pH Measurement in Refining Crude Unit Overhead

Process Overview

Oil refineries use distillation columns to separate light components such as gasoline and heavy components such as lubricants from crude oil. The distillation towers consist of a series of re-boiling and condensation steps through which the heavier components become concentrated in the lower sections of the distillation tower and the lighter components are concentrated in the upper sections.

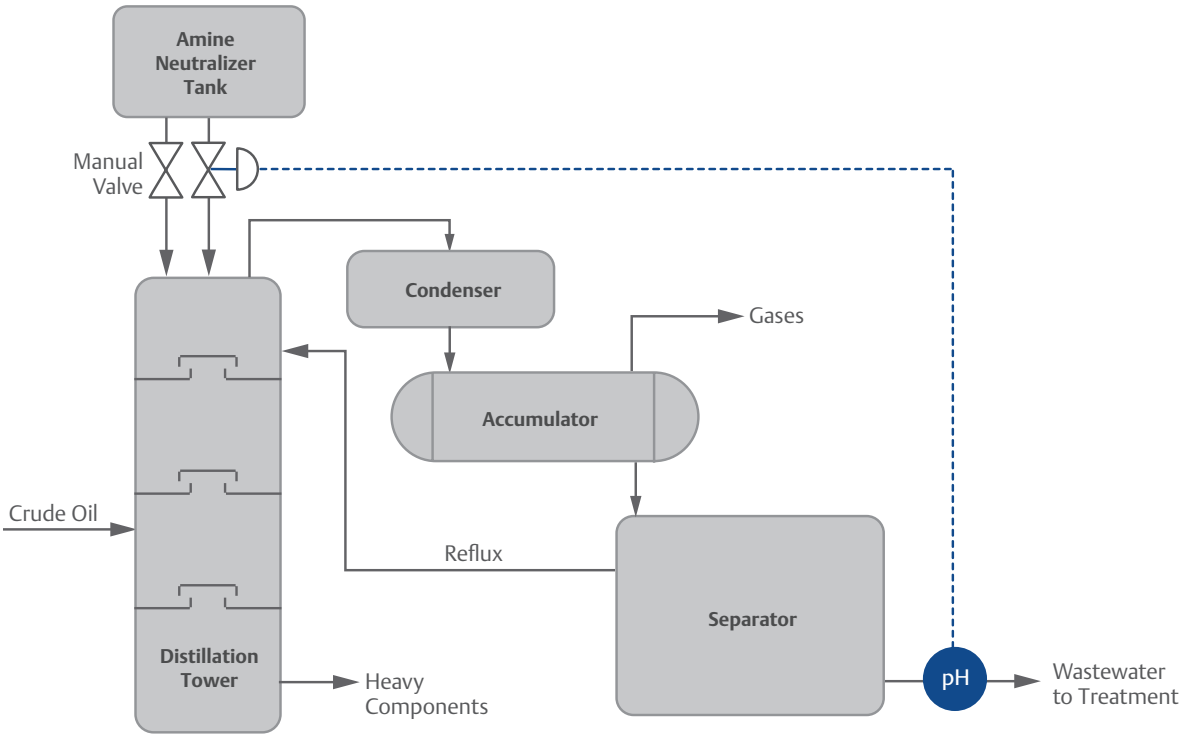
The upper third of the distillation tower produces light oil with substantial amounts of water that must be allowed to drop out of a separator vessel. Salt impurities found in most crude oils are more soluble in water than in oil and tend to accumulate in the distillate (or overhead) product. These impurities cause the separated water to become acidic.

The water/oil vapors from the top of the crude tower are passed through a condenser and the resulting liquid is separated into oil and water. The oil is mostly transferred to another column, though some may be recycled to meet process specifications. Unless neutralizing chemicals are added to control pH, the corrosive acidic water will attack metal process equipment, particularly the upper portion of the crude tower, over-head piping, condensers, and accumulators (see Figure 1).

pH Measurement

pH is monitored and controlled to reduce corrosion and extend the life of the expensive equipment. A sample is drawn from the bottom of the accumulator and, after another separation step, is measured for pH. A neutralizing chemical is added overhead to raise the pH and prevent corrosion in the tower. The flow system creates a time lag of 15 to 45 minutes between injection of the neutralizer and pH measurement at the sensor. This time lag can cause inadequately slow response to large changes and oscillations for periodic changes. To minimize these problems, the pH is neutralized in two stages:

Figure 1 - Refining Crude Unit Overhead Diagram



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1. A film-forming corrosion inhibitor (an organic amine), which also has neutralizing properties, is manually fed into the overhead to neutralize about 80% of the stream acidity. If process flow rates are inconsistent, flow-paced control addition can be used. This coarse pH adjustment also forms a protective film on the metal surfaces.
2. A proportional control algorithm is used to “trim” the pH to within 0.2 pH units of the setpoint (usually between 5.5 and 6.5). This is achieved by separately injecting the neutralizing amine to correct only the final 20% of the acidity.

The presence of residual oil in the pH sample stream makes this a challenging application for pH sensors. Over time, the oil coats the pH sensor reference junction, interfering with the electrical connection between the reference and measurement electrodes and causing and unstable and unreliable measurement. As a result, pH sensors in this application usually require frequent cleaning and maintenance.

The Emerson Solution

The Rosemount™ 3500P pH/ORP Sensor is the top recommendation for continuous pH measurement in this application because it is offered with an oil resistant electrolyte that resists coating from trace oil. The double junction design uses two layers of porous junctions to separate the process chemicals from the silver reference and allows the outer reference solution to be conveniently refilled with a preloaded syringe. Rosemount 3500P design can be customized for different application situations and includes a titanium solution ground for complete diagnostics of the reference and glass portions of the sensor. This sensor is also available with the convenient VP connector and in a retractable metal housing (Rosemount 3400), which allows sensor removal without shutting down the process.

The Rosemount 3500P pH sensor is compatible with all Rosemount liquid analysis transmitters including the Rosemount 5081 Explosion Proof Transmitter which is often preferred in refineries due to its robust electronics and rugged explosion proof enclosure. This transmitter also has several hazardous area certifications and includes complete pH sensor diagnostics that can immediately notify the user to problems such as sensor coating, glass breakage, or non-immersed sensor.

Rosemount™ 3500P pH/ORP Sensor

Operation Tips

- A separator should be installed upstream of the pH sensor to remove large amounts of oil.
- Don’t remove the sensor immediately if a drift is noticed. Wait a couple of hours, and then standardize to a grab sample when the pH value is steady.
- Clean an oil-coated pH electrode (as necessary) with a mild detergent solution or water, but do not rub the glass surface.
- Use a jet-spray cleaner (PN 12707-00) to reduce maintenance time. The jet-spray is highly effective at removing oil coatings on glass.

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