FEATURES

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Electro-organic Syntheses for Green Chemical Manufacturing

by Elizabeth J. Biddinger and Miguel A. Modestino

While large-scale electrochemical manufacturing is currently practiced in processes such as chloro-alkali production or aluminum refining,[1,2] significant opportunities exist to implement electrosynthesis routes more broadly for the sustainable production of organic chemicals. Electro-organic syntheses offer an alternative to traditional thermochemical approaches to organic syntheses. In electro-organic syntheses, electrons are used as "green" reactants/products in reduction and oxidation reactions, enabling the utilization of renewable electricity to decarbonize the chemical manufacturing industry. Additionally, environmental advantages of electro-organic syntheses such as minimizing waste generation, utilizing non-fossil feedstocks, and on-demand chemical manufacturing are also large drivers for sustainability in chemical processes across multiple sectors. In this article, we discuss the potential advantages of electro-organic syntheses for green chemical manufacturing (highlighted in Fig. 1), and we provide a perspective on the research and development (R&D) needs to implement electrosynthesis processes at scale.

Green Chemistry Advantages of Electro-Organic Syntheses

Decarbonization of Chemical Manufacturing

The chemical industry outputs >70,000 products that impact >96% of all manufactured goods. This industry supports 25% of the U.S. GDP directly and indirectly and is responsible for ~5 and ~10% of the US and global primary energy consumption, respectively. Thermochemical processes in this industry account for >93% of the energy utilization, >86% in the form of fossil fuel derived heat, leading to 5.5% and 7% of the global CO_2 and total greenhouse gas emissions, respectively.[3-5] Decarbonization of this industry through renewable-energy-powered electrochemical manufacturing would represent a major step towards mitigating global warming. The largest opportunity in this industrial transformation lies in electro-organic synthesis processes, which could result in sustainability improvements for the production of a large number of industrial chemicals, across the commodity organic, specialty, and fine chemicals sectors.

While decarbonizing the thousands of organic processes in this industry is a colossal challenge, electrification of a small subset of the top 18 commodity chemicals would transform >80% of the energy utilization and avoid the emission of >75% of the GHG emissions of the whole industry[5] (Fig. 2(a)). The development of electro-organic manufacturing for some of these products would have a major impact in the wide-spread deployment of electrochemical processes across the industry. Table 1 presents some example opportunities where electrification through electrosynthesis can have a large impact in CO_2 emission reduction. Notably, the electrochemical production of petrochemical feedstocks, such as olefin (e.g., ethylene, propylene) and aromatic (e.g., benzene) compounds from saturated hydrocarbons (e.g., methane, ethane, propane) could have the largest sustainability impact. Recent high-temperature electrolysis examples of these reactions can serve as a starting point to the development of these processes at scale.[6, 7] Further downstream electrochemical functionalization of these feedstocks via selective redox processes can lead to higher value products produced via green and sustainable routes. For example, the selective electrocatalytic oxygenation of ethylene or propylene leading to epoxides,[8, 9] or the electrocatalytic hydrogenation of benzene to cyclohexane,[10] can impact large volume

processes and allow for the integration of renewable electricity as a primary source of energy into chemical manufacturing. Figure 2(b) shows an example network of reactions in commodity chemical manufacturing that could be electrified through electrosynthesis. Most of these reactions are oxidative in nature and if performed electrochemically could be coupled with the reduction of protons (or water) to potentially produce H_2. These paired electrolysis approaches for the production of bulk organic chemicals would result in the production of large amounts of emissions-free H_2, which could support other processes in the industry. For example, the H_2 production rates from a few electro-organic processes could exceed the needs of ammonia synthesis (Figure 2(c)), which source their hydrogen from steam methane reforming leading to stoichiometric amounts of CO_2 emissions.[5]

Waste Minimization

The E(nvironmental)-factor, introduced in 1992, was one of the first metrics developed for the fine chemical and pharmaceutical industries to recognize that the yield of a desired product was not the only important measure of a chemical process; the waste that was generated in the process has a significant environmental impact.[11] The E-factor is calculated as the ratio between the mass of waste generated to the mass of product formed and has led to the re-evaluation of many processes in the fine chemical and pharmaceutical industries. Typically, as the complexity of the synthesis of the chemical product and the value of the product goes up, so does the E-factor. For example, the common E-factors for the major chemical sectors are the following: oil refining <0.1 kg waste/kg product, bulk chemicals <1-5 kg waste/kg product, fine chemicals 5-50 kg waste/kg product, and pharmaceuticals 25 - >100 kg waste/kg product.[11] The use of stoichiometric reagents and non-recyclable solvents drive the E-factors up significantly. While replacing many reactions that use
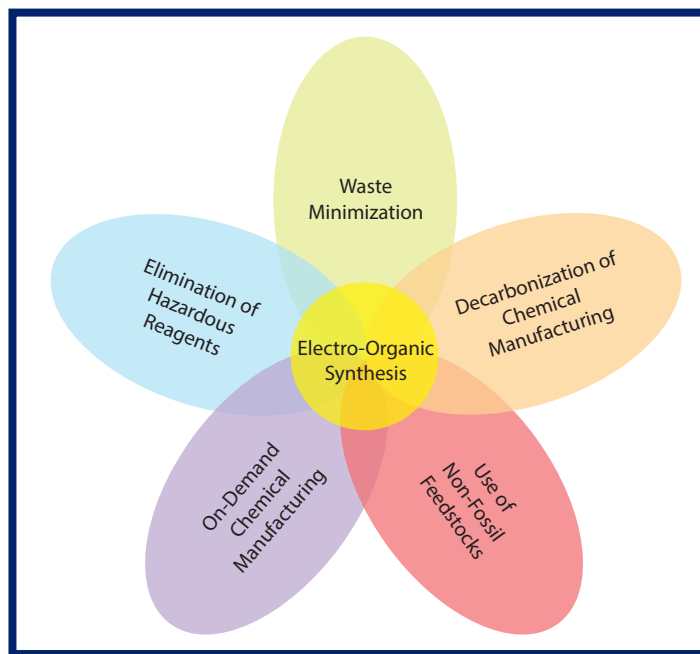
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Fig. 1. *Green chemistry advantages of electro-organic synthesis.*

stoichiometric reagents with catalytic reactions has been a significant step forward, many of the homogeneous catalysts implemented are only used once in the process, resulting in significant downstream waste generation.

Electrochemical syntheses can be used as a replacement to stoichiometric reagents as well. In this case, the electron replaces the reducing agent as a reactant or the oxidizing agent as a product, eliminating a significant waste stream. For example, the industrial synthesis of DL-homocysteine, an intermediate for the drug Citiolone, from DL-homocystine was switched from a conventional homogeneous method that used zinc and acid as the stoichiometric reducing agents to an electrochemical method.[12] In the conventional method, undesired hydrogen gas was evolved, and more than 2 tons of zinc salt waste were formed per ton of reactant processed. In the electrochemical process, both the zinc salt and hydrogen gas were eliminated as emissions. The electrochemical process was successfully implemented at a scale of 30 tons/year and operates at a conversion of 95%.[12]

Elimination of Hazardous Reactants or Intermediates

While reducing waste generated in a process lowers the E-factor, the E-factor does not distinguish the wastes generated in terms of environmental or safety risks associated with the use of harsh reactants or intermediates. The use of these reactants can be eliminated through the in-situ generation of reactive intermediates via electro-organic syntheses.[13] For example, through the use of

TEMPO $(2,2,6,6$-tetramethyl-1-piperidin-1-oxo,R_2N-O$^-$/R_2N=O$^+$) – mediated electrochemical reactions, toxic chromium VI compounds can be eliminated from oxidation reactions.[13] The selectivity of the reaction can be controlled through tuning the length of the R-groups in TEMPO and the potential that the reaction is operated at. In mediated electrochemical reactions, the electron is transferred between the electrode and the mediator compound and then the mediator acts as an activated homogeneous catalyst with the reactant before being regenerated at the electrode. This also means that only a catalytic, rather than a stoichiometric, quantity of the mediator is required in the reaction, reducing the quantity of chemicals required for a reaction to proceed.

Using Non-Fossil Feedstocks

The ability to tune reactions using potential as a driving force and the modular nature of electrochemical reactions also lend themselves well to the utilization of non-fossil distributed feedstocks.

Carbon dioxide is probably the most researched of non-fossil feedstocks for the production of chemicals electrochemically. CO_2 is a notoriously stable compound and requires significantly high temperatures and pressures to reduce it using thermochemical methods. Electrochemically, CO_2 can be readily reduced at atmospheric temperatures and pressures. CO_2 to carbon monoxide has been demonstrated at scale, and is on a path towards commercialization using electrochemical reactors[14-16] as a means of obtaining a renewable syn gas component. At ambient to near ambient conditions, a variety of products can be formed through the electroreduction of CO_2, including carbon monoxide, formic acid, methane, ethylene, and ethanol, depending upon the catalyst and
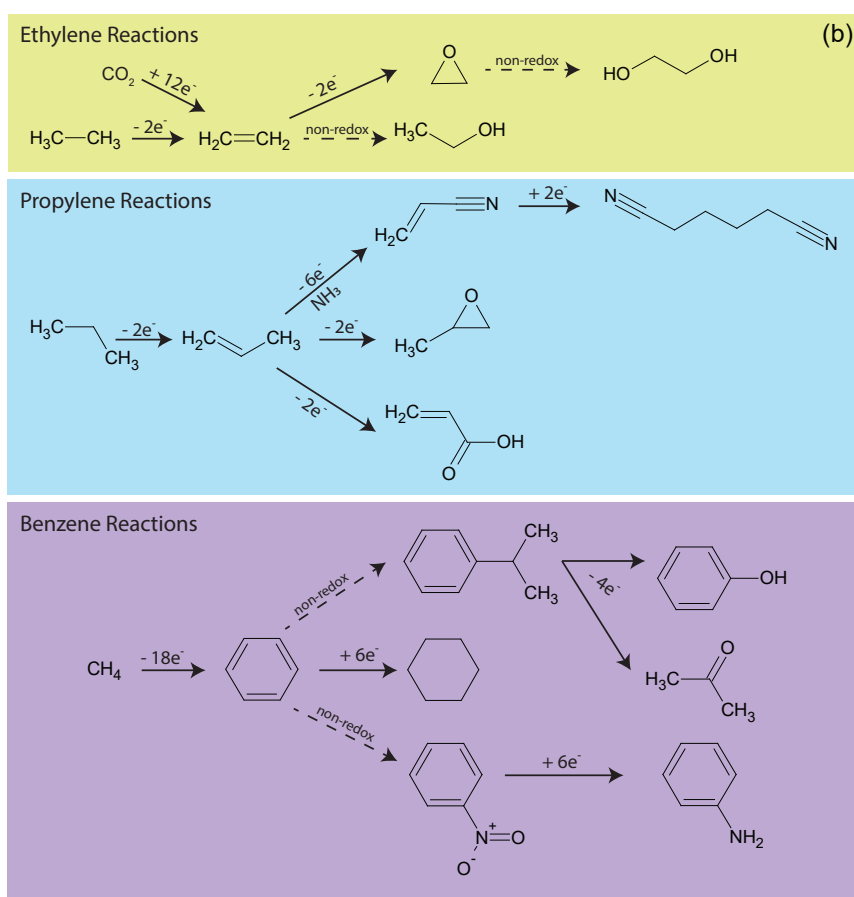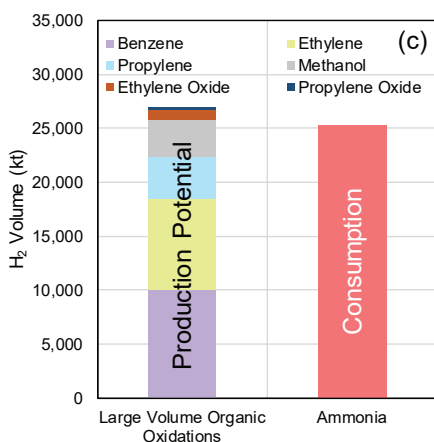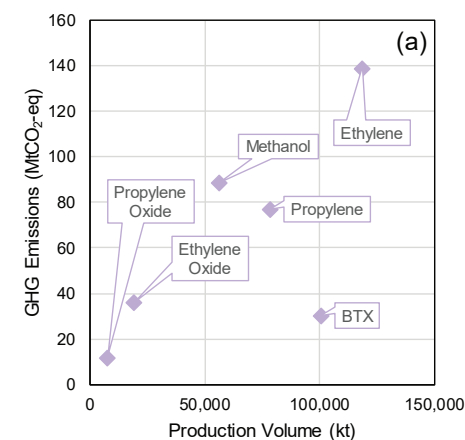

Fig. 2. *(a) Global production volumes and greenhouse gas emissions from large commodity organic chemicals. (b) Network of reactions involving ethylene, propylene, and benzene, including possible redox and non-redox reactions. (c) Possible hydrogen production volumes from paired electrolysis involving electro-organic oxidations and proton reduction at a global scale. The hydrogen production level obtained from the production of six major chemical products would exceeds the needs for ammonia synthesis. Values calculated based on information from Ref. 5.*

Table 1. Current typical production methods and possible electro-organic routes for the production of example commodity organic chemicals.

Chemical Product	Current Typical Production Method	Possible Electro-organic Reactions
Ethylene	Steam cracking of ethane	$C_2H_6 \rightarrow C_2H_4 + 2H^+ + 2e^-$ or $2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$
Propylene	Steam cracking of propane	$C_3H_8 \rightarrow C_3H_6 + 2H^+ + 2e^-$
Benzene	Catalytic reforming of naphtha	$6CH_4 \rightarrow C_6H_6 + 18H^+ + 18e^-$
Ethylene Oxide	Direct oxidation of ethylene	$C_2H_4 + H_2O \rightarrow C_2H_4O + 2H^+ + 2e^-$
Propylene Oxide	Cl_2 mediated oxidation of propylene	$C_3H_6 + H_2O \rightarrow C_3H_6O + 2H^+ + 2e^-$
Methanol	Syngas Conversion	$CH_4 + H_2O \rightarrow CH_3OH + 2H^+ + 2e^-$ or $2CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$

reaction conditions.[16, 17] When renewable electricity is utilized in the reactions, the products carbon monoxide, formic acid, ethylene, and ethanol can all be synthesized with negative net CO_2 emissions when high energy conversion efficiencies are obtained.[18]

The modular nature of electrochemical systems also is amenable for use in the upgrading of biomass-derived species. To maintain economic and environmental value, biorefineries will be distributed, small facilities located within only a few miles of the source of the raw biomass (to reduce costs and CO_2 emissions from transportation). Many products from the biorefinery (beyond ethanol) obtained through fermentation or pyrolysis, require additional upgrading to improve stability and add value. Biomass upgrading depots (BUDs)[19, 20] have been proposed as skid- or multi-skid-sized facilities co-located with the biorefinery to upgrade the initial products. These facilities will not have the universal feedstocks that are regularly available at the petrochemical facilities (e.g., high-pressure hydrogen), will likely operate more intermittently than traditional chemical plants, and will be much smaller than the oil and gas refinery. Electrochemical hydrogenation units have been proposed as an alternative to having high pressure, high temperature catalytic hydrogenation units at the BUDs and when paired with solar energy exhibit favorable energy, mass, and carbon efficiencies.[20] Biomass-derived species, such as phenolic compounds,[21, 22] furanics,[23, 24] other aldehydes[25] and pyrolysis product mixtures,[21, 26] for example, are particularly amenable to electrochemical hydrogenation. There are also opportunities to perform electro-oxidation reactions on biomass feedstocks, including lignin[27] and furanics,[24, 28] or for processing of the aqueous waste stream obtained during pyrolysis of biomass.[29] The electrochemical oxidation reactions could be paired with the electrochemical hydrogenation reactions to double the electron efficiency, lower the cell voltage compared to using oxygen evolution as the anodic reaction and minimize capital costs.[13, 28, 30]

On-Demand Chemical Manufacturing

The modular nature of electrochemical systems and ambient operating conditions can allow for the production of chemicals on-demand in a distributed fashion. This can reduce emissions and safety risks from transporting feedstocks or products long distances and from storage in large quantities. On-demand ammonia for fertilizer is one such case that could be possible. While the electroreduction of nitrogen into ammonia currently struggles with very low Faradaic efficiencies,[31] an additional outcome beyond decarbonization is that ammonia could be synthesized on-demand for the production of fertilizers. This reduces the need to store and ship large quantities of hazardous ammonia, lowers the carbon footprint of transportation, and provides access of valuable fertilizer to regions of the world where distribution channels for ammonia are not readily available. Similar opportunities exist to install electro-organic syntheses for on-demand delivery of many other chemicals.
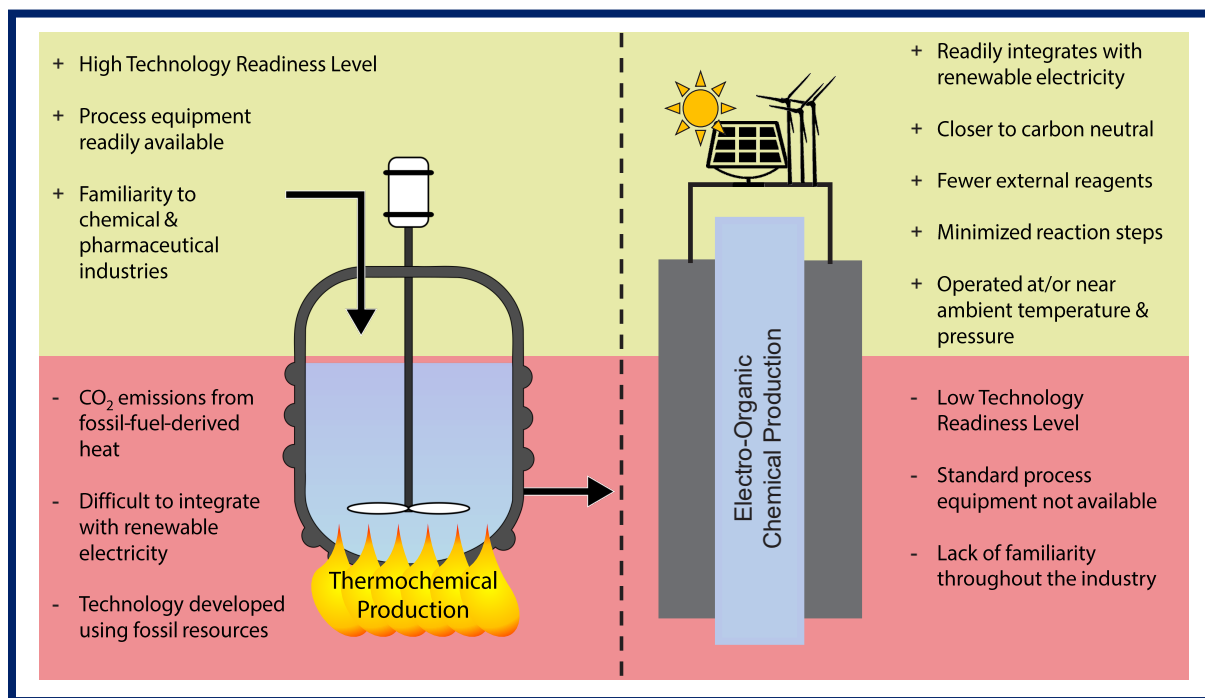
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FIG. 3. *Comparison of advantages and disadvantages for traditional and electro-organic chemical production.*

Pathways to Green
Electro-organic Manufacturing

Achieving wide-scale implementation of electro-organic syntheses in chemical manufacturing would require the development of stable, scalable and cost-effective processes that operate at high production rates (i.e., current densities), high selectivity and high-energy conversion efficiency. Meeting these performance metrics in electro-organic processes is particularly challenging as most reactions are limited by the low solubility of organic reactants in inexpensive aqueous electrolytes and the presence of multiple reaction pathways that lead to undesired by-products and lowers the reaction selectivity.[32] In addition to these fundamental challenges, the scale-up and implementation of these processes for bulk-chemical production is hindered by significant barriers due to a lack of standard and easily accessible electrochemical manufacturing equipment, an issue further compounded with the limited expertise on electrochemical manufacturing methods in most industrial settings.

Electrochemical engineering strategies can enable pathways to achieve practical processes that are highly selective and efficient at production scales. Electrocatalyst design approaches can aid in lowering the overpotential of reactions, enhancing their energy conversion efficiency, and can promote selective bond formation or cleavage events to enhance their selectivity. Electrocatalytic approaches have been demonstrated to assist in the selective hydrogenation of unsaturated hydrocarbons,[10] oxygenates,[33] nitriles,[34] or nitro[35] compounds. Electrocatalysis can also play a key role in oxidative reactions such as the epoxidation of olefins,[8, 9] the activation of C-H bonds in hydrocarbons,[6, 7] or the selective oxidation of oxygenates.[36] Additionally, electrochemical reaction engineering approaches can enhance the performance of reactors by mitigating mass transport challenges associated with the low solubility of organic reactants. These approaches include formulating electrolytes with enhanced solubility for organic reactants (e.g., addition of surfactants,[37] co-solvents,[34] controlling the pH,[23] use of novel solvents like ionic liquids[38]), or controlling the electrolyte environment in the electrochemical double layer (EDL) or the near-electrode region to facilitate desired reactions and suppress the production of byproducts (e.g., implementing supporting electrolytes that passivate the electrode surface and prevent undesired species from participating in electrochemical reactions[37]). Process intensification strategies can also improve the economic viability of electro-organic processes. The mesoscale structure of electrodes plays a key role on the performance of electrochemical devices, and can help to increase the active surface area of the electrocatalysts and the achievable current densities. Electrode nanostructuring strategies have already led to high current density devices in many other electrochemical technologies, including water[39] and CO_2 electrolyzers,[40, 41] and would certainly play a role in electro-organic synthesis at scale. Membrane-separated reactors will also be important in the future implementation of organic electrosynthesis processes, as they can lead to significant enhancements in energy conversion efficiency and reductions in manufacturing costs. In these reactors, the cathodic and anodic compartments are separated by ion-conducting membranes that enable the simultaneous but physically separated co-production of valuable oxidation and reduction products. Membranes also allow for the independent optimization of cathodic and anodic reaction conditions and can reduce the inter-electrode distance to minimize ohmic losses – especially in zero-gap reactors where membrane-electrode assemblies are implemented. Membrane-separated electrolysis approaches are already implemented in large-scale electrochemical processes (e.g., chloro-alkali, water electrolysis), but are much less developed for electro-organic reactions where the organic reactants and products can significantly lower the conductivity and stability of membranes.[42]

Learnings from existing large-scale organic electrosynthesis processes, such as adiponitrile (ADN) production (the largest electro-organic synthesis process implemented in industry[43-45]), can help accelerate the deployment of new promising electro-organic reactions in industry. This process is based on the cathodic electro-hydromerization of acrylonitrile (AN) to ADN in an undivided electrochemical cell.[43, 46] The cell uses a two-phase liquid electrolyte composed of an aqueous ion-conducting phase and an organic rich phase containing the reactants and products. The aqueous electrolyte implements a combination of a phosphate buffer, which controls the pH and provides supporting ions to lower the ohmic resistance of the cell, tetra alkyl ammonium salts that enhance the solubility of the organic reactants and controls the environment near the EDL to promote high-selectivity towards ADN production, and a chelating agent to prevent the electrodeposition of undesired metal cations in the cathode.[37] Cadmium or lead are commonly used as cathodes given their high overpotential for the hydrogen evolution reaction (HER), which helps minimize this parasitic cathodic reaction. Given the low solubility of AN in the aqueous electrolyte, the electro-organic reaction rates are mass transport limited, which is usually mitigated by increasing convection transport rates (e.g., by introducing turbulence promoters), or as recently proposed by dynamically modulating the electrode potential.[47] Similar electrochemical cell design, electrolyte formulation, and transport control strategies are translatable to other emerging electro-organic synthesis processes.[48]

Ultimately, for electro-organic syntheses to be implemented industrially, it will need to outcompete traditional thermochemical production methods at scale. The promising technical, economical, and/or environmental advantages highlighted in this article (and summarized in Fig. 3) have led to an increased interest towards organic electrosyntheses in recent years, but realizing significant environmental and economic gains will require large R&D and workforce development efforts aimed at bringing technological advances from the lab to manufacturing scale.

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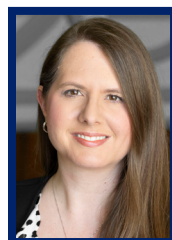
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