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Improving uncertainty evaluation of process models by using pedigree analysis. A case study on CO_2 capture with monoethanolamine

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ABSTRACT

This article aims to improve uncertainty evaluation of process models by combining a *quantitative* uncertainty evaluation method (data validation) with a *qualitative* uncertainty evaluation method (pedigree analysis). The approach is tested on a case study of monoethanolamine based postcombustion CO_2 capture from a coal power plant. Data validation was used to quantitatively assess the uncertainty of the inputs and outputs of the MEA model. Pedigree analysis was used to qualitatively assess the uncertainty in the current knowledge base on MEA carbon capture systems, the uncertainty in the MEA process model, and the uncertainty of the MEA model results. The pedigree review was done by 13 international experts in the field of postcombustion carbon capture with chemical solvents.

The data validation showed that our MEA model is accurate in predicting specific reboiler duty, and CO_2 stream purity (4% and 1% difference respectively between model and pilot plant results), but in first instance it was less accurate in predicting liquid over gas ratio, and cooling water requirement (54% and 23% difference respectively between model and pilot plant results). The pedigree analysis complemented these results by showing that there was fairly high uncertainty in the thermodynamic, and chemistry submodels, as reflected in the low pedigree scores on most indicators. Therefore, the model was improved to better resemble pilot plant results.

The results indicate that using a pedigree approach improved uncertainty evaluation in three ways. First, by highlighting sources of uncertainty that quantitative uncertainty analysis does not take into account, such as uncertainty in the knowledge base regarding a specific phenomenon. Second, by providing a systematic approach to uncertainty evaluation, thereby increasing the awareness of modeller and model user. And finally, by presenting the outcomes in easy to understand numerical scores and colours, improving the communication of model uncertainty. In combination with quantitative validation efforts, the pedigree approach can provide a strong method to gain deep insight into the strengths and weaknesses of a process model, and to communicate this to policy and decision-makers.

1. Introduction

1.1. Background

Process modelling plays an important role in the research and development of (novel) technologies. A process model is defined here as a model containing a flowsheet of connected unit operations, with underlying physical property data, thermodynamic, and chemistry models, which transforms specified inputs into specified outputs (Fig. 1). A major reason for constructing a process model is allowing the researcher to simulate the performance of a real chemical process, without having to build or perform experiments in an actual plant, which is a costly and time consuming exercise. By using process models, significant understanding of a process can be gained in a relatively short time and at relatively low costs (Kvamsdal et al., 2011; Tobiesen and Schumann-Olsen, 2011).

Many process simulation models have been constructed to screen the technical performance of novel chemical technologies (e.g. Rao and Rubin, 2002; Peeters et al., 2007; Vicari et al., 2012; Patel et al., 2010; Eerhart et al., 2014). The outcomes are often used by policy and decision-makers as a basis for policy and R&D strategies. Other users include cost engineers, and life cycle engineers, that use the process model results as input for their cost, or LCA analysis. It is thus very common that the users of process model outputs are other than the modeller, and therefore they tend to

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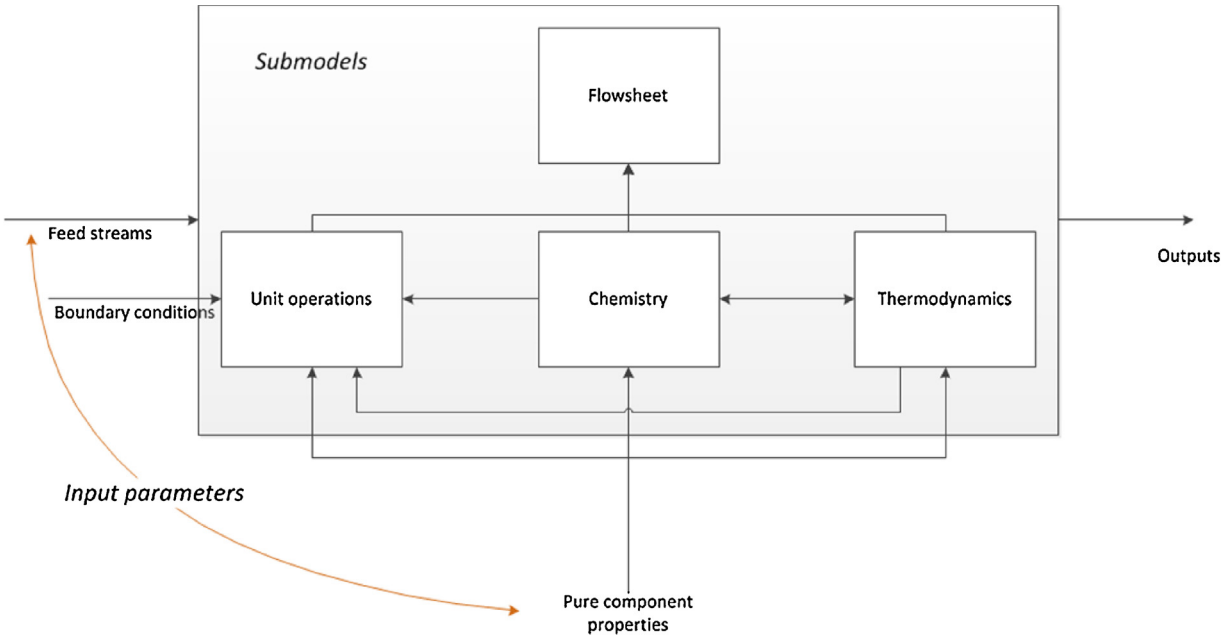

Fig. 1. Schematic representation of a process model.

have a limited understanding of how the process model came into being. Consequently, they use the model outputs, but are often unaware of the *uncertainty*[1] of this data. This in turn, may lead to biases in policy and decision-making. A systematically harmonized assessment of model uncertainty, and/or model output uncertainty, can support users to understand the quality, and limitations of the model, and can lead to more informed use of the model and the results it provides. Model uncertainty is thus a relevant concept in construction and dissemination of process models.

1.2. Definitions of model uncertainty

In scientific modelling literature, many definitions of uncertainty can be found. Examples include "incomplete information about a particular subject" (Ascough et al., 2008: 387), "lack of confidence in knowledge related to a specific question" (Sigel et al., 2010: 504), and "any deviation from the unachievable ideal of completely deterministic knowledge of the relevant system" (Walker et al., 2003: 5). Uncertainty may come in many forms, such as contextual uncertainty,[2] model structure uncertainty,[3] parameter uncertainty, and input data uncertainty (Knol et al., 2009). It can be caused by such aspects as lack of knowledge, the methods used, natural variability, and measurement errors (Walker et al., 2003; Knol et al., 2009). Uncertainty is partly quantifiable, e.g. natural variability and measurement errors, but also resides in parts of models, and in parts of the modelling process, that cannot be quantified (Alexandrov et al., 2011). Examples of the latter are methodological,[4] or epistemic uncertainty[5] (Van der Sluijs et al., 2005).

Following the definition of Sigel et al. (2010), we acknowledge that uncertainty resides in all types of knowledge that form the underlying basis of a process model, including both qualitative, and quantitative uncertainty. Another aspect of Sigel's definition that we consider relevant to process modelling studies, is that it makes a connection between uncertainty, and the modelling question. This implies that the modeller's strive is not for models with the least amount of uncertainty, but rather to match the right level of model uncertainty, with the uncertainty requirement of a specific type of question. For example, for an early stage technology screening, it may not be required to develop a very detailed process model.

1.3. Currently used uncertainty evaluation methods in (process) modelling

There are many methods, approaches and tools, to evaluate, manage, or analyse model uncertainty. A few examples used in process modelling will be discussed in this section, a more exhaustive list of approaches used in modelling in general can be found in Appendix A in Supplementary data, or for instance in Pohjola et al. (2013).

1.3.1. Quantitative uncertainty evaluation methods

Typical *quantitative* methods include validation, sensitivity analysis, and error analysis. *Validation* of model outputs against an independently collected dataset is one of the most commonly used uncertainty evaluation methods (Matthews et al., 2011). In this case the model is generally compared with experimental data to establish the goodness of fit of the model output. Validation thus aims to provide insight into how accurately the model describes reality, and how big the difference is between model and experiment.

[1] Section 1.2 further elaborates on model uncertainty.

[2] "Contextual uncertainty stems from choices made about system boundaries and definitions used in an assessment" (Knol et al., 2009). Examples are which unit operations to include in the flowsheet, or which impurities to incorporate in the model.

[3] "Model structure uncertainty relates to uncertainty about the causal structure of the model" (Knol et al., 2009). An example is the ways unit operations are connected to one another in the flowsheet, but also the structure and interplay of the physical property models underlying the flowsheet.

[4] Methodological uncertainty relates to the methods used to obtain a specific result. It applies to input parameters as well as (sub)models.

[5] Epistemic uncertainty relates to the state of the knowledge base underlying a modelling study. Is the knowledge well-established or preliminary? Is it generally accepted by peers or is there debate about its reliability?

Sensitivity analysis aims to understand the sources of uncertainty in model calculations and to identify those parameters that contribute with the largest share of uncertainty in a given outcome of interest (Van der Sluijs et al., 2004; Reagan et al., 2005). Sensitivity analysis preferably includes running some extreme cases in input parameters, to test if the model responds as it would be expected to (Colonna, 2013).

Error analysis and *probabilistic uncertainty analysis* can provide extra insight into the *numeric* uncertainties of model outputs. They focus on quantitative representation of the uncertainty, or error, in model inputs, and translate that into compiled errors (or probabilities) of the outputs. Often Monte Carlo simulation and error propagation are used as tools for these types of uncertainty analysis (Rao and Rubin, 2002; Van der Sluijs et al., 2004; Nord et al., 2010), but also more novel mathematical tools are available, for instance polynomial chaos expansion (Red-Horse and Benjamin, 2004; Reagan et al., 2005). All these methods have in common that they put a quantitative figure of merit on model output in the form of a probability distribution function (PDF), or error bars (Colonna, 2013).

1.3.2. Limitations of quantitative uncertainty evaluation methods

The strength of quantitative evaluation methods is that they provide a measure for model quality that is relatively easy to understand and can be perceived as objective, because it is calculated following stringent mathematical principles. However, these methods also show clear weaknesses and limitations. A first limitation for validation is that it is only useful if you are able to retrieve a representative and independent dataset, preferably from a pilot or commercial plant, to compare with model outputs (Colonna, 2013). A second, similar limitation applies to Monte Carlo simulation, where the premises that every parameter can be described by a PDF often has no reasonable basis, for instance because of a lack of empirical data (Van der Sluijs et al., 2004). The uncertainties represented in the output of a Monte Carlo simulation are no more than a compilation of uncertainties of model inputs. This means that if there is not sufficient, good quality data to fit the PDF of the inputs, this will lead to underrepresentation of reality, whilst creating a false sense of certainty. A third, major limitation of quantitative methods, is that they are only able to capture parameter uncertainty, for instance the input parameters depicted in Fig. 1. They fail to provide insight however, into A) uncertainty in the model structure, and B) uncertainty in the knowledge base underlying both input parameters and the process model (epistemic and methodological uncertainty, Section 1.2). This also strongly relates to the fact that not all sources of uncertainty can be quantified, as was explained in Section 1.2. Thus quantitative uncertainty analyses "only provide a partial insight into what usually is a very complex mass of uncertainties" (Van der Sluijs et al., 2005: 482), and thus do not provide insight into uncertainties that are unquantifiable, but that are very relevant for the user of the process model and its output.

1.3.3. Pedigree analysis as a complementary approach to quantitative uncertainty methods

An uncertainty evaluation method that is able to fill the gaps left by quantitative methods is expert elicitation with the use of so-called pedigree analysis (Van der Sluijs et al., 2005; Knol et al., 2009, 2010; Pohjola et al., 2013). To the best of our knowledge, this *qualitative* uncertainty evaluation method is not currently used in chemical process modelling. In environmental sciences however, it is more commonly applied and it is typically combined with quantitative methods like data validation and sensitivity analysis. Environmental modellers, like process modellers, are often confronted with highly complex, non-linear systems, as well as incomplete data or knowledge on specific natural phenomena. In that sense, environmental modelling is, to some extent, analogous to chemical process modelling, which gives reason to believe that uncertainty evaluation tools used in environmental modelling may also prove useful in process modelling.

The idea behind expert elicitation as a means of uncertainty evaluation is that the modeller explicitly provides insight to third parties into the inputs, submodels, assumptions, and details, which together form the process model. The modeller thus provides evidence to experts, so that the latter can independently judge the model's quality (Alexandrov et al., 2011). To mitigate subjectivity and provide useful insights, pedigree matrices are used (Van der Sluijs et al., 2005). A pedigree matrix is a tool that systematically scores (sub)model and/or parameter strength with respect to a number of predefined quality indicators, called *pedigree criteria*. Pedigree matrices were first introduced by Funtowicz and Ravetz (1990), as a measure of the quality of data used for modelling purposes. The idea is to "code qualitative expert judgment for a set of problem-specific *pedigree criteria* into a numerical scale, with criteria as columns of the table, the numerical codes as table lines, and linguistic descriptions for each value in each cell of the table" (Ciroth, 2009: 1586). The strength of this method is that it provides a structure to critically appraise the knowledge base behind quantitative policy relevant scientific information, and that it fosters an enhanced appreciation of the issue of uncertainty in model outputs.

Pedigree matrices have been used as a support tool for decision-making in a number of cases to help making results more transparent. Some examples include:

- A model study into NO_x, SO_x, and NH_3 emissions in The Netherlands (Van der Sluijs et al., 2005);
- Evaluation of uncertainties in the Integrated Model to Assess the Global Environment (IMAGE), of the Netherlands Environmental Assessment Agency (Van der Sluijs et al., 2005);
- Cost data quality considerations for eco-efficiency measures (Ciroth, 2009);
- Evaluating the Data Quality in a Quantitative Microbial Risk Assessment Model for Salmonella in the Pork Production Chain (Boone et al., 2009).

1.4. Goal of this paper

This paper aims to improve process model uncertainty evaluation by combining quantitative and qualitative methods for uncertainty evaluation in process simulation models. It will combine data validation (quantitative) with pedigree analysis (qualitative). In this way we aim to improve insights into uncertainty of process models and results, thereby increasing the informed and more transparent use of process models for policy, and decision-making. Providing a more complete view of the uncertainties and their significance can also provide useful information for R&D strategies. This approach will be tested in a process model developed to assess the technical performance of a CO_2 capture process based on monoethanolamine solvent (MEA) from a coal power plant flue gas. This case study has been chosen because the technology has been developed up to the large pilot scale, and hence validation data is available. Secondly, it is a widely studied case in the field of CO_2 capture, and hence the chemical engineering aspect is already well understood, which provides the room to focus on uncertainty management, as to exemplify our approach.

2. Research method

2.1. Case study

Chemical absorption of CO_2 with MEA is a mature technology in the fields of natural gas sweetening and CO_2 capture for the food

industry. It is however not commercially used for the purpose of CO_2 capture and storage from power plant flue gasses, but it is currently considered the most mature technology for this purpose (Figueroa et al., 2008; Rubin et al., 2012). A detailed description of the process is shown in Section 3.1.1. Chemical absorption of CO_2 contains many different sources of complexities and uncertainty. Complex chemical engineering aspects play a role, including electrolyte chemistry, highly non-ideal thermodynamics, mass transfer limitations and reaction kinetics (see e.g., Tobiesen et al., 2007, 2008; Darde et al., 2012). This implies there is a vast knowledge base underlying models of these systems.

2.2. Modelling procedure and uncertainty analysis

The modelling procedure of the MEA carbon capture technology in this study contained four distinct stages: literature review; model specification; model runs; and interpretation of results. Uncertainty evaluation was pursued between all these stages (Fig. 2):

- *After the literature review*. At this point the quality of current (state of the art) scientific knowledge on MEA system modelling was reviewed. This review allows understanding which data is available as input for MEA models, and how (un)certain this data is. This information can be compared to the uncertainty of the process model, which is evaluated after the second stage. For this uncertainty evaluation, pedigree matrices were used (see Section 2.4).
- *After model specification*. At this point the uncertainty of the specified model was reviewed to understand the quality of the model, and how it compares to the state of the art. Data validation and pedigree matrices were used.
- *After running the model*. At this point the quality of the model results was evaluated. Data validation and pedigree matrices were used.

2.3. Data validation

Data validation was applied twice in the modelling procedure: to the model inputs and to the model outputs (Fig. 2). For our case study, the validated inputs include the flue gas feed stream to the carbon capture unit and the boundary conditions for simulating the carbon capture unit (e.g., pressure and temperature settings, and pressure drops over equipment). Preferably, the inputs and characteristics of process models would be validated against performance measurements of a full size, commercial plant, if the model is meant to simulate the performance of a full size plant. In the particular case of emerging technologies however, this is not possible, since by definition they have not reached commercial deployment yet. If this is the case, the model can be validated against pilot, or even bench scale results, in descending order of preference. In case a large pilot is available, the characteristics are likely to resemble that of a commercial technology. In the case of a small pilot, or bench scale plant however, this is often not the case, and only parts of the design and output characteristics can be used for validation purposes.

The input data of our MEA model were validated against the Esbjerg (large pilot) and ITC (small pilot) plant results (Knudsen et al., 2007, 2009; Ahmadi, 2012) where possible, and against other modelling studies were necessary. The output data were validated against published results of the Esbjerg pilot plant. This plant was chosen because the design of its main equipment is close to a commercial design, i.e., the columns have a height representative of a commercial plant, and packing that would also be used in commercial absorber/stripper configurations. Therefore, the Esbjerg plant is considered an acceptable proxy for a commercial PCC process.

2.4. Pedigree analysis

Pedigree analysis was applied three times in the modelling procedure: to the state of the art in literature, to the various model components, and to the model results (Fig. 2).

The pedigree analysis of the *state of the art* included the chemical components and their properties, MEA chemistry, thermodynamics, and potential process line-ups. The pedigree analysis of the *model outputs* included a selection of relevant performance indicators for the MEA system, further specified in Section 3.1.6. The pedigree analysis of the *model itself*, includes the evaluation of both *input parameters* and *submodels*. Table 1 shows the model components that were considered relevant for pedigree review of the MEA system, because they are the main building blocks of a carbon capture system with chemical solvents. Note that the table distinguishes between input parameters and submodels,

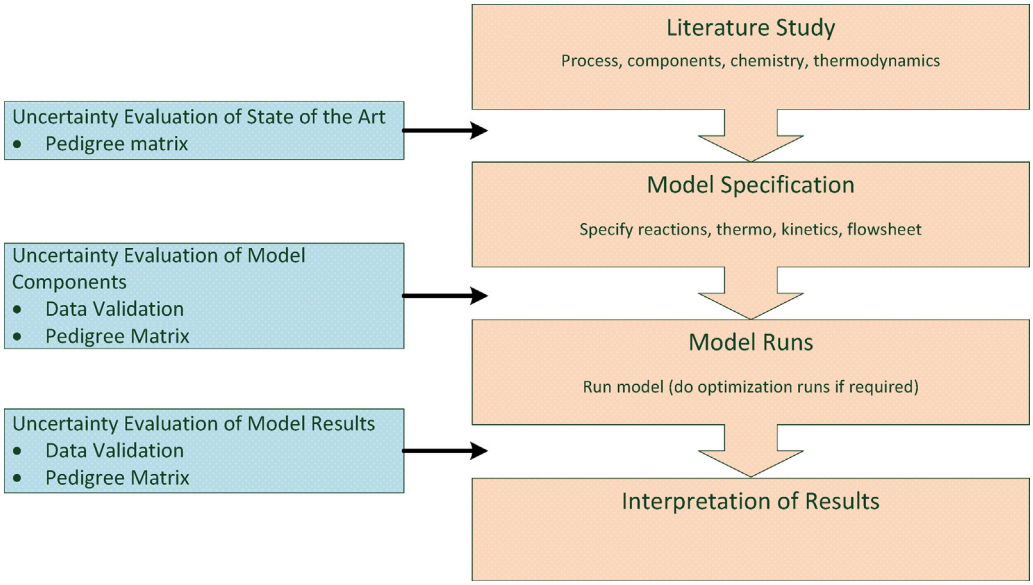

Fig. 2. Graphic representation of the modelling procedure followed in this study. The blue boxes indicate the points where uncertainty evaluations were carried out and which evaluation tools were used.

Table 1
Model components that were reviewed using pedigree analysis. A distinction was made between input parameters, and submodels.

Input parameters	• Feed streams • Boundary conditions • Pure component properties
Submodels	• Flowsheet • Thermodynamics • Chemistry • Unit operations

following Fig. 1, and the definition of a process model in Section 1.1. Input parameters are the data that are fed into the model, submodels are aggregated groups of model equations and coefficients, for example, the equations and coefficients that together form the thermodynamic submodel.

2.4.1. Selected pedigree matrices

For the pedigree assessment of data uncertainty in this work (state of the art, model input, and model outputs), we used a pedigree matrix that was originally developed for the assessment of parameter strength of Integrated Assessment Models (Fig. 3). We selected this matrix because it displays a strong scientific approach to the assessment of data uncertainty by assessing if proxies were used for data points; by assessing how strong the empirical basis of data is, and which method was used to collect the data; by including a measure of the theoretical understanding of data; and by assessing the level of validation of the data. Note that the column headings of Fig. 3 list the five pedigree criteria used in our approach (proxy, empirical basis, theoretical understanding, methodological rigour, and level of validation). The row headings list the strength of the criteria (in an ordinal scale from 0 to 4), and each box presents a linguistic description of a specific criterion and numeric score. Definitions of the pedigree criteria are given in Appendix B in Supplementary data.

Besides data, submodels were also evaluated with pedigree matrices (Table 1). However, as specific pedigree matrices for assessment of *submodel uncertainty* are unavailable, the matrix in Fig. 3 was adapted. As a result, the pedigree criteria *proxy* and *empirical basis* were removed, because they strictly relate to parameters, and not to submodels or model equations. Instead, we added the criterion *skills and time*. This criterion reflects the type and amount of resources available to execute the modelling task. The last change is the linguistic descriptions of the criterion *validation so that it represents* validation of submodels instead of data. Fig. 4 shows the resulting pedigree matrix for the assessment of submodel quality.

2.4.2. Expert review procedure

An important aspect of model quality review with pedigree matrices is that the review is undertaken by independent experts. The problem with having the modeller review the quality of his own work is that he may be biased, willingly, or unwillingly. In this study a group of experts in carbon capture modelling participated in the quality review. The experts were selected based on their experience with i) development of carbon capture solvents, ii) technical

Strength	Proxy	Empirical Basis	Theoretical understanding	Methodological Rigour	Level of Validation
4	An exact measure of the desired quantity	Controlled experiments and large sample, direct measurements	Well established theory	Best available practice in well established discipline	Compared with independent measurements of same variable over long domain
3	Good fit to measure	Historical/field data, uncontrolled experiments, small sample, direct measurements	Accepted theory with partial nature (in view of the phenomenon it describes)	Reliable method common within established discipline; best available practice in immature discipline	Compared with independent measurements of closely related variable over shorter period
2	Well correlated but not measuring the same thing	Modelled/derived data, indirect measurements	Accepted theory with partial nature and limited consensus on reliability	Acceptable method but limited consensus on reliability	Measures are not independent, include proxy variables or have limited domain
1	Weak correlation but commonalities in measure	Educated guesses, indirect approximation, rule of thumb estimate	Preliminary theory	Preliminary methods, unknown reliability	Weak and very indirect validation
0	Not correlated and not clearly related	Crude speculation	Crude speculation	No discernable rigour	No validation performed

Fig. 3. Pedigree matrix for the assessment of data uncertainty. This matrix was originally developed to assess parameter strength of Integrated Assessment Models (Van der Sluijs et al., 2002). Definitions of the pedigree criteria are given in Appendix B in Supplementary data.

Strength	Skills and time	Theorethical Understanding	Methodological Rigour	Level of Validation
4	High expertise from multiple practitioners in subject matter and no time constraints	Well established theory	Best available practice in well established discipline	The (sub)model as a whole has been compared with independent measurements
3	Good expertise from single practitioner but limited time available	Accepted theory with partial nature (in view of the phenomenon it describes)	Reliable method common within established discipline; Best available practice in immature discipline	Parts of the (sub)model have been compared with independent measurements
2	Limited expertise but enough time to build skill for the specific purpose	Accepted theory with partial nature and limited consensus on reliability	Acceptable method but limited consensus on reliability	Measures are not independent, include proxy variables or have limited domain
1	Limited expertise and limited time available	Preliminary theory	Preliminary methods ; unknown reliability	Weak and very indirect validation
0	No expertise in the subject matter and big time constraints	Crude speculation	No discernable rigour	No validation performed

Fig. 4. Pedigree matrix for assessment of submodel uncertainty.
Source: Adapted from Van der Sluijs et al. (2002). Definitions of the pedigree criteria are given in Appendix B in Supplementary data.

assessment of CO_2 capture from power plants, and/or iii) generic chemical process simulations. The 14 experts taking part in this evaluation are either employed by academia or research institutes, including leading research institutes in carbon capture technologies such as the Norwegian University of Science and Technology (NTNU), University of Texas at Austin, and CSIRO (Australia). After the pedigree review, one of the respondents indicated his expertise on the topic was too low to be assumed an expert. His contribution to the assessment was therefore not included in the analysis leading to a total amount of respondents of 13.

To limit the amount of work for the reviewers, pedigree scores were pre-assigned by the modeller. The filled matrices were then sent by email to the reviewers and they were asked to review the scores assigned in the pedigree matrices. If they did not agree with the scores assigned by the modeller, they should change them into a score that represented their opinion. In the file containing the scoring matrices, there was room for the reviewers to explain their choice, or to provide any other comment with respect to the pedigree analysis. After reviewing, they returned the updated matrices by email. In addition to the pedigree matrices, background information was also provided. This information pack described the characteristics of the MEA model (see Supplementary data).

2.4.3. Processing of Pedigree results

The scores in pedigree matrices follow an ordinal scale, hence ordinal scale statistics were used for determination of averages and spreads. The results of the 13 respondents were averaged into an overall result, by taking the median score. To determine the spread, initially the Interquartile Range (IQR)[6] was used. However, as is shown in Appendix C in Supplementary data, in this study the result of this statistic is zero in most cases,[7] and hence provides very little information about the spread. Therefore, instead of the IQR, the standard deviation is used in the results section of this work.

The medians and standard deviations were presented in tables, where a median of 0 indicates very high average uncertainty, and a median of 4 indicates very low average uncertainty. As a visible representation of uncertainty, scores were complemented with coloured shading: red (score 0), orange (1), yellow (2), light green (3), dark green (4).

2.5. Analysis of the combined validation and pedigree results

In the final step, the results from both data validation and pedigree matrices were analysed to assess the overall uncertainty of the model, and model results. For this assessment all pedigree analyses and data validations were assumed equally important during interpretation of final uncertainty and quality.

[6] The Interquartile Range, or IQR, is a measure of statistical variability used for ordinal scale statistics. It is defined as the difference between the first and the third quartile or a dataset: IQR = Q3 − Q1.

[7] An IQR score of zero occurs if the values for the first and third quartile are equal to each other. This is generally a sign of high agreement amongst, i.e., low variability in, the dataset.

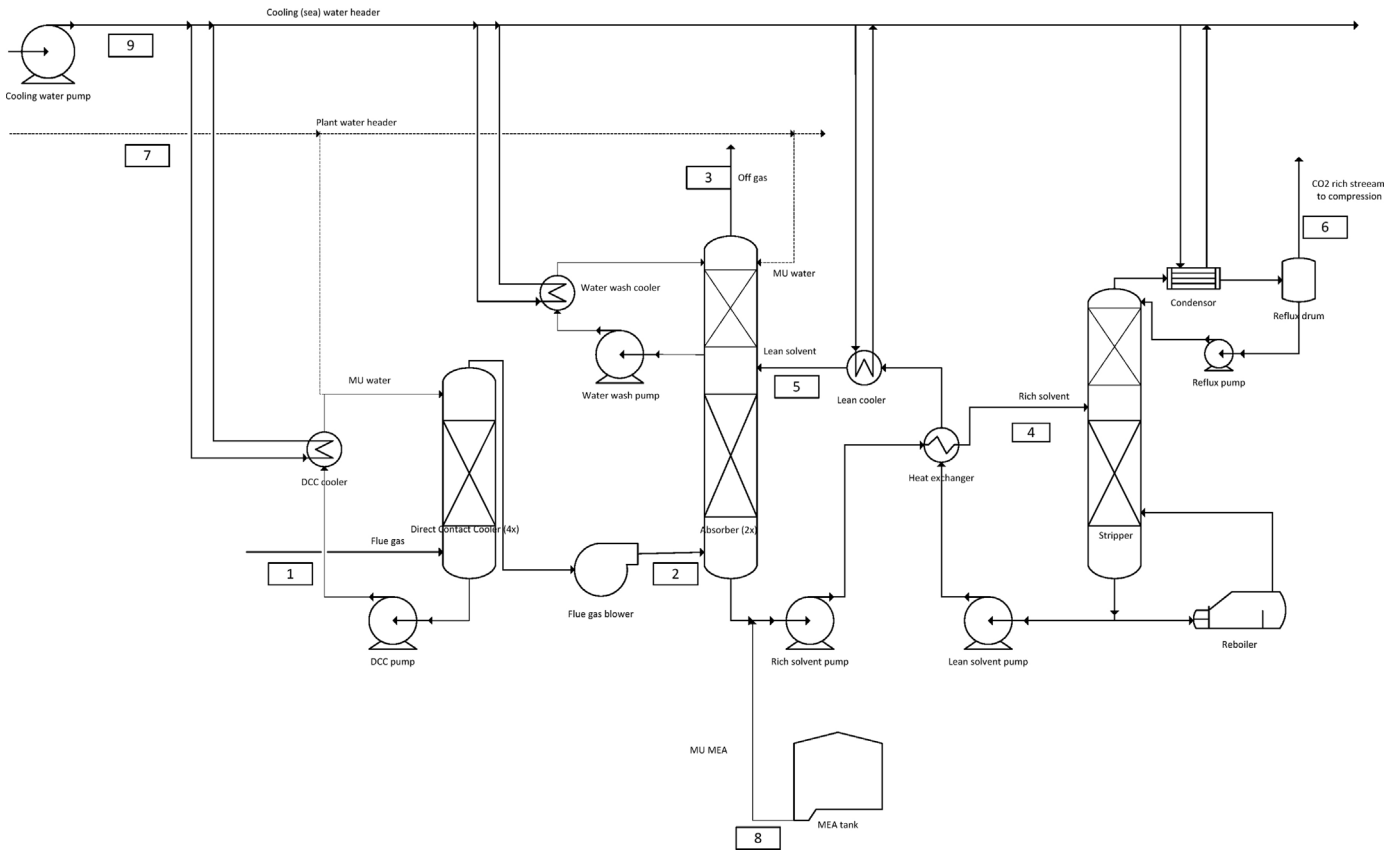

Fig. 5. Process flow diagram of the MEA model.

3. Results

3.1. Quality evaluation of the state of scientific knowledge on MEA carbon capture modelling

3.1.1. Process description

A MEA system is a process for post combustion capture of CO_2 from a flue gas. Typical line-ups consist of an absorber-stripper combination in which the solvent, a 30 wt% solution of monoethanolamine in water, is circulated (Fig. 5). In the absorber, the solvent binds CO_2 at low temperature and pressure. This "rich" solvent is sent to the stripper where the CO_2 is released at elevated temperature, typically 120 °C. Carbon dioxide comes over the top of the column, while lean, regenerated solvent goes through the bottom of the stripper, back to the absorption column. The stripping heat is supplied by low pressure steam in the stripper reboiler. For heat integration typically a cross heat exchanger is placed between absorber and desorber. Both absorber and stripper are equipped with a water wash. In the absorber it washes entrained MEA droplets from the flue gas. In the stripper the water wash rectifies the desorbed CO_2 stream. The MEA process contains a direct contact cooler (DCC) to cool flue gas to the required temperature, and a flue gas blower to overcome pressure drop in the DCC and absorber. Most commercial line-ups include highly optimized energy integration measures, in order to lower the MEA system's energy penalty. Examples of these measures are reported in, e.g., Ahn et al. (2013).

3.1.2. Components

The chemical components are summarised in Table 2. A vast amount of information is available in literature for the main flue gas components, the main solvent components and some of the electrolytes. This also applies to most of the flue gas impurities. For the solvent degradation products, and for the MEA electrolytes, the amount of available data is scarcer, especially for some physical properties.

Table 2
Chemical components typically found in coal plant flue gas, and in MEA systems (Sanchez Fernandez et al., 2012).

Main flue gas components	N_2, CO_2, H_2O, O_2, Ar
Possible flue gas impurities	SO_x, NO_x, HCl, HF, CO, NH_3, particulates, Hg, trace metals
Main solvent components	H_2O, C_2H_7NO
Solvent electrolytes	OH^-, H_3O^+, CO_3^{2-}, HCO_3^-, $C_3H_6NO_3^-$, $C_2H_8NO^+$
Solvent degradation products	Heat stable salts of MEA and S, N or O

3.1.3. Chemistry

The main chemical reactions in the MEA—H_2O—CO_2 system are well-known, and are given in Eqs. (1)–(5) (Kim et al., 2009):

$$H_2O + HCO^-{}_3 \leftrightarrow CO^{2-}{}_3 + H_3O^+ \quad (1)$$

$$2H_2O + CO_2 \leftrightarrow HCO^-{}_3 + H_3O^+ \quad (2)$$

$$2H_2O \leftrightarrow OH^- + H_3O^+ \quad (3)$$

$$H_2O + MEA^+ \leftrightarrow MEA + H_3O^+ \quad (4)$$

$$H_2O + MEACOO^- \leftrightarrow MEA + HCO^-{}_3 \quad (5)$$

Besides the main reactions, there are side reactions between MEA and impurities in the flue gas. Examples are oxidative degradation of MEA into heat stable salts, MEA degradation with acid components, and polymerization of the MEA electrolytes. These mechanisms and reaction rates are currently under investigation,

Table 3
Pedigree scores for the process line-ups, thermodynamics and chemistry of components of the main system (pedigree results of impurity and degradation reactions shown in Table 4). Medians and standard deviation of scores assigned by the experts. Median scores range from 0 (high uncertainty) to 4 (low uncertainty). Colours used as visual aid.

	Pedigree Criteria of State of Art MEA Knowledge									
Pedigree Criterion	Proxy		Empirical basis		Theoretical understanding		Methodological rigor		Level of validation	
Data	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.
Process line-ups	3	0.00	3	0.00	4	0.28	4	0.44	3	0.00
Thermodynamics	3	0.28	3	0.41	3	0.38	3	0.28	3	0.71
Chemistry	3	0.28	3	0.38	4	0.44	4	0.38	3	0.64
Component (properties)	3	0.28	3	0.41	3	0.38	3	0.28	3	0.49

Table 4
Pedigree scores for the process, thermodynamics and chemistry of impurities and degradation products (pedigree results of the main system shown in Table 3). Medians and standard deviations of scores assigned by the experts. Median scores range from 0 (high uncertainty) to 4 (low uncertainty). Colours used as visual aid.

	Pedigree Criteria of State of Art MEA Knowledge									
Pedigree Criterion	Proxy		Empirical basis		Theoretical understanding		Methodological rigor		Level of Validation	
Data	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.
Process line-ups	3	0.28	3	0.28	3	0.00	3	0.00	3	0.00
Thermodynamics	2	0.00	2	0.00	2	0.28	2	0.44	1	0.38
Chemistry	3	0.66	3	0.48	2	0.28	2	0.00	2	0.49
Component (properties)	2	0.28	2	0.28	2	0.28	2	0.28	2	0.41

but knowledge on this topic is currently incomplete and inconclusive (Goff and Rochelle, 2004; Lepaumier et al., 2009; Supap et al., 2009; Sexton and Rochelle, 2011; Voice and Rochelle, 2013). Note that most data have been collected from lab experiments, and limited data from pilot plants are available. Moreover, most of these lab experiments use different experimental methods, leading to difficulties in comparing results, and therefore on deriving robust conclusions on MEA degradation.

3.1.4. Thermodynamics

As can be derived from components and chemistry, CO_2—H_2O-amine systems contain multiple components and electrolytes. This leads to complex thermodynamics and phase equilibria that are governed by multiple simultaneous reactions. There are three ways to model the vapour–liquid equilibria in this system. Soft or non-rigorous models consist of simple mathematical relations to predict phase equilibria. Examples are the modified Kremser equation and the "soft" thermodynamic model implemented in the software CO_2SIM (Kvamsdal et al., 2011; Notz et al., 2011). On the other end of the spectrum there are rigorous thermodynamic models, based on activity coefficients, such as the electrolyte-NRTL or the UNIQUAC model (Hessen et al., 2010; Zhang et al., 2011). In between these extremes are simplified activity coefficient models (Tobiesen, 2014). All these types of models are available for the MEA—CO_2—H_2O system and are frequently refined to better predict phase equilibria, and in some cases, component speciation.

3.1.5. Uncertainty evaluation of current state of knowledge

As explained in the methods section, the pedigree matrix for assessment of data uncertainty (Fig. 3) was used to assess the current state of knowledge on MEA systems (scores provided by each individual experts are included in Supplementary materials). Table 3 shows the matrix for the main system, i.e., the system described by the reactions in Eqs. (1)–(5). The matrix includes the medians of the scores assigned by the 13 experts, as well as the standard deviation in the experts' scores.

The matrix shows that all median scores for the main system are greater than three, reflecting agreement among the experts that the quality of currently available knowledge of the main system is high. More specifically, it means that they think there is a large amount of empirical data available on MEA system components, chemistry, thermo and line-ups (criterion empirical basis), and that this information is a good measure for the values that are needed for our process models (criterion proxy). Furthermore, the matrix shows that the theoretical understanding of the MEA system is high, that the measurement methods of data are reliable and that the data have been well validated. The scores of indicators *theoretical understanding*, and *methodological rigour*, for line-ups, and chemistry are the highest (4), indicating that these particular sets of data are best understood, and the best regarded measurement methods are used to generate these data. In their responses, many experts made the comment that a great deal of data on the MEA system is currently available from lab, and small pilot plants. In case there is a need to further increase the quality of data, i.e., get all scores up to a value of 4, more data need to be generated in large demo plants, and preferably in commercial plants.

Looking at the standard deviations of the expert scores in Table 3, the individual scores showed little variability. The pedigree indicator *proxy* shows the lowest standard deviations, meaning that the experts agree on the value assigned to this indicator. The largest standard deviation is observed for the criterion *validation*. This is explained by the fact that some experts believe current data are well validated, assigning a higher value of three or four, while other experts stress that current validation is done with lab values with limited validity, assigning a lower score of 2.

Table 4 shows that the quality of data on MEA degradation and impurity reactions is clearly lower than that of the main reactions, with median scores between one and three. As pointed out in Section 3.1.3, current knowledge is still incomplete and inconclusive. Not all reaction products and reaction mechanisms have been identified, and if they have been identified, it is mostly in lab conditions that do not match actual plant conditions (see e.g.,

Table 5
Flow and composition of the flue gas feed stream to the MEA unit.

Unit	Value (ASC PC in-house model)	Validation (Cesar, 2011)
Flow (kg/s)	780	782
Pressure (bar)	1.0	1
Temperature (°C)	50	50
Composition (%$_{vol}$)		
N_2	72.2	72.9
CO_2	13.6	13.7
O_2	3.4	3.7
H_2O	9.5	9.7
Ar	0.8	0.005

Fredriksen and Jens, 2013; Sanchez Fernandez et al., 2012). The small standard deviations show that there is general agreement amongst experts: the state of current knowledge of degradation and impurity reactions is that research and experiments have been performed, but that the amount of empirical studies, and hence the theoretical understanding is still average; the research methods are not best in class yet and differ amongst research institutes, and validation has mostly been done to small lab experiments, limiting the applicability of these results for use in models of commercial scale plants.

As a general conclusion, the state of the art on MEA is that the main system has been elaborately studied: much and good quality data are available. This is an important conclusion for modelling purposes, because it means that there is sufficient high quality data available that can be used to construct detailed, first principle process models. The degradation and side reactions are less studied, and data on this topic are of average quality. As a consequence, it is not possible to include these reactions into rigorous process models yet. However, the information should be sufficient to make simple mass balances of the amine degradation process.

3.1.6. Model description

This section describes the choices that were made in process model selection. The steps followed can be summarised as: understanding the process; defining the modelling objective; specifying selection criteria; selecting model attributes; specifying model; and running the model (see Van der Spek and Ramirez, 2014).

The objective of this MEA simulation model was to assess the technical performance of a commercial size carbon capture plant. The following output parameters were selected as a measure of technical performance:

- Specific Reboiler Duty (SRD; GJ/t CO_2 captured)
- Liquid/gas ratio ($kg_{solvent}/kg_{flue\ gas}$)
- Electric power requirement (kJ/t CO_2)
- Cooling water requirement (GJ/t CO_2)
- Plant water requirement (m^3/t CO_2)
- CO_2 in stripper overhead (%)

Flue gas from an Advanced Super Critical (ASC) Pulverized Coal (PC) power plant was used as feed stream to the MEA unit (stream 1 in Fig. 5). The feed stream flow and composition (Table 5) are the outputs of an in-house ASC power plant model, based on the European Best Practice Guidelines for Assessment of CO_2 Capture Technologies (Cesar, 2011). The values of our in-house model are well in line with the original values from the European Best Practice Guidelines (Table 5). For the purpose of this modelling work, it was not necessary to include flue gas impurities and MEA degradation reactions.

The MEA system was modelled in the software package Aspen Plus V8.4, according to the flowsheet in Fig. 5. As stated in Section 3.1.1, more advanced process configurations exist for MEA carbon capture technology. Especially, commercial vendors have developed their proprietary line-ups, in order to increase their technology's energy performance (e.g. Scherffius et al., 2013). Note that in this paper we model a generic MEA system, and consequently proprietary line-ups have not been taken into account in the model. The e-NRTL-RK model was selected for prediction of CO_2 solubility in the MEA solvent. E-NRTL coefficients were retrieved from the Aspen databanks (AspenTech, 2014). Equilibrium reactions in Eqs. (1)–(5) were used; the equilibrium coefficients were also retrieved from the Aspen databanks. To include diffusion limitations of the gases into the solvent, the Aspen Ratesep blocks were selected for modelling of DCC, absorber, stripper, and water washes. The boundary conditions in Table 6 were used to specify the building blocks of the process model. Also these were validated against external data points, if validation values could be retrieved.

3.1.7. Uncertainty evaluation of simulation model

Data validation: as part of the uncertainty evaluation, we validated the feed stream, flowsheet and boundary conditions. The Feed stream (Table 5) was validated against the European Best Practice Guidelines for Assessment of Carbon Capture Technologies (Cesar, 2011), and showed good accordance with values retrieved from this study. The European Best Practice Guideline is an independent source, by the European Benchmarking Task Force (EBTF), which provides guidelines for baseline performance of power plants with and without carbon capture.

The boundary conditions were validated against values retrieved from the Esbjerg (Knudsen et al., 2007, 2009, 2011; Ahmadi, 2012), and ITC (Ahmadi, 2012) pilot plants (Table 6). Note that not all values could be validated because of missing public data. The values that could be validated are generally in good accordance with the pilot plant values. Only the values for packing heights show some differences, especially with the ITC pilot. This is due to different performance requirements for the pilot plant and a commercial plant that is simulated with our model. The flowsheet, or process line-up, was validated against flowsheets presented in Cesar (2011), IEAGHG (2010), and the Esbjerg pilot plant.

The thermodynamics and chemistry that are retrieved from the Aspen databank were not validated against pilot plant results. Instead, they were validated by comparing the coefficients to coefficients found in other modelling studies (Kim et al., 2009; Hessen et al., 2010; Zhang et al., 2011). Some of the coefficients match the coefficients in the Aspen Plus databank, but some do not. It is assumed that the physical properties retrieved from the Aspen databank are regressed based on experimental data, but it is not possible to retrieve the original source, so there is no certainty on validation. The pure component properties are not validated by the authors, but are assumed to be validated by AspenTech. The unit operation models were not validated by the authors, because they are assumed to be correctly implemented in the Aspen Plus software.

Pedigree matrices: as explained in the methods section, the pedigree matrix for assessment of process model uncertainty (Fig. 4) was used to assess the strength of the chosen submodels (line-up, thermodynamics, chemistry, and unit operations). Table 7 shows the resulting median scores and standard deviations of the expert review (scores of each individual respondent are included in Supplementary material).

The table shows that the quality of the line-up used in this model is above average, scoring a three on all pedigree criteria. The weaknesses of the model, according to the reviewers, lie especially with type of validation, and with resource skills and time. As mentioned in the previous section, validation of thermodynamics and chemistry was only done by comparing VLE and chemical equilibrium coefficients from the Aspen Plus databanks, with coefficients found in scientific literature. During the pedigree review, some experts indicated that, as a minimum, they expect a comparison of absorber

Table 6
Boundary conditions for unit operations in the MEA simulation model. The letters in the Ref column represent the source of the value. Validation data are retrieved from Knudsen et al. (2007, 2009, 2011) and Ahmadi (2012).

Boundary condition	This study	Ref[a]	Validation
CO_2 capture rate (%)	90 (design spec)	A	Esbjerg: 90%
Lean solvent loading	0.25	A	Esbjerg: 0.166–0.275; ITC: 0.19–0.232
Absorber inlet temperature (°C)	40	A	ITC: 39–50
Lean solvent inlet temperature (°C)	30	A	Esbjerg: 40; ITC: 37.6–40.8
Flue gas temperature (°C)	50	C	Esbjerg: 47
Stripper inlet temperature (°C)	Model output	–	–
Reboiler temperature (°C)	Model output	–	Esbjerg: 120
Condenser temperature (°C)	30	B	–
Cross-HX temperature approach (°C)	6	C	Esbjerg: 4–10
Cooling water inlet temperature (°C)	12	B	–
Cooling water outlet temperature (°C)	19	B	–
Plant water inlet temperature (°C)	15	C	–
HX pressure drop (bar)	0.4	C	–
DCC top pressure (bar)	0.99	–	–
DCC pressure drop (bar)	0.01	–	–
Absorber pressure (bar)	1.148	A	–
Absorber pressure drop (bar)	0.048	A	–
Stripper pressure (bar)	1.7	A	Esbjerg: 1.85–1.94
Stripper pressure drop (bar)	0.2	A	–
Packing height (m) and type			
DCC	7 m Norton IMTP-50	–	–
Absorber	15 m Mellapak 250Y	–	Esbjerg: 17 m Mellapak 2X; ITC: 6.5 m Flexipack 700Y
Absorber water wash	10 m Mellapak 250Y		Esbjerg: 3 m Mellapak 250Y; ITC: 2 m Flexipack 700Y
Stripper	7 m Mellapak 250Y	–	Esbjerg: 10 IMTP-50; ITC: 6.5 m Flexipack 700Y
Stripper water wash	3.5 m Mellapak 250Y		Esbjerg: 3 m IMTP-50; ITC: 8.3 m Flexipack 700Y

[a] A: Abu-Zahra et al. (2007), B: IEAGHG (2010), C: Cesar (2011).

Table 7
Pedigree matrix of submodels used in this MEA model. Medians and standard deviations of scores assigned by the expert reviewers. Median scores range from 0 (high uncertainty) to 4 (low uncertainty). Colours used as visual aid.

	Submodel Pedigree Criteria (this study)							
Pedigree Criterion	Skills & Time		Theoretical understanding		Methodological rigor		Level of Validation	
Submodel	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.
Process line-up	3	0.28	3	0.28	3	0.44	3	0.28
Thermodynamics	1	0.63	3	0.28	2	0.28	1	0.78
Chemistry	1	0.63	3	0.41	2	0.28	1	0.77
Unit Operations	2	0.00	3	0.00	3	0.44	1	1.04

and stripper temperature profiles with experimental values. Other suggestions to validate VLE were to construct a diagram comparing CO_2 partial pressure with amine loading, as done for instance in the paper by Hessen et al. (2010). With respect to skills and time, the modeller was accustomed to process modelling, but was new to the field of modelling postcombustion CO_2 capture with chemical solvents. Within the research institute, there is much experience in process modelling, but not in modelling of this particular technology. Hence the scores for this criterion are in the low range for thermodynamics, and chemistry (one), and in the medium range for line-ups, and unit operations (two–three). A last point is that thermodynamics, and chemistry, were assigned an average score of two on the *methodological rigour* criterion. This was done because it is not stated by AspenTech how these submodels were derived, and on which sources they are based, which adds to the uncertainty. The AspenTech databanks are somewhat of a black box in that sense. Perhaps the methodological rigour behind these submodels is high, but the fact that this is an unknown, and hence uncertain, makes it difficult to assign a higher score than two.

The standard deviations of the scores are low, implying general agreement between the reviewers. The exceptions are the scores for validation. Some reviewers have the opinion that all submodels in the Aspen databanks are well validated, and hence assign a high score to this criterion (scores of three and four have been recorded). Most reviewers however believe these submodels need explicit validation and assign a low score, typically a one.

The quality of the input parameters is generally considered high (Table 8). The reviewers believed that theoretical understanding of the parameters is high and data were retrieved using reliable methods. The input parameters give a good representation of the quantity they represent and were based on directly measured empirical data. Most of the parameters were validated against independent measurements. This is illustrated by all scores being greater than three. Standard deviations are low, indicating that there is overall agreement between reviewers on the quality of input parameters.

In conclusion, there is significant uncertainty in some components of our model. In fact, the pedigree matrices of our model

Table 8
Pedigree matrix of input parameters used in this MEA model. Medians and standard deviations of scores assigned by the expert reviewers. Median scores range from 0 (high uncertainty) to 4 (low uncertainty). Colours used as visual aid.

	Pedigree Criteria of Input Parameters (this study)									
Pedigree Criterion	Proxy		Empirical basis		Theoretical understanding		Methodological rigour		Level of Validation	
Data	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.
Feed streams	3	0.28	3	0.28	4	0.00	4	0.00	3	0.28
Boundary conditions	3	0.00	3	0.28	3	0.28	3	0.00	3	0.28
Pure component properties	3	0.28	3	0.28	3	0.49	3	0.38	3	0.64

Table 9
Case study performance indicators and validation results.

	Validation	1st model	Difference to validation values	Revised model	Difference to validation values
Specific Reboiler Duty (GJ/t CO_2)	Esbjerg: 3.6–3.9	3.9	~4%	3.6	~4%
Liquid/gas ratio ($kg_{solvent}/kg_{flue\ gas}$)	Esbjerg: 3–3.5	5.0	~54%	3.8	~17%
Electric power requirement (MJ/t CO_2)	–	128.6		122.3	
Cooling water requirement (GJ/t CO_2)	Esbjerg: 3.2–3.9	4.3	~21%	4.1	~15%
Plant water requirement (m^3/t CO_2)	–	0.56		0.53	
CO_2 stream purity (%)	Esbjerg: 96.9	95.9	~1%	95.9	~1%

Table 10
Pedigree matrix of the output parameters. Medians and standard deviations of scores assigned by the expert reviewers. Median scores range from 0 (high uncertainty) to 4 (low uncertainty). Colours used as visual aid.

	Pedigree Criteria of model output									
Pedigree Criterion	Proxy		Empirical basis		Theoretical understanding		Methodologic rigour		Level of Validation	
Data	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.	Med.	St. Dev.
Spec. Reboiler Duty (GJ/t CO_2)	4	0.60	2	0.38	3	0.28	2	0.28	3	0.41
Liquid/gas ratio (kg/kg)	4	0.63	2	0.38	3	0.28	2	0.28	3	0.29
Electric power (kJ/t CO_2)	4	0.60	2	0.49	3	0.28	2	0.00	0	0.60
Cooling water (GJ/t CO_2)	3	0.28	2	0.38	3	0.28	2	0.00	3	0.28
Plant water (m3/t CO_2)	4	0.60	2	0.38	3	0.28	2	0.00	0	0.75
CO_2 in stripper overhead (%)	4	0.63	2	0.38	3	0.41	2	0.28	3	0.53

(Tables 7 and 8) show lower scores than the pedigree matrix for the state of the art (Table 3). This is mainly because it is unknown how the thermodynamic and kinetic properties in the Aspen databanks were retrieved and if they were well validated. This raises the question whether or not we should continue with these thermodynamic and chemistry submodels. Given time restrictions, we decided to keep the standard models from the Aspen Plus databank, run the model, and assess the quality of the output parameters, with the option to later change the thermodynamic and/or kinetic coefficients, if the output requires this.

3.2. Uncertainty evaluation of output parameters

This section assesses the uncertainty of the MEA model results. First, the results and the data validation are shown, then the quality of the outputs is assessed using the pedigree matrix for data quality.

3.2.1. Data validation

Table 9 shows the model outputs (1st model) and the reference values used for the validation. It also shows the results of the revised model (see Section 3.2.4). When comparing the outputs of the MEA model (1st model) to the validation values, the specific reboiler duty and CO_2 stream purity are in line with Esbjerg values. However, the liquid over gas ratio and cooling water requirement show significant differences of around 54% and 21%, respectively. Electric power requirement and plant water requirement could not be validated since pilot data is lacking.

3.2.2. Pedigree results

Following the procedure described in Section 2, the output parameters were assigned pedigree scores (Table 10). The scores on the indicator "proxy" are high (all fours and one three), because all but one parameter are an exact measure of the desired quantity, rather than a proxy variable. Scores on "empirical basis" and "methodological rigour" were assigned a median score of 2. For "empirical basis" this is inherent to its definition: a modelled result is always assigned a two. If a higher score is desired, the score should be retrieved from controlled empirical experiments, i.e., values from operating carbon capture plants. The scores for "methodological rigour" are explained by the uncertainty in quality of the submodels, as mentioned in Section 3.1.7. This score means that the followed modelling method is acceptable, but there is uncertainty about its reliability. The "theoretical understanding" of these parameters is above average, with all output parameters assigned a median score of three, stemming from high understanding of the input values and submodels. "Level of Validation" is high for all but two parameters since it was possible to validate the results against the Esbjerg pilot plant. Only the parameters "electric power requirement" and "plant water requirement" score a one, because it was only possible to validate those in an indirect way.

3.2.3. Integration of results on uncertainty analysis

As described in Section 2.5, the insights from validation, and pedigree assessment of the output results can be combined to obtain a better overall picture of output uncertainty. The results indicate that the values of output parameters "liquid over gas ratio", and "cooling water requirement" of our MEA model, diverge from values found in the Esbjerg pilot plant (54% and 21% respectively), see Table 8. This implies that the predictability of our MEA model is low, at least for these performance indicators. To complement this insight, the pedigree analysis identified the following weaknesses in the process model: in the thermodynamic and chemistry submodels (Table 7), and in some of the output indicators (Table 10).

3.2.4. Revision of MEA model

As discussed in Section 1.2, an acceptable level of model uncertainty is related to the purpose of a specific modelling task. The present case study aimed to assess the technical performance of a commercial size, MEA based carbon capture plant. Given the uncertainties shown by the validation, and pedigree analysis (Tables 7 and 9), this model was considered unable to meet the desired aim. Therefore, it was decided to revise the model so that it would be better fit for purpose. The pedigree review pointed out clear weaknesses in the thermodynamic and/or chemistry submodels of the first version of the model. Therefore, improvements were made to these submodels until satisfactory output values were reached. As a first improvement, the coefficients for prediction of the chemical equilibrium constants were revised. Instead of the values from the Aspen Plus databanks, the values from Kim et al. have been used as they have been shown to provide accurate predictions of CO_2 solubility in MEA (Kim et al., 2009).

As a result of this first improvement, the revised version of the MEA model was able to better predict L/G ratio and cooling water requirement. The differences in these indicators between the model and pilot plant (which is used for validation purposes) improved from 54% to 17%, and from 21% to 15%, respectively (Table 9). Therefore, it was decided to accept this revised model, and not make any further improvements to, e.g., the thermodynamic submodel.

The pedigree of the revised model was not assessed with the external experts, but the improvement has probably increased the scores for methodological rigour and validation of the chemistry submodel, because the equilibrium coefficients presented in Kim et al. are taken from sources that provide solid research methods and were properly validated.

4. Discussion of the pedigree approach for process model quality review

This section evaluates the usefulness, and robustness of the pedigree approach, for quality assessment of carbon capture process models. This discussion is partly based on feedback received from the experts. This full feedback is presented in Appendix D in Supplementary data.

4.1. Pedigree matrix design

Meaningful use of pedigree matrices for process model evaluation requires clear pedigree criteria, and understandable linguistic descriptions. In this study a pedigree matrix for the assessment of data quality (Fig. 3) and a pedigree matrix for the assessment of process model quality (Fig. 4) were used. Appendix D in Supplementary data describes that reviewers had difficulty interpreting some of the criteria, and some of the linguistic descriptions. This was especially the case for the criterion *proxy*. One way to look at this is that in this case study hardly any proxies were used, so it may be confusing to have to score the level of proxy on a scale from 0 to 4, when all values are an exact measurement of the quantity they represent. Proxies are hardly used in this case study because it deals with a well-known technology, for which it was possible to construct a detailed process model. Consider however a model that predicts the degradation of a MEA solvent. In this case, not all reaction products and reaction pathways are known, and proxies will need to be used to generate a basic understanding of the degradation process. So for a less understood research subject, the insight of where actual values are used, and where proxies are used, may become more meaningful.

4.2. Which data items to score?

Another topic of reflection is which data should be scored when either reviewing a process model, or its output. A process model can have several tens (sometimes hundreds) of input values and model equations. A very rigorous way to assess the quality of a model would be to scrutinize every single one of these parameters and equations. That would however add much complexity to the review process affecting its applicability, and it is questionable whether this would provide significantly more insights or not. In this study we opted to aggregate data items into aggregates of knowledge (Table 3), aggregates of submodels (Table 7), and aggregates of input parameters (Table 8). As an example, rather than reviewing every equation involved in calculating the energy balance, we rather reviewed the aggregated submodel *thermodynamics*. This does lead to less detail in the quality assessment, but makes the pedigree approach more feasible in terms of time, and hence expert resources.

One could also opt to only review those parameters and equations that have most impact on model outputs. Van der Sluijs et al. (2005) did this by first evaluating the sensitivity of the model to the input parameters. Only the most sensitive input parameters are then screened on their respective uncertainty. This would however require a different approach to pedigree than ours, since it would require screening of individual parameters and equations, rather than aggregated groups of parameters and equations as done in this study. In turn, this would have led to a very time consuming sensitivity analysis, given the large number of parameters and equations in a process model, as discussed before. An intermediate solution, that could be tested in a next study, is instead of doing a full sensitivity analysis to find the most important input parameters, one could ask the experts to select (groups of) parameters and model equations that they expect most important given a specific technology. In a second step, the experts could score the strength and uncertainty of the selected (groups of) parameters and model equations.

4.3. Scoring procedure

As explained in the methods section, for this study we preassigned scores to the items to be reviewed, and had the respondents review this score individually, in their own office. This was done to minimize the time effort for the reviewers. One could argue however that a better setting would be to have the experts in the same room, where they can ask questions about the procedure, pedigree matrices, and model information provided (Risbey et al., 2001). This could lead to a better understanding of the procedure, and improve the outcomes of the pedigree review. Besides that, pre-assigning scores by the original modeller could lead to a scoring bias amongst the reviewers. Reviewers may tend to keep the original scores as much as possible, and only diverge from the original scores if in their opinion, they are really incorrect.

Therefore, in a next study, it would be interesting to use a different procedure, where no scores are pre-assigned, and possibly the experts do the reviewing individually, but in the same venue, as to ask questions and clarifications when required.

4.4. Expert selection, group size, and repeatability

Additional issues with expert judgement are the amount of experts to include, and the type of expertise to invite for elicitation. In this study 14 respondents participated in the pedigree review, but one of them indicated afterwards that he actually lacked the background knowledge to give a meaningful assessment, so his contribution was excluded from the results. As Knol et al. (2010) point out, including the right type and amount of experts is key to the robustness of the expert elicitation. The combined skills and expertise of the participants should preferably cover all aspects of the reviewed model. They indicate that when the right experts are included in the elicitation, a minimum of six of them is required, in order arrive at robust results. This implies that the results of the expert elicitation with pedigree analysis should be repeatable to a large extent, if the review were to be done by a similar group of experts. Furthermore, the experts are asked to judge the model based on evidence provided by the modeller. This decreases subjectivity, because all experts are asked to judge the same information. This aspect of the pedigree approach also fosters repeatability of the results.

In this study, the expert scores were very similar to each other, which resulted in a low standard deviation of scores. This supports the notion that the results are robust repeatable. From a practical perspective, it may also mean that a smaller group of experts could have been consulted for the results to still be robust. This may increase the practical applicability of the pedigree approach, especially when it needs to be applied in the case a large pool of experts is not readily available. To establish if this premises holds, it is necessary to perform the pedigree review with different sizes of expert groups. This is subject to future studies.

5. Conclusions

In this work, we introduced a novel approach to uncertainty evaluation of process models which combines pedigree analysis and data validation. The approach was tested in a case study of CO_2 capture with monoethanolamine from a coal power plant flue gas. Data validation was used to quantitatively assess the uncertainty of the inputs and outputs of the MEA model. Pedigree analysis was used to qualitatively assess the current knowledge base on MEA carbon capture systems, the strength of the MEA process model, and of the MEA model results. The pedigree review was done by 13 international experts in the field of postcombustion carbon capture with chemical solvents.

The data validation showed that the model accurately predicts specific reboiler duty, and CO_2 stream purity (4% and 1% difference respectively between model and pilot plant), but is less accurate in predicting liquid over gas ratio, and cooling water requirement (54% and 21% difference respectively between model and pilot plant). The pedigree analysis complemented this result by showing that there is fairly high uncertainty in the thermodynamic, and chemistry submodels used for this simulation model, as reflected in the low pedigree scores on most indicators (ones and twos on a scale from zero to four), which could be the cause of the differences found during validation. The low scores in the pedigree matrix led us to further investigate the weaknesses in the chemistry submodel, and to improve this by adding new values for calculation of chemical equilibrium constants. As a result, the prediction of L/G ratio and cooling water requirement improved significantly, leading to increased overall confidence in the model.

The results show that including a pedigree approach improved uncertainty evaluation in three ways. First, by highlighting sources of uncertainty that quantitative uncertainty analysis does not take into account, such as the knowledge base of specific phenomenon. In this case study, it was fundamental in highlighting weaknesses in the thermodynamic and chemistry submodels. Second, by providing a systematic approach to uncertainty evaluation, thereby increasing the awareness of modeller and model user. And finally, by presenting the outcomes in easy to understand numerical scores and colours, improving the communication of model uncertainty. In combination with quantitative validation efforts, the pedigree analysis provides a strong method to gain deep insight into the strengths and weaknesses of a model, to identify important knowledge gaps, and to communicate this to decision-makers.

The pedigree approach was perceived as a useful method by the experts that participated in this study. There are however issues that should be further investigated. One being the potential impact of carrying out the review via email instead of face-to-face, and whether or not there is a bias by providing the experts pedigree matrices with pre-assigned scores. Future work will focus on improving the pedigree approach with respect to these concerns. We will also focus on applying the pedigree approach to more novel carbon capture technologies, to establish whether further modification of the approach is required.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.compchemeng.2015.10.006.

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