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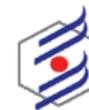
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Integrated Process Design–Computational Chemistry Framework for Process Intensification: H₂S Recovery and Conversion

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Abstract

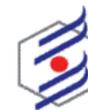
Phase transfer catalysis (PTC) is a general methodology with importance in intensified extraction-reaction processes, and it is applicable to a large number of chemical reactions. This technique accommodates reactions that are generally not achievable through conventional synthesis methods due to the introduction of a homogeneous catalyst for biphasic systems that can transfer a reactant species between two immiscible phases. This two-phase system offers several advantages, such as high conversion yields, high purity of products, operational simplicity, mild reacting conditions, suitability for scale-up of the process, and an environmentally benign reaction system. The economic viability and successful implementation of the large-scale process are heavily contingent on the design and modeling of these kinds of systems.

Although a number of attempts have been made to develop case-specific and generalized models for PTC, the proposed models and accurate thermodynamic parameters are not fully developed. The lack of published theoretical process modeling for scale-up hurts the commercialization potential of PTC. In this study, an integrated and multi-scale modeling framework is proposed for overcoming these limitations for liquid-liquid (LL)-PTC. The framework needs little to no experimental data and combines different tools at different time and space scales to model virtually any LL-PTC system. The goal of this work is to utilize this framework for the recovery and conversion of H₂S from an aqueous alkanolamine solution into value-added products as a way to improve economics and sustainability of the process, specifically at offshore oil and gas platforms.

Keywords: Phase transfer catalysis, multiscale modeling, resource recovery, biphasic system, hydrogen sulfide, sustainability, process intensification

Introduction

The combination of the advancements in computing and the progress in the natural and technical sciences in the past century has significantly contributed to the continual evolution in the fields of chemistry and chemical engineering, eventually giving rise to the sub-disciplines of computational chemistry and process systems engineering (PSE). These two sub-disciplines have a major role in introducing new understandings and developments in computational methods for the simulation, design, and operation of process systems ranging from atomic and molecular up to industrial-scale; this tremendous span in scales forms the chemical supply chain. Although they belong to the same overarching field, chemistry and chemical engineering have typically remained two separate areas working at varying scales. While computational chemistry focuses on the sub-micrometer scale, PSE focuses on the intermediate and macro-scales. However, over the past two decades, it has become increasingly clear that the modeling, design, and development of new and innovative reaction and separation processes requires going below the scale of unit operations – the holy ground



of traditional process engineering – towards the underlying molecules, clusters and their behavior that make up the functions/tasks carried out by the unit operations (Babi et al., 2016). This trend of moving beyond traditional chemical engineering has emerged because the concept of unit operations, although useful and easy to understand, inherently restricts the solution space to a limited number of well-known and ready-made solutions (Freund and Sundmacher, 2008).

To overcome these limitations, engineers and industrial researchers have been working on novel equipment and techniques that could potentially transform our concept of chemical plants and lead to compact, safe, energy-efficient, and environment-friendly sustainable processes (Stankiewicz and Moulijn, 2000). These developments share a common theme: process intensification. In this regard, bridging computational chemistry and PSE to achieve process intensification could qualitatively change the way chemical products and processes are designed.

Phase transfer catalysis is one such case of process intensification that could hugely benefit from a multiscale outlook. In L-L PTC, the reactions take place in heterogeneous two-phase systems (organic-aqueous) with negligible mutual solubility of the phases. The catalyst, located in the aqueous phase, acts as a source of lipophilic cations and continuously introduces the reacting anionic species in the form of lipophilic ion pairs into the organic phase. However, the downside of PTC is the need to quantify exacting reaction conditions and parameters that are difficult to uncover and, in some cases, are counterintuitive. Although there has been some progress in terms of mathematical modeling of PTC systems (Anantpinijwatna et al., 2016), availability of accurate thermodynamic parameters still proves a major limitation as the chemical domain in the group contribution methods is inherently limited to the portion of the chemical design space for which every binary interaction parameter is available.

Modeling Framework

Anantpinijwatna et al. (2016) presented a systematic procedure for modeling biphasic systems that is based on the model generation method of Cameron and Gani (2011). The procedure serves to reduce the complexity of the modeling problem by breaking it into a series of sub-problems. A schematic of the various steps in the procedure can be seen in Figure 1.

The heart of a successful PTC modeling framework lies in the methods and/or tools used to describe the system in the three modules shown in

Figure 1 since the methods used to calculate the molecular and mixture properties largely determine the breadth, accuracy and performance of the framework. The present work employs sequential multiscale modeling by using different tools for different scales of time and space to model and predict the behavior of the PTC system. Although modules 2 and 3 remain largely the same as defined in Anantpinijwatna et al. (2016), the methods used in module 1 make the framework much more generic in terms of its application; the integration of quantum chemical calculations into a process modeling framework greatly expands the envelope of chemical species that can be modelled at a high level of accuracy. A more thorough description of the framework can be found in Pudi (2019).

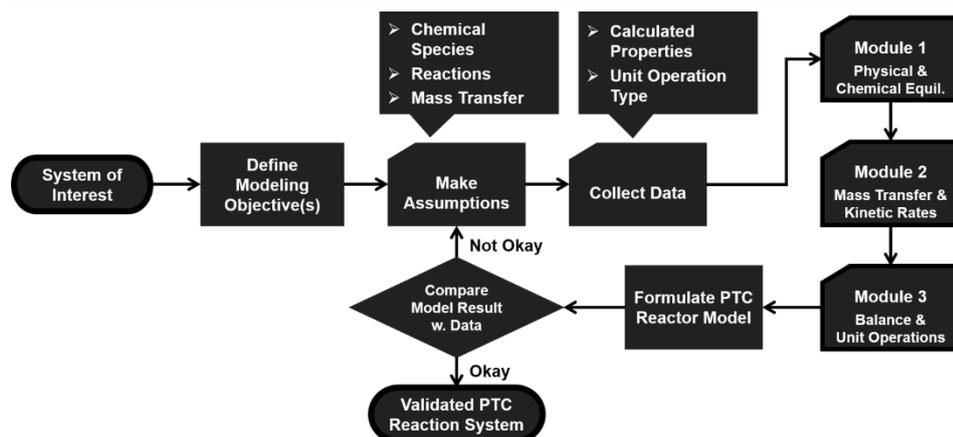
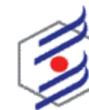


Figure 1 Generic Modeling Procedure for Biphasic Reaction Systems. Adapted from Anantpinijwatna et al. (2016)

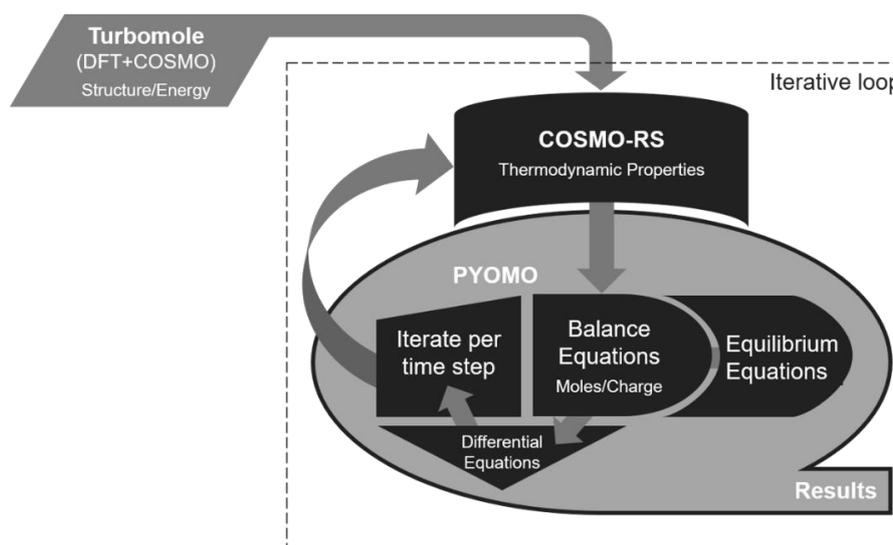


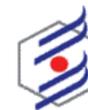
Figure 2 Solution Algorithm for the Proposed Framework

The algorithm is illustrated in

Figure 2. With Python as the high-level interface, three different tools are employed at three different levels of space and time as follows:

- Molecular/electronic level: Turbomole
- Transport and reaction thermodynamics level: COSMOtherm
- Reactor level: Pyomo

For each species in the system, geometric optimization calculations are performed in Turbomole to obtain their ground-state and gas-phase energies and screening charge density profiles. These are then transferred to COSMOtherm to obtain partition coefficients, activity coefficients, and chemical equilibrium constants, which are all parameters for the PTC model. These parameters are then input in Pyomo where the equations for equilibria, kinetics, and balances are solved to model the system behavior.

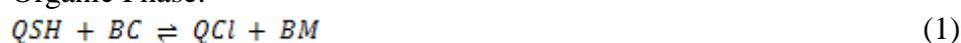


Application towards H₂S Valorization

Hydrogen sulfide is a highly toxic chemical that is found as an impurity or an inhibitor in many petrochemical, chemical and biochemical processes. In fact, it is classified as a hazardous industrial waste. Environmental and/or process constraints often require the removal of this compound to trace amounts. This is usually accomplished by capturing H₂S and later oxidizing it to elemental sulfur, a process generally referred to as sulfur recovery. Recovered elemental sulfur is produced primarily during the processing of natural gas and crude petroleum. Due to the depletion of sweet oil and gas reserves around the world, players in the O&G industry are increasingly looking toward sour fields to meet our energy needs. In the past 2-3 decades, sulfur production has consistently outpaced the demand leading to the large stockpiles of block sulfur *waste* in several countries around the world. At a time when the world is striving to achieve a zero-waste and circular economy, sulfur disposal poses a serious barrier to such a transition. Therefore, it is vital to develop a viable alternative to the practice of converting H₂S to elemental sulfur.

L-L PTC offers one such alternative by converting H₂S to value-added products. Since alkanolamine-based processes are widely used for the removal of acid gases from gaseous streams, it is assumed that the capture of H₂S from a gas phase to a liquid phase uses a 30 % solution of methyldiethanolamine (MDEA). Traditional approach for the next step is the use of a stripping column to separate H₂S and regenerate MDEA; MDEA is then sent back to the absorber while H₂S is directed towards further process steps to convert it to elemental sulfur. However, the regeneration step requires high operational costs. In order to overcome the drawbacks of this process, PTC is explored as the cornerstone for the capture and utilization of H₂S. One major advantage of this route is the ability to target a wide variety of products, instead of only elemental sulfur or inorganic sulfates. Using L-L PTC in a continuous stirred tank reactor, the H₂S-rich aqueous phase is put in contact with an organic phase (here toluene) containing benzyl chloride (BC) to produce benzylmercaptan (BM) in the presence of a PT catalyst such as tetrabutylammonium bromide (QBr). The objective is to model the complex interlinked phenomena—multiple reactions in each phase and partitioning of various species between the phases—occurring in such a system. The reactions presumed to occur in this biphasic system are given below.

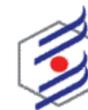
Organic Phase:



Aqueous Phase:



The PT catalysts, QBr & QCl, react with the inorganic sulfide anion in the aqueous phase to produce the active catalyst species, QSH. These active catalysts species partition into the organic phase transporting the hydrosulfide ion to participate in the nucleophilic substitution reactions with BC. A few of the reactor specifications are taken from the experimental data reported by Singh et al. (2016).



Results and Analysis

Phase Partitioning

From the phase equilibrium calculations in COSMOtherm, affinities of each species in the system to each of the two phases can be understood. To this end, the partition coefficient values of a few important components calculated in the first iteration of the implicit solution method are listed in Table 1.

Table 1 Partition Behavior Characteristics

Chemical Species	Partition Coefficient	Preferential Phase
H ₂ O	0.06	Aqueous
Toluene	1104.57	Organic
BM	1040.48	Organic
BC	912.15	Organic
QSH	100.86	Organic
QBr	26.82	Organic
QCl	24.31	Organic
MDEA	0.44	Aqueous
HS ⁻	0	Aqueous

A partition coefficient greater than 1 implies a relatively higher affinity towards the organic phase, while a value less than 1 implies a relatively higher affinity towards the aqueous phase. In this context, the reported values are consistent with and explain the experimental behavior observed by Singh et al. (2016). The main reactant and product in the organic phase reaction, benzyl chloride, and benzylmercaptan, are heavily partitioned into the organic phase. This provides for a cleaner product separation in the downstream purification processes. The three catalyst species (QSH, QBr, and QCl) mildly prefer the organic phase. Among the three, the active catalyst form of QSH exhibits about four times higher affinity to the organic phase than the two inactive catalyst species. This enables the preferential partition of the necessary active form into the organic phase to undergo the reaction to form the required product BM.

General Performance

The first iteration found a 23 % conversion of benzyl chloride to benzylmercaptan. Although the final rate of conversion is expected to be high, it is worth noting that the value from the first iteration matches the first data point obtained by Singh et al. (2016) in the first 5-10 minutes of the experiment. This shows that the current version of the modeling framework does indeed work and is headed in the right direction.

Conclusions

A rigorous multiscale-modeling framework to describe the behavior of a PTC system is presented. The framework incorporates a series of computational tools covering different scales of time and space in a sequential/dynamic modeling approach. The current implementation offers great advantages over the previously developed modeling framework reported in Anantpinijwatna et al. (2016). Due to the incorporation of quantum chemical and continuum solvation methods, the limitation due to the unavailability of accurate thermodynamic model parameters has been overcome in the present work. Further work is expected to fully develop the tool integration in the framework.



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