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PROJECT FINAL REPORT

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Project acronym: NEW-PMR

Project title: New Frontiers in (Trans)esterification Pervaporation Membrane Reactors

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[1] Usually the contact person of the coordinator as specified in Art. 8.1. of the Grant Agreement.

4.1 Final publishable summary report

This section must be of suitable quality to enable direct publication by the Commission and should preferably not exceed 40 pages. This report should address a wide audience, including the general public.

The publishable summary has to include **5 distinct parts** described below:

- An executive summary (not exceeding 1 page).
- A summary description of project context and objectives (not exceeding 4 pages).
- A description of the main S&T results/foregrounds (not exceeding 25 pages),
- The potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and exploitation of results (not exceeding 10 pages).
- The address of the project public website, if applicable as well as relevant contact details.

Furthermore, project logo, diagrams or photographs illustrating and promoting the work of the project (including videos, etc…), as well as the list of all beneficiaries with the corresponding contact names can be submitted without any restriction.

Executive summary (not exceeding 1 page)

The project New Pervaporation Membrane Reactor (New-PMR) has provided **groundbreaking research on the development, application and modelling of (trans)esterification pervaporation membrane reactors**. Pervaporation membrane reactors (PMRs) integrate the reaction and separation steps and it is a recognized concept that provides significant synergetic effects, so that a drastic improvement of the performance of the reactor is obtained. PMRs have been applied successfully for equilibrium-limited reactions involving water as one of the side products. However, **the fundamentals and feasibility of this integrative approach had not yet been demonstrated for chemical conversions yielding an organic by-product such as methanol or ethanol.** This project has provided a scientific basis for this and this report shows the main results obtained during the project execution. The reference reaction between butanol and methyl acetate to produce methanol and butyl acetate is deeply studied in this project. In addition, the study has been extended to other transesterification reactions, *i.e.,* the reaction between methanol and ethyl acetate to produce ethanol and methyl acetate, which is a reference reaction in biodiesel production; production of methyl tert-butyl ether (MTBE).

Experimental results with commercial membranes have demonstrated the capability of some membranes to separate butanol from the reaction medium due to a higher permeance of this component through the membrane. Using those membranes in an industrial schema would reduce the energy of separation considerably since the azeotrope between butanol and butyl acetate is not an issue if pervaporation is used prior to distillation. The potential of these membranes allocates them as a very attractive solution in combination with distillation of in a cascaded approach. In addition, **a deep experimental study for multicomponent mixtures** have demonstrated the critical importance of the driving force in the separation. Most of the commercial membranes enhance the permeance of components with the lowest driving force, indicating that the membrane is acting against the natural tendency of separation based on thermodynamics. This behavior may have a negative effect on the economics of the process since the permeate become less pure and the separation is not working under optimal conditions. A clear methodology to determine the performance of the separation has been proposed.

Pervaporation has been integrated in conventional processes in combination with distillation and as stand-alone technology, and the applicability of several flowsheets has been determined. It was estimated that performing the separation of methanol-methyl acetate using pervaporation requires over 90% less energy to the utilities in comparison with distillation. Also, in addition to pervaporation, the alternative use of membrane contactors for the specific case of purification of biodiesel has been evaluated.

Life cycle assessment analyses have been also performed together with exergy analyses. The integration of membrane technology in a hybrid configuration (i.e. pervaporation-distillation) has shown advantages to be considered in the design and development of more environmentally friendly processes (e.g., processes involving azeotropic mixtures such as those that appear in transesterification reactions). A guideline based on the impact during the production stage of the main solvents used in the chemical industry has been also developed. This guideline allows the selection of the best environmentally friendly treatment depending on the composition of the liquid mixture. Incineration (heat recovery) versus distillation (material recovery) represents the technological alternatives.

The CIG Marie Curie Grant has initiated a new research line at the Université catholique de Louvain that continues after the termination of the Grant. Thanks to the impulse given by the grant, I have developed **my own independent research as professor at the Université catholique de Louvain (UCL in Louvain-la-Neuve, Belgium).**

Summary description of project context and objectives (not exceeding 4 pages)

The overall objective of this project is **to understand how pervaporation membrane reactors can be used to enhance transesterification reactions.** The reference reaction that is considered is the transesterification of methyl acetate with n-butanol to n-butyl acetate, with methanol as by-product:

$$CH_3COOCH_3 + CH_3(CH_2)_3OH \leftrightarrow CH_3COO(CH_2)_3CH_3 + CH_3OH$$

(methyl acetate) (butanol) (butyl acetate) (methanol)

The transesterification reaction is reversible and the equilibrium constant is close to unity, with a low reaction rate and complex phase equilibrium behavior. A traditional separation based on phase equilibrium such as distillation after the reaction step involves the formation of two azeotropes: methanol-methyl acetate and butanol-butyl acetate. Thus, the purification of products is not straightforward and effective strategies have to be developed. The approach that is developed in this work is to use pervaporation directly for the separation of the resulting products or by-products in the reactor. In this case, pervaporation is integrated with a chemical reactor. The only requirement to be competitive with conventional separation processes is a high permeability for the target compound, this is, high production and high selectivity. Thus, the membrane plays a key role in the efficiency of the separation, and the development of new membranes and/or new process configurations (e.g., hybrid process distillation-pervaporation) is required to fill the technological gap existing in a commercial level.

The overall objective of this project is to understand how pervaporation membrane reactors can be used to enhance (trans)esterification reactions. This comprises two specific objectives: i) development of an in-depth experimental study of a (trans)esterification reactor, which includes the construction of the lab-scale plant and the synthesis of novel membranes based on polyphenylsulfone (objective 1), intertwined with the development of system modelling based on reaction kinetics, reactor configuration and transport through pervaporation membranes (objective 2). The separation that can be achieved by pervaporation has been determined in the project, yielding answers to the following questions:

- Do currently available membranes cover the technical requirements to allow their use in a PMR for the studied (trans)esterification reactions?
- What are the requirements for a hypothetical membrane optimised for use in this application?
- To what extent is it possible to achieve a complete conversion of the product?
- Which (trans)esterification reactions also have potential in PMRs?
- Is continuous operation possible?
- Which reactor configuration has the best performance for the conversion?

In addition, the system has been modelled; this is an essential requirement for further understanding, extending and simulation of the proposed reactors. The research questions related to modelling are the following:

- Can the selective separation of the involved compounds be described by advanced models for organic-organic separations in polymeric and ceramic pervaporation?
- To what extent should reaction kinetics be consistent with by-product transport through the membrane?
- Is it possible to discriminate between various reactor configurations using calculation tools?
- How do PMRs compare to reactive distillation?

- How do membrane characteristics influence the reactor conversion or efficiency?

This project has explored new frontiers in PMRs and has developed the basis for further research in this field by the intensification and integration of processes in the chemical industry.

The *experimental work* has been focused on the separation that can be achieved by pervaporation, aiming at a **maximal product purity and minimal losses**. In addition to the reference transesterification reaction of methyl acetate and *n*-butanol to yield *n*-butyl acetate and methanol, other transesterifications have been studied, such as those that yield a larger alcohol (e.g., ethanol) as the by-product. One of the obvious parameters that has been studied is the temperature, which influences not only the reaction, but also the separation that can be achieved.

The modelling of pervaporation has been a strong core of this project. This part of the project has built on expertise to describe the mass transfer phenomena. In this project, the technical viability of pervaporation as stand-alone technology or integrated with distillation has been evaluated by using simulation of real industrial processes, and it has been completed with energetic, exergetic and environmental analyses**.**

The proposed methodology is concreted by means of three work packages: WP1 (Experimental study of reaction and pervaporation); WP2 (Transport model for organic-organic separation in pervaporation); WP3 (Hybrid reaction and separation model).

The **Work Package WP1** refers to the experimental study to achieve a sufficient separation of the components in the reaction mixture of the transesterification of n-butanol. This experimental work is focused on the separation that can be achieved by pervaporation aiming at **maximal conversion with maximal product purity and minimal losses**. The separation of the compounds present in **the transesterification of methyl acetate with *n*-butanol to *n*-butyl acetate, with methanol as by-product** is studied**.** A pervaporation unit is the core of the experimental study and it will allow evaluating the performance of different membranes in terms of permeability of each compound through the membrane and selectivity in order to determine the target separation compound for each membrane.

The **Work Package WP2** includes the development of a transport model for organic-organic separations in pervaporation. In this project, due to the intrinsic complexity of the pervaporation membrane reactors, **models developed in the literature have to be completed and/or modified to achieve a good description of mass transfer.** A model based on the solution-diffusion model has been developed in order to describe the mass transfer of the studied compounds through the membrane. In addition to this, a novel methodology to obtain thermodynamic data (i.e., activity coefficients) that is critical to the correct application of the models has been developed. It is based on the use of Head-Space Gas Chromatography (HSGC). A comparison of the obtained experimental data with those obtained with conventional models (e.g. UNIFAC, Wilson) has been done, indicating the good performance of the method. In addition, **a methodology to determine diffusional transport parameters from binary and multicomponent pervaporation has been developed.**

The **Work Package WP3** involves the modelling and simulation of various hybrid reactor and separator configurations: **batch or continuous, and incorporation of the hybrid model in process flowsheeting software package** and the **comparison between reactive distillation and pervaporation for transesterification reactions having methanol as by-product using state-of-the-art membranes**.

The following section presents the main results obtained for each work package.

Description of the main S&T results/foregrounds (not exceeding 25 pages)

The **Work Package WP1** involves the experimental study of the separation of organic-organic mixtures. The reference reaction in the project is **the transesterification of methyl acetate with *n*-butanol to *n*-butyl acetate, with methanol as by-product.** A pervaporation unit is the core of the experimental study and allows evaluating the performance of different membranes in terms of permeability of each compound through the membrane and selectivity in order to determine the target separation compound for each membrane. In this work, the selective removal of methanol or butyl acetate is studied by using several commercial specialty membranes with different nature at three different temperatures (30, 40 and 50°C) and a feed concentration ranging from 20 to 80 mole% in order to obtain a general view of the real possibilities to apply this technology in a short term. The studied membranes are: Typ M1, Typ M2, Pol AL M1, Pol AL M2, Pol AR M1, Pol AR M2, Pol OL M1 and Pol OL M2, supplied by PolyAn GmbH, Germany, and the membranes Pervap 1201 and Pervap 2255-50, supplied by Sulzer Chemtech, Switzerland. The pervaporation experiments were performed using a Lab Test Cell Unit from GFT-Le Carbone (Neunkirchen-Heinitz, Germany). The fluxes and permeances and the separation factors and selectivities of the studied membranes were obtained experimentally for each membrane. One example of the obtained results for the membranes Poly OL M1 and Poly OL M2 at 30°C are shown in Figure 1.

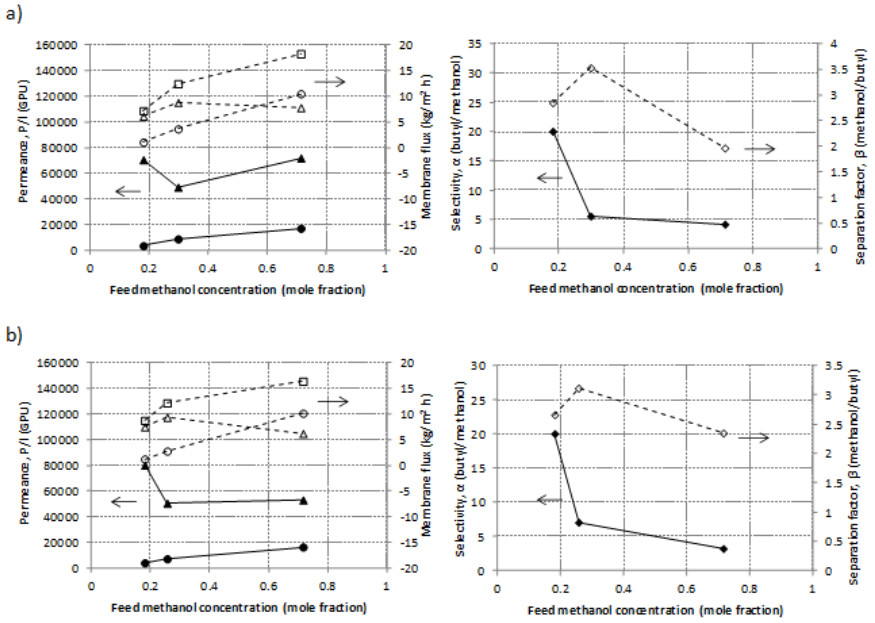


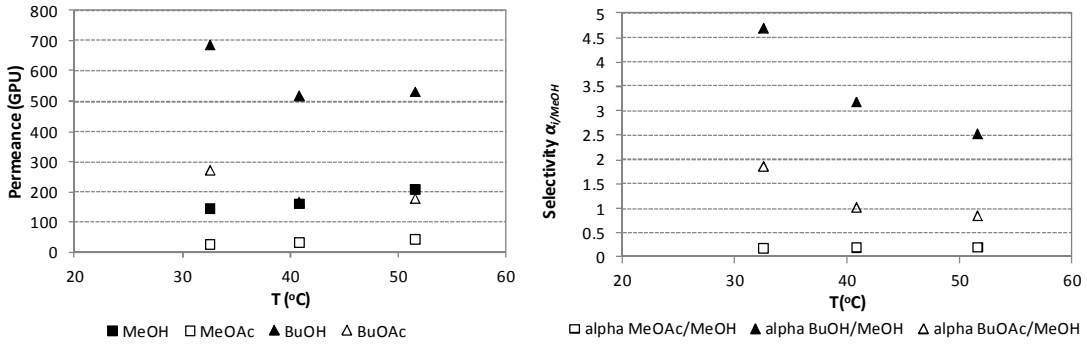
Figure 1. Permeance and flux (left) and selectivity and separation factor (right) of Poly OL M1 (a) and Poly OL M2 (b) membranes. Triangles refer to butyl acetate, circles refer to methanol and squares represent the total flux.

As general conclusions, it can be stated that the selectivity of the studied membranes is dependent on the concentration of the feed solution, showing selectivity towards butyl acetate. The PolyAn membranes and the Pervap 2255-50 membrane have shown the best performance when the concentration of the feed solution is rich in butyl acetate. On the other hand, the membrane Pervap 1201 is the best choice when an intermediate or low concentration of butyl acetate is present in the mixture, achieving very high values of selectivity compared to the other membranes. Regarding the effect of the temperature on the membrane performance, only the membrane Pervap 2250 shows an

increase in the permeance of butyl acetate and selectivity when the temperature is increased. The other membranes show a worse performance at higher temperatures.

From these results, five of those membranes (*i.e.,* Pervap 2255-50, Pervap 1201, Poly OL M1, Poly OL M2 and Poly AR M2) were selected considering their permeability and selectivity to be evaluated in a mixture composed of the four components present in the reaction: methyl acetate, butanol, methanol and butyl acetate. This approach is required to obtain a clear vision of the real applicability of these membranes since the reaction medium will always contain the reagents due to the fact that the reaction is conditioned by the equilibrium. In this case, very promising results were obtained with the membranes Pervap 2255-50 and Poly OL M2 since they achieve a remarkable separation of one or two components of the mixture, respectively. Figure 2 shows the main results for these two membranes in terms of permeance and selectivity defined as the ratio of permeances of the component *i* divided by the permeance of methanol (taken as the reference compound).

a) Pervap 2255-50:



b) Poly OL M2:

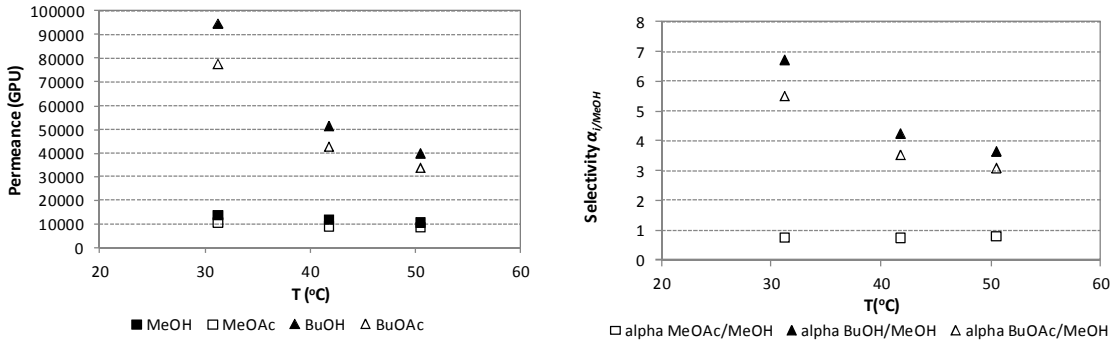


Figure 2. Permeance (left) and selectivity (right) of Pervap 2255-50 (a) and Poly OL M2 (b) membranes as a function of the temperature.

As observed in Figure 2, the membrane Pervap 2255-50 achieves the separation of butanol from the reaction medium due to a higher permeance of this component through the membrane. Using this membrane in an industrial schema would reduce the energy of separation considerably since the azeotrope between butanol and butyl acetate is not an issue if pervaporation is used prior to distillation. Regarding the membrane Poly OL M2, a very high permeation for butanol and butyl acetate (around 95000 GPU and 75000 GPU, respectively) is observed, ensuring a good separation of these two components from the mixture. A combination of this membrane with the Pervap 2255-50, for example in cascade, could be an interesting solution to separate first the butanol and butyl acetate

and secondly the butanol in a second membrane unit. The potential of these membranes allocates them as a very attractive solution in combination with distillation or in a cascaded approach.

In order to study the industrial application of the transesterification reaction between n-butanol and methyl acetate, the pervaporative concentration of the MM20 waste (~16 mole% methyl acetate in methanol) was assessed. This was studied with the intent of producing a reagent stream of higher methyl acetate content, which is necessary in order to shift the reaction equilibrium. For this scope polyvinylidene fluoride (PVDF) pervaporation membranes were synthesized and tested. **The outcomes demonstrate that methyl acetate selective membranes based on PVDF are realistic and can be used in order to concentrate low content methyl acetate-methanol industrial waste streams.** The PVDF membranes were also compared to two other in-house synthesized membranes, selected based on the Hansen solubility parameters theory. The pervaporative separation of all chosen membranes revealed the inadequacy of the Hansen solubility parameters theory for selection of membranes to be used in pervaporation of alcohol/ester mixtures.

Other transesterifications have been also considered (deliverable 1.4): (a) the production of MTBE (methyl *tert*-butyl ether) from the reaction of isobutene with methanol, and (b) other reactions yielding the same by-product, i.e., methanol or related reactions yielding a larger alcohol (e.g., ethanol), such as those involved in the biodiesel production.

In this sense, pervaporation was investigated for **the separation of methanol-methyl tert-butyl ether** (MTBE). Two commercial membranes were tested. The Poly Al M1 membrane was found to have a separation factor up to 350 and Poly Ol M1 a flux ranging from 2.26 to 25 kg/m^{2}h. These two membranes from PolyAn were investigated in an industrial context as a possible alternative to reduce the impact caused by distillation. A pervaporation unit was modeled with Aspen Custom Modeler and then imported in Aspen Plus to verify the improvement on the application of this membrane technology. It was concluded that **the pervaporation unit brings a benefit in terms of energy consumption reducing the energy costs by 9-14% respect to the conventional process**.

In the **biodiesel process** the introduction and evaluation of a membrane contactor unit was considered to purify biodiesel from the main impurities as methanol and glycerol. A setup was built and several flat sheet commercial membranes were tested to evaluate if a membrane extraction can replace an extraction unit that requires a lot of water and its consequent further separation steps. **All the membranes used were able to purify biodiesel but it was shown that only the hydrophobic ones can be used in an industrial context because of their high breakthrough pressure.** The most suitable membrane, PTFE, was selected and the effects of the concentration of methanol, the flow rate variation and the presence of glycerol were investigated. The overall mass transfer coefficient observed was compared with that calculated using a model present in the literature, and was in the range of 3.5-7 E-03 (cm/min) for methanol.

Currently, the use of ionic solvents (*i.e* ionic liquids) to prepare supported ionic liquid membranes is under study, as well as the development of catalytic membranes that allows performing the reaction on the surface of the membrane while the reaction products are separated through the membrane. This novel approach tries to intensify the process to the maximum by minimizing the size of the required equipment and maximizing the reaction yield.

The expected milestone for WP1 are:

M1.1 Selectivity of the target compounds by using the proposed membranes has been determined.

M1.2 Reaction kinetics of the reference reaction is known.

In addition, the deliverables are:

D1.1 Assessment of state-of-the-art membranes and newly developed membranes specifically for the target compounds selectivity in binary and ternary mixtures and mimicked reaction media (publication).

D1.2 Reaction kinetics of the studied reactions.

D1.3 Publication on the performance of the performance of an integrated reactor and pervaporation separation unit for the reference reactions.

D1.4 Determination of the limits of applicability of the proposed concept from comparison with other reactions.

The milestones as well as the deliverables have been successfully achieved according to the planning.

The **Work Package WP2** includes the development of a methodology to determine the mass transfer through the membrane for organic-organic multicomponent separations in pervaporation. A model based on the solution-diffusion model has been applied in order to describe the mass transfer of the studied compounds through the membrane.

The objective is to emphasize the importance of a prior evaluation of the driving force of each compound in order to determine when pervaporation is an appropriate technique to perform the separation of multicomponent mixtures. From the results obtained in WP1 using the three commercial membranes from PolyAn GmbH (Germany) and two membranes from Sulzer Chemtech (Switzerland), d for the separation of equimolar mixtures of methanol-methyl acetate-butanol-butyl acetate, at around 30, 40 and 50^{o}C, it was determined that all the studied membranes present a preference for the permeance of butanol, reaching permeances of butanol until 95 000 GPU. However, methanol and methyl acetate are the compounds with the higher driving force due to their higher volatility, leading to their higher concentration in the permeate and their preferential separation instead of butanol. Thus, the study of permeances/permeabilities and selectivities is required but not sufficient to evaluate the real performance of pervaporation. The driving force has to be evaluated separately, and membranes that enhance the effect of the driving force by permeating the species with the highest driving force should be preferably selected. Thus, pervaporation is used under conditions of maximum performance.

From the discussion developed in this study, taking the quaternary mixture composed of methanol-methyl acetate-butanol-butyl acetate as case of study, **the following methodology is proposed to evaluate in-depth the potential of pervaporation membranes**:

Step 1) Evaluation of the driving force and determination of target compounds for permeation (i.e., those compounds with the largest driving force). As an example for one of the studied membranes (Pervap 2255-50 membrane), Figure 3a shows that methanol and methyl acetate are the components of the highest driving force in the reference mixture. In principle, according to the discussion elaborated in the present research, these two compounds should permeate preferably through the membrane, this is, the membrane should enhance the permeation of these two compounds.

Step 2) Experimental evaluation of permeances (or permeabilities) and selectivites of the membranes. In the best case, the membranes will enhance the permeation of the target compounds selected in the previous point. Figures 3b and 3c present the results of permeance and selectivity of the Pervap

2255-50 membrane. It can be observed that butanol has the highest permeability and selectivity, in contradiction with the highest driving force of methanol and methyl acetate.

Step 3) Elaboration of McCabe-Thiele diagrams and comparison with distillation. Thus, the real advantages obtained by pervaporation can be evaluated. Figure 3d includes the comparison between distillation and pervaporation. This is an important comparison that allows determining the real effect of the membrane and its competitive character against distillation. The results for the Pervap 2255-50 membrane indicate that this membrane allows a better performance than distillation for the separation of the studied mixture.

This procedure will allow us to see if the pervaporation process is operating under optimal conditions and to obtain the best performance of pervaporation.

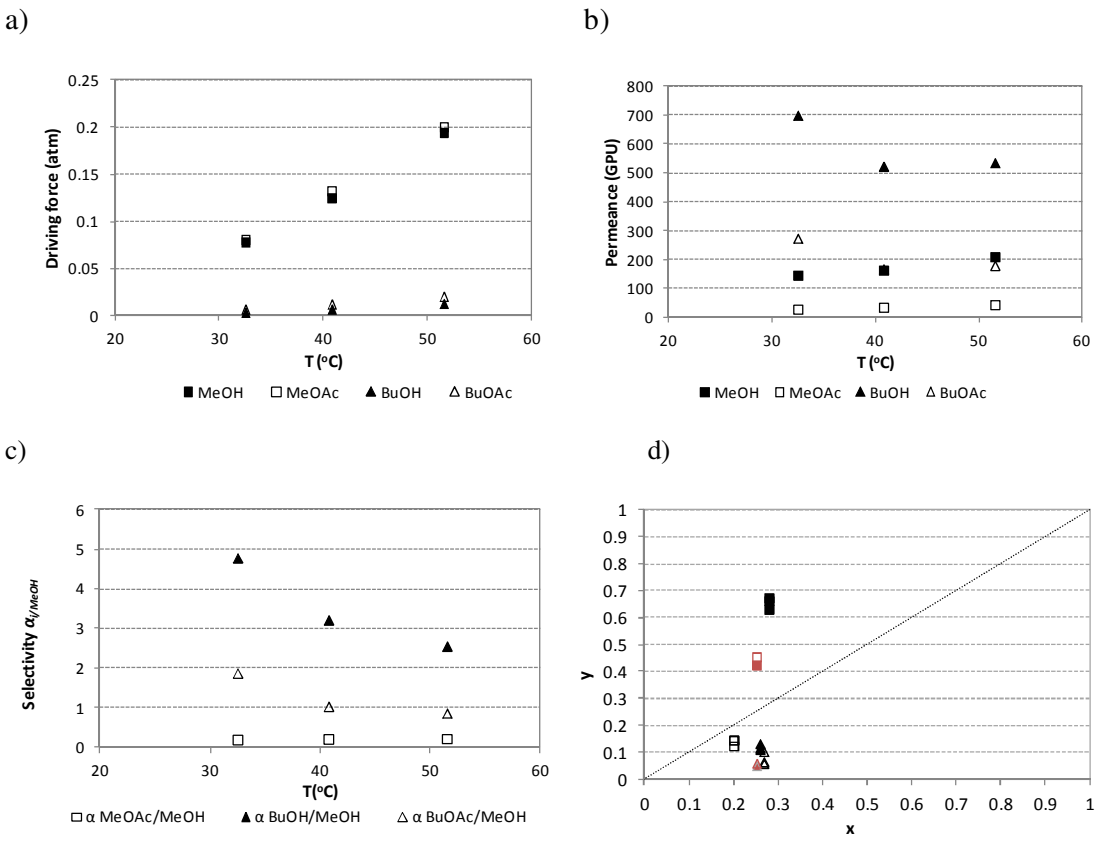


Figure 3. a) Driving force of methanol (MeOH), methyl acetate (MeOAc), butanol (BuOH) and butyl acetate (BuOAc) as a function temperature, for the membrane Pervap 2255-50. **b)** Permeance of methanol (MeOH), methyl acetate (MeOAc), butanol (BuOH) and butyl acetate (BuOAc) through the commercial membranes Pervap 2255-50; **c)** Selectivity of methyl acetate (MeOAc), butanol (BuOH) and butyl acetate (BuOAc) on the commercial membranes Pervap 2255-50 (methanol is taken as the reference compound); **d)** McCabe-Thiele separation diagram that shows the pervaporation selectivity for each compound (■: methanol; □: methyl acetate; ▲: butanol; △: butyl acetate) and the membranes Pervap 2255-50. The dotted line indicates no selectivity (feed concentration 'x' equals to permeate concentration 'y'). The variation of each point shows the effect of temperature (30, 40 and 50 ºC). The red symbols correspond to the separation obtained by simulation of distillation flash at 75 ºC.

The developed methodology is applicable independently of the complexity of the model (solution-diffusion, Maxwell-Stefan, etc) and lead to the right interpretation of the membrane performance.

In addition to the experimental evaluation of the potential of pervaporation for the separation of products from transesterification reactions, a **thermodynamic approach that allows the further application of transport models for organic-organic separations** (i.e. *n*-butyl acetate and methanol) by using pervaporation is being developed. One of the main issues to describe the mass transfer in pervaporation is the determination of the activity coefficients, which define the vapour-liquid equilibrium in the membrane interface. The role of experimental data is essential and novel fast and reliable techniques need to be developed. In this project, headspace gas chromatography (HS-GC) is proposed as a novel technique to measure vapour-liquid equilibrium data. The mixtures ethylacetate-water, ethylacetate-isooctane, acetonitrile-toluene and acetonitrile-toluene-tetrahydrofuran were considered as reference in order to contribute with new data of azeotropic mixtures at the same time that the great potential of HS-GC is shown. The effect of the temperature (35, 50 and 70^{o}C) was also evaluated and the results were fitted with the Redlich-Kister expansion for the mixtures acetronitrile-toluene and ethylacetate-isooctane, and compared with those obtained with results calculated from thermodynamic models (i.e., Wilson, UNIFAC) by using Aspen Engineering Suite V7.2 or from the literature, when available.

The isothermal VLE measurements (x_1, y_1) together with the calculated pressure and the activity coefficients (γ_1-γ_2-x_1 diagrams) were calculated for all the mixtures and the best operating conditions were determined. Figure 4 shows an example for the mixtures acetonitrile-toluene, which has a minimum-boiling point homoazeotrope with an azeotropic composition of around 90 mole% acetonitrile. Literature data obtained by means of a stage-Muller ebulliometer and a multicell apparatus and the data obtained from the Redlich-Kister and Wilson models are included for comparison. From this study, it can be concluded that HS-GC is a potential technique for the measurement of vapour-liquid equilibrium and thermodynamic properties. Further studies will be focused on the integration of reaction and equilibrium in order to apply this technique for transesterification reactions.

From this research, a general procedure to obtain experimental values of activity coefficients for binary mixtures by using HS-GC has been developed. The deviations that the fractional volume of liquid in the vial can cause have been studied since it was observed that the reproducibility of the results may be affected. If too small volumes of liquid are used, the amount of helium introduced during the pressurization step influences the magnitude of the peak areas, which will condition the reproducibility and reliability of the data. Thus, an easy procedure is recommended in order to select the optimal liquid fill for VLE and activity coefficient measurements of mixtures.

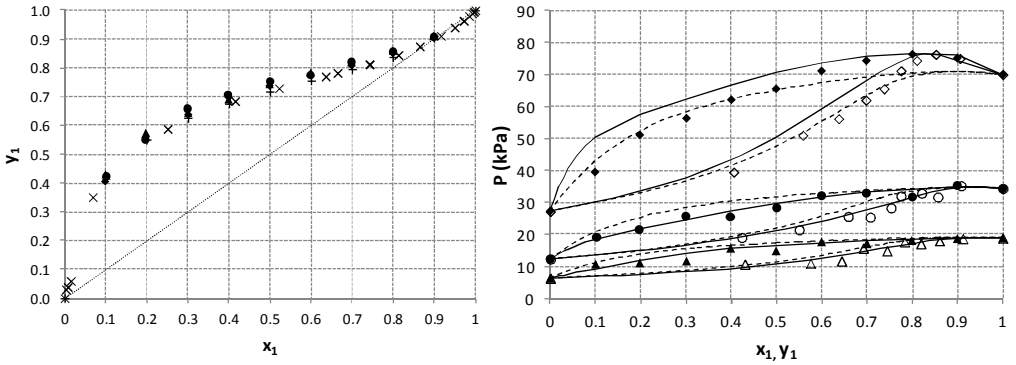


Figure 4. a) VLE measurements for the acetonitrile (1) – toluene (2) mixture. Literature data at 70°C are represented by: x and +; b) Total pressure–composition diagram for the acetonitrile (1) – toluene (2) mixture; closed symbols refer to the liquid phase and open symbols refer to the vapour phase. Dashed lines show results calculated from Wilson's model and solid lines show results from the Redlich-Kister expansion.
Temperatures: ▲ 35°C; ● 50°C; ◆ 70°C

This research is linked to the research stay performed during October-December 2011 at the University of Delaware under the supervision of Prof. Stanley Sandler, an expert in Thermodynamics and Chemical Engineering and a reference in the application of thermodynamic models. Together with the application of high throughput techniques to obtain fast and reliable experimental data, the development of thermodynamic models that consider the compounds at molecular level is critical. Thus, the COSMO-SAC approach that Prof. Sandler is developing is a reference for the international community since activity coefficients can be estimated from the molecular structure of compounds. In this framework, my work in Delaware was focused on the study of the grade of applicability of COSMO-SAC to predict the activity coefficients of several water-organic and mainly, organic-organic mixtures. In total, 23 mixtures were evaluated and compared with experimental results obtained from the literature.

The milestones for the WP2 are:

M2.1 A model based on Maxwell-Stefan equations is performed.
M2.2 Model parameters are obtained.

And the deliverables:
D2.1 A model-based and methodology for extraction of diffusional transport parameters from binary and multicomponent pervaporation flux experiments.

Both the milestones and the deliverables have been obtained successfully.

The **Work Package 3 includes the study of the hybrid reaction and separation model.** The **integration of reaction and separation** allows the study of proposed hybrid configuration. The integration has been carried out using a multi-stage-batch pervaporation unit (MSBP unit), as indicated in Figure 5.

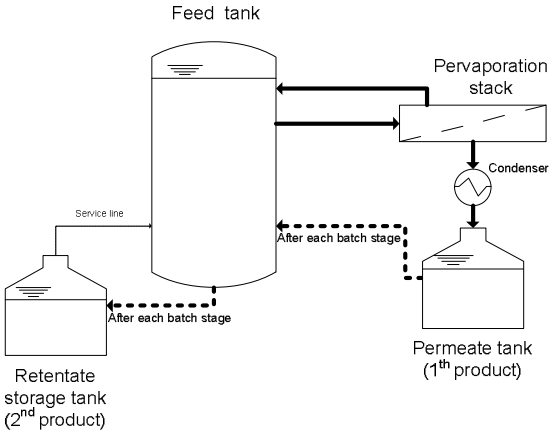


Figure 5. Scheme of the MSBP unit studied in WP3.

Hence, in order to increase the purity of the permeate to be obtained as the product, at the end of each stage what is left in the feed tank is sent to the storage tank, and what has been permeated, condensed and collected in the permeate tank, is returned to the feed tank for further purification. Therefore, the *retentate product* (hereinafter always reported referring to the concentration of the component not selective for the membrane, e.g., methyl acetate concentrations, if the membrane is methanol selective) is the product accumulated in the storage tank; the *permeate product* (hereinafter always reported in concentration unit of component selective for the membrane) is the product obtained at the end of the entire MSBP process and contained in the permeate tank; the *stage-termination condition* is the condition that terminates an MSBP stage; the *process-termination condition* is the condition that ends an MSBP process; the *operation mode* indicates the way in which the MSPB unit is run and depends on the stage-termination condition; a component *stage-recovery* and *total-recovery* are the ratios between the amount of the component at the end (in the respective tanks) over the amount of the same component (in the feed tank) at beginning of the stage or at the very beginning of the process, respectively.

Considering that the energy of permeation comes from the retentate-side and that during condensation the permeate rejects heat to the cooling utility, during each stage both retentate and permeate have to be heated in a heat exchanger system. However, this step was not assessed here as it is outside the scope of this study.

Medium-low performance membranes may lead to the design of expensive pervaporation units made of a long series of membrane modules, discouraging the use of this technology. The MSBP unit described may allow to overcome this problem. Here, after each batch-stage it is possible to increase the purity of the permeate product by recycling to the feed tank using a single condenser system. Figure 6a-b, shows two proposed (basic) operation modes, represented schematically, to operate an MSBP unit. Figure 6a and 6b were produced simulating an imaginary membrane separation; in particular, Figure 4a shows the case in which each stage is terminated once a fixed stage-recovery of the component enriched in the permeate is reached, and Figure 6b the case in which each stage is terminated when reaching a desired retentate product purity. Starting from the feed point and following the time direction it is possible to see the dynamics of the purity of the permeate and retentate products for each stage. When terminating each stage at the desired retentate product purity (Figure 6b), at the end of the entire process it is possible to obtain both products, i.e., storage and permeate tank products, with the desired purities. On the other hand, when terminating each stage after reaching a certain value of stage-recovery of the component enriched in the permeate, only the permeate product can be extracted pure as the membrane limits the retentate product purity.

However, in this case the retentate product accumulated in the storage tank, can be recycled to the feed tank for further processing or be treated by other separation systems, e.g., pervaporation, distillation, etc.

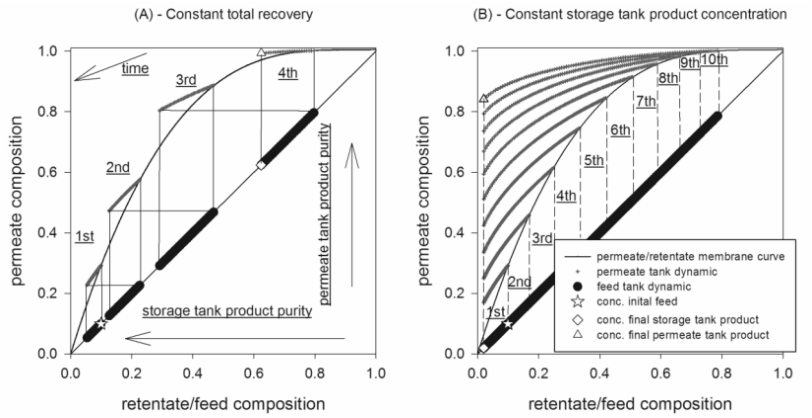


Figure 6. Two schemes for variation of compositions of permeate vs. retentate with the number of stages: (a) multi-stage-batch-pervaporation mode in which each stage is terminated after reaching a certain value of stage-recovery of the component enriched in the permeate; (b) each stage is terminated when a constant purity value of the retentate product is reached.

These two ways of operating the MSBP unit are basic examples. More elaborate combinations may be designed and employed depending on the particular separation. However, it is not the purpose of the present work to explore them.

As extension to the evaluation of the technical viability of the pervaporative process, an energetic and environmental study of different processes have been performed.

As example, an exergy analysis has been applied for the biodiesel process. The chemical process was first revised because some inconsistencies were found in the literature. Then, since in Aspen v.7.3 exergy is not presented, a new and very simple method was developed using the calculator block. The exergy concept was compared with energy for the production process of biodiesel. It was found that the reaction section has the largest losses, whereas in the energy study the separation steps are the most critical.

During the development of the method to calculate exergy, the importance of the mixing term was determined. The results of the exergy analysis for the butyl acetate production were compared with the calculation of exergy by using Aspen Plus 8.4. It is shown that the current implementation of exergy in the simulator has to be improved for the mixing term but also for the contribution of chemical exergy due to the formation of the components, otherwise the error can be large.

The application of life cycle assessment as a tool during the decision making allows determining which technology (pervaporation, distillation or incineration) is the most appropriate for the treatment of waste solvents from an environmental point of view depending on the waste composition. From the obtained results, it was observed that the main impact is caused during the solvent production. This means that those compounds of which the production entails a large environmental burden, such as tetrahydrofuran, should be recovered. In a first study, a comparison between distillation and incineration was performed. A lower impact of recovery by means of distillation involves that environmental credits obtained by the recovery are higher than those led by

the energy production from incineration. In general terms, when the impact caused during the solvent production is similar for the compounds in the mixture (e.g. acetonitrile–toluene), the recovery by means of distillation shows significant advantage when the target compound is highly concentrated in the mixture. In addition, organic–water mixtures are expected to produce lower environmental impact than organic–organic mixtures due to the significant impact caused during solvent production. Regarding batch and continuous distillation, no differences with statistical significance were observed. In Figure 7, an example of the Ecoindicator-99 for the mixture methanol-tetrehydrofuran is shown. Clearly, the recovery of tetrahydrofuran by batch or continuous distillation shows a higher decrease of the total impact (Eco points) when compared with the recovery of methanol or with using incineration.

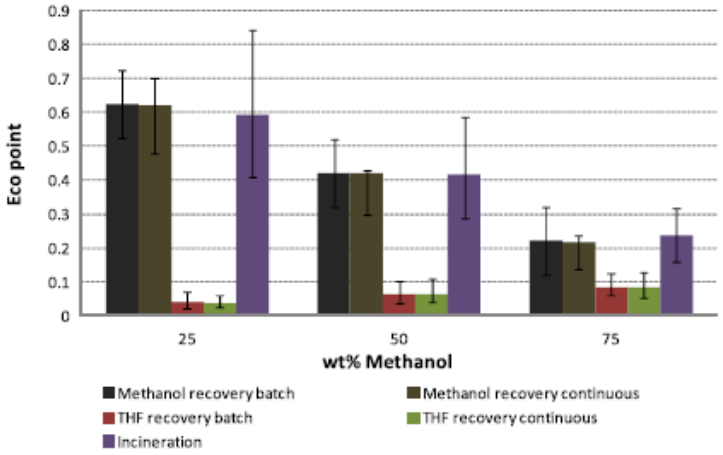


Figure 7. Eco-indicator 99 of the mixture methanol–tetrahydrofuran for incineration and batch and continuous distillation with methanol or THF as target compounds to be recovered (best case scenario).

In a second study, the design of a hybrid process consisting of distillation and pervaporation has been exposed as an alternative for the separation of mixtures composed of methanol and tetrahydrofuran. From the technical and environmental comparison between the hybrid and pressure swing distillation and incineration, it has been demonstrated that the hybrid shows clear benefits, making the recovery of tetrahydrofuran competitive compared to incineration while pressure swing distillation causes more impacts than the hybrid process. Thus, the hybrid process can be considered a real alternative to pressure swing distillation and incineration, saving materials and energy in an overall scenario. Figure 8 shows the environmental impact of pressure swing distillation, the hybrid distillation-pervaporation and incineration for a reference mixture methanol-tetrahydrofuran. The integration of membrane technology in a hybrid configuration should be considered in the design and development of more environmentally friendly processes and its application in azeotropic mixtures, such as those that appear in transesterification reactions, is worth of consideration in an industrial approach.

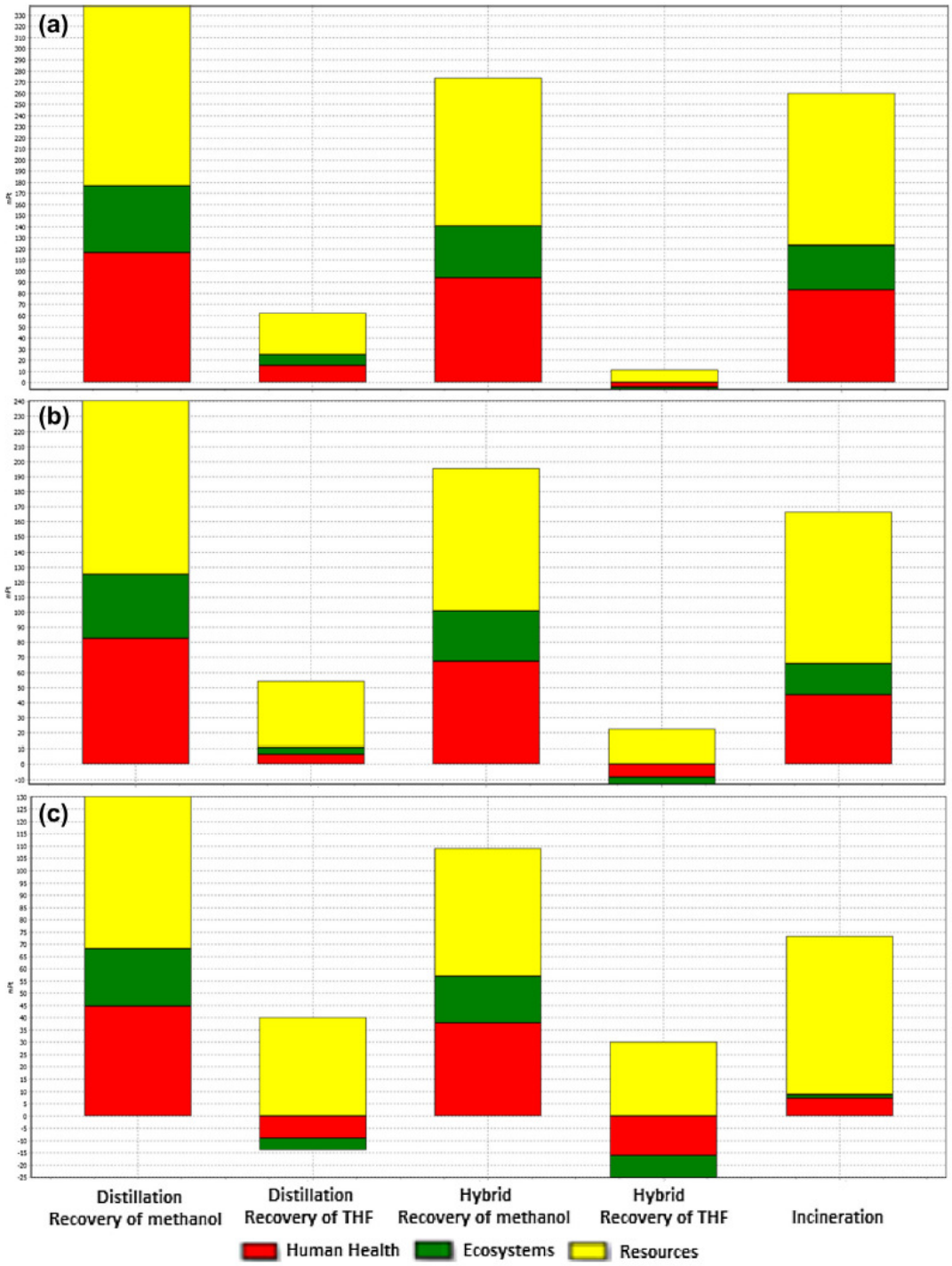


Figure 8. Environmental impact (ReCiPe) caused in the end-points (i.e. Human Health, Ecosystem Quality and Resources) when pressure swing distillation (focused on methanol – first column or THF recovery – second column), hybrid distillation–pervaporation (focused on methanol – third column – or THF recovery – forth column) and incineration are considered for: (a) 25 wt% methanol; 50 wt% methanol; 75 wt% methanol.

Furthermore, life cycle assessment was considered to evaluate the treatment of the mixture isopropanol-water. A hybrid system distillation coupled with pervaporation to produce alcohols with high purity was compared with two alternatives to incinerate the mixture in a conventional waste

solvent incineration unit or in a cement kiln plant after a pre-concentration step by distillation. The LCA results, performed in SimaPro using the ReCiPe methodology, showed that the main impact is related to the solvent production. Thus, solvent recovery is the best option if minimization of the use of resources is paramount. Nevertheless, incineration in a cement kiln becomes relevant in terms of human health for the avoided use of fuels.

Finally, the LCA was compared with the exergy analysis for the butyl acetate production via reactive distillation. The results showed that the two methodologies are speculative and both are important to be used.

The expected milestones for WP3 are:

M.3.1 A simulation model for various hybrid reactor and separator configurations (batch or continuous, with the latter based on the mixed flow reactor or the plug flow reactor) has been performed.
M3.2 The simulation model has been validated.

Regarding the deliverables:

D3.1 A validated simulation model for various hybrid reactor and separator configurations: batch or continuous, with the latter based on the mixed flow reactor or the plug flow reactor (and each of these considered with or without recycle).
D3.2 Incorporation of hybrid model in process flowsheeting software package (Aspen Plus or Aspen HYSYS).
D3.3 Comparison between reactive distillation and pervaporation for transesterification reactions having methanol as by-product using state-of-the-art membranes.

Both milestones and deliverables have been achieved successfully.

Potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and exploitation of results (not exceeding 10 pages).

The present project funded by the Marie Curie Integration grant has enhanced my international visibility by means of the publication of research articles in peer-review journals and the attendance and active participation in international conferences. As consequence, The CIG Marie Curie Grant has allowed the initiation of a new research line at the Université catholique de Louvain that continues after the termination of the Grant. Thanks to the impulse given by the grant, I have developed **my own independent research as professor at the Université catholique de Louvain (UCL in Louvain-la-Neuve, Belgium). Thus, the CIG Marie Curie Grant gave me the required support to grow up from postdoc at KU Leuven (Leuven, Belgium) to professor at UCL.**

The impact and transfer of knowledge are in a way related to each other. Dissemination of research is a key issue in order to establish a closer bond with the society. In my research, I have contributed to spreading science in society by means of three mechanisms:

- Teaching at university level:
  I have participated in the teaching of thermodynamics, separation processes and process design in Chemical Engineering at KUL during the first two years of the grant and, at UCL during the last two years of the grant as well as currently. These subjects are cornerstone in the knowledge that a chemical engineer has to develop and the most recent information in these fields is required. In this sense, my research contributes to the formation of chemical engineers that are updated with the last generation techniques and technology for application in the industry, including not only technical aspects but also environmental, economic and cultural. This interrelationship between research and teaching has a direct impact in the society. In addition, my contribution to supervise MSc and PhD theses is part to the dissemination of results and continuation of the research started with the Marie Curie grant.

- Participation in conferences:
  Dissemination of results in international conferences is an opportunity to interact with the main stakeholders in the development of new processes in the industry. Researchers, industrial partners, press, etc, sit together to discuss about the most innovative processes and the challenges that need to be solved. A very rich and fruitful interaction is obtained in this kind of events.

- Interaction with the industry:
  A direct contact with the industry by means of face-to-face meetings is essential to understand specific problems that the closer industry is suffering. Research cannot be isolated from the real necessities of the society and the industry is a clear mirror of the society needs. Thus, several meetings with industrial partners (*i.e.,* De Neef Chemical Processing, Janssen Pharmaceutica, Omnichem en Nitto) have enriched the performed research and addressed towards real applications. In addition, in my role as holder of the Solvay Chair (more info: **http://www.uclouvain.be/en-solvay-chair.html**), a very close interaction with Solvay and Rhodia has led to a very fruitful exchange of ideas to give solutions to industrial concerns.

Currently, I am supervising the following PhD candidates in collaboration with KUL:

- Fred Molelekwa, Production of Potable Water for Small Scale Communities using Low-Cost Membrane Filtration, 2011-2015, KU Leuven - Tshwane University of Technology, promoters: Bart Van der Bruggen and Patricia Luis (UCL).

  Fred Molelekwa's PhD is the result of a developing cooperation project with the Tshwane University of Technology funded by VLIR (VLIR-UOS Own Initiative). The main objective is the application of membrane technology to the purification of water in small communities in South Africa. He is in the second year of his PhD.

- Antonio Amelio, Process Intensification in Transesterification: membrane pervaporation reactor and biodiesel production, 2012-2016, KU Leuven, promoters: Bart Van der Bruggen and Patricia Luis (UCL).

  Antonio Amelio is performing his last year of PhD. His research is focused on the study of transesterification reactions for biodiesel production, evaluating the technical applicability of pervaporation and the environmental impact, and optimizing the process from an energetic and exergetic point of view. Antonio Amelio carries out his work under the umbrella of the OT Project: "Pervaporation Membrane Reactors for Transesterifications: Development and Modeling" (Promoter: Prof. Bart Van der Bruggen. Co-promoter: Prof. Patricia Luis).

- Giuseppe Genduso, Development of a pervaporative membrane reactor for transesterification reactions, 2012-2016, KU Leuven, promoters: Bart Van der Bruggen and Patricia Luis (UCL).

  Giuseppe Genduso is in last year of PhD. His works involves the integration of a transesterification reaction (industrial framework) with pervaporation (low energy consumption separation technology) in order to develop an integrated chemical unit for the conversion of methyl acetate, capable to be environmental friendly and remunerative at the same time. Giuseppe Genduso carries out his work under the umbrella of the OT Project: "Pervaporation Membrane Reactors for Transesterifications: Development and Modeling" (Promoter: Prof. Bart Van der Bruggen. Co-promoter: Prof. Patricia Luis).OT Project: "Pervaporation Membrane Reactors for Transesterifications: Development and Modeling". Promoter: Prof. Bart Van der Bruggen. Co-promoter: Prof. Patricia Luis

- Dessalegn Dadi, Sustainable industrial production: Coffee - Valorization of waste products, 2013-2017, KU Leuven, promoters: Bart Van der Bruggen, Patricia Luis (UCL); Jimma University, promoter: Abebe Beyene.

  Dessalegn Dadi is performing his second year of PhD in a Joint program between KUL and Jimma University. His main research will consist on developing a sustainable treatment method to valorize the coffee waste.

These PhD candidates are developing their research under the umbrella of KUL, which may be considered as a strong point in my collaboration with KUL.

Regarding my independence as researcher at UCL, I am currently promoter of three PhD students, one of them (Wenqi Li) having been contracted under the Marie Curie grant to perform his first year of PhD:

- Wenqi Li, Enhancing (trans)esterification reactions by pervaporation, started in 2014 at UCL, promoters: Patricia Luis (UCL).

- Israel Ruiz-Salmon, CO_2 capture with NaCl: An approach based on membrane technology, started in 2014 at UCL, promoters: Patricia Luis (UCL).

- Raphael Janssens, Targeting the elimination of antineoplastic compounds in hospital wastewaters: novel frontiers in sustainable treatment, started in October 2015 at UCL. Promoters: Patricia Luis (UCL).

In addition to my integration as professor at UCL, the Marie Curie grant has allowed me to continue a very fruitful research. The following publications have been obtained under the umbrella of this grant:

Articles in international peer reviewed academic journals under the umbrella of the Marie Curie grant

1. Amelio A., C. Creemers, F. Vereyden, C. Andecochea, J. Degrève, S. Darvishmanesh, B. Van der Bruggen, P. Luis. Complete methodology for the evaluation of exergy in chemical engineering applications. (Submitted October 2015 at Applied Energy Journal).

2. Amelio A., L. Loise, R. Azhandeh, S. Darvishmanesh, V. Calabró, Jan Degréve, P. Luis, B. Van der Bruggen. Purification of Biodiesel stream using membrane contactor: liquid-liquid extraction.(Submitted July 2015 at Fuel Processing Technology)

3. Amelio A., T. Van de Voorde, C. Creemers, J. Degrève, S. Darvishmanesh, P. Luis, B. Van der Bruggen. Energy or Exergy analysis? Study of the production of biodiesel .(Submitted January 2015 at Energy Journal).

4. Amelio A., Genduso G., Vreysen S., Luis P., Van der Bruggen B. (2014). Guidelines based on life cycle assessment for solvent selection during the process design and evaluation of treatment alternatives. Green Chemistry, 16, 3045-3063.

5. Amelio, A., E. Curcio, V. Calabró, Jan Degréve, S. Darvishmanesh, P. Luis, B. Van der Bruggen A complete study of pervaporation: experiments, modeling and simulation for the separation of MTBE and methanol. (Submitted October 2015 at Computers & Chemical Engineering).

6. Genduso G., Amelio A., Colombini E., Luis P, Degrève J, Van der Bruggen B., (submitted for publication) Retrofitting of extractive distillation columns with high flux, low separation factor membranes: a way to reduce the energy demand?

7. Genduso G., Farrokhzad H., Latré Y., Darvishmanesh S., Luis P. and Van der Bruggen B. (2015). Polyvinylidene fluoride dense membrane for the pervaporation of methyl acetate-methanol mixtures. Journal of Membrane Science, 482, 128-136.

8. Genduso G., Luis P., Van der Bruggen B., (submitted for publication) Techno-economical assessment of a pervaporation based production of n-butyl acetate from methyl acetate waste streams

9. Genduso G., Amelio A., Luis P., Van der Bruggen B., Vreysen S. (2014). Separation of methanol-tetrahydrofuran mixtures by heteroazeotropic distillation and pervaporation. AIChE Journal, 60 (7), 2584-2595.

10. Genduso G., Luis, P., Van der Bruggen B. (2015). Overcoming any configuration limitation: an alternative operation mode for pervaporation and vapour permeation. Journal of Chemical Technology and Biotechnology. n/a (n/a), n/a-n/a

11. Jullok N., Deforche T., Luis P., Van der Bruggen B., 2012. Sorption and diffusivity study of acetic acid and water in polymeric membranes, Chemical Engineering Science, 78, 14-20.

12. Jullok N.; Luis P.; Degrève J.; Van der Bruggen B, 2014. A cascaded pervaporation for dehydration of acetic acid, Chem Eng Sci, 105, 208-212.

13. Jullok, N.; Martinez, R.; Wouters, C.; Luis, P.; Sanz, M.T.; Van der Bruggen, B. 2013 A biologically-inspired hydrophobic PDMS/PPSU membrane for application in pervaporation. Langmuir, 29 (5) 1510-1516.

14. Luis P., 2013. Exergy as a tool for measuring process intensification in chemical engineering, Journal of Chemical Technology and Biotechnology, 88, 1951–1958.

15. Luis P., A. Amelio, S. Vreysen, V. Calabro, B. Van der Bruggen: Life cycle assessment of alternatives for waste-solvent valorization: batch and continuous distillation vs incineration. The International Journal of Life Cycle Assessment, 18 (5): 1048-1061 (2013).

16. Luis P., A. Amelio, S. Vreysen, V. Calabro, B. Van der Bruggen: Simulation and environmental evaluation of process design: Distillation vs. Hybrid distillation–pervaporation for methanol/tetrahydrofuran separation. Applied Energy, 2014 113: 565-575.

17. Luis P., J. Degrève, B. Van der Bruggen, 2013. Separation of methanol – n-butyl acetate mixtures by pervaporation: Potential of ten commercial membranes, Journal of Membrane Science, 429, 1–12.

18. Luis P., Van der Bruggen B., 2014. Exergy analysis of energy-intensive production processes: Advancing towards a sustainable chemical industry, Journal of Chemical Technology and Biotechnology, 89, 1288–1303.

19. Luis P., Van der Bruggen B., The driving force as key element to evaluate the pervaporation performance of multicomponent mixtures, Separation and Purification Technology, 148 (2015) 94–102.

20. Luis P., Wouters C., Sweygers N., Creemers C., Van der Bruggen B., 2012. The potential of Head-Space Gas Chromatography for VLE measurements, Journal of Chemical Thermodynamics, 49, 128-136.

21. Luis P., Wouters C., Van der Bruggen B., Sandler S.I., 2013. Measurement of activity coefficients of mixtures by head-space gas chromatography: General procedure to obtain reliable data, Journal of Chromatography A., 1302, 111-117.

22. Meyer RN., D. A Figueroa Paredes; M. Fuentes; A. Amelio; B. Morero; P. Luis; B. Van der Bruggen; J. Espinosa. Conceptual Model-Based Optimization and Environmental Evaluation

of Waste Solvent Technologies: Distillation/Incineration versus Distillation/Pervaporation. (Submitted June 2015 at Separation Purification Technology)

23. Parvez, A.M., Luis, P,, Ooms, T., Vreysen, S., Vandezande, P., Degrève, J., Van der Bruggen, B., 2012. Separation of ethyl acetate–isooctane mixtures by pervaporation and pervaporation-based hybrid methods. Chemical Engineering Journal, 210, 252-262.

24. Van der Bruggen B., Luis P., Pervaporation as a tool in chemical engineering: a new era?, Current Opinion in Chemical Engineering 2014, 4:47–53.

Book chapters under the umbrella of the Marie Curie grant

1. Genduso G., Luis P., Van der Bruggen, B. (2015). Pervaporation membrane reactors (PVMRs) for esterification. In: Basile A., Di Paola L., Piemonte V. (Eds.), Membrane Reactors for Energy Applications and Basic Chemical Production, Woodhead Publishing, 1-616.

2. Amelio, C. Lopresto, A. Verardi, V. Calabro', P. Luis, B. Van der Bruggen: Pervaporation membrane reactors: biomass conversion into alcohols . 'Membrane technologies for biorefining', Elsevir. In Press.

Scientific Conferences-Symposia Proceedings under the umbrella of the Marie Curie grant

1. Amelio A., L. Loise, T. Van der Voorde, S. Darvishmanesh, V. Calabró, Jan Degréve, P. Luis, B. Van der Bruggen. Process integration of membrane extraction in the biodiesel production process: experiments and simulation. Submitted on EMS Conference, Aachen 2015 (September 6-10)

2. Amelio, A., E. Curcio, S. Darvishmanesh, V. Calabró, P. Luis, B. Van der Bruggen: Design of a hybrid system (distillation pervaporation) for the mixture Methanol-MTBE (methyl tert-butyl ether). Proceeding CAPE Forum Milan 2014.

3. Amelio, A., E. Curcio, S. Darvishmanesh, V. Calabró, P. Luis, B. Van der Bruggen. Separation of Methanol-MTBE (methyl tert-butyl ether) by hybrid system (distillation pervaporation) using commercial membranes. IV PV-VP-DM Conference, Torun 2014 (September 21-24)

4. Amelio, A., E. Curcio, S. Darvishmanesh, V. Calabró, P. Luis, B. Van der Bruggen. Separation of Methanol-MTBE (methyl tert-butyl ether) by hybrid system (distillation pervaporation) using commercial membranes. Poster Session Aachen (6 September 2014).

5. Genduso G., Osorio V., Amelio A., J. Degrève, P. Luis, B. Van der Bruggen From a methanolmethyl acetate industrial waste stream to n-butyl acetate, ethyl acetate or acetic acid - How can pervaporation help in increasing the value of these conversions? Submitted on EMS Conference, Aachen 2015(September 6-10)

6. Genduso G., Farrokhzad H., Colombini E., Latré Y., Darvishmanesh S., Luis P., Van der Bruggen B. (2014). Two relevant pervaporation membranes for the separation of methyl-

acetate-methanol industrial streams. 4th International Scientific Conference on Pervaporation, Vapor Permeation and Membrane Distillation. International Scientific Conference on Pervaporation, Vapor Permeation and Membrane Distillation. Torun, Poland, 21-24 Sep 2014 (art.nr. SL 18).

7. Luis P., Van der Bruggen B., Enhancing Transesterification Reactions by using Pervaporation, 20th International Congress of Chemical and Process Engineering (CHISA 2012), 25-29th August 2012, Prague, Czech Republic. Participation: oral.

8. Luis P., Van der Bruggen B., Key issues in the measurement of VLE with balanced-pressure head-space gas chromatography, 26th European Symposium on Applied Thermodynamics ESAT (ESAT 2012), 8-10th October 2012, Postdam, Germany. Participation: poster.

9. Luis P., Van der Bruggen, B, Enhancing Transesterification Reactions by Pervaporation, International Scientific Conference on Pervaporation, Vapor Permeation and Membrane Distillation, Toruñ, Poland, 12th-15th May 2013. Participation: oral.

4.2 Use and dissemination of foreground

A plan for use and dissemination of foreground (including socio-economic impact and target groups for the results of the research) shall be established at the end of the project. It should, where appropriate, be an update of the initial plan in Annex I for use and dissemination of foreground and be consistent with the report on societal implications on the use and dissemination of foreground (section 4.3 – H).

The plan should consist of:

- Section A

  This section should describe the dissemination measures, including any scientific publications relating to foreground. **Its content will be made available in the public domain** thus demonstrating the added-value and positive impact of the project on the European Union.

- Section B

  This section should specify the exploitable foreground and provide the plans for exploitation. All these data can be public or confidential; the report must clearly mark non-publishable (confidential) parts that will be treated as such by the Commission. Information under Section B that is not marked as confidential **will be made available in the public domain** thus demonstrating the added-value and positive impact of the project on the European Union.

Section A (public)

This section includes two templates

- Template A1: List of all scientific (peer reviewed) publications relating to the foreground of the project.
- Template A2: List of all dissemination activities (publications, conferences, workshops, web sites/applications, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters).

These tables are cumulative, which means that they should always show all publications and activities from the beginning until after the end of the project. Updates are possible at any time.

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES

NO.	Title	Main author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Year of publication	Relevant pages	Permanent identifiers[2] (if available)	Is/Will open access[3] provided to this publication?
1	*Separation of methanol – n-butyl acetate mixtures by pervaporation: Potential of ten commercial membranes*	*Luis P., J. Degrève, B. Van der Bruggen*	*Journal of Membrane Science*	*429*			*2013*	*1-12*		*no*
2	*Exergy analysis of energy-intensive production processes: Advancing towards a sustainable chemical industry*	*Luis P., Van der Bruggen B*	*Journal of Chemical Technology and Biotechnology*	*89*			*2014*	*1288–1303*		*no*

[2] A permanent identifier should be a persistent link to the published version full text if open access or abstract if article is pay per view) or to the final manuscript accepted for publication (link to article in repository).

[3] Open Access is defined as free of charge access for anyone via Internet. Please answer "yes" if the open access to the publication is already established and also if the embargo period for open access is not yet over but you intend to establish open access afterwards.

3	*The driving force as key element to evaluate the pervaporation performance of multicomponent mixtures*	*Luis P., Van der Bruggen B.,*	*Separation and Purification Technology*	*148*			*2015*	*94–102*		*no*
4	*Exergy as a tool for measuring process intensification in chemical engineering*	*Luis P*	*Journal of Chemical Technology and Biotechnology*	*88*			*2013*	*1951–1958*		*no*
5	*Life cycle assessment of alternatives for waste-solvent valorization: batch and continuous distillation vs incineration*	*Luis P., A. Amelio, S. Vreysen, V. Calabro, B. Van der Bruggen*	*The International Journal of Life Cycle Assessment*	*18*			*2013*	*1048-1061*		*no*
6	*Simulation and environmental evaluation of process design: Distillation vs. Hybrid distillation–pervaporation for methanol/tetrahydrofuran separation*	*Luis P., A. Amelio, S. Vreysen, V. Calabro, B. Van der Bruggen*	*Applied Energy*	*113*			*2014*	*565-575*		*no*
7	*Pervaporation as a tool in chemical engineering: a new era?*	*Van der Bruggen B., Luis P.,*	*Current Opinion in Chemical Engineering*	*4*			*2014*	*47-53*		*no*
8	*Complete methodology for the evaluation of exergy in chemical engineering applications*	*Amelio A., C. Creemers, F. Vereyden, C. Andecochea, J. Degrève, S. Darvishmanesh, B. Van der Bruggen, P. Luis.*	*Applied Energy Journal*	*Submitted*						*no*
9	*Purification of Biodiesel stream using membrane contactor: liquid-liquid extraction*	*Amelio A., L. Loise, R. Azhandeh, S. Darvishmanesh, V. Calabró, Jan Degréve, P. Luis,*	*Fuel Processing Technology*	*Submitted*						*no*

		B. Van der Bruggen								
10	*Energy or Exergy analysis? Study of the production of biodiesel*	*Amelio A., T. Van de Voorde, C. Creemers, J. Degrève, S. Darvishmanesh, P. Luis, B. Van der Bruggen*	*Energy Journal*	*Submitted*						*no*
11	*Guidelines based on life cycle assessment for solvent selection during the process design and evaluation of treatment alternatives.*	*Amelio A., Genduso G., Vreysen S., Luis P., Van der Bruggen B*	*Green Chemistry*	*16*			*2014*	*3045-3063*		*no*
12	*A complete study of pervaporation: experiments, modeling and simulation for the separation of MTBE and methanol.*	*Amelio, A., E. Curcio, V. Calabró, Jan Degréve, S. Darvishmanesh, P. Luis, B. Van der Bruggen*	*Computers & Chemical Engineering*	*Submitted*						*no*
13	*Retrofitting of extractive distillation columns with high flux, low separation factor membranes: a way to reduce the energy demand?*	*Genduso G., Amelio A., Colombini E., Luis P, Degrève J, Van der Bruggen B.,*		*Submitted*						*no*
14	*Polyvinylidene fluoride dense membrane for the pervaporation of methyl acetate-methanol mixtures*	*Genduso G., Farrokhzad H., Latré Y., Darvishmanesh S., Luis P. and Van der Bruggen B.*	*Journal of Membrane Science*	*482*			*2015*	*128-136*		*no*
15	*Techno-economical assessment of a pervaporation based production of n-butyl acetate from methyl acetate waste streams*	*Genduso G., Luis P., Van der Bruggen B*		*Submitted*						*no*
16	*Separation of methanol-tetrahydrofuran mixtures*	*Genduso G., Amelio A., Luis*	*AIChE Journal*	*60*			*2014*	*2584-2595*		*no*

	by heteroazeotropic distillation and pervaporation	*P., Van der Bruggen B., Vreysen S*								
17	*Overcoming any configuration limitation: an alternative operation mode for pervaporation and vapour permeation*	*Genduso G., Luis, P., Van der Bruggen B*	*Journal of Chemical Technology and Biotechnology.*	*In Press*			*2015*			*no*
18	*Sorption and diffusivity study of acetic acid and water in polymeric membranes*	*Jullok N., Deforche T., Luis P., Van der Bruggen B*	*Chemical Engineering Science*	*78*			*2012*	*14-20*		*no*
19	*A cascaded pervaporation for dehydration of acetic acid*	*Jullok N.; Luis P.; Degrève J.; Van der Bruggen B,*	*Chem Eng Sci*	*105*			*2014*	*208-212*		*no*
20	*A biologically-inspired hydrophobic PDMS/PPSU membrane for application in pervaporation*	*Jullok, N.; Martinez, R.; Wouters, C.; Luis, P.; Sanz, M.T.; Van der Bruggen, B*	*Langmuir*	*29*			*2013*	*1510-1516*		*no*
21	*The potential of Head-Space Gas Chromatography for VLE measurements*	*Luis P., Wouters C., Sweygers N., Creemers C., Van der Bruggen B.,*	*Journal of Chemical Thermodynamics*	*49*			*2012*	*128-136*		*no*
22	*Measurement of activity coefficients of mixtures by head-space gas chromatography: General procedure to obtain reliable data*	*Luis P., Wouters C., Van der Bruggen B., Sandler S.I.,*	*Journal of Chromatography A*	*1302*			*2013*	*111-117*		*no*
23	*Conceptual Model-Based Optimization and Environmental Evaluation of Waste Solvent Technologies: Distillation/Incineration versus Distillation/Pervaporation*	*Meyer RN., D. A Figueroa Paredes; M. Fuentes; A. Amelio; B. Morero; P. Luis; B. Van der Bruggen; J. Espinosa*	*Separation Purification Technology*	*Submitted*						*no*
24	*Separation of ethyl acetate–isooctane*	*Parvez, A.M., Luis, P,, Ooms, T.,*	*Chemical Engineering*	*210*			*2012*	*252-262*		*no*

	mixtures by pervaporation and pervaporation-based hybrid methods.	*Vreysen, S., Vandezande, P., Degrève, J., Van der Bruggen, B*	*Journal*							

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES

NO.	Type of activities[4]	Main leader	Title	Date/Period	Place	Type of audience[5]	Size of audience	Countries addressed
1	*Conference*	*P.Luis*	*Euromembrane*	*6-10 September 2015*	*Aachen (Germany)*	*Scientific Community*	*800*	*International*
2	*Conference*	*A. Amelio*	*CAPE Forum*	*2014*	*Milan (Italy)*	*Scientific Community*	*500*	*International*
3	*Conference*	*P. Luis*	*4th International Scientific Conference on Pervaporation, Vapor Permeation and Membrane Distillation. International Scientific Conference on Pervaporation, Vapor Permeation and Membrane Distillation*	*21-24 Septembre 2014*	*Torun (Poland)*	*Scientific Community*	*150*	*International*
4	*Conference*	*P.Luis*	*20th International Congress of Chemical and Process Engineering*	*25-29 August 2012*	*Prague (Czech Republic)*	*Scientific Community*	*900*	*International*

[4] A drop down list allows choosing the dissemination activity: publications, conferences, workshops, web, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters, Other.

[5] A drop down list allows choosing the type of public: Scientific Community (higher education, Research), Industry, Civil Society, Policy makers, Medias, Other ('multiple choices' is possible).

5	*Conference*	*P. Luis*	*26th European Symposium on Applied Thermodynamics*	*8-10 October 2012*	*Postdam (Germany)*	*Scientific Community*	*250*	*International*

Section B (Confidential[6] or public: confidential information to be marked clearly)
Part B1

The applications for patents, trademarks, registered designs, etc. shall be listed according to the template B1 provided hereafter.

The list should, specify at least one unique identifier e.g. European Patent application reference. For patent applications, only if applicable, contributions to standards should be specified. This table is cumulative, which means that it should always show all applications from the beginning until after the end of the project.

TEMPLATE B1: LIST OF APPLICATIONS FOR PATENTS, TRADEMARKS, REGISTERED DESIGNS, ETC.					
Type of IP Rights[7]:	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant (s) (as on the application)

[6] Note to be confused with the "EU CONFIDENTIAL" classification for some security research projects.

[7] A drop down list allows choosing the type of IP rights: Patents, Trademarks, Registered designs, Utility models, Others.

Part B2

Please complete the table hereafter:

Type of Exploitable Foreground[8]	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application[9]	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
	Ex: New supercond uctive Nb-Ti alloy			*MRI equipment*	*1. Medical 2. Industrial inspection*	*2008 2010*	*A materials patent is planned for 2006*	*Beneficiary X (owner) Beneficiary Y, Beneficiary Z, Poss. licensing to equipment manuf. ABC*

In addition to the table, please provide a text to explain the exploitable foreground, in particular:

- Its purpose
- How the foreground might be exploited, when and by whom
- IPR exploitable measures taken or intended
- Further research necessary, if any
- Potential/expected impact (quantify where possible)

[19] A drop down list allows choosing the type of foreground: General advancement of knowledge, Commercial exploitation of R&D results, Exploitation of R&D results via standards, exploitation of results through EU policies, exploitation of results through (social) innovation.

[9] A drop down list allows choosing the type sector (NACE nomenclature) : http://ec.europa.eu/competition/mergers/cases/index/nace_all.html

4.3 Report on societal implications

Replies to the following questions will assist the Commission to obtain statistics and indicators on societal and socio-economic issues addressed by projects. The questions are arranged in a number of key themes. As well as producing certain statistics, the replies will also help identify those projects that have shown a real engagement with wider societal issues, and thereby identify interesting approaches to these issues and best practices. The replies for individual projects will not be made public.

A General Information *(completed automatically when **Grant Agreement number** is entered.*	
Grant Agreement Number:	PCIG09-GA-2011-294218
Title of Project:	New Frontiers in (Trans)esterification Pervaporation Membrane
Name and Title of Coordinator:	Professor Patricia Luis

B Ethics	
1. Did your project undergo an Ethics Review (and/or Screening)? • If Yes: have you described the progress of compliance with the relevant Ethics Review/Screening Requirements in the frame of the periodic/final project reports? Special Reminder: the progress of compliance with the Ethics Review/Screening Requirements should be described in the Period/Final Project Reports under the Section 3.2.2 *'Work Progress and Achievements'*	***NO*** ***0Yes 0No***
2. Please indicate whether your project involved any of the following issues (tick box) :	***NO***
RESEARCH ON HUMANS	
• Did the project involve children?	
• Did the project involve patients?	
• Did the project involve persons not able to give consent?	
• Did the project involve adult healthy volunteers?	
• Did the project involve Human genetic material?	
• Did the project involve Human biological samples?	
• Did the project involve Human data collection?	
RESEARCH ON HUMAN EMBRYO/FOETUS	
• Did the project involve Human Embryos?	
• Did the project involve Human Foetal Tissue / Cells?	
• Did the project involve Human Embryonic Stem Cells (hESCs)?	
• Did the project on human Embryonic Stem Cells involve cells in culture?	
• Did the project on human Embryonic Stem Cells involve the derivation of cells from Embryos?	
PRIVACY	
• Did the project involve processing of genetic information or personal data (eg. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?	
• Did the project involve tracking the location or observation of people?	
RESEARCH ON ANIMALS	
• Did the project involve research on animals?	
• Were those animals transgenic small laboratory animals?	
• Were those animals transgenic farm animals?	

• Were those animals cloned farm animals?	
• Were those animals non-human primates?	
RESEARCH INVOLVING DEVELOPING COUNTRIES	
• Did the project involve the use of local resources (genetic, animal, plant etc)?	
• Was the project of benefit to local community (capacity building, access to healthcare, education etc)?	
DUAL USE	
• Research having direct military use	0 Yes 0 No
• Research having the potential for terrorist abuse	

C Workforce Statistics

3. Workforce statistics for the project: Please indicate in the table below the number of people who worked on the project (on a headcount basis).

Type of Position	Number of Women	Number of Men
Scientific Coordinator	1	
Work package leaders		
Experienced researchers (i.e. PhD holders)		
PhD Students		1
Other		

4. How many additional researchers (in companies and universities) were recruited specifically for this project?	**1**
Of which, indicate the number of men:	1

D Gender Aspects

5. Did you carry out specific Gender Equality Actions under the project?

○ Yes
● No

6. Which of the following actions did you carry out and how effective were they?

	Not at all effective				Very effective
❑ Design and implement an equal opportunity policy	○	○	○	○	○
❑ Set targets to achieve a gender balance in the workforce	○	○	○	○	○
❑ Organise conferences and workshops on gender	○	○	○	○	○
■ Actions to improve work-life balance	○	○	○	○	●

○ Other:

7. Was there a gender dimension associated with the research content – i.e. wherever people were the focus of the research as, for example, consumers, users, patients or in trials, was the issue of gender considered and addressed?

○ Yes- please specify

● No

E Synergies with Science Education

8. Did your project involve working with students and/or school pupils (e.g. open days, participation in science festivals and events, prizes/competitions or joint projects)?

○ Yes- please specify

● No

9. Did the project generate any science education material (e.g. kits, websites, explanatory booklets, DVDs)?

○ Yes- please specify

● No

F Interdisciplinarity

10. Which disciplines (see list below) are involved in your project?

○ Main discipline[10]: 2.3

○ Associated discipline[10]: 1.3

○ Associated discipline[10]: 1.1

G Engaging with Civil society and policy makers

11a Did your project engage with societal actors beyond the research community? *(if 'No', go to Question 14)*

○ Yes
● No

11b If yes, did you engage with citizens (citizens' panels / juries) or organised civil society (NGOs, patients' groups etc.)?

○ No

○ Yes- in determining what research should be performed

○ Yes - in implementing the research

○ Yes, in communicating /disseminating / using the results of the project

[10] Insert number from list below (Frascati Manual).

11c In doing so, did your project involve actors whose role is mainly to organise the dialogue with citizens and organised civil society (e.g. professional mediator; communication company, science museums)?	○ ○	Yes No

12. Did you engage with government / public bodies or policy makers (including international organisations)

- ○ No
- ○ Yes- in framing the research agenda
- ○ Yes - in implementing the research agenda
- ○ Yes, in communicating /disseminating / using the results of the project

13a Will the project generate outputs (expertise or scientific advice) which could be used by policy makers?

- ○ Yes – as a **primary** objective (please indicate areas below- multiple answers possible)
- ○ Yes – as a **secondary** objective (please indicate areas below - multiple answer possible)
- ○ No

13b If Yes, in which fields?

Agriculture		Energy		Human rights	
Audiovisual and Media		Enlargement		Information Society	
Budget		Enterprise		Institutional affairs	
Competition		Environment		Internal Market	
Consumers		External Relations		Justice, freedom and security	
Culture		External Trade		Public Health	
Customs		Fisheries and Maritime Affairs		Regional Policy	
Development Economic and Monetary Affairs		Food Safety		Research and Innovation	
		Foreign and Security Policy		Space	
Education, Training, Youth		Fraud		Taxation	
Employment and Social Affairs		Humanitarian aid		Transport	

13c If Yes, at which level?

- ○ Local / regional levels
- ○ National level
- ○ European level
- ○ International level

H Use and dissemination

14. How many Articles were published/accepted for publication in peer-reviewed journals?	**24**
To how many of these is open access[11] provided?	**0**
How many of these are published in open access journals?	**0**
How many of these are published in open repositories?	**0**
To how many of these is open access not provided?	**all**
Please check all applicable reasons for not providing open access:	
❑ publisher's licensing agreement would not permit publishing in a repository ❑ no suitable repository available ❑ no suitable open access journal available ❑ no funds available to publish in an open access journal ■ lack of time and resources ❑ lack of information on open access ❑ other[12]: ……	

15. How many new patent applications ('priority filings') have been made? *("Technologically unique": multiple applications for the same invention in different jurisdictions should be counted as just one application of grant).*		**0**
16. Indicate how many of the following Intellectual Property Rights were applied for (give number in each box).	Trademark	**0**
	Registered design	**0**
	Other	
17. How many spin-off companies were created / are planned as a direct result of the project?		**0**
Indicate the approximate number of additional jobs in these companies:		

18. Please indicate whether your project has a potential impact on employment, in comparison with the situation before your project:

■	Increase in employment, or	❑	In small & medium-sized enterprises
❑	Safeguard employment, or	❑	In large companies
❑	Decrease in employment,	❑	None of the above / not relevant to the project
❑	Difficult to estimate / not possible to quantify		

19. For your project partnership please estimate the employment effect resulting directly from your participation in Full Time Equivalent (*FTE = one person working fulltime for a year*) jobs:	*Indicate figure:* *1*

[11] Open Access is defined as free of charge access for anyone via Internet.
[12] For instance: classification for security project.

Difficult to estimate / not possible to quantify	❑

I Media and Communication to the general public

20. As part of the project, were any of the beneficiaries professionals in communication or media relations?

○ Yes ● No

21. As part of the project, have any beneficiaries received professional media / communication training / advice to improve communication with the general public?

○ Yes ● No

22 Which of the following have been used to communicate information about your project to the general public, or have resulted from your project?

❑	Press Release	■	Coverage in specialist press
❑	Media briefing	❑	Coverage in general (non-specialist) press
❑	TV coverage / report	❑	Coverage in national press
❑	Radio coverage / report	❑	Coverage in international press
❑	Brochures /posters / flyers	❑	Website for the general public / internet
❑	DVD /Film /Multimedia	❑	Event targeting general public (festival, conference, exhibition, science café)

23 In which languages are the information products for the general public produced?

❑	Language of the coordinator	■	English
❑	Other language(s)		

***Question F-10*:** Classification of Scientific Disciplines according to the Frascati Manual 2002 (Proposed Standard Practice for Surveys on Research and Experimental Development, OECD 2002):

FIELDS OF SCIENCE AND TECHNOLOGY

1. NATURAL SCIENCES

1.1 Mathematics and computer sciences [mathematics and other allied fields: computer sciences and other allied subjects (software development only; hardware development should be classified in the engineering fields)]

1.2 Physical sciences (astronomy and space sciences, physics and other allied subjects)

1.3 Chemical sciences (chemistry, other allied subjects)

1.4 Earth and related environmental sciences (geology, geophysics, mineralogy, physical geography and other geosciences, meteorology and other atmospheric sciences including climatic research, oceanography, vulcanology, palaeoecology, other allied sciences)

1.5 Biological sciences (biology, botany, bacteriology, microbiology, zoology, entomology, genetics, biochemistry, biophysics, other allied sciences, excluding clinical and veterinary sciences)

2 ENGINEERING AND TECHNOLOGY

2.1 Civil engineering (architecture engineering, building science and engineering, construction engineering, municipal and structural engineering and other allied subjects)

2.2 Electrical engineering, electronics [electrical engineering, electronics, communication engineering and systems, computer engineering (hardware only) and other allied subjects]

2.3. Other engineering sciences (such as chemical, aeronautical and space, mechanical, metallurgical and materials engineering, and their specialised subdivisions; forest products; applied sciences such as

geodesy, industrial chemistry, etc.; the science and technology of food production; specialised technologies of interdisciplinary fields, e.g. systems analysis, metallurgy, mining, textile technology and other applied subjects)

3. MEDICAL SCIENCES

3.1 Basic medicine (anatomy, cytology, physiology, genetics, pharmacy, pharmacology, toxicology, immunology and immunohaematology, clinical chemistry, clinical microbiology, pathology)

3.2 Clinical medicine (anaesthesiology, paediatrics, obstetrics and gynaecology, internal medicine, surgery, dentistry, neurology, psychiatry, radiology, therapeutics, otorhinolaryngology, ophthalmology)

3.3 Health sciences (public health services, social medicine, hygiene, nursing, epidemiology)

4. AGRICULTURAL SCIENCES

4.1 Agriculture, forestry, fisheries and allied sciences (agronomy, animal husbandry, fisheries, forestry, horticulture, other allied subjects)

4.2 Veterinary medicine

5. SOCIAL SCIENCES

5.1 Psychology

5.2 Economics

5.3 Educational sciences (education and training and other allied subjects)

5.4 Other social sciences [anthropology (social and cultural) and ethnology, demography, geography (human, economic and social), town and country planning, management, law, linguistics, political sciences, sociology, organisation and methods, miscellaneous social sciences and interdisciplinary , methodological and historical S1T activities relating to subjects in this group. Physical anthropology, physical geography and psychophysiology should normally be classified with the natural sciences].

6. HUMANITIES

6.1 History (history, prehistory and history, together with auxiliary historical disciplines such as archaeology, numismatics, palaeography, genealogy, etc.)

6.2 Languages and literature (ancient and modern)

6.3 Other humanities [philosophy (including the history of science and technology) arts, history of art, art criticism, painting, sculpture, musicology, dramatic art excluding artistic "research" of any kind, religion, theology, other fields and subjects pertaining to the humanities, methodological, historical and other S1T activities relating to the subjects in this group]

2. FINAL REPORT ON THE DISTRIBUTION OF THE EUROPEAN UNION FINANCIAL CONTRIBUTION

This report shall be submitted to the Commission within 30 days after receipt of the final payment of the European Union financial contribution.

Report on the distribution of the European Union financial contribution between beneficiaries

Name of beneficiary	Final amount of EU contribution per beneficiary in Euros
1. KUL	50 000 Euro
2. UCL	50 000 Euro
Total	*100 000 Euro*