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## Design and simulation of rate-based CO<sub>2</sub> capture processes using carbonic anhydrase (CA) applied to biogas

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### Abstract

Today the mix of the energy sector is changing from reduction of CO<sub>2</sub> emission from fossil fueled power industry into a general focus on renewable industry which is emitting less greenhouse gases. Renewable fuels like biomass for electricity production or biogas for bio-methane production have a potential to create negative emissions using bio-energy carbon capture and storage (BECCS).

All sectors are still in the need for applying more sustainable carbon capture and storage (CCS) technologies which result in lower energy consumption while reducing the impact on the environment. Recently several promoters have been developed for solvent based technologies, but there is still a need to develop new approaches which can potentially reduce energy consumption even further.

Solvents typically used for CCS have the tendency to form carbamate. They are characterized by the speed at which they react with CO<sub>2</sub>. Advantageous kinetics results in smaller equipment size. But this is not the only benefit.

In this study we deliberately apply a slow reacting solvent, MDEA (methyldiethanolamine). It is in the category of non-carbamate forming tertiary amines, for the same reason it binds less hard to CO<sub>2</sub>. The advantage is a noticeably lower regeneration energy compared to primary and secondary amines. As a result the cost for stripping is significantly lower.

Reactivated slow tertiary amines are applied in this study with the aim of reducing energy consumption. This is achieved by using carbonic anhydrase (CA) enzymes as additives in the slow solvent.

The aim of this work is to develop a rate-based model for tertiary MDEA mixed with various amounts of CA. The results show that the properties for biogas are significantly different compared to air and may need to be treated accordingly accurate. This

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work proves that the typical mass transfer resistance observed in the biogas gas phase is low compared to the resistance in the liquid phase. The consequence is a reduced requirement for accurate properties for the biogas and the biogas can easily be modelled as being similar to air.

In this work we create a calculation engine which is capable of BECCS, thereby enabling prevention of CO<sub>2</sub> emissions from renewable technologies giving a potential for zero-emission scenarios which can help to reach the new low emission CO<sub>2</sub> target set up by COP21.

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*Keywords:* Biogas upgrading, carbonic anhydrase, rate based model, simulation, absorption, desorption

## 1. Introduction

The major energy source today is the combustion of fossil fuels. According to the International Energy Agency (IEA), 81.4% of the world's total energy supply was produced from fossil fuels in 2013, whereof 21.4% from the combustion of natural gas. The World Energy Outlook (WEO) predicts that fossil fuels will remain the major energy source in 2030 and will meet about 84% of the expected energy consumption. As fossil fuels are not sustainable and eventually will run out, substitutes are essential to solve the energy challenge of the future.

Substitutes for fossil fuels have to be sustainable, green and cheap. Substitutes like wind, solar and hydro power have the potential of solving the energy problem, but do still have a long way to go. Only a fraction, around 8.5%, of today's energy production comes from these renewable energy sources [1]. Especially the lack of economically viable storage opportunities hinders these renewable substitutes [2]. Another renewable alternative is biogas, which can be used as a direct substitute for natural gas. Biogas can be combusted to produce power and heat, or liquefied to be used in vehicles in the transportation sector. Biogas together with other biofuels and waste accounted for 10.2% of the total energy production in 2013. Currently, biogas alone has the potential to replace about 6.7% [1] of the world primary energy supply, or a quarter of the current natural gas consumption. Biogas is thus not the whole solution, but an important element in a sustainable future.

As for most engineering solutions, biogas also has some challenges to overcome. When biogas is produced, around 30-40% of the gas is CO<sub>2</sub>. This lowers the heating value of the gas significantly and makes it expensive to store. To make biogas suitable for gas grid injection and vehicle usage, the biogas has to be upgraded to almost pure bio-methane.

In this work we aim to construct a rate based model for packed column applied to solvent based CO<sub>2</sub> removal, using absorption and desorption, applied to biogas systems.

In this study we deliberately apply a slow reacting solvent, MDEA (methyldiethanolamine). It is in the category of non-carbamate forming tertiary amines, for this reason, the bonds between CO<sub>2</sub> and the solvent are relatively weak. Amines are classified in three groups: primary, secondary and tertiary amines. The reaction between CO<sub>2</sub> and primary/secondary amines (MEA, DEA) is significantly faster than the reaction between CO<sub>2</sub> and tertiary amines (MDEA). However, the advantage of tertiary amines is a noticeably lower regeneration energy compared to primary and secondary amines. As a result the cost for stripping is significantly lower. An ideal approach would be a combination of fast absorption and low regeneration energy – such as activated/promoted tertiary amine solutions.

The aim is to reduce energy consumption using MDEA, but MDEA reacts slowly with CO<sub>2</sub>. MDEA is re-activate using CA in this study.

## 2. Carbon anhydrase to improve solvent performance

The CO<sub>2</sub> absorption into MDEA-H<sub>2</sub>O mixtures occurs through 3 reactions. CO<sub>2</sub> reacts with MDEA forming bicarbonate, see R1 below. In this, MDEA acts as a proton receptor. Secondly, CO<sub>2</sub> reacts with OH<sup>-</sup> to form carbonate ions, R2, while the third reaction, R3, represent hydration of CO<sub>2</sub> in water.



Generally, tertiary amines like MDEA have significantly lower reaction rates than primary or secondary amines like MEA or DEA. [3]. In the MDEA-H<sub>2</sub>O systems, the contributions of R2 and R3 can be neglected. This is not possible in CA systems.

CA is a family of metalloenzymes capable of catalysing the hydrolysis of CO<sub>2</sub> (R2 and R3). CA is found in many variations in nature, where it is among other things responsible for the absorption and desorption of CO<sub>2</sub> into the blood stream. Thermostable strains of CA capable of handling up to 80-90°C have been discovered. In the presence of CA, R3 contributes significantly to the reaction scheme during CO<sub>2</sub> absorption in MDEA-H<sub>2</sub>O [3, 4]. The capture process therefore needs to be modelled as at least a 2-reaction scheme.

### 3. Model basis: thermodynamics, properties, rate based scheme

The rate based model presented in this work is based on the initial work of Gabrielsen et al. [5]. It has undergone a significant development process the last decade and is now called the CapCO<sub>2</sub> model. The package is a model of multi-coupled partial differential equations (PDE) solved as a boundary value problem (BVP) using design specification for inlet flows. It allows for simple design considerations on column height and diameter with the possibility to easily vary the packing type. Currently it is implemented as a standalone module. It is also interfaced to Aspen Plus as a user unit operation model. It can take advantage of the CAPE-Open principles if the user finds a need for it. The model is valid at both absorber and desorber conditions. Recently it was consistently extended for blended amine solvents with multiple reactions [6] applying the so called GM enhancement factor model. It has been used in advanced slurry simulations [7] and also dynamic applications [8,9] and it was benchmarked against well-known models within CO<sub>2</sub> capture [10]. In this study it implements the advanced thermodynamic model called extended UNIQUAC for the CO<sub>2</sub>-MDEA-H<sub>2</sub>O system [11].

#### 3.1. Model development for the MDEA-H<sub>2</sub>O solvent with CA

The model presented here is for rate-based column calculation. The solvent applied is MDEA with dissolved CA. The enzyme is only present in minute amount, <1 kg/m<sup>3</sup>, it is therefore rightfully assumed that physical chemical properties and phase equilibria is not impacted. Only the net kinetic performance of the solvent is increased.

All thermodynamic properties like vapor pressures, heat capacities, heat of absorption and similar properties are calculated using the extended UNIQUAC model. The physical-chemical properties which cannot be calculated with an activity coefficient model are outlined in table 1.

Table 1. Physical-chemical properties used in CapCO<sub>2</sub> for the CO<sub>2</sub>-MDEA-H<sub>2</sub>O liquid phase.

Property	Author	Year	$W_{MDEA}$ range wt frac.	AARD %
Density ( $\rho$ )	Al-Ghawas et. al.	1989	0.0-1.0	0.05%
Viscosity ( $\mu$ )	Al-Ghawas et. al.	1989	0.0-0.7	1.16%
Surface tension ( $\sigma$ )	This work	-	0.0-0.9	1.12%
Diffusion coefficient of CO <sub>2</sub> in the liquid ( $D_{CO_2}$ )	This work	-	0.0-0.5	10.8%
Diffusion coefficient of MDEA solvent ( $D_{MDEA}$ )	This work	-	0.0-1.0	4.11%

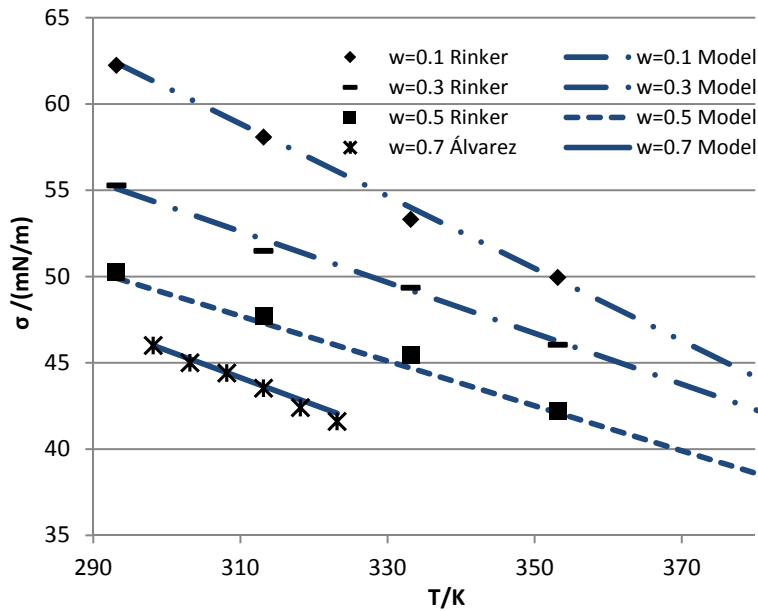


Figure 1. Correlation and model of surface tension used in CapCO<sub>2</sub> for the MDEA solvent.  $w$  is wt. fraction MDEA.

The table shows 5 basic properties which were used in order to estimate mass transfer coefficients. Note that a sub-section of the parameters are currently not valid at high concentration due to lack of sufficient measurement. If new data are published there are no obstacles to fit the properties in the whole concentration range. Currently the properties are correlated to physically meaningful values in the whole range. For the specific CO<sub>2</sub> application it is of less importance. MDEA is not used for concentration >50 wt% in this work.

The density and viscosity of the liquid were both correlated previously [12]. In this work they were validated against 15 other works from literature. For the sake of simplicity the viscosity correlation was not extended further for MDEA weight fraction >0.7. Data are available, but not in the scope of this study. The can easily be extended to include this range.

Surface tension and diffusivities of MDEA and CO<sub>2</sub> were refitted for this study in an extended range of temperature and concentration. An exemplification is given in figure 1 for surface tension on a subset of the used data. The AARD is low, approximately 1% and the behavior is strictly linear as function of concentration and therefore easy to correlate.

### 3.2. Correlations for air and biogas type systems

The typical CO<sub>2</sub> removal is conducted on spent air or air type systems. In biogas upgrading, the gas is not burnt. It consists mainly of biomethane (CH<sub>4</sub>), water vapor and small amounts impurities. The gas properties are significantly different compared to air since it contains 30-40% CO<sub>2</sub>. The gas phase is in this work modelled using the following correlations given in table 2.

Table 2. Physical-chemical properties used in CapCO2 for the biogas phase.

Property	Property basis
Gas density ( $\rho$ )	Ideal gas law
Gas viscosity ( $\mu$ )	Wilke [13]
Diffusion coefficient of CO <sub>2</sub> in gas ( $D_{G,CO_2}$ )	Fuller [18]
Diffusion coefficient of H <sub>2</sub> O in gas ( $D_{G,H_2O}$ )	Fuller [18]
Gas heat capacity ( $C_{p,g}$ )	This work
Gas thermal conductivity ( $\lambda_g$ )	Wilke [13]

The viscosity of the system is modelled using the Wilke [13] mixing rule based on pure gas viscosities estimated with the simple Chapman-Engskog equation as function of temperature. The heat capacities were estimated using ideal mixing of CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub>. Pure property heat capacities of the three species were refitted to experimental NIST data. Thermal conductivity of the gas mixture is calculated from pure component thermal conductivities using the Eucken's approximation. The mixtures were estimated by the Wilke [13] mixing rule. Impurities were correctly, as seen later, modelled without the impact of impurities.

### 3.3. Kinetics and mass transfer

The kinetics of the CO<sub>2</sub> reaction with MDEA catalyzed by CA was recently studied by Penders-van Elk [3]. In this work the kinetics were also based on the model and parameterization by Gaspar et al. [14]. The mass transfer coefficient and effective packing area was estimated using available correlations [15,16] incorporating the above physical-chemical properties.

### 3.4. Model validation

The model created in this work was recently validated against pilot data using enzymes [14,17].

### 3.5. Gas property impact of biogas compared to air

As mentioned above, biogas and air have significantly different properties. Figure 2 exemplify viscosity of the two gas phases. The axis to the right show approximately 25% difference on the two conditions. These results suggest that there could be a significant difference on model results by applying biogas upgrading. The same comparison at 45% CO<sub>2</sub> shows a milder difference of 15%.

The viscosity of biogas is always higher than the viscosity of air. This is due to the higher molecular weight of air compared to methane. The difference is seen to be smaller at higher CO<sub>2</sub> concentrations. The observed behavior is due to the higher molecular weight of CO<sub>2</sub> compared to air and methane.

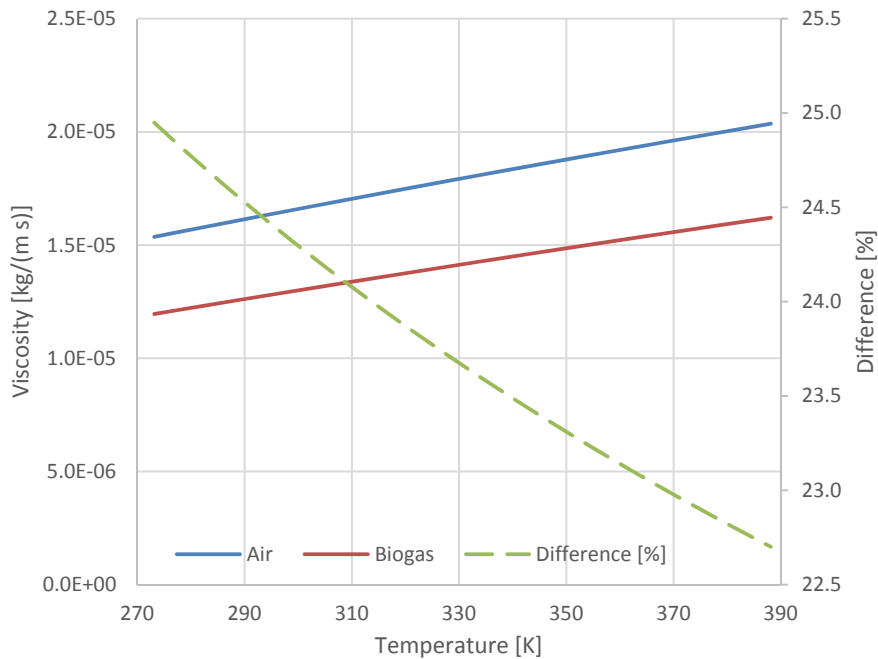


Figure 2. Comparison of viscosity for water saturate 30% CO<sub>2</sub> biogas and air as function of temperature.

Figure 3 also exemplifies an opposite trend for diffusivities. There is little to no difference on CO<sub>2</sub> diffusivities in biogas and air. The same conclusion is even stronger for water.

The typical range of difference for heat capacity in biogas and air is 10-20%. It is approximately 20-30% for densities and thermal conductivity.

In conclusion, it would be natural to expect that there could be a significant difference on modelling biogas upgrading systems compared to air cleaning setups or industrial gas cleaning.

#### 4. Absorption simulation

In order to test the impact of biogas properties compared to air, a small section of simulations were performed. The used physical size of the column is not based on industrial operating conditions. The focus here is to study the impact of biogas cleaning compared to air cleaning and the difference on the results. The liquid composition was 30 wt% MDEA with CA (0.05%) in a 6.6 m column using a diameter of 0.2 m.

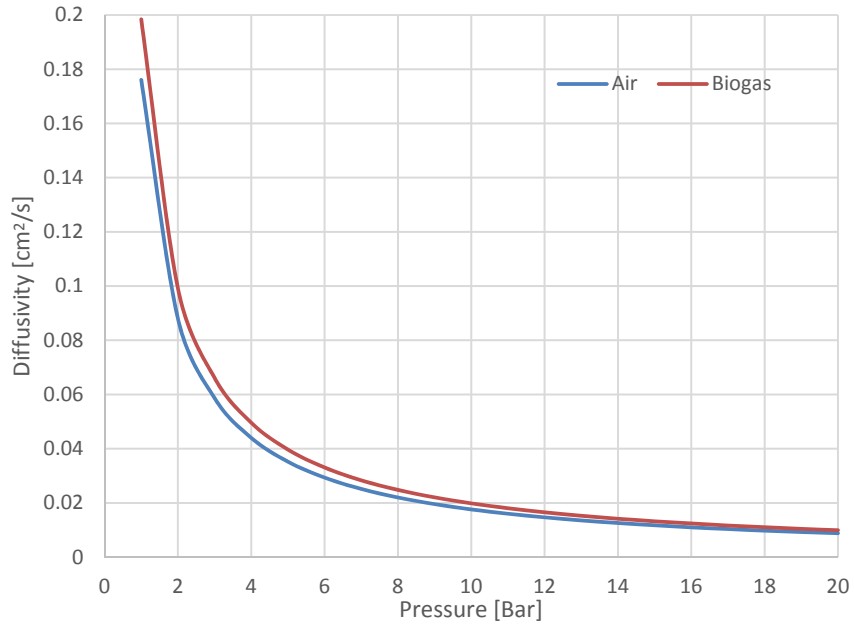


Figure 3. Comparison of CO<sub>2</sub> diffusivity in water saturated biogas and air as function of pressure.

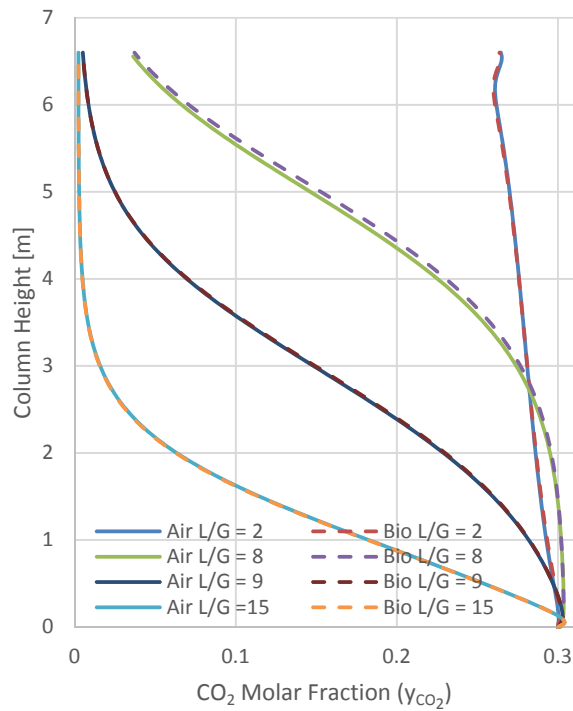


Figure 4. CO<sub>2</sub> profiles in a 6.6 m column comparing results from biogas upgrading and air cleaning as function of L/G ratio.



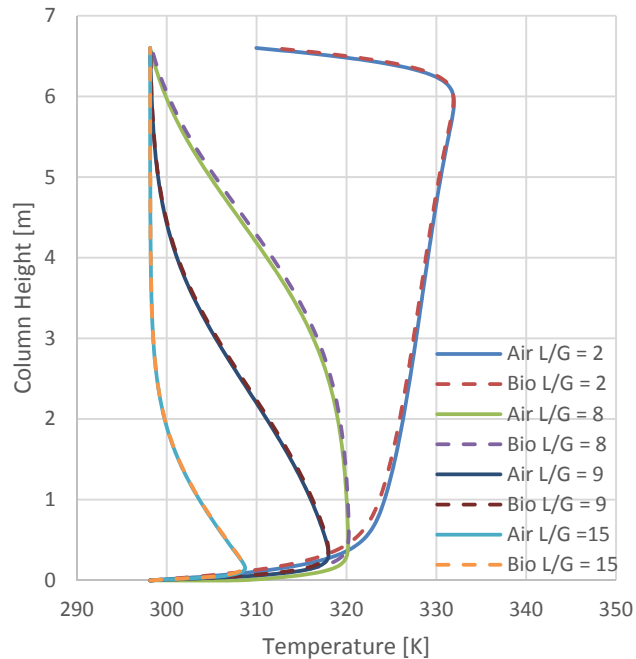


Figure 5. Temperature profiles in a 6.6 m column comparing results from biogas upgrading and air cleaning as function of L/G ratio.

By studying figure 4 and 5, it is clear that there is little to no difference on the calculated absorber efficiencies. A minor difference is observed for the low L/G ratios on the temperature profiles in figure 5 for the high gradient cases in the bottom of the column.

This same conclusion can also be made from studying the overall mass transfer coefficient,  $K_G$ , which is calculated from the two film theory with each a mass transfer resistance of,  $k$ , applying an overall enhancement factor  $E$  and a Henry's constant  $H$ , figure 6:

$$\frac{1}{K_{G,CO_2}} = \frac{1}{k_{G,CO_2}} + \frac{H_{CO_2}}{E \cdot k_{L,CO_2}} \quad (1.1)$$

The resistance to mass transfer in the gas phase for these systems is negligible. It therefore does not matter if the gas phase properties are accurately simulated. The result eventually depends mainly on the liquid side coefficients.

## 5. Conclusions

Based on this basic study of rate based modelling for biogas upgrading it can be concluded that gas phase properties can easily be correlated with a simple modelling approach for the gas phase properties. It can be concluded that the CapCO2 model is now available for enzyme enhanced amine solutions and that it can be applied for biogas upgrading. Since gas phase properties play an insignificant role in the calculations, impurities are also expected to have no impact on the final rate based calculation and column performance.

The model is available using Excel, Cape-Open, and the Aspen Plus user-model interface. DTU has created a custom programming interface (API) for users who like to apply the model in other larger customized simulation scenarios using C++, C# or Fortran language programming. The model can be run stand-alone.

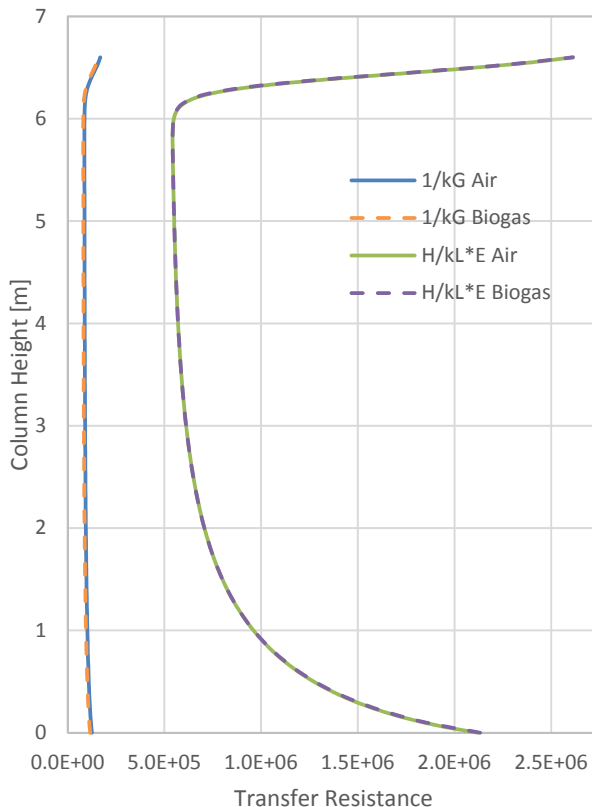


Figure 6. Mass transfer resistance in gas and liquid phases at L/G=8.

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