Western European refineries and acidity in crude oil

Oil special report
May 2017
Richard Warner, Pricing Analyst
In the past few decades, driven by the growing availability of higher acid crudes, more and more refiners have become adept at processing such crudes, with various strategies emerging to handle them.

According to PIRA Energy, a part of S&P Global Platts, production of crude oil grades with an acidity identified as “high” or “very high” reached 12.9 million b/d in 2015, representing more than 15% of global production. Looking more specifically at the North Sea, the profile of crude oil produced in the region has become more acidic since the 1990s, peaking in 2005 at an average of over 0.35 TAN (Total Acid Number) and remaining close to that level since.

Europe’s refineries, with a comfortable supply of light, sweet and low acid feedstock from the North Sea, somewhat lagged behind in the process of becoming more adept at using acidic crude oils as feedstock, with higher acid crude oil from the area typically being exported to other regions. However since 2010, amid an overall contraction in the sector, refineries have reduced their intake of light sweet crude oil by 193,000 b/d, compared to a reduction of just 43,000 b/d for other qualities. This has resulted in the average crude oil slate in the region becoming heavier, sourer and more acidic.

Europe’s refiners have faced an increasingly competitive market in recent years. Declining regional fuel demand and growing international competition from the Middle East, the former Soviet Union and the United States has placed considerable pressure on European refiners’ profitability. As a result, over 1.9 million b/d of refining capacity has closed or been converted to other purposes in Europe since the beginning of 2009. This consolidation in the sector has been a key driver of change. Much of the refining capacity that has shut down has been smaller, less sophisticated plants, averaging only 108,000 b/d in capacity. The remaining capacity tends to be larger, more modern and more sophisticated facilities that are more optimally prepared for utilizing higher acid crude, as well as other crudes that are not light and sweet. They also tend to have more storage available for crude oil blending and larger budgets for employing software and instrumentation to optimize their processing of higher acid crudes.

There has consequently been greater appetite to evaluate the attributes of differing crude oils, and take advantage of market discounts where available, in order to maximize profitability in the increasingly tough global refining market. Higher acid crude oil has become a much more typical part of the European refining market as a result, accompanied by more sophisticated strategies to mitigate that acidity.

Why acidity matters to refiners
The combination of high pressure and high temperature in a refinery’s units and pipelines increases the risk of corrosion. Because of the flammable nature of the liquids in a refinery, alongside very high temperatures, a failure in a particular pipeline or unit could quickly become catastrophic. Moreover, even a non-catastrophic failure could result in a refinery being partially or fully shut for an extended period of time. Having unexpected refinery downtime can be extremely expensive for a refinery, resulting in additional labor and maintenance costs, as well as the lost production income. As a result, refiners take safety and maintenance extremely seriously.

Corrosion in a refinery can be broadly categorized into three types: general, localized and stress based. General corrosion refers to a broadly similar level of corrosion across units, pipelines and other infrastructure. This can increase the need to perform shutdowns for major overhauls, usually carried out by refiners every few years. Localized acid corrosion refers to when acidity...
attacks metal at particular locations, often exacerbated by conditions at that location, such as flow, heat and pressure. In contrast, stress based refers to the ability of acid, in combination with tensile stress, to cause cracks in a refinery's units or pipeline without significant metal corrosion.

Localized and stress based corrosion are particularly problematic for refineries. One damaged component can result in significant production loss or cause further catastrophic damage to a facility even without corrosion generally being a problem.

There are other headaches for refiners that can come from utilizing high acid crude oils including, but not limited to, the following:

- A tendency towards higher metals content, which can poison the catalysts utilized refineries with units such as fluidic catalytic crackers (FCCs) and hydrocrackers.
- A strong association with fouling problems in pipelines, units and storage. The processing of high TAN crude oils can produce salts as a byproduct, which can create blockages.
- Salts, in particular when combined with naphthenic acids, can create strong emulsion effects (making water mix with a crude oil), which can make desalting and generally handling a crude oil problematic.
- A tendency towards refinery output being heavier and having a smaller yield of lighter distillate material.

These issues persuaded many refiners, particularly in the Northwest European market, to stay away from higher acid crudes, seeing any likely price discount as not worth the risk of interrupting refining operations to check for or repair corrosion problems, or even worse, risk an accident.

Explaining acidity
As a rule, the higher the TAN of a crude oil the higher potential there is for corrosion and other related problems. However, there is no generally measurable relationship between TAN and corrosion. Naphthenic acid, found particularly in heavier sweeter crude oils, shows a stronger causal link to corrosion; but total acidity is a not a measure of specific acid types.

Refiners have considered crude with a TAN below 0.5 KOH/g (milligrams of potassium hydroxide per gram) to be low acid, 0.5 to 1 mg KOH/g to be medium acid, and anything above 1 mg KOH/g to be high acid.

Typically, refiners without specialist experience or knowledge have shied away from using crude oils rated above 0.5 and most definitely those above 1. This was particularly the case for companies with a single smaller less sophisticated refinery asset they would prefer not to see hit by unscheduled maintenance, severely interrupting operations. Moreover, the understanding of price discounts associated with higher TAN crude oils was not well understood in the region.

Mitigating high TAN in crude oil – passing the acid test
With the growth of high TAN crude oil production, refiners globally have become increasingly adept at dealing with more acidic feedstocks, employing a variety of strategies to mitigate the issues involved.

The principle method refiners use to manage TAN levels in crude oils is blending. Refiners routinely take in numerous crudes as part of what is known as their crude slate. These crudes are often mixed in order to mitigate certain characteristics such as viscosity, sulfur and metals content, or TAN, in order to provide a more suitable and profitable feedstock for the production of finished products.

For larger sites, higher TAN crudes can more easily be accommodated as a proportion of their feedstock while keeping overall acidity within acceptable levels.

Adoption of blending has been encouraged by tightening product specifications (in particular on sulfur) as well as the greater availability of heavier crudes in many global markets. Its increasing use has been accompanied by a growing body of knowledge among refiners, with better monitoring technology in tanks and refineries.

It has also been facilitated by the introduction of more sophisticated blending software. As a result, refiners are more able than ever before to utilize crude oil blending to achieve maximum value from their feedstocks and to cater for issues such as sulfur, viscosity and other contamination issues, as well as acidity.

In the case of TAN, acidity tends to blend linearly. This means that as high TAN crude oils are blended into lower TAN crude oils, measured acidity will progressively increase on a linear scale.

If a refiner was to begin with a crude oil slate of 100% high TAN crude oil, such as Heidrun (3 mg KOH/g), Grane (2.5 mg KOH/g) or Troll (0.7 mg KOH/g), then the acidity level of the feedstock would likely be above their upper TAN tolerance level of about 0.5. However, by progressively adding volumes of a low TAN crude oil (as example perhaps Forties), the average TAN of the crude slate can be lowered.

In the case of Troll, by blending in to the feedstock less than 30% Forties, the crude slate acidity can be brought within tolerance levels. For higher TAN crude oils, such as Heidrun and Grane, much greater volumes of lower TAN crude need to be added to bring the feedstock within tolerance. In both cases, a mixture in excess of 85% of
lower TAN crude oil must be mixed in to bring the created feedstock within comfortable acid tolerance.

Utilizing modern refinery technology, which can control the blending of crude oil in real time, the feedstock flow into a refinery can be modified as necessary. Another important advantage is that the capital and operation costs of blending are relatively low compared to other methods of acid mitigation.

The primary capital costs relate to additional monitoring and control equipment, as well as extra tank space needed to carry out the actual blending, which are relatively limited as compared to alternatives. The primary operational costs relate to the cost of the crude oils being blended.

Dependent on the crude oils being blended, the output of more valuable refined products may be increased, improving the economics of blending despite the possible additional cost related to crude oil purchasing.

There are however challenges and limitations with blending. For very high TAN crude oils, the volumes of low crude oil that need to be added to reach refinery acidity tolerance levels can be very high.

Sulfur is another area of consideration. Lower levels of sulfur can mitigate acid corrosion, with the flipside that higher sulfur levels can actually worsen it, so refiners have to keep a keen focus on levels in feedstock. Moreover, with regulated sulfur levels in transport fuels globally heading downwards, sulfur has become an increasingly undesirable attribute to refiners. With a global limit of 0.5% on marine bunker fuels due to come into force in 2020, sulfur mitigation, rather than acid mitigation, will become a key area of focus.

What makes this even more complicated is that sulfur and acidity may not correlate in the distillation cuts. TAN levels tend to vary along distillation cuts. Similarly, sulfur also tends to change along distillation cuts, although not necessarily at the same rate.

When blending crude oils, this can create an added layer of complexity that may on paper create a blendstock that is suitable for a refinery, but in reality may be quite problematic.

Other qualities of crude oils being blended can also create issues, such as metals contamination, viscosity (whether too low or too high) as well as other issues. Also, some crude oils may not blend easily, reflecting differences in their chemical makeup. For example, blending a very light crude oil with a very heavy one can result in them separating back out into their constituent parts.

Rather than blending, there are alternative methods to reduce the corrosive impact of acidic crude oil. One is the use of specialist steels, with additional elements such as chromium and molybdenum, in a refinery's units and pipelines. This can create a relatively robust element of protection from acid corrosion, in particular of the localized type.

However, with molybdenum's costs often at some thirty times that of steel, to protect an entire refinery is economically unviable, so tends to be done only at especially vulnerable locations. One example of this is to use these steels in particularly vulnerable feedstock pipelines.

The ability of metallurgy to cope with higher TAN crude oils is limited however. This is particularly the case for naphthenic acids, which present a problem even for acid resistant steels. Moreover, different crude oils with high TAN can have different corrosion profiles.

As such, the corrosion vulnerability of particular refinery units and pipelines can shift between different crude oils, making protecting them with specialist materials problematic. This tends to see this type of protection especially utilized by refiners who know a particular high TAN crude oil very well.

Moreover, considering the upfront investment needed, a refinery owner would need to be comfortable with making their investment back over an extended period of time.

Another method employed by refiners in order to reduce the corrosive impact of a high TAN crude oil is to utilize chemical additives. These chemicals broadly fall into three main groups:

- **Corrosion inhibitors** provide a protective layer around the steel and other metal in a refinery's units, pipelines or other infrastructure. This layer acts to prevent the acid in a high TAN crude oil directly attacking the metal.

- **Neutralization agents** reduce the acidity of a high TAN crude oil. However, these agents generate emulsions, which can be extremely problematic for refiners, as well as other unwanted by-products.

- **Extracting agents** allow the easy separation out of acids from a crude oil. However, similarly to neutralization agents, these agents can generate unwanted emulsions.

Over the last 20 years or so, these additives have improved tremendously, prompting some refiners that had traditionally stayed away from higher TAN crude oils to evaluate wider feedstock options.

Also, more sophisticated corrosion monitoring processes have improved the application of these chemical additives, allowing a greater degree of corrosion prevention to be achieved using less material and thus lowering costs.
Conclusion

Overall, it is clear that the acidic crude oils are here to stay as a key part of Europe’s crude slate. While this has been prompted by a growth in upstream production and driven by refinery competitiveness, it has been underpinned by the development and improvement of acid mitigation methods.

In particular, blending has become a key tool in a refinery’s tools in the modern competitive market. With competitive pressures only expected to increase in Europe and highly acidic crudes expected to remain a key source of feedstock in the coming years, the market is likely to adapt further to embrace them, as long as they continue to provide good value.

Testing regime

In order to ascertain acidity of crude oils, as well as other chemicals, a standard test was developed to give results that are repeatable and accurate. This test has come to be known as ASTM D 664. Under the conditions of the test, a chemical (typically potassium hydroxide) is titrated from a buret into a flask below containing the chemical in question until the acidity of the solution in the flask is neutralized.

The acidity of the liquid in the flask is determined using a potentiometer, which measures the electrical resistance of the liquid in the flask as the chemical from the buret is gradually added.

An alternative test, ASTM D 974, utilizes a reaction agent in the flask which changes color as the acidity of the liquid in the flask is neutralized by the chemical from the buret. This has the disadvantage of relying on the eyesight of lab technicians, meaning there is larger potential for error in repeat testing.

The test is used to produce an output figure known as a Total Acid Number (TAN), which is measured in mg KOH/g (milligrams of potassium hydroxide per gram). This number reflects how much titrated neutralization agent is needed to reduce the acidity of the solution in question.

There are limits to the capabilities of the test, which restricts its usefulness to refiners. Firstly, as a crude oil is run through a CDU, it is separated into different distillation cuts but the ASTM D 664 test does not indicate in what distillation cuts and to what degree acidity will concentrate. However, the test can be conducted on the various cuts as desired.

Acidity tends to concentrate at the heavier end of the barrel, primarily because of the greater density of the material. This can cause problems in particular parts of a refinery, dependent on where and to what degree acidity is concentrated, as well as particular refinery processes. As example, units which utilize heavier material as feedstock, such as a thermal cracker taking in Residual Fuel Oil, tend to be particular vulnerable.

Also, these cuts are distilled using temperature to separate them out. The corrosive impact of an acid on a refinery is accelerated by high temperature.

Moreover, the test cannot indicate what type of acid is present in the solution included in the test and how it will behave in a refinery. It can only tell how much neutralization agent is needed to remove the acidity of the solution in question. The particular breakdown between light organic acids, naphthenic acids and other types of acids, each of which will impact a refinery in different ways, is not determined.

Finally, the remaining chemistry of a refinery blendstock needs to be considered. For example, higher sulfur levels in a crude oil can impede or accelerate acid corrosion. Higher sulfur levels in a crude oil can coat the internal parts of a refinery in sulfides.

However, at even higher sulfur levels corrosion may increase, reflecting the corrosive characteristics of sulfur, as well as other unwanted chemical reactions.

The lack of a general relationship between TAN and corrosion levels of metals severely limits the ability of a TAN result to predict the corrosiveness of a refinery feedstock. As such, its usefulness to a refinery is limited.