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March 13, 2023 | 19th Global Congress on Process Safety

Green, Blue, Grey, or Brown - Pressure Relief Systems Consideration for Methanol in Decarbonization Processes

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QMS_7.3_7.4.F06 Rev.9

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- B.S. Chemical Engineering, Texas A&M University
- 14+ years of process & pressure relief systems engineering
- Technical Experience
  - Refinery relief systems revalidations and design correction
  - Offshore production platform relief systems revalidations
  - Gas fractionation plants relief systems revalidations and design correction
  - Inland terminal facility relief systems revalidations and design corrections
  - Flare hydraulic evaluations ranging from simple converging networks to complex looped refinery networks, including time-based transient analyses
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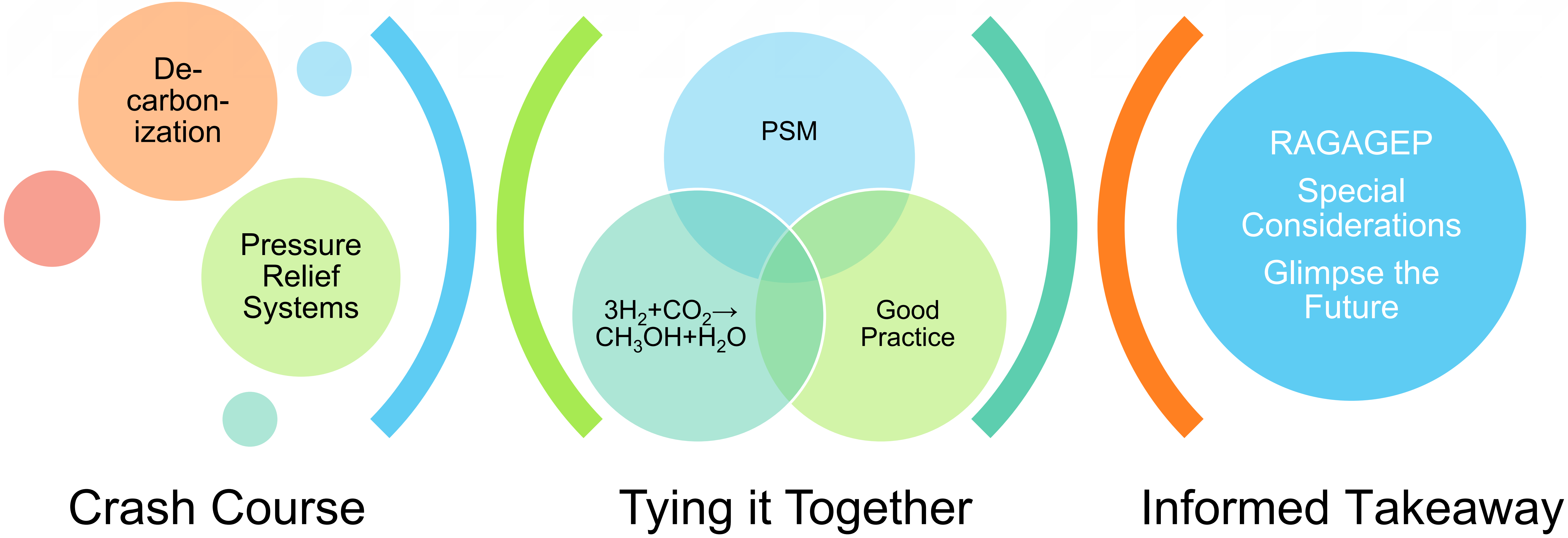
(Ice Breaker)

Source: Microsoft 365

Overview

This presentation weaves together decarbonization via methanol and pressure relief system design considerations



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Decarbonization?

- *Decarbonization* is a broad term for reducing or eliminating carbon emissions into the environment (nominally carbon dioxide, CO_2). Carbon capture & storage (CCS), Carbon capture & use (CCU).
- Intensive, but incentives and synergies have popularized methanol production from carbon dioxide hydrogenation technology.

Source: Microsoft 365

Decarbonization?

- The terms green, blue, grey, and brown are contextual modifiers describing how a process might include:
  - renewable sources
  - hydrocarbon fuels with CCS or CCU
  - hydrocarbon fuels without CCS or CCU
  - coal and heavy hydrocarbons without CCS or CCU
- Clearly, these terms are evocative. Green and blue are considered attractive, like verdant trees beneath an open sky; gray and brown are considered less attractive, like smoke and filth.

Source: Microsoft 365

Decarbonization ✓
What about methanol or pressure relief systems?

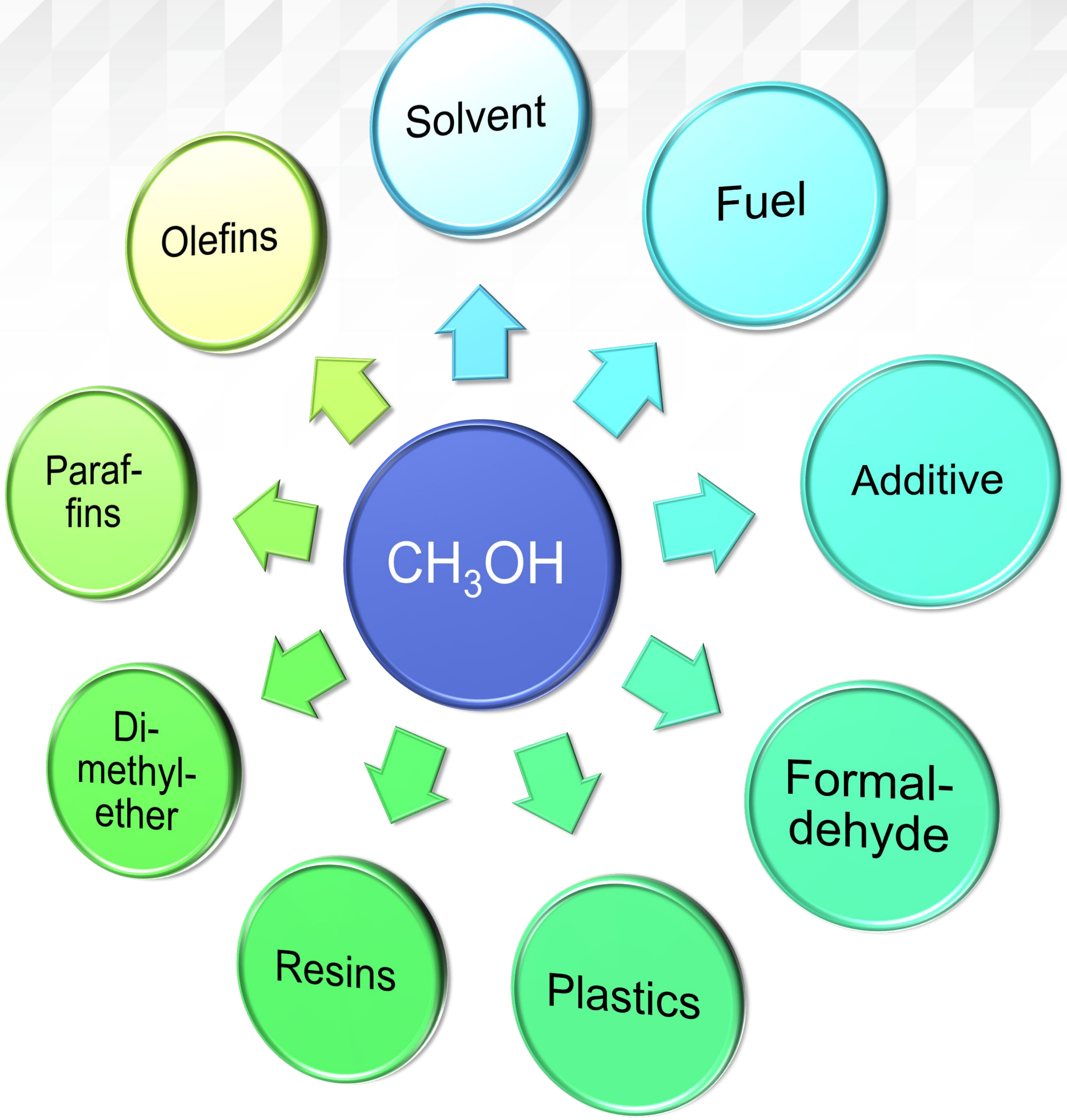
- In the context of methanol production, decarbonization is be achieved by capturing CO_2 for use in feedstock, and by storing the carbon within the product methanol molecule.
- But what does this have to do with pressure relief systems? As with any chemical manufacturing process, pressure relief systems must be considered for methanol decarbonization plants, including the unique characteristics of the feedstocks, intermediates, products.

Source: Microsoft 365 & ioMosaic Corporation

Crash Course

Crash Course – Methanol

- Methanol, CH_3OH, is the simplest of alcohols.
- The NFPA classifies methanol as a Class IB flammable liquid because it has a flash point lower than 73 °F and boiling point greater than 100 °F [1].
- Poisonous! ☠



Source: ioMosaic

Crash Course – Methanol

- Historically, methanol was created by pyrolysis of wood.
- In the past century, large scale manufacture achieved with syngas.
  - Partial oxidation of carbon-rich fuel sources or steam-methane reformation yields carbon monoxide, CO, a versatile chemical that is ready to react. (H_2, too!)
  - CO reacts with H_2 gas in the presence of a metal catalyst (e.g., copper) to produce methanol. Competing reactions yield other products, which complicates separation.

Source: Microsoft 365

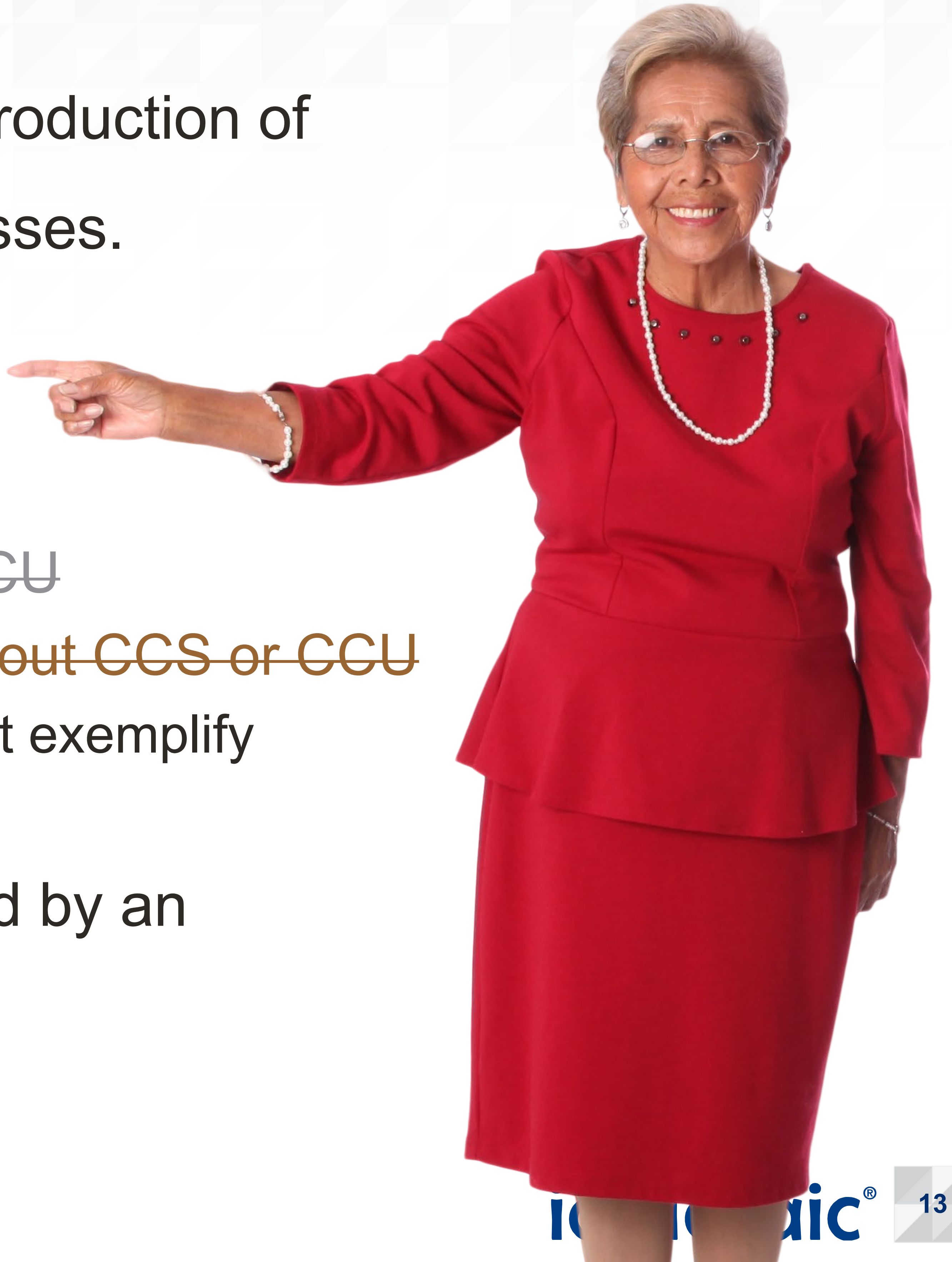
Crash Course – Methanol

- The scientific community also recognized the ability to produce methanol from CO_2 within the past century, but industry has not favored this approach.
  - Abundant coal or methane make endothermic gasification or steam reforming attractive
  - Like syngas methanol, synthesis from CO_2 also involves a metal catalyst, like copper, but with potential mixes of common or rare metals depending on selectivity and desired activity.
- In other words, CO is easier to manipulate and react than its stable cohort CO_2.
- However, because there are emerging social, regulatory, and commercial incentives to decarbonize, methanol production from carbon dioxide hydrogenation technology is gaining popularity and industrial deployment.

Source: Microsoft 365

Crash Course – Methanol

- Hydrogen gas, H_2, is the other feedstock in the synthetic production of methanol. It is likewise sourced from "multi-colored" processes.
  - green H_2 from water electrolysis
  - turquoise H_2 from methane pyrolysis
  - blue H_2 from steam-methane reforming with CCS or CCU
  - ~~grey H_2 from steam-methane reforming without CCS or CCU~~
  - ~~brown H_2 from coal or heavy hydrocarbon gasification without CCS or CCU~~
    - Obviously, grey and brown H_2-producing processes do not exemplify decarbonization.
- Bonus question: What color is H_2 from electrolysis powered by an upstream non-renewable? 🤔



Source: Microsoft 365

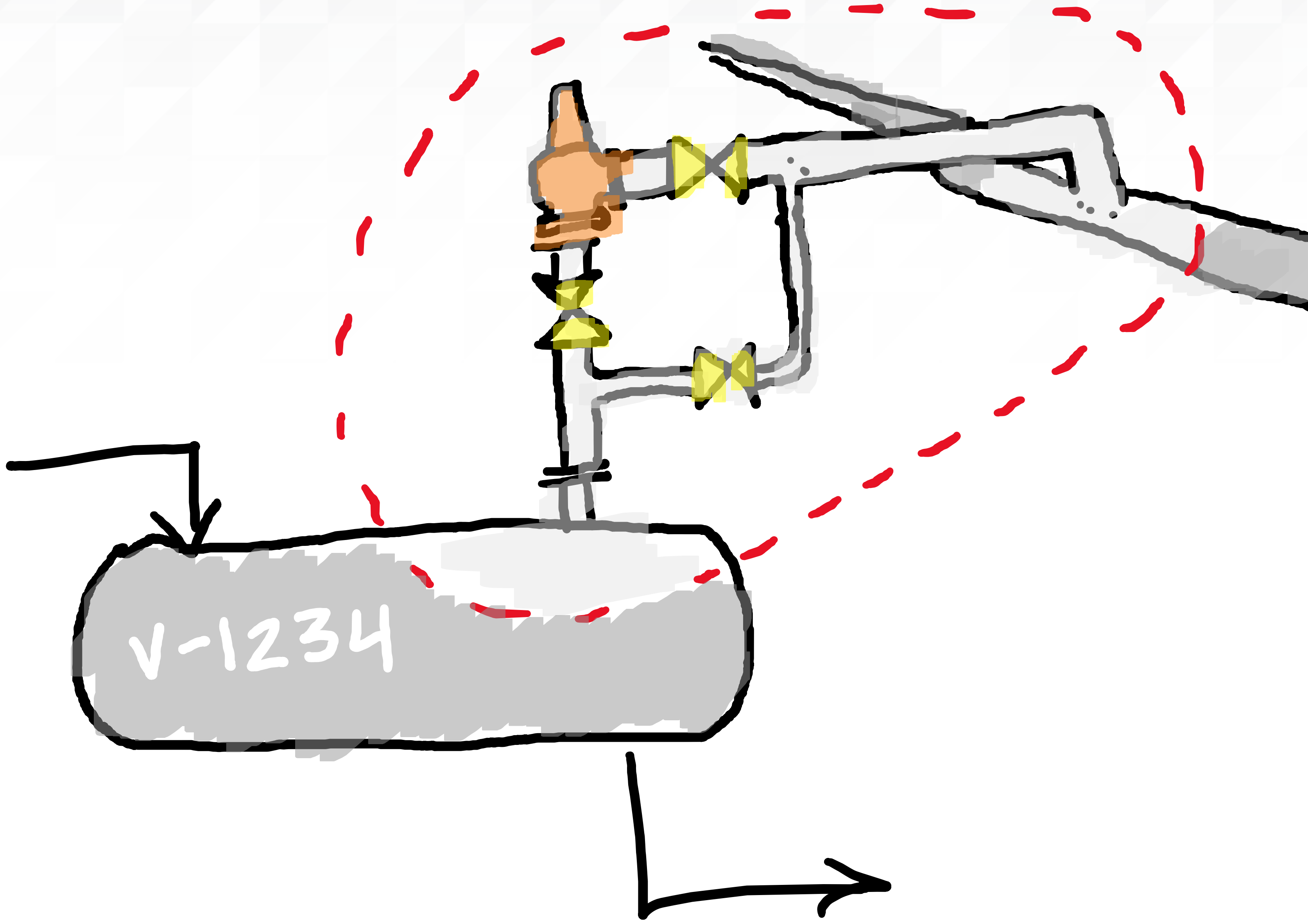
Crash Course #2 – Pressure Relief Systems

- Equipment is not infinitely strong, so all contemporary codes of construction, such as ASME VIII [2] for pressure vessels, require protection against overpressure, most often with pressure relief devices (PRDs).
  - PRDs are the last layer of defense against a loss of containment from pressure-containing equipment onto people and into the environment.
  - Pressure relief devices may take the form of a reclosing pressure relief valve (PRV), a rupture disk, or even an open vent to atmosphere (where permitted).

Source: ioMosaic

Crash Course #2 – Pressure Relief Systems

- A *pressure relief system* (PRS) is a pressure relief device, its piping, and to a degree its protected equipment (the vessel, tank, rotating equipment, or other equipment that could experience overpressure), and its effluent destination.
- PRS evaluation is essential for
  - new facilities
  - as-built facilities



Source: Microsoft 365, ioMosaic Corporation

Crash Course #2 – Pressure Relief Systems

- Engineers evaluate PRS in three (3) easy steps:

1. Analyze isolable sections of a process to qualify potential causes of overpressure.
    - *Isolability* is an important concept because PRS design is intentional and specific. PRDs relieve at predetermined pressures specific to their protected equipment
        - Isolation valves that are not controlled open are isolation points
        - Control valves are isolation points because of the potential spurious behavior
        - Rotating equipment are isolation points
    - Piping & instrument diagrams (P&IDs) aid evaluation

Crash Course #2 – Pressure Relief Systems

- Engineers evaluate PRS in three (3) easy steps:

1. Analyze isolable sections of a process to qualify potential causes of overpressure.
   - Use industry standards or process-specific knowledge to consistently qualify potential causes of overpressure
   - Document the rationale
   - DOCUMENT THE RATIONALE
   - DOCUMENT THE RATIONALE

Crash Course #2 – Pressure Relief Systems

- Engineers evaluate PRS in three (3) easy steps:

2. Determine the required relief rates for qualified overpressure scenarios.
   - After *qualifying* scenarios, *quantify* them.
     - simple material balances
     - empirical relationships
     - natural laws
     - theoretical relationships
     - some combination of those things

Crash Course #2 – Pressure Relief Systems

- Engineers evaluate PRS in three (3) easy steps:

2. Determine the required relief rates for qualified overpressure scenarios.
   - Ex: The required relief rate for a hydrogen gas booster (a type of reciprocating compressor) that has been inadvertently blocked in is equal to the capacity of that booster.
   - Ex: For a liquid methanol storage vessel, the rate at which methanol vaporizes due to an external fire is two-part:
     - Heat input from external fire, Q, may come from empirical methods underpinned by radiant and convective heat transfer theory.
     - Vaporization rate comes from heat input divided by latent heat of vaporization, $W = Q/\lambda$.
   - Ex: A distillation column that separates methanol from byproducts, waste streams, and recycle streams may experience a reflux failure scenario. A H&MB around the system determines the imbalance of heat and material compared to normal conditions; excess heat may result in vaporization, and the net product of accumulated heat and material is balanced as a relief load through a pressure relief device.

Crash Course #2 – Pressure Relief Systems

- Engineers evaluate PRS in three (3) easy steps:

3. Rate or create the pressure relief systems for the relief requirements.
   - For new facilities: Design PRS to meet contemporary construction requirements; expect:
     - Frequent iterations
     - Design compromises
     - Competing interests
     - Constructability concerns
     - Unforeseen restraints
     - Hidden agendas
   - Remain engaged with piping designers, project engineers, and others throughout the design phase because constructing an improper PRS design can be **costly**.

Crash Course #2 – Pressure Relief Systems

- Engineers evaluate PRS in three (3) easy steps:

3. Rate or create the pressure relief systems for the relief requirements.
   - For existing facilities: Rating is straightforward…
     - …unless the piping layout, PRD, equipment, or process conditions are unknown
     - Check relief capacity, acceptable piping and PRD installation, and conformity to good industry practices such as RAGAGEP.
   - If the rating of a PRS design is unacceptable
     - Perform a more rigorous evaluation ("sharpen the pencil")
     - Mitigate <u>legitimate</u> design deficiencies in a process design cycle

Crash Course #2 – Pressure Relief Systems

- Engineers evaluate PRS in three (3) easy steps:

3. This last step also encompasses effluent handling.
   - For atmospheric discharge:
   - Pay great attention to *safe discharge locations* to avoid harming personnel, equipment, or the environment.
     - Flammable H_2 gas and pressurized steam are discharged to atmosphere frequently
   - Closed systems provide safe destruction for multiple PRDs. The trick is to:
     - Recognizing *global scenarios* that cause an increase in backpressure
     - Modeling the flare header hydraulics in a realistic way (is it *really* all vapor? is it *really* all at once?)

Tying These Threads Together with RAGAGEP

Tying These Threads Together with RAGAGEP

- Ever heard of the EPA or OSHA?
- Ever heard of OSHA's PSM Standard [3]?
  - Both H_2 and methanol are covered
  - 29 CFR 1910.119(a)(1)(ii) if their quantities are 10,000 lbs or greater
- But why mention the PSM Standard if it doesn't apply?
  - It is a good model and performance-based.

1910.119(a)(1)
This section applies to the following:

1910.119(a)(1)(i)
A process which involves a chemical at or above the specified threshold quantities listed in appendix A to this section;

1910.119(a)(1)(ii)
A process which involves a Category 1 flammable gas (as defined in 1910.1200(c)) or a flammable liquid with a flashpoint below 100 °F (37.8 °C) on site in one location, in a quantity of 10,000 pounds (4535.9 kg) or more except for:

1910.119(a)(1)(ii)(A)
Hydrocarbon fuels used solely for workplace consumption as a fuel (e.g., propane used for comfort heating, gasoline for vehicle refueling), if such fuels are not a part of a process containing another highly hazardous chemical covered by this standard;

1910.119(a)(1)(ii)(B)
Flammable liquids with a flashpoint below 100 °F (37.8 °C) stored in atmospheric tanks or transferred which are kept below their normal boiling point without benefit of chilling or refrigeration.

Source: 29 CFR 1910.119

Tying These Threads Together with RAGAGEP

- RAGAGEP Applicable to Methanol Synthesis Production Facilities

American Petroleum Institute (API)	
API 521: Pressure-Relieving and Depressuring Systems [7]	Standardized overpressure scenario identification and relief rate determination for high-pressure applications; Effluent disposal considerations
API 2000: Venting Atmospheric and Low-Pressure Storage Tanks [8]	Standardized overpressure and vacuum scenario identification and relief rate determination for low-pressure storage tanks; Low-pressure PRD specification and installation
API 520, Part I: Sizing and Selection of Pressure-Relieving Devices [9]	Description of PRD types; Sizing PRDs for single- and two-phase flow
API 520, Part II: Installation of Pressure-Reliving Devices [10]	Installation of PRDs; Pressure drop, backpressure, valve stability, and pipe stress considerations
National Fire Protection Association (NFPA)	
NFPA 2 Hydrogen Technologies Code [11]	Broad application of safety and construction requirements for a range of H_2 facilities; Excludes large scale electrolyzers making ≥100 kg/h H_2
NFPA 30: Flammable and Combustible Liquids	Nearly equivalent to API 2000
American Institute of Chemical Engineers – Design Institute for Emergency Relief Systems and the Center for Chemical Process Safety (AIChE DIERS & CCPS)	
Guidelines for Pressure Relief and Effluent Handling Systems [12]	Rate determination for reactive and nonreactive overpressure scenarios; Sizing pressure-relief devices (PRDs) for single- and two-phase flow; Effluent disposal

Tying These Threads Together with RAGAGEP

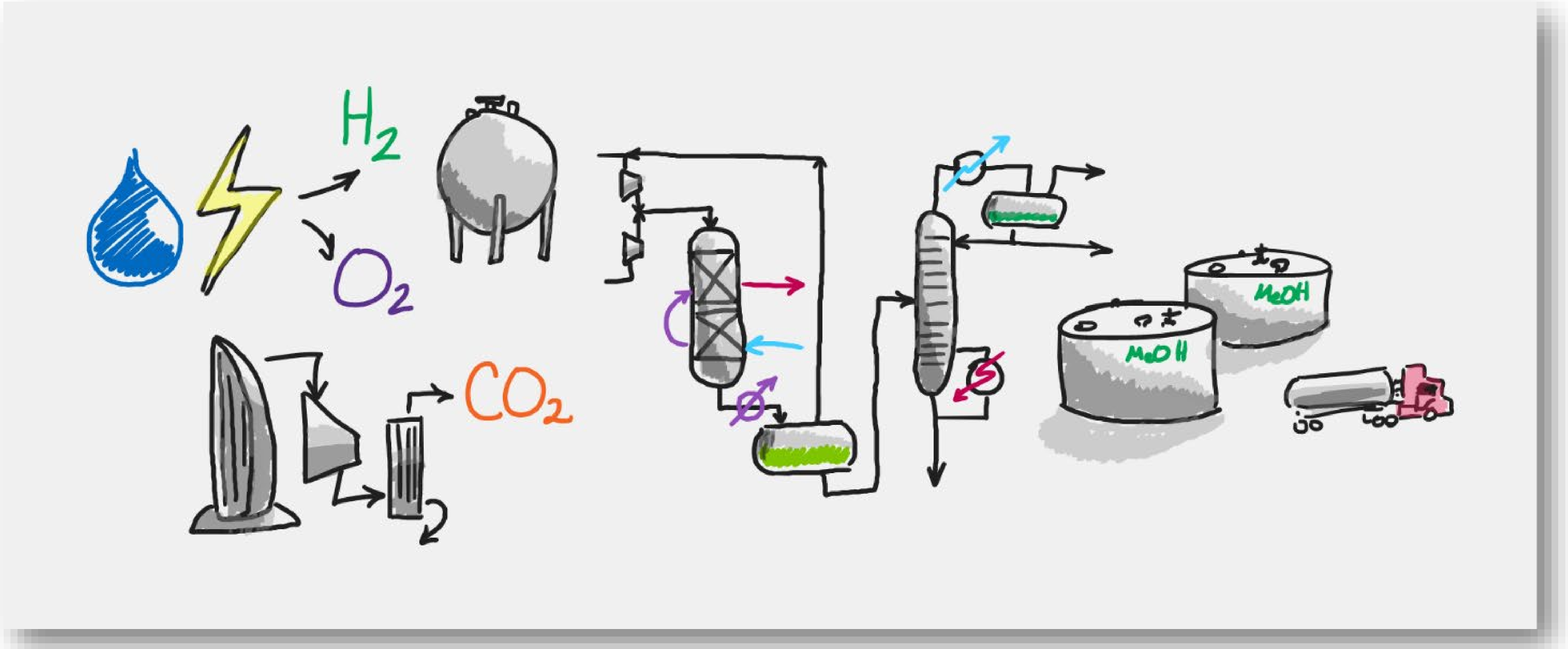
RAGAGEP Applicable to Methanol Synthesis Production Facilities

National Aeronautics and Space Administration (NASA)	
Safety Standard for Hydrogen and Hydrogen Systems [13]	Contains guidance on vents to atmosphere and to flare systems
Compressed Gas Association (CGA)	
S-1.3: Pressure Relief Device Standards, Part 3, Stationary Storage Containers for Compressed Gases	Description of PRD types; PRD design and installation requirements; Minimum PRD capacity including fire scenario relief rate determination
G-5.5 Hydrogen Vent Systems [14]	Description of H_2-specific vent system from pressure relief devices; Installation requirements
H-3 Standard for Cryogenic Hydrogen Storage [15]	Contains guidance on liquid H_2 pressure relief
Pacific Northwest National Laboratory	
H2 Tools (h2tools.org) [16]	Public website containing myriad H_2 safety guidance including references to relevant standards
Methanol Institute	
Methanol Safe Handling Manual [17]	Contains myriad safety guidance for methanol

Special Considerations

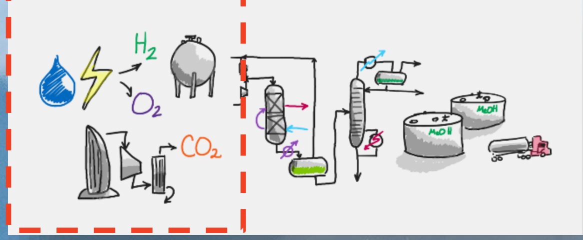
Special Considerations

- New facilities that synthesize methanol from H2 and CO2 can be broken into three (3) areas illustrated in Figure 2:
  - Sourcing & Storage
  - Reaction & Separation
  - Product Storage



Source: ioMosaic Corporation

Special Considerations



- Sourcing & Storage
  - Liquid CO_2 relief or pressurized gaseous CO_2 can chill downstream piping systems,
    - Use the right steel.
    - Maintain downstream piping free of accumulated water, which can freeze on contact and *really* create a blockage.
    - External freezing of atmospheric moisture (icing on the outside of pipes) is also possible, especially on uninsulated piping.
  - CO_2 is an asphyxiant, so relief to atmosphere must never be to an enclosed area where personnel are present. ☠

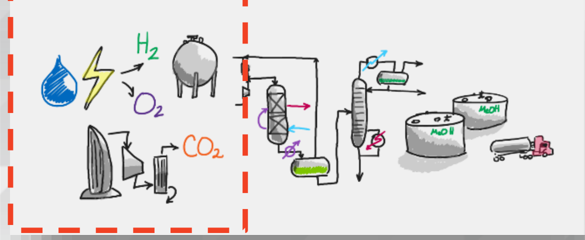
Source: Microsoft 365

Special Considerations

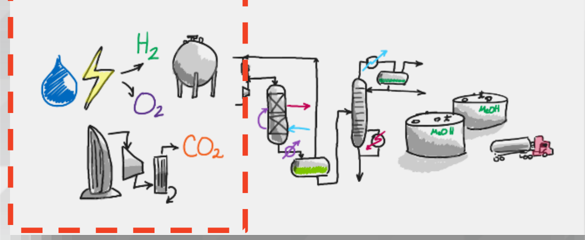
- Sourcing & Storage
  - Liquid H_2 and cold gaseous H_2 pressure relief systems can chill downstream piping systems, instantly freezing any accumulated water and creating a blockage.
  - Furthermore, H_2 can be cold enough to freeze atmospheric air. How about that! At sea level:
    - H_2 melting pt -435 °F (-259 °C); boiling pt -423 °F (-253 °C)
    - N_2 melting pt -346 °F (-210 °C); boiling pt -320 °F (-196 °C)
    - O_2 melting pt -361 °F (-218 °C); boiling pt -297 °F (-183 °C)
  - See CGA G-5.5 and H-3 for additional details

Source: Microsoft 365

Special Considerations

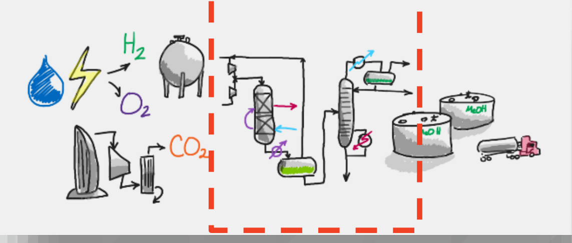


- Sourcing & Storage
  - Despite historical use and any notion to the contrary, using a broom to check for invisible H_2 fires is neither accurate nor especially safe.
  - Specialized adhesives, tapes, gas detectors, and thermal detectors are the safest way to check for fugitive H_2 emissions and flames.
  - A dispersion and radiation analysis is recommended to document the reasonable extent that unignited effluent can travel and the thermal radiation it exhibits after ignition.



Special Considerations

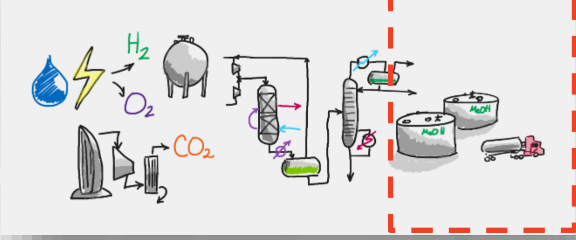
- Sourcing & Storage
  - Electrolyzers are often sold as packaged skids that “plug and play” into a facility
  - Take the time to understand the potential causes of overpressure in this technology
    - external fire on liquid-containing vessels
    - overproduction of gas
    - blocked outlet
  - Ensure that pre-packaged PRDs are installed according to RAGAGEP, especially those with atmospheric termination points



Special Considerations

- Reaction & Separation
  - The separation technology used purify reactor products are just as unique as the choice of reactor.
  - There are three important considerations that can be learned from refining and petrochemical industries:
    - (1) Column imbalance, where the failure of a cooling utility or a blocked outlet can alter the heat and material balance in the system.
    - (2) Series fractionation, where the failure of a heating utility can cause volatile liquids (or dissolved gas) to leave the bottom and then flash in a lower-pressure, downstream recipient system.
    - (3) Gas blow-by from the reactor effluent separator, where a loss of liquid level control can cause hot gas or vapor streams from the reactor to enter the distillation system.

Product Storage



- Product Storage
  - Check for flammable dispersion and thermal radiation of ignited methanol effluent.
  - Perform toxic dispersion analysis from atmospheric discharge points.
    - Consider reasonable AEGL exposure times [22].
  - As with the upstream distillation system, consider gas blow-by if storage is interconnected with the separation process

A Glimpse of the Future

A Glimpse of the Future

- AIChE positioned itself years ago for this stuff
  - Center for Energy Initiatives [23] and Center for Hydrogen Safety [24]
  - For direct and practical applications, the Center for Hydrogen Safety promotes the use of www.H2Tools.org, a useful and free-to-use web resource developed and maintained by The Pacific Northwest National Laboratory with support from the US Department of Energy
- For the world of pressure relief systems, API offers some of the most influential and widely used RAGAGEP available, such as API 521. API 521 was created with refinery processes in mind, but over the years it has been readily applied to all manner of facilities.
  - Based upon recent meetings within the API Subcommittee on Pressure Relieving Systems, it is likely that API 521 will begin addressing pressure relief in energy transition technologies such as decarbonization with CCS & CCU, electrolysis, and more.

Conclusion

- This paper attempts to bridge the gap between decarbonization via methanol synthesis and pressure relief systems design. It is the presenter's experience-based approximation that there are few organizations and industry professionals that have deep expertise in decarbonization technologies, associated methanol synthesis, and pressure relief system design. The presenter therefor attempts to promote interest in all these areas by including relevant concepts and technologies such as H_2 generation from electrolysis, methanol synthesis from CO_2 hydrogenation, distillation, Process Safety Management, RAGAGEP, specific standards and best practices, and special considerations.

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