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Optimal Solvent Design for CO_2 Capture Process

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Development of alternative CO_2 capture, utilization and storage (CCUS) have become important for sustainable and environmental reasons. Various promising solvents are used to capture CO_2 such as MEA, DEA, potassium carbonate and recently co-blending of solvents. However, the major drawbacks of using these solvents are degenerative issue, energy intensive for regeneration process and environmental impact. Traditionally, designing a solvent for carbon capture involves a trial and error approach where potential candidates are subjected to laboratory testing. However, this process is time-consuming and often has no guarantee that the tested solvent properties adhere to the desired property range. Hence, a systematic framework for optimal solvent design for CO_2 capture is discussed in this paper. The solvent design problem has been formulated using model-based approach to meet specified target properties such as density, solubility, viscosity, vapour pressure, CO_2 absorption capacity and thermal stability. The number of blend solvent was then systematically ranked according to a desired process performance, cost and environmental friendliness.

1. Introduction

Rapid economic growth nowadays has contributed to the increasing in global warming effect especially the effect from anthropogenic emission of greenhouse gasses (GHG). This is consequence from the reliance of the world economies on the use of fossil fuels (i.e. coal, natural gas and oil) as primary source of energy, which contributes to the high emission of CO_2 in the atmosphere. Statistic shows that the global concentration of CO_2 in atmosphere has increased from 280 ppm during pre-industrial time (UNEP, 2005) to approximately 400 ppm in May 2013 (IEA, 2013) which is the highest in history at that time. The increase of the emission of CO_2 in atmosphere has contributed to the adverse effects on environment. For instance, rise in global surface temperature, continuous rise in sea level and increasing occurrence of storms and floods (IPCC, 2007).

With growing concern over the adverse effect on the environment, different approaches on effective CO_2 abatement strategies are considered to combat these phenomena. As stated by Leung et al. (2014), the feasible way to mitigate this global climate change are by increase energy efficiency, increase the usage of low carbon fuels, change the usage of fossil fuels to renewable energy, and to create the CO_2 sinks with the help of Carbon Capture and Storage (CCS) technologies. Each approach to mitigate global climate change has their own advantages and limitations, but amongst the different approaches, the most promising way is CCS technology since it's reconcile the continued use of fossil fuels, while at the same time minimising the effect of CO_2 on the earth climate system. Besides, CCS also can capture up to 90 % of CO_2 from large point emission sources such as fossil fuels fired power plants (Leung et al., 2014).

CCS is define as the process that involve the separation of CO_2 from industrial emission source, transport to storage location and then either stored permanently or reutilised industrially (IPCC, 2005). CCS technology can be divided into three basic stages which is separation or capture of CO_2, transportation and storage. The most important stage in CCS is the first stage which is the capture and separation stage. This is due to the operating and capital cost of capture stage will contribute up to 70 - 80 % of the total cost of the full CCS technology (Blomen et al., 2009). Besides, it is the biggest challenge to capture CO_2 in the flue gasses from industries since it has larger volume, and low CO_2 concentration.

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One of the most promising ways to capture CO_2 is by using post combustion, chemical absorption process. This process is preferred since it can easily integrate or retrofitted to any existing power plant. Moreover, chemical absorption process is highly selective with very high carbon capture efficiency at low CO_2 concentration and low pressure (Sreenivasulu et al., 2015). However, chemical absorption has some drawbacks. As listed by Knudsen et al. (2009) in their research, chemical absorption requires high energy consumption for solvent regeneration process, degradation of solvent in the presence of oxygen, and promotes the corrosion of equipment. Besides, some of solvent is lost through evaporation due to thermal degradation and will cause the impact on the environment.

Currently, a lot of research has been done to overcome this problem such as screened the current available solvent based on thermodynamics properties (Porcheron et al., 2011), studied the interaction between process design and solvent to improve the energy performance of CO_2 capture process (Neveux et al., 2013) used phase equilibrium model to identify an optimal solvent (Hopkinson et al., 2014), and developed an equation-base methodology to optimise the design of absorption and desorption process (Khalilpour and Abbas, 2014). Besides, design new improved liquid solvents with reduce capture cost and energy penalties also have been paid much more attention. Several types of chemical solvents have been introduced for chemical absorption process such as ammonia, monoethanolamine (MEA), methyldiethanolamine (MDEA), piperazine, potassium carbonate, ionic liquid and blending of MDEA and DEA (Toro-Molina and Bouallou, 2013). All of these solvents have their own advantages and drawbacks. For example the commonly employ solvents for carbon capture which is MEA is relatively cheap, has high reactivity and higher absorption rate (Rao et al., 2004). However MEA also has some drawback which could degrade easily in oxidizing atmosphere, energy intensive during regeneration process, has limited CO_2 capacity and corrosive (Davidson, 2007).

Besides, the main problem in designing solvent for carbon capture is time consuming, difficult, and expensive since the process of designing a solvent traditionally involves a trial and error approach where potential candidates are subjected to laboratory testing. Therefore, this research applies Computer Aided Molecular Design (CAMD) approach in order to quickly identify the most suitable solvents and to avoid spending efforts on infeasible regions of the search space (Conte et al., 2011). The purpose of this research is to develop a systematic framework using model-based approach that can be used to design an optimal solvent for carbon capture with reduced solvent cost, reduced energy requirement for solvent regeneration process, low environment impact and acceptable solvent degradation and corrosion.

2. Methodology

The systematic methodology for optimal solvent design of carbon capture process using CAMD approach is illustrated in Figure 1. This methodology applies the reverse design approach introduced by Gani and Pistikoupoulos (2012), where the target properties of the desired solvent are specified first, then the solvent that match the target is identified. The method consists of four main steps which is problem definition, property model identification, optimal solvent design and model based verification. The potential CO_2 solvent that can satisfy solvent performance criteria and environmental friendliness will be generated through step 1, step 2, and step 3 (stage 1 only). However, the remaining step and other attributes such as safety and cost will be presented in future work.

2.1 Problem definition

Problem definition is the step to identify the user attributes and needs. First, in this step, the problem for solvent design in carbon capture process is defined, where the performance criteria of the desired solvent for chemical absorption process are identified from knowledge based or from literature review. The aspect of this performance criteria include the properties of the commonly employ solvent, the properties of solute and the carbon capture process performance. Second, the important performance criteria that have been listed will be translated into physicochemical target properties. Then, the constraint value for each of desired target properties is set based on the literature search.

2.2 Property model identification

Different problem need different set of property models. Therefore the purpose of this step is to assign the appropriate property models for selected process. The required property models are retrieved from the model library which contains the property models for mixture and pure component.

2.3 Optimal solvent design

The next step is to design the optimal solvent. This step consists of two stages. In the first stage, the input data which is the list of chemicals/solvents candidates with their associated properties is selected. Then, the list of feasible solvent is generated based on the target properties constraint that is specified in step 1. If no feasible solvent is generated within desired target properties constraint, the problem can be solved

again by revised the values of constraint in step 1. At this stages only general target properties of the desired solvent is consider such as solubility parameter, normal boiling point, vapour pressure, surface tension and density. This is due to principal that it is better to start with relaxed and simple constraints to generate many solvent candidates where these candidates are screened and ranked in the second stage to obtain the optimal solvent.

In order to screen and rank the solvent, several criteria need to be considered which are environmental impact, solvent degradation, energy for solvent regeneration and cost. The candidate that not specified any of the criteria is eliminated through screening process. The candidate that satisfied all the criteria is ranked and then the best optimum solvent is selected. In this paper, the detailed calculation and model for stage 2, step 3 will not be presented.

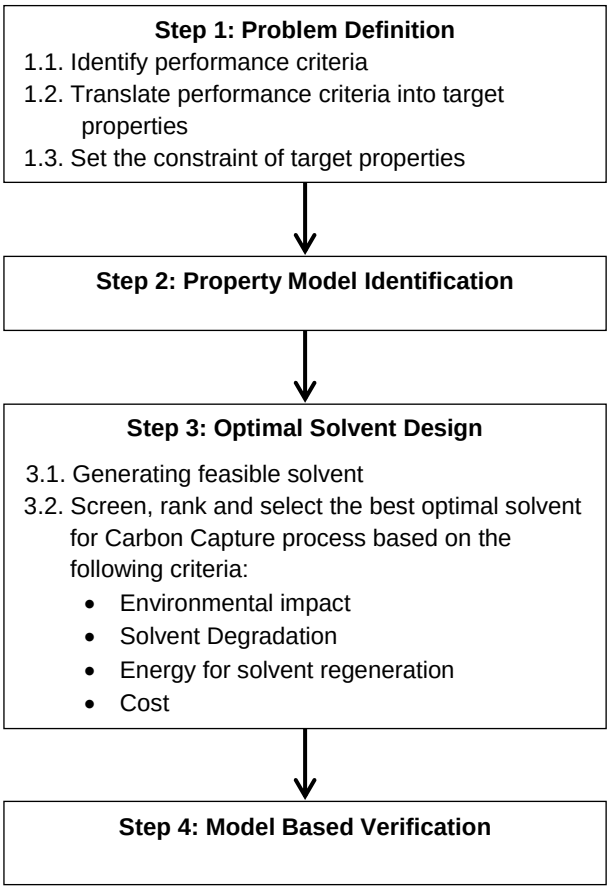

Figure 1: Systematic methodology for optimal solvent design of CO_2 capture process

2.4 Model based verification

The last step in solvent design is model based verification. This step is to verify the target properties of the design solvent that estimated using simple mixing rules. They will be verified using rigorous model. If the target properties estimate with rigorous model is not satisfying the constraint, the solvent will be rejected.

3. Case study

In this section, the case study of fossil fuels fired power plant is used to demonstrated the systematic framework for optimal solvent design of CO_2 capture process. As stated by Freund (2003) in their research, the fossil fuel fired power plants are the single largest lump source of CO_2 emissions. Therefore, in order to capture the CO_2 from this power plant, post combustion chemical absorption process is retrofitted to the existing power plant. The typical process flow diagram for post combustion chemical absorption process is shown in Figure 2. In this process, the cooled flue gas (basically the concentration of CO_2 is around 12 - 14 w/w%, where the balance is nitrogen and water) is contacted counter-currently with the lean solvent (usually aqueous amine). The scrubbed gas is then water washed of solvent and vented

to the atmosphere. The lean solvent gradually heats up as it absorbs CO_2. The temperature inside the absorber is basically between 40 °C to 60 °C. The rich solvent is heated in a cross heat exchanger by the regenerated lean solvent from the stripper column. Then the rich solvent is pumped to the top of the stripper column. In this stripper column, the solvent is regenerated at increased temperature which is around 100 °C to 120 °C and at slightly higher than atmospheric pressure (1.5 – 2 atm) (IPCC, 2005). Heat is supplied into the stripping column through the reboiler. This is the major energy penalty of the process. The regenerated solvent is then pumped back to the absorber through the cross heat exchanger to reduce the temperature of solvent before entering back the absorber column.
The objective of this case study is to design a new improved liquid solvent which can capture CO_2 form fossil fuels fired power plants with reduced energy requirement for regeneration, low environment impact and acceptable solvent degradation and corrosion. As stated before, only Step 1, Step 2 and stage 1 of Step 3 is demonstrated in this case study. The remaining step will not be presented in this work.

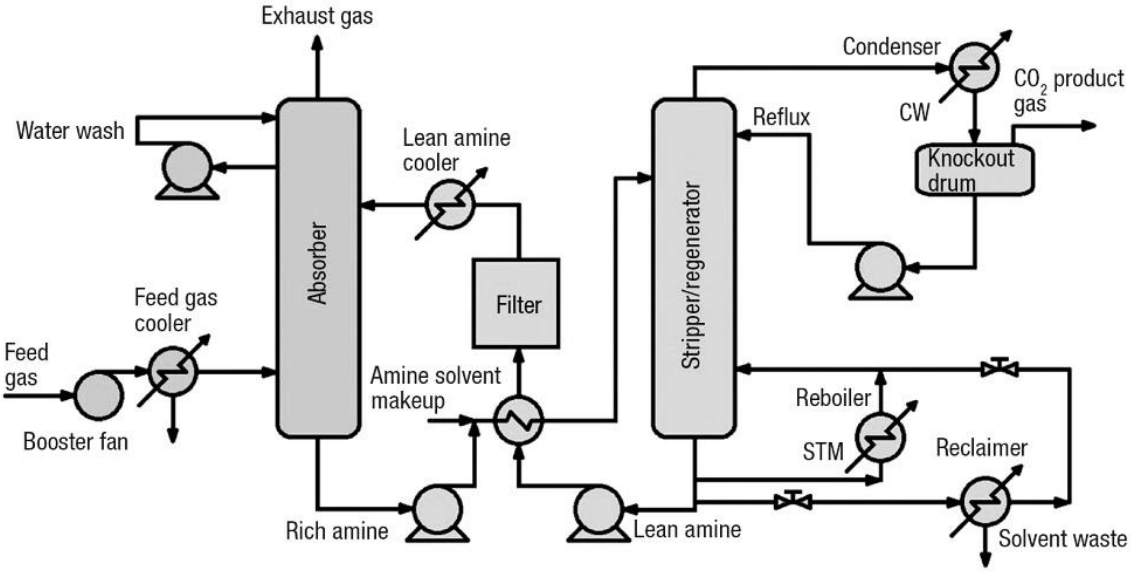

Figure 2: The typical process flow diagram for post combustion CO_2 capture by chemical absorption (IPCC, 2005)

3.1 Problem definition

Based on the knowledge base and literature search, the best solvent for chemical absorption carbon capture process should have the following performance criteria: high reactivity and absorptivity with respect to CO_2, low energy for solvent regeneration, low vapour pressure, high thermal and chemical degradation stability, low environment impact and low solvent cost. In addition, the solvent should not perform an azeotropic mixture with CO_2 (solute) and can easily be separated.
After the important performance criteria of the solvent are identified, these performance criteria are translated into appropriate target properties. The range of value for each target properties is specified based on the literature search on commonly employ solvent properties and the properties of CO_2 as a solute. Table 1 summarize the target properties used in this case study with their corresponding constraint values.

3.2 Property model identification

In this case study, all the general target properties used to design the solvent for CO_2 capture process which is total solubility parameter, normal boiling point, surface tension, density, vapour pressure and viscosity are estimates using linear mixing rule model.

Table 1: The target properties used in this case study with their corresponding constraint value

Target Properties	Lower boundary	Upper boundary
Solubility parameter ($MPA^{1/2}$)	13.6	25
Normal boiling point (K)	400	-
Surface tension (dynes/cm)	25	60
Density (g/cm^3)	1.0	1.5
Vapour pressure (kPa)	-	7.00
Viscosity (cP)	1.0	3.0

3.3 Optimal solvent design

The next step is to design the optimal solvent for carbon capture process. This step is done using CAMD tool in ICAS software. The input data required for CAMD are the functional group, type of chemicals (acyclic, cyclic or aromatic), and the most important is the target property values that has been defined in step 1. The list of functional group that has been chosen for this case study is amine, alcohol, ketone and aldehyde. In this case study, the search for feasible solvent is done for acyclic chemical compound only. The target properties and values in Table 1 are settled in CAMD. As the result, 1,211 chemical structures have been generated. Among 1,211, only 50 chemicals are identified as solvents for carbon capture process. The rest of generated structures are not in the chemical database or unknown and some of them might be not exist. The summary of this result is shown in Table 2.

These 50 feasible solvent candidates are subjected to the second stage of this step where this candidate will be screened, rank and then optimal solvent will be selected. This step and verification model step will be demonstrated in future work.

Table 2: Summary of the result for feasible solvent candidates generated in Step 3

Functional group	Number of feasible solvent candidate generated.
Amine	18
Ketones	19
Amine and alcohol	8
Alcohol	4
Aldehydes	1

4. Conclusion

A systematic methodology for optimal solvent design of CO_2 capture process has been developed in this paper. This systematic methodology was then demonstrated using fossil fuels fired power plant case study. In this case study, 50 solvent candidates for chemical absorption process of CO_2 has successfully been generated from amine, alcohol aldehyde and ketone functional group. In the future work, the shortlisted solvent candidates are subjected to further screening and ranking process in order to select the best optimal solvent candidates. Besides, further verification of the resulting solvent candidates is needed. The verification step is important in order to verify the predicted solvent properties before moving into production.

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