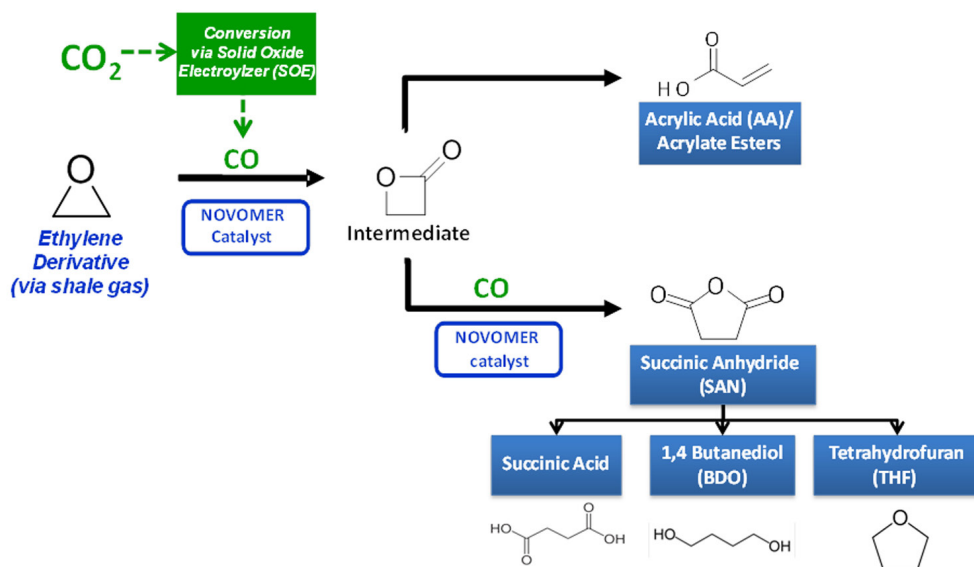


Conversion of Waste CO₂ and Shale Gas to High-Value Chemicals

Enabling high-yield, low-cost, low-temperature production of chemical intermediates

Chemical intermediates, typically derived from crude oil, are building blocks that undergo additional reactions to produce a wide variety of commercial products. For example, acrylic acid can be used to make the components of paints, adhesives, or absorbent polymers used in personal hygiene products such as diapers. Currently, imports account for about half of the total U.S. crude oil supply, are subject to major price swings, and are relatively expensive. Additionally, typical chemical production processes tend to be energy intensive due to low selectivity and high operating temperatures.

This project will combine two unique systems into one semi-integrated laboratory-scale continuous process that can produce a variety of chemical intermediates—including acrylic acid—with significantly lower energy requirements and a smaller carbon footprint, and at a lower projected cost than today's petrochemical versions. The first process will convert waste carbon dioxide (CO₂) from industrial sources to carbon monoxide (CO) using a solid oxide electrolyzer (SOE). The SOE cell will be adapted for combustion-assisted electrolysis, which provides the energy required for the reduction process as well as reduces the electrical potential to initiate the reduction reaction. The CO from this process will be combined with an ethane derivative from shale



Schematic illustrating the Novomer/Praxair semi-integrated process to produce high-value chemical intermediates. *Graphic image courtesy of Novomer.*

gas, ethylene oxide, using a novel highly selective catalyst to form a versatile intermediate called beta-propiolactone (BPL). The BPL can be converted into acrylic acid using known technologies or combined with another CO molecule to make succinic anhydride (SAN). SAN can be easily converted into succinic acid by adding water or through hydrogenation to make butanediol or tetrahydrofuran.

Benefits for Our Industry and Our Nation

Using waste CO₂ and ethane derivatives as feedstocks for high-value drop-in chemicals has many benefits, including the following:

- Increasing energy productivity of chemical manufacturing by 30%–70% compared to existing technologies, depending on the target chemical.
- Waste CO₂ is converted to CO and incorporated into certain organic chemicals, providing a significant portion of the carbon structure.

- Increasing production of chemical intermediates from domestically-produced, ethane-rich shale gas.
- Decoupling the price of chemicals produced using this technology from crude oil, as well as reducing oil imports.

Applications in Our Nation's Industry

This technology could provide the chemical industry with a low-energy, cost-effective method of producing important chemical intermediates. The technology can be integrated seamlessly into the existing infrastructure. In addition to the chemical industry, a range of industries throughout the supply chain will benefit from the technology, including the paint and coating, textile, and polymer industries.

Project Description

The project objective is to develop, build, operate, and validate a semi-integrated laboratory-scale continuous process that converts waste CO₂ from industrial sources and ethane derivatives from shale gas into commodity chemical intermediates. The chemicals include acrylic acid, acrylate esters, butanediol, tetrahydrofuran, and succinic acid, which have applications in paints, coatings, textiles, diapers, and polymers, among other products. The technology relies on a catalyst that is 99% selective, operates at a lower temperature, and utilizes domestic shale gas in addition to waste CO₂, resulting in dramatically reduced energy and carbon footprints and potentially much lower production costs compared to current technology.

Barriers

- Establishing a cost-effective, low-energy process for generating CO using a combustion-assisted SOE cell.
- Producing sufficient amounts of CO to adequately test the semi-integrated technology.
- Developing a reactor system that satisfies both performance and economic requirements while operating in semi-continuous mode.

Pathways

Project partners are developing the carbonylation process and the SOE technology separately before semi-integrating them in a laboratory-scale process. For the carbonylation process, the major unit operations have been tested and evaluated individually to ensure key process parameters are well

understood before integrating into a single process. As a result, Novomer has connected the major unit operations and the system is being operated continuously with catalyst recycle.

SOE cell electrode and electrolyte materials have been tested and preferred compositions have been selected and used to manufacture SOE cells. Single SOE cells have been operating continuously for extended periods of time. A multi-cell SOE short stack will be assembled and tested to assess potential issues with combustion-assisted electrolysis technology scale-up.

To semi-integrate the two processes, the research team will analyze the CO generated from the SOE process to determine its purity and composition. The team will prepare CO gas to the same specifications and deliver it to the carbonylation process. The team will adjust the carbonylation design to accommodate the CO from the SOE cell.

Milestones

This 2.5 year project began in 2013.

- Develop a detailed process diagram of an integrated laboratory-scale carbonylation process based on individual evaluation of the test reactor and separation systems (Completed).
- Assemble the SOE cell and select preferred cathode and anode compositions for combustion-assisted CO/CO₂ electrolysis (Completed).
- Assemble a continuous carbonylation process, including process control instrumentation, to ensure system monitoring and data collection (Completed).

- Demonstrate successful operation of combustion-assisted electrolysis for reduction of CO₂ to CO at both ambient and elevated pressure (2015).
- Produce high-value chemicals from the carbonylation process using CO from the SOE cell (2016).

Commercialization

At the conclusion of the project, researchers will work with an industrial chemical partner to build a pilot plant capable of producing 2,000 metric tons (MT) of acrylic acid per year. Researchers will also work with partners to design, build, and operate an SOE engineering prototype capable of producing 20 MT of CO per year. An integrated commercial unit that combines both technologies will be built after the successful operation of the pilot plants. The technology will be further licensed to other chemical companies to ensure wide adoption and rapid deployment.

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