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DISCUSSIONS

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Modelling – from molecules to mega-scale: general discussion

Berend Smit, Peter Styring, Grant Wilson, Gary Rochelle, Felix Donat, Joseph Yao, Martin Trusler, Claire Adjiman, Stephen Lyth, Jet-Sing M. Lee, Thomas Hills, Patrick Brandl, Matteo Gazzani, Rosa Cuellar-Franca, Paul Fennell, Daniel Sutter, Mai Bui, Colin Scholes, George Dowson, Jon Gibbins, Lisa Joss, Geoffrey Maitland, Stefano Brandani, Pelayo Garcia-Gutierrez, Yue Zhang, Christoph Müller, George Jackson, Raffaella Ocone, Lennart Joos, Robert Bell and Richard Graham

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Gary Rochelle opened discussion of the paper by **George Jackson**: Have you attempted to use the implicit speciation of SAFT to model mass transfer with fast reaction in the boundary layer using kinetics?

George Jackson answered: No, we have not used the SAFT treatment to describe mass transfer in the boundary layer using kinetics. This is an interesting proposition which we will certainly be looking into in the near future.

Martin Trusler remarked: It appears that the parameter τ that you use to modify the effective diffusion coefficient plays a very strong role in the overall performance of the model. I think it would be interesting to model a solvent system which has simpler chemistry in CO_2 capture, where the bound species is a known molecule with a diffusion coefficient known from experiment. This would provide a more rigorous test for your overall modelling approach.

George Jackson responded: This would certainly be a very good way of testing the applicability of our modelling approach for the effective diffusion of carbon dioxide in a reactive amine solvent. Which particular solvent system did you have in mind?

Martin Trusler commented: My suggestion is to look at an aqueous solution of a tertiary amine.

Martin Trusler continued: In the paper, you describe obtaining the diffusion coefficient of CO_2 and N_2 in water from a "predictive" empirical model. My comment is that these diffusion coefficients are available experimentally and one

could eliminate the (possibly large) uncertainty of the "predictive" empirical model by using the experimental data or a simple representation thereof.

George Jackson replied: We feel that the issue is not so much determining the diffusion coefficients of carbon dioxide or nitrogen in neat water (for which there are extensive experimental data and reliable correlations), but the availability of such data for carbon dioxide in the reactive amine solvent. It would be extremely useful to have reliable experimental data of the diffusion coefficients (and other transport thermophysical properties) for the various reaction species, including the unreacted carbon dioxide, the carbamate, the bicarbonate, and the protonated amine.

Yue Zhang observed: To match the pilot plant data, you chose to vary the single diffusivity parameter based on the sensitivity analysis. Have you tried to regress multiple adjustable parameters simultaneously to get a better fit?

George Jackson responded: The key goal of our approach is to minimize the number of adjustable parameters to describe the system, retaining as much of the predictive capability of the model as possible. By varying more of the parameters in the model (to better describe the diffusivity, viscosity, enthalpies, surface tensions *etc.*) one could in principle achieve a better overall description of the process. We are aiming however to develop a tractable predictive platform for integrated computer aided molecular and process design (CAMPD) of a broad range of solvents including amines, ethers and multifunctional alkanolamines, for which very limited (or no) experimental data are available. The fact that the diffusivity parameter is found to be transferable to different pilot plant runs and conditions is a clear advantage in this regard. We are planning to assess the transferability of the parameter to other carbon capture solvents in the near future.

Peter Styring enquired: The model works well for MEA, however, does it work for other systems, other amines or other sorbents where the number of interactions is different? For example, 1 : 1 chemisorption as opposed to 1 : 2 chemisorption, or even physisorption?

George Jackson answered: The SAFT approach has been used to successfully describe the thermodynamics and fluid-phase behaviour of a wide range of amine systems of relevance in carbon dioxide separation and capture processes, including: monoethanolamine (MEA);[1,2] ammonia and 2-amino-2-methyl-1-propanol (AMP);[2,3] linear alkylamines;[4] diethanolamine (DEA) and methyldiethanolamine (MDEA);[2] poly(oxyethylene)dimethylethers (Selexol) and poly(oxymethylene)dimethylethers (OME).[5] The group contribution version of the theory (SAFT-γ)[6,7] has also been used predictively to assess a broad range of alkanolamine solvents, and offers promise in computer aided molecular process design (CAMPD).[8–10]

1 N. Mac Dowell *et al.*, *Ind. Eng. Chem. Res.*, 2009, **49**, 1883.
2 Rodriguez *et al.*, *Mol. Phys.*, 2012, **110**, 1325.
3 N. Mac Dowell *et al.*, *Computer Aided Chem. Eng.*, 2010, **28**, 1231.
4 N. Mac Dowell *et al.*, *J. Phys. Chem. B*, 2011, **115**, 8155.

5 J. Burger *et al.*, *AIChE J.*, 2015, **61**, 3249.
6 A. Lymperiadis *et al.*, *J. Chem. Phys.*, 2007, **127**, 234903.
7 A. Lymperiadis *et al.*, *Fluid Phase Equil.*, 2008, **274**, 85.
8 A. I. Papadopoulos *et al.*, *Chem. Eng. Trans.*, 2014, **39**, 211.
9 A. Chremos *et al.*, *Fluid Phase Equil.*, 2016, **407**, 280.
10 A. I. Papadopoulos *et al.*, *Mol. Sys. Design and Eng.*, 2016, **1**, 313–334.

Gary Rochelle commented: I suggest that you attempt to represent the data by Dugas (dissertation) on the absorption of CO_2 into MEA and into PZ. Frailie (dissertation) has also modelled the PZ data by ASPEN/eNRTL.

George Jackson replied: This is a good suggestion, thank you. Could you please provide full details of the references?

Mai Bui queried: Pilot plant data tends to have variations due to amine degradation and heat loss. The degree of influence from these effects can vary from one set of pilot plant data to another. How does your model compensate for data uncertainty due to these effects?

George Jackson answered: At this stage our process model does not account for the degradation of the amine solvent. In our paper we assessed one set of pilot plant data[1] and we have not in this case found the need to compensate for the solvent degradation, though of course this may be taken into account in an effective manner with our model of the speciation equilibrium. It would be possible to account for the degradation of the amine, but one would need to specify the degradation species and obtain intermolecular interaction models for the key products.

1 P. Tontiwachwuthikul *et al.*, 1992, *Chem. Eng. Sci.*, **47**, 381.

Gary Rochelle remarked: Data for the heat capacity of amine solvents are generally not accurate enough to determine the partial heat capacity of the total CO_2. Therefore, the eNRTL representation also has difficulty getting a reasonable C_P. Where does the SAFT model account for the excess enthalpy of the interactions? Since that enthalpy must account for the "heat of reaction", is there a second term that addresses the heat capacity effect?

George Jackson replied: The SAFT equation of state is formulated in terms of the Helmholtz free energy and all thermal thermodynamic properties (including the heat capacity, enthalpy, entropy *etc.*) can therefore be obtained as appropriate temperature derivatives of the free energy. In physical approaches to reactive systems, such as the Wertheim treatment of association at the heart of the SAFT approach, the heat of reaction is treated at the level of an association energy between the various reacting/associating species. In the case of the reaction of carbon dioxide in aqueous solutions of monoethanolamine (MEA), there are two association/bonding energies in the model corresponding to the 2 : 1 stoichiometry of the reaction; the heat of reaction is therefore treated implicitly in this type of approach. Due to the fact that the SAFT treatment provides an accurate representation of the concentrations of the various species (protonated amine, bicarbonate, carbamate *etc.*), the equilibrium constant (and its temperature

dependence) is also well captured. Because the slope of the (natural) logarithm of the equilibrium constant as a function of the inverse (absolute) temperature corresponds to the enthalpy of reaction, this means that the heat of reaction is also obtained in an implicit manner.

Grant Wilson opened discussion of the paper by **Lennart Joos**: I just wondered if anyone had considered CCS to a lower specification for local needs and transport, and then a shared facility that would take this local specification and upgrade it to transmission and storage level specifications?

Lennart Joos answered: I don't know if anyone has considered this already, but it's certainly an interesting idea. I think indeed that "lower-grade" CO_2 is only practical for local (and small-scale) applications of CO_2, *e.g.* use in greenhouse gases. You don't want to transport diluted CO_2, because you're going to be moving around dead volume, and small impurities might also corrode the pipelines. However, once a transport network for CO_2 exists, for instance when you're close to an Enhanced Oil Recovery site, you could indeed envisage an upgrade facility to inject pure CO_2 in this network.

Pelayo Garcia-Gutierrez asked:

(i) What applications using direct capture are competitive?

(ii) If you want to do direct capture in the UK you may be capturing CO_2 emitted elsewhere; therefore, who pays for it?

Lennart Joos responded:

(i) For small-scale applications of CO_2, at a significant distance from large concentrated CO_2 sources. For instance, to increase the CO_2 level in greenhouses, so as to increase crop production. If you're far away from a fossil-fuel-fired power plant, it doesn't make sense to build a long pipeline for such a small amount. You could burn methane, but this would be a rather costly source. You can buy food-grade CO_2 in bottles, which has a market price of about 50 EUR/tonne (also note that these bottles have to be transported). However, as we showed in our manuscript, Direct Air Capture may have a price below that, down to 25 EUR/tonne for CO_2 at 1 bar and 50%, which would suffice for this specific application.

(ii) In the case outlined above, you need the CO_2. So no matter what the source is, you have to pay for the CO_2. Whether from bottles or from Direct Air Capture, for this specific scenario, you are going to pay for the CO_2. Admittedly, the number of applications for CO_2 is relatively small, so this will not make a large dent in global CO_2 emissions, but this just illustrates that in some cases, "useful" CO_2 has a market price.

Paul Fennell queried: What sort of an effect would the cleanup of trace and minor species have on the results discussed here? Does it change the economics of some of the very low-cost reuse options?

Lennart Joos replied: This is hard to say without additional simulations. SO_x and NO_x are notorious for poisoning nanoporous materials, but I don't know what their effect would be on the economics.

Peter Styring observed: It is clear that we need to look at air capture, where the air is 500 times more dilute than flue gas. Does this mean that the plant must be 500 times bigger for DAC, or the sorbents 500 times more efficient or faster? The big problem is the volume of air that needs to be processed under compression to get relatively small volumes of pure CO_2.

Stefano Brandani addressed **Lennart Joos** and **Berend Smit**: Reducing the purity requirement clearly simplifies the separation, and single-stage vacuum swing adsorption processes could produce the gas mixtures used in this study efficiently. It is not surprising that the process simplification would reduce the importance of the properties of the adsorbent materials.

What is not clear though in the thermodynamic analysis is why the assumption is made that the utilization process will start with CO_2 under atmospheric conditions. In most cases it is very likely that some sort of hydrogenation will be needed, *e.g.* if one makes methanol, both CO_2 and H_2 are needed, and in this case the reaction pressure will be dictated by the pressure at which hydrogen is generated. One would also opt for high pressures in view of the reduced size and footprint of the plant. From a thermodynamic point of view it would appear to be better to go through a gasification step and produce syngas, from which one would arrive at the desired product.

As for the previous comment on carbon capture and utilization, one needs to establish what the realistic market is for utilization that can deliver an impact at a scale large enough to mitigate climate change. If in reality this market is only a niche one, it is difficult to arrive at general conclusions on energy requirements as a function of final purity, because the final viability of a specific process will depend on a range of external conditions that are not thermodynamic in nature.

Furthermore, as long as natural gas remains relatively cheap and widely available it is unlikely that CCU would out-compete steam methane reforming (SMR), which also produces hydrogen, coupled to the reaction to form the product directly from syngas. This is particularly true for direct air capture as part of a CCU scheme. Should the comparison on thermodynamic efficiency be made with reference to SMR in order to more clearly determine the commercial viability?

Lennart Joos answered: That would be an interesting extension for sure.

Berend Smit added: We have chosen to conduct this study on CO_2 at atmospheric conditions as this would be the best-case scenario, meaning the maximum gain in saving energy compared to geological sequestration, which involves compression to 150 bar. Obtaining captured CO_2 at atmospheric pressure does not require any additional compression work, while using it for some sort of hydrogenation would demand pumping work, which immediately increases the energy demand substantially. Of course, a higher pressure would reduce the size and footprint of the plant, but this was not the initial aim of our work.

We agree on both of your statements on the market for utilization. The point we wanted to make with this study is that the energy requirement for CCU could be significantly smaller compared to general CCS, and this has not been considered yet, as far as we know. Making CCU attractive for niche industries by reducing their recurring cost of material will not solve the problem of effectively reducing the emission of CO_2 to mitigate climate change. However, it would be

a step in the right direction and might open up avenues for stronger regulations and potential subsidies, which would make it even more attractive.

Lisa Joss observed: In the presented analysis, a clear distinction is made between the imposed purity and the final purity. The two following questions concern clarifications on these quantities.

(i) The final purity depends on the amount of CO_2 and N_2 desorbed as well as on the bed porosity. Could you comment on the porosity considered for the different materials, and how it affects the final purity?

(ii) The results of the optimization seem to contain many configurations that do not reach the purity targets (visible in Figures 6 and 7 and Table 6 in the paper). What is the exact formulation of the optimization problem (objectives, constraints and decision variables)? Do the optimal materials (*e.g.* those reported in Tables 4 and 9 in the paper) achieve the imposed purity?

Lennart Joos replied:

(i) We considered a fixed void fraction of 0.35 throughout the simulations. When extending the model to include more process-technical aspects, this would be a very interesting suggestion.

(ii) When the purity target is not reached, a second, third... step can be added to increase the final purity. Of course, this increases the parasitic energy. The best performing materials usually reach their target in the first step.

Geoffrey Maitland remarked: I would like to make a comment about the general issue of impurities raised by the paper of Joos *et al.* This paper shows the large reductions in parasitic capture energy which can result from relaxing some of the constraints imposed by conventional CCS process requirements: pressurisation up to the supercritical state (where typically 150 bar is used) and requiring 99% CO_2 purity. Whilst this paper focuses on how these constraints may be relaxed in the case of CCU, the potentially significant cost savings this presents for CCS should not be forgotten. Whilst there may be some constraints on levels of purity imposed by materials selection for both CO_2 transportation and injection, many CCS processes will be feasible at lower levels of purity. Since it is necessary for transportation, injection and storage efficiency to operate with a GHG stream above its critical point, more use could be made of systems which capture GHGs at pressure, or use available energy from the process (*e.g.* waste heat) to increase the gas stream pressure before the (relatively high cost) compression stage. Although some research is being carried out on these issues, it is an area worthy of more attention in the quest to bring overall CCS costs down.

Geoffrey Maitland opened discussion of the paper by **Richard Graham:** You have two methods for estimating molecular interactions: semi-empirical, where parameters are fitted to dense phase data and so represent effective multi-body, rather than pairwise, interactions, as is appropriate for the VLE and other data relevant to impure CO_2 CCS processes considered in the paper; and *ab initio* quantum mechanics calculations, which give highly accurate numerical anisotropic pairwise intermolecular potentials, for which you have developed rather smart fitting approaches to enable them to be used in molecular simulations. Accurate though these are for two-body interactions, they do not include the multi-body interactions that are required in the dense gas, liquid and supercritical regions

relevant to CCS processes. How do you intend to include such effects so as to give confidence in your thermophysical property predictions for mixed dense phases?

Richard Graham replied: The three-body interaction problem has been investigated for pure CO_2 by my co-author, Richard Wheatley, who showed *via* quantum-chemical calculations and Gibbs ensemble Monte Carlo simulations that pairwise potentials are, indeed, insufficient to predict the phase behaviour.[1] However, by adding *ab initio* calculations on trimers of CO_2, thus including non-additive three-body interactions in the simulations, they were able to predict coexistence behaviour, from first-principles, with reasonable accuracy. This includes the density of the coexisting liquid.

We have made some early tests of how well our Gaussian Process algorithm captures the non-additive part of a 3-body interaction. These results suggest that generalising our algorithm to these non-additive interactions is straightforward and effective. Further testing of the GP algorithm and implementation in a simulation is needed to confirm whether accounting for 3-body interactions is sufficient to predict fluid properties of CO_2 mixtures.

1 M. T. Oakley and R. J. Wheatley, Additive and nonadditive models of vapor-liquid equilibrium in CO_2 from first principles, *J. Chem. Phys.*, 2009, **130**, 034110.

George Jackson commented: The determination of the interaction pair-potential energy between pairs of unlike molecules is the bane of chemical engineering applications of equations of state. The unlike dispersion energy parameter is commonly obtained from approximate relations such as the Berthelot or Hudson-McCoubrey combining rules,[1] which fail for highly non-ideal mixtures. The detailed first-principles quantum mechanical calculations outlined by Graham and co-workers offer a promising route to the accurate determination of the unlike interaction energy (or so-called k_{ij}) parameter based on a knowledge of the like interactions.

1 A. J. Haslam *et al.*, *Fluid Phase Equil.*, 2008, **266**, 105–128.

Richard Graham responded: Indeed, translating insight from our quantum calculations into usable information for equations of state is a key focus of our work.

Berend Smit asked: On the issue of three body interactions, I can see that for Ar–Ar interactions a quantum calculation does not include any 3-body interactions, but a CO_2–CO_2 calculation does. So I would not be surprised if the liquid state behavior may actually be better than you expect. Is this what you see?

Richard Graham answered: Indeed, work by my co-author, Richard Wheatley, on pure CO_2 shows that 3rd order non-additive interactions are sufficient to account for phase behaviour experiments. It would be very interesting to test whether monatomic fluids, such as pure Ar, require interactions beyond 3rd order to account for dense fluid properties, as your explanation suggests.

Martin Trusler remarked: You describe application of molecular simulations to prediction of the VLE of CO_2-diluent binary systems, but I would comment that

the VLE of these systems is mostly well-known from experiment. The few gaps in the literature are being filled rapidly. I would also argue that engineering thermodynamic models, when tuned to these binary VLE data, are capable of providing highly-accurate predictions for multi-component systems that will be very hard to beat by molecular simulation. However, mixtures of CO_2 with more difficult partners such as water and toxic acid gases are problematic from the experimental perspective. Do you think that your simulation approaches can provide new information on these more difficult systems?

Richard Graham responded: We began with binary systems where the VLE is well-known experimentally, in order to establish the robustness of the simulation predictions. Even here, the issue of tuning engineering thermodynamic models to binary VLE data, relevant to CCS, is not fully solved. For example, our simulations in this article compare more accurately to CO_2–O_2 and CO–H_2 VLE measurements than the widely used GERG EoS. Furthermore, the simulations are comparable to and, in places, better than very recently derived EoS.[1,2] From this baseline, predicting multi-component systems with EoS seems rather uncertain. When considering also the need to predict a wide range of other physical properties for mixtures, such as viscosity, speed of sound and specific heat, the stronger physical basis for molecular simulation becomes an important advantage. Ultimately, we should be looking for ways to exploit together the complementary advantages of experiments, EoS and simulations.

For the problematic experimental systems that you mentioned, there is considerable potential for simulations to contribute. However, we might anticipate difficulties in interpolating the molecular potential and running the simulations when the constituent molecules are larger and their interactions stronger or more complicated. I suspect that generalising our approach to such mixtures will be possible but not completely straightforward.

1 T. A. Demetriades and R. S. Graham, A new equation of state for CCS pipeline transport: Calibration of mixing rules for binary mixtures of CO_2 with N_2, O_2 and H_2, *Journal of Chemical Thermodynamics*, 2016, **93**, 294–304.

2 G. J. Gernert, A new Helmholtz energy model for humid gases and CCS mixtures (Ph.D. thesis), Faculty of Mechanical Engineering, University of Bochum, 2013. Available from: http://www-brs.ub.ruhr-uni-bochum.de/netahtml/HSS/Diss/GernertGeorgJohannes/diss.pdf

Peter Styring enquired: Have you looked at modelling of other systems for inspiration, for example liquid crystal simulations, hydrogen bonding interactions, ionic liquid crystals, or surfactant lyotropic systems? Large arrays of molecules in bulk phase simulation have been achieved in these systems. Lots of data are out there for multiple body simulations at a molecular level as well as *ab initio* simulations and quantum mechanics to include charges on species.

Richard Graham replied: Yes, we are actively engaged in using insight, techniques and code from the enormous range of systems to which molecular simulation has been applied. A particular feature of CCS modelling is the number of impurities, and hence mutually interacting species, that are relevant to the problem. This suggests that characterisation of very many binary, and higher order, interactions must be interpolated. Our Gaussian Process interpolation

appears to generalise straightforwardly to new binary pairs, which will be an important advantage over parametric methods.

Berend Smit addressed **Richard Graham** and **George Jackson**: We have now seen two methods of predicting properties of gases and liquids: SAFT and molecular simulations. Could each of you outline under which conditions one would like to use one approach or the other approach?

Richard Graham responded: I would advise the use of SAFT or another equation of state (EoS) under the following circumstances: when there are existing high quality experimental data that are fitted well by the EoS and one wants to predict in a region that is well covered by experiments. Under these circumstances the cheap cost of computing accurately with an EoS is a clear advantage. In contrast, if the predictions involve extrapolation to regions that are not well-covered by experiments then one should use the most detailed approach available, namely molecular simulation. Here, the stronger physical basis of molecular simulation is important to the robustness of the predictions when extrapolating. Regions where experimental data are not comprehensive are somewhat common in CCS modelling as the number of potential impurities is high and many physical properties are of interest beyond VLE behaviour, such as viscosity, speed of sound and specific heat. There are potential ways to use simulations and EoS together. For example, where experimental data are not available to fit EoS, simulation predictions could be used as surrogate data so that the EoS inherits some of the superior robustness of the simulations.

George Jackson answered: The statistical associating fluid theory (SAFT) is a molecular-based equation of state developed as a perturbation expansion from a hard-sphere reference system (*e.g.*, see the latest incarnations of the theory based on the Mie (generalized Lennard-Jones) potential by Lafitte *et al.*).[1] As such, SAFT approaches provide a reliable and efficient algebraic description of the thermodynamic properties and fluid-phase equilibria of complex fluids (ranging from mixtures of small polar and associating fluids to solutions of macromolecules). The group-contribution reformulations of SAFT are particularly useful for predictions based solely on a knowledge of the chemical functionality of the molecules in the system (*e.g.*, see SAFT-γ Mie).[2] Equations of state do not, however, directly inform on structural, interfacial, or transport properties. On the other hand, molecular simulation offers a direct route to all thermodynamic, surface and dynamical properties, providing one has an accurate force field for the intermolecular interactions between the chemical groups of the molecules of interest; simulation methods employ numerical algorithms to solve the statistical mechanics (Monte Carlo) or equations of motion (molecular dynamics) and hence are more computationally intensive to implement than algebraic theories. There is therefore a certain synergy in the roles played by equations of state and molecular simulation: the former can be used for a rapid early assessment of the thermodynamics and phase equilibria, and the latter can then provide a more detailed microscopic description of the structure and dynamics of the system. Accurate equations of state such as SAFT-γ can also be used in the development of dependable force fields based on the Mie potential for direct use in molecular simulation, extending the capability of SAFT-based approaches.[3,4]

1 T. Lafitte *et al.*, *J. Chem. Phys.*, 2013, **139**, 154504.
2 V. Papaioannou *et al.*, *J. Chem. Phys.*, 2014, **140**, 054107.
3 C. Avendaño *et al.*, *J. Phys. Chem. B*, 2011, **115**, 11154.
4 E. A. Müller and G. Jackson, *Ann. Rev. Chem. Biomolec. Eng.*, 2014, **5**, 405.

Matteo Gazzani opened discussion of the paper by **Raffaella Ocone**: In order to achieve an efficient chemical looping process in terms of energy requirements, it is key to design a proper system for managing the sensible heat of the circulating solids. From a system point of view, one should try to transfer the heat of the hot solids to the cold solids being circulated. Do you consider this as a feasible option?

Raffaella Ocone replied: This is certainly a possibility which would make the process more efficient (and more complex). We have not analysed this option in our current work, but we could include it in future developments.

Paul Fennell queried: Is there any issue with the slip of carbon monoxide in your system? This can be an issue with nickel-based materials in the CLC context.

Raffaella Ocone responded: Whilst the slip of carbon monoxide is certainly a possibility in real systems, we have neglected such an effect in our simulations.

Thomas Hills asked: In your paper you looked at the performance of a nickel-based oxygen carrier. The residence time required to make this process competitive even with MEA-based systems is very long (4000 h) and it is likely to be difficult to produce particles which can last that long; a shorter lifetime per particle will push up costs. Do you think that cheaper sorbents will be more suitable for chemical looping given that they can be replaced more cheaply and more often?

Raffaella Ocone answered: The main concept behind CLC is that the solid has to have oxidising and reducing properties. I think that sorbents do not have the ability to behave as oxygen carriers.

Felix Donat questioned: For this type of modelling, how important is reliable kinetic data and how sensitive is the model (or the outcome/the conclusions of the model) to changes in kinetic parameters? Are there situations where models can be simplified, *e.g.* when mass transfer in a reactor system is dominant?

Raffaella Ocone responded: The kinetics model is taken from the literature (as referenced in the paper). A different kinetics will affect the results but I do not think that the overall conclusion will change drastically when the kinetics change. Should the process be mass limited, then the kinetics will have even less effect (the predominant time would be the time taken for the diffusing species to get to the particles).

Paul Fennell queried: Can you clarify your statement on structured (*i.e.* artificially produced) and non-structured materials with respect to gas and coal? Structured materials could be very useful for gas fired systems, but for coal fired systems there are a lot of impurities so you won't be able to use these materials.

Raffaella Ocone replied: I agree.

Joseph Yao commented: You have a nice two phase bed model to describe the bubbling fluidised bed for CLC; however, you have taken kinetic data from another source, so what is the purpose of the model if not for determining kinetics?

Raffaella Ocone responded: The reason for developing a model for the bubbling bed (to be used in conjunction with ASPEN) is to take into account the bed hydrodynamics. The purpose was not to determine the kinetics. Concerning the kinetics, we assumed that the shrinking core model could be applied to the oxygen carrier solid particles and the kinetics was taken from the literature. We did not attempt any kinetic modelling in this work and we did not undertake any experimental measurements. I hope this clarifies the issue.

Christoph Mueller asked: You say that you need 4000 h to make it comparable to MEA; did you assume a certain material cost? How many redox cycles are 4000 h?

Raffaella Ocone answered: The estimation is made based on the material used in Ref. 33 in the paper, which does not make an explicit mention of the cycles. A very quick estimation of the number of cycles required to reach 4000 h can be done by considering the residence time in the reactors (which is in the order of a tenth of a second). If 4000 h can be reached (I doubt it), then the number of cycles would be very high.

Paul Fennell remarked: Regarding the need for 4000 h of lifetime, nobody has run any of these things in an industrial context to see where the nickel comes out and if you can recondition the particles. If we build these CO_2 processes with improved thermodynamics/energy penalty, then there will be engineering challenges, and particle attrition would need to be optimised. This is a problem for the next generation of research.

Raffaella Ocone replied: I fully agree with these statements. Although 4000 h of lifetime is reported in the reference in the paper, we think that this is not for continuous operation.

Raffaella Ocone addressed **Paul Fennell**: Do you think that the material available at present would work at a large scale?

Paul Fennell responded: Yes, I think that some materials available now could work at a large scale and are good enough to demonstrate the technology with; however, I also believe that until a CO_2 price comes along there is little incentive for development of 2nd generation CLC materials. When a price is forthcoming, the invisible hand will push for rapid development of both the technology (outside of development and into deployment) and new materials.

Jon Gibbins remarked: Rather than just taking it as a given that it makes sense to design power plants with CCS to run at low load factors to accommodate large

amounts of intermittent renewable generation connected to the grid, the overall system costs of doing this need to be considered. If the CCS power plants have to be there anyway then it may make sense to run them more of the time and not bother with the intermittent renewables; see for example David MacKay's final interview (http://www.marklynas.org/2016/04/david-mackay-last-interview-tribute/).

Peter Styring added: Just to clarify, there are prizes for carbon capture, albeit through carbon dioxide utilisation prizes which still need a capture stage. These include the 1.5 million euro Horizons Prize in CO_2 Reuse and the COSIA Carbon XPrize worth US $10 million.

Patrick Brandl said: In order to comment on the presentation, which showed that an increase in complexity for CO_2 capture was predicted: Gary Rochelle pointed out in his talk (paper 10818) that the simplicity of a layout is of highest importance in commercial realisation and effectiveness. Daniel Sutter discussed the chilled ammonia process (paper 10822), which is not as simple as the advanced flash configuration but could be linked to further simulations analysing for example load following operation. So it might be that the predicted complexity is not linked to the capture process itself but more to the depth of simulation.

Raffaella Ocone responded: I am not sure that I fully understand this question. However, if anything, the model simplifies the real system.

Christoph Mueller asked: How do the results of your study compare to other studies concerning the stability of the materials?

Raffaella Ocone replied: We have not attempted such a study. This is a good point to consider for future work.

Martin Trusler opened discussion of the paper by **Yue Zhang**: In the absorber without the direct-contact cooler, hot oxygen-containing flue gases contact the solvent at the bottom of the column; does this create a problem with thermal and/or oxidative degradation of the solvent?

Yue Zhang replied: For absorber design without the direct contact cooler, pump-around cooling at the bottom of the absorber can effectively manage the temperature of the hot flue gas. The model predicts that the rich solvent outlet temperature never exceeds 70 °C. Concentrated PZ can tolerate temperatures up to 150 °C, so there is no degradation issue. Nevertheless, the absorber gas inlet must be designed properly to avoid localized complete solvent evaporation with resulting excessive temperature.

J.-S. M. Lee enquired: In your proposed plant, you install an extra membrane system in the recycling process that enriches the CO_2 concentration of the flue gas from 4% to 18%. Can the original burner and turbine withstand the higher CO_2 levels, or would you have to consider replacing this?

Yue Zhang answered: Conventional exhaust gas recirculation (EGR) is used to increase the concentration of CO_2 in flue gas (from ~4% to ~7% at a 35% EGR rate)

as a way to reduce the cost of capture. Various studies have examined the effects of EGR on gas turbines. The primary constraint is lower O_2 concentration resulting from the dilution of combustion air with recirculated flue gas, rather than elevated CO_2 concentration. Vendor studies and tests have examined combustion performance and flame stability over a range of O_2 inlet concentrations. The consensus finding is that the combustion air should not contain less than 16% O_2 unless modifications are made to the turbine. This correlates to a 35% EGR rate. In MTR's selective exhaust gas recycle (S-EGR) design, the S-EGR recycle rate is held to the same limit, *i.e.* not less than 16% O_2 in the combustion air. However, CO_2 is more concentrated with S-EGR compared to EGR. Analysis of the higher inlet CO_2 concentrations indicates a reduction in the burning velocity in the combustor, an increase in the volume of the flame, and a decrease in the consumption rate of fuel in the flame region. These conditions generally produce more CO and lower NO_x emissions. There may also be impacts on the overall NGCC power plant efficiency, and pilot scale tests are being performed at the UK PACT Pilot Plant to evaluate this.

J.-S. M. Lee asked: In your absorber configuration, you cool the flue gas by pump-around intercooling rather than perhaps pumping the gas out, cooling it and returning it through the same system. What is the advantage of your design that uses this pump-around intercooling loop?

Yue Zhang responded: There are two major types of intercooling for the absorber: in-and-out intercooling and pump-around intercooling. In-and-out intercooling cools the solvent and sends it back to the same place, while pump-around intercooling cools the solvent and pumps it back to the upper bed. Both in-and-out and pump-around intercooling can reduce the temperature bulge and improve CO_2 mass transfer driving force. The advantage of pump-around intercooling is that it can generate extra turbulence and enhance liquid film mass transfer. The disadvantage is the reduced driving force by back-mixing the solvent.

Daniel Sutter questioned: I would like to ask you to comment on the water balance in the case where you skip the DCC. Aren't you condensing water out of the flue gas that would accumulate in the capture process?

Yue Zhang replied: For the absorber design with DCC, water balance is controlled by DCC and water wash. For the absorber design without DCC, the absorber inlet gas carries more water, so the water wash needs to be operated at a higher temperature (around 48 °C) to maintain the water balance.

Jon Gibbins addressed **Yue Zhang** and **Gary Rochelle**: Did you consider using the higher CO_2 concentration obtained using the membrane to get higher capture levels? While using a standard 90% capture is satisfactory as one ideal hypothetical test case for comparison purposes, it seems likely that in practice such a plant would achieve its optimum performance at a higher capture level due to the higher inlet CO_2 concentration to the absorber.

Yue Zhang answered: It is a good point. Further optimization needs to be carried out to find the optimal capture levels of the entire system.

Gary Rochelle added: We considered several cases with greater CO_2 removal in the absorber and recognize that this is an important degree of freedom in the process optimization.

Claire Adjiman addressed **Gary Rochelle** and **Yue Zhang:** Can you comment on the impact of the proposed flowsheets on desorber design and performance, *e.g.* due to reduced solvent flowrate?

Gary Rochelle answered: With a high T/P stripper as used with piperazine, the desorber will use a somewhat lower diameter with the reduced solvent rate.

Yue Zhang added: The advanced flash stripper (AFS) with cold and warm rich solvent bypass has been used in our design and its energy performance is affected by both lean solvent rate and Δloading. The hybrid capture system gives a higher absorber inlet CO_2 concentration, which results in a higher rich loading. From the perspective of the minimum total equivalent work, AFS always benefits from high rich loading. Also, since there is a higher CO_2 driving force across the absorber, a higher lean loading has been used. As a result, the hybrid capture system gives a slightly higher lean solvent rate and lower Δloading. According to the AFS modeling results of the hybrid system, its energy performance remains almost the same from 6% to 18% CO_2.

Patrick Brandl addressed **Yue Zhang** and **Gary Rochelle**: The detailed analysis of flowsheet configurations in this paper should be acknowledged by the CCS community, since it is time and resource-consuming but an inevitable task in improving the capture process.

(i) Could the authors please give a reference for the characterisation of the membrane used in the hybrid capture process and comment on the long term stability with respect to the operating conditions?

(ii) Does the CAPEX calculation take the liquid collectors and distributors for the absorber intercooler into account?

Yue Zhang replied:

(i) MTR's Polaris™ membrane is a high-permeance, polymeric membrane developed for the separation of CO_2 from N_2 (post-combustion capture from various flue gases). The membrane properties used in the simulation for this paper and in the economics are: Membrane replacement rate = 3 years; CO_2 permeance = 2,000 gpu; CO_2/N_2 selectivity = 50. Polaris is a derivative of MTR's other commercial membranes used to perform separations in, almost exclusively, harsher conditions. The replacement interval for those membranes can exceed 5 years, so the long term stability assumptions and replacement interval used in this paper are conservative.[1,2]

(ii) Yes, the CAPEX calculation does include incremental costs of these column internals – chimney trays, liquid distributors, and packing supports.

1 T. C. Merkel, X. Wei, Z. He, L. S. White, J. G. Wijmans and R. W. Baker, Selective Exhaust Gas Recycle with Membranes for CO_2 Capture from Natural Gas Combined Cycle Power Plants, *Ind. Eng. Chem. Res.*, 2013, **52**, 1150–1159.
2 Current and Future Technologies for Power Generation with Post-Combustion Carbon Capture, DOE/NETL-2012/1577, March 16, 2012.

Gary Rochelle added: The CAPEX includes the chimney tray, packing support, and distributor required to break the packing and insert intercooling.

The model assumes a Polaris membrane. MTR has good operating experience with these membranes tested on coal-fired flue gas at the National Carbon Capture Center.

Rosa Cuellar-Franca communicated: In your paper you mentioned that the addition of the membrane-amine hybrid system helps to reduce the absorber CAPEX by 60%. What would be the approximate cost difference between the process configurations shown in Figures 1 and 3 in the paper if you take into account the installation and operation of all the equipment required, *i.e.* absorber plus the additional equipment required for the pre-enrichment of CO_2?

Yue Zhang communicated in response: The major cost difference between simple NGCC (Figure 1) and hybrid capture (Figure 3) is the additional membrane. Technical economic analysis of the membrane for each hybrid case has been completed by MTR, which was not included in this paper. If both membrane CAPEX and absorber CAPEX are taken into account, compared with simple NGCC, total CAPEX decreases by 14% for Case 4, decreases by 10% for Case 1, and increases by 29% for Case 3.

Patrick Brandl addressed **Yue Zhang** and **Gary Rochelle**:

(i) How does the water usage of the total plant change when wet cooled intercoolers are used instead of a direct contact cooler (DCC)?

(ii) How would a load following NGCC operation affect those intercoolers?

Yue Zhang responded:

(i) By using the absorber bottom pump-around intercooling instead of DCC, the cooling load at DCC transfers to the absorber bottom intercooler. As a result, total plant water usage will not change.

(ii) Intercooler operation will not be affected.

Gary Rochelle added: Without a direct contact cooler the flue gas leaving the absorber will contain more water vapor. Less "waste" water will be produced at the direct contact cooler and less water will be evaporated from the cooling water loop.

We have not yet considered load following conditions.

Colin Scholes communicated: This is a very interesting paper, and highlights the potential of hybrid approaches combining membranes and absorption technology to achieve more efficient capture. It also demonstrates that more coordination and collaboration between the different capture technologies is needed, as there is significant potential for process gains.

There is however little information about the performance of the membrane stage in the hybrid processes – and while I understand the expertise on this unit operation is with MTR, I believe more information is required, as the recycling of CO_2 through the process is critical to the improved absorber performance. As such, I have the following questions I would like the authors to address.

Firstly, how was the membrane process simulated? As the absorber was modelled in ASPEN Plus, was the membrane unit also modelled using the same design package? I am unaware of a membrane process module in ASPEN.

Gary Rochelle communicated in response: The membrane performance was modelled by MTR in a ChemCad customized model.

Colin Scholes communicated: What is the pressure ratio across the membrane process? Did it differ for the various strategies? The process diagram in Figure 3 in the paper has no compressors/blowers around the membrane unit, while those in Figures 13 and 14 do. Can the authors provide any information on whether the pressure ratio was optimized? I am also curious to know if the authors can relate the membrane operating pressure to the absorber pressure – and if any process simulations were undertaken to optimize this variable between the two process units as a method to minimize the compression requirement.

Gary Rochelle communicated in reply: The sweep membrane used in this analysis has little or no total pressure ratio. The concentration driving force for the CO_2 transfer is small, on the order of 2 to 5 mol% CO_2. Blowers are included to deal with pressure drop through the membrane contactor. There is no "compressor" needed to drive the sweep membrane separation.

Colin Scholes communicated: Also, following on from the discussion about water in the absorber column – was the water flux around the membrane unit simulated? For almost all membranes, water has a much higher permeability than CO_2, and hence the permeate stream will have a higher water content than the feed. Hence, a significant water recycle will develop within the process because of the water permeance through the membrane. From the reported inlet feeds to the absorber (Table 5 in the paper) it does not appear that the water flux across the membrane was accounted for, as these are lower than the NG composition. This is actually a serious issue, because higher water content will impact the gas turbine performance, and lead to additional water in the absorber – which the prior discussion has highlighted is an issue if the DCC is removed. Can the authors provide some comment on this?

Gary Rochelle communicated in response: Water has been considered in the analysis. There is some water recycle, but the process also includes additional water knockout with cooling steps that are not shown.

George Dowson opened discussion of the paper by **Robert Bell**: The interactions of these ionic liquids with CO_2 can be both positively and negatively affected by the presence of water. In the case where the presence of water improves performance, is it possible to elucidate computationally whether the water is supplying a chemical effect to the ionic liquid rather than just a physical improvement in diffusion rate (for example)?

Or put more simply, can we model chemical interactions of these types of ionic liquids with both water and CO_2 to determine any synergy?

Robert Bell replied: Yes, this can be looked at computationally. It would be quite feasible to study chemical interactions of both water and CO_2 with models of an ionic liquid. For instance, if water molecules interacted with an anion in such a way as to alter its polarisation or basicity towards CO_2, we would expect to model this.

Claire Adjiman remarked: This is a question of clarification on the DFT calculations. Did you use a solvation model or were the calculations carried out in the gas phase?

For the calculations with a solvation model, to what extent can these be validated quantitatively against experimental data?

Robert Bell answered: We have used a solvation model in studying ionic liquids, though not in the work presented in this paper, which involves up to two ion pairs in the gas phase. In the cases we have looked at with a solvation model, we found that, although absolute energies may have differed somewhat, trends were qualitatively the same as without the solvation model, *i.e.* where competing reaction mechanisms were considered, the same ones were predicted to be energetically favourable. Quantitatively, one would need data such as enthalpies of sorption of CO_2 in the ionic liquid, which are infrequently available. Using the SMD-GIL solvation model for ionic liquids, the group of Truhlar found very close agreement with experimental free energies of sorption.[1]

1 V. S. Bernales, A. V. Marenich, R. Contreras, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2012, **116**, 9122–9129.

Berend Smit queried: Could you comment on whether your calculations can provide recommendations on the type of ILs one would like to use for carbon capture?

Robert Bell replied: That is a very general question, and it depends also on what the desired criteria are for carbon capture. If the strongest enthalpy of sorption is required, this can be optimized by increasing the basicity of the N-donor atom in the heterocyclic anion. This is likely to be a general feature across many types of task-specific IL, though the aprotic anions are also known for minimal viscosity increase with CO_2 uptake. It seems further that increasing the ion pairing strength can decrease the enthalpy of CO_2 sorption, essentially by creating competition between physisorption and chemisorption. This could be manipulated if a lower energy is required, *e.g.* for easier regeneration. Studies of amino acid ILs suggest that molar uptake can be maximised by favouring a particular carbamate-formation mechanism, *e.g.* by introducing substituents that have a steric or inductive effect.

Stephen Lyth asked: Can these computational techniques be applied to CO_2 adsorption onto *e.g.* graphitic surfaces?

Robert Bell responded: Yes, periodic DFT can be applied to study CO_2 sorption on graphene and graphitic surfaces. There are a number of reports in the literature on this type of work.