



Thermal degradation kinetics of morpholine for carbon dioxide capture

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ARTICLE INFO

Keywords:

CO₂ capture
Morpholine
Thermal degradation
Kinetic model
Reaction mechanism

ABSTRACT

Deterioration of amines under process operating conditions for sour gas treatment is a severe problem. New amines are being investigated to replace conventional amines which face operational, economic and environmental challenges. Morpholine (MOR) is an understudied amine for carbon dioxide (CO₂) capture which comes with good CO₂ capture characteristics like CO₂ absorption rate, CO₂ solubility etc. This study investigates the stability of aqueous morpholine under stripper conditions. Effect of CO₂ loading and temperature have been investigated on the degradation kinetics of MOR. CO₂ loading is varied from 0 to 0.48 mol CO₂/mol alkalinity and temperatures is varied 135–190 °C. Thermal degradation experiments were conducted using 316 stainless steel cylinders, closed with Swagelok® endcaps. The degraded samples were analyzed by using Gas Chromatography-Mass Spectrometry (GC-MS), Gas Chromatography-Flame Ionization Detector (GC-FID) and Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometry (LC-QToF-MS) for morpholine concentration and identification of degradation products. Morpholine demonstrated higher stability up to 150 °C. However, higher degradation rate is found at temperatures 175 °C and above. Degradation rate increases with CO₂ loading. Identified degradation products are tabulated in the text and reaction mechanisms for formation of some of the key degradation products are also provided. A kinetic model for the rate of degradation of morpholine is proposed, which shows a decent agreement with experimental data. Comparison shows that morpholine is thermally more stable compared to monoethanolamine (MEA), diethanolamine (DEA), methyl-diethanolamine (MDEA) and piperazine (PZ).

1. Introduction

Increasing emissions of greenhouse gases has led to increased global average temperatures and catastrophic climate change events [1]. Apart from other greenhouse gases, CO₂ is a key man-made greenhouse gas. Records of Mauna Loa Observatory show that very unfortunately we already crossed the mark of 415 ppm of CO₂ in atmosphere in May 2019 [2]. The heat and electricity sectors have been reported as the highest CO₂ emission contributors [3]. This may be attributed to the urbanization, economic growth, energy consumption and minimal use of renewable resources of energy [4,5].

The factual data shows operation of a huge number of coal-fired power plants, and other CO₂ emitting plants which cannot be phased out. Under such circumstances, when there is no choice of redesigning the existing plants, amine-based post-combustion carbon capture process comes as a retrofit approach [6–8]. However, green methods for

CO₂ mitigation may also be explored [9–11]. Historically, the amine-based post-combustion carbon capture technology comes with chemical absorption of sour gases like hydrogen sulphide (H₂S) and CO₂ for natural gas sweetening [12]. Currently the technology is being widely used for natural gas processing. At the same time it has made significant advancement to be used for CO₂ capture from flue gases, particularly for coal-fired power plants [13]. Even after significant progress, the technology has several operational, environmental and economic challenges. Solvent escape due to volatility, solvent degradation, fouling, foaming, corrosion, solvent regeneration and emissions of environmentally non-friendly amine derivatives are some of the major hassles in front of its largescale operation.

Several amines like monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), aminomethylpropanol (AMP), diglycol amine (DGA), piperazine (PZ) etc. are some of the commonly tested amines for post-combustion CO₂ capture [14–16]. However,

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<https://doi.org/10.1016/j.jece.2020.103814>

Received 17 January 2020; Received in revised form 24 February 2020; Accepted 27 February 2020

Available online 28 February 2020

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most of the amines have their own limitations, none have a complete package of desired properties like fast CO₂ absorption kinetics, cyclic capacity, minimal regeneration energy, stability under process operating conditions, less corrosion, fouling and foaming, less volatility, less formation of environmentally hazardous derivatives, cost effectiveness etc. [17]. Among others, MEA and PZ have made more progress in terms of research and testing, specially at pilot and largescale plants. Apart from benign CO₂ capture characteristics like CO₂ capacity and absorption rate, MEA has been found very corrosive in nature, which ultimately contributes to operational problems and lowers the plant life. Other than corrosion, MEA is known for its lower stability under process operating conditions and forms harmful products like formaldehyde, nitrosamines and nitramines. Regeneration energy for MEA is also high, which increases the operational cost. PZ is a stable solvent under process operating conditions and comes with double CO₂ capture capacity compared to MEA due to two nitrogen groups with a very fast CO₂ absorption rate. However, precipitation at higher and lower CO₂ loading is one of the problems, which is causing operational deficiencies. Apart from precipitation, energy required for regeneration is very high than that of MEA. One of the chronic issues with PZ is nitrosation, where it forms very high concentrations of nitrosamines as compared to other amines [18].

Tetrahydro-1,4-oxazine also known as morpholine (MOR) is a secondary amine, which has chemical formula $O(CH_2CH_2)_2NH$. It is a developing solvent for CO₂ capture, which has better reactivity with CO₂, consequentially producing a higher rate of CO₂ absorption than monoethanolamine. Liu et al. [19] reported that overall mass transfer coefficient of CO₂ increases as MOR concentration increases, while they tested 4, 5 and 6 M solutions respectively. They also reported that MOR CO₂ absorption kinetics is three times higher as of MEA under the same operating conditions. MOR forms a strong carbamate bond while reacting with CO₂ compared to linear amines, which results in higher rate for CO₂ absorption [20]. Its maximum estimated stripper temperature (MEST) is 170 °C [21], this reduces the energy usage for carbon capture plant due to the greater efficiency of thermal compression compared to mechanical compression which will ultimately lower the overall capture cost [22]. Secondary amines are known for their nitrosation, similarly morpholine is not an exception, it also produces relatively higher amounts of nitrosamines than MEA, however lower than PZ [23].

Stability of amine solvents is an important aspect as solvent degradation causes not only economic losses but operational problems [6]. Screening experiments show that morpholine is a stable amine at elevated temperatures [24]. However, no detailed studies are available on chemical kinetics of thermal degradation of morpholine for CO₂ capture. This study focuses on evaluation of thermal stability of MOR under different CO₂ loadings and temperatures. CO₂ loading is varied

from lean to rich and temperatures from lowest minimum for stripper to above stripper temperatures. Experiments above MEST may not necessarily be applicable in industrial applications. However, these provide an understanding of degradation behavior of morpholine at elevated temperatures in aqueous carbonated environment. Thermal degradation products of MOR are identified and reaction pathways are described for major degradation products. With the help of gas chromatography amount of concentration loss of morpholine is quantified. An empirical model has also been developed to predict the rate of degradation of morpholine. In the end, a comparison of degradation kinetics of morpholine with other amines like MEA, DEA, MDEA and PZ is also provided.

2. Experimental

2.1. Methodology

Merck Sdn Bhd, Malaysia provided morpholine (99 %) for synthesis. Based on CO₂ solubility results from literature for morpholine, the concentration was chosen as 30.34 wt.%, which becomes a 3.5 M solution. The solutions were prepared gravimetrically as the mother liquor for all set of experiments. A fixed amount (in grams) of morpholine was transferred in a 2-liter volumetric flask. Later, deionized and degassed water with resistivity of 18 MΩ from Millipore was added to the flask to achieve the needed molar concentration. Solution was given time and stirred using a magnetic stirrer for 15 min, no additional heat was provided due to exothermic nature of MOR and water reaction. Using 0.1 M H₂SO₄, concentration of prepared solutions was determined by titration. CO₂ was also loaded gravimetrically through a pure saturated stream of CO₂. A gas saturator (absorber) filled with with required amount of amine solution was placed on a digital balance, and saturated CO₂ stream was bubbled through it until the required weight was achieved. From 0.1 to 0.3 mol CO₂/mol alkalinity; CO₂ loading was achieved gravimetrically.

However, 0.48 mol CO₂/mol alkalinity was achieved in a jacketed glass reactor on stirring plate mounted with a pH probe under atmospheric conditions. Saturated CO₂ steam was stopped once the solution pH reached the equilibrium. The experimental setup contained of a stirred tank reactor, pure CO₂ gas cylinder, stirring plate, magnetic stirrer, pH probe, Metrohm titrator system and computer. A predefined amount of aqueous morpholine solution was poured into the stirred tank reactor. CO₂ stream coming from the gas cylinder was connected to the saturator, placed in water bath so that gas attains the saturation. The saturated CO₂ stream from the saturator enters to the reactor containing aqueous morpholine. Chemical equilibrium was monitored through change in pH using a pH probe mounted within the reactor. CO₂ was bubbled through the reactor until a linear plot of pH with time

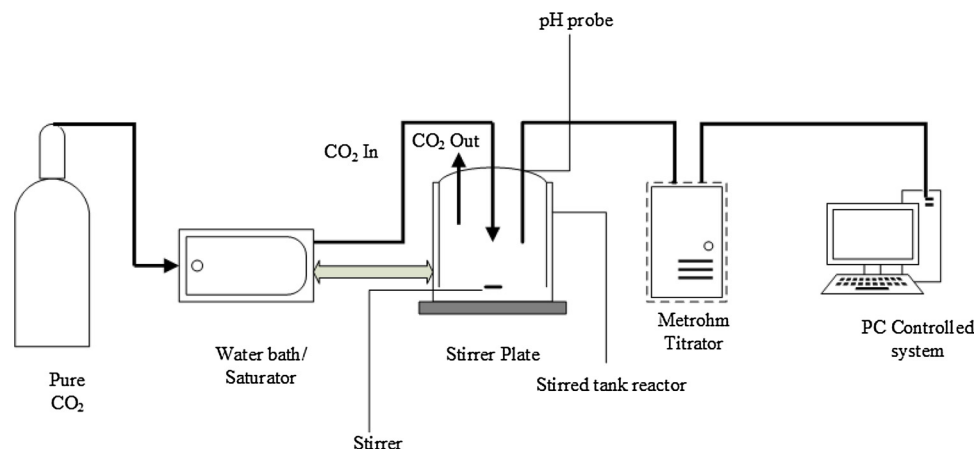


Fig. 1. The experimental setup used for CO₂ loading until the amine – CO₂ saturation.

was attained. The pH probe was integrated with the Metrohm system to get the online and real time pH of the solution. Fig. 1 provides an overview of the experimental setup used for amine–CO₂ chemical equilibrium.

Confirmation of CO₂ loading was carried by using titration method [25–27]. The same method is also used in our previous work [28]. Two samples of 0.5 g were taken for each CO₂ loading. The taken samples were then kept in 250 ml Erlenmeyer flask and then 25 ml of BaCl₂ (0.5 M) and 50 ml NaOH (0.1 M) were poured into the flask. The samples in Erlenmeyer flask were heated until the boiling, then cooled. The help of vacuum pump, the white crystal formed during the heating of samples were filtered by using 0.45 µm pore size silicon papers. The white solid crystals were then poured into a beaker and 45–55 ml deionized water was then added so that no unreacted CO₂ remains in the sample. The watery samples of white crystals were then ionized using 0.1 M HCl. The acidified samples then were titrated using 0.1 M NaOH. All the titration tasks were performed using 785 DMP Titrimo auto-titrator installed with Tiamo 1.3 software.

2.2. Reactions in thermal reactors

The thermal stability evaluation experiments were conducted in thermal reactors (stainless steel cylinders). This method have been used by several researchers for the same purpose, which originally was proposed by Hillard [29]. The thermal reactors were made of ½ inches outer diameter (OD) 316 stainless steel cylinders. The cylinders were cut into the segments of 5 in. and closed with 316 stainless steel Swagelok® endcaps. The CO₂ loaded and unloaded solutions after the confirmation of CO₂ loading through titration. The filled stainless-steel cylinders were kept in convection ovens for heating at predefined temperatures. Cylinders were double checked and weighted, prior filling the of liquid carbonated amine samples. From each sample 10 cylinders were prepared with 8 g of sample in each cylinder. N₂ was purged into the filled cylinders to evacuate the dissolved oxygen from the samples. The oven temperatures were achieved well before the introduction of samples so that stabilized temperature conditions are achieved. The reactions were carried out at 135, 150, 175 and 190 °C. In parallel, two ovens were run at two different temperatures with all CO₂ loading ranges for a single temperature. Labels were put on each cylinder accordingly for the identification of samples. Each sample was experimented for a minimum of 7 weeks, however, periodically a sample cylinder was removed from the oven for analyses. After removing the sample from oven, each of them was analyzed for quantification of parent amine loss and identification of degradation products within 48 h.

2.3. Gas chromatography analyses

Gas chromatography (GC) was used as the major equipment for sample analyses for quantification of morpholine loss and identification of degradation products. Two GC systems were used separately, one with Mass Spectrometer (MS) as the detector and other with Flame ionization Detector (FID) as the detector. GC–MS was from Shimadzu (GC–MS–QP2010). This came with an ultra-auto sampler (AOC 20I + S). The column used was RTX-5MS, with 30 m length, 0.25 mm film thickness and 0.25 µm internal diameter. The method used for GC–MS was adopted from Lepaumier [30]. GC–MS was helpful in identification of degradation products. GC–FID was also from Agilent (7890A). This came with an autosampler (G4513A). A nonpolar column, CP–Sil 8 CB, with dimensions 15 m, 530 µm, and 1 µm Length, internal diameter, and thickness respectively was used with GC–FID. Ethanol was used for the dilution of samples for analyses, which was purchased from Merck Millipore. Two samples from each cylinder were prepared for analyses. The method used for the analyses of samples is reported in our previous study [31]. GC–FID helped in determining concentration of MOR using known concentration standard solution

straight line equation.

2.4. Liquid chromatography

Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometry (LC–QToF–MS) was also used for the identification of degradation products. Agilent 1260 Infinity Liquid Chromatography coupled with 6224 Time-of-Flight (TOF) MS was used for the analyses. Database was created by using Agilent Personal Compound Database Library (PCDL). In LC–QToF–MS, molecules are converted into ions by electrospray ionization (ESI) source. To achieve the ionization, both positive and negative ion mode were used in the Atmospheric Pressure Chemical Ionization (APCI) interface. The column used was Zorbax Eclipse Plus (2.1 X 100 mm). 20 µl was used as the injection volume. 0.10 % formic acid in water (1) and methanol (2) was used as the eluent. A gradient profile of eluents was used with the ratio of 49:1 for (1) and (2) respectively for the first 6.0 min and then changed to 1:4 for next 2 min, and from 8 to 14 min, the ratio of (1) and 2 was set back to 49:1. The flow rate was set at 0.200 ml/min for the entire span of analyses. A detailed method of analysis using LC–QTOF is provided elsewhere [32].

3. Results and discussion

3.1. Degradation products of morpholine

Degradation products of partially degraded morpholine samples were identified by using C–MS and LC–QToF–MS. Detailed list of degradation products identified by both methods is provided in Table 1.

3.2. Pathways of formation of major products

Gilbert and Lamarre [33] reported that Samuel T. as cited by Tuck and Osborn [34] found that aqueous morpholine decomposed up to 40 % at 308 °C within 48 h, giving ethanolamine, diethanolamine and some primary amines. Furthermore, traces of diethanolamine are also reported during morpholine degradation at 260 °C [33]. MEA is detected as a degradation product of morpholine in boiler feed water and steam condensate samples [35]. Based on supporting literature on degradation of morpholine, we propose the degradation mechanism of morpholine. The reaction occurs by protonation of oxygen of morpholine, which turns it into a leaving group followed by nucleophilic attack of water, which then leads to ring opening of morpholine by producing DEA. Diethanolamine further splits down by protonation of nitrogen to produce MEA (3) and ethylene oxide (EO) (4). MEA will further react with MOR molecule to produce 2-morpholinoethanol (ME) (5). On the other hand, MOR can also reacts with EO to produce 4-(2-Aminoethyl) morpholine AEM (6). Ethylene oxide being volatile is suspected to escape from the cylinders on their opening, whereas MEA and DEA are potentially intermediate products of the reaction, as these have not been identified through analyses as stable degradation products. (Scheme 1)

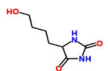


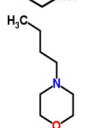





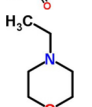
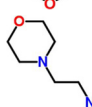
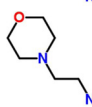
The reaction of formation of N-[2-(4-Morpholinyl)ethyl]ethanedi- amide (MEAD) begins with reaction of acetamide (1) with formamide (2) to produce oxamide (3), which further reacts with 2-morpholinoethanol (4) to produce MEAD (5). (Scheme 2)

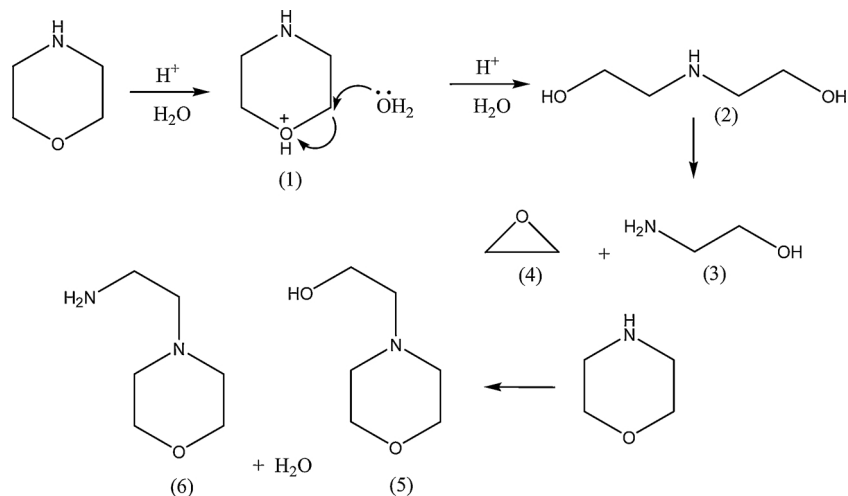
The formation of 4-morpholinylacetaldehyde (MAA) takes place by aldolization of formic acid and morpholine as shown in scheme 3 [36].

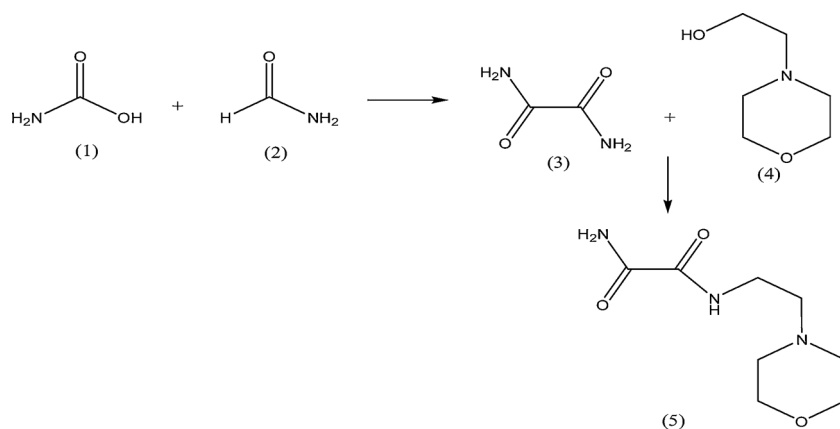
The reaction mechanism of formation of N-(2-Aminoethyl)acet- amide (AEA) starts by the reaction of acetic acid with ammonia fol- lowed by the reaction with intermediate MEA to generate N-(2- Aminoethyl)acetamide. (Scheme 4)

Scheme 5 shows the reaction mechanism for formation of 5-(4-Hy- droxybutyl)-2,4-imidazolidinedione (HOBID). The reaction begins by dehydration of MEA followed by ring opening of ethylene oxide, which further attacks MEA molecule to form 4-amionbutanol (AB). The

Table 1List of degradation compounds of 30.34 % morpholine with CO₂ loading of 0 to 0.48 mol CO₂/mol alkalinity at temperatures 135 to 190 °C.

SNo.	Compound	Abb.	CAS-number	Structures	Analytical technique	
					GC-MS	LC-QToF-MS
1	5-(4-Hydroxybutyl)-2,4-imidazolidinedione	HOBID	25860-42-8		×	×
2	2-Morpholinoethanol	ME	622-40-2		×	×
3	2,2-Dimethylmorpholine	DMM	147688-58-2		×	×
4	4-Butylmorpholine	BM	1005-67-0			×
5	4-Methyl-2-morpholinone	MM	18424-96-9			×
6	4-Morpholinylacetaldehyde	MAA	21977-09-3			×
7	Propionamide	PA	79-05-0		×	×
8	N-Formylmorpholine	FM	4394-85-8		×	×
9	N-(2-Aminoethyl) acetamide	AEA	1001-53-2		×	
10	N-Ethylmorpholine	NEM	100-74-3		×	
11	4-(2-Aminoethyl) morpholine	AEM	2038-03-1		×	
12	N-[2-(4-Morpholinyl) ethyl] ethanediamide	MEDA	5625-80-9		×	

**Scheme 1.** In presence of water morpholine splitting into its derivatives and diethanolamine.



Scheme 2. Formation of N-[2-(4-Morpholinyl) ethyl]ethanediamide.

formamide which is formed by the reaction of ammonia with formic acid, reacts with AB through dehydration of water of AB to form 4-hydroxybutyl urea, which again react with formamide to give diurea, where intermolecular amidification occurs to produce 5-(4-Hydroxybutyl)-2,4-imidazolidinedione by internal cyclization of diurea.

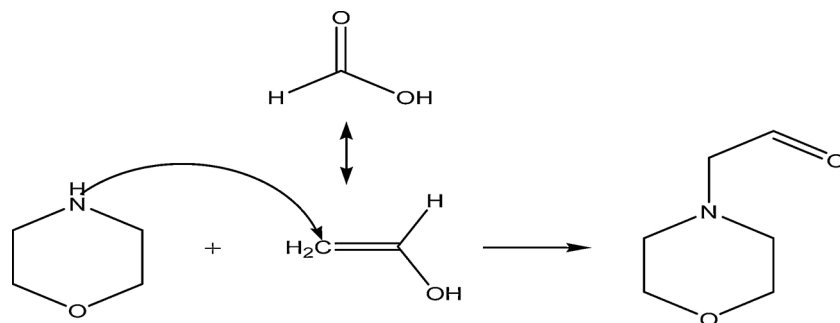
Reaction of formation 4-Methyl-2-morpholinone commences through the reaction of protonated EO with amino acetic acid by ring opening of EO, which leads to the formation of (2-Hydroxy-ethylamino)-acetic acid followed by internal cyclization to form 2-morpholinone (MO). MO further reacts with formic acid and formaldehyde through Eschweiler-Clarke reaction. Amine methylation process takes place with reaction of amine with the protonated formaldehyde by producing an intermediate iminium ion. A methylated ammonium ion forms and carbon dioxide gas gets released in the process when the iminium ion reacts with the formic acid. This keeps process moving in forward direction. A final methylated amine product is formed due to deprotonation of the ammonium ion. These steps repeat twice to produce the tertiary amine final product in case of primary amine. [Scheme 6](#) presents the formation of 4-Methyl-2-morpholinone.

3.3. Amine loss

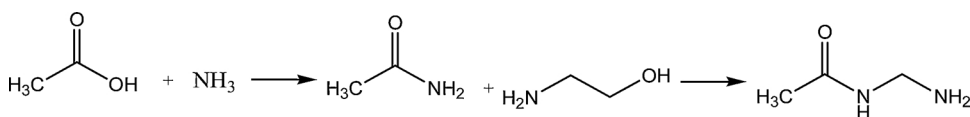
Degradation quantification of morpholine was conducted using GC-FID. Quantification was conducted at temperatures 135, 150, 175 and 190 °C with five different CO₂ loadings like 0, 0.1, 0.2, 0.3 and 0.48 mol CO₂/mol alkalinity. A small concentration loss of morpholine was observed at 135 °C and this remained linear for almost 10 weeks. Morpholine loss although was minimal, however it augmented with rise in CO₂ loading. This indicated that CO₂ loading has a direct relation with morpholine degradation. However, at relatively higher CO₂ loading like 0.48 mol CO₂/mol alkalinity a small decline is noted in the loss of morpholine. This may be because of the active influence of protonated morpholine species at lower CO₂ loading and higher influence of unprotonated species at 0.4 mol CO₂/mol alkalinity [27].

However, effect of temperature has been observed consistent with the loss of morpholine concentration.

Results indicate that unloaded solutions degraded at a very slow rate. For example, a loss of 1.1 % in concentration of morpholine was experienced over a duration of 10 weeks at 135 °C. Increase in CO₂ loading increased the degradation rate of morpholine. At the same temperature for the same duration, highest loss of 2.1 % in the concentration of morpholine was observed at 0.48 mol CO₂/mol alkalinity. Almost a three-fold surge in the loss of morpholine was observed at the same CO₂ loading when temperature increased from 135 to 150 °C for the same duration of experiment. The concentration loss observed for morpholine at 150 °C was 5.42 %. Not only at the highest CO₂ loading but a similar trend is experienced at different CO₂ loadings. However, the highest concentration loss of morpholine at 150 °C was 5.63 %, which was observed at 0.30 mol CO₂/mol alkalinity. A very sharp increase in concentration loss of MOR has been experienced at 175 °C compared to the loss at 135 and 150 °C. Even without CO₂ loading the MOR loss was up to 15.8 % for a duration of 9 weeks. As observed in previous trends the loss of concentration of MOR increases as the CO₂ loading increases. Similarly, degradation of MOR increased as CO₂ loading increased. At this temperature, the highest morpholine concentration loss was observed at 0.48 mol CO₂/mol alkalinity. For initial 6 weeks, the degradation rate of morpholine was higher for 0.3 mol CO₂/mol alkalinity but afterwards, a sharp increase was observed at 0.48 mol CO₂/mol alkalinity and this caused the maximum loss of morpholine. This may indicate the degradation of less reactive intermediate and formation of active or protonated intermediates, which catalyzed the reaction. The highest loss in the initial concentration of MOR was experienced at 190 °C. A maximum of 42 % of morpholine concentration declined at CO₂ loading of 0.3 mol CO₂/mol alkalinity for 10 weeks at 190 °C. At this temperature, morpholine concentration decline was lower at 0.48 mol CO₂/mol alkalinity compared to 0.3 mol CO₂/mol alkalinity.



Scheme 3. Formation of 4-morpholinylacetaldehyde by aldolisation of formic acid and morpholine.



Scheme 4. Formation of N-(2-Aminoethyl)acetamide.

3.4. Degradation rate determination

Thermal stability evaluation of morpholine has been conducted at various CO₂ loadings and temperatures. The concentration time data were fitted against zeroth, first and second order rate laws. The experimental data better fitted the first order rate law compared to others. Hence, based on data fitting, the following rate equation was formulated for degradation of morpholine.

$$\frac{-dC_{MOR}}{dt} = k_1 C_{MOR} \quad (1)$$

Integrating Eq. (1) gives:

$$C_{MOR} = C_{MOR,0} \cdot e^{-k_1 t} \quad (2)$$

Taking natural log (ln) from both sides of Eq. (2), it becomes,

$$\ln C_{MOR} = \ln C_{MOR,0} - k_1 t \quad (3)$$

Where, $C_{MOR,0}$ is the initial concentration of morpholine, C_{MOR} is the concentration of morpholine at time t , k_1 is the first order rate constant, and t is the time in seconds.

In order to determine the apparent first order rate constants (k_1) for each reaction, values of $\ln C_{MOR}$ were fitted against t . Fig. 2 provides a representative plot for the determination of first order rate constants, k_1 .

Data at 175 °C and 0.48 mol CO₂/mol alkalinity does not behave consistently, this may be attributed to the mechanism of reaction happening at different stages of the reactions. Regression coefficient (R^2) from fit at 175 °C and 0.48 mol CO₂/mol alkalinity is 0.903. However, data at 190 °C behaved with better consistency and achieved a R^2 of 0.968 as indicated in Fig. 2. Similarly, other data sets are also regressed to obtain the k_1 values. In most of the cases R^2 was higher than 0.90. Table 2 provides a detailed list of k_1 values along with their

corresponding R^2 values.

3.5. Temperature dependence and Arrhenius equation

Temperature plays an important role in the chemical kinetics. Hence, this makes it necessary to carry out an analysis that how reaction depends on temperature. In the current study, reactions are conducted at four different temperatures like 135, 150, 175 and 190 °C. To explore influence of temperature on degradation chemical kinetics of morpholine, Arrhenius Eq. (4) is used in this study. To determine the effect of temperature on the degradation kinetics of morpholine the Arrhenius equation was at first linearized into Eq. (5), and then $\ln k$ was plotted against inverse of temperature ($1000/T$).

$$k = Ae^{(-E_a/RT)} \quad (4)$$

Taking natural log of Eq. (4), it becomes:

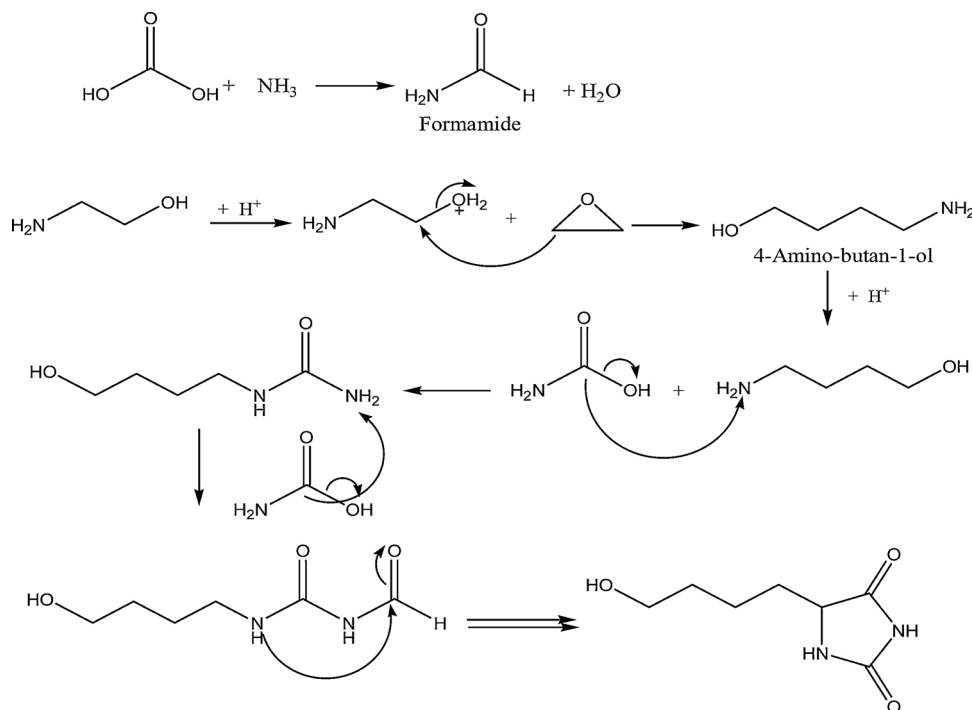
$$\ln k = \ln A - E_a/RT \quad (5)$$

Where k is the rate constant, A is the pre-exponential factor (s^{-1}), E_a is the activation energy (joules/mole), R is universal gas constant and T is the operating temperature (K). Degradation kinetics of morpholine at CO₂ loadings of 0 to 0.48 mol/mol alkalinity at temperatures 135–190 °C is provided in Fig. 3.

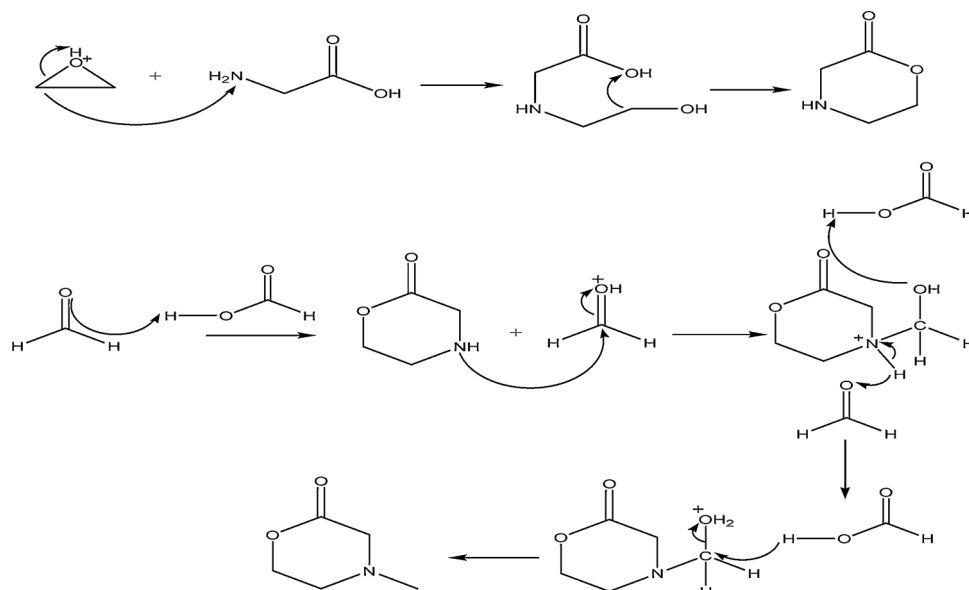
Fig. 3 shows that degradation kinetics of morpholine increases with temperature. At initial the trend follows an exponential behavior, which slows down with time. This may be because of consumption of protonated morpholine into derivatives of morpholine in degradation reactions, hence reducing its nucleophilic reaction opportunity.

3.6. Overall rate constants

The process conditions for CO₂ stripping vary within the process,



Scheme 5. Formation of 5-(4-Hydroxybutyl)-2,4-imidazolidinedione.



Scheme 6. Formation of 4-Methyl-2-morpholinone.

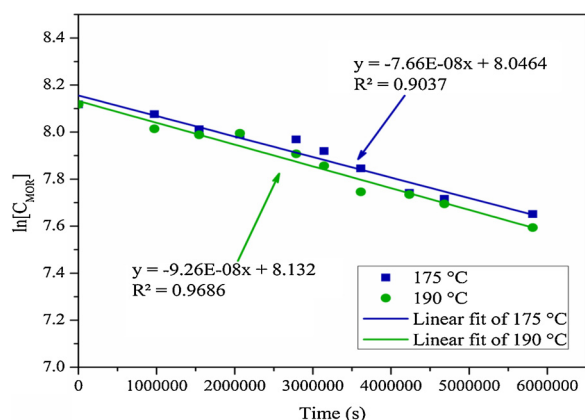


Fig. 2. A representative plot of $\ln C_{\text{MOR}}$ against time (t) to determine the first order rate constants (k_1) at 175 and 190 °C at the CO_2 loading of 0.48 mol CO_2 /mol alkalinity.

Table 2

First order rate constants (k_1) for thermal degradation of morpholine at 0 to 0.48 mol CO_2 /mol alkalinity from 135–190 °C.

Temperature (°C)	CO_2 loading	k_1 , (10^{-8})	R^2
135	0.0	0.21	0.950
	0.1	0.28	0.900
	0.2	0.30	0.970
	0.3	0.43	0.987
	0.48	0.41	0.981
150	0.0	0.68	0.932
	0.1	0.87	0.961
	0.2	1.08	0.965
	0.3	1.10	0.986
175	0.0	0.99	0.960
	0.2	2.75	0.971
	0.3	7.05	0.993
	0.48	7.66	0.908
190	0.0	7.17	0.901
	0.1	4.02	0.982
	0.2	8.67	0.984
	0.3	9.26	0.968
	0.48	8.95	0.982

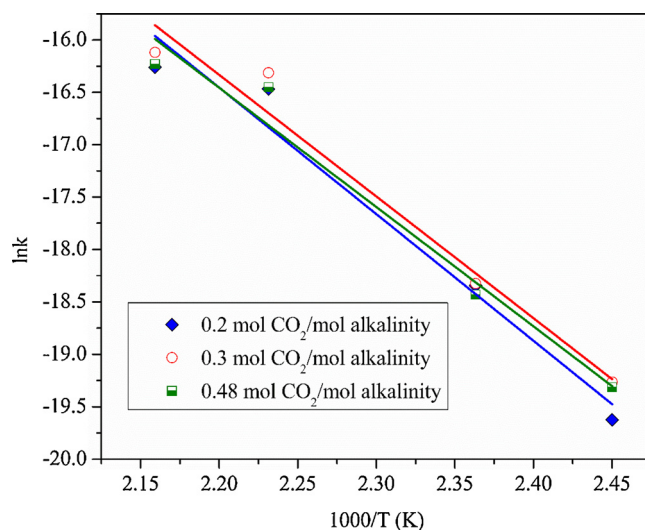


Fig. 3. The temperature dependence degradation kinetics of morpholine at 35 to 190 °C with CO_2 loadings of 0 to 48 mol CO_2 /mol alkalinity.

hence effect of that varies with solvent location. An overall rate constant may be required to determine the solvent loss due to its degradation in the process. Considering the different data points of the study obtained at different temperatures and CO_2 loadings, Arrhenius Eq. (5) has been used to demonstrate an overall effect of different temperatures under various CO_2 loadings. Data for three different CO_2 loadings like 0.2, 0.3 and 0.48 mol CO_2 /mol alkalinity is used for an overall rate constant under different temperatures. A comparison of experimental first order rate constants against determined overall first order rate constants is provided in Fig. 4. The graph shows a linear relationship between calculated and experimental values of rate constants in an acceptable limit. R^2 of the fit is provided within the figure.

4. Degradation kinetic model

4.1. Model development

Thermal stability evaluation of aqueous morpholine in presence of CO_2 at 135–190 °C provides more or less stripper operating conditions.

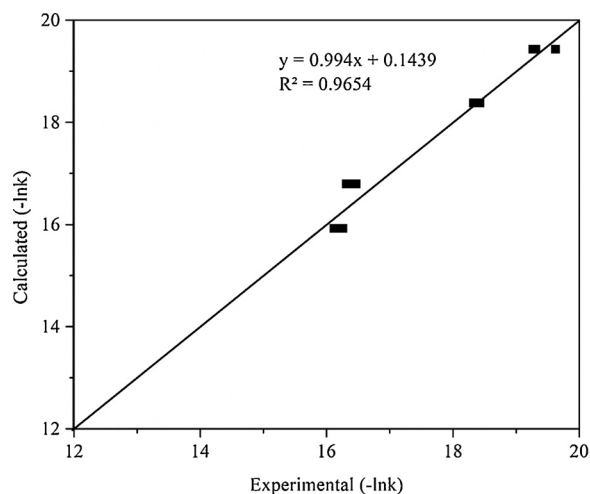


Fig. 4. Comparison of calculated $-\ln k$ values against experimental $-\ln k$ values with CO_2 loading of 0.2, 0.3 and 0.48 mol CO_2 /mol alkalinity at each temperature.

The process may be taken as an example of gas-liquid contact reaction, where CO_2 is shifting from bulk of the liquid to bulk of the CO_2 . In this study, an experimentation to determine the degradation kinetics of morphine spanned up to 10 weeks. An empirical rate equation by using power law rate of reaction model is proposed as equation under (6).

$$-r_{\text{MOR}} = k[\text{C}_{\text{MOR}}]^a[\text{C}_{\text{CO}_2}]^b \quad (6)$$

Where $-r_{\text{MOR}}$ (mmol/L.s) is the rate of degradation of morpholine, C_{MOR} is the concentration of morpholine (in mmol/L) at time t , C_{CO_2} is the initial concentration of CO_2 (in mmol CO_2 /mol alkalinity) and k is the first order reaction of rate constant (s^{-1}). a and b are exponents for C_{MOR} and C_{CO_2} respectively.

Effect of temperature on the rate of degradation reaction of morpholine is added by using Arrhenius Eq. (7).

$$k = Ae^{-E_a/RT} \quad (7)$$

Where, A is the pre-exponential factor (units depend on the units of k), E_a is the activation energy (J/mol), R is universal gas constant (8.314 J/K mol) and T is temperature (K).

Substituting Eq. (7) in (6) and linearizing, it gives:

$$\ln(-r_{\text{MOR}}) = \ln A - \frac{E_a}{RT} + a \ln[\text{C}_{\text{MOR}}] + b \ln[\text{C}_{\text{CO}_2}] \quad (8)$$

In this study five batches of experiments with CO_2 loadings of 0, 0.1, 0.2, 0.3 and 0.48 mol CO_2 /mol alkalinity have been conducted at a single temperature. The data obtained with zero CO_2 loading have not been added to the model as none of the species concentration should be zero for proposed equation. Moreover, data with 0.1 mol CO_2 /mol alkalinity was also not added in the model. At this CO_2 loading, experiments were not conducted at 175 and 190 °C. The model is built using data-points at 0.2, 0.3 and 0.48 mol CO_2 /mol alkalinity, tested at all temperatures. This study is conducted at a single concentration of morpholine with different concentrations of CO_2 . So, concentration taken after one week was assumed as the initial concentration corresponding to their initial rates. Furthermore, this is also assumed that initial degraded concentration of morpholine, which is negligible does not contribute to the overall rate of degradation of morpholine. Table 3 shows the data used for the development of the kinetic model.

4.2. Parameter optimization

$\ln A$, a , b and E_a are the parameters involved in the rate Eq. (8). The parameters were obtained by regressing the experimental data by using multiple linear least-squares regression with a confidence interval of 95

Table 3

The database for the development of degradation kinetic model.

$-r_{\text{MOR}}$ (mmol/L.s)	$[\text{C}_{\text{MOR}}]$ (mmol/L)	$[\text{C}_{\text{CO}_2}]$ (mmol/mol alkalinity)	T(K)
0.000010710	3342.3706	200	408.15
0.000035447	3342.7321	300	408.15
0.000096958	3325.945	480	408.15
0.000270486	3341.3435	200	423.15
0.000307672	3340.3404	300	423.15
0.000346395	3307.581	480	423.15
0.000222483	3204.0261	200	448.15
0.000323909	3158.6959	300	448.15
0.000300732	3017.0366	480	448.15
0.000257104	3161.3435	200	463.15
0.000363668	3078.0363	300	463.15
0.000316358	2922.8308	480	463.15

Table 4

Optimized parameters of morpholine degradation kinetic model.

Parameter	Value
$\ln A$	-10.97
a	32.09
b	2.29
E_a (Joules/mole)	142165

%. The coefficient of each operating parameter is taken as the optimized parameter with reference to their respective parameter. The statistical parameters for model like regression coefficient (R^2), F value and significance F values were found as 0.80, 10.96 and 0.0033 respectively. This indicates that experimental data fitted the model at a reasonable agreement. The regressed parameters are provided in Table 4. Exaggeration in the values of $\ln A$ and a is due to use of the same concentration of morpholine.

To determine the statistical agreement of the degradation kinetic model, Absolute Average Deviation (AAD) of the predicted rate data against experimental data was taken. The AAD obtained for the model is 2.88 %, which indicates that model predicted results are in good agreement with experimental data. MEA thermal degradation activation energy is reported to be 138.07–144.21 KJ/mol [37]. In our study, we found that morpholine degradation activation energy is higher compared to MEA under similar operating conditions. This also shows that morphine is more stable than MEA. A comparison of predicted rate $\ln(r_{\text{MOR}})$ data against experimental values of $\ln(r_{\text{MOR}})$ is provided in Fig. 5.

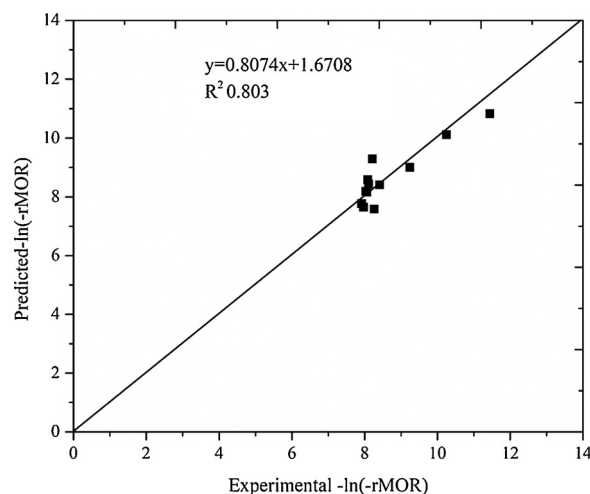


Fig. 5. Comparison of model predicted degradation rate of morpholine versus experimental rate values of $-\ln(r_{\text{MOR}})$.

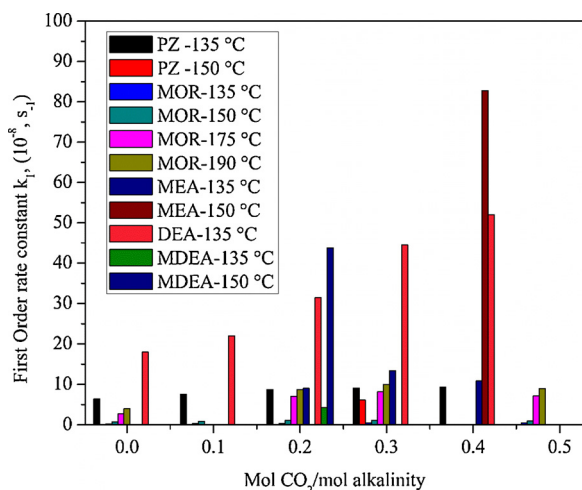


Fig. 6. Thermal degradation kinetics comparison of MEA, DEA, MDEA, PZ and MOR [18].

5. Thermal stability comparison of morpholine with other amines

No studies provide a detailed degradation kinetics of morpholine at stripper conditions except some screening experiments. This investigation brings to light the detailed investigation of thermal stability of morpholine and comparison with other amines. Data for degradation of other amines is taken from the open domain literature. To compare the degradation kinetics of morpholine, the first order rate constants of various commonly tested amines with respect to CO₂ loading and temperature is provided in Fig. 6. Under similar operating conditions and experimental setup used, morpholine is the most stable amine so far. Contrarily, MEA, DEA and MDEA are very vulnerable to higher temperatures. However, piperazine is very stable compared to MEA, DEA and MDEA but less than morpholine.

Degradation activation energy plays an important role in relating and determining the stability of amines. Various studies have reported degradation activation energy of different amines. Table 5 presents thermal degradation activation energies of different amines.

Tabulated results on thermal degradation activation energies exhibit that MOR is a stable amine compared to others. The energy varies with overall temperature range and CO₂ loading. From the table it may be observed that highest activation energy of 300.94 KJ/mol is required at lowest CO₂ loading of 0.2 mol CO₂/mol alkalinity. Whereas, at highest loading of 0.48 mol CO₂/mol alkalinity the lowest activation of 131.65 KJ/mol is required. The similar trend may also be noted in other

studies as shown in Table 5. This may also be noted that PZ has higher activation energies after MOR. Some studies have determined activation energies using rate constants at different conditions and average values with their upper and lower difference have been published as shown in Table 5. However, our study and study of Léonard et al. [37] reports activation energies by using the proposed rate equations. Activation energies by using rate equations can incorporate all the parameters with different ranges in a single equation.

6. Conclusions

Thermal stability of 3.5 M morpholine is studied at temperatures from 135–190 °C with CO₂ loadings of 0 to 0.48 mol CO₂/mol alkalinity of the solution. Several degradation products have been identified using GC–MS and LC–QTOF–MS and pathways for the formation of major degradation products are discussed. Most of the degradation products of morpholine are amides, aldehydes and ketones in ring structure formation. Carbonated solutions of morpholine produced more degradation products compared to non-carbonated solutions indicating the influence CO₂ on the rate of degradation of morpholine. It is proposed that reaction of morpholine degradation begins with oxygen protonation of morpholine followed by nucleophilic attack of water. Minimal loss in concentration due to degradation have been experienced at temperatures like 135 and 150 °C. However, loss of concentration of morpholine increased sharply at high temperatures like 175 and 190 °C.

Comparison of concentration loss of morpholine with other amines show that it is the most stable amine solvent. CO₂ loading has shown a direct effect on the degradation of morpholine. However, at 190 °C, the higher CO₂ loading 0.48 mol CO₂/mol alkalinity resisted the degradation compared to 0.3 mol CO₂/mol alkalinity. Effect of temperature and CO₂ loading is also evidenced by the required activation energies. The degradation kinetics of morpholine follows the first order rate of reaction. A rate model has been proposed for the degradation morphine. The predicted results of degradation kinetics of morpholine are in good agreement with experimental results with an AAD of 2.88 %.

CRediT authorship contribution statement

Shaukat Ali Mazari: Conceptualization, Methodology, Writing - original draft. **Rashid Abro:** Validation. **Abdul Waheed Bhutto:** Writing - review & editing. **Idris M. Saeed:** Data curation. **Brahim S. Ali:** Supervision. **Badrul M. Jan:** Project administration, Supervision. **Lubna Ghalib:** Validation. **Mushtaque Ahmed:** Software. **N.M. Mubarak:** Visualization.

Table 5
Thermal degradation activation energies of different amines.

Amine	Amine Conc: (M)	Degradation Activation Energy (KJ/mol)	Temperature Range (°C)	CO ₂ loading (mol/mol alkalinity)	Reference
MOR	3.50	142.16	135, 150, 175, 190	0.2, 0.3, 0.48	This Study
MOR	3.50	175.77	135, 150, 175	0.2, 0.3, 0.48	This Study
MOR	3.50	300.94	135, 150, 175, 190	0.20	This Study
MOR	3.50	212.17	135, 150, 175, 190	0.30	This Study
MOR	3.50	131.65	135, 150, 175, 190	0.48	This Study
MEA	2.88	60	100, 120, 135	0.2	[27]
MEA	2.88	129	100, 120, 135	0.4	[38]
MEA	4.91	157	100, 120, 135, 150	0.3	[38]
MEA	4.91	144.21	120, 140	0.44	[37]
PZ	4.54	185	135, 150, 165, 175	0.3	[21]
PZ	4.54	191	135, 150, 165	0.4	[27]
Diethylethanolamine (DEEA)	2, 3, 4	82.60 ± 2.07	120, 135, 150, 175	0.3, 0.5, 0.7	[39]
AMP	1.12, 1.68, 2.24, 3.36	109.53 (± 15.32) 112.61 (± 11.95)	120, 135, 150	0.17 to 0.7	[40]
AMP	3.88	112	120, 135, 150	0.4	[38]
MDEA	4.28	100	100, 120, 140, 160, 180	2.6 MPa	[27,41]
Ethylenediamine (EDA)	5.21	154	100, 120, 135	0.4	[27,42]

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Authors are thankful to Institute of Research Management & Services (IPPP), University of Malaya for financial assistance under grant PG030-2014B.

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