

Modern Spectroscopies for Characterizing the Chemical Composition of Kerogen and Bitumen

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Abstract

Producing mobile hydrocarbons from shale depends in part on the chemistry of the immobile hydrocarbons in shale. In addition to mobile oil and gas, shales typically contain two phases of immobile hydrocarbons: bitumen, a viscous material defined as soluble in organic solvent; and kerogen, a solid material defined as insoluble (pyrobitumen is included in this definition). These phases control many of the key processes involved in economic recovery from shales, and their detailed chemistry is relevant to understanding fundamental mechanisms involved in shale production. For example, oil and gas are formed by the decomposition of kerogen and bitumen, such that the chemistry of the initial kerogen dictates when producible fluids are generated and what their properties are. Oil and gas generation leaves nanoscopic pores in kerogen, and kerogen's surface chemistry and structure dictate how different components in the mobile phase are stored and transported through kerogen, similar to the role of the stationary phase in chromatography. Additionally, kerogen is typically the most ductile component of shale and can be bonded to minerals in complex manners, so the chemistry of kerogen may impact fracture propagation.

Despite their importance, kerogen and bitumen are complex mixtures that are not amenable to chemical characterization by common experimental techniques. As a result, relatively little is known about their detailed chemistry, hindering the development of first-principles understanding of these fundamental mechanisms. However, several advanced spectroscopic methods able to characterize kerogen and bitumen at the molecular level have been implemented recently. These methods include X-ray absorption near-edge structure (XANES) spectroscopy, which can measure the distribution of sulfur-containing functional groups; high-resolution ^{13}C NMR spectroscopy, which can measure the relative abundance of aromatic carbon (similar to benzene) and aliphatic carbon (similar to wax); X-ray Raman scattering (XRS) spectroscopy, which can measure the geometry of fused aromatic ring systems; and infrared (IR) spectroscopy, which can measure the configuration of aliphatic carbon and some oxygen-containing functional groups. Taken together, these analyses are beginning to paint a picture of the molecular composition of kerogen and bitumen, including their evolution with thermal maturity. We find that immature kerogen contains mostly aliphatic carbon and sulfur, as well as several oxygen-containing functionalities. During maturation, carbon and sulfur in kerogen become more aromatic, the size of fused rings grow, and all oxygen-containing functionalities are diminished. Like kerogen, bitumen converts from mostly aliphatic carbon at low maturities to mostly aromatic carbon at high maturities. However, several chemical differences between kerogen and bitumen are observed: kerogen is dominated by reduced sulfur (which is non-polar), while bitumen is dominated by oxidized sulfur (which is polar); aliphatic chains monotonically shorten with maturity in kerogen, while they reach a maximum length at intermediate maturities in bitumen; and aromatic ring systems grow with maturity in kerogen, while their size remains unchanged in bitumen. These measurements provide some insights into the mechanisms involved in petroleum generation, hydrocarbon storage, and oil/water transport in shale.