Final Report Summary - CASCATBEL (CAScade deoxygenation process using tailored nanoCATalysts for the production of BiofuELs from lignocellulosic biomass)

Executive Summary:
CASCATBEL is a project co-funded by the European Commission’s Seventh Framework programme. It has brought together 17 partners, including 4 research institutions, 6 universities, 5 large industries and 2 SME from 10 different European countries. CASCATBEL started its activities in November 1st of 2013 and finished on October 31st of 2017.
CASCATBEL project has been aimed to the development of a novel and feasible process for the production of advanced biofuels having composition and properties very similar to petroleum-derived fuels. This is a very relevant advantage regarding the commercial implementation of this technology, as it would not require any significant changes in the already existing infrastructures and engines. Thereby, CASCATBEL has investigated the sequential coupling of three catalytic steps as an essential factor for achieving a progressive and controlled biomass deoxygenation, reducing the hydrogen consumption, and avoiding the problems that hinder other bio-oil upgrading processes. The results obtained have confirmed the feasibility of this approach, leading to the production of advanced biofuels (mainly in the gasoline and diesel ranges) showing a low oxygen content (about 6 wt%).

The design of tailored catalysts for each of the chemical steps considered in the cascade scheme has been one of the essential aspects of the project as it has allowed the optimization of the reaction yields (increasing bio-oil and energy yield). Thereby, a large variety of catalytic systems have been prepared and tested in those reactions, selecting the most convenient ones for each transformation. Product selectivity and deactivation rates have been major factors to take into account during the selection and optimization of the catalysts. Likewise, the scaling-up of the process has been a very important issue for fully exploring and understanding the catalytic and reaction dynamics, assessing the catalyst behavior in a relevant environment. In this way, the experimental work has been performed in three different scales (laboratory, bench and pilot plant scales), using both model compounds and real biomass feedstock.

The commercial feasibility of this process has been assessed based on the experimental results obtained. In this way, the typical sustainable plant size was set at 400 kt/year of dry and ash free biomass feed, corresponding to 61 kt/year of fuel grade liquid products. For this plant, the estimation of final energy yield achieves at least 53%, including the production of 41 MWel of electricity (16.5% energy yield) and the production of 60.5 kt/year biofuels (36.4 % energy yield). The estimated GHG reduction is, in the most favourable case, higher than 90%, compliant with the current RED European Directive mandate (60%) and also with the possible REDII revised target (70%). The capital cost estimated for a typical plant with 400 kt/year biomass input is 171 M€, corresponding to 1,840 €/MWth liquid fuels output. The investment is attractive from a financial point of view since IRR (21%) is considerably higher than the Cost of Capital (WACC 4% was considered). Break even time, calculated on the basis of the most promising process options, is 4 years.

In conclusion, after the overall assessment, the commercial process designed based on the CASCATBEL results has proved to be feasible from technological, environmental and socio-economic points of view.

Project Context and Objectives:

BACKGROUND

First generation biofuels (bioethanol and biodiesel) have shown important limitations to achieve targets for oil-derived product substitution, climate change mitigation, and economic growth, mainly due to the high water and energy consumption during their production, and the biofuel versus food controversy. The cumulative impacts of these concerns have increased the interest in developing biofuels produced from non-food biomass. Lignocellulosic biomass, either from forestry or agriculture, offers such potential.
Lignocellulose is the most abundant source of continental biomass and it is usually a low-cost raw material. Accordingly, the use of non-edible lignocellulosic biomass from agriculture and forestry represents a very interesting alternative resource for the production of second-generation biofuels with reduced environmental impact. Additionally, lignocellulosic biomass can be supplied on a large-scale basis from different low-cost raw materials such as municipal and industrial wastes, wood and agricultural residues.

Lignocellulosic biomass holds the key for the sustainable production of liquid transportation fuels without impacting the food supply. Furthermore, the use of lignocellulose resources not only allows the production of a valuable biofuel, but the utilization of a wide range of residues from domestic, agricultural and industrial activities.

However, lignocellulose is a very complex material that requires an intensive labour and high capital cost for its processing. Although conversion of lignocellulose into transportation fuels has been attempted by a number of different routes, it is not a trivial goal due to its chemical complexity, elevated stability and high oxygen content. Three main pathways can be considered for the conversion of lignocellulose into fuels and chemicals based on hydrolytic, biochemical and thermochemical transformations, respectively. Among the various thermochemical transformation processes, biomass pyrolysis has shown to be a very promising option for the conversion of large volumes of solid biomass to liquids. In this route, biomass is treated under inert atmosphere to yield gases, liquids (bio-oil) and a solid residue (char). The use of high heating rates (fast pyrolysis), combined with moderate temperatures (around 500 ºC) and short residence times, leads to an enhanced production of bio-oil.

Bio-oil presents a high potential as liquid fuel since it retains up to 70% of the energy stored in the raw biomass and contains less N and S than petroleum fractions. However, bio-oil possesses 15 - 25 wt% water, more than 40 wt% of oxygen and shows a dark red-brown colour. It has a very complex composition (up to 400 different components have been identified) and several shortcomings, such as relatively low heating value (16–19 MJ/Kg; less than half that of petroleum-derived fuels), strong corrosiveness (pH = 2–4), high viscosity, immiscibility with conventional fuels and poor chemical stability with polymerisation of components observed on storage. Consequently, biomass pyrolysis into liquid fuels suffers from important limitations that can be only overcome if the bio-oil is subjected to upgrading treatments to improve its properties. The production of advanced liquid fuels from solid lignocellulose by biomass pyrolysis / bio-oil upgrading requires a decrease in the O/C ratio (by removal of oxygen) and an increase in the H/C ratio (by the addition of hydrogen).

Catalytic pyrolysis has been investigated as an interesting alternative to convert lignocellulosic biomass into transportation fuels that produces bio-oil. This process does not require external hydrogen and takes place at atmospheric pressure with the use of a proper catalyst, which allows the pyrolysis vapours to be upgraded into low oxygen-containing bio-oil. However, this strategy suffers from significant limitations which include reduced liquid yield (secondary cracking is favoured), high polycyclic aromatic hydrocarbons (PAHs) content in the bio-oil and fast deactivation of the catalyst as high levels of coke and contaminant metals (from biomass) are deposited. Accordingly, a compromise between the deoxygenation degree and coke formation is required.
Hydrodeoxygenation (HDO) has also been proposed as an option for upgrading biomass pyrolysis bio-oil. It involves removal of most of the oxygen groups contained in the bio-oil via hydrogenation under high pressure (up to 200 bar) and temperatures in the range 300-400 °C. HDO yields a naphtha-like and diesel product that could be blended in refineries with conventional transportation fuels. However, since bio-oil contains over 40 wt% oxygen, full HDO involves high hydrogen consumption, making this process hardly competitive in economic terms with conventional fossil fuels. Therefore, minimizing the hydrogen consumed in HDO is especially important to reduce the operation costs.

In recent years, a variety of catalytic treatments, based on the occurrence of condensation reactions between oxygen-containing polar groups, have been investigated for reducing the oxygen content of bio-oil and decreasing its water-affinity. Although the degree of oxygen removal so achieved is not complete, it is here envisaged that this kind of process could be highly beneficial for the process economics if coupled to a subsequent HDO treatment to produce low-oxygen synthetic biofuels. Accordingly, CASCATBEL project is aiming at designing a cascade process to make transformation of lignocellulosic biomass into advanced biofuels a competitive alternative to petrol-based fuels.

On the other hand, recent developments in materials chemistry have led to novel generations of nano-structured catalysts, allowing fine control of their properties at the nano-scale (shaping nanoparticles and other nano-structures, nano-pores, nano-crystallinity, precise control over size, etc.). The present project has taken full advantage of these advances in order to design nano-catalytic materials with tailored properties for optimizing the different chemical transformations considered in the biomass conversion cascade process here proposed.

CONCEPT AND GENERAL OBJECTIVE OF THE PROJECT

The CASCATBEL project focused on designing, optimizing and scaling-up a novel multi-step process for the production of second-generation liquid biofuels from lignocellulosic biomass in a cost-efficient way through the use of next-generation high surface area tailored nano-catalysts. On one hand, the sequential coupling of catalytic steps is an essential factor for achieving a progressive and controlled biomass deoxygenation and reduce hydrogen consumption, avoiding the previously highlighted problems that hinder one/two-step bio-oil upgrading processes. On the other hand, the use of tailored nano-catalysts led to optimised reaction yields (increasing liquid yield and preventing bio-oil contamination), facing limitations of current catalysts in terms of selectivity and deactivation rates. Finally, the scaling-up of the process was a very important aspect for fully exploring and understanding the catalytic and reaction dynamics, assessing catalysts life-cycles and demonstrating the viability of the CASCATBEL process in relevant environments, from both technical and economic perspectives.

The strategy followed in CASCATBEL led to the preparation of advanced biofuels having composition and properties very similar to petroleum-derived fuels. This is a very relevant advantage regarding the commercial implementation of this technology, as it would not require any significant changes in the already existing infrastructures and engines. Four aspects (cascade processing of lignocellulosic biomass, synthesis of competitive tailored nano-catalysts, demonstration at pilot plant scale and synthesis of low-oxygen advanced biofuels) were the main elements of the CASCATBEL project.
The proposed process was based on the cascade combination of up to three catalytic transformations: catalytic pyrolysis, intermediate deoxygenation and hydrodeoxygenation. This strategy led to the production of liquid biofuels, with enhanced yield and energy density, and miscible with oil-derived fuels. Consequently, these biofuels could be co-processed and mixed with conventional ones in a wide range of proportions. Furthermore, since HDO was outlined as the ultimate deoxygenation treatment, the overall hydrogen consumption was found to be strongly minimized, resulting in a significant improvement of the process economy.

For achieving the project aim and optimizing the different chemical transformations included in the biomass conversion cascade process, catalytic materials with tailored properties at the nano-scale were designed and synthesized. These materials were selected because they possess high surface areas, narrow pore size distribution and large pore volumes. Moreover, a number of effective methods were applied for the functionalization of solid surfaces with acid/base moieties, as well as for the preparation of metals and metallic compounds with a narrow nanoparticle size distribution.

In most cases, the studies so far published on the conversion and upgrading of biomass pyrolysis products have been conducted using just model compounds and model reactions at laboratory scale. In contrast, the feasibility of the CASCATBEL cascade process was proved under relevant conditions, including pilot plant tests. Thus, the experimental work in the present project employed real biomass and bio-oil feedstocks, whereas the size of the equipment was progressively scaled-up from laboratory up to bench scale and, finally, up to pilot plant. In this way, one of the main challenges of the CASCATBEL project was how to successfully combine catalytic tests at different scales (laboratory, bench and pilot plant scales) with fundamental studies, such as theoretical modelling and in-situ catalyst monitoring.

Fundamental studies (theoretical modelling and in situ monitoring) were performed simultaneously with the above commented experiments with the objective of getting insights of the phenomena taking place at nano- and micro-scale, so these results can be used for understanding the behaviour of the nano-catalysts in the reaction tests and aiding in the selection of the most convenient ones. On the other hand, assessment of the results obtained at the different scales was carried out according to different criteria (technical, environmental, toxicological, safety and economic) to ensure that the best catalysts and reaction systems are really selected along the progress of the project.

**SCIENTIFIC AND TECHNOLOGICAL OBJECTIVES**

The following scientific and technological goals were pursued in the CASCATBEL project:

1. To optimize lignocellulose catalytic pyrolysis (1st step in the cascade process). Tailored catalysts, with mild acidity or basicity, were tested at different scales and optimised to obtain partially deoxygenated bio-oil in order to avoid overcracking of the pyrolytic vapours and to reduce the coke deposition for increased catalyst durability. Compared to conventional catalytic pyrolysis, this resulted in higher bio-oil yields, lower production of gases and coke and reduced catalyst deactivation.

2. To optimize bio-oil upgrading through intermediate deoxygenation (2nd step in the cascade process).
Three different types of reactions (ketonization, aldol condensation and esterification) were investigated in order to select the most effective one as intermediate bio-oil upgrading treatment.

3. To optimize the ultimate bio-oil hydrodeoxygenation (3rd step in the cascade process). In this last step, bio-oil deoxygenation was completed by working at moderate temperatures (200-350 °C) and under moderate to high hydrogen pressures (20-150 bars). The HDO catalysts tested consisted of transition metal phases loaded with very high dispersion onto supports specially designed to stand the aggressive conditions present in the bio-oil, minimizing leaching of the active phase.

4. To improve the fundamental understanding of the different catalytic reactions considered in the project, which is of high relevance for aiding in the selection of the optimum characteristics of the nano-catalysts. Quantum mechanical modelling was used to establish the interactions between components in the catalysts, as well as between reactant molecules and active sites (in particular DFT, Density Functional Theory). Similarly, in-situ spectroscopic techniques were applied to characterize the behaviour of the catalysts under real operating conditions and to determine the mechanism of the reactions at a molecular scale, as well as for in-situ monitoring of coke formation and catalyst deactivation.

5. To compare the nano-catalyst performance at different reaction scales: in-situ catalytic tests, laboratory and bench-scale reactors and pilot plant reaction systems.

6. To determine the viability of the cascade process according to economic (production and investments costs), social (impact on the employment and the rural development), environmental (life cycle analysis, LCA), safety and toxicological (regarding both nano-catalysts and bio-oil) criteria.

Project Results:
The main activities performed and the most relevant results obtained are next summarized according to the scientific WPs that have integrated the CASCATBEL project.

1. WP1 - FEEDSTOCK SELECTION AND CHARACTERIZATION

1.1. Objectives

WP1 was devoted to the analysis in the European context of the biomass availability and the selection and characterization of the optimum raw materials to be used for bio-oil production.

1.2. Tasks

Task 1.1. Selection of the biomass raw materials.
Task 1.2. Supply and characterization of the biomass raw materials.

1.3. Significant results

Four main types of biomass resources were considered to be of interest:
Forestry residues. In general, they have the advantage of a huge appearance in Europe, so they could play a key role in advanced biofuel production. However, this comes with the disadvantage of potential transportation problems and the need of regulating tree-cutting rates, which leads to a difficulty in terms of long time prediction of availability of this feedstock. Scandinavian countries and Romania could cover a high-energy demand in the transport sector with biofuels coming from forestry residues. The species Norway spruce and pine are dominant in the Northern, Central and Eastern countries. For Italy and France, non-coniferous trees are dominant species.

Agricultural residues. They could offer over 20% of the total energy potential from lignocellulosic biomass. France, as a leader in European agriculture, has the highest energy potential from agricultural residues, based mainly on straw from barley. Likewise, wheat straw could also have an impact to lignocellulosic energy production in Germany and in the United Kingdom. Wheat straw shows an advantage in transportation, since it is usually offered balled and to a reasonable price. Nevertheless, it has to be mentioned that price prediction, especially for wheat straw, seems difficult.

Energy crops. There is significant technical potential for energy crops, especially for Spain, Poland, Romania and Italy. It could be a possibility to use fallow lands for short rotation coppice (Spain, Poland, Romania and Italy) or perennial grass (in Poland).

Industrial wood residues, such as scrap wood. They could also be used as a lignocellulosic feedstock for advanced biofuel production. In this field, Finland shows a huge potential due to its large forest industry, but also in Germany industrial wood residues could be considered. Nevertheless, competing uses can decrease the availability of this feedstock for energy purposes. Today, almost all industrial wood residues are being used.

The analysis concluded that lignocellulosic biomass possesses a significant energy potential in Europe, not only for power generation and thermal energy, but also for fuel production as a second-generation biofuel. The considered lignocellulosic feedstocks have the potential to cover a significant share of fuel consumption in the transport sector. Thus, even based on conservative estimations, it was concluded that most of the assessed European Countries have the technical potential to cover more than 10% of the energy demand in the transport sector using these feedstocks.

The types of lignocellulosic biomass to be employed in the project were selected based on this analysis. The criteria applied for the selection were as follows: availability, environmental issues, cost and diversity. Industrial wood was excluded because of the high variability of its composition depending on the industry and also the country. The following six biomass types were selected as raw materials for the project: Forestry residues: coniferous wood (pine) and non-coniferous wood (oak). Agriculture residues: wheat straw and barley straw. Energy crops: short rotation crops (eucalyptus) and perennial grasses (miscanthus).

2. WP2 - CATALYSTS DEVELOPMENT AND PREPARATION AT LABORATORY AND BENCH SCALES

2.1. Objectives
Within WP2, a wide range of catalysts was prepared, characterized, and made available for catalytic testing. They are in a great part based in already known nanomaterials, which have been adapted for the catalytic processes relevant to the cascade reactions being undertaken in WP5. The catalyst samples were subjected to basic characterization techniques to check that the syntheses were successful and that they show the expected physicochemical properties.

2.2. Tasks

Task 2.1. Synthesis and basic characterization of catalysts for biomass catalytic pyrolysis.
Task 2.2. Synthesis and basic characterization of catalysts for bio-oil ketonization.
Task 2.3. Synthesis and basic characterization of catalysts for bio-oil aldol condensation.
Task 2.4. Synthesis and basic characterization of catalysts for bio-oil esterification.
Task 2.5. Synthesis and basic characterization of catalysts for bio-oil HDO.
Task 2.6. Catalyst shaping and pelletization.

2.3. Significant results

At laboratory scale (in amounts of a few grams), a large variety of catalysts (about 225) were prepared, characterised, and made available for further catalytic testing in WP5. This figure denotes the strong effort performed within this WP to synthesize catalysts showing different and tuneable properties.

The families of materials prepared were based on known nanomaterials, adapted for catalytic processes relevant to the cascade reactions being undertaken in WP5 of CASCATBEL project. These materials included: i) Hierarchical and 2D delaminated zeolites for catalytic pyrolysis; ii) Metal oxides prepared by nanocasting with silica or under hydrothermal conditions for ketonisation reactions; iii) Alkali-activated zeolites and hydroxyapatite solid base catalysts for aldol condensation; iv) Mesoporous sulfated zirconia/SBA-15 and high loaded sulfonic acid SBA-15 for esterification; v) Carbon encapsulated Pd and CuPd, along with nanostructured supported metal phosphides and carbides catalysts for HDO.

The catalysts selected for bench scale tests were subsequently prepared in larger amounts. Thereby, the synthesis procedures and equipment were adapted from those employed at laboratory scale to increase the production of the materials in appropriate amounts. This means that at this stage the synthesis scale was multiplied by a factor of around 10 (up to 50 – 100 g batches). Regarding their preparation in technical forms two main procedures were applied: shaping by pressure and agglomeration with binders.

All samples prepared at both laboratory and bench scales were subjected to basic characterization applying conventional techniques in order to assess their main physico-chemical properties.

3. WP3 - Theoretical studies and modelling

3.1. Objectives

Theoretical studies using DFT models were carried out to understand at molecular level the behaviour and
deactivation phenomena of selected representative catalytic systems. In addition, the reaction kinetics of the different chemical steps in the cascade process were determined, as well as the catalyst deactivation rates based on the results of pilot plant scale experiments.

3.2. Tasks

Task 3.1. Modelling of the catalytic systems.
Task 3.2. Modelling of the reactant/products adsorption and interaction with the active sites.
Task 3.3. Modelling of the catalyst deactivation phenomena.
Task 3.4. Modelling of the reaction kinetics and catalyst deactivation rates.

3.3. Significant results

Zeolite-, metal oxide- and carbon-based catalysts were investigated theoretically at the density functional theory level. The following significant results were obtained from the analysis performed in Task 3.1 and Task 3.2:

- The differences in acidic/basic properties of hierarchical zeolites with respect to corresponding regular zeolites were analysed. The Brønsted acidity remains unaffected by the 3D → 2D transformation. The Lewis acidity of 2D zeolites is decreased in case of samples with large concentration of surface silanols and thin layers. However, the Lewis acidity of 2D ZSM-5 is similar to that of 3D ZSM-5. The basicity of zeolites was evaluated based on acetone deprotonation energies, concluding that the basicity of hierarchical Na-hUSY is larger than that of regular Na-FAU, but lower than the basicity of over-exchanged Na-FAU.

- Deposition of metal nanoclusters (Ru and Ni) on the regular and defective surfaces of titania and zirconia was investigated with the aim to elucidate the role of chemical reduction of the catalysts in the enhancement of its activity in ketonization reactions. The direct charge transfer from the Ru or Ni nanoparticles to the oxide surface, with consequent reduction of the oxide, has been ruled out. Instead, the reverse oxygen spillover on Ni clusters supported on anatase TiO2 (101) surface has been suggested as possible mechanism of formation of low-coordinated sites on titania surfaces.

- The alkali-metal containing hierarchical zeolites, Ru nanoparticles supported on transition metal oxides and on carbon, and nickel phosphide and molybdenum carbide nanoparticles were investigated computationally for their catalytic activities in deoxygenation reactions. The interaction of catalysts with reactants, reaction intermediates and products was investigated and the full reaction pathways, including transition states of elementary reaction steps, were obtained. The calculations were carried out at the density functional theory (DFT) level.

- The reaction mechanism of aldol condensation of furfural and acetone was investigated over sodium-grafted hierarchical USY zeolite (Na-hUSY). The activity of this material can be explained by a relatively strong basic character of the active sites, consisting of ionic pairs of silonate groups and Na+ ions. Silanolate acts as the basic center for acetone activation by deprotonation/enol formation, while Na+ provides activation for the furfural. The silanol groups in the vicinity of the active site provide additional
interaction with organic molecules.

- The mechanism of hydrogen spillover promoted by Ru metal particles on oxide surfaces was investigated. The role of the supported metal particle is essential as it favours the spontaneous dissociation of H2, a process that does not occur on the bare oxide surface. In both TiO2 and ZrO2 surfaces, the migration of an H atom from the Ru cluster to the surface is accompanied by an electron transfer to the empty states of the support with the reduction of the oxide surface.

- The role of carbon support on the activity of Ru nanoparticles was also investigated in hydrodeoxygenation reactions using phenol as a model reactant. For Ru nanoparticles with only small hydrogen coverage the hydrogenation pathway (HYD) is much preferred over more desirable hydrogen-efficient direct deoxygenation pathways (DDO). However, when the Ru nanoparticle is saturated with hydrogen both HYD and DDO pathways become possible.

- Phase diagrams of hydrogen coverage on Ni2P and Mo2C surfaces were studied at the ab initio thermodynamics level. Calculations show that the barrier for DDO process is relatively high (250 kJ/mol) but it becomes significantly smaller at higher hydrogen pressure. Nevertheless, the barriers found along the HYD pathway are lower than those found for DDO pathway.

From the theoretical studies about catalyst deactivation (Task 3.3) the most relevant mechanisms affecting the stability of selected catalysts and with potential to cause their deactivation during reaction were identified. The following conclusions are emphasized:

- For zirconia nanoparticles, one potential route of deactivation is the formation of carbonates as they may lead to complete deactivation of the oxide active phase. This is particularly important in chemical processes, such as catalytic pyrolysis, where CO2 is present as reactant, (sub) product, or carbonates are formed as reaction intermediates. Other deactivation route identified is sintering by metal diffusion on oxide supports. Nevertheless, the presence of OH groups can reduce the mobility of atomic species, thus slowing down the growth of metal particles via Ostwald ripening mechanism.

- For molybdenum carbide nanoparticles (active phase in HDO reactions), it was found that they are deactivated by adsorption of polar compounds (e.g. water, alcohols) due to the formation of adsorbate layers which hinder the accessibility of reactants to the catalytically active sites. This effect is more severe with small alcohols than with water although in both cases deactivation is reversible under mild conditions and the catalyst can be regenerated. However, a longer exposition of the nanoparticle surface to water at elevated temperatures leads to an irreversible phase change of catalytic surface.

Regarding the kinetic modelling of the CASCATBEL cascade process performed in Task 3.4 a lumped-reaction kinetic modelling scheme was developed and evaluated for the following reactions:

a) Biomass thermal pyrolysis (absence of catalyst).

b) Catalytic upgrading of produced vapors (catalytic pyrolysis ex-situ), using the final selected catalysts based on metal oxide nanoparticles supported into acidic zeolite and agglomerated with natural clays.

c) Intermediate deoxygenation, using commercial ZrO2 and the K-USY agglomerated with a natural clay
d) Hydrodeoxygenation (HDO) of the derived catalytic pyrolysis oil, over four different catalysts, based on Ni and Mo deposited over silica and carbon supports.

In all cases the proposed kinetic models predicted accurately the reactions evolution, even at long residence times and under progressive catalyst deactivation.

4. WP4 - Advanced characterization and in-situ monitoring

4.1. Objectives

A number of advanced characterization and in-situ techniques were applied to gain insights into the different phenomena including deactivation events that take place during the catalytic reactions. These results and conclusions were used to aid in the selection of the best catalytic systems to be scaled up.

4.2. Tasks

Task 4.1. In-situ monitoring and advanced characterization of catalytic systems employed at laboratory scale.
Task 4.2. In-situ monitoring and advanced characterization of catalytic systems employed at bench scale.
Task 4.3. In-situ monitoring and advanced characterization of the deactivation of catalysts at pilot plant scale.

4.3. Significant results

Some of the most relevant results obtained in WP4 are summarized below:

a) Laboratory scale catalyst samples

- The acidity of different ZSM-5 zeolite catalysts employed in the biomass pyrolysis was evaluated. The addition of metal oxides to the parent ZSM-5 sample decreases the amount of Brønsted acid sites and creates new Lewis acid centers with stronger acidity. The pillared ZSM-5 samples are more accessible in comparison with the lamellar-structured ZSM-5 materials. This shows that having pillars is advantageous when bulky molecules have to be converted.

- Different metal oxide catalysts, based on Fe and Ti, were investigated for bio-oil ketonization. The results demonstrate that the nature of the metal, the oxidation state of the metal and the phase of the oxide all affect the amount of surface coverage, the nature of the adsorption and hence the catalytic performance.

- The results obtained in aldol condensation tests suggest that the alkali-activated USY zeolites prepared in alcoholic media are promising materials for the aldol condensation of propanal in the gas phase. Using these materials, the formation of coke species, which might deactivate the catalysts, is suppressed. The nature of USY zeolite active sites and micropores structure might account for this reduced coke formation.
The acidic properties of different sulfated ZrO2 (SZ) were studied for their application in esterification reactions. Quantification of the acid site loading shows the number of acid site almost doubles from 1-2 ML ZrO2, suggesting the optimum acid density of the SZ film requires two layers of ZrO2. Further grafted layers did not have any beneficial effect on acid loading suggesting a ZrO2 bilayer is required to optimise acid site loading. The overall acid site loading for SZ/SBA-15 is approximately three times that achievable for bulk SZ.

b) Bench scale catalyst samples

The acidity of different catalysts selected for the pyrolysis of bio-oil at the bench scale was evaluated. For this purpose, pyridine was adsorbed on the catalyst and studied by IR spectroscopy. In this way, the type, strength, concentration and accessibility of the catalyst acid sites could be assessed. The adsorption of pyridine shows that the addition of metal oxides and binder to the parent zeolite leads to changes in the acid properties of the catalysts, with a general decrease in the concentration of Brønsted acid sites. Furthermore, new Lewis acid sites are detected for the metal oxide-containing samples.

In addition to pyridine adsorption, other model compounds (acetone and acetic acid) were adsorbed and followed by FTIR in order to investigate their transformations via ketonisation over a large temperature range. The adsorption of acetone shows that addition of the metal oxide to the parent zeolite partially blocks the access to some centers and modifies their behaviour in catalysis. Even more, it was shown that the inclusion of binder into the catalyst composition modified the adsorption behaviour and impeded the ketonisation process.

The activity, selectivity and stability of ZSM-5 based catalysts and their corresponding extruded counterparts were tested in the aldol condensation of propanal. Operando results suggest that the use of bentonite as binder for the extruded catalysts has a detrimental effect on the catalytic performance, in terms of activity and selectivity. Nevertheless, the mixture of catalyst with binder shows a better resistance against aromatics and coke formation, i.e. improved stability, probably related to the lower activity. The same finding was confirmed also by TGA analyses of the spent catalysts. The effects of the binder on the physicochemical properties of the zeolite may originate from modification of catalyst morphology, porosity and acidity.

Clays used as binder for the catalyst shaping, such as bentonite and attapulgite, can induce dramatic changes in zeolite acidity mainly as a result of cation exchange between the acidic protons of zeolite and metal cations of binder. As a consequence, zeolite Brønsted acid sites were reduced, and even disappeared when bentonite was used as binder.

c) Pilot plant scale catalyst samples

Spent catalysts from the catalytic pyrolysis step were characterized by FT-IR and Raman spectroscopy to investigate the functional groups of coke precursors. In addition, temperature treatments were used to study catalyst regeneration and adsorption studies were performed on regenerated catalysts. About 40% of these carbonaceous deposits were volatile. Highly aromatic coke was observed in all the samples, being produced most in the catalysts without binder. A significant drop of the concentrations of acid sites...
was detected for the used catalysts. However, full regeneration of almost all catalysts was achieved by burning them in static air conditions at 450 °C. Under these conditions, usually approximately 90% of active sites were restored. Pore blocking by coke formation was found to be the main cause of deactivation. Some loss in crystallinity and dealumination seemed to occur, being favored at longer reaction times. The regeneration procedure applied provided a good recovery of properties affected by coke buildup. Nevertheless, regeneration did not seem to restore the partial zeolite dealumination.

- Regarding the intermediate deoxygenation step, both MnO and ZrO2 catalysts retained most of their catalytic activity in deoxygenation reaction after one cycle of operation in the pilot plant and also no change in the selectivity was observed. Indeed, most of their physicochemical properties were preserved after reaction. In the case of commercial ZrO2 catalyst, the impact of calcination temperature on its physicochemical properties was explored. It was observed that up to 300 °C zirconia remains as an amorphous material, while at 400 °C crystallization starts and transitions into different phases occur as temperature is increased. Such phase changes were accompanied by crystallite size increases, leading to significant loss of surface area and lower capacity to adsorb acetic acid, as evidenced by acetic acid adsorption/DRIFTS analysis.

5. WP5-Laboratory and bench scales reaction tests

5.1. Objectives

The performance of the catalysts prepared in WP2 was assessed in the different reactions of the cascade scheme: catalytic pyrolysis, bio-oil intermediate deoxygenation and bio-oil hydrodeoxygenation. In addition, non-catalytic biomass pyrolysis tests were also carried out to study the effect of the biomass pre-treatment and bio-oil stabilization. For each of the cascade steps, convenient and efficient catalysts were identified an optimized. In addition to lab scale experiments, bench scale tests were performed, which implied operating larger and more complex experimental setups and working under more realistic industrially-relevant conditions.

5.2. Tasks

Task 5.1. Tests of biomass pyrolysis.
Task 5.2. Tests of biomass catalytic pyrolysis.
Task 5.3. Catalytic tests of bio-oil ketonization.
Task 5.4. Catalytic tests of bio-oil aldol condensation.
Task 5.5. Catalytic tests of bio-oil esterification.
Task 5.6. Catalytic tests of bio-oil hydrodeoxygenation.

5.3. Significant results

a) Laboratory scale tests

The main findings derived from the extensive work performed in WP5 at laboratory scale are as follows:
Although the non-catalytic bio-oil quality was more or less the same for all feedstocks, there were significant differences in bio-oil yield. Oak, pine and miscanthus were found to produce more bio-oil compared to wheat and barley straw and eucalyptus. Bio-oil analysis by GC/MS detected in all cases high concentrations of phenols, organic acids and unidentified compounds.

Washing biomass with 1% aq. solution of HNO3 was determined as the most effective method for removing all the abundant elements of ash from biomass. De-ashing the feedstocks had a positive effect in the pyrolysis performance, increasing the liquid organic yields, while decreasing the coke and gas yields.

Cold filtration is not effective at reducing solid content. In contrast, hot filtration of the bio-oil vapours in-situ, directly after pyrolysis, showed to be highly efficient for the removal of solid particles. The reduced solid content leads to less severe aging and very low metal of the bio-oil.

For each of the cascade steps (tasks 5.2-5.6) generally suitable catalysts were identified. These catalysts were as follows according to the different types of reactions considered in the cascade process:

- Catalytic pyrolysis: catalysts based on ZSM-5, MCM-22 and SBA-15 materials.
- Ketonization: catalysts based on TiO2, ZrO2 and MnO2.
- Aldol condensation: catalysts based on alkali-modified USY zeolite and hydroxyapatite.
- Esterification: catalysts based on sulphated zirconia and grafted sulfonic acid/SBA-15.
- Hydrodeoxygenation: catalysts based on Ni, Mo and W phases supported on silica, SBA-15 and carbon materials.

b) Bench scale tests

Bench scale biomass pyrolysis tests were carried out with three of the most promising types of biomasses identified in the project: oak, wheat from straw and miscanthus. All feedstocks exhibited high liquid bio-oil yield, in the range of 50-57 wt%. Oak produced the most bio-oil accompanied by lower gas yield, followed by miscanthus and wheat straw.

The biomasses were treated with 1% aq. solution of HNO3, which was determined as the most effective method in removing all of the abundant elements of ash from biomass. The results of the bench scale thermal pyrolysis of the de-ashed samples confirmed previous lab scale tests showing that deashing has a positive effect in the pyrolysis performance of all biomass types. Bio-oil yields increased in all cases and ranged between 56-63 wt%.

Regarding bench scale biomass catalytic pyrolysis experiments, the following main conclusions were derived:

- While the pure binders have little catalytic activity, their incorporation to the active phases causes important changes in their catalytic behaviour. This finding was related to the modifications provoked by the binder in the textural and acid properties of the catalyst.

- The best combination of catalytic activity in biomass catalytic pyrolysis, measured through the bio-oil...
The best performance in biomass catalytic pyrolysis corresponds with metal oxides containing MCM-22 and ZSM-5 catalysts. These systems led to significant reductions in the oxygen content of the bio-oil while keeping the energy yield over 60%.

In reaction systems with continuous bio-oil feeding the catalysts undergo a fast deactivation at short times on stream, being then stabilized for prolonged period of time as denoted by the steady deoxygenation removal that takes place, mainly through dehydration reactions.

Bench scale catalytic pyrolysis experiments were also performed for the production of bio-oil samples to be distributed to the project partners for the intermediate deoxygenation processes. Detailed analyses of the bio-oils obtained at bench scale show substantial differences between the thermal and catalytic products, which are consistent with the previous findings at lab scale. All the obtained catalytic bio-oils were biphasic, with a remarkably higher O/C in the case of the aqueous fraction, although in overall they present a significantly higher degree of deoxygenation with respect to the thermal bio-oil. The main components of the organic fraction of the bio-oil are oxygenated aromatics, furans and aromatic hydrocarbons. On the other hand, the aqueous phase contains most of the organic acids and sugars.

In respect to the intermediate deoxygenation results at bench scale, the results obtained show the difficulty of achieving in some cases an efficient deoxygenation of the bio-oils by condensation reactions. Likewise, one of the problems encountered is the formation of additional solid residues when processing the already produced bio-oils, which implies an important loss of both mass and energy yield. This fact is especially pronounced when processing liquid bio-oils by vapour phase treatment as a high carbonization takes place during the bio-oil vaporization process. Moreover, significant catalyst deactivation was observed, in particular for the liquid phase processing of bio-oils by esterification and ketonization. However, it is worth to point out that relevant and positive results were obtained with a number of systems, as it is the case of vapour phase ketonization over K-USY zeolite and vapour phase ketonization over Zr- and Mn-containing catalysts that promote further upgrading and deoxygenation of the bio-oil. Using a two-bed reaction system for coupling the catalytic pyrolysis and aldol condensation/ketonization steps avoids the extensive formation of carbonaceous residues that takes place when feeding liquid bio-oil.

Finally, in respect to the hydrodeoxygenation catalytic tests at bench scale, the following main conclusions were derived:

- Both Ni2P/SiO2 and MoCx/HCS HDO catalysts could be effectively shaped into cylindrical pellets by preparing physical mixtures of the catalyst powders and binder. However, both catalysts suffered from oxidation during the pelletization process and lost their activity for HDO reactions. By reducing the catalyst pellets, ca. 50% of the original activity could be regenerated.

- High concentrations of water decrease the catalyst activity and the catalyst lifetime. Regarding MoCx/HCS, an inhibiting effect of water was indicated.

- Under reasonable operation parameters (e.g. larger autoclave, more solvent), a total or high HDO degree
can be expected at bench scale with both thermal pyrolysis oil and catalytic pyrolysis oil, using a continuous supply of hydrogen.

- To carry out continuous flow experiments by feeding of condensed catalytic bio-oil probed to be challenging because this liquid can easily plug the reactors lines. Two strategies were successfully used to facilitate continuous operation: working at relatively low temperature (in the range 250-300 °C) and use of bio-oil with low sugar content as feed, which is quite less prone to suffer polymerization.

- Catalytic tests performed with pure catalytic bio-oils in the continuous fixed reactor showed that the selected catalysts were able to achieve a moderate but significant deoxygenation, as monitored by the global oxygen content in the liquid phase and the increment of the water fraction. Moreover, this HDO activity showed to be reasonably stable for some of the catalytic systems after several hours of time on stream.

Based on the bench scale catalytic results, the most promising catalysts were selected for being investigated at pilot plant scale:

- Catalytic pyrolysis: based on ZSM-5 zeolite agglomerated with clays.
- Intermediate deoxygenation: based on alkali-modified USY, MnO2 and ZrO2, used for upgrading the bio-oil vapours coming directly from the catalytic pyrolysis step.
- Hydrodeoxygenation: Ni2P and Ni-Mo phases supported on silica and carbon materials.

6. WP6-Catalyst development and preparation at pilot plant scale

6.1. Objectives

The objective of WP6 was to prepare the selected catalysts for pilot plant tests in a sufficient quantity and with suitable physico-chemical and mechanical properties.

6.2. Tasks

Task 6.2. Catalyst preparation at pilot plant scale for intermediate bio-oil deoxygenation.
Task 6.3. Catalyst preparation at pilot plant scale for bio-oil hydrodeoxygenation.
Task 6.4. Basic characterization of the catalysts prepared at pilot plant scale.

6.3. Significant results

Preparation of catalysts at pilot scale demanded the adaptation of the bench scale synthesis recipes for every catalytic step of the project in order to produce the selected catalysts in enough quantity (1-5 kg) and with suitable physico-chemical and mechanical properties. This work was successfully carried out thanks to the close collaboration between the project partners responsible for the catalysts synthesis at both bench and pilot plant scale. The main actions performed were focused on facilitating the easy production of large amounts of catalysts, while reducing the waste amounts and keeping the structural
stability of the materials. Likewise, shaping of catalysts was adapted and carried out in industrial facilities of project partners.

According to the characterization results, the physicochemical characteristics of the catalysts prepared at larger scale for the different stages of the cascade process are comparable in terms of phase distribution and textural properties to those obtained for small-scale experiments in lab scale tests. However, some minor differences were observed, which can be related to the modification of the preparation routes and/or to the use of additional component commercial materials.

7. WP7-Pilot plant catalytic tests

7.1. Objectives

WP7 involved the performance tests of the catalysts prepared in WP6 at pilot plant scale in continuous reactors. In addition, relatively large amounts of upgraded bio-oil were produced allowing its characterization according to standard tests, in order to establish their possible commercial application.

7.2. Tasks

Task 7.1. Pilot plant scale tests of biomass catalytic pyrolysis.
Task 7.2. Pilot plant scale tests of intermediate bio-oil deoxygenation.
Task 7.3. Pilot plant scale tests of bio-oil hydrodeoxygenation.
Task 7.4. Determination of the properties of the produced bio-oil and char.

7.3. Significant results

The catalysts selected based on the bench scale results were tested in biomass pyrolysis in a medium scale pilot plant fluid bed unit. It was concluded that by increasing the catalyst loading (increasing C/B ratio) more cracking reactions take place, resulting in less organic fraction. Among the catalysts tested, the metal oxide/ZSM-5/clay system was the most selective, achieving the lowest oxygen content at the same organic yield. Additional tests performed with this catalyst validated its best performance in a much wider range of operating conditions.

These catalysts were also tested for their performance under deactivation by measuring their activity and selectivity versus pyrolysis run time. It was concluded that all catalysts deactivate during pyrolysis by coke deposition, small differences between them being detected. This coke deposition alters the catalyst performance making the catalyst more inactive and producing higher amounts of oil but with more oxygen, as deoxygenation degree decreased with run time between 4-6% units depending on the catalyst.

The bio-oil samples from all the biomass catalytic pyrolysis tests at pilot plant scale were characterized regarding their water content, elemental composition and (for the organic phase only) the TAN number and High Heating Value (HHV). It was found that higher catalyst loadings produced bio-oils with lower TAN number and higher High Heating Value (HHV). The organic phase of the bio-oil sample from metal oxide/ZSM-5/clay catalyst seems to have the lowest TAN number and the highest HHV of all. Semi-
quantitative GC-MS was performed on the organic phase of the bio-oils produced over the five catalysts at C/B ratio of 0.25. The main compounds that were identified were aromatic hydrocarbons, phenols, polyaromatic hydrocarbons and oxygenated phenols.

In the intermediate bio-oil deoxygenation step, the three catalysts selected (ZrO2, K-USY/clay and MnO2 nanowires) were tested in pilot scale using a lignocellulosic biomass feedstock by means of coupled experiments with the previously selected optimum pyrolysis catalyst (metal oxide/ZSM-5/clay).

Pilot plant tests were then performed with the dual catalyst bed consisting of the pyrolysis catalyst and each deoxygenation catalyst on top. The addition of the deoxygenation catalyst in reactor-2 decreased the organics obtained from the process and increased the formation of gases, primarily that of CO2. Small differences were observed between the reference case (only pyrolysis catalyst) and the coupled experiments with both the pyrolysis and deoxygenation catalysts, except in the case of reduced MnO. However, the presence of the intermediate deoxygenation catalysts was not found to improve the selectivity of the upgrading process.

The hydrodeoxygenation catalysts selected in the previous step (Ni2P/SiO2, Ni2P/mesoporous carbon and Ni-doped MoCx/mesoporous carbon) were also tested in pilot scale. The feedstock employed was the organic phase of bio-oil produced from ex-situ catalytic pyrolysis of lignocellulosic wood-based biomass over metal oxide/ZSM-5/clay catalyst. In addition, reference tests were also performed with a commercial pre-sulfided NiCoMo/Al2O3 catalyst, using the same feedstock and experimental procedure.

The general conclusion is that the HDO of the catalytic oil produced by CASCATBEL process is feasible in a continuous process. From the three tested catalysts, the Ni2P/SiO2 was the best, but the initial HDO degree with the commercial catalyst was higher. However, there were many limitations in the application of this catalyst. The commercial catalyst requires an initial presulfidation step and the continuous spiking of the bio-oil feed with sulphur-containing compounds in order to keep the catalyst activity. This sulphur finally goes to the HDO oil and deteriorates its quality. The Ni2P/SiO2 catalyst does not need any presulfidation or any S spiking for keeping its activity. Moreover, the commercial catalyst has higher hydrocracking activity, giving less oil compared to the new catalysts. Finally, and most importantly, the stability of the commercial catalyst was low since it deactivated with time. After 11 h of operation, its performance was similar to the best CASCATBEL catalyst. The stability of the best CASCATBEL catalyst (Ni2P/SiO2) was therefore concluded to be better than that of the commercial catalyst.

Oxygen content of HDO oil over Ni2P/SiO2 catalyst was 6.2 wt% and the hydrogen consumption was 3 wt% on dry catalytic oil. Analysis of the oily phase of the HDO product showed that the total organic product consists mainly of gasoline and diesel. For the boiling ranges used, gasoline was slightly higher than diesel. However, in all cases there was a heavy fraction of around 12%. Among the investigated catalysts, the Ni2P/SiO2 and NiMoCx/C had similar gasoline and diesel distribution. Ni2P/C however had a different performance, producing more gasoline and slightly less diesel with much less heavy compounds, indicating that this material promotes the cracking of the heavier components to gasoline range components. Analysis of the gasoline fraction by PIANO showed that it consists mainly of saturated naphthenes (44 wt%), aromatics (37 wt%) and paraffins (18 wt%). These results indicate that this gasoline is an excellent fraction and could be also suitable for aviation jet fuel. Regarding the other compounds in
the HDO organic oil the analysis performed by GCxGC-TOFMS showed that these samples are especially rich in hydrocarbons and aromatic hydrocarbons.

Another valuable product from the cascade process is char produced in the thermal pyrolysis step. As part of WP7, four char samples were produced from thermal pyrolysis tests with two different biomass feedstocks (oak and wheat straw) at two different temperatures (500 °C and 600 °C). The chars were characterized using ultimate and elemental analysis, ICP-MS for determining the metals in the ash and TGA analysis. The use of wood-based biomasses, like oak, was found to lead to the production of chars with heating values higher than 30 MJ/kg and relatively low ash content. On the contrary, when wheat straw was used as feedstock, the chars contained a high amount of ash (>40%) that decreased proportionally the heating value of the solids.

8. WP8-Overall process assessment

8.1. Objectives

The main goal of WP8 was to aid in the decision-making process throughout the duration of the CASCATBEL project, especially in those key steps implying a higher risk and associated to the most important Milestones. Thus, WP8 was a transversal activity collecting and evaluating the results from the experimental work packages (WP1 to WP7) and giving as output a complementary assessment integrating four types of criteria: a) process parameters; b) economic and cost factors; c) environmental impacts and d) nanosafety and toxicological issues. Thereby, a series of indicators associated to the above mentioned criteria were defined specifically for each experimental step to be assessed. This set of indicators formed the basis for making the decisions related to the main milestones of the project.

8.2. Tasks

Task 8.1. System definition.
Task 8.2. Assessment of the results obtained at laboratory scale.
Task 8.3. Assessment of the results obtained at bench scale.
Task 8.4. Assessment of the results obtained at pilot plant scale.

8.3. Significant results

8.3.1. Assessment of laboratory scale results

Assessment of the results obtained in laboratory scale allowed the following decisions to be taken:

- Selection of the biomass pre-treatment before the pyrolysis reaction: Acid washing straw-type biomass was proposed due to its beneficial effects in terms of process parameters whereas no critical economical neither toxicological, nor environmental issues were detected.

- Selection of the most convenient pyrolysis bio-oil stabilization method: Hot vapour filtration and the most appropriate filter size were proposed.
Selection of the most promising catalytic systems. Based on the integrated assessment of the defined indicators for each catalytic reaction, together with the results reported in related work packages (WP2, WP3, WP4 and WP5), 6 catalytic systems were finally proposed for being studied at bench scale in each chemical step.

8.3.2. Assessment of bench scale results

Likewise, WP8 aimed to aid in the selection of a minimum of 3 types of catalysts to be tested at pilot plant scale for the different catalytic reactions proposed in the CASCATBEL project. From the analysis of both the experimental results reported in related WPs, as well as the specific indicators defined, the following key parameters were identified:

- Bio-oil* (water free basis) energy yield and bio-oil* oxygen concentration, as process parameters.
- Cost of catalyst synthesis, as economic/cost factor criteria.

No significant differences regarding the rest of indicators (e.g. those from environmental, toxicological and nanosafety criteria) were evidenced. Accordingly, 3 catalytic systems were proposed for their evaluation at pilot plant scale:

a) Catalytic pyrolysis at bench scale

Catalysts based on metal oxide nanoparticles supported on acidic zeolites and shaped in technical form with natural clays were proposed, since they presented the best balance between process parameters, catalyst cost and scale-up feasibility.

b) Intermediate catalytic deoxygenation at bench scale

- Vapor phase reactions were preferred as they allowed coupling the catalytic fast pyrolysis reactor on line with that of intermediate deoxygenation without phase changes.

- Due to the complexity of real feedstocks, a combination of different reaction pathways take place simultaneously during this catalytic step, including aldol condensation and ketonization, among others.

- Scale-up and cost of catalyst was a key parameter. Some catalysts were discarded due to the difficulty to be scaled-up. The final 3 catalysts proposed for testing at pilot plant scale included modified zeolites and bulk metal oxides with good catalytic performances and whose synthesis was adapted to fulfill economic and scale-up criteria.

c) Catalytic HDO at bench scale

- Some catalysts were discarded due to their poor catalytic performance, rapid deactivation and difficulty to scale-up.
The three catalytic systems proposed for being investigated in HDO at pilot plant scale were based on supported metallic phases. Supports proposed were commercially available or developed by the project partners, being easy to scale-up.

8.3.3. Assessment of pilot plant scale results

The assessment of all the experimental work carried out at pilot plant scale was performed. Based on the integrated assessment of the established indicators (process parameters, economic factors, environmental, toxicological and nanosafety criteria), together with the results reported in related work-packages (WP3, WP4, WP6 and WP7), the final catalyst and optimal reaction conditions were proposed for each catalytic step.

The most relevant conclusions for each catalytic step derived from this assessment are as follows:

a) Catalytic pyrolysis

- Optimal balance between process parameters (bio-oil yield, oxygen concentration and deactivation rate) and cost factors (price and scale-up) was achieved by a catalyst formed by metal oxide nanoparticles supported on an acidic zeolite and agglomerated into technical shape by a natural clay.

- Regarding the reaction conditions, highest catalyst/biomass ratios increase the cost of this catalytic step, but it allows achieving a quite low oxygen concentration, as this catalyst includes also some intermediate deoxygenation functionality.

b) Intermediate catalytic deoxygenation

The optimal catalyst was proposed according to cost and synthesis scale-up criteria, as they were identified to be the most critical indicators together with process parameters. Optimal reaction conditions were also selected. Nevertheless, it was proposed to consider also the possibility of using only the optimum catalytic pyrolysis material with high catalyst/biomass ratios coupled to the hydrodeoxygenation step. This would imply the exclusion of the intermediate catalytic deoxygenation step, and would allow simplifying the cascade process. This is possible since the catalytic pyrolysis system incorporates a metal oxide able of catalyzing intermediate deoxygenation reactions.

c) Catalytic HDO at bench scale

The most critical indicators were identified and compared. As a result, the optimal catalyst and reaction conditions were proposed. The catalyst selected was based on a metallic phase supported on a commercially available, inexpensive and harmless porous solid. This composition provided the highest HDO degree leading to oxygen contents in bio-oil about 6 wt% and slower deactivation rates than the commercial catalyst.

9. WP9-Process design and feasibility study at commercial scale
9.1. Objectives

Based on the results of the pilot plant experiments in WP7 and the overall process assessment in WP8, WP9 aimed to elaborate the conceptual design of the integrated process and determine its viability at commercial scale. Process was optimized considering different plant capacities and types of lignocellulosic biomass, and minimizing the external energy needs and generation of waste streams.

9.2. Tasks

Task 9.1. Process design.
Task 9.3 Determination of environmental impacts.
Task 9.4. Socio-economic study.
Task 9.5. Overall process feasibility.

9.3. Significant results

A detailed process flow diagram for the integrated cascade process proposed in CASCATBEL project was developed, including the most important equipment and operations. Using this flow diagram, the simulation and optimization of the process was performed, including optimization of mass and energy balances, operation conditions, utilities and energy requirements, as well as relevant process conditions for all main equipment so their sizing and economic estimations could be also carried out.

Finally, for the socio-economic and environmental evaluation, two different process designs were simulated and optimized, based on different biomass feedstock:

• Northern Europe location - Biomass available: forestry residues (wood). High quality. No biomass pretreatment is required.

• Central Europe location - Biomass available: agricultural residues (wheat straw). Lower product quality compared to forestry residues. Acid washing pretreatment is required.

Concerning the plant capacity, for scale economy reasons, the centralized option was preferred to the decentralized one.

Taking into account the biomass availability and the transport distance, the typical sustainable plant size was set at 400 kt/year of dry and ash free biomass feed, corresponding to 61 kt/year of fuel grade liquid products.

Five different hydrogen provision chains were assessed and compared regarding their environmental impact for both plant locations, including:

• Hydrogen production via PEM electrolysis and electricity according to the national electricity mix.
• Hydrogen production via PEM electrolysis and electricity from renewable sources; i.e. wind in France and hydroelectricity in Finland.
• Hydrogen production via cracking of fossil residues in a crude oil refinery.
• Hydrogen provided by the national market mix for hydrogen.
• Production via PEM electrolysis using the electricity produced internally by utilizing the excess heat from the conversion process.

For a plant size of 400 kt/year of dry biomass, the estimation of final energy yield achieves at least 53%, including the production of 41 MWel of electricity (16.5% energy yield) and the production of 60.5 kt/year biofuels (36.4 % energy yield). The overall CASCATBEL energy yield, is comparable to that calculated for a BtL process (Gasification/ Fischer-Tropsch synthesis, starting from wood biomass and producing liquid drop-in hydrocarbon fuels and electricity.), typically ranging between 50-60%. The produced advanced biofuels need further validation activities, including blending, engine and car tests, in order to assess the actual specifications and performances as automotive or aviation fuels.

The estimated GHG reduction is in the most favourable cases higher than 90%, compliant with the current RED European Directive mandate (60%) and also with the possible REDII revised target (70%), according to the valid reference values. Among the assessed scenarios, differing in biomass feedstock and H2 supply chain, both the Northern Europe and Central Europe location turned out to be sustainable in terms of GHG reduction. In the case of wheat straw feedstock, the biomass uptake has to be regulated in order to minimize the fertilizer consumption for soil nutrition, and the accounting methods for agricultural waste streams have to be defined further. The GHG reduction estimated for CASCATBEL process is comparable, or even higher, than those reported as reference values by the RED Directive for advanced biofuels produced by different technologies.

The capital cost estimated for a typical plant with 400 kt/year biomass input is 171 M€, corresponding to 1,840 €/MWth liquid fuels output. These costs are lower than those reported for a waste wood Biomass-to-Liquids diesel plant with the same capacity, chosen as a benchmark for alternative thermochemical technologies for the production of advanced biofuels. The investment is attractive from a financial point of view since IRR (21%) is considerably higher than the Cost of Capital (WACC 4% was considered). Break even time, calculated on the basis of the most promising process options, is 4 years. The accuracy of the economical assessment is affected by the typical uncertainties (+50%/-30%) related to the early development stage of the technology.

The expected European market demand for advanced biofuels (diesel + gasoline) is growing, driven by the RED European Directive mandate (approximately 0.7 Mt/year by 2020, corresponding to 0.5% of the total fuel demand, reduced by the double counting bonus). If the updated more ambitious targets included in the REDII draft are to be confirmed, the demand of advanced biofuels could expand up to 9.7 Mt/year by 2030 (double counting bonus not included). Considering an expected market price for advanced biofuels around 1,000€/t, the global European market size turns out to be 0.7 Billion €/year by 2020 and up to 9.7 Billion €/y by 2030. Assuming that the CASCATBEL technology could contribute for a fraction of this total market (20%), the relative market size would be 0.14 Billion € by 2020 and 1.9 Billion € by 2030. Nevertheless, an accurate and affordable market assessment could be done only in presence of a stable long term policy on advanced biofuels.
After the overall assessment, the process proved to be feasible from a technological point of view and sustainable from the environmental and socio-economic points of view, taking into account the typical uncertainties (+50%/-30%) due to the early development stage of the technology.

Further activities would be needed to reduce the degree of uncertainty prior a possible commercial application, in particular:

• The validation of the technology up to the integrated demo/pilot scale.
• The production of biofuel samples in a suitable quantity to conduct blending, engine and car tests.
• A stable long term policy on advanced biofuels for an accurate estimation of the market demand and market price.

Potential Impact:
Main innovations developed in the project were identified and their market potential was analyzed within the Innovation Radar. These are summarized as follows:

1. Two-step catalytic process for producing advanced biofuels and renewable electricity.

The process is aimed to produce advanced biofuels, with low oxygen content and boiling points in the gasoline and diesel range, from lignocellulosic biomass. It consists of two main steps: i) production of a partially deoxygenated bio-oil by catalytic pyrolysis and ii) removal of most of the remaining oxygen by catalytic hydrodeoxygenation. Moreover, renewable electricity is co-produced by combustion of the side streams (char and gases).

2. Catalyst for the production of liquid fuels by pyrolysis of a variety of feedstocks.

The catalyst consists of a nanocrystalline ZSM-5 zeolite having a high accessibility due to its large external surface area. It has been modified by metal oxide impregnation and agglomeration with clays. It exhibits remarkable properties in the catalytic pyrolysis of different raw biomasses, including both forestry and agriculture residues. In addition, this material may have application in the pyrolysis of other feedstocks, such as plastic wastes and the organic fraction of MSW.

3. Synthesis and supply of metal-containing HDO carbon catalysts up to a bench scale.

The innovation comprises an easily scalable method for the preparation of nanostructured carbon based HDO catalysts. Mesoporous carbons are prepared by the carbonization of resorcinol-formic acid resin, followed by shaping in wet the dough to get cylinder shapes. Impregnation of Ni2P is performed in the shaped carbon, while for Ni-doped MoCx phases the impregnation is carried out in the resin. Activation of the catalysts is carried out by hydrogen reduction at high temperature. The resulted catalysts show excellent activity towards HDO of fast pyrolysis bio-oils in the plant scale tests. Other different active metal phases can be easily loaded with similar methods.

4. Synthesis and supply of K-USY/attapulgite catalyst in technical form for organics condensation.
This material is based on alkali metal-grafted high-silica USY zeolite than can be exploited in coupling reactions. An efficient method has been developed for the preparation of K-USY/attapulgite catalysts in technical form consisting in the shaping of the zeolite with the binder followed by the grafting of potassium with a KOH methanolic solution and the subsequent stabilization by calcination. The resulting material has shown very promising results in bio-oil upgrading reactions.

5. Multitechnique-based assessment of acidity, basicity and coke deposition and removal in shaped catalyst particles.

Acidity/basicity of (shaped) zeolite-based catalysts and the influence of coke thereon are determined with probe-molecule FTIR spectroscopy. Diffusivity, distribution of acidity and coke deposition over (spent) catalyst particles is assessed by UV-Vis and confocal fluorescence microscopy. Two cells were developed for in situ analysis of catalyst wafers: 1) for in situ FTIR, a high-temperature FTIR cell with an on-line gas chromatograph was built, which allows sample manipulation at different temperatures and under different gas atmospheres; 2) a cell for in-situ, combined UV/IR/MS analysis of performance in probe reactions such as aldol condensation.

6. Consultancy services in the design and assessment of biomass conversion processes based on thermochemical treatments.

Based on the extensive experience gained in WP8 and WP9 of CASCATBEL project, the key partners can offer a consulting service, providing valuable advice on the efficient design of demonstration plants for the production of advanced biofuels not only from the engineering and economic points of view, but also taking into account environmental considerations using LCA analysis methodologies. This expert counselling can contribute to increase the overall energy efficiency, reduce the investment and minimize the impacts of biofuel production.

7. Prototype consisting in a pilot plant for biomass catalytic pyrolysis and bio-oil upgrading.

Design of a prototype pilot plant facility to convert lignocellulosic biomass into high quality liquid biofuel comprising 3 steps: thermal pyrolysis, catalytic upgrading of pyrolysis vapours and liquid-phase catalytic hydrodeoxygenation. The pilot plant will enable research activities for process optimization and catalysts screening, generating bulk volumes of products (char, gases and bio-oil) optimal for mass balances/yields calculations and their analytical characterization.

MAIN DISSEMINATION AND EXPLOITATION ACTIVITIES

1. Main dissemination activities performed

1.1. Project website

A specific project website www.cascatbel.eu managed by the project Coordinator, has been used as
primary tool for the dissemination of project general objectives, progress towards the workplan, main achievements and events.

The sections on the website are:
• Home, with a permanent link to the project information and a section dedicated to news and events, continuously being updated.
• Information about the project, including general facts, stages of the project, and the work-programme containing information about all work-packages of the project.
• Consortium composition, with information of all consortium partners, their locations, principal investigator and a link to their websites.
• Main project dissemination activities, including the details on scientific publications and congress communications, as well as the project public deliverables and newsletters available for downloading.
• News and events, which are linked to the Home.
• Relevant links, including Bioenergy and Catalysts Organizations, as well as related projects.
• Contact at project Coordination.

1.2. Publications

The most relevant project results were published in international peer-review journals as a means of dissemination to the scientific community and to industries with interest in the particular research topics. The journals for these publications were selected for providing high impact and priority coverage in the fields of the results generated: biomass resources, biofuel production, catalysis, nanomaterials, sustainability and environmental impact assessment. The previous outstanding publication records of the partners participating in CASCATBEL project was a guarantee for the significant number of scientific articles published during the project lifetime. Publication of results only occurred after the evaluation of the potential protection of Intellectual Property Rights (IPR) by the Innovation Committee, and consideration of the legitimate interest of associated IP owners.

A total number of 52 scientific publications in peer-review journals were produced during the project. Most of them were published in journals with impact factor (47) and some in a journal without impact factor (5). The total number of citations of these publications (dated October 2017) is 649, which is very high considering that 16 articles were published in the last year. This is indicative of the high impact of this dissemination activity.

Besides, a special issue in the journal “Biomass Conversion and Biorefinery” has been published with a collection of selected papers originally presented at the “Thermochemical lignocellulose conversion technologies workshop” that was organized in Chalkidiki (Greece) in the frame of the CASCATBEL project. Five works of CASCATBEL project were published in this special issue.

In addition, three chapters in books were published during the project.

1.3. Public deliverables

A public deliverable was prepared every year containing CASCATBEL main achievements and highlights
of the project. These deliverables were uploaded in the project website.

1.4. Conferences, congresses and other scientific events

Participation in conferences and other external events has been considered crucial not only for dissemination of the project status, goals and achievements but for networking and exchange of professional experiences. These activities were promoted within the consortium as an efficient means of increasing the dissemination impact of the project within both academia and industry, and providing updates on the progress of research carried out by other groups and projects. Priority was given to international workshops, congresses and conferences having both scientific and technological profiles.

The project activities and obtained results were presented in 106 conferences, congresses and other scientific meetings and events during the project, either with oral communications including lectures and keynotes (total number of 142 contributions during the project) or poster presentations (total number of 48 posters presented during the project).

1.5. General audience publications and events

Communication actions oriented to the general audience serve to ensure that various groups, public bodies and agencies outside of academia utilize the knowledge produced and/or are aware of the benefits and challenges of the project. To this effect, CASCATBEL carried out the following actions:

• Publication of the project information in institutional websites, press releases or non-specialist journals, to provide information about the main objectives and activities of the project, as well as the potential benefits to society. A total of 16 general publications were produced.

• Publication in The Parliament Magazine, a journal dedicated to European deputies, with the objective of informing policy-makers of the project objectives and achievements. At least one publication was expected along the project and it was produced, in cooperation with the projects FASTCARD and BIOGO.

• Participation in science dissemination events to the general public, such as The Week of Science, and The European Researchers’ Night. Outreach activities were performed by CASCATBEL researchers in several editions of (i) the Madrid’s Week of Science, focused to students in secondary school, with a workshop of biofuels production at laboratory scale and a visit to the pilot plant of pyrolysis and HDO; and (ii) the European Researcher’s Night of Madrid, focused to young children, where benefits of renewable energies and biofuels for environment and climate change were explained through workshops. Participation in 5 science dissemination events was produced during the project.

• Participation in other general audience events, either presenting the project or with distribution of the CASCATBEL project leaflet.

• Other communications in media. An interview in COPE, a Spanish radio, was performed after one year of project duration to raise awareness at national level of the relevance of the research project activities and challenges in the transport, energy and environment sectors, as well as impacts to society of project
1.6. Summer School

A Summer School on “Catalysis of Biomass” was organized by CASCATBEL project in Castle Liblice, Czech Republic. The main goals of the School were to summarize the up-to-date knowledge of the development of new catalysts for biomass transformations, to discuss the appropriate routes in biomass upgrading, and to propose new ways for biomass utilization.

This event mainly targeted young (predoctoral and postdoctoral) researchers involved in the CASCATBEL consortium, although it was also open to young researchers from other groups and institutions external to the project interested in this topic.

The Summer School focused on reviewing the main catalytic transformations currently under development for biofuels production, highlighting the relevance of controlling and tuning catalyst properties to optimize performance towards the complex feedstock mixtures typically present during biomass conversion.

The program consisted of 12 plenary lectures, 12 short oral presentations of PhD students and postdoctoral researchers, and 16 posters. A total number of 75 students attended to School, which is considered a great success in terms of impact achieved. The lectures were compiled in a specialized book that was distributed among the attendees.

1.7. Workshop

A three-day workshop on “Thermochemical Lignocellulose Conversion Technologies”, organized by CASCATBEL project, was held in Chalkidiki, Greece. The main goal of the workshop was to present the most up-to-date technological and research advances in the field of lignocellulosic biomass valorization via thermochemical process routes: gasification, pyrolysis and liquefaction. Prominent scientists and experts from both academia and industry working on these topics were selected and invited to share their knowledge and expertise. The invited speakers were from inside and outside the CASCATBEL project. Special attention was paid in having a balanced mix of speakers from academia and industry, in order to also have the views of the industrial sector about the advances required in the field of thermochemical biomass conversion. The program consisted of 23 invited lectures and 23 posters.

An informative flyer was prepared and was distributed both in electronic and printed form. In addition, information of the workshop was distributed by email to more than 800 recipients from relevant universities, research organizations, and companies.

In terms of impact, the workshop was very successful, with 71 participants, coming from 15 countries and representing important academic and industrial institutions. The workshop served as a means to disseminate important results and advances that were realized in the frame of the CASCATBEL project. It was also very successful in terms of networking and fostered interesting discussions between the participants from industry and academia for future collaborations and the outlook for the biomass thermochemical conversion technologies.
1.8. Networking and cooperation with other projects

CASCATBEL partners participate in different forums and platforms that were supportive with the approach to stakeholders and served to amplify the impact of CASCATBEL’s communications. International, European and National associations were contacted and informed about the project goals, results and dissemination initiatives.

In addition, cooperation with the projects FASTCARD and BIOGO was realized, either in the preparation of joint events or joint publications. These projects were selected in the same call and topic as CASCATBEL project (NMP.2013.1.1-1 - Exploration, optimisation and control of nano-catalytic processes for energy applications), so special synergies were found with them.

On the other hand, the following networking activities were performed during the project with the aim of exploring synergies with different groups working on thematic areas related to CASCATBEL. In this way, the project joined the following clusters and participated in the following events:

- Nanosafety cluster.
- European cluster on catalysis.
- Engineering and upscaling cluster.
- Industrial Innovation Liaison (i2L).
- SPIRE PPP Workshops.
- KETs for regional growth: Synergies between Horizon 2020 and ESIF.
- The Business Booster (TBB) by KIC Innoenergy.
- Joint workshop of ENMIX, FASTCARD, CASCATBEL, BIOGO.
- Sustainable Energy Week (EUSEW).
- Special session in the WCCE 2017.
- BBI JU Infoday and brokerage event.
- IV Forum SusChem.

1.9. Dissemination material

Both the CASCATBEL logo and brand were developed by graphic design and communication experts. The logo was used on any document related with the project (presentations, posters, leaflets or reports).

A template for presentations was prepared, as well as a general presentation of the project. This presentation was used for project dissemination within the partners’ organizations or for stakeholders.

A general information leaflet of CASCATBEL project was prepared (1,000 units printed) and widespread in conferences and events, especially during first years in order to create awareness of the project among stakeholders.

Besides, two different electronic leaflets were prepared for the CASCATBEL Summer School and the Workshop. Leaflets were uploaded in the project website and delivered to participants.
Finally, an electronic newsletter was issued periodically with an average of three issues per year. A total number of 11 issues were prepared during the project. The newsletter was distributed by email to more than 300 identified stakeholders and it was made available to be downloaded through the website.

2. Main exploitation activities performed

2.1. Innovation Committee

The Innovation Committee was a permanent body within the CASCATBEL consortium, composed by representatives of all industrial partners and the project Coordinator, aimed to analyze project achievements in order to identify foreground that should be protected for further commercialization, and assist the partners in the selection of the best exploitation strategy.

2.2. Standardization

The Spanish Association for Standardization and Certification (AENOR), as a European Standardization Body, was subcontracted in the CASCATBEL project to provide support regarding the standardization tasks included in the project.

2.3. Patentability Study

In view of the potential of results obtained at bench scale, a patentability report was performed, to analyze the novelty and inventive step of an invention, which could lead to the protection of results.

2.4. Stakeholders Event

The purpose of the CASCATBEL Stakeholders Event was to join experts from industries (including potential-end users) and other stakeholders of the nanotechnology, catalysts and biofuels fields in order to present and discuss main achievements of the CASCATBEL project, so relevant feedbacks could be received regarding the potential of project results, to be commercially exploited.

Nine external experts in the field of catalysts and biofuels production joined the event, included representatives from UPM Biorefining, BTG-BTL, Evonik Industries, IFP Energies Nouvelles, Johnson Matthey, BASF, Neste, EERA Bioenergy (SP1 Thermo-Chemical Platform) and the Cluster of Excellence on Tailor-Made fuels from biomass (TMFB) at RWTH Aachen University. This was a restricted event in which external participants were selected and invited for the maximum impact of the activity.

Consortium partners presented the actual scenario in advanced biofuels, the project and its objectives, main results in the three different steps in the cascade process and the potential industrial impact of the project. Presentations were followed with the feedback from the external participants and a final discussion on strategies for exploitation of project results and its potential impact.

2.5. Market Study
The economic viability of the CASCATBEL process was assessed.

2.6. Innovation Radar

Main Innovations developed in the project were identified and their market potential was analyzed within the Innovation Radar.

List of Websites:
- CASCATBEL project public website:
  www.cascatbel.eu

- Relevant contact details:
  Dr. David P. Serrano Granados
  E-mail: david.serrano@imdea.org
  Phone: +34 917 37 11 20