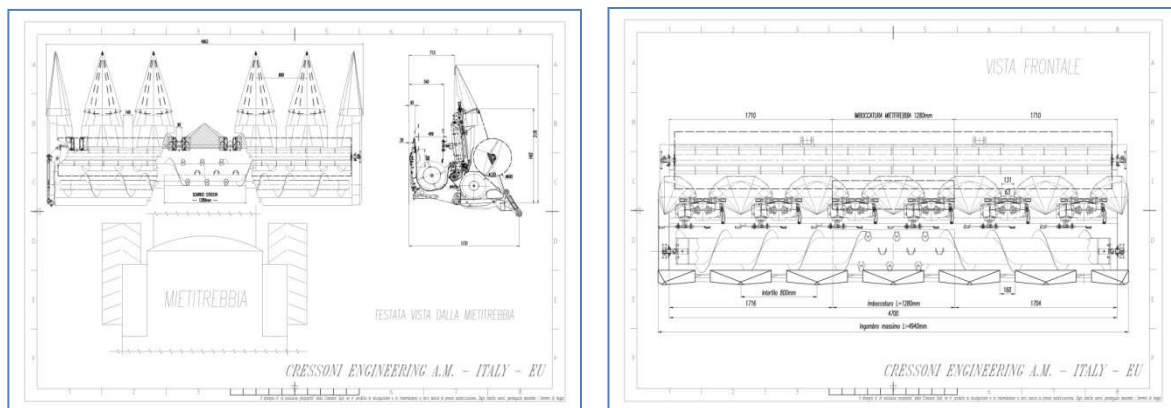


Fig 8. Left: Top view of the Cynara head. Right: Front view of the Cynara head.

Task 1.6 Low cost cynara pre-treatment

This task focused on the stage of the bioenergy chain that mediates between the stages of feedstock production and energy use. Co-firing biomass in coal fired boilers has progressed from engineering concepts and parametric testing to demonstrations. It is the most promising near term method of increasing the use of biofuels in electricity generation. Biomass co-firing is a low capital cost application that permits the introduction of fuels such as wood waste, energy crops and other forestry and agricultural residues into high efficiency boilers.

In the case of the energy crops, the biomass is harvested and delivered by the farmer in a rough presentation, generally in the form of round bales or chopped material. For the purpose of co-firing the biomass size particle has to be reduced by means of a convenient pre-treatment. Required particle size for co-firing applications depends mainly on the combustion technology, type of biomass and residence time of particles in the boiler. Previous co-firing experiences have operated in a range of 2-6 mm particle sizes and biomass percentages lower than 10% in energy basis. Within these ranges and biomass moisture contents lower than 10% in average, biomass co-firing does not generate relevant impacts to the boiler. In addition, pelletizing is another way to improve the market penetration of Cynara biomass, which requires further particle size reduction. Within Task 1.6 tests of

cynara biomass pre-treatment were conducted to determine the milling and handling behavior of the final biomass material.

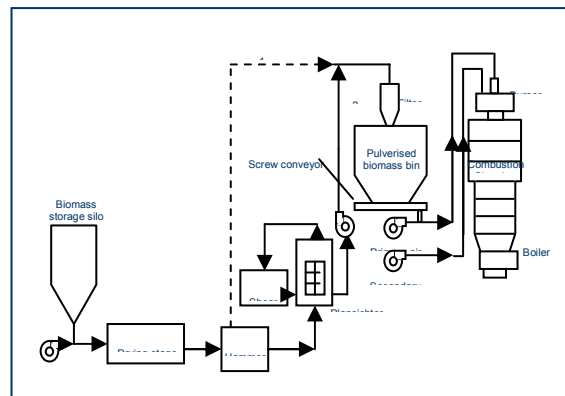


Fig 9. Pre-treatment line of biomass

The results showed that the specific electrical energy for the milling process ranged between 10-40 kWh/t. Large differences were found between the results of the tests. The stems were the most difficult fraction to mill. These differences were more remarkable for milling to target diameters < 2 mm. The milling process caused a reduction of the sample moisture where that reduction depended mainly on the feeding flow-rate and the initial moisture. The higher the initial moisture, the bigger the moisture decrease in the milling tests. Therefore, as the moisture content of the cynara biomass is low, it would not be necessary to add a drying stage. The results of granulometry of pelletized biomass showed the highest fine particle content. This fact makes that, for this material, a bigger sieve diameter could be used in the milling chamber which would diminish the electrical consumption for this material. The soil contamination detected in pellets analyses could be another reason of the fine particle content obtained at milling. When milling material to a target diameter between 2 and 1 mm, a low consumption was obtained. This result was due to the milling configuration used. With that configuration, it was prioritized the recirculation of the rough part of the material to reach the maximum particle size considered over the production of too small material. Finally the tests showed that when a small target diameter is required, an adequate option is to mill with a mill sieve of higher size than the target diameter and re-circulate the coarse fraction obtained in the classifier to the mill. Lower electric consumptions were obtained in such tests.

Task 1.7 Cynara logistics analysis

A tool to optimize biomass transportation logistics was made. The aim was to find the cheapest logistic solution to feed both the Endesa power plant based in Los Barrios – Cadiz (Project partner) with cynara lignocellulosic biomass and to transport the seed production in biodiesel esterification plants to feed MAN engines (Project partner). The considered area is that of a circle with a 100 km radius, around Cadiz (Spain), encompassing 89 Communes.

To take into account the impact of the transportation cost depending of the road type and the mean of transportation, the local road network was included.

The application, based on ArcGIS v9.2 software, was developed with Visual Basic for Application. The following steps were performed to obtain the final result:

- **Cartographic data acquisition and processing.** At an early stage, the necessary cartography was acquired and processed to isolate the area around Cadiz. Then a road network database and an mdb with numerical input were prepared.
- **SW_Cadiz.mxd tool development.** The second step involved the development of the tool to simulate the transportation logistics in the area around Cadiz. The add-on modules allow the users to:
 - choose the final product: a) biodiesel b) electrical energy
 - choose between: a) biomass b) seeds c) whole plant
 - choose the transportation mean
 - choose the case between: a) CASE I: 50% of fallow land, b) CASE II: 50% of fallow land + 10% of current Herbaceous crops c) CASE III: 50% of fallow land + 30% of current Herbaceous crops, d)CASE IV: 100% of fallow land + 30% of current Herbaceous crops
 - choose a set of Communes in the area
- The computation was carried out according the following formulas:

$$\text{Costocs} = \text{CostoRac} \cdot \text{Ton} + \sum_i (K_i \cdot S \cdot \text{Dist}(i-S)) \cdot \text{Ton}$$

$$\text{Costotot_cs} = (\sum_i (\text{CostoRaci} \cdot \text{Toni} + \sum_i (K_i \cdot S \cdot \text{Dist}(i-S)) \cdot \text{Toni})) / \sum_i \text{Toni} + (K_S \cdot PP \cdot \text{Dist}(S-PP))$$

Costocs: total cost at a generic stocking centre (€/t)

Costotot_cs: total cost at the power plant of the product coming from the stocking centre S (€/t)

CostoRaci: generic harvesting cost per tonne (€/t)

Toni: Commune “i” production (t)

Ki-j: cost per kilometre and per tonne for the considered length i-j (€/km·t)

Dist(i-j): distance between network nodes i and j (km)

KS-PP: cost per kilometre and per tonne for the considered length stocking centre-power plant (€/km·t)

Dist(S-PP): distance between stocking centre and power plant (km)

The final cost (€/t) is the summation of the total cost at the chosen stocking centre and the transportation cost of the total collected product from the stocking centre to the power plant.

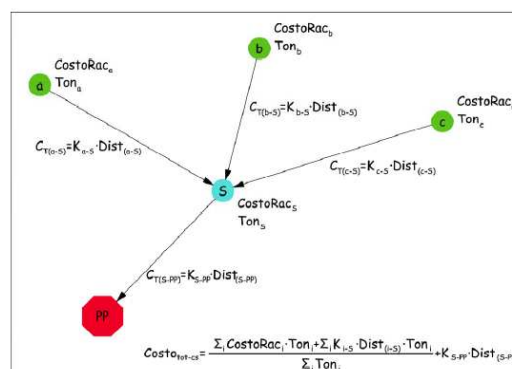


Fig 10. Layout of transport costs

1.1.3 Impact on the industry or research sector

Since the very beginning of the Project, the Tasks in WP1 entailed activities addressed to the agrarian sector, agronomists, industries of agricultural machinery, end-users and research teams. Direct and indirect contacts, calls, collaborative actions, demonstration activities, seminars, workshops, technical fairs, international conferences and scientific journals were the means of broadcasting the progress of the work in WP1.

Some indices of the impact of WP1 are the following:

- Collaborative actions established with two research institutes: IMIDRA (research institute of Spain) and AFLOPS (research institute of Portugal)
- Collaborative actions with the agrarian sector: one agrarian agency of Spain (DAP, agrarian agency of the Andalusia region), local farmers (cynara plantations) and local workshops of agricultural machinery (Fontanar)
- Involvement of large and medium size machinery firms: New Holland, Cressoni Engineering SA.
- Know-how transfer to farmers and investors by direct consultancy regarding the cynara cultivation for biomass purposes
- Participation in six dedicated international fairs (FIMA, Saragossa 2006; EIMA, Bologna 2005, IPACK-IMA, Milano 2006) and biomass exhibitions (Paris 2005, Berlin 2007, Valencia 2008)
- Two articles in scientific journals (1 published + 1 submitted)
- Six articles published in proceedings of international conferences (Berlin-Germany 2007, Antalya-Turkey 2008, Jonkoping-Sweden 2008, Valencia-Spain 2008)
- Three articles in technical magazines (Agrotecnica, 2007 and 2008, Tecnica 2007)
- Dissemination activities addressed to end-users (technical workshop in Rome 2007), university and local authorities (inauguration of pre-treatment facilities), students (pre-graduated students, post-graduated students, Master students, high school students)

1.2 BIOMASS VALORISATION FOR ENERGY CONVERSION

1.2.1 Description of project objectives

This section summarizes the work performed in Work Package 2 under BIOCARD project. Work package 2 was focused in the biomass valorization for energy conversion. The objective of the work package was to demonstrate the technical feasibility of the use of *Cynara cardunculus* for co-firing with coal in fossil power plants, analyzing different technical configurations for using this fuel as a substitute of a percentage of coal, and to determine the most efficient method for biomass combustion. For this purpose, three different technologies for biomass energy conversion were selected for research and comparison:

- Co-combustion in fluidized beds.
- Co-combustion of pulverized fuel in swirl burners.
- Combustion in grate-fired boilers.

Research activities were focused on the analysis and evaluation of combustion efficiency, deposition and corrosion problems from the use of *cynara* biomass in the different combustion technologies. Moreover, feasibility studies of *Cynara* combustion at full scale coal power plant by means of Computational Fluid Dynamics (CFD) simulations were carried out, in order to analyze the problems for adapting the existing power plants to the secondary fuel. Performed tests will serve to the energy industry sector, by providing useful information for co-firing coal and *Cynara* at full-scale power plants.

Activities under WP2 were divided into three different tasks:

- Task 2.1 studied the characteristics and quality of biomass as fuel, which may vary widely influencing the combustion process and the suitable combustion technology. Different analyses were used for characterizing fuels for combustion applications. Relevant characteristics analyzed were particle size, moisture, ash and volatile content and High Heating Value (HHV), as well as advanced analytical techniques (Scanning Electron Microscopy SEM/EDS, chemical fractionation, among others).
- Task 2.2 dealt with performing experimental energy conversion tests and analyses of operating problems. The presence of high amount of alkalis in biomass ashes is frequently related to slagging and fouling problems in furnaces. CIRCE, VTT and DTU performed combustion tests with some *Cynara* and *Cynara*-coal blends.
- Finally, task 2.3 was based on studying the co-combustion process of coal and *cynara* in an existing PF power plant by a set of CFD simulations.

1.2.2 Work performed and end results

Task 2.1 Preliminary combustion analysis

CIRCE, DTU, VTT and ENDESA were involved in some experiments to determine the relevant properties to use *cynara* as fuel in thermal conversion applications such as ultimate and proximate analysis, tests in Laminar Flow Reactor (LFR), SEM/EDS, ash analysis, and thermogravimetric analysis.

Primary characterization

Results of the proximate, ultimate and heating values are shown in Table 1 for Cynara samples. Since Cynara is harvested in summer, moisture content is quite low in all samples. Pelletized Cynara ash content is 19 % which is caused by soil contamination at harvesting. Regarding fractions, the highest ash content is located in the leaves (15.1% in weight). Volatile matter content is high in every fraction analyzed (70-80 w. %). The ultimate analysis shows the highest chlorine content in leaves compared to other fractions. Nevertheless, the weight percentage is even higher in the pelletized Cynara sample. The reason is that most of the chlorine present in this type of crops comes from fertilizers, and depending on the harvest method, this factor may vary. Heating values are similar among fractions, being lower for the case of pelletized Cynara, again caused by the soil contamination.

Table 1. Cynara primary characterization results

	Pellets	Leaves	Stems	Capitula
Moisture (as received, %w.b.)	12.4	10.6	10.1	9.6
Ash (550°C)	19.0	15.1	5.1	6.7
Proximate (% d.b.)				
Volatile matter	63.8	71.2	75.6	77.7
Fixed Carbon	17.2	13.7	19.3	15.6
C	39.4	42.7	45.4	44.5
H	4.70	5.60	6.30	6.00
Ultimate (% d.a.f.)				
N	0.98	1.79	0.99	1.45
S	0.16	0.26	0.07	0.12
Cl	1.76	1.73	1.28	0.47
HV (MJ/kg)				
HHV (d.b.)	15.57	17.5	17.8	17.9
LHV (d.b.)	14.54	16.4	16.5	16.6

LFR tests

Cynara stems of 0.3-0.4 mm particle size were used for LFR tests. The fraction above 400 µm (38% in mass) was mainly composed of a whitish down (27% of the total in mass), corresponding to the centre of the stem, accompanied by large particles of straw (11%). the fraction 300-400 µm represented 5% of the total, and had the appearance of straw of different lengths (the lowest diameter is that one limited by the sieve and therefore shows low variations). Finally, 57% of the Cynara mass was in the finest fraction (<300 µm), with a more granular and compact appearance.

Cynara represents a heterogeneous composition, both because of the morphology of the product (difference between the different parts of the stem etc.) and because of the chemical composition (as shown in the thermo gravimetric analysis).

Table 3 shows the highest devolatilization kinetic parameters found. The volatile content of the fuel derived from the tests in realistic conditions (especially regarding final temperature and speed of particle heating) is approximately 86%, expressed in terms of UT. Table 2 summarizes the oxidation kinetic parameters of Cynara char (including the assumed reaction order, 1, and the average value α , that determine the development of the diameter of particles in combustion).

Table 2. Kinetic oxidation parameters of Cynara char

$E_{ad}(\text{J/mol})$	$k_d(\text{s}^{-1})$
11000	47.17

Table 3. Kinetic devolatilization parameters of Cynara

Order of reaction	$E_{a_{opt}} \quad (\text{J/mol})$	$k_{c_{opt}} \quad (\text{kg/m}^2 \cdot \text{s} \cdot \text{Pa})$	a
n = 1	63000	0.000457	0

Approximately 90% of the nitrogen contained in the Cynara particles was released in the devolatilization tests. The chemical analysis of samples collected throughout this process and the following oxidation indicate a release similar to the consumption of carbon, being slightly quicker in the first stages.

The importance has been shown of a correct drying model for the Cynara particles for the case of “big” particles; similarly this has thrown into relief the need to take into account, for its use in large-scale combustion installations, the relative velocity of the particle with respect to the gas surrounding it, and how that affects the combustion curves.

Scanning Electron Microscopy combined with Energy Dispersive Spectroscopy analysis (SEM/EDS)

SEM images of ashed and fresh samples from Cynara leaves are shown in Fig 11.

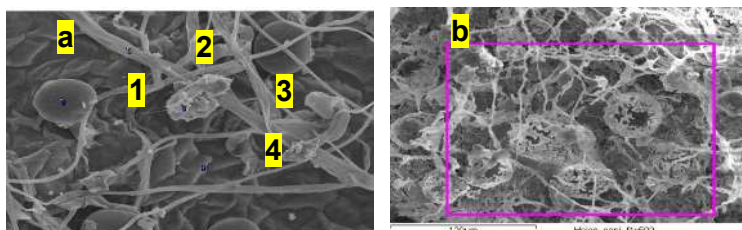


Fig 11. SEM images of a) untreated leaves (x500) b) ashed leaves (x500)

The structure of the fresh leaves (Fig 11a) differs strongly from the structure after ashing (Fig 11b), but some filaments can still be found in the latter figure. Fig 12 and Fig 13 represent the elements that are present in the samples. The most important element was Ca, although Na and Cl were also concentrated in the ash leaves, mainly as NaCl. Silicon can be present either as inherent AFM (Ash Forming Matter) introduced into the plant by absorption of silicic acid from the soil or as extraneous material probably from soil contamination. Regarding to Fig 13, relative concentrations of Al and Si in point 3 suggests their presence as aluminum silicates. In this point Fe is also found, which would come from soil components.

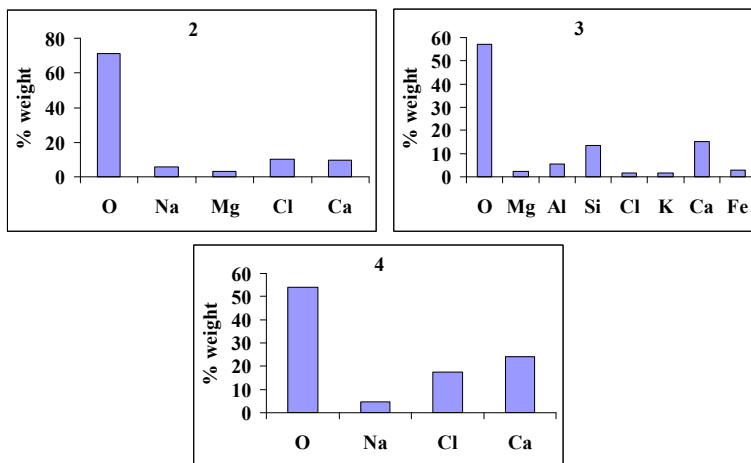


Fig 12. Qualitative weight Composition fresh leaves x500

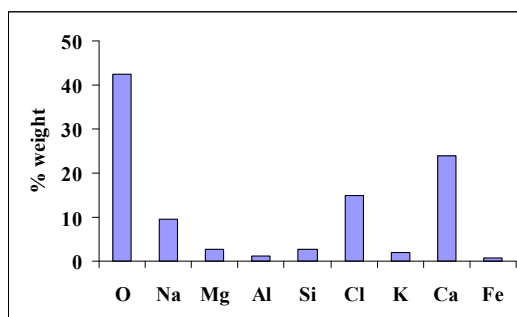


Fig 13. Qualitative Weight Composition ashed leaves x500

An optical 1000 magnification analysis was done for the ashed sample. The area considered is shown in Fig 14 and the composition regarding the area in Fig 15:

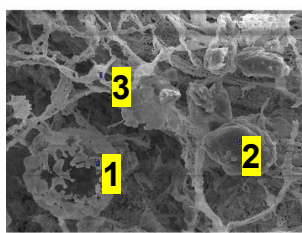


Fig 14. SEM image of ashed leaves (x1000)

Separate mineral particles were found in the ashed leaves formed mostly by Al, Si and O indicating mixing of soil and leaves during the harvesting (spot 2 in Fig 14). This finding is confirmed by Fig 15 where high variety of inorganic compounds was found. Discrete particles, mainly composed of Al and Si, were identified within the ashed leaves. They had probably incorporated into the fuel during harvesting.

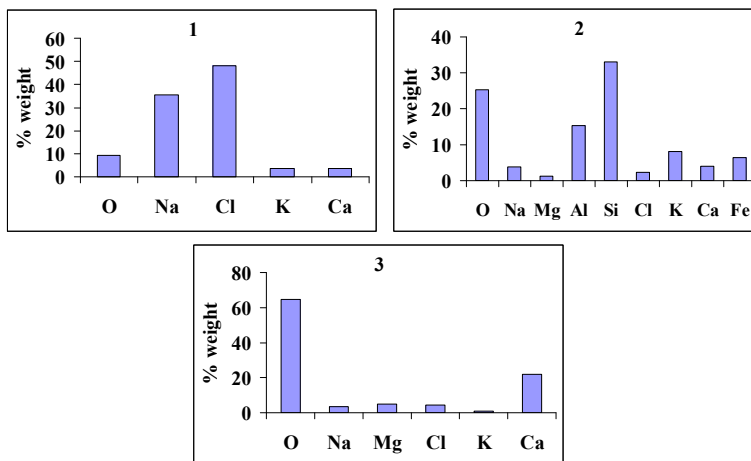


Fig 15. Qualitative weight composition ashed leaves (x1000). Points 1,2-3 of figure 4.

Further 2000x magnification analyses were done to the ashed leaves sample for comparison with the previous 1000x analysis. The photograph and elemental composition of selected points are illustrated in Fig 16 and Fig 17. Results revealed important differences in the compositions between the two spot areas of the sample. In the second point, more elements are present. This point appears to be a soil particle since Fe, Si and Ti are common elements in soil composition.

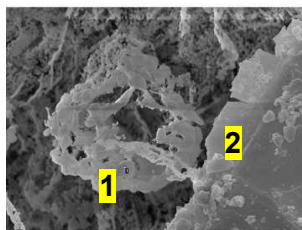


Fig 16. SEM image of ashed leaves (x2000)

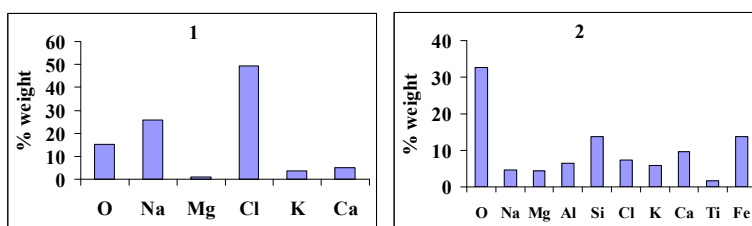


Fig 17. Qualitative weight composition ashed leaves (x2000).

Summarizing, lots of soil-originated particles were found in the ashes of different Cynara fractions. Potassium is one of the most important elements in all the samples. Cl most probably occurs as KCl within the fuel. On the other hand K appears also taking part of other compounds. Si can be present either as inherent AFM or as extraneous material probably from soil pollution. Si and Al take part of aluminosilicates molecules from soil, so does Fe or even Ti. There is an important presence of chlorine in the ashed samples. To use biomass as fuel, this component has to be studied. Regarding Cl concentration in the different parts of

cynara plants, Cl presence is more important in leaves and stem but it has to be considered in all of them as the minimum amount of this component is in receptacle samples with a 5 %.

ASH ANALYSIS

Three fractions of Cynara ashes were analyzed by this method: capitula, leaves and stem. Minerals were mostly concentrated in the leaves.

Although the conditions of the standard ash melting analyses can not strictly predict ash related problems at real combustion conditions, the low measured ash melting temperatures usually mean operational problems. Fig 18 shows the result: The ash of stem melted at very low temperature predicting severe fouling and slagging problems when combusting alone, whereas there were no problems in the ash melting properties of leaves and capitula. The maximum temperature used in the analyzer was 1450 °C. Therefore, ash melting temperatures were not found in cases they exceeded 1450 °C.

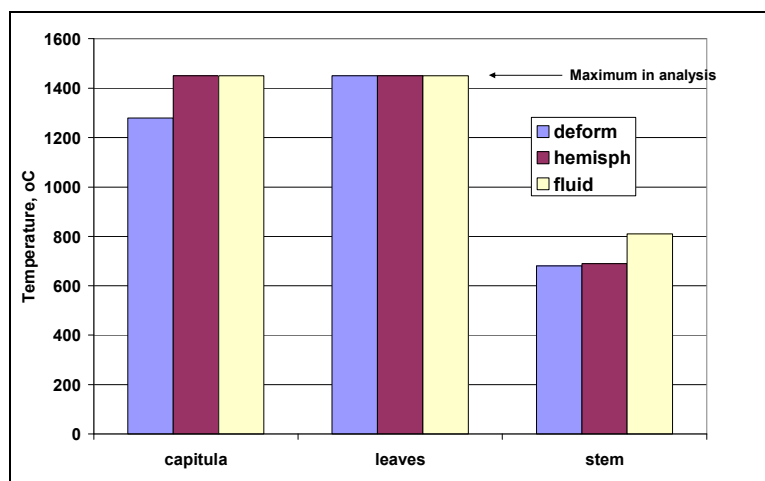


Fig 18. Ash melting temperatures for the Cynara

Because of the great difference in ash melting temperatures between stem and the other Cynara fractions, one would suppose large differences also in the compositions of these fractions. Fig 19 shows the concentrations of main ash constituents (calculated as oxides) in the ashes obtained at 550 °C. The composition of the studied ashes differs clearly. Very little sodium was present in the ash of Capitula whereas leaves and stem were rich in Na at about equal concentrations. Capitula was strongly enriched with potassium and contained about two times as much potassium as the leaves. The concentrations of so called acid oxides (Al_2O_3 , SiO_2 and P_2O_5) were very low in leaves and stem, but Capitula was enriched with phosphor. Different indexes can be calculated from the elemental composition of the ash aiming the explanation in the variations in the ash melting properties (included in deliverable 2.1). Increasing sum of alkali oxides has been suggested to decrease ash melting temperatures and increase slagging and fouling. The sum was largest with stem with very low ash melting temperature. The molar ratio of basic to acid oxide is one prediction tool because acid basic oxides tend to form low melting “salts”. The critical value is 0.4-0.7, this index was originally applied to coals, but the index is not useful in values > 1 and < 0.1 . In the case of the studied ashes the value is > 6 in all cases and very high with stem. One index mentioned in the literature is B/A multiplied by Na_2O concentration. This value is very high with stem.

To summarize, the stem ash with much lower ash melting temperature than the other Cynara fractions was most enriched with Na + K and its B/A and B/A * N₂O ratios were clearly higher than with the other ashes. Fractionation analysis might give still better explanation to the very low ash melting temperature of the Cynara stem ash.

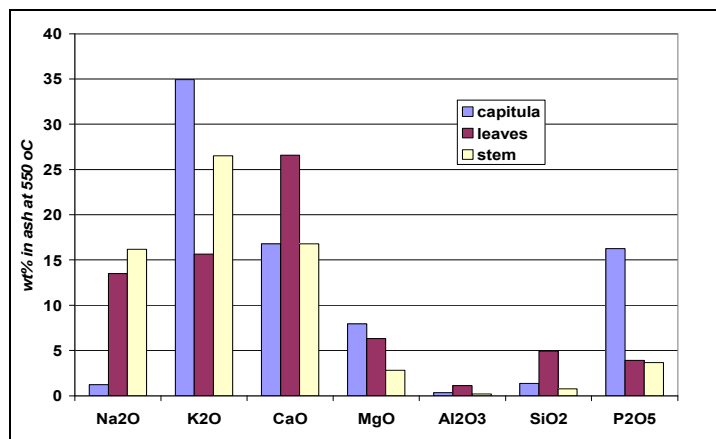


Fig 19. Concentrations of the main ash constituents in the Cynara fractions ashed at 550°C

Although some portion of sulfur and chlorine probably released from the samples during the ashing at 550 °C, concentrations of these elements in the Cynara fractions obtained through ashing and ash analysis are given in Fig 20. On the basis of this analysis the main source of Cl is leaves. Capitula contained only one fifth of the Cl concentration in leaves. The obtained Cl concentrations can be nearly correct if almost all Cl is present in inorganic components, because they vaporize at higher temperature than the ashing temperature used. Instead, largest part of the possible organic Cl compounds would vaporize at the ashing temperature.

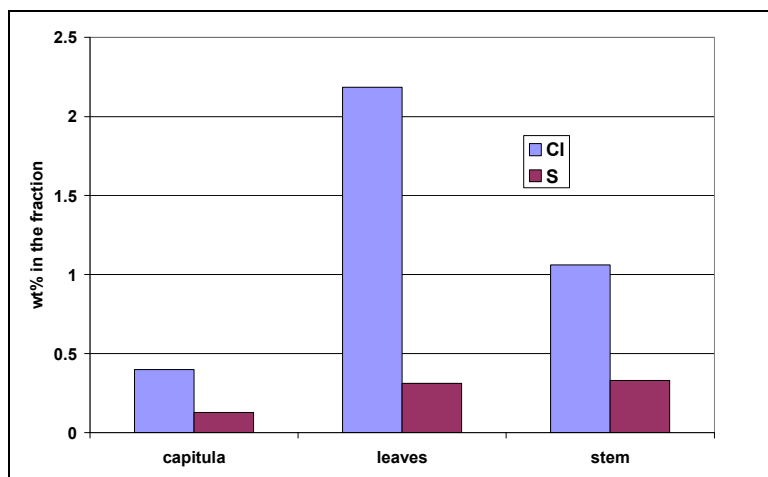


Fig 20. Cl concentrations of the Cynara fractions obtained from ashes at 550°C and calculated back to concentrations in the dry fractions

Inorganic elements Analysis

The elements in this sample (2007 harvest) were measured using Inductively Coupled Plasma Spectroscopy (ICP-OES) techniques. The most abundant elements in the Cynara 2007 sample are K (1.7 %), Cl (1.7 %) and Ca (1.2 %), followed by Si (0.7 %). When comparing with the results from the fractionated samples from 2006 harvest it is seen that the concentration of the various elements in the 2007 sample generally is similar to, or slightly higher, than the concentrations found in the fractions Stems, Capitula and Crushed Cynara, whereas, on the other hand, it is generally lower than in the Leaves fraction. These results seem to reflect the fact that the 2007 sample is unfractionated (containing the whole plant – i.e. all stems, leaves and capitula) and consequently it may have a composition that is similar to a combination of the different 2006 fractions. However the concentration of Si in the 2007 sample is still higher than in any fraction from the 2006 harvest (maybe due to a higher degree of soil contamination).

Fig 21 shows the chemical fractionation analysis of the Cynara 2007 sample, according to the 4-step leaching procedure described previously. Fig 22 summarizes some of the previous results of chemical fractionation analysis on Cynara 2006 samples, for comparison.

The chemical fractionation analysis of the Cynara 2007 sample reveals a similar distribution as in the previously analyzed samples: K, Cl and Na is highly mobile, with > 80 % leached in the first step (H₂O), indicating a high potential risk of these risky elements during combustion.

The ash content at 550 °C and 815 °C is approximately 8.7 % and 6.9 %, respectively, in the Cynara 2007 sample. This is substantial higher than the ash content found in the fractions Stems, Capitula and CRU, but lower than in the Leaves fraction. Again, this may reflect that the 2007 sample is unfractionated, (thus containing all stems, leaves and capitula).

When analyzing inorganic elements in ash samples, the element present in the highest concentration (% w/w, ash basis) in ash from Cynara 2007 harvest is K, followed by Ca, Cl, Si and Na. The trends are similar to the results from the fractionated (2006) samples, although it is noted that the relative content of Cl and Si is higher in the 2007 samples as compared to any of the 2006 fractions.

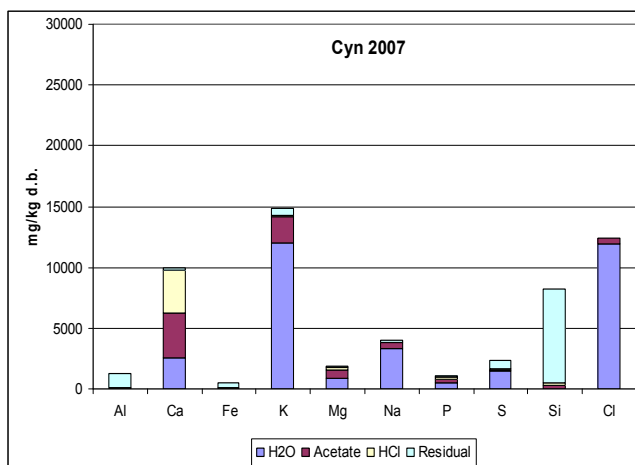


Fig 21. Chemical fractionation of Cynara 2007 sample

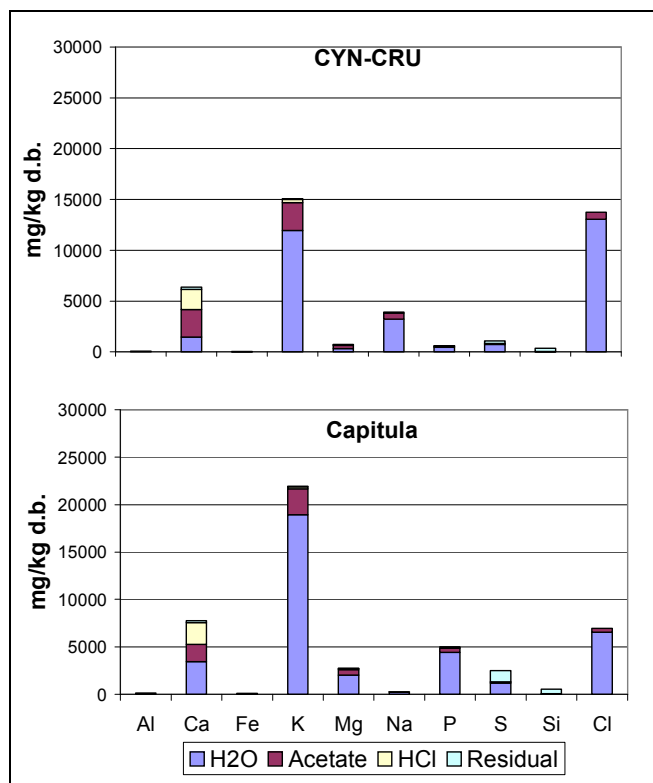


Fig 22. Chemical fractionation of Cynara fractions from 2006 harvest. Crushed Cynara and Capitula.

TGA analyses

Pyrolysis and combustion tests were done to selected cynara samples in order to evaluate devolatilization and combustion processes. Table 4 shows the test matrix. In combustion tests, a maximum temperature of 1000 °C was maintained during 30 min to assure complete combustion of the sample. Pyrolysis tests were performed at different heating rates, particle diameters and final reached temperature; maintaining a 100% N₂ composition in the flue gases.

Table 4. TGA test matrix

Test	Fuel type	O ₂ (%)	Particle size (100%<D _p), μm	Heating rate (°C/min)	Final T (°C)
1	Crushed Cynara	21	150	10	1000
2	Capitula				
3	Stem				
4	Filaments				
5	Leaves				
6	Crushed Cynara	0	150	10	1000
7	Capitula				
8	Stem				
9	Filaments				
10	Leaves				
11	Crushed Cynara (2007 Harvest)	0	500	5	800
12				10	
13				20	
14				30	
15				1000	

Results of selected TGA experiments from the set 1-10 are shown in Fig 23, where DTG (differential thermogravimetric) curves are represented for pyrolysis tests. Similar behavior can be observed for all the Cynara fractions analyzed. It is shown that there is one main zone of weight loss, due to volatile matter content.

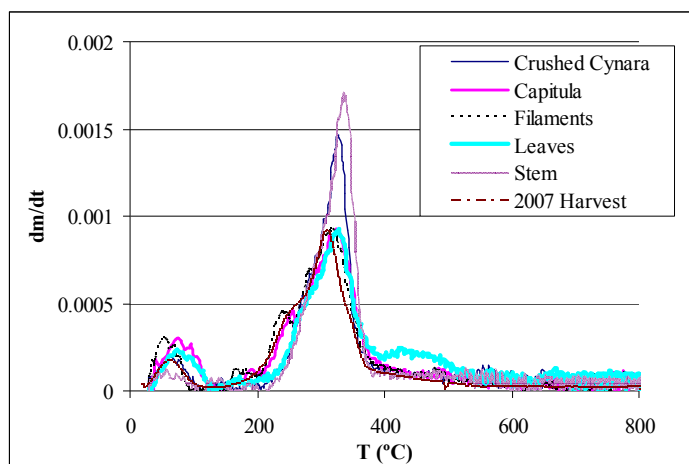


Fig 23. DTG pyrolysis results

On the other hand, combustion results show three main zones of mass loss, see Fig 24. The first peak may be due to moisture loss ($T < 100^\circ\text{C}$), the main one to cellulose decomposition ($T < 400^\circ\text{C}$) and the third one to hemicellulose thermal decomposition ($T > 400^\circ\text{C}$). Coal usually present only one peak at higher temperatures than the second in this thermogram. On the other hand, no clear peak can be detected due to thermal decomposition of lignin. This is because the lignin decomposition occurs over a very broad temperature range.

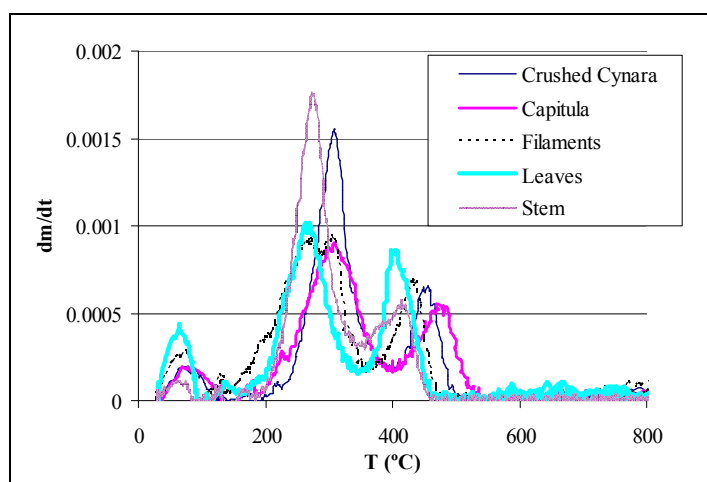


Fig 24. DTG combustion results

Regarding the differences among the different Cynara fractions, it can be mentioned that crushed Cynara and Cynara capitula have a similar behavior. Both the pyrolysis and

combustion curves show similar trends until temperatures of 350 and 400 °C are achieved, respectively. This fact is surprising, as the composition of both samples is not the same, i.e. 2006 harvest crushed Cynara is mainly composed of Cynara stem. It needs additional research. The higher slope of the curve is the higher is the volatile content of the biomass. Table 1 shows that stem is the fraction with the lowest ash content. This fact can be detected also in Fig 24 as the weight reached at the higher temperature is lower than in the other samples. This ash content is important as it can affect the char combustion stage.

Task 2.2 Experimental energy conversion tests and analysis of operating problems

Co-combustion tests in fluidized bed

Co-combustion tests of Cynara with selected coals were performed at fluidized bed combustion conditions in order to find out the possible risks and give solution concepts to these risks.

The combustion experiments were conducted in a 20 kW FB reactor (Fig 25) with blends of Cynara- Spanish coal and Cynara- South African coal. VTT co-operated with CIRCE in handling and publishing these results. Advanced analytics were used for the analysis of fuel, flue gases, finest fly ash and deposits. Use of impactors to share the finest fly ash particles to detailed analysis required an advanced sampling method to minimize changes in the flue gas and in the fine fly ash particles in the sampling line. Deposits were collected on well-controlled probes and were analyzed at several locations by SED EDS.

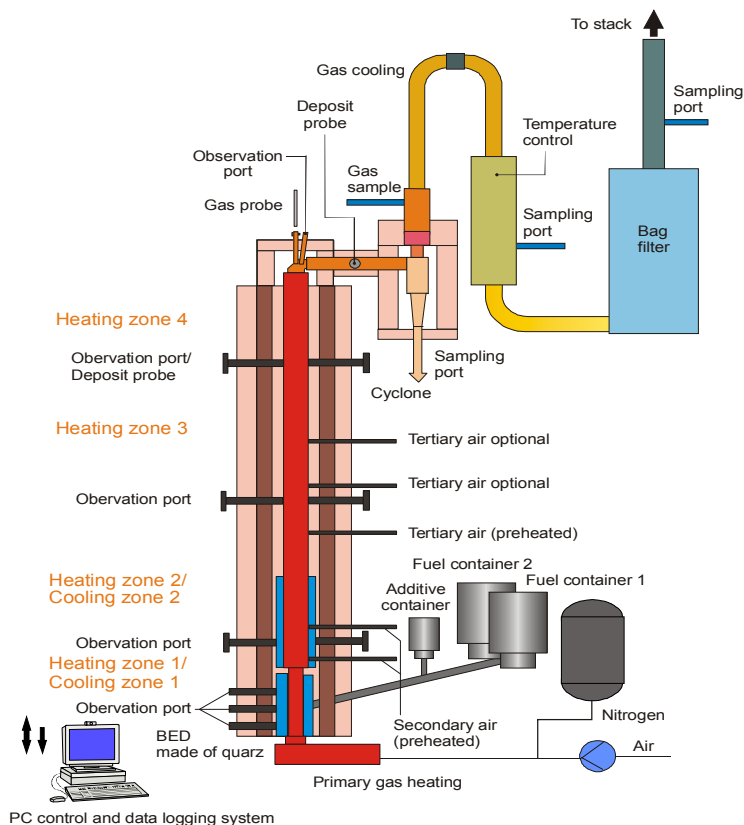


Fig 25. Schematic diagram of the 20 kW FB reactor

The Cynara sample of this study (CYN) had high chlorine and alkali contents. When burned alone, the deposition of alkali chlorides would strongly damage superheaters through high temperature corrosion if the steam values exceed 420 °C. The coals in co-combustion were sulfur rich Spanish coal (SPA) and aluminum silicate rich South African coal (SAC).

Alkali chlorides were destroyed during all combustion tests of CYN-SPA blends with CYN percentages up to 30% on energy basis. We suggest that sulfation strongly dominated over alkali aluminum silicate formation as alkali capture mechanism. SPA is very rich in pyrite (FeS₂), which easily decomposes to SO₂ in oxidizing atmosphere, producing SO₂ concentrations close to 16000 mg/Nm³. A significant quantity of this high-SO₂ gas probably oxidized to SO₃, effectively sulfating the alkali chlorides in the flue gases. With CYN-SAC blends, autocapture of SO₂ with the reactive calcium in CYN was effective, and SO₂ concentrations measured for the CYN-SAC blends were two magnitudes lower than the SO₂ concentrations measured for the CYN-SPA blends. We suggest therefore, that the alkali capture with SAC blends is based not on sulfation but on alkali aluminum silicate formation. In case of the 20CYN-SAC this mechanism was effective, but its protective power was insufficient at higher CYN percentages.

The results presented suggest that FB co-combustion of Cynara in small portions (up to 10% on energy basis) with SAC coal is safe. On the other hand, it is difficult to find higher portions of Cynara than this limit value to large power plants because of restrictions of production and transporting logistics. At this portion, SO₂ emissions are low and there should be no need for limestone addition, and HCl emissions would be less than 400 mg/Nm³. At present, there are no limits on HCl emissions from coal-biomass fired power plants, and a traditional ESP would be sufficient for flue gas cleaning.

The very high concentrations of SO₂ produced during combustion of high portions of Spanish coal need to be captured by limestone in the flue gas line after the superheaters. Addition of limestone to the furnace would lead to strong reduction in SO₂ concentration, and probably result in Cl deposition. Binding of about 16000 mg SO₂/Nm³ requires high mass flows of limestone.

The problem how to burn 100% Cynara in power plants can be solved a) with low vapor temperatures which lead to low efficiency of electricity production which is not the best way or (b) to test in pilot scale and then utilize additives destroying the corrosive compounds before entering to the superheater area (c) to use very expensive superheater material and different construction and location of the superheaters compared to a traditional furnace construction.

Co-combustion tests of pulverized fuel in swirl burners.

CIRCE performed some tests in a pulverized fuel combustor using South African Coal and Spanish Coal co-fired with cynara. A 500 kWt premixed multifuel burner, on top of a cylindrical combustion chamber vertically arranged is used for the research. Fig 26 shows the layout of the combustion test rig.

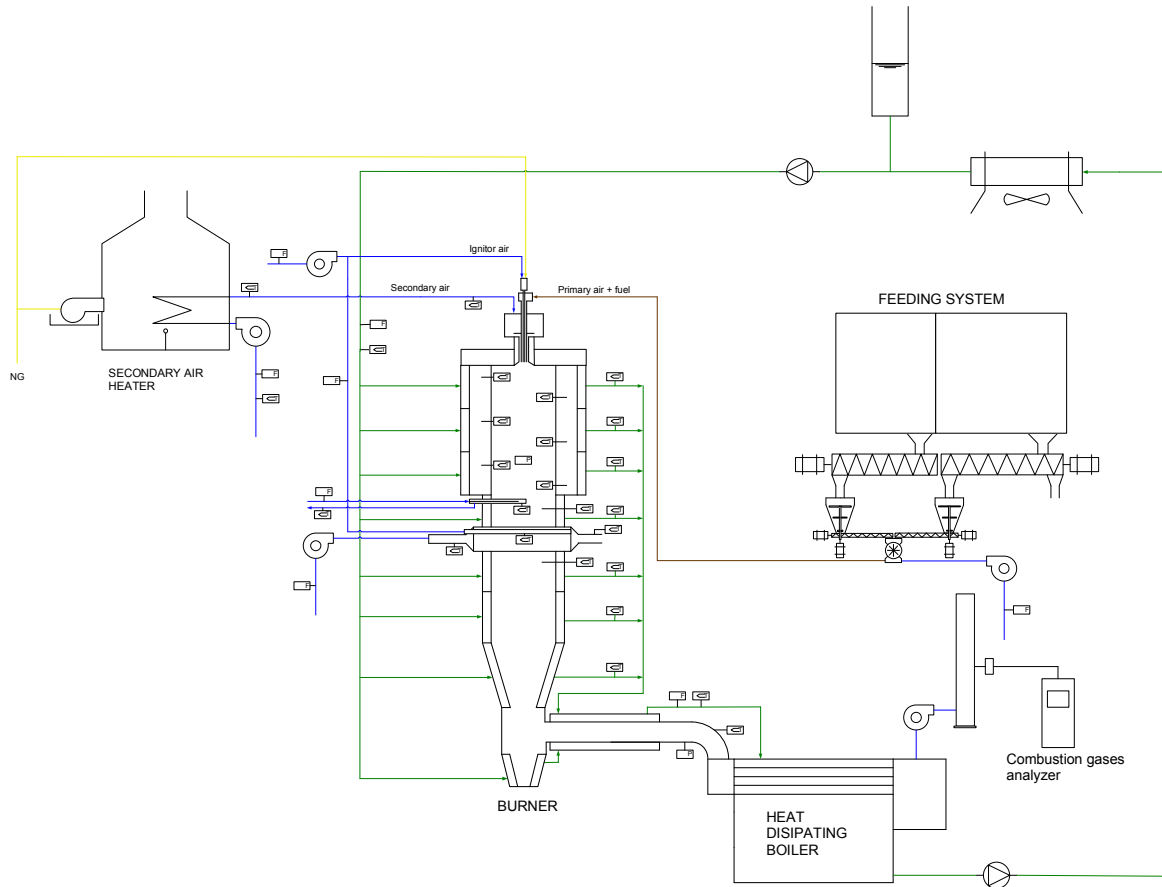


Fig 26. Layout of the test rig

Table 5 shows the experimental test matrix. Coals selected for the tests are South African coal and Spanish coal whose properties are presented in D2.1 in the characterization analysis. The biomass fuel is raw crushed Cynara. Combustion tests are planned at 5-10-15% of Cynara in energy basis. These shares are usual values for co-firing biomass and coal in PF combustion power plants. Higher shares were not scheduled to be burned in the pilot plant, due the high alkali and chlorine content of Cynara.

Table 5. Set of experiments in CIRCE

TEST N°	Coal	Biomass	% Biomass
1	South African Coal	Crushed Cynara	0
2			5
3			10
4			15
5	Spanish Coal	Crushed Cynara	0
6			5
7			10
8			15

Results were divided in two main subjects, **cofiring** and **deposition**. Table 6 shows a brief summary of the most important results in cofiring tests. At the same time, tests are divided in two series, the first one using South African Coal - Crushed Cynara (test 1 to 4) and the second one, Spanish Coal – Crushed Cynara (tests 5 to 8).

The main objective of these tests was to achieve stable combustion of the coal-biomass blends while maintaining the CO levels as low as possible. The heat input of the pilot test rig was maintained constant at 500 kW_{th} of thermal input power. Due to the very different chemical composition of the two coals tested, the mass flow rates of the Spanish and South African coals necessary to obtain the required energy were very different.

Table 6. CIRCE tests results

a	1	2	3	4	5	6	7	8
Coal-biomass %	100-0	95-5	90-10	85-15	100-0	95-5	90-10	85-15
CO (mg/m ³ N, d.b., 6% O ₂)	162.70	153.01	102.45	100.82	187.45	88.75	141.99	177.35
SO ₂ (mg/m ³ N, d.b., 6% O ₂)	434.65	589.97	712.19	697.45	16956.99	15992.41	13639.08	13204.52
NO _x (mg/m ³ N, d.b., 6% O ₂)	690.26	771.93	602.25	595.91	534.44	556.51	556.22	516.02
O ₂ (%vol)	7.96	6.82	6.74	6.98	7.02	7.12	7.25	6.64
CO ₂ (%vol)	11.82	13.38	13.04	13.20	12.21	12.29	12.89	13.24
Coal Flow Rate (kg/h)	62.20	59.70	54.90	51.30	94.64	89.37	86.40	80.30
Biomass Flow Rate (kg/h)	0.00	7.25	13.06	18.87	0.00	7.25	13.06	18.87
Sec. Air (m ³ /h)	584.31	606.59	579.61	573.41	600.53	593.24	616.70	607.97
Prim. Air (m ³ /h)	174.96	173.04	185.19	182.88	235.15	234.99	211.32	211.16
T _{gas} (°C)	922.42	1004.58	962.63	1004.58	900.47	932.09	869.91	925.44
T _{sec} (°C)	242.28	212.40	212.55	211.29	214.44	212.62	215.10	213.96

Ash samples were analyzed by SEM/EDS, to obtain images and qualitative composition of the different samples got in the tests. They were subjected to optical-magnification and EDS analyses, with a map of the elements present in the sample, or a spot/bulk analysis. Every sample was analyzed with two different magnifications, x100 and x400.

Flue gas composition (emissions)

CO concentrations were lower than 200 mg/m³N in all tests (at 6% O₂). Results for CYN-SPA blends were slightly higher in the majority of the tests. Due to its low heating value, it was necessary to transport 44% plus of coal than in South African coal tests. Primary air flow rate levels were higher when burning Spanish coal.

NO_x levels do not show a clear trend when increasing the biomass percentage in co-firing. Biomass nitrogen content is lower than SAC nitrogen content so NO_x emissions were expected to be lower in SAC-CYN blends combustion than in SAC test. This trend has to be further investigated.

Regarding SO₂ emissions, they are around 15000 mg/m³N in SPA burning tests; this is due to the high S content of this coal, 8%. In the first series of tests, using SAC, SO₂ concentration in flue gases was not very high. The tendency observed in these first 4 tests should not be taken into account because when some of these tests were performed, SPA tests had already been done. Due to the high SO₂ levels obtained with this coal, the measurement module of the gas analyzer was saturated and the data are not completely reliable.

Deposition results

Detailed results are shown in deliverable 2.2 but the main conclusions are that Cl deposition in ash is lower than expected, so it is suggested that the majority of the Cl is released as HCl in combustion gases. Aluminosilicates are the most abundant inorganic components in ash, which indicates a big influence of coal as they come from coal clays. Some other metals are present in ashes but they do not sum up more than 5 %.

Combustion tests in grate-fired boilers

A fixed-bed setup at the CHEC Research Centre, Technical University of Denmark (DTU) was applied for the combustion tests, simulating grate-firing. The setup includes a gas mixing system, an electrically heated, horizontal tube reactor, a gas conditioning system, gas analyzers, a thermocouple and a data acquisition system, and it allows for pyrolysis and combustion under well-controlled conditions.

Table 7 shows the experimental matrix:

Table 7. Complete test matrix for fixed-bed combustion experiments performed on Cynara samples.

Experiment series	Fuel	Sample mass (g)	Temperature range (°C)	O ₂ concentration in oxidizer
A: Variation of sample weight	Pelletized Cynara	1; 1.5; 2.5; 5; 10	Fixed at 750	Fixed at 10 %
B: Variation of oxygen content	Pelletized Cynara	Fixed at 2.5	Fixed at 750	5 %; 10 %; 20 %
C: Variation of temperature	Pelletized Cynara	Fixed at 2.5	500; 750; 1000; 1050	Fixed at 10 %
D: Fuel pre-treatment (particle size)	Shredded pellets (< 5 mm; < 1 mm)	Fixed at 2.5	Fixed at 750	Fixed at 10 %
E: Fuel fractionation	Stems; Leaves; Capitula; CRU; Cyn 2007	Fixed at 2.5	Fixed at 750	Fixed at 10 %

Series A: The sample weight was varied from 1 to 10 g, while the temperature was fixed at 750 °C and O₂ concentration in oxidizer was fixed at 10 % (vol.)

Series B: The O₂ concentration in the oxidizer was varied between 5 % and 20 %, while sample mass was fixed at 2.5 g and the temperature was fixed at 750 °C.

Series C: The reactor temperature was varied from 500 to 1050 °C, while sample mass (2.5 g) and O₂ concentration (10 %) was fixed.

Series D: The fuel particle size was reduced from whole pellets (2 – 5 cm long, 5 mm in diameter) to < 1 mm, while sample mass (2.5 g) and O₂ concentration (10 %) was fixed.

Series F: Different types/fractions Cynara samples were tested: milled fractions of raw Cynara from 2006 (stems, leaves, capitula), crushed stems from earlier harvest (also milled) (CRU), and crushed raw Cynara from 2007 (Cyn2007), while sample mass (2.5 g) and O₂ concentration (10 %) was fixed.

Some results and recommendations from the test performed are listed below:

- The burn-out time decreased with decreasing sample mass, increasing O₂ content in oxidizer, increasing reactor temperature, and decreasing particle size.
- Leaves differed significantly from the other Cynara fractions, burning with higher CO₂ and (initial) CO levels, lower levels of O₂, and slightly longer burn-out time.
- Emissions of NO and SO₂ varied only slightly from one experiment to another, and emissions tended to increase with increasing concentrations of N and S in the fuel.
- The temperature monitoring showed that the temperature within the fuel bed increased a little shortly after ignition of the samples (< 25 °C at reactor temperature 750 °C, < 35 °C at reactor temperature 1000 °C). The temperature increase was less in the pelletised samples as compared to the milled samples.

Ash melting problems were observed already at T = 750 °C when firing Stems fractions (Stems and CRU), as part of the ash was sticking to the bottom of the crucible, being difficult to remove. At 1000 °C initial ash melting problems were also seen when firing non-fractionated Cynara (pelletized Cynara and Cyn 2007), and at 1050 °C severe ash melting took place (parts of the ash could not be removed from the crucible). (Only pelletized Cynara and Cyn 2007 were tested at 1000 °C, and only pelletized Cynara was tested at 1050 °C).

The fixed-bed combustion tests largely confirm the findings from the preliminary fuel characterization, pointing out that Cynara is a problematic fuel with respect to potential slagging and fouling problems. Ash melting problems are observed at higher temperatures, and the combustion tests on the different fractions identified stems as a particular problematic fraction with respect to potential slagging and fouling problems, as ash melting was observed already at a combustion temperature of 750 °C. The findings suggest that due to the potential slagging and fouling problems, Cynara should not be combusted alone, as would be the case in grate-fired boilers.

Task 2.3 Cynara combustion feasibility at full scale

CFD simulations of co-firing coal with cynara in an existing power plant were performed. Detailed results and methodology obtained from a set of CFD simulations conducting to the study of the co-combustion process of coal and *Cynara Cardunculus* in the Teruel Power Plant (Spain) are presented in deliverable 2.3.

Table 8 summarizes the main operational conditions, under full load conditions, considered in the simulation.

With regard to the combustion model, kinetic parameters for the devolatilization and the char oxidation processes used in the CFD calculations are presented in Table 9.

Table 8. Coal analysis and main operational conditions

Ultimate Analysis			Proximate Analysis		
C	42.29	% weight	Fixed Carbon	23.25	% weight
H	2.98	% weight	Moisture	18.54	% weight
O	0.59	% weight	Ash	23	% weight
N	8.24	% weight	Volatiles	35.21	% weight
S	4.01	% weight	HHV	17000	kJ/kg

FUEL AND AIR MASS FLOWS			
Coal Consumption	<i>Total</i>	60	kg/s
	<i>Per mill / per burner</i>	10 / 2.5	"
Total air mass flow into the furnace		391.62	kg/s
Primary Air + Atemperation Air		120	kg/s
Secondary Air		271.62	kg/s
Product Gases mass flow		406.4	kg/s
% Coal distribution per burner respect to the total		4.17	%
Primary Air / Coal Ratio		2	kg air / kg coal
Air Excess at the boiler exit (estimated)		12.07	%
% Oxygen at the boiler exit (estimated)		2.13	% (w.b.)
Primary Air Temperature		85	°C
Secondary Air Temperature		360	°C

Table 9. Combustion kinetic parameters of coal

Devolatilization parameters	
Ea (kJ/kmol)	200000
Aa (s ⁻¹)	1.00E+13
Char oxidation parameters	
Ec (kJ/kmol)	83370
Ac (kg/m ² s Pa)	0.6374

The full boiler simulation was run on a cluster with 3 AMD Opteron 248 2.2 GHz processors, 4 GB RAM each one. The commercial code used was FLUENT 6.3. The process took about 30 hours until convergence was obtained. Average results from the simulation at the boiler outlet were compared against averaged plant data measurements for the same operational conditions on Table 10.

Table 10. Average results on the boiler outlet on CFD simulation and on simulated plant data

	T (°C)	% O ₂	%CO	%CO ₂	%SO ₂	%H ₂ O	%N ₂	Combustion particles (%)
CFD SIMULATION	1112	2,76	0,137	13,85	0,495	10,92	71,838	100
PLANT DATA	950	2,13	0 - 0,1	14,14	0,505	12,64	70,59	98,23

In this work, main aspects affecting the boiler performance when co-firing coal and *Cynara Cardunculus* in the Teruel power plant (Spain) have been simulated. To achieve this, three main factors known to have a relevant impact on the combustion behavior have been considered: particle size, biomass substitution percentage and biomass injection locations and the conclusions are divided depending on the factor.

Particle size is one of the three parameters studied, the most influential factor in biomass burnout. As particle diameter decreases the specific surface increases. This fact means that there will be a greater active contact surface between the fuel and air, enhancing fuel surface oxidation. In addition, heat and species transfer also increase. In the study 2 different particle diameters have been considered:

- a. 0.5 mm target size. This size represents the diameter for grinding the biomass without excessive milling energy consumption, and for ensuring a complete combustion of the biomass particles in the operating conditions of the study.
- b. 2 mm diameter target size. It represents a significant saving of energy, compared to 0.5 mm. However, although milling energy requirement is lower, biomass unburned carbon presented in the fly ash may be too high for an efficient industrial application.

Substitution percentage: Combustion efficiency is strongly dependent on the mean particle size, but also on the intrinsic and reactive characteristics of the fuel, and furnace conditions (Temperature and oxygen concentration). In particular, in this work, results evidence that there is a competing process between coal and biomass for the oxygen presented into the furnace. Therefore, since coal combustion dominates the global combustion behavior in the boiler, increasing the percentage of biomass substitution results in a decrease of the overall burnout attained. On the other hand, it has been also obtained a low increase in the temperature of the exits gases when the percentage of biomass substitution increases, suggesting an increase of the steam production. This result, together with the positive balance in the global emissions of the unit, opens a new line of research in order to quantify these aspects.

Burners situation: two different locations of the biomass burners have been studied: One placed at the upper row of burners and another in an intermediate row. The choice of a burner at the upper row was done to interfere as little as possible on the coal burners fluid dynamic, and to introduce the biomass particles in a zone with a relative higher concentration of O₂. The burner located in the intermediate zone aims to increase the residence time of biomass particles respect to the previous configuration, and to introduce the biomass particles into a higher temperature area. Biomass burnout is higher in the burner placed in the upper row than in the intermediate row. This fact was explained due to the competing process between coal and biomass for the oxygen, suggesting oxygen concentration as a parameter much more critical than residence time on biomass burnout under the operational conditions analyzed in the study. Another factor to consider is that burners are not specific biomass burners; they have been designed for pulverized coal combustion. Cynara requires less air for combustion than the study coal; hence, the air amount introduced to the burner is significantly lower than the nominal of the coal burner, leading to biomass burner velocities slower than optimal settings for biomass combustion.

Therefore, a good solution to improve the biomass combustion (compared with the theoretical data of air needs to burn biomass) would be to increase the air/fuel ratio. This change will get a double benefit for biomass burnout. First, it would increase the concentration of oxygen in the vicinity of the burner when the most of the combustion takes place, increasing their conversion. On the other hand, burner velocities would be increased up to a typical range of specific biomass burners.

In this work we have studied the substitution of one burner in two rows. It would be also interesting to examine the substitution on two burners of the same row to assess the symmetrical combustion impact on the furnace.

Another aspect that could be extended in subsequent studies is to simulate the biomass combustion on specific biomass burners on different positions of the boiler. This substitution configuration presents two advantages: the interferences between biomass and coal flames would be avoided, and the competing process among coal and biomass for the oxygen presents into the furnace would be reduced.

1.3 CYNARA SEEDS VALORISATION FOR ENERGY CONVERSION

1.3.1 Description of project objectives

The main objective of workpackage 3 has been the development of a process for cynara seeds valorisation for producing biofuel for energy conversion. Main activities in this workpackage include:

- Design the optimum pre-treatments of the Cynara oil for biofuel production.
- Validation and demonstration of the Cynara oil as new renewable resource for production of biofuel by the homogeneous process.
- Develop new low cost solid catalyst for transesterification reactions applied to biofuel production and Identification of the deactivation routes of catalyst to increase their life cycle and reduce cost.
- Develop a new biofuel production process by heterogeneous catalyst to reduce cost production and environmental impacts.
- Study of innovative mixing techniques for transesterification of vegetable oil with methanol.
- To test biofuel and Cynara biofuel obtained in laboratory engines for electric production.

1.3.2 Work performed and end results

1. Batch and fixed bed re-circulating reactors for the esterification of palmitic acid in sunflower oil using solid acid catalysts.

The transesterification of the triglycerides contained in vegetable oil with methanol to yield fatty acid methyl ester (FAME, biodiesel) is homogeneously catalysed by NaOH and KOH bases. Free fatty acids (FFA) are a poison to the catalyst, and also lead to soap formation. The FFA content is low (<1 wt.%) in refined oil, but can exceed 10 wt.% for some crude and recycled oils and greases. The esterification of FFA with CH₃OH using a solid catalyst prior to the esterification reactor is a promising method to convert FFA into valuable FAME [see for example: Ramadhas, A.S., Jayaraj, S., and Muraleedhara, C. Fuel 84, 335 (2005)]. Many solid acids display an activity for the esterification of short carboxylic acids and alcohols, but deactivates upon reuse. When the Biocard project started, there was also a lack of data on the esterification of long-chain FFA in realistic reaction media (i.e. oils). Therefore, the work presented here aimed at determining active and durable solid catalysts for the esterification of palmitic acid (PA, C₁₆H₃₂O₂) in sunflower oil.

The catalysts, i.e. sulfated (SZ, Aldrich) and tungstenated zirconia (MELCat, X20861/02), silica-alumina (Davicat, CL5600) and Nafion/SiO₂ (SAC-13 from Aldrich), were typically calcined at 600°C, except for the SAC-13, which was used as received. In the case of the batch reactor, 30 ml of commercial sunflower oil (Tesco brand) containing 10 wt.% of PA (Aldrich, 99% purity) was placed into a round bottom flask fitted with a reflux condenser. No organic solvent was used. 9 ml of methanol mixed with a known amount of catalyst was then added to the oil. The reaction mixture was stirred at 1000 rpm to increase the dispersion of the reactants, as those were not fully miscible at the temperature used (around 60°C). In the case of the re-circulating reactor, a peristaltic pump was used to circulate the reaction mixture. Three-fold larger proportion of reactants were used, which were stirred in a round

bottom flask prior to contacting the fixed-bed holding the catalyst. Contrary to the case of experiments realised at high dilution in an organic solvent or in pure FFA medium (in which methanol is fully soluble), the lack of full miscibility constitutes a challenge in the type of work reported here. Samples were collected at regular intervals and the PA content was titrated with a solution of KOH in ethanol.

The SZ and the SAC-13 were the most active catalysts under our conditions (60°C: TOF were 0.24 and 0.16 min⁻¹, respectively) and received further attention. The SZ was essentially not active if not calcined above 400°C before reaction. An in situ diffuse reflectance FTIR study of the activation of the SZ revealed that the higher calcination temperatures are necessary to form the highest proportion of a band at 1403 cm⁻¹, which is associated with the presence of highly covalent surface sulfate species. The effect of the reactants and reaction products of the esterification were investigated over the activated SZ. Neither the methanol nor the mixture oil+palmitic acid had any deleterious effect on the activity. This indicates that SZ can actually be stored in the alcohol or the oil once activated. On the contrary, water almost fully inhibited the activity of the catalyst. Recycling experiments also showed that leaching of sulfate occurred, in agreement with earlier reports [see, e.g., Omota, F., Dimian, A.C., and Bliet, A. Chem. Eng. Sci. 58, 3175 (2003)]. The SZ showed a marked loss of activity with the first recycling, and thereafter a slower gradual loss (Fig 27, right). The SZ could not be fully regenerated by calcination at 500°C, probably because of the carbon residues derived from adsorbed oil. As a matter of fact, calcination of SZ following exposure to various reaction mixtures showed that all oil-containing mixtures led to poor activity (Fig 27, left). The SAC-13 did not deactivate upon reuse and required no activation and therefore appears as a most promising catalyst for the esterification of FFA in oil. The origin of these observations may lie in the hydrophobicity of the SAC-13, which favours water removal away from the catalyst and the sulfonic acid group. It is interesting to note that the SAC-13 used elsewhere with various carboxylic acids up to C₈H₁₆O₂ (in the presence of a large excess of tetrahydrofuran solvent) exhibited a marked deactivation upon each reuse cycle [Liu, Y., Otero, E., and Goodwin, J.G. J. Catal. 243, 221 (2006)]. The origin of this discrepancy probably lies in the different nature of the reactants and/or reaction media used. The activity of the SAC-13 was also investigated in a fixed-bed re-circulating reactor to allow monitoring the durability of the catalyst and re-usability without the need to filter off the material. While some limited deactivation was observed following the first run, a reproducible time/conversion plots were subsequently obtained.

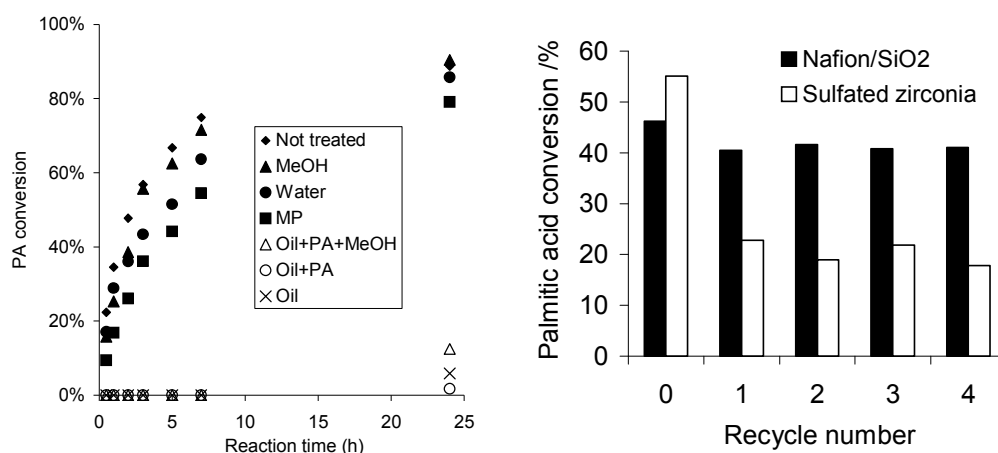


Fig 27. Left: Effect of various pre-treatments followed by a calcination at 500°C on the activity of activated SZ for the methanol-esterification of PA in sunflower oil. Catalyst loading: 3 wt%. T = 60°C. Right: Conversion of PA after 3h over SZ and Nafion/SiO₂ (SAC-13) over a number of recycled uses. Catalyst loading = 3 wt.%.

Nafion/SiO₂ appears as an active and durable heterogeneous catalyst for the esterification of FFA with methanol in oils, requiring no activation before use. This catalyst could be used in a fixed bed reactor for a cost-effective pre-treatment of FFA-rich oils for biodiesel production.

2. Transesterification of in sunflower oil using solid basic catalysts.

Finding active and durable solid bases for the transesterification of vegetable oil would allow lowering significantly the cost of biodiesel production, by avoiding the use of alkali bases that lead to separation and soap formation problems. QUB was supporting CSIC in the quest for such new materials, by helping in the characterisation of materials and by testing a few catalysts. Three characterisation setups were used for investigating the surface and bulk structure of our catalysts:

- situ DRIFT with on-line MS analysis of the effluent gases
- in situ XRD,
- CO₂-TPD with on-line analysis of the effluent gases.

The characterization of CaO, CaCO₃ and Ca(OH)₂ by CO₂-TPD, in situ XRD and in situ DRIFTS was carried out. The experimental condition for CO₂-TPD and in situ DRIFTS was that the temperature rose from room temperature 20 °C to 750 °C at the rate of 10°C/min, then held for 30 min and cooled down to room temperature. In case of XRD experiment, increment of 100 °C from room temperature to 800 °C up the ramp of 10°C/min was used. Each temperature would hold for 30 min and data collection was performed afterward with the variation of 2θ from 5.02 to 79.98 degree. This series of DRIFT analysis (not shown here) shows that the CaO is initially highly hydrated and carbonated, and that a temperature of ca. 400 °C is necessary to dehydrate and 750 °C to decarbonate. These observations are in agreement with the CO₂-TPD results. The results obtained by XRD, which gives an indication of the composition in term of crystalline phases present, are quite different. The XRD pattern observed at RT is that of CaO, but an intermediates Ca(OH)₂ and carbonate phases are observed. The whole data indicate that there is a significant proportion of amorphous hydrated and carbonate phase at RT, which then partly crystallise (also leading to the destruction of the CaO phase) before being decomposed at the higher temperature back to CaO.

A number of basic and acidic catalysts were tested in the transesterification reaction of sunflower oil. The only catalysts presenting a high catalytic activity and that were not dissolved in the reaction media (by visual observation) were CaO and MgLaO_x. However, CaO requires high activation temperature (750°C) to remove surface hydroxyl and carbonates and can be easily deactivated even exposure to air for few seconds, which has been confirmed by the characterisation methods (DRIFTS, TPD and XRD) of the activated calcium oxide catalyst. Finally a more controlled evaluation of Ca homogeneous catalytic contribution of calcium oxide has revealed the reaction between CaO and glycerol forming Ca glyceroxide which is the main cause of the blockage in the fixed bed reactor, rendering it unrealistic heterogeneous catalyst.

CsF-based materials have been recently reported as promising transesterification catalysts. The durability of the CsF/alumina catalyst has been tested and shown to be poor. This is probably due to the gradual leaching of the CsF in the reaction medium, as suggested by an experiment which showed that a catalyst washed with an oil+methanol mixture was almost inactive (Fig 28). These data are important as those emphasise that durability and reusability is rarely checked and lead to wrong direction. A possible way to stabilise the CsF in the

sample could be to use much higher calcination temperatures, but this may result in the formation of aluminates.

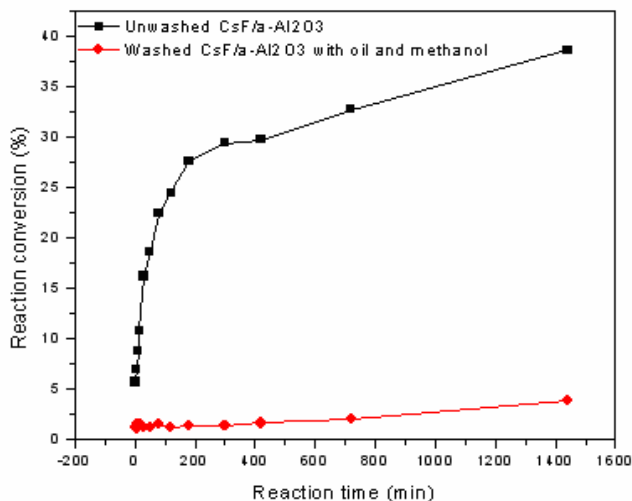


Fig 28. Catalytic activity of a washed and original (i.e. “unwashed”) powder of CsF/ α -Al₂O₃

A new heterogeneous catalyst has been published in the open literature (Lingaiah, Energy & fuels, 2008, 22, pages 1965-1971) and a sample was kindly sent to us by the authors. The activity of the sample is extremely high and full conversion of the oil to FAME was obtained at 65 °C after 120 min (see Fig 29) (Experimental conditions: 1.0 g of MgLaOx powder was mixed with 21.4 ml of sunflower oil and 50 ml of methanol, corresponding to a molar ratio of methanol/oil of 53). QUB has tried to prepare the MgLaOx sample according to the published method, but the activity obtained was lower, although it was still an active catalyst (Fig 29). The original sample from Lingaiah was analysed by X-ray photoelectron spectroscopy and traces of alkali metals were found. It is therefore possible that part of the activity on the original sample was due to the presence of (soluble) hydroxide of alkali metals. In any cases, this shows another difficulty in the field of transesterification is that results or preparation from the literature are difficult to reproduce.

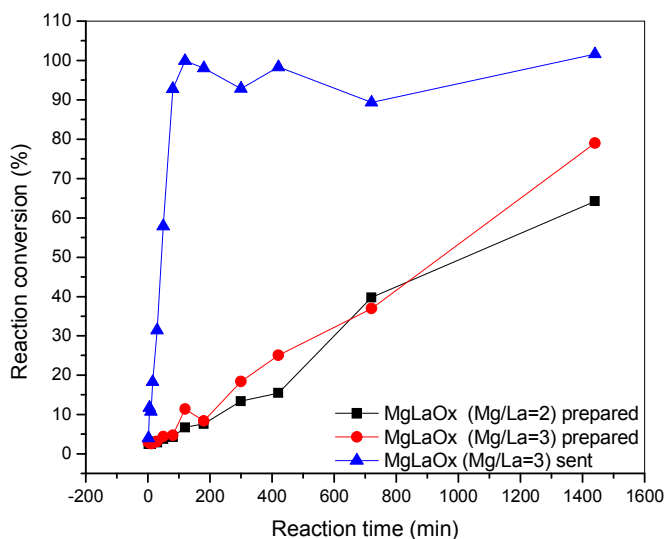


Fig 29. Catalytic activity of MgLaOx. The sample “sent” was sent to us by Lingaiah, while the “prepared” samples were made at QUB.

3. Competitive basic solid catalysts to produce biodiesel.

The *methodology* following by ICP-CSIC was addressed to reach the objective of identify and improve some competitive basic solid catalysts against the conventional homogeneous process to produce biodiesel. This partner has prepared and used a high number of basic solid catalysts. These samples were activated adequately and a scanning for tested their catalytic properties was carried out. The catalysts with the best catalytic behaviour were characterized (activated and used samples) establishing a correlation structure-activity. New preparations were carried out to improve the catalytic properties (activity, selectivity and durability) of the samples.

Concerning to the *reaction system*, a microreactor and an adequate analysis procedure (Gases Chromatographic) to testing the catalytic performance in the transesterification reaction of vegetal oil with methanol has been carried out. To check and validate the reaction system (reproducibility and accuracy) we have studied the homogeneous reaction with KOH catalyst diluted in methanol. The crude cynara oil can not be used for the transesterification reaction when basic catalysts are used (both KOH or solid). The large FFA content consumes the basic catalyst and a previous esterification step to transform the FFA to FAME is required. Thus, we have considered opportune to use edible grade sunflower oil, which is very similar to refined cynara oil with respect to composition and physical properties. In relation with reaction conditions, we have selected for these tests the following conditions: Oil amount of 50 g, MeOH/oil molar ratio of 12 and catalyst/oil ratio of between 0.2-1 % wt (100-500 mg), temperature at 60 °C, atmospheric pressure and a stirring rate of 1000 rpm. After some time of reaction, depend on the catalyst loading, the conversion reached under above conditions were higher than 90% of methylester content. These values have been replicate several times and the progress of the transesterification reaction was estimated after the evaluation of correspond aliquots extracted a different times. The more relevant found solid catalysts were:

Alkaline oxide supported on γ -Al₂O₃. ICP-CSIC has prepared several oxide basic solid samples supported on γ -Al₂O₃ to be tested in the transesterification reaction of sunflower oil with methanol. Activation procedure have been carefully studied by N₂ isothermal (BET specific area), EGA-MS, FTIR, XPS, XRD and DRIFT techniques. The catalytic performance for potassium and strontium oxide supported was very promising. However, the leaching of these active phases in reaction mixture was evidenced and the methyl esters yield (%) after reutilization on several runs decay strongly. Thus the contribution of homogeneous process is very high by the leaching.

Activated bulk calcium oxide. ICP-CSIC has also studied commercial calcium oxide which has been tested in the transesterification reaction of sunflower oil with methanol. Activation procedure of calcium oxide catalyst seems a key factor in its catalytic performance. The loading of catalyst has also been studied, suggesting that the contribution of homogeneous process is not the main responsible of this performance. However, the evaluation of the homogeneous contribution by possible leaching has been studied further as it will see below. Several strategic were carried out to improve the samples based in CaO.

- I. *CaO supported γ -Al₂O₃.* These samples were prepared by impregnation method to establish the active species of CaO (avoiding a possible leaching) and increase the exposed calcium oxide surface area. Unfortunately activity results suggested that this type of catalyst was deactivated by leaching of active phase. Characterization of supported, fresh and used catalyst in transesterification reaction confirmed the calcium leaching.
- II. *CaO promoted by lithium.* The promotion of CaO by the addition of Li catalyst has been investigated. Lithium incorporation was carried out to increase the basicity of surface sites. Lower temperatures of activation are required for the Li promoted

catalyst to become as active as the unpromoted CaO catalyst. It required a lithium amount above 4.5 wt % to promote the catalytic activity of CaO. The catalyst starts to be active when activation temperature was higher than the melting point of LiNO₃ (492 K). Above 773 K, the influence of the activation temperature is not significant for catalytic activity, but it is for homogeneous contribution. When Li₂O has been formed, active species are leached in the reaction medium and catalysis is mainly homogeneous; nevertheless, at lower temperatures when LiNO₃ is present on CaO, heterogeneous contribution must be responsible for the activity because any possible LiNO₃ leached in the reaction medium is not active.

- III. *Bulk CaO from different calcium salt (different surface area).* To obtain calcium oxide with higher surface area the preparation of CaO by different methods (activation of other salts besides CaCO₃, precipitation of Ca(OH)₂ from different Ca salts, microemulsion). The intention is found a method of preparing the CaO with the large amount of strong basic sites at its surface. It was concluded that the surface area is important (more area normally derives in more activity) but this is not the unique important factor. Calcium oxide with similar surface area showed different catalytic behaviour.

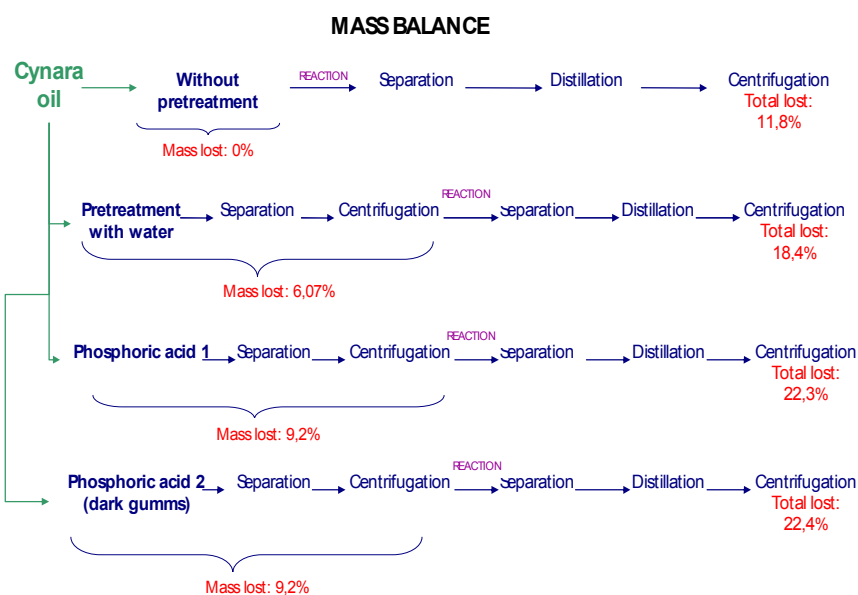
CaO reutilization and leaching (homogeneous contribution). The activities of ICP-CSIC were directed in the search of solids that are active and stable in the transesterification of triglycerides with methanol. The unique catalyst with high catalytic activity that was not dissolved in the reaction media was CaO. Moreover this catalyst showed a high stability by reutilization (8 times). Therefore, an important research activity was addressed to a more controlled evaluation of the homogeneous catalytic contribution of calcium oxide catalyst. The study of the leaching of active species by two different methods demonstrates that although a small amount CaO (< 3%) is dissolved, the contribution of these leached species to the activity is negligible. The activity of the solids is due to the sites present at the surface of the solid. The solubility of activated CaO methanol, methanol with glycerol, and reaction media (methanol, glycerol and biodiesel) was determined by in-situ conductivity measurements. CaO is quite insoluble in methanol whereas when glycerol is present Ca glyceroxides are formed that are more soluble in the alcoholic phase than CaO in methanol. In any case the Ca²⁺ concentration in alcohol and FAME phases is significantly lower than that found when a homogeneous catalyst is used under frequently used reaction conditions. Thus the solid can be reutilised for a reasonably large number of runs under the catalyst loading frequently used (larger than 1 wt % referred to oil). The research allowed us to conclude that, although the intrinsic activity of the leaches species was larger than that of the sites of the surface, the homogeneous contribution is much smaller than that arising from the heterogeneous sites provided that the catalyst loading is larger than 1 wt % of CaO.

4. Suitability of Cynara oil to produce biodiesel that fulfils European standard 14214 for automotive uses.

The objective of this work has been the evaluation of the cynara oil as raw material for biofuel production.

The first activity has been to produce oil from cynara seeds. After this, different oil pre-treatments have been studied in order to optimize the biodiesel production in a commercial process (homogeneous catalysis). The produced biodiesel must carry out the demanded requirement for diesel engines compiled in UNE:EN 14214.

A very important point of this study is the mass balance assessment. The mass lost connected to each step are very important under an economic point of view. Moreover the final reaction yield must be considered.



From the data obtained the first conclusion was that the crude cynara oil is suitable to produce biodiesel for diesel engines in homogeneous catalyst conditions.

Moreover, under an economic point of view it is very important to consider the mass lost during the whole process. The use of crude oil presents the best mass balance and this is an additional advantage over the rest of the treatments.

5. Design and construction a pilot plant for biofuel production under homogeneous and heterogeneous catalytic reaction

The objective of this work has been the design, construction and verification of the designed biodiesel pilot plant. For this purpose, some tests have been carried out in order to start the machine, to prove that all the components were working properly and the produced biodiesel fulfilled the biofuel standard (UNE EN 14214)

A pilot plant for biodiesel production, under either homogeneous or heterogeneous catalytic conditions, has been designed and constructed. A cylindrical body jacketed reactor made of stainless steel, that presents a useful volume of 50 L. The reactor is equipped with a stirrer and baffles to improve the quality of the mixture oil, catalyst (solid or liquid) and methanol. The rest of the components of the plant were designed and dimensioned (pumps, centrifuges, tanks, distillation system decanter, etc) to allow the production of a biodiesel of quality for car use. All components are assembling and automated.

The biodiesel pilot plant could be useful for big-scale experiments, using multi feedstock oils. The expertise in oil treatment is applied to other vegetable oils.



Fig 30. GAIKER Bio-diesel pilot plant

6. Innovative mixing techniques for transesterification of vegetable oil with methanol

A large number of bench-scale literature studies on homogeneous-catalyzed processes examined the effect of the different operational parameters on the rate of biodiesel production and on the equilibrium conversion of the transesterification reaction. In particular, the investigations focused on the role of alcohol type, alcohol:oil molar ratio, type and concentration of catalyst, temperature, and intensity of agitation. Because vegetable oil and alcohol form two almost immiscible phases, no matter what type of catalysis is selected, an intense mixing of the two reagents is required in order to break the alcohol phase into small drops, thus providing sufficient interfacial area for the reaction. The vast majority of the studies on transesterification focused on mechanically agitated systems, either with impellers or with magnetic stirrers.

Recent analysis relative to the energy balance associated with biodiesel production evidenced that the energy input required for the transesterification reaction seems to represent a minor fraction of the overall cost of biodiesel production. On the other hand, in terms of energy balance, the energy required for oil transesterification can represent a significant fraction of the overall energy input. Therefore, the improvement of the energetic efficiency of the biodiesel synthesis reaction can lead to a significant improvement of the biodiesel energy balance and is therefore worthy of investigation.

The experimental investigation carried out by the UNIBO research group in the BIOCARD project focused on the investigation of innovative mixing techniques for the alkali-catalysed transesterification of vegetable oil with methanol. We tested the employment of static mixers and of mechanical agitation configurations characterized by the combination of different types of impellers and by the variation of agitation speed with time. The different mixing techniques were compared in terms of reaction time required to attain a given conversion of the transesterification reaction and corresponding specific energy requirement. The main

goal of the study was to determine, for each type of mixing device, the optimal experimental configuration in terms of reaction time required to attain a given conversion and corresponding energy consumption.

A first part of the experimental programme was dedicated to the use of static mixers (SM). Static Mixers consist of motionless mixing elements placed within a tube or column. The utilization of SM for dispersing two immiscible liquids finds applications in liquid–liquid extraction, metal extraction, emulsification processes, and some liquid–liquid reactions. Static mixing generally require less power input than mechanical agitation at equivalent performance, and thanks to the absence of moving parts they are characterized by minimum maintenance requirements.

We investigated the alkali-catalyzed sunflower oil transesterification with methanol in a 22 L batch reactor preceded by a SM section: oil and methanol (the latter containing the dissolved KOH as catalyst) were initially loaded into two tanks. The two streams were mixed in a tee connection and then fed to the reactor by air displacement, utilizing a tube containing the SM section.

The main activities of the research were:

- ✓ the investigation of the effect of the number of SM and of the SM superficial velocity on the profiles of oil conversion versus time, with particular focus on the detection of possible mass transfer limitations to the transesterification reaction;
- ✓ to evaluation of the specific energy requirement associated with SM utilization for biodiesel production, both in our laboratory-scale pilot and at the industrial scale.

The best reaction performances were obtained with the utilization of 1 SMV static mixer operated at a 1.3 m/s superficial velocity.

In a second part of the experimental programme the same type of optimization applied to SM was extended to mechanical agitation, by varying the type of impellers and the agitation speed. This allowed to perform an overall comparison of the results obtained with SM and with mechanical agitation. This study was also aimed at evaluating the influence of the mass-transfer resistance under different mixing conditions and the effect of various distributions of mixing power within the stirred reactor. In this study the KOH-catalysed transesterification of sunflower oil with methanol was conducted in batch conditions in a 22 L temperature-controlled stirred-tank reactor (height = 0.45m, diameter = 0.25 m). The main activities carried out were:

- ✓ study of different mechanical agitation systems;
- ✓ evaluation of the effect of different distributions of mixing power within the stirred reactor;
- ✓ development of criteria for the energetic optimization of mechanical agitation in the biodiesel synthesis reaction;
- ✓ evaluation of the influence of the mass-transfer resistance under different mixing conditions.

The best reaction performance was obtained by combining a radial (Rushton) and an axial (A310) impeller and stopping the agitation after just 1 minute. This configuration resulted in a 200 fold reduction of specific energy consumption in comparison with traditional, non-optimized mixing configurations. An evaluation of the reaction and mass-transfer characteristic times evidenced the crucial role of mass-transfer in the first part of the reaction. The supply of a sufficiently high mixing power in proximity of the initial methanol/oil interface resulted to have a fundamental role for the rapid advancement of the reaction.

These optimised configurations studied in these studies resulted in a 7-130 fold reduction of specific energy consumption in comparison with the traditional, non-optimized mixing

configurations. The work done therefore allowed the individuation of mixing configurations characterized by a drastic reduction of the specific energy consumption in comparison with the traditional, non-optimized mixing configurations. In particular, the best reaction performances were obtained with the presence of a high-energy event at the beginning of the transesterification reaction followed by a low-power or null mixing. These results ensure the attainment of a significant improvement of the energy balance associated with biodiesel production.

The analysis of the energetic consumptions showed that SM can perform favourably in comparison with mechanically agitated reactors. This indication was confirmed by the extension of the energetic assessment to biodiesel production facilities of medium and large size. The overall results indicate that static mixing represents an interesting option for the biodiesel production process.

Finally, this research unit has analysed the fluid dynamics of gas-liquid and of liquid-liquid separators moreover of gas-liquid distributors/equalisers. Liquid-liquid separators are installed in horizontal and vertical vessels to increase the efficiency of separation between two liquid phases, that cannot mix together, in order to reduce the loss of expensive products, increase the purity of each phase, stop the corrosion of downstream equipment and reduce pollution due to products that could be drained out into the surrounding environment. These internals are used not only in the sector of offshore platforms but also for all steps of natural gas and oil treatment in the post-extraction phases. Gas-liquid distributors/equalizers are installed on the feed inlet nozzles of vessels (horizontal or vertical) or distillation columns to allow for uniform gas distribution in the inlet area and to promote a primary separation of the liquid present in the gas. Flow equalisers are normally installed in horizontal vessels to uniformly distribute the vapour stream, break the waves and stop any foam present on the surface of the liquid, obtaining pre-separation of the larger droplets carried by the vapour stream upstream of the gas-liquid separators.

The results obtained in present research program could allow to improve the equipments needed in Biodiesel process production to separate the Esters from the Glycerine.

7. Liquid biofuel characterization test for applications in stationary engines power production.

The objective has been to determine if the biofuels coming from cynara - cynara oils and biodiesel or fatty acid methyl ester (FAME) - are able to be burned in diesel engines without mechanical problems and low costs for diesel engines.

For this purpose, different proportions of cynara oil and (cynara) biodiesel, were blended with different Heavy Fuel Oil (HFO) and characterised.

As comparison three fuels were chosen for blending into HFO:

- I. Marine Diesel Oil (MDO) according the specification ISO 8217, ISO-F-DMB. This is a fuel often used in marine applications. The compatibility of MDO with HFO is normally very good.
- II. Marine Gas Oil (MGO). This is another fuel frequently used in marine application. The compatibility with HFO is worse compared to MDO. The MGO used for this investigation is a very light one with a very low sulphur content. Such a fuel quality can cause incompatibility problems with some HFO. This particular fuel fulfils even the specification EN 590 and is a typical automotive diesel fuel.
- III. FAME according EN 14214. This is biodiesel made from rape seed oil. This is common biodiesel used mainly in automotive applications as a 5 % blend to mineral diesel or even pure. As FAME from rape seed oil is the most common biodiesel today, this fuel was selected as a reference for biodiesel made from cynara oil.

These fuels were used to produce blends (25 %, 50 % and 75 %) with 4 different HFO (that represent the big variety of HFO qualities available around the world):

- HFO 1 is a typical marine HFO quality available in Europe.
- HFO 2 is a fuel used in Central America for power production in large diesel engines.
- HFO 3 is a Chinese fuel used for offshore power production.
- HFO 4 is a fuel in marine applications, bunkered in Far East.

The stability was analysed using two different methods:

- **Spot test.** A drop of the mixture was applied on a chromatographic paper and dried in an oven. In case of asphaltene precipitation a separation of the different fuels can be observed on the chromatographic paper.
- **Hot filtration test.** The mentioned mixtures were aged at 100°C for 24h. Then the aged mixture was filtered hot and the remaining sediment on the filter was measured. In case of incompatibilities the amount of sediment would increase. For pure heavy fuel oil, the maximum allowed content of this so called sediment potential is 0.1%. Each filtering was repeated three times.

The blends and analysis were done in Augsburg laboratory at the Man Diesel factory.

The results of these experiments show:

a) Hot filtration test

As expected, the blends of MDO in HFO are stable.

The expected poorer stability of the blends with this ultra low sulphur MGO has been confirmed.

The stability of biodiesel (FAME) in HFO can be compared with the stability of blends of MDO. There is no significant difference between FAME from cynara oil or rape seed oil.

Blends of cynara oil in HFO have the poorest stability of all blends that have been tested.

b) Spot test

As expected from field experience, blends of MDO in HFO show an acceptable stability.

The ultra low sulphur MGO shows a poorer compatibility with HFO but in most cases still acceptable.

FAME (both from cynara and from rape seed oil) has a compatibility with HFO comparable to MDO. Blends of FAME from rape seed oil seem to be slightly better compatible with HFO than FAME from cynara oil.

Cynara oil itself shows a poor compatibility with HFO.

The results from the spot test correlate very well with the results from the hot filtration test.

The conclusions are:

- Blends of FAME (both from cynara oil and rape seed oil) have a compatibility with HFO comparable to MDO and better than ultra low sulphur MGO.
- Blends of non-transesterified cynara oil in HFO have a poor stability.
- These results have been obtained from two different methods.

- Blends of biofuel in HFO should be done by using transesterified FAME and not the non-transesterified oil. The stability of FAME in HFO is much higher.
- The selection of 4 different HFO was made to cover a broad range of HFO quality. Nevertheless it cannot be excluded, that some other HFO qualities might show a poor compatibility even with FAME.
- As the conditions for ageing the fuel inside an engine are different from the conditions of this investigation, the obtained results must be verified in an engine test.

1.3.3 Impact on the industry or research sector

Each end result are related to an impact on the industry:

1. **Batch and fixed bed re-circulating reactors for the esterification of palmitic acid in sunflower oil using solid acid catalysts.**

The results that were obtained are very important for the industry sector (biodiesel producers) because we have shown the viability of the refining of crude or recycled vegetable oils containing large concentrations of free fatty acids. Nafion/SiO₂ appears as an active and durable heterogeneous catalyst for the esterification of free fatty acids with methanol in oils, requiring no activation before use. This catalyst could be used in a fixed bed reactor for a cost-effective pre-treatment of free fatty acids -rich oils for biodiesel production. This would limit the formation of soap and therefore facilitate the separation of biodiesel from the phases containing the glycerol/alcohol and the catalyst.

2. **Transesterification of in sunflower oil using solid basic catalysts.**

Our results show that the development of viable solid catalysts for the transesterification of vegetable oil at low temperature requires additional work. Many promising formulations reported in the literature are actually either not stable (dissolution in the reaction mixture, formation of slurry) or not reproducible.

3. **Competitive basic solid catalysts to produce biodiesel.**

Concerning to the *impact on the research sector*, we can said that the work carried out under this project has derived in four publications in scientific journals with high impact factor (IF):

- I. "Biodiesel from sunflower oil by using activated calcium oxide"; M. López Granados, M. D. Zafra Poves, D. Martín Alonso, R. Mariscal, F. Cabello Galisteo, R. Moreno-Tost, J. Santamaría y J. L. G. Fierro; Appl. Catal B: Environmental 73, 317-326 (2007). (IF=4,651, in 2007).
- II. "Potassium leaching during triglyceride transesterification using K/γ-Al₂O₃ catalysts"; D. Martín Alonso, R. Mariscal, R. Moreno-Tost, M. D. Zafra Poves y M. López Granados; Catal. Commun. 8, 2080-2086 (2007). (IF=2,394, in 2007).
- III. "Biodiesel preparation using Li/CaO catalysts: activation process and homogeneous contribution"; D.Martín Alonso, R. Mariscal, M. López Granados, P.Maireles-Torres; Catalysis Today (2009) (doi:10.1016/j.cattod.2008.09.021) in press (IF=2,764 in 2007).

- IV. “Leaching and homogeneous contribution in liquid phase reaction catalysed by solid: the case of triglycerides methanolysis using CaO”; M. López Granados, D. Martín Alonso, I. Sádaba, R. Mariscal, P. Ocón; submitted in Applied Catalysis B: Environmental (2009).

To our knowledge, the activated calcium oxide is the best solid catalyst described in the literature under reaction conditions equal to industrial homogeneous process. We have to remark that our first paper was one of the pioneering works relative to activated calcium oxide as a promising heterogeneous catalyst for the transesterification reaction of vegetable oil with methanol to obtain biodiesel. It was during several months one of the top twenty downloaded articles of the Applied Catalysis B: Environmental scientific journal. This article has already received 28 cites, according to the SCOPUS database.

In relation to the *impact on the industrial* we have to mention that the first article was deserving of a note in the electronic journal *focus on catalysis* (page 6, June 2007) entitled “Inexpensive transesterification process for biodiesel” emphasizing its relevance in this topic. The main barriers to industrial implementation are the weak but progressive solubility in the reaction media and the solid catalyst shape.

4. y 5. Suitability of Cynara oil to produce biodiesel that fulfils European standard 14214 for automotive uses and Design and construction a pilot plant for biofuel production under homogeneous and heterogeneous catalytic reaction

The industrial partner should be interested in improving or researching in the biofuel and renewable energies fields:

- Multi-feedstock biodiesel production technologies with currents, available technology to improve overall process economy.
- Modelling and experimental verification of the reactions during the biodiesel synthesis in a dynamic multi phase regime.
- Improved catalyst recovery and phase separation technology.
- Improved low-cost multi-feedstock oil pre-processing techniques

6. Innovative mixing techniques for transesterification of vegetable oil with methanol

In general, the experimental investigation of innovative mixing techniques for the transesterification of vegetable oil with methanol carried out by the UNIBO research group in the BIOCARD project allowed the individuation of mixing configurations characterized by a drastic reduction of the specific energy consumption in comparison with the traditional, non-optimized mixing configurations. In particular, the best reaction performances were obtained with the presence of a high-energy event at the beginning of the transesterification reaction followed by a low-power or null mixing. These results ensure the attainment of a significant improvement of the energy balance associated with biodiesel production.

During the project the UNIBO research group has reached the following results, that have a potential for industrial application or for developing and improving the process of biodiesel production from oil:

- development of an optimization methodology for biodiesel production reactors based on different ways to generate the liquid-liquid dispersion using traditional agitation systems (stirred tank reactor) and innovative devices (static mixer reactor). The methodology comprises fluid dynamic tests in the absence of the reaction;

- development of an enhanced liquid-liquid separation plant based on plate pack, coalescer, coalescer plus plate pack.

The fluid-dynamic information acquired on the different devices studied to generate the methanol/ oil dispersion is valid in the case of both a homogeneous and heterogeneous catalysis reactor, such as conventional batch reactors, static mixing plug flow reactors, slurry reactors (stirred tank reactor with the solid catalyst loaded as fine particles), batch or continuous fixed-bed reactor.

Static mixing, deeply studied during the project, proved to be an innovative and flexible tool for generating the methanol/oil dispersion. Static mixers are suitable for both homogeneous and heterogeneous catalysis, both in the batch and continuous operating modes.

An operation modality was proposed for batch stirred tank reactors based on a limited agitation time at a fixed rotational speed followed by the completion of the reaction without agitation. This alternative operational modality is supposed to lead to a significant reduction in the total agitation power consumption.

The optimisation of the stirred tank reactor carried out in this research work is also applicable to both homogeneous and heterogeneous catalysis in a batch plant, as the problem of a fast and effective dispersion of the initial methanol layer addressed in our research is common to both the catalytic systems.

The experimental procedures developed during the project can be used to investigate: i) possible other techniques or devices suitable for generating the liquid-liquid dispersion; ii) the reaction performance of biodiesel production, as well as of other liquid-liquid processes.

The main achievements that can have an impact on the industry or research sector are:

- development of a fast and reliable analytical method for the oil conversion assessment (FAME content) by refractive index;
- development of low cost fluid dynamic tests to investigate the characteristics and stability of a liquid-liquid dispersion. This tool is suitable for studying the influence of the operating conditions for the formation and maintenance of liquid-liquid dispersion with different dispersion generation devices (stirred tank reactor, static mixing);
- development of an apparatus for the generation of a high quality liquid-liquid dispersion using the static mixer;
- experimental procedures for the optimisation of a static mixing apparatus to generate the liquid-liquid dispersion in the case of biodiesel production;
- optimisation of the configuration of the conventional batch stirred tank reactor and of the operating conditions;
- development of a operation modality based on a limited agitation time at a fixed rotational speed followed by the completion of the reaction without agitation;
- the design of an innovative heterogeneous catalysis fixed bed reactor working in batch conditions and using static mixing to generate and maintain a liquid-liquid dispersion suitable to avoid mass transfer limitations on the reaction rate.

The study of fluid dynamic behaviour in tanks equipped with special inlet devices and/or inertial separator is necessary when two/three non miscible phases have to be separated. The results obtained in present research program show that an improvements of the separation performances are possible. For liquid-liquid separations, when plate packs are coupled with liquid-liquid coalescers, high separation efficiency could be reached also if the dispersed droplets are really tiny. The results obtained in present research program could

allow to improve the equipments needed in Biodiesel process production to separate the Esters form the Glycerine.

7. Liquid biofuel characterization test for applications in stationary engines power production.

Considering the results from the analysis carried out during “Liquid biofuel characterization test for applications in stationary engines power production”, we could conclude that blends of biodiesel and HFO and MDO, as well as pure vegetable oil (not blended) could be used as fuel for power generation, since their good stability in the lab test and no causing problems by precipitation of asphaltenes.

Likely such blends and pure cynara oil will be stable in real applications. As the conditions for ageing the fuel inside an engine are different from the conditions of this investigation, the obtained definitive results must be verified in an engine test.

Considering that the raw material is the base for a further development, a good collaboration with an adequate partner involved in the agriculture production, would be the most interesting partnership. This could be concluded in a very fruitful collaboration covering the necessities of integral agriculture-energy projects around the World and mainly in developing countries.

This kind of project can produce a very positive socio-economic impact at a local level contributing to Host Country’s Sustainable Development, covering the following aspects:

- Social well-being: improvement of employment, promotion of local people development, removal of social disparities between rural and urban areas, etc.
- Economic well-being: Diversification of energy sources, economic development and competitively.
- Environmental well-being: Reduction of GHG emissions and improvement of air quality, etc.
- Technology well-being: Technology transfer in power engines: fully substitution of fossil fuels in power plants by biofuels, research in new fuels, plantation areas, etc.

2 DISSEMINATION AND USE

This section provides a publishable summary of each exploitable result the project has generated. Only results usable outside the consortium are included.

2.1 DESCRIPTION OF RESULT #1

2.1.1 Description of the result

No. & TITLE OF RESULT

No.	Self-descriptive title of the result
1	Expertise (know-how) of the cultivation of cynara at large scale

CONTACT PERSON FOR THIS RESULT

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URL	
Specific Result URL	

SUMMARY

The cultivation of the cynara energy crop has been experimented at large scale (20 ha) as a field mechanized crop. Management techniques and mechanization have been worked out. Know-how potentially transferable to future cynara growers has been developed. Benefits of that might be the promotion of a rainfed energy crop native to the Mediterranean region, in which it would not run into biodiversity or sustainability issues.

SUBJECT DESCRIPTORS

Subject descriptors codes	142	CROP, CROP INPUTS/MANAGEMENT/YIELD ESTIMATION
	16	AGRONOMY

CURRENT STAGE OF DEVELOPMENT

Scientific and/or Technical knowledge (Basic research)	
Guidelines, methodologies, technical drawings	
Software code	
Experimental development stage (laboratory prototype)	
Prototype/demonstrator available for testing	
Results of demonstration trials available	X
Other (please specify.):	

INTELLECTUAL PROPERTY RIGHTS

Type of IPR	
Patent applied for	
Patent granted	
Patent search carried out	
Licence agreement(s) reached	
Partnership / other contractual agreement(s)	
Exclusive rights	
Registered design	
Trademark applications	
Copyrights registered	
Secret know-how	
Other - please specify : University	X

MARKET APPLICATION SECTORS

Possible sectors for application based on NACE classification.

Market application sectors	01	Agriculture, hunting and related service activities
	73	Research and development

2.1.2 Further collaboration, dissemination and use of the result

COLLABORATIONS SOUGHT

R&D	Further research or development	X	FIN	Financial support	
LIC	Licence agreement		VC	Venture capital/spin-off funding	
MAN	Manufacturing agreement		PPP	Private-public partnership	
MKT	Marketing agreement/Franchising		INFO	Information exchange	
JV	Joint venture		CONS	Available for consultancy	
			Other	(please specify)	

POTENTIAL OFFERED FOR FURTHER DISSEMINATION AND USE

Input, value and interest of the applications and the dissemination and use opportunities offered to potential partner(s).

Input: Know-how on the cultivation and mechanization of the cynara energy crop.
Opportunities: Promotion of an energy crop in the Mediterranean Region

PROFILE OF ADDITIONAL PARTNER(S) FOR FURTHER DISSEMINATION AND USE

Profile and expected input from the external partner(s).

Researchers and biomass investors.

2.2 DESCRIPTION OF RESULT #2

2.2.1 Description of the result

No. & TITLE OF RESULT

No.	Self-descriptive title of the result
2	Development of a stationary machinery chain for the separation of value-added cynara biomass fractions

CONTACT PERSON FOR THIS RESULT

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URL	
Specific Result URL	

SUMMARY

The concept of a biomass treatment facility for the separation of value-added cynara biomass fractions has been developed in a stationary machinery chain. Such facility would be fed with bales of whole biomass and would permit the valorization of the cynara fractions (seeds, stalks, pappi, floral hairs). In this way the harvest of cynara whole biomass could be easily achieved in only one run with advantages over other options involving several passes of machinery, i.e. lower energy inputs, less soil-ground risk. Components of the chain have been tested and designed at the prototype scale. Further development would be needed to scale it up.

SUBJECT DESCRIPTORS

Subject descriptors codes	503	POST HARVEST TREATMENT – NON-FOOD
	13	AGRICULTURAL PRODUCTION SYSTEMS

CURRENT STAGE OF DEVELOPMENT

Scientific and/or Technical knowledge (Basic research)	
Guidelines, methodologies, technical drawings	
Software code	
Experimental development stage (laboratory prototype)	
Prototype/demonstrator available for testing	X
Results of demonstration trials available	
Other (please specify.):	

INTELLECTUAL PROPERTY RIGHTS

Type of IPR	
Patent applied for	
Patent granted	
Patent search carried out	
Licence agreement(s) reached	
Partnership / other contractual agreement(s)	
Exclusive rights	
Registered design	
Trademark applications	
Copyrights registered	
Secret know-how	
Other - please specify : University	X

MARKET APPLICATION SECTORS

Possible sectors for application based on NACE classification.

Market application sectors	01	Agriculture, hunting and related service activities
	29	Manufacture of machinery and equipment n.e.c.

2.2.2 Further collaboration, dissemination and use of the result

COLLABORATIONS SOUGHT

R&D	Further research or development	X	FIN	Financial support	
LIC	Licence agreement		VC	Venture capital/spin-off funding	
MAN	Manufacturing agreement		PPP	Private-public partnership	
MKT	Marketing agreement/Franchising		INFO	Information exchange	
JV	Joint venture		CONS	Available for consultancy	
			Other	(please specify)	

POTENTIAL OFFERED FOR FURTHER DISSEMINATION AND USE

Input, value and interest of the applications and the dissemination and use opportunities offered to potential partner(s).

Input: Prototype developing the concept of cynara biomass treatment facility.
Opportunities: To scale-up machinery

PROFILE OF ADDITIONAL PARTNER(S) FOR FURTHER DISSEMINATION AND USE

Profile and expected input from the external partner(s).

Manufacturers of agricultural machinery.

2.3 DESCRIPTION OF RESULT #3

2.3.1 Description of the result

No. & TITLE OF RESULT

No.	Self-descriptive title of the result
3	Design, construction and operation of a new constant temperature deposition probe for evaluating ash deposition in combustion flue gases.

CONTACT PERSON FOR THIS RESULT

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URL	
Specific Result URL	

SUMMARY

Implementation of a new probe for evaluating ash deposition in combustion flue gases.

This probe is A 550°C controlled temperature deposition probe that has been specially designed for this purpose. The probe is equipped with a removable part which can be analyzed by Scanning Electron Microscopy (SEM) to study both the structure and composition of the ashes collected during the tests.

The objective of the probe is to evaluate the fouling tendency when burning different biomass fuel blends with coal.

SUBJECT DESCRIPTORS

Subject descriptors codes	349	LARGE SCALE GENERATION OF ELECTRICITY/HEAT
	137	CONTROL ENGINEERING
	201	ENERGY PRODUCTION FROM BIOMASS/WASTE
	197	ENERGY AND CLIMATE CHANGE

CURRENT STAGE OF DEVELOPMENT

Scientific and/or Technical knowledge (Basic research)	
Guidelines, methodologies, technical drawings	
Software code	
Experimental development stage (laboratory prototype)	
Prototype/demonstrator available for testing	X
Results of demonstration trials available	
Other (please specify.):	

INTELLECTUAL PROPERTY RIGHTS

Type of IPR	
Patent applied for	
Patent granted	
Patent search carried out	X
Licence agreement(s) reached	
Partnership / other contractual agreement(s)	
Exclusive rights	
Registered design	
Trademark applications	
Copyrights registered	
Secret know-how	
Other - please specify :	

MARKET APPLICATION SECTORS

Possible sectors for application based on NACE classification.

Market application sectors	40	Electricity, gas, steam and hot water supply
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2.3.2 Further collaboration, dissemination and use of the result

COLLABORATIONS SOUGHT*

R&D	Further research or development	X	FIN	Financial support	
LIC	Licence agreement		VC	Venture capital/spin-off funding	
MAN	Manufacturing agreement		PPP	Private-public partnership	
MKT	Marketing agreement/Franchising		INFO	Information exchange	
JV	Joint venture		CONS	Available for consultancy	
			Other	(please specify)	

POTENTIAL OFFERED FOR FURTHER DISSEMINATION AND USE

Input, value and interest of the applications and the dissemination and use opportunities offered to potential partner(s).

CIRCE can use the new developed probe design for experimental testing of the fouling phenomena in furnaces for many combustion applications: in grate, FB and PF furnaces, for instance.

PROFILE OF ADDITIONAL PARTNER(S) FOR FURTHER DISSEMINATION AND USE

Profile and expected input from the external partner(s).

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2.4 DESCRIPTION OF RESULT #4

2.4.1 Description of the result

No. & TITLE OF RESULT

No.	Self-descriptive title of the result
4	Cynara cannot be burnt alone in effective power plants with steam values > 420 C

CONTACT PERSON FOR THIS RESULT

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URL	
Specific Result URL	

SUMMARY

Cynara cannot be burnt alone in effective power plants with steam values > 420 C. Such trials would lead to strong superheater corrosion (when usual material are used) and big damages in that power plant.

This result was obtained at fluidised bed (FB) conditions in VTT. VTT and CIRCE co-operated in reporting stage. The value of that result might be to prevent big repairing costs in power plants aiming at burning Cynara directly. The production capacity and transporting logistics allow the combustion of Cynara alone only in small power plants. Then is essential

to a) a use low vapour temperature which lead to low efficiency of electricity production or (b) to test in pilot scale and then utilise additives destroying the corrosive compounds before entering to the superheater area (c) to use very expensive superheater material and different construction and location of the superheaters compared to a traditional furnace construction.

SUBJECT DESCRIPTORS

Subject descriptors codes	349	LARGE SCALE GENERATION OF ELECTRICITY/HEAT
	71	BIOMASS PROCESS INTEGRATION AND ENVIRONMENTAL IMPACTS
	389	METALLURGY
	197	ENERGY AND CLIMATE CHANGE

CURRENT STAGE OF DEVELOPMENT

Scientific and/or Technical knowledge (Basic research)	
Guidelines, methodologies, technical drawings	X
Software code	
Experimental development stage (laboratory prototype)	
Prototype/demonstrator available for testing	
Results of demonstration trials available	
Other (please specify.):	

INTELLECTUAL PROPERTY RIGHTS

Type of IPR	
Patent applied for	
Patent granted	
Patent search carried out	
Licence agreement(s) reached	
Partnership / other contractual agreement(s)	X
Exclusive rights	
Registered design	
Trademark applications	
Copyrights registered	
Secret know-how	
Other - please specify :	

MARKET APPLICATION SECTORS

Possible sectors for application based on NACE classification.

Market application sectors	40	Electricity, gas, steam and hot water supply
	27	Manufacture of basic metals
	29	Manufacture of machinery and equipment n.e.c.

2.4.2 Further collaboration, dissemination and use of the result

COLLABORATIONS SOUGHT

R&D	Further research or development	X	FIN	Financial support	X
LIC	Licence agreement		VC	Venture capital/spin-off funding	
MAN	Manufacturing agreement		PPP	Private-public partnership	
MKT	Marketing agreement/Franchising		INFO	Information exchange	
JV	Joint venture		CONS	Available for consultancy	
			Other	(please specify)	

POTENTIAL OFFERED FOR FURTHER DISSEMINATION AND USE

Input, value and interest of the applications and the dissemination and use opportunities offered to potential partner(s).

VTT has unique pilot plant facilities and newest analytical tools to determine and solve the detected operational problems at fluidised bed (FB) and grate (GC) combustion conditions. Furnace measurements can also be applied to full scale tests at GRATE, FB and PF furnaces. In addition VTT has high potential to test the effect of additives in preventing superheater corrosion.

PROFILE OF ADDITIONAL PARTNER(S) FOR FURTHER DISSEMINATION AND USE

Profile and expected input from the external partner(s).

Power producing companies in Spain and in other Mediterranean area where Cynara and other risky biomass types can be produced.

2.5 DESCRIPTION OF RESULT #5

2.5.1 Description of the result

No. & TITLE OF RESULT

No.	Self-descriptive title of the result
5	Cynara can be burnt together with Al silicate rich coals with shares 10% enb. in maximum without risks to superheater corrosion IF the Cynara feeding is even

CONTACT PERSON FOR THIS RESULT

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URL	
Specific Result URL	

SUMMARY

Cynara can be burnt together with Al silicate rich coals with shares 10% enb. in maximum without risks to superheater corrosion IF the Cynara feeding is even. This result was obtained both at fluidised bed (FB) conditions in VTT and at pulverised fuel (PF) conditions in CIRCE. It offers the possibility to decrease CO₂ emissions from a big power plant a little bit which can save costs and also give better imago to that plant. This result also helps to select the optimal coal and emphasizes the importance to invest to good feeding equipment for Cynara to guarantee even feeding to the furnace. Even feeding is important because

peaking shares of Cynara in the feedstock of the power plant might lead to superheater corrosion although the following higher portions of coal can partly compensate the corrosive reactions. < 10% share of Cynara in a power plant with > 100 MW_e is also in a good agreement with the production potential of Cynara at reasonable distances from the power plant (to keep the transporting costs reasonable)

SUBJECT DESCRIPTORS

Subject descriptors codes	349	LARGE SCALE GENERATION OF ELECTRICITY/HEAT
	71	BIOMASS PROCESS INTEGRATION AND ENVIRONMENTAL IMPACTS
	389	METALLURGY
	197	ENERGY AND CLIMATE CHANGE

CURRENT STAGE OF DEVELOPMENT

Scientific and/or Technical knowledge (Basic research)	
Guidelines, methodologies, technical drawings	X
Software code	
Experimental development stage (laboratory prototype)	
Prototype/demonstrator available for testing	
Results of demonstration trials available	
Other (please specify.):	

INTELLECTUAL PROPERTY RIGHTS

Type of IPR	
Patent applied for	
Patent granted	
Patent search carried out	
Licence agreement(s) reached	
Partnership / other contractual agreement(s)	X
Exclusive rights	
Registered design	
Trademark applications	
Copyrights registered	
Secret know-how	
Other - please specify :	

MARKET APPLICATION SECTORS

Possible sectors for application based on NACE classification

Market application sectors	40	Electricity, gas, steam and hot water supply
	27	Manufacture of basic metals
	29	Manufacture of machinery and equipment n.e.c.

2.5.2 Further collaboration, dissemination and use of the result

COLLABORATIONS SOUGHT*

R&D	Further research or development	X	FIN	Financial support	X
LIC	Licence agreement		VC	Venture capital/spin-off funding	
MAN	Manufacturing agreement		PPP	Private-public partnership	
MKT	Marketing agreement/Franchising		INFO	Information exchange	
JV	Joint venture		CONS	Available for consultancy	
			Other	(please specify)	

POTENTIAL OFFERED FOR FURTHER DISSEMINATION AND USE

Input, value and interest of the applications and the dissemination and use opportunities offered to potential partner(s).

VTT has unique pilot plant facilities and newest analytical tools to determine and solve the detected operational problems at fluidised bed (FB) conditions and CIRCE at pulverised fuel (PF) conditions by deposit quality analysis. In addition, VTT has special technology to analyse the corrosive compounds directly from VTT's pilot plants and full scale power plant furnaces.

PROFILE OF ADDITIONAL PARTNER(S) FOR FURTHER DISSEMINATION AND USE

Profile and expected input from the external partner(s).

Power companies with big coal-fired power plants in Mediterranean area with significant CO₂ payments and bad imago as fossil fuel users

2.6 DESCRIPTION OF RESULT #6

2.6.1 Description of the result

No. & TITLE OF RESULT

No.	Self-descriptive title of the result
6	Even low shares of sulphur rich Spanish lignite mixed with Cynara can protect the superheaters against corrosion. Such lignite may enable Cynara shares up to 50-70% enb

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E-mail*	martti.aho@vtt.fi
URL	
Specific Result URL	

SUMMARY

Even low shares of Spanish sulphur rich Spanish lignite (about 8 wt% S) mixed with Cynara can protect the superheaters against corrosion if there is a need to feed Cynara at high shares to a power plant. Such lignite may enable Cynara portions up to 50-70% on energy basis. However, this option is realistic only to small power plants let's say < 20 MW electricity. It is impossible to get as high portions of Cynara to big power plants for restricted production capacity per hectare and for logistic reasons (the transporting costs and distances

would be too high).

This result was obtained at fluidised bed (FB) conditions in VTT. VTT and CIRCE co-operated in reporting stage.

This result might be useful to small power plant with grate or FB technique. This might also help to utilise sulphur-rich low quality lignite in power production in a reasonable way. Such lignite can be found close to the production fields of Cynara in Mediterranean area.

SUBJECT DESCRIPTORS

Subject descriptors codes	349	LARGE SCALE GENERATION OF ELECTRICITY/HEAT
	71	BIOMASS PROCESS INTEGRATION AND ENVIRONMENTAL IMPACTS
	389	METALLURGY
	197	ENERGY AND CLIMATE CHANGE

CURRENT STAGE OF DEVELOPMENT

Scientific and/or Technical knowledge (Basic research)	
Guidelines, methodologies, technical drawings	X
Software code	
Experimental development stage (laboratory prototype)	
Prototype/demonstrator available for testing	
Results of demonstration trials available	
Other (please specify.):	

INTELLECTUAL PROPERTY RIGHTS

Type of IPR	
Patent applied for	
Patent granted	
Patent search carried out	
Licence agreement(s) reached	
Partnership / other contractual agreement(s)	X
Exclusive rights	
Registered design	
Trademark applications	
Copyrights registered	
Secret know-how	
Other - please specify :	

MARKET APPLICATION SECTORS

Possible sectors for application based on NACE.

Market application sectors	40	Electricity, gas, steam and hot water supply
	27	Manufacture of basic metals
	29	Manufacture of machinery and equipment n.e.c.

2.6.2 Further collaboration, dissemination and use of the result

COLLABORATIONS SOUGHT

R&D	Further research or development	X	FIN	Financial support	x
LIC	Licence agreement		VC	Venture capital/spin-off funding	
MAN	Manufacturing agreement		PPP	Private-public partnership	
MKT	Marketing agreement/Franchising		INFO	Information exchange	
JV	Joint venture		CONS	Available for consultancy	
			Other	(please specify)	

POTENTIAL OFFERED FOR FURTHER DISSEMINATION AND USE

Input, value and interest of the applications and the dissemination and use opportunities offered to potential partner(s).

VTT has unique pilot plant facilities and newest analytical tools to determine and solve the detected operational problems at fluidised bed (FB) and grate (GC) combustion conditions. Furnace measurements can also be applied to full scale tests at GRATE, and FB furnaces which are realistic options in this size class (< 20 MWe). In addition VTT has high potential to test the effect of additives in preventing superheater corrosion. CIRCE can assist VTT in coal quality optimisation (when Mediterranean sulphur rich coals are utilised)

PROFILE OF ADDITIONAL PARTNER(S) FOR FURTHER DISSEMINATION AND USE

Profile and expected input from the external partner(s).

Power production companies and individual power plants smaller than 20 MWe

2.7 DESCRIPTION OF RESULT #7

2.7.1 Description of the result

No. & TITLE OF RESULT

No.	Self-descriptive title of the result
7	Evaluation of the combustion and emissions characteristics of Cynara biomass during grate-firing and identification of potential operational problems.

CONTACT PERSON FOR THIS RESULT

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URL	
Specific Result URL	

SUMMARY

A fixed-bed combustion setup at the CHEC Research Centre, Technical University of Denmark (DTU) was applied for combustion tests on Cynara biomass, simulating grate-firing. A series of experiments were conducted on samples of Cynara while varying parameters such as combustion temperature [500 – 1050 °C], oxygen content in oxidiser, fuel particle size and fuel fractionation. The aim of the combustion tests was to evaluate the combustion characteristics and emission levels during grate-firing of Cynara biomass, thereby identifying potential operational problems.

From online measurements of the sample temperature and the O₂, CO₂, CO, NO and SO₂ concentrations in the outlet gas, the conversion process was monitored during an experiment.

The obtained results suggest that due to potential slagging and fouling problems, caused by a low ash melting point and a potentially high release to the gas phase of risky elements (alkali metals and Cl), Cynara is a problematic fuel if combusted alone, as would be the case in grate-fired boilers. However the results also suggest that the fuel quality may be improved by fuel fractionation or fertilizing and harvesting means. Stems was identified as a particular problematic fraction, as ash melting was observed already at a combustion temperature of 750 °C.

SUBJECT DESCRIPTORS

Subject descriptors codes	71	BIOMASS PROCESS INTEGRATION AND ENVIRONMENTAL IMPACTS
	117	COMBUSTION BASICS AND EFFICIENCY
	201	ENERGY PRODUCTION FROM BIOMASS/WASTE

CURRENT STAGE OF DEVELOPMENT

Scientific and/or Technical knowledge (Basic research)	X
Guidelines, methodologies, technical drawings	
Software code	
Experimental development stage (laboratory prototype)	
Prototype/demonstrator available for testing	
Results of demonstration trials available	
Other (please specify.):	

INTELLECTUAL PROPERTY RIGHTS

Type of IPR	
Patent applied for	
Patent granted	
Patent search carried out	
Licence agreement(s) reached	
Partnership / other contractual agreement(s)	
Exclusive rights	
Registered design	
Trademark applications	
Copyrights registered	

Secret know-how	
Other - please specify :	

MARKET APPLICATION SECTORS

Possible sectors for application based on NACE classification.

Market application sectors	73	Research and development
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2.7.2 Further collaboration, dissemination and use of the result

COLLABORATIONS SOUGHT

R&D	Further research or development	X	FIN	Financial support	
LIC	Licence agreement		VC	Venture capital/spin-off funding	
MAN	Manufacturing agreement		PPP	Private-public partnership	
MKT	Marketing agreement/Franchising		INFO	Information exchange	X
JV	Joint venture		CONS	Available for consultancy	
			Other	(please specify)	

POTENTIAL OFFERED FOR FURTHER DISSEMINATION AND USE

Input, value and interest of the applications and the dissemination and use opportunities offered to potential partner(s).

Potential offered: Research within characterisation and evaluation of biomass based fuels for valorization in grate-fired boilers. Dissemination through scientific journals, conferences, workshops etc.

PROFILE OF ADDITIONAL PARTNER(S) FOR FURTHER DISSEMINATION AND USE

Profile and expected input from the external partner(s).

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2.8 DESCRIPTION OF RESULT #9

2.8.1 Description of the result

No. & TITLE OF RESULT

No.	Self-descriptive title of the result
9	A durable acid catalyst for the esterification of free fatty acids in vegetable oil using a fixed bed reactor.

CONTACT PERSON FOR THIS RESULT

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URL	http://www-lcs.ensicaen.fr/spip.php?auteur103
Specific Result URL	

SUMMARY

Vegetable oils or recycled cooking oils can be used to produce bio-diesel (fatty acid methyl esters, FAME) by transesterification. However, the free fatty acids (FFA) often present in these liquids poison the transesterification catalyst.

The esterification of FFA present in vegetable oils with CH₃OH using a solid catalyst is a promising method to convert FFA into FAME and obtain a FFA-free oil that can be further transesterified using alkali bases. A silica-supported Nafion® resin (SAC-13) appeared as the most promising catalyst, requiring no activation and being only mildly and reversibly

affected by water. The combination of SAC-13 and a fixed bed-reactor system could lead to a practical and cost-effective FFA removal unit in front of typical oil transesterification units.

End-user may be small or medium size businesses interested in converting natural or recycled vegetable oils into fuel.

The durability of the catalyst was excellent. Note that other cheaper resins could probably be used. The possibility to use a fixed bed reactor offer marked advantages in terms of operating and separation cost as compared to traditional homogeneous processes.

The process has not yet been used with real recycled cooking oil and the effect of some related impurities are not known.

SUBJECT DESCRIPTORS

Subject descriptors codes	102	CHEMICAL TECHNOLOGY AND ENGINEERING
	103	CHEMISTRY/HOMOGENEOUS AND HETEROGENEOUS CATALYSIS/THEORETICAL/NANOCHEMISTRY
	201	ENERGY PRODUCTION FROM BIOMASS/WASTE
	246	FUELS: ALTERNATIVE FUELS IN TRANSPORTS

CURRENT STAGE OF DEVELOPMENT

Scientific and/or Technical knowledge (Basic research)	X
Guidelines, methodologies, technical drawings	
Software code	
Experimental development stage (laboratory prototype)	
Prototype/demonstrator available for testing	
Results of demonstration trials available	
Other (please specify.):	

INTELLECTUAL PROPERTY RIGHTS

Type of IPR	
Patent applied for	
Patent granted	
Patent search carried out	
Licence agreement(s) reached	
Partnership / other contractual agreement(s)	
Exclusive rights	
Registered design	
Trademark applications	
Copyrights registered	

Secret know-how	
Other - please specify : Published in scientific journal	X

MARKET APPLICATION SECTORS

Possible sectors for application based on NACE classification.

Market application sectors	37	Recycling
	50	Sale, maintenance and repair of motor vehicles and motorcycles; retail sale of automotive fuel
	73 I	<i>Research and experimental development on natural sciences and engineering</i>

2.8.2 Further collaboration, dissemination and use of the result

COLLABORATIONS SOUGHT.

R&D	Further research or development		FIN	Financial support	
LIC	Licence agreement		VC	Venture capital/spin-off funding	
MAN	Manufacturing agreement		PPP	Private-public partnership	
MKT	Marketing agreement/Franchising		INFO	Information exchange	
JV	Joint venture		CONS	Available for consultancy	X
			Other	(please specify)	

POTENTIAL OFFERED FOR FURTHER DISSEMINATION AND USE

Input, value and interest of the applications and the dissemination and use opportunities offered to potential partner(s).

The catalyst is already commercially available but cheaper version based on different resins can most likely be used. We would welcome more research work on other resins.

PROFILE OF ADDITIONAL PARTNER(S) FOR FURTHER DISSEMINATION AND USE

Profile and expected input from the external partner(s).

The external partners should fund a PhD student and basic research equipment (glassware, gas-chromatograph) that would allow us investigating the activity and stability of cheaper acidic resins.

We are primarily interested in publishing but patent protection would be sought if requested by the partner.

The market might become limited to recycled cooking oil if food prices pressurize the cost of vegetable oils.

2.9 DESCRIPTION OF RESULT #10

2.9.1 Description of the result

No. & TITLE OF RESULT

No.	Self-descriptive title of the result
10	Development of an optimization methodology for biodiesel production reactors based on different ways to generate the liquid-liquid dispersion using traditional agitation systems (stirred tank reactor) and innovative devices (static mixer reactor). The methodology comprises fluid dynamic tests in the absence of the reaction. Side results are: a) the development of a fast, easy and reliable analytical method for the assessment of oil conversion (FAME content), utilizing the refractive index, b) the design and assembly of an innovative heterogeneous catalysis fixed bed reactor working in batch conditions and using static mixing to generate and maintain a liquid-liquid dispersion suitable to avoid mass transfer limitations to the reaction rate.

CONTACT PERSON FOR THIS RESULT

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Specific Result URL	http://www.dicma.unibo.it/DICMA/Ricerca/Progetti+e+attivita/Biodiesel.htm

SUMMARY

The main achievements are:

- development of a fast and reliable analytical method for the assessment of oil conversion (by refractive index);
- development of low cost fluid dynamic tests to investigate the characteristics and stability of a liquid-liquid dispersion. This tool is suitable for studying the influence of the operating conditions on the formation and maintenance of a liquid-liquid dispersion with different dispersion generation devices (stirred tank reactor, static mixing);
- development of an apparatus for the generation of a high quality liquid-liquid dispersion using static mixers;
- optimisation of a static mixing apparatus to generate the liquid-liquid dispersion in the case of biodiesel production;
- optimisation of the configuration of a conventional batch stirred tank reactor and of the operating conditions;
- development of an operation modality based on a limited agitation time at a fixed rotational speed followed by the completion of the reaction without agitation. This alternative operational modality is supposed to lead to a significant reduction of the total agitation power consumption.
- an innovative heterogeneous catalysis fixed bed reactor using static mixing to generate and maintain a methanol-oil liquid-liquid dispersion suitable to avoid mass transfer limitations on the biodiesel reaction rate.

SUBJECT DESCRIPTORS

Subject descriptors codes	28	ANALYTICAL CHEMISTRY
	176	ECONOMIC AND ENVIRONMENT IMPACTS
	356	LIQUID BIOFUELS
	507	PROCESS EFFICIENCY

CURRENT STAGE OF DEVELOPMENT

Scientific and/or Technical knowledge (Basic research)	
Guidelines, methodologies, technical drawings	
Software code	
Experimental development stage (laboratory prototype)	X
Prototype/demonstrator available for testing	
Results of demonstration trials available	
Other (please specify.):	

INTELLECTUAL PROPERTY RIGHTS

Type of IPR	
Patent applied for	
Patent granted	
Patent search carried out	
Licence agreement(s) reached	
Partnership / other contractual agreement(s)	
Exclusive rights	
Registered design	
Trademark applications	
Copyrights registered	
Secret know-how	
Other - please specify :	

MARKET APPLICATION SECTORS

Possible sectors for application based on NACE classification.

Market application sectors	24	Manufacture of chemicals and chemical products
	29	Manufacture of machinery and equipment n.e.c.
	73 I	<i>Research and experimental development on natural sciences and engineering</i>

2.9.2 Further collaboration, dissemination and use of the result

COLLABORATIONS SOUGHT

R&D	Further research or development	X	FIN	Financial support	
LIC	Licence agreement		VC	Venture capital/spin-off	
MAN	Manufacturing agreement		PPP	Private-public partnership	
MKT	Marketing agreement/Franchising		INFO	Information exchange	
JV	Joint venture		CONS	Available for consultancy	
			Other	(please specify)	

POTENTIAL OFFERED FOR FURTHER DISSEMINATION AND USE

Input, value and interest of the applications and the dissemination and use opportunities offered to potential partner(s).

The experimental investigation of conventional and innovative mixing techniques allowed the individuation of mixing configurations characterized by a drastic reduction of the specific energy consumption in comparison with the traditional, non-optimized mixing configurations. In particular, the best reaction performances were obtained with the presence of a high-energy event at the beginning of the transesterification reaction followed by a low-power or null mixing. These results ensure the attainment of a significant improvement of the energy balance associated with biodiesel production.

The fluid-dynamic information acquired regarding the different devices studied to generate the methanol/ oil dispersion is valid in the case of both a homogeneous and heterogeneous catalysis plant, such as conventional batch reactors, static mixing plug flow reactors, slurry reactors (stirred tank reactor with the solid catalyst loaded as fine particles), batch or continuous fixed-bed reactor.

Static mixing, deeply studied during the project, proved to be an innovative and flexible tool for generating the methanol/oil dispersion. Static mixers are suitable for both homogeneous and heterogeneous catalysis, both in the batch and continuous operating modes.

An operation modality was proposed for batch stirred tank reactors based on a limited agitation time at a fixed rotational speed followed by the completion of the reaction without agitation. This alternative operational modality is supposed to lead to a significant reduction in the total agitation power consumption.

Finally, the heterogeneous catalysis fixed bed reactor is available in the laboratories of the UNIBO research group. This reactor can be used to test heterogeneous catalysts, as well as to investigate the influence of a fixed bed on a liquid-liquid dispersion passing across it.

PROFILE OF ADDITIONAL PARTNER(S) FOR FURTHER DISSEMINATION AND USE

Profile and expected input from the external partner(s).

The UNIBO research group can cooperate with research groups operating in the field of heterogeneous catalysis for liquid-liquid reactions, to test heterogeneous catalysts in the above-described heterogeneous catalysis fixed bed reactor.

2.10 DESCRIPTION OF RESULT #11

2.10.1 Description of the result

No. & TITLE OF RESULT

No.	Self-descriptive title of the result
11	Development of an enhanced separation plant for the liquid-liquid based on plate pack, coalescer, coalescer plus plate pack.

CONTACT PERSON FOR THIS RESULT

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Fax	+390516347788
E-mail*	alessandro.paglianti@mail.ing.unibo.it
URL	http://www.unibo.it/SitoWebDocente/default.htm?UPN=alessandro.paglianti@unibo.it
Specific Result URL	

SUMMARY

This research unit has analysed the fluid dynamics of gas-liquid (not in present research program) and of liquid-liquid separators moreover of gas-liquid distributors/equalisers:

b) Liquid-liquid separators are installed in horizontal and vertical vessels to increase the efficiency of separation between two liquid phases, that cannot mix together, in order to reduce the loss of expensive products, increase the purity of each phase, stop the corrosion of downstream equipment and reduce pollution due to products that could be drained out

into the surrounding environment. These internals are used not only in the sector of offshore platforms but also for all steps of natural gas and oil treatment in the post-extraction phases. Gas-liquid distributors/equalizers are installed on the feed inlet nozzles of vessels (horizontal or vertical) or distillation columns to allow for uniform gas distribution in the inlet area and to promote a primary separation of the liquid present in the gas. Flow equalisers are normally installed in horizontal vessels to uniformly distribute the vapour stream, break the waves and stop any foam present on the surface of the liquid, obtaining pre-separation of the larger droplets carried by the vapour stream upstream of the gas-liquid separators.

The results obtained in present research program could allow to improve the equipments needed in Biodiesel process production to separate the Esters form the Glycerine.

SUBJECT DESCRIPTORS

Subject descriptors codes	102	CHEMICAL TECHNOLOGY AND ENGINEERING
	155	DESIGN, DESIGN ENGINEERING
	194	EMISSION
	213	ENVIRONMENTAL TECHNOLOGY/ENGINEERING, POLLUTION CONTROL
	447	OFFSHORE TECHNOLOGY, SOIL MECHANICS, HYDRAULIC ENGINEERING

CURRENT STAGE OF DEVELOPMENT

Scientific and/or Technical knowledge (Basic research)	
Guidelines, methodologies, technical drawings	
Software code	
Experimental development stage (laboratory prototype)	
Prototype/demonstrator available for testing	X
Results of demonstration trials available	
Other (please specify.):	

INTELLECTUAL PROPERTY RIGHTS

Type of IPR	
Patent applied for	
Patent granted	
Patent search carried out	
Licence agreement(s) reached	
Partnership / other contractual agreement(s)	
Exclusive rights	
Registered design	

Trademark applications	
Copyrights registered	
Secret know-how	
Other - please specify :	

MARKET APPLICATION SECTORS

Possible sectors for application based on NACE classification.

Market application sectors	11	Extraction of crude petroleum and natural gas; service activities incidental to oil and gas
	24	Manufacture of chemicals and chemical products
	29	Manufacture of machinery and equipment n.e.c.
	73I	<i>Research and experimental development on natural sciences and engineering</i>

2.10.2 Further collaboration, dissemination and use of the result

COLLABORATIONS SOUGHT

R&D	Further research or development	X	FIN	Financial support	
LIC	Licence agreement		VC	Venture capital/spin-off funding	
MAN	Manufacturing agreement		PPP	Private-public partnership	
MKT	Marketing agreement/Franchising		INFO	Information exchange	
JV	Joint venture		CONS	Available for consultancy	
			Other	(please specify)	

POTENTIAL OFFERED FOR FURTHER DISSEMINATION AND USE

Input, value and interest of the applications and the dissemination and use opportunities offered to potential partner(s).

The study of fluid dynamic behaviour in tanks equipped with special inlet devices and/or inertial separator is necessary when two/three non miscible phases have to be separated. The results obtained in present research program show that an improvements of the separation performances are possible.

For liquid-liquid separations, when plate packs are coupled with liquid-liquid coalescers, high separation efficiency could be reached also if the dispersed droplets are really tiny.

Finally, a new experimental rig is available by UNIBO research group and can be used to

test inlet distributors, vane type demisters, wire mesh demisters, plate packs, axial cyclones etc.

PROFILE OF ADDITIONAL PARTNER(S) FOR FURTHER DISSEMINATION AND USE

Profile and expected input from the external partner(s).

The UNIBO research group can cooperate with research groups operating in the field of inertial two/three phase separation to test/analyse inlet distributors and/or special separators.

