
Question 16: What is the typical carbon monoxide (CO) concentration in the reformer net gas? How is the CO content measured? What are the potential effects to downstream units from the CO?

MELDRUM (Phillips 66)

Carbon monoxide can form in reformer units as the hydrocarbon reacts with moisture under very low-unit pressure conditions. Typically, semi-regeneration reformer net gas would have nil CO and only a minimal amount in a CCR-type unit. I expect it to probably be on the order of 5 ppm (parts per million), though some units report routine measurements of 10 to 20 ppm CO in their net hydrogen off gas.

One of our cyclic units that was operating at 400-pound had CO as high as 20 ppm in its net hydrogen stream when the recycled moisture rose to around 300 ppm. The excessive water entered the reformer from a leaking side reboiler on a wet debutanizer that used a slipstream of the reformer reactor effluent as the heat source. The water then returned to the reformer product separator. The high CO caused deactivation in the catalyst in a downstream isomerization unit.

Accurate measurements of CO in the net gas are difficult. Reformer units are not expected to have much CO, so they seldom have an online analyzer. A colorimetric tube – Gastec or Dräger type – can be used to give an indication of the presence of CO, but accuracy for a quantified number is difficult and requires the use of a carbon pre-tube to remove the hydrocarbons.

CO is detrimental to downstream hydrogen-using units in three principal areas. CO in hydrogen being fed to a distillate hydrotreater will methanate, consuming the hydrogen that would have otherwise been used for the desulfurization reactions. This will have the effect of lower catalyst activity. CO in hydrogen fed as a makeup stream to an isomerization unit will also methanate and form moisture that will deactivate the isomerization catalyst. CO that did not methanate in the second example could act as a poison to the platinum metal function of the isomerization catalyst. UOP suggests a CO limit of 1 ppm max for isomerization hydrogen makeup gas. My Answer Book response also includes some of the common steps used to minimize CO formation in reformer units, particularly in a CCR unit.

BULLEN (UOP LLC, A Honeywell Company)

As you can see in this table, we have correlated some different types of operation and ranges of CO levels. As Craig alluded, the numbers vary quite a bit, which can be due to conditions in the unit, as well as analytical capabilities. There seems to be a trend that the lower pressure units generate more CO than higher pressure units.

CO concentration in the reformer net gas



CCR Platforming Process Unit Type	Typical CO in Net Gas, mol ppm
Lower Pressure (50-65 psig)	5-25
Higher Pressure (85-100 psig)	3-14
SR Platforming Unit (250-450 psig)	<1

The laboratory method we recommend using is UOP 603, which is a laboratory method for CO and CO₂ and hydrogen. However, a lot of refiners cannot do this method. The gas detection tube route is fairly common. Our point of view is that with the gas detection tubes, if one carbon pre-tube is good, then two is better. So, we usually ask them to use two tubes instead of one to help eliminate the breakthrough of hydrocarbons that can make a false high value for CO.

As Craig said, the issue with chloride and alumina isomerization catalyst is that you will deactivate the catalyst. However, if you are using another type of catalyst, like the Par-Isom catalyst or zeolitic catalyst, the actual suppression you will get will be very dependent on what temperatures you are running. As you approach the 400°F temperature, you tend to methanize the CO in the first part of the bed. So CO tends to have less of an effect on the metal function of the isomerization catalyst and becomes more of an issue of activity suppression due to the water on the acid sites. The same would apply if you had a saturation unit with platinum catalyst. It would also behave in a similar manner to these higher temperature isomerization units.

R.K. (RICK) GRUBB (Chevron Products Company)

Another aspect needs to be mentioned for the lower pressure reforming units. You have to take into consideration your nickel carbonyl formation when you shut down a hydroprocessing unit that is using the reformer hydrogen. You may have to either swap the hydrogen source or think of another shutdown procedure that will ensure no nickel carbonyl formation.

CRAIG MELDRUM (Phillips 66)

CO is detrimental to downstream hydrogen using units for three principal reasons:

- 1) CO will methanate in HDS (hydrodesulfurization) units consuming hydrogen, which will take away catalyst activity.
- 2) Much of the CO will methanate in isomerization units, forming water that will deactivate the isomerization unit catalyst.
- 3) The non-methanated CO in the isomerization unit will poison the metal function of platinum on the catalyst.

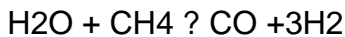
Note: The UOP suggested CO limit on isomerization unit hydrogen makeup gas is 1 ppm (10 ppm for CO + CO₂). UOP reports that CO levels greater than 6 ppm will not allow the isomerization unit catalyst to meet its cycle life guarantee.

The common steps to minimize CO formation in the reformer are:

- Minimize moisture in the system (feed water control and good regeneration drying),
- Minimize the last reactor temperature,
- Maximize the H₂/HC ratio, and
- Minimize catalyst circulation rate in a CCR.

PATRICK BULLEN (UOP LLC, A Honeywell Company)

The CO concentration in reforming unit net gas can be impacted by a number of factors: system pressure, temperature, and moisture in the recycle gas, as well as the H₂/HC (hydrogen/hydrocarbon) of the operation. Operating pressure has the most significant impact on CO production in a reforming unit. CO formation in reforming operation is produced via steam reforming of hydrocarbons:



Thermodynamically, this CO formation reaction is more favorable at lower pressures. CO production is inversely proportional to the pressure squared. As such, a semi-regeneration reforming unit, being significantly higher pressure than typical continuous reforming units, will tend to produce less CO than a typical continuous reforming operation. Likewise, the lower pressure high severity reforming unit operation is more favorable for CO productions.

Commercial reforming net gas CO data from CCR Platforming™ process units can range from 1 to 40 mol ppm. The table below indicates typical ranges for various unit types. Typically, CO levels in the semi-regeneration reforming units are at trace ppm levels due to the high pressure and low-moisture range operation.

CCR Platforming™ Process Unit Type	Typical CO in Net Gas, mol ppm
Lower Pressure (50-65 psig)	5-25
Higher Pressure (85-100 psig)	3-14
SR Platforming™ Unit (250-450 psig)	<1

For testing of CO in reformer net gas, UOP recommends method UOP 603 for trace CO and CO₂ in hydrogen. For CO in light gaseous hydrocarbons, analysis by GC is recommended. Analysis by gas detector tubes can also be considered for measuring CO at elevated levels when used with several carbon adsorbing pre-tubes.

CO in reforming net gas can have an impact on downstream users that may be sensitive to CO or H₂O that may be formed due to the reverse steam reforming reaction, also known as the methanation reaction. In the case of a Butamer™ and Penex™ catalyst, water is a permanent deactivator. A typical rule of thumb is that 1 pound of H₂O kills 62 pounds of Butamer™ and Penex™ catalyst.

For other types of catalysts, such as Par-isom™ Process and zeolitic isomerization catalysts that operate at higher temperature, the water generated from methanation of CO is a temporary activity suppressant. Platinum-based BenSat™ catalyst behaves similarly to these isomerization catalysts.

GARY HAWKINS (Emerson Process Management)

With respect to the second part of the question, the carbon monoxide content, as well as other components in the net gas of a naphtha reforming unit, can be measured with a variety of measurement principles depending upon the accuracy and reliability required, other species present that may interfere with a particular technology, and the expected range of concentration of carbon monoxide. These same comments apply to measuring other refinery gases, such as the net hydrogen and PSA (pressure swing adsorption) tail gas from steam reforming units for hydrogen production.

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