

# Response Surface Modelling to Reduce CO<sub>2</sub> Capture Solvent Cost by Conversion of OZD to MEA

Federico Mereu <sup>a</sup>, Jayangi D. Wagaarachchige <sup>a</sup>, Maths Halstensen <sup>a</sup>, Zulkifli Idris <sup>a</sup>, Klaus-J. Jens <sup>a, \*</sup>

<sup>a</sup> University of South – Eastern Norway, Kjølnes ring 56, 3918 Porsgrunn, Norway  
Klaus.J.Jens@usn.no

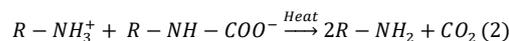
## Abstract

The increasing CO<sub>2</sub> concentration in the atmosphere is the most urgent global challenge. The most mature CO<sub>2</sub> abatement option is post-combustion CO<sub>2</sub> capture employing Monoethanolamine (MEA) solvent. One challenge of using MEA is its in-service degradation to 2-oxazolidinone (OZD), a heterocyclic five-membered organic ring compound. Furthermore, OZD degrades more MEA leading to CO<sub>2</sub> capture solvent loss and hence increased operational cost. It is therefore of interest to investigate methods to convert OZD back to MEA. This work reports the conversion of 2-oxazolidinone to MEA by heat treatment at an alkaline condition. Raman spectroscopy and Ion-Exchange chromatography were applied to qualify and quantify the reaction. The optimal reaction parameters were identified by an experimental design model using the Response Surface Methodology (RSM). A second-order model with three variables and five levels of focus was employed, with the OZD conversion percentage as the response. This methodology was chosen because such a model could estimate the main effects, interactions and quadratic terms by relying on a relatively small number of experiments. 17 experimental runs were designed by the software using this method. At a reaction time of 35 minutes, reaction temperature of 100°C, and 2.5 mole of hydroxide per mole of OZD resulted in a complete conversion of OZD to MEA.

## 1. Introduction

Carbon dioxide capture and storage (CCS) is so far considered the most promising technology to sequester CO<sub>2</sub> from large emission point sources (Rochelle, 2009). Post-combustion carbon capture (PCC) gas-liquid chemical adsorption is the predominant CCS technology today because of the development status (*US Department of Energy*, 2017) and that it can be retrofitted to existing CO<sub>2</sub> emitting plants.

Aqueous 30 wt% Monoethanolamine (MEA) is one of the most investigated CO<sub>2</sub> absorption solvents due to its good operational properties and relatively low price (Kohl & Nielsen, 1997; Buvik, 2021). Figure 1 shows the typical CO<sub>2</sub> absorption-desorption process scheme. The flue gas enters the absorber bottom after pre-treatment and flows upwards while the solvent solution e.g., aqueous 30 wt% MEA moves downwards in counter flow. Through a contact of these two streams, the CO<sub>2</sub> flue gas content is absorbed into the amine solution, forming mainly amine carbamate (equation (1)) which can release CO<sub>2</sub> upon heating to 120-140°C in the process stripping section according to equation (2) (Eimer, 2014). For simplicity, MEA is expressed by R-NH<sub>2</sub>, where R stands for a -CH<sub>2</sub>-CH<sub>2</sub>OH group.



However, aqueous MEA solvent has a high energy need in the solvent regeneration section and it is degrading in service due to contact with air in the absorption section and high temperature in the stripping section of the process (Fredriksen & Jens, 2013). These degradation reactions reduce solvent absorption capacity. Furthermore, these degradation products have to be removed and replaced with fresh MEA solvent which adds to operational cost. This degradation (reclaimer waste) varies in the range of 0.1-14.9 kg waste /ton CO<sub>2</sub> captured (IEAGHG, 2014).

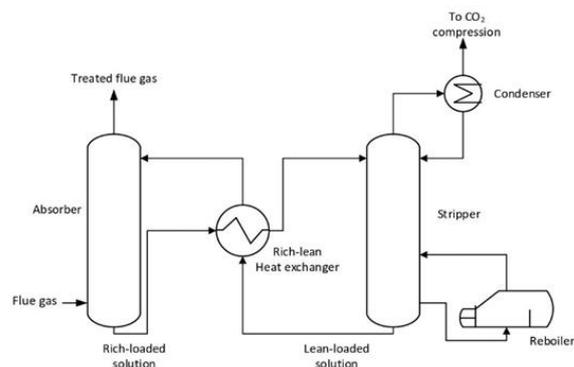


Figure 1: Basic schematic diagram of the chemical absorption-desorption CO<sub>2</sub> capture process.

The first step of thermal MEA degradation is the formation of oxazolidone (Davis & Rochelle, 2009; Dyen & Swern, 1967; Poldermann et al., 1955) from the reaction of MEA with CO<sub>2</sub>. Several patents (Miller, 1985; Pottiez & Verbeest, 1972; Snoble, 1981; Turoff et al., 2008) claim hydrolytic alkaline splitting of the alkanolamine derived oxazolidone back to the original alkanolamine and carbonate anion as shown in Figure 2.

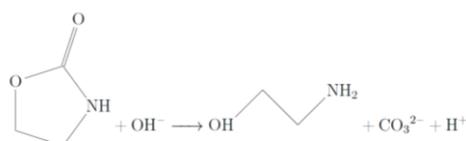


Figure 2: Reaction for Splitting of oxazolidone by alkali to MEA and a carbonate anion.

It is therefore desirable to understand the optimum reaction conditions for splitting of oxazolidone type thermal degradation products back to the original CO<sub>2</sub> capturing alkanolamine. Hence, this work determines optimal reaction conditions for splitting of oxazolidone by Design of Experiment utilizing the Response Surface Methodology (RSM) (Myers et al., 2016). Furthermore, a process integration concept into a CO<sub>2</sub> capture plant is proposed.

## 2. Methodology

### 2.1 Design of Experiments

A screening design (Eriksson et al., 2008; Esbensen & Swarbrick, 2017) was used to identify the most important parameters, thus reducing the number of experiments needed. For the optimization experiments, a Central Composite Design (Eriksson et al., 2008; Esbensen & Swarbrick, 2017) was used to vary the parameters at 5 levels as indicated in Figure 3.

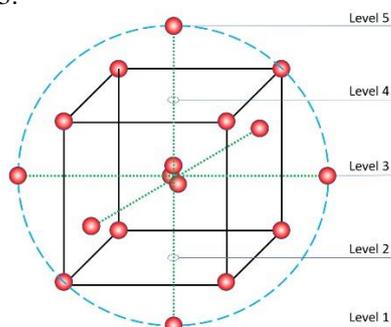


Figure 3. Central composite design with three center samples resulting in 17 experiments. The 5 different levels of the vertical variable are indicated.

The optimal reaction parameters were identified by an experimental design model using the RSM provided by the JMP software.

### 2.2 Chemicals

Chemicals were used as received and are summarized in Table 1. All aqueous solutions were prepared with Milli-Q® water (18.2 MΩ·cm at 25°C).

Table 1. Chemicals used in the experiments.

Chemical name	CAS number	Supplier	Mole Fraction purity (%)
Ethanolamine	141-43-5	EMSURE	≥ 99.5
2-Oxazolidinone	497-25-6	Sigma-Aldrich	98
Sodium carbonate	497-19-8	Sigma-Aldrich	99.9

### 2.3. Chemical Analysis

Cation chromatography and Raman spectroscopy were used to determine the reference concentrations.

#### 2.3.1 Cation chromatography

The samples were analyzed by a Dionex 5000 Cation chromatograph controlled by Chromeleon® software and equipped with a Dionex IonPac CS16 2 mm column. The eluent was methanesulfonic acid run at a gradient method (Table 2) and a constant flow rate of 0.5 mL/min at 60°C temperature. Samples were diluted with 0.3 ppm Li<sup>+</sup> containing Milli-Q water (internal standard) to a factor of 900 and filtered before injection using a 0.2 mm syringe filter.

Table 2. Eluent gradient concentrations

Time [min]	Concentration [mM]
0	6
13	8
25	55
30	60
32	60
34	6
40	0

#### 2.3.2 Raman spectroscopy.

The spectra were acquired with a RXN2 Raman spectrometer fitted with a 785nm laser delivered by Kaiser Optical Systems Inc. The samples were placed inside a black sample holder covered with an aluminium foil to suppress background light and were measured using a fiber optic immersion probe. The probe was washed with deionized water

followed by acetone before each measurement. The analysis exposure time was 30 seconds with 6 scans for each sample. A blank water sample preceded each analysis run. All Raman spectra were baseline corrected using the Whittaker filter (Eilers, 2003; Whittaker, 1922) (available in PLS toolbox in the MATLAB @software suite) before further processing.

#### 2.4 Oxazolidone (or 2-Oxazolidinone) splitting experiment.

The experimental set-up is shown in Figure 4. A sample of aqueous 3M oxazolidone stock solution and NaOH pellets or 0.1M NaOH solution was placed in a flask connected to a reflux condenser and heated under stirring to a pre-determined temperature and time. The pH of the reaction mixture was monitored by a pH electrode.

In a typical experiment, 25g 3M aqueous oxazolidone solution was titrated with 0,1 M NaOH solution using a Mettler Toledo T50 titrator pH 14 or a total solution volume of 80 ml whatever happened first. The latter produced a pH value of 12.4 at 80 ml solution. The solution was heated to 110°C for a few minutes, cooled to room temperature and analyzed for oxazolidone conversion by Raman spectroscopy. An alternative typical experiment of the above procedure substituted the 0.1 M NaOH solution by anhydrous NaOH pellets followed by water dilution to pH14. The aqueous dissolution of NaOH pellets is an exothermic process. Hence, the reaction solution was cooled to room temperature before Raman spectroscopic analysis.

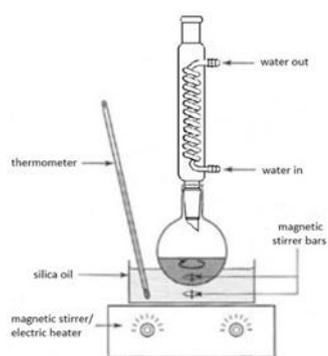


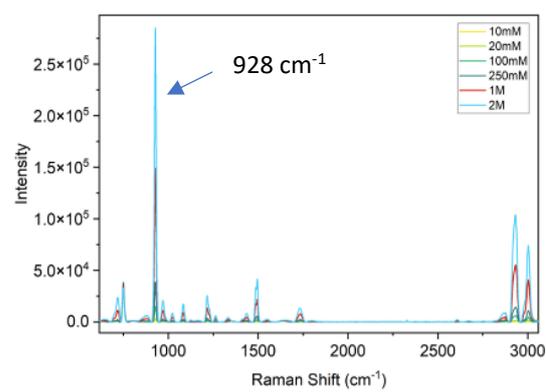
Figure 4: Experimental set-up

### 3. Results and Discussions

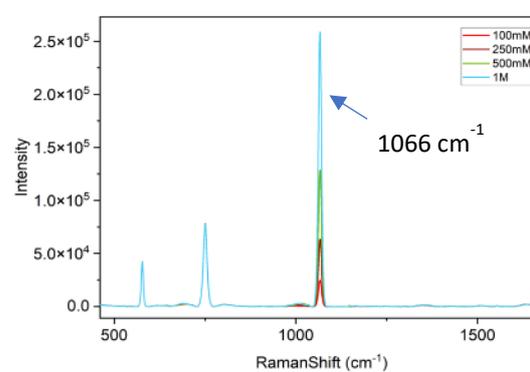
#### 3.1. Chemical Calibration for MEA and OZD Quantification

Concentrations of OZD were quantified using Raman Spectroscopic analysis. The spectral peaks of oxazolidone at 928  $\text{cm}^{-1}$  (Figure 5 (a)) (ref: McDermott (1986)) and of  $\text{Na}_2\text{CO}_3$  at 1066  $\text{cm}^{-1}$

(Figure 5 (b)) were chosen for subsequent qualitative and quantitative analysis.



(a)



(b)

Figure 5: (a) Raman spectra of oxazolidone (b) sodium carbonate at various concentrations

Cation chromatography was then used for the quantification of MEA. The MEA peak was identified in the chromatogram (Figure 6) by spiking it with an authentic MEA sample. Quantitative analysis was based on a calibration curve in the appropriate concentration range.

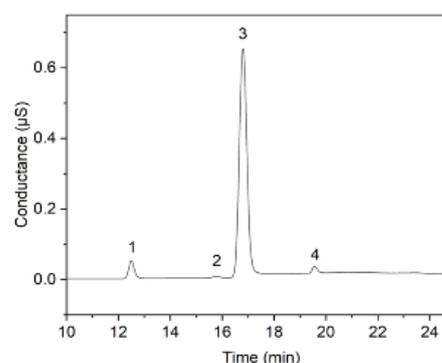


Figure 6: MEA chromatogram: MEA (3); Na<sup>+</sup> (1); NH<sub>4</sub><sup>+</sup> (2); K<sup>+</sup> (4).

### 3.2 Optimization of conversion of OZD to MEA

#### 3.2.1 Phase 1

screening investigations. The initial experiments in this phase verified oxazolidone splitting to MEA. As a preliminary study to verify the conversion of OZD to MEA, four tests were carried out using the alternative typical experiment procedure with solution reflux at 120°C and 2 hour duration (Table 3).

Table 3: Parameters for the oxazolidone (OZD) splitting experiment

Experiment	OZD conc. [mM]	OH <sup>-</sup> /OZD	Temp. [°C]	Time [min]
3	200	28	90	100
4	400	14	140	60
5	600	12	100	120
6	80	73	130	30

Three parameters were identified based on the initial screening experiments. The parameters were varied at two levels and three parameters were identified. Reaction time, reaction temperature, and the relationship between mole of hydroxide per mole of OZD were all found as the most significant contributors to the conversion of OZD to MEA.

#### 3.2.1 Phase 2

Optimization model for OZD conversion percentage. In phase 1, 3 three variables were chosen for the second phase: temperature (°C), time (min), and OH<sup>-</sup>/OZD molar ratio. The Response Surface Methodology was chosen because it can fit a second-order polynomial model that estimates main effects, interactions, and quadratic terms relying on a relatively small number of runs. The quadratic terms are useful because they can capture a possible curvature in the relationship between the response and the experimental factors. The three main variables are represented by the coefficients A, B, and C; the three two-way interactive terms are described by AB, AC, and BC; the three quadratic terms by A<sup>2</sup>, B<sup>2</sup>, and C<sup>2</sup>.

With these considerations, the number of central points (cp) was set to 3, the number of factorial points (Cube) was 8, and the number of axial points was 6. Three additional runs (No NaOH (3a), 1a and 2a) were added to the design resulting in a total of 20 experimental runs. Experimental plan details and the

responses (OZD conversion %) are given in Table 4. Figure 7 (a) and (b) show the response surface contour plots of OZD conversion for 100°C (temperature) and 35 min (time), respectively.

Table 4: Optimization model data and results

Exp. No.	Data			Results
	Temp. [°C]	Time [min]	OH <sup>-</sup> /OZD	OZD conversion [%]
1	100	38	4	100
2	118	51	3.2095	99.88
3	118	24	3.2095	99.94
4	82	24	3.2095	99.83
5	82	51	3.2095	99.93
6	70	38	2.05	89.2
7	130	38	2.05	99.53
8	100	38	2.05	98.83
9	100	60	2.05	99.58
10	100	38	2.05	98.92
11	100	15	2.05	94.52
12	100	38	2.05	98.69
13	82	51	0.8905	53.34
14	82	24	0.8905	48.17
15	118	24	0.8905	59.52
16	118	51	0.8905	74.63
17	100	38	0.1	10.48
1a	130	60	0.8905	72.21
2a	130	60	0.1	13.54
3a	130	60	0	0

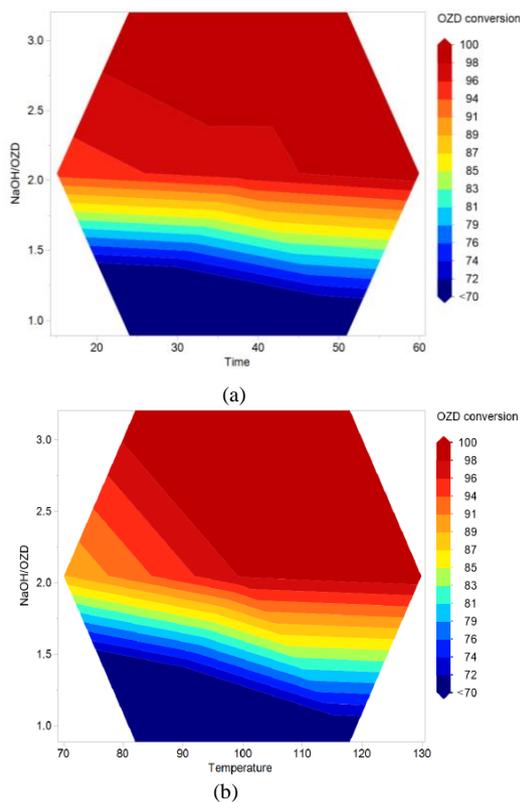


Figure 7: OZD conversion in function of OH-/OZD mole ratio (a) and time at 100°C (fixed temperature) (b) and temperature at 35 min (fixed time)

The summarizing prediction performance (Table 5) and the coefficient values of the optimization model (Table 6) indicate it to be satisfactory.

Table 5: Optimization model: prediction performance

RMSE	P-value	R <sup>2</sup>	Adj. R <sup>2</sup>
2.1958	<0.0001	0.99727	0.993167

Table 6: F-ratios and P-values of coefficients values (A: temperature, B: time, C: OH-/OZD)

Coefficient	F-ratio	P-value
A	37.7291	0.00085
B	12.5534	0.01217
C	803.7899	0.00000
AB	2.4178	0.17096
AC	27.5179	0.00193
BC	10.5144	0.01763
A <sup>2</sup>	3.4492	0.11266
B <sup>2</sup>	0.1520	0.71013
C <sup>2</sup>	507.2047	0.00000

The model shows several sets of possible variable combinations (Table 7) depending on desired reaction condition application.

Table 7: Model responses for selected variable sets

OH-/OZD	Temp. [°C]	Time [min]	OZD conversion achieved [%]
1	130	60	83.46
1.5	130	60	98.59
1.8	100	60	96.97
1.8	120	45	99.01
2	100	47	99.12
2	110	36	99.11
2.2	100	24	98.96
2.5	76	15	98.99

Analytic chemical evidence of reaction response for selected variable combinations is given in Figure 8.

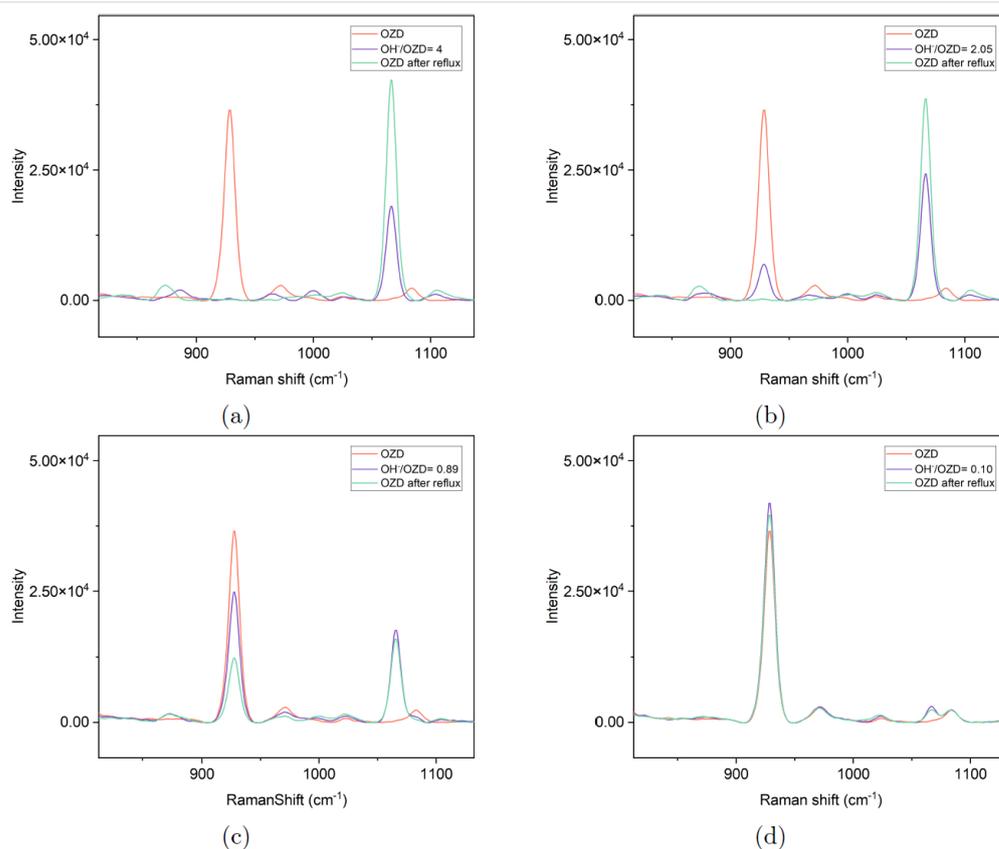


Figure 8. Raman spectra of selected experiments: Axial C (high) (a); Axial B (high) (b) and Axial C (low) (d).

### 3.3 Potential integration of the oxazolidone splitting reaction into a carbon dioxide capture unit.

The optimal reaction conditions for oxazolidone (OZD) splitting (Table 7) depend mostly on the OH-/OZD mole ratio. The reaction itself could be run in the reboiler of the CO<sub>2</sub> stripper or in a separate reactor connected to it (Figure 1). This would provide a temperature of the reaction vessel in excess of 100°C (Poldermann et al., 1955). As suggested by a US patent (Turoff et al., 2008), a slipstream of the stripper bottoms could be sent to a separate reactor where NaOH is added, the reaction is conducted and the recovered alkanolamine is separated from the caustic by phase splitting. Some caustic could be recycled to the reaction vessel while the rest is treated as solvent reclaiming waste. The US patent (Turoff et al., 2008) teaches this proposal for splitting of the oxazolidone hydroxypropyloxazolidone (HPOZD) to diisopropanolamine (DIPA) and CO<sub>2</sub>. Our optimal reaction conditions for OZD splitting would fit well with the above process integration proposal.

## 4. Conclusion

- Society needs to stabilize and reduce CO<sub>2</sub> emissions. Large-scale post-combustion

carbon capture is expected to be necessary in the near future. Our contribution puts focus on the cost reduction of aqueous alkanolamine carbon capture solvent.

- Alkanolamine recovery by splitting of oxazolidone (OZD) to the original MEA alkanolamine solvent and CO<sub>2</sub> can be satisfactorily modeled and optimized by the RSM method.
- The model variables are in order of importance OH-/OZD ratio, reaction temperature and reaction time.
- A CO<sub>2</sub> capture process integration concept for splitting of OZD to MEA is proposed.

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