



Cyanide Analysis of Wastewater Samples from FCC and Hydrocracking Operations

Introduction

Fluid catalytic cracking (FCC) is a major unit operation in refineries around the world. FCC is used to convert low-value, high molecular weight feedstocks such as shale oil, tar sands oil, and coker gas oils into lighter, high-value products by “cracking” C-C bonds. These feedstocks may contain high levels of organic nitrogen compounds such as indole, carbazole, pyridine, and quinoline (Figure 1), which form ammonia and cyanide in the reactor of FCC units. The nitrogen content of crude petroleum is generally in the range of 0.1 - 0.9%, however, some crude may contain up to 2% nitrogen. The more asphaltic the oil the higher the nitrogen content.⁽¹⁾

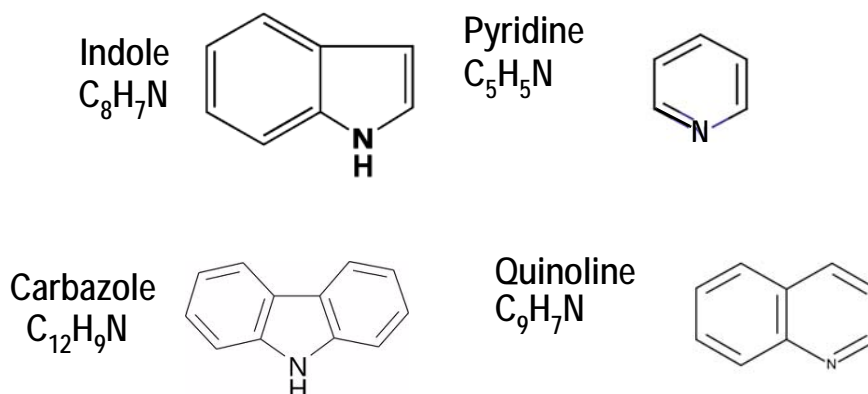


Figure 1. Common Organic Nitrogen Compounds in Petroleum

Hydrocracking is a thermal process (>350 °C) in which hydrogenation is performed concurrently with catalytic cracking. Hydrocracking converts high-boiling feedstocks to lower boiling products by cracking the hydrocarbons and hydrogenating the resulting unsaturated reaction products. Polycyclic aromatics are partially hydrogenated before the aromatic nucleus is cracked. Sulfur and nitrogen atoms are converted into hydrogen sulfide, ammonia, and cyanide.

Hydrocracking reactions are catalyzed by dual-function catalysts. Cracking is performed by silica-alumina (or zeolite) catalysts, and hydrogenation by platinum or nickel catalysts.

Hydrogenation helps minimize catalyst poisoning by nitrogen, oxygen, and sulfur compounds in feedstocks. Some reactions involved in nitrogen removal are depicted in Figure 2.

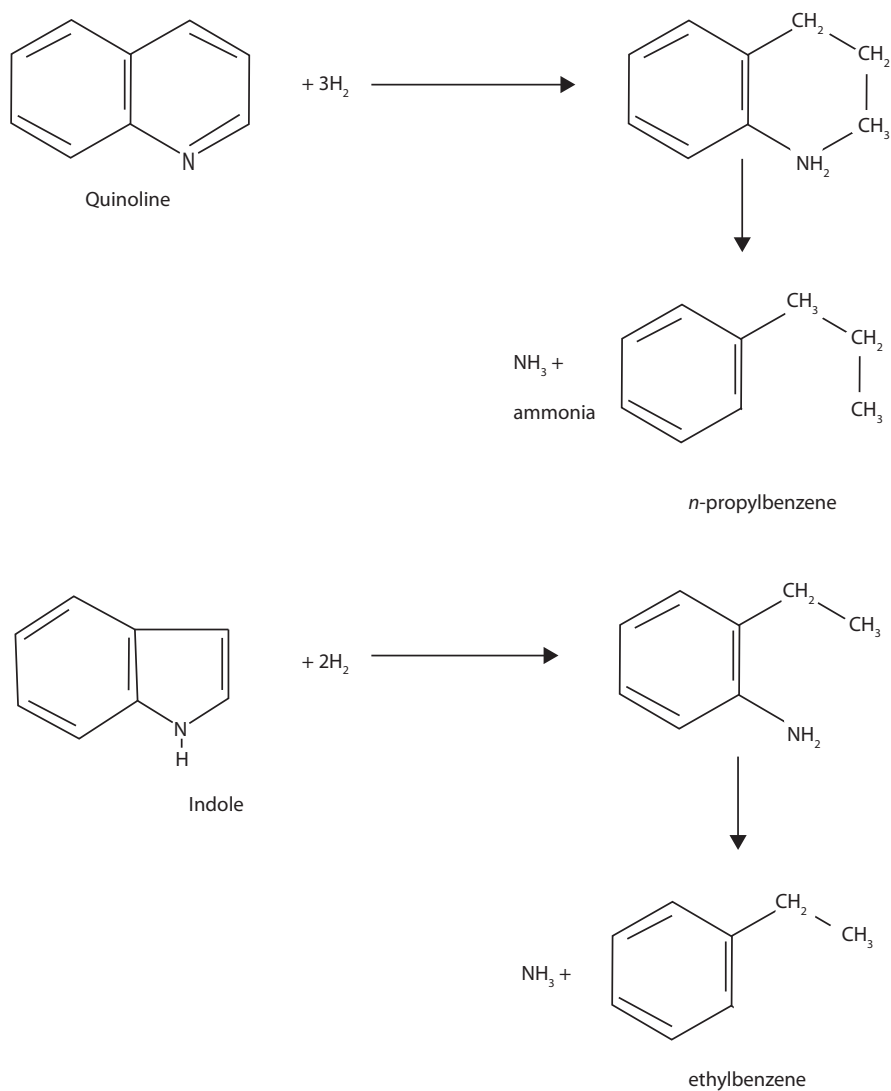


Figure 2. Hydrogenation Reactions Involving Nitrogen Compounds in Petroleum

Cyanide Generation and Corrosion

Cracking organic nitrogen compounds in petroleum feedstocks liberates hydrogen cyanide (HCN), ammonia, and other nitrogen compounds. The formation and downstream effects of cyanide are a major concern in FCC and hydrocracking operations.⁽²⁾

Gas phase reaction products; hydrocarbons, HCN, H_2S , and NH_3 formed in the FCC reactor are transferred to a distillation column where steam is injected into the overhead stream to reduce hydrocarbon partial vapor pressure allowing operation under lower temperatures. Sour water is formed in this step, which also entrains HCN and NH_3

that react and form ammonia cyanide (NH_4CN). The NH_4CN ionizes in the sour water liberating ammonium (NH_4^+) and cyanide (CN^-) ions.

Cyanide ions react with insoluble iron sulfide to form a soluble ferrocyanide complex. This reaction attacks the protective iron sulfide film on metal surfaces and exposes fresh metal. This corrosion liberates hydrogen atoms that penetrate into the steel surfaces causing hydrogen blistering and leads to stress corrosion cracking.⁽³⁾

Cyanide Analysis of NPDES Wastewater Samples

Petroleum refineries generate large volumes of wastewater, (0.4 - 1.6 times the volume of oil processed).⁽⁴⁾ A survey of water use at 27 refineries conducted by the U.S. EPA found that 19.6% of the total wastewater discharged from refineries was from sour water stripping.⁽⁵⁾

Sour wastewater from FCC and hydrocracking operations contains emulsified oils, phenols, sulfides, mercaptans, ammonia, and cyanide. The chemical composition of sour wastewater complicates the measurement of cyanide species because other constituents are known matrix interferences. In fact, the U.S. EPA Solutions to Analytical Chemistry Problems with Clean Water Act Methods⁽⁶⁾ (“Pumpkin Guide”) notes; “Next to oil and grease, cyanide is the pollutant for which the most matrix interferences have been reported.”

Sulfides in particular are of concern in sour wastewater samples because they can cause low or high cyanide recoveries depending upon the analytical technique and methodology employed for testing. Sour wastewater was determined to contain 15–23 mg/L of sulfide on average, 5.1 to 21.1 mg/L of ammonia, and 98-128 mg/L of phenol.⁽⁴⁾

Refineries in the U.S. have National Pollution Discharge Elimination System (NPDES) permits with limits for cyanide in wastewater. Data submitted for NPDES compliance reporting must be obtained using U.S. EPA approved methods.

The first generation of U.S. EPA cyanide analysis methods from the 1970’s employ an acid distillation step to dissociate cyanide from metal-cyanide complexes and separate cyanide from the matrix. Acid distillation is known to cause either negative or positive analytical biases depending upon the chemical composition of the sample matrix being tested. Sulfide is known to cause interferences during sampling, sample preparation, and measurement steps of U.S. EPA methods such as 335.4.

During sampling, sulfide reacts with cyanide to form thiocyanate decreasing the cyanide concentration. This reaction is especially rapid if metal sulfides such as lead sulfide are present.

During acid distillation, sulfide distills over into the basic absorber solution and reacts with cyanide forming thiocyanate and decreasing its concentration.

Cyanide methods that employ colorimetry will erroneously detect sulfide as cyanide when the sulfide concentration is >10 mg/L causing a positive bias.

ASTM Method D 7511-09e2 for Total Cyanide Analysis

ASTM D 7511-09e2⁽⁷⁾ defines a method for the determination of total cyanide in aqueous samples including industrial effluents. This automated method is applicable to a mass concentration range of 3-500 $\mu\text{g/L}$ CN. Higher

concentrations can be determined by performing dilutions or adjusting operating conditions. ASTM D 7511-09e2 was specifically developed to mitigate interferences commonly encountered with other cyanide methods, especially those that utilize a high temperature acid distillation step. Sulfide concentrations below 50 mg/L do not interfere with analysis by ASTM D 7511-09e2. Testing samples with a lead acetate test strip will indicate samples with sulfide > 50 mg/L. Samples containing sulfide concentrations >50 mg/L can be diluted or treated with a sulfide scrubber reagent to reduce the level of sulfide for interference-free analysis.

On April 17th, 2012, the U.S. EPA Administrator signed a Methods Update Rule (MUR) approving new analytical methods for testing of pollutants in wastewater under the Clean Water Act.⁽⁸⁾ Six ASTM methods (including ASTM D 7511-09e2) covering sampling, preservation, and analysis of free, available and total cyanide species were included in the final MUR published in the Federal Register of May 18, 2012.⁽⁹⁾ Refineries can now use ASTM D 7511-09e2 to test wastewater samples for NPDES regulatory compliance reporting.

Principle of Operation

A flow diagram for performing total cyanide analysis by ASTM D 7511-09e2 is shown in Figure 3. In operation, a sample is injected into a carrier stream, segmented, and acidified. Under acidic conditions, the weak acid dissociable cyanide complexes convert to HCN (1) and the strong metal-cyanide complexes are irradiated by ultraviolet light in the UV digestion module (2) where they break down and release HCN. The HCN gas from all cyanide species present in the sample diffuses across a hydrophobic membrane into a basic acceptor solution (3), where it converts back to CN⁻ and is carried into a flow cell of an amperometric detector. Cyanide ions react with a silver electrode and generate current proportional to the cyanide ion concentration (4). The detector response is displayed as a peak. The resulting peak height is proportional to the cyanide concentration present in the sample.

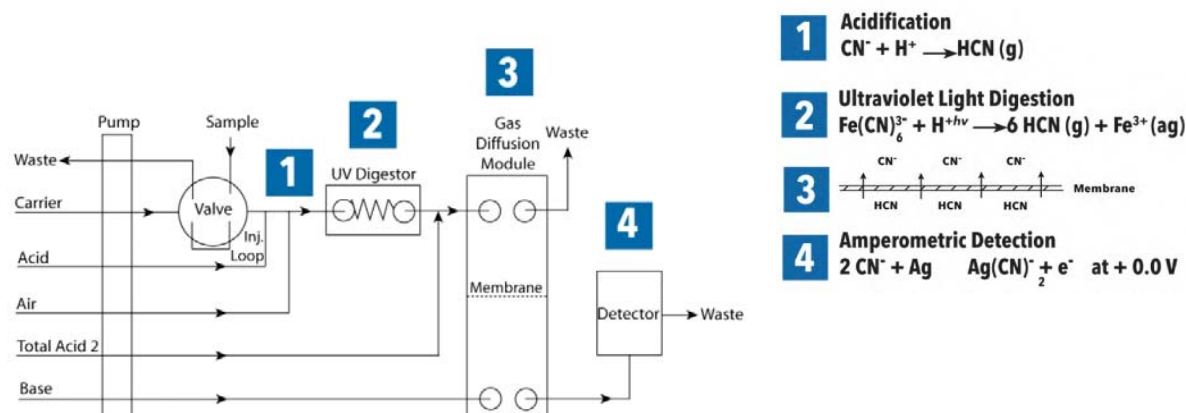


Figure 3. Flow Diagram for Total Cyanide Analysis by ASTM D 7511-09e2

Instrumentation for Cyanide Analysis by ASTM D 7511-09e2

ASTM D 7511-09e2 defines design and performance characteristics a flow injection analysis (FIA) instrument should possess to perform the method. Among the design features needed for this in-line UV digestion, gas-diffusion amperometry method are a UV digestion module with a 312-nm lamp, a gas diffusion manifold with a hydrophobic membrane, an amperometric detector equipped with a silver working electrode, an AgCl reference electrode, and a Pt or stainless steel counter electrode.

The CNSolution™ 3100 Cyanide Analyzer (Figure 4) is a compact, modular, laboratory instrument that meets the requirements stated in ASTM D 7511-09e2.



Figure 4. OI Analytical CNSolution™ 3100 Cyanide Analyzer for ASTM D 7511-09e2

Summary and Conclusions

The chemical composition of sour wastewater complicates the analysis of cyanide due to the presence of matrix interferences such as sulfide. Analytical methods that employ an acid distillation step and colorimetry are most prone to sulfide interferences commonly encountered in sour wastewater samples. ASTM D 7511-09e2 is a U.S. EPA-approved method for total cyanide analysis of NPDES wastewater samples. Sour wastewater samples containing sulfide at concentrations <50 mg/L can be analyzed for cyanide by ASTM D 7511-09e2 without the interferences encountered with other methods.

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