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A Modular Oxygen-Selective System for Combustion Systems

September 2024

Deepika Malhotra Eric D Walter Jared O Kroll Yuan Jiang



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Summary

Small-scale modular systems for oxygen generation offer clear benefits, including improved energy efficiency, reduced operating costs, and the flexibility to meet location-specific needs. We propose that a compact modular system could be developed using a solvent-based method for capturing and releasing oxygen, enabling "oxygen on demand" for various combustion technologies. In this project, we aim to develop and demonstrate a modular oxygen-selective approach based on Battelle IPID 31740. The use of designer solvents, which are reversible, single-component solvents capable of dissolving and separating oxygen from air, offers the advantage of unlimited chemical tunability to achieve desirable properties for efficient oxygen separation. While various air separation technologies, such as sorbents and ion transport membranes, have been explored by DOE programs, they often face challenges such as high energy requirements or substantial capital costs. The DOE is keenly interested in advancements in air separation that will facilitate the use of abundant domestic coal resources in modular gasification systems, thereby enhancing energy security. The study is aligned with the DOE's mission to develop innovative methods for providing high-purity oxygen for gasification and other energy applications. We filed U.S. Patent (32845-E, iEdison No. 0685901-23-0184).

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1.0 Introduction

State-of-the-art oxygen generation technologies primarily rely on cryogenic air separation systems. This method, developed by Dr. Carl von Linde, involves the compression and heat exchange of air to produce high-purity molecular oxygen (O₂) through a distillation process. Air liquefaction begins at temperatures below -140°C, making it an energy-intensive process. During hot summer months, air separation plants often reduce production to avoid overwhelming the electrical grid, highlighting the significant energy demands of this technology. While cryogenic distillation can achieve nearly pure oxygen, it is only economically viable at large production scales of 100-7,000 tonnes per day, compared to the 10-90 tonnes per day required for a 1-5 MWe system. The substantial heat generated during compression necessitates pre-cooling with water, which acts as an energy sink and can account for up to 15% of the total capital cost of a gasification plant. As a result, these processes are not suitable for modular applications due to their energy intensity and scale requirements.

This project aims to develop an oxygen-selective material capable of delivering pure oxygen to energy-conversion technologies such as oxy-combustion and various oxidation technologies involving oxygen concentrator modules. These oxygen-selective materials function as reversible, single-component solvents that selectively dissolve and separate oxygen from air. Their unique properties, including strong ionic interactions and non-flammability, make them promising candidates for O₂ capture. Additionally, their chemical tunability offers limitless possibilities for designing materials with characteristics optimized for oxygen separation. Since oxygen constitutes a smaller fraction of air than nitrogen (21% vs. 78%), using designer O₂selective materials can result in more efficient systems with a smaller footprint and lower energy requirements compared to N_2 -selective technologies. Recognizing the need for alternative, costeffective oxygen production methods, DOE/NETL has been exploring various approaches, including Ion Transport Membrane (ITM) technology, which has been under development since the 1990s and is currently in the engineering validation phase. Other innovative approaches funded through Small Business Innovation Research (SBIR) grants include oxygen separation using magnetic gradients and redox swing-assisted biomimetic processes. Globally there is considerable interest in the 50 MW demonstration plant being developed in La Porte, Texas, which employs the Allam cycle. This oxy-fuel power cycle has the potential to achieve efficiencies of up to 59% with zero carbon emissions, though it still relies on an air separation unit to supply pure oxygen. Our proposed research methodology aligns with the DOE's mission to develop novel approaches for providing high-purity oxygen for gasification and other energy applications, offering a pathway to more flexible and scalable oxygen generation technologies.

2.0 Research Approach and Findings

Our previous study provided preliminary insights into the O_2 binding mechanism, and we conducted an initial Electron Paramagnetic Resonance (EPR) analysis on the first-generation O_2 -selective materials (Figure 1). EPR spectra were obtained using a Bruker 580 Elexsys X-band spectrometer. The initial findings indicated that the binding process follows first-order kinetics with respect to oxygen, contrary to the second-order kinetics in nitroxide previously reported by Turro and colleagues. Additionally, the observed slight sublinear dependence on nitroxide concentration may be attributed to the solvent system used, warranting further investigation. This research study was focused on achieving the design, synthesis, and fine-tune selective materials with high adsorption capacity for oxygen separation. This will be accomplished by synthesizing and modifying structural analogues of symmetrical imidazolium-based task-specific ionic liquids (TSILs) incorporating two TEMPO units, as illustrated in Figure 2 (left panel). The material will be evaluated to determine whether its symmetry promotes effective oxygen removal or if steric hindrance impedes its performance.



Figure 1: EPR spectra showing variation of O₂ pressure on TSIL.



Figure 2: Symmetrical O₂ selective material and preliminary TEA analysis.

As of next step, to modulate/tune selective materials with high adsorption capacity for oxygen separation we designed and synthesized and symmetrical imidazolium based TSIL with two units of TEMPO installed on it as shown in Figure 4. Our TEMPO derived biradical analogue 6 has shown high absorption capacity of 15wt% which is a huge stride towards designing these Task-specific ionic liquids (Figure 4).





Next, we installed the TEMPO derived biradical analogue 6 on MCM-41 to design a reversible oxygen absorbing system. TEMPO derived biradical 6 (squares) shows that the biradical maintains 3-4 times higher loading at all temperatures which is a significant progress in the practical application of these task-specific ionic liquids.





-20

0

20

40

O₂ gauge pressure (psi)

60

80

Preliminary techno-economic and life-cycle assessment (TEA/LCA) were conducted for air separation using the proposed TSIL-based vacuum pressure swing adsorption (VPSA) technology operating at ambient temperature. As shown in Figures 4 and 5, air is compressed and sent to the VPSA beds filled with TSIL sorbent. A number of sorbent beds is operated in parallel with different absorption/desorption schedule to continuously produce O_2 . In the adsorption step, O_2 is absorbed under pressure, while N_2 and other gases in the air do not interact with the sorbent and are directly vented to the atmosphere. In the desorption step, then the bed is depressurized to release O_2 product. The main energy consumption of the VPSA technology is the electricity used in air compressor and O_2 vacuum compressor.



Figure 6: Process configuration of TSIL based VPSA for air separation.

In this study, a process model was developed in Aspen Plus V14 to estimate the mass and energy balance, where the VPSA beds were modeled as a component separator due to the lack of breakthrough curves and other necessary experimental data for developing a rigorous adsorption cycle model. The O_2 recovery rate (the percent of O_2 in air recovered in the product stream) was set to 50%, similar to that of a commercial VPSA-based air separation technology using zeolite to adsorb N2 (Budner et al., 1999). The experimentally measured O_2 loading data at different O_2 partial pressure as shown in Figure 4 was used to calculate O_2 uptake on the sorbent at different adsorption and desorption pressure. The plant scale was set to 19.7 ton/day, similar to the commercial VPSA technology. In the proposed process, the VPSA beds were sized based on a 200 sec adsorption time and 25 sec desorption time for a 15wt% O₂ uptake on the sorbent, observed through the laboratory operation. The equipment price was estimated using Aspen Process Economic Analyzer (APEA) V14. An overnight cost approach used by PEP Yearbook was used to calculate the minimum O_2 selling price with 15% return on investment before taxes in 2020 U.S. dollars. The prices of TSIL sorbent, cooling water and electricity were set to \$300/kg. ¢12.7/MGAL, ¢3.77/kWh, respectively, to calculate the variable cost. A preliminary LCA study was conducted to estimate the cradle-to-gate greenhouse gas (GHG) emission per kg of O_2 produced based on the life cycle inventory data generated from the Aspen Plus model. Due to the lack of TSIL data, in this study, we only considered the GHG emission associated with utility consumption, of which the carbon intensity of the U.S. grid was collected from GREET database (466 kg CO₂eg/MWh electricity).

A sensitivity study was conducted to evaluate the impact of adsorption and desorption pressure on the economic and environmental performance of the proposed air separation technology, of which the results are shown in Table 1 and Figure 7. As shown in Table 1 and Figure 8, tradeoffs exist between the capital and operating costs. Higher adsorption pressure and lower desorption pressure are preferred to maximize the working capacity of the sorbent (O_2 removal per kg sorbent per cycle) and reduce the capital investment of the adsorption beds. At meanwhile it will result in high power consumptions and capital investment for the air compressor and O_2 vacuum compressor, as well as higher GHG emission. An adsorption pressure of 45 bar (corresponding to a 60 psig O₂ adsorption pressure) and a desorption pressure of 1 bar gives the lowest estimated minimum O₂ selling price (\$0.52/kg). An adsorption pressure of 21 bar (corresponding to 20 psig O_2 adsorption pressure) and a desorption pressure of 1 bar gives the lowest estimated GHG emission (0.57 kg CO_2 eg/kg O_2). The benchmark GHG footprint of O_2 in the 2022 GREET model is 0.20 kg CO₂ eq/kg O₂, estimated based on the large-scale cryogenic process. Figure 6 provides a comparison with the commercial technology and TSIL technology development progress in the past few years. A TEA based on one single experimental point available at the time with an absorption pressure of 60 psig, a desorption pressure of 15 millitorr, a sorbent working capacity of 15 wt% O₂ was conducted in 2020, which gave an estimated minimum O_2 selling price of \$1.11/kg for the TSIL technology. A target case was evaluated at the time assuming O_2 can be regenerated at a much higher pressure with the same sorbent working capacity. The newly collected O₂ loading data collected in 2023's experimental work enabling a data driven sensitivity study to identify the optimal adsorption and desorption pressure to simultaneously reduce cost and GHG emission of the proposed TSIL technology. With the current state of technology (SOT), the minimum O₂ selling price of the TSIL technology is higher than that of the commercially available zeolite technology, because of its higher absorption pressure (>21 bar vs 1.2 bar). One important advantage of TSIL sorbent over zeolite sorbent for O₂ production is that TSIL adsorb O_2 instead of N_2 and therefore has the potential to produce O_2 product with a much higher purity. The commercially available zeolite based VPSA technology can only produce O₂ from air with 90-95% purity. The proposed TSIL technology may become competitive or even better than the industrial benchmark with further development to improve O_2 adsorption at relatively lower pressure and reduce sorbent manufacturing cost.

technology									
Cases	1	2	3	4	5	6	7	8	9
Adsorption									
O ₂ partial pressure (bar)	5.15	5.15	5.15	3.77	3.77	3.77	2.39	2.39	2.39
O ₂ loading (wt%)	15	15	15	11	11	11	7.5	7.5	7.5
Desorption									
O ₂ partial pressure (bar)	1.01	0.46	0.25	1.01	0.46	0.25	1.01	0.46	0.25
O ₂ loading (wt%)	4	2	1	4	2	1	4	2	1
Adsorption pressure ⁽¹⁾ (bar)	45	45	45	33	33	33	21	21	21
Working capacity (wt%)	11	13	14	7	9	10	3.5	5.5	6.5
Sorbent makeup ⁽²⁾ (kg/kg O ₂)	0.07	0.06	0.06	0.11	0.09	0.08	0.23	0.15	0.12
Utility consumption									
Electricity (kWh/kg O ₂)	1.457	1.487	1.511	1.376	1.407	1.431	1.202	1.233	1.257
Cooling water (Gal/kg O ₂)	52.17	51.62	51.09	49.19	48.64	48.12	42.95	42.40	41.88

Table 1: Impact of operating pressure on	O ₂ adsorption p	performance a	and utility	consumptions	of the	TSIL			
technology									

(1) With an O₂ recovery rate of 50%

(2) assuming a sorbent lifetime of 1 year



Figure 7: Impact of operating pressure on key economic and environmental measures of the TSIL technology.



Figure 8: Progress on TSIL technology development and comparison with the commercial technology.

Conclusions:

The escalating demand for pristine energy sources and the quest for enhanced energy efficiency represent some of the most formidable challenges currently confronting the energy sector. Addressing the critical need for advanced approaches to oxygen separation is essential to meet these emerging demands. In this study, we successfully synthesized TSIL-TEMPO ILs and conducted EPR studies, which provided valuable insights into the O_2 binding mechanism. Our findings revealed that the binding is first-order in oxygen, not second-order in nitroxide, as previously reported by Turro and coworkers for other nitroxides.

To enhance selective materials with high adsorption capacity for oxygen separation, we designed and synthesized a symmetrical imidazolium-based TSIL with two TEMPO units. The TEMPOderived biradical analogue 6 demonstrated an impressive absorption capacity of 15 wt%, representing significant progress in the design of task-specific ionic liquids. Furthermore, the installation of the TEMPO-derived biradical analogue 6 onto MCM-41 resulted in a reversible oxygen-absorbing system. This biradical maintained 3-4 times higher loading at all temperatures, highlighting substantial advancements in the practical application of these task-specific ionic liquids. Our preliminary techno-economic and life-cycle assessments indicate that the proposed TSIL technology has the potential to become competitive or even superior to the current industrial benchmark with further development. Improvements in O_2 adsorption at relatively lower pressures and reductions in sorbent manufacturing costs could position this technology as a leading solution in the field. We believe that our research approach has the potential to significantly impact the energy industry by providing a cost-effective and energy-efficient solution for modular gasification and other applications. By leveraging the latest technological advancements, we aim to help reduce the carbon footprint of the energy sector and contribute to the overall sustainability of our planet.

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