Continuous Emissions Monitoring Systems

Engineering & Design

For Refinery Processes

*a technical solution to meet every need*

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Fractional distillation is useful for separating a mixture of substances with narrow differences in boiling points, and is the most important step in the refining process.
You can change one fraction into another by one of three methods:

- **breaking large hydrocarbons into smaller pieces** (cracking)
- **combining smaller pieces to make larger ones** (unification)
- **rearranging various pieces to make desired hydrocarbons** (alteration)

**Thermal** - you heat large hydrocarbons at high temperatures (sometimes high pressures as well) until they break apart.

- **steam** - high temperature steam (1500°F / 816°C) is used to break ethane, butane and naptha into ethylene and benzene, which are used to manufacture chemicals.

- **visbreaking** - residual from the distillation tower is heated (900°F / 482°C), cooled with gas oil and rapidly burned (flashed) in a distillation tower. This process reduces the viscosity of heavy weight oils and produces tar.

- **coking** - residual from the distillation tower is heated to temperatures above 900°F / 482°C until it cracks into heavy oil, gasoline and naphtha. When the process is done, a heavy, almost pure carbon residue is left (**coke**); the coke is cleaned from the cokers and sold.
You can change one fraction into another by one of three methods:

- breaking large hydrocarbons into smaller pieces (cracking)
- combining smaller pieces to make larger ones (unification)
- rearranging various pieces to make desired hydrocarbons (alteration)

**Catalytic** - uses a catalyst to speed up the cracking reaction. Catalysts include zeolite, aluminum hydrosilicate, bauxite and silica-alumina.

**fluid catalytic cracking** - a hot, fluid catalyst (1000°F/538°C) cracks heavy gas oil into diesel oils and gasoline.

**hydrocracking** - similar to fluid catalytic cracking, but uses a different catalyst, lower temperatures, higher pressure, and hydrogen gas. It takes heavy oil and cracks it into gasoline and kerosene (jet fuel).
You can change one fraction into another by one of three methods:

- breaking large hydrocarbons into smaller pieces (cracking)
- combining smaller pieces to make larger ones (unification)
- rearranging various pieces to make desired hydrocarbons (alteration)

**Unification**

Sometimes, you need to combine smaller hydrocarbons to make larger ones -- this process is called unification. The major unification process is called catalytic reforming and uses a catalyst (platinum, platinum-rhenium mix) to combine low weight naphtha into aromatics, which are used in making chemicals and in blending gasoline. A significant by-product of this reaction is hydrogen gas, which is then either used for hydrocracking or sold.
You can change one fraction into another by one of three methods:

- breaking large hydrocarbons into smaller pieces (cracking)
- combining smaller pieces to make larger ones (unification)
- rearranging various pieces to make desired hydrocarbons (alteration)

**Alteration**
Sometimes, the structures of molecules in one fraction are rearranged to produce another. Commonly, this is done using a process called **alkylation**. In alkylation, low molecular weight compounds, such as propylene and butylene, are mixed in the presence of a catalyst such as hydrofluoric acid or sulfuric acid (a by-product from removing impurities from many oil products). The products of alkylation are high octane hydrocarbons, which are used in gasoline blends to reduce knocking.

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Descriptions courtesy of www.howstuffworks.com
Fractional Distillation and Chemical Processing CEMS

- Most units utilized in fractional distillation and chemical processing utilize heaters burning refinery and/or natural gas and require CEMS. Process heaters may utilize Selective Catalytic Reduction (SCR) for NO\textsubscript{x} control.

CEMS Design Considerations

- Area classification of shelter/cabinet placement
  
  If shelter/cabinet is placed in a classified area
  - Can a positive pressure purge system be used to de-classify shelter/cabinet interior to general purpose area?
  - Site requirements for conduit, receptacle, misc. equipment whether in a classified or general purpose area.

- Space limitations including access for HVAC maintenance and I/O connections.

- Shelter ambient gas monitors for worker safety.
Fractional Distillation and Chemical Processing CEMS

CEMS Design Considerations Continued

- If SCR is utilized for NO\textsubscript{X} control
  - Dual range NO\textsubscript{X} analyzer for post-SCR measurement including associated cal gas equipment.
  - How will NH\textsubscript{3} slip be measured?
    - Tunable Diode Laser (TDL)
    - Differential NO\textsubscript{X} calculation
    - Converted NH\textsubscript{3} measured as NO\textsubscript{X}

- Calibration gas supply for startup and certification.

- Site specific boilerplate specifications required to be met.

Data Acquisition

- How will CEMS data be handled and stored?
  - Data Acquisition System (DAS) for data handling and storage.
  - DCS to handle CEMS data
  - Co-mingling of data issues

- Most refinery processes subject to 40CFR Part 60 compliance. Some processes may be large enough to be subject to 40CFR Part 75, requiring data substitution routines.

NO\textsubscript{X} & O\textsubscript{2} CEMS on refinery heater with stack mounted NH\textsubscript{3} measurement using TDL (tunable diode laser)
Auxiliary Refinery Processes

Additional support processes are required for refinery operation to aid in refining of the crude oil and handling of the process waste:
- **power and steam production for process heat (Co-Gen Plant)**
- **hydrogen production for hydro treating processes (Hydrogen Plant)**
- **sulfur recovery for processing waste acid gases (Sulfur Recovery Unit)**

**Cogeneration Plant**

Cogeneration Plants are used to produce power and steam for use in the refinery processes. Steam specifically can be used for process heat and is integral in the operation of the hydrogen plant and sour water steam stripper.
Most Cogeneration Plants utilize combined cycle turbines burning natural gas and require CEMS. The turbines typically utilize Selective Catalytic Reduction (SCR) for NO\textsubscript{X} control.

CEMS Design Considerations

- Area classification of shelter/cabinet placement is typically general purpose as the CoGen plant is remotely located from the refinery.

- If SCR is utilized for NO\textsubscript{X} control
  - Dual range NO\textsubscript{X} analyzer for post-SCR measurement including associated cal gas equipment.
  - How will NH\textsubscript{3} slip be measured?
    - Tunable Diode Laser (TDL)
    - Differential NO\textsubscript{X} calculation
    - Converted NH\textsubscript{3} measured as NO\textsubscript{X}

- Calibration gas supply for startup and certification.
Cogeneration Plant CEMS

CEMS Design Considerations Continued

- Site specific boilerplate specifications required to be met.

- Data Acquisition
  - Stand alone data acquisition system (DAS) typically utilized for data manipulation and storage.
  - System may be subject to 40CFR Part 60 or 40CFR Part 75, depending on the amount of power sold to the grid.

NEMS (NO\textsubscript{X} Emissions Monitoring System)
Auxiliary Refinery Processes

Additional support processes are required for refinery operation to aid in refining of the crude oil and handling of the process waste:
- power and steam production for process heat (Co-Gen Plant)
- hydrogen production for hydro treating processes (Hydrogen Plant)
- sulfur recovery for processing waste acid gases (Sulfur Recovery Unit)

Hydrogen Plant
Hydrogen plants are used to produce hydrogen gas used in the hydro treating refinery processes, particularly the hydrocracker and hydrotreater units. Natural gas is converted to hydrogen through the steam reforming process.
Most Hydrogen Plants utilize steam reformer burners burning natural gas and require CEMS. The burners may utilize Selective Catalytic Reduction (SCR) for NO\textsubscript{X} control.

CEMS Design Considerations

- Area classification of shelter/cabinet placement
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  - Can a positive pressure purge system be used to de-classify shelter/cabinet interior to general purpose area?
  - Site requirements for conduit, receptacle, misc. equipment whether in a classified or general purpose area.

- If SCR is utilized for NO\textsubscript{X} control
  - Dual range NO\textsubscript{X} analyzer for post-SCR measurement including associated cal gas equipment.
  - How will NH\textsubscript{3} slip be measured?
    - Tunable Diode Laser (TDL)
    - Differential NO\textsubscript{X} calculation
    - Converted NH\textsubscript{3} measured as NO\textsubscript{X}
Hydrogen Plant CEMS

CEMS Design Considerations Continued

- Calibration gas supply for startup and certification.
- Site specific boilerplate specifications required to be met.

Data Acquisition
- How will CEMS data be handled and stored?
  - Data Acquisition System (DAS) for data handling and storage.
  - DCS to handle CEMS data
  - Co-mingling of data issues
- Most refinery processes subject to 40CFR Part 60 compliance. Some processes may be large enough to be subject to 40CFR Part 75, requiring data substitution routines.

CEMS measuring NO\textsubscript{x}, CO, wet and dry O\textsubscript{2}, ammonia and stack flow on Hydrogen Plant.
Additional support processes are required for refinery operation to aid in refining of the crude oil and handling of the process waste:

▪ power and steam production for process heat (Co-Gen Plant)
▪ hydrogen production for hydro treating processes (Hydrogen Plant)
▪ sulfur recovery for processing waste acid gases (Sulfur Recovery Unit)

Sulfur Recovery Unit
Sulfur Recovery Units remove the sulfur compounds ($\text{H}_2\text{S}, \text{SO}_2$) from the waste stream gases and convert them to elemental sulfur using a process developed by Carl Claus. The unit uses both thermal and catalytic reductions for removal of the sulfur compounds. Post recovery gases may be passed to a Tail Gas Incinerator or Caustic Scrubber for further cleanup.
Most Sulfur Recovery Units (SRU) exhaust waste acid gas through a Tail Gas Incinerator or Caustic Scrubber and require CEMS. Tail Gas Incinerator and Caustic Scrubber CEMS are the most difficult refinery CEMS applications due to variable fuel compositions and wide range of expected emissions.

CEMS Design Considerations

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  - Site requirements for conduit, receptacle, misc. equipment whether in a classified or general purpose area.

- Space limitations including access for HVAC maintenance and I/O connections.

- Shelter ambient gas monitors for worker safety.
CEMS Design Considerations Continued

- Calibration gas supply for startup and certification.
- Site specific boilerplate specifications required to be met.

Data Acquisition
- How will CEMS data be handled and stored?
  - Data Acquisition System (DAS) for data handling and storage.
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- Co-mingling of data issues
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Tail Gas Incinerator
CEMS Design Considerations Continued

**Tail Gas Incinerator CEMS**
- Wide range of SO\(_2\) emissions, ~10ppm during normal operation and % level during plant upsets.
  - Separate SO\(_2\) analyzers may be required to cover both controlled and uncontrolled plant operation.
  - Worker safety while working with % level gases.
- Stack flow measurement typically required due to variable heat input capacity of waste gas. (Mass emissions reporting)

**Caustic Scrubber CEMS**
- Measurement of SO\(_2\) in the presence of NH\(_3\)
  - Formation of ammonia salts
  - Knockout of NH\(_3\) at probe location to avoid loss of SO\(_2\) sample. Critical for low level SO\(_2\) measurements.
- Stack Flow measurement typically required.
Gas Chromatographs are used at different points throughout the refinery process for both process control and regulatory reporting:

- flare gas composition for 40CFR60, Subpart J compliance (H₂S, SO₂, TRS)
- refinery gas sulfur and heat content used by heaters (H₂S, SO₂, TRS, BTU)
- product composition (Ethane, Propane, Butane, Pentane, C₄+, C₆+)

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Since 2005, Cemtek Environmental has been responsible for the service of all 26 CEMS at a local SCAQMD Refinery. Cemtek is also performing the routine maintenance and calibration on the ambient air monitoring systems and fuel flow transmitters. To provide 7 day a week service, Cemtek has 8 full time service technicians dedicated to this site.
CEMTEK supplied a new CEMS for monitoring sulfur recovery unit tail gas incinerator emissions. The new CEMS was integrated into the existing Class 1, Div 2 CEMS shelter measuring NO\textsubscript{x}, SO\textsubscript{2}, CO, wet & dry O\textsubscript{2}, and stack flow. Also provided was a custom built, 18 foot multi-point heated probe for measurement of a stratified stack.
SCAQMD Refinery RECLAIM CEMS Application

Supplied CEMS in a NEMA 4X Class I, Div II Stainless Steel shelter to measure NO$_x$, SO$_2$, & O$_2$. 
Supplied CEMS in a NEMA 4X Class I, Div II Stainless Steel cabinet to measure NO\textsubscript{x}, CO, wet and dry O\textsubscript{2}, ammonia and stack flow. Included field installation supervision services, start-up, training and certification services. Certified 2005
Cemtek provided a new SCAQMD RECLAIM CEMS in a NEMA 3R cabinet for measuring $\text{NO}_x$, $\text{O}_2$, & ammonia.
Cemtek provided four new NEMS (NO$_X$ Emissions Monitoring Systems) in a NEMA 3R cabinet for measuring inlet NO$_X$. These replaced 20 year old KVB process systems.
Cemtek provided a new CEMS in a Class I, Div II shelter for measuring inlet NO\textsubscript{X} and stack NO\textsubscript{X} & O\textsubscript{2} utilizing ABB analyzers and M&C Products probes for classified areas.
Cemtek provided a new CEMS in a shelter for measuring SO$_2$ & O$_2$ in a wet gas scrubber application.
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- Most Cemtek Environmental staff members currently have TWIC cards.

- Cemtek Environmental is an active participant in the OSCA/ASAP Drug Solutions testing program.