

# BioRECO<sub>2</sub>VER

## Biological routes for CO<sub>2</sub> conversion into chemical 'building blocks'

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### D2.4 - Packed-bed reactor using amine-ionic liquid -immobilized CAs blends for optimal capture of CO<sub>2</sub> from off gas

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Author(s)		
Name	Organization	Email
Io Antonopoulou	LTU	
Ulrika Rova	LTU	
Paul Christakopoulos	LTU	

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Internal reviewer(s)		
Name	Organization	Email
Metin Bulut	VITO	
Christopher vom Berg	Nova Institute	

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## 1 Executive summary

The goal of BioRECO<sub>2</sub>VER is to develop and validate the technical feasibility of more energy efficient and sustainable non-photosynthetic biotechnological processes for the capture and conversion of CO<sub>2</sub> from industrial point sources into valuable platform chemicals. One of the specific objectives of the project is the development and application of robust enzymes for CO<sub>2</sub> capture from industrial point sources and the improvement of a novel concept combining enzymatic absorption with ionic liquid-amine blends. It is aimed to achieve energy and cost reduction compared to the monoethanolamine (MEA)-based state-of-the-art technologies, increased resistance to major impurities and yield a concentrated gas stream of at least 95% CO<sub>2</sub>.

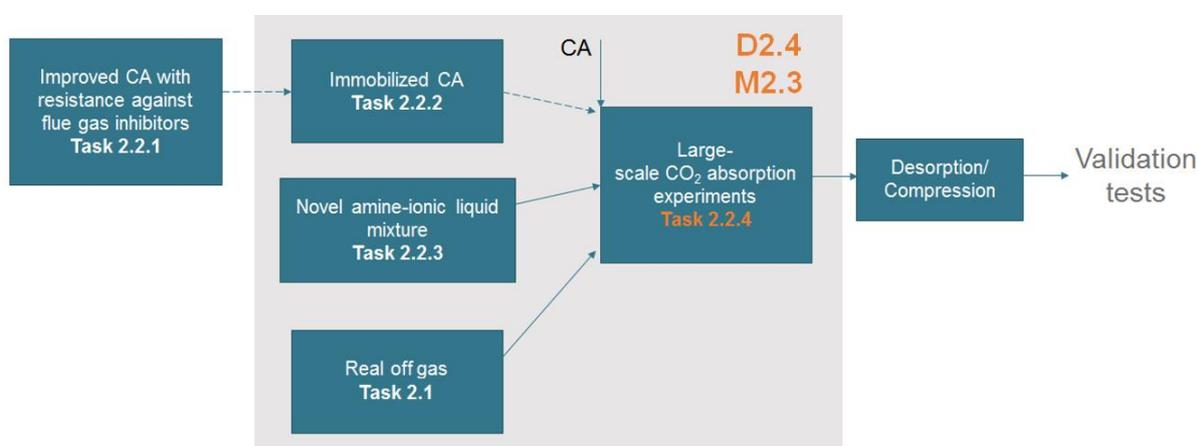
The objective of D2.4 was to demonstrate the operation of a packed-bed reactor using amine-ionic liquid-immobilized CAs blends for optimal capture of CO<sub>2</sub> from off gas. Scaling up of the CO<sub>2</sub> capture process using a packed-bed reactor requires the exploitation of the research outcomes of the project regarding CA improvement and the solvent development. The combination of CA with an MDEA-ionic liquid mixture would result in a ternary solvent with exceptional absorption properties compared to standard MDEA solvents and reduced regeneration temperatures compared to MEA-based technologies. Integration of immobilized and/or improved CA proved not to be a viable option for scaling up the CO<sub>2</sub> capture. Nevertheless, integration of CA in free form with an amine-ionic liquid mixture for the CO<sub>2</sub> capture from off gas using a packed-bed reactor on an automated absorption and stripping pilot plant, resulted in several fold higher absorption rates and CO<sub>2</sub> recovery compared to aqueous solution of MDEA. CA-assisted CO<sub>2</sub> absorption resulted in higher initial absorption rates, reduced absorption times and overall 25% higher CO<sub>2</sub> recovery compared to absorption using only the ionic liquid-amine blend. This would improve the economics of CO<sub>2</sub> capture technologies by reducing operation times and energy consumption due to regeneration, yielding a pre-treated concentrated gas stream of at least 92% CO<sub>2</sub>. The set-up is now ready to perform real off gas pre-treatment for validation testing during the project.

## 2 Introduction

Conventional CO<sub>2</sub> absorption processes are based on amine solvents. The current state-of-the-art for CO<sub>2</sub> capture is the primary amine MEA that is highly reactive and shows high absorption rates. However in turn, this results in high desorption temperatures (120-140°C) due to formation of carbamates, requiring high energy consumption for solvent regeneration. On the contrary, tertiary amines, such as MDEA, form bicarbonates requiring lower regeneration temperatures but suffer from significantly lower absorption rates. Blending amines and ionic liquids in aqueous solutions have shown promising results coupling advantages of both sorbents. In particular, introducing an amino functional group in ionic liquids by the use of an amino acid generates so called amino acid ionic liquids which, when blended with MDEA, have shown increased CO<sub>2</sub> absorption rates maintaining the good desorption properties of both solvents.

The enzyme carbonic anhydrase (CA) is one of the fastest enzymes known and catalyzes the hydration of CO<sub>2</sub>. Although CA is known to improve CO<sub>2</sub> absorption rates in aqueous methyldiethanolamine (MDEA) solvents, its use in industrial settings is often limited. High temperature and inhibitors forming and accumulating in the solvent during continuous CO<sub>2</sub> capture processes lead to degradation and/or inactivation. The development of a thermostable carbonic anhydrase with enhanced tolerance to off gas inhibitors and reusability potential is critical for the economical use of this efficient enzyme in conventional amine scrubbers. Directed evolution and immobilization are enzyme improvement strategies that have shown to increase the resistance of enzymes to harsh conditions. Immobilization of the enzyme could also facilitate a more efficient recycle and recovery of the enzymes contributing to a more economical process.

The objective of Deliverable D2.4 is the demonstration of operating a packed-bed reactor at optimized conditions for large scale CO<sub>2</sub> capture from real off gas using a novel ternary solvent comprised of amine, ionic liquid and immobilized CA. D2.4 is related to the activities performed in WP2 of the project (Figure 1).



**Figure 1** Overview of CO<sub>2</sub> capture activities in the BioRECO<sub>2</sub>VER project.

The general objective of Task 2.2 in WP2 is to develop a hybrid chemo-enzymatic CO<sub>2</sub> capture process with novel or improved enzymes in order to reduce energy demands and related costs in CO<sub>2</sub> capture processes. One of the key components for this task is the use of CA which is known to improve CO<sub>2</sub> absorption rates, particularly in aqueous solutions of MDEA by catalysing the hydration of CO<sub>2</sub> towards bicarbonate.

CA was improved by directed evolution in Task 2.2.1 and immobilized with various techniques in Task 2.2.2. One of the objectives of Task 2.2.3 was the integration of CA with conventional absorption using novel amine-ionic liquid blends at small (0.1 L) and large scale (up to 80 L). Since the start of the project:

- A CA mutant library was constructed and screening methods were developed and optimized.
- Extensive screening revealed several enhanced mutants of which three showed 50% increased resistance to selected off gas inhibitors compared to the original CA.
- Sequencing analysis was performed to confirm and characterize the produced mutants. Immobilization techniques were applied for further enhancing the stability and allow the reusability of CA.
- The first immobilization method chosen was cross-linked enzyme aggregates (CLEA). Influence of precipitant and cross-linker on the activity of CA was investigated where low concentrations of glutaraldehyde were giving the most promising results although a significant drop in residual activity was observed.
- Alternative cross-linkers and other immobilization methods were investigated, including adsorption, covalent binding and encapsulation.
- Different combinations of ionic liquids and tertiary amine were tested against appropriately defined evaluation criteria, such as high CO<sub>2</sub> absorption rates and load capacity, reduced desorption temperature and good enzyme compatibility.
- The most promising amine-ionic liquid aqueous mixture was tested in the presence of CA to further enhance the CO<sub>2</sub> absorption potential of the resulting solvent.
- The mixture offered approximately 5-fold higher initial absorption rate compared to MDEA and a 2-fold higher regeneration compared to MEA.
- Integration of CA in the mixture offered a 31.7% further increase in the mass of absorbed CO<sub>2</sub> and reduced absorption times compared to the absorption reaction using only the developed amine-ionic liquid mixture

The final Task 2.2.4 is focused on the upscaling of CO<sub>2</sub> capture where large-scale packed-bed absorption equipment at LTU is operated to selectively capture CO<sub>2</sub> and produce sufficient amounts of pre-treated CO<sub>2</sub> to be supplemented for adaptation and validation testing. The flow rate, temperature, pressure were optimized and compositions of CO<sub>2</sub> in the gas entering and leaving the absorber were measured and used for real-time mass balance calculations of percent carbon capture.

D2.4 is also related to Milestone M2.3 - Large-scale packed-bed absorption ready for CO<sub>2</sub> capture from real off gases for validation testing. D2.4 together with M2.3 were delayed by 5 months till Month 30, mainly due to unforeseen circumstances related to the COVID-19 crisis.

### 3 Packed-bed reactor for optimal CO<sub>2</sub> capture

The objective of D2.4 is the demonstration of a packed-bed reactor for optimal capture of CO<sub>2</sub> from off gas, exploiting research outcomes achieved in Task 2.2, regarding hybrid enzymatic CO<sub>2</sub> capture. For optimal CO<sub>2</sub> capture at large scale, a CHE626 automated absorption and stripping pilot plant (Figure 2A) accompanied by a CHE906 hot water generator (Figure 2B) were acquired (HFT Global Ltd, Derbyshire, UK). The pilot plant was placed under a ceiling-mounted fume hood with air flow rate of 92 L/s. Adequate safety measures have been adopted to ensure safe operations during experiments including personal protective equipment and online determination of air quality in the laboratory area. In this paragraph, the experimental set-up, operation mode and operation limits of the packed-bed reactor are presented.



**Figure 2** A) CHE626 Automated Absorption and Stripping Pilot Plant and B) CH906 Hot Water Generator (HFT Global Ltd, Derbyshire, UK) at LTU.

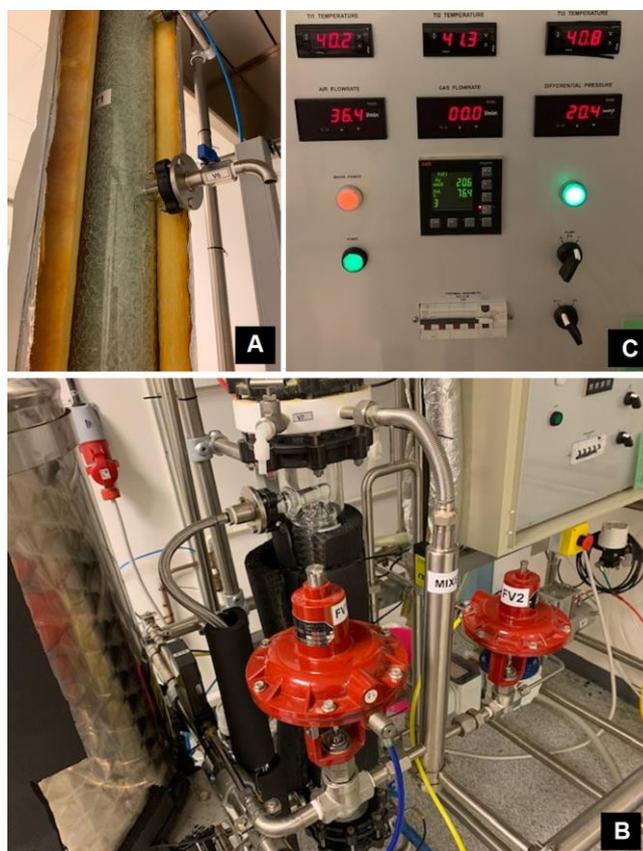
#### 3.1 Experimental set-up

The CHE626 absorption and stripping pilot plant unit includes a 1 m (ID 80 mm) glass column packed with Raschig rings (Figure 3A). Three thermocouples (TI1, TI2 and TI3) provide temperature measurements at the top, middle and bottom of the column. Solvent is pre-heated and heated during operation, maintaining a constant temperature of 40°C via a heat exchanger (E1): warm water is inserted from the CHE906 hot water generator system to E1 through a valve (V11). A manometer measures the pressure drop (PdI, mmH<sub>2</sub>O) in the column. CO<sub>2</sub> capture takes place at atmospheric pressure (1 bar) while the pressure drop in the column,

during the reaction, is monitored. Valves (V5, V6 and V7) are placed at different heights of the column for sampling.

The solvent is placed in a tank (TK1) with a maximum capacity of 80 L. During CO<sub>2</sub> capture, the solvent is fed to the column top by a pump (P1). Solvent and CO<sub>2</sub>-rich gas are contacted in the column in counter-current flow mode. The solvent exits the system at the column's bottom (valve V10). Gas can be inserted in the system by two different valves (V8 or V9) which provides the opportunity to create tailored-made gas mixtures. Each gas input is controlled by a flow meter (FT, FI, FC) equipped with a flow control valve (FV) (Figure 3B). During Task 2.2, different synthetic gas mixtures were tested by mixing commercial gases (AGA, Luleå, Sweden) at different proportions. In case the gas was already pre-mixed or industrial off gas was used, it was inserted through valve V8. After mixing, the gas enters in the middle section of the column where it is directed towards the column top, contacting the solvent. Given CO<sub>2</sub> amounts are absorbed by the solvent while residual gas exits the system from the column top. The output is directed through a tube to a CO<sub>2</sub>/O<sub>2</sub> analyser (Geotech G110, Geotechnical Instruments Ltd, Warwickshire, UK) for the online monitoring of the output gas composition. The calculation of mass balances during CO<sub>2</sub> absorption is made based on the known composition of input and output gas over time.

A PID controller is used to regulate solvent and gas flow rates and monitor pressure drop and temperature in the column. The parameters can be adjusted through a control panel (Figure 3C) or via a PC, using an acquisition software.



**Figure 3** A) Column packed with Raschig rings B) Flow-controllers of two gas inputs (FV1 and FV2) and mixer C) Control panel.

### 3.2 Modes of operation

The CHE626 automated absorption and stripping pilot plant can be operated by two different modes: continuous and batch. Continuous mode is simulated as the solvent is pumped from the tank (TK1) to the column top and is collected at the column bottom by opening valve V10 at fixed aperture (Figure 4). Fresh solvent is continuously fed to the column and CO<sub>2</sub> concentration of the output gas is recorded. After few seconds a steady state is achieved, as the CO<sub>2</sub> concentration in the output gas is stabilized at a fixed value. During steady state operation, the absorption rate is constant and does not change over time while the solvent is absorbing CO<sub>2</sub> at the maximum capacity given the applied flow conditions. Batch mode is achieved by recirculating the solvent through the column. To achieve this, V10 is connected to the back of the tank with a hose (Figure 4). The solvent that reaches the bottom of the column is fed back to the tank and then pumped again to the column top. The minimum solvent volume required for a batch experiment was determined to be 8 L. During recirculation, the initial absorption rate is observed to be constant until the whole amount of solvent has passed through the column while it starts decreasing over time, as the solvent is recirculated and gets saturated with CO<sub>2</sub>. The solvent is considered fully saturated when the CO<sub>2</sub> concentration of the input gas is equal to the CO<sub>2</sub> concentration of the output gas.



**Figure 4** CHE626 automated absorption and stripping pilot plant operating at batch mode (recirculation).

### 3.3 Operation limits

According to the manufacturer's instructions (HFT Global Ltd, Derbyshire, UK), gas flow rates in the pilot unit can be increased up to 50 L/min only when operating under low or medium solvent flow rates (0.7-1.48 L/min) (1). It is reported that the system can be operated at full capacity without flooding for solvent flow rates ranging between 0-3.73 L/min and gas flow rates ranging between 0-30 L/min at any combination (1) (Table 1). CO<sub>2</sub> absorption trials under different solvent and gas flow rates have been performed at continuous mode, using the developed amine-ionic liquid mixture as solvent and a commercial synthetic gas mixture (20% CO<sub>2</sub>, 80% N<sub>2</sub>, AGA, Luleå, Sweden) to validate the instructed limits. It was determined that a

maximum flow rate of 30 L/min (50% FI1) and a maximum solvent flow rate of 3 L/min solvent (76.4% P1) can be safely implemented for system operation without flooding.

**Table 1** Pressure drop Pdl (in mm H<sub>2</sub>O) at different gas and solvent flow rates.

Pressure drop Pdl (mm H <sub>2</sub> O)					
Gas flow rate FI1, 1 bar (NL/min)	Pump P1 flow rate (L/min)				
	0.77	1.48	2.25	2.96	3.73
20	7.6	10.9	14.9	15.3	22.8
30	12.4	16.3	22.0	21.0	47.8
40	23.0	37.4	47.0	65.2	Flooding
50	60	72.3	Flooding	Flooding	
60	Flooding	Flooding			

## 4 Optimal CO<sub>2</sub> capture from off gas using amine-ionic liquid-CA blends

### 4.1 Selection of CA form suitable for scale up of CO<sub>2</sub> capture

In the BioRECO<sub>2</sub>VER project, a thermostable CA was used for the development of a hybrid enzymatic CO<sub>2</sub> capture process. In particular, an evolved CA from the bacterium *Desulfovibrio vulgaris* has been selected ascribed to its (reported) exceptional properties regarding thermal stability (2). The increased thermal stability of this evolved enzyme makes it an important candidate for integration in conventional amine-based CO<sub>2</sub> scrubbing technologies, where absorption temperatures vary between 40-60°C (3).

Different strategies for further improving CA as biocatalyst were implemented. The two main improvement strategies for the enzyme performance were directed evolution and immobilization. Directed evolution resulted in three mutant forms with 50% increased resistance to selected inhibitors that are commonly found in industrial off gases (NO<sub>x</sub>, SO<sub>x</sub>). Immobilization using different techniques such as adsorption, covalent binding, cross-linked enzyme aggregates and encapsulation resulted in enzyme forms with good immobilization yield and residual activity. Immobilization offers many advantages such as reduced enzyme costs due to the potential of reusing the enzyme over several consecutive cycles, potentially higher stability and more feasible enzyme separation and recovery, leading to pure product isolation. The results from these studies have been reported in D2.2 - Immobilized CA-improved by protein engineering mutants.

In order to select the most promising CA form for use in large scale CO<sub>2</sub> capture, different improved CA forms were screened in small-scale absorption experiments, using the developed amine-ionic liquid mixture and off gas (supplied by a project partner). The CA improved forms were evaluated for their stability in amines and reusability potential. It was revealed that the improved CA forms, in general, had limited stability under real CO<sub>2</sub> capture conditions, showing limited reusability. It was concluded that the implementation of neither of the improvement strategies would improve substantially the economy of the developed process. Therefore, it

was decided not to use evolved or immobilized CA forms for the CO<sub>2</sub> capture using the packed-bed reactor. Instead, CA in free form would be applied for further experiments.

#### 4.2 Selection of amine-ionic liquid mixture suitable for scale up of CO<sub>2</sub> capture

Different amine-ionic liquid aqueous mixtures were screened for their CO<sub>2</sub> absorption and desorption properties and enzyme compatibility. The results obtained from this study have been reported in Deliverable D2.3 - Optimum amine-ionic liquid–CA blends, and published as a scientific article in the journal ACS Sustainable Chemistry & Engineering (4). The developed amine-ionic liquid mixture demonstrated approximately a 5-fold higher initial absorption rate than MDEA and a 2-fold higher regeneration compared to MEA. Thus, it was selected as a promising candidate for use in scale up experiments in the packed-bed reactor.

#### 4.3 Determination of overall volumetric mass transfer coefficients

To quantify the superiority of developed amine-ionic liquid mixture in the upscaled demonstration experiments, CO<sub>2</sub> absorption using the CHE626 automated absorption and stripping pilot plant unit was performed. The reaction was carried out at 20°C, fixed solvent (0.58 L/min) and gas flow rate (65 L/min) and using a synthetic gas mix containing 8 % CO<sub>2</sub> and 92% N<sub>2</sub> (4). The in- and outlet CO<sub>2</sub> concentrations were monitored continuously. The overall volumetric mass transfer coefficient, KG<sub>a</sub>, was calculated for dilute conditions (CO<sub>2</sub><10%) according to following equation, assuming ideal gas behavior in the vapor phase, which is derived from a general mass balance over a packed absorption column:

$$KG_a = \frac{PN}{AZ} \left( \frac{\ln\left(\frac{P_i}{P_o}\right)}{(P_i - P_o)} \right)$$

Where P=total pressure in the column (atm), P<sub>i</sub>=partial pressure of CO<sub>2</sub> in the inlet stream (atm), P<sub>o</sub>=partial pressure of CO<sub>2</sub> in the outlet stream (atm), A=cross-sectional area of the column (m<sup>2</sup>), N= gram moles CO<sub>2</sub> absorbed/s, Z=height of packing (m).

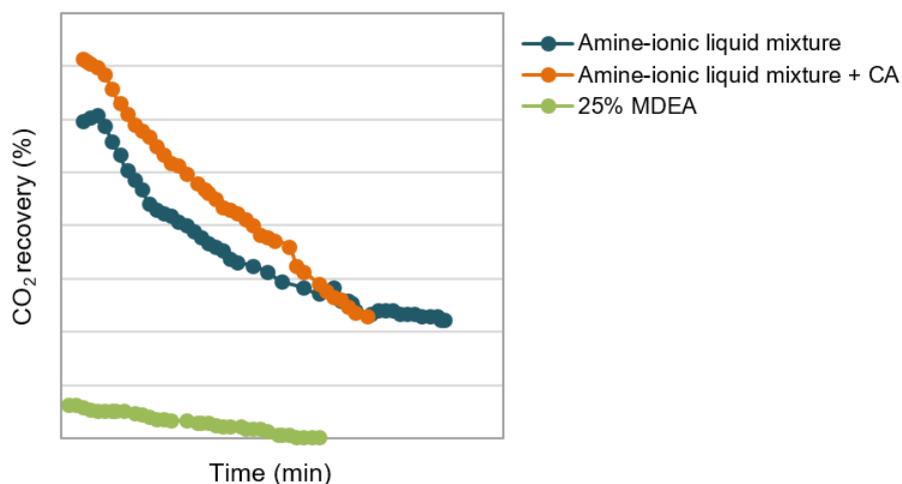
As presented in Table 2, the developed amine-ionic liquid mixture displayed 9.6 times higher KG<sub>a</sub> than 25% MDEA, which could save capital costs compared to MDEA-based plants (4). MEA remains the solvent with the highest mass transfer coefficient. This is expected due to the high reactivity of MEA as a primary amine. Nevertheless, the developed amine-ionic liquid mixture displayed only 3.3 times lower KG<sub>a</sub> than MEA, underlining its potential as promising solvent for CO<sub>2</sub> absorption. KG<sub>a</sub> is a lumped parameter that represents the absorption performance per unit volume of the reactor. It is a combination of thermodynamics, kinetics, and hydrodynamics of the CO<sub>2</sub> absorption system and provides an important insight for the design and manufacturing of an absorber.

**Table 2** KG<sub>a</sub> for selected solvents under the same conditions.

Solvent	KG <sub>a</sub> (mol/ (m <sup>3</sup> s mol fraction))
25% MEA	15
25% MDEA	0.48
Amine-ionic liquid mixture	4.6

#### 4.4 Integration of CA in an amine-ionic liquid mixture for enhanced CO<sub>2</sub> capture from off gas

CO<sub>2</sub> capture from real off gas using amine, ionic liquid and CA was performed on the CHE626 absorption and stripping pilot plant unit. Real off gas was supplied by a project partner. The reaction was carried out at 40°C under batch mode (recirculation). A several fold increase in the CO<sub>2</sub> recovery and CO<sub>2</sub> absorption rate was observed compared to 25% MDEA using synthetic gas (Figure 5). Integration of CA in the amine-ionic liquid mixture resulted in further improvement in the CO<sub>2</sub> absorption rate and CO<sub>2</sub>% recovery compared to only using the amine-ionic liquid mixture. A significant decrease in the absorption time and a 25% increase in the CO<sub>2</sub> recovery was achieved compared to the non-enzymatic reaction that involves only use of the amine-ionic liquid mixture (Figure 5). Combined with the good desorption properties of the developed amine-ionic liquid mixture, integration of CA in CO<sub>2</sub> capture could result in short operating times and reduced energy use, factors directly related to the operating cost of CO<sub>2</sub> scrubbing. This approach highlights the potential for application of greener and more sustainable bioprocesses for CO<sub>2</sub> capture from CO<sub>2</sub>-rich industrial streams. The full details of the study performed on the integration of CA in amine-ionic-liquid blends using a packed-bed reactor is planned to be published as a research article in an international journal imminently.



**Figure 5** CO<sub>2</sub> capture from off gas using the novel ternary solvent comprising of amine-ionic liquid mixture and CA using the packed-bed reactor of the CHE626 absorption and stripping pilot plant unit. CO<sub>2</sub> capture from synthetic gas (20% CO<sub>2</sub>, 80% N<sub>2</sub>) in 25% MDEA using the packed-bed reactor is shown for comparison.

## 5 Conclusion

The objective of D2.4 was to demonstrate the operation of a packed-bed reactor using amine-ionic liquid-immobilized CA blends for optimal capture of CO<sub>2</sub> from off gas. Under D2.4, measurements characterizing CO<sub>2</sub> absorption from synthetic gas mixture as well as real off-gases should be available. D2.4 is also connected to M2.3 - Large-scale packed-bed absorption ready for CO<sub>2</sub> capture from real off gases for validation testing.

In this report, the following achievements have been described:

- The operation of a packed-bed reactor using a ternary system of amine-ionic liquid-CA for optimal CO<sub>2</sub> capture from off gas has been demonstrated.
- A several fold increase in the absorption rate and CO<sub>2</sub> recovery was observed for using the ternary amine-ionic liquid CA blend compared to 25% MDEA using a packed-bed reactor.
- Use of real off gas from a cement plant indicated that the developed blend has good stability against potential impurities or inhibitors in the off gas.
- Measurements characterizing CO<sub>2</sub> absorption from synthetic gas mixture as well as real off-gases were performed.
- CO<sub>2</sub> capture conditions using a packed-bed reactor have been tuned in order to perform large absorption from real off gases for validation testing.

The main issue was encountered during the CA selection process for its application in the packed-bed reactor, i.e. the developed immobilized/evolved CA forms showed low stability under real CO<sub>2</sub> capture conditions in the amine-ionic liquid mixture, resulting in reduced reusability potential hence limited economic benefits for the process. It was therefore decided that CA would be applied in its free form for further CO<sub>2</sub> capture experiments and campaigns. This adjustment did not affect the activities for scaling-up of the process and will not affect the gas pre-treatment activities for validation testing.

Last, the automated absorption and stripping pilot plant unit is now set and available for the performance of real off gas pre-treatment for validation testing in later work packages, and therefore implies the achievement of Milestone 2.3.

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