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FINAL PROJECT REPORT

Cost-Effective Carbon Capture Using Chemical Compounds

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PREFACE

The California Energy Commission's (CEC) Energy Research and Development Division supports energy research and development programs to spur innovation in energy efficiency, renewable energy and advanced clean generation, energy-related environmental protection, energy transmission and distribution and transportation.

In 2012, the Electric Program Investment Charge (EPIC) was established by the California Public Utilities Commission to fund public investments in research to create and advance new energy solutions, foster regional innovation and bring ideas from the lab to the marketplace. The CEC and the state's three largest investor-owned utilities—Pacific Gas and Electric Company, San Diego Gas & Electric Company and Southern California Edison Company—were selected to administer the EPIC funds and advance novel technologies, tools, and strategies that provide benefits to their electric ratepayers.

The CEC is committed to ensuring public participation in its research and development programs that promote greater reliability, lower costs, and increase safety for the California electric ratepayer and include:

- Providing societal benefits.
- Reducing greenhouse gas emission in the electricity sector at the lowest possible cost.
- Supporting California's loading order to meet energy needs first with energy efficiency and demand response, next with renewable energy (distributed generation and utility scale), and finally with clean, conventional electricity supply.
- Supporting low-emission vehicles and transportation.
- Providing economic development.
- Using ratepayer funds efficiently.

Cost-Effective Carbon Capture Using Chemical Compounds is the final report for the New Chemical Compounds for Cost-Effective Carbon Capture Project (Contract Number: EPC-15-072) conducted by the University of California, Davis. The information from this project contributes to the Energy Research and Development Division's EPIC Program.

For more information about the Energy Research and Development Division, please visit the <u>CEC's research website</u> (www.energy.ca.gov/research/) or contact the CEC at ERDD@energy.ca.gov.

ABSTRACT

California's current portfolio of energy sector decarbonization strategies is not enough to achieve economy-wide net-zero carbon emissions by 2045. Negative emission technologies that physically sequester carbon dioxide from the atmosphere or from sources such as power plants are essential to reaching carbon neutrality. A recent report by Lawrence Livermore National Laboratory suggests that to reach its goals, California must achieve approximately 125 megatons of carbon dioxide equivalents per year of negative emissions. Negative emission technologies include natural solutions such as ecological restoration, bioenergy with carbon capture and sequestration, and direct air capture. The research presented here lies at the nexus of carbon capture and sequestration for fossil fuel and bioenergy, as well as direct air capture, all of which can benefit from development of new and improved carbon dioxide capture compounds. Amine-based chemical absorption post-combustion capture is the most technologically mature approach. However, amines have large regeneration energy, high production cost, and toxic byproducts. Bioinspired phosphoenol compounds derived from Crassulacean acid metabolism show promise as amine alternatives by potentially alleviating these implementation barriers. A novel effort is made here to screen these compounds in terms of their relevant physicochemical properties using a suite of computational chemistry tools to assess their suitability as post-combustion capture solvents in existing process architectures. Group contribution methods show reaction enthalpies within the optimal range and identify core gateway structures while nonreactive molecular dynamics simulations indicate that aqueous solution properties like solubility are comparable to the monoethanolamine benchmark. This is important since the theoretical capture efficiency of phosphoenol compounds is twice that of monoethanolamine, meaning a potentially significant reduction in energy penalty and thus cost. Reactive molecular dynamics simulations accurately describe the reaction thermodynamics and kinetics, and process modeling demonstrates encouraging trends for using these compounds in commercial-scale carbon capture and sequestration.

Keywords: climate change, carbon capture and sequestration, negative emissions, carbon dioxide scrubbing, amines, biomimetic carbon capture solvents

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EXECUTIVE SUMMARY

Background

There is wide scientific consensus the world must adopt mitigation strategies that collectively limit mean global warming to less than 1.5 degrees Celsius (°C) (2.7 degrees Fahrenheit (°F)) above preindustrial levels to avoid the most catastrophic climate change predictions, as outlined in Intergovernmental Panel on Climate Change reports and agreed upon in the 2016 Paris Agreement. The panel further predicted the planet is on track to reach 3.2°C warming by the end of the century due to widespread governmental inaction. Reducing global greenhouse gas (GHG) emissions to net zero within the next 30 years and radical actions to achieve this goal must begin in the next decade. These actions must include directly sequestering (removing and storing) carbon from industrial emissions and the atmosphere.

California's GHG emission reduction targets were established in the Global Warming Solutions Act of 2006 (Assembly Bill 32, Nuñez, Chapter 488, Statutes of 2006), expanded upon in then-Governor Edmund G. Brown, Jr.'s 2015 Executive Order B-30-15, and culminating in the most ambitious goal to date of statewide carbon neutrality — which requires sequestering as much carbon as is emitted by 2045 (Governor Brown's Executive Order B-55-18 signed in 2018). Despite impressive progress on these goals through a combination of renewable energy, increased energy efficiency, electric vehicles, zero-emission transit, land restoration, cleaner fuels, and a carbon cap-and-trade program, a recent report by Lawrence Livermore National Laboratory concluded that even if California's ambitious emissions reductions strategies are successful, the state is on track to significantly surpass the 2045 emissions reduction target for carbon dioxide (CO_2). Accordingly, a portfolio of negative emissions strategies must be implemented to compensate.

International agreement is quickly emerging that the most viable, technologically ready, and widely applicable collection of negative emissions technologies include (1) natural solutions like tree-planting, ecological restoration, forest management, and soil carbon sequestration; (2) bioenergy with carbon capture and sequestration focused on biomass waste streams like agricultural residue, municipal solid waste, and forest debris that would otherwise release GHGs to the atmosphere from fugitive emissions, decay, or combustion; and (3) physically removing CO_2 directly from the atmosphere, referred to as direct air capture.

The Lawrence Livermore National Laboratory report provides a comprehensive and feasible roadmap that considers the potential roles of these negative emissions technologies in achieving carbon neutrality by 2045. The report estimates that of the roughly 125 megatons of CO_2 equivalents per year that would be emitted in 2045 if California's current suite of emissions reduction strategies is successful, 20 percent could be removed through natural solutions and 67 percent by bioenergy with carbon capture and sequestration, with the remaining 13 percent relegated to direct air capture. The research reported here lies at the intersection of bioenergy with carbon capture and sequestration and direct air capture, which both require innovative approaches in CO_2 capture and separation technologies and chemistries.

Amine-based carbon capture, which has been widely used in industry for decades, is by far the most heavily studied, technologically mature, and economically viable approach. As such, this type of capture currently sets the benchmark for new and emerging technologies in terms of

cost, energy penalty, CO₂ capture efficiency, and physicochemical properties (for example, stability, corrosivity, absorption capacity, and toxicity). It is a retrofit technology that can be implemented at existing facilities like power plants; however, a major drawback of this technology is that it is energy intensive and thus significantly increases operational costs. For example, sequestering 90 percent of CO₂ emissions from pulverized coal and combined cycle natural gas power plants increases the levelized cost of electricity (\$US 2016) by 30 percent. Process modeling of modern absorber-stripper architectures reveals capture chemistry as the variable with the largest potential to further reduce costs. This is the rationale for further research on cost-effective amine alternatives.

Research on direct air capture is still in its infancy. With only a few companies demonstrating products at scale, there is a general lack of data. However, although the mechanical and chemical processing systems will be vastly different given orders of magnitude smaller CO₂ concentrations in the atmosphere (approximately 400 parts per million) relative to power plant emissions (approximately 4–15 percent), the fundamental CO₂ separation mechanisms will be the same. Therefore, the research presented in this report on new carbon capture compounds is potentially applicable to post-combustion fossil-fuel and bioenergy carbon capture and sequestration and direct air capture.

Project Purpose

Biomimetic carbon capture is the effort to mimic chemical mechanisms used by living organisms to capture CO_2 to improve upon current post-combustion capture technologies. This work used sophisticated chemistry techniques as exploratory tools to investigate the suitability of bio-inspired carbon capture compounds as substitutes for amines. The origin of this research was a unique group of plants that have adapted to arid climates using a process called Crassulacean acid metabolism. In this process, to conserve water, the plants accept CO_2 by opening their stoma at night, rather than during the day, and then immediately activate it with another compound to store it overnight. The reaction is reversed in the morning when the sun rises, releasing the CO_2 to participate in photosynthesis. In essence, the plant is performing regenerative chemical absorption carbon capture.

This project demonstrated the proof of concept for three hypotheses:

- 1) That the underlying CO₂ capture chemistry of the Crassulacean acid metabolism photosynthetic pathway is suitable for negative emissions technologies like post-combustion carbon capture and direct air capture.
- 2) That current state-of-the-art chemical modeling platforms could accurately predict relevant thermodynamic and molecular properties of phosphoenolpyruvate and its variants.
- 3) That phosphoenolpyruvate variants could be custom tailored to optimize molecular and thermochemical properties for improved performance in existing system architectures.

Project Approach

The CO₂ capture compound in Crassulacean acid metabolism is used here as a template for designing similar molecules that are investigated against the amine benchmark for performance in current carbon capture systems using process models. A suite of state-of-the-art chemical modeling platforms is employed to simulate and predict the properties of the new carbon capture compounds. The objective is to identify those compounds with the largest

confluence of optimal properties and feed them back through the process model to evaluate the net reduction in energy penalty.

Project Results

Results of multiple modeling efforts demonstrate proof of concept for biomimetic carbon capture chemistry and identify encouraging trends in terms of usability, cost, and flexibility of using Crassulacean acid metabolism-inspired CO₂ sequestration in post-combustion and direct air capture systems. However, more research is required to validate estimates from these modeling efforts.

Although the effort to demonstrate proof of concept for the three stated hypotheses has been successful, it is still in its infancy. Given the scarcity of literature, experimental data, and modeling studies on the compounds being explored, the bulk of this effort has been spent in developing and validating the models, including building the force fields, optimizing the parameterization space, and minimizing uncertainties in the predicted data.

With the concept and computational machinery firmly in place, additional research is needed to expand the pool of candidate compounds, refine the molecular modeling, further investigate the reaction kinetics, increase accuracy of the thermochemical data, and optimize molecular design. The latter can be accomplished via iterative analyses using process models and technoeconomic analytics to identify the most viable amine substitutes. Biomimetic carbon capture is a novel and promising approach to helping propel and accelerate California into its carbon neutral future.

Knowledge and Technology Transfer

The long-term goal of this research is commercializing phosphoenolpyruvate variants that can be used in existing carbon capture technologies to improve process efficiency and reduce costs. The intended market audience is the electric utilities sector, high CO₂ emitting industries like cement production, and direct air capture research and development companies. However, the maturity of this research is still insufficient to initiate these conversations, and the target remains additional funding opportunities to continue validation and quantification of benefits. As such, knowledge transfer thus far has been limited to funding agencies via reports, presentations, and proposals until intellectual property rights are established. Three manuscripts have been written and will be submitted for publication in scientific journals pending filing of a patent application.

Although the research presented here is at a low technology readiness level, the process technologies into which it would be embedded are mature. The underlying architecture of current absorber-stripper and direct air capture systems is not being altered. Rather, new carbon capture compounds are being proposed that can substitute existing compounds to optimize efficiency and thus reduce resistance to implementation. The natural trajectory of this work is further refinement of the modeling methods, laboratory synthesis of select variants, benchtop validation of thermodynamic and kinetic properties, pilot scale demonstrations, and commercial scale up. Given existing infrastructure, an accelerated research to market pathway is projected.

Benefits to California

Regardless of successful execution of California's current portfolio of decarbonization strategies, negative emission technologies must be implemented at a scale of approximately 125 megatons of CO₂ equivalents per year to achieve carbon neutrality by 2045. This can be accomplished by adopting the priority recommendations of the recent Lawrence Livermore National Laboratory report and would benefit Californians by creating jobs, redistributing burden and opportunity, stabilizing infrastructure, invigorating ingenuity, retaining talent, reducing risks, restoring ecosystems, and building resiliency into all vital societal and life support systems. Negative emissions are paramount to the path of carbon neutrality, and a majority fraction will have to be through a flexible blend of post-combustion fossil fuel and bioenergy carbon capture and sequestration and direct air capture. CO₂ separation systems are a cornerstone to these technologies, and biomimetic computational chemistry represents uniquely uncharted territory with a promising trajectory to significantly reduce projected costs.

A combination of results reinforces this narrative. First, the theoretical CO₂ capture efficiency of phosphoenolpyruvate variants is already twice that of the amine benchmark. Second, the capture capacity of phosphoenolpyruvate variants is only limited by solubility while that of amines is capped by corrosivity considerations. Third, fugitive amine emissions are potentially toxic while phosphoenolpyruvate variants are benign. Finally, phosphoenolpyruvate variants have the potential to increase process efficiency. Ultimately, if these model predictions come to fruition and the compounds are brought to market, it would result in significant cost savings to ratepayers and industry by reducing the energy penalty of carbon capture while also achieving carbon neutrality and averting the worst impacts of climate change. The scale, complexity, and urgency of the issues and efforts compel and justify this research.

CHAPTER 1: Introduction: Framing the Issue

Significance

There is wide scientific consensus the world must adopt mitigation strategies that collectively limit mean global warming to less than $34.7^{\circ}F(1.5^{\circ}C) - 35.6^{\circ}F(2^{\circ}C)$ above preindustrial levels to avoid the most catastrophic climate change projections, as outlined in the Intergovernmental Panel on Climate Change (IPCC) report (2018) and agreed upon in the 2016 Paris Agreement. According to a recent National Oceanic and Atmospheric Administration (NOAA) report (NOAA 2021), however, the average global surface temperature is already 1.25°C warmer than in the preindustrial period 1850–1900, and the IPCC predicts the planet is on track to reach $3.2^{\circ}C$ warming by the end of the century due to widespread governmental inaction.³ The United Kingdom Meteorological Office (UK Met Office) recently forecasted that atmospheric carbon dioxide (CO₂) concentrations will cross the threshold of being 50 percent higher than before the Industrial Revolution in 2021, exceeding 417 parts per million (ppm) compared to 278 ppm in the late 18^{th} century. To attain greenhouse gas (GHG) emissions reduction targets, we must take actions that include directly sequestering carbon from industrial emissions and the atmosphere.

The reason is threefold: (1) the world has been slow to reduce GHG emissions; (2) many GHG sources are difficult to control, including natural (for example, wildfire, biogenic), agricultural (methane and nitrous oxide), and land-use change emissions; and (3) it is likely not possible to completely decarbonize the economy given the projected persistence of legacy sources like aviation and industry. These latter two are collectively referred to as residual emissions, that is, emissions remaining after full implementation of the current portfolio of mitigation strategies that will continue to raise atmospheric GHG concentrations and thus warm the planet. This is depicted graphically in Figure 1 adopted from the United Nations Environment Program's 2017 Emissions Gap Report (UNEP 2017). The solid yellow line is the business-asusual GHG emissions profile, while the solid red line is the projected emissions trajectory required to meet the 2°C warming target. The green shaded area represents avoided emissions from implementation of currently planned mitigation technologies, the brown shaded area is the residual emissions — divided between CO₂ and other GHGs by the dotted line — and the blue area is the negative emissions required to offset the residual emissions to maintain the 2°C target. A critical distinction is made between avoided and negative emissions, where the former refers to removal of CO₂ that would have otherwise been emitted via implementation of negative emissions technologies (NETs) like retrofitting existing power plants with carbon capture and sequestration (CCS) technology. Negative emissions are strictly defined as physically sequestering carbon from the atmosphere for long-term, near-permanent storage like increasing terrestrial carbon uptake (biomass and soils), bioenergy with carbon capture and sequestration, and direct air capture.

California is particularly vulnerable to the impacts of climate change owing to a confluence of factors, including a vast latitudinal and coastal expanse (1,100 miles), semi-arid climate, rich and diverse ecosystems, intensive agricultural and tourism industries, iconic landscapes, densely populated urban centers, and high energy and water demands. Effects of climate

change include wildfires; drought; flooding; heat waves; invasive species; infectious diseases; desertification; loss of habitat, biodiversity and arable land; sea level rise; and declining air and water quality, as well as the economic, social, infrastructure, food security, and public health volatilities accompanying these extreme events and shifting trends. Concomitantly, as the fifth largest economy in the world with an internationally recognized portfolio of progressive climate policies and targets, abundant natural resources, massive ingenuity pool, academic prowess, and immense clean energy potential including wind, solar, geothermal, waves, and biomass, California has the opportunity and is also uniquely positioned to lead the world in ameliorating climate change.



Figure 1: Greenhouse Gas Trajectories: Avoided, Residual, and Negative Emissions

Source: UNEP. 2017. The Emissions Gap Report. United Nations Environment Program, Nairobi.

California's greenhouse gas emission reduction targets were initiated in the Global Warming Solutions Act of 2006 (Assembly Bill 32), expanded upon in 2015 via Executive Order B-30-15, and culminated in the most ambitious goal to date of statewide carbon neutrality — which requires sequestering (removing and storing) as much carbon as is emitted — by 2045 via Executive Order B-55-18 signed in 2018. Despite impressive progress on these goals through a combination of renewable energy, increased energy efficiency, electric vehicles, zero-emission transit, land restoration, cleaner fuels, and a carbon cap-and-trade program, a recent report by Lawrence Livermore National Laboratory (LLNL) concluded that extrapolation of current emission plans significantly overshoot the 2045 target by 125–150 megatons of CO₂ equivalents (Mt CO₂e) per year and that a portfolio of negative emissions strategies must be implemented to compensate (Baker et al. 2020). This is shown graphically in Figure 2 adapted from that report. The brown line is the extrapolated emission trend according to current reduction targets, the red line depicts the carbon neutrality goal, and the green line shows the gradual transition to NETs necessary to offset the residual emissions. This is comparable to national and global assessments of carbon neutrality recently reported by the National Academies of Sciences, Engineering, and Medicine (NASEM) that contend NETs must constitute a major fraction of our global climate mitigation portfolio — removing roughly 20

percent of current emissions by midcentury and 40 percent by century's end — if the world is to realize the goals of the 2016 Paris Agreement (NASEM 2019).



Figure 2: Extrapolation of California Emission Reduction Targets

International agreement is guickly emerging that the most viable, technologically ready, and widely applicable collection of NETs include (1) natural solutions like afforestation, ecological restoration, forest management, soil carbon seguestration, and climate-smart agriculture; (2) bioenergy with carbon capture and sequestration (BECCS) focused on biomass waste streams like agricultural residue, municipal solid waste, biogases from manure lagoons and landfills, and forest debris that would otherwise release GHGs to the atmosphere via fugitive emissions, decay, or combustion; and (3) physically removing CO_2 directly from the atmosphere, referred to as direct air capture (DAC). The LLNL report provides a comprehensive and feasible roadmap to applying these NETs to offset California's residual emissions and achieve carbon neutrality by 2045. It estimates that of the roughly 125 Mt CO₂/year emission gap, 20 percent could be removed through natural solutions and 67 percent via BECCS with the remaining 13 percent relegated to DAC, by far the most expensive technology on a normalized cost basis by a factor of 2:10. The report also provides a priority scenario that could achieve this target at a modest cost of \$65 per ton of CO₂ captured, or roughly \$8 billion per year, which is only 0.34 percent of California's current gross domestic product. The research reported here lies at the intersection of BECCS and DAC, which both require refinement and development of existing and new CO₂ capture and separation technologies and chemistries.

A schematic of current combustion-capture technologies is provided in Figure 3, including post-combustion capture (PCC), pre-combustion capture (gasification), oxyfuel combustion, and chemical looping combustion (Leung, DYC, et al 2014). The relevant physicochemical CO₂ separation processes are (Angelidaki, I, et al. 2019): (1) physical absorption like organic solvent scrubbing (for example, Selexol), (2) chemical absorption where CO₂ reacts with other compounds like amines, (3) adsorption on solid surfaces like zeolites, (4) cryogenic distillation, (5) membrane separation, and (6) chemical hydrogenation.

Source: Baker et al. 2020. Getting to Neutral: Options for Negative Carbon Emissions in California, LLNL.



Figure 3: Schematic of Current Combustion-Capture Technologies

Amine-based chemical absorption PCC, which has been widely used in industry for decades and relies on well-established aqueous phase chemistry between an organic base (amines) and acid gas (CO₂), is by far the most heavily studied, technologically mature, and economically viable approach. As such, it currently sets the benchmark for new and emerging technologies in terms of cost, energy penalty, CO₂ capture efficiency, and physicochemical properties (for example, stability, corrosivity, absorption capacity, and toxicity). It is a retrofit technology that can be implemented at existing facilities like power plants and employs a regenerative process wherein gaseous CO₂ from industrial emissions dissolves into aqueous amine solutions in an absorber and reacts at low temperature to form carbamates. The solution is then transferred to a stripper and heated by steam to high temperature to reverse the reaction, regenerating the amines and releasing gaseous CO₂. The regenerated amines are recirculated to the absorber, and the CO₂ is dried, compressed, and transported for storage in geological formations. A major drawback of these systems is that they are energy intensive and thus significantly increase operational costs. For example, sequestering 90 percent of CO₂ emissions from supercritical pulverized coal (SCPC) and combined cycle natural gas (CCNG) power plants increases the levelized cost of electricity (\$US 2016) by 30 percent (Adams et al. 2017) Process modeling of modern absorber-stripper architectures reveals capture chemistry as the variable with the largest potential to further reduce costs.

Research on DAC is still in its infancy with only a few companies demonstrating products at scale (Keith et al. 2018) so there is a general paucity of data. However, although the mechanical and chemical processing systems will be vastly different given orders of magnitude smaller CO_2 concentrations in the atmosphere (approximately 400 ppm) relative to power

Source: Leung et al. 2014. Renewable and Sustainable Energy Reviews, 39: 426-443.

plant emissions (approximately 4–15 percent), the fundamental CO₂ separation mechanisms will be the same. Thus, the research presented here on carbon capture compounds will be mutually beneficial to fossil-fuel CCS, BECCS, and DAC.

As shown later in Chapter 5, thermal energy required to regenerate the solution during carbon capture is the sum of sensible heat for heating the solution, latent heat for generating steam, and enthalpy of reaction (ΔH_{rxn}) for CO₂ desorption. Despite complex interdependencies between these energy terms, effort has been made to minimize regeneration energy by optimizing process parameters and/or solution properties. Either specific compounds are chosen, and the process parameters varied to find energy minima, or the process is held constant — typically a standard absorber/stripper configuration — and the optimal solution properties are determined.

In total, solution optimization aims to maximize absorption capacity, mass transfer kinetics, and reaction kinetics while minimizing enthalpy of desorption, specific heat capacity, viscosity, degradation tendency, volatility, toxicity, production costs, and fouling tendency (Mathias et al., 2013). The most critical variables, however, are (1) absorption kinetics, (2) cyclic capacity of the solution — that is, the difference in absorption capacity (moles CO_2 /volume solution) between the absorption and desorption temperatures, which is determined from vapor-liquid equilibria (VLE) – and (3) the enthalpy of desorption. The aim is VLE that changes substantially with temperature to maximize CO_2 capture in combination with low desorption enthalpy to minimize sensible and latent heat requirements in the stripper. Modeling efforts thus search for the optimal desorption enthalpy that minimizes total energy costs. Although results vary and are system dependent (that is, SCPC versus CCNG), there is general agreement that the value falls in the range of -80 ± 20 kilojoules per mole (kJ/mol) (Lin and Rochelle 2016; Herberle and Bhown 2014; Van Nierop et al. 2011).

Studies to date have focused on different amines or amine mixtures to explore the interplay between solvent properties and process parameters on the energy penalty of absorption-based PCC. Results from these efforts have quantified the challenges of current technology while describing the desired properties for new solution systems and capture chemistry.

Purpose of This Work: Innovation

Biomimetic carbon capture describes the effort to mimic the CO₂ capture prowess of the biosphere to improve upon current chemical absorption PCC technologies. The purpose of this work is to use sophisticated computational chemistry techniques as exploratory tools in a nascent attempt to investigate the suitability of bioinspired carbon capture compounds as substitutes for amines. The genesis of this effort was a unique group of plants that have adapted to arid climates using a process called Crassulacean acid metabolism (CAM), as shown in Figure 4, where, to conserve water, plants uptake CO₂ by opening their stoma at night, rather than during the day, and then immediately activate it with another compound to store it overnight. The reaction is reversed in the morning when the sun rises, releasing the CO₂ to participate in photosynthesis. In essence, plants are performing chemical absorption carbon capture. The compound, called phosphoenolpyruvate (PEP), is used here as a template for designing similar molecules that are investigated against the amine standard, monoethanolamine (MEA), for performance in current absorber-stripper systems using industry process models. A suite of state-of-the-art molecular modeling platforms is employed to simulate the thermochemical properties of the PEP derivatives.

A schematic of the reaction mechanism for CAM carbon capture using a generalized phosphoenol compound is shown in Figure 5. There are two major steps: (1) nucleophilic attack on the phosphate group by a bicarbonate ion forming carboxy phosphate and a highly reactive enolate ion, where the charge is delocalized over the oxyanion and carbanion forms and (2) exothermic decomposition of carboxyphosphate into CO₂ and hydrogen phosphate followed by nucleophilic attack on CO₂ by the enolate ion to form the corresponding keto-carboxylate anion. This work aims to use a combination of computational chemistry tools to explore the physicochemical properties of PEP and other phosphoenol compounds and model their subsequent reaction with CO₂ to evaluate their suitability as PCC compounds relative to amine-based benchmarks.

Approach

An initial assessment of the suitability of PEP and similar compounds as PCC solvents was performed using group contribution methods to estimate the reaction enthalpies to determine if they fall within the optimal range derived from process modeling of standard absorber/stripper architectures previously discussed. For compounds found to be in the optimal enthalpy range, nonreactive molecular dynamics simulations were performed to quantify their aqueous solution properties, like solubility, viscosity, and diffusivity. Furthermore, reactive molecular dynamics was used in conjunction with quantum mechanical calculations to simulate the energetics and kinetics of reaction with the bicarbonate ion. The objective is to identify those compounds with the largest confluence of optimal properties and feed them back through the process model to evaluate the net reduction in energy penalty relative to the amine benchmark.





Figure 4: Schematic of Crassulacean Acid Metabolism C4 Carbon Fixation Pathway

Source: Wikimedia Commons. Retrieved May 7, 2020. https://commons.wikimedia.org/w/index.php?curid=48991839

Figure 5: Reaction Mechanism for Carbon Capture by Phosphoenol Compounds



Source: Keith Bein, University of California, Davis

To the authors' knowledge, this is the first time that a combination of biomimetics and computational chemistry has been used to design and characterize carbon capture compounds suitable as amine substitutes. These computational techniques are routinely used in other research areas, like lithium-ion battery technology, but have not been applied to the search for alternative PCC technologies. The phosphoenol compound family is an entirely new exploratory route with novel CO₂ capture chemistry that may better optimize process inefficiencies.

The report proceeds as follows: Chapter 2 presents the first modeling approach on Phosphoenol Compound Discovery. Chapter 3 presents the second modeling approach on Atomistic Molecular Dynamics Simulations. Chapter 4 presents the third modeling approach on Reactive Molecular Dynamics Simulations. Chapter 6 presents the knowledge transfer. Chapter 7 describes the conclusions and recommendations. Chapter 8 defines the Benefits to California."

CHAPTER 2: Project Approach – Phosphoenol Compound Discovery

Objective

As discussed in Chapter 1, process modeling of conventional absorber/stripper architectures in PCC systems reveal ideal solvent properties for minimizing the energy penalty of carbon capture. A critical solvent parameter is the absorption enthalpy of the capture chemistry and studies have shown the optimal value to be in the range of -80 ± 20 kJ/mol. As a first approach to accessing the aptness of CAM-inspired phosphoenol compounds for chemical absorption-based PCC, group contribution methods were used to estimate reaction enthalpies of these PEP variants according to the reaction mechanism shown in Figure 5 to determine whether they fall in this range.

Methods

It is well understood that intermolecular forces are determined by the properties of the atoms and bonds making up the molecules and that these, in turn, determine macroscopic properties. This is the basis of group contribution methods wherein weighting factors are assigned to the atoms, atomic groups, and bonds constituting a given molecule and these values are algebraically summed to estimate certain properties of the molecule. The most accurate methods at the limit of estimation also allow for nearest neighbor and next nearest neighbor interactions of the atoms and functional groups comprising the molecule of interest to factor into the overall sum. The method of Benson (1978) is an example and is the basis of the American Society for Testing and Materials Chemical Thermodynamic and Energy Release Evaluation (CHEETAH) program distributed by the National Institute of Standards and Technology and widely used in industry. In the current work, CHEETAH (Harrison 2009) is used to estimate the enthalpies of formation ΔH_f for the various reactants and products in the reaction of phosphoenol compounds with bicarbonate according to the generalized and balanced reaction equation given below:

$$RCR'PO_4^{2-}(aq) + HCO_3^{-}(aq) \leftrightarrow RC_2HR'O_3^{-}(aq) + HPO_4^{2-}(aq)$$

The reaction enthalpy ΔH_{rxn} can then be calculated as the difference in the stoichiometric sum of formation energies between the products and reactants according to

$$\Delta H_{rxn}^{o} = \sum \Delta H_{f}^{o}(products) - \sum \Delta H_{f}^{o}(reactants).$$

These calculations are repeated as the molecular structure of PEP is varied to determine the sign, magnitude, and trends in the reaction enthalpy of CO₂ capture. The phosphoenol backbone is held constant while the variables *R* and *R'* are changed by adding functional groups ranging from a simple hydrogen atom to increasingly more complex chemical structures like alkenes, alkynes, aryls, and ketoacids. The nomenclature in what follows simply hyphenates the phosphoenol backbone with the added functional group, for example, phosphoenol-alkenes, where *R* and *R'* could be any number of different alkenes and alkene derivatives. For PEP, *R* is a carboxylate anion CHO_2^- while *R'* is a methyl group CH_2 .

Results

Starting with PEP, which belongs to the phosphoenol-ketoacid group where ketoacids consist of both a carboxylic acid ($O = R - O^-$) and ketone (R - C = O) group, Figure 6 shows the enthalpy of formation for the reactants and products and the overall enthalpy of reaction ΔH_{rxn}^o . It is promising that the PEP-HCO₃⁻ reaction already has enthalpy within the optimal range of -80 ± 20 kJ/mol even before modifying its chemical structure.



Source: Keith Bein, University of California, Davis

Similar data are plotted in Figure 7 and Figure 8 for simple alkene, alkyne, aryl, and ketoacid additions to the core phosphoenol structure. Again, reaction enthalpies fall within the target range. More interesting, however, is that these compounds represent core gateway structures where any number of additional atoms and/or functional groups can be added to the terminal carbons of these structures without changing the reaction enthalpies — the reason being that the functional groups are added far from the reactive sites and thus do not contribute to the nearest and next-nearest neighbor weighting factors applied to the reactive atoms. Therefore, contributions from the additional functional groups simply cancel out when calculating ΔH_{rxn}^o . This opens the gateway to countless possible phosphoenol compounds with optimal reaction enthalpies.

Figure 7: Phosphoenol Reaction Enthalpies: Ketoalkenes and Ketoalkynes



Source: Keith Bein, University of California, Davis



Source: Keith Bein, University of California, Davis

Conclusions

First approach estimates of reaction enthalpies via group contribution for reaction of phosphoenol compounds with bicarbonate revealed (1) core gateway structures that can be built upon with any number of different atoms and/or functional groups to customize molecular properties without changing reaction enthalpy and (2) that these reaction enthalpies are within the optimal range for use as solvents in absorption-based PCC.

CHAPTER 3: Project Approach – Atomistic Molecular Dynamics Simulations

Methods

These investigations were carried out using non-reactive molecular dynamic (MD) simulations. The General Assisted Model Building with Energy Refinement Force Field was used to parameterize molecules for the simulation because it is applicable to modeling interactions of small organic compounds, including PEP (Wang et al. 2004; Duffy and Jorgenson 2000). The simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), which is a molecular dynamics program from Sandia National Laboratories (Plimpton 1995).

All simulations were established by organizing the necessary molecules periodically in a specified simulation box. Each system was run a total of six times with the orientations of the molecules randomized in each version. The molecules were situated approximately 6 angstroms away from each other to avoid collisions during set up. At the onset of each simulation, the energy of the system was minimized, thus reducing the size of the system. After this minimization, a Gaussian distribution was used to randomly assign kinetic energies to the molecules based on temperature. The system was then allowed to equilibrate for one nanosecond. Measurements were taken over a 10-nanosecond period following equilibration.

All simulations were run at typical absorber conditions of 40°C and 1 atmosphere. All bonds and angles were treated as harmonic, and water molecules were treated as rigid bodies to prevent angular vibrations. These simplifications were included because this investigation was focused on solution properties as a whole and not the individual interactions between molecules. Table 1 describes the concentration of PEP/water mixtures studied by MD.

Dissociation of Acids

Non-reactive MD is unable to simulate the dissociation of an acid; therefore, it is necessary to place the appropriate number of "predissociated" ions in the simulation during setup. The runtime of a few nanoseconds is often insufficient for free protons to move away from their conjugate bases, as this process requires water molecules to interpose themselves between the charges. Therefore, hydronium ions (H_3O^+) were randomly distributed across the system during setup and a set of independent simulations were performed with different proton distributions. Since only the first dissociation constant (K_a) for PEP is available in the literature, only singly charged PEP molecules were considered (Wishart et al. 2017).

$$C_3H_5O_6P + H_2O \to C_3H_4O_6P^- + H_3O^+$$

It was assumed that it was significantly more difficult for a PEP ion to lose its second or third hydrogen, as that would result in multiple like charges on the same molecule. Even if triply charged PEP would more accurately represent the state in solution than the singly charged state, results are conservative since the triply charged state is likely to be more soluble. Less than half of the PEP molecules in the solution were dissociated at modeled conditions. However, for the simulations including bicarbonate, a much higher pH was assumed, and

essentially all PEP molecules were dissociated. It seems likely that under these conditions, doubly and possibly triply dissociated PEP ions would have been present, which decreases bond dissociation energies and decomposition barriers as shown later via reactive MD simulations.

Weight% PEP	# PEP molecules	# PEP+ ions	# Water molecules	# Water molecules difference to baseline	Initial Box Size (Å)
31.93	92	408	9940	+2795	136.4
39.49 (Baseline)	113	387	7145	NA	124.0
45.38	129	371	5612	-1533	117.8
48.23	137	363	5005	-2140	111.6
49.49	141	359	4759	-2386	111.6
50.41	144	356	4587	-2558	111.6
51.76	148	352	4346	-2799	105.4
52.77	150	350	4173	-2972	105.4
54.62	156	344	3874	-3271	105.4
56.64	162	338	3569	-3576	99.2
58.81	168	332	3266	-3879	99.2
59.99	172	328	3110	-4035	99.2

Table 1: Simulation Parameters for Phosphoenolpyruvate Modeling

Source: Keith Bein, University of California, Davis

Estimation of Solubility via Energy of Mixing

The solubility of PEP is key to its energy-efficient use for PCC. The solubility was estimated by constructing a potential energy versus concentration curve in addition to the entropy of solution effects, which were approximated as an ideal solution by $S = -R\chi \ln \chi$ where χ is the mole fraction of PEP in solution. The energy of mixing is

U = Thermal Energy + Interaction Energy

Energy change by mixing = $U_{3,solute \& N+M water} - (U_{1,solute \& N water} + U_{2,M water})$

Additionally, pure water simulations were performed to calculate the difference in energy caused by simply changing the number of water molecules. This allows for the direct comparison of energy between various simulations.

 $U_3 - U_1 - U_2 = \Delta Interaction Energy$

Benchmarks and Validation

Benchmark materials were used to check the accuracy of the simulation method. Acetic and formic acids were chosen as the initial benchmarks due to readily available literature values on their solution enthalpy (Rumble, Bruno, and Doa 2018). The enthalpy of mixing was calculated in a similar manner to the free energy of mixing, using the default LAMMPS enthalpy

calculation. Simulations were run for 3, 4, and 5 mol/L of both materials. Comparative results between literature and calculated values are shown in Table 2; all values are reported at kJ/mol. Although the solubility trends are well reproduced, the values are not quantitative. This was expected for the simple approach taken here, which nonetheless proved sufficient.

Acetic Acid mol/L	Acetic Acid Literature value	Acetic Acid Calculated Value	Formic Acid mol/L	Formic Acid Literature	Formic Acid Calculated Value
3m to 4m	-0.193	-0.283	3m to 4m	0.000	-0.093
4m to 5m	-0.368	-0.543	4m to 5m	0.000	-0.127
3m to 5m	-0.175	-0.061	3m to 5m	0.000	-0.104

 Table 2: Enthalpy of Solution for Acetic and Formic Acid (kJ/mol)

Source: Keith Bein, University of California, Davis

Simulation for 30 percent by Weight Aqueous Monoethanolamine Solution

MD simulations with 30 percent (by weight) aqueous MEA solution (500 MEA molecules, 3955 water) were also performed to directly compare predicted performance measures of PEP against the current industry standard. These simulations were performed under the same conditions and with the same force field as the PEP simulations.

Radial Distribution Functions

The system's radial distribution functions (RDFs), which are statistical mechanics descriptions of how density varies as a function of distance from a reference point, determine solution structure. The water position was defined by the oxygen atom; the inset of Figure 8a shows the PEP centers. RDFs were normalized by density so that they converged to one at large distance.

Diffusion

The diffusivity of PEP in solution *D* was found via the Stokes-Einstein equation.

$$D = \lim_{\Delta t \to 0} \frac{1}{6\Delta t} \langle [x(t + \Delta t) - x(t)]^2 \rangle$$

Mean squared displacement data were obtained every 5 picoseconds from trajectories. Diffusivity is important in the PCC process because it influences the kinetics of the PEPbicarbonate reaction, which essentially determines the speed of CO_2 absorption. An additional simulation was performed to find the diffusivity of bicarbonate in an equilibrium PEP-water solution. For this simulation, the optimum PEP concentration was used (48.23 weight percent), and the pH was set to 1.5 to allow PEP to fully dissociate and enough bicarbonate to form in solution to obtain meaningful statistics. In a realistic system, the number of PEP ions would be the same but most counter ions would be sodium (Na⁺) instead of H₃O⁺. However, the simulation is nonreactive, meaning molecules cannot react, so there is no significant difference since PEP concentration governs the results.

Viscosity

The shear viscosity of a liquid can be computed through several different atomistic simulation methods. The Green-Kubo relation was used to calculate the viscosity of the specified systems because it can be used on any equilibrated liquid and is easily implemented in LAMMPS (Kirova and Norman 2015; Zang, Otani, and Maginn 2015). A running average of the viscosity was

periodically revised every 3 picoseconds using this technique. In this method, the shear viscosity is obtained from the integral over time of the pressure tensor autocorrelation function:

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{xy}(0) P_{xy}(t) \rangle dt$$

where *V* is the volume of the system, k_B is the Boltzmann constant, *T* is temperature, P_{xy} denotes the element xy of the pressure tensor, and the angle bracket refers to the ensemble average. Viscosity plays an important role in pumping costs for moving aqueous PEP solutions between the absorber and stripper. To contrast aqueous PEP solutions with the current amine-based benchmark, a simulation of 30 weight percent (wt%) MEA was run to find its viscosity.

Results

Energy of Mixing

A solubility curve for aqueous PEP solutions is shown in Figure 9 and demonstrates the expected features. As PEP is charged and polar, it has an energy minimum at a concentration of about 50 wt% in water, which corresponds to a mole fraction of about 10 percent. This puts it slightly below the benchmark MEA concentration of 11 percent (OGUK 2019). Mixing energy plateaus between 45 percent and 55 percent, which may indicate that this mole fraction could be somewhat higher at small energy penalty. The wide energy minimum is indicative of good solubility over a range of conditions.



Figure 9: Potential Energy Difference Between Mixed and Unmixed Solution

Source: Keith Bein, University of California, Davis

Solution Structure and Radial Distribution Functions

As PEP solution concentration increases, no significant structural changes are observed in the radial distribution functions of water around PEP, as shown in Figure 10. There is a trend of increasing magnitude of the first peak in the RDF as concentration is increased. This is likely due to the higher concentration simulations having fewer waters, resulting in increasingly large portions of the total water in PEP hydration shells and indicating a slightly better solubility of PEP with decreasing water (Wexler 2019). The lack of any significant change in RDF implies that the structure of the hydration shells is the same across the entire range of concentrations and correspondingly that the solvation mechanism is unchanged. No indications of structural transition or unmixing are observed.



Figure 10: Radial Distribution Functions of Carbon and Phosphorous Atoms

Source: Keith Bein, University of California, Davis

Viscosity

Figure 11 shows viscosity as a function of percent wt aqueous PEP concentration determined using the Green-Kubo relation. The values obtained are about 50 percent below the

experimentally expected value where available. This is not unusual for simulations of this type, thus trends can be expected to be robust (Hess 2001). The value obtained for pure water was 0.342 millipascal-second (mPa*s), whereas its expected value is around 0.79. Simulations of a 30 wt% aqueous MEA solution were also performed to compare relative numbers and were found to have a value of 0.647 mPa*s (marked with orange x in Figure 11), against a literature value of 1.536 mPa*s (Nazrul Islam et al. 2004). The relative error in viscosity is comparable for water and 30 wt% aqueous MEA solution and within the range expected. The small statistical error in the pure water measurements (0.024 mPa*s) determined from independent runs indicates that the starting conditions do not have a significant impact on viscosity. It appears that PEP viscosity is similar to MEA over the same concentration range such that there would be no disadvantage from a viscosity standpoint to move from MEA to PEP. Again, the continuous increase of viscosity indicates that there is no qualitative change in structure or dynamics over the concentration range studied, indicating molecular stability.





PEP = phosphoenolpyruvate; MEA = monoethanolamine.

Source: Keith Bein, University of California, Davis

Diffusion Coefficient

The mean square displacement over time was used to calculate the diffusion coefficient of PEP over a range of concentrations. As shown in Figure 12, diffusivity drops linearly with increasing PEP concentration from 30 to 60 wt%. At 48 wt% PEP, the diffusion coefficient of bicarbonate HCO_3^- is 2.381 ± 0.392x10⁻⁵ cm²/s, roughly a third of the literature value for water (orange dot in Figure 12).



Figure 12: Diffusion Coefficient versus Percent Weight Aqueous Phosphoenolpyruvate Concentration

Bicarbonate transport was also included in the simulations with concentration given by:

$$[HCO_3^-] = \frac{K_{c1}H_{CO_2}p_{CO_2}}{[H^+]}.$$

Values for constants were taken from the literature (Brune 2019). The equilibrium constant K_{c1} had a value of 2.5 x 10⁻⁴, and the Henry's law constant for CO₂ is approximately 0.034 mol/L atm at neutral pH value. The mole fraction of CO₂ was 0.205 based on the assumption that all oxygen in the air had been converted to CO₂ in the combustion process.

Due to the concentration of HCO_3^- being very low at low pH value (explicit pH was 1.5 for the PEP simulations), it was necessary to significantly raise the pH of these simulations to have a useful concentration of bicarbonate at a reasonable simulation size. It is expected that all PEP molecules would likely have at least one dissociated proton and a significant amount would have more. But due to the limitations mentioned previously, only singly charged ions could be simulated; simulation parameters are shown in Table 3.

Source: Keith Bein, University of California Davis

wt%	# Water molecules	# PEP ⁺ ions	#Bicarbonate molecules
31.93	29820	1500	94
39.49	21435	1500	69
48.23	15015	1500	49
54.62	11622	1500	39
56.64	10707	1500	37

Table 3: Diffusion Coefficient Simulation Parameters

Source: Keith Bein, University of California, Davis

Free Energy of Phosphoenolpyruvate Variants

PEP appears to be a suitable replacement for MEA in PCC based on its properties in aqueous solution. However, it is possible that slight variations on the PEP structure by removing or adding different atoms and functional groups could lead to even better PCC solvent alternatives. A preliminary assessment of some possible PEP variants is given here. Figure 13 displays both the original PEP molecule and its free energy diagram. Subsequent analyses of PEP variants are judged solely on the merit of their free energy diagrams compared to that of the original. For the variant to have any advantage over the original PEP molecule, they should have lower energy of dilution in water. For the sake of simplicity, the three points enclosed by the red circle in Figure 13 were the only points compared across all variants since they represent the energy minimum.

Figure 13: Phosphoenolpyruvate Molecular Structure and Free Energy Diagram (C₃H₅O₆P)



Source: Keith Bein, University of California, Davis

The first PEP variant is depicted in Figure 14 and eliminates the terminal double bonded carbon. Comparing this free energy diagram with that of PEP demonstrates that it has higher energy of dilution. These simulations do not suggest this variant to be a better replacement to PEP.

Figure 14: Phosphoenolpyruvate Variant V1 (C₂H₅O₆P) Molecular Structure and Free Energy Diagram



Source: Keith Bein, University of California, Davis

Substituting one of the hydrogen atoms bound to carbon atom C2 with a hydroxyl group, as shown in Figure 15, also results in higher free energy. Again, this suggests the variant shows no improvements over PEP, although the difference between the curves is small.

Replacing a hydrogen atom on C2 with a carboxylic acid group (O = C - OH) instead of hydroxyl group increases the energy of dilution even more than the previous two variants, as shown in Figure 16. It is not immediately clear why the addition of a carboxylic group increases the dilution energy, but it may involve steric hindrances to the hydration shell. A possible explanation is that the carboxylic group aids the dissociation of the first proton but makes it more difficult for the second proton to dissociate due to electrostatic attraction to the nearby carboxylate anion.

Figure 15: Phosphoenolpyruvate Variant V2 (C₂H₅O₇P) Molecular Structure and Free Energy Diagram



Source: Keith Bein, University of California, Davis

Figure 16: Phosphoenolpyruvate Variant V3 (C₃H₅O₈P) Molecular Structure and Free Energy Diagram



Source: Keith Bein, University of California, Davis

For the fourth PEP variant, the hydrogen atom attached to C2 is substituted with a double bonded oxygen (oxy-group). Figure 17 shows that the energy of dilution in this case is lower than the original PEP molecule. Although further simulations are required for validation, this result shows the possibility of improving the aqueous solution properties of PEP by changing the functional groups in the nonreacting parts of the molecule.

Figure 17: Phosphoenolpyruvate Variant V4 (C₂H₃O₇P) Molecular Structure and Free Energy Diagram



Source: Keith Bein, University of California, Davis

The final PEP variant is shown in Figure 18, where a carbon atom bonded to a hydroxyl group (C - OH) substitutes the hydrogen on the C2 atom. Like the previous variant but to a lesser extent, the minimum in the energy of dilution is lower than that found in original PEP. Again, this demonstrates the ability to optimize the properties of PEP by modifying the chemical structure of the nonreacting regions.

Figure 18: Phosphoenolpyruvate Variant V5 (C₃H₅O₇P) Molecular Structure and Free Energy Diagram



Source: Keith Bein, University of California, Davis

Conclusions

The chemical potential-concentration curve shows that the expected solubility of PEP at 20°C is 9.8 mol%. This is slightly lower than the 11 mol% of the standard MEA solution. However, the stoichiometric ratio of MEA to CO₂ during absorption is 2:1 as shown in the following equation while that of the PEP-CO₂ reaction is 1:1. Therefore, the absorption capacity of the PEP solvent for CO₂ is almost doubled compared to most primary and secondary amines, which all follow the same general reaction stoichiometric ratio: where NR_3 can be any primary, secondary, or tertiary amine and NHR_2 is either a primary or secondary amine (Hoff et al. 2013).

$$CO_2 + NHR_2 + NR_3 \leftrightarrow NR_2CO_2^- + NR_3H^+$$

Higher temperatures present in absorber systems may further improve the solubility of PEP, especially given the curve is very shallow up to 55 wt% (11 mol%).

The viscosity of PEP solutions in the 45 to 55 wt% (9.8 mol%) range is estimated to be roughly triple that of the standard MEA solution, with a real viscosity of about 3 mPa*s. Based on the viscosity alone, a rough calculation shows that the same pipe infrastructure would require about 6 percent more power to pump PEP than MEA solution (Milnes 2014). Fortunately, the amount of power required to pump MEA is already a negligibly small part of the PCC energy cost.

Hydration shells, viscosity, and self-diffusion coefficient trends for PEP showed no notable behavior change over the examined range of concentrations. It is therefore unlikely that any sort of relevant phase or structure change is taking place.

Preliminary simulations of the change in free energy of dilution as the original PEP molecule is modified by adding or removing atoms and functional groups demonstrated the ability to change the solvent properties. Some variants decreased the minimum free energy while others increased it, substantiating the concept that solvents can be optimized for the PCC process. In total, the observations made here show the promise of alternative PCC solvents based on phosphoenol compounds to increase the desired solvent properties relative to benchmark amines such as MEA. Further research is needed to elaborate on these preliminary findings and reactive simulations are necessary to compare CO_2 absorption kinetics between MEA and PEP.

CHAPTER 4: Project Approach – Reactive Molecular Dynamics Simulations

Objective

Nonreactive MD simulations of the chemical potential, viscosity, and diffusion coefficient of aqueous PEP solutions described in the previous chapter showed that PEP is comparably efficient to MEA in PCC. This suggests that PEP or PEP variants have the potential to be good alternative CO₂ solvents for lower regenerative energy. Further investigation of the reaction mechanism of PEP and PEP variants with CO₂ can be accomplished by reactive MD simulations, which use empirical reactive force fields that allow bond formation and dissociation. The reactive force field (ReaxFF) uses an interatomic potential that implicitly describes chemical bonding using a bond-order formulism without explicit quantum mechanical (QM) calculations and thus can handle the dynamics of larger systems than pure QM simulation (Senftle et al. 2016). A schematic of the possible applications of reactive MD using ReaxFF is shown in Figure 19.



Figure 19: Applications of Reactive Molecular Dynamic Modeling Using

Source: Senftle et al. npi Computational Materials 2 (2016); 15011.

The branches represent different modeling applications like combustion chemistry and aqueous phase reaction, which is the application used in this research. In terms of molecular

(a) ReaxFF for Hydrocarbons

(b) Si/O/H

size, this is closest to glycine. This chapter presents an optimized ReaxFF for aqueous PEP solutions with CO₂. Force fields are computationally trained against an extensive data set including density functional theory (DFT) calculations of reaction pathways of the dissociation of PEP³⁻, bond dissociation energies, and structures and partial charges of all molecules and ions. The parametrization process uses a parallelized search algorithm developed at the University of California, Davis (Deetz and Faller 2014).

Methods

Quantum chemistry-based methods including DFT are powerful tools to describe chemical reactions on the atomistic scale. However, these types of calculations are very computationally expensive and thus limit the time and length scales. This is depicted schematically in Figure 20.



Source: Roland Faller, co-investigator.

Alternatively, empirical force field methods like classical molecular dynamics (MD) simulation can study the system's dynamic evolution for comparatively long times (nanoseconds) with thousands of atoms but loses the reaction information since the atomic connectivity is predefined. Therefore, to describe the reaction step of PEP with HCO₃⁻ (Figure 5) and compare potential PEP variants, ReaxFF-based reactive MD simulations are used that fill the gap between quantum chemistry methods and classical empirical force field methods. ReaxFF is a reactive force field that allows bond formation and dissociation. The total system energy is comprised of bond order dependent energies and non-bonded energies, as shown in Figure 21 (van Duin et al. 2001). Bond order is a smooth function of atom distance. For example, as two carbon atoms starting from close to each other separate further and further, the bond order gradually goes from three (triple bond) to zero (fully dissociated).

Figure 21: Bond Order and Non-Bond Order Dependent Energies in Reactive Molecular Dynamic



Source: van Duin et al. JPC A 105.41 (2001); 9396-9409.

The ReaxFF P/N/C/O/H/Na was previously published for CO₂ capture using the ionic liquid tetrabutylphosphonium glycinate (Zhang, van Duin, and Johnson 2014). The CO₂ related parameters were optimized, and the parameterization contains the important element P and the counter ion element Na to neutralize the charged system in the MD simulations. However, the important P-O interactions were not specifically developed, and the H/O parameters are from a first generation water force field for which the constant pressure water density is known to be significantly smaller than the experimental value. Furthermore, the H₂O, H₃O⁺, and OH⁻ diffusion constants are more than an order of magnitude off (Zhang and van Duin 2017). The current application is an aqueous system, so the water behavior needs to be more accurate. Therefore, all the water-related parameters from the P/N/C/O/H/Na force field were replaced with those from the second generation water force field that corrects the first generation water parameters. Also, many of the C/P atom parameters and O/P interaction parameters were reoptimized to better describe the PEP-HCO₃⁻ reaction. Table 4 shows which parameters were chosen and why.

Parameters Chosen	Reasons
Electrostatic: Electronegativity equalization method parameters for C, P	Bonding prediction
Valence bond: All bond radii/order/dissociation energy, and under/over coordination energy parameters for C, P atoms and C-C, C-O2, P-O pairs	Bonding prediction Reaction pathway Reaction/product/transition state structure
Valence angle: All angle parameters for C, O, P related angles in the molecules	Geometry prediction
Van de Waals: Vdw radii/dissociation energy/shielding for C, P	Bonding prediction

 Table 4: Choice of Force Field Parameters

Source: Keith Bein, University of California, Davis

The optimization process consists of two parts: training set generation and parallel search algorithm. The new parameter values are accepted so that they reduce the error between training set features and ReaxFF fitted features.

The training set has four sections: charge, geometry, energy, and reaction. The charge and geometry sections collect the partial charges, bond lengths, and angles of all neutral molecules related to $PEP-HCO_3^-$ reaction step and their charged states. Since the LAMMPS (Plimpton 1993) modeling software requires a neutral system, H_3O^+ was used as counter ions. The bond section collects dissociation energy scans for P-O and O-H bonds in neutral PEP and carboxyphosphate.

The reaction section has the reaction energy of the PEP-HCO₃⁻ reaction and the activation energy of the splitting of PEP³⁻ into the phosphate ion PO₃²⁻ and the enolate form of pyruvate since the transition state structure of this reaction step is not stable in vacuum. Therefore, this activation energy is not appropriate to include in the training set. Figure 22 shows the training set features and the workflow of the optimization process. The scripts are written in MATLAB and Bash, and the parallel search optimization part is run in parallel on a high-performance cluster at the University of California, Davis (HPC1). The training set data is from DFT calculations using the Gaussian software, and the MD calculations using ReaxFF are done in LAMMPS. In the total weighted error function, the inverse weight w_i for each feature in the training set is selected first so that each section of the training set (charge, geometry, energy, reaction) weighs similarly to the error function. Then after the error function converges, the parameters are fine-tuned by changing the wt. This process is repeated until (1) the overall performance of the new force field matches the training set with acceptable errors and (2) the most important features like kinetics are well matched to the training data.

Figure 22: Workflow of Overall Optimization Process for Reactive Force Field Parameterization



Source: Keith Bein, University of California, Davis

Results

After reoptimizing parameters, as previously discussed, the new ReaxFF force field accurately reproduces the partial charges of CO₂, the neutral and charged bicarbonate, PEP, carboxyphosphate, enolate, oxaloacetate, and the transition state relative to DFT values. Bond dissociation energy scans in Figure 23 show good agreement between DFT and ReaxFF. Using DFT calculations, the O-P and O-H bonds at the active sites for both neutral PEP and neutral carboxyphosphate were scanned from very short distances to equilibrium distances and then to very large distances without relaxing the whole structure to acquire the energies along the scans. To account for the multiple spin states as molecules break, both singlet and triplet scan were calculated, and the lower energies were taken as bond dissociation scan energies. Some energy data points at extreme distances were removed to reduce the computational cost. The structures corresponding to each DFT data point along the scans were then fed to ReaxFF MD simulations to calculate ReaxFF energies. The fitted ReaxFF energies generally match the DFT energies, especially at the regions near the equilibrium distances.

The bottom right panel of Figure 23 shows the comparison of the energies along the reaction pathway and the reaction energy between DFT and ReaxFF. The energies along the reaction pathway were obtained from intrinsic reaction coordinate (IRC) calculation using DFT, and the ReaxFF energies were fitted using for the structures along the DFT IRC curve. The barrier energies from DFT and ReaxFF are 8.87 kcal/mol and 7.08 kcal/mol respectively, and the reaction energies from DFT and ReaxFF are -16.90 kcal/mol and -11.06 kcal/mol respectively. Both the barrier energy and the reaction energy prove that the optimized force field can accurately describe the kinetics and thermodynamics of the PEP-HCO₃⁻ reaction step. Furthermore, the bond and angle errors between ReaxFF and DFT calculations are all less than

6 percent. All these comparisons show that the optimized ReaxFF can be used for the PEP solution of interest.

The optimized ReaxFF parameters were also used to explore the bond lengths and bond dissociation energies of neutral PEP and PEP variants. As discussed previously, PEP variants are obtained by adding and removing atoms and functional groups from the original PEP molecule to vary the reaction energetics. Using the same two variants shown in Figure 14 and Figure 15 for the nonreactive MD simulations of Chapter 3, and an additional variant containing an extra oxygen atom between the central carbon and phosphate group, Figure 24 shows the results of these simulations. Although the differences in bond dissociation energies are relatively small, this exercise again demonstrates the ability to alter PEP to obtain other phosphoenol compounds with more favorable properties, for example, reaction energetics in this case. Of the compounds tested, the variant with a hydroxyl group added to the C2 carbon (V5: $^{a}C_{3}H_{5}O_{7}P$) shows the lowest bond dissociation energy, meaning lower reaction energetics and potentially faster reaction kinetics. This variant also showed lower minimum energy of dilution than PEP.

Simulations were similarly performed on the triply charged PEP and PEP variants to evaluate the energy barrier for decomposition into the phosphate and enolate ions, a critical step in the reaction mechanism. Results are shown in Figure 25. Simulations of the quadruple charged V5 and V6 variants, denoted as Case 5' and 6' in the figure, are also included. The effect of modifying the PEP structure and charge on the decomposition barrier energy are striking in this case with several variants showing significantly reduced energy barriers compared to PEP. Of note is the quadruple charged V5 variant with essentially a zero-energy barrier.



Figure 23: Bond Dissociation Energy Comparisons Between Density Functional Theory and Reactive Force Field

Source: Keith Bein, University of California, Davis

Figure 24: Bond Length and Bond Dissociation Energy for Phosphoenolpyruvate and Phosphoenolpyruvate Variants



Source: Keith Bein, University of California, Davis

Figure 25: Decomposition Barrier for Triply Charged Phosphoenolpyruvate and Phosphoenolpyruvate Variants



Source: Keith Bein, University of California, Davis

Conclusions

The optimized ReaxFF reproduces atomic partial charges, geometries, and bond energies of the target reaction exceptionally well. The bond and angle errors between ReaxFF and DFT calculations are all less than 6 percent. More importantly, the reaction energy and barrier calculated from ReaxFF shows that the optimized force field can accurately describe the thermodynamics and kinetics of the first step in the PEP-HCO₃⁻ reaction pathway. Water

density calculated using this force field and at 300 Kelvin and 1 atmosphere with isothermalisobaric ensemble is 1.005 ± 0.015 grams/cubic centimeter. Furthermore, first results from simulations of bond dissociation energies and decomposition energy barriers for PEP and PEP variants offer proof of concept for the ability to modify the phosphoenol structure to optimize compound properties and performance for PCC. Additional effort is required to validate these preliminary findings and further characterize aqueous solutions of phosphoenol compounds in terms of CO₂ absorption kinetics.

CHAPTER 5: Project Approach – Process Modeling Carbon Dioxide Capture Chemistry in Post-Combustion Capture Systems

Objective

State-of-the-art process models of various absorber/stripper architectures in first-generation post-combustion capture (PCC) systems are used to quantify the total thermal energy demand of the CO₂ absorption-desorption process, termed the regeneration energy Q_{reg} . As mentioned previously, Q_{reg} comprises three highly interdependent thermal energy terms, including (1) the sensible heat Q_{sen} required to heat the aqueous carbon capture solvent, (2) the latent heat of vaporization Q_{lat} for producing steam, and (3) the heat of reaction Q_{rxn} for desorption of CO₂.

$$Q_{reg} = Q_{sen} + Q_{lat} + Q_{rxn}$$

The most common objective of PCC process modeling is to minimize Q_{reg} by varying either process parameters, like solvent flow rate, stripper pressure and reboiler temperature, or solvent parameters, like CO₂ vapor-liquid equilibrium (VLE), reaction enthalpy ΔH_{rxn} , and mass transfer properties. A typical absorber/stripper configuration is shown in Figure 26.



Figure 26: Standard Absorber/Stripper Configuration in Post-Combustion Capture Systems

Source: Source: Keith Bein, University of California, Davis

Counterpropagating flows of CO_2 -rich flue gas entering from the bottom of the boiler (Figure 26: point $1_{(g)}$) and CO_2 -lean aqueous solutions of the carbon capture compound from the top

of the boiler $(1_{(liq,c)})$ mix, and CO₂ is transferred from the flue gas to the solution via dissolution into the aqueous phase, dissociation to the bicarbonate ion, and reversible reaction with the carbon capture compound, typically referred to as the solvent. The CO₂-rich solvent collected at the bottom of the absorber is pumped through a heat exchanger, where the thermal energy of the hot CO₂-lean solvent on the return cycle from the stripper is transferred to the CO₂-rich solvent, to the top stage of the stripper ($3_{(liq,h)}$). Counterpropagating flows of steam from the reboiler at the bottom of the stripper and CO₂-rich solvent from the top mix, and CO₂ is transferred from the aqueous phase to the vapor phase via a thermally driven reverse in the carbon capture reaction. Gaseous CO₂ then exits the top of the stripper ($3_{(g)}$) to the compressor and CO₂-lean solvent collects at the stripper bottom ($4_{(liq,h)}$) and is recycled through the heat exchanger, transferring its thermal energy to the CO₂-rich solvent and then fed back to the absorber top.

Process modeling studies to date have shown that operational variables — solvent flow rate and stripper pressure and temperature — are constrained in their degrees of freedom to influence the regeneration energy. One variable must be set to satisfy operational targets (for example, 90 percent capture efficiency) while the others are limited by the chemical stability of the carbon capture compound. Therefore, it is widely recognized that the solvent is the most critical variable in minimizing Q_{reg} . Much effort has been made to quantify optimal solvent properties, but these studies have exclusively focused on various amines and amine mixtures. There has been no effort to study alternative, non-amine carbon capture chemistry. In the current work, well established state-of-the-art process models within the Aspen Plus architecture are used to study phosphoenol-based CO₂ capture chemistry starting with the base PEP molecule.

Methods

The Electric Power Research Institute maintains and operates Aspen Plus process models based on the traditional absorber/stripper configuration shown in Figure 26 and standard operational parameters previously discussed. These models are configured to accept generalized solvent properties and calculate the resulting energy penalty. They are used here to quantify the energy penalty of PEP carbon capture chemistry relative to the MEA benchmark. Required model inputs include the solubility, viscosity, and heat capacity of PEP, as well as the CO₂ VLE of the underlying PEP-bicarbonate reaction equilibrium.

CO2 Vapor Liquid Equilibrium

Reaction reversibility is cornerstone to carbon capture chemistry and is characterized by the temperature dependence of the reaction equilibrium constant $K_{rxn}(T)$, which decreases with increasing temperature. At low temperature (for example, 40°C absorber), products are favored, and gaseous CO₂ is drawn into aqueous solution via reaction of the bicarbonate ion HCO_3^- with the solvent (absorption). At higher temperature (such as 120°C stripper), reactants are favored and HCO_3^- desorbs, releasing CO₂ back into the gas phase for capture and compression. The difference ΔCO_2 between these temperature extremes determines the absorption capacity of the solvent, or cyclic capacity of the absorber/stripper system, and thus is perhaps the most critical solvent property. The CO₂ VLE for the generalized phosphoenol-bicarbonate reaction is a multistep process encompassing (1) dissolution of CO₂ into the aqueous phase via Henry's law, (2) hydrolysis/ionization of aqueous CO₂, (3) carbonic acid dissociation into singly (HCO₃⁻) and doubly (CO₃²⁻) charged states, (4) water self-ionization, (5)

phosphoenolpyruvic acid dissociation into singly, doubly, and triply charged states, (6) reaction of bicarbonate and triply charged PEP, (7) oxaloacetic acid dissociation into singly and doubly charged states, and (7) phosphoric acid dissociation into singly ($H_2PO_4^-$), doubly (HPO_4^{2-}), and triply (PO_4^{3-}) charged states. The reaction system and thermodynamic mathematical formalism are currently in preparation for publication.

Results

Figure 27 shows the CO_2 VLE curves for pure water, 11 percent mole fraction MEA solution, and 10 percent mole fraction PEP solution at the temperatures of the absorber (40°C) and stripper (120°C).



Figure 27: Carbon Dioxide Vapor Liquid Equilibrium Curves

Source: Keith Bein, University of California, Davis

The solid horizontal lines are the CO_2 partial pressures in the flue gas emissions of SCPC and CCNG power plants. VLE describes the number of moles CO_2 per unit volume solution absorbed via reaction and dissolution as a function of CO_2 partial pressure above solution. For example, the absorber VLE curve for MEA shows that the system is in thermodynamic equilibrium at CO_2 partial pressures significantly below that of SCPC and CCNG flue gas

concentrations, meaning that further raising CO₂ partial pressure above the value where the curve terminates will not increase the molality of absorbed CO₂ in solution. The cyclic capacity is simply the difference between the molality of absorbed CO₂ in rich conditions at the absorber (SCPC: 2.38 mol/kg at 12,880 Pa; CCNG: 2.38 mol/kg at 3,910 Pa) and lean conditions in the stripper assuming 90 percent reduction in CO₂ partial pressure (SCPC: 0.70 mol/kg at 1,288 Pa; CCNG: 0.37 mol/kg at 391 Pa), which gives 1.43 and 1.86 mol/kg for SCPC and CCNG, respectively. This equates to 71 percent and 84 percent cyclic efficiency, that is, 71 percent and 84 percent of CO₂ reacting with MEA at absorber conditions for SCPC and CCNG, respectively, are desorbed and released for compression at stripper conditions. The remaining 29 percent and 16 percent remain bound in solution during repeated cycling.

Full integration of the thermodynamic formalism for the PEP reaction system into the Aspen Plus model is still a work in progress. Furthermore, all the equilibrium constants for the various acid dissociation and PEP-HCO₃⁻ reactions, as well as their temperature dependence, are not well constrained at this point given a paucity of available data and since different estimation methods give significantly different results for Gibbs free energy of reaction ΔG_{rxn} . Equilibrium constants vary as the exponential of ΔG_{rxn} and so are extremely sensitive to even small errors in these estimates. Additional research is required to model these parameters in aqueous solutions to obtain more accurate and consistent data. As a result, best estimates of the various parameters were used in the process model and all PEP was assumed to be fully reacted with HCO₃⁻ at the absorber conditions. This represents a best-case scenario for the VLE curves and sets the upper limit on cyclic capacity and efficiency. As shown in Figure 27, these data for PEP are 3.91 mol/kg and 99.9 percent for SCPC and 1.64 mol/kg and 99.9 percent for CCNG, highlighting significant potential for PEP variants to reduce the cost of carbon capture. Further research on the true VLE is required.

Conclusions

The fact that the reaction stoichiometry of PEP is half that of MEA, that is, each PEP molecule can absorb one CO₂ molecule while it takes two MEA molecules per CO₂, gives PEP and PEP variants a stark advantage in terms of the energy efficiency of the absorber-stripper process. Since PEP is noncorrosive, unlike MEA, the possibility of raising the solubility for PEP variants, as exhibited previously, will act to decrease the energy penalty even further. Additional effort is required to model PEP variants as the thermochemical data required for the VLE calculations feeding the process models are nonexistent and must be estimated using MD and DFT simulations. Kinetic data for the reactions are also absent but are the focus of the next step in this nascent effort.

CHAPTER 6: Knowledge Transfer

The long-term goal of this research is commercialization of PEP variants that can be implemented into existing carbon capture technologies to improve process efficiency and reduce costs. Thus, the intended market audience is the electric utilities sector, high CO₂ emitting industries like cement production, and direct air capture research and development companies. However, the maturity of this research is still insufficient to initiate these conversations and the target remains additional funding opportunities to continue validation and quantification of benefits. As such, knowledge transfer thus far has been limited to funding agencies via reports, presentations, and proposals until intellectual property rights are established. Three manuscripts have been written and will be submitted for publication in scientific journals pending filing of a patent application.

Although the research presented here is at a low technology readiness level, the process technologies into which it would be embedded are mature. The underlying architecture of current absorber-stripper and direct air capture systems is not being altered. Rather, new carbon capture compounds are being proposed that can substitute existing compounds to optimize efficiency and thus reduce resistance to implementation. The natural trajectory of this work is further refinement of the modeling methods, laboratory synthesis of select variants, benchtop validation of thermodynamic and kinetic properties, pilot scale demonstrations, and commercial scale-up. Given existing infrastructure, an accelerated research to market pathway is projected.

CHAPTER 7: Conclusions/Recommendations

Results of multiple modeling efforts demonstrate proof of concept for biomimetic computational carbon capture chemistry and identify encouraging trends in the viability of using Crassulacean Acid Metabolism-inspired CO₂ sequestration in post-combustion and DAC systems. In brief, first estimates of the thermodynamics for the reaction of PEP and several PEP variants with HCO₃⁻ demonstrate that the energetics, e.g., enthalpy and Gibbs free energy, are within the optimal range for use in current absorber-stripper post-combustion systems based on process modeling optimization of the MEA benchmark. This is important since these variables ultimately determine the energy penalty, and thus cost, of carbon capture. Furthermore, it was determined that the PEP variants could be tailored to customize molecular properties like solubility without changing the thermodynamics. This provides tremendous flexibility to design PEP variants that can potentially meet and exceed current benchmarks. More research is required to validate the accuracy of these estimates.

Molecular dynamics, which are currently the most sophisticated chemical modeling techniques available, were also performed on PEP and select PEP variants to estimate the aqueous solution properties of these compounds, including solubility, viscosity, and diffusivity. Solubility is vital to determining the maximum CO_2 that the solution can uptake during one cycle between the absorber and stripper. The higher the solubility, the larger the absorption capacity, and the more energy efficient the process. Simulations showed that solubility is comparable to MEA and that the PEP variants could further improve this, which is important for two reasons. First, the reaction stoichiometric ratio of MEA to CO_2 is 2:1 - i.e., two amine molecules are required to absorb one CO_2 molecule – while that of the PEP- CO_2 reaction is 1:1, i.e., it only takes one PEP or PEP variant molecule to absorb one CO_2 molecule. Therefore, the theoretical CO_2 absorption capacity of PEP and its variants is already twice that of amines, which translates into significant potential cost savings. Secondly, amines are caustic, which places upper limits on solution concentration due to corrosivity considerations, while PEP and its variants are only limited by solubility. Increasing solubility through custom tailoring of the PEP variants would further increase cyclic efficiency and reduce costs more.

The energy barriers and kinetics for reaction of PEP and its variants with CO₂ were investigated using reactive MD simulations. These variables are important as they determine how fast the reactions happen and thus what the optimal processing parameters, and associated costs, would be. The faster the reaction, the more efficient and cost-effective the process. Initial results clearly demonstrate the ability of these models to accurately reproduce the molecular properties of the compounds like atomic partial charges, geometries, and bond energies, as well as describe the thermodynamics and kinetics of the first step in the PEP-CO₂ reaction pathway. Analysis of the variants show improvement over PEP with significant decreases in both bond dissociation energy and decomposition energy barrier, key metrics in reaction potential. The smaller the energy barrier, the more likely the reaction will proceed quickly. Although these results are very promising, additional research is required to validate these preliminary findings and further characterize aqueous solutions of PEP and its variants in terms of reaction kinetics.

The objective of this project was to demonstrate proof of concept for three hypotheses. First, that the underlying CO₂ capture chemistry of the CAM photosynthetic pathway is suitable for NETs like PCC and DAC. Second, that current state-of-the-art chemical modeling platforms could accurately predict relevant thermodynamic and molecular properties of PEP and its variants. Third, that PEP variants could be custom tailored to optimize molecular and thermochemical properties for improved performance in existing system architectures. Although this effort has been successful, it is still in its infancy. Given the paucity of literature, experimental data, and modeling studies on PEP and its variants, and organophosphates in general, the bulk of this effort has been spent in developing and validating the models, including building the force fields, optimizing the parameterization space, and minimizing uncertainties in the predicted data.

With the concept and computational machinery firmly in place, additional research is needed to expand the pool of candidate compounds, refine the molecular modeling, further investigate the reaction kinetics, increase accuracy of the thermochemical data, and optimize molecular design. The latter can be accomplished via iterative analyses using process models and technoeconomic analytics to identify the most viable amine substitutes. Biomimetic carbon capture is a novel and promising approach to helping propel and accelerate California into its carbon neutral future.

CHAPTER 8: Benefits to California

California is particularly vulnerable to the effects of climate change owing to a confluence of factors, including a vast latitudinal and coastal expanse (1,100 miles), semi-arid climate, rich and diverse ecosystems, intensive agricultural and tourism industries, iconic landscapes, densely populated urban centers, and high energy and water demands. The effects of climate change include wildfires, drought, flooding, heatwaves, invasive species, infectious diseases, desertification, loss of habitat, biodiversity, and arable land, sea level rise, and declining air and water quality, as well as the economic, social, infrastructure, food security, and public health volatilities accompanying these extreme events and shifting trends.

As the fifth largest economy in the world with an internationally recognized portfolio of progressive climate policies and targets, abundant natural resources, massive ingenuity pool, academic prowess, and immense clean energy potential including wind, solar, geothermal, waves, and biomass, California is uniquely positioned to assume a leadership role in the global fight against climate change by using these resources to demonstrate a viable regional scale model of a carbon neutral economy that can be adopted by others. A key corollary here is that problems provide opportunity, which, when acted upon, translates into natural, social, and economical gains. Irrespective of successful execution of California's current portfolio of decarbonization strategies, NETs will need to be implemented at a scale of roughly 125 megatons of carbon dioxide equivalents per year to achieve carbon neutrality by 2045. This can be accomplished by adopting the priority recommendations of the Lawrence Livermore National Laboratory report, which would immensely benefit Californians by creating jobs, redistributing burden and opportunity, stabilizing infrastructure, invigorating ingenuity, retaining talent, reducing risks, restoring ecosystems, and building resiliency into all vital societal and life support systems. Negative emissions are paramount to the path and a majority fraction will have to be through a flexible blend of fossil fuel CCS, carbon capture and sequestration, bioenergy with carbon capture and sequestration, and direct air capture. Carbon dioxide separation systems are cornerstone to these technologies, and biomimetic computational chemistry represents uniquely uncharted territory with a promising trajectory to significantly reduce projected costs.

A combination of results reinforces this narrative. First, the theoretical carbon dioxide capture efficiency of phosphoenolpyruvate variants is already twice that of the amine benchmark. Second, the capture capacity of phosphoenolpyruvate variants is only limited by solubility while that of amines is capped by corrosivity considerations. Third, fugitive amine emissions are potentially toxic, while phosphoenolpyruvate variants are environmentally benign. Finally, PEP variants have the potential to increase process efficiency. Ultimately, if these model predictions come to fruition and the compounds are brought to market, they would result in significant cost savings to ratepayers and industry by reducing the energy penalty of carbon capture while also achieving carbon neutrality and averting the worst impacts of climate change. The scale, complexity, and urgency of the issues and efforts compel and justify this research.

LIST OF ACRONYMS

Term	Definition	
°C	degrees Celsius	
atm	atmosphere	
BECCS	bioenergy with carbon capture and sequestration	
С	carbon	
САМ	Crassulacean acid metabolism	
CCNG	combined cycle natural gas	
CCS	carbon capture and sequestration	
CEC	California Energy Commission	
CHEETAH	Chemical Thermodynamic and Energy Release Evaluation	
cm²/s	square centimeters per second	
CO ₂	carbon dioxide	
CO3 ²⁻	carbonate ion	
DAC	direct air capture	
DFT	density functional theory	
EPIC	Electric Program Investment Charge	
°F	Degrees Fahrenheit	
g/cc	grams/cubic centimeter	
GHG	greenhouse gas	
Н	hydrogen	
H ₃ O ⁺	hydronium ion	
HCO3 ⁻	bicarbonate ion	
IPCC	Intergovernmental Panel on Climate Change	
IRC	intrinsic reaction coordinate	
К	Kelvin	
kcal/mol	kilocalories per mole	
kJ/mol	kilojoules per mole	
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator	
LLNL	Lawrence Livermore National Laboratory	

Term	Definition	
MD	molecular dynamic	
MEA	monoethanolamine	
Mol/L atm	moles per liter atmosphere	
mPa*s	millipascal-second	
Mt CO ₂ e/yr	megatons of carbon dioxide equivalents per year	
N	nitrogen	
Na	sodium	
Na ⁺	sodium ion	
NASEM	National Academies of Sciences, Engineering, and Medicine	
NETs	negative emissions technologies	
NOAA	National Oceanic and Atmospheric Administration	
0	oxygen	
Р	phosphorous	
PCC	post-combustion capture	
PEP	phosphoenolpyruvate	
Ppm	parts per million	
QM	quantum mechanical	
RDF	radial distribution functions	
ReaxFF	reactive force field	
SCPC	supercritical pulverized coal	
UK Met Office	United Kingdom Meteorological Office	
UNEP	United Nations Environment Program	
VLE	vapor-liquid equilibrium	
Wt%	weight percent	

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