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A comparison of different parameter correlation models and the validation of an MEA-based absorber model

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Abstract: Considerable effort on research in CO_2 capture technologies has been directed towards steady state systems while less seems to have been done for the same systems in transient state. This work presents a dynamic model for CO_2 absorption using aqueous mono-ethanolamine (MEA). Validation against experimental results both obtained at steady state and dynamic conditions is included. A parametric sensitivity study of the underlying model equations is carried out based alternative parameter correlations for the reaction rate constant. It is concluded that validated results for one specific pilot plant don't necessarily apply to other plants of different sizes under other operational conditions. Furthermore, a parametric sensitivity study for the other parameters as well as for the rest of the CO_2 capture process is also warranted.

1. Introduction

Post-combustion CO_2 capture using MEA is generally accepted as the most mature and documented technology. As such, it is widely regarded as some kind of standard against which other similar upcoming technologies are compared. Consequently, the quest to develop rigorous models appropriate for design and operation, in order to increase efficiency and reduce cost has naturally resulted in contributions of different parameter-correlations with varying degrees of complexity from various researchers. In a way, these parameter-correlations seem to be competing yet without comparison. The choice of which parameter to use in a particular model is largely subjective to the model-developer's discretion, usually premised on a limited set of arguments. Even the commercial and popular software programs like ProTreat, Aspen HYSYS or gPROMS, just to mention a few, are as-a-matter-of-factly based on one parameter or the other. Several works, where only the predicted results from such simulators have been compared and contrasted abound in literature. However, not much seem to have been done regarding comparative exploration of the resultant effects that arise from using different parametric models.

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Another important challenge related to modelling is the validation of the model. One thing is the lack of appropriate data in literature, especially obtained from dynamic tests. The other thing is lack of application on large/full scale-facilities. In such cases, the usual approach is to compare the model with pilot-plant data and adjust the model parameters to make a proper fit. However, the model may not be valid for other plants operating at different conditions.

While most efforts at present have focused on the development of steady state models, Kvamsdal et al. (2009)[1] developed a dynamic absorber model (with appreciable rigorousness) to study problems inherent to transient operation, e.g. start-up, shut-down, load reduction, etc. The model was first validated against four different cases from an MEA campaign at the University of Texas at Austin (UT) in 2006. Unfortunately, only steady state data were available, but some of the model parameters were adjusted to fit: the steady state liquid phase temperature profile, the capture rate (%) and the rich loading. The gist of the present study is to validate this dynamic absorber model further and investigate the effect (on the general performance) of fitting different correlations of the same parameter. In essence, this could be construed as some kind of 'sensitivity study' based on parameter-correlations inputted from different literature sources. As an example, the effects of using four different correlations of the reaction rate coefficient compared against an appropriate steady state data-set (from the pilot plant at UT) as well as against a dynamic data-set (from a pilot plant at NTNU/SINTEF) are shown in the present paper.

2. Absorber Model

A diagram illustrating the concept of an absorber column is shown in Figure 1. The liquid solvent and flue gas are in conventional counter flow. In this case, the packing material, which determines the specific absorption area is packed from Z=0 to L. During operation, the packing material is assumed to be completely wetted by the liquid as it flows down the column, preferably at flow rates that maximize its contact surface area with the counter-flowing flue gas. In our case, plug flow is assumed since post-combustion CO_2 capture is characterized by low gas velocities and low pressures: conditions under which chances for back-mixing and flooding are very low. The conceptual flows for a control volume are indicated; with the broken line representing the gas-liquid interface.

The present model has been developed based on the following assumptions: axial differential mass and energy balances for both gas and liquid phases, linear pressure drop, ideal gas phase (owing to low pressure), mass and heat transport are based on the two film theory, no accumulation in gas and liquid films, MEA is the solvent (i.e. all thermodynamic issues are tailored accordingly), thermal

Figure 1: Illustration of the absorber. dz is the height of the control volume.

equilibrium between the liquid and packing material, condensation of water vapour occurs at gas-liquid interface as well as at the walls and that the effective contact area is equal to the specific area of the packing material.

The dynamic model is described by Kvamsdal et al. 2009[1]. The model, which was originally implemented in gPROMS[1] has now been re-implemented in MATLAB[2] with a slight improvement of the approach described in Astarita ([2]). The spatial discretization of the column is based on the orthogonal collocation method. An in-depth description of the orthogonal collocation method can be found in [3]. The resulting differential-algebraic equations are solved by the *ode15s* solver in MATLAB.
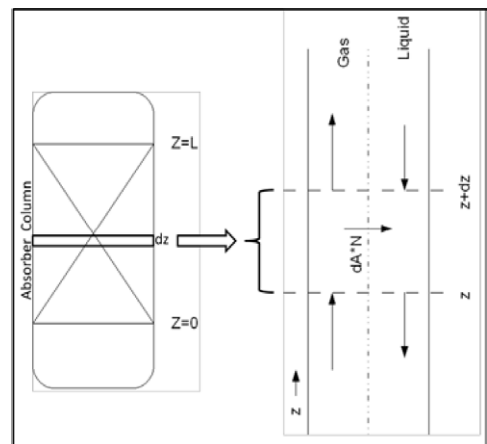

2.1. Reaction rate coefficient

The reaction-rate coefficient is generally described by an Arrhenius type of expression:

$$k_{r,CO_2} = k_{r,CO_2,0} \cdot \exp\left(\frac{-E_A}{RT_l}\right) \tag{1}$$

Based on measurements, several values have been proposed for both the constant $k_{r,CO_2,0}$ and the activation energy E_A. Here, three different sets of values found in the literature have been compared to an adjustment based on the above mentioned measurements at the University of Texas at Austin (UT) ([4]). The first is proposed by Versteeg et al. (1996) [5] and the second one is proposed by Hikita et al. (1977)[6]. Since both proposals were based on much lower concentration of MEA (less than 1 M), Freguia (2002)[7] adjusted the values from Hikita et al. [6] and Kvamsdal and Rochelle (2008) [4] adjusted the latter even further . The constants used in Equation 1, based on these 4 different references are given in Table 1.

Table 1: Constants used in Equation 1 based on different references.

Reference	$k_{r,CO_2,0}$ (m³/mol s)	E_A/R (K)
Versteeg et al (1996)[5] (*Versteeg*)	$4.40 \cdot 10^8$	5400
Hikita et al. (1977)[6] (*Hikita*)	$9.77 \cdot 10^7$	4955
Freguia (2002)[7] (Freguia)	$3.20 \cdot 10^3$	1348
Kvamsdal and Rochelle (2008)[4] (Kvamsdal)	$2.95 \cdot 10^3$	1500

The reaction rate coefficient is included in the Enhancement factor:

$$E_{CO_2} = \frac{\sqrt{k_{r,CO_2} \cdot C_{MEA}^* \cdot D_{CO_2}}}{k_{CO_2}^l} \tag{2}$$

Where $k_{r,CO2}$ is the reaction rate coefficient for the reaction of CO_2 with the aqueous MEA, C_{MEA}^* is the liquid concentration of free MEA in the solution, D_{CO2} is the diffusivity of CO_2 in the aqueous MEA solution, and k_{CO2}^l is the liquid mass transfer coefficient for CO_2. The Enhancement factor is incorporated in the total mass transfer coefficient (for absorption of CO_2) follows:

$$K_{tot,CO_2} = \frac{1}{\dfrac{RT_g}{k_{CO_2}^g} + \dfrac{H_{E,CO_2}}{k_{CO_2}^l E_{CO_2}}} \tag{3}$$

H_{E,CO_2} is the Henry's Law constant and $k^g_{CO_2}$ is the gas mass transfer coefficient for CO_2.

3. Model validation

In the present work, the model has been validated against one steady state model implemented in an in-house simulation tool (CO2SIM) as well as against both steady state and dynamic results obtained from an MEA campaign carried out at the VOCC (Validation Of Carbon Capture) rig, owned by NTNU and SINTEF.

3.1. Comparison with CO2SIM

CO2SIM is an in-house albeit professional (developed by SINTEF) software dedicated to research in post-combustion chemical CO_2 capture processes at steady state. It uses a rigorous rate-based approach for mass transfer.

For convenience in comparing our model against CO2SIM, all the input data (for simulation) were taken from [1] (case 32) except for the packing material, which is at present limited to Mellapak 2X in CO2SIM. The discripancy in the corresponding input values means that the resulting temperature profiles are slightly different from those reported in [1]. As seen in Figure 2, there are some differences in the steady state temperature profiles and the capture level for the two models. The equilibrium model is based on the same approach in the two models so it is believed that the discrepancies are mainly related some simplifications in the energy balance of the dynamic model. All the same, differences in liquid outlet temperature and the capture level are within an acceptable margin of less than 2 %.
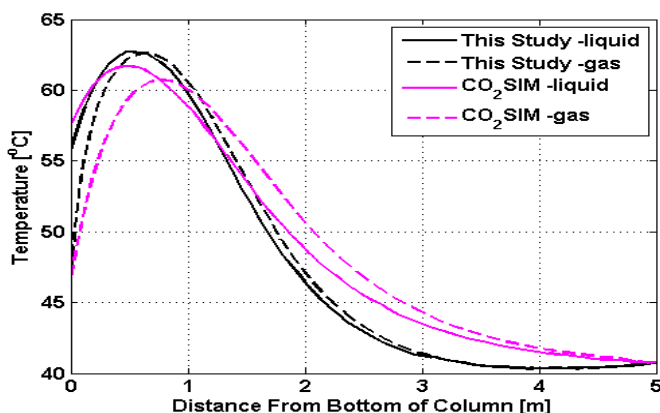

Figure 2 Simulation at steady state - comparing the performance of the dynamic model against CO2SIM using input data from case 32 reported by Kvamsdal et al. (2009)[1] except for the packing material (Mellapak 2X).

3.2. Validation against Pilot Plant measurements

The NTNU and SINTEF laboratory has a pilot plant rig tailor-designed for the *validation of CO₂ capture* (usually abbreviated VOCC by the users) both in steady state and dynamic mode. For the purpose of this study (CO_2 absorption), the stripper section was decoupled. Structured packing material (Mellapak 2X) was used. Temperature readings inside the column are assumed to approximate liquid temperature. The inlet liquid solution contained 30 wt% MEA with a CO_2 loading of 0.25 (i.e. mole fractions: x_{co_2}=0.0293, x_{H_2O}=0.8538, x_{MEA}=0.1169). The gas temperature and pressure were fairly stable, thus assuming x_{H_2O} to be constant and that ideal gas laws applies, was considered good enough. The VOCC dimensions are summarized in Table 2.

Table 2 Dimensions of the VOCC rig.

Contact area	Inside diameter	Packing Height	Hydraulic diameter	Void fraction	Liquid hold-up
205 m^2/m^3	0.5 m	5.4 m	0.019	0.98	0.07

During the VOCC campaign, the plant was first run in steady state mode before shifting to the dynamic mode. That implies that both the liquid and gas flows were operated in a once-through fashion until stable output values and the associated profiles were achieved. In the dynamic mode, the rig was run under a set of two different conditions, dubbed case-A and case-B for reference. In case-A, the liquid and gas flows were changed as summarized in Table 3. The gas was recycled for case-A, so CO_2 content at gas inlet was constantly decreasing with time. The rest of the gas was assumed to be saturated air.

Table 3: Summary of conditions and inlet/outlet values for Case-A

Time (min)	Liquid flow rate (m^3/h)	Gas flow rate (m^3/h)	Average in- and out-let input values	
0	1.56	1742	T_{inlet} , T_{outlet} (^oC)	41, 40
2.5	1.98	1742	Inlet $x_{CO2,g}$	0.036
14	1.98	1090	Inlet $x_{H2O,g}$	0.085
21	1.98	1742	Inlet $x_{inerts,g}$	1-($x_{H2O,g}$ + $x_{CO2,g}$)
25	1.56	1742	p_{inlet} , p_{outlet} (kPa)	102.0, 101.4

An example of the steady state temperature profile for case A is shown in Figure 3. From these plots, it can be seen that the predictions (for both the liquid and gas phases) from our model compares very well with the rig measurements at steady state.

On the other hand, the outcome of running the VOCC rig in the dynamic mode corresponding to the set of conditions for case-A as summarized in Table 3 are shown in Figure 4. In this case, the discrepancy between the simulation and the measurements is much higher compared to the steady state mode. For the CO_2 capture level, the margin is systematic and to the order of ∓10%. Figure 4 (b) shows that the model generally over-predicts the rich loading, albeit, its values are acceptably within the neighbourhood of the VOCC measurements.
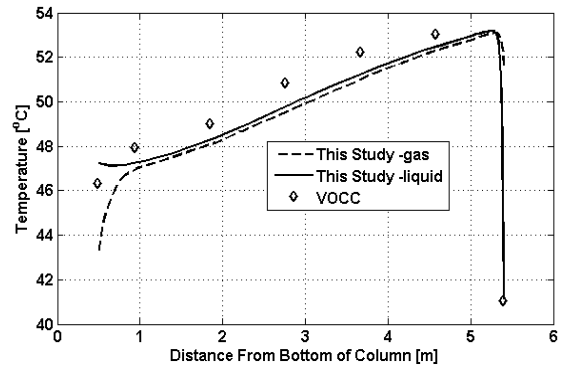

Figure 3: Plots showing the steady state gas/liquid temperature profile for case A predicted by the dynamic model versus VOCC
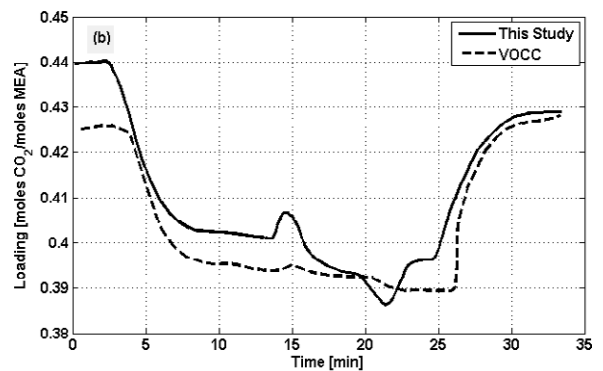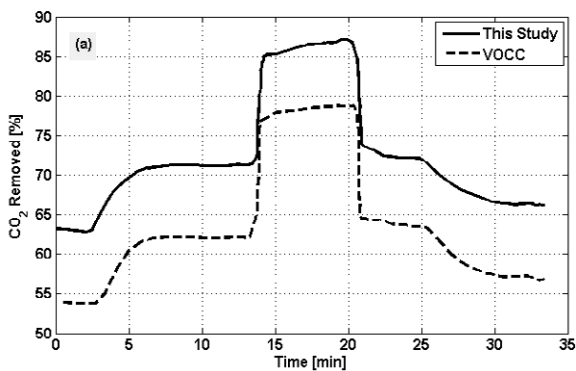

Figure 4: Inlet conditions and flow rates for case-A (see Table 2): (a) shows the corresponding CO2 removed while (b) shows the corresponding loading.

4. Sensitivity Study based different parameter correlations for reaction rate

The governing equations (on which our dynamic model is based) are, as a matter of fact, subject to and affected (either weakly or strongly) by the parameters constituting them. However, for each parameter, there exist in many cases, several alternatives. This implies that the existing models developed for CO_2 absorption are based on rather arbitrary sets of these parameter correlations, the choice of which is largely dependent on the model-developer's discretion and or experience. Nevertheless, in this section we seek to explore the effects of inputting the different parameter correlations in the dynamic model and then compare the outcome.

The performance of using the four different correlations was first validated against case 32 from the UT campaign. Although there are some differences in the temperature profiles, the differences in other performance-data are not significant as seen in Table 4.

Table 4: Sensitivity study based on parametric correlations (reaction rate coefficient) constituting model equations for CO_2 absorption. Numbers in italics - corresponding % deviation (for loading & CO2 removal respectively) from UT measurements

Correlation	Bottom temp (^{o}C)	Rich loading		CO$_2$ Removal (%)	
Pilot plant UT	-	0.428	*0*	93.8	*0*
*Kvamsdal et al., (2009)[1]	54.0	0.436	*1.8*	94.9	*1.2*
Freguia, (2002) [7]	54.9	0.440	*2.7*	98.0	*4.3*
Hikita et al.,1977 [6]	54.0	0.434	*1.4*	93.4	*-0.4*
Versteeg et al., 1996 [5]	54.3	0.435	*1.6*	94.5	*0.7*

* Correlation used in the dynamic model

The performance of the different parameters were also validated against case-B of the VOCC dynamic campaign, in which the flow rates (gas=2141 m^3/h, liquid=1.98 m^3/h) were kept constant while the CO_2 content was changed as depicted in Figure 5. The in- and out-let temperatures were the same for case-A while the corresponding pressures were 103.6 and 101.3 kPa respectively. The change with temperature for the different parameter correlations is shown in Figure 6 (a) while Figure 6 (b) shows the resultant corresponding temperature (at steady state i.e. CO_2 content is fixed before time=0) when the correlations are applied in the model for case-B conditions.
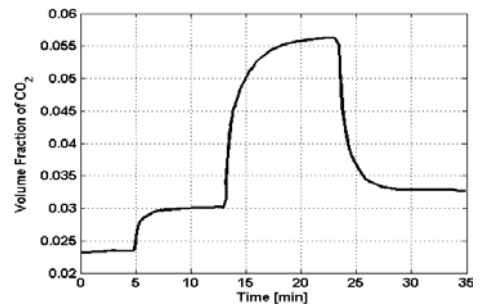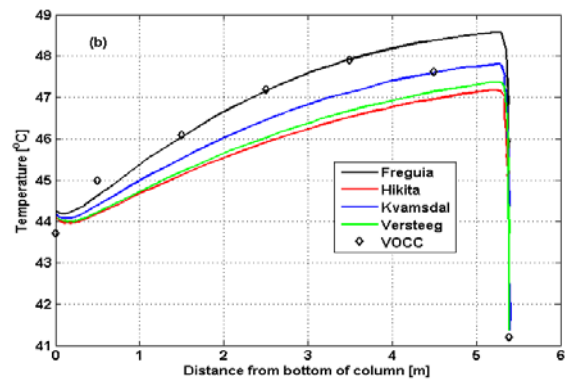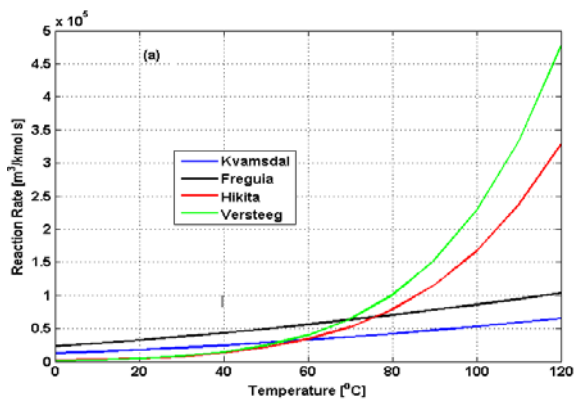

Figure 5: CO$_2$ content at gas inlet for case-

Figure 6: (a) Shows variation with temperature (b) shows the resultant (or corresponding) absorber temperature profiles.

It can be seen that the correlation by Freguia et al. agrees better with pilot plant measurements compared to the other correlations regarding the temperature profile. However, this is not the case when considering the two most important indicators (CO_2 capture level and rich loading) as is revealed by Figure 7 which showcases the situation in the dynamic mode.

   Although the difference in value of the reaction rate constant within the operating range of the absorber for correlations shown in Figure 6 (a) is not very big, the correlation by Versteeg shows better performance for CO_2 removal as depicted by Figure 7 (a). However, all four correlations are significantly but systematically (thus warranting further investigation to establish the cause) off-target regarding prediction of the rich loading.
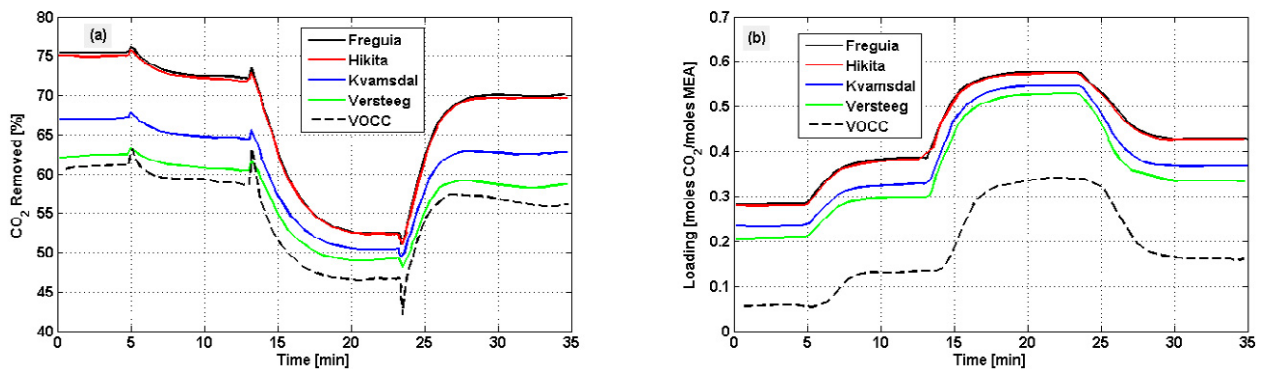

Figure 6: (a) Compares CO2 removal levels for the different correlations (b) the corresponding rich loading.

   A tabulated overview of the resultants effects on the general performance of the model at steady state conditions (based on the parameter correlations selected for this study) is summarized in Table 5.

Table 5: Sensitivity study on parametric correlations (reaction rate coefficient) in model equations for CO2 absorption. Numbers in italics - corresponding % deviation (for loading & CO2 removal respectively) from VOCC measurements

Correlation	Bottom temp (^{o}C)	Rich loading		CO_2 Removal (%)	
Pilot plant VOCC	43.75	0.317	*0*	60.5	*0*
*Kvamsdal et al., (2009) [1]	44.15	0.379	*16*	66.9	*9.6*
Freguia, 2002　　[7]	44.16	0.394	*20*	75.4	*20*
Hikita et al.,1977 [6]	44.15	0.393	*19*	75.5	*20*
Versteeg et al., 1996 [5]	44.15	0.368	*14*	62.1	*3.4*

   * Correlation used in model

5. Results and discussion.

   The dynamic model performs satisfactorily, both in terms CO_2 capture level (less than 5% relative difference) and the temperature profile when compared with corresponding outcomes from CO2SIM. In regards to the VOCC measurements, it should be emphasized that running a campaign to obtain pertinent data for CO2 absorption in the dynamic mode is in general, a challenging task. This perhaps could be one of the factors why data for dynamic campaigns has hardly been reported elsewhere in literature to date.

The general performance of the dynamic model in comparison to the dedicated campaigns from the VOCC rig is reasonably good, with prediction of the temperature profile for both dynamic and steady state mode being quite satisfactory, but the results at steady state deviate more (the model over-predicts the CO2 removal level with 10% and rich loading with 16%) compared to the validation against the UT campaign. However, the model is tuned specifically to the data obtained at UT and as such, not necessarily applicable for direct simulation in regards to the VOCC rig. Further investigation is therefore needed to generalize the model while simultaneously minimizing the discrepancies between simulation and measurements.

The study on parametric sensitivity has been showcased using four different correlations for the reaction rate coefficient. The difference in the absorber performance by simulation of the case 32 from the UT campaign is not significant. However, the corresponding scenario for case-B (based on the VOCC rig) exhibited deviations of appreciable margins the same correlations. Most likely, the reason is that the condition in the bottom at UT (for case 32) was closer to equilibrium compared to those of the VOCC rig. Thus, the influence of the reaction rate coefficient is more important for the mass-transfer in the latter case. Another important factor is that; while the differences in the reaction rate itself (as seen in Figure 6a) are rather insignificant at typical absorption conditions (i.e. around 40 oC) the differences are much larger at stripper conditions. The latter implies that, in any case, the whole process should be studied in the dynamic mode.

6. Conclusions

Validation of dynamic models for CO_2 absorption is rather challenging due to lack of reported data in literature, and those which are available are limited to small scale pilot plants tested mainly at steady state conditions. This likely gives rise to scale-up problems when implementing full scale modelling. Agreement between the dynamic model and pilot plant measurements are reasonably good, but some further adjustments are necessary. The parametric sensitivity study based on the reaction rate coefficient correlations reveals that: conclusions based on results accredited from the validation one specific pilot plant don't necessarily apply to other plants of different sizes under other operational conditions.

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