How to Save Cash in Refineries by using Online TOC Analysers

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Steam and hot water are of a big concern in crude oil refinement. The processing of these is very energy intensive and their contamination may lead to corrosion in pipes, boilers and heat exchangers causing mineral oils to leak into the return condensate. An oil-in-water analyser would be required. However, as organics may cause corrosion as well, an online TOC analyser is more preferable.

An oil refinery has many petrochemical facilities like crude oil distillation columns, reformers, crackers, hydrogen generation units as well as fuel oil and gasoline blending units in operation. Beside this, huge cogeneration plants are in operation. The production of steam and hot water is significant for the operation of many types of these installations and facilities. While high pressure steam is used for generating electrical power, driving turbines, utility pumps and for process heating, medium pressure steam is typically used for heat transfer to refinery products via heat exchangers and the low pressure steam is used for a variety of purposes such as pipe tracing, process heat exchange and deaerators. If the temperature of the steam decreases, it will become hot condensate which still contains a lot of energy and, hence, remains very valuable. By re-using this so-called return condensate, enormous cost savings can be attained. Nevertheless, its purity should be continuously monitored in order to avoid any pollution and damages of the pipes, boilers and heat exchangers.

Why use a TOC analyser in such case? An online TOC anlayser will not only measure any type of oil but also organics that do not belong to oil groups. At refineries, the alarm thresholds are much lower than drinking water, in a range of 10 ppb to 100 ppm C. Therefore, the analytical performance of the TOC analyser installed must be outstanding, since tough demands are made by the industry regarding accuracy, response times and traceability.

Condensates' purity is vital

A cogeneration plant consists of a demineralisation water plant and a steam boiler. Basically, the process starts with the production of make-up water. The temperature and pressure in the boiler is very high. At such conditions carbon dioxide (CO_2) will be transformed to carbonic acid, a corrosive substance that causes pit corrosion. The same applies to dissolved oxygen when the temperature increases rapidly. Hence, even the smallest impurity can lead to corrosion or scaling within the transport pipe system or the boiler itself. Oxygen pitting is a costly problem which can be minimised when traces of dissolved oxygen are removed from the make-up water using a deaerator. Here, this make-up water is heated using steam whereby the oxygen is purged out consequently. Any remaining traces of oxygen are removed through the introduction of oxygen scavengers. Additionally, a variety of other chemicals are dosed such as amines to build up a protective film over the metal surfaces, anti-scaling chemicals to maintain the heat distribution and anti-foam chemicals to prevent the forming of foam in the boiler.

The costs involved in the production of pure make-up water are very high and re-using the steam condensate saves a lot of money. Every ton of steam that has passed numerous heat exchangers and is returned to a feed water holding tank at the boiler facility returns as condensate, saving the production of one ton of demineralised water. However, the disadvantage of this well thought out cost saving system would be again the risk of importing contaminated steam condensate.

The steam's energy is transferred to process fluids such as crude, mineral oils and other products by use of heat exchangers. A common type is the pipe bundle heat exchanger of which there are hundreds in use at a refinery. Due to the high temperature of the steam and the presence of traces of oxygen that penetrate into the plant's steam piping system, these heat exchangers are also subject to pit corrosion. Despite the associated inspections, there is always a risk of a break through, leading to pure products, for example hydrocarbons, crude oil, petrol, kerosene and lube oils, leaking into the return condensate. This polluted condensate can flow into the holding tank, finally entering the boiler, where it can lead to disastrous metal corrosion. Additionally, all organics, either non-oily types as well any other type of organics, will harm the boiler as well.

Therefore, it is recommended to monitor the quality of the return condensate by using a quick online TOC analyser and to drain it off as soon as a trip alarm TOC level is exceeded. This total organic carbon measured will also contain the smallest amounts of hydrocarbons and oil traces.

The TOC analyser system should respond quickly to the breakthrough of an oily matter, triggering an alarm as fast as possible to allow the prevention of oil entering and fouling the installations. This early warning system should activate a process valve allowing the contaminated condensate to be drained off. The leaking heat exchanger can then be located and repaired.

Tough requirements on the TOC analyser

The tendency of hydrocarbons to stick to or penetrate the wetted parts of the sample transfer pipes and the analyser's parts is called adsorption or absorption. The release of these hydrocarbon molecules from the surface of the wetted parts into the sample is called desorption. Not only are the analytical TOC results influenced by this cross contamination, but the memory effects can cause the entire analyser system to operate very slowly. The extent of these

Figure 1: A large site with refinery and petrochemical facilities

Figure 2: Cogeneration Plant

Figure 3: Heat exchanger with 5 plugged heat pipes

Figure 4: Commissioning and start-up of a QuickTOCpurity TOC analyser

phenomena depends on the type of material of the wetted parts, the flushing velocity, the flushing time, the temperature of the fluid and, more specifically, the type of organic matter. Oily matter in particular is subject to adsorption and desorption. This all becomes especially challenging when a single TOC analyser is used to monitor several sample streams. This multi-stream TOC system should rapidly and sequentially measure samples with different TOC levels and different compositions as well as be able to rapidly return to accurate TOC values, even after having been exposed for hours to a highly oily mixture. Many TOC analysers, however, continue to suffer from severe memory effects because of the pollution of the wetted parts by the sticky oil. As a consequence, these analysers show very high measurements over long periods, during which plant operators keep flushing expensive pure condensate down the drain.

The TOC analyser is usually placed in the centre of a refinery, where the CO_2 and volatile organic carbon (VOC) content of the ambient air is often at a higher level than normal. These gases, however, should not be able to influence, penetrate, permeate or leak into the analyser system and the sample. They would cause wrong readings. On the other hand, at refineries the sample may contain volatile and purgable organic carbons as well. Hence, the system should not only be sealed to prevent penetration of these but also to avoid them to leak out. Due to the fact that POC and VOC are a part of the total organic carbon to be measured, they must not be neglected.

In the case the TOC analyser measures a TOC peak, it immediately becomes suspect to the plant operators, as they are not happy to drain their expensive return condensate. The analyser engineer must prove immediately that this TOC analyser is taking correct measurements. An ad hoc certified standard is needed. However, it is not possible to prepare such a standard in an instant. Calibration and validation is usually performed by the use of wet chemical standards, which are prepared under stringent circumstances, needing a considered time frame, and using an expensive water purifier, often in combination with reverse osmosis, highly pure ion exchange resins etc. resulting in a TOC purity of about 10 ppb. As soon as they are ready, they are subject to degradation and contamination. They can only be stored at ideally cooled conditions in totally filled, sealed bottles for a few days at a time. Hence, a calibration and validation feature ready at any time would be necessary.

Figure 5: Cylinder with calibration gas

Analyser building blocks

In general, an online TOC analyser consists of sample transfer, injection system, reactor, carrier gas circuit, gas detector and calibration system. There are different types on the market of which most cannot meet the requirements of the application in discussion. However, the quick LAR TOC anlysers for pure water stand out with their well designed multi-loop injection system as the pre-eminent methodology for sample transference and injection of oily samples. During a programmed time period all parts, including the sample injection loop, are flushed with a fresh sample. Then a precise volume of the sample is blocked inside the injection tube and pushed by carrier gas via the injection port into the 1,200°C reactor. This loop injection system avoids absorption and memory effects by the use of inert materials such as Teflon. Moreover, the analyser is able to measure samples of up to 90°C.

The second important analyser building block is the ultra high temperature reactor, based on non-catalytic thermal oxidation. At the temperature of 1,200°C catalysts are not necessary whereby it is physically impossible for compounds to survive. Hence, the full recovery rate for very hard to oxidise compounds like fluorocarbons, chlorinated hydrocarbons and amines is guaranteed. Without exception all hydrocarbon compounds are completely oxidised forming CO_2. A carrier gas flows through the reactor and transfers this CO_2 to a non-dispersive infrared detector (NDIR detector). The amount of carbon dioxide that is measured, is linearly proportional to the amount of organic carbon molecules (TOC) in the sample. This shows that the LAR ultra high oxidation technique is free from memory effects, giving excellent low TC (total carbon) and TOC level performances in comparison to other oxidation techniques. Experience shows that catalytic combustion systems do suffer from memory effects and, in addition, show the 'blind' value phenomena. This means that beyond a certain point in the lower ppb range, values cannot be measured due to the catalytic memory effect, peak tailing and a shifting of the CO_2 baseline.

The LAR QuickTOCpurity uses a smartly designed carrier gas system of which the flow circuit is kept at a stable overpressure. This design eliminates the risk of any ambient air interferences. Moreover, the patented injection port avoids any leaking out of purgable and volatile organic carbon. Hence, the analysers measure the TRUE TOC of the sample.

The third remarkable analyser building block is the innovative calibration and validation system which offers a unique feature: Whenever needed, the operator can easily and immediately calibrate or validate the analyser by using a cylinder filled with a certified gas mixture. This gas mixture is very stable and can be stored over a period of several years, making it always ready for use. For calibration or validation the before-mentioned injection loop is filled with the gas and injected into the reactor, where it is oxidised to CO_2. The amount is then measured by the NDIR detector. This routine takes only a few minutes.

A TOC analyser as a money maker in refineries

Money cannot be saved only through cutting energy costs by re-using return condensate. Experience shows that the effective analysis of its purity is of importance as well. The monitoring system installed needs to be fast, reliable and be able to measure many types of hydrocarbons at the same time. The LAR QuickTOC's patented thermal oxidation technique guarantees the complete oxidation of all carbons without exception, negating the need to use expensive catalysts. This totally sealed system, maintained at a stable overpressure, means that only the sample is measured without any environmental interferences. Its well designed multi-loop injection system has reduced internal dimensions and minimised wetted surfaces, as well as no dead volumes, resulting in the prevention of memory effects. The quick and easy calibration and validation feature of the LAR analysers confirms the accuracy of the results within minutes. Hence, using these analysers the operators are not pouring expensive condensate down the drain.

Figure 6: QuickTOCpurity in a NEMA4X housing

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