Emissions from Delayed Cokers

An analysis of the emissions and air quality challenges from delayed coking units

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Introduction

A delayed coker is one of several types of coker process units used in oil refineries to convert heavy oils to useful lighter products. All cokers use heat to thermally crack the larger hydrocarbon molecules. In delayed cokers, heavy oil is heated in a continuously operating process furnace, then enters a large, vertically-oriented cylindrical vessel, in which the coking reactions take place. This vessel is called a coke drum. The term "delayed" coker refers to the fact that the coking reactions do not take place in the furnace, but rather are delayed until the oil enters the coke drum. In the coke drum, large oil molecules are cracked to lighter products and residual coke, which forms on the vessel walls. The lighter hydrocarbons flow out of the drum and are further processed into fuel products. Gradually the layer of coke builds up until the coke drum is almost filled with coke. When the drum is nearly filled, then the hot oil from the furnace is directed to a clean coke drum, while the full one is decoked. The decoking cycle involves cooling and depressuring the drum, sweeping it with steam to remove residual hydrocarbon vapor, opening up the top and bottom heads, and then using high pressure water lances to cut the coke out of the drum. The coke falls out the bottom of the drum into a pit, where the water is drained off and conveyers take it to storage or rail cars. Then the drum is closed up and is ready for another coking cycle.

The feedstocks for delayed cokers are typically the heaviest (highest boiling) fractions of crude oil that are separated in a crude fractionator. This stream usually is taken directly from the bottom of the crude fractionator, while still hot, into the delayed coker furnace.

The nature of the coke formed is highly dependent on the characteristics of the feedstock to the coker. Most cokers produce what is known as sponge coke, which is relatively easy to quench, strip and cool. Certain heavy feeds produce shot coke, which is more difficult to cool and quench and, on occasion, can cause coke bed eruptions or blowouts. Other heavy feeds can produce a very dense coke, which can have a tendency to burn spontaneously in the coke pit.

The majority of the heavy oil upgraders and conventional oil refineries are relying on delayed cokers to process their heaviest fractions. As more and more heavy crude oils are refined to meet demand for fuel products, the quantities of coke produced continue to increase. In addition, massive quantities of coke are produced in the upgrading of Canadian tar sands, Venezuelan Orinoco tars and other heavy oils.

Most coke contains high concentrations of metals and sulfur compounds, which makes it a poor quality fuel. However, it is sold as a low quality fuel for applications that have flue gas cleanup facilities, or are in parts of the world not having emissions regulations. Smaller quantities of specialty cokes are used for carbon black in tire manufacture, for electrodes, and other applications.

Sources of emissions

Delayed cokers are unique among refinery units in that the coke drums do not operate continuously, but rather go through cycles of coking and decoking. For continuous processes, and the continuous portions of the delayed coking units, the hydrocarbons are contained in closed systems and only get into the atmosphere if there is a leak. However, the coke drums must be opened to the atmosphere in order to get the coke out. During this sequence of operations there are opportunities for emissions of hydrocarbons and particulate matter.

At the start of a coke drum decoking cycle, the pressure is gradually lowered by allowing vapors to vent to a closed blowdown system, which may then lead them to either a flare or a gas recovery system. Once the pressure in the coke drum is too low to push the vapor into the blowdown system, typically 5 psi, the drum is then vented to the atmosphere. This venting has the potential to release significant volumes of volatile organic compounds.

The other major opportunity for hydrocarbon emissions is when the coke is dumped out of the drum into the pit below and then transported away. At this time, vapors trapped in the coke may escape to the atmosphere. The amount of volatile hydrocarbons will depend on many factors, such as the temperature of the coke when it is dumped, the size of the coke particles or chunks, the density and porosity of the coke and other factors relating to the properties of the feedstock.

Throughout the coke cutting, dumping, loading and transporting operations, fine particulate matter can escape to the atmosphere unless controls are employed.

Delayed Cokers in the Houston-Galveston Region

There are four large delayed coking units or complexes located in the Houston-Galveston region: one in Houston, two in Texas City, and one in Deer Park. Some of these are complexes comprised of two units. The total charge capacity of these units is 281,800 barrels per calendar day.

There are two other coking units in the area, one a fluid coker and the other a Flexicoker. Although the emission of particulates could be a concern with these units, both of them are continuous processes that do not present the unique opportunities of delayed coking for emitting volatile organics.

Uncertainties regarding delayed coker emissions

Although the potential for significant emissions exists, the actual amounts of hydrocarbon emissions are not very well characterized. Few, if any, refiners measure air emissions from cokers. There is a severe lack of data from any source for emissions from venting, coke dumping and handling. Moreover, the limited data that are available are inconsistent and not always correlated with coker operating cycles.

The lack of data and variation in results from measurements of delayed coker emissions is evident by a comparison of two studies using DIAL technology[1]. The first study, performed at a refinery in Canada, found that the coker and vacuum units were responsible for just over seventeen percent of total emissions of alkane and larger hydrocarbons (465 lbs/hr), over forty-two percent of methane emissions (276 lbs/hr), and over one quarter of total benzene emissions (2.8 lbs/hr). This study found significant variations in emissions during different phases of the coking process. Hydrocarbon emissions from the closed coking unit were measured at 251 lbs/hr. These emissions spiked to 657 lbs/hr during the drilling and decoking phases of the coke process.[2]

By contrast, a DIAL study of the BP Texas City refinery found average emissions of benzene from the coker unit to be between 1.5 and 2.1 lbs/hr of benzene while measured during the last six hours of the coking process, including the decoking phase. Benzene levels were at or below the detection limits during most of the coking cycle. The DIAL measured total VOC concentrations at the coker of between 10 and 32 lbs/hr. While there is still a great deal of difference in measured VOC numbers, it is still far less in volume and size of variation than the emissions measured in the Alberta study.[3]

Current regulations and EPA activities

In June 2008 EPA issued the final New Source Performance standard for refineries, including coking units. The final standards in 40 CFR part 60, subpart Ja includes work practice standards for reducing emissions of VOC from delayed coking units. The final work practice standard for delayed cokers requires affected delayed coking units to depressure to 5 pounds per square inch gauge (psig) during reactor vessel depressuring. The standard requires that the exhaust gases be vented to the fuel gas system or to a flare.

Although the MACT rules date to 1998, the final petroleum refinery MACT residual risk rule was anticipated to be promulgated in mid-January 2009. It has been stalled as the Obama administration and new leadership at the Environmental Protection Agency review the rule.

[1] DIAL (Differential Absorption LIDAR) uses a laser as a light source to quantify and speciate air emissions from refinery process units. DIAL's value is that it can effectively and efficiently take "snapshot" measurements of emissions from units such as cokers for which there are no other reasonably viable constant monitoring technologies.

[2] (Alberta Research Council Inc.)

[3] (Nettles)

Recommendations

1. Establish comprehensive testing of delayed cokers during the decoking cycles of the coke drums. Test results must be correlated with the steps in the decoking cycle.
   a. EPA and TCEQ to sponsor testing with DIAL and infrared cameras
   b. New regulations are needed that require all coker operators to run routine tests on air emissions and VOCs in water effluent from coke drums during decoking cycles, and to report the results.
2. The new NSPS refinery rules for delayed cokers should be extended to cover all existing units.
3. Test results should be analyzed to determine what additional controls and regulations are needed. For example, the decision to require coke drum vapors to be contained down to a pressure of 5 psi should be revisited. If data support it, this rule should be revised to 2 psi. Updated regulations should be implemented within two years.
4. All cokers should be required to control particulate emissions from coke handling through use of enclosures, water sprays or other dust-minimization measures.

Works Cited

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