Molecular Weight Distribution of Kerogen with MALDI-TOF-MS

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Abstract

Kerogen is an amorphous organic matter (AOM) in fine grain sediments, which produces petroleum and other byproducts when subjected to adequate pressure and temperature (deep burial conditions). Chemical characteristics of kerogen by considering its biogenic origin, depositional environment, and thermal maturity has been studied extensively with different analytical methods, though its molecular structure is still not fully known. In this study, conventional geochemical methods were used to screen bulk rock aliquots from the Bakken Shale with varying thermal maturities. Organic matter was isolated from the mineral matrix and then a mass spectrometry method was utilized to quantify molecular weight distribution (MWD) of four different kerogens at various thermal maturity levels (immature to late mature). Furthermore, to complement mass spectrometry, Fourier transform infrared (FTIR) spectroscopy was employed as a qualitative chemical and structural investigation technique. The MWD of four samples was obtained by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, and the results are correlated with the absorption indices (CH_3/CH_2 ratio and aromaticity) calculated from the FTIR attenuated total reflectance (ATR) method. The results showed when the degree of maturity increases, the aliphatic length shortens, and the branching develops, as well as the aromatic structure becomes more abundant. Moreover, based on the MWD results, higher maturity kerogen samples would consist of larger size molecular structures, which are recognized as more developed aromatic, and aliphatic branching stretches. The combination of infrared spectroscopy (AFT-FTIR) and mass spectrometry (MALDI-TOF) provided MWD variations in kerogen samples as a function of maturity based on varying absorption indices and revealed the rate of change in molecular mass populations as a function of thermal maturity.

Keyword: Kerogen, organic matter, Bakken, MALDI-TOF, molecular weight distribution (MWD), FTIR, EOR

Introduction

In the past few years, there has been growing attention to organic-rich shale reservoirs due to their importance in hydrocarbon production and CO_2 sequestration [1,2]. The high abundance of total organic carbon (TOC) in shale layers, which are deposited in these rocks hundreds million years ago, would lead to the generation of oil and gas through thermal maturation. This process takes place due to the exposure of rocks containing organics to adequate temperature and pressure as the depth of burial increases. During this geologic process, the organic matter known as kerogen, which has a complex and amorphous molecular structure, breaks down and goes through a significant structural and compositional transformation [3,4].

Thermal maturity of organic matter is an important phenomenon that still requires further studies at the molecular scale from various perspectives to help us better explain this process [3] which enables us to better explain the phenomenon that'd generate hydrocarbons from the organic matter. In this regard, there has been a limited number of studies to investigate molecular structure of organic matter (kerogen) at different stages of thermal maturity using various spectroscopy methods such as: 13-C nuclear magnetic resonance (^{13}C-NMR), X-ray photoelectron spectroscopy (XPS), and X-ray absorption near-edge structure (S-XANES) [5], Raman [6], and infrared (IR) [7] spectroscopy. Even though these studies have clarified the structural evolution of kerogen to some extent, this task still demands further analysis since kerogen has different biogenic origins (e.g., lacustrine and marine algae and plankton or terrestrial higher-order plants). One of the methods in better characterizing the molecular structure of organic matter during thermal maturation is measuring its molecular weight (MW) and relating that to the existing chemical compounds or functional groups at every stage of maturity.

Mass spectrometry (MS) technique has been widely utilized in biology [8] and chemistry [9] for decades to identify the molecular weight of various materials such as proteins and synthetic polymers, which is now extended to petroleum and fossil fuels arena. This being said, in the first attempt to characterize kerogen with MALDI by Li et al., [13], a relationship between the minimum laser power sufficient for activating the MALDI-ionization process and the thermal maturity level (reported in the age of samples) of kerogens, was established. This study was later continued by Herod et al. [14], where several isolated kerogens from various thermal maturities and mixed depositional environments (marine, lacustrine and terrestrial) were analyzed by MALDI-TOF-MS (Matrix-assisted laser desorption ionization-time of flight mass spectrometry). Authors found that spectra of isolated kerogens from 'younger' deposits (less mature or less buried) showed larger molecular mass distributions compared to the spectra obtained from extracts of older sediments. Furthermore, kerogen molecular weight estimation measured by MALDI-TOF was in agreement with the values obtained by conventional techniques, such as SEC-chromatograms [13,14]. The issue with these two studies that employed MALDI spectroscopy is that neither of them studied a single origin kerogen specimen, and there was a mixture of samples without a systematic maturity trend among them. The importance would be to reveal the rate of molecular weight alteration at specific thermal maturity stage and the rate of change in the population of molecular fragments, which is missing.

Recently, molecular weight of the organic matter that was artificially matured in a semiopen pyrolysis system to various levels of thermal maturities from Green River Shale Formation was quantified using various mass spectrometry methods including laser desorption laser ionization (L^2MS), surface assisted laser desorption ionization (SALDI) [10], and matrix-assisted laser desorption ionization (MALDI) [11,12]. Results showed a systematic change in molecular weights and correlation between elemental analysis and mass spectroscopy results. It should be mentioned that although chemical information that is provided by MALDI-TOF is considered accurate for both identification and in quantification of chemical substances in a material, it would be difficult to determine the existing functional groups (e.g. carboxyl/amide/carbonyl/methylene/methine functional groups), and non-degradable fractions in the studied compounds. This adds a drawback to MALDI-TOF-MS, which makes it inevitable to be coupled with other analytical techniques such as IR, Raman or nuclear magnetic resonance (NMR) spectroscopy, as was done on these limited studies of kerogen, to provide us more detailed information about the components and materials that are being analyzed [15].

In this study, four isolated (extracted) kerogens from the mineral matrix at four different stages of natural thermal maturity (immature to late mature) from the Bakken Shale were examined by MALDI-TOF-MS combined with FTIR spectroscopy for molecular weight quantification along with chemical and structural analysis. This study enabled us to identify structural characteristics of organic matter as it undergoes thermal advance in nature to relate these variations to both qualitative information from chemical structures and quantitative molecular weight distributions (MWD). Additionally, the outcome helps us to delineate the rate of change in molecular weight intervals populations as thermal maturity progresses.

Materials and Methods

Samples

Kerogen samples (type II representing a marine environment) were collected from the Bakken Formation which is one of the largest unconventional shale oil plays in North America and is currently being studied for potential CO_2-EOR and sequestration [16,17]. Samples were retrieved from four different wells that are drilled at different locations in the Williston Basin in ND, where the Bakken has different thermal maturities. Aliquots of the bulk samples were examined with programmed pyrolysis (Rock Eval 6) for determining the thermal maturity level of the samples. To be more accurate, samples were also analyzed for the solid bitumen reflectance in the absence/scarcity of the vitrinite maceral, and the measured values then converted to the equivalent vitrinite reflectance using the appropriate conversion equations. Results are summarized in Table 1, where it shows sample A is immature and sample D is late mature. Selected kerogen samples were isolated using HCl and HF, and liquid state hydrocarbon was extracted before MALDI-TOF-MS experiment. Further details about these samples and conventional geochemical analysis, organic matter extraction and the Bakken Formation can be found in Khatibi et al. [18], and Abarghani et al. [19].

Table 1 Properties of Four Kerogen Samples (type II)[a].

Sample No.	**T_{max} (°C)**	**TOC (wt %)**	**HI (mg/g C)**	**SBRo (%)**
A	428	14.56	569	0.33
B	432	15.76	531	0.49
C	449	12.69	260	0.72
D	452	16.36	171	0.94

[a]The values were examined by the solid bitumen reflectance (%SBR$_o$) and Rock−Eval 6 derived parameters including Tmax, TOC (Total organic carbon), and HI (hydrogen index).

ATR-FTIR

Infrared spectra of kerogen samples were recorded in adsorption between 450 and 4000 cm^{-1} wavelengths using a Thermo Fisher Scientific, Nicolet iS50 FTIR Spectrometer. Four kerogen samples were pulverized using a ball mill before the characterizations. Fourier transform infrared (FTIR) spectroscopy using attenuated total reflectance (ATR) was utilized to analyze the isolated kerogens. Unlike transmittance FTIR, ATR does not require that kerogen samples to be mixed with potassium bromide and form into pellets under high pressure, which reduces the time needed to prepare the samples. Kerogen samples were placed in contact with an internal reflection material, and IR spectra were obtained based on the excitation of the molecular vibrations of chemical bonds by the absorption of light. The stretching absorption of a vibrating chemical bond is observed at higher frequencies (wavenumbers) than the corresponding bending or bond deformation vibrations [22,23]. Although the bending vibrations can support to obtain more details from the chemical structure, we'd face limitations in the analysis of integrated bands in bending vibration areas because kerogen is a complex macromolecule. In this study, it was decided to analyze the C-H set of stretch vibrations that are observed in kerogen samples, which is also done in previous studies [7]. It should be noted that recorded bands of the absorption were identified through comparison with the published spectra shown in table 2.

Table 2 Saturated aliphatic group and aromatic ring group frequencies [23].

Origin	**Group frequency (cm^{-1})**	**Functional Group/ Assignment**
Methyl(-CH_3)	2970-2950	Methyl C-H asymmetric stretch
	2880-2860	Methyl C-H symmetric stretch
Methylene (>CH_2)	2935-2915	Methylene C-H asymmetric stretch
	2865-2845	Methylene C-H symmetric stretch
Aromatic (C-H)	3130-3070	Aromatic C-H stretch

Table 2 presents the stretching absorption for C-H stretch vibrations for methyl (-CH_3), methylene (>CH_2), and aromatics (C-H). These are the most common characteristics of an organic compound containing the aliphatic fragments. The intensities observed are corresponding to the asymmetric and symmetric stretching and bending of the C-H bonds of the central carbon atom. The C-H stretching vibrations for the saturated aliphatic occur between 3000 and 2800 cm^{-1}, and the aromatic ring stretch vibrations occur between 3130 and 3070 cm^{-1}. IR structural evaluations, which has been established in earlier studies [24], were calculated from acquired spectra. The intensities of bands assigned by the functional groups were deconvoluted through a curve fitting procedure [22,23]. The CH_3/CH_2 ratio ($I_{(2970\text{-}2950)}/I_{(2935\text{-}2915)}$) indicates the average chain length of aliphatic and the degree of chain branching. Moreover, aromaticity index ($I_{(3130\text{-}3070)}/(I_{(2970\text{-}2950)}+I_{(2935\text{-}2915)})$) represents the degree of aromatic structures to aliphatic chain structures [7,27]. These ratios were considered to better analyze MWD that is acquired by MALDI-TOF at different stages of maturity and were related to alterations in the overall molecular weight of the specimens.

MALDI-TOF-MS

The AB SCIEX TOF/TOF 5800 mass spectrometry system was used for the identification and relative quantitation of kerogen molecular weight. A dilution series of kerogen powder were prepared for two different test setups, in the absence and the presence of the matrix. In the second set up where the matrix is presented, dilutions were mixed with α-Cyano-4-hydroxycinnamic acid (α-CHCA) in 1:1 ratio. The matrix, α-CHCA, is commonly used in conjunction with organic molecules, particularly for relatively higher-weight ones [28]. Each sample (1 µL) was spotted onto a standard stainless steel plate and allowed to air-dry. Spectra were acquired with MS reflector mode for 1,000 shots, and the analysis was conducted over a range of 60 to 5000 Da by use of an adjusted accelerating voltage.

It should be noted that MALDI-TOF-MS analysis has been utilized to characterize kerogen in a very limited scope. However, previous studies conducted on heavy fossil fuels and aromatic compounds have demonstrated the applicability of MALDI-TOF to characterize similar macromolecules [11,12]. These studies suggested that the matrix would not always be necessary to obtain MALDI mass spectra, because lower molecular weight aromatics, can play the role of the matrix for the ablation of the higher molecular weight compounds. Even though suggestions have been made regarding the matrix, its role in the analysis of kerogen has not yet fully understood. Therefore, in our study, the MALDI-TOF spectrum of kerogen samples at various maturations is obtained in the absence and presence of the matrix, and the results are compared and reorganized to delineate the MWDs more accurately and help us investigate the necessity of having a matrix.

In order to confirm accurately the compound measurements validating the technique, we performed control procedures for MALDI-TOF [29,30]. MS technique is possible to detect varying components (fragments) of a complex structure. Hence, we made a 1:1 and 1:1:1 mixture of model compounds including kerogens spanning the mass range occurred for kerogen samples. Then, we checked that MALDI can detect all of these model compounds with about the same cross-section, and that the results give a spectrum with peaks regarding references and kerogens. Additionally, we confirmed that the measured molecular weight (WD) is not adjusted changed by the laser pulse energy. Furthermore, to find optimum laser power for kerogen samples, the multiple tests with model compound were performed to obtain clear and exact signals. Hence, we set of laser intensity at 5000 (instrument-specific units) for the absence of matrix with ??? Hz pulse rate and at 4200 for the presence of matrix with ??? Hz pulse rate.

Results and Discussions

Since kerogen consists of amorphous and complex chemical compounds, spectroscopy analysis would be inadequate to evaluate its chemical structure quantitatively. As a result, in this study, FTIR and MALDI-TOF-MS are integrated, to assist the chemical characterization of this geo-macromolecule. We have interpreted spectra obtained from several extracted kerogens at different stages of thermal advance to reveal the relationship between various functional groups and molecular weight distributions and chemical alterations in a type II kerogen.

Structural Characterization by FTIR

Considering the FTIR intensities, a given absorption band that is assigned to a specific functional group has a direct relationship with the amount of that functional group overall existence in the structure of the macromolecule [23]. We noted that the methyl group (CH_3) is considered as the terminal for the aliphatic chain, where a methylene group (CH_2) is linked to a neighboring group which can also be attached to another methylene group. This framework presents a carbon to carbon bond, forming the aliphatic chain. Because each section of this group has its corresponding C-H stretching and bending vibrations, identification of this group and skeletal frequency would help to estimate a carbon-based organic compound such as the kerogen. Especially, a strong methylene band (2935-2915 cm^{-1}) and a weak methyl band (2970-2950 cm^{-1}) indicates a longer-chain aliphatic structure. In contrast, the strong methyl band and a comparatively weaker methylene band indicate shorter-chain branching.

Figure 1 represents the intensities measured for frequency absorptions assigned to methyl, methylene, and aromatic on a relative basis in the spectrum of each kerogen samples. The reason for the overlapped original spectra is due to the same amount of energy required for various vibrations [23]. To analyze each functional group at desired frequencies, the FTIR spectrum area from 2700-3200 cm^{-1} was fitted (Figure 2). In order to do so, intensities and frequencies of the bands in the desired regions were estimated by curve fitting where the peak separation and quantitative calculation were performed using the Fourier self-deconvolution method.

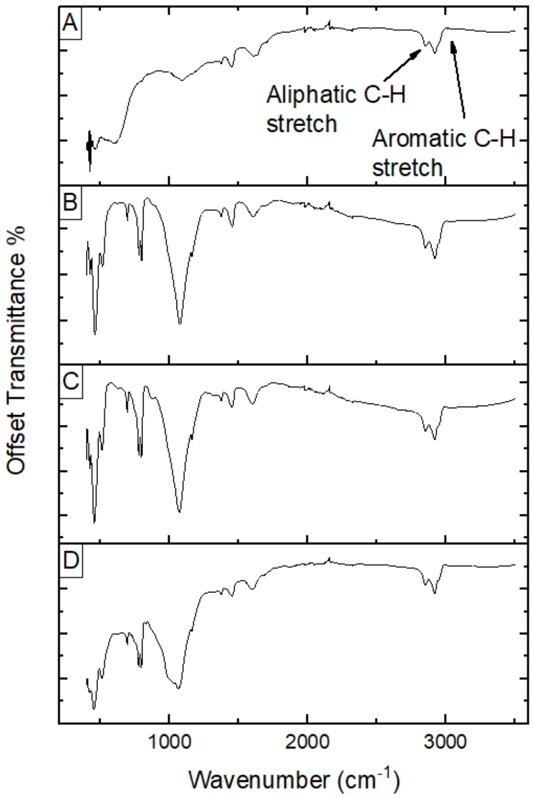
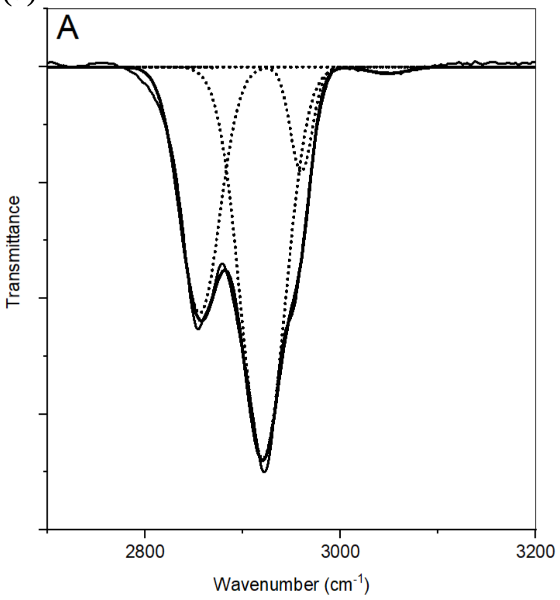


Figure 1 FTIR spectra of four kerogen samples with varying maturity.

(a)



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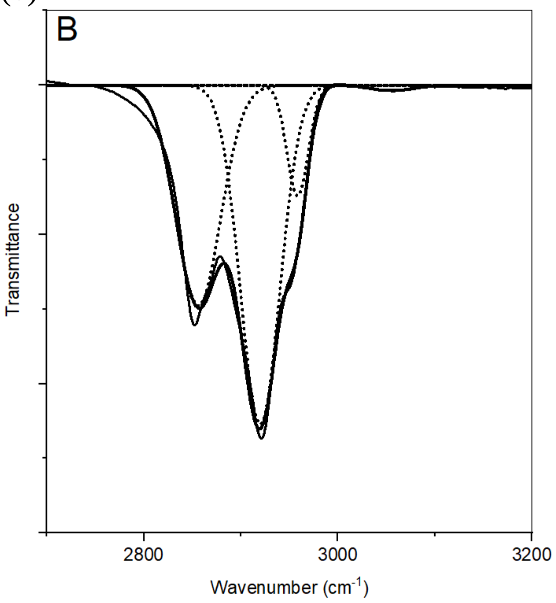

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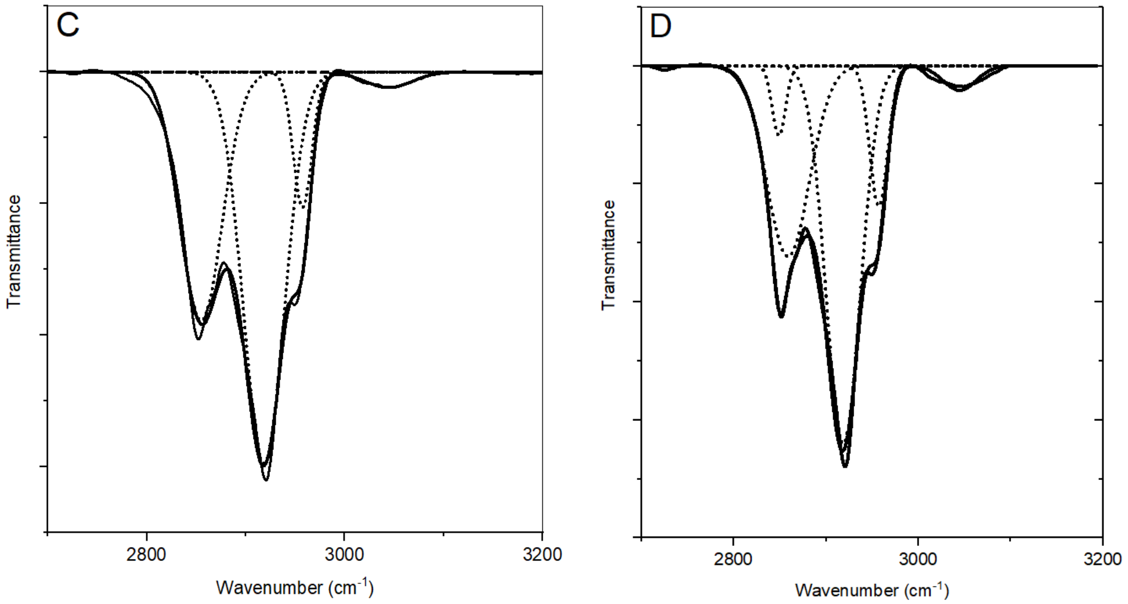


Figure 2 Peak fitting results for the C-H stretch vibration area for samples A to D respectively. The black line is the original observed spectrum, while the solid line is the fitted spectrum. The coefficients of determination (R^2) of the peak fitting for the region 3200–2700 cm^{-1} in all spectra were between 0.998 and 0.994.

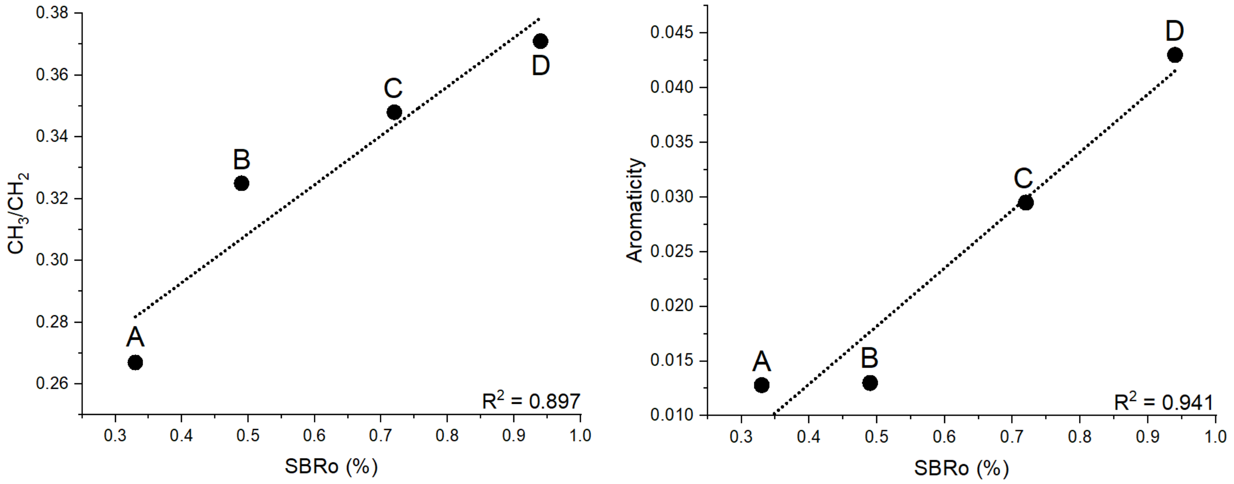
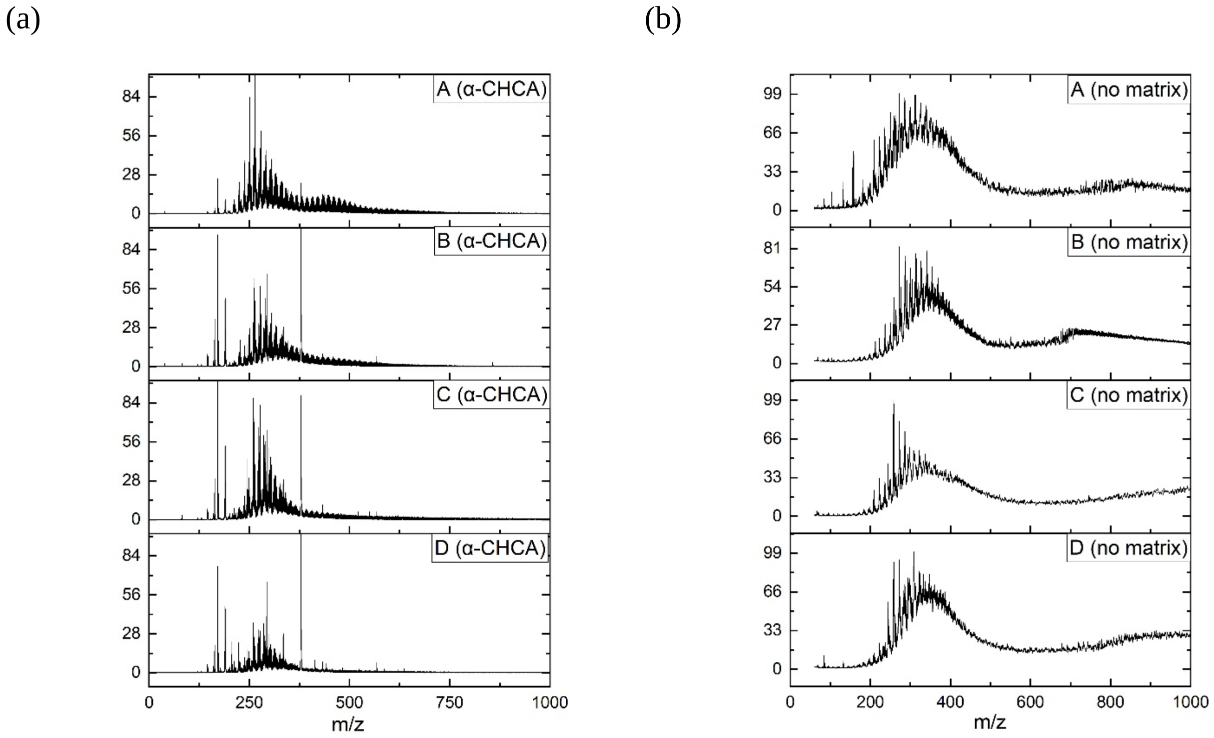


Figure 3 Thermal maturity index (SBRo (%)) versus two major FTIR structural indices, (Left) CH_3/CH_2 and (Right) Aromaticity.

Here, we examined the C-H stretching band intensities for CH_3, CH_2 and, aromatic ring CH-based that was obtained from the deconvolution results. CH_3/CH_2 ratio and the aromaticity indices were calculated based on the relationships that were stated earlier. Considering CH_3/CH_2 ratio, smaller values (sample A) implies comparatively longer and straight chains, whereas larger values (sample D) means shorter and more branched chains (Figure 3-Left). In other words, when kerogen thermal maturation is advanced, relatively, the aliphatic chain length will become shorter, and branching is developed. As a result, the aromaticity index (Figure 3-Right), representing the abundance of aromatic structures in the kerogen molecule is also increased as thermal maturity is increased. Furthermore, at a higher degree of thermal maturation where the abundance of aromatic rings and the reduction of methyl/methylene is observed, it is expected this phenomenon to result in a significant change in the molecular weight of the remaining substance. The observed trends in Figure 3 are consistent with the results from previous findings, which proved that the aliphatic chain lengths have shortened and increased aromaticity during the maturation [7]. It should be stated again during the maturation process, as a result of organic matter exposure to temperature, hydrocarbons are generated and expelled from the organic matter and the remaining molecule is undergone major molecular alteration as being investigated here.

Molecular Characterization by MALDI-TOF MS

The ionization process in MALDI-TOF proceeds through the capture of a proton, which forms a charged adduct with the molecular species of the sample. As the number of charged adducts reflects the signal intensity of the molecular weight, quantitative MWD analysis of any chemical compound is conducted. Four kerogen samples of this study were analyzed by MALDI-TOF to attribute maturation effects on the MWD of organic matter. Furthermore, systematic naturally matured kerogens with single biogenic origin have rarely been researched with MALDI-TOF, which limits the guidelines for an optimal and effective matrix selection based on the literature. Hence, in our study, kerogen samples were examined in both the presence and in the absence of the matrix (α-CHCA) for comparison and more accurate results.



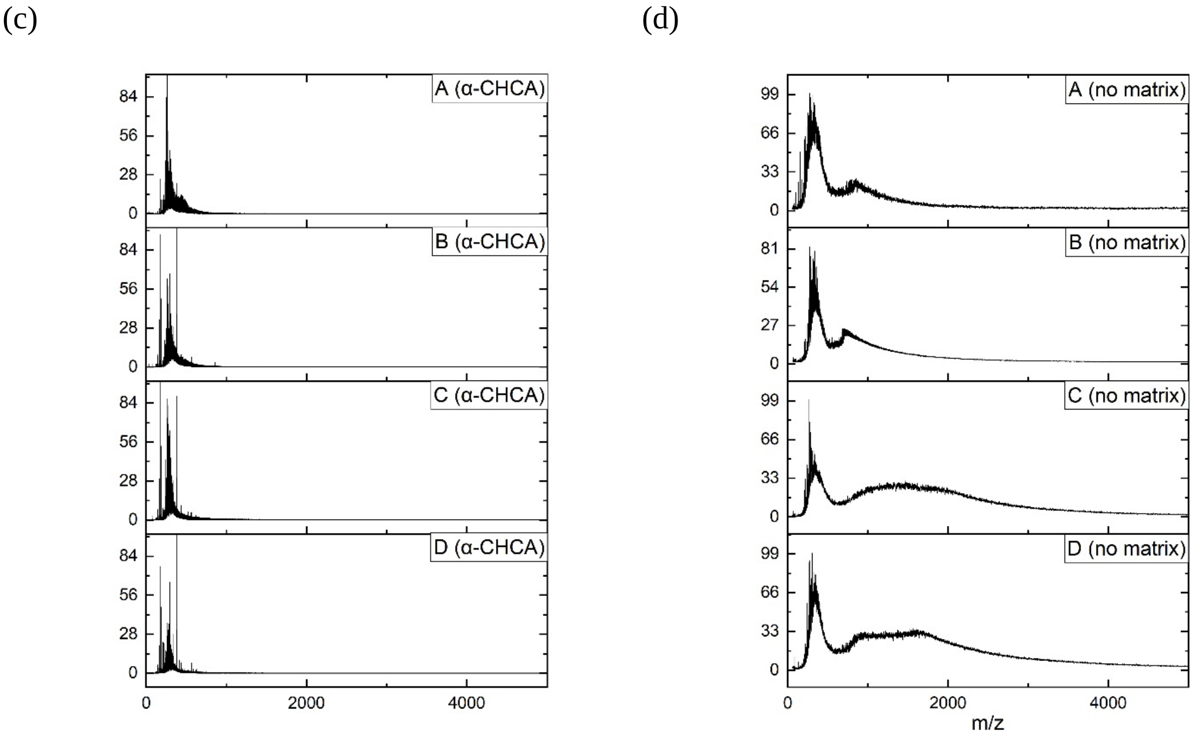


Figure 4 Normalized MALDI-TOF spectra of kerogens in the order of increasing maturity from A-D (a and c) in the presence of the matrix (α-CHCA) and (b and d) in the absence of the matrix. The spectra are plotted over (a and b) a range of 60 to 1000 Da and (c and d) a range of 60 to 5000 Da.

Figure 4 exhibits the mass spectra of kerogen samples obtained both in the presence and in the absence of the matrix. In all of these spectra for the presence of the matrix, unidentified high-intensity signals were observed in the relatively low-mass region between 200 and 400 m/z. Also, we could not find a regular ionization and pattern overall. This confirms that kerogen does not have a specific chemical structure and contains various functional groups which are differently ionized, which hinders the signal interpretation from analyzing molecules in kerogen. Also, overall spectra representing the samples in Figure 4 does not show a particular relationship with signal intensities unlike polymers and proteins. However, we found that signal intensity changes with respect to the degree of thermal maturation. As a result of this alteration in the intensity, it is conclusive that the maturation process would change the molecular structure of kerogen in terms of the molecular mass of the organic matter. This infers that the chemical structure of kerogen has been evolved while bond-breaking and forming have occurred [31]. Thus, we can at least conclude that MALDI result confirms the chemical structure changes by maturation. Sample A, the immature kerogen, exhibits signals between 250 to 350 m/z with the highest intensity regardless of the presence or absence of the matrix. In addition, when the maturation is progressed, strong signals become evident in the presence of the matrix, near 170 m/z and 370 m/z.

On the other hand, in the absence of the matrix, the highest intensity signals are recorded in the similar mass region in all maturation stages, while molecular alterations have occurred in the higher mass region of the spectra. When the degree of maturation is higher, it was seen that signals become more transparent in the relatively heavier mass regions. This observation was not quite similar to the changes of signals in the presence of the matrix. In the latest experimental conditions, the spectra do not display any clear signals over 800 m/z. Therefore, it is probably understood not only that α-CHCA is not the best matrix to investigate complex mixtures of organic matter (kerogen) for the higher mass regions, but also that an excess of matrix inhibits to precisely conduct the ionization process. Based on this, in our study, the mass spectra without any matrix was utilized for the MWD analysis of the kerogen samples to avoid erroneous results.

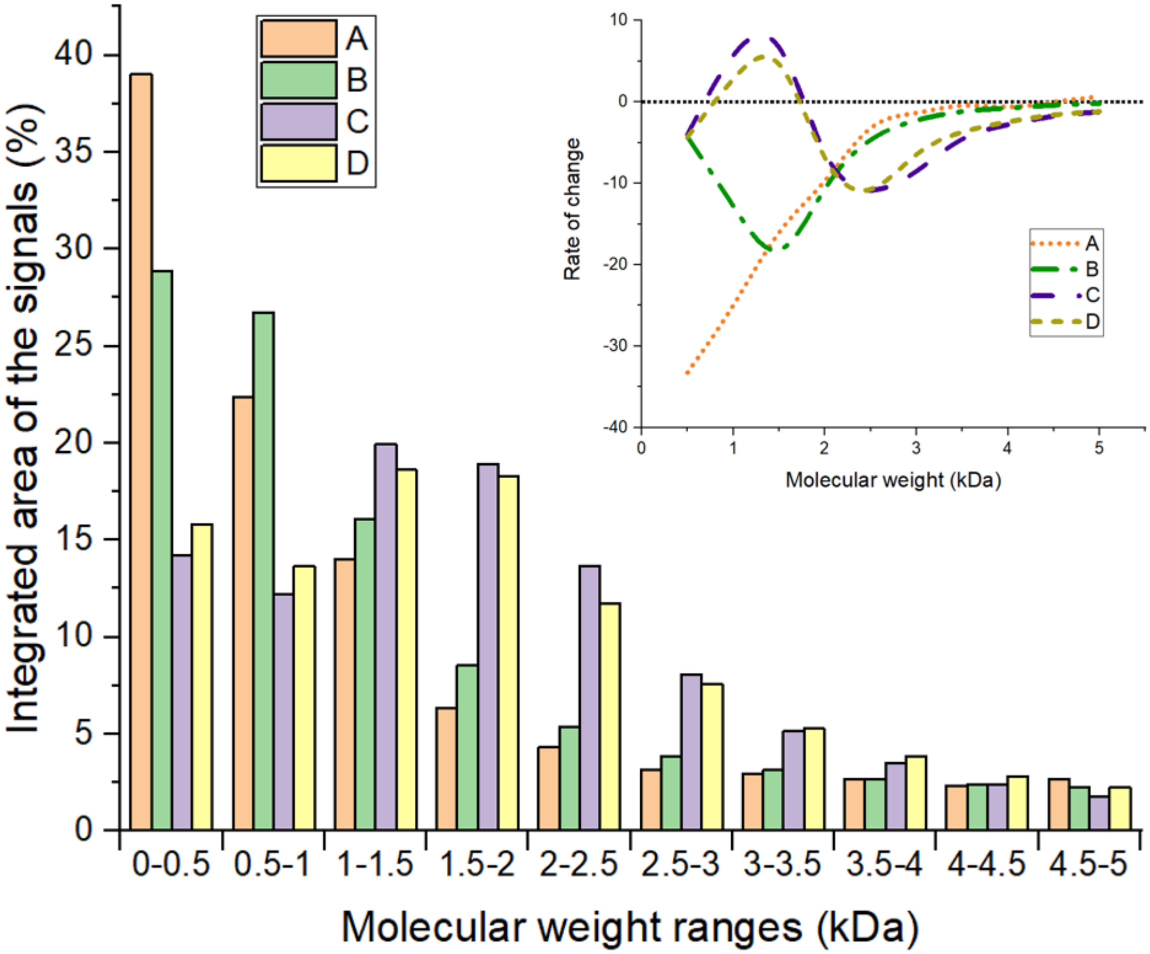


Figure 5 Molecular weight distribution (MWD) diagrams of four samples presents different molecular weight ranges at different thermal maturity stages in the absence of the matrix. The relative areas of each sample are compared within the designated intervals. This specific MWD and intervals are used since this particular format showed the most distinct variation in MWs. The smaller image is based on MWD, rate of change (derivatives) of integrated MALDI-TOF signals with respect to molecular weight over the interval 0 to 5 kDa.

Figure 5 exhibits four molecular weight distribution (MWD) diagrams in separate intervals obtained from immature to late mature organic matters. Each independent value of four samples was created through the summation of the area under molecular weight signals based on the normalized spectra (Figure 4). Furthermore, this particular partitioning (distribution) of MWs is decided through trying different molecular weight intervals and plotting MWDs of these four different samples when the most distinct and meaningful trends are delineated. We also note that the quantitative value in Figure 5 disregards total MW and solely pertains to the comparative change of MWD regarding the maturity since the area ratio was adopted. It was found that, for relatively immature kerogen (A and B), around 60% of the signals are under 1 kDa range, whereas the majority of recorded signals for relatively higher maturity kerogen samples (C and D) are found between 1 to 2 kDa range. Immature sample (A) has the highest signal in the range under 500 Da; this indicates that relatively lighter molecular structures exist in kerogen compound prior to maturation. Meanwhile, the MWD for samples A and B continuously decreases in higher mass ranges. Remarkably, as the degree of the maturation increases, the higher signal distribution in the heavier range is observed in Figure 5. It is verified that the MWD variation is certainly a function of the degree of thermal maturation, reflecting the existence of separate molecules detected through the MALDI-TOF-MS process. Although in all kerogen samples, the distributions are almost similar in the ranges over 5 kDa, generally higher maturity kerogens should contain larger size molecular compounds and fragments than lower maturity ones.

Additionally, the rate of change in MW is also investigated for each maturity stage over the entire range from 0 to 5 kDa. The smaller graph in Figure 5 is obtained through taking the derivatives of integral of MALDI-TOF spectra to represent the rate of change in the quantity of that specific MW interval for each sample. The most important aspect of this graph is that at a specific MW (around 2.5 kDa) all of four samples start to show relatively similar increasing trends in the rate of MW quantities, and then this becomes constant regardless of their maturity at higher MW region (> 4 kDa). This means there isn't any change in the molecule's population at higher weights regardless of the maturity. In sample A, the most immature kerogen, relatively large negative rate of change in the lower MW region is observed and the degree of change presents a decreasing trend as the molecular weight increases. The rate of change in sample B rapidly decreases up to around 1.5 kDa MW, then alleviates in higher MW ranges showing similar positive rate over 2 kDa similar to sample A. Unlike immature kerogens, two higher maturity specimens (C and D) have comparable MW rate of changes over the entire MW range. Positive change is observed near lower MW region (< 2kDa), which means the molecules in 1 to 2 kDa are becoming more abundant than other MW regions, then the rate of popularity decreases and becomes unchanged like other samples. The difference in MWD and rate of change in MWs between the immature (A and B) and late mature (C and D) kerogens could refer to the boundary from pre-oil to oil generation window and to the phenomenon where hydrocarbons are generated and expelled from the OM through a nonlinear trend [21]. This major change in molecular structure corresponds to the onset of oil-window, when a major alteration is expected to take place (molecular structure and molecular weight) around 2.5 kDa where all MW rate of change graphs in the smaller image in Figure 5 coincide and start to perform with a similar increasing trend. These two graphs combined illustrate, although we have a relatively linear increase in thermal maturity index (in Table 1) from samples, the variations are nonlinear which is at the onset of oil generation.

The MWD results can be correlated to the structural indices from the FTIR as well. As we discussed in this study, the carbon chain (aliphatic) length has shortened and branching has developed as the degree of maturation is increased, as well as the aromatic structure becomes more abundant. From Sample A to D, the abundancy in lower MW intervals decreases which corresponds to the increase in CH_3/CH_2 ratio. On the contrary, the higher quantity of heavier MW intervals is correlated to the aromaticity index where it increases from Sample A to D. These two combined, as a function of increasing the maturity, kerogen should contain a greater number of heavier molecules that are more developed aromatic and aliphatic branching structures. We state that the trend could not directly convey the change of total weight of kerogen. In other words, the structural changes that kerogen undergoes due to the abundance of the aromatic and shorten aliphatic chain length as its maturity progresses is well correlated with the heavier molecular weight of the product.

Conclusion

This article presented a characterization of kerogen at 4 different maturity levels using infrared spectroscopy and mass spectrometry. Spectrums obtained by FTIR and MALDI-TOF from organic matters (kerogens) isolated from the bulk rock aliquots collected from the Bakken Shale were analyzed. The results were useful to better understand hydrocarbon generation and maturation process through investigation of a chemical structure and molecular weight variations during the expulsion of hydrocarbons as maturity progresses. Based on the results, the following conclusions can be made:

- MALDI-TOF spectra in the presence of the matrix (α-CHCA) show irregular ionization and pattern between 200 and 400 m/z for all maturity stages. It follows that kerogen does not have a specific chemical structure and hardly can be analyzed regarding its composition and molecular weights for specific fragments in the presence of the matrix. Since kerogen is a complex macromolecule, the matrix (α-CHCA) maybe inappropriate to be used during the ionization/mass spectroscopy experiments and existing lower MW aromatic fragments can take the role of the matrix.
- It was found while the increase in the maturation takes place, the results of MALDI-TOF in the absence of the matrix demonstrates that kerogen consists of heavier molecules. The result without the matrix shows obvious signals in the heavier mass regions (over 1,000 m/z). Based on this, MWD was generated from MALDI-TOF spectra in the absence of matrix.
- The MWD variation provided different molecular weight ranges at different thermal maturity stages in the absence of the matrix. Relatively immature kerogens exhibited around 60% of the signals under 1 kDa range, with the strongest signals in the range under 500 Da, whereas the majority of signals of mature kerogens were found between 1 to 2 kDa range.
- In terms of major changes (molecular structure and molecular weight) through maturation, the boundary from pre-oil to oil generation window can be distinguished based on the rate of change of integrated MALDI-TOF signals with respect to molecular weight. After a specific MW (over 2.5 kDa), all kerogens would show a similar increasing trend in the rate of change of the population of MW intervals.
- The shorter aliphatic chain length and abundant aromatic structure are expected and delineated based on FTIR structural indices (CH_3/CH_2 and Aromaticity) when the degree of maturity increases which was correlated to the MWDs. The structural kerogen

alteration in the abundance of the aromatic and shorten aliphatic chain length as its maturity progress tends to make the weight of molecules/fragments in kerogen heavier.

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