Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 153 (2015) 37–71

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Petroleum alteration by thermochemical sulfate reduction – A comprehensive molecular study of aromatic hydrocarbons and polar compounds

Clifford C. Walters[a,*], Frank C. Wang[a], Kuangnan Qian[a], Chunping Wu[a], Anthony S. Mennito[a], Zhibin Wei[b]

[a] *ExxonMobil Research & Engineering Company, 1545 Route 22 East, Annandale, NJ 08819, United States*
[b] *ExxonMobil Upstream Research Company, 3120 Buffalo Speedway, Houston, TX 77098, United States*

Received 2 July 2014; accepted in revised form 24 November 2014; available online 27 December 2014

Abstract

Thermochemical sulfate reduction (TSR) alters petroleum composition as it proceeds towards the complete oxidation of hydrocarbons to CO_2. The effects of TSR on the molecular and isotopic composition of volatile species are well known; however, the non-volatile higher molecular weight aromatic and polar species have not been well documented. To address this deficiency, a suite of onshore Gulf coast oils and condensates generated from and accumulating in Smackover carbonates was assembled to include samples that experienced varying levels of TSR alteration and in reservoir thermal cracking. The entire molecular composition of aromatic hydrocarbons and NSO species were characterized and semi-quantified using comprehensive GC × GC (FID and CSD) and APPI–FTICR-MS.

The concentration of thiadiamondoids is a reliable indicator of the extent of TSR alteration. Once generated by TSR, thiadiamondoids remain thermally stable in all but the most extreme reservoir temperatures (>180 °C). Hydrocarbon concentrations and distributions are influenced by thermal cracking and TSR. With increasing TSR alteration, oils become enriched in monoaromatic hydrocarbons and the distribution of high molecular weight aromatic hydrocarbons shifts towards more condensed species with a decrease in the number of alkyl carbons. Organosulfur compounds are created by the TSR process. In addition to the increase in benzothiophenes and dibenzothiophenes noted in previous studies, TSR generates condensed species containing one or more sulfur atoms that likely are composed of a single or multiple thiophenic cores. We hypothesize that these species are generated from the partial oxidation of PAHs and dealkylation reactions, followed by sulfur incorporation and condensation reactions. The organosulfur species remaining in the TSR altered oils are “proto-solid bitumen” moieties that upon further condensation, oxidation or sulfur incorporation result in highly sulfur enriched solid bitumen, which is chemically distinct from pyrobitumen formed by thermal cracking reactions.

Although TSR involves the oxidation of hydrocarbons to CO_2, prior studies of TSR-altered oils have not identified intermediate products. Using NESI–FTIRC-MS, the presence and distribution of oxygenated species become evident. All oils possess minor amounts of O_2 and O_4 species, presumable mono- and di-naphthenic acids originating from the source. As TSR progresses, the distribution of oxygenated species shifts towards increasing species with higher oxygen content, up to O_8. Similar trends are observed for the SO_x species. We hypothesize that these are partially oxidized condensed hydrocarbons and that these species are likely formed by the reaction proposed by Püttmann et al. (1989) for the oxidation of PAHs associated with Kupferschiefer mineralization, whereby hydrocarbons with aryl–aryl bonds incorporate sulfur to form thiophenic species.

---

[*] Corresponding author.
E-mail address: clifford.c.walters@exxonmobil.com (C.C. Walters).

http://dx.doi.org/10.1016/j.gca.2014.11.021

The rate of TSR is influenced by reservoir temperature and the presence of H_2S. Typically, high reservoir temperatures (>140 °C) are needed for extensive TSR alteration to occur. Oil from the Gin Creek Field appears to have received a charge of H_2S, presumably from TSR alteration of a down dip reservoir, which has accelerated the TSR reaction within a relatively cold reservoir (∼109 °C). This condition has allowed for the generation and preservation of abundant sulfur containing species that would be thermally cracked at higher temperatures.

1. INTRODUCTION

Petroleum hydrocarbons may react with sulfate in relatively hot (>100 °C) non-clastic reservoirs. This process, termed thermochemical sulfate reduction (TSR) (Orr, 1974; Nöth, 1997) involves a complex series of redox reactions whereby hydrocarbons and other compounds present in petroleum are oxidized to CO_2 and sulfate is reduced to H_2S. The reaction is promoted initially through the formation of contact ion-pairs that destabilize the sulfate tetrahedron (Zhang et al., 2007; Ma et al., 2008).and is further advanced by H_2S (Orr, 1977; Zhang et al., 2008a,b). As H_2S is a product of TSR, the reaction can be viewed as "auto-catalytic" as suggested by early investigator of the process (Feely and Kulp, 1957; Orr, 1974; Powell and Macqueen, 1984; Goldhaber and Orr, 1995), although H_2S itself is not a catalyst but promotes the formation of bisulfate and or contact ion pairs (Ma et al., 2008) that accelerates the reaction. H_2S also is generated by the thermal cracking of organosulfur compounds and, hence, the rate of TSR alteration is dependent on the hydrocarbon composition (Zhang et al., 2007; Amrani et al., 2008). Xia et al. (2014) found that once the C_{3+} hydrocarbons have been oxidized, the TSR reaction is no longer promoted by H_2S and proceeds at a significantly slower rate.

Oils altered by TSR exhibit compositional and isotopic changes that are distinct from thermal cracking and other reservoir alteration processes. In some aspects, TSR mimics thermal cracking that would occur at higher reservoir temperatures and oils become increasingly dominated by lighter more volatile hydrocarbons, increasing the API gravity. Ultimately, condensates containing only the most stable diamondoids and thiodiamondoids remain (Wingert, 1992; Mankiewicz et al., 2009). TSR alteration result in heavier $\delta^{13}C$ values of the whole oils and oil fractions (Sofer, 1988; Claypool and Mancini, 1989; Connan and Lacrampe-Couloume, 1993; Manzano et al., 1997). The selective reactivity of the light (C_2–C_8) normal and branched alkanes compared to monoaromatic hydrocarbons can result in compositional (Whiticar and Snowdon, 1999; Peters et al., 2005; Xiao et al., 2011) and isotopic (Rooney, 1995; Connan et al., 1996; Whiticar and Snowdon, 1999; Xiao et al., 2011; Amrani et al., 2012) values that are diagnostic of the extent of TSR.

Organosulfur compounds are formed by TSR either through the oxidative process or by back reaction of hydrocarbons with H_2S or elemental sulfur. With increasing extent of TSR alteration, the $\delta^{34}S$ of oils and evolved H_2S shifts from the values derived from the source kerogen towards that of the inorganic sulfate (Orr, 1974; Krouse et al., 1988) and thermally stable organosulfur compounds, such as dibenzothiophenes (Manzano et al., 1997; Cai et al., 2009; Wei et al., 2012) and thiadiamondoids (Hanin et al., 2002; Wei et al., 2011, 2012) increase in relative abundance. Less thermally stable organosulfur compounds, such as thiophenes, benzothiophenes and benzonaphthothiophenes as well as metastable species, such as thiols, alkylsulfides and alkylthiolanes, are enriched suggesting that these species are being created by the TSR process faster than they are being destroyed (Ho et al., 1974; Manzano et al., 1997; Cai et al., 2003; Li et al., 2011; Zhu et al., 2011).

Solid bitumens are commonly observed in nearly all reservoir rocks where TSR has occurred (e.g., Powell and Macqueen, 1984; Sassen, 1988; Shew and Garner, 1990; Machel et al., 1995; Li et al., 2005; Hao et al., 2008; Cai et al., 2010; Hu et al., 2010). Filling vugs, cracks, and pore spaces, these materials were once fluid components that have become insoluble through thermal and TSR-induced processes. Solid bitumens associated with TSR are chemically distinct from reservoir bitumens arising from asphaltene precipitation or pyrobitumens. TSR-bitumens are largely insoluble, exhibit high reflectivity (>1.5%R_o) (Stasiuk, 1997), and are highly aromatic with high concentrations of thiophenic sulfur (Kelemen et al., 2008, 2010). The origin of these sulfur-rich bitumens are not fully known, but laboratory simulations of TSR can create similar solids starting with *n*-alkane reactants, suggesting that TSR-bitumens form not only from precipitated polars and asphaltenes that back react with reduced sulfur but from the TSR redox process (Zhang et al., 2008b) or sulfur cross-linking vulcanization type reactions (Kowalewski et al., 2010).

Until recently, the characterization of organosulfur species in crude oils was limited largely to volatile compounds amenable to gas chromatographic separation. The application of ultrahigh resolution mass spectrometry (FTICR-MS, Fourier transform ion cyclotron resonance-mass spectrometry) to petroleum fluids has expanded the detectable range to higher molecular weight, less volatile species. Using a method developed by Müller et al. (2005), where sulfur compounds are converted to methylsulfonium salts that are suitable for electrospray ionization (ESI), Li et al. (2011) analyzed several Lower Ordovician oils from Tarim Basin that included samples possibly altered by TSR. Purcell et al. (2006) showed that atmospheric pressure photoionization (APPI) is effective in ionizing organosulfur compounds in crude oil, though the method is not effective for non-aromatic species. Utilizing this method, Walters et al. (2011) reported that TSR-altered oils contain highly condensed polynuclear aromatic and naphthenoaromatic