Elemental analysis of hydrocarbon streams using Dry colorimetry analyzers, a catalyst saviour

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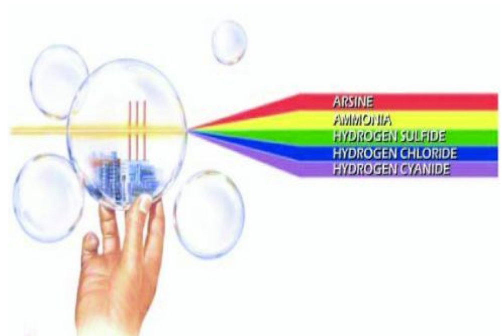


The Petrochemical industry has refined technological developments to improve product quality. One, in particular, is the ability to measure trace impurities at extremely low levels. This is a crucial step for the industry to reduce agents that can eventually cause pollution as they can cause harmful health and environmental effects. In addition, it is essential for the industry to reduce agents that can eventually cause catalyst poisoning and corrosion in the metal structures where processes are being held. Indeed, companies need to protect their expensive catalysts used in the chemical reactions performed during the cracking, isomerisation, reforming and many other processes. This article explains how the tape detection technique saves catalysts used in different industrial processes.

Introduction to dry colorimetric method

Since the creation of oil refining, a variety of treatment methods have been used to remove non-hydrocarbon impurities and other constituents. These compounds reduce the efficiency of the conversion processes and reduce the quality of the finished products. It is necessary to remove impurities from blending stocks in several processes such as treatment, drying and sweetening. There are many analytical methods used in industrial settings for the quantitative analysis of impurities, but not all are efficient and cost effective. Companies need methods that are fast, precise, versatile and virtually interference-free. One technique that fulfills these demands is the dry colorimetric method. This technique can measure at ultra-low detection ranges from parts per million (ppm), to parts per billion (ppb). In addition to meeting ultra-low-levels, it is considered safe and non-toxic. For the user, simple care as you would for household cleaners would suffice. The dry colorimetric method is a simple and easy way to measure impurities in reactions where hydrocarbons are used as reactants. This method is suited for elemental analysis as well as total analysis in process or in a laboratory setting depending on the application. Many chemical and petrochemical processes require expensive catalysts to materialize their final product, however, their catalyst can be destroyed by impurities or by-products contained in the reaction. Some of those processes are discussed below.

Haber - Bosch process

The Haber–Bosch process is used for Nitrogen fixation intended for production of ammonia in large quantities. This innovation is the most important process in history for feeding the increasing global population. In this process nitrogen is obtained from air and hydrogen is obtained from natural gas. Natural gas is used to obtain methane, which is processed to get hydrogen gas, which is obtained from the following reaction:

$$CH_{4(g)} + H_20_{(g)} \leftrightarrow CO_{(g)} + 3H_{2\,(g)}.$$

Hydrogen can also be produced from coal or naphtha in order to be used as reactant for Haber-Bosch process. No matter what process is used to produce hydrogen, it is important to remove all impurities, in particular sulfur and hydrogen fluorides from the process. Purified Nitrogen and hydrogen gases are mixed in a 1:3 volume ratio and heated at 400-500°C in about 200atm pressure and in presence of the iron catalyst. Liquid ammonia is obtained upon cooling the resulting gases. The catalyst is actually not just pure iron, it contains potassium hydroxide which increases its efficiency. It is crucial to keep those catalysts free from contamination because a high surface area is needed for adsorption of nitrogen and hydrogen. The measurement and handling of the impurities involved in these processes can save the catalysts before they get destroyed by contaminants. Gas analyzers can also be used to monitor the natural gas purification for purity of hydrogen by measuring the amounts of impurities. This can further contribute to enhance the rate of the reaction by increasing surface area of the catalyst.

Sulfur recovery process

The iron oxide sulfur recovery catalyst is not only used in reactions involved to make chemical fertilizers but it also participates in other reactions such as removing hydrogen sulfide from coal gas and various feeds of refining, chemical modification of coal and chemical fiber. Before, during and after processing, crude oil is desulfurized using sweetening compounds and acids. The reaction involved in removing sulfur using iron oxide sulfur recovery catalyst is as follows:

$$2Fe_2O_3+3H_2S \rightarrow FeS+FeS_x+S+3H_2O$$

In most cases it is important to measure the contaminants of the reactants in contact with catalysts to prevent their degradation. Hydrodesulphurization process is a prerequisite prior to exposure of the stream to platinum catalyst in order to prevent the poisoning of the catalyst. Removing sulfur from various processes can protect the companies from problems such as corrosion of material, harmful gas formation, decomposition of expensive catalysts, etc. This makes it crucial to measure the quantities of Sulfur impurities remaining as H_2S after the Sulfur removal process. Dry colorimetry analyzers are equipped for on-line and laboratory usage for measurements at ultra-low-ppb levels for catalytic purification analysis.

Isomerisation process

Catalysts are used in many organic reactions and industrial processes to enhance the rate of the reaction by lowering the activation energy. Consider the following example: the industrial isomerisation process uses expensive catalysts such as aluminum chloride ($AlCl_3$) for alkanes reactions. For example, 2,2,4-trimethylpentane (isooctane, a component of high-octane gasoline) needs 2-methylpropane (isobutane) as a starting material, where 2-methylpropane can be obtained from an isomerisation process of butane[1]. The trace amounts of impurities in the isomerisation process of butane, isobutane, isooctane and various other paraffin hydrocarbons can cause costly problems. Another interesting reaction catalyzed by aluminum chloride ($AlCl_3$) is the alkylation reactions, for example, between benzene and alkylhalides resulting in alkylbenzene and hydrogen chloride formation:

$C_6H_6 + RCl + AlCl_3$ (catalyst) $\rightarrow C_6H_5R + HCl$ where R is alkyl group

Corrosion occurs in the reforming units and in the hydrotreating units upon excessive humidity presence due to the exposure of hydrogen chlorides. In these areas of the petrochemical process, an analyzer can quantitatively determine the concentration of hydrogen chloride, which is considered a contaminant in certain feed stocks. This simple precaution prevents from spending excessive amount of money in repairs from corrosion.

Hydrogenation process

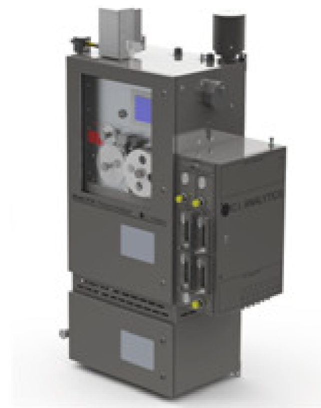
Gas analyzers are also required for the impurity analysis of the reactant gas or liquid of the hydrogenation process of methane derivatives (alkenes and alkynes) in presence of catalysts such as platinum, palladium or nickel to form alkanes. The purpose of these catalysts is to adsorb dihydrogen and activate them to react with ethene and produce ethane. This hydrogen fixation reaction is very suitable for ethylene and benzene. Another important reaction using this process and using the steam reforming concept is used to convert methane to a mixture of gases as in the following reaction:

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$

This reaction is conducted at high temperatures and is catalyzed by nickel. This catalyst must also be protected from numerous impurities in the methane stream. In the industrial environment, ethane is obtained from natural gas and processed to make ethylene and hydrogen. Both are widely used reagents in petrochemical reactions. As mentioned above, the hydrogen obtained from this reaction is used in the Haber-Bosch process. It is important that these reactions are conducted in a chemically controlled environment. It is crucial to immediately trace the impurities that can generate by-products or destroy expensive catalysts. For instance, hydrogen chloride can be measured using dry colorimetry analysers by simply selecting the appropriate tape for this compound placing gas analyzers at different parts of the process can save time, effort and money but automatically measuring the level of impurity flowing through the streams. For these reasons dry colorimetric detection method is the best method to conduct impurity analysis of petrochemical reagents. This technology allows for the detection and monitoring of hydrocarbon impurities. It offers high reliability with low maintenance.

Test method

Samples can be analysed in either liquid or gaseous form.



Model 9730
Process Analyzer

Chemical testing of samples can be done automatically or by using an injection valve. At the injection port of the elemental analyzer gaseous arsine, ammonia, phosphine or hydrogen sulphide are injected and analyzed directly. However, if a chemical modification is required, as in the case of Nox or total nitrogen, liquid or gas samples are directly injected into the preheated section of the reaction tube. The liquid samples are heated to achieve a gaseous state. Once the sample reaches the furnace in a gaseous state it is mixed with the reaction gas. In the case of sulfur, sulfur compounds are reduced to hydrogen sulfide (H_2S) through the reductive method or oxidized to sulfur dioxide (SO_2) through the oxidative method. The method used is application specific. After several filtrations, sample gas reacts with the sensi-tape specific to the target impurity. This reaction generates a colour stain on the sensi-tape that is directly proportional to the concentration of the target gas present in the sample gas. This analysis method gives accurate results within minutes and in some instances within seconds (application specific). As for the measurement of total sulfur, the gaseous sample flows through a sample loop. The sample can be measured at atmospheric or high pressure. In the case of sulfur species, the gas chromatography column is used to separate the species. By simply changing a few parameters, these instruments can, in addition to handling different gas pressures, switch between detection levels (ppb and ppm) and between different impurities (sensi-tape change required). For example, a laboratory purchased a total sulfur tape analyzer apparatus that complies with ASTM D4045, ASTM D4468, to detect and measure total sulfur and with ASTM D5623 and ASTM D5504 for sulfur species in gas and liquid samples that can measure at as low as 1 ppb in gas (Application specific).

The tape detection method is a unique technique which requires minor changes to the analyzer to switch from one impurity to another. In addition to total sulfur, total chlorides, total nitrogen and total arsenic, below is a list of some of the impurities that can also be detected.

Measurable impurities using this method are:

Table 1. Detectable Impurities with analytical range

Impurities	Lower detectable limits*
Ammonia (NH_3)	5 ppb
Arsine (AsH_3)	1 ppb
Chlorine (Cl_2)	5 ppb
Hydrogen Chloride (HCl)	5 ppb
Hydrogen Cyanide (HCN)	5 ppb
Hydrogen Fluoride (HF)	500 ppb
Hydrogen Sulfide (H_2S)	1 ppb
Nitrogen Dioxide (NO_2)	25 ppb
Phosphine (PH_3)	1 ppb
Sulfur Dioxide (SO_2)	1 ppb

*Detection range can be optimized to meet application requirements

Elemental analysis of gaseous streams is fairly easy to perform. All one needs is to place this instrument on-line where samples can be automatically collected and analyzed. The Tape-detection technique is one of the rare methods which allows a visual inspection of the results in addition to the concentration determined by the instrument; you can actually see that a reaction occurred; no false positives. Crude oil refineries and chemical processing companies need to reduce compounds that contain sulfur for environmental compliance, for saving expensive catalysts and prevent corrosion from some other impurities in their metallic refinery structure. Companies are acquiring dry colorimetry elemental analyzers to track impurities such as H_2S, NO_2, AsH_3, PH_3, chlorine, etc. Tape based analyzers can also be configured for the measurement of total species in hydrocarbon streams.

Conclusion

Amongst all the analytical techniques, the dry colorimetric method truly is second to none. This method can be applied in both laboratory and process analysis depending on the application it will be serving and it is virtually free from interference and maintenance problems. As explained in this article, dry colorimetric method can be applied for impurity analysis of several processes such as Haber-Bosch, sulfur recovery, isomerisation, hydrogenation and many others. This method is a saviour of catalysts and reagents used in different processes by tracking contaminants before problems occur. As described in the test method section elemental analysis of hydrocarbon impurities can be performed using an analyzer that functions with dry colorimetric means. This method is good for a variety of chemical impurities at ultra low PPB levels, but only few applications are mentioned.

Reference

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2. Richard S. Kraus , "Petroleum refining process". *Encyclopedia Of Occupational Health And Safety* . 4th Edition, volume 3, Geneva, 2011