Final Report Summary - M4CO2 (Energy efficient MOF-based Mixed Matrix Membranes for CO2 Capture)

Executive Summary:
This report covers the work performed in the M4CO2 (MOF-based mixed matrix membranes for CO2 capture) project and the final conclusions, carried out under the EU framework-7 program by a consortium of groups from academia, research institutes and industry with complementary expertise.

The M4CO2 project targeted the development of cost-effective (=energy-efficient) membranes for CO2 capture from both pre- and post-combustion coal based processes meeting the European SET-plan targets of 90% CO2 recovery at costs less than 25 Euro/MWh or better. The principal approach was applying high performance composite mixed matrix membranes based on polymeric materials modified with nanoparticles of metal-organic framework (MOF) materials.

Unique theoretical modeling and experimental in-situ spectroscopic techniques have been developed which provided significant understanding and insight in the interaction between nanoMOFs and polymers.
and how they affect membrane performance. In addition, a unique key performance indicator was developed based on the wealth of characterization information.

For both applications, three composite membrane generations and related materials have been developed successfully, reaching pre-defined target performances. Based on these developments the materials for the two proof-of-principle prototypes were selected, scaled up and hollow fiber (HF) membranes were developed, scaled-up, and produced by industrial partners and technology institutes. The scale-up of HF membranes and implementation into a module turned out challenging, and requires further development. The performance of a prototype of the most promising second-generation membrane for both applications did not meet the lab-scale results, but was stable over a longer period.

Innovative conceptual process designs indicate that the SET targets can be met for pre-combustion (<20 Euro/ton CO2), while for post-combustion capture costs could be reduced to ~28 Euro/ton CO2. Life cycle assessments (LCA) confirm a far more favorable (lower) environmental impact of these energy efficient membrane applications than classical scrubbing techniques, the recommended EBTF benchmark cases.

The project has seen a large dissemination activity. 58 scientific papers have appeared in international scientific journals, also 51 contributions to international conferences were submitted, and a final dissemination meeting was organized back-to-back with the EuroMOF-2017 conference. The results of the project were published in a downloadable brochure.

In conclusion, this project constitutes a successful development of a new energy efficient CO2 capture technology from TRL-1 to TRL-4. This technology will be further developed in a follow up H2020-NMBP project (MEMBER) targeting TRL-7 level.

Project Context and Objectives:
The M4CO2 project aimed at developing and prototyping Mixed Matrix Membranes based on highly engineered Metal organic frameworks and polymers (M4) for energy efficient CO2 Capture in power plants and other energy-intensive industries, both for pre-combustion and post-combustion applications. The developed highly selective high flux membranes should allow CO2 capture at prices below 15 €/ton CO2 (≈ 10-15 €/MWh), amply meeting the targets of the European SET plan (90% of CO2 recovery at a cost less than 25€/MWh).

By applying the innovative concept of M4 by a consortium of world key players, continuous separation processes of unsurpassed energy efficiency should be achieved because:

i) membrane separation, in contrast to other relevant technologies, does not require a gas-liquid phase change, reducing the energy penalty and resulting in smaller CO2 footprints, and
 ii) gas separation membrane units are safer, environmentally friendly and, in general, have smaller physical footprints than other types of plants like amine stripping.

In this way, this project aimed at a quantum leap in energy reduction for CO2 separation with associated cost efficiency and environmental impact reduction.

In order to achieve these objectives, new membranes needed to be developed. Despite the superior
In order to achieve these objectives, new membranes needed to be developed. Despite the superior performance of membranes based on purely crystalline materials like zeolites or metal organic frameworks (MOFs) polymeric membranes rule the commercial scene thanks to their easy processing and mechanical strength. By developing optimized M4s, it should be possible to combine the best of both worlds:

i) easy manufacturing,
ii) high fluxes per unit volume
iii) high selectivity through advanced tailoring, thereby breaking the so-called Robeson upper bound that hampers advancements in pure polymeric membranes.

The main barriers that were addressed were the optimization of the MOF-polymer interaction and selective mass transport through the composite. This is very challenging because chemical compatibility, filler morphology and dispersion as well as polymer rigidity all play a key role. Innovatively, the project planned to the first systematic, integral study into this type of membranes with investigations at all relevant length scales; including the careful design of the polymer(s) and the tuning of MOF crystals targeting the application in M4s.

The key objective of the project was to provide MOF based mixed matrix membranes that outperform current technology for CO2 capture and meet the targets of the European SET plan. This was underpinned experimentally as well as through conceptual process designs and economic projections by the industrial partners.

A platform approach was constructed around the proposed M4 concept:

First Phase (months 1-12): most of the R&D was focused on the main components of the M4’s and on the preparation and initial screening of 1st generation composite membranes, the core of the M4CO2 project. The objective was to obtain as much information as possible on their achievable performance and their potential.

Second Phase (months 13-24): the development of 2nd generation composite membranes, integrating components developed within the project entered its testing stage. At the Mid-Term-Assessment Clause (month 24) only the two most interesting 2nd generation composites were selected for further prototype development purposes.

Third Phase (months 25-46): the 2nd generation membrane prototype development was undertaken to prove the achievement of the overall project objectives. In parallel, 3rd generation membranes will be developed at lab scale during this phase.

The following targets were set for the development of the various M4CO2 components, with an approach exploiting basic science and cutting edge technologies:

- Identification of the most interesting MOF – polymer couples for their use in M4.
- MOF tuning at the particle level, this involves:
  o the preparation of MOF nanoparticles
  o the MOF surface functionalization: synthesis of core-shell fillers
  o the synthesis of hierarchical MOF nano-fillers combining meso and micro-pores
  o the control of MOF particles with extreme aspect ratios (lamellae)
- The development of new high flux polymers bearing tailored functional groups to optimise polymer-MOF interactions.

- The optimization of membrane preparation conditions:
  - Flat sheet, lab scale MOF membranes
  - Langmuir-Blodgett model ultra-thin membranes
  - Hollow fiber (HF) M4s with thin separating layers for real application
- Gaining insight into the separation performance and into the physicochemical properties of the new composites under working conditions
- The development of accurate engineering models based on experimentally determined fundamental parameters to describe permeation through the selected types of M4
- The thorough economic evaluation and conceptual process designs for the real life applications of the new membranes

After successful completion, this extremely ambitious program should constitute a breakthrough for membrane technology in a broad sense, not only from the application but also from the fundamental point of view. It should provide separation technology with a new class of unrivalled hybrid membranes.

Project Results:
WP2: Synthesis

UEDIN was focused on enhancing selectivity via increasing the rigidity of the PIM polymer chain. A key strategy was the use of methanopentacene as the structural component, for which molecular modelling showed that both the short methano-bridged bicyclic system and the greater contribution from aromatic rings enhanced rigidity. The synthetic route to PIM-MP-TB proved remarkably simple from commercially available reactants in only three steps.

Polymer PIM-MP-TB proved soluble in chloroform and could be cast into robust films. Initial analysis showed that selectivity was enhanced over that of similar TB-based PIMs containing ethanoanthracene for O2/N2 and H2/N2 gas pairs, presumably due to its greater rigidity, but its ideal gas performance was unremarkable for CO2/N2 or H2/CO2. Mixed gas measurements planned by ITM may be more interesting.

UEDIN synthesized new TB monomers, which gave high molecular mass polymers following TB polymerization. These polymers have yielded high quality self-standing films suitable for gas permeability measurements and have been sent to ITM for analysis.

In addition, UEDIN has optimized the synthesis of PIM-TMN-Trip, which has previously shown exceptionally high values of CO2 permeability (>30000 Barrer) and moderate selectivity. A paper describing the remarkable ultrapermeability of PIM-TMN-Trip (denoted as PIM-BTrip-cy-6 in earlier report) with 2-dimensional polymer chains (Fig. 1) was published in Nature Materials (2017, 16, 932) and highlighted in an accompanying News and Views article (Nature Materials, 2017, 16, 880) and as a news article in Chemical and Engineering News (2017, 95(32), 6). Further elaboration of the 2D-PIM concept was achieved by the synthesis of PIM-HMI-Trip, which shows slightly improved performance over PIM-TMN-Trip due to the enhanced rigidity of its hexamethylindane (HMI) substituents. Attempts to improve the CO2 selectivity of these 2D ultrapermeable PIMs, by reduction of the nitrile groups to introduce amine functionality, has been performed successfully. Ideal gas measurements show that CO2/N2 selectivity is enhanced, however, the benefit of the –NH2 functionality may only become apparent, for mixed gas permeability studies which are to be performed at ITM, as was the case for reduced PIM-1.

A novel polymer was finally prepared using the highly rigid structural unit dibenzomethanopentacene (DBMP) formed using TB polymerization. The gas permeability of films of TB based polymer PIM-DBMP
Polymer inclusion into large pore MOFs has been studied to mimic PAF-1 (Porous Aromatic Framework) anti-ageing property observed on some PIMs. USTAN worked on PCN-224(Zr) and prepared some MMMs with PIM-1; aging data will be acquired with time. CNRS-ILV/IMAP proposed several alternative MOFs to PAF-1 with two new tetracarboxylate MOFs denoted MIL-177 (Ti-mdip) and MIL-179 (Zr-mdip) possessing large accessible channels in the structures (1.1 nm and 1.3 nm respectively) along with the MIL-101(Cr) which has already produced promising results with PIMs. These films demonstrated accelerated aging (e.g. PCO2 reduced from >20 000 Barrer to 15 000 Barrer within days) but maintained this high permeability for over 200 days. This may be evidence of ageing modulation by the physical cross-linking by trapping of the polymer chains within the large windows provided by these MOFs.

Enhancement of performances through Post-Synthetic Modification (PSM).

USTAN developed a post synthetic modification (PSM) strategy to give superior water stability by reacting different amines with the aldehyde functionality of the imidazole linker (ZIF-94(Zn)). This produced negligible change in adsorption properties and maintained the nm sized particles (<200 nm). External surface modification was studied by CNRS-ILV/IMAP on MIL-100(Fe) and ZIF-8. Short chains (10 or 100 monomers) of PEG were grafted at the surface of the nanoparticles while maintaining the porosity for MIL-100(Fe). Such a functionalization of the outer surface of the MOFs seems to provide a better affinity with polymers, e.g. PVA (see WP4 for more results). Also, modification of the promising second generation MIL-91(Ti) has been achieved by USTAN using a linker with an additional methyl group to reduce the pore size and so the diffusivity of small molecules. MIL-91(Ti) doped with 10% showed a steady decrease in adsorption while the 100% Me-form was non porous. In this way it is possible to increase the selectivity of the MIL-91(Ti) structure without significantly reducing the CO2 uptake. Finally, an opportunity arose for USTAN to follow the rate of uptake of CO2 in crystals of ZIF-78 and Zn(nIm)2 prepared in this project by synchrotron IR microcrystal studies at the Diamond Synchrotron. These studies indicated that CO2 uptake in even large ZIF crystals is very rapid of the order of seconds and this method offers a route to direct measurements of CO2 diffusion in MOFs of relevance to MMMs.

UNIZAR worked also on the synthesis of MOF-MOF core-shell materials: ZIF-8/ZIF-7 and ZIF-93/ZIF-11. The idea was to use ZIF-8 nano-sized particles of 150 nm (or ZIF-93 of ca. 70 nm) and attach ZIF-7 (or ZIF-11) as precursor to be crystallized in the proper solvent. A conversion of ZIF-8 into ZIF-7 via post-synthetic modification with blm was monitored and the reaction kinetics calculated leading to a wide variety of hybrid frameworks, being the ones containing 10 and 44% blm the most promising. These materials were applied for membrane fabrication in WP4. PBI based MMMs at 20 wt% loading were tested obtaining an important augment of H2 permeability together with a huge increase of selectivity H2/CO2 up to 10.1 (at 180°C and 3 Bar). This is the best H2/CO2 separation result obtained within M4CO2 for pre-combustion with dense MMMs. ZIF-7 was synthesized in its three forms ZIF-7-I, ZIF-7-II and ZIF-7-III. The denser phase, ZIF-7-III, more interesting for H2/CO2 separation, was obtained after additional exfoliation and sent to WP4 partners.
The synthesis and characterization of several new water stable Fe, Ti or Zr polycarboxylate MOFs has been carried out by CNRS-IMAP/ILV. The crystal structures of porous Zr tetracarboxylate MOFs MIL-178 and MIL-179 were successful solved leading to either a 3D cubic microporous architecture or an hexagonal 1D large pore material, respectively. Their synthesis conditions were finally optimized using green solvents. Series of narrow pores Zr dicarboxylate MOFs based on aliphatic linkers, including aminoacids with free pending basic NH2 groups suitable for CO2 capture, were also discovered. Their structures are still under investigation while their synthesis (green) conditions have been optimized. Note that two patents have been filed in 2017 accordingly and a third one is to be filed. The room temperature synthesis of new hydrothermally stable Fe polycarboxylate MOFs bearing free COOH groups has been developed leading to a microporous 1D coordination polymer with a high CO2/N2 selectivity (>150) and a new phase whose structure is still unknown but highly porous (~1000 m2/g). More recently new mesoporous Zr-MOFs based on commercial dicarboxylic acids have been obtained with a large variety of functionalized linkers bearing polar or apolar groups. Finally, two new porous Ti-MOFs based on formic acid or trimesic acid have recently been isolated and their characterizations are under progress. First sorption tests indicate that these solids possess a high CO2/N2 selectivity above 100.

CNRS-ICGM explored the crystal structure solution/prediction of 3rd generation MOFs using a recent computational toolbox they recently developed which is based on the Automated Assembly of Structure Building Units (AASBU). This approach was successfully applied to a series of existing MOFs and the structure resolution of a few novel Zr-based MOFs incorporating short-linkers (succinic, aspartic...) was assisted by this computational effort. A step-further consisted of predicting the CO2/CH4 and CO2/N2 separation performances of these novel solids. In addition to this, CNRS-ICGM performed DFT-calculations to assist the structural revisit of the Al-based MIL-96(Al) that was supported by an intensive experimental characterization effort combining X-ray diffraction and NMR from CNRS-ILV/IMAP.

Layered MOFs were studied both by USTAN and UNIZAR with ZIF-7-III(Zn) which is non-porous to CO2 (suitable for pre-combustion) and stable in humid conditions. The syntheses of layered zinc benzimidazolates was achieved in order to selectively allow permeance of smaller molecules, such as H2 over CO2, with the aim of subsequent exfoliation for inclusion in membranes. The work on the reported Zn2(OH)BzIm3 (right) has resolved details of the structure of this material and shown that the material adsorbs CO2 slowly. If this was not possible to produce nanosheets of ZIF-7-III, UNIZAR reported a successful exfoliation by using DMAc and multiple sonication steps. NTU-9, more prone to post-combustion CO2 capture, was studied by CNRS-ILV/IMAP for exfoliation tests. Al-pda compound, a new Al pyrazole dicarboxylate material isolated previously, of interest due to its scalable synthesis in water, excellent thermal and water stability, large surface area (SBET~1500 m2/g) and a good selectivity of CO2/N2 (>20) was obtained with particles of 200-400 nm in diameter and then as platelet-like nanoparticles below 50nm in average. Similarly TUDelft reported MIL-53(Al)-NH2 nanoparticles, nanorods and microneedles as well as carried out the synthesis optimization of Cu-BDC nanosheets. The XRD pattern and TGA analysis of scale-up synthesis were compatible to the related characterization of small-scale synthesis. In comparison with the small-scale nanosheets preparation, reported previously, the yield of scaled up reaction was slightly lower (~5%, instead of the ~8% for the small-scale production), probably because of a loss of more products during the washing procedure in scale up synthesis, compared to the small-scale route.

A work on morphology control was done on MIL-96(Al) by CNRS-ILV (microrods, nanorods, hexagonal platelets, nanospheres) leading to nanospheres of MIL-96(Al) of 70 or 200 nm. Very small particles of MIL-140A Br could also be obtained by decreasing the synthesis time and using more concentrated solutions.
MIL-140A-Br could also be obtained by decreasing the synthesis time and using more concentrated solutions. Finally UNIZAR synthesized ZIF-11 nanoparticles (36±6 nm) via a centrifugation based synthesis route.

JM carried out the synthesis optimization and scale-up of selected second generation nanoMOFs. JM led experimentations to improve the synthetic concentration of the four second generation MOF materials. ZIF-94 and MIL-91(Al) were shown to produce phase pure nano-MOF materials at 1.5 times and 2.0 times initial concentration respectively. Above these concentrations impurity phases were detected by PXRD. Increasing the reaction concentration for the synthesis of MIL-69(Al) proved to be non-trivial. At low concentrations, the synthesis was shown to be irreproducible with mixed phase samples being produced, further work on this MOF is continuing.

MIL-140A-Br was successfully produced at 2.0 times initial concentration. This allowed for the scale-up of MIL-140A-Br in a single synthesis, producing enough pure phase nano-MOF to fulfil JM’s commitment of 30 g to collaborators at TECNALIA.

The pH of the reaction mixture of MIL-91(Ti) presented problems during the scale-up but was overcome with the help of USTAN (December 2016). USTAN developed also new methods of syntheses (mild solvents, reaction conditions) for MIL-91(Al) and ZIF-94(Zn) passed on to JM for scale-up.

The MOF MIL-91(Ti), was initially dropped from the 2nd generation MOF list due to difficulties in producing the material. Work on the synthesis was completed at USTAN and MIL-91(Ti) was successfully produced at JM. Current work is focused on improving the reaction concentration before test scale-up.

WP3: Fundamentals and Characterization

WP3 links materials synthesis (WP2) and membrane development (WP4-6). The main objective of this WP is to obtain fundamental information about the interactions between the two components (polymer and MOFs), the fundamental thermodynamic (heats of adsorption, working capacities, selectivities) and kinetic (diffusivity) properties of these individual components and their composites with respect to single gases and mixtures.

Which MOFs are suitable for integration into a mixed matrix membrane?

This question has been asked at the start of this project and indicators have been able to be established in order to choose materials for upscale and testing. This approach has been refined at the CNRS-Marseille in order to be more adapted to the particular case of membranes. Indeed, the results obtained from the approach where working capacities, selectivities and adsorption heats are combined has led to the identification of a number of MOFs of which the majority have been further tested and incorporated into membranes. Apart from the initially identified MIL-53(Al)_NH2, other materials of interest have been highlighted as MIL-96(Al), MIL-91(Ti), MIL-69(Al), ZIF-94 and Zn(2-nlm)2. When factoring in the effect of water on CO2 uptake, it would seem that the MIL-96(Al) material is of particular interest.

A deeper investigation of the interactions between the target molecules and MOFs of potential interest has been undertaken at BAS-Sofia. The acid-base nature of the available surface has been probed with a number of molecules. More specifically, the CO2 adsorption has been followed and the effect of water on CO2 uptake equally studied for some materials. Notable results include the identification of strong adsorption sites for CO2 on MIL-91(Ti) and the possibility for CO2 to displace water in the MIL-96(Al).

Further results have been obtained with materials such as STA-26, ZIF-93(Zn), MIL-81(Fe), MIL-53(Al).
Further results have been obtained with materials such as STA-26, ZIF-93(Zn), MIL-61(Fe), MIL-53(Al).

The study of mixture gas adsorption on identified materials has been studied at UMONS. Notably in the case of the MIL-96(Al) material, CO2/N2 selectivities in the order of 30 were measured both at 1 bar and 3 bars. These values are in good agreement with predicted selectivities using general relationships (IAST) obtained with the single gas isotherms. Further mixture experiments were carried out with other novel materials such as MIL-160(Al), Al-pda, Fe-btc and MIL-69(Al).

The group at CNRS-Montpellier have used molecular modelling methods to reconstruct various MOF-polymer interfaces. This has been carried out in order to try and understand the structure at this crucial part of the membrane. Various effects have been observed including (i) poor connectivity leading to voids, (ii) polymer penetration into the pores of the MOF and various intermediate behaviours between these two extremes. A rationalization of the various studies has led to beliefs that it is the rigidity of the polymer that plays an essential role concerning the effectiveness of this interface.

Experimental work has accompanied these numerical studies and this has been carried out at UNILEIP using IR microimaging. In this study a ZIF-8/6FDA-DAM membrane was taken and clear microvoids have been observed for several areas. CO2 was observed to accumulate in these microvoids.

This work has helped WP3 in constructing membranes and has led to the development of novel methodologies for MOF incorporation including the use grafting with organic functions on the exterior of the MOF crystals for example.

A further question that can be asked is to what size or shape of MOF crystal should be incorporated into the membrane. UNILEIP has used modelling to predict the effect of these parameters on transport through the membrane. Depending on the separation mechanism required, different filler aspect ratios have shown to be optimal. The effect of crystal size has equally been carried out experimentally with respect to gas uptake (CNRS Marseille) and the external surface may play a significant role on CO2 uptake.

Operando testing conditions of mixed matrix membranes has been carried out at CNRS-Caen. It has been shown that adsorption is highest on the membranes for which permeability is also high. Conversely, low permeating polymers did not adsorb much CO2. This would suggest that adsorption is thus a necessary step for permeation. In the membranes explored, water impurities most often have a negative effect on CO2 permeability but conversely a slight positive influence on the CO2/N2 selectivity. The methods developed have allowed the relative contribution of MOF and polymer to CO2 adsorption to be evaluated using the ratios of CO2 adsorbed on the MOF vs. that adsorbed on the polymer. Of the several influences observed, it is of note that the MOF have always the highest contribution to the overall adsorption, largely above the contribution of the polymer. Further impurities such as O2 and SO2 were also tested, specifically on a ZIF-94 40%/6FDA-DAM. Oxygen did not impact the membrane performance, neither in a dry feed gas nor with 1% H2O in the feed. SO2 only slightly lowered the permeability.

WP4: Fundamentals of Membrane preparation, performance and modelling

The main objective of this WP is the development of laboratory mixed matrix membranes (MMMs) for CO2 capture. The work is structured in four tasks, relating to membrane synthesis, membrane characterization,
The work is structured in four tasks, relating to membrane synthesis, membrane characterization, and membrane gas separation performance testing and modelling. WP4 collaborates with other WPs from the consortium, such as WP2, which provides new materials for the membrane synthesis. Besides, there are also interactions with WP3 and WP5 through the characterization of composites and the comparison of separation performance with hollow fiber membranes. With the results from WP4, the best MOF-polymer couples will be selected for prototyping in WP6.

Three membrane generations were prepared as flat membranes (with self-supported and asymmetric supported configuration) with different MOF and polymer generations provided from WP2. The study of asymmetric flat membranes and thin film composites has become more relevant in this period with the aim of fabricating films with reduced selective thicknesses to achieve the pre- and post-combustion targets.

Among the different membrane developments the following stand out:

1. The fabrication of PBI MMMs embedding more than 20 different MOFs by UNIZAR (from 1st, 2nd and 3rd generation fillers (MIL-61(Fe), MIL-69(Al); MIL-140A_Br, MIL-140A_NO2, MIL-96(Al) and Fe/1,2,4-BTC, from CNRS-IMAP/ILV; ZIF-93, MIL-91(Al) and ZIF-III in the form of spheres and plates, from USTAN; and ZIF-7 (phases I, II and III) and ZIF-7-III exfoliated, ZIF-8 (three different particle sizes), ZIF-11, nanoZIF-11 and the core-shells ZIF-7/8 (with sod structure) and ZIF-11/93 (with rho structure), synthesized at UNIZAR). The best performing materials correspond to ZIF based MMMs, specifically the ZIF-7/8 core-shell filler (J. Mater. Chem. A, 5 (2017) 25601-25608, see also Deliverable 4.9 for a better description of the optimization of the preparation conditions of for 3rd generation polymers and MMMs).

2. The study of the influence MOF topology (four different types of MOF with 1D, 2D & 3D pore structure, i.e. NH2-MIL-53(Al), MIL-96(Al), MIL-69(Al) & ZIF-94) on 6FDA-DAM and Pebax MMMs, by TUDELFT (J. Membrane Sci. 550 (2018) 198-207).

3. The fabrication of membranes with novel polymers of intrinsic microporosity (PIMs) acting as efficient molecular sieves. A large number (>60) of dense pure polymer and MMM films were prepared at UEDIN and sent to ITM for gas permeation. Third generation polymers include the 2D ultrapermeable polymers PIM-TMN-Trip, PIM-HMI-Trip and highly rigid polymers PIM-MP-TB and PIM-DBMP-TB. MMM films were prepared comprised of PIM-1, PIM-EA(Me)-TB, PIM-EA(H)-TB and the ultrapermeable PIM-TMN-Trip including Ti-mdip, MIL-101(Cr), MIL-61, PCN-224[Zr] and MIL-177 (MOFs mainly provided by USTAN, JM or CNRS-IMAP/ILV).

4. The preparation of PBI/PIM-EA-TB blending membranes containing ZIF-8, by UNIZAR and films comprising the mixed polymers PIM-1&Matrimid® (called PIMAT) and NH2-MIL-53(Al), MIL-96(Al), MIL-69(Al) & ZIF-94(Zn) and Cu-BDC nanosheets, by TUDELFT.

5. The validation of MMMs for pre- and post-combustion for 3rd Round-Robin (R-R) testing, involving UNIZAR, TUDELFT, ITM, LUH and CNRS-CAEN. 20 wt% Fe-1,2,4-BTC and PBI were selected for H2/CO2 whereas ZIF-94 and 6FDA-DAM for CO2/N2. UNIZAR prepared the membranes for pre-combustion while TECNALIA did for post-combustion. The conditions for the measurements were arranged between the partners to ensure comparability and reproducibility. The R-R tests demonstrated a fair agreement between the different teams, generally with differences near or below 25%. The discrepancies may be due to: a) membrane reproducibility/handling, b) use of different membrane modules, c) differences between the experimental setups, d) different membrane testing conditions (see Deliverable 4.11). A more exhaustive study was published regarding the 1st R-R testing (J. Membrane Sci. (2016) 45-53).

6. The study of modelling membrane modules and simulating the effect of hydrodynamics in modules with...
The study of modelling membrane modules and simulating the effect of hydrodynamics in modules with different flow patterns and establishing models to predict the permeability and selectivity of MOF/polymer MMMs, by TUDELFT and CNRS-ICGM (see Deliverable 4.8 and Milestone MS7).

In addition, novel procedures for MMM fabrication were developed in the project:

1. Preparation of ultrathin films: a) Langmuir Blodgett (LB) films by depositing PIM-EA-TB monolayers (1 nm each) on top of PTMSP dense membrane by Langmuir-Schafer technique (LS, i.e. horizontal deposition of Langmuir films), by UNIZAR. Composite membranes with a selective PIM-EA-TB layer only 30 nm thick (i.e. only 0.04% of the PIM dense membrane content) present CO2/N2 selectivity values close to the dense PIM membranes; with CO2 permeances 7 times higher (ChemSusChem, 10 (2017) 4014-4017; see also Deliverables 4.7 and 4.10). b) Thin film nanocomposite (TFN) membranes of ZIF-8/polyamide (<100 nm) by interfacial polymerization onto P-84® support, by UNIZAR, task not initially planned but yielded very good, next to the target performance for H2/CO2. c) Thin membranes by spin coating of pure and MMMs comprising MIL-96 and 6FDA-DAM/Matrimid® solutions (> 450 nm) on glass and then transferred to PAN support, by TUDELFT. While CO2/N2 selectivity remains constant, a significant enhancement in permeance was achieved.

2. The simple preparation of a new membrane architecture called PSPMs (Polymer Stabilized Percolation Membranes) with high loadings (90 wt%), initially with ZIF-8, MIL-140A, zeolite X, consisted of a pressed/condensed filler phase, by LUH (Chem. Eur. J. 23 (2017) 6522-6526; patent EP17151687.5). New membranes based on narrow pore MOF scandium chloro-terephthalate (Sc2(BDC-Cl)3, from USTAN were studied for CO2/N2, while ZIF-7/8 core-shell, from UNIZAR, was used for H2/CO2 obtaining a clear enhancement of selectivity.

3. Preparation of ZIF-8/PIM-1 colloidal suspensions by mixing modified MOF particles and PVA, by CNRS-IMAP/ILV. In addition, short chains of PEG were selective grafting on the outer surface of MIL-100(Fe) and ZIF-8 to enhance the compatibility between MOF particles and the polymer (ACS Appl. Mater. Interfaces 8 (2016) 27311–27321).

4. The fabrication of ZIF-8 PBI asymmetric MMMs with ca. 1 µm selective thickness, by UNIZAR. A broad study of the optimization conditions using a range of dope concentrations (15-26 wt% PBI in DMac) was done. The membranes, repaired when needed with PDMS for defect healing, were submitted to high temperature (250 ºC) and pressure (6 bar feed) obtaining extraordinarily high selectivities. This was explained due to the saturating effect of the CO2 adsorption while H2 constantly increase with pressure (paper submitted to J. Membr. Sci.).

Conclusions
For post-combustion, membranes using 6FDA-DAM as polymer achieved CO2 permeabilities above the Milestone MS8, hugely increasing when employed PIM series. However, with membranes based on Pebax the CO2/N2 target selectivity was managed with the consequent reduction on the permeability. MOFs such as MIL-96 or NH2-MIL-53 proved that the effect of the polymer in their performance is more accused. In pre-combustion application, highly permeable membranes (with permeabilities above the Milestones MS9) are obtained with PIMs and PBI, the latter being more favored when testing at higher temperatures (up to 250 ºC) and pressures (up to 6 bar). The best results in dense membranes arise when using a 3rd generation functionalized ZIF (ZIF-7/8 core-shell) or with the Polymer Stabilized Percolation Membrane system (PSPMs). Fortunately, when reducing the selective thickness in the form of TFN membranes and asymmetric PBI membranes the targets for MS9, both in terms of permeation and selectivity, were managed. The overall status of WP4: in line with the DoW and in time.
WP5: Development and Testing of M4 Hollow Fibers (M25-48)

The main objective of WP5 was the development and characterization of first and second generation mixed matrix asymmetric hollow fiber membranes (M4 HFs) for pre- and post-combustion CO2 capture. This implies on one hand the development and screening of suitable porous hollow fiber membranes to be used as support in the coating process. On the other hand, the identification of proper spinning parameters and dip-coating conditions for the preparation of dual layer hollow fiber membranes and composite hollow fiber membranes respectively. The best HFs have been selected to prepare the HFs for the prototype on WP6.

Mixed matrix asymmetric hollow fiber membranes have been prepared with commercially available polymers and polymers synthetized by consortium partners (UEDIN). MOFs have been supplied by consortium partner (JM).

M4 HFs were prepared by two different strategies. The first strategy is direct spinning of dual layer MM HF membranes where both the support and the selective layer of the fiber are prepared in a single operation (Tecnalia). On the second strategy, supported composite membranes were prepared in two steps. First the porous support is spun and after that the support is dipcoated to form a dense separating layer (ITM, Polymem and Tecnalia). Porous metallic supports were developed for pre-combustion CO2 capture and porous polymeric support for post-combustion CO2 capture.

ZIF-8 and MIL\textsubscript{140A}(Zr)\textsubscript{Br} containing PBI hollow fibers were spun with a polymer supplied by PBI Performance Products. An increase on H2 permeance was observed by the addition of the MOF for single layer M4 hollow fibers. Single and dual layer hollow fibers with PBI polymer in both the inner and outer layer were fragile and difficult to handle. To overcome this issue inner polymer was replaced by P84. ZIF-8 MIL\textsubscript{140A}(Zr)\textsubscript{Br} containing dual layer HFs were prepared. Obtained dual layer HFs were mechanically more resistant. Moreover, good adhesion between inner and outer layer was observed. However, lower permeances than the previous M4 PBI hollow fibers were obtained due to the high resistance to gas transport of the P84 support.

A new PBI has been purchased, Fumion AP PBI powder from Fumatech, with a higher molecular weight than the earlier used PBI from PBI Performance Products. The hollow fibers prepared by the new PBI show a better mechanical resistance than the ones prepared with the previous PBI. The improvement in the mechanical resistance of the fibers allows preparing dual layer fibers with PBI in both the inner and outer layer, and therefore reducing the resistance to gas flow of the inner support. Few dual layer spinning were performed with the new PBI, composed of an inner layer of PBI and an outer layer of 20 wt% of ZIF-8. Dual layer PBI/PBI fibers with good mechanical resistance were obtained. H2 permeance was improved regarding P84/PBI dual layer fibers. However, selectivity is quite low. Spinning parameters need to be further modified and tuned to obtained defect free fibers. More spinning sessions are needed for that purpose.

The second strategy for pre-combustion consists in using porous metal supports for the MMMs. Experimental work was performed for depositing a mixed matrix membrane layer directly on the metallic support, i.e. without the intermediate gutter layer. This approach is considered to be feasible given the relatively large size of 2nd generation MOF (MIL-140-Br) of 200 nm. We considered that the MOF will not penetrate into the 2 micrometer pores of the support fiber and a layer might be formed directly on the
penetrate into the 2 micrometer pores of the support fiber and a layer might be formed directly on the surface. We based this consideration on the tortuosity of the support and asymmetry of the MOF particles. For the proof of principle vacuum assisted dip coating experiments have been carried out using dispersions of bare MIL-140-Br in ethanol (no polymer) at different vacuum levels, by the consecutive layer deposition approach. A defect-free layer mixed matrix layer has been obtained (0.71 GPU H2 and H2/CO2 selectivity of 15).

Several polymers and MOFs were used for post-combustion CO2 capture. P84 polyimide fibers containing UIO-66-COOH particles and 6FDA-DAM containing NH2-MIL-53 (Al) particles were prepared by the first strategy of direct spinning. Pebax and PIM based composite hollow fiber membranes were prepared following the second strategy. An automatic system was used for the external coating of the fibers that are partially immersed in the coating solution and extracted at a constant velocity. The supports were PAN support for PIM based M4 HFs and PSU-based ultrafiltration for Pebax based M4 HFs. The M4-HFs were developed using PIMs supplied by UEDIN and the commercial copolymer polyamide-polyethylene oxide, referred to as Pebax® 1657, that meets the project objective in terms of selectivity. Pebax® 1657 polymer was the selected polymer for the preparation of the fibers of the prototype and therefore it was further studied by the addition of MOF particles. The MOFs (ZIF-94 or MIL-91) were loaded at a concentration up to 27 wt.%. Gas permeation tests confirm the achievement of defect-free layers for the coated M4-HFs with Pebax®1657 and upon the addition of ZIF-94 or MIL-91 (coating layer of ca. 1 micron). The nanoZIF-94 are capable of increasing the gas permeance with respect to the HFs produced with the neat polymer. Pebax based composite fibers present a smaller permeance than the one expected for the deposited layer thickness. For instance, pure Pebax® 1657 composite fibers had a permeance of 10-15 GPU while 76 GPU was expected. This could be due to a relatively low surface porosity, which is inherent to all porous hollow fibers and limits the surface of active film. The proposed solution to overcome this issue was to incorporate a highly permeable gutter layer between the support and the active layer to collect all the permeate coming from all the surface. PSU porous support was first coated with a layer of PDMS (gutter layer) and then a layer of Pebax 1657 was deposited. The performance of the new membranes went from 10-15 to >100 GPU. The best membrane obtained with a PSU hollow fiber covered by a 1-2 µm of PDMS and coating by a 0.5 µm of Pebax had a permeance of 123 GPU and a CO2/N2 selectivity of 48.

Conclusions
Permeance was improved at almost constant selectivity by the addition of the filler in both pre- and post-combustion CO2 capture. In case of pre-combustion, a selectivity close to the targeted one was obtained. The targeted selectivity value for the fibers could be reached by the increase of testing temperature, as demonstrated by dense film permeation study performed on WP4 at temperatures as high as 250ºC. In the case of post-combustion CO2 capture developed M4HFs can be classified in two categories: high permeable and low selective membranes (PIMs and 6FDA-DAM based M4) and high selective and low permeable membranes (P84 and Pebax based M4). In the first category targeted permeance values were reached, while in the second category targeted selectivity was reached.

The research activity on Life Cycle Assessment (LCA) of post-combustion CO2 capture based on membrane separation was performed on WP7. CO2 capture based on membrane separation was accomplished in a dual stage membrane system. Two membranes with complementary separation properties were selected for investigation: a polymer with a relatively low CO2 permeability, but a high CO2/N2 selectivity and another polymer with an excellent CO2 permeability and lower selectivity. It was
It was demonstrated that a CO₂ capture system combining a highly permeable membrane (e.g., PIMs or 6FDA-DAM based M4) with a highly selective membrane (e.g., Pebax based M4) provides the best compromise between environmental impacts. Future research activities will be devoted to the improvement of M4 permeance in both pre- and post-combustion CO₂ capture. The following promising approach has been identified in each separation process: in the former case a new PBI candidate has been identified, which will allow preparing mechanically resistant PBI M4 single layer HFs or dual layer HFs using PBI both in the inner and outer layer of the fiber, overcoming the issue related to the high resistance to gas flow of the inner porous substructure. In the latter separation process, the use of a PDMS gutter layer was demonstrated to be a promising approach. Using the gutter layer theoretical permeance of the Pebax layer can be reached.

On the other hand, third generation materials have been identified for hollow fiber module manufacture (milestone M12). Material selection was performed based on MOF scalability and separation performance of dense MMMs prepared on WP4 with these materials. Best performing dense MMMs were based on the following materials and therefore are the identified third generation materials for hollow fibers: PBI polymer / ZIF-8/ZIF-7 hybrid material for pre-combustion CO₂ capture and Pebax 1657 polymer / MIL-96 (Al) for post-combustion CO₂ capture.

WP6: Membrane Prototyping and long term Testing

The work package 6 did experience experimental and technical challenges related to the manufacturing of the hollow fibres. As a result, the delivery of the first and second batches of hollow fibres were delayed by 4 and 1 month, respectively.

Tecnalia has prepared the three batches of dual layer hollow fibres by the dry jet, wet quench method. The first batch consisted of an inner layer of P84 (thickness of 113µm) and an outer layer of 10wt% of ZIF-8 in PBI (thickness of 27µm). The second batch was composed of an inner layer of P84 and an outer layer of 10wt% of MIL-140A(Zr)_Br in PBI (thickness of 21µm). Finally, for the third batch a different PBI than that used for 1st and 2nd batch was used for fibre production, PBI from Fumatech; it has a higher molecular weight and therefore a higher mechanical resistance, which allows using the same polymer both in the inner and outer layer of the hollow fibre. The third batch dual layer fibres are composed of an inner layer of PBI and an outer layer of 20wt% of ZIF-8 in PBI. The fibres of all three batches were defect healed by dip coating with a 3wt% PDMS solution in hexane. Crosslinking of the PDMS was performed at 100°C for 24 h. In total, 200, 250 and 220 fibres were produced, also a lab-scale module was prepared by Tecnalia for TU-Delft containing first batch type hollow fibres. The fibres were tested at Tecnalia for mixed gases at 150°C and 114 psia; the following results were achieved:

- Batch 1: H₂ permeance 14.5 GPU, H₂/CO₂ selectivity 11;
- Batch 2: H₂ permeance 25 GPU, H₂/CO₂ selectivity 12;
- Batch 3: H₂ permeance 52 GPU, H₂/CO₂ selectivity 6.4

Hollow fibres for post-combustion were prepared by ITM by dip-coating of porous hollow fibre support in a solution containing the components for the active layer. Based on the work carried out in WP5, the
solution containing the components for the active layer. Based on the work carried out in WP5, the operating conditions for coating of the external surface with PEBAX® 1657 have been identified; solution with 3 wt.% of Pebax dissolved in EtOH/H2O (70/30 wt/wt), constant withdrawal velocity = 500 mm/min, atmosphere at Room T and RH=50% and T solution = 25-30 °C.

The first batch consisted of PSU-based HFs with a PEBAX® 1657 coating. The second batch consisted of PSU-based HFs with a PEBAX® 1657 coating containing 27wt% nanoZIF-94 as filler. The third batch was similar to the second batch with the intent to add a silicone-based protective layer by Tecnalia before module making. During transport from ITM to Tecnalia the fibres were damaged. In total 100, 100 and 100 fibres were produced. Some fibres were tested at ITM for single gases at 25 ºC prior to shipment; the following results were achieved:

Batch 1: CO2 permeance 11 GPU, CO2/N2 selectivity 46.5
Batch 3: CO2/N2 selectivity ca. 70

Modules of length of 560mm and 660mm were manufactured respectively for post- and pre-combustion. The module shell is composed of a stainless steel pipe of 1/2 inch with Swagelok-T fittings at its two ends. Fibres were incorporated into the tube. After potting step with epoxy resin, the two ends of the modules are cut in order to reveal the lumen of the hollow fibres. For each module the potting integrity is checked up to 0.5 bar.

Modules have been made from the three batches of hollow fibres for post-combustion. For pre0combustion only fibre batches 1 and 2 were used as the third batch hollow fibres were very corrugated, which made them not possible to use.

At HyGear and TU-Delft an experimental facility has been set-up to test pre-combustion hollow fibre modules. At HyGear full size modules, whereas at TU-Delft one (batch 1) small size, small scale module. At HyGear the performance of a pre-combustion membrane module is tested using a slipstream of the off-gas line of the PSA sub-system of a HyGear hydrogen generator system, Hy.GEN. At TUD the module is tested in a lab environment.

At TOTAL an experimental rig for studying the post-combustion CO2 capture by continuous permeation method has been build.

At TU Delft the performance of the hollow fibre module provided by Tecnalia was assessed and evaluated up to a temperate of 200 oC and 10 bar. Under this condition, the hollow fibres can effectively separate H2 from CO2 with a H2 permeance of ca. 28.5 GPU (1 GPU = 3.35 ×10−10 mol m−2 s−1 Pa−1) and a H2/CO2 selectivity of approximately 9.5. Both the permeance of H2 and CO2 increased with temperature. This is probably due to the enhanced gas diffusivity. The enhancement of H2 permeance is higher than CO2, due to a decreased sorption of CO2, resulting in an improvement of selectivity.

By increasing the feed pressure from 5 to 10 bar the permeability and selectivity remained constant which confirmed the good sealing of the module together with non-defective structure of the HFs. The adsorption isotherms of the ZIF-8, PBI and HFs at 423 K represent the enhancement in CO2 adsorption properties of the pure membranes by loading the ZIF-8 particles in PBI.

The first module tested at HyGear proofed not to be gas tight. During the initial characterisation tests the second module showed a nitrogen permeance of 65 GPU.
At TOTAL three modules were received and tested. The first generation module \{PSU + Pebax\} was received in May 2017. Due to its poor performances \((S \text{ CO}_2/\text{N}_2 = 2)\) compared to those measured at ITM on a single hollow fibre, testing was stopped and the module was sent back to Polymem for investigation. The second generation module \{PSU + Pebax + ZIF94\} was received by May 2017. Even though its performances were lower than expected \((S \text{ CO}_2/\text{N}_2 = 8)\), testing phase was pursued with short tests as well as a long testing period (over 2 months), which was a key objective of M4CO2 project. The endurance test showed an almost stable performance during 2 months of testing. The selectivity was constant, and the permeance only showed a slight decrease, -10%.

The third generation module \{PSU + Pebax + ZIF94 + PDMS\} was received by mid October 2017. After initial testing at Total’s facilities, it was decided to not pursue testing as the performance was very poor (selectivity of 1.2 only).

WP7: Life Cycle Analysis and economic assessment

During the last period M25-48, the WP7 partner have consolidated their models to deeply evaluate both costs Capex and Opex using M4CO2 membranes and optimized plant design for pre-combustion and post-combustion.

In the meantime, from the 2 optimized designs the partners have finished the Life Cycle Assessment and have compared them with the current carbone capture i.e. Selexol for pre-combustion and Amine absorption for post combustion.

Pre-combustion: Based on analysis of the 536 MWe coal-fired IGCC power plant and on a multi-criteria evaluation the most cost-effective process for CO2 capture consisting of syngas upgrading (WGS) and membrane separation in three stages has been designed.

The scope of the design comprised identification of the most suitable configuration of the separation process, design of process equipment with an emphasis on hollow fibre membrane modules, techno-economic evaluation of the process leading to a removal of 90% of highly pure CO2, sensitivity analysis underlying the recommendations for the future development of the membranes and life cycle assessment of the membrane based capture process.

A pressure of 110 bar is advantageous for the process economics due to more efficient separation and smaller equipment size. The optimal design using state of the art membrane is estimated to result in CO2 capture costs of 15.6 €/t. This corresponds to a reduction of plant efficiency from 42.9% to 39.2% (39.5% at 35 bar operation and 18.2 €/t). Simulations with membranes of a wide range of permeability and selectivity indicate that the capture costs can be more effectively reduced by increasing the H2/CO2 selectivity to at least 20 than by increasing the permeability. Increasing the selectivity further beyond 30 does not bring any remarkable benefit to the costs.

Post-combustion : Considering as case study the CO2 capture from the flue gas of a coal-fired power plant \((x\text{CO}_2=13.5\%)\), simulation results confirmed that single stage membrane systems are not able to reach the target for CO2 transport and storage \((CR=90\%, y\text{CO}_2=95\%)\). Assuming a capture ratio of 90%, the maximum CO2 permeate purity is around 70-80% in the case of PolyactiveTM1500, with the maximum value attained with a partial permeate recirculation \((RC=60\%)\). In order to increase the CO2 purity of
value attained with a partial permeate recirculation (RC=60%). In order to increase the CO2 purity of permeate stream, a dual-stage membrane system was definitely chosen.

Setting as design conditions CR=90% and yCO2=95%, two main options were envisaged. The one combining a PIM-1 membrane at the first stage and a PolyactiveTM1500 at the second stage allows to provide the minimum area requirement (28.1*10^3 m^2), while that based on PolyactiveTM1500 at both stages the minimum specific energy requirement 347.1 kWh/tonne). The research activity on conceptual design also investigated the potential for improving energy performances of dual stage membrane systems, by using 3rd generation polymeric membranes and varying pressure ratio across membrane stages and system layout. Simulation results highlighted that membrane area and specific energy requirement drastically reduce for an increase of selectivity αCO2/N2 up to 100. Less significant is the potential improvements of higher selectivity values. Furthermore, it exists an optimal membrane pressure ratio, allowing to minimize the specific energy requirement and the penalty on power plant efficiency. A further improvement in energy performances can be achieved eliminating the energy recovery system at second stage and reducing the pressure ratio of downstream membrane unit accordingly. Assuming a PolyactiveTM1500 membrane at both stages, the minimum specific energy requirement is reached for a pressure ratio of around 23 and states at less than 300 kWh/tonne, thus enabling a plant efficiency penalty of 8.5% pts (equals 22% of the design efficiency of 38.2%) and specific CO2 emissions of around 110kg/MWh. Moving to a selectivity αCO2/N2 of 200, specific energy requirement reduces to 240kWh/tonne, while plant efficiency penalty and specific CO2 emissions remain to 7% pts and 105 kg/MWh. In the case of CO2 capture from a natural gas boiler, the lower CO2 molar fraction in the exhaust flue gas (xCO2=8.7%) involves an increase of specific energy requirement of around 30% (395.5 kWh/tonne) and 25% (298.3 kWh/tonne) for a PolyactiveTM1500 and an improved membrane selectivity (αCO2/N2=200), respectively.

Simulation results revealed that in the case of CO2 capture from a coal-fired power plant, the dual-stage membrane system combining a high permeable membrane (PIM-1) and a high-selective membrane (PolyactiveTM1500) allows to minimize the specific cost of CO2 capture (33 €/tonne). On the other side, when a reduction in membrane thickness is considered, the configuration based on PolyactiveTM1500 at both stages becomes the best option (28 €/tonne). Focusing on the last configuration and assuming an increase of membrane selectivity to 200, cost of CO2 capture approaches a minimum value of 20 €/tonne. In the case of CO2 capture from a gas boiler, cost of CO2 capture states at around 50 €/tonne, even in the case of an improved membrane. This is due to the reduced CO2 molar fraction in the exhaust flue gas, allowing for an increase of specific energy consumption, and to the increased specific cost of system equipment.

Life cycle assessment for pre- and post-combustion
The process of CO2 capture has been designed for a coal-fired IGCC power plant with electricity to coal efficiency of 42.9 % and a net power output of 536 MWe without capture, operated 7450 hours per year. The annual capture capacity corresponds to 2.8 Mt of CO2. Battery limits of the CO2 capturing process are given by the feed of clean, desulphurised syngas and, at the outlet, by a hydrogen-rich fuel gas stream used in power generation island and the stream of captured CO2. Within the capture process syngas is upgraded by means of a water gas shift reaction, compressed, then hydrogen is separated and CO2 concentrated in a two-stage membrane separation process. Subsequently, most of the CO2 is condensed at elevated pressure and ambient temperature and remaining hydrogen in the uncondensed gas is...
at elevated pressure and ambient temperature and remaining hydrogen in the uncondensed gas is recovered in third membrane stage. The rest is burned, cooled and CO₂ is recovered in a low temperature condenser.

The Life Cycle Assessment (LCA) utilising MOF-based membrane indicates a smaller impact in all categories compared to the Selexol capture process. For instance, the relative impacts on human health, resource depletion and exo-toxicity are reduced by factor of 2.2 indicating a substantial improvement. The relative environmental impacts caused by membrane application and by burning coal in a power plant with capture results in a ratio of the two burdens of approximately 104.

Post-combustion: Life cycle emissions of post-combustion capture based on membrane separation were evaluated assessing their sensitivity to the variation in membrane material and thickness of the dense active layer. Then, environmental impacts of CO₂ capture based on membrane separation were compared to monoethanolamine (MEA) absorption, considering the commercial Fluor Econamine FG Plus technology as a reference. Simulation results highlighted that life cycle emissions of CO₂ capture based on membrane separation process were strongly related to membrane material and thickness of the dense active layer, influencing the net power consumption and membrane area requirement. Membrane configurations investigated allowed to reduce to such an extent environmental impacts compared to CO₂ capture based on monoethanolamine (MEA) absorption. The greatest reduction potential was observed for human toxicity and impacts on freshwater and marine ecosystems, because of the elimination of environmental concerns related to solvent manufacturing and disposal of amine reclaimer wastes.

Potential Impact:
The main potential impact of the project was to create a novel separation route for CO₂ containing gas streams that is cheaper than the ones currently available by using membrane technology. This way, the whole separation of CO₂ process could be made more cost (and energy) efficient. With CO₂ separation being one of the main cost drivers for the implementation of carbon capture and sequestration (CCS) or carbon capture and utilisation (CCU), there is a lever to implement these in the technological advances of the M4CO₂ project.

The results of the project in separation performance and price per ton separated CO₂ approach the numbers in the SET plan. This indicates that the membrane technology can be a imaginable alternative for separation of flue gasses from power plants.

Furthermore, the knowledge and network created within the project, help to lift the scientific excellence of the partners from all over Europe within their specific fields of activities and beyond. The advances in knowledge also reflects in 58 peer reviewed publications and 51 contributions to scientific events all over the world. Noticeable were especially one publication in “Nature Materials” and a cover of “Angewande Chemie” by partners from the consortium with topics from the research agenda of the project.

The general public was addressed by press releases, contributions in newspapers (e.g. Heraldo de Aragon (Spain)) and by all information put of the public homepage www.m4co2.eu. A brochure, published in October 2017 and downloadable from the homepage, presents the most important results of the project.

Impact beyond the European Borders was especially made by the fruitful collaboration with the Australian twinning project “CO₂MOF”. Collaborators from both continents met regularly to discuss possible cooperation’s, like the exchange of samples and staff.
Cooperations, like the exchange of samples and staff. This cumulated into a joint dissemination workshop by both project, together with the European Project ProDIA, that was organised and held back to back with the European Flagship event on MOFs and porous polymers, the EuroMOF2017.

List of Websites:
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