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**"Carbon4PUR - Turning industrial waste gases (mixed CO/$CO_2$ streams) into intermediates for polyurethane plastics for rigid foams/building insulation and coatings"**

Research and Innovation Action

Topic: [SPIRE-08-2017] Carbon dioxide utilisation to produce added value chemicals

# Deliverable 5.5: *Pilot scale rigid foam fulfilling rigid foam specifications*

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# The Carbon4PUR Consortium

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| 2. | Recticel N.V. | Recticel | Belgium |
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| 4. | Universiteit Gent | UGent | Belgium |
| 5. | Universiteit Leiden | UL | Netherlands |
| 6. | Dechema Gesellschaft für chemische Technik und Biotechnologie e.V. | Dechema | Germany |
| 7. | Technische Universität Berlin | TUB | Germany |
| 8. | Commissariat à l'énergie atomique et aux énergies alternatives | CEA | France |
| 9. | ArcelorMittal Maizières Research SA[1] | AMMR | France |
| 10. | South Pole Carbon Asset Management Ltd.[2] | SPG | Switzerland |
| 11. | Grand Port Maritime de Marseille | MFPA | France |
| 12. | Rheinisch-westfälische technische Hochschule Aachen[3] | RWTH | Germany |
| 13. | PNO Consultants BV | PNO | Netherlands |
| 14. | Imperial College of Science Technology and Medicine | ICL | UK |

[1] At ArcelorMittal two legal entities are involved as linked third parties: ArcelorMittal Méditerranée (AMMED) and ArcelorMittal Belgium NV (AMB)

[2] At South Pole the following legal entity is involved as linked third party: South Pole UK (SP UK)

[3] At RWTH three departments are involved: *Chair of Fluid Process Engineering* (RWTH-AVT), *Catalytic Center* (RWTH-CAT), and *Chair of Communication Science & Human-Computer Interaction Center* (RWTH-COMM)

# Acronyms and Definitions

| Acronym | Defined as |
|---|---|
| **CO** | Carbon monoxide |
| **$CO_2$** | Carbon dioxide |
| **COOH#** | Acid number |
| **EO** | Ethylene oxide |
| **SA** | Succinic anhydride |
| **MDI** | 4,4′-Methylenebis(phenyl isocyanate) |
| **OH#** | Hydroxyl number |
| **PEG** | Polyethyleneglycol |
| **PIR** | Polyisocyanurate |

# Table of Contents

# 1. The Carbon4PUR project

Carbon4PUR aims at turning industrial waste gases (byproduct exhaust gas streams and flue gas streams of steel industry / mixed carbon monoxide (CO) / carbon dioxide ($CO_2$) / $CO/CO_2$ streams) into intermediates for polyurethane plastics for rigid foams/building insulation and coatings. The industrially driven, multidisciplinary consortium is developing a novel process based on direct chemical flue gas mixture conversion, avoiding expensive physical separation, thus substantially reducing the carbon footprint, and also contributing to high monetary savings. The interdisciplinary consortium consists of 14 partners from seven European countries (Germany, France, Belgium, The Netherlands, Greece, Switzerland and United Kingdom) and across sectors: four industries (Covestro Deutschland AG – short: COV, Recticel N.V. – short: Recticel, Viomichania Ritinon Megaron Anastasios Fanis Anonymos Etairia – short: Megara, ArcelorMittal – short: AMMR), five universities (Universiteit Gent – short: UGent, Universiteit Leiden – short: UL, Technische Universität Berlin – short: TUB, Rheinisch-westfälische technische Hochschule Aachen – short: RWTH, Imperial College of Science Technology and Medicine – short: ICL), one association (Dechema Gesellschaft fuer chemische Technik und Biotechnologie e.V. – short: Dechema), one research organization (Commissariat à l'énergie atomique et aux énergies alternatives – short: CEA), two service providers (PNO Consultants BV – short: PNO, South Pole Carbon Asset Management Ltd. – short: SPG) and the Grand Port Maritime de Marseille-Fos (short: MFPA).

Both the consortium and the work are organized along the full value chain starting with the provision and conditioning of industrial emissions from a steel *(AMMR, UGent)* to a chemical company *(COV)* in line with the concept of industrial symbiosis exemplarily at *Marseille Fos*, going through the transformation into chemical building blocks *(CEA, RWTH and COV),* which both will be further transformed into polymer intermediates *(RWTH, COV)* and flow into desired sustainable polyurethane applications of rigid foams and coatings *(Recticel, Megara)*. Life Cycle Assessment (LCA) and technology evaluation will be done *(UL, RWTH, TUB, SPG)* and replication strategies to transfer the technology to other applications will be elaborated *(Dechema, PNO, ICL)*.

The distinctive feature of the developed process is avoiding resource-intense separation of the gas components before the synthesis, and developing a chemo-catalytic process to deal directly with the gas mixture instead. The challenge and innovation is coming up with an adjustable process in terms of on-purpose and demand tailor-made production of required products, taking into account all variables at the same time: the available flue gases characteristic from the steel plant, material and process parameters, and the market requirements for the end product, thus flexibly involving the whole value chain with best results and possibly lower the prices.

# 2. Objectives and Overview

This deliverable refers to work package (WP) 5 which deals with further semi-industrial processing and tests of polyols based on the new Carbon4PUR CO technology. In lab-scale new CO-based polyols were successfully produced from CO-based anhydride in WP3. To accelerate the upscaling, commercial anhydride was used for the production of the semi-industrial scaled samples in WP4. Therefore, the resulting polyols do not yet contain CO. However, based on the lab-scale polyol production from CO-based anhydride in comparison to lab-scale polyol production from commercial anhydride, it can be assumed, that the polyols produced from CO-based anhydride and commercial anhydride do not differ. To distinguish the polyols, the commercial anhydride-based polyol is called polyol based on the new Carbon4PUR CO technology or in short Carbon4PUR polyol. The polyol produced from CO-based anhydride is called CO-based polyol.

The purpose of this deliverable is to report on the outcomes of Task 5.3 on the processing of sample polyols at Recticel on pilot scale in order to prove the suitability of the Carbon4PUR polyol in rigid foam application. Polyols were tested to produce polyisocyanurate foams, also referred to as PIR foams, which are thermoset materials and used mainly as rigid thermal insulation.

Before performing the large scale semi-industrial trials, many hand-mix trials were performed for initial screening of different polyols and to obtain crucial information about the behaviour of polyols during foaming reaction. Hand-mix trials are simple and straightforward tests that are performed in the laboratory in small scale, but they are essential to acquire an initial feeling about the performance of the tested raw material. As depicted in Figure 1a, polyol mixture containing other components of the formulation such as surfactant, catalyst, blowing agent etc. is mixed with the isocyanate in a container and the resulting mixture is vigorously mixed for a short period of time before it is poured into a wooden mold. The foam starts to rise immediately after and fills the mold to have the final shape as shown in Figure 1b. Therefore, during the first stage of the project, nine different polyols produced by Covestro were tested in hand-mix trials to assess the performance of the polyols at laboratory scale. The formulations were tested to optimize the concentration of Carbon4PUR polyol in the formulation and quantities of formulation components were fine tuned to be able to have reference system comparable foams. It was seen that up to 70% of the standard polyol can be replaced by Carbon4PUR analogue in laboratory scale samples and higher surfactant levels were required. Use of Carbon4PUR polyol more than 70% replacement of the standard polyol deteriorated the properties, therefore 70% was chosen as the highest use level. Taking into account the different nature of the Carbon4PUR polyols compared to standard polyol and based on earlier experiences with analogue polyol substitutions, it was not expected to reach an exchange range of 70% with such experimental polyols. These small-scale tests allowed us to designate two promising polyols to be further tested in semi-industrial setting to produce PIR based insulation boards.

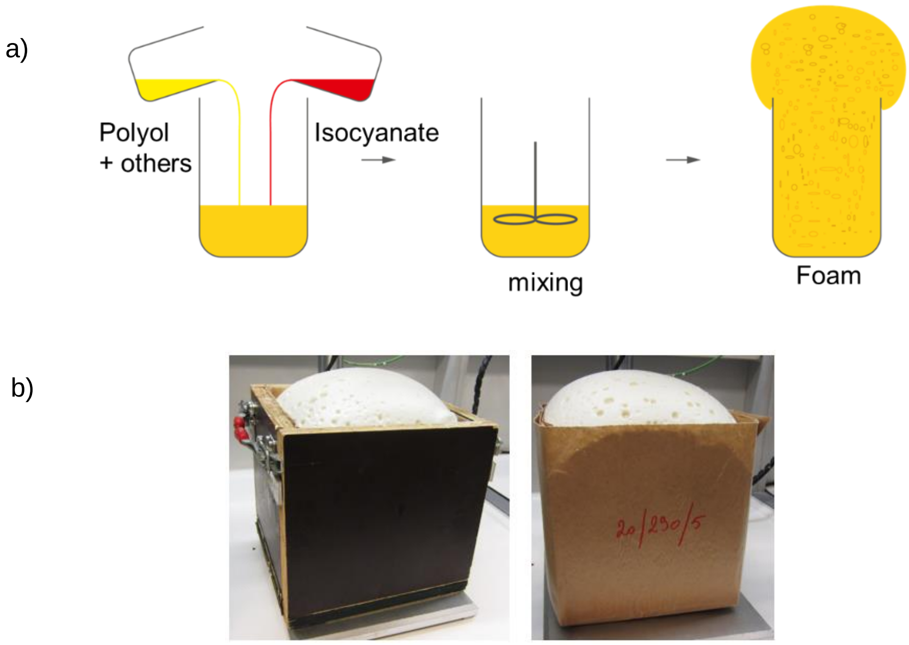


**Figure 1**: *a) Simple illustration of handmix foaming process;* b) *Wooden mold (left) to produce handmix laboratory sample in brown paper (20x20 cm) (right).*

Initial semi-industrial trials were performed by using two different polyols. One of the polyols was based on succinic anhydride – ethylene oxide (PEGSAEO) chemistry whereas the other one was based on succinic anhydride – glycol (PEGSA) chemistry. It was seen during these semi-industrial trials that PEGSAEO-5 based system displayed substantial mixing problems when processed under semi-industrial conditions. The resulting foams were not homogeneous due to this issue observed. PEGSA-5 based polyol system was found to be more promising in terms of processing. The evaluation performed on the properties of the resulting foams showed that the several key properties, e.g., thermal conductivity, were still not in-line with the reference system. Although not all the properties were met, it was still possible to produce insulation boards by using Carbon4PUR polyols as 70% replacement of the standard polyol system.

**Figure 2:** *Pictures of boards produced during pilot trials*

As a result of internal discussions held, it was decided that the compatibility of the PEGSA-5 polyol needs to be improved and hence requires further optimization. Therefore, further work on the improvement of the PEGSA-5 polyol was performed by Covestro. It was seen that the introduction of a stabilizer additive into the polyol improves the compatibility. Hence, the modified PEGSA-5 polyol was further tested in laboratory scale to verify the properties of the resulting foams are fulfilling the requirements.

As a continuation, PEGSA-5 modified with a stabilizer additive was received in large scale to perform semi-industrial trials in order to produce rigid PIR based insulation boards. In order to assess the performance of the Carbon4PUR polyol, two different concentrations were selected to be tested. Therefore, trials were performed by using 60% and 70% of Carbon4PUR polyol as a replacement of the standard polyol system and formulation was adapted to contain higher surfactant levels. It was seen the adapted formulation was substantially better in terms of mixing compared to previous trials on pilot scale. Further details about the trials and the properties are provided below.

# 3. Rigid foam semi-industrial trials

Carbon4PUR polyol is tested in the formulation as a partial replacement of the standard polyol. Based on previous trials, Carbon4PUR polyol modified with a stabilizer additive was used.

## 3.1 Formulations

***Table 1:*** *Carbon4PUR polyol sample received for semi-industrial trial*

| Sample name | “CO”$_{theo}$ [wt.-%] | Components | OH# [mgKOH/g] | COOH# [mgKOH/g] | Viscosity [mPas] at 25°C | Sample size [kg] |
|---|---|---|---|---|---|---|
| Modified PEGSA-5/1 | 28 | SA + diol | 213 | 0.4 | 2730 | 347 |

***Table 2:*** *Carbon4PUR formulations used for trials*

| Component | Parts |
|---|---|
| Standard polyol | 40 or 30 |
| Carbon4PUR polyol | 60 or 70 |
| Surfactant | 5 |
| Other components | 40 |
| Polymeric MDI | Index: 320 |

*Formulations are based on 100 parts of total polyol content. Density is kept around 31 kg/m$^3$.
**Carbon4PUR polyol: PEGSA-5/1 is modified with a stabilizer additive to improve compatibility.

Small adjustments on catalyst and blowing agent levels were done to have similar reaction and density profiles.

## 3.2 Processing

Processing of the formulation to produce rigid foam insulation boards is an important part of the overall operation. Formulation components, e.g. polyol, isocyanate etc., are separately transferred from their corresponding storage tanks by means of high pressure pumps to a mixing head where mixing of the formulation components take place. The pressures reached to achieve a proper mixing in the mixing head are more than 100 bar which is crucial to obtain a homogeneous mixture of all formulation components. The final reaction mixture that is containing all the components is then laid down on a moving double belt conveyor. The foam is sandwiched between two facers moving simultaneously with the conveyor to form the final insulation board. The board enters into a curing chamber where the temperature of the double belt and the surroundings are around 55°C - 70°C to assure a proper curing of the foam components. The board is then cut into the desired size by means of a cutting tool at the end of the curing period.

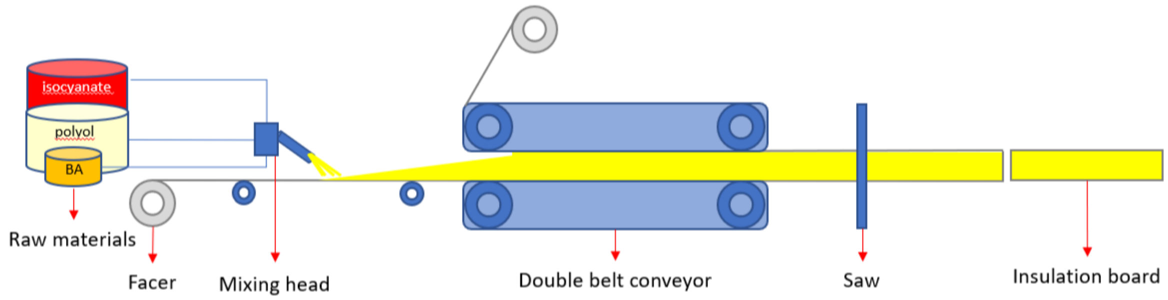


***Figure 3:*** *Representative sketch of a double belt conveyor system.*


***Figure 4:*** *Picture of an insulation board produced during semi-industrial trials (width:1.2 m; length:6 m).*

Carbon4PUR polyol is chemically distinct from standard polyol systems commonly used for rigid foam production. Therefore, the behaviour of the polyol in a semi-industrial setting is not alike. Hence, it was seen that the processing with 60% Carbon4PUR polyol composition was smoother compared to 70% Carbon4PUR polyol formulation. The main processing differences observed during the trials with Carbon4PUR polyol were lack of sufficient mixing of the components and the tendency to over expand. The mixing issues observed with Carbon4PUR system was overcome by introducing higher surfactant levels into the formulation. Other processing issues observed were handled by playing with processing parameters such as conveyor speed, dosing output and reaction profile. As a result, insulation boards were produced successfully.

## 3.3 Properties

Properties of the resulting foams are important for the final performance of the insulation board. Therefore, various properties are tested in order to verify whether the requirements are fulfilled. Mechanical, fire, and dimensional stability plus thermal conductivity are along the vital properties to have a quality board. The comparison of the foam properties are provided below where reference formulation does not contain any Carbon4PUR polyol.

***Table 3:*** *Properties of the boards produced*

| Sample / Property | Reference | Carbon4PUR – 70% | Carbon4PUR – 60% |
|---|---|---|---|
| **Compressive strength** | | | |
| **Tensile strength** | | | |
| **Dimensional stability** | | | |
| **Under extreme conditions** | | | |
| **Flammability** | | | |
| **Thermal conductivity** | | | |
| **Normality** | | | |
| **Water absorption** | | | |

: good  : slightly worse, but above required specifications  : worse

Compressive strength, dimensional stability and stability under extreme conditions are various physical tests performed in order to verify the mechanical properties of a foam under certain conditions. These are measured on a foam sample cut in certain dimensions from the board produced and provides information about the ability of the material to withstand loads and bear stresses. Due to changes in outside temperatures, e.g. summer or winter times, during the service life of an insulation board, the external and internal pressures acting on the foam differs substantially. Hence, these mechanical properties become a crucial property so that the foam stays stable under changing conditions during its service. Another important test performed on the foams is the flammability test. The foam is exposed to a flame source for a certain period of time and the response of the foam is recorded for classification. The final result will provide valuable information about the fire safety of that insulation board. Main application purpose of an insulation board is related to its thermal conductivity and is vital for the insulation performance. Therefore, thermal conductivity is measured on the insulation boards cut in certain dimensions to verify this unique property. However, due to very long service life of an insulation board, e.g. 25 years, ageing studies are also conducted to verify that the board thermal insulation property will perform as promised even after long years. Then, normality test becomes a crucial property which relates the long term thermal insulation property of an insulation board. Within this context, considering that all the tested properties are important elements of the overall performance of the board, a comparison between different formulations has been made in Table 3. As it can be seen, the performance of Carbon4PUR formulations are comparable to the reference system. Slightly lower compression values were recorded for both Carbon4PUR formulations, but the values were above required specifications. Stability performance of 70% Carbon4PUR formulation under extreme conditions was slightly worse compared to reference and 60% Carbon4PUR formulations. All in all, the properties were found to be promising to be able to prove the suitability of Carbon4PUR polyol in rigid foam application.

The tests performed on the produced insulation boards with Carbon4PUR polyol allows us to verify that the properties recorded are fulfilling the requirements of rigid foam and are summarized in Table 4.

***Table 4:*** *Insulation board fulfilling the requirements of rigid foam*

| | Property | Norm | EN-code | Value | Unit |
|---|---|---|---|---|---|
| Carbon4PUR – 60 to 70% | **Thermal conductivity** | EN 13165 | $\lambda_D$ | 0.022 | W/mK |
| | **Normality** | EN 13165 | | ≤ 0.0060 | W/mK |
| | **Compression strength** | EN 826 | CS(10/Y)120 | ≥ 120 | kPa |
| | **Dimensional stability** | EN 1604 | DS(70,90)2 | ≤ 3 | change in length |
| | | | | ≤ 3 | change in width |
| | | | | ≤ 8 | change in thickness |
| | **Tensile strength** | EN 1607 | TR80 | ≥ 80 | kPa |
| | **Flammability** | EN 13501-1 | Euroclass | E | |

# 4. Conclusion and Outlook

Polyurethane/polyisocyanurate based insulation boards are among the best insulation products due to their superior performance which is essential to mitigate the energy consumption of buildings. However, it is of great interest to utilize sustainable raw materials for the production of such products without sacrificing their favorable properties such as low thermal conductivity. The Carbon4PUR project is dedicated to develop sustainable polyols which are one of the crucial components of a rigid foam formulation. Within this context, various polyols prepared within the framework of Carbon4PUR project were tested in rigid foam formulation in order to determine the promising candidates that can replace partially the standard polyol analogue. As a result of a series of hand-mix trials, possible candidates were selected to perform large scale trials on semi-industrial line. Consecutive semi-industrial trials showed that the 60% or 70% of standard polyol can be replaced by Carbon4PUR polyol to result in insulation boards fulfilling the requirements of rigid foam specifications. It is also worth mentioning that the processing with 60% Carbon4PUR formulation was observed to be smoother compared to 70% formulation. Considering the fact that replacement of any formulation component by different alternatives can become a long and tedious process, successful production of insulation boards containing the Carbon4PUR polyol proves the potential of sustainable polyols as a replacement of non-sustainable analogs currently in use. Further works on the enhancement of the chemistry of the Carbon4PUR polyol will pave the way for increased use levels in the formulations.