



Review article

Molecular characterization of sulfur-containing compounds in petroleum

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ABSTRACT

Sulfur-containing compounds (SCCs) are the most abundant heteroatom compounds in petroleum. The characterization of SCCs in crude oils and petroleum products has great importance not only for the downstream refining process control/optimization and environmental compliance but also for upstream geochemical studies for exploration and production. In recent years, a variety of methods to analyze SCCs have been developed and practiced where chromatography and mass spectrometry have played major roles. This review summarizes the analytical strategy and some of the most important and promising technologies, from sample pretreatment to molecular level characterization. For the convenience of discussions and practical applications, we divide the petroleum mixtures containing sulfur components into gas chromatography (GC)-amenable and nonvolatile fractions. For the former, gas chromatography (GC) and comprehensive two-dimensional gas chromatography (GC × GC) utilizing sulfur-selective detectors or mass spectrometry (GC–MS) are predominant analytical techniques. For the latter, molecular characterization is much more difficult and challenging. High performance liquid chromatography (HPLC) or direct liquid infusion and its combination with mass spectrometry (LC–MS), especially ultra-high resolution mass spectrometry, such as Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and Orbitrap MS, associated with various atmospheric ionization techniques are the most practical approaches. Some ionization techniques are underutilized, such as atmospheric pressure chemical ionization (APCI). The use of surface desorption ionization techniques, direct electrospray ionization (DSEI) and desorption atmospheric chemical ionization (DAPCI), for the molecular characterization of insoluble kerogens that has been characterized by X-ray near edge structure spectroscopy (XANES) and X-ray photoelectron spectroscopy (XPS) remain to be explored.

1. Sulfur-containing compounds in petroleum

Petroleum is a very complex mixture of hydrocarbons and non-hydrocarbons (heteroatom-containing compounds). In common language, petroleum includes not just crude oil, but all liquid (crude oil, condensate), gaseous (natural gas) and solid (bitumen, oil sand, tar) hydrocarbon mixtures [1–4]. The main elements of petroleum are carbon and hydrogen, as well as small amounts of heteroatoms (sulfur, nitrogen, oxygen, metals, etc.). Sulfur is the most abundant heteroatom, account for 0.03–6 wt% in petroleum (natural gas and crude oils) of commercial importance [4,5]. The New York Mercantile Exchange designated crude oil as “sweet” when the total sulfur is less than 0.42%, and “sour” when it contains higher levels of sulfur [6].

Sulfur-containing compounds (SCCs) are generally the most abundant heteroatom-containing components in petroleum. SCCs can be categorized into six basic types according to their functional groups:

hydrogen sulfide (H₂S), elemental sulfur, mercaptans (thiols), sulfides (acyclic and cyclic), polysulfides (disulfides, trisulfides, etc.) and thiophenes [7,8], with general structures shown in Fig. 1. The first two are inorganic compounds that are commonly associated (soluble) with crude oils and fractions due to thermochemical decomposition of sulfur organics, bacteria sulfate reduction and incorporation of inorganic sulfur that over time react with organic compounds during burial or petroleum processing. The first four types are reactive and corrosive. Many fatal incidents were caused by the accidental release of H₂S in the exploration and/or production of high-sulfur reservoirs [9]. The composition and quantities of SCCs vary significantly in different crude oils around the globe [4,10], affected by source characteristics (marine versus terrigenous), presence or absence of dissolved sulfate, depositional environment (carbonate versus clastic formation), thermochemical or bacteria sulfate reduction, and extent of biodegradation [11]. There are other types of SCCs, such as sulfones and sulfoxides,

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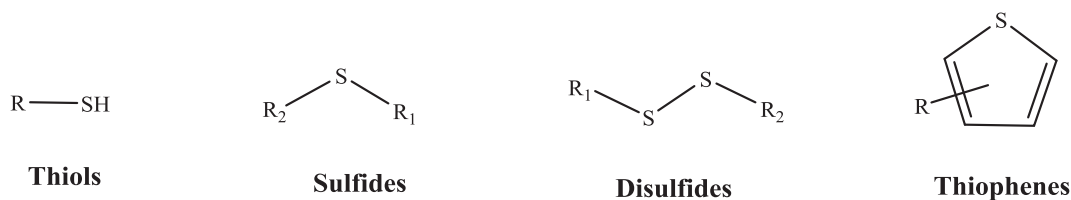


Fig. 1. Category of organic SCCs in petroleum.

that are generated through oxidation in shallow reservoirs exposed to oxic water or during transportation and storage exposed to air. Trace amounts of carbonyl sulfide can be found in natural gas. Most of the oxidized sulfur organics are concentrated in heavy oils (or fractions) and bitumen.

The volatile SCCs are readily detected by their smell of pungent rotten-egg odor. They can be converted into toxic H_2S upon burial (thermal stress) or heat. The pungent mercaptans are usually oxidized into disulfides through Merox process prior to transportation to meet specifications because they are also highly corrosive to pipelines, tankers and storage tanks. During petroleum refining processes, sulfur compounds can deactivate the catalysts and etch equipment. SCCs in products are of environmental concerns. The combustion of organic sulfur in fuels emits SO_x (SO_2 and SO_3), which are the major contributors to acid rain that can damage plants, crops and structural surfaces. The toxic SO_x released into air can interact with ozone, other gases and particulates to form airborne sulfonated smog particles that are hazardous to human health. Several sulfur heterocyclic hydrocarbons from combustion exhausts are suspected carcinogens and mutagens. Hence, the refining processes and environmental regulations limit the SCCs in processed fuels to small amounts [12,13]. For example, United State Environmental Protection Agency (US EPA) Tier 3 vehicle emission and fuel standards and China V standard have lowered the allowed sulfur content in gasoline to 10 ppm by weight, beginning in 2017 in U.S. and 2016 in China, respectively [14]. In the European Union, the legal limit of 10 ppm on sulfur in gasoline has been mandatory since 2008. Hence, desulfurization is a critical process in refining.

SCCs with different structures behave very differently in the desulfurization processes [12,15–19], and a better understanding of the molecular structures or compound types of the sulfur species in petroleum is needed for developing improved strategies. In addition, the characterization of the sulfur species could provide potential molecular indicators, such as petroleum biomarkers, for the source inputs and maturity as well as depositional environments of the crude oils and source rocks [20]. Therefore, the characterization of SCCs in crude oils and petroleum products has great importance not only for the downstream refining process control and environmental compliance but also for upstream geochemical studies for exploration. In this article, some recent progresses in the SCC characterization will be highlighted and discussed.

2. Analytical strategy

Other than natural gas and light petroleum, such as condensate, crude oils are complex mixtures containing thousands of components. Hence, no single analytical method can completely characterize the SCCs found in the oils. Any analytical scheme that attempts to do so will have to separate oil into distillation or chemical group type fractions and apply multiple analytical techniques [21].

Prior to compositional analysis, it is important to obtain the boiling range and total sulfur content of the sample being analyzed. The boiling range would help the determination if the sample can be analyzed in details by gas chromatography (GC) and associated techniques. The total sulfur content is used as a reference for the quantitation of sulfur-containing components in the mixtures. It can also be used to determine

if pre-concentration would be necessary for more reliable analytical results.

Both boiling range and sulfur content of whole crude oil and its distillation fractions are usually available in crude assay [8,22]. Boiling range of petroleum fractions also can be determined in a short analysis time using a minute amount of sample by simulated distillation (Sim-Dist) utilizing gas chromatography with flame ionization detection [23,24]. With a sulfur-selective detector, such as sulfur chemiluminescent detector (SCD), SimDist can also be used for the sulfur distribution as a function of boiling point [25].

Gas chromatography (GC) has proven a powerful analytical technique to analyze individual components in a complex mixture. However, it has limitation in operation temperature, normally $350^\circ C$, due to the thermal stability of column stationary phase. Thermally labile compounds can also degrade at the high operating conditions needed for vaporization and elution. Hence, our strategy is to divide oil and oil fractions containing SCCs into GC-amenable (low boiling) and nonvolatile (high boiling) fractions. The light distillation fractions, including gas, naphtha, middle distillates (kerosene, jet fuel, diesel oil) and gas oils, are GC-amenable. For whole crude oil containing higher boiling fractions (heavier than gas oils), the identification of many individual components is possible utilizing high efficiency capillary GC columns although many isomers remain partially or completely unresolved. Compound type analysis by hydrocarbon groups (classes) has been commonly adopted for analysis.

Quantitative GC analysis is conventionally carried out using flame ionization detection (FID) due to its uniform response to mass. For sulfur compounds, many selective detectors can be used [26,27], which are discussed in details below. In practice, FID and one of the sulfur-selective detectors are used in parallel or tandem for quantification of the eluting peaks identified as sulfur species. Compound identification and confirmation is normally conducted using mass spectrometry. Electron impact ionization (EI) at 70 eV is a standard method so that the compounds can be identified based on their unique fragmentation patterns either by comparing with library (reference) spectra or through spectral interpretation. There is no ionization method, including chemical ionization (CI) and photoionization (PI), that selectively ionizes only sulfur components.

For nonvolatile components or mixtures that are not amenable to GC, the volatile components are usually removed by distillation. The nonvolatile fraction can then be separated further into chemical fractions by preparative liquid chromatography (LC). The latter techniques range from open column to high performance liquid chromatography (HPLC) or ultra-high performance liquid chromatography (UPLC). The high boiling sulfur compounds are several magnitudes more diverse than those in the GC-amenable fractions and LC separation into separate individual compounds is not possible. LC separates the SCCs, along with hydrocarbons, into only a few different chemical groups with similar polarity or functionality. The most commonly used LC detectors in hydrocarbon analysis include refractive index (RI), ultraviolet/visible (UV/VIS) and evaporative light scattering detector (ELSD) [28]. However, there is no sulfur-selective detector for LC effluent because of the requirement of exciting sulfur species into higher electronic states under severe interference of excess amounts of solvent. Again, mass spectrometry has proven the most powerful analytical tool for the molecular characterization of the LC eluent. The mass spectrometric

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