Practice makes perfect

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discuss the best practices for using Coriolis flowmeters in sulfuric acid alkylation units.

Coriolis flowmeters have evolved since they were first introduced as Micro Motion technology in 1977. Likewise, as new and challenging applications are tried, Emerson's understanding of specialised processes continues to grow. One such challenge is in alkylation units found in refineries all over the world. Coriolis flowmeters, with their high accuracy density measurement capability, offer an opportunity for refineries to eliminate some of the tradeoff between safety and cost savings. This article provides background information and best practices developed since some of the first Coriolis meters were used in alkylation units.

The balance of acid concentration

Alkylation units are a sensitive but key process in many refineries. They produce a gasoline blending component that is high in octane and contains no aromatics, olefins or sulfur, a necessity in some US states and other parts of the world.

Sulfuric acid is used as a catalyst to produce alkylates out of hydrocarbons. 'Fresh' (high concentration) acid enters the process and is mixed with the hydrocarbons in a series of reactors and settlers. To create alkylates, the acid is 'spent' down to lower concentrations until it reaches a point when it must be replenished. The spent acid is recycled by a third party and later sold back to the refinery as fresh acid.

Maintaining the correct acid concentration in the system is a delicate balance. If the concentration is higher than required, acid consumption costs are too high. If the concentration is lower than required, the efficiency of the process is reduced. But more importantly, if the acid concentration drops too low it spirals quickly into a condition known as 'acid runaway'. The concentration continues to drop and the corrosive power goes up accordingly.

The consequences of acid runaway far outweigh the cost of high concentration. Refineries must endeavour to eliminate the possibility of runaway before being able to worry about using too much fresh acid. The traditional, but less than ideal practice is to err on the side of caution by overshooting the concentration level sufficient to guarantee the absolute minimum is maintained. A better practice is to use methods and equipment that can provide fast, accurate, and reliable measurement data so fresh acid can be metered in only when necessary and never to overcompensate for bad data pointing to a potential runaway situation.

Titration test and adjust method

The traditional way to monitor the acid concentration in alkylation units is to sample the process at multiple points and perform an acid titration test on each sample. Based upon the results of the tests, the addition rate of fresh acid is increased or decreased. This test and adjust process can be repeated as often as necessary, but it is usually done once per shift unless there is an abnormal test result.

The main problem with this method is that the amount of test data is limited to the number of tests performed and the data always lags behind the instantaneous state of the acid concentration. Acid runaway can occur rapidly once the concentration is low enough, and therefore a timely response is necessary to ensure that conditions do not deteriorate faster than the testing method can detect. There may not be time to even confirm a test result before action is required to prevent runaway.

The inefficiency of the test and adjust method leads to much higher than necessary fresh acid costs. The ideal acid concentration operating range runs from fresh acid at 98 wt% to spent acid at 88 wt% (below 88 wt% it is not possible to produce acceptable alkylate; below 87 wt% acid runaway begins). In reality, the margin for error of the testing method determines the alkylation unit's target spent acid strength. Because of the infrequent nature of the test and adjust method, the target spent acid strength is frequently 90 - 94 wt%. For every one percentage point the target spent acid can be dropped, the total amount of fresh acid needed by the unit drops by at least 10%.

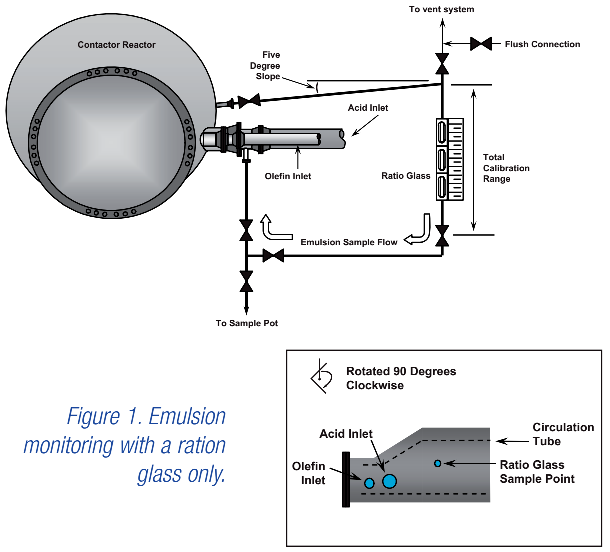

Figure 1. Emulsion monitoring with a ration glass only.

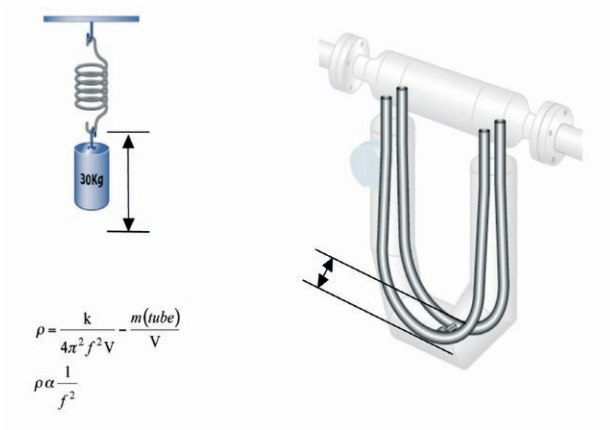

Figure 2. Coriolis flowmeter as a spring mass system.

Emulsion monitoring

Monitoring the emulsion in an alkylation unit is important for quality and productivity. The ideal hydrocarbon to acid ratio provides adequate surface area between reagents to permit only the reactions that are desired. The ideal ratio is around 45 - 50% acid. If there is too much acid, unwanted competitive reactions can occur, causing a loss of selectivity. If there is not enough acid in the mixture, the reaction surface area goes down, causing a drop in productivity and product quality.

Ratio glass monitoring

In a typical alkylation unit, emulsion monitoring is accomplished by a ratio glass: a sample of the emulsion is taken and permitted to settle for 30 - 40 minutes, then viewed through a sight glass. Once the lighter hydrocarbons float to the top it is possible to determine what percentage is hydrocarbon and what percentage is acid.

Rather than actually handling a sample separate from the process, a small sampling line, with shutoff valves on each end, is connected between the contactor reactor and its acid return line. To obtain a sample, operators open the valves long enough to permit a valid sample to enter the sampling line, then the valves are closed and the operator waits while the emulsion settles.

The incoming sample line from the contactor reactor is installed in the centre of the reactor to ensure a representative sample, and the elevation of the sight glass is centred within the total hydrocarbon to acid ratio so its reading range is centered on the desired ratio.

There are some problems with the standard ratio glass method. The biggest is settle time, which could leave the emulsion at an ineffective ratio for an unnecessarily long time, resulting in a costlier process. Also, because the testing process requires human action every time it is performed, there is opportunity for neglect and human error, such as leaving an outlet valve closed. Finally, the method is susceptible to mechanical failure including fouling and plugging of ball valves and check valves, and material buildup on the sight glass that makes it difficult or impossible to read accurately.

Coriolis technology for alkylation processes

Overview of Coriolis flowmeters

Coriolis flowmeters are among the most accurate and reliable measurement technologies for both mass flow rate and in-situ density in a growing number of common and specialty applications. In principle, they are a spring mass system that works just like any other type of vibrating element densitometer. Because the flowmeter's sensor tubes are fixed at one end and free on the other, it is easy to compare their motion to that of the mass on the end of the spring.

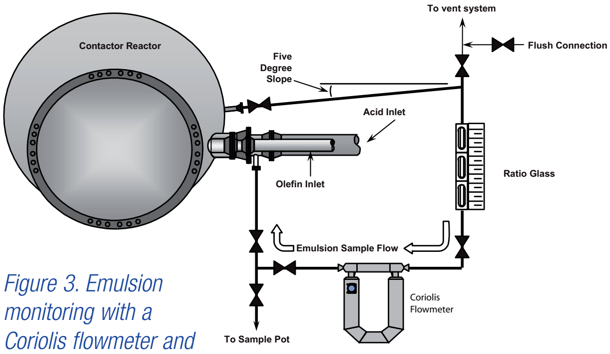

Figure 3. Emulsion monitoring with a Coriolis flowmeter and ratio glass.

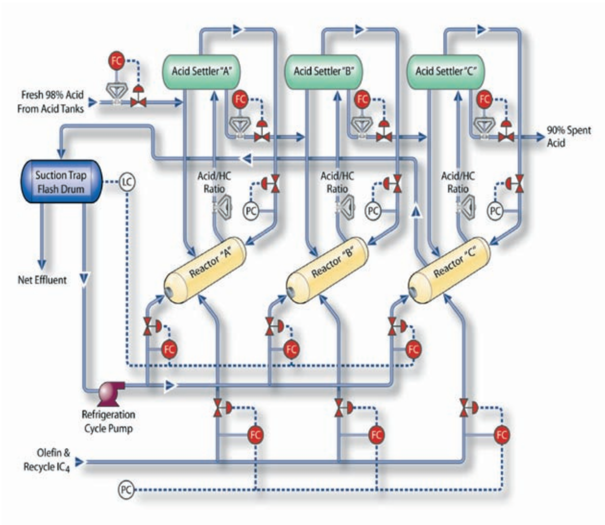

Figure 4. Coriolis flowmeters throughout the alkylation unit.

A Coriolis sensor uses a drive coil and feedback circuit to cause the flow tubes to vibrate. Like in all other spring mass systems, the flow tubes vibrate at their resonant frequency, which is a function of the geometry, material of construction, and mass of the assembly. The tube assembly mass is comprised of two parts: the mass of the tube and the mass of the fluid in the tube. Because the mass of the tubes is constant, the change in resonating frequency represents the change in mass of the fluid in the tube. The volume inside of the tubes is also constant, therefore measuring the mass of the fluid reveals the fluid's density (density = mass/volume).

The flowmeter measures the temperature and period of the flow tubes. The density of the fluid is directly proportional to the square of the time period; therefore a linear response is obtained, which means the Coriolis flowmeters can be calibrated very accurately using air and water under precisely controlled conditions.

Using density measurement to determine concentration

In pure sulfuric acid, there is a direct connection between acid concentration and density. (Even though the sulfuric acid in an alkylation unit is not pure, it is still possible to effectively trend the concentration.) By using Coriolis flowmeters as the process density analyser, it is typically possible to reduce the target spent acid concentration by as many as four percentage points (from 94 to 90 wt%) without reducing product quality or adding risk of acid runaway.

Using density for emulsion monitoring

Density measurement also indicates hydrocarbon to acid ratio in the contactor/reactor. Instead of, or in addition to, a sight glass, a Coriolis flowmeter can be installed between reactors and settlers to provide a realtime density measurement that can be used to monitor and adjust the emulsion.

Putting it all together

Figure 4 shows an example of an alkylation unit that takes advantage of Coriolis flowmeter technology wherever possible. In addition to flow metering and control, the Coriolis meters are used for their ability to report acid strength and acid to hydrocarbon ratio. Note that the flowmeters are shown in their logical location, not necessarily in their exact location, particularly with the emulsion monitoring meters, which are usually in an isolated circuit as shown in Figure 1.

Best practices

While Coriolis flowmeters have proven to be a very valuable technology in alkylation processes, there are some best practices that should be followed to increase the likelihood of successful operation.

Account for hydrocarbons

Some hydrocarbons inevitably fail to separate from the acids in the settler. They can potentially skew the density reading used to determine acid concentration. However, the presence of hydrocarbons tends to be consistent during steady state operation and a variation can be anticipated whenever feed rates, hydrocarbon composition, or other routine process changes are made.

To establish the correlation between acid density and concentration, density and temperature data should be gathered after the Coriolis meter is installed. The values can be imported in a spreadsheet and a correlation developed to infer spent acid strength. Different correlations can be developed for each situation known to affect the amount of hydrocarbons that do not separate from the acid.

Mitigate coating and corrosion

Acid contains acid soluble oils, which means material eventually builds up on the inside of the flow tubes, increasing their mass. Likewise, gradual corrosion and/or erosion of the flow tubes decrease their mass. Because the mass of the tubes affects the frequency of oscillation of the tubes, the density measurement is affected. To mitigate the potential error, a bias updating programme should be implemented. The spent acid concentration readings from daily laboratory samples are compared to the output from the meter, and then the equation is updated accordingly. In this manner the accuracy of the device is continually validated.

Also, it pays to ensure that the newest technology is being used. Many of the latest generation of Micro Motion flowmeters are now equipped with a special in-situ diagnostic tool called 'meter verification' that verifies the mechanical condition of the flow tubes. If corrosion were significant enough to skew the density measurement accuracy, the meter verification tool would

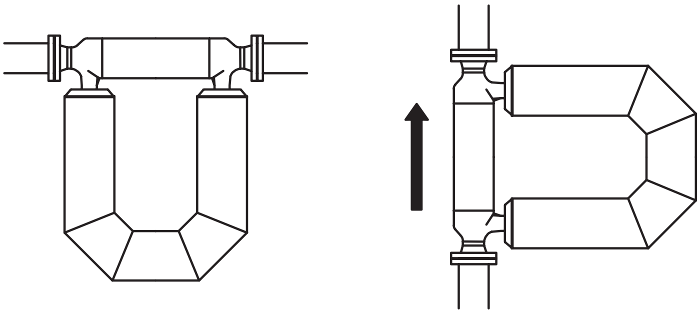

Figure 5. Best Coriolis flowmeter orientation.

be able to detect it. Thereafter, a decision can be made whether to make an adjustment to the equation or service or replace the sensor.

Meter selection and sizing

Accuracy and velocity (along with several other factors) are dynamically related for a given process. To assist customers, manufacturers (should or do) provide a sizing tool that takes customer inputs of flow rate, temperature, pressure, density and viscosity. The tool then shows the options for meter models and sizes, accuracy of the density measurement and flow rate, velocity through the tubes, pressure drop, and reynolds number.

It is impossible to establish an effective correlation between density and concentration by monitoring to the hundredth (0.01) of a g/cc. The measurement must be accurate to at least the thousandth (0.001). While most Coriolis flowmeters are very accurate, some may not be accurate enough for this type of application.

In sizing Coriolis flowmeters for an alkylation unit, the most important factor to consider is the velocity at which the acid will flow through the meter. Sulfuric acid flowing at velocities greater than 5 ft/s can cause flow tube erosion. Similarly, the flow tubes should be made of hastelloy, which has the best track record against erosion and corrosion in alkylation units.

Installation

The number and placement of Coriolis meters is important to ensure successful operation. In early installations, flowmeters were used on the spent acid line only. Recent experience has demonstrated that the meters should also be installed on inter stage lines. Depending upon variables within each stage, the amount of acid depletion can vary significantly from one stage to another. Also, because of the residence time in each reactor and settler, an upset in the first or second reactor may take hours before it can be detected in the final settler.

The meters should be installed in locations where the pressure is high enough to prevent dissolved hydrocarbons from flashing. For instance, locating the instrument upstream of the final flow control valve on the spent acid is a good location. The latest high frequency signal processing available on many Micro Motion flowmeters has eliminated many previous entrained gas problems of the past. However, vaporisation of hydrocarbons can still cause wild swings in the instrument readings.

Orientation of the meter is also important in this application. For liquid streams, Coriolis meters should be mounted in one of two possible orientations. The first is with the flow tubes pointed down, and the second is in the ‘flag’ orientation with the flow of fluid up through the sensor, as shown in Figure 5.

Many Coriolis flowmeters are now designed to make them more impervious to some types of mechanical stress, but it is still best to install the sensors according to best piping practices and minimise torque and bending loads on process connections.

Conclusion

Given the high cost of fresh acid and the even higher cost of allowing the acid concentration to slip into runaway condition, Coriolis flowmeters offer an attractive opportunity to permit tighter control of the delicate balance between one extreme and another in alkylation units. Over recent years, better understanding and practice in the field have shown that there are ways to improve the application of Coriolis flowmeters in these processes. It begins with careful product selection, placement, and installation practices and continues to succeed with diligent monitoring, analysis of data, and recognition when something has changed. When applied correctly, these efforts have yielded significant and immediate savings in acid costs, along with improved product quality and refinery safety.