# 2023 - 2024 AIChE Student Design Competition Problem Statement

Sustainable Power-to-Gas System Design: Integrating Renewable Energy Storage and Environmental Responsibility

1.0 Introduction to Power-to-Gas

Renewable energies play a pivotal role in ensuring a sustainable energy supply while keeping greenhouse gas emissions in check. However, the incorporation of renewable power into the global energy framework faces challenges due to the erratic nature of renewable energy sources. Specifically, wind and solar energy exhibit significant fluctuations, necessitating enhanced storage technologies for grid stability and optimal utilization of renewable resources (Thema et al., 2019).

One effective strategy to address this variability is the use of chemical energy storage systems. Excess electrical energy generated by wind and solar power can be stored in the form of chemical molecules like hydrogen (H_2) or methane (CH_4) through processes known as "power-to-gas" (PtG) methods (Götz et al., 2016). In PtG, the process of electrolysis splits water molecules using electric current, resulting in the production of hydrogen. Subsequently, renewable hydrogen can be converted into methane through a process called methanation. When compared to hydrogen, methane offers two significant advantages: higher energy density per unit volume and the ability to inject large quantities of methane into the gas grid (Sterner & Stadler, 2014). The gas grid itself has substantial storage capacity and enables the versatile use of methane in various sectors, including power generation, heating, and transportation.
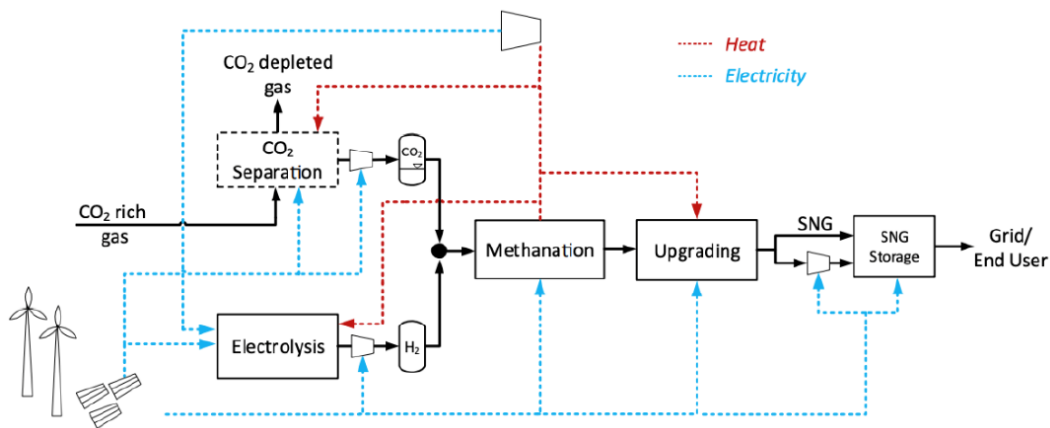
PtG is a critical step in ensuring the usability of renewable energy. The PtG process (highlighted above) contains several key processes (Gorre et al., 2019):

1. **Electrolysis of water to produce hydrogen:** Electrolysis employs electric power to divide water into hydrogen (H_2) and oxygen (O_2), thereby storing the electric energy within the H_2 component. Currently available industrial-scale electrolysis units include alkaline electrolysis (David et al., 2019) and proton exchange membrane electrolysis (Carmo et al., 2013).

2. **CO/CO₂ separation:** A typical PtG process uses CO_2 from biogenous (from a living organism) or other sources (Gorre et al., 2019).
3. **Methanation:** The hydrogen produced from renewable energy sources and carbon dioxide are then reacted to form synthetic methane. This process can be carried out using either thermochemical, photothermal, electrochemical, or biochemical processes (Schaaf et al., 2014; Thema et al., 2019; Xu & Froment, 1989).

Your design project will focus on processes 2 and 3.

2.0 Objectives for Power-to-Gas Unit Design

The purpose of this design project is to assess the economic feasibility of a PtG plant using hydrogen produced from renewable energy. With this in mind, the prioritized project objectives are:

1. Effectively manage all high-consequence process safety risks.
2. Select a suitable CO_2 source to maximize economic and environmental performance and reliably deliver on specification CO_2 as a feedstock for the methanation reaction.
3. Reliably deliver on-specification methane so that the methane can be used in the current distribution system.

3.0 Selection of CO₂ Source

Numerous industrial processes release carbon dioxide directly through the combustion of fossil fuels and indirectly via electricity generation from fossil fuels. Cement production is the largest industrial source of carbon dioxide emissions. The production of 1000 kg of cement results in nearly 900 kg of carbon dioxide emissions. Steel production also produces a large amount of carbon dioxide. On average, the production of one ton of steel leads to 1.9 tons of carbon dioxide. Moreover, the usage of fossil fuels in the production of chemicals and petrochemical goods contributes to carbon dioxide emissions. The industrial fabrication of ammonia and hydrogen often relies on natural gas or other fossil fuels as foundational components, producing carbon dioxide in the process. Petrochemical products, including plastics, solvents, and lubricants, are manufactured from petroleum. These products tend to release additional carbon dioxide during their lifespan through evaporation, dissolution, or wear and tear. Additionally, livestock are a large source of CO_2 emissions, accounting for 14-17% of global emissions (*Main Sources of Carbon Dioxide Emissions*, n.d.).

In this task, you must survey several possible sources (i.e., industrial, agricultural, environmental sites) for carbon dioxide and assess their economic and environmental potential (i.e., purity of C0₂ and impurities released when burning) for use in PtG facilities. List your possible sources and explain why you chose your final selection.
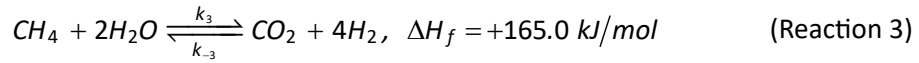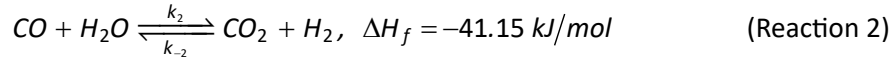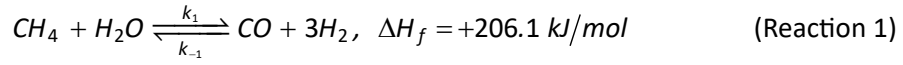
4.0 Design of Methanation Unit

The discovery of methanation reactions involving carbon monoxide and carbon dioxide dates back to the early 19th century (Götz et al., 2016). Methanation of carbon dioxide is an exothermic, catalytic reaction. In thermochemical processes, the reaction is carried out between 200 and 550 °C, depending on type of catalyst used.

The overall reaction is:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O, \quad \Delta H_f = -165 \ kJ/mol$$
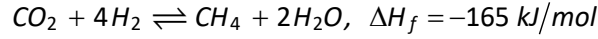
The following mechanism has been proposed (Xu & Froment, 1989):

$$CH_4 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO + 3H_2, \quad \Delta H_f = +206.1 \ kJ/mol \qquad \text{(Reaction 1)}$$

$$CO + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CO_2 + H_2, \quad \Delta H_f = -41.15 \ kJ/mol \qquad \text{(Reaction 2)}$$

$$CH_4 + 2H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CO_2 + 4H_2, \quad \Delta H_f = +165.0 \ kJ/mol \qquad \text{(Reaction 3)}$$

In addition to methane and water, higher saturated hydrocarbons can also be produced. The most stable hydrocarbon produced in this reaction is ethane. Additionally, carbon precipitation can occur. The kinetic equations for reactions 1-3 are as follows (Xu & Froment, 1989):

$$r_1 = \frac{\dfrac{k_1}{\left(P_{H_2}\right)^{2.5}}\left(P_{CH_4}P_{H_2O} - \dfrac{P_{CO}\left(P_{H_2}\right)^3}{K_1}\right)}{\left(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + \dfrac{K_{H_2O}P_{H_2O}}{P_{H_2}}\right)^2} \quad \frac{kmol}{(kg\,cat)(hr)}$$

$$r_2 = \frac{\dfrac{k_2}{P_{H_2}}\left(P_{CO}P_{H_2O} - \dfrac{P_{CO_2}P_{H_2}}{K_2}\right)}{\left(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + \dfrac{K_{H_2O}P_{H_2O}}{P_{H_2}}\right)^2} \quad \frac{kmol}{(kg\,cat)(hr)}$$

$$r_3 = \frac{\dfrac{k_3}{\left(P_{H_2}\right)^{3.5}}\left(P_{CH_4}\left(P_{H_2O}\right)^2 - \dfrac{P_{CO_2}\left(P_{H_2}\right)^4}{K_3}\right)}{\left(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + \dfrac{K_{H_2O}P_{H_2O}}{P_{H_2}}\right)^2} \quad \frac{kmol}{(kg\,cat)(hr)}$$

$$r_{CO_2} = -r_2 - r_3$$
$$r_{CH_4} = -r_1 - r_3$$
$$r_{CO} = r_1 - r_2$$

Standard Arrhenius and Van't Hoff equations are used to model the temperature dependance of the rate and adsorption constants:

$$k_i = k_{i0}\,e^{-E_i/RT}, \ i = 1,2, \text{ or } 3$$

$$K_i = A_i e^{-\Delta H_i/RT}, \ i = 1,2, \text{ or } 3$$

$$K_n = A_{K_n}\,e^{-\Delta H_n/RT}, \ n = CO, H_2, CH_4, \text{ or } H_2O$$

Reaction rate and equilibrium constants are tabulated below.

k_{10}	4.225×10^{15}	E_1 (kJ/mol)	240.1
k_{20}	1.955×10^6	E_2 (kJ/mol)	67.13
k_{30}	1.010×10^{15}	E_3 (kJ/mol)	243.9
A_1	1.198×10^{17}	ΔH_1 (kJ/mol)	223.06
A_2	1.767×10^{-2}	ΔH_2 (kJ/mol)	-36.58
A_3	2.117×10^{15}	ΔH_3 (kJ/mol)	186.40
$A_{K_{CO}}$	8.23×10^{-5}	ΔH_{CO} (kJ/mol)	-70.65
$A_{K_{H_2}}$	6.12×10^{-9}	ΔH_{H_2} (kJ/mol)	-82.90
$A_{K_{CH_4}}$	6.65×10^{-4}	ΔH_{CH_4} (kJ/mol)	-32.28
$A_{K_{H_2O}}$	1.77×10^5	ΔH_{H_2O} (kJ/mol)	88.68

These reaction kinetics are valid from 300-400 °C and a maximum pressure of 10 bar. The catalyst is made up of 15.2% nickel on a magnesium spinel. The catalyst is crushed into particles of 0.18-0.25 mm in diameter with a void fraction of 0.528 and a density of 44 kg/m³.

Given the highly exothermic nature of the thermochemical methanation reaction, effective thermal management within the system is crucial. Currently, two advanced reactor types are suitable for this process: two-phase fixed bed reactors or fluidized bed reactors. Regardless of the chosen reactor design, effective removal of the heat generated during the methanation reaction is essential. In the context of carbon dioxide methanation (as per Reaction 3), a mere 1% rise in the molar gas fraction of methane in the product gas can lead to a temperature increase of approximately 60 K (Schaaf et al., 2014).

One strategy to mitigate temperatures within the reactor involves decreasing the reactive feed through a controlled dilution strategy for the gas stream at the reactor inlet. This can be executed by cooling and recirculating a portion of the reactor's outlet gas stream. However, cooling the product gas results in undesirable energy losses.

An alternative approach entails maintaining an isothermal reactor operation. In this scenario, a cooled reactor is necessary to transfer the reaction heat from the reaction zone to a cooling medium. Due to the intense exothermic nature of the methanation reaction and the limited heat transfer capabilities in a fixed bed reactor in both radial and axial directions, achieving isothermal conditions in a single fixed bed reactor is challenging. Effective temperature control in a fixed bed reactor necessitates connecting at least two adiabatic reactors in series with recirculation of the reactor outlet gas. Temperature management can be achieved through the recirculation of reactor outlet gas streams (as previously discussed) and intermediate cooling between reactors (Schaaf et al., 2014).

In addition to fixed bed reactors, fluidized bed reactors have been explored as an alternative. Within these reactors, the methanation reaction occurs within a fluidized bed of catalyst particles. The fluidized bed's excellent gas-solid catalyst particle mixing facilitates robust mass and heat transfer, facilitating near-isothermal conditions. Moreover, fluidized bed reactors offer superior process control. Nevertheless, issues like catalyst particle abrasion and entrainment in the gas flow pose challenges if this reactor type is chosen (Schaaf et al., 2014).

Emerging as a promising technology, biological methanation facilitates the conversion of hydrogen and carbon dioxide (CO_2) into methane. This process involves a multi-phase system with microorganisms, specifically members of Archaea, residing in the liquid phase (Thema et al., 2019). Due to concentration differences between the phases, the gaseous inputs dissolve into the liquid phase. The microorganisms absorb the dissolved H_2 and CO_2, subsequently transforming them into CH_4 (as depicted in Fig. 1). Enzymes within the microorganisms catalyze the methanation reaction (also known as the Sabatier reaction) through biochemical processes (Sterner & Stadler, 2014).

A typical biological methanation reactor contains a growth medium consisting of modified basal anaerobic medium: salt solutions (NH_4Cl, 100 g/L; NaCl, 10 g/L; $MgCl_2 \cdot 6H_2O$, 10 g/L; $CaCl_2 \cdot 2H_2O$, 5g/L), vitamin solution (biotin, 2 mg/L, folic acid, 2 mg/L; pyridoxine-HCl, 10 mg/L; riboflavin-HCl, 5 mg/L; thiamine-HCl, 5 mg/L; p-aminobenzoic acid, 5 mg/L; lipoic acid, 5 mg/L, D-pantothenic acid hemicalcium salt, 5 mg/L, trace metal solution ($FeCl_2 \cdot 4H_2O$, 2000 mg/L; H_3BO_3, 50 mg/L, $ZnCl_2$, 50 mg/L, $CuCl_2$, 30 mg/L, $MnCl_2 * 4H_2O$, 50 mg/L; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 50 mg/L; $AlCl_3$, 50 mg/L, $CoCl_2 \cdot 6H_2O$, 50 mg/L; $NiCl_2$, 50 mg/L; $Na_2SeO_3 \cdot 5H_2O$, 100 mg/L; $Na_2WO_4 \cdot 2H_2O$, 60 mg/L), sodium bicarbonate solution ($NaHCO_3$, 52 g/L), potassium phosphate dibasic solution (K_2HPO_3, 152 g/L), chelating agent solution (Nitrilotriacetic acid, 1 g/L) and reducing agent solution ($Na_2S * 9H_2O$, 25 g/L). The incubation temperature of the system is 37 °C for mesophilic and 60 °C for thermophilic enrichments (Grimalt-Alemany et al., 2020).

The thermodynamic feasibility of the metabolic network can be evaluated and modeled based on the Gibbs free energy change ($\Delta_f G^0$) of the overall biochemical reaction. The Gibbs free energy of formation can be corrected for temperature and ionic strength using the following equations:

$$\Delta_f G_T'(T) = \Delta_f G_i'(298.15K)\frac{T}{298.15K} + \Delta_f H_i'(298.15K)\frac{298.15 - T}{298.15K}$$

$$\Delta_f G_i'(T) = \Delta_f G_i^0(I=0) - \frac{RTAz_i^2\sqrt{I}}{1 + B\sqrt{I}}$$

In these equations, z_i is the charge number of compound i, I is the ionic strength of the medium, A was calculated as a function of temperature and B is an empirical constant of value of $1.61(I)^{0.5}$ within a range of ionic strength of 0.05-0.25 M (Grimalt-Alemany et al., 2020). Therefore, the Gibbs free energy change of reaction ($\Delta_r G_T'$) can be corrected for the partial pressure of gases based on the following equation:

$$\Delta_r G_T' = \Delta_r G_T^0(I=0.08M) + RT \ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

The thermodynamic potential factor (F_T) was first introduced by Jin and Bethke to introduce thermodynamic consistency in kinetic models (e.g., Monod kinetics) and to determine the minimum threshold concentration for each microbial group.

$$F_T = 1 - exp\left(\frac{\Delta G_A - \Delta G_C}{\chi RT}\right)$$

$$\Delta G_C = Y_{ATP}\Delta G_P$$

ΔG_A is equal to $-\Delta_r G'_T$ in kJ per reaction, ΔG_C is the energy conserved and is calculated from the ATP yield of each metabolic pathway multiplied by the Gibbs free energy of phosphorylation (ΔG_P), and χ is the average stoichiometric number. For methanogenesis, a typical ATP yield is 0.5 and χ is 2 (Grimalt-Alemany et al., 2020).

The biomethanation reaction can be model as either an equilibrium reactor, Gibbs reactor, kinetic reactor, or a stoichiometric reactor (Leonzio, 2016).

In this task, you must optimize the design the methanation reaction scheme based on economic and environmental factors. The design should be assessed using the CO_2 sources researched in Section 3.

5.0 Design Considerations for Methane Separations

After the methanation reaction, the methane produced must be separated from the unreacted CO_2 and H_2 and produced water.

1. The methane produced should have a water composition of no more than 7 lbs H_2O/MCF.
2. The methane produced should have less than 2 wt% hydrogen
3. The methane produced should have 1-8 mol% carbon dioxide.
4. The methane produced should be 90-95 mol% purity, overall.

6.0 CO_2 Emissions

Using the Greenhouse Gas Equivalent calculator, determine the reduction in CO_2 emissions based on your proposed design(s).

Calculator: https://www.epa.gov/energy/greenhouse-gas-equivalencies-calculator

7.0 Economics

We are committed to address the variability of renewable energy sources by producing a Power-to-Gas plant, but the economics are challenging, meaning the designer must deliver a design that accomplishes the key project priorities for Safety, Reliability, and Cost Effectiveness described in Section 2.0.

Your design team's work is considered to be critical input for hydrogen and methane pricing. In preparation, your team must prepare:

- A Capital Cost estimate for the facility. Basis: US dollars, year 2022, US location.
  - The cost estimate must include all process facilities including
    - Emission Control
    - Gas Storage
- Determine the impact of the hydrogen price and the selling price of methane.
- Fixed Operating Cost (labor, maintenance, catalyst & chemicals allowance).
- Variable Operating Cost estimate based on the following price set (Turton):

Utility	Description	Cost ($/Common unit)
Air Supply	Pressurized and dried air: a. 6.3 barg (90 psig) b. 3.3 barg (50 psig) c. Instrument air	 a. $0.49/100 std m^3 b. $0.35/100 std m^3 c. Add 20%
Steam from Boilers	Process steam: a. 5 barg, 160 °C b. 10 barg, 184 °C c. 41 barg, 254 °C	 a. $14.05/GJ b. $14.83/GJ c. $17.70/GJ
Cooling Tower Water	Process cooling water: a. 30 °C to 40 or 45 °C	 a. $0.354/GJ
Other Water	High-purity water for: a. Process use b. Boiler feed at 115 °C c. Potable	 a. $0.067/1000 kg b. $2.45/1000 kg c. $0.26/1000 kg
Electrical Substation	Electric distribution: a. 110 V b. 220 V c. 440 V	 a. $0.06/kWh b. $0.06/kWh c. $0.06/kWh
Fuels	a. Fuel oil b. Natural gas c. Coal	a. $14.2/GJ b. $11.1/GJ c. $1.72/GJ
Refrigeration	a. Water at 5 °C b. Refrigerant at -20 °C c. Refrigerant at -50 °C	a. $4.44/GJ b. $7.89/GJ c. $13.11/GJ
Thermal Systems	Cost based on thermal efficiency of fired heater using natural gas: a. 90% efficiency b. 80% efficiency	 a. $12.33/GJ b. $13.88/GJ
Waste Disposal	a. Nonhazardous b. Hazardous	a. $41/tonne b. $200-$2000/tonne
Wastewater Treatment	a. Primary (filtration) b. Secondary (filtration + activated sludge) c. Secondary (filtration + activated sludge + chemical processing)	a. $41/1000 m^3 b. $43/1000 m^3 c. $43/1000 m^3

8.0 Environmental, Health, and Safety:

Environmental, Health and Safety (EHS) aspects are critical to the economic viability, sustainability and social responsibility of business and operations. These aspects must be carefully considered during design to ensure that processes minimize raw material consumption, safely contains process materials, and effectively treats potentially harmful discharges prior to release to the environment.

These aspects are especially important when processes employ or produce toxic and flammable materials. Your design will be judged in part on your recognition of the potential environment, health and safety hazards inherent in the process, as well as on the mitigation steps you incorporate to ameliorate these potential hazards.

1. Minimizing Environmental Impacts

  a. You should assume that regulatory authorities require the application of Best Available Control Technology (BACT) to minimize and treat gaseous and liquid waste generated by the process.
  b. Prepare a detailed process and instrumentation diagram (P&ID) for methanation reactor. Your P&ID should include automatic controllers for pressure, level, and composition (temperature) management as well as alarms informing operators of abnormal conditions.
  c. Size a pressure relief for this methanation reactor assuming an onsite flare is available for the safe and complete combustion of vented material.
  d. Calculate the Scope 2 of your emissions plant. (Please reference https://www.epa.gov/climateleadership/scope-1-and-scope-2-inventory-guidance#:~:text=Scope%202%20emissions%20are%20indirect,of%20the%20organization's%20energy%20use).

2. Assessing and Mitigating Potential Health Impacts

Your design must recognize the hazards associated with potential human exposure to process materials, including raw materials, intermediate and finished products, by-products and wastes. To recognize hazards, compile a table of OSHA chemical exposure limits, NFPA diamond classifications, and lethal dose (LD50) limits for process chemical constituents. This information is often found on Safety Data Sheets (SDS), formerly known as Material Safety Data Sheets MSDS. Screening for potential health risks is an essential element of process safety that informs personnel protective equipment and standard operating protocols.

3. Safety – Learning from Experience

The design must consider relevant lessons learned from the industry, especially with respect to hydrocarbon explosions.

  a. Highlight the risks in hydrocarbon processing by performing a TNT equivalency calculation for the atmospheric detonation of all chemicals from the largest, by inventory, process distillation column. For worst-case consideration assume all fractionator contents instantly vent to atmosphere in gas-phase.
  b. To mitigate risks, tabulate a Hazard and Operability (HAZOP) study for the reactor.

9.0 References

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