AN INVESTIGATION INTO THE EFFECTS AND IMPLICATIONS OF GAMMA RADIATION ON ORGANIC MATTER, CRUDE OIL, AND HYDROCARBON GENERATION

by

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Abstract

The current model of hydrocarbon generation involves the thermogenic maturation of organic material as a consequence of burial. This process only considers energy generated from temperature increase due to burial. The majority of organic rich source beds contain high concentrations of radioactive elements, hence the energy produced from radioactive decay of these elements should be evaluated as well. Previous experiments show that α-particle bombardment can result in the generation of hydrocarbons from oleic acid. This study investigates the effects of γ-rays in a natural petroleum generating system. In order to determine the effects of γ-rays, experiments were conducted using cesium-137 as the γ-ray source at the KSU nuclear facilities to irradiate crude oil and organic material commonly found in petroleum systems. The samples were then analyzed using Fourier Transform Infrared Spectroscopy (FTIR) and Rock-Eval pyrolysis to determine changes in the samples.   The FTIR results demonstrated that γ-radiation can cause the lengthening and/or shortening of hydrocarbon chains in crude oils, the dissociation of brine (H_2O (aq)), the production of free radicals, and the production of various gases. These changes that come from γ-radiation hold the possibilities to distort the configuration of organic molecules, dissociate molecular bonds, and trigger oxidation-reduction reactions, all of which could provide an important step to the onset of dissociation necessary to create hydrocarbons in petroleum systems. Further understanding the effects of γ-radiation in hydrocarbons systems could lead to more information about the radiolytic processes that take place. This could eventually lead to further understanding of oil generation in organic-rich source beds.

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Chapter 1 - Introduction

The thermogenic mechanics of hydrocarbon production involve the heating of a parent kerogen while it is under pressure to cause the thermal degradation of the kerogen to yield petroleum-range hydrocarbons (Hunt 1996). This is the most widely accepted model for the generation of hydrocarbons. Experiments, such as Engler (1913), have heated oleic acid and other organic materials at temperatures below 250°C and obtained paraffin, naphthene, and aromatic hydrocarbons in the entire petroleum range (Hunt 1996). This idea of hydrocarbon generation, while probable in deep basin environments with adequate temperature regimes, only focuses on the temperature increase on organic matter and does not take into account all five regimes present in a petroleum source beds. Those regimes are the atmosphere or gases, lithosphere or mineral matrices, hydrosphere or H_2O, biosphere or organic material, and the energetics or energy produced from temperature increase and other sources, including the radioactive decay of isotopes present in the source beds.

Organic-rich shales, often the source beds for natural generation of hydrocarbons, are known to contain high amounts, as much as 200 ppm, of radioactive U, Th, and K (Beers et. al 1944, Swanson 1961). The spontaneous radiations produced from the decay of the radioactive isotopes include: α-particles, β-particles, and γ-rays from the decay of U and Th isotopes, and β-particles and γ-rays from the decay of K isotopes. It has been known that excited product nuclei emit their excess energy as γ-rays between 0.25 MeV to about 2 MeV when they go from an excited state to a ground state. Gamma rays can also be produced by the process of annihilation which involves the reaction between β⁻ and β⁺ particles. Annihilation can occur during the decay of ^{40}K but does not happen often because of the rare production of β⁺ particles. When annihilation does occur, it will produce a γ-ray with the energy of 1.02 MeV. The energy produced from one γ-ray has the potential to break bonds as shown in Table 1.

Table 1. Table of the potential bonds that can be broken by one γ-ray.

1 γ-ray=0.25-2 MeV=$4.0*10^{-14}$-$3.2*10^{-13}$J				
Potential to break:				
~$6.0*10^4$	C-H bonds		~$4.4*10^4$	O-H bonds
~$6.7*10^4$	C-O bonds		~$5.5*10^4$	H-H bonds
~$3.9*10^4$	C=C bonds		~$4.8*10^4$	HO-H bonds
~$3.0*10^4$	C=O bonds		~$4.8*10^4$	O=O bonds
~$8.6*10^4$	C-C bonds		~$1.03*10^5$	C-N bonds

Throughout the decay series of one ^{235}U isotope and one ^{238}U isotope, 7 gamma rays and 7-10 gamma rays are produced respectively. Our calculations indicate that if the entire amount of gamma radiation emitted by 1.0 g shale source rock with 10-30 ppm U concentrations is allowed to break or dissociate bonds between atoms in a molecule, nearly 10^{-6} moles of carbon-hydrogen or carbon-carbon bonds could be broken in a period of 500,000 years. The average U concentration is never a good measure for an assessment of the impact of gamma radiation, in light of the fact that U is unevenly distributed in natural materials, as are many other minor and trace elements. It has been well known that radioactive elements are distributed highly unevenly, even within a single small grain of zircon. Our own studies have shown that plant materials have highly inhomogeneous U and Th distributions, some leaves have higher U concentrations than other leaves in a small plant, and the same aspect of uneven distributions is seen among leaves, stems, and roots of a small plant. Hence it is not unreasonable to assume that similar inhomogeneous distributions exist for U and other radioactive elements in shale source rocks. In other words, micro-sized to mega-sized zones with very high radioactive element concentrations will be surrounded by domains with highly spotty occurrences of the radioactive elements. Therefore, the average concentration of a mass of shale source rock does not portray the real distribution pattern of the radioactive elements. Conceivably, numerous zones of different dimensions exist in shale source rocks with U concentrations tens to thousands times higher than the average 10-30 ppm. The U in these high concentration zones will then be offering quanta of gamma radiations with a capacity for breaking C-H or C-C bonds by an amount as much as 10^{-3} to 10^{-2} moles per half a million years. Therefore, gamma radiation impact on the organic materials could be of appreciable magnitude at these high uranium-concentrated sites.

Investigation of the γ radiation impact on hydrocarbon material may provide some clue to the transformation of organic materials from a state of saturated carbon to a state of an unsaturated carbon or vice versa. This research is intended to shed some light on this question and has helped with the development of an unpublished petroleum system model.

Chapter 2 - Materials and Methods

Experiments were conducted using gamma rays produced from a cesium-137 core to see how organic matter and crude oil react to the gamma radiation. Crude oils and solid organic matter were targets for this investigation. Crude oils for this investigation included those that are enriched in both saturates and unsaturates, the heavy oil was gathered in a 1.0 L bottle from the Woodford Shale from the wellhead of Taylor 1-22 in Payne County, Oklahoma, and the light oil was gathered in a 1.0 L bottle from the Lansing-Kansas City Groups from the wellhead of McElhaney #3A in Rooks County, Kansas. These two oils were each put into a 50 mL centrifuge tube using a pipette and then centrifuged to ensure that the oils were separated from the formation brines. Organic matter used in this study include an average of samples, both mature and immature shale separates, taken from multiple locations of the Woodford Shale in the midcontinent of the USA as shown in Appendix A. The clay minerals, Arizona calcium montmorillonite and Illinois Fithian illite, along with brine (H_2O (aq)) were included as variables in these irradiation experiments. Table 2 shows the different oil samples that were irradiated.

Table 2. Table of the different oil sample combinations that were irradiated.

Sample	Wt. Clay (g)	Wt. Oil (g)	Wt. Brine (g)	Dose (rads)
Heavy Oil	-	2.0	-	~100
Light Oil	-	2.0	-	~100
Heavy Oil + Brine	-	1.0	1.0	~100
Light Oil + Brine	-	1.0	1.0	~100
Heavy Oil + Brine + Arizona Calcium Montmorillonite	0.1	1.0	0.9	~100
Heavy Oil + Brine + Illinois Fithian Illite	0.1	1.0	0.9	~100

2.1. Oil Sample Preparation

Each sample was put into a PowerSoil™ DNA Kit 2.0 mL tube for irradiation. The samples including brine were filled with melamine foam cut into strips <1mm thick. This foam is microporous which allows for maximum oil-to-brine surface contact. This microporous texture is similar to the micropores that are present in source beds thus coming closer to

mimicking a natural system. Maximizing the oil-to-brine contact gives the greatest possibility for chemical reactions to occur. One sample containing heavy oil and one sample containing light oil were made. Two mixtures were made consisting of only oil and brine while two more mixtures were made consisting of each clay mineral in combination with the brine. One mixture was a combination of Arizona calcium montmorillonite and brine while the other mixture consisted of Illinois Fithian illite and brine. The mixtures were then soaked up with melamine foam strips and put into two individual 2.0 mL tubes along with the crude oil. The mixtures were then sealed and irradiated with ~100 rads of γ-radiation using a panoramic irradiator with a cesium-137 core at the KSU nuclear facilities.

2.2. Oil Sample Analysis

The pure crude oil samples were analyzed using Fourier transform infrared spectroscopy (FTIR) (Appendix B). The mixtures containing brine with/without clay minerals were centrifuged and the brine was separated from the oil. The controls that were compared with these samples were also centrifuged in order to keep the preparations uniform. The lighter fractions of the irradiated and control samples were then analyzed using FTIR. Next, the oil samples were stirred individually by hand to make a more homogeneous sample and analyzed using FTIR once again. The samples were then compared with the control samples, which received no dosage of radiation, to determine the changes that took place due to the irradiation by γ-rays.

2.3. Organic Matter Preparation

Organic matter was separated from rock samples taken from eight different Woodford Shale samples in the midcontinent of the USA as shown in Appendix A. The organic matter was chemically separated for previous experiments by Daniel Ramirez-Caro (Ramirez-Caro 2013). The silicate portion of the rock samples was dissolved using HF(aq) and the carbonate portion of the rock samples was dissolved using HCl(aq) leaving only the organic matter. The organic matter used in this study was then mixed together to obtain an average organic matter composition of the Woodford Shale. Four individual samples were made as shown in Table 3 and each sample was put into a PowerSoil™ DNA Kit 2.0 mL tube for irradiation.

Table 3. Table of the various kerogen samples and the dosage of irradiation.

Sample	Organic Wt. (g)	Dose (rads)
Kerogen Sample 1	0.3	0
Kerogen Sample 2	0.3	~100
Kerogen Sample 3	0.3	~225
Kerogen Sample 4	0.3	~400

The samples were then sealed and irradiated with various amounts of γ-radiation using the panoramic irradiator.

2.4. Organic Matter Analysis

The irradiated samples then underwent Rock-Eval pyrolysis (Appendix C) to determine if there were changes in the maturity of the organic matter when compared with the control. The Rock-Eval temperature readings ranged from 300 ⁰C to 550 ⁰C.

Chapter 3 - Results

3.1. Heavy and Light Crude Oils

After irradiation, both the heavy and light crude oils were analyzed using FTIR. The results were then compared respectively with controls by subtracting the control FTIR spectra from the irradiated FTIR spectra. The comparison showed positive anomalies at wavenumbers 2922 cm^{-1} and 2850 cm^{-1} and negative anomalies at wavenumbers 2952 cm^{-1} and 2875 cm^{-1} as shown with the heavy oil in Figure 1 and the light oil in Figure 2.
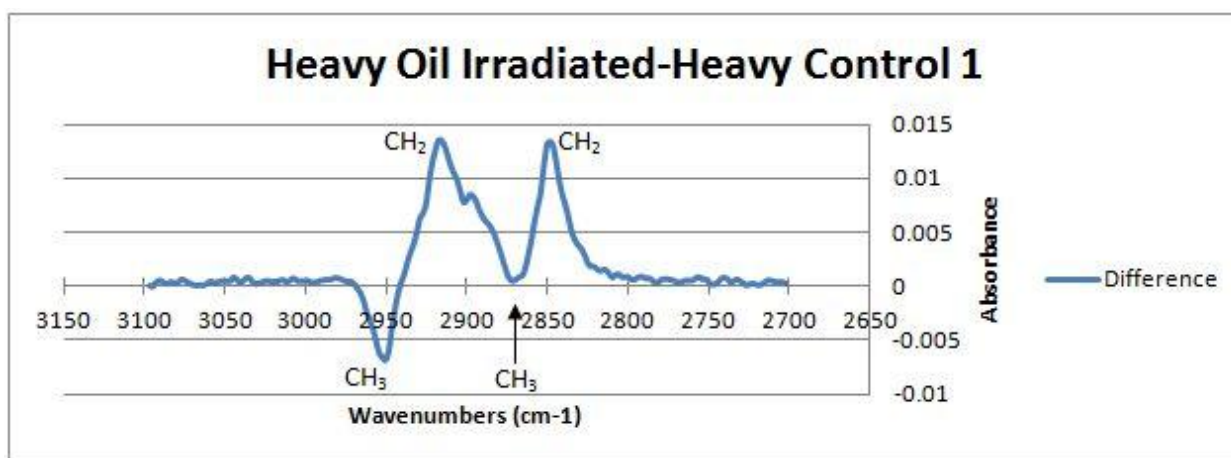
Figure 1. Difference in FTIR Spectras of heavy crude oil and heavy control 1 (Heavy Irradiated Oil-Control Heavy Oil). ~100 rad (0.001 J/g)
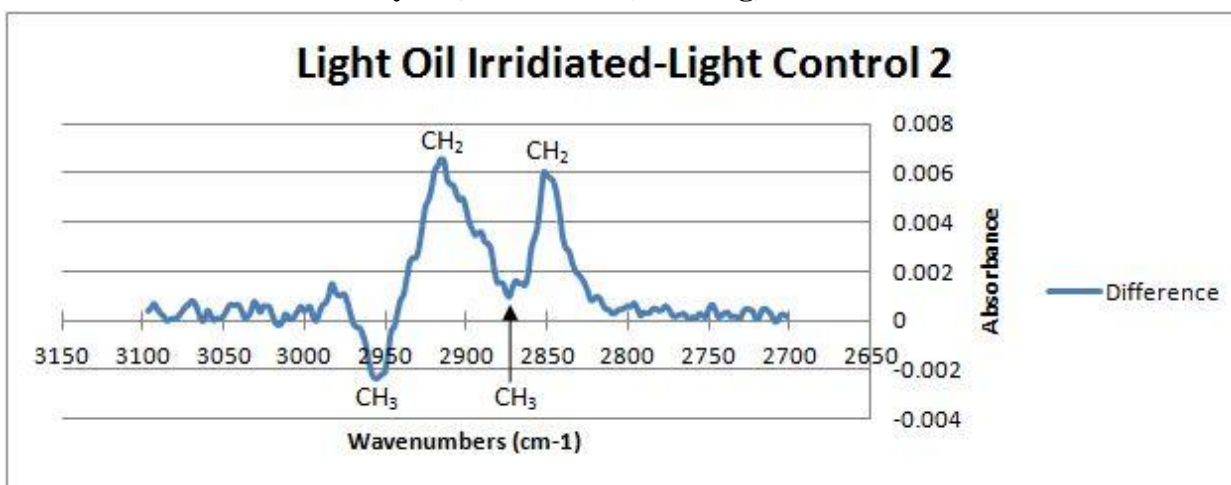
Figure 2. Difference in FTIR Spectras of light crude oil and light control 2 (Light Irradiated Oil-Control Light Oil). ~100 rad (0.001 J/g)

3.2. Heavy and Light Crude Oils+Brine

After irradiation, the mixtures were centrifuged to separate the oils from the brine then analyzed using FTIR. The initial FTIR results were taken from the top of the centrifuged oil samples and then compared with the FTIR of the appropriate control samples by subtracting the control FTIR values from the irradiated FTIR values. This comparison of the lighter fraction of the heavy oil/brine sample showed a positive anomaly at wavenumber 2922 cm^{-1} and a negative anomaly at wavenumber 2910 cm^{-1} as shown in Figure 3. The comparison of the lighter fraction of the light oil/brine sample may have possible positive anomalies at wavenumber 2922 cm^{-1} and 2875 cm^{-1} but the FTIR does not yield definitive results for the identification of the organic molecules of interest as shown in Figure 4.

Figure 3. Difference in FTIR Spectras of heavy crude oil+brine (lighter fraction) and heavy control 1 (Light Fraction of Irradiated Heavy Oil+Brine Sample-Control Heavy Oil). ~100 rad (0.001 J/g)

Figure 4. Difference in FTIR Spectras of the light crude oil+brine (lighter fraction) and light control 2 (Light Fraction of Irradiated Light Oil+Brine Sample-Control Light Oil). ~100 rad (0.001 J/g)

The samples were then stirred individually by hand to make more homogeneous mixtures, and then they were once again analyzed using FTIR. These samples were compared with their respective control samples and the differences in the analyses were calculated. The comparison of the homogeneous heavy oil/brine sample exhibits possible negative anomalies at wavenumbers 2952 cm^{-1}, 2922 cm^{-1}, and 2850 cm^{-1} and a possible positive anomaly at wavenumber 2875 cm^{-1} as shown in Figure 5. The homogeneous light oil/brine sample comparison showed negative anomalies at wavenumbers 2952 cm^{-1}, 2922 cm^{-1}, and 2850 cm^{-1} as shown in Figure 6. It showed a positive anomaly at wavenumbers 2933 cm^{-1} and a possibly 2860 cm^{-1}.

Figure 5. Difference in FTIR Spectras of the heavy crude oil+brine (homogeneous oil) and heavy control 1 (Homogeneous Irradiated Heavy Oil+Brine Sample-Control Heavy Oil). ~100 rad (0.001 J/g)

9
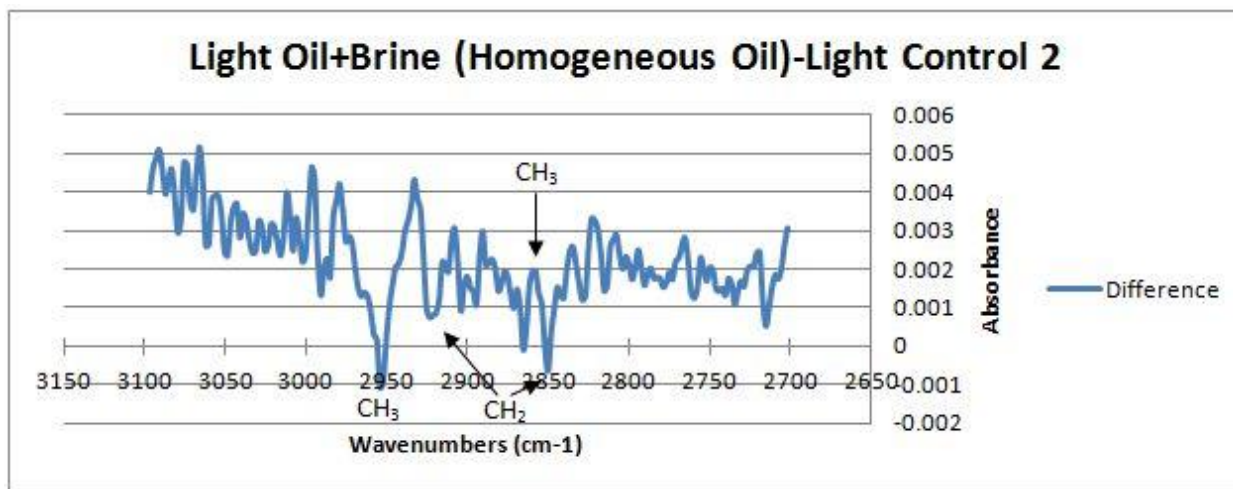
Figure 6. Difference in FTIR Spectras of the light crude oil+brine (homogeneous oil) and light control 2 (Homogeneous Irradiated Light Oil+Brine Sample-Control Light Oil). ~100 rad (0.001 J/g)

3.3. Heavy Oil+Brine+Arizona Calcium Montmorillonite or Illinois Fithian Illite

After being centrifuged, the lighter fractions of the oils that had been combined with both clay and brine taken from the top of the vials were analyzed. The control FTIR results were subtracted from the irradiated samples FTIR results and the changes from irradiation are shown. The lighter fraction of the samples show positive anomalies at wavenumbers 2950 cm^{-1} and 2875 cm^{-1} and negative anomalies at wavenumbers 2922 cm^{-1} and 2852 cm^{-1}. Figure 7 represents the changes in the sample containing the light fraction of heavy oil, brine, and Arizona calcium montmorillonite. Figure 8 represents the changes in the sample containing the light fraction of heavy oil, brine, and Illinois Fithian illite.
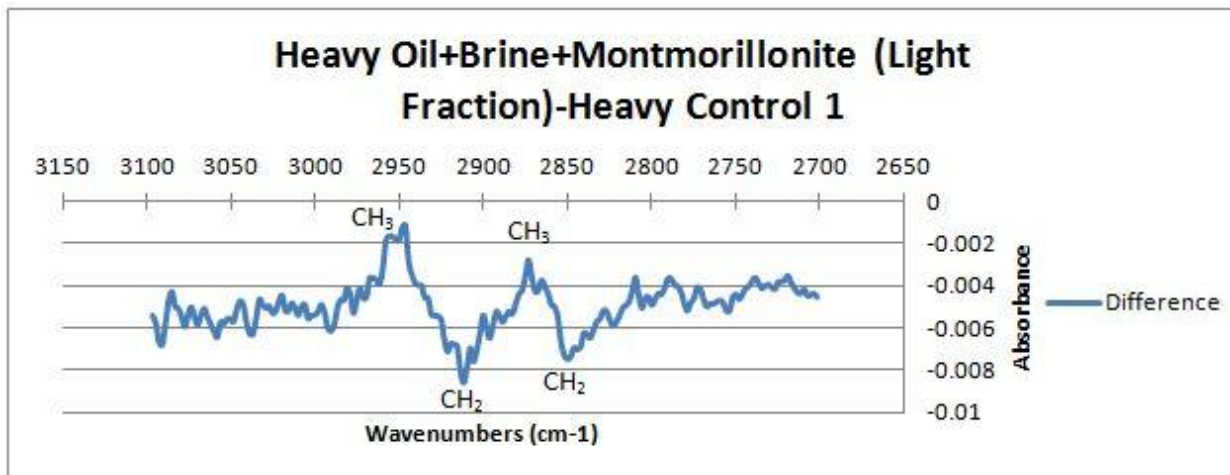
Figure 7. Difference in FTIR Spectras of the heavy crude oil+brine+montmorillonite (lighter fraction) and heavy control 1 (Light Fraction of Irradiated Heavy Oil+Brine+Montmorillonite Sample-Control Heavy Oil). ~100 rad (0.001 J/g)
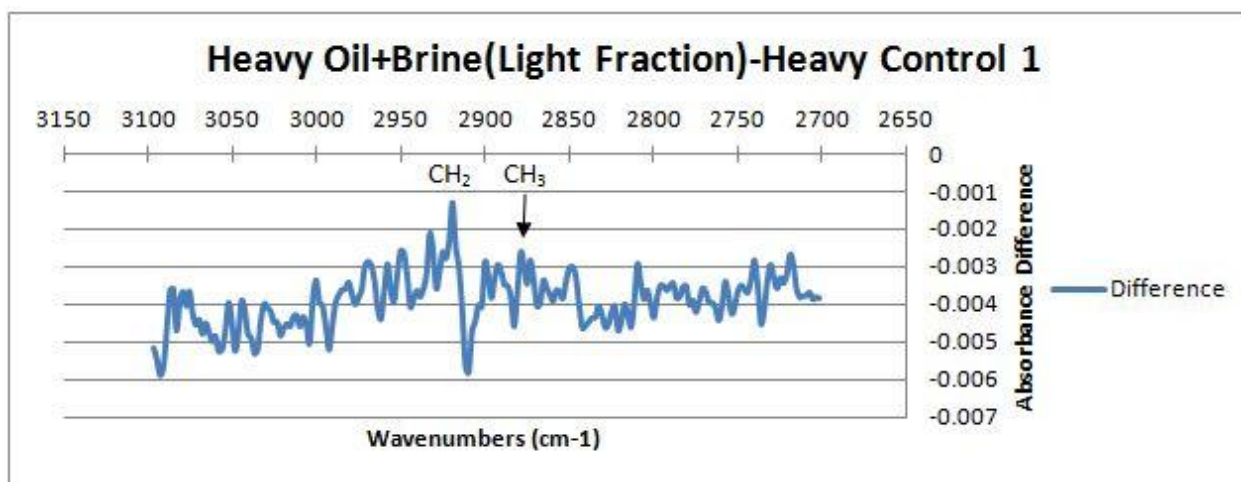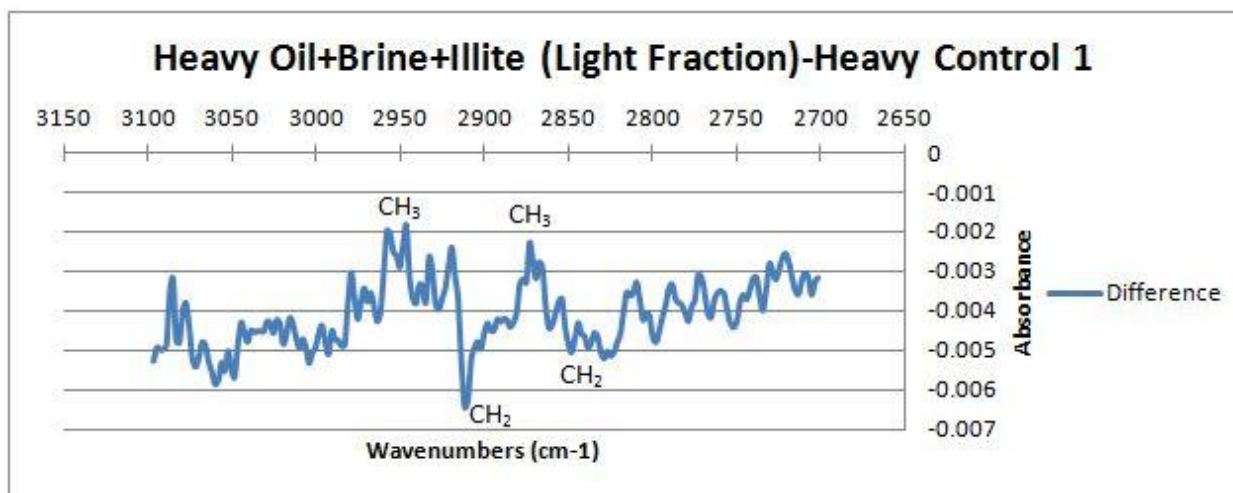

Figure 8. Difference in FTIR Spectras of the heavy crude oil+brine+illite (lighter fraction) and heavy control 1 (Light Fraction of Irradiated Heavy Oil+Brine+Illite Sample-Control Heavy Oil). ~100 rad (0.001 J/g)
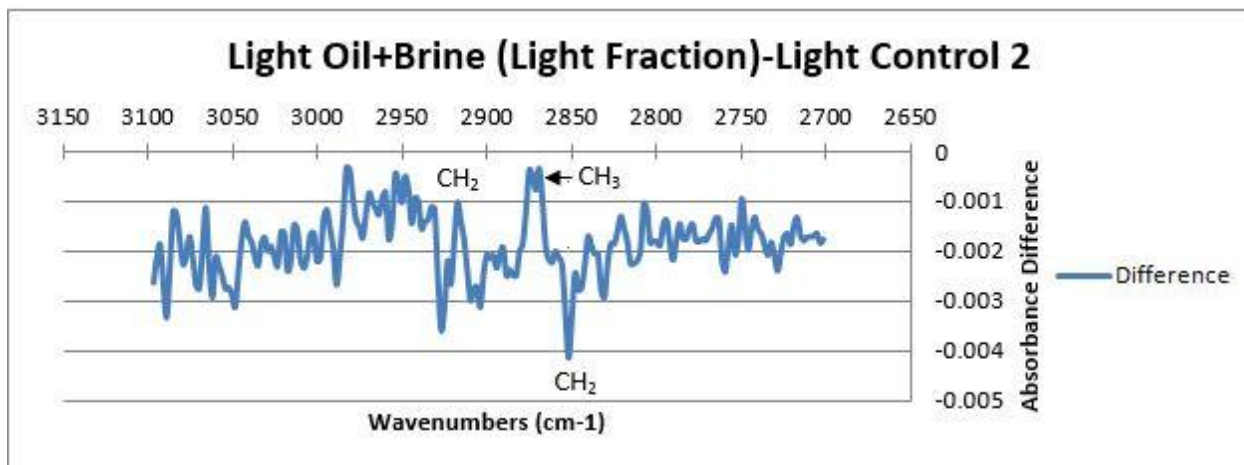
The samples were then stirred individually by hand to get more homogeneous samples and each of those samples were analyzed again using FTIR. The control FTIR results were subtracted from the homogeneous irradiated samples FTIR and changes from irradiation were determined. The homogeneous samples show positive anomalies at wavenumbers 2922 cm^{-1} and 2852 cm^{-1} and negative anomalies at wavenumbers 2952 cm^{-1} and 2870 cm^{-1}. Figure 9 represents the changes in the homogeneous sample containing heavy oil, brine, and

montmorillonite. Figure 10 represents the changes in the homogeneous sample containing heavy oil, brine, and illite.
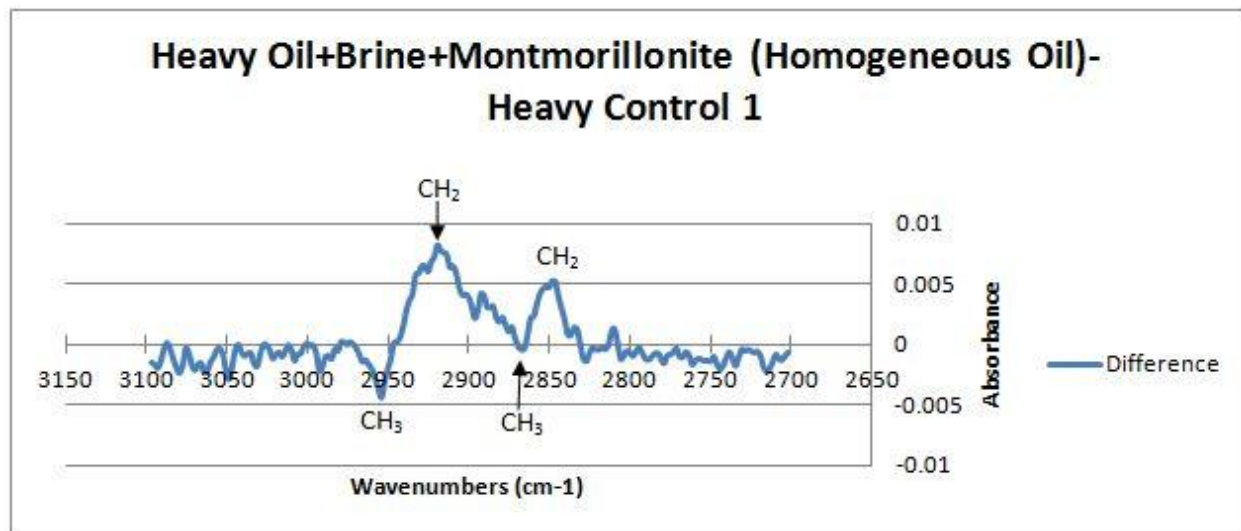
Figure 9. Difference in FTIR Spectras of the heavy crude oil+brine+montmorillonite (homogeneous oil) and heavy control 1 (Homogeneous Irradiated Heavy Oil+Brine+Montmorillonite Sample-Control Heavy Oil). ~100 rad (0.001 J/g)
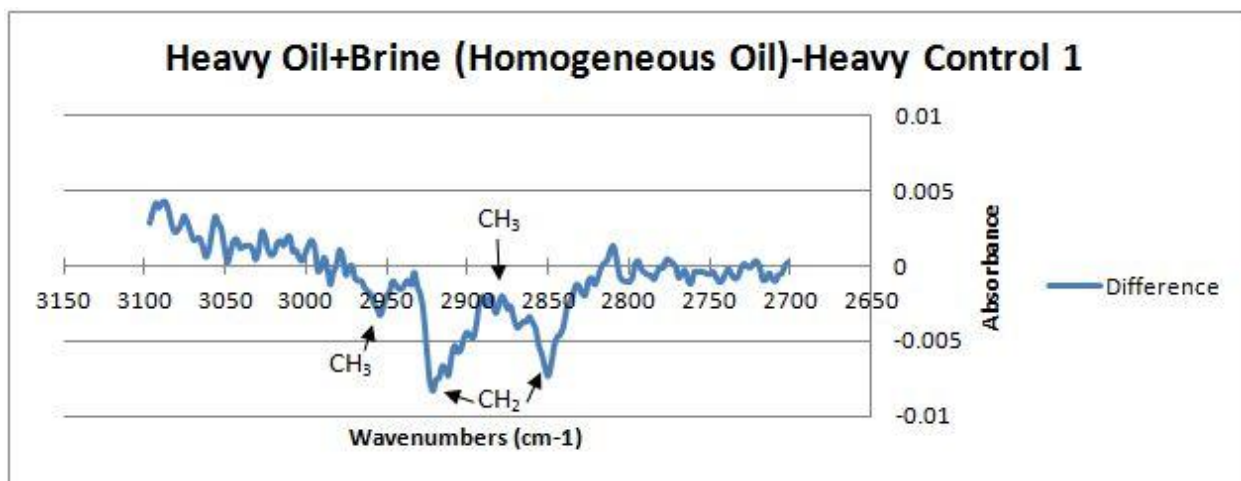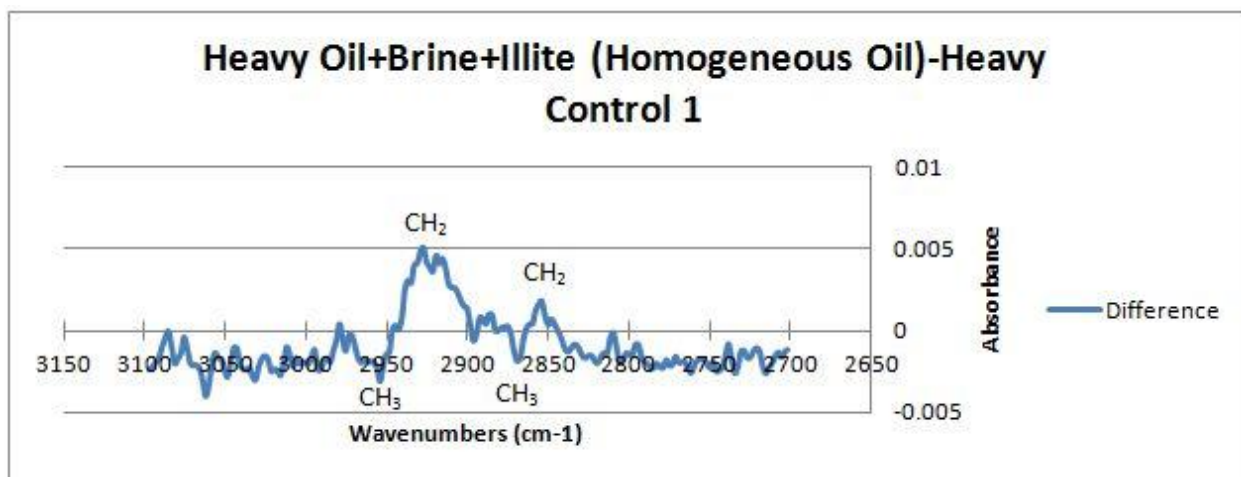

Figure 10. Difference in FTIR Spectras of the heavy crude oil+brine+illite (homogeneous oil) and heavy control 1 (Homogeneous Irradiated Heavy Oil+Brine+Illite Sample-Control Heavy Oil). ~100 rad (0.001 J/g)

3.4. Organic Separates

Each kerogen sample received different doses of gamma radiation ranging from 0 to 400 rads. Those samples were then analyzed using a Rock-Eval pyrolysis and compared with the control sample that was not irradiated. The control sample (Kerogen Sample 1) had a T_{max} of

429 °C and a S1 value (i.e. the free hydrocarbons in the sample) of 2.40 mg HC/g. Kerogen Sample 2, which received ~100 rads of gamma radiation, had a T_{max} of 428 °C and a S1 value of 2.29 mg HC/g. Kerogen Sample 3, which received ~225 rads of gamma radiation, had a T_{max} of 429 °C and a S1 value of 2.31 mg HC/g. Kerogen Sample 4, which received ~400 rads of gamma radiation, had a T_{max} of 429 °C and a S1 value of 2.19 mg HC/g. Figure 11, 12, 13, and 14 show the pyrograms of each individual kerogen.
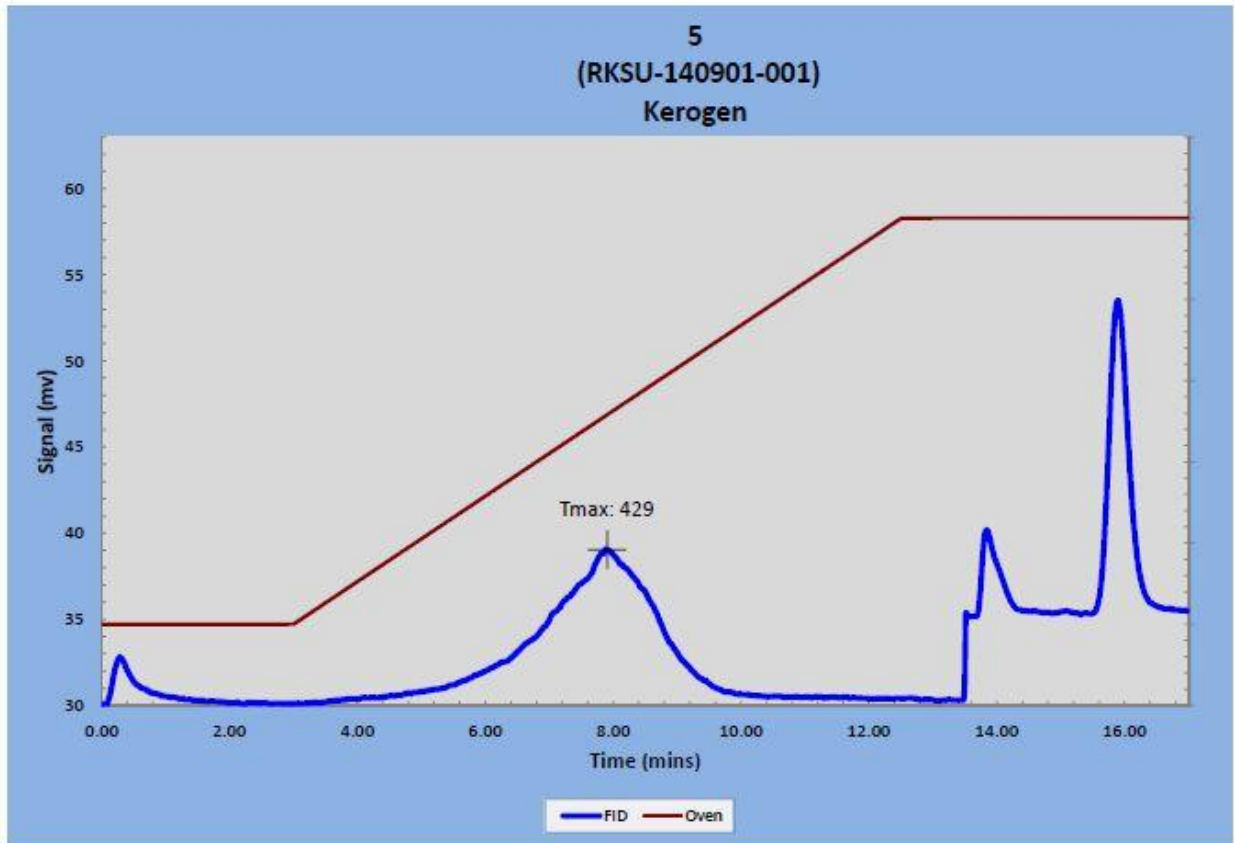
Figure 11. Rock-Eval of Kerogen Sample 1 (Control Kerogen which received no radiation).
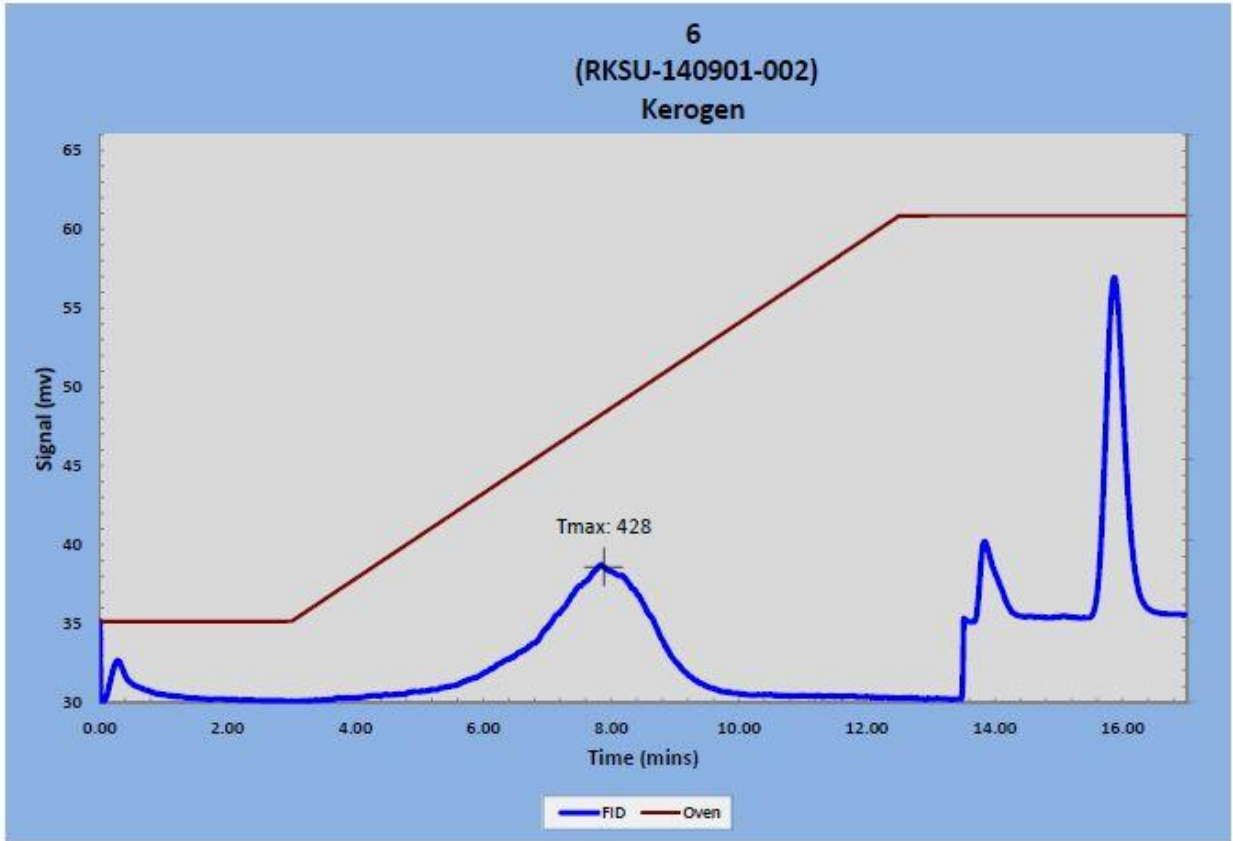
Figure 12. Rock-Eval of Kerogen Sample 2 (Kerogen which received ~100 rads of gamma radiation).
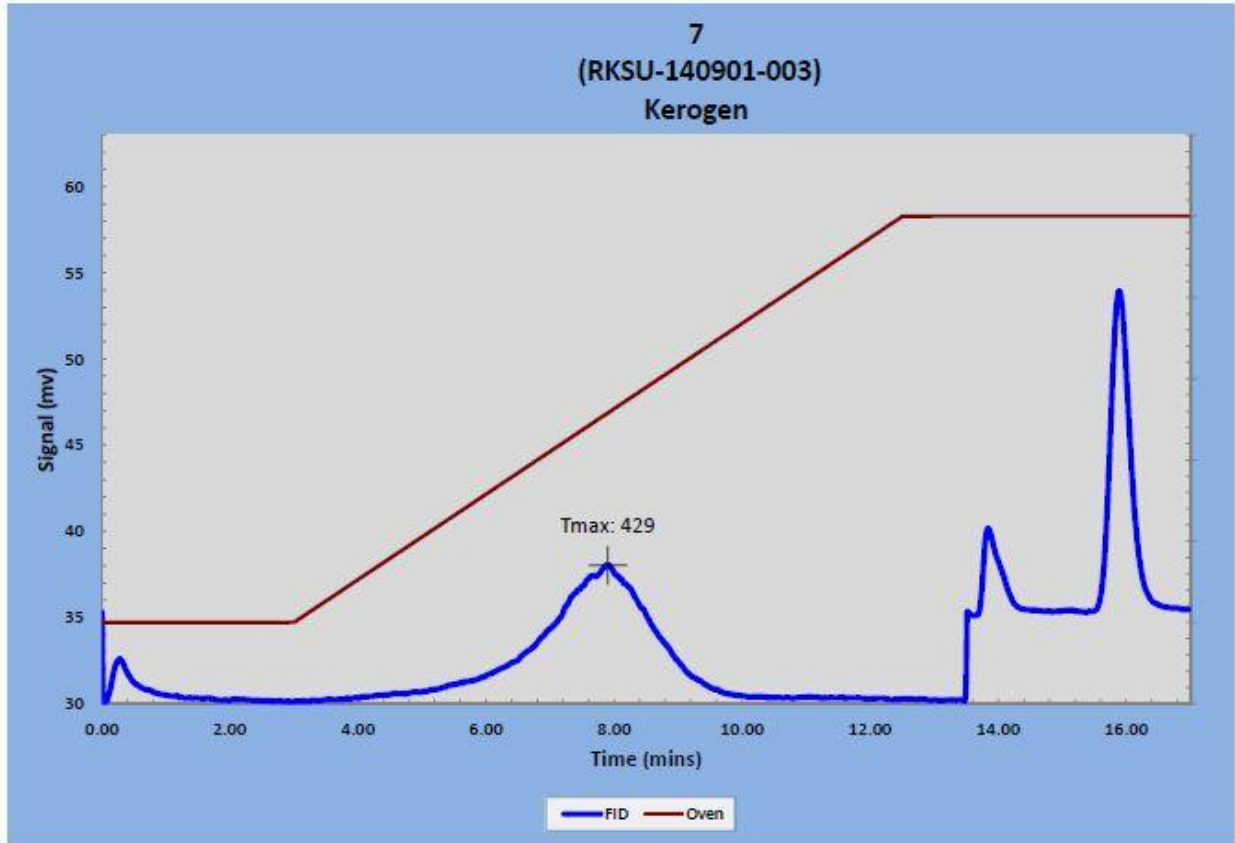
Figure 13. Rock-Eval of Kerogen Sample 3 (Kerogen which received ~225 rads of gamma radiation).
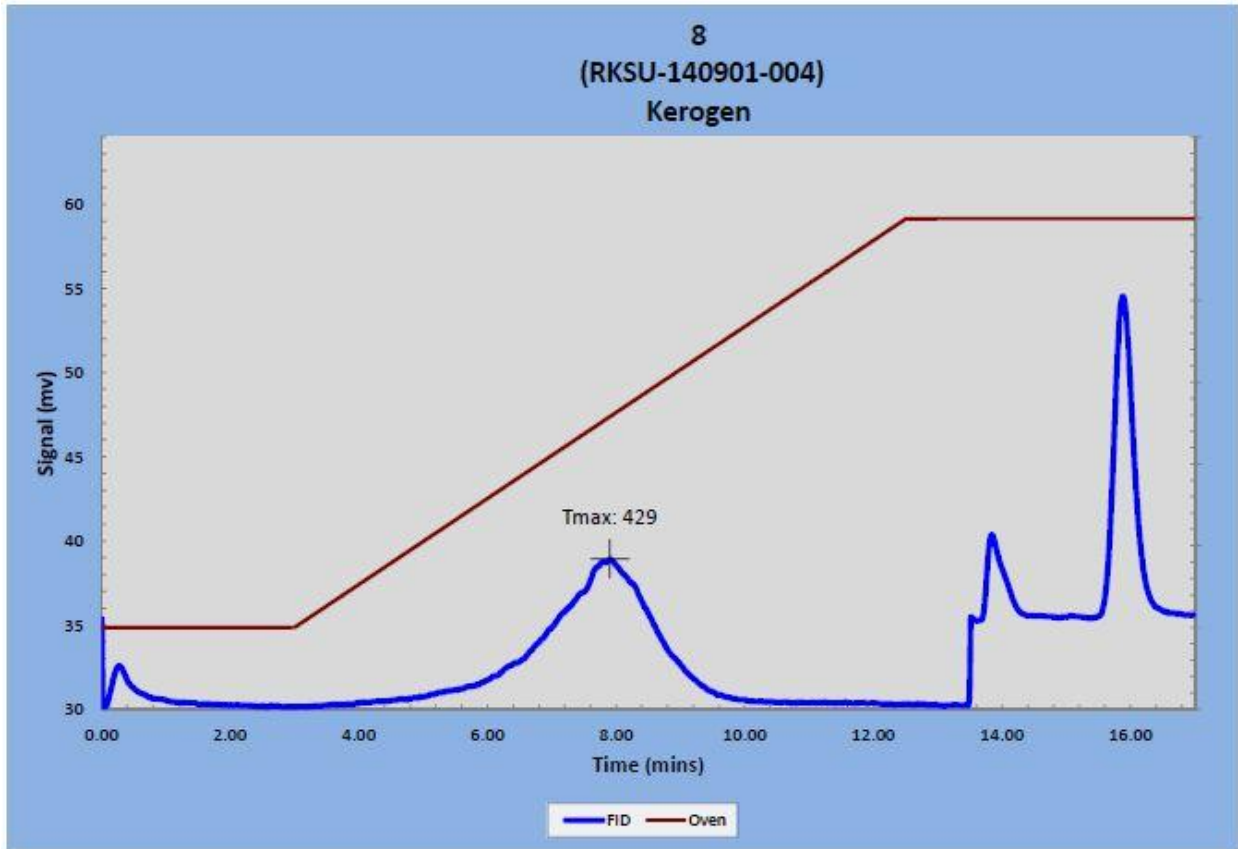
Figure 14. Rock-Eval of Kerogen Sample 4 (Kerogen which received ~400 rads of gamma radiation).

Chapter 4 - Discussion

4.1. Impact of Irradiation on Heavy and Light Crude Oil

The positive anomalies at wavenumbers 2922 cm^{-1} and 2850 cm^{-1} in Figures 1 and 2 suggest an increase in CH_2 groups, and the negative anomalies at wavenumbers 2952 cm^{-1} and 2875 cm^{-1} suggest a decrease in CH_3 groups relative to the original (non-irradiated) control samples. This suggests that smaller hydrocarbon chains are combining to form longer hydrocarbon chains when gamma irradiation occurs as shown below:

$$C_5H_{12}+\gamma \rightarrow C_5H_{12}^{+}+e^{-}$$
$$C_5H_{12}^{+}+C_5H_{12} \rightarrow (C_{10}H_{24})^{+}$$
$$(C_{10}H_{24})^{+}+e^{-} \rightarrow C_{10}H_{22}+H_2$$
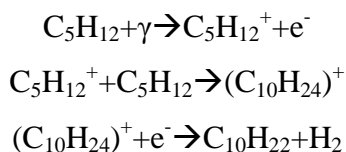
This step equation can then be applied to produce the following reactions:

$$C_8H_{18}+C_8H_{18}+\gamma \rightarrow C_{15}H_{32}+CH_4$$
$$C_6H_{12}+3C_2H_6+\gamma \rightarrow C_6H_6+6CH_4$$
$$C_8H_{18}+C_8H_{18}+\gamma \rightarrow C_{16}H_{32}+2H_2$$
$$C_8H_{16}+C_8H_{18}+\gamma \rightarrow C_{16}H_{32}+H_2$$
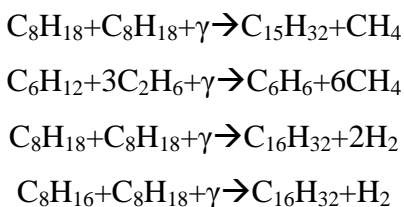
This reaction not only created longer hydrocarbon chains from shorter chains, but also may have produced H_2 (g) and a small hydrocarbon as a product.

4.2. Impact of Irradiation on Heavy and Light Crude Oil+Brine

The positive anomaly in the light fraction of the heavy oil/brine sample at wavenumber 2922 suggests an increase in CH_2 groups (Figure 3). The possible positive anomalies in the light fraction of the light oil/brine sample at wavenumbers 2922 cm^{-1} and 2875 cm^{-1} would suggest an increase in CH_2 groups and an increase in CH_3 groups respectively (Figure 4). This increase in CH_2 groups would signify the lengthening of hydrocarbon chains and can be shown in the step reaction below:
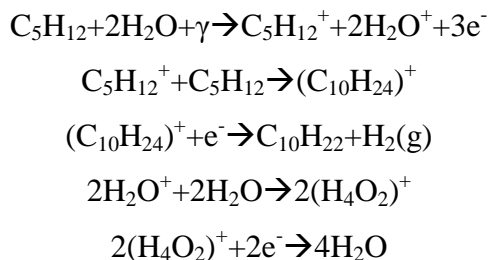
$$C_5H_{12}+2H_2O+\gamma \rightarrow C_5H_{12}^{+}+2H_2O^{+}+3e^{-}$$
$$C_5H_{12}^{+}+C_5H_{12} \rightarrow (C_{10}H_{24})^{+}$$
$$(C_{10}H_{24})^{+}+e^{-} \rightarrow C_{10}H_{22}+H_2(g)$$
$$2H_2O^{+}+2H_2O \rightarrow 2(H_4O_2)^{+}$$
$$2(H_4O_2)^{+}+2e^{-} \rightarrow 4H_2O$$

This reaction involves the formation of a longer hydrocarbon chain from two smaller hydrocarbon chains. It also involves the production of $H_2(g)$ and breaking then reformation of H_2O as a result of the movement of electrons. The possible increase in CH_3 groups would signify a formation of a lighter fraction of hydrocarbons or shortening of hydrocarbon chains.

The negative anomaly in the homogeneous heavy oil/brine sample at 2952 cm^{-1} would suggest a decrease in CH_3 and the negative anomalies at wavenumbers 2922 cm^{-1} and 2850 cm^{-1} would suggest a decrease CH_2 groups (Figure 5). The positive anomaly at 2875 cm^{-1} would suggest an increase in CH_3 groups. The negative anomalies in the homogeneous light oil samples at wavenumber 2952 cm^{-1} would suggest a decrease in CH_3 groups and at 2922 cm^{-1} and 2850 cm^{-1} suggest a decrease in CH_2 groups (Figure 6). The positive anomaly at 2860 cm^{-1} suggests an increase in CH_3 groups. An example of this increase in CH_3 groups is represented in the following step equation:
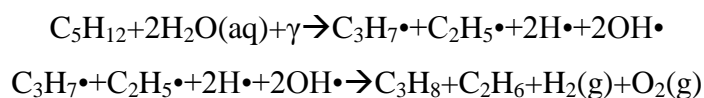
$$C_5H_{12}+2H_2O(aq)+\gamma \rightarrow C_3H_7\bullet+C_2H_5\bullet+2H\bullet+2OH\bullet$$

$$C_3H_7\bullet+C_2H_5\bullet+2H\bullet+2OH\bullet \rightarrow C_3H_8+C_2H_6+H_2(g)+O_2(g)$$

The initial breaking of the C_5H_{12} and H_2O causes free radicals to be produced in the samples. Those free radicals then react randomly producing various amounts of $H_2(g)$, $O_2(g)$, and shortened carbon chains.

It should be considered that the differences in the control and irradiated light oil/brine samples (Figures 3-6) are very small and it is possible that bandwidth interferences and/or interferences of different weights of oil created during irradiation could cause destructive interferences during the FTIR analysis. These differences between irradiated and non-irradiated control samples still show that radiation can change the molecular compositions and/or geometry of crude oil by randomly breaking bonds and as a consequence of breaking bonds, creating new bonds.

The composition of the brine may also influence the impact of gamma radiation. During the irradiation process, many radical species will be produced as shown above. These radicals may react differently depending on the composition of the brine, such as brine enriched in Na compared to brine enriched in Ca.

4.3. Impact of Irradiation on Heavy Oil+Brine+Arizona Calcium Montmorillonite or Illinois Fithian Illite

The positive anomalies in the light fraction of the oil /brine/clay samples at wavenumbers 2950 cm^{-1} and 2875 cm^{-1} suggest increases in CH_3 groups. The negative anomalies at wavenumbers 2922 cm^{-1} and 2852 cm^{-1} suggest decreases in the CH_2 groups (Figures 7 and 8). These positive and negative anomalies signify shortening of carbon chains in the oil samples along with the production of $H_2(g)$ and $O_2(g)$ from the brine. An example of this reaction is shown below:

$$C_5H_{12}+2H_2O(aq)+\gamma\rightarrow C_3H_7\bullet+C_2H_5\bullet+2H\bullet+2OH\bullet$$

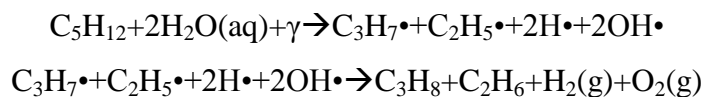$$C_3H_7\bullet+C_2H_5\bullet+2H\bullet+2OH\bullet\rightarrow C_3H_8+C_2H_6+H_2(g)+O_2(g)$$

The initial breaking of the C_5H_{12} and H_2O causes free radicals to be produced in the samples. Those free radicals then react randomly producing various amounts of $H_2(g)$, $O_2(g)$, and shortened carbon chains.

The positive anomalies in the homogeneous oil /brine/clay samples at wavenumbers 2922 cm^{-1} and 2852 cm^{-1} suggest an increase in CH_2 groups and the negative anomalies at wavenumbers 2952 cm^{-1} and 2870 cm^{-1} suggest a decrease in CH_3 groups (Figures 8 and 9). This signifies a lengthening of hydrocarbon chains in the oil samples combined with the production of $H_2(g)$ and H_2O. A step equation of this reaction is shown below:
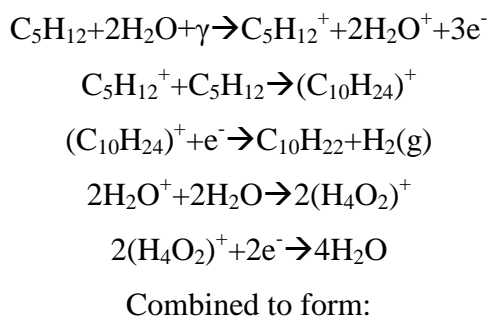
$$C_5H_{12}+2H_2O+\gamma\rightarrow C_5H_{12}^{+}+2H_2O^{+}+3e^{-}$$

$$C_5H_{12}^{+}+C_5H_{12}\rightarrow (C_{10}H_{24})^{+}$$

$$(C_{10}H_{24})^{+}+e^{-}\rightarrow C_{10}H_{22}+H_2(g)$$

$$2H_2O^{+}+2H_2O\rightarrow 2(H_4O_2)^{+}$$

$$2(H_4O_2)^{+}+2e^{-}\rightarrow 4H_2O$$

Combined to form:

$$2C_5H_{12}+4H_2O+\gamma\rightarrow C_{10}H_{22}+4H_2O+H_2(g)$$

This reaction involves the formation of a longer hydrocarbon chain from two smaller hydrocarbon chains. It also involves the production of $H_2(g)$ and breaking then reformation of H_2O as a result of the movement of electrons.

4.4. Organic Separates

The samples did not seem to show any trend with increasing radiation dosage (Figures 11-14). It should be noted that any kerogen that may have been converted to gaseous bitumen would have escaped through the capsules or when the capsules were opened for the Rock-Eval.

4.5. Effects of Clay Minerals

When comparing the oil samples irradiated with clay minerals Arizona calcium montmorillonite and Illinois Fithian illite with the samples irradiated without clay minerals, there seems to be positive anomalies at wavenumbers 2922 cm^{-1} and 2850 cm^{-1}. Figure 15 shows this difference in the sample containing montmorillonite clay and Figure 16 shows this difference in the sample containing illite clay. These anomalies suggest that more CH_2 bonds were created in the samples that had clay minerals included in the systems than the samples that did not contain clay minerals. The clay minerals appear to act as catalysts in the irradiation experiments. Shimoyama and Johns (1971) previously determined that clay minerals have acted as catalysts in a thermal experimental study on $C_{21}H_{43}COOH$ (behenic acid), in which they contributed to the decarboxylation the fatty acid molecules. This catalytic effect may come from the various charge differences in the clay minerals. These ionic effects may allow valence electrons and free radicals to not immediately react with each other or the brine in the system but react with the various hydrocarbon chains thus creating longer and/or shorter hydrocarbon chains.

Figure 15. Difference in FTIR Spectras of the heavy crude oil+brine+montmorillonite (homogeneous oil) and heavy crude oil+brine (homogeneous oil) (Homogeneous Irradiated Heavy Oil+Brine+Montmorillonite Sample-Heavy Oil+Brine Sample). ~100 rad (0.001 J/g)

Figure 16. Difference in FTIR Spectras of the heavy crude oil+brine+illite (homogeneous oil) and heavy crude oil+brine (homogeneous oil) (Homogeneous Irradiated Heavy Oil+Brine+Illite Sample-Heavy Oil+Brine Sample). ~100 rad (0.001 J/g)

The difference between how Arizona calcium montmorillonite and Illinois Fithian illite were then determined and evaluated as shown in Figure 17. There are positive anomalies at wavenumbers 2922 cm^{-1} and 2850 cm^{-1} with negative anomalies at wavenumbers 2952 cm^{-1} and 2860 cm^{-1}. The positive anomalies suggest an increase in CH_2 groups and the negative anomalies suggest a decrease in CH_3 groups. When irradiated, the crude oil sample containing montmorillonite created more CH_2 groups than the crude oil sample containing Fithian illite. An explanation to this may lie in the composition of the clay minerals. The Fithian illite contains an adequate amount of Fe^{2+} and Fe^{3+} while the montmorillonite is poor in Fe. During the irradiation process, radical species are being created. Those radicals will react with other radicals, the brine, the clay minerals, and the crude oil. In the samples containing Fithian illite, the radicals may react with the Fe^{2+} and Fe^{3+} causing reduction-oxidation reactions. If the radicals are reacting with the Fe^{2+} and Fe^{3+}, they will be less likely to react with the crude oil giving reason to why there is more change in the functional groups in the samples containing crude oil and montmorillonite rather than the samples containing crude oil and Fithian illite.
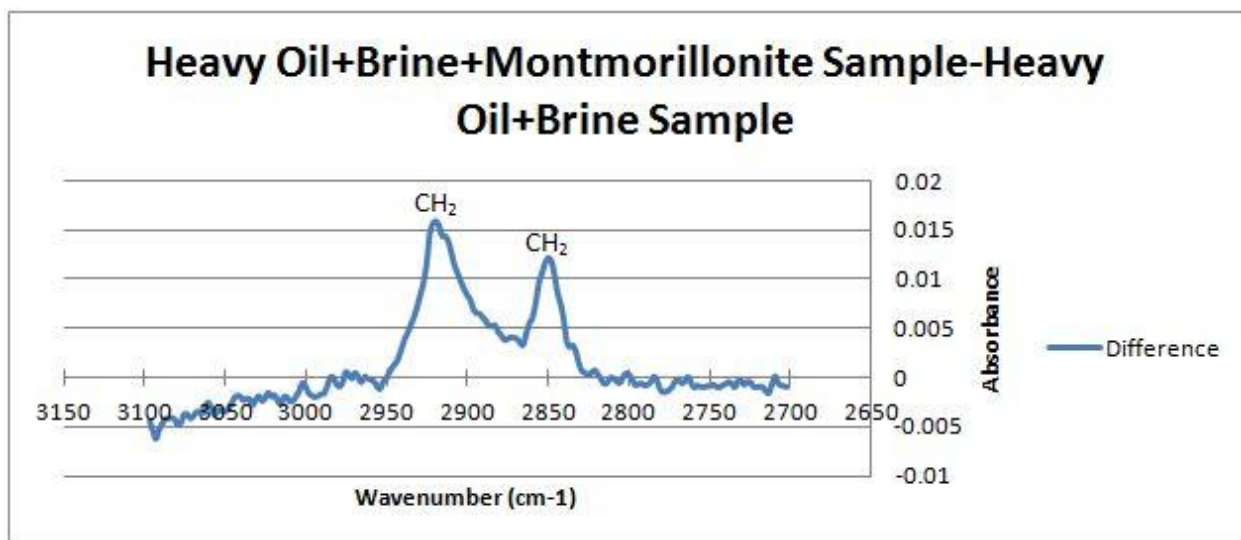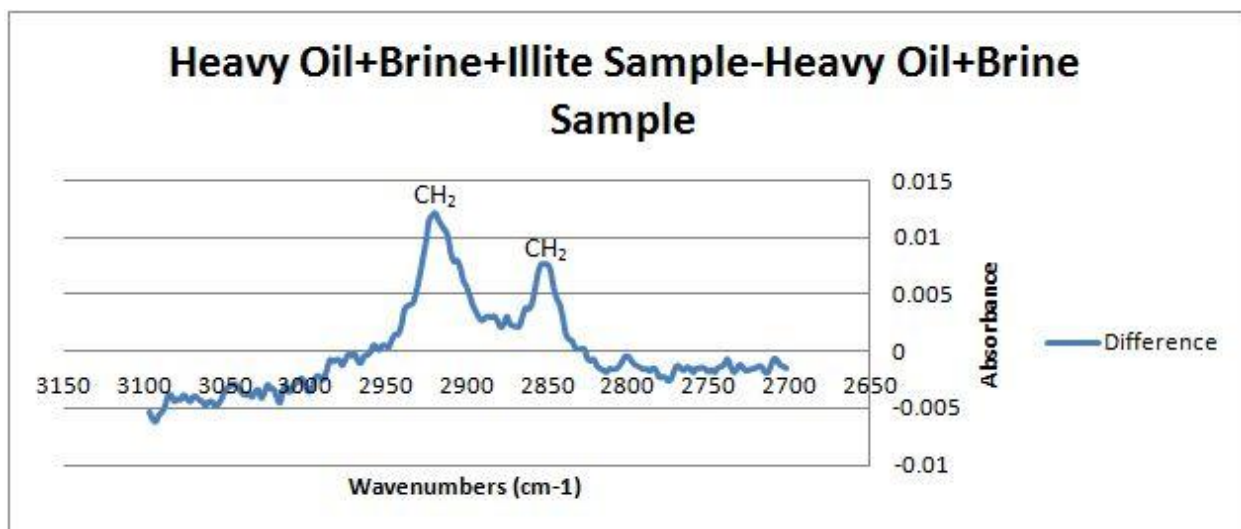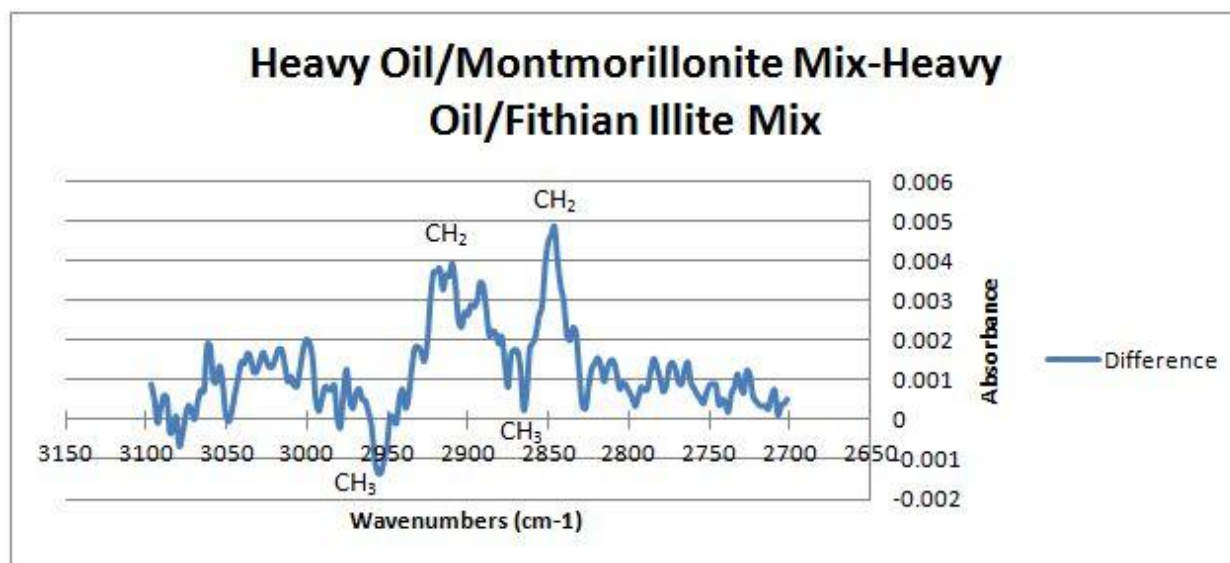
Figure 17. Difference in FTIR Spectras of the heavy crude oil+brine+montmorillonite (homogeneous oil) and heavy crude oil+brine +Fithian illite (homogeneous oil) (Homogeneous Irradiated Heavy Oil+Brine+Montmorillonite Sample-Heavy Oil+Brine+Fithian Illite Sample)

4.6. Production and Effects of Free Radicals

A common process that takes place in the oil irradiation experiments containing brine in various systems is the dissociation of water molecules. Gamma radiation released from the decay of radioactive elements (e.g., U, Th, and K) dissociates water molecules into H●, OH●, H_2, H_2O_2, a hydrous electron (e_{aq}^-), and H^+ (Lin et al. 2004). As shown through previous step equations, radical hydrocarbon chains are also created due to gamma radiation. These various radical molecules are very reactive and can be powerful components in initiating chemical reactions. The creation of a radical species often initiates a chain of radical reactions. Hence one quantum of energy creates manifold opportunities for initiating chemical reactions. An inherently potent power of a radical chemical species is that it is a powerful oxidizing agent. How a radical can be a powerful impact on an organic compound can be illustrated with the presence of iron in a reduced form, such as in porphyrins. The oxidation of the iron promoted by a radical reaction can weaken the configuration of the porphyrin molecule. Thus it is conceivable that just a small amount of high energy gamma radiation can create a significant amount of distortion in the molecular configurations of the organic molecules. This could be an important first step in denaturing the molecules which would prepare the way to their ultimate dissociation to hydrocarbon fluid products.

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4.7. $H_2(g)$, $O_2(g)$, and Short Hydrocarbon Chain Production

As shown during the irradiation of all the oil samples, there are several potential gases produced from radiation. These gases include but are not limited to $H_2(g)$, $O_2(g)$, $CH_4(g)$, $C_2H_6(g)$, $C_3H_8(g)$, $C_4H_{10}(g)$, and $C_5H_{12}(g)$. As these gases are produced from the combined radiolysis of crude oil and/or H_2O, the individual gas particles can transfer energy initially received from the γ-rays as a change in translation state or an increase in kinetic energy thus making it possible to break more bonds. $H_2(g)$ for example, when struck by a weak gamma ray with only $1.0*10^{-14}$J of energy, will be deflected at a speed of ~$2.4*10^6$ m/s. The gas molecules may then strike other gaseous or organic molecules in the system and break additional bonds or cause distortions in the stable configuration of an organic molecule, without breaking any organic molecular bonds. This possible cascade effect would exponentially increase the possibilities of breaking or distorting organic molecules. Depending on what bonds are broken or distorted, this transfer of energy may replicate the certain processes of the well-known thermogenic degradation of a kerogen into bitumen. Any form of energy transfer that aids in increasing the kinetic energy of gas molecules should aid in driving chemical reactions.

Chapter 5 - Conclusions

As shown from the experiments conducted, as crude oil is irradiated by gamma radiation, a number of reactions can take place, varying between the lengthening and shortening of hydrocarbon chains, the production of free radicals, and the production of gases. From these experiments, it can be said that gamma radiation can be used to cause a change in the electronic state of molecules leading to their dissociation with free radicals as intermediates in these chemical processes. The production of these free radicals from gamma radiation will further trigger oxidation-reduction reactions in the organic compounds weakening their configurations. It should be assumed that gases present before and/or after these chemical reactions will be affected by the gamma radiation and that effect on the gases can be in the form of a change in the translation state. An energy input to gas molecules can be significantly important, as part of the input can cause an increase in the kinetic energy of the molecules, enabling them to target reaction points and potentially promote bond dissociation or distortion of the configuration of organic molecules. Any form of energy transfer that aids in increasing the kinetic energy of gas molecules should aid in driving chemical reactions. With the possibilities to ionize molecules, distort the configuration of organic molecules, dissociate molecular bonds, and trigger oxidation-reduction reactions, it appears that the radiation energy could help provide an important step for the onset of necessary dissociation processes to be completed by other energy sources within the environment. The influences of the clay minerals possibly acting as catalysts only magnifies the possibilities that reactions are taking place in source rocks since clay minerals makeup a large portion of these shales. The various roles of gamma radiation on shale source rocks in a subsiding basin may be depicted as small, but they can be an important partner to the activity of geothermal heat energy. The radiation energy can be seen as a significant subtext in the energy clause relating to oil and gas generation in shale source rocks, particularly in the confines of uranium-rich domains.

Chapter 6 - Future Work

This idea of how radiation may affect hydrocarbon generation opens up numerous possibilities for future work. Analysis of the clay minerals that have been irradiated should be conducted. The irradiation of clay minerals with brine present in the system may change the structure of the clay minerals and possibly hold clues about the transformation of smectite to illite. Further investigation of the change in translation state and the kinetic energy of gases should also be evaluated to show how gas particles react to gamma radiation and how those gases then react with their surroundings in organic rich source beds. GCMS along with carbon isotope data of the irradiated crude oils may give further insight to how gamma radiation changes the chemical makeup of crude oil or if certain carbon isotopes are more prone to dissociating than other carbon isotopes. The composition of the brine should be looked into further as well. Brine rich in Na may react to radiation differently than brine rich in Ca and the composition of the brine may change due to irradiation. The brine may also affect the clays and vice versa when irradiation occurs and additional research should be conducted to determine if and how much brine composition may influence FTIR absorption peaks in the oils. Irradiation of a more immature organic kerogen with and without brine in the system may hold more answers about how gamma radiation affects organics in source beds. By having a more immature kerogen, there will be a higher H-C ratio which may hold potential in breaking less hindered bonds by using radiation. Using a gas chromatograph to capture and analyze potential gas created by both crude oil and kerogen irradiation may show more details in hydrocarbon generation.

References

Aske, Narve, Harald Kallevik, and Johan Sjöblom, 2001, Determination of Saturate, Aromatic, Resin, and Asphaltenic (SARA) Components in Crude Oils by Means of Infrared and Near-Infrared Spectroscopy: Energy & Fuels, v. 15.5, p. 1304-312.

Beers, Roland F., and Clark Goodman., 1944, Distribution of Radioactivity in Ancient Sediments: Bulletin of the Geological Society of America, v. 55, p. 1229-54.

Engler, K.O.V., 1913, Die Chemie und Physik des Erdols. Vol.1. Leipzig: S. Hirzel.

Honig, Richard E., 1946, Radiochemical Changes in Some Fatty Acids: Science: v. 140. p. 27-28. Print.

Howton, David R., and Guey-Shuang Wu., 1967, γ Radiolysis of Oleic Acid: Journal of the American Chemical Society, v. 89:3, p. 516-525.

Hunt, John M., 1995, Petroleum Geochemistry and Geology, Second Edition: W. H. Freeman and Company.

Lin, Li-Hung, Greg F. Slater, Barbara Sherwood Lollar, Georges Lacrampe-Couloume, and T.C. Onstott., 2005, The Yield and Isotopic Composition of Radiolytic H_2, a Potential Energy Source for the Deep Subsurface Biosphere: Geochimica Et Cosmochimica Acta, v. 69.4, p. 893-903.

Ramirez-Caro, Daniel., 2013, Rare Earth Elements (REE) as Geochemical Clues to Reconstruct Hydrocarbon Generation History

Sheppard, Charles W., 1944, Radioactivity and Petroleum Genesis: Bulletin of the American Association of Petroleum Geologists, v. 28, no. 7, p. 924-52.

Sheppard, Charles W., and Virginia L. Burton., 1946, The Effects of Radioactivity on Fatty
        Acids: Bulletin of the American Association of Petroleum Geologists, v. 68, p. 1636-39.

Shimoyama A. and Johns W. D., 1971, Catalytic conversion of fatty acids to petroleum-like
        paraffins and their maturation: Nature, v. 232, p. 140-144.

Swanson, Vernon E., 1961, Geology and Geochemistry of Uranium in Marine Black Shales:
        Geological Survey Professional Paper 356-C, p. 51.

Appendix A - Locations of Kerogen Samples

Sample Name	Latitude	Longitude	Section	TWP	RNG	County	Sample Depth (ft)	Formation
WF # 1 Shell McCalla Ranch	35.0912	-97.78539	12	07N	06W	Grady	12309	Woodford
WF # 2 Mobil Sara Kirk	36.72669	-97.93513	15	26N	07W	Grant	5567	Woodford
WF # 3 Mobil Rahm Lela	36.5809	-97.82898	03	24N	06W	Garfield	6729	Woodford
WF # 4 Shell Guthrie	36.25138	-97.45871	31	21N	02W	Noble	4165	Woodford
WF # 6 Mobil Cement Ord	34.90223	-98.07862	18	05N	08W	Grady	17581	Woodford
WF # 5 Mobil Dwyer Mt	36.23352	-98.22134	01	20N	10W	Major	8716.5	Woodford
WF # 7 Amerada Chenoweth	36.40693	-97.73539	04	22N	05W	Garfield	6513	Woodford
WF # 8 Apexco Curtis	35.39349	-97.72205	27	11N	05W	Canadian	8520	Woodford
WF # 9 Jones and Pellow	35.03079	-98.53458	35	07N	13W	Caddo	6793	Woodford
WF # 10 Lonestar Hannah	36.15513	-99.79674	06	19N	24W	Ellis	14323	Woodford

Appendix B - Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to obtain an infrared spectrum of absorption of specific functional groups such as CO, CH_2, or CH_3. At certain wavenumbers, (cm^{-1}), functional groups will absorb the infrared energy emitted by the machine and the amount of absorbance is calculated. By matching absorbance and the wavenumbers that the absorbance takes place at, specific functional groups present in medium can be identified. This technique has previously been used in crude oils in the spectra range 4000-400 cm^{-1} to identify different C, O, S, N, and H functional groups (Arske 2001). By using FTIR, it is possible to get the functional group composition of a medium.

Appendix C - Rock-Eval Pyrolysis

During Rock-Eval pyrolysis, a sample is placed inert atmospheric conditions and heated to 550 $^{\circ}$C. During this heating process, hydrocarbons already present in the sample will burn off and the amounts of hydrocarbons burnt off are represented by the S1 peak. The kerogen present will then crack or convert to bitumen and that process is represented by the S2 peak and the temperature at which the S2 peak takes place at is the T_{max} which is a tool used to represent the maturity of a source rock. As heating continues, the CO_2 will be generated from the mineral matrices and that will be represented by the S3 peak.

For this experiment, the kerogen was separated from the silicate minerals and carbonate minerals. Because of this separation, there should be no S1 or S3 peaks in the Rock-Eval of the control sample which received no dose of radiation. If bitumen was created during the irradiation process, an S1 peak would in the irradiated samples' pyrograms would represent conversion of kerogen to bitumen by means of irradiation. A change in the S2 peak and T_{max} in the irradiated samples would also represent a change of kerogen to bitumen or a change in maturity according to the Rock-Eval. When comparing the control with the irradiated samples, no changes were apparent.