# Zero-Emissions Combined Cycle and Beyond – rev c

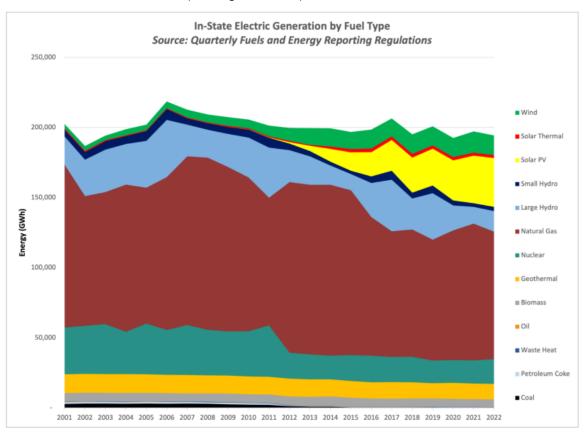
By John Benson May 2023

### 1. Introduction

This post is about combined-cycle generating plants, and mainly in California. The last time I wrote about these was over a year and a half ago, and that is linked below.

### https://www.energycentral.com/c/pip/old-and-new-cycles

The above linked paper was a thorough examination of combustion turbines, steam turbines, combined-cycle and other similar forms of generation. At that time (2016) California produced about half of its electricity using natural gas. As of 2022, those numbers are down to 46.9% (See figure below).<sup>1</sup>



Gas powered peakers (combustion turbines) and older gas-fueled plants are being closed where possible without impacting local grid stability. Also no new gas-fueled plants have been permitted in a few years. Requirements for new peakers are being met by battery energy storage systems (BESS).

1

<sup>&</sup>lt;sup>1</sup> California Energy Commission, "Electric Generation Capacity & Energy", <a href="https://www.energy.ca.gov/data-reports/energy-almanac/california-electricity-data/electric-generation-capacity-and-energy">https://www.energy.ca.gov/data-reports/energy-almanac/california-electricity-data/electric-generation-capacity-and-energy</a>

This paper has a proposal that will keep combined cycle power plants running by converting them to (nearly) zero greenhouse gas (GHG) emission operation. Ultimately these can be converted to negative emissions technology to offset other GHG sources.

## 2. The Second and Third Greenhouse Gases

Most people focus on CO<sub>2</sub> when it comes to greenhouse gas. This is good, because it is gas with the most climate change potential. And then there is methane. Although there is much less methane in the atmosphere than CO<sub>2</sub>, it makes up for it by having a much stronger global warming potential per unit volume. Methane has a global warming potential for equal volumes that is 104 times greater than CO<sub>2</sub> in a 20-year time-frame, but only 28 times in 100-years. As it degrades, it forms CO<sub>2</sub>.

Then there is the third greenhouse gas: nitrous oxide. Although it is present in the atmosphere in even lower quantities than methane, it (again) makes up for it by having a bigger punch. In equal volumes, nitrous oxide has 265–298 times the global warming potential of CO<sub>2</sub> for a 100-year timescale. N<sub>2</sub>O emitted today remains in the atmosphere for more than 100 years, on average. Outside of being shown in a table of greenhouse gasses in the above linked paper (Section 2.3), I have not written on this gas until now.

#### 2.1. Biomethane

Biomethane is a rapidly expanding industry in California. At the end of this subsection, there is a summary of current major projects that I found in a quick search of the web. This new industry is also attracting major players (see below). Currently, the primary feedstock for producing biomethane is cow manure from dairies, feed-lots and other bovine operations. The process is anaerobic fermentation (a.k.a. anaerobic digestion). Rather than explaining this process, A link to a UK site that explains this process below. <a href="https://anaerobic-digestion.com/anaerobic-digestion-basics/what-is-anaerobic-digestion/">https://anaerobic-digestion.com/anaerobic-digestion-basics/what-is-anaerobic-digestion/</a>

Also note that many organic materials can be used to produce biogas and ultimately, biomethane. Thus there is no shortage of feedstock.

Projects in California producing (currently or planned) biomethane include;

"Southern California Gas Co. (SoCalGas) today announced the utility received approval from the California Public Utilities Commission (CPUC) to begin the next phase in construction of four new dairy biomethane projects in California. Last week, the CPUC approved the contracts signed between SoCalGas and the developers of the four projects for the construction of infrastructure that will connect each biomethane facility to the SoCalGas pipeline system. This approval now allows SoCalGas to move forward, starting with the design and engineering phase. When completed, biogas from anaerobic digesters at 35 dairies will be collected and then cleaned to produce pipeline-quality renewable natural gas. The new projects represent four of six pilot projects in the San Joaquin and Sacramento Valleys selected by the CPUC, the Air Resources Board (CARB) and the Department of Food and Agriculture in December 2018. These new dairy biomethane facilities will significantly reduce greenhouse gas emissions by harnessing methane emissions from dairy digesters and converting that energy into renewable natural gas (RNG) which can be used to heat homes and businesses, for cooking and to fuel trucks and buses.<sup>2</sup>

2

<sup>&</sup>lt;sup>2</sup> PR Newswire, "SoCalGas Granted Approval from California Public Utilities Commission to Move Forward with Dairy Biomethane Projects", May 16, 2019, <a href="https://www.prnewswire.com/news-releases/socalgas-granted-approval-from-california-public-utilities-commission-to-move-forward-with-dairy-biomethane-projects-300851792.html">https://www.prnewswire.com/news-releases/socalgas-granted-approval-from-california-public-utilities-commission-to-move-forward-with-dairy-biomethane-projects-300851792.html</a>

"The facilities are targeted to be completed by December 2020 and combined, will have the ability to produce enough renewable natural gas to fuel close to 40,000 homes each year. Today, there are about 37 dairy methane capture projects either operating or in development, and experts estimate there could be as many as 120 projects funded and operating in the next five years. In addition, as the state seeks to divert organic waste from landfills and capture emissions from wastewater treatment plants, more locally produced RNG will become available."

Regarding these quotes, another term for biomethane is renewable natural gas (RNG).

A new technology being developed by Lawrence Livermore National Lab may be tested in one or more of the above projects as described below by one of this project's participants.<sup>3</sup>

"Xebec Adsorption Inc., a global provider of clean energy solutions is pleased to announce today its inclusion in the U.S. Department of Energy's (DOE) \$24 million commitment to a public-private collaboration funding 77 energy technology projects.

"With matching funds from the private sector, the Office of Technology Transition's (OTT) Technology Commercialization Fund (TCF) will advance the commercialization of promising energy technologies and strengthen partnerships between DOE's National Laboratories and private sector companies to deploy these technologies to the marketplace.

"Xebec's a supporting Industrial partner on this project as a result of its collaboration with Southern California Gas (SoCalGas), and a California treatment facility...

"This \$500,000 grant to the Lawrence Livermore National Laboratory will be used to develop and seek to commercialize their composite sorbent technology to more effectively remove CO<sub>2</sub> from biogas. This proposed technology has the potential for significant improvements over the current state-of-the-art adsorbents used for biogas upgrading.

"Xebec will play an important advisory role with our expertise in sorbents and biomethane production. Also, there is the opportunity to commercialize the technology in a small-scale biogas upgrading plant if proven successful in early stages."

Another project from another firm is below.

"Aemetis, Inc. (NASDAQ: AMTX) announced today that it has initiated the permitting and construction phase of its multi-dairy renewable biomethane digester cluster. In July 2018, the California Department of Food & Agriculture (CDFA) awarded two matching grants for a total of \$3 million to build biomethane digesters at the first two dairies in the Aemetis biogas project."

3

<sup>&</sup>lt;sup>3</sup> Sandi Murphy, Xebec Adsorption Inc., "Xebec Announces Inclusion in DOE Project to Enable Economical Biomethane Production", July 11, 2019, <a href="https://www.globenewswire.com/news-release/2019/07/11/1881402/0/en/Xebec-Announces-Inclusion-in-DOE-Project-to-Enable-Economical-Biomethane-Production.html">https://www.globenewswire.com/news-release/2019/07/11/1881402/0/en/Xebec-Announces-Inclusion-in-DOE-Project-to-Enable-Economical-Biomethane-Production.html</a>
<sup>4</sup> Aemetis, "Aemetis Dairy Biomethane Digester Project Achieves Milestones", February 7, 2019, <a href="https://www.globenewswire.com/news-release/2019/02/07/1712058/0/en/Aemetis-Dairy-Biomethane-Digester-Project-Achieves-Milestones.html">https://www.globenewswire.com/news-release/2019/02/07/1712058/0/en/Aemetis-Dairy-Biomethane-Digester-Project-Achieves-Milestones.html</a>

"The CDFA grant program provides California state funding support for dairy digester projects to reduce methane emissions, decrease air pollution, improve the environment and lower carbon emissions. In addition to the on-dairy covered lagoon digesters, Aemetis plans to construct a local pipeline designed to connect about a dozen dairies to the Aemetis biorefinery in Keyes, California, then clean the biomethane for use in ethanol production or for powering compressed renewable natural gas (RNG) vehicles.

"The \$3 million set of CDFA grants supports the engineering and construction of digesters at two dairies to collect waste dairy biogas,' stated Eric McAfee, Chairman and CEO of Aemetis. 'The Aemetis Biogas project is an example of the public and private support created by California's sincere commitment to stable long-term policies to improve air quality and reduce greenhouse gas emissions, including SB 1383, Cap-and-Trade and the Low Carbon Fuel Standard. These programs also demonstrate California's strong support for the state's vital dairy industry,' said McAfee.

"The CDFA grant is in addition to the recently announced \$30 million equity financing for the Aemetis Biogas project, of which \$8 million was funded in December 2018 to launch design, engineering and construction of the initial phase of the project. Preliminary engineering for the initial phase has been completed and permitting is underway."

And finally a project where Chevron is one of the partners:

"Chevron U.S.A. Inc. and California Bioenergy announced a joint investment in a holding company with California dairy farmers to produce and market dairy biomethane as a vehicle fuel in the state.<sup>5</sup>

"The holding company, CalBioGas, secured funding from Chevron to build infrastructure for dairy biomethane projects in California's San Joaquin Valley, adding to the investment from dozens of dairy farmers.

"Manure storage on dairy farms results in the release of methane, a highly potent greenhouse gas. CalBio brings technology, operational experience and capital to help dairy farmers build digesters and methane capture projects to convert this methane to a beneficial use as renewable natural gas.

"The dairy biomethane projects are designed to send dairy biogas to a centralized processing facility, where it will be upgraded to RNG and injected into the local gas utility's pipeline. The RNG is then marketed as an alternative fuel for heavy-duty trucks, buses, and eventually off-road and farm equipment."

### 2.2. Nitrous Oxide

In earlier posts (linked below) I defined the primary sources of CO<sub>2</sub> and methane. However, I've never done this for nitrous oxide, until now.

https://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-1-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-2-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-2-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-2-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-1-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-1-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-2-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-2-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-2-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-2-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-2-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-2-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-2-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-%E2%80%93-part-2-rev-bhttps://www.energycentral.com/c/ec/path-net-zero-weightps://www.

The primary sources for biogenic nitrous oxide are land-use change, fertilizer production and use and manure application.<sup>6</sup> The "manure application" can by the original appliers

<sup>&</sup>lt;sup>5</sup> Transport Topics, "Chevron, California Bioenergy to Produce Biomethane", June 24, 2019, https://www.ttnews.com/articles/chevron-california-bioenergy-produce-biomethane

<sup>&</sup>lt;sup>6</sup> A.R. van Amstel & R.J. Swart, Kluwer Academic Publishers, "Methane and nitrous oxide emissions: an introduction", <a href="https://link.springer.com/article/10.1007/BF00748940">https://link.springer.com/article/10.1007/BF00748940</a>

(cattle) or by farmers using manure for fertilizer. In either case the manure releases nitrous oxide as it degrades and releases nitrogen into the soil.

Any process that converts the manure to another product (like biomethane production and combustion) has the potential to be greenhouse gas neutral. The release of nitrous oxide is precluded, but CO<sub>2</sub> is produced during the combustion.

The same is true is plant-based biomass is converted biomethane and which is combusted. The original plant material absorbs roughly as much carbon, as the methane produces when it is combusted.

Process efficiency and the specifics of the chemical conversions will determine how close to greenhouse-gas-neutral each process is.

## 3. Combined Cycle Generation – A Modest Proposal

Initially an administrative-step will transition combined-cycle generators from greenhouse gas emitting to (almost) zero emissions. I will leave the specifics to our good legislators, public utility commission, and other administrators, but the following should be included.

- A floor-price for biomethane that steadily increases over time (to encourage the development of more biomethane production facilities).
- A requirement for combined-cycle generators to use biomethane as an increasing percentage of the natural gas that they consume.

The second step (described in the subsections below) is the heavy lift. However the positive outcome of the complete process is that these combined-cycle generators will end up being greenhouse-gas-negative, and thus negative emissions technology. Thus operating these generators can potentially offset the emissions from other greenhouse gas sources. Again, process efficiency and the specifics of the processes described below will determine how greenhouse-gas-negative the processes are, thus a simulation would be a good starting point, and LLNL would be a good first contact (go through reference 3 above).

## 3.1. Carbon Dioxide Capture Process

There are two architectures for carbon dioxide capture: pre-combustion and post-combustion. There have been recent technological advancements for each of these processes, and they are very different in their methods and applications. Each of these will be covered in the following two subsections.

#### 3.1.1. Pre-Combustion

The good news is that an exciting new technology has been developed over the last decade for pre-combustion carbon dioxide capture of methane (natural gas, including biomethane) –fired generation. This technology, the Allam Cycle (a.k.a. Allam-Fetvedt Cycle), uses carbon dioxide as its primary working fluid, and thus intrinsically captures this gas.

The bad news is that this process uses completely different mechanical components than existing combined-cycle plants, thus is not a reasonable retrofit. This will probably only be considered for replacement of existing older combined cycle (or other gas-fired generators) where a base-load-like application is required.

The Allam Cycle was invented by 8-Rivers Capital, and the first demonstration plant, a 25 MWe Plant in La Porte, Texas has been operating for over a year, and was developed by NET Power and others.<sup>7</sup>

The diagram and explanatory text below is from a 2016 paper published by the developers of this process.<sup>8</sup>

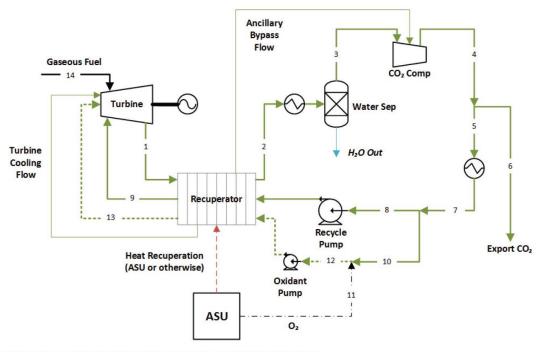


Figure 1: Process schematic of a simplified commercial scale natural gas Allam Cycle

The Allam Cycle is a power cycle that utilizes a recirculating, trans-critical CO<sub>2</sub> working fluid in a high-pressure, low-pressure-ratio, highly recuperated Brayton cycle. The cycle operates with a single turbine that has an inlet pressure of approximately 300 bar and a pressure ratio of 10. The basic schematic employing natural gas fuel is depicted in Figure 1... These values are a simplified representation of a commercial scale plant without depicting additional detail for optimized heat exchanger, compressor, and turbine performance. A pressurized gaseous fuel (14) is combusted in the presence of a hot oxidant flow containing a mixture of CO<sub>2</sub> and nominally pure oxygen (13), provided by a co-located Air Separation Unit (ASU) and a hot CO<sub>2</sub> diluent recycle stream (9) at approximately 300 bar under lean combustion conditions. The exhaust flow exiting the combustor is expanded through a turbine to approximately 30 bar, reducing in temperature to above 700°C (1).

<sup>&</sup>lt;sup>7</sup> Sonal Patel, Power, "Pioneering Zero-Emission Natural Gas Power Cycle Achieves First-Fire", May 30, 2018, <a href="https://www.powermag.com/pioneering-zero-emission-natural-gas-power-cycle-achieves-first-fire/?printmode=1">https://www.powermag.com/pioneering-zero-emission-natural-gas-power-cycle-achieves-first-fire/?printmode=1</a>

<sup>&</sup>lt;sup>8</sup> Rodney Allam et al, Demonstration of the Allam Cycle, July, 2017 <a href="https://www.sciencedirect.com/science/article/pii/\$187661021731932X">https://www.sciencedirect.com/science/article/pii/\$187661021731932X</a>

Following the turbine, the exhaust flow enters a recuperating heat exchanger which transfers heat from the hot exhaust flow to the aforementioned high pressure CO2 recycle stream which acts as diluent quench for the combustion products and lowers the turbine inlet temperature to an acceptable level of 1150°C, as well as the oxidant flow providing oxygen to the combustor flame zone. Exiting the primary heat exchanger (2), the turbine exhaust flow is cooled to near ambient temperature and combustion derived water is separated (3). The predominantly CO<sub>2</sub> fluid stream is then recompressed (4), cooled (7), and pumped to approximately 300 bar pressure where it then reenters the cold end of the recuperative heat exchanger. At a point before entering the heat exchanger, a portion of the recycle CO<sub>2</sub> (10) is mixed with oxygen (11) to form an oxidant mix stream (12) which is fed separately to the heat exchanger and turbine. Within the main process heat exchanger, the recycle flows undergo reheating against the hot turbine exhaust before returning to the combustor at temperatures exceeding 700°C. In order to maintain mass balance within the semi-closed cycle, a portion of the high purity CO<sub>2</sub> process gas is exported at a point within recompression to a high pressure CO<sub>2</sub> pipeline for sequestration or utilization. This net export is approximately 5% of the total recycle flow, meaning the majority of the process inventory is recirculated.

There is a second good explanation (more marketing oriented) of this process by the developers of the demonstration plant, referenced here.<sup>9</sup>

#### 3.1.2. Post Combustion

The good news here is that these processes have been developed and tested over time, and are suitable for retrofits to existing combined-cycle plants. Thus this will probably be suitable for use in newer combined cycle plants.

The three paragraphs below are each about an existing post-combustion carbon dioxide capture technologies. These all use CO<sub>2</sub> absorbing solutions mixed with the heat-exchanger exhaust of the combined-cycle plant.

"Shell Cansolv CO<sub>2</sub> capture technology: The first commercial post combustion CO<sub>2</sub> capture plant, based on regenerable amine technology, designed by Shell Cansolv was started successfully in Q3, 2013. Subsequently, the plant conceded 72 hrs. warranty test run and since then, the CO<sub>2</sub> capture plant has been running smoothly. The plant performance met requirements for a successful warranty test run and in most cases results were considerably better than expected.<sup>10</sup>"

<sup>&</sup>lt;sup>9</sup> Net Power, Technology, https://www.netpower.com/technology/

<sup>&</sup>lt;sup>10</sup> Ajay Singh, Karl Stéphenne, Shell Cansolv, "Shell Cansolv CO2 capture technology: Achievement from First Commercial Plant", 2014, <a href="https://core.ac.uk/download/pdf/82015698.pdf">https://core.ac.uk/download/pdf/82015698.pdf</a>

"Aker Solutions Carbon Capture: Our proprietary carbon capture process uses a mixture of water and organic amine solvents to absorb the carbon dioxide. The process can be applied on emissions from various sources such as fossil and bio fuel, cement, urea, steel, aluminum, refineries and waste-to-energy.

The process has been qualified for commercial scale application after extensive testing and verifications. Our ACC™ process is offered as a license package including key equipment and proprietary solvents.<sup>11</sup>"

"Alstom CAP carbon capture technology: Based on a successful pilot (5 MW, We Energies, US) as well as a validation plant operation (54 MW, AEP Mountaineer, US), the Chilled Ammonia Process (CAP) has demonstrated its potential to be a world class technology. The Alstom validation program has confirmed expected performance levels, without any detrimental environmental impact. Alstom offers a full portfolio of the most advanced carbon capture technologies for power and industrial applications, and is committed to 16 pilots and large scale Carbon Capture and Storage (CCS) projects with various major utility and industrial partners throughout the world.<sup>12</sup>"

## 3.2. Carbon Transport and Sequestration Processes

The good news here is that almost all if California's combined cycle power plants are over or near sequestration sites (see the map on the next page).<sup>13</sup> In addition to the map below, the linked site also has links to preliminary site assessments for each plant. Although short CO<sub>2</sub> pipelines may be necessary for most plants, only a few will need long pipelines.

### 3.3. Government's Role

Again, government agencies should step in and help to fund (via public-private partnerships) (1) the initial simulation (modeling) of these processes and (2) a series of full-scale demonstration plants. Hopefully at that point our cap and trade system will provide the incentive to convert other combined cycle plants to negative emissions technology.

 $<sup>^{11}~</sup>Aker~Solutions, \underline{https://www.akersolutions.com/what-we-do/products-and-services/carbon-capture-\underline{utilization-and-storage/}$ 

<sup>&</sup>lt;sup>12</sup> Michelle Marcher Lidén, Alstom Press Release, "Inauguration of worlds largest CO<sub>2</sub> Capture test facility at Technology Centre Mongstad, Norway", May 7, 2012, <a href="https://www.alstom.com/press-releases-news/2012/5/inauguration-of-worlds-largest-co2-capture-test-facility-at-technology-centre-mongstad-norway">https://www.alstom.com/press-releases-news/2012/5/inauguration-of-worlds-largest-co2-capture-test-facility-at-technology-centre-mongstad-norway</a>

<sup>&</sup>lt;sup>13</sup> West Coast Regional Carbon Sequestration Partnership, "Assessment of CCS for Gas-Fired Power Plants", <a href="https://www.westcarb.org/ngcc-ccs-study.html">https://www.westcarb.org/ngcc-ccs-study.html</a>

Many of California's existing and planned NGCC plants are near sedimentary basins identified as having  $CO_2$  storage potential (shown in green).  $CO_2$  captured from in-state NGCC plants and other sources could also supply  $CO_2$  for enhanced recovery operations in California's oil and gas fields (shown in dark green and red, respectively).

