

Fossil Energy Topic 1: Multi-functional Catalyst Research and Development –

Methane Upcycling for Sustainable Domestic Oil Production through Reduction of Flaring

The conversion of natural gas associated with oil production into value-added products is potentially an attractive alternative to flaring in areas where pipelines do not exist to move the gas to markets. However, in most instances, existing technologies are not economical for this application. The development of transportable, low-cost, modular processes for converting natural gas to marketable products (e.g., CNG, LNG, synthetic fuels, chemicals, electricity) in the field are needed to sustain current domestic oil production, reduce the waste of natural resources, and mitigate emissions associated with flaring.

Significant anthropogenic emissions of the greenhouse gases methane (CH₄) and carbon dioxide (CO₂) often occur together or in proximity to one another. Examples include oil and gas production sites, gas processing plants, landfills, and anaerobic digesters used in wastewater and other organic waste treatment. The primary strategy being employed by the oil and gas industry today to dispose of this “stranded gas” is flaring, which can be effective in reducing methane emissions by better than 98%, if operated efficiently. However, the CO₂ produced via combustion is subsequently released to the atmosphere. Since CH₄ is roughly a twenty times more potent greenhouse gas than CO₂, this results at best in a net greenhouse gas emissions reduction of 95% on a CO₂ emissions-equivalent basis, not accounting for any CO₂ originally present in the gas being flared. At face value, this would appear to be an efficient strategy for addressing anthropogenic methane emissions. However, globally, the amount of methane emissions being mitigated by flaring is huge and is increasing with the growth in demand for oil and gas.¹ This has prompted the World Bank to promote a worldwide effort to achieve zero routine flaring by 2030. The cumulative amount of natural gas being disposed of by flaring is also a tremendous lost economic opportunity. New technologies to productively capture and utilize this methane, as well as ethane or CO₂ often associated with it, could provide both meaningful greenhouse gas reductions and economic benefits.

R&D Need

Commercial technologies are available to convert natural gas to liquid fuels and chemicals; however, currently all rely on conversion of the gas, primarily methane, into synthesis gas, a mixture of hydrogen and carbon monoxide. The synthesis gas is then converted in subsequent process steps into methanol, dimethyl ether, synthetic jet and diesel fuel, or other products. This *indirect* conversion approach is thermodynamically inefficient and capital intensive, requiring large production facilities in order to achieve sufficient economies of scale to be profitable. Thus, the process is only commercially competitive where natural gas deposits are large and it is uneconomical to transport to market (i.e. remote locations), or the desired product (e.g., methanol) cannot be easily produced from other resources. The indirect conversion pathway going through synthesis gas to produce fuels and chemicals is almost one hundred years old and existing commercial technologies are mature. Therefore, it is unlikely that more than incremental improvements can be achieved through further R&D

¹ Thousands of gas flares at oil production sites around the globe burn approximately 140 billion cubic meters of natural gas annually, causing more than 300 million tons of CO₂ to be emitted to the atmosphere (World Bank).

on the indirect pathway.

The *direct* conversion of methane to fuels and chemicals has the potential to be more efficient and lower cost. However, R&D to date has been unable to solve a key technical challenge for this approach. Methane is a very stable molecule and must be activated to a high-energy transition state before it can further react to produce more-stable, complex chemical products. The activation process is very difficult to control, resulting in poor selectivity to desirable products. Substantial R&D in this area was sponsored by DOE (METC and PETC, predecessors to NETL) in the 1980s and 1990s.

More Recently, DOE ARPA-E has funded R&D focused on developing transformational technology to solve this problem by employing biological systems (REMOTE program). *Methanotrophic* organisms are capable of metabolizing methane. Natural methanotrophs display high selectivity but low methane conversion rates. Research teams are attempting to genetically evolve/modify organisms to solve this problem, but progress has been slow and major biological hurdles still remain for this pathway. The province of Alberta and the not-for-profit Climate Change and Emissions Management Corporation (CCEMC) have also sponsored R&D aimed at developing breakthrough technologies to convert methane, along with carbon dioxide, via both direct and indirect chemical pathways. The ARPA-E and CCEMC efforts represent less than twenty distinct R&D projects for the direct conversion of methane (and carbon dioxide) to fuels and chemicals, which have Technology Readiness Levels (TRLs) ranging from two to four.

Elements of DOE-AMO's Advancement in Process Intensification Deployment (RAPID) Institute and NSF's recently launched Engineering Research Center for Innovative and Strategic Transformation of Alkane (CISTAR) are relevant to the reduction of associated gas flaring. However, these efforts have a broad focus and are not directly aligned with DOE-FE program goals. The EPSCoR opportunity could leverage the research under these other initiatives to accelerate the deployment of methane conversion technologies to reduce flaring. While considerable progress has been made in recent years, no single technology has been able to solve all the problems associated with the direct conversion of methane alone, or in combination with ethane and/or CO₂, into value-added products, and none have been able to advance much beyond small-scale demonstration. Additional R&D examining other novel conversion pathways and technologies is needed to adequately explore this important and challenging R&D space. DOE's Fossil Energy R&D Program is in the early stages of identifying and assessing the viability of new and novel materials, equipment and processes that could be used to address associated gas flaring, and direct conversion of methane is one area of interest.

Other Challenges

In addition to the activation of methane, the development of technology for the direct conversion of methane (along with ethane and carbon dioxide to fuels and chemicals), as a means of reducing flaring, possesses some unique challenges. These are:

1. Remote locations and decentralized nature of oil and gas production and gas processing operations

2. Short duration of oil and gas field operations generating flare gas
3. Intermittency of methane releases and variability in the quantity of gas to be processed
4. Relatively small amounts of gas to be processed at a single production site
5. Quality of gas to be processed including variable methane, ethane and carbon dioxide content
6. Gas treatment requirements to remove natural gas liquids (NGL) and other impurities upstream of the conversion step

For a conversion technology to be effective under these circumstances will require major breakthroughs in the areas process intensification and modularization. The ideal technology should possess high conversion and selectivity, and involve a minimum number of process steps. High reaction and mass and heat transfer rates will be necessary to minimize equipment size, while low operating severities will be required due to the lack of utility services at remote locations. Mobile systems that can be easily commissioned, de-commissioned and relocated to a new drilling site are desirable. *These constraints will need to be addressed from the start of any development program to ensure all aspects of the proposed conversion technology move forward at a meaningful pace.*

Benefits

In the immediate future and beyond, increasing flaring of natural gas could stifle oil and gas production in the U.S. Methane upcycling is a means of addressing both the environmental and climate impacts of flaring, while improving the bottom line for oil and gas producers. If they can be successfully developed and demonstrated, direct conversion technologies may also have applications outside of the oil and gas industry for controlling emissions from landfills, refineries and chemical plants, and possibly controlling some types of fugitive emissions (e.g., within the U.S. and globally, abandoned oil and gas wells, some dating from the 1800s, are leaking methane and other emissions into the atmosphere). Other spin-off technology applications based on the invention of new materials, equipment and processes are also likely outcomes from this transformational R&D effort.

Fossil Energy Topic 2: Selenium Reclamation from Amine Solvents

Carbon Capture

Carbon capture involves separating and removing carbon dioxide (CO₂) from a gas stream before it is emitted to the atmosphere. Separation of gases requires energy. The minimum energy required for gas separation can be calculated based on thermodynamic principles associated with mixing. If you start with pure nitrogen (N₂) and pure CO₂ in a box separated by a divider and then remove the divider, the N₂ and CO₂ will mix spontaneously, increasing entropy (disorder) and decreasing exergy (useful work or energy). The gas separation process involves re-separating the CO₂ and N₂. The exergy lost by mixing represents the minimum work (energy) required for separation. The minimum work required for CO₂ separation is a function of partial pressure, or CO₂ concentration. The work required for separation increases rapidly as the partial pressure decreases. This results in increased energy requirements and costs associated with capture from low-CO₂-concentration gas streams such as flue gas from coal- and natural gas-based power production.

Amine-Based Capture

Removal of CO₂ from industrial gas streams is not a new process. Gas absorption processes using chemical solvents, such as amines, to separate CO₂ from other gases have been in use since the 1930s in the natural gas industry and to produce food and chemical grade CO₂ from gas streams containing three to 25 percent CO₂. Amine absorption systems are still the most common technology used for CO₂ separation. These systems are typically installed downstream from conventional pollution control equipment. Flue gas exiting conventional treatment is contacted with the amine solvent in an absorption column, also referred to as an absorber, and CO₂ in the gas is transferred to the solvent. The CO₂-rich solvent from the absorber is then regenerated so that it can be re-used. Chemical solvents are usually regenerated by raising the temperature to release CO₂. This typically occurs in a desorption column, also referred to as a stripper. Advances in technology supported by the Carbon Capture R&D Program have resulted in increased efficiencies for amine-based capture systems that have reduced costs from over \$100/tonne captured in the 2005 timeframe to values approaching \$40/tonne captured for 2nd-generation amine-based technologies.

Concentration of Flue Gas Contaminants

One of the remaining challenges associated with amine-based capture technologies is that the amine solvents tend to concentrate contaminants present in flue gases. It is widely recognized that amine solvents selectively capture sulfur, resulting in the formation of heat stable salts that degrade CO₂ capture performance. Solvent reclaimers are commonly used to periodically remove these salts and extend the useful life of the solvent. However, metals commonly found in flue gas such as barium, selenium, arsenic, cadmium, lead, mercury, and silver, present additional challenges. Analysis of monoethanolamine solvent that had been exposed to flue gas for 1,000 hours at the National Carbon Capture Center indicated that selenium concentrations were elevated. The presence of toxic substances such as selenium would have significant cost and environmental implications associated with disposal of spent solvent. Selenium is particularly problematic because its chemical behavior mimics sulfur due to its similar electron structure.