FLAMELESS COMBUSTION: CHEMICAL LOOPING ETHANE TO ETHYLENE

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ORIGINAL PROJECT TITLE: Electrogenerative System for Co-Production of Green Liquid Fuels and Electricity from Methane
PROGRAM: OPEN 2012
AWARD: $4,665,228
PROJECT TEAM: EcoCatalytic (Bio2Electric, LLC) (Lead), North Carolina State University, Particulate Solid Research Inc., KBR, Inc.
PROJECT TERM: February 2013 – July 2017
PRINCIPAL INVESTIGATOR (PI): John Sofranko

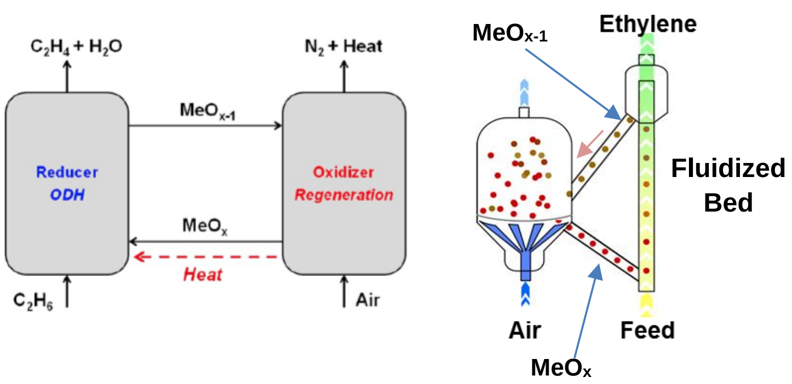
TECHNICAL CHALLENGE

Ethylene is a major chemical feedstock, with 24 million metric tons produced domestically as of 2010[1]. In the United States, ethylene is primarily produced in steam crackers from ethane, a byproduct of natural gas production. Domestic ethylene production consumes over 400 Trillion British Thermal Units (TBtu) per year and releases over 30 million tons of carbon dioxide and harmful nitrogen oxides. One alternative to steam cracking of ethane is oxidative dehydrogenation (ODH), where ethane and oxygen react over a catalyst to form ethylene. ODH has a modest external heat requirement, and because air is exluded from the reactor, no nitrogen oxides are formed. However, supplying pure oxygen typically requires a cryogenic air separation unit, which negates the cost and energy savings. The highly volatile, capital intensive, commodity chemicals industry requires new technologies to be competitively priced as well as environmentally beneficial to enable adoption.

TECHNICAL OPPORTUNITY

An alternative to providing pure gas-phase oxygen is to combine the catalyst with oxygen in a metal-oxide compound (MeOx). Circulating fluid bed chemical looping reactors use such oxygen transfer agents to promote chemical reactions, as illustrated in Figure 1. The oxygen transfer agent catalytically provides the oxygen to oxidize ethane to ethylene, producing water as the only major byproduct. The oxygen transfer agent then reacts with oxygen (regeneration) in a stream of air, at the same time producing heat to support the reduction process. By avoiding an air separation unit, these reactors are net exporters of energy in contrast to the energy intensive conventional processes. Chemical looping reactors have traditionally been used in combustion-related applications, and with innovation, chemical looping oxidative dehydrogenation offers an opportunity to reduce the energy emissions footprint of production of ethylene from ethane.

Figure 1: Chemical looping oxidative dehydrogenation technology prevents air exposure for the reaction, ensures simultaneous engagement of the reactant with oxygen and the catalyst, and reduces energy use and emissions. A fluidized bed reactor design enables continuous processing.



INNOVATION DEMONSTRATION

The EcoCatalytic team's goal was to convert ethane to ethylene with reduced energy and emissions by way of chemical looping oxidation. This required developing an oxygen transfer agent that is chemically and physically robust to cycling between air and

[1] Bandwidth Study on Energy Use and Potential Energy Saving Opportunities in U.S. Chemical Manufacturing, U.S.DOE Advanced Manufacturing Office, June 2015.

feed reactors and that will facilitate ethylene production from ethane with high conversion and selectivity. They also needed to design a reactor system that balances the mass and heat flows for maximum efficiency.

The team adapted a metal-oxide catalyst to provide the properties needed to carry out the reaction in a fluidized bed configuration. This requires that the metal oxide material be fabricated into robust particles of similar size and strength to fluid catalytic cracking (FCC) catalysts (70-100 μm diameter). The development process involved adding different metal oxides to the mix of materials, and testing them for activity, selectivity, cyclability, and physical durability through experimentation and simulation. Cost has also been a crucial criterion in the selection process. The team developed a cyclable oxygen transfer agent that charges in air and reacts with ethane to produce 70% yield of useful products, of which ethelyne is the primary output.

The team expended considerable effort in developing the reactor design, shown schematically in Figure 1. After extensive simulation of different designs, the team is now comissioning a 10 kWth[2] chemical looping reactor that they will use to test their materials and reactor design. This laboratory-scale reactor, which will produce ethylene at a rate of up to 30 kg per day, is scheduled to be complete by June 2017. Their process models, validated by industrial partners and external consultants, indicate that their chemical looping oxidative dehydrogenation is projected to reduce total ethylene production costs by at least 20% and reduce carbon dioxide emissions, nitrogen oxide emissions, and production energy each by over 80%.

PATHWAY TO ECONOMIC IMPACT

EcoCatalytic partnered with engineering, procurement, and construction company KBR to develop a techno-economic analysis of their technology and to validate estimates of energy use and emissions. Their analysis indicates that chemical looping oxidative dehydrogenation of ethane to ethylene has an improved emissions profile over the state of the art and an improved economic profile, with a total cost of production that is 20% less than traditional steam cracking. Thus, EcoCatalytic's technology has the potential to displace exisiting ethylene production, resulting in increased energy efficency and reduced emissions.

Upon validating these models in their 10 kW reactor, EcoCatalytic will work with commercialization partners to validate their results at a larger pilot scale of 100 kW to 2 MW, equivalent to 0.5 to 10 metric tons of ethylene per day. To achieve this scale, the team is looking for opportunities in retrofitting existing reactors with an estimated initial capital investment of about $5 million. The company is currently targeting business development for applications where reduced nitrogen oxide is a compelling value proposition, such as in the EPA non-attainment zones along the U.S. Gulf Coast.

LONG-TERM IMPACTS

EcoCatalytic's technology is showing potential to lower the cost of ethane to ethylene production by 20%, thereby injecting competitive advantages into this industry that provides about 85,000 jobs nationwide[3]. As of 2010, the United States produces 24 million metric tons of ethylene per year[1], constituting an output of $30 billion in a global market worth over $150 billion.[4]

Ethylene production in the United States consumes 400 TBtu of energy per year and releases 30 million tons of carbon dioxide into the atmosphere. Replacement of conventional ethylene production technology with chemical looping oxidative dehydrogenation has the potential to decrease energy consumption by over 300 TBtu per year and carbon dioxide emissions by over 25 million tons per year.

More broadly, the demonstration of a successful dehydrogenation process for ethane, may also open development opportunities for similar improvements in other industrial chemical processes.

INTELLECTUAL PROPERTY AND PUBLICATIONS

As of January 2017, the EcoCatalytic team's project has generated three invention disclosures to ARPA-E and one U.S. Patent and Trademark Office (PTO) patent application. The team has also published the scientific underpinnings of this technology in the open literature. A list of publications is provided below:

Haribal, V. P., Neal, L. M., & Li, F. (2016). Oxidative dehydrogenation of ethane under a cyclic redox scheme–Process simulations and analysis. Energy. http://dx.doi.org/10.1016/j.energy.2016.11.039

[2] Thermal, as opposed to electric.

[3] Estimated based on the total U.S. production volume and employment projections released by Louisiana Economic Development: https://www.opportunitylouisiana.com/led-news/news-releases/news/2016/06/14/lotte-chemical-axiall-break-ground-on-$3-billion-complex-in-louisiana

[4] http://mediatracking.com/npcapp/bounce.aspx/mynewsclips/30076/0/bXlOZXdzQ2xpcHMgUlNTIFVzZXI~/1193056782

Neal, L. M., Yusuf, S., Sofranko, J. A., & Li, F. (2016). Oxidative Dehydrogenation of Ethane: A Chemical Looping Approach. Energy Technology, 4(10), 1200-1208.