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Molecular characterization of kerogen and its implications for determining hydrocarbon potential, organic matter sources and thermal maturity in Marcellus Shale

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ABSTRACT

Organic-rich shales are a vital component of the US energy sector. Kerogen, a high molecular weight macromolecule is the largest reservoir of organic carbon on earth and serves as the starting material for the oil and gas generation in these shales. Despite its importance, kerogen structure and its evolution on maturation are still not well understood, especially for mature shales (VRo > 1). Moreover, most of the models built to determine hydrocarbon (HC) potential and thermal maturity of the source rocks have used the structural parameters of kerogen extracted from immature shales (VRo < 1). Therefore, these models might not yield accurate results for mature and over-mature shales like Marcellus. In this study, we determine the structural parameters of kerogen extracted from three Marcellus Shale cores using ^{13}C solid-state Nuclear magnetic resonance (NMR). Samples were acquired from the upper and lower Marcellus Shale Formation from a dry gas well WV-6 (VRo > 2.5), a wet gas well WV-7 (VRo ~ 1.4) and an oil window well BG-1 (VRo ~ 0.81) in Monongalia, Wetzel and Brooke County, West Virginia, respectively. Our results indicate that the percentage of carbon chains such as mobile (freely rotating) and immobile alkyl without heteroatoms (with restricted rotation), and alkyl-substituted aromatic carbons decrease with increasing maturity indicating that these chains are more prone to thermal degradation and might have higher HC generating potential. However, carbon chains such as O- substituted alkyl (ether), O_2 substituted alkyl (dioxy alkyl), amine, protonated aromatic carbons, O- substituted aromatic (phenol) and bridgehead aromatic carbons does not decrease directly with thermal maturity suggesting that these groups are either more refractory in nature or their carbon fraction is influenced by changing sources of OM. Our results also indicate that the previous models based on the structural parameters of kerogen derived from immature shales overestimate the HC generation potential and underestimate the thermal maturity in mature shales from the Marcellus. In addition, H, O, C ratios derived from structural parameters of kerogen can be utilized to determine the kerogen type in these mature shales where traditional pyrolysis analysis fails to characterize the kerogen.

1. Introduction

Kerogen, the insoluble fraction oforganic matter (OM) in sedimentary rocks, is the largest and economically most important reservoir of organic carbon and source of all hydrocarbons in the subsurface. Therefore, it is essential to accurately characterize the structure of kerogen and its HC generation potential. However, there is a significant gap in understanding the mechanism of kerogen cracking and HC generation especially for mature shales (VRo > 1) mostly due to the insolubility and chemical heterogeneity of kerogen. Additionally, limited analytical techniques have the ability to provide quantitative molecular-level information of the structure of kerogen [7,16,48].

Kerogen is formed by the degradation, condensation, and polymerization of biomolecules contributed by different sources of OM (e.g., [21,45,18,48]. Kerogen formed in the diagenetic stage of burial later cracks to form oil and gas in catagenetic and metagenetic stages of burial. Most of the current studies on kerogen have been focused on methods such as visual kerogen analysis and pyrolysis using a Source Rock Analyzer (SRA). These methods are helpful in determining the type of kerogen, maturity, and oil vs. gas generating potential but do not provide any information on the chemical structure or composition of kerogen [48]. Moreover, for mature/over-mature source rocks SRA produces biased results about the OM sources and maturity due to low amounts of free/bound hydrocarbons, and incomplete combustion of

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refractory OM, and/or the hydrocarbons bound in a mineral matrix [48]. Biomarker ratios have also been used to determine the thermal maturity of source rocks [40,24,3,26]. However, due to thermal degradation and alteration of biomarkers on maturation and low extraction efficiency in high maturity samples, the results can be biased.

To understand kerogen cracking mechanism at the molecular level and to accurately predict HC potential from any source rock, it is vital to understand the molecular structure of kerogen [5,47,48]. Several analytical techniques have been developed for characterization of the chemical structure of kerogen, which are commonly classified into two major groups: destructive (pyrolytic) and non-destructive (spectroscopic) methods [46,8,9]. The pyrolytic analyses can provide valuable information about the labile/pyrolyzable fraction of kerogen [5,20,42,29]. However, the products generated from pyrolysis can interact among themselves and yield biased results about the components present in the labile fraction of kerogen [20]. Moreover, most of the kerogen models developed using the yield from pyrolysis experiments are conducted under elevated temperature (~250–650 °C) and then extrapolated to ~100 to 170 °C [17,49]. These results may not be reliable as the time span differs by ~4 orders of magnitude [17,49]. Additionally, the pyrolysis results depend on whether the reaction is conducted in an open vs. closed or hydrous vs. anhydrous conditions [6,28]. Therefore, the reactions taking place in laboratory conditions might not be representative of sedimentary basin conditions. Due to these limitations, non-destructive methods such as Fourier transform infrared (FT-IR), Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and ^{13}C solid-state nuclear magnetic resonance (^{13}C NMR) have been employed for the qualitative, semi-quantitative, and quantitative measurements of kerogen [13,52,25,41,46].

The ^{13}C solid-state NMR techniques provide the maximum amount of structural information on kerogen due to its higher accuracy and quantification capacity compared to other direct analytical methods, [33]. The most extensively used solid-state NMR technique for kerogen characterization is ^{13}C cross polarization/magic angle spinning (CP/MAS) [13,52,39,32,29,50]; [25]; [51,31,30]. However, by using ^{13}C CP/MAS alone, the fraction of non-protonated carbons and mobile groups (with non-restricted rotation) cannot be determined. Therefore, advanced solid-state NMR techniques such as multiple CP /MAS, multiple CP /MAS plus dipolar dephasing have been developed and applied in the recent years for systematically characterizing kerogen [33,23]. These advanced ^{13}C NMR techniques can be used for determining specific functional groups, aromaticity, and aromatic cluster size and better understanding the chemical structure of kerogen. A few researchers have used advanced NMR techniques, to determine the molecular structure of kerogen (For, e.g. [25,46,31,30]. However, most of these studies were conducted mainly on low maturity or immature samples. The models developed using these immature shales [27,31,50] can result in underestimation/overestimation of HC potential (especially gas) and thermal maturity, especially in mature shales with VRo > 1. For accurate estimation of HC potential in newly emerging mature shale plays like Marcellus, there is a need to develop a better understanding of the molecular structure of kerogen in mature shales with VRo > .1

The goal of the study is to determine changes in structural parameters of kerogen using ^{13}C solid-state NMR in Marcellus Shale maturity series with VRo ranging from 0.8 to 2.5. Kerogen was extracted from sediments from upper and lower Marcellus Shale Formation from three wells lying in the oil window (BG-1), wet gas window (WV-7) and in the dry gas window (WV-6). The location of the three wells is shown in Fig. 1. The easternmost WV-6 core has a thermal maturity of VRo > 2.5, WV-7 core has VRo ~ 1.4 [1,53], and the BG-1 core has VRo ~ 0.81–1.05. The depositional environment of the wells WV-6 and WV-7 has been established using geochemical, isotopic, pyrolysis and biomarker proxies [12,1]. The depositional model proposed by these studies suggest that the terrestrial sediment influx was from east to west

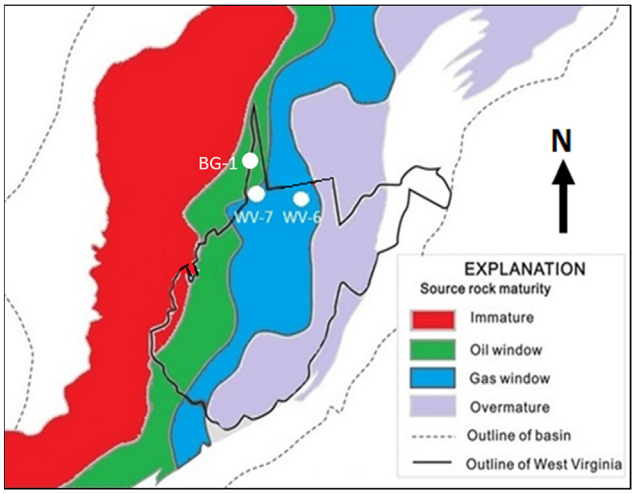

Fig. 1. Location of wells BG-1, WV-7 and WV-6. Modified from [54].

part of the basin, and the model suggests that sediments in dry gas WV-6 well were deposited in shallower part of the basin and received higher terrestrial OM influx as compared to WV-7 shale that was deposited in the deeper and anoxic part of the basin. Further, it was shown that upper Marcellus Formation received more terrestrial OM input as compared to lower Marcellus Shale Formation. Detailed isotopic and geochemical study is not available for the well BG-1. However, since this well is located in the western part of the basin (Fig. 1), the sediments must have been deposited further away from the terrestrial sediment source.

2. Materials and methods

2.1. Sampling

Core samples have been collected from three wells (WV-6, WV-7, and BG-1) in the upper and lower zones of the Marcellus Shale Formation. Location of WV-6 is in Monongalia County, WV-7 is from Wetzel County, and BG-1 is from Brooke County, West Virginia. (as shown in Fig. 1). To avoid any effects of contamination due to contact with drilling fluids and oxidation of OM [37,15] at least 5 mm of the outer layer of samples was removed before kerogen extraction. It is highly unlikely for fluids or air to penetrate > 5 mm of shale layer and contaminate/oxidize the inner part of the core. After paring, the inner portion was crushed to 200 mesh and homogenized using a sterile SPEX mixer mill and oven dried for 24 h at 50 °C.

2.2. Kerogen extraction

Kerogen was extracted from shale cores using methods modified from previous studies [14,48,22]. Soluble OM was extracted by sonicating 50 g of powdered samples in approximately 120 ml of dichloromethane DCM multiple times till the color of the solution was transparent. The residue was sonicated again with ~20 ml MeOH–acetone–$CHCl_3$ (15:15:70 v/v) mixture to dissolve the remaining polar soluble OM. The carbonates mineral was then dissolved from the residue by adding 6 N HCl for 48–72 h. This step was done multiple times until no effervescence was observed. Silicate minerals and the carbonates bound in silicate minerals were dissolved using a 1:1 mixture of 6 N HCl and 50% HF for 24 h. The residue was thoroughly rinsed with distilled water to avoid the formation of fluoride minerals. Remaining silicate minerals were dissolved by using 50% HF multiple times. Each HF step was followed by multiple rinses with distilled water to avoid neo-fluoride formation. Heavy minerals such as pyrite were removed by separating the denser phase by using 2.4gm/cc zinc bromide. The