Project acronym:	**EuroBioRef**
Project Title:	EUROpean multilevel integrated BIOREFinery design for sustainable biomass processing
Instrument:	Large Scale Collaborative Project
Thematic Priority:	FP7-ENERGY.2009.3.3.1
Grant Agreement:	241718
Start Date of Project:	01/03/10
Duration:	48 Months

SP7 –Conceptual process design and integration of the whole process chain/grid into a biorefinery
WP7.3 – Preliminary function tests

Deliverable report

Due Date of Deliverable: M24 - 29/02/2012
Actual Submission Date: M24 – 15/02/2012

Deliverable Identification	
Deliverable Number:	D7.3.5.1 (Part1 – an update (D7.3.5.2) is planned at M35)
Deliverable Title:	Production of at least 0.1 kg of each product. Analysis of reaction products. Life tests for catalytic activation.
Responsible Beneficiary:	CNRS-UCCS
Contributing Beneficiaries:	CNRS-UCCS, ARKEMA, UMICORE, FEUP, RWTH, CIRCC, HTAS, SINTEF, OBRPR
To be Submitted to the EC:	Yes

History			
Version	**Author**	**Modification**	**Date**
V1	Franck DUMEIGNIL	Creation of a first draft	30/01/2012
V2	Wei Zhao	Modification and approval	15/02/2012

Approval				
	Name	**Organization**	**Date**	**Visa**
Deliverable Responsible	Franck DUMEIGNIL	CNRS-UCCS	30/01/2012	OK
Work Package Leader	Coordinator on behalf of METEX	CNRS-UCCS	30/01/2012	OK
Sub-Project Leader	Wei Zhao	PDC	15/02/2012	OK
Coordinator	Franck DUMEIGNIL	CNRS-UCCS	15/02/2012	OK

Dissemination level		
PU	Public at the end of the project (M48)	X
PP	Restricted to other programme participants (including the Commission Services)*	
RE	Restricted to a group specified by the consortium (including the Commission Services)*	
CO	Confidential, only for members of the consortium (including the Commission Services)	

* In case of dissemination level of PP/RE, the persons (or group of personnes) agreed to have an access to the document are: Non applicable.

Content

Executive summary

Description of the deliverable objective and content

This deliverable is split in two parts. The present part is the first one due at M24 (D7.3.5-Part1) and the second is due at M35 (D7.3.5-Part2).

In this deliverable, we must report about the quantity/quality of products synthesized at a 'pre-demo' scale (SP7). The present first part of the deliverable presents the current progress that has been done to achieve the targets at M35.

Deviation from objectives and corrective actions

As this deliverable is divided in two parts, this can be considered as the first assessment. The objective of completion is at M35. Anyway, the absence of work of METEX delayed the delivery of biotech-derived platform molecules, but amendment 2 will compensate for this by integrated two new partners, namely TUHH and BKW, who will be able to deliver samples in sufficient quantities to enable these SP7 demonstrations.

Analysis of the results

For the moment, the results indicate that we will be able to deliver the products at M35 without having to face too difficult issues.

Impact of the results

The results will enable evidence for the possibility of further up-scaling in SP8.

Related IPR

IPR is not directly concerned here as the results are derived from SP5 experimental work that has been potentially previously protected.

Publishable information

This deliverable will be made public at the end of the project.

Conclusion

This first part of D7.3.5 shows that, despite some experimental complications, we are well on line with the objectives. Thus, we should be able to deliver the materials at M35, and declare their delivery in part 2 of this deliverable.

Table of achievements

Reactions	Tests and work	Production of samples	OK?	Comments
Fatty acid/nitrile Cleavage	Life tests in metathesis synthesis, to confirm that the TurnOver Number can be maintained on a long period (1 week) without detrimental effect of accumulation of minor impurities Life test in Oxidative cleavage to confirm a catalyst life of at least 5 days. Life tests of Catalytic cracking of hydroxylated fatty acids, for at least one week. UMICORE will provide catalyst on required scale based in fatty acid/nitrile cleavage. **(ARKEMA, UMICORE)**	**Production of several grams of product purified at lab scale**  © ARKEMA	**N**	UMICORE provided the following catalysts: CNRS-UCCS: 10 g of **Umicore M1** (68.1874.2611), Dichloro-(3-phenyl-1H-inden-1-ylidene)bis(tricyclohexylphosphine)ruthenium(II); 10 g of **Umicore M11** (68.1874.3114), Dichloro-(3-phenyl-1H-inden-1-ylidene)bis(isobutylphobane)ruthenium(II); 10 g of **Umicore M2** (68.1874.2911), [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(3-phenyl-1H-inden-1-ylidene)(tricyclohexylphosphine)ruthenium(II); 10 g of **Umicore M31** (68.1874.3312), [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(3-phenyl-1H-inden-1-ylidene)(pyridyl)ruthenium(II); 10 g of **Umicore M51** (68.1874.3415), [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro[[2-(1-methylacetoxy)phenyl]methylene]ruthenium(II). CNRS-RENNES: 5 g of **Umicore M31** (68.1874.3312); 5 g of **Umicore M41** (68.1874.3111), [1,3-Bis(mesityl)-2-imidazolidinylidene]-[2-[[(4-methylphenyl)imino]methyl]-4-nitro-phenolyl]-[3-phenyl-indenyliden]rutheniumchloride; 5 g of **Umicore M51** (68.1874.3415); 5 g of **Umicore M52** (68.1874.5116) [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro[[2-(2-oxopropoxy)phenyl]methylene]ruthenium(II). ARKEMA: 5.0 g of **Umicore M51** (68.1874.3415); 0.5 g of **Umicore M71 SIPr** (68.1874.6213) [1,3-Bis(2,6-diisopropylphenyl)-2-imidazolidinylidene]dichloro[(2-isopropoxy)(5-trifluoroacetamido)benzylidene]]ruthenium(II); 0.5 g of **Umicore M71 SIMes** (68.1874.7113), [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-[(2-isopropoxy)(5-trifluoroacetamido)benzylidene]ruthenium(II). RWTH**:** 0.5 g of **Umicore M10** (68.1874.3011)**,** Dichloro(3-phenyl-1H-inden-1-ylidene)bis(triphenylphosphine)ruthenium(II)**;** 0.5 g of **Umicore M31** (68.1874.3312)**;** 0.5 g of **Umicore M1Py2** (-)**,** Dichloro(3-phenyl-1H-inden-1-ylidene)bis(pyridine)(tricyclohexylphosphine)ruthenium(II)**;**

				0.5 g of **Umicore M51** (68.1874.3415). **M12 achievement:** ARKEMA has begun scale-up tests of the metathesis reactions. The first test reaction is the cross-metathesis of unsaturated C_{18} diester (commercially available) with acrylonitrile (feasibility studied in task 5.1.2). Tests have been performed on a 2 litres batch reactor at 20g diester scale. This means a 100-150 scale-up factor compared to the work done in Rennes University. Turnover numbers of 500 have been obtained. This is about 4 times lower than the academic results likely due to the influence of the purities of reactants and solvent. **M18 achievement:** Arkema has continued the optimization and the scale-up of the metathesis reaction. The selected reaction in 5.1.2 is the cross-metathesis between 10-undecenenitrile and methyl acrylate to give a nitrile-ester compound that is a precursor for a polyamide monomer. Basic process conditions have been optimized with Umicore M71 SIPr catalyst (temperature=100°C, 2-3 equivalents of methyl acrylate, catalyst addition time=15-30 minutes). For the scale-up, tests have been performed with 25g of undecenenitrile (compared to 5g in the screening phase). We have obtained turnover numbers of 17.000 that are consistent with those obtained in the screening phase (18.000). No issue is currently identified for a future pilot plant scale-up. Arkema further worked on separation issues linked to the oxidative cleavage of fatty acids (WP5.1.5). At the end of the cleavage reaction, a mixture of unreactive saturated fatty acids, cleavage products and by-products are obtained. Separation by distillation and solvent extraction were done. Both techniques are suitable for separation. Extraction with organic solvent allows separation of saturated fatty acids from bi-functional products like diacids. Cleavage products (mono and bi-functional) containing 9 carbon atoms have been successfully distilled. The purity after separation has to be improved further. Then, Arkema prepared larger amounts of raw materials for WP 5.1. and for blending into fuel. On our pilot plant, we have tested different sources of fatty acids. These acids were characterized by the level of oleic acid contained. The expected nitriles obtained by kg scale will be tested in metathesis, oxidations reaction and for fuels applications. **M24 achievement:** Oxidative cleavage: Arkema recovered > 80% of the catalyst after reaction. Recycling of the catalyst is foreseen. A pilot plant run is prepared for oxidative cleavage of oleonitrile. The reaction

				conditions on a pilot plant scale were specified and logistic issues like raw materials, transportation MSDS. Arkema also worked on extraction sequences in order to improve products separation. Experiments were carried out to improve the understanding of by-product formation with the goal to improve yield during the pilot run.
Acetals synthesis	Life tests of direct oxidation catalysts. At least 5 consecutive days with a loss of activity below 5 %. SMBR tests of the production of acetals in a continuous mode. **(FEUP)**	**Production of acetals at a few grams scale: CNRS-UCCS will produce DMM and DEE by direct oxidation of methanol and ethanol, respectively**	**N**	In order to implement the SMBR process for the acetals production it is necessary the knowledge of some fundamental data, as kinetics of reaction and adsorption multicomponent equilibrium. In the literature no data was available regarding the GEA system. Therefore, until now these kind of studies have been performed (details in the report from Task 5.2.4). A mathematical model, based in the fundamental data acquired, will be soon completed in order to describe the SMBR unit. Then, this model will be used to define the SMBR operating conditions. The SMBR tests in the previous defined conditions will be performed within the next period report and at month 35 we expect to deliver 100 grams of GEA with around 99 % purity. An efficient catalytic formulation for methanol reaction to produce DMM has been proposed based on a well-known commercial FeMo catalyst with 50% yield to DMM. The life test of the catalyst in methanol reaction will be carried out within the next reporting period as soon as proper modification of the catalytic setup will be made allowing continuous feeding of methanol for at least 5 consecutive days. Delivering of few grams scale of DMM, with some amounts of impurities, is possible regarding the productivity of 4 $g_{DMM}.h^{-1}.g_{cat}^{-1}$ obtained by far. For ethanol reaction, screening catalysts based on FeMo formulation present rather low DEE yield. Intensive studies dealing with optimizations of both catalytic system and experimental working conditions are in progress.
Guerbet Chemistry	Catalysts life tests on 5 consecutive days. Production in a continuous mode to evaluate the accumulation of side products **(CNRS-UCCS)**	**Production of samples of 100 grams.**	**N**	So far, we identified some interesting catalytic systems but further optimisation is required. At the moment such a life test is thus not worth carrying out. This will be made during the next reporting period.
Glycerol	Synthesis at lab scale of product	**Production of 100 g samples**	**N**	**M12 Achievement**: A sample of 10 g of oxazolidinone was isolated, characterized and transferred (CIRCC) to Arkema for their evaluation.

upgrading Synthesis of a cyclic carbonate	for quality control. **(CIRCC)**			**M18 Achievement**: The sample was shown to contain glycerol H-bonded to the oxazolidinone (CIRCC, ARKEMA). The bonding energy has been estimated (CIRCC) at over 20 kcal/mol: this makes difficult the elimination of glycerol H-bonded to oxazolidinone. **M24 Achievements**: Additional **60 g** of oxazolidinopne-glycerol have been prepared (CIRCC). The synthesis, still under study, has been improved (CIRCC) with a yield increased from 14 to 25 % per single passage. New catalysts are under study The reaction mechanism has been fully elucidated. Attempts to purify the oxazolidinone and to esterify such product are now ongoing.
Maleic anhydride	Identification of catalyst giving the best yield to MA at lab scale **(CIRCC)**	**Production of maleic anhydride at the lab-scale (less than 1 g). Synthesis of catalyst at lab scale (few grams).**	**N**	**M12 Achievement**: (a) identification of the key-steps and key-catalyst requirements for the one-step oxidehydration of 1-butanol into maleic anhydride. (b) identification of a possible alternative process configuration (originally not included in the DoW), for the transformation of 1-butanol into maleic anhydride: a two-step process. (c) set up of a pilot unit (which may load 1.5 kg of catalyst in the industrial-like shape) at Orgachim. **M24 Achievement:** (a) identification of the catalyst type giving the best yield in the one-step oxidehydration of 1-butanol: vanadyl pyrophosphate. The optimization of the reaction parameters at lab-scale level is under study. (b) identification of a catalyst-type offering the optimal performance in the first step of the two-step process configuration. Investigation of the reactivity of industrially-shaped catalysts is currently going-on; a sample of 1.5 kg of this latter catalyst will be delivered to Orgachim for tests in pilot-unit. The identification of the catalyst giving the best yield to MA in the second step of the two-step process configuration is under evaluation. **Obtained product**: maleic anhydride, with 38% yield, in the one-step approach.
Acrylic acid	Dehydration of 3-hydroxypropanoic acid **HTAS** will perform continuous dehydration of 3-HPA to acrylic acid.	**Continuous production of acrylic acid for esterification**	**N**	**M12 achievement:** Several potential catalysts (found in WP5.5) for the dehydration of 3-HPA to acrylic acid are tested by HTAS, optimized and verified in a pulsed micro reactor. Materials such as high-surface silica and a number of modified sulfate salts show promising performances for catalyzing the reaction at about 200 ^{o}C, 1 atm, with high yields and selectivity for acrylic acid. Currently a lab-scale continuous flow reactor is being configured, in order to validate the findings in the pulsed reactor,

				and to collect further information such as the life time of the optimized catalyst, the reaction kinetics data, and the purity profile of the products under continuous flow conditions, etc. **M18 achievement:** Based on the catalyst screening results of M0-M12 obtained using a pulsed micro-reactor, a series of continuous flow tests was carried out by HTAS during M12-M18. NZ-AS provided 100 mL of 3-HPA aq. solution to enable these tests. 3 potential catalysts have been figured out as results of the continuous flow tests. Under the test conditions, i.e., 20 wt% 3-HPA aq. solution as the feed at LHSV = 2 h-1, reaction temperatures between 150-250C, and TOS = 6 h, 100% 3-HPA conversion and 100% selectivity of acrylic acid can be obtained over these 3 catalysts, specifically, a Amberlyst at 150°C, a tungstated zirconia at 200°C and a HTAS silica at 250°C. The lifetime of these catalysts needs to be verified in further tests. Based on these results and considerations, we have chosen the HTAS silica as the candidate of the 1st generation catalyst, and have conducted optimizations with respects both to the catalyst and process conditions. The durability and scale-up synthesis of the catalyst has been tested. The process condition parameters have been optimized. It is recommended to use aqueous solutions of 3-HPA as the feed at LHSV 2-10 h^{-1}, and convert the lactic acid to acrylic acid at 100% yield in a single pass using a fixed bed reactor operating at around 250^{o}C and 1-10 atm pressure. The separation of acrylic acid from water and other contaminants is realized in a post-reactor unit.
Production of ButylAcrylate	Obtained by esterification of Acrylic Acid and Bio-Butanol A smaller part of this task will also address the esterification of isobutene and acrylic acid. (**RWTH**).	**Production of 300 g sample**	**N**	This is pending till the project did not produce yet bio-butanol. Amendment 2 will enable the new partners, namely TUHH and BKW, to take over the related tasks initially supposed to be handled by METEX.
Sugar hydrogenation to alkyl-THF, diols and	The 4 catalysts identified in task 5.7.3/4 will be subjected to synthesis on a larger scale to obtain the necessary quantity of the material for pilot-scale	**Production of 100 – 1000 kg of each of the target products will be performed.**	**N**	The search and selection for good catalysts are still on going. Good results are achieved in the laboratory tests both on Sugar dehydration and on alcohol hydrogenation.

alcohols and isoparaffins	testing of the processes. To demonstrate the utility of the improved process developed during this work package, pilot lots of 100 – 1000 kg of each of the target products will be produced at WP8.2. **OBRPR** will share in examinations of hydrogenation processes according to technology provided by **SINTEF**.	 © OBRPR lab pilot	[redacted]	