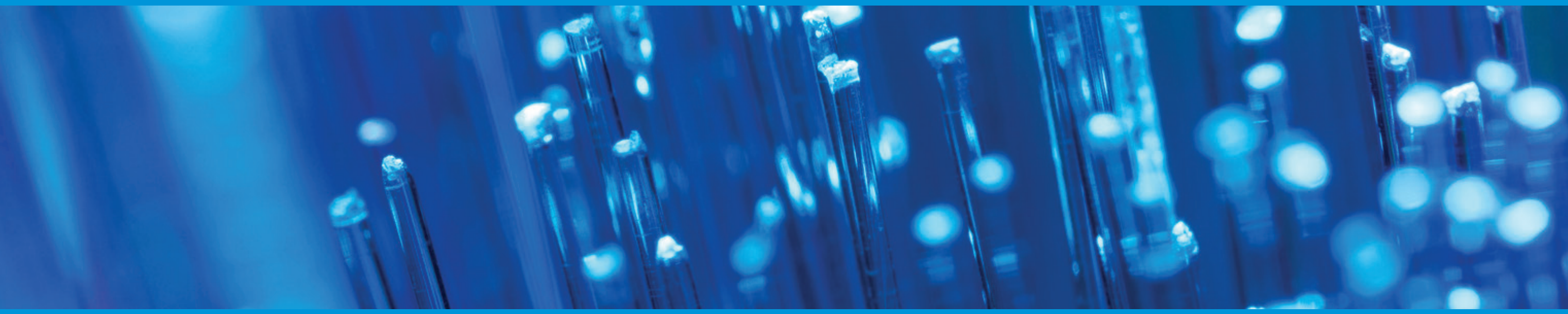
THE DRY COLORIMETRIC APPROACH TO POLYMER GRADE OLEFIN FEEDSTOCK ANALYSIS



The increasing demand of ethylene and propylene gas lies in their importance for polymer production. These olefins are the basic molecular forms of more complex macromolecular structures known as polymers. Given the specificity of determinate chemical and physical properties of some polymers, the polymerization process requires extensive amounts of pure raw material to guarantee high yields of products. Dry colorimetric method is presented as a solution for olefins production to monitor the quality and to control the presence and concentration of minor components that may compromise the performance of catalyst materials during the polymers manufacturing.

Introduction

Olefins, also known as alkenes, are unsaturated hydrocarbons produced by numerous processes in the petrochemical and oil refining industry. Given its wide reactivity and versatility, more specifically light olefin products such as ethylene, propylene, butane, butadiene etc., are the preferable precursors of industrial and consuming products including polymers, fertilizers, detergents, dyes, other chemical intermediates and synthetic rubber. Conventionally, olefins are produced by steam cracking of light alkanes (natural gas processing products) or different fractions of crude oil (essentially naphtha).

Ethylene, the shortest olefin, is the precursor of intermediate chemical products counting acetaldehyde, ethylene chloride, ethyl alcohol, ethylene oxide, ethyl benzene listed as the top 30 most common chemicals in the United States in the past 20 years[1]. Ethylene is increasingly used for the production of polymers such as polyethylene, polystyrene, polyethylene terephthalate and polyvinyl chloride used in food packaging, textiles and construction materials. Ethylene is obtained from cracking naphtha, gas oil and condensates in European and Asian counties. In the United States, Canada and the Middle East ethylene is manufactured as a product of ethane and propane cracking. Because of the global concern to develop environmentally friendly technologies to produce polymeric products, mostly polyethylene, a Brazilian company developed a plant for cracking fermentation-based ethanol to ethylene. Since the ethylene produced comes from a renewable resource, polyethylene-based packaging was labelled as a "green" product[2].

About 60 % of ethylene is used to produce polyethylene. Polyethylene (PE) is a polymeric thermoplastic material comprising long chains of ethylene monomers. Polyethylene is categorized based on its density and branching. Specific mechanical properties are conferred as the result of engineering variables such as the extent and the degree of branching, the crystal structure and the molecular weight. High Density Polyethylene (or HDPE) is characteristic by its density greater or equal to 0.941 g/cm^3. HDPE has low branching chains and as a result stronger molecular forces and tensile strength. This material is commonly used in blow and injection moulding applications of which containers, drums and household goods are the end result. This material can be made into pipes for water irrigation, gas, carrier bags and industrial lining. Low Density Polyethylene or LDPE is characteristic for its density ranging between 0.910 and 0.940 g/cm^3. LDPE is characterized by its high degree of short and long chain branching, which makes it a poor crystal packaging structure. For instance, these polymers have low tensile strength and high ductility. LDPE products are found for rigid containers and plastic films. Linear Low Density Poly Ethylene (LLDPE) has density values ranging between 0.915 and 0.925 g/cm^3. LLDPE is a significantly linear polymer with high content of short branches. LLDPE reveals high tensile strength, compared to LDPE, and as a result high impact and puncture resistance. LLDPE is used predominantly in film applications given its toughness, flexibility and relative transparency for multilayer and composite films[3].

Propylene is the simplest mono substituted alkene, and it is a resourceful petrochemical with even more derivatives than ethylene. In 2015, 67 % of the propylene was dedicated to the production of polypropylene. Nearly 7% of global propylene demand was committed to propylene oxide synthesis, an intermediate product of polyols, propylene glycols and propylene glycol ethers for the manufacturing of a wide variety of products including polyurethane foams and insulation materials, personal care products, aircraft deicers, cleaning and household products, glues, inks, etc. Propylene is obtained as a by-product of steam cracking of naphtha for ethylene production or recovered from fluid catalytic cracking. By moderating the severity of the cracking conditions, it is possible to tune the propylene/ethylene ratio increasing the production of high value by-products such as propylene. Propylene, generated as a product of fluid catalytic cracking, accounts about 30 % of the global production and this trend tends to be increasing given ethylene production through ethane steam cracking is growing. Given the availability of propane in shale gases, propylene synthesis via a dehydrogenation mechanism is an alternative source for this olefin.

Four carbon chain olefins include compounds such as butadiene, isobutylene and n-butene. These compounds are raw materials of commercial products including synthetic rubber, polymer gasoline and as precursors to methyl tert-butyl ether and ethyl-tert-butyl ether as octane enhancers and methyl ethyl ketone for higher olefins synthesis[4].

For polyolefin synthesis purposes, olefins feedstock must be substantially pure, especially when the catalyst used presents high activity and any appreciable concentration of impurities can eventually have a negative impact with the catalyst activity. Table N.1 presents some non-hydrocarbon impurities found in polymer grade ethylene and propylene.

Along with the sulfur contaminants (mainly, H_2S, carbonyl sulfide and short chain mercaptans) light olefins may contain small amounts of arsine. Generally, light olefin hydrocarbon feedstock may have several hundred ppb of AsH_3. Even though, the typical concentration expected is low (about 20 ppb), AsH_3 is a powerful reducing agent that significantly decreases the yield of production of polymers by interfering with the catalytic activity of catalyst such as Ziegler-Natta for polypropylene production[7]. Hence, critical point monitoring to control the impurities content during light olefin production is needed. In addition, it is known that the levels of nitrogen oxides (commonly known as NOx) must be controlled during ethylene recovery since these nitrated compounds may form ammonium nitrite and ammonium nitrate salts which are highly reactive near ambient temperature.

Aware of the necessity to develop a method able to produce reliable results for low concentration impurities, CI Analytics developed a fully automated technique capable to measure a wide variety of compounds including ammonia, hydrogen sulfide, arsine and phosphine, phosgene, chlorine, and total content of heteroatoms including sulfur, nitrogen and chlorides. The principle of the analytical technique relies on the dry colorimetric method where a targeted compound produces different colour intensities proportional to the concentration in the gas phase. The

Table N.1 Possible composition of propylene and ethylene for polymers manufacturing

Component	Ethylene[5]	Propylene[6]
Hydrogen sulfide, H_2S	<0.1 to 1 ppm	<0.1 to 10 ppm
Total sulfur	<0.1 to 5 ppm	<1 to 10 ppm
Total nitrogen	-	<1 to 5 ppm
Ammonia, NH_3	<0.1 to 2 ppm	-
Total NO_x (nitric oxide NO, and nitrogen dioxide NO_2)	<0.1 to 10 ppm	-
Total chloride	<0.1 to 2 ppm	<1 to 5 ppm
Arsine, AsH_3	-	<0.1 to 1 ppm

colorimetric detection is carried out with a photodiode system sensing the colour changes of a chemically impregnated paper that reacts selectively to the target impurity. The main advantage of this technique is that the major stream components (mostly hydrocarbon based) do not represent an interference issue with the detection system, as it may occur with other methods such as Chemiluminescence and UV fluorescence. In addition, CI Analytics method is suited to analyze on-line processes as well as laboratory locations depending on the area classification required. Table N. 2 presents a summary of the typical detection limits available for some non-hydrocarbon impurities.

Table N.2 Detection limit for typical gas impurities with CI Analytics dry colorimetric method.

Compound	Low detection limit, LDL*
H_2S	1 ppb
NH_3	30 ppb
AsH_3	1 ppb
NO_2	5 ppb
HCN	35 ppb
Total sulfur	1 ppb
Total chlorides	200 ppb
Total NO_x	5 ppb

** LDL can be optimized depending on specific application parameters.*

Conclusion

Petrochemicals are known to be a group of the most relevant derived products from crude oil besides the refining products, designated predominantly to fuel production. Olefins as part of petrochemicals are unsaturated hydrocarbons source of industrial chemicals and plastics. Within the most versatile olefinic compounds are ethylene and propylene, considered the building blocks of polymers with a wide variety of applications including packaging, coatings, adhesives, inks, detergents, furniture, textiles, etc. Ethylene and propylene as raw material of polymers must be produced with high degree of purity to be economically viable in an industrial polymerization process. The presence of minor components as contaminants of ethylene and propylene steams may interfere with the catalytic production of polyethylene and polypropylene. The dry colorimetric method offers an analytical solution for on-line and laboratory application during different olefin stages of production.

References

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