



GHGT-9

## Comparison of solvents for post-combustion capture of CO<sub>2</sub> by chemical absorption

Anusha Kothandaraman<sup>\*a</sup>, Lars Nord<sup>b</sup>, Olav Bolland<sup>b</sup>, Howard J. Herzog<sup>c</sup> and Gregory J. McRae<sup>a</sup>

<sup>a</sup>*Department of Chemical Engineering, Massachusetts Institute of Technology, 77, Massachusetts Avenue, Cambridge, MA 02139*

<sup>b</sup>*Department of Energy and Process Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway*

<sup>c</sup>*MIT Energy Initiative, Massachusetts Institute of Technology, 77, Massachusetts Avenue, Cambridge, MA 02139*

---

### Abstract

Post combustion absorption technologies represent one of the most commercially ready technologies for CO<sub>2</sub> capture. Solvent selection is the critical consideration in post-combustion absorption capture technology. In order to compare the performance of different solvents, it is necessary to perform simulations on a consistent basis and perform a process analysis of the system. The focus of this work was to develop consistent simulations for MEA and K<sub>2</sub>CO<sub>3</sub> systems in ASPEN. The simulations have been developed within the ASPEN RateSep framework and are valid for both natural gas and coal fired power plants. This paper describes the methodology of the simulations and some results from the two systems. The MEA base case was validated with reported values in literature. Potassium carbonate was found to be particularly useful for pressurized combustion and for CO<sub>2</sub> removal from product gases of reforming of natural gas or coal.

© 2009 Elsevier Ltd. All rights reserved.

*Keywords:* Carbon capture and storage; CO<sub>2</sub> capture, Post combustion capture

---

### 1. Introduction

Post-combustion capture is a downstream process that is analogous to flue gas desulphurization. It involves the removal of CO<sub>2</sub> from the flue gas produced after the combustion of the fuel. A schematic of post-combustion capture is presented in Figure 1 .

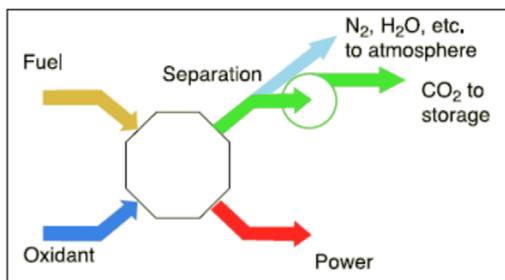


Figure 1: Schematic of post-combustion capture ( Adapted from [1])

In most cases, the power plant operates at atmospheric pressure and hence, the partial pressure of CO<sub>2</sub> in the flue gas is low. In the case of pressurized combustion or with IGCC and IRCC, the partial pressure of CO<sub>2</sub> is much higher. Table 1 presents the conditions of flue gas from different situations.

Table 1: CO<sub>2</sub> partial pressure in flue gases of different combustion systems. (Data taken from [1])

Flue gas	CO <sub>2</sub> concentration % vol (dry)	Pressure of gas stream MPa	CO <sub>2</sub> partial pressure MPa
Natural gas fired boilers	7-10	0.1	0.007-0.01
Gas turbines	3-4	0.1	0.003-0.004
Oil fired boilers	11-13	0.1	0.011-0.013
Coal fired boilers	12-14	0.1	0.012-0.014
IGCC after combustion	12-14	0.1	0.012-0.014
IGCC synthesis gas after gasification	8-20	2-7	0.16-1.4
IRCC synthesis gas after reforming	13-17	2-4	0.26-0.68

Post combustion absorption technologies represent one of the most commercially ready technologies for CO<sub>2</sub> capture. Solvent selection is the critical consideration in post-combustion absorption capture technology. In order to compare the performance of different solvents, it is necessary to perform simulations on a consistent basis and perform a process analysis of the system. The focus of this work was to develop consistent simulations for MEA and K<sub>2</sub>CO<sub>3</sub> systems in ASPEN. The simulations have been developed within the ASPEN RateSep framework and are valid for both natural gas and coal fired power plants. This paper describes the methodology of the simulations and some results from the two systems.

## 2. Process description

Chemical absorption systems at present represent the most preferred option for post-combustion capture of CO<sub>2</sub>. Chemical absorption systems have been in use since the 1980s for the capture of CO<sub>2</sub> from ammonia plants for food plants and hence, are a commercially realized technology, though not at the scale required for power plants. CO<sub>2</sub> is separated from the flue gas by passing the flue gas through a continuous scrubbing system. The system consists of an absorber and a desorber. Absorption processes utilize the reversible chemical reaction of CO<sub>2</sub> with an aqueous alkaline solvent [2]. A schematic of the absorption system is presented in Figure 2.

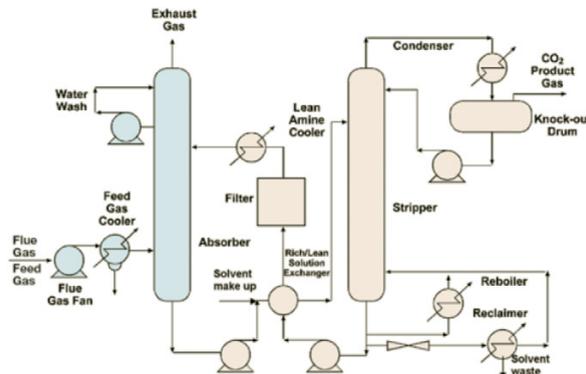


Figure 2: Schematic of chemical absorption system (Figure from [1])

The topic of this paper is to study in detail the performance of MEA and  $K_2CO_3$  solvents for  $CO_2$  capture.

### 3. Methodology

The simulations were developed using the ASPEN RateSep framework. It was found that it was necessary to model the systems using a rate-based method as opposed to equilibrium methods which have been utilized before. The thermodynamics for the system were modeled according to the parameters described by Freguia et al. [3] for MEA and Hilliard [4] for  $K_2CO_3$ . This was necessary in order to correct the thermodynamics representation in ASPEN for both MEA and  $K_2CO_3$ . The kinetics of the reaction were also modeled using the rate module in ASPEN.

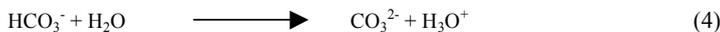
#### 3.1. Reactions

The reactions for the systems are modeled as:

##### 3.1.1. Reactions with MEA



##### 3.1.2. Reactions with $K_2CO_3$



#### 3.2. Flowsheet development

The simulations were developed in ASPEN as open loop simulations in order to perform parametric simulations. The simulations were designed to incorporate a number of design specifications on the reboiler duty and the heat exchangers in order to converge in a closed loop, in a manner similar to Freguia et al. [5]. The flowsheet model used to simulate the system for MEA is shown in Figure 3. A similar flowsheet was developed for  $K_2CO_3$ .

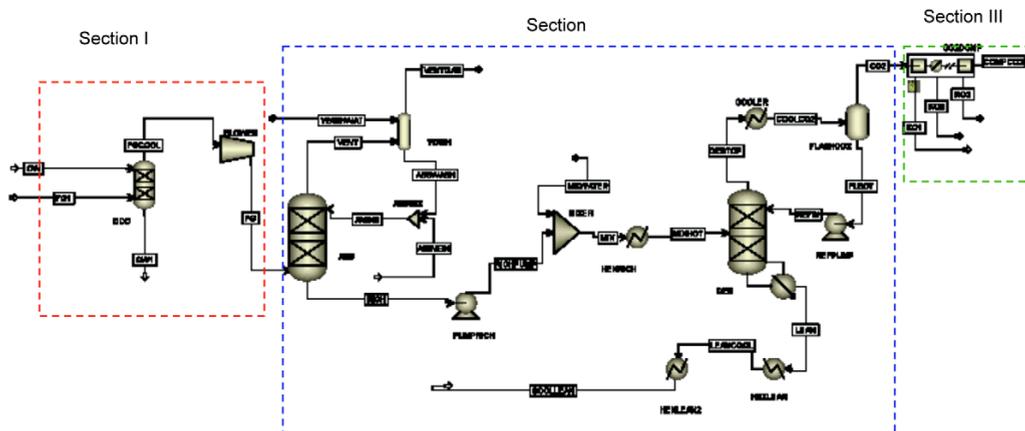


Figure 3: Schematic of ASPEN flowsheet

The flowsheet is composed of three distinct sections. Section I is the flue gas cooling and saturation section. Section II is the CO<sub>2</sub> absorption and desorption section while Section III refers to the CO<sub>2</sub> compression section. In Section I and II, the ENRTL model was used to model the system while in Section III the Reidlich-Kwong-Suave equation with the Boston-Mathias correction (RKS-BM) was used.

### 3.3. Rate based modeling

In order to truly capture the behavior of the system, it is necessary to employ a modeling approach wherein the reaction rates and rigorous mass transfer and heat transfer calculations are incorporated. ASPEN RATESEP allows the incorporation of kinetic and hydrodynamic effects in the modeling of the system. The effect of different packing types on the performance of the system can also be studied.

### 3.4. Film discretization

RateSep allows the calculation of reaction rate in the film. For systems in which there are rapid reactions, it is necessary to discretize the film properly in order to accurately account for the amount of reaction in the film. If the reaction is very fast and the film is not discretized, then RateSep will calculate the reaction in the film based on the concentration at the interface. This will be higher than the actual film reaction and hence will not accurately model the system. Also, the number of discretization points should be such that the solution is stable while at the same time not compromising on the computation time. This process of optimizing the film discretization was performed for both the MEA and the K<sub>2</sub>CO<sub>3</sub> systems.

### 3.5. Sizing considerations

While performing rate based calculations, it is necessary to provide the diameter and height of the column. ASPEN has an option wherein diameter calculations can be performed based on certain design factors. It was decided to size the columns on an approach to flooding basis. A design factor of 70% approach to flooding was chosen since this also allows some safety factor incase the operating conditions change suddenly. Since the flowrate of flue gas from a power plant is very high (~800 kg/s from a 500MWe natural gas power plant), it was decided to divide the CO<sub>2</sub> capture operation into 4 trains. This allowed the use of absorbers and strippers with diameters which are found in commercial units now. The range of diameters looked at was from 9-13m. There was also a limit set on the pressure drop of the column and this provided a constraint on the calculation of the diameter of the column.

## 4. Results and discussion

This section details the results that we obtained with the MEA and  $K_2CO_3$  systems

### 4.1. Results with MEA system

The MEA system was modeled with the specifications presented in the previous section. The simulations predict a reboiler duty of 4500 kJ/kg for natural gas and a duty of 4200 kJ/kg for gas from a coal power plant. The difference between the two is due to the higher rich loading that can be obtained with the coal system. These results match very well with the reported results from the Fluor Econamine FG<sup>TM</sup> process which reports a reboiler duty of 4200 kJ/kg [6]. The PH4-33 report [7] states a lower value but that is based on the Fluor Econamine Plus FG<sup>TM</sup> process which incorporates a better solvent formulation and significant heat integration. A number of parametric simulations were performed in order to optimize the system. Some of the important parameters are discussed below.

#### 4.1.1. Effect of capture percentage

As the capture percentage increased, the reboiler duty increased as well. There was a steep increase observed once the capture percentage approached 95%. This is due to the higher sensible heat requirements for the solvent.

#### 4.1.2. Effect of packing

Different packing types were investigated in the absorber, primarily for the effect on the rich loading that could be achieved. Table 2 presents a comparison of the different packings for the minimum reboiler duty obtained.

Table 2: Effect of packing in absorber on reboiler duty

Packing	SA (sqm/cum)	Lean load	Rich Load	Reb Duty (kJ/kg)
IMTP	226	0.22	0.491	4292
SuperPak	300	0.22	0.498	4219
MellaPak	495	0.22	0.504	4152

Hence, the rich loading increases and the required solvent flow decreases which leads to a decrease in the reboiler duty required. An economic optimization is required to determine the trade offs between the cost of packing and the reboiler duty. In this study, it was decided to proceed with the Norton IMTP packing.

#### 4.1.3. Effect of absorber height

Keeping the column diameter constant, the absorber height was varied to see the effect on the reboiler duty. The absorber height is normalized by the base height used in the other simulations and the reboiler duty is normalized by the minimum reboiler duty obtained from the equilibrium simulations. As the absorber height increases, the attainable rich loading increases and hence, the reboiler duty decreases. However as the absorber height increases, the pressure drop in the absorber increases and the capital cost of the absorber increase. Hence, an economic optimization needs to be performed to determine the feasible height.

#### 4.1.4. Effect of solvent temperature

As the temperature of absorption decreases, the driving force for absorption increases. However, the rate of the reaction and diffusivity decrease as temperature is decreased. An analysis was performed to see the effect of temperature on the performance of the system. Simulations were run at solvent temperatures of 20, 30 and 40 C. The reboiler duty for these runs did not differ significantly. Hence, the temperature of the solvent does not have a significant effect on the performance of the system. This is mainly because the solvent has a low specific heat and it takes up the heat of absorption quickly.

#### 4.1.5. Energy integration in the MEA system

The work lost in the MEA system due to CO<sub>2</sub> capture and compression was calculated to be 0.013 kWh/gmol CO<sub>2</sub> for coal fired power plants for 85% capture. This amounted to an efficiency decrease of 25% in the power plant. The breakdown of energy consumption is given in Figure 4 and the breakdown of regeneration requirements is given in Figure 5.

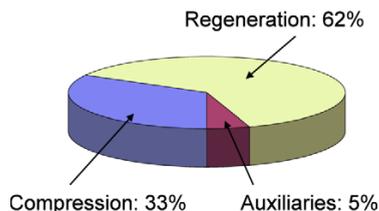


Figure 4: Breakdown of energy consumption in MEA absorption

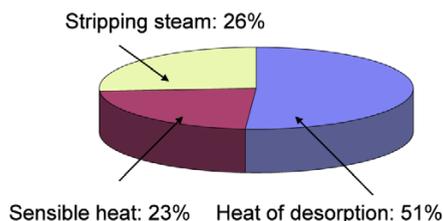


Figure 5: Breakdown of regeneration energy for MEA

The main opportunity for energy recuperation in the MEA system is in the reduction of sensible heat requirements. This will however require a larger heat exchanger and will come with the attendant trade-offs of increased cost. There is not much other scope to improve the performance of the MEA system as given beyond this.

#### 4.2. Results with K<sub>2</sub>CO<sub>3</sub> system

The potassium carbonate system is a pressure swing absorption desorption system [8] and the absorber was designed to operate at a high pressure of 15 atm. This system is useful in applications of pressurized combustion and IGCC and IRCC applications [9]. For a CO<sub>2</sub> content of 12% in the flue gas, the minimum reboiler duty obtained without energy recuperation was 3200 kJ/kg. A point of difference between the two systems was found to be in the design of the desorber. In the MEA system, the reactions in the desorber are very fast due to the high temperature in the desorber and it was the absorber which was the critical piece of equipment due to the high volumes of gas flows through it. However, in the case of K<sub>2</sub>CO<sub>3</sub>, the reactions are not faster in the desorber since both the absorber and desorber operate at nearly the same temperatures. In addition, the pressure is lower in the desorber. As compared to the MEA system, the equilibrium pressure of CO<sub>2</sub> over the K<sub>2</sub>CO<sub>3</sub> system in the desorber is much lower. Hence, the kinetics of the stripping reaction and the mass transfer of CO<sub>2</sub> to the vapor phase in the desorber are very important and the desorber becomes the critical piece of equipment. An important consideration in the K<sub>2</sub>CO<sub>3</sub> system is the precipitation of the bicarbonate species [10]. It is necessary that the system not be operated at very high conversions to bicarbonate since this can precipitate out especially in sections where the liquid stream is cooled.

##### 4.2.1. Effect of packing

The effect of packing on the performance of the system is quite pronounced in the case of K<sub>2</sub>CO<sub>3</sub>. The rich loading obtained in the absorber is influenced significantly by the packing employed.

The effect of packing in the desorber is even more pronounced. This is because a high mass transfer packing is essential in the desorber to transfer the CO<sub>2</sub> into the vapor phase. Table 3 presents the reboiler duties obtained with different packings.

Table 3: Effect of packing in desorber on reboiler duty

Packing	Size (mm)	Surface area (sqm/cum)	kJ/kg
Raschig	6	814.5	3180.33
Raschig	10	543	3422.3
Raschig	16	325.5	3796.72
Raschig	25	185	4215.41
IMTP	50	102	4557.38

#### 4.2.2. Effect of desorber pressure

For K<sub>2</sub>CO<sub>3</sub>, the ratio of the heat of absorption to the heat of vaporization of water is very close to 1 and hence, there is a lot of H<sub>2</sub>O vapor which exits with CO<sub>2</sub> at the top of the column. Energy has to be supplied in the reboiler to produce this steam and this represents a major portion of the energy consumption in this system. As the pressure increases, the amount of water vapor increases. Hence, for the potassium carbonate system, it is particularly beneficial to operate at vacuum conditions. By operating under a slight vacuum, it is possible to reduce the energy consumption by 100 kJ/kg. However, when operating under vacuum, it will be necessary to have larger diameter columns due to the higher vapor flows.

#### 4.2.3. Energy recuperation in the system

There are a number of schemes for energy recuperation in the potassium carbonate system.

##### 4.2.3.1. Flashing of rich solution:

The rich solution leaving the absorber is at a high pressure. If this solution is flashed before it enters the desorber, some of the dissolved CO<sub>2</sub> would be desorbed. This would then correspondingly reduce the heat duty in the desorber. However, the problem with this strategy is that the temperature of the rich stream leaving the flash vessel is low (adiabatic flash) and hence, sensible heat needs to be provided in the desorber to heat up this stream. This negates the heat savings obtained by flashing the stream. To overcome this, an alternative flowsheet modification is proposed wherein the liquid stream is heated by the lean stream leaving the desorber. This necessitates the addition of a heat exchanger, but can result in significant savings in the heat required in the desorber. Using this approach, the energy consumption can be reduced to 2850 kJ/kg. This represents a reduction of around 10% in the reboiler duty from the base case and hence offers significant savings.

##### 4.2.3.2. Split flow absorber

In the K<sub>2</sub>CO<sub>3</sub> system, significant savings in energy can be obtained if the system can be operated at higher lean loadings using a split flow absorber as described by Kohl et al. [2]. This will result in savings in both stripping steam and in reducing the heat of desorption. In this setup, only a part of the solution is thoroughly stripped to low lean loadings. This solution is then cooled and sent to the top of the absorber where there are the lowest driving forces. The rest of the solution is stripped less thoroughly and is introduced into the absorber at an intermediate point. Around 25% of the total rich stream is stripped completely and cooled to 60 C and fed to the top of the absorber. The rest of the stream is removed from an intermediate point in the desorber and fed to the top of the absorber. The reboiler duty for such a setup is approximately 2650 kJ/kg. This represents a significant savings over the base case scenario. The size of the equipment will however be greater in this setup because of the greater flows of liquid required.

## 5. Conclusions

A consistent framework for comparing different solvents for CO<sub>2</sub> capture has been developed using the ASPEN RateSep framework. The simulation for MEA produced results that matched well with those from experimentally reported values. There was not much scope for energy recuperation within the MEA system. The potassium carbonate system was found to be particularly useful for CO<sub>2</sub> capture from pressurized combustion power plants and from IGCC and IRCC applications. Substantial energy recuperation was possible in the potassium carbonate system.

## 6. Acknowledgements

We would like to thank the Norwegian Research Council and SatoilHydro for providing the funding for the project.

## 7. References

1. B. Metz, O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.), IPCC Special Report on Carbon Dioxide Capture and Storage, 2005.
2. Kohl, A. and R. Nielsen, *Gas Purification*, 5<sup>th</sup> ed., 1997, Houston, Texas, USA:Gulf Publishing Company.
3. Freguia, S., *Modeling of CO<sub>2</sub> removal from flue gases with monoethanolamine*, in *Chemical Engineering*. 2002, University of Texas: Austin.
4. Hilliard, M., *Thermodynamics of aqueous piperazine/potassium carbonate/ carbon dioxide caharacterized by the Electrolyte NRTL Model within ASPEN Plus*, 2004, University of Texas:Austin.
5. Freguia,S. and G.T. Rochelle, Modeling of CO<sub>2</sub> capture by aqueous monoethanolamine, *AIChE J.* **49** (7) (2003), pp. 1676–1686
6. Chapel, D., Ernst, J. and C. Mariz, 1999. *Recovery of CO<sub>2</sub> from flue gases: commercial trends*. Can. Soc. Chem. Eng. annual meeting.
7. IEA Greenhouse Gas R&D Programme, 2004. *Improvement in power generation with post-combustion capture of CO<sub>2</sub>*. Report No. PH4/33.
8. Benson, H.E., Field, J.H. and R.M. Jameson, CO<sub>2</sub> absorption employing hot potassium carbonate solutions. *Chemical Engineering Progress*, 1954. **50**: p. 356-364.
9. Sanyal, D., N. Vasishtha, and D.N. Saraf, *Modeling of carbon dioxide absorber using hot carbonate process*. *Industrial & Engineering Chemistry Research*, 1988. **27**(11): p. 2149-2156.
10. Tosh J.S., F.J.H., Benson, H.E. and W.P. Haynes., *Equilibrium Study of the System Potassium Carbonate, Potassium Bicarbonate, Carbon Dioxide, and Water*. U.S. Bur. Mines, Rept. Invest, 1959. **5484**: p. 23.