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Project concept and objectives: Key information

The EuroBioRef project (European Multilevel Integrated Biorefinery Design for Sustainable Biomass Processing; [www.eurobioref.org](http://www.eurobioref.org)) was a 4 years program coordinated by CNRS, France, launched on March 1st, 2010 and closed on February 28th, 2014. It was supported by a 23 M€ grant from the European Union Seventh Framework Program (FP7). EuroBioRef had this unique feature of dealing with the entire process of transformation of biomass, from non-edible crops production to final commercial products. It involved 29 partners (industry, SMEs, academics) from 15 different countries (see map next page) in a highly collaborative network, including crop production, biomass pre-treatment, fermentation and enzymatic processes, catalytic processes, thermochemical processes, assessed by a life cycle analysis and an economic evaluation of the whole development chain (scheme p. 7). With this strategy to develop next generation biorefineries (scheme p. 7), the project generated a lot of results, with an important impact on the European bioeconomy, including new energy & new chemicals (figure p.8) production strategies.
EUROpean multilevel integrated BIORefinery design for sustainable biomass processing

EuroBioRef Consortium

COORDINATOR
M. Franck DUMEIGNIL, CNRS-UCCS – franck.dumeignil@univ-lille1.fr

PARTNERS
1. CNRS, Centre National de la Recherche Scientifique (UMR8181, UMR6256, UMR6509), France
2. ARKEMA FRANCE SA /CECA, France – jean-luc.dubois@arkema.com
3. BORREGAARD Industries. Ltd., Norway
4. NOVOZYMES A/S, Denmark
5. Partner 5 left the project without contributing and was replaced by partners 29 and 30 below
6. CRES, Centre for Renewable Energy Sources, Greece
7. HALDOR TOPSØE A/S, Denmark
8. CERTH, Centre for Research & Technology Hellas, Greece
9. PDC, Process Design Center BV, the Netherlands
10. QUANTIS, Switzerland
11. EUBIA, European Biomass Industry Association, Belgium
12. DTI, Danish Technological Institute, Centre for Renewable Energy and Transport, Denmark
13. Technische Universität Dortmund, Germany
14. MERCK KGaA, Germany
15. FEUP Faculdade de Engenharia da Universidade do Porto, Portugal
16. RWTH Aachen, Germany – retired from the project on 31/08/2011
17. CIRCC, University of Bari, Italy
18. WSK «PZL-Rzeszow» S.A, Poland
19. OBRPR, Ośrodek Badawczo-Rozwojowy Przemysłu Rafineryjnego Spółka Akcyjna, Poland
20. SINTEF Materials and Chemistry, Norway
21. SOABE, Société Agricole de Befandriana-Sud & Partners Sarl, Madagascar
22. UMICORE AG & Co KG, Germany
23. Nykomb Synergetics AB, Sweden
24. Alma Consulting Group SAS, France
25. Ruse Chemicals AD, Bulgaria (deremerger from Orgachim AD, Bulgaria from 1st January 2014)
26. Imperial College of Science and Technology, United Kingdom
27. Novance, France
28. University of Warmia and Mazury in Olsztyn, Poland
29. Technische Universität Hamburg – Hamburg, Germany – entered the project from M24
30. BKW Biokraftwerke Fürstenwalde GmbH, Germany – entered the project from M24

ACKNOWLEDGEMENTS
The research leading to these results has received funding from the European Union’s Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 241718 EuroBioRef.
A success story that was closely followed by the EC, with high expectations

“EuroBioRef – How a radical re-design is strengthening economic viability in the bioeconomy”. “For most people, the bioeconomy is the way of the future. A shift towards an economy based on renewable resources not on fossil fuels is no longer just an option, it’s a necessity.”

View the article online: http://ec.europa.eu/research/infocentre/article_en.cfm?item=Result%20of%20search&id=/research/star/index_en.cfm?p=ss-eurobioref&calledby=infocentre&artid=25553

Main results

- 5 lignocellulosic plants (willow, giant reed, miscanthus, switchgrass, cardoon) and 10 oil crops (castor, crambe, cuphea, lesquerella, lunaria, jatropha, safflower, as well as sunflower, camelina and rapeseed for comparison) were grown in test fields;
- Large test fields were set for willow and crambe in Poland, giant reed and safflower in Greece and castor in Madagascar, with ultimately the production of ca. 10 t for the latter;
- Win-win culture rotation strategies between food and non-food crops have been developed and proven;
- Efficient biotech technologies have been developed to yield platform molecules from glycerol and biomass hydrolyzates, which outperform even the current state of the art;
- A biomass supply logistics model has been developed, which operates in an optional mode in terms of biomass quality (new and unexplored biomass types), system efficiency and reduced operational costs. It was exemplary populated with data for willow, castor, safflower and giant reed. Scenarios have been considered based on different plant capacities;
- A brand new pilot plant in Norway able to operate more than 50 kg of dry lignocellulosic materials per hour has been constructed, using a new and feedstock agnostic pretreatment process validated at the lab scale on miscanthus, giant reed and switchgrass;
- So far, 24 patents were filed, mostly related to vegetable oils conversions, which means that, to date, EuroBioRef reached 1.04 patent application per Million Euro of public money spent;
- So far, 29 scientific papers were published, and more are in preparation. Then, to date, EuroBioRef reached 1.26 publications per Million Euro of public money spent;
- A 20 min video explaining the project is available on the EuroBioRef Website (www.eurobioref.org);

- A 6 min video summarizing the outcomes of the project is available on the EuroBioRef Website: http://www.eurobioref.org/index.php/eurobioref-results

• **Value chains corresponding to different scenarios of biorefineries** integrating results and concepts developed in EuroBioRef have been designed, and were multidimensionally assessed, to realize demonstrations of the developed technologies, but also to test scenarios of industrial exploitation;

• On 11-12 February 2014, we organized two one-day conferences in Brussels with our sister biorefinery research projects Biocore and Suprabio *‘Tomorrow’s Biorefineries in Europe’*, notably to present our results and propose our technologies to stakeholders. More information here: [https://colloque.inra.fr/eubiorefineryprojectsfinalconf](https://colloque.inra.fr/eubiorefineryprojectsfinalconf);

• A new web-based integrated life cycle assessment tool was designed and is fully operational to check the socio-economical validity of the biorefinery scenarios.

EuroBioRef is a clear demonstration on how to re-energise the European economy through bioeconomy. This will create activity thanks to new technological options, with job creation and job savings by revamping of existing units to high tech applications.

### Global summary of the achievements

6 value chains have been generated:

**Value Chain 1:** Castor oil to polymers;
**Value Chain 2:** Crambe/Safflower oils to polymers;
**Value Chain 3:** Alcohols to fuels (ATF);
**Value Chain 4:** Lignocellulosics to acrylates (abandoned due to low technological advancement);
**Value Chain 5:** Syngas based products;
**Value Chain 6:** Integrated productions in existing Assets.

A short description of these value chains is given below. Full details are provided in the next part of the document for the reader who would like more information.

**VALUE CHAINS 1 & 2: CASTOR/CRAMBE/SAFFLOWER OILS TO POLYMERS.**

Both value chains are dealing with vegetable oils and are technologically the most advanced ones. The purpose of VC1 is to start from castor and produce a high value monomer with some co-products being used as fuel. VC2 starts with oleaginous crops (Crambe, Safflower) producing high value monomers and short fatty acids, suitable for fuel application once esterified. VC1 and VC2 have several steps in common: Beside the market for end products, several transformation steps are in common. Both VCs have the possibility to start from castor, crambe and safflower. Further, a route was proposed to the Castor Oil (VC1) and combines it with the chemistry of VC2 to deliver monomers even more interesting than those initially planned in VC2. Thus, as previously mentioned, due to similarities and to common outputs, these Value Chains have been merged.

**VALUE CHAINS 3 & 5: FUELS AND SYNGAS DERIVED PRODUCTS.**

These Value chains relate to the production of “ATF” used for aviation fuels (VC3) and to the conversion of black liquor to syngas-derived products (VC5) including alcohols. Then, VC3 is closely related to VC5 as both share the same route of syngas production via gasification and its consecutive conversion to alcohols. However, VC3 also considers another way of production of heavy alcohols/branched paraffins via advanced chemical routes to be blended as components of aviation gasoline and jet fuel.

**VALUE CHAIN 4: BIOBASED ACRYLATES.**

This Value chain deals with conversion of lignocellulosic crops to hydrolysates, fermentation to 3-hydroxypropionic acid, then dehydration to acrylic acid, and in parallel fermentation of sugar hydrolysates and glycerol to n-butanol before a...
final esterification step by reactive distillation to produce butyl acrylate. Due to lack of technological maturity / economical viability, it was decided to drop the demonstration of this value chain and to redistribute some useful competencies in the other value chains.

VALUE CHAIN 6: INTEGRATION OF EUROBIOREF TECHNOLOGIES IN EXISTING ASSETS.
VC6 offers a framework to consider EuroBioRef chemistries and technologies as additions to existing, preferably European plants. Several such “co-location” scenarios have been proposed as modifications of VCs 1 to 4, VC5 being a co-location model by itself. On the other hand, 11 co-location models have been identified for EuroBioRef conversions, which are not studied in any of the other VCs. The work was re-focused on the most promising value chains. With the addition of the 2 products coming from VC4, Value chain 6 seeks to demonstrate the cases in which it makes sense to add a biobased production in an existing asset (plant) and capitalize on skilled personnel, available infrastructure, and plant integration. In this case, the Integrated Biorefinery is looking at the integration of a biobased product in a fossil (or bio) existing asset.

Final results, intentions for use and impact

BUSINESS RESULTS WERE OBTAINED ON:
- Demonstration of the economic and technical performance of biobased products including bio-aviation fuels and chemicals;
- Demonstration of the increase in economic performance due to use of second-generation feedstock by using the whole plant in a zero waste concept;
- Demonstration of the sustainable value chain of non-food crops cultivated in synergy with food-crops, through rotation strategies that benefit to both food and non-food crops yields;
- Definition of final products specifications and tests of new products to be able to propose them directly to the customers.

SCIENTIFIC INNOVATION IS FOCUSED ON:
- Methods for conceptual process design widely applied in the chemical sector towards bio-/chemical applications;
- Heterogeneous, homogeneous and enzymatic catalytic systems including fermentation and optimization of the formulations taking into account the purity of the feedstock;
- New low energy separation techniques and adaptation to biomass-derived products, which enable lowering of the overall cost;
- New reactor technologies for minimizing production of by-products while enabling substantial energy savings;
- Co-products reutilization technologies in order to further increase the attractiveness of the process;
- Integrated reaction/separation technologies for optimized process design;
- Development of new purification technologies for the fermentation broth using green solvents, which further improve the overall sustainability.

SUBSTANTIAL ADVANCEMENTS WERE MADE ON:
- Crop rotations optimization for Northern/Southern Europe and Africa, selection of appropriate sustainable biomass feedstock for diverse EU environments;
- Rationalization of the chain elaborated to yield each product and global integration/optimization of the whole process;
- Quality control of a variety of feedstock for a variety of end-products to set high level standards;
• Demonstration at the lab/bench scale of sub-units and demonstration at the pilot scale of integrated chains for significant products;
• Integration of several reaction and separation steps for high selectivity and conversion, energy and Capital (CAPEX) reduction.

SUSTAINABILITY ASSESSMENT AND PERFORMANCES
• Specific logistic methodology for cultures in Northern and Southern Europe;
• LCA methodology for evaluation of environmental performances;
• Economic modelling for assessment of economic viability;
• Sustainable assessment of the whole chain for economics.

SOCIO-ECONOMIC IMPACT AND SOCIETAL IMPLICATIONS OF THE PROJECT
• Creation of specialized jobs in rural areas;
• Developing business/side businesses in local economies;
• The investigated value chains could contribute to about 100 to 200 direct jobs, and up to 3,600 jobs when taking into account the indirect jobs and farming jobs corresponding to each implementation.

PREPARATION OF THE EXPLOITATION PLAN OF THE PROJECT (FIGURE BELOW)
EuroBioRef prepared its exploitation plan taking into account sales from each partner in 2017 and at mature market, and self-assessing a probability of success. The workplan was accordingly adjusted in order to increase the chances to reach the market and to cross the so-called “Valley of Death”.

Exploitation of the Results @ Year 2017 (each color corresponds to a partner) - Results at M48
Value Chains 1 & 2:
Vegetable oils to high value monomers .............................................................. 14

Value Chain 3:
Lignocellulosics (aviation fuels) biorefinery ..................................................... 24

Value Chain 5:
Syngas-based biorefinery towards higher alcohols, $H_2O_2$ and MeSH .......... 32

Value Chain 6:
Integration of technologies in existing units ...................................................... 39
Both Value Chains 1 (VC1) and 2 (VC2) are dealing with vegetable oils. The purpose of VC1 is to go from castor to a high value monomer for polyamides with some co-products being used as fuel. VC2 starts with oleaginous crops (crambe, safflower) producing high value monomers and short fatty acids, suitable for fuel application once esterified. VC1 and VC2 have several steps in common. Besides the market for end products, there are also several transformation steps in common. In fact, both value chains have the possibility to start from castor, crambe and safflower and some routes have been proposed, which combine VC1 and VC2. Thus, these value chains have been merged for their analyses.

a) General description of the Value Chain (Figure 1)

Figure 1: VC1&2 general description

Four main options have been investigated in the project:

CASTOR → PA12
Metathesis base case (Chemistry A)

CASTOR → PA12
Metathesis best case (less steps → lower CAPEX: Chemistry B)
Hydroformylation (high TON number: Chemistry C)

CASTOR → PA11-PA12 (no need for expensive catalyst: chemistry D)

Concerning the castor production, a specific scenario has been proposed in Madagascar (Figure 2):

The key issues for the Madagascar scenario are identified. We propose an annual crop rotation with a leguminous plant such as black-eyed bean in order to get savings in terms of fertilizers, pesticides and herbicides. This is also a way to bring more value to the farmers compared to a single leguminous culture. We established that manual harvest, optimizing the seeds yield (2-3 harvests a year) and leaving the straw on the field as a carbon source are optimum. At a reasonable scale for Soabe (15,000 ha), solvent extraction could be avoided for oil recovery. The scenario involves crushing the castor seeds in Madagascar using oil-powered generators that could be powered by jatropha oil. The oily cake will be partly used as a fertilizer, but also for biogas production with the knowledge that other sources for biogas such as fruit wastes, or unused biomass from available land, are available in Madagascar. These can be blended for biogas production. The biogas digestate rich in nitrogen can also be used as a fertilizer. Finally, the hull will be transformed in activated carbon.

The final monomer application would require additional 30,000 ha of castor cultivation. A European scenario has been investigated by CRES, showing that production of castor and safflower can be made basically in similar areas in Southern or Eastern Europe (Figure 3). A variety improvement program will also be profitable for castor in order to get homogeneous ripening and shorter cycling time.
b) Competition

The final application targets the polyamides market and will compete with existing polymers: PA12 from butadiene, PA11 from castor oil, and PA10,10 from castor oil. PA9 and PA13 are new polymers that would also compete with these existing polymers.

The polyamides market (Figure 4) can be segmented in short-chains polyamides (PA6, PA6,6) and long-chains polyamides (PA6,10, PA6,12, PA10,10, PA11, PA12). Short chains polyamides are commodity polymers with huge volumes and low prices. Long-chains polyamides bring more technical performance in terms of flexibility, moisture resistance, stress cracking resistance and polar fluid resistance. Price is very dependent on performance and end-use application. With VC1&2, we are targeting the high performance segment of long-chains polyamides. The main applications are automotive (fuel lines, flexible pipes, air-brake tubing systems), energy (off shore pipes for oil recovery) and sport and leisure (shoe soles). It is a growing market (about 5% per year, mainly in Asia and South-America) and the market is estimated to grow at a rate of 10,000 tons/year. The main competitors are Arkema (EuroBioRef partner), Evonik, Ube and EMS.

Figure 4 : Polyamides market
The worldwide castor oil production is about 600,000 tons/year (www.castoroil.in) with more than 80% coming from India (Figure 5). The main applications are lubricants, polymers (polyurethanes, polyamides, polyesters) and cosmetics. Main competitors are India (Wilmar, Jayant), China and Brazil.

**Figure 5 : Castor oil trade flows**

The worldwide safflower oil production is about 130,000 tons/year. Main producers are India, USA, Mexico and Argentina (Figure 6). There is only little production in Europe (Russia, Spain). Price fluctuates around the world due to trading issues, but it is possible to get safflower oil at around 1200 $/t.

**Figure 6 : Safflower oil production and trade flows**

**MARKET SUMMARY**

**Need:** There is a need for high performance polymers based on renewable resources. There is also a growing market for castor oil for polyurethane, lubricants, cosmetics…

**Value to the customer:** The polymers have high technical properties such as chemical resistance and mechanical properties at high temperatures and offer a renewable alternative to metals.

**Market Opportunity:** There is a growing need for polymers to substitute metals in transportation (cars, airplanes,…) and then reduce carbon dioxide emissions.

**Impact:** Technical polyamides find applications in cars (under the hood), but also sports, crude oil transportation, low-pressure natural gas transportation, electrical industry…
c) Technology

VC1&2 both rely on existing and innovative technologies. Castor oil production is already established at the industrial scale and the challenge of the project was to evaluate and adapt this production in Europe and Madagascar/Africa. Transesterification of castor oil and thermal cracking of methylricinoleate are already industrially operated by Arkema, while the purpose of the project was to improve the cracking process bringing a 30% energy saving. Metathesis is a key innovative technology. The final PA12 is an existing polymer, but currently obtained from the fossil-based lactam-12 (Laurolactam) or amino-acid monomers.

Safflower and Crambe plantations are known, but need to be adapted to European conditions. Oil extraction and hydrolysis rely on commercial technologies. Nitrilation is already carried out at an industrial scale from different fatty acids. The main challenge lies in the oxidative cleavage of the nitrile compound especially with the separation/purification issues of the products.

The different options investigated for VC1&2 have been ranked with the IPscore tool and compared with the current commercial reference (Figure 7).

Figure 7: IPscore of the VC1&2 options

**TECHNOLOGY SUMMARY**

**TECHNOLOGY AND SPONSORSHIP**

**Technology description:** From castor seeds production, oil is produced and refined, transesterified and thermally cracked to produce methylundecenoate. Then, a cross-metathesis step, followed by hydrogenation leads to 12-amino-dodecanoic acid, which is a PA12 monomer (commercially available petrochemical polymer). Seed meal is used as a fertilizer, or converted to Biogas/Biosyngas. Castor co-products (hull) are converted to activated carbons or energy.

An alternative option is to transform the castor oil ester into 12HSA (12-hydroxystearic acid through hydrogenation and hydrolysis), which is then transformed to nitrile. The fatty nitriles undergo oxidative cleavage and hydrogenation reactions to give the PA11 and PA12 monomers.

From safflower and crambe plantations, the corresponding oil is obtained and refined. After hydrolysis, a mixture of fatty acids is obtained. The acids are transformed to nitriles. Reaction of the fatty nitriles with hydrogen peroxide leads to cleavage of the unsaturated nitriles. The obtained acid-nitrile molecule is hydrogenated leading to the monomer for PA9 and PA13 depending on the type of starting oleaginous plant. The produced short fatty acid, after esterification, can be used as a fuel or a lubricant. The remaining biomass fraction is used as a fertilizer or converted to energy. Hull and cake are valorized as activated carbons.

**Project sponsorship:** EuroBioRef is providing support – FP7 Project.
d) Risk analysis, SWOT analysis, LCA analysis

### Strengths
- High performance and high value products
- Good seed yield potential
- Partners know-how about castor
- Some existing technologies
- Flexible technologies
- PA9, 11, 12, 13 with similar technologies
- Diacids also possible
- Low CAPEX
- Strong IP for metathesis
- Valorization of co-products
- Energy self-sufficiency

### Weaknesses
- Castor adaptation in Europe
- No mechanical harvesting (castor)
- Non homogeneous ripening (castor)
- Toxicological issues (castor)
- Dedicated crushing units (non-edible crops)
- Metathesis catalyst cost
- Process with several products
- Products separation
- New monomer (PA12). Customer homologation
- PA9 and PA13 new polymers

### Opportunities
- Alternative to India castor monopoly
- Madagascar complementarities in Southern hemisphere
- Availability of seeds and oils on the market
- New business for European farmers
- Polyamides growing market
- Demand for bio-based polymers. Energy saving through metal substitution in transport (lighter materials)
- Promotion of biodiversity

### Threats
- Costs
- Competitive markets (oils, existing polymers, potential competing technologies from palm, soybean, canola…)
- Raw material reliability (weather issues…)

The key technology challenges have been identified and back-up solutions defined.

### Risks
- Castor in Europe:
  - Mechanical harvesting, profitability, sustainability
- Thermal cleavage:
  - Energy and CAPEX demanding
- Nitration of fatty esters:
  - Technology not mature yet
- Metathesis:
  - Key new technology, catalyst cost
- Polymerization:
  - New monomer

### Back up
- Castor in Madagascar
- Ethenolysis and oxidative cleavage options
- Metathesis with acrylonitrile
- Hydroformylation or oxidative cleavage options
- Additional step to reach existing monomer

### LCA - VC1/CASTOR
A comparison of the VC1 base case and best case has been made though EuroBioRef developed methodology/software (Figure 8):

**Figure 8: LCA results for VC1 from castor to PA12 using IMPACT 2002+ indicator**

Progression along the project shows significant impact on the resources, climate change and human health indicators from the base case to the best case. The ecosystem quality is worse than the reference due to the substitution of a fossil base polymer by a renewable polymer (negative land use impact).
The same analysis was carried out for safflower and crambe, which showed better performances for the resources, climate change and human health indicators (Figure 9).

Figure 9: LCA results for VC2 from safflower and crambe using IMPACT 2002+ indicators

e) Value Creation

Figure 10: Production cost estimation – Castor → PA12 best case/base case

CASTOR

The CAPEX data has been evaluated from the literature or from existing similar units in the best case option (Figure 10). The total CAPEX is between 120 and 160 M€ for 10,000 t/year of the final monomer (EU location). A CAPEX of 150 M€ has been assumed for comparison and for job creation estimates, which were indexed on CAPEX.

From these hypotheses, the production costs have been estimated. In the Best case, the monomer production cost is representing 21% savings achievement compared to the Base case. Step 1 is the critical step for cost reduction. This confirms that the alternative scenarios for removing this step could probably make more sense.

SAFFLOWER-CRAMBE

Historically, safflower was grown for the dyes produced from its flowers, but nowadays it has little importance due to cheaper synthetic dyes. Its oil (high linoleic) is used in paints and varnishes, as it produces paint that will not yellow with age. Seeds are sold for the birdseeds market. EuroBioRef technologies would need to use the high oleic type of safflower. The polyamides obtained from safflower and crambe are longer (PA13) and shorter (PA9) than the known polyamides on the market (PA10,10, PA11, PA12). Markets addressed by crambe oil are much diversified: pharmaceuticals, lubricants, heat transfer fluids, dielectric fluids, waxes, fish food, coating agent. Erucic acid is used as a plasticizer, an antistatic and as a corrosion inhibitor. The main value of crambe is its erucic acid content, and it is therefore in competition with high erucic acid rapeseed.

The CAPEX data has been estimated for 10 kt/y of PA9 monomer from safflower (Figure 11). The total CAPEX is between 110 and 160 M€. Additional 150 M€ would be necessary for straw valorization by gasification.

The monomer production costs have been evaluated and Step 7 of the figures hereafter is the critical step for cost reduction.
f) Job creation

Jobs creation has been estimated by correlation with literature data related to investment cost of existing biorefineries (Figure 12). Between 200 and 300 direct jobs would be created for VC1.

**Figure 12: VC1 job creation evaluation (excluding farming)**

- **Capital Cost M€ (assuming plant constructed in France, April 2011)**
  - 100 M€ Capex --> 50-70 direct and 200-280 construction jobs

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g) Company/Team & Business Model

**Commercial Applications:** Commercial applications of all the technologies developed include castor seeds, oil, meal (Soabe), polyamides (Arkema), biogas units (BKW), activated carbon (CECA) and homogeneous catalyst (Umicore).

**Energy Applications:** Castor oil can be used for jet fuels once hydrogenated to isoparaffins, and fatty esters (C18, methyl undecenoate, methyl nonenoate, methyl octanoate) can be used in road fuels. Biogas, BioSyngas, Jatropha oil are considered for on-site energy production.

**Business Model:** Production of castor seeds in Madagascar and Europe, with large crushing unit in Europe. Castor oil to be sold to customers or traders. Polyamide unit could be located next to the raw material or near the customers. Production of safflower seeds in Southern Europe and crambe seeds in Northern Europe. Seed processing unit should be located next to the raw material or near customers.

**Objective:** Develop the castor chain in Madagascar and Europe to provide an alternative to India monopoly. Take advantage of the growing polyamides market.

Develop new access route to bio-based polyamides, generate short esters for fuel applications. Enlargement of specialty polyamides product range to PA9 and PA13.

**Partners / expertise needed in following areas:** Fuel company (fatty esters). Industrial partner for castor crushing in Europe. Industrial partner for safflower and crambe production.
h) Co-location in existing assets (Value Chain 6 model) (Figure 13)

Ramp up of the castor value chain could take advantage of some existing equipments. Seeds crushing could be done in an existing non-edible crop crushing unit (same for safflower and crambe). The transesterification and thermal cleavage of castor oil are already practiced at the industrial scale. We have proposed an option to debottleneck this plant by better valorizing the co-product as a fuel.

Concerning safflower and crambe, hydrolysis would be possible in oleochemical plants. Transesterification of safflower oil should be possible in any biodiesel plant.

i) Actual demonstration status

Castor production is well advanced. Field tests are successful in Madagascar (Figure 14). Next step is to check the results over several years including the crop rotation strategy. In Europe, we are still at the R&D level. Castor oil extraction is already an industrial technology and we do not foresee any issue for this step as long as the oil composition in the seeds conforms to what already exists on the market. The transesterification step is also an existing industrial technology and no innovation was expected in the project. Metathesis is the key new technology of the value chain. The demonstration (Best Case) has been performed at a 100 L scale showing that there was not any scale up issue. Hydrogenation and polymerization steps have also been demonstrated.

A crambe demonstration field of 10 ha has been established in Poland (Figure 15). While plantation of safflower and crambe at a larger scale in Europe needs still to be proven, refining oil and hydrolysis to fatty acid are commercial technologies that should apply to the obtained material. 60 L of crambe oil have been produced by UWM, and refining was carried out by Novance. Oxidative cleavage was demonstrated at the pilot scale and the pilot run confirmed the good laboratory results.

The demonstration field-test of a high oleic variety of safflower was established in Greece in autumn 2013 and the field will be harvested in late summer 2014 (i.e., after the official end of the project) to confirm the yield potential of the crop in large scale plantations.
j) Conclusions and global assessment
Summary of the different steps with Technology Readiness Level

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<td>Hull/cake conversion to activated carbon</td>
<td>7</td>
</tr>
<tr>
<td>Hull/cake/straw conversion to biogas</td>
<td>2</td>
</tr>
<tr>
<td>Seed crushing</td>
<td>9</td>
</tr>
<tr>
<td>Oil hydrolysis</td>
<td>9</td>
</tr>
<tr>
<td>Nitrilation</td>
<td>9</td>
</tr>
</tbody>
</table>
VALUE CHAIN 3:
LIGNOCELLULOSICS (AVIATION FUELS) BIOREFINERY.
PARTNERS: ARKEMA, BORREGAARD, BKW, CERTH, CNRS-UCCS, CRES, DTI, IMPERIAL, NOVANCE, OBRPR, PDC, QUANTIS, SINTEF, TUHH, UWM, WSKFZ

a) General description of the Value Chain

The main target of this VC is the production of heavy alcohols/branched paraffins to be blended as components of aviation gasoline and jet fuel. This VC is closely related with VC5 as both share the same route of syngas production via gasification and its consecutive conversion to alcohols. A simplified diagram of this VC is shown in Figure 16. Two main routes for the production of alcohols are considered, one via syngas production and alcohol synthesis and the other via fermentation of sugars hydrolysates with butanol as a platform molecule. The main process steps leading to the target products are:

1. Gasification of black liquor and gas cleaning to syngas (common with VC5);
2. Fermentation of sugar hydrolysates to butanol;
3. Higher alcohols synthesis from syngas (common with VC5);
4. Gas phase process to higher alcohols C4-C8;
5. Liquid phase process to alcohols C8-C12;
6. Hydrogenation/dehydration of branched alcohols to alkanes/alkenes;
7. Blending of the alcohols/paraffins to aviation gasoline and jet fuel.

Figure 16: Simplified flow scheme of the main process routes and products

Figure 17: Effect of alcohols addition to the AVGAS100LL octane number

Detailed data on the six process steps (conversion, selectivities, efficiencies etc) were collected from the involved partners. Based on this technical data, a detailed process scheme with associated mass and energy balances was completed. The suitability of mixed branched alcohols and/or mixed branched paraffins was evaluated as components of avgas and jet fuel. The results showed that the addition of C3-C5 and C3-C6 alcohols to AVGAS100LL results in lower octane number as shown in Figure 17. However, addition of up to 8% is still possible as the final product fulfills the specifications. Overall, the addition of the C3-C6 alcohols and the corresponding alkanes did not improve the octane number of avgas.
OBR completed the measurement of the properties of C8 branched alcohols (10%) in jet fuel blends, and confirmed that the mixture properties fall within the range of the ASTM specifications. WSKRZ tested the performances of jet fuel blends containing 10% and 20%, and compared them with those of the pure jet fuel. The operation of the engine was smooth with no significant differences in power and temperature characteristics (Figure 18). Emissions of the flue gases, measured at various engine ratings, were in a range similar to that of the pure Jet fuel, except for SO\textsubscript{2}, of which the emissions were lower.

Figure 18: Comparative performance characteristics of the 10% EuroBioRef blend and of the pure jet fuel used in a jet engine

---

**b) Competition**

As the final product proposed to the market will be a jet fuel blended with up to 10% bio-originated compound(s), the competition with the pure fossil and alternative aviation fuels should be considered in this VC. The new product and the production train should compete with established and mature processes and products, which have large shares in the fuel market. The main competitive products are the 100% fossil-based jet fuel, the synthetic jet fuel produced from Fischer-Tropsch (FT), the hydrogenated oils and the drop-in jet fuels produced from isobutanol. The technologies available and the main technology licensors are included in Table 1.

Table 1: Competitive products and processes for Jet fuel

<table>
<thead>
<tr>
<th>Technology</th>
<th>Process</th>
<th>Feedstock</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Companies</td>
<td>Refining</td>
<td>Petroleum</td>
<td>Jet fuel, gasoline, diesel</td>
</tr>
<tr>
<td>UOP/Eni (Ecofining process)</td>
<td>Hydrotreating and isomerization</td>
<td>Triglycerides and/or free fatty acids</td>
<td>Green diesel and jet fuel</td>
</tr>
<tr>
<td>Haldor Topsoe</td>
<td>Hydrotreating</td>
<td>Raw tail oil</td>
<td>Green diesel and jet fuel</td>
</tr>
<tr>
<td>The Neste Oil (NExBTL process)</td>
<td>Hydrotreating</td>
<td>Palm oil and waste animal fat</td>
<td>Green diesel</td>
</tr>
<tr>
<td>Syntroleum Corporation</td>
<td>Hydrotreating</td>
<td>Animal fats</td>
<td>Green diesel and jet fuel</td>
</tr>
<tr>
<td>Sasol</td>
<td>FT synthesis</td>
<td>Coal, natural gas</td>
<td>Diesel and jet fuel</td>
</tr>
<tr>
<td>Shell</td>
<td>FT synthesis</td>
<td>Natural gas</td>
<td>Diesel and jet fuel</td>
</tr>
<tr>
<td>Gevo</td>
<td>Dehydratation, oligomerization</td>
<td>Isobutanol from biomass fermentation</td>
<td>Jet fuels</td>
</tr>
</tbody>
</table>
The complete picture of competitors regarding the technology step of alcohols production from syngas is presented in Table 2. The competition is very high as commercial units for the production of ethanol from syngas either thermochemically or via fermentation are already in operation. The world map indicating the locations of the commercial and pilot units is illustrated in Figure 19. It is clear that the majority of them are located in the US, while in Europe there is only one unit (Lurgi-Octamix) that already stopped its operation before commercialization.

Table 2: Syngas-based units producing higher alcohols

<table>
<thead>
<tr>
<th>Company</th>
<th>Scale</th>
<th>Capacity, Mliters/year</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coskata, Clewiston, U.S.</td>
<td>Commercial</td>
<td>381</td>
<td>Stopped</td>
</tr>
<tr>
<td>Celanese, TCX™ technology, Clear Lake TX</td>
<td>Commercial</td>
<td>254</td>
<td>Operational</td>
</tr>
<tr>
<td>Coskata, Flagship, Southeast U.S.</td>
<td>Commercial</td>
<td>236</td>
<td>Stopped</td>
</tr>
<tr>
<td>Fulcrum, Sierra Biofuels Plant</td>
<td>Commercial</td>
<td>38</td>
<td>Operational</td>
</tr>
<tr>
<td>Enerskem, Pontotoc, Mississippi</td>
<td>Commercial</td>
<td>38</td>
<td>Planned</td>
</tr>
<tr>
<td>Enerskem, Varennes, Quebec</td>
<td>Commercial</td>
<td>38</td>
<td>Planned</td>
</tr>
<tr>
<td>Enerskem, Waste-to-Biofuels complex</td>
<td>Commercial</td>
<td>36</td>
<td>Under constr</td>
</tr>
<tr>
<td>Power Energy Fuels Inc (PEFI)-Ecalene</td>
<td>Demo</td>
<td>15.9</td>
<td>Stopped</td>
</tr>
<tr>
<td>Tembec Chemical Group, Canada</td>
<td>Demo</td>
<td>15.3</td>
<td>Operational</td>
</tr>
<tr>
<td>Enerskem, Westbury, Quebec</td>
<td>Pilot</td>
<td>5.07</td>
<td>Operational</td>
</tr>
<tr>
<td>IFP-Idemitsu</td>
<td>Pilot</td>
<td>1.11</td>
<td>Stopped</td>
</tr>
<tr>
<td>Lurgi-Octamix</td>
<td>Pilot</td>
<td>0.89</td>
<td>Stopped</td>
</tr>
<tr>
<td>Colorado State University, Boone, U.S.</td>
<td>Pilot</td>
<td>0.253</td>
<td>Operational</td>
</tr>
<tr>
<td>Coskata, Lighthouse, Pennsylvania</td>
<td>Pilot</td>
<td>0.152</td>
<td>Stopped</td>
</tr>
<tr>
<td>Research Triangle Institute, Durham, U.S.</td>
<td>Pilot</td>
<td>0.028</td>
<td>Under constr</td>
</tr>
</tbody>
</table>

Figure 19: Map of commercial and pilot units for higher alcohols production from syngas
MARKET SUMMARY

Need: There is a need for aviation fuels (mostly jet fuels) based on renewable resources. Renewable alcohols may have a market also in cosmetics, pharmaceuticals, while alcohols and paraffins (obtained after hydrogenation) could be used as fuel constituents.

Value to the customer: Green fuels are attractive to the customers – minimum carbon footprint is expected, but the price that the customers will pay for this product will be over 1 €/liter.

Market Opportunity: Tax reduction for (partly) sustainable fuel, increase in CO₂ emission prices, future mandates for a minimum sustainable fraction. There is a growing need for aviation fuels due to the increase in air transport and the environmental regulations to reduce CO₂ emissions.

Impact: Bio-alcohols currently find application as octane boosters in gasoline (ethanol), gasoline substitutes (ethanol, butanol), boosters or substitutes of aviation gasoline, in cosmetics etc. Bio-derived products will not fully replace fossil fuels any time soon. Therefore, their consumption is not expected to affect the market value.

c) Technology

With the use of the IPscore software, it was possible to evaluate the risk and opportunities for the new EuroBioRef product. The EuroBioRef blended jet fuel is compared with other competing products: the pure fossil based jet fuel, the synthetic diesel, the green diesel and the Gevo jet fuel. It is clear from this graph (Figure 20) that the new fuel has high opportunity with medium risk and that there is room for improvements compared to the other competing products. Risks will be lowered as the patent will be granted, and the product certified.

TECHNOLOGY SUMMARY

Technology description: Syngas derived from black liquor & biomass gasification is used, after cleaning, as a feed to the higher alcohol synthesis unit. The mixture of C4- alcohols is further processed via gas phase process, while the C4+ fraction is processed in the liquid phase process to increase the carbon number of alcohols. This latter stream is further hydrogenated/dehydrated to produce branched paraffins (C8-C12) and olefins. Two main end products are considered in the VC3 biorefinery: C3-C5 alcohols for blending with aviation gasoline and C8-C12 branched components for blending with Jet Fuel.

In parallel to the route of syngas, the production of butanol from sugar hydrolysates via fermentation to butanol and its addition to the mixture of alcohols is considered. Butanol is further processed via liquid phase process to C8-C12 compounds.

Project sponsorship: EuroBioRef is providing support - FP7 Project.
POSSIBLE DEVELOPMENT IN HORIZON 2020

From the process development route, more work is needed to develop catalysts with higher activity and most importantly selectivity to the target products, and to design an integrated processes for each of the steps that are presently not yet at an adequate TRL to be industrialized.

d) Risk analysis, SWOT analysis, LCA analysis

For the upstream of the VC3 the risk analysis is to be managed jointly with VC5.

<table>
<thead>
<tr>
<th>Strengths</th>
<th>Weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>• IP on the potential use of branched alcohols and paraffins as blending components for jet fuel</td>
<td>• Catalyst cost for the liquid phase reaction</td>
</tr>
<tr>
<td>• The target products are high volume and high value</td>
<td>• Catalyst recovery</td>
</tr>
<tr>
<td>• Partners know-how on process steps</td>
<td>• Relatively low selectivity in the syngas to alcohol step</td>
</tr>
<tr>
<td>• Sustainable production</td>
<td>• Low productivity in the hydrolysates to butanol step</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Opportunities</th>
<th>Threats</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Tax reduction for (partly) sustainable fuel, increase in CO₂ emission prices, future directives for a minimum sustainable fraction. Parts of the technologies developed do not exclusively rely on biomass</td>
<td>• Costs</td>
</tr>
<tr>
<td>• Subsidies to ease the commercial development of bio-fuels</td>
<td>• Competing technologies for syngas conversion to alcohols via thermochemical and/or biochemical routes</td>
</tr>
<tr>
<td>• New business for European farmers</td>
<td>• Several products or mix of products could compete</td>
</tr>
<tr>
<td>• New business for jet fuel-producing companies</td>
<td>• Alternative technologies (FT, NexBTL, Ecofining, Gevo) producing synthetic and bio-jet fuel</td>
</tr>
</tbody>
</table>

LCA

Quantis assessed VC3 in terms of environmental impact based on a consolidated scenario and improved mass and energy balances provided by PDC. The scope was also extended to include the distribution, the use and the end-of-life of the biorefinery products and avoided products. The final LCA results of VC3 are shown below.

Figure 21: LCA results as per IMPACT 2002+ for VC3 (black liquor-to-aviation fuel)

VC3 shows a significant benefit in terms of climate change and resources with respect to conventional production routes for the specific set of co-products (kerosene and sulphuric acid). While being slightly unfavourable according to actual results and numbers, the performance of VC3 in terms of water withdrawal is considered to be similar to conventional production routes considering the uncertainty of the data and of the LCA model. VC3 is unfavourable in terms of ecosystem quality and human health compared to conventional production routes. The impacts for both indicators are very much dominated by the supply and combustion of wood to compensate for the energy loss from the recovery boiler in the paper mill.

An alternative scenario (including biobutanol issued from fermentation as a source for C4+ alcohols) was also addressed.

e) Value creation

The capital cost estimation for the implementation of VC3 was finalized by PDC. Accordingly, the total CAPEX is around 400 MEuros for a capacity of 67,200 t/year C6+ Guerbet alcohols. The annual turnover (sales) considering Guerbet alcohols (P1) and sulfuric acid as well (P2) are shown in Figure 22A.
Figure 22A compares the potential sales that can be generated with the same capital cost. VC3 first (main) product (Guerbet alcohols for aviation fuels, P1) and with secondary products (sulfuric acid, P2) are indicated. Since the branched alcohols are taken at their fuel value, the total generated value is low. However, the total value that could be generated would be 5 to 10 times higher if branched alcohols for chemical applications were targeted.

Figure 22B compares the potential direct job creations in Value Chains 3 and 5 with similar projects for fuels production, and also with projects requiring a high capital cost. In VC3, it is estimated that 150 to 170 direct jobs will be created. These numbers do not include the jobs created during construction and the jobs related with farmer businesses.
f) Cost analysis

Imperial College analyzed several scenarios to make Value Chain 3 more attractive. Influenced by the process units associated with higher alcohols synthesis in particular, Value Chain 3 is dominated by extremely high capital costs, namely over 400 M€, which result in a negative mean NPV. While there is a small (1%) chance of returning a positive NPV, this Value Chain still does not present a favourable investment opportunity (Figure 23).

The best route for reducing costs is found by assuming a premium payment (or a product subsidy) or by targeting a different end product of higher value, or by diversifying the end product mix. The creation of a higher value product, at a sales price not less than 1035 €/t (for the same product volume) results in a positive mean NPV. If the whole product pathway would be directed to the use of the alcohols as chemicals (with all the other process costs kept as equal), this would result in the return of a mean NPV of nearly 115 M€, with nearly 80% probability of returning a positive NPV.

g) Company/team & business model

**Commercial Applications:** Commercial applications of all the developed technologies include black liquor gasification (Nykomb), higher alcohols synthesis from syngas (CERTH/Nykomb), chemistry in the liquid phase (ARKEMA), chemistry in the gas phase (CNRS-UCCS), production of biomass hydrolysates (Borregaard), fermentation of sugars/biomass hydrolysates (TUHH), hydrogenation (SINTEF/OBR/CERTH), and blending of aviation fuels (OBR).

**Energy Applications:** The main target product is to be blended in jet fuel, improving its properties.

**Business Model:** Upstream based on the CHEMREC black liquor gasification, as it is today the most probable option, but other biomass gasification processes are also considered. Alternatively, the higher alcohols unit could be located near a biomass fermentation unit, where butanol and other alcohols will be readily available.

**Objective:** To produce air-transport biofuels with a lower carbon footprint at a competitive price. Volumes to be determined, depending on the amount of product admissible in blending with aviation fuel.

**Partners / expertise needed in following areas:** Fuel company / Air transportation company.

h) Co-location in existing assets

At the center of VC3 stands the reaction carried out in the liquid phase for the production of heavy branched alcohols. This needs a feed of primary C4+ alcohols. This mixture can be prepared from syngas produced as a by-product by a pulp mill with Chemrec’s technology. Another alternative for the present VC is to be part of a biomass to liquid (BTL) asset, where part of the produced syngas should be directed to the HAS reactor for the production of higher alcohols in parallel to methanol and/or FT units. Concerning the route based on butanol, a better location choice would be at the proximity of the plant with a fermentation site, where the butanol will be easily available and the production cost will be lower. Sites already producing fossil equivalent might also find some advantages to add a biobased alternative in their portfolio, and oil refineries already blending aviation fuels could collocate a plant producing the targeted compounds.

i) Actual demonstration status

ARKEMA delivered 2 tons of product to OBR for blending in aviation fuels. Novance upscaled the recipe provided by Arkema for the production of the biosourced equivalent via liquid phase synthesis. About 210 kg of biobased 2-EH have then been subsequently provided to OBR for blending with aviation fuels. WSKRZ ran an engine on the EuroBioRef fuel over a long period without any issue. The fuel efficiency was confirmed, together with lower emissions of pollutants compared to a conventional jet fuel.
Hydrogenation of side streams of heavier compounds (heavier than C8 alcohols) has been successfully performed at CERTH.

### j) Conclusions and global assessment

Summary of the different steps with Technology Readiness Level

<table>
<thead>
<tr>
<th>Step</th>
<th>TRL</th>
<th>Risk</th>
<th>Measure of Success</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher alcohols synthesis from syngas</td>
<td>4</td>
<td>Medium</td>
<td>Stable catalyst performance</td>
</tr>
<tr>
<td>Gas phase synthesis</td>
<td>4</td>
<td>High</td>
<td>Stable catalyst performance in long time testing</td>
</tr>
<tr>
<td>Liquid phase synthesis</td>
<td>6</td>
<td>High</td>
<td>210 kg made by Novance</td>
</tr>
<tr>
<td>Hydrogenation of branched alcohols</td>
<td>5</td>
<td>Low</td>
<td>30 kg of branched hydrocarbons produced</td>
</tr>
<tr>
<td>Fermentation of sugar hydrolysates to butanol</td>
<td>5/8</td>
<td>Low</td>
<td>Demonstration completed by TUHH/BKW</td>
</tr>
</tbody>
</table>

**Black liquor gasification**

7/8 (7 at end of the project, and 8 if Chemrec can build a demonstration unit)

**Measure of Success**

- Production Capability
- Commercialisation
- Fuel Approval
- Full-Scale Technical Evaluation
- Process Validation
- Preliminary Technical Evaluation
- Proof of Concept
- Technology Concept Formulation
- Basic Principles
- Observed and Reported

**Fuel Readiness Level**

- FRL 9
- FRL 8
- FRL 7
- FRL 6
- FRL 5
- FRL 4
- FRL 3
- FRL 2
- FRL 1

**Technology Readiness Level**

- TRL 10
- TRL 9
- TRL 8
- TRL 7
- TRL 6
- TRL 5
- TRL 4
- TRL 3
- TRL 2
- TRL 1
VALUE CHAIN 5: SYNGAS-BASED BIOREFINERY TOWARDS HIGHER ALCOHOLS, $H_2O_2$ AND MeSH.

PARTNERS: ARKEMA, ČERTH, CNRS-UCCS, IMPERIAL, NYKOMB, PDC, QUANTIS

a) General description of the Value Chain

The main target of this VC is the production of a variety of chemicals and fuels via gasification of black liquor or solid biomass. This VC is closely related with VC3, as the latter exploits higher alcohols for the production of jet fuels. A simplified diagram of this VC is shown in Figure 24. Higher alcohols have to be separated from MeOH or EtOH (which are the main by products from the alcohol synthesis process). In the case of black Liquor gasification within a pulp a paper industry, $H_2O_2$ is produced from the tail gas $H_2$. MeSH can be produced by using the $H_2S$ content of the black liquor product gas. Sulphur make up for the overall process integrity would then have to be added to the pulping process.

The main process steps leading to the target products are:
1. Gasification of black liquor or biomass and gas cleaning to syngas;
2. Higher alcohols synthesis from syngas;
3. $H_2O_2$ synthesis using $H_2$ tail gas;
4. MeSH synthesis either in single step $CO/H_2S/H_2$ reaction process or a two-step reaction process using the produced MeOH and its further reaction with $H_2S$.

Figure 24: Simplified flow scheme of the main process routes and products in VC5

b) Competition

The new product and the production train should compete with established and mature processes and products that have large shares in the fuel market. The main competing products are the 100% fossil-based fuels and chemicals, Fischer-Tropsch products, hydrogenated oils and fats, higher alcohols, $H_2O_2$ and MeSH. The complete picture of competitors regarding the technology step of alcohols production from syngas is presented in Table 3. The competition is very high as commercial units for the production of ethanol from syngas either thermochemically or via fermentation are already in operation. A map indicating the locations of the pulp and paper industries that could employ the BL gasification is shown in Figure 25. These paper production units would have to give up their combustion recovery process and undertake gasification to be able to still cover their energy demands and perform the cooking chemicals recycling and engage in biorefinery operations.
The world map indicating the locations of the commercial and pilot units producing HA is illustrated in Figure 26. It is clear that the majority of them are located in the US, while in Europe there is only one unit (Lurgi-Octamix), which already stopped its operation before commercialization.

**Table 3: Syngas-based higher alcohols (ethanol)**

<table>
<thead>
<tr>
<th>Company</th>
<th>Scale</th>
<th>Capacity, Liters/year</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coskata, Clewiston, U.S.</td>
<td>Commercial</td>
<td>381</td>
<td>Stopped</td>
</tr>
<tr>
<td>Range Fuels, Inc.</td>
<td>Commercial</td>
<td>381</td>
<td>Closed company</td>
</tr>
<tr>
<td>Celanese, TCX® technology, Clear Lake TX</td>
<td>Commercial</td>
<td>254</td>
<td>Operational</td>
</tr>
<tr>
<td>Coskata, Flagship, Southeast U.S.</td>
<td>Commercial</td>
<td>236</td>
<td>Stopped</td>
</tr>
<tr>
<td>Fulcrum, Sierra Biofuels Plant</td>
<td>Commercial</td>
<td>38</td>
<td>Operational</td>
</tr>
<tr>
<td>Enerkem, Pontotoc, Mississippi</td>
<td>Commercial</td>
<td>38</td>
<td>Planned</td>
</tr>
<tr>
<td>Enerkem, Varennes, Quebec</td>
<td>Commercial</td>
<td>38</td>
<td>Planned</td>
</tr>
<tr>
<td>Enerkem, Waste-to-Biofuels complex</td>
<td>Commercial</td>
<td>36</td>
<td>Under construction</td>
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<td>Stopped</td>
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<tr>
<td>Lurgi-Octamix</td>
<td>Pilot</td>
<td>0.89</td>
<td>Stopped</td>
</tr>
<tr>
<td>Iowa State University, Boone, U.S.</td>
<td>Pilot</td>
<td>0.253</td>
<td>Operational</td>
</tr>
<tr>
<td>Coskata, Lighthouse, Pennsylvania</td>
<td>Pilot</td>
<td>0.152</td>
<td>Stopped</td>
</tr>
<tr>
<td>Research Triangle Institute, Durham, U.S</td>
<td>Pilot</td>
<td>0.028</td>
<td>Under construction</td>
</tr>
</tbody>
</table>

**Figure 25: Map of recovery boilers in Europe – potential BL gasification sites**
EUROpean multilevel integrated BIOREFinery design for sustainable biomass processing

MARKET SUMMARY

Need: There is a need for 2nd generation biofuels based on renewable resources (MeOH and EtOH). Furthermore, renewable alcohols may have a market also in cosmetics, pharmaceuticals, while H₂O₂ is required for on-site bleaching purposes in pulp and paper industries. H₂S produced on-site can be turned into MeSH, DMDS, DMS or DMSO.

Value to the customer: Green fuels and block and fine chemicals.

Market Opportunity: Tax reduction for (partly) sustainable fuel, increase of CO₂ emission credits value, future mandates for a minimum sustainable fraction. For H₂O₂, on-site production, reducing the global CO₂ footprint in the paper production (no H₂O₂ transportation, and renewable product).

Impact: Bio-alcohols currently find applications as octane boosters in gasoline (ethanol), gasoline substitutes (ethanol, butanol), boosters or substitutes of aviation gasoline, in cosmetics etc. Bio-derived products will not fully replace fossil fuels any time soon. Therefore, their consumption is not expected to affect the market value. H₂O₂ would have a greener added value for the pulp and paper industry.

c) Technology

LEGEND

TECHNOLOGY SUMMARY

Technology description: Syngas derived from black liquor & biomass gasification is used, after cleaning, as a feed to the (higher) alcohols synthesis unit. MeOH or EtOH can be separated and used as fuels. H₂O₂ can be produced using the residual H₂ from the HA synthesis reactor (or any other type of synthesis reactor employed). MeOH can be used together with H₂S separated from the BL gasification product gas to produce MeSH. Alternatively, a direct route of CO/H₂/S reaction is also possible. A makeup sulphur stream would be needed for sustaining proper levels of cooking agent for the pulping process.

Project sponsorship: EuroBioRef is providing support - FP7 Project.
POSSIBLE DEVELOPMENT IN HORIZON 2020
From the process development route, more work is needed to develop catalysts with higher activity and, most importantly, selectivity to the target products, and to design integrated processes for each of the steps that are not presently at an adequate TRL to be industrialized. Solid biomass gasification and gas cleaning require robustness strengthening. Such application will therefore not be only limited to the fate of pulp and paper industry. Separation technologies need to be improved for the separation of diverse mixtures. Process integration aspects have to be optimized in the operation of such a diverse product scheme.

d) Risk analysis, SWOT analysis, LCA analysis
For the upstream of the VC5, the risk analysis is to be managed jointly with VC3.

<table>
<thead>
<tr>
<th>Strengths</th>
<th>Weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Diversified products, both chemicals and fuels</td>
<td>• Stability of the catalysts</td>
</tr>
<tr>
<td>• On-site H$_2$O$_2$ production has increased cost reduction (no need for transportation)</td>
<td>• Biofuel market needs to be created in parallel (MeOH and EtOH)</td>
</tr>
<tr>
<td>• The target products are high volume</td>
<td>• Relatively low selectivity in the syngas to alcohol step</td>
</tr>
<tr>
<td>• Partners know-how on process steps</td>
<td>• MeSH production from natural gas is currently far less costly</td>
</tr>
<tr>
<td>• Sustainable production</td>
<td>• MeSH is a toxic material not easily transported. So, an additional step to transform it on site to DMDS or other products such as DMSO would be needed</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Opportunities</th>
<th>Threats</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Tax reduction for (partly) sustainable fuel, increase in CO$_2$ emission prices, future (company) directives for a minimum sustainable fraction. Parts of the technologies developed do not exclusively rely on biomass</td>
<td>• Costs</td>
</tr>
<tr>
<td>• Subsidies to ease the commercial development of biofuels</td>
<td>• Several competing products derived from natural gas-based syngas chemical industries.</td>
</tr>
<tr>
<td>• New business for European farmers</td>
<td>• Biomass-based alternative technologies (FT, NexBTL, Ecofining, Gevo)</td>
</tr>
<tr>
<td>• New business for jet fuel-producing companies</td>
<td>• Biomass cost</td>
</tr>
<tr>
<td></td>
<td>• Papermills lack in financial resources</td>
</tr>
</tbody>
</table>

LCA
Quantis assessed VC5 in terms of environmental impact, based on consolidated scenario and improved mass and energy balances provided by PDC. The scope was also extended to include the distribution, use and end-of-life of the biorefinery products and avoided products. The final LCA results of VC5 are shown below (Figure 28).

Figure 28: LCA results for VC5 using IMPACT 2002+ indicators

As for all VCs, VC5 performs well for Climate Change, but, on the other hand, does not have significant benefits as far as the required resources are concerned. VC5 is performing considerably better than all the other examined VCs for environmental scoring (including Water Withdrawal, Human Health, and Ecosystem Quality). In particular, from an ecosystem quality perspective, the biorefineries systems show a clear disadvantage, mainly due to the land use associated with biomass cultivation, except for VC5 where the main avoided product is ethanol from biomass (from sugarcane - in particular, field burning in sugarcane cultivation and bagasse combustion in ethanol manufacturing).
e) Value Creation

The capital cost for the implementation of VC5 was finalized by PDC. According to this, total CAPEX is around 400 M€. The annual turnover (sales) considering all the products as well as P1 (Higher Alcohols) are shown in Figure 29A. The number of jobs created is illustrated in Figure 29B. It is estimated that 120 direct jobs will be created.

Figure 29A: Economic Impact Evaluation of VC

Figure 29B: Direct jobs creation potential

LEGEND
- Direct Jobs Construction
- Direct Jobs Operation
- Public Support M€
- Direct Jobs Operation (Bio)Chemical plants

What do we get for 400M€ CAPEX?

100 M€ Capex --> 50-70 direct and 200-280 construction jobs

Direct Jobs created

Capital Cost M€ (assuming plant constructed in France, April 2011)
f) Company/Team & Business Model

**Commercial Applications:** Commercial applications of all the developed technologies include black liquor gasification (Chemrec/Nykomb), higher alcohols synthesis from syngas (CERTH/Nykomb/ARKEMA), MeSH synthesis (CNRS-UCCS/ARKEMA), H₂O₂ synthesis (CNRS-UCCS/ARKEMA).

**Energy Applications:** MeOH and EtOH are produced in large quantities as by-products from the HA synthesis step. If properly separated, these are first class 2nd generation biofuels.

**Business Model:** Based on the CHEMREC black liquor gasification, as it is today the most probable option, but other biomass gasification processes are also considered.

**Objective:** To produce a variety of chemicals (H₂O₂, MeSH, higher alcohols) and MeOH or EtOH for fuel applications in an integrated scheme.

**Partners / expertise needed in following areas:** Solid biomass gasification company, gas cleaning company, air separation, pulp and paper industry.

g) Co-location in existing assets (as Value Chain 6 model)

Value Chain 5 is already a co-location model, since it should be integrated in a paper mill. All three major products, namely H₂O₂, MeSH and HA, can be prepared from syngas produced as a by-product in a pulp mill with Chemrec® technology. In this case, H₂O₂ production for bleaching purposes is one of the most promising options. Apart from a chemicals production orientation, VC5 is to be part of a biomass to liquid fuel (BTL) concept, where part of the syngas produced should be directed to chemicals in parallel to methanol and/or FT units.

h) Actual demonstration status

It has been decided that the envisaged H₂O₂ demo scale production is a promising aspect with low risk. Nevertheless, it was also decided to give weight to the syngas to higher alcohols route, towards aviation fuels additives (VC3). Higher alcohols and MeSH production are below demo scale TRLs, and thus not considered for a demo.

i) Conclusions and global assessment

**SUMMARY OF THE DIFFERENT STEPS WITH TECHNOLOGY READINESS LEVEL**

Gasification technologies are close to demo scale, i.e., TRL 6 and above. The progress for gas cleaning is similar. Downstream catalytic syntheses further require development by testing with actual product gas.
## Market Summary

**Technology description:** Syngas derived from black liquor & biomass gasification is used, after cleaning, as a feed to the (higher) alcohol synthesis unit. MeOH or EtOH can be separated and used as fuels. H₂O₂ can be produced using the residual H₂ from the HA synthesis reactor (or any other type of synthesis reactor employed). MeOH can be used together with H₂S separated from the BL gasification product gas to produce MeSH. Alternatively, a direct route of CO/H₂S reaction is also possible. A makeup sulphur stream would be needed for sustaining proper levels of cooking agent for the pulping process.

**Project sponsorship:** EuroBioRef is providing support - FP7 Project.

<table>
<thead>
<tr>
<th>Step</th>
<th>TRL</th>
<th>Risk</th>
<th>Measure of Success</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher alcohols synthesis from syngas from EuroBioRef technology</td>
<td>4</td>
<td>Medium</td>
<td>Stable catalyst performance</td>
</tr>
<tr>
<td>MeSH synthesis from methanol</td>
<td>9</td>
<td>Low</td>
<td>Already at commercial scale, but not biobased</td>
</tr>
<tr>
<td>MeSH synthesis through direct syngas</td>
<td>4</td>
<td>Medium</td>
<td>Stable catalyst performance</td>
</tr>
<tr>
<td>H₂O₂ synthesis</td>
<td>7</td>
<td>Low</td>
<td>Stable catalyst performance</td>
</tr>
<tr>
<td>Gas cleaning</td>
<td>6</td>
<td>Low</td>
<td>Proper gas cleaning</td>
</tr>
<tr>
<td>Solid biomass gasification</td>
<td>6</td>
<td>Low</td>
<td>Robust performance without downtime due to agglomeration/ defluidization</td>
</tr>
<tr>
<td>Black liquor gasification</td>
<td>7 at end of project - 8 if Chemrec can build a demonstration unit</td>
<td>Low</td>
<td>In operation in Chemrec at large pilot scale under pressure (level 7 or 8). Would be 9 if at atmospheric pressure and with air.</td>
</tr>
</tbody>
</table>
**VALUE CHAIN 6: INTEGRATION OF TECHNOLOGIES IN EXISTING UNITS.**

**PARTNERS:** ARKEMA, CIRCC, CNRS-UCCS, FEUP, RUSE, PDC, TUDO

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**a) General description of the CO-LOCATION SCENARIO: n-BUTANOL TO MALEIC ANHYDRIDE**

The co-location scenario considered is a (partial) revamp of a phthalic anhydride (PA) plant. Such a plant is already producing some maleic anhydride (MA) as a by-product. Therefore, facilities to separate MA from the main product PA are already available, even though they need an upgrade when more MA is being produced by co-feeding bio-n-butanol.

Since there is a great interest for using butanol as a fuel component, it can be foreseen that there will be considerable trade volumes of this bio-alcohol in the future, and that it will be produced by various suppliers. For that matter, there are already several small-scale biobutanol producers or technology providers: Cathay Industrial Biotech (China), Cobalt Technologies (announced in Brazil), Butalco, Tetravitae (now Eastman), Green Biologics, Abengoa (US), see Figure 30. Apart from Abengoa, all these companies offer biobutanol from fermentation. Abengoa recently announced that they will produce n-butanol through Guerbet coupling of bio-ethanol.

Note that, until now, there are no production plants in Europe. If this does not change in the future, biobutanol will have to be sourced from overseas.

---

**b) Competition**

MA is used for the production of polyester resins, alkyd resins, for the agriculture sector and for obtaining fumaric acid. Currently, the European MA market is structurally short. Figure 31 displays the maleic anhydride producers currently operational in Europe. Potentially, there are more producers of MA, as it is coproduced in PA plants where it is currently often converted into other products such as fumaric acid. Otherwise, most of the MA is produced by a selective oxidation of benzene or butane, where the latter is economically more favourable. MA is currently produced at the largest scale by Sasol-Huntsman in Moers, Germany. The production scale there is 105 kton per annum (kta). The joint production scale of Polyn’s plants in Bergamo and Ravenna, Italy, is similar. The total production scale in Europe is about 300 kta. The case studied in EuroBioRef is a 50 kta PA production plant, which, after reconversion, produces 27 kta of PA and 9 kta of MA. The eventual target is to obtain an MA production cost lower than the current market price. This may require green credits.
MARKET SUMMARY

Need: Develop new technologies for the synthesis of renewable products, the production of which does not affect the production of food. Specifically, delivery to the market of maleates (from ex-butanol MA) with a bio-share value, as a co-monomer for various polymers. Retrofit current productions of phthalates (being phased-out) with bio/based maleates, using the same process facility currently used by phthalates producers. Preserve jobs and production in Europe.

Value to the customer: Added value of maleates produced from renewable sources, as an alternative to maleates from fossil-derived raw materials. Possibility to tune the maleic vs. phthalic anhydride production. Opportunity for the producer to retrofit an existing plant.

Market Opportunity: Reasonably, it may be expected that, at a European level, the new technology for MA production from bio-butanol might initially cover between 20 kt/year and 100 kt/year, in function of the considered option (see above for the different options). Production of maleic acid by direct fermentation does not seem to gain a lot of attention, probably due to major difficulties. However, Myriant (US) and Genomatica (US) have bio-fumaric acid in their product pipelines.

Impact: The market of MA and maleates covers several sectors of the polymer industry. Impact foreseen for stakeholders, since this conversion technology could be used to preserve jobs, endangered by the phase out of phthalates in Europe.

c) Technology

Figure 32 shows the risk/opportunity profile for the production of MA through conventional technology (butane and benzene oxidation) and through a revamped PA plant. At the cost of a slightly increased risk (due to a new technology, not fully protected by patents – Arkema has a patent, which has been granted in France and in the US: FR2933978 and US8394973), the co-location scenario shows a higher opportunity than the conventional partial oxidation of butane. The partial oxidation of benzene is an old technology, which today is neither longer well protected nor economically favoured. This is reflected in a lower opportunity and a higher risk.
TECHNOLOGY AND SPONSORSHIP

Technology description: PA is being produced by partial oxidation of o-xylene with air in a multitubular reactor. The idea is to replace the PA catalyst by an MA catalyst in part (say half) of the tubes. This catalyst will convert biobutanol to MA. Alternatively, it will convert 1-butene, resulting from a prior n-butanol dehydration, to MA.

n-butanol can be obtained by means of two routes studied in EuroBioRef: (a) by means of enzymatic transformations using specifically selected microorganisms, and (b) by advanced catalytic processes.

Project sponsorship: EuroBioRef is providing support to the development of the optimal catalyst for the oxodehydration of n-butanol to MA, and for the selection of the best reactor and process configuration.

POSSIBLE DEVELOPMENT IN HORIZON 2020

The main hurdle for future implementation is, in this case, the development of an oxodehydration catalyst that would exhibit high selectivity at (near) full conversion. The alternative is a two-step approach, in which n-butanol is first dehydrated to 1-butene, which is consequently partially oxidized to MA.

Future support is therefore needed for further engineering of a catalytic reaction route from n-butanol to MA. Alternatively, butane oxidation could be considered, but we would lose the “Green” advantage of the product in return for the cheaper starting material. What remains important, in a goal to retrofit existing plants, is to find catalysts that could operate in similar reaction conditions (especially temperature). This is where there is an advantage of using butanol, since this is a molecule more reactive than butane.

d) Risk analysis: 6 Forces analysis

<table>
<thead>
<tr>
<th>Category</th>
<th>Relative Power</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bargaining Power of Suppliers</td>
<td>Medium</td>
<td>n-Butanol (1-butanol) can be obtained by means of different routes starting from biomass. Since there is a great interest for using n-butanol as a fuel component, it can be foreseen that it will become available from various suppliers. Moreover, there is an opportunity to create some competition between n-butanol suppliers, so fostering the generation of new value chains starting from this bio-alcohol. If biobutanol becomes too expensive, it is possible to switch to fossil grade.</td>
</tr>
<tr>
<td>Bargaining Power of Customers</td>
<td>Medium</td>
<td>The MA market is still growing, albeit at a lower rate than in the past. Driven by an arising consciousness of customers, companies producing chemicals are looking for technologies that enable increasing the bio(renewable)-share of products delivered to the market.</td>
</tr>
<tr>
<td>Threat of New Competitors</td>
<td>Medium</td>
<td>In regard to the bio-n-butanol production, there is a need for a strong know-how and scientific/technological background in order to be implemented at an industrial level with economic profit. The transformation of n-butanol to MA is less challenging, but requires infrastructures and facilities that only a few companies hold.</td>
</tr>
<tr>
<td>Threat of Substitute Products</td>
<td>Medium</td>
<td>Currently, there is no possible substitute for maleic anhydride and maleates derived from it. Direct fermentation to maleic acid does not seem to attract attention and would need a dehydration step to get to maleic anhydride. Myriant and Genomatica have listed fumaric acid in their product pipeline.</td>
</tr>
<tr>
<td>Competitive Rivalry</td>
<td>High</td>
<td>Maleic anhydride and maleates production are well established processes, with producers both in the Eastern and European countries. Existing plants are medium- to large-sized, and due to the moderate (yet positive) market growth for these chemicals, and to large investment costs required to install new plants, it is expected that no new players will enter this business area.</td>
</tr>
<tr>
<td>Stakeholders: Government / Public</td>
<td>High</td>
<td>Public is favouring renewable products. Governments can positively favour renewable products through subsidies. The PA market is fading, phthalates being banned. Therefore, converting current reactors from PA to ex-n-butanol MA production is an opportunity, especially to preserve jobs and local revenues.</td>
</tr>
</tbody>
</table>

e) Value Creation

MA is used for the production of polyester resins, alkyd resins, for the agriculture sector and for malic and fumaric acids. The overall capacity is larger than 3 Mt/year. Food grade malic acid is now used as a new acidulent in the food and beverage industry, it can enhance special fruit aroma and improve the taste in food. The food industry might be in favor of the production of bioderived chemicals.
As the PA market is shrinking, revamping European PA plants for an increased co-production of MA, for which there is still a growing market, is expected to save jobs. We estimate the number of full-time jobs in a PA plant at about 28 (some 19 of them being operators). This figure should be fairly independent of the production capacity. The capital investment costs required for revamping a 50 kta PA plant are estimated at 18 million Euros.

**f) Company/Team & Business Model**

**Commercial Applications:** Commercial application of the developed technology include the catalyst for n-butanol oxidehydration to MA, and production of MA (Arkema, Orgachim).

**Energy Applications:** none.

**Business Model:** Production of MA by means of n-butanol oxidehydration in Europe, production of catalyst for MA in Europe. Low investment costs foreseen, because the reactors and facilities currently used for PA (or MA) production might be fed directly with n-butanol.

**Objective:** The progressive replacement of at least 10% of the MA anhydride currently produced from oil-derived feedstock with renewable source.

**Partners / expertise needed in following areas:** Producers of bio-n-butanol, MA.

**g) Co-location in existing assets (Value Chain 6 model)**

Figure 33 shows a map of European PA plants. Mainly small European PA plants are targeted for a revamp, for example the 24 kta Grupa Azoty plant in Poland or the 20 kta Orgachim plant in Bulgaria. Considering that Grupa Azoty and the relatively nearby Perstorp are also producers of n-butanol, see Figure 34, the former is probably the most appropriate choice. Indeed, having fossil n-butanol available decreases the risk associated with a (temporary) unavailability of bio-n-butanol. It ensures that the revamped plant will be able to operate at full scale, even if bio-n-butanol is not yet available (at start-up) or temporarily unavailable.
h) Actual demonstration status

Design and economic evaluation of the revamp scenario of a 50 kta PA plant was made. The capital costs for reconversion are now estimated at 18 M€.

Tests have been performed in Orgachim’s pilot unit (loading 2 litres of catalyst prepared by Arkema, in an industrial-like tube from an industrial unit used for gas phase selective oxidation). The process configuration now adopted is the one-pot oxodehydration of \( n \)-butanol to MA, in a dedicated reactor and using a dedicated catalyst. The results indicate a good correspondence with results obtained by CIRCC in the lab scale reactor. At full butanol conversion, MA and PA selectivities of, respectively, 43 % and 5 % have been obtained in the pilot reactor – much better results are expected from a wider catalyst screening and optimisation. Tests done on biobutanol at CIRCC have shown some differences with chemical butanol, but not to an extent endangering the project.

Figure 34: \( n \)-butanol plants in Europe

i) Conclusions and global assessment

Summary of the different steps with Technology Readiness Level

![Technology Readiness Level Diagram](image-url)
## EUROpean multilevel integrated BIOREFinery design for sustainable biomass processing

<table>
<thead>
<tr>
<th>Step</th>
<th>TRL</th>
<th>Risk</th>
<th>Measure of Success</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABE fermentation</td>
<td>9</td>
<td>Low</td>
<td>Operational at the industrial scale: technology applied by Cathay Industrial Biotech (China), promoted by Green Biologics (UK), etc.</td>
</tr>
<tr>
<td>Other fermentation technologies (e.g., Green Biologics, Tetravitae, Cobalt)</td>
<td>7</td>
<td>Moderate</td>
<td>Pilot experiments successful, but no industrial implementation</td>
</tr>
<tr>
<td>EuroBioRef fermentation</td>
<td>4</td>
<td>High</td>
<td>17 kg of butanol coproduced with a larger quantity of 1,3-propanediol in the BKW's pilot unit – Poor separation of PDO has been achieved in the project time frame (both PDO and n-butanol purifications are needed in this co-fermentation process)</td>
</tr>
<tr>
<td>n-butanol produced by advanced catalytic process</td>
<td>4</td>
<td>High</td>
<td>n-butanol produced and delivered for downstream transformation</td>
</tr>
<tr>
<td>n-butanol purification</td>
<td>5 - (9 when taking into account that commercial product exist)</td>
<td>Low</td>
<td>Successfully performed in the lab (TUHH) up to about 96 %, and in the pilot unit up to 99.5 % (BKW)</td>
</tr>
<tr>
<td>n-butanol oxidation</td>
<td>6</td>
<td>Medium</td>
<td>Pilot experiments successfully carried out, with 40 Mol.% yield in maleic anhydride and 12 Mol.% yield in phthalic anhydride, using bio-butanol as a reactant and a catalyst in an industrial shape</td>
</tr>
<tr>
<td>Purified n-butanol oxidation to MA by the one pot approach</td>
<td>6</td>
<td>Low</td>
<td>Successful tests in pilot unit</td>
</tr>
</tbody>
</table>
Summary of technologic & scientific results

in the various involved fields

Sub-project 1:
General strategy framework for a sustainable integrated biorefinery

Sub-project 2:
Studies on biomass feedstock and optimisation for the selected value chain

Sub-project 3:
Development of innovative biomass pre-treatment for the up-stream separation of added value products

Sub-project 4:
Integrated biochemical conversion and separation processes

Sub-project 5:
Advanced catalytic conversion processes to chemicals and integrated separation technologies

Sub-project 6:
Advanced catalytic conversion process

Sub-project 7:
Conceptual process design and integration of the whole process chain/grid into a biorefinery

Sub-project 8:
Integrated biorefinery concept demonstration and assessment

Sub-project 9:
Sustainability analysis for EuroBioRef biorefinery concept

Sub-project 10:
Exploitation, dissemination, communication, standardisation and training activities
SUB-PROJECT 1:
GENERAL STRATEGY FRAMEWORK FOR A SUSTAINABLE INTEGRATED BIOREFINERY

PARTNERS: ARKEMA, BORREGAARD, NZ, BKW, SOABE, CRES, CERTH, PDC, QUANTIS, OBRPR, IMPERIAL, NOVANCE, TUHH

The objective of this SP was to ensure efficient project coordination adapted to the specificities of the EuroBioRef project, and to achieve the project objectives and goals within a specific general strategy network (figure below).

GENERAL POLICY SUGGESTIONS
ARE BIOFUELS FEASIBLE?

Technically, biofuels are possible, but, economically, it will be difficult. They can be produced at high cost CAPEX and OPEX. «Subsidies» are often mentioned as an incentive, but co-production with higher value products can help to tackle the cost issue.

WHAT ARE THE SPECIFIC POLICY NEEDS (i.e., INCENTIVES) FOR THE USER?

Consumer education should be seen as a driver. If tax incentive policies are put in place, it means that, one way or the other, consumers are taking part of the bill. Promotion of biofuels and ecofriendly solutions are as important as legislation to get public acceptance on these issues for a sustainable development, in view of the high capital costs for biofuel plants.
WHAT SHOULD BE DONE IN THE POLICY FOR RESEARCH, ENERGY, ENVIRONMENT AND AGRICULTURE?

R&D projects, industry-driven, as has been EuroBioRef through the Value Chains, which have been created after the initial technology screening during the first 2 years.

WHAT IS NEEDED TO IMPROVE SIGNIFICANTLY THE TECHNOLOGY COMPETITIVENESS, EVEN FOR THOSE THAT ARE READY TO BE OR ARE COMMERCIAL?

There is clearly a need for new separation technologies adapted to the biomass issues (fluctuating raw material quality). Several purification technologies are listed. Low CAPEX technologies, which could benefit from the replication in several local biorefineries, are to be developed.
WHAT IS THE POTENTIAL IN EU (AND POSSIBLY ABROAD)?

Europe is characterized by a high labour cost and a high biomass cost. The first one for social reasons, the second one mostly for climatic conditions. To preserve its social model, high-value applications should be a first target, and the use of residues (agricultural residues and bio-wastes) should be considered, but meaning also limited plant capacity to cope with local sourcing.

ARE BIO-BASED PRODUCTS (BIOCHEMICAL, BIOMATERIALS, ETC.) FEASIBLE?

The answer is definitively yes. Several products have been developed within EuroBioRef such as butanol, acrylates, monomers for polyamides, maleic anhydride..., and have reached a TRL above 5.
**WHAT ARE THE POLICY NEEDS?**

Here again, incentives are needed to promote bio-based products and to avoid the unfair competition with subsidised biofuels. For example, policies to cover part of the high capital cost should allow reducing the risks for investors.

**WHAT IS NEEDED TO IMPROVE SIGNIFICANTLY THE TECHNOLOGY COMPETITIVENESS?**

Again, separation technologies need to be developed, in order to be able to deliver high quality products.

**WHAT IS THE EU POTENTIAL?**

EU should capitalize on its potential to develop innovative technologies, and facilitate the Intellectual Property protection. High-value products can generate jobs in Europe, and, here, the high technicity of the processes should be seen as a protection.
WHAT IS SUGGESTED ON BIOMASS SOURCING? IS THE ASSUMPTION THAT MANY OF THE BIOREFINERY CONCEPTS RELY ON EXTERNAL (NON-EU) SOURCES CORRECT? WHAT ARE THE RISKS?

Research on agricultural residues is often mentioned together with the designation on some dedicated crops for industrial usage, such as oil seed crops that can also be used to promote biodiversity.
SUB-PROJECT 2:
STUDIES ON BIOMASS FEEDSTOCK AND OPTIMISA-
TION FOR THE SELECTED VALUE CHAIN
PARTNERS: ARKEMA, CIRCC, CRES, DTI, QUANTIS, SOABE, UWM

The aim of this sub-project (SP) was to review, evaluate, configure and analyse sustainable biomass chains for several biorefinery options. The analysis comprised feedstock production, supply logistics chain including storage and referred to different regional scales (South, Central, Northern Europe), but also to sustainable possibilities offered by African feedstocks. This aimed at enabling capture of the geographic specificities in terms of ecosystems, climate variation, land use patterns as well as resource types, crop management, feedstock handling and associated logistics. The suitability of the crops for each environmental zone was mainly based on the climate requirements of each crop, as they are defined by the crop ecology (area of origin), biology (tolerance in abiotic stresses, etc.) and physiology (nutrients and soil requirements, growing season, radiation use efficiency, water and nutrients use efficiency, etc.)

A variety of oil crops and lignocellulosic feedstocks was studied in field trials in small and demonstration scale. Castor (Ricinus communis L.), crambe (Crambe abyssinica Hochst ex R.E. Fries), cuphea (Cuphea spp L.), lesquerella (Lesquerella fendleri L), lunaria (Lunaria annua L.), safflower (Carthamus tinctorius L.) were tested in small field trials in Greece and Poland. Along with the selected crops, rapeseed (Brassica napus L.), sunflower (Helianthus annuus L.) and camelina (Camelina sativa L.) were also grown as reference crops. Their selection has been based on their favourable oil characteristics that will serve the biorefinery concept of this project. They are all non-food crops, thus not in competition with the food market and can be grown in arid conditions, not competing with food crops over good quality agricultural lands and water resources. In addition, they can be grown in rotation with food crops that can ensure their smooth introduction into the existing cropping systems, internal nutrient recycling and limitations of pests and diseases, avoidance of mono-cultures, as well as better management of the land, of the agricultural inputs and infrastructure and of the human resources.

The lignocellulosic plant options included cardoon (Cynara cardunculus L.), giant reed (Arundo donax L.), miscanthus (Miscanthus x giganteus GREEF et DEU) switchgrass (Panicum virgatum L.) and willow (Salix viminalis L.). Their selection was based on their higher biomass yields compared to annual bioenergy crops, better water and nitrogen use efficiencies, positive environmental impact compared to annual crops in terms of CO2 and energy balance and ability to be grown in marginal lands avoiding the competition with areas used for food production. Due to their long lifetime (15-20 years), they also positively affect soil erosion problems.

SP2 activities processed through two work-packages (WP), WP2.1 dedicated to study and map land use and cultivation strategies for growing selected non-food oil and lignocellulosic crops that match the biorefinery concepts and value chains of the project, and WP2.2 on the biomass logistics and supply chains.

In WP2.1, after 3-year field trials, it can be stated that castor and safflower are the best suited plants to be grown in the Mediterranean agro-climatic zone, compared to the rest of the oil crops studied in this project. They grew satisfactorily and produced considerably high seed yields. Likewise, in Poland, representing the continental agro-climatic zone, it may be stated that safflower is proved to be unsuitable for cultivation, whereas crambe and camelina performed the best. Crambe plants were sown in a commercial size plantation (2 ha) with very good establishment and seed production, and the plantation was harvested with existing commercial machinery.

In Madagascar, the rotation trials of castor demonstrated that the use of a leguminous plant such as cowpea as rotation crop can reduce fertilizer use by 40% and results in a good soil structure. The consecutive exploitation of castor beans and the use of the perennial castor variety result, however, in a higher risk of disease.
Lignocellulosic crops are performing well in Greece and Poland, proving their good adaptability and yielding capacity.

In WP2.2, information on the harvesting (time & equipment) and storage operations for the harvested materials, as well as on their handling requirements has been collected. Specific harvesting and storage trials have been performed for willow to assess the quality of biomass with several storage methods.

A comprehensive tool for optimizing biomass logistics has been developed. This new tool can handle multiple feedstock/source input into the supply chains as well as multiple outputs for the biorefinery (or other consumer of biomass) and takes into account losses throughout the supply chains, including losses during storage (depending on duration of storage). Results are given as optimization of total costs or energy consumption or CO₂ emissions or any weighed combination of those 3 parameters.

More than 250 data sheets have been elaborated describing all the handling elements for crops such as willow, castor, safflower, crambe or giant reed. Any crop or biomass product can be included in the model and 15 (or more) handling elements can be included in each supply chain.
SUB-PROJECT 3:
DEVELOPMENT OF INNOVATIVE BIOMASS PRE-TREATMENT FOR THE UP-STREAM SEPARATION OF ADDED VALUE PRODUCTS

PARTNERS: ARKEMA, BORREGAARD, CIRCC, CRES, NOVANCE, SOABE

SP3 has been divided into two parts, the first one handling pre-treatment and hydrolysis of lignocellulosic biomass, and the other one handling extraction and processing of non-edible oil crops, the EuroBioRef project considering multi-biomass input.

PRE-TREATMENT OF LIGNOCELLULOSIC BIOMASSES

WP3.1: The objective was to develop solvent-free chemical pre-treatment and enzymatic hydrolysis processes from lignocellulosic materials provided by the EuroBioRef partners. We thus developed these processes first at the lab scale and prepared the processes for subsequent operation at the demo scale. Very few biorefinery processes have reached full-scale production yet. Most of the intended processes are based on steam explosion pre-treatment and enzymatic saccharification combined with incineration of the lignin and other residues to produce heat and power. The biggest challenge with these types of technologies (steam explosion, weak acid and ammonia pre-treatment, etc.) is the relatively low yield of products from the different parts of biomass.

The BALI-process successfully developed within EuroBioRef aims at utilizing low value biomass and converting both the carbohydrates and lignin to various competitive products. The entire process consists of four major steps, first a pretreatment or fractionation where lignin is made water soluble and separated from cellulose. The hemicellulose fraction is either preserved or hydrolyzed into soluble monosaccharides. The entire BALI process is schematically described in Figure 35A and Figure 35B.

Figure 35A: Schematic illustration of the BALI process
Pretreatment processes for switchgrass, giant reed, miscanthus, sunflower oil cake, willow, bagasse and spruce have been developed. Pretreated miscanthus, giant reed, switchgrass, willow and bagasse can be hydrolyzed at high glucose yields. On the contrary, sunflower cake showed to be very difficult to hydrolyze. Willow, bagasse and spruce were the three raw materials that gave the best performance of the produced lignin. Optimal pretreatment and hydrolysis conditions for bagasse (used as a reference material) were determined in the lab. The results were used as a basis in the scale-up work for bagasse and willow. For pretreatment, critical scale-up factors included going from batch to continue process and mechanical issues, and for the hydrolysis, bacterial contamination and process control strategies. These factors have been identified and addressed within the subproject.

PRE-TREATMENT OF OIL CROPS

The objective was to proceed with the oil extraction and refining from the various studied candidate crops. The obtained oils were supplied to SP5 and the co-products processed in SP6. Commercial grade quality of vegetable oils and fatty acids were obtained through available purification technologies and then delivered to the other downstream WPs, especially for chemistry developments.

In more details, jatropha and castor meals were crushed to extract oil, in which fatty acids profiles were very close to the commercial ones. Lunaria, castor and crambe oils were also refined. Their distribution in fatty acids fell in the expected range for the corresponding commercial oils. Lunaria and crambe oils were then saponified and crambe fatty acids further distilled to isolate erucic acid.

In parallel to this work, a new clean process for enzymatic hydrolysis was fully set up at a prototype lab scale, enabling positive environmental benefits. Fatty acids are commonly produced by a high temperature process, which has several disadvantages, such as high water consumption, partial recycling of water, by-products generation implying cost consuming purification steps and huge energy consumption.

In order to reduce the content of side-products, reactive oils, as, for example, castor oil, are preferably saponified. However, this level still remains too high, especially for food applications.

Enzymatic catalyzed reactions, taking place under milder conditions than thermal ones, provide high purity end-products and consequently reduce the release of waste into the environment and water treatment costs. This type of reaction often operates with relatively slow kinetics, being further slowed down above hydrolysis rate of around 80-90%, which is very time-consuming and hence expensive. Thanks to simulation works coupled with experiments on a lab prototype using castor oil, a new process has been completely designed and set up, which enables:

- Reaching hydrolysis rates above 95% in a reasonable reaction time, and thus without by-product formation, such as cracking products, estolide polyesters and fatty acid oligomers. The distillation yield is increased by around 5%, as referred to the current process;
- Up to 70% reduction of water consumption;
- Full recycling of the hydrolysis water;
- And, finally, the last but not the least, a huge reduction of energetic consumption.
SUB-PROJECT 4: INTEGRATED BIOCHEMICAL CONVERSION AND SEPARATION PROCESSES

PARTNERS: ARKEMA, BKW, CIRCC, NZ, MERCK, TUDO, TUHH

PLATFORM CHEMICALS PRODUCTION

Wood hydrolysates, glycerol (side product from plant oil processing and biodiesel production) and oil seed cake (residuals from oil plant processing) are cheap and abundant substrates for the biochemical conversion into value-added fuels and chemicals by different microorganisms. In this subproject, n-butanol and 1,3-propanediol (PDO) were selected as two target products because of their industrial importance as a fuel and as a polymer building monomer, respectively, together with possibilities of downstream functionalization into commodity chemicals.

We have successfully developed a fermentation process to produce n-butanol from raw substrates from the project partners with bacterial strain of *Clostridium pasteurianum* (Figure 36). In contrast to the conventional aceton-butanol-ethanol ("ABE") fermentation using classic Clostridia strains, no significant amounts of aceton and ethanol are produced with the *C. pasteurianum* strain used in this project, leading to a substantial simplification of the downstream processing. We have successfully adapted this strain to grow on pure biomass hydrolysate, as well as on raw glycerol from biodiesel production. A mixture of both carbon sources and further optimization of the cultivation media led to 21 g/L n-butanol in the fermentation broth, which is higher than the highest n-butanol titer reported so far in the literature for this organism.

For the bioconversion of raw glycerol to PDO, a microbial consortium, mainly consisting of Clostridia species was initially used for fermentation under unsterile conditions. Initial attempts with technical glycerol from the project partners resulted in a rather low product titer. A key component in the culture medium was then identified to significantly affect the selectivity of the bioconversion. Using an optimized culture medium with a controlled concentration of this component, we were able to produce PDO at a concentration of 50-60 g/L and with a yield of 0.4 g/g glycerol under unsterile conditions. Unsterile fermentation of raw glycerol to PDO was then successfully realized at the pilot scale (4 m³ bioreactor).

PDO production from raw glycerol was also studied in parallel with *Lactobacillus*. Using a selected *Lactobacillus* strain in a batch glycerol-glucose co-fermentation process, medium optimization led to a high productivity with a yield significantly higher than the benchmark value set at the beginning of the project. The selected strain is resistant to the inhibitory compounds contained in the raw glycerol issued from the biodiesel industry and is able to convert it mainly to PDO. Furthermore, biomass hydrolysate could substitute for glucose even though the efficiency of the process was significantly hampered in the presence of spruce lignocellulosic hydrolysate issued from the aforementioned BALI® process.
For separation of PDO and \(n\)-butanol from fermentation broth, different techniques including distillation, extraction and pervaporation and gas stripping were examined (Figure 37). Specifically, promising ionic liquids as extraction solvents were developed and successfully tested in lab and bench scale units for \(n\)-butanol. Furthermore, different membrane materials on a polymer and an ionic liquid basis were tested and evaluated regarding their performances. Extraction, pervaporation and gas-stripping showed promising results for efficient recovery of \(n\)-butanol. In comparison, gas stripping is the easiest downstream solution for setting up the pilot scale fermentations. Additionally, it performs very well as an \textit{in situ} process for product removal within the cultivation.

New innovative efficient technologies were accordingly developed for the production of \(n\)-butanol and of PDO (Figure 38), which are still confidential at the moment. However, among the obtained benefits, we can state that:

- With an especially developed medium and a \textit{C. pasteurianum} strain grown on glycerol in a fed batch process, butanol titer could be largely optimized;
- Stripping out inhibiting components enabled considerably increasing the 1,3-PDO production;
- A product solution of high concentration (up to 70\% \(n\)-butanol) with a high purity was easily obtained in a phase separation vessel after condensation of the stripping gas.

\textbf{BIOGAS PRODUCTION}

Biogas production was implemented as a part of the biorefinery concept to completely use residuals or “waste” materials from biomass processing and conversion. In particular, studies were carried out to convert seed mill cakes from processing of oil plants (e.g., castor) into biogas. These residual materials are known as quite refractory substrates for biogas production. With an adapted thermophilic consortium, we could anyway achieve a biogas yield as high as 380 to 400 L/kg organic dry substance (oTS) from castor meal issued from the project. This is about twice as high as that reported in the literature with a similar substrate, but lower than the biogas yield (about 700 L/kg oTS) using cellulosic materials as a substrate. The high lignin content (about 55\% w/w) in the oil cake was found to be the reason for the relatively low biogas yield.

The biogas production process was further optimized in terms of organic loading and residence time of the substrate. In a continuous biogas culture, the loading rate was increased from 1.5 to 3.5 g oTS/L*-day, whereas the residence time was reduced from 25 to 9 days without significant effects on the biogas yield. To further increase the biogas yield, fermentations with either cow dung or bioethanol stillage as a co-substrate were studied in different reactors with increasing loading rate. Although no increase in biogas yield could be observed in both cases, the use of bioethanol stillage as a co-substrate proved to be promising, since it can result in a stabilized reactor performance and does not lead to ammonium inhibition.
SUB-PROJECT 5:
ADVANCED CATALYTIC CONVERSION PROCESSES TO CHEMICALS AND INTEGRATED SEPARATION TECHNOLOGIES

PARTNERS: ARKEMA, CIRCC, CNRS-IRCÉLYON, CNRS-RENNES, CNRS-UCCS, FEUP, HTAS, NOVANCE, NZ, OBRPR, ORGACHIM, RWTH, SINTEF, TUDO, UMICORE

The general objective of SP5 was to screen catalytic processes to yield a variety of products with tailored properties for aviation fuel and niche applications. Several biomass sources have been identified as suitable for catalytic transformations. Castor, crambe and safflower have been successfully used for the vegetable oils, while willow, giant reed and miscanthus are lignocellulosic materials precursors for other chemical raw materials. This SP used the product delivered through the cultivation / pretreatment chain developed from SP2 to SP4.

A key technology for fuel and chemical applications is the cleavage of fatty acids and derivatives (esters, nitriles) to give shorter molecules. For this purpose, three methods were investigated. The thermal cleavage of methyl ricinoleate has been improved with new conditions allowing 30% energy saving. Much progress has been made with the olefin metathesis reaction. Even if the ethenolysis reaction did not reach the literature performances, metathesis has been proven to be a powerful tool for the synthesis of ester and nitrile compounds. High catalyst efficiencies (TON) have been obtained with different homogeneous catalysts. The oxidative cleavage is an alternative technology for the cleavage of unsaturated fatty chains with original results obtained for some nitrile compounds.

Different process technologies were studied to make acetals and alcohols. For acetals production, new processes were developed. Direct oxidation, SMBR (Simulated Moving Bed Reactor) (Figure 39) and catalytic distillation are promising solutions to substitute a conventional batch process by a continuous process. For alcohols synthesis, we have focused on advanced catalytic reactions to make heavy alcohols (Figure 40). A large heterogeneous catalysts screening has been carried out through the development of a new parallel testing equipment with 4 reactors, which will be commercialised through a startup under creation at UCCS.

Figure 39: SMBR
Figure 40: New parallel equipment for advanced catalytic reactions
Different routes for the valorization of \( n \)-butanol and \( 1,3 \)-propanediol (issued from SP4 research outcomes) have been proposed. The feasibility to transform propanediol into a useful carbonate compound has been shown. Detailed process studies have been performed for the \( n \)-butanol transformation to butyl acrylate and maleic anhydride. A catalytic distillation process has been set up for butyl acrylate production. For maleic anhydride, different process options have been studied and a new catalyst has been discovered and scaled up. This is a nice opportunity to retrofit existing maleic or phtalic anhydride plants in Europe (see Value Chain 6).

The transformation of sugar hydrolysates into fuels through the HMF (5-hydroxymethylfurfural) intermediate failed, but the hydrogenation reaction of sugar derivatives or alcohols remains interesting to make paraffins.

Several products from SP5 (nitriles, esters, acetics, alcohols, alkanes) have been evaluated for the aviation fuel application. Two products have been selected for the aviation gasoline and jet fuel demonstrations, respectively. Three other products failed for aviation fuel (ester and acetal compounds), but have been proposed for diesel fuel. Apart from the fuel application, SP5 has highlighted several opportunities to make high value monomers for polyamides or acrylics in a chemical-driven biorefinery concept (Figure 41).

Figure 41: SP5 summary scheme

SP5 has contributed to the development of key technologies for the Value Chains: thermal cleavage, metathesis, oxidative cleavage, hydrogenation, heavy alcohols synthesis, esterification, and oxidation to maleic anhydride. All these technologies have moved to the demo phase in SP8 and 21 patent applications have been filed during the project from this SP (8 on metathesis, 5 on oxidative cleavage, 2 on hydroformylation, 3 on nitriles, 2 on glycerol derivatives, and 1 on the new parallel equipment for assessing catalytic performances).
EUROpean multilevel integrated BIORefinery design
for sustainable biomass processing

**SUB-PROJECT 6: ADVANCED CATALYTIC THERMOCHEMICAL CONVERSION PROCESS**

**PARTNERS:** ARKEMA, CIRCC, CNRS-IRCELYON, CNRS-RENNES, CNRS-UCCS, FEUP, HTAS, NOVANCE, NZ, OBRPR, ORGACHIM, RWTH, SINTEF, TUDO, UMICORE

SP6 was dedicated to the development of ADVANCED CATALYTIC THERMOCHEMICAL CONVERSION PROCESSES. The EuroBioRef concept is a zero waste biorefinery that includes the lignin/black liquor and solid residues conversion to syngas as an intermediate for the production of power and value added chemicals.

A primary objective of SP6 was to test and assess the gasification processes of biomasses that is available from the pre-treatment processes of SP3, i.e., a) woody materials, b) lignocellulosics, c) spent cakes from oil crops (crambe cakes), d) plants originating from Africa (such as castor and jatropha). Tests under fluidized gasification conditions and examination of ash-related problems deriving from the inorganics were investigated. Cardoon seems to be the worst fuel and almost impossible to gasify with a fluidized bed technology (Figure 42 and Figure 43) failing to reach adequate temperatures (namely ~800°C) without agglomeration and defluidisation. The quality of gasification of the tested fuels was assessed comparatively, and, for chosen materials, long duration tests have been performed in SP7. A model for residual liquid biomass gasification was elaborated for predicting the gasification of different qualities of black liquor materials. Furthermore, the project assessed the potential uses or safe disposal of residues (ash) from gasification processes. The second target to achieve dry gas cleaning to reduce liquid effluents includes two processes. A gas cleaning test facility has been designed and implemented. In parallel a thermal / catalytic oxidation TPOX/CPOX was also successful in reducing tars from syngas for energetic applications. The reported results from tests for removing a model tar (naphthalene) include a wide screening of different process parameters impact on gas quality and heating value. On the TPOX, the conversion rate of toluene and naphthalene is higher than 99.8 %, and, on the CPOX, higher than 99.9 %.

**Figure 42:** Picture of the circulating fluidized bed gasification unit

**Figure 43:** Flow sheet of the 100 kWth pilot plant gasifier facility
One of the predominant applications of syngas in SP6 was the production of \( \text{H}_2\text{O}_2 \), which can be used on-site in the pulp and paper industry. The most efficient catalytic system for the production of \( \text{H}_2\text{O}_2 \) was chosen. The anthraquinone process was revamped in several novel aspects. The different impurities in the hydrogen supplied from the black liquor gasification and DME/Methanol unit of an integrated Chemrec Unit for the production of \( \text{H}_2\text{O}_2 \) were assessed. \( \text{H}_2\text{S} \)- or \( \text{CO} \)-poisoning of the production process has been assessed. The PSA technology, which was selected, can achieve the purity goals for the hydrogen used for \( \text{H}_2\text{O}_2 \).

SP6 investigated upgrading of biosyngas to MeSH and higher alcohols with an integrated approach of systematic catalyst synthesis, catalytic testing and physicochemical characterization that enabled determining of composition-structure performance relations and gave clear insights on the detailed property requirements for efficient higher products synthesis. Several catalysts were prepared, characterized and tested in the reaction of syngas with hydrogen sulfide for obtaining methyl mercaptan (MeSH). Conversions of around 60% and yields in MeSH above 5.0 kg/day.L were observed for the developed catalysts. For the HA production, the effect of \( \text{Zn} \) and \( \text{Al} \) substitution by \( \text{Cr} \) and \( \text{Mn} \) was investigated in \( \text{K} \)-promoted \( \text{Cu/X/Al} \) and \( \text{Cu/Zn/X} \) catalysts. Furthermore, a series of bulk carbides \( \text{Mo}_2\text{C} \) showed the highest productivity in alcohol synthesis (70 mg/kgcat.h) followed by \( \text{Fe-CuZnAl} \) catalysts. Preliminary tests showed stability of the prepared catalysts in the presence of 13 ppm of \( \text{H}_2\text{S} \) during the first 60 h on stream. Space time yields of up to 70 g\( \text{C}_2\text{OH} \)/kgcat.h have been reached and further enhancements are expected with increased pressures, as a proposal for a next project.

The existing and newly developed gas cleaning techniques proved sufficient for avoiding serious detrimental effects on the catalysts operation.

Finally, residual biomasses were also screened with batch carbonization / activation for the production of highly added value activated carbons. Several recipes for both carbonisation and activation have been tested on the most promising materials. The products were analysed for their hardness, BET, DFT and indexes, and, by these means, the consortium identified promising applications. In total, 30 physically activated and 88 chemically activated carbons have been produced from a variety of biomasses (Figure 44).

*Figure 44: Examples of microscope pictures of various activated carbons elaborated from biomass in the project*
SUB-PROJECT 7:
CONCEPTUAL PROCESS DESIGN AND INTEGRA-
TION OF THE WHOLE PROCESS CHAIN/GRID INTO A
BIOREFINERY

PARTNERS: ARKEMA, BKW, BORREGAARD, CECA, CERTH, CIRCC, CNRS-RENNES,
CNRS-UCCS, DTI, FEUP, HTAS, MERCK, NOVANCE, NZ, OBRPR, RUSE, PDC, QUAN-
TIS, RWTH, SINTEF, TUDO, TUHH, UMICORE, WSKRZ

With the application of a systematic methodology for conceptual design, individual processes developed
in EuroBioRef have been designed with their economics evaluated. Diverse aspects of process intensifi-
cation have been considered, e.g., reactor systems, hybrid separation technologies, integrated reaction
and separation.

All these individual process steps have then been integrated into value chains, which convert biomass
as a raw material into fuels and/or chemicals for end-use. The value chains have been mass and energy
integrated. The co-/by- products have been valorized, and waste streams have been identified. Where
necessary, the technologies developed in EuroBioRef have been supplemented with other technology to
fill the gaps in the value chains. This entailed extra design work, sometimes involving reverse engineering
on existing commercial technologies. A techno-economic study has identified the critical steps for cost
reduction in order to achieve an overall optimal economic and sustainable biorefinery.

During the development of the value chains, Quantis’s Life-Cycle Assessment (LCA) software suite, in
a version tailored for EuroBioRef, has been used to guide the integration work and enable a ranking of
alternatives.

In order to validate the products, raw materials, optimized catalysts and process conditions, preliminary
function tests in lab and bench scale units have been carried out in a decentralized way, making use of
existing equipment where possible. The results of these tests have also been used as input towards pilot
scale demonstration.

Among the range of products generated in EuroBioRef, those potentially suitable as aviation fuel
constituents have been identified by measuring the relevant performance properties (e.g., energy content,
lubricity, fluidity, non-corrosivity, electrical conductivity, cleanliness).

Thereafter, the combustion characteristics (including flame stability, temperature profile of the flame, flow
field) have been tested (Figure 45 and Figure 46). The best performing compounds have then been tested in
an engine, measuring performance and emission characteristics (Figure 47 and Figure 48). Simultaneously,
aspects of safety effect have been investigated (reaction between fuel/flame and engine parts).

Those components, which were positively evaluated on all criteria, i.e., the components that showed a
comparable performance to conventional fossil aviation fuel but without negative safety effects on engine
parts, have been proposed to be blended into aviation fuel.
Figure 46: Sample photographs of the flame stability test viewed by revision window

Figure 47: Engine exhaust emission pick up

Figure 48: Measurement of the engine exhaust emissions
The objective of this SP was to demonstrate the whole biomass chain conversion, starting from the biomass feedstock culture, harvesting and logistics, through the developed pre-treatment and conversion routes at the demo level (pilot and industrial plants) to the potential marketable bio-products in a viable economic, socioeconomic and sustainable way. These demonstration tests have been realized in various sites in prepared pilot plants or in adapted industrial units.

The program was divided into 3 work packages:

**PREPARATION AND ADAPTATION OF DEMONSTRATION PILOTS FOR EUROBIOREF**

This WP comprised the construction and/or adaptation of pilot units of the various sub processes according to the process design developed in SP7, expected by the project in a scale that can be considered as industrial or that, at least, easily enables the extrapolation of the process at the industrial scale production. A main success of this part is the Borregaard pilot plant (BALI), of which the lab achievements are presented in the SP3 section above. The BALI process has also been automated to be in line with the full-scale biorefineries of lignocellulosic biomass. This was done in order to gain maximum knowledge from the pilot plant when moving from pilot to full scale. All unit operations are continuous and it is possible to monitor and control them via computers from the control room. All the other unit operations (feedstock handling, chemical preparation, pretreatment, lignin processing, enzymatic hydrolysis and fermentation) have been successful.

Biomass feedstock production for the demonstration was provided by UWM. Willow plantation area being in Poland, 40 tons of chips were delivered by trucks to Borregaard in Norway for further tests. As a main result from the three batches, in the third hydrolysis, 80% glucan conversion was achieved after 48 h with an actual enzyme loading of 40% w/w.

**PILOT DEMONSTRATION OF EUROBIOREF SPECIFIC MODULES AND THE WHOLE CHAIN INTEGRATED IN SELECTED SCENARIOS**

EuroBioRef project demonstrates the technical and economic feasibility in logistics, pilot plants of biomass pre-treatment, first conversion, and bioproducts production. This WP thus targeted a demonstration scale at which the industrial partner would be sufficiently confident to move the results to a commercial scale production.

Concerning the agronomic part, the objectives were to select the best species and prove and optimize the agronomic feasibility in different countries. 5 species were then selected to go to the demonstration phase:

- Lignocellulosic biomass: Willow in Poland and giant reed in Greece;
- Oleaginous plants: Castor in Madagascar, safflower in Greece, and crambe in Poland.

The main results are:

- Validation of these species potential;
- Production at the demo scale of samples and data to elaborate the scenarios of Value Chains 1, 2 & 3;
- Confirmation of agronomic interest and performance of willow species and giant reed for lignocellulosic biomass and of castor, safflower and crambe for polymer applications.

A guide for castor oil plant cultivation in Madagascar was further prepared to guide the farmers for good practices and to show them the economic interest of this cultivation.
Further, in this WP, we showed the good operation of specific units in the project and demonstrated their production capacities, efficiency and their eventual optimization for the piloting of:

- Biomass first transformation/pretreatment: biomass pretreatment/delignification, castor seed dehulling and seed crushing, fermentation to 1,3-propanediol and to n-butanol;
- Final products (applications) manufacturing (monomers, acetics, butylacrylate, castor oil methyl esters separation, maleic anhydride, aviation fuel);
- Thermochemical conversion technologies applied in a specific site, starting from the gasification of lignin and solid residues, through gas cleaning and going to syngas conversion of alcohols.

The main successes of these tasks are:

- A first successful transformation of glycerol to 1,3-propanediol (TRL = 4; Final separation raised several issues);
- Production process of acetics is ready to scale-up level, a demonstration was done in Arkema (TRL = 6) and a sample supplied to DTI for further fuel testing;
- Butanol fermentation of hydrolysate of BORREGAARD has been done by TUHH/BKW (TRL = 4);
- Butylacrylate was produced using biobutanol and acrylic acid with a new reactive distillation technology by TUDO;
- Castor oil methyl esters were separated by a new technology promoted by Arkema and TUDO (TRL = 6);
- Preparation of biobased branched paraffins was demonstrated by OBR (TRL = 6) at CERTH on heavier molecules;
- Downstream chemical transformation: maleic anhydride by bio-butanol oxdehydration has been performed by Orgachim/CIRCC/Arkema (TRL = 6);
- Improved H_2O_2 process for small units was piloted at Arkema (TRL = 6);
- For thermochemical conversion, syngas was generated from several biomass resources by CERTH (TRL = 5).

**INDUSTRIAL DEMONSTRATION OF SPECIFIC APPLICATIONS**

For some bio-products close to the market (4-5 year), the feasibility was directly demonstrated in relevant industrial environment, which is a remarkable achievement of EuroBioRef. Namely, the following demonstrations were carried out in existing industrial units:

- Guerbet alcohols synthesis process developed by Arkema was up-scaled by Novance (210 kg);
- Acetics were synthesized at several 100 kg scale by Arkema (TRL = 6), and the product was supplied to DTI for fuel tests;
- Fatty nitriles of several new compounds were synthesized on an equipment used to directly up-scale to the commercial production unit (TRL = 7);
- Short chain esters were obtained through several cleavage technologies – metathesis, oxidative cleavage, thermal cleavage (TRL = 6);
- New bio-based aviation fuels blended by OBRPR were demonstrated by WSKRZ (test with 15 m^3 of product; TRL = 6, FRL - Fuel Readiness Level = 6 out of 9).
These results have enabled the establishment of different production scenarios that are validated both at the pilot and the industrial scales and demonstrated within the value chains.

CONCLUSIONS

- Confirmation of the agronomic interest and of the performance of willow species and giant reed for lignocellulosic biomass and castor (TRL = 7 to 8, by SOABE), safflower and crambe (TRL = 5 to 7);
- The first transformation of these species is validated and is integrated in the value chain concept and demonstration. The scale up with the continuous reactor BALI pilot plant is in demonstration for hydrolysis of biomass. Dehulling unit (Figure 49) and oil extraction pilot is validated (full scale BALI unit to be constructed by 2017 in Norway by Borregaard). The castor production in Madagascar is now “en route” to commercialization and should start sampling first customers for validation soon after the end of the project (TRL = 8);
- Further, as listed above, several products have reached a TRL equal or above 5 (Figure 50).

![Figure 49: Castor dehulling unit](image)

![Figure 50: Schematics explaining how the project managed to reach its objectives including demonstration at TRL equal or above 5 (right part of the scale 100 % of the objective achieved)](image)

<table>
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<tr>
<th>EuroBioRef Achievements vs. Objectives</th>
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<tr>
<td><strong>Biodiversity</strong></td>
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<td>Produc...</td>
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<td><strong>High Energy Aviation Fuel</strong></td>
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<td>High specific energy bio-jetfuel (42 MJ/kg)</td>
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<td><strong>Produce Multiple Products (Reaching TRL &gt; 5)</strong></td>
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<td>(Chemicals, polymers, materials) in a flexible and optimised way...</td>
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<tr>
<td><strong>Improve Cost Efficiency by 30%</strong></td>
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<tr>
<td>through improved reaction conditions and separation effectiveness, improved plant and feedstock flexibility, reduction in production time and logistics</td>
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<tr>
<td><strong>Reduce Energy Consumption by 30%</strong></td>
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<td><strong>Product Zero Wastes</strong></td>
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<td>and rationalize the use of raw materials</td>
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<td><strong>Reduce Time to Market (Month)</strong></td>
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SP9 focused on providing economic and socio-economic analysis of the biorefinery value chains. This was done in order to generate discussions around project feasibility, identify areas of cost sensitivity, and help to prioritise value chains and future research. The analysis took place in two parts: one quantitative, based on a stochastic modelling technique, and the other qualitative, based on a survey of potential barriers to future project development and a detailed case study of Madagascan socio-economic impacts.

The EuroBioRef value chains represent an early stage of concept development and the costs of many supply chain elements are highly uncertain. This uncertainty compounds the more general uncertainty around product and chemical costs that will strongly influence future commercial viability.

The approach taken in SP9 successfully demonstrated a stochastic cost modelling approach (Figure 50), which was able to quantify and incorporate the uncertainties in costs. Full, detailed models were developed for location-based scenarios within each of Value Chains 1 and 2 (oil seed feedstocks) and Value Chains 3 and 5 (lignocellulosic feedstocks). Cost data was obtained from databases, quotations, and expert judgment, and the model used specialist software to fit probability distributions for each of these. These distributions were used to run Monte Carlo simulations and produced probability distributions of success and failure for the complete value chain. Focusing on commonly used economic metrics, such as net present value (NPV), internal rate of return (IRR) or levelised cost of production (LCOP), the models provided an informed basis to allow analysis of the cost drivers and feasibility of each of the value chains, and discussion and comparison between them. This methodology resulted in flexible models that represent the inherent uncertainty and risk involved in each value chain, whilst enabling swift numerical and graphical comparison between value chain scenarios and value chains.

Of the EuroBioRef Value Chains, Value Chain 5 (syngas-based products from black liquor) generated the most attractive NPV. This model returned a mean NPV of over €140 million, associated with 90% probability of returning a positive NPV. The IRR for this Value Chain was 17%, representing a relatively high return on capital and indicating that this project is an attractive investment even considering the technological immaturity of some of the process steps.

The next most economically viable option was found to be Value Chain 1 (castor oil to polymers) where the castor crop is harvested from a Madagascan plantation. This Value Chain returned a mean NPV of over €30 million, with a 70% probability of returning a positive NPV. However, the IRR for this value chain was found to be slightly lower at just less than 8%, suggesting that the perceived riskiness associated with such a ‘first of a kind’ project could negatively influence the investment profile. The socioeconomic investigation of the Madagascan scenario also suggested potential project risks arising from the possibility of hidden costs, child labour and political unrest. However, the socioeconomic framework also revealed potentially positive impacts on the target population, and, overall, the Madagascan scenario for Value Chain 1 looks to present an attractive investment opportunity.

The rest of the proposed value chains returned negative mean NPVs, with French and Spanish safflower returning negative mean NPVs of around -€10 and -€40 million, respectively. However, while the probabilities of positive NPVs were relatively low for these two scenarios, the very early stage of project development means that the investment potential is expected to improve as the concept matures. Results were similar for Value Chain 3 (heavy alcohols to fuels) with a negative mean NPV and a low probability of positive NPV both expected to improve over time.
Sensitivity analyses revealed the dominant influence of feedstock costs, electricity and gas prices in determining each of the Value Chains’ economics. The EuroBioRef processes are highly energy intensive and overall NPV values are significantly dependent on the price of feedstock. Plant location and feedstock selection are therefore expected to be important determinants of the economic feasibility of each of these Value Chains. The qualitative assessment of the economic and financial barriers complements these findings, identifying subsidies for oil crops coupled with relevant mandates and standardization schemes for bio-products as important factors for future development of the EuroBioRef concepts (Figure 52). Furthermore, large-scale demonstration plants for the concepts that are closer to commercialisation stage are deemed critical in order to prove the feasibility of the technology. These measures would reduce uncertainties and help to realise the attractive investment opportunities presented within these Value Chains.

Figure 51: Cost modelling was used to examine future economic performance

Figure 52: The legal framework for EU biorefineries was assessed

<table>
<thead>
<tr>
<th>Madagascar</th>
<th>France</th>
<th>Spain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>82, 386, 702, 90</td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>202, 200, 476, 75</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>51, 483, 798, 79</td>
<td></td>
</tr>
<tr>
<td>Std Dev</td>
<td>47, 385, 338, 73</td>
<td></td>
</tr>
<tr>
<td>Values</td>
<td>10000</td>
<td></td>
</tr>
</tbody>
</table>
The objective of this SP was to continuously monitor and provide means for the EuroBioRef partners to share their knowledge within the consortium and to integrate the research activities as well as to exploit the research results and/or communicate and disseminate the results to the scientific community, to standardization bodies and to the wider audience (e.g., by training).

This SP was organized in four WPs that are listed below with their major achievements.

- **Management of IPR, exploitation roadmap**
  An IPR committee was set in year 1 that took care of the patent filing issue. This WP has also produced the following information relevant to the products generated in the project:
  - Exploitation Plan (ExPl) of results;
  - Probability of Success of innovative technologies;
  - Sustainability index of new processes developed in the project;
  - The new assessment methodology Technological Readiness Level-TRL, has also been used as an additional tool to be introduced for the evaluation of the advancement of the project;
  - The Commercialization plan has been implemented for selected products.

- **Dissemination and communication**
  Awareness about the project’s goals and objectives was generated by executing a dissemination strategy to reach different groups, such as the scientific and industrial communities, the general public, other on-going projects including sister projects, potential end-users and interested stakeholders, or standardisation bodies. The project has then stepped from the conceptual to the demonstration phase. As the technical maturity has grown, the capacity of self-critical assessment and the academia-industry integration has made the Project more productive of applications. The start of the activity of the Interest Group (external industrial partners interested to either use the results of the project or to provide raw materials to the project for testing in innovative processes and linked to the Project by a non disclosure agreement) is providing new life to the Project beyond its end.

- **Training activities**
  A School on “The concept of Biorefinery comes into operation” was organized in year one and the book “Biorefinery: from biomass to chemicals and fuels”, De Gruyter was published in year two. Additional training activities for professionals, PhDs, Post Docs were also performed. Moreover, an Erasmus Master on Biorefineries has been planned.

- **Standardization**
  International standardization bodies were contacted and new EU standards for bio-fuels, bio-products and bio-processes were elaborated. Also, new cellulose-sourced molecules were selected and tested as potential avio-fuels. EuroBioRef also worked at the definition of a new methodology for identifying the origin of the biomass from which biofuels are produced. This methodology is the “Traceability of Biofuels and Chemicals” based on the use of sophisticated spectroscopic techniques and measurements that make use of isotopes of various elements for labeling the origin of the raw materials.
PARTNERS CONTACT DETAILS

CNRS - UCCS, Centre National de la Recherche Scientifique - Unité de Catalyse et Chimie du Solide (UMR8181) (France)
Franck Dumeignil
Coordinator
franck.dumeignil@univ-lille1.fr

CNRS, Centre National de la Recherche Scientifique – Institut de recherches sur la catalyse et l’environnement de Lyon (UMR5256) (France)
Aline Auroux
aline.aurox@ircelyon.univ-lyon1.fr

CNRS, Centre National de la Recherche Scientifique – L’Institut des Sciences Chimiques de Rennes (UMR6226) (France)
Jean-François Carpentier
jean-francois.carpentier@univ-rennes1.fr

ARKEMA FRANCE SA (France)
Jean-Luc Dubois
SP1 leader
Industrial and Exploitation Manager
jean-luc.dubois@arkema.com
Jean-Luc Couturier
SP5 leader
jean-luc.couturier@arkema.com

CECA (France)
Philippe Bour
philippe.bour@ceca.fr

FEUP Faculdade de Engenharia da Universidade do Porto (Portugal)
Alírio Rodrigues
arodrig@fe.up.pt

RWTH Aachen, (Germany)
Retired from the project on 31/08/2011

CIRCC (Ita)
Michele Aresta
SP10 leader
michele.aresta@uniba.it

WSK «PZL-Rzeszow» S.A (Poland)
Antoni Gnot
antoni.gnot@wskrz.com

OBR Joint Stock Company
Jacek Muszyński
jacek.muszynski@obr.pl
Janusz Pilarczyk
janusz.pilarczyk@obr.pl

BORREGAARD Industries, Ltd. (Norway)
Anders Sjöde
SP3 leader
anders.sjode@borregaard.com

NOVOZYMES A/S (Denmark)
Nils Isbæk
SP4 leader
nisb@novozymes.com

CRES, Center for Renewable Energy Sources (Greece)
Myrsini Christou
SP2 leader
mchrist@cres.gr
Angeliki Lemonidou
alemonidou@cheng.auth.gr

HALDOR TOPSØE A/S (Denmark)
Irantzu Sabada Zubiri
irsz@topsoe.dk

CERTH, Centre for Research & Technology Hellas (Greece)
Kyriakos Panopoulos
SP6 leader
panopoulos@certh.gr
Angeliki Lemonidou
alemonidou@cheng.auth.gr

PDC, Process Design Center BV (the Netherlands)
Hans Keuken
SP7 leader
keuken@process-design-center.com

QUANTIS (Switzerland)
Arnaud Dauriat
arnaud.dauriat@quantis-intl.com
By buying products with the FSC® label you are supporting the growth of responsible forest management worldwide.

CONSORTIUM

EuroBioRef is coordinated by UCCS, CNRS Délégation Nord Pas-De-Calais et Picardie. This 29 partners project from 15 countries gathers actors from the whole biomass value chain:
• Biomass producers, culture developers and logistics specialists (SOABE, CRES, DTI, UWM);
• Advanced biomass pretreatment industries (BORREGAARD, NOVANCE);
• Catalytic and enzymatic reactions developers (CNRS, TUDO, FEUP, CIRCC, RWTH, TUHH, BKW);
• Thermochemical reactions developers (CERTH, NYKOMB);
• Catalyst and enzymes producers (HTAS, NZ, UMICORE);
• Process designers and engineers (PDC, CERTH, SINTEF);
• Final chemical and biochemical producers and end-users (ARKEMA, RUSE, MERCK, NYKOMB, OBRPR).

The consortium includes also an aviation refinery (OBRPR) and a jet-engines maker (WSKR2) for bio-aviation fuel testing. The sustainability of the whole project will be analysed and optimised by socio-economics and life cycle analysts (IMPERIAL, QUANTIS), civil organisation analysts (EUBIA) as well as specialists for project management (ALMA).

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CONTACT

Project Coordinator:
CNRS-UCCS: M. Franck DUMEIGNIL,
+ (33) 3 20 43 45 38 – franck.dumeignil@univ-lille1.fr

EC Project Officer:
DG-Research G4: Ms. Maria GEORGIADOU,
+ (32) 2-2-29-59846 – maria.georgiadou@ec.europa.eu

With the support of:
ALMA: Project Manager Ms. Maud BOSSARD,
+ (33) 4 72 35 51 15 – mbossard@almacg.com

Official website of the EuroBioRef project: www.eurobioref.org