Geochemical investigation of the origin of hydrocarbon occurrences in up-dip Wilcox Group reservoirs at Raccoon Bend field, southeast Texas Gulf Coast basin

A Thesis Presented to

the Faculty of the Department of Earth and Atmospheric Sciences

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Allison McConnell

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ABSTRACT

Raccoon Bend field is a densely-drilled salt dome field in Austin County, Texas located within the southeast Texas Gulf Coast basin. Successful commercial drilling of the Wilcox Group at the Raccoon Bend field has presented a rare opportunity to study the organic geochemical attributes of hydrocarbons in Wilcox-aged reservoir in this basin. Molecular geochemistry of hydrocarbons was integrated with local stratigraphy, subsurface temperature and pressure, and reservoir brine isotope geochemistry to evaluate the source, maturity, and possible migration pathways of the hydrocarbons at Raccoon Bend field. Additionally, rock samples were collected from the Wilcox Group at Raccoon Bend field and were analyzed for total organic carbon, vitrinite reflectance, visual kerogen analysis, and stable isotopes of carbon. Organic geochemical attributes of the rocks, combined with the hydrocarbon geochemistry, were used for oilsource rock comparison at Raccoon Bend field.

Geochemical investigation of hydrocarbons at Raccoon Bend field suggests that these oils belong to a single family, and therefore likely sourced from the same rock. Whole-oil gas chromatography and biomarker chemistry suggest that the chemistry of the oils are influenced profoundly by non-marine humic organic matter (Type III kerogen). Raccoon Bend oils correlate with other oils studied from younger reservoirs within the basin. However, there are several geochemical characteristics that suggest that the molecular chemistry of these oils is influenced by the immature coal-rich, high-energy proximal carrier-bed and reservoir rocks where the oils have accumulated. Pr/Ph ratios, $n-C_{15}+$ distribution, and some saturate biomarker parameters show unusual characteristics for Gulf Coast oils that cannot be explained by source rock facies variations. Rock analyses confirm the Wilcox Group at Raccoon Bend is currently in the 'early generative window' and therefore the Wilcox Group is not responsible for the commercial quantities of oil and gas at Raccoon Bend. The low organic carbon content and the dominance of re-worked organic matter in the Wilcox Group. It is possible that the Raccoon Bend oils are not likely sourced from the Wilcox Group. It is possible that the Raccoon Bend oils are sourced from laterally more mature, more distal facies of the Wilcox or from older source rocks such as Midway, Austin Chalk, or Eagle Ford.

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1. INTRODUCTION

The southeast Texas Gulf Coast basin contains many salt-related oil fields that have been active exploration targets since the discovery of Spindletop in 1901 (Halbouty, 1979) (Figure 1.1). Recent studies have revealed the lack of understanding of the origin and migration paths of the oils in this region (Guo, 2004; Banga et al., 2011). Geochemical inversion analysis is the process of analyzing oils for molecular characteristics that can be used to infer the source rocks of an oil (Bissada et al., 1993). Biomarkers, the chemical "fossils" in hydrocarbons, can be used for geochemical inversion analysis (Walters and Dusang, 1988; Bissada et al., 1993). Biomarker analysis is a useful tool for identifying source rocks in the southeast Texas Gulf Coast basin because many of the potential source rocks are not penetrated by wells and therefore only the hydrocarbon-bearing reservoirs are available for sampling. The biomarker-inversion studies completed on oils from other southeast Texas fields were all done on the Claiborne Group and Frio Formation oils, and in each case, vertical migration from the underlying Wilcox Group, or possibly deeper units, was invoked as the likely sourcing mechanism (Sassen et al., 1994; Guo, 2004; Banga et al., 2011).



Figure 1.1 Hydrocarbon reservoirs associated with salt domes in the southeast Texas Gulf Coast basin. Previous geochemical inversion studies in the Basin are indicated in this figure. The approximate location of the E. Sorsby well in Waller County is also labeled and Eagle Ford and Austin Chalk cuttings were obtained from this well. Map modified from Galloway et al. (1983).

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Figure 1.2. Stratigraphic column for the southeast Texas Gulf Coast basin modified from Sheets and Cockrell (1962). Symbols indicate formations that produce oil and gas. Potential source rocks suggested for this basin include Wilcox, Midway, Austin Chalk, and Eagle Ford (Warwick, 2009; Sassen, 1990; Philippi, 1974).

2. PREVIOUS STUDIES

The Gulf of Mexico Basin hosts multiple source rocks of different ages. Kennicutt et al. (1992) outlines five distinct genetic families of oils: Jurassic Smackover oils, Flexure Trend oils, South Florida oils, Upper Cretaceous oils, and Paleogene oils (Wilcox Group) based on differences from whole oil gas chromatography analysis, biomarker analysis, and carbon isotope analysis of 309 oil samples. Along the Texas and Louisiana Coast, many of the reservoirs deposited during the Tertiary, including those that are the focus of this study, have oils with similar geochemical characteristics (based on high concentrations of oleannane, C_{15} + n-paraffin distributions, and C_{30} hopane to C_{29} norphane ratios) and those characteristics suggest the deltaic Wilcox Group as a sourcerock (Sassen et al., 1988, 1994; Hanor and Sassen, 1990; Sassen, 1990; Wenger et al., 1990; Kennicutt et al., 1992; Guo, 2004; Banga et al., 2011).

The distinct biomarker and isotopic compositions of Wilcox reservoir oils in Louisiana and Mississippi differ from those of oils found in stratigraphically older reservoirs suggesting that Wilcox source rocks are an important contributor to the Wilcox oils (Sassen et al., 1988; Sassen, 1990; Wenger et al., 1990; McDade et al., 1993). Although a genetic relationship was hypothesized between Wilcox source rocks and Wilcox oils, Sassen (1990) acknowledged that Wilcox oils in Louisiana, especially those in the Louisiana salt basin, could have a substantial contribution from older source rocks due to vertical migration. There are no previous biomarker analyses of oils from Wilcox reservoirs in the southeast Texas Gulf Coast basin.

Previous biomarker studies of oils from the younger Claiborne Group and Frio Formation reservoirs in the southeast Texas Gulf Coast basin suggest the Wilcox Group

as a likely source rock with the possibility of contributions from older source rocks such as the Eagle Ford Group (Sassen et al., 1994; Guo, 2004; Banga et al., 2011). All of these studies suggest that vertical migration is a dominant pathway for hydrocarbon migration to the sampled reservoirs, as it is for hydrocarbon migration in other parts of the Gulf Coast Basin (Bissada et al, 1990).

3. Study Area

The Raccoon Bend field is located in the southeast Texas Gulf Coast basin, about 97 km northwest of Houston in Austin County (Figure 1.1). Raccoon Bend is classified as an intermediate salt dome field with the top of salt at approximately 2,329 m (7,640 ft) below sea level (Halbouty, 1979) (Figure 3.1). The stratigraphy of the southeast Texas Gulf Coast basin penetrated by drilling consists of Mesozoic and Cenozoic deposits (Figure 1.2). However, very few wells drilled in the basin penetrate the deeper Mesozoic section therefore little is known about the Mesozoic stratigraphy (Sheets, 1987). The Raccoon Bend field lies basinward of the Cretaceous shelf edge by approximately 10 km. Mesozoic stratigraphy in the Katy Field just southeast of Raccoon Bend consists of Cretaceous carbonate Sligo and Edwards basinal facies equivalents identified from seismic lines (Ewing, 1986). Above these carbonate Cretaceous units lies "undifferentiated marine Gulfian (U.Cretaceous) and Midway Groups (L. Paleocene)". These Late Cretaceous and Midway Group sediments in the area are believed to be continental slope deposits (Ewing, 1983, 1986).

The Wilcox Group, which is the focus of this study, was the first major depositional episode in the Cenozoic (Fisher and McGowen, 1967; Galloway, 1982;

Galloway et al., 2000). Wilcox deposition in the southeast Texas Gulf Coast Basin resulted from the large fluvial-dominated Rockdale Delta System (Fisher and McGowen, 1967; Galloway et al., 2000). The Rockdale Delta covered most of southeast Texas with the major axis of deposition occurring near the Raccoon Bend field (Fisher and McGowen, 1967; Galloway, 1982; Galloway et al., 2000). Seismically, the Wilcox Group in the area can be identified by a sequence of prograding clinoforms showing the seaward movement of the shelf edge during this time (Ewing, 1986). Ewing (1984, 1986) describes both the lower Wilcox formation and the upper Wilcox formation in the area as sandstone-rich, meaning they have 40-75% sand, whereas the middle Wilcox formation is a sandstone/shale sequence with only 20-40% sand. There are two major transgressive shales that mark the beginning and the end of the middle Wilcox formation: respectively, the Big Shale and Yoakum shale (Xue, 1994; Xue and Galloway, 1993,1995). This study will focus on these two shales as likely Wilcox source rocks because transgressive sequences are favorable conditions for source rock deposition (Tissot and Welte, 1984, p.654).

From the depositional environment described, a source rock composed of the Wilcox Group should be deltaic in origin and therefore contain both marine and terrestrial organic components, which is supported by previous work (Philippi, 1965; Sassen et al., 1988, 1994; McDade et al., 1993; Sassen, 1990; Guo, 2004; Banga, 2011). However, the Wilcox Group in the vicinity of the Raccoon Bend field is predominantly composed of deltaic sandstones with a low percentage of shale (Ewing, 1983, 1986; Swenson, 2012, personal communication). The high percentage of sandstones in the Wilcox Group in the Raccoon Bend area suggests a high energy depositional

environment with significant terrestrial organic matter contribution but perhaps lacking the necessary anoxic conditions required for accumulation of hydrogen-rich, oil-prone organic matter (Demaison and Moore, 1980). This depositional environment suggests that the Wilcox Group at Raccoon Bend field may not include much shale deposited in an adequate oil-prone source environment.

Raccoon Bend field lies approximately 30 km updip of the Wilcox Group growth fault zone. The growth fault zone is created by gravitational failure of the shelf edge during Wilcox progradation (Bebout et al., 1982). Fault zones along the Gulf Coast are commonly associated with vertical migration of hydrocarbons (Bissada et al., 1990; Sassen, 1990). Past studies in the southeast Texas Gulf Coast Basin suggest that Wilcox source rocks may be downdip of this growth fault trend (Guo, 2004; Banga et al., 2011) and therefore Wilcox hydrocarbon migration from source rocks downdip of the fault trend may be constrained to that area.

Historical production from the Raccoon Bend field has been predominantly from the Jackson and Yegua Formations (Galloway et al., 1983). Recent drilling, however, has resulted in commercially successful production from the underlying Wilcox Group. Oil production from the Wilcox Group is due to creation and preservation of trapping structures and migration pathways that are likely caused by timely salt movement. Although the salt does not appear to pierce any of the producing reservoirs at Raccoon Bend, salt diapirism can cause extensive faulting on the flanks and crest of salt domes directly leading to both the traps and migration pathways critical to the local petroleum system (Halbouty, 1979) which is believed to be the case at Raccoon Bend field (Swenson, 2012, personal communication). The top of the Wilcox Group is over 609m

(2,000 ft) higher on the dome crest than off the structure (Swenson, 2012, Figure 3.1 and 3.2).

The Wilcox oil samples were collected from wells located on the north side of the salt dome. All of the reservoirs sampled are from either the upper Wilcox or the lower Wilcox formations according to the classification of Xue and Galloway (1993, 1995) and Xue (1994) [1933m-2092m]. The deepest sample originated from a depth of 2027m that was initially gas/condensate productive but is now producing oil and gas. A map of sampled wells is shown in Figure 3.2.



Figure 3.1. Schematic cross-section of Raccoon Bend field, omitting all faults, from Swenson (2012, personal communication). This study contains samples from Miocene (included in Pliocene-Oligocene Vicksburg), Jackson, upper Wilcox, and lower Wilcox oil reservoirs. Also, middle Wilcox rock samples are used for source rock-oil correlations.



Figure 3.2. Simplified structure map on the top of the upper Wilcox formation at Raccoon Bend field modified from Swenson (2012, *personal communication*). Diamond shapes indicate the seven wells chosen for oil geochemical analysis. Circles mark other Raccoon Bend wells used for pressure and temperature calculations.

4. HYDROGEOLOGIC SETTING

The subsurface fluid-pressure regimes of the Gulf of Mexico Basin, including Raccoon Bend field, consists of hard geopressured sediments at depth, and normal pressures above (Kharaka et al., 1977; Dutton et al., 2002, 2006). There is also a transitional zone between hard geopressured sediments and normally pressured referred to as the soft geopressured, or transitional, zone (Bethke, 1986; Harrison and Summa, 1991; Dutton et al., 2002, 2006). The pressure-depth gradients for these three zones are shown in Figure 4.2a. Geopressured sediments characteristic of the Gulf of Mexico Basin are likely due to a combination of (1) rapid burial of uncompacted sediments, (2) low-permeability seals that prevent release of fluids buried at greater depths, and (3) temperature-induced phase change from smectite to illite causing bound water to change to pore water (Bethke, 1986; Harrison and Summa, 1991).

The normally pressured zone within the Wilcox formation lies updip of the geopressured transitional zone and consists of a very productive aquifer system composed of major sandstones, the Carrizo aquifer (Fogg and Kreitler, 1982; Thorkildsen and Price, 1991; Dutton, 1999). The updip normally pressured zone is above the base of potable water line in Figure 4.1. Dutton et al. (2002, 2006) studied the hydrogeology of the soft-geopressured or transitional zone of the Wilcox Group beneath the central part of the Texas Coastal Plain where Raccoon Bend field lies. The characteristics for the geopressured zone, in addition to the pressure-depth gradient, include formation water with salinity typically much greater than seawater and the presence of major oil and gas

fields (Galloway et al., 1983; Bethke et al., 1988; Land and Macpherson, 1992; Kosters et al., 1989).

Raccoon Bend Wilcox reservoirs lie in the transitional or soft-geopressured zone with pressure-depth gradient between the hydrostatic gradient (P_h) and the lithostatic gradient (P_L) ((Figure 4.2a). Mixing from meteoric water above and geopressured brines and hydrocarbons below can occur in the soft-geopressured zone (Dutton et al., 2002, 2006; Banga et al., 2011, 2002). Figure 4.3 shows a schematic cross-section of Raccoon Bend field and other previously studied fields in the basin.



Figure 4.1. Geopressured and meteoric water pathways for the Tertiary Gulf Coast progradational packages from Dutton et al. (2006) modified from Galloway (1982) and Galloway et al. (1982). Location of this study's Wilcox-producing wells is circled and labeled based on depth and pressure information (see Method 5.1 for well information).



Figure 4.2. (a) Pressure versus depth plot and (b) temperature versus depth plot of Raccoon Bend samples and additional Raccoon Bend wells. Data was obtained from well-log headers (Sandalwood Oil & Gas and Railroad Commission of Texas, 2012). A hydrostatic gradient of 10.74 MPa/km and a lithostatic gradient (P_L) of 23.1 MPa/km (1 psi/ft) are used for Gulf Coast brines (Fertl, 1975; Kharaka et al., 1977). The calculated pressure gradient for Raccoon Bend wells is 12.3 MPa/km and the temperature gradient is 33°C/km (see Methodology 5.1).



Figure 4.3. Modified schematic cross-section of Raccoon Bend salt dome field and previously studied southeast Texas Gulf Coast basin fields from Banga, 2006. Sources of stratigraphic data: Miller (1942), Halbouty and Hardin (1951), Bebout (1976), Moran (2003), Teas and Miller (1933), and Swenson (2012, personal *communication*). Grey boxes indicate sampling zones: W.Columbia (Hyeong and Capuano, 2001), Chocolate Bayou (Hyeong and Capuano, 2001), South Liberty (Banga et al., 2011; Banga, 2006), and Sabine Tram (Moran, 2003). Star indicates formation where rock sample was obtained. Abbreviations used: M= Miocene, An= Anahuac, Fr= Frio, V-J= Vicksburg-Jackson, Y-C= Yegua-Cook Mountain, W= Wilcox, LWX= lower Wilcox, MWX= middle Wilcox, and UWX= upper Wilcox. Wilcox formations are defined based on Xue and Galloway (1993, 1995) and Xue (1994).

5. METHOD

For this study oil, water, and rock samples were collected from the Wilcox Group at the Raccoon Bend field, and water and oil samples were collected from the Jackson Group and Miocene formation at Raccoon Bend. Rock samples from the Austin Chalk and the Eagle Ford were obtained from a well near the dome, the E.Sorsby #1 well. In addition, geophysical well logs for selected wells were obtained from a field operator, Sandalwood Oil & Gas.

5.1 Temperature and pressure calculations

Temperature and pressure data were obtained from 52 well logs at Raccoon Bend field. This data is from both sampled wells and wells not sampled. All well data was obtained from well log headers obtained from Sandalwood Oil and Gas or from the Railroad Commission of Texas website (Railroad Commission of Texas, 2012a). The temperatures obtained from well logs are bottom-hole temperatures (BHT) that are measured during each logging run. BHTs in older wells have to be corrected because they are not accurate values for formation temperatures due to the drilling fluid circulation that causes cooling of the borehole fluids (Hanor, 1987). Once drilling is stopped, the temperature of the borehole begins to equilibrate with the formation temperature; this is called equilibrium temperature (T_e). Equilibrium temperatures can be estimated by the following equation from Kehle (1971):

 $T_e(^{\circ}F)=T_1(^{\circ}F)-8.819\times10^{-12}\times D^3(ft)-2.143\times10^{-8}\times D^2(ft)+4.375\times10^{-3}\times D(ft)-1.018$ (1) where T₁ is the BHT obtained from well log and D is depth in feet. Wells that were corrected for BHT are noted in Appendix 1. Formation pressure (P_f) can be calculated from mud weight information obtained from well logs. Mud weights were converted to formation pressure (P_f) using the equation from Hanor (1988):

$$P_f(MPa) = mudweight\left(\frac{lbs}{gal}\right) \times 0.052 \,\left(\frac{gal}{in^2 ft}\right) \times D(ft) \times 0.0069 \,\left(\frac{MPa}{psi}\right)$$
(2)

Using a best fit line for the measured and corrected data an average temperature gradient of ~33°C/km and an average pressure gradient of 12.3 MPa/km (0.55 psi/ft) was calculated for Raccoon Bend field. The calculated average temperature gradients and pressure gradient were used to extrapolate the average temperature and pressure at sampling depths from the bottom-hole data because those depths are shallower than the bottom-hole depths. These values are shown in Appendix 1.

5.2 Oil samples

Seven oil samples were collected from the Raccoon Bend field. Five of these oil samples were collected from the Wilcox Group, one from the Lower Wilcox formation and the other four from the Upper Wilcox formation. The remaining two samples were collected from younger formations at Raccoon Bend, the Jackson and Miocene, for comparison with Wilcox oils. All seven of these samples were analyzed by gas chromatography (GC) and then two were selected for biomarker analyses. Information on these seven samples is given in Table 6.1 and their location on the map in Figure 3.2.

This study focuses on the comparison of the Wilcox oil molecular chemistry to other recent studies in the basin. The other oils used for comparison come from the S.

Liberty field (Frio, Yegua, and Cook-Mountain) (Banga et al., 2011; Banga, 2006) and from the Frio formation sampled from several Brazoria County fields, including Chocolate Bayou, West Columbia, Danbury, Damon Mound, Old Ocean, and Algoa-Orchard (Guo, 2004). The Frio oils from Brazoria County will be referred to as "Brazoria Oils" throughout the rest of this study.

5.2.1 Molecular chemistry of oil samples

The high-resolution whole-oil gas chromatography analyses on seven oil samples determined the C₄-C₃₅ molecular composition using a Hewlett Packard (HP) 6890 GC with HP 7673 liquid auto sampler, a split/splitless injector, a flame ionization detector (FID), and 100m x 0.25mm x 0.25 μ m HP-1 column. API gravities were calculated for the seven oils using a density meter (DMA 48 by PAAR) to measure each oil samples density. Then the densities were plugged in to the API equation below (American Petroleum Institute):

$$API(^{\circ}) = 141.5 / oil \ sample \ density - 131.5 \tag{3}$$

Two samples were selected for SARA separation (saturates, aromatics, resins, asphaltenes) and PIN fractions (n-paraffins, iso-paraffins, and naphthenes, respectively). The two oil samples selected for SARA separation were fractionated into their different SARA components using the multidimensional, high-performance liquid chromatography (HPLC) method developed by Bissada et al. (2003). Saturate fractions were also separated into PIN components using the same HPLC method and then further analyzed in the Gas-Chromatography-Mass Spectrometry (GC-MS) for biomarkers. The biomarker compositions are used to help determine the source and maturity of the

respective oils. SARA and PIN data are given in Table 6.2. Biomarker data from the GC-MS analyses is given in Table 6.4 and 6.5. Saturate and aromatic components for the two samples were also used for stable carbon isotope analysis.

5.2.2 Stable carbon isotopes ($\delta^{13}C$) of oil samples

Stable carbon isotope values of the saturate and aromatic fractions were determined for the two oil samples subjected to biomarker analysis (UWX4-1 and LWX2-1). Saturates and aromatics were separated from the original oil sample using the HPLC machine as described above in Methodology 5.2.1. In addition, all seven whole oil samples were also analyzed for stable carbon isotope values for comparison and correlation with other studies and within the oils at Raccoon Bend. All stable carbon isotope analyses were performed using a Finnigan MAT 252 Isotope Ratio Mass Spectrometer (IRMS). The method for preparation and analysis can be found in Silverman and Epstein (1958) and Kennicutt et al. (1992). Analyses of the fractions and whole oil were used for oil-oil correlations and oil-source rock correlations. The equation for calculating the stable carbon isotope values of each oil fraction compared to the PDB standard is shown below (Faure, 1998):

$$\delta_{13}C_{sample} = \frac{\binom{{}^{13}C/{}^{12}C}_{sample} - \binom{{}^{13}C/{}^{12}C}_{stan\,dard}}{\binom{{}^{13}C/{}^{12}C}_{stan\,dard}} \times 1000(\%)$$
(4)

Stable carbon isotope values for the Raccoon Bend oils are shown in Tables 6.1 and 6.3.

5.3 Rock samples

Rock cuttings were collected from the Wilcox Group from a well in Raccoon Bend field and, for comparison, from the Cretaceous from a well off the salt dome flank. These cutting were analyzed for total organic carbon (TOC), percent vitrinite reflectance (R_0), and carbon isotopes (δ^{13} C). The Raccoon Bend well cuttings were obtained from the operator, Sandalwood Oil & Gas, and the cuttings from the well off the dome, E. Sorsby #1, were obtained from the Bureau of Economic Geology Core Center in Houston, Texas. The well locations are shown in Figure 1.1. The Raccoon Bend cuttings were selected based on well log characteristics and lithology for the Wilcox-aged Yoakum Shale and Big Shale. The E. Sorsby #1 cuttings were chosen from the Eagle Ford (5639m) and the Austin Chalk (5182m) based on well log interpretation and confirmed by micropaleontology reports (Swenson, *personal communication*, 2012). Well log correlation combined with micropaleontologic information indicates that the Eagle Ford sample is probably from the upper Eagle Ford, the lower Eagle Ford is apparently missing due to an unconformity.

5.3.1 Total organic carbon (TOC) of cuttings

Total organic carbon (TOC) analyses of the cuttings were conducted at the University of Houston Center for Petroleum Geochemistry (Elrod et al., 1985). Rock cuttings were ground and acidized, and heated to remove inorganic carbon before they were measured for TOC. TOC is used as an approximate measure of source rock's potential to generate hydrocarbons upon thermal maturation. Bissada et al. (p.124, 1990) reasons, "Although it is probably unrealistic to preclude any section from being considered a potential source rock bed solely on the basis of a rigidly establish minimum value of organic carbon content, empirical observations in producing and non producing areas suggest that potential source beds must contain at least 1.0% TOC in order to yield significant amounts of hydrocarbons."

5.3.2 Vitrinite reflectance (R_o) of organic matter in the cuttings

Vitrinite Reflectance (R_o) is used as a measure of the level of thermal maturity of sedimentary organic matter (e.g. Tissot and Welte, 1984). Vitrinite reflectance measurements require a photomultiplier-photometer to measure the proportion of incident light reflected from a polished specimen of vitrinite. Five grams of cuttings for each source interval were sent to National Petrographic Service, Inc. in Bellaire, Texas to be polished and prepared in thin-section. Measurements were conducted at the University of Houston Center for Petroleum Geochemistry using the methodology from the International Handbook of Coal Petrology (1963, 1971, 1975). Surfaces of polished vitrinite particles exhibit higher reflectivity with increased thermal maturity (Bissada et al., 1990). Vitrinite reflectance is a measure of percent (% of incident light that is reflected off the polished vitrinite surface and received by the photometer). Vitrinite reflectance measurements are used to create histograms where indigenous R_0 values can be distinguished from caved and recycled populations. Then the mean vitrinite reflectance values are calculated from the indigenous population along with the range, mode, and standard deviation.

5.3.3 Thermal alteration index (TAI) of sedimentary organic matter

Thermal alteration index (TAI) is another useful indicator of thermal maturity of sedimentary organic matter. Calculating thermal alteration index involves looking at the rock sample in thin section using transmitted light (Tissot and Welte, 1984, p. 515). Spores, pollen, and other microfossils are identified and using their progressive change in color, one can identify that microfossils' maturation (International Handbook of Coal Petrology, 1963, 1971, 1975).

5.3.4 Stable carbon isotopes of kerogen

Stable carbon isotope values of kerogen can be used to rule out a relationship between a parent source rock and oil. Stahl (1977, 1978) tested the relationship between known source rocks' stable carbon isotope values and its related oils' values. He found that the kerogen of the source rock should have carbon isotope signatures less negative when compared to the standard Pee Dee Belemnite values than the oils that were generated from the source rock. Carbon isotope analyses in this study are used to evaluate if Wilcox-aged shale can be the source of oil at Raccoon Bend field.

Stable carbon isotope analyses of kerogen from cuttings were conducted at the University of Houston Center for Petroleum Geochemistry using the method described in Silverman and Epstein (1958). Preparation of the samples included: grinding, weighing, and then twice soaking in hydrochloric acid overnight. Acid was removed from grinded sample by extensive washing with deionized water and then samples were dried in the oven at 70°C. Samples were ready for analysis after they were dry and all inorganic carbon was removed.

Hydrocarbon Generation vs. Kerogen Therma Maturity									
Hydrocarbon Generation Zones	Vitrinite Reflectance (Ro)	Thermal Alteration Index							
I Immature	>0.55%	<2.4							
II Initial oil	0.55-0.7%	2.4-2.6							
III Peak Oil Generation	0.7-1.3%	2.6-3.2							
IV Thermal degradation	1.3-2.0%	3.2-3.75							
V Intense orga nic metamorphi sm	>2.0%	>3.75							

Figure 5.1. Hydrocarbon generation zones identified by kerogen thermal maturity. Zone boundaries are from Bissada (1983). Vitrinite reflectance values have been added to their respective zones. Using the vitrinite reflectance values determined in this study, the Wilcox shales (Yoakum and Big Shale) are in the hydrocarbon generation Zone II. The Austin Chalk and Eagle Ford samples off the salt dome are currently in Zone III.

5.4 Water Samples

Water samples were collected in order to better understand the reservoir fluids and their subsequent migration pathways. Most of the wells sampled at Raccoon Bend that produced water from the Wilcox Group could not be sampled at the wellhead due to water-in-oil emulsions. The only well that provided a water sample of the Wilcox Group was UWX5-1, which was sampled at the wellhead and analyzed for δ^{18} O. Water was also collected from the Jackson Group (well RGP-45) and from the Miocene formation (well RBM3-1) and analyzed for δ^{18} O.

Stable isotopes of oxygen (δ^{18} O) were analyzed by Geochron Laboratories using a VG Micromass gas source stable isotope ratio mass spectrometer (Ghosh and Brand, 2003). These ratios are standardized to VSMOW using the equation:

$$\delta^{18} O = \frac{\left(\frac{18}{0} O/\frac{16}{0} O_{stan} \frac{18}{dr d}\right)^{16} O_{stan} \frac{dr d}{dr d}}{\frac{18}{0} O/\frac{16}{0} O_{stan} \frac{dr d}{dr d}} \times 1000(\%)$$
(5)

 δ^{18} O values are given in Table 6.1.

6. RESULTS

GC chromatographs for the seven Raccoon Bend oils studied are shown in Figures 6.1 and 6.2. Well name abbreviations, reservoir formations, sample depths, temperatures, pressures, API gravities, gas/water ratios, and GC parameters for these seven wells are reported in Table 6.1. It is apparent from the GC chromatographs that three of the samples (RBM3-1, RGP-45 and UWX8-1) are biodegraded. The GC traces and API values correlate well within the non-biodegraded and biodegraded groups with higher API values (34°) corresponding to minimum biodegradation and lower API values (18-24°) belonging to biodegraded oils (Figures 6.1 and 6.2).

Based on the similarity between the four non-biodegraded samples, SARA, PIN and biomarker analyses were completed on only two of these samples, UWX4-1 and LWX2-1. One sample is from the upper Wilcox (UWX4-1) and the other from the lower Wilcox (LWX2-1). They are from two neighboring fault blocks within the field, one uplifted relative to the other. The results of the SARA and PIN analyses are given in Tables 6.2, source biomarkers in Table 6.4 and maturity biomarkers in Table 6.5. SARA separations of UWX4-1 and LWX2-1 indicate that the Raccoon Bend oils consist of 60-70% saturates, 21% aromatics, 4-9% asphaltenes, and 6% resins (Table 6.2). Pin analyses of the saturate fraction (Table 6.2) show these oils are predominantly normal paraffins (39.6-50%) and naphthenes (47.3-50.6%) and iso-paraffin percentages are relatively low (2.7-9.8). The biomarker parameters are discussed in the following section.

Cuttings of possible source rocks were collected from two wells, one well from the Raccoon Bend field (UWX1-1) and the other samples from another well (E. Sorsby)
located 15 km northwest of the Raccoon Bend field. The well locations are shown on Figure 1.1. The two Raccoon Bend samples are of the Yoakum Shale (2082m) and Big Shale (2277m) both of the Wilcox Group, whereas the E. Sorsby well samples are of the stratigraphically older and deeper Austin Chalk (5182m) and Eagle Ford (5639m). These cuttings were analyzed for total organic carbon (TOC), percent vitrinite reflectance (R_0), Thermal Alteration Index (TAI), and carbon isotopes (δ^{13} C) and the results are presented in Table 6.6.

TOC of the Wilcox Group shale samples are 0.7 and 1.5%, of the Austin Chalk is 1.1% and of the Eagle Ford is 1.7% (Table 6.6). According to Bissada et al. (p.124, 1990), potential "source beds must contain at least 1.0% TOC in order to yield significant amounts of hydrocarbons." Thus, one of the Wilcox samples, the Austin Chalk, and the Eagle Ford shale samples all contain enough organic carbon to be a potential source rock. However, vitrinite reflectance and visual kerogen analyses of the Wilcox shale samples indicate that although Big Shale and Yoakum Shale are currently in the oil generation zone (Figure 5.1) they are probably not effectively releasing hydrocarbons at the present time (R_0 values 0.60-0.64%; T.A.I.: 2.4-2.6) (Figures 6.3, 6.4). In contrast, the Austin Chalk and Eagle Ford cuttings have R_0 values of 0.74% and 0.81% respectively and T.A.I. values of 2.6-3.0 (Figure 6.3, 6.4). These values correlate to Zone III in Figure 5.2 where hydrocarbon generation and expulsion occurs. However, all vitrinite reflectance histograms show a significant contribution of re-worked organic matter (Figure 6.3). High amounts of re-worked organic matter in combination with relatively low TOC values (less than 2) poses serious doubts that these rocks are the likely source rocks of the Raccoon Bend field oils.

Stable carbon isotope values (δ^{13} C) are shown in Table 6.1 for whole-oil samples and Table 6.3 for UWX4-1 and LWX2-1 for saturate and aromatic fractions. Whole-oil δ^{13} C values of the seven samples studied range from -26.9 to -28.9 ‰. The whole oil δ^{13} C values for UWX4-1 and LWX2-1 (-27.3 and -27.6 ‰) fall between the saturates δ^{13} C values (-30.6 and -29.9 ‰) and the aromatic δ^{13} C values (-25.6 and 27.1‰) which is expected since these oil samples are composed of predominately saturate and aromatic fractions. The heaviest δ^{13} C (-26.9‰) belongs to the shallowest and most biodegraded oil, RBM3-1.

 δ^{13} C kerogen values for the Wilcox-aged Big Shale and Yoakum Shale as well as the Upper Cretaceous Austin Chalk and Eagle Ford shale are shown in Table 6.7. The values range from -26.0 to -26.8 ‰ for all samples. All four rock samples have δ^{13} C values heavier (less negative) than the Raccoon Bend oils.

The stable oxygen isotope values are shown in Table 6.1 with other chemical properties obtained from the operating company. Stable oxygen isotopes values for the three samples show increasing values with depth a trend noted in other Gulf Coast water studies (Banga et al., 2011; Gell, 1999; Moran et al., 2003; Bourgeois, 1997; and Kharaka et al., 1977). This increase is interpreted to show increased mixing from geopressured fluid from below with meteoric water from above (Kharaka et al.1977; Banga et al., 2011). Using this interpretation, the Wilcox reservoirs at Raccoon Bend field are capable of receiving fluids, including hydrocarbons, from the geopressured section below through vertical or long-distance lateral migration.



Figure 6.1a-d. Whole-oil gas chromatographs from Wilcox Group oils at Raccoon Bend field. These oils show minimum biodegradation (normal paraffins and light-ends are still present).



Figure 6.2a-c. Whole-oil gas chromatographs of a Wilcox oil (UWX8-1), and two oils from reservoirs of younger formations (RGP-45 and RBM3-1). All three samples are biodegraded.

Table 6.1 Sample depth, API gravity, gas-oil ratio, brine chemistry, whole-oil GC attributes, biodegradation ranking, and whole oil carbon isotope values for Raccoon Bend Field.

							Brine C	hemistry Whole-Oil GC Attributes (Peak Area))	D 1	013 0 0 0 0					
Well Name	Short Name	Formatio n	Depth* (m)	Р ^ь (MPa)	T ^c (°C)	API ^d (°)	GOR	δ ¹⁸ Ο ^f (‰)	TDS ^g (mg/L)	Ргь	Phi	Pr/P h	Pr/ nC ₁₇	Ph/ nC18	P1/IIC ₁₇ :Ph/nC ₁	OEP"	on ranking ⁱ	oil ^k (‰)
Raccoon Bend UWX Unit 4-1	UWX 4-1	upper Wilcox	1939- 1997	25	66	34.2	562	n/a	n/a	2381	379.7	6.27	2.06	0.38	5.40	0.42	none	-27_3±.033
Raccoon Bend UWX Unit 5-1	UWX 5-1	upper Wilcox	1933- 1983	25	65	34.7	407	0.5	95243	3045	464	6.57	2.27	0.41	5.50	0.42	none	-27.3±.034
Raccoon Bend UWX Unit 8-1	UWX 8-1	upper Wilcox	2086- 2092	26	69	24.3	15699	n⁄a	n/a	155	31.30	4.96	1.82	0.43	4.24	0.42	very slightly	-27.2±.048
Raccoon Bend UWX 27-1	UWX 27-1	upper Wilcox	1979- 1992	25	66	34.2	1908	n/a	n/a	2651	414.6	6.38	2.19	0.41	5.32	0.42	none	-28.9±.282
Raccoon Bend LWX Unit 2-1	LWX2- 1	lower Wilcox	2019- 2025	26	67	34.4	n/a	n⁄a	n/a	3525	501.3	7.04	2.34	0.41	5.73	0.42	none	-27.6±.085
Robert G. Paine No.45	RGP- 45	Jackson	850- 855	11	28	21.8	n/a	-4.3	19781	142	54.11	2.62	1.74	0.55	3.16	n/a	moderately	-27.4±.033
Raccoon Bend Miocene Unit 3-1	RBM3 - 1	Miocene	633- 668	8.4	22	18.4	218	-3.8	2169	n/a	n/a	n/a	n/a	n/a	n/a	n/a	heavily	-26.9±.033

^aDepth: sampling depth

^bP: pressure at sampling depth

°T: temperature at sampling depth

^dAPI: API gravity (equation 3, section 5.2.1)

*GOR: gas/oil ratio obtained from operators and Railroad Commission of Texas (2012)

 $^{f\delta^{18}O:Stable}$ oxygen isotope value ($^{18}O/^{16}O$) relative to standard VSMOW (equation 5, section 5.4)

gTDS: total dissolved solids, calculated from equation 6, section 5.4

^hPr: pristane

ⁱPh: phytane

^jBiodegradation ranking:bioegradation ranking from Wenger et al., 2003

 $k\delta^{13}$ C Whole oil: stable carbon isotope values (13 C/ 12 C) relative to standard PDB (equation 4, section 5.2.2)

¹n/a: data not available

^mOEP: odd/even predominance calculated using $(nC_{27}+nC_{29}+nC_{31})/(4C_{28}+4C_{29})$ (Peters and Moldowan, 1993, p.219)

		Hydrocarb	ons	N	lon-hydro	ocarbons	Saturates (PIN)				
Well Names	Total (%)	Saturates (%)	Aromatics Total (%)		Resins (%)	Asphaltenes (%)	Normal Paraffins (%)	Iso-Paraffins (%)	Naphthenes (%)		
UWX4-1	89.8	68.0	21.8	10.2	6.2	4.0	39.6	9.8	50.6		
LWX2-1	85.0	64.0	21.0	15.0	5.9	9.1	50.0	2.7	47.3		

Table 6.2 Group-type separations of the Raccoon Bend oils into hydrocarbon and non-hydrocarbon components.

Table 6.3 Stable carbon isotope values (‰) for whole-oil and saturate and aromatic fractions of two Wilcox oil samples.

Well Names	$\delta_{13}C_{saturates}$	$\delta_{13}C_{aromatics}$	$\delta_{13}C_{whole \; oil}$
UWX4-1	-30.6	-25.6	-27.3
LWX2-1	-29.9	-27.1	-27.6

Table 6.4 Source-related biomarker attributes of the Raccoon Bend oils and interpreted source rock environments. South Liberty and Brazoria oils are shown for comparison.

Source Biomarker Attributes	Raccoon	Bend Oils	South Liberty Oils Range of	Brazoria Oils Range of	Inferred Source-rock Environment for			
	UWX4-1	LWX2-1	Values ^a	Values	Kaccoon Bend Field Olis			
(C35/C3135) homohopane index	0.03	0.03	0.00-0.04 °	0.00-0.04	Oxic			
Gammacerane index	0.01	0.02	0.00-0.03 ^d	0.01-0.03	Not hypersaline			
Tricyclics/17 α hopanes	0.01	0.06	0.04-0.08 ^h	0.02-0.03	Terrestrial organic matter			
Regular steranes/17 α hopanes ^g	0.34, 0.24	0.15, 0.21	0.19-0.34, 0.12-0.24 ^h	0.1-0.14	Terrigenous and/or microbially reworked organic matter			
Bisnorhopane/hopane	0.17	0.14	0.06-0.39	n/a ⁱ	Not anoxic			
Oleanane/hopane	0.21	0.13	0.08-0.14	0.07-0.19	Some angiosperm input			
C ₃₂ (S/S+R) homohopane	0.56	0.56	0.55-0.66	n/a ⁱ	No recent contamination			
(C ₃₅ /C ₃₄) homohopane	0.60	0.53	0.31-0.70*	n/a ⁱ	Clastic/oxic			
Diasterane/regular sterane ^f	0.55-1.03	0.57-1.10	0.94-1.43	0.73-1.19	Inconclusive			
(C_{27}/C_{29}) Regular sterane ⁸	1.19, 0.40	1.03, 0.30	1.33-1.84, 0.42-0.55 ^h	n/a ⁱ	Inconclusive ⁱ			
(C_{29}/C_{27}) Regular sterane ^g	0.84, 2.47	0.96, 3.36	0.54-0.75, 1.82-2.38 ^h	n/a ⁱ	Inconclusive			
$C_{21}/(C_{21}-C_{20})$ sterancs ⁸	0.42, 0.20	0.40, 0.16	0.44-0.51, 0.20-0.24 ^h	0.39-0.48	Inconclusive			
$C_{22}/(C_{27}-C_{29})$ steranes ⁸	0.23, 0.32	0.21, 0.29	0.15-0.23, 0.23-0.33 ^h	0.21-0.26	Inconclusive ⁱ			
$C_{29}/(C_{27}-C_{29})$ sterancs ⁸	0.35, 0.49	0.39, 0.55	0.28-0.34, 0.43-0.54 ^h	0.32-0.35	Inconclusive ⁱ			
C ₃₀ /(C ₂₇ -C ₂₉) steranes ⁸	0.04, 0.05	0.04, 0.05	0.03-0.08, 0.04-0.23 ^h	0.01-0.09	Terrestrial (higher plant input)			

^aSouth Liberty oils from Banga et al., 2011

^bBrazoria oils from Guo, 2004

°0.00-0.04: 3 out of 5 samples had C35 homohopane absent

^d0.00-0.03: 4 out of 5 samples had gammacerane absent

e0.31-0.70: 3 out of 5 samples had C₃₅ homohopane absent

¹Diasterane/regular sterane: ratio is given in range for Raccoon Bend oils due to coelutions of $C_{27}R-\alpha,\beta,\beta$ -cholestane with $C_{29}S-\beta,\alpha$ -diacholestane and (20R)-24-methyl-13 α ,17 β -diacholestane with (20S)-24-methyl-5 α ,14 β ,17 β -cholestane (section 7.4.5)

^gsterane(s):g. sterane calculations for Raccoon Bend oils and S.Liberty oils were calculated with the coelution values for C_{27} 5 α , 14 β , 17 β -cholestane (S&R) to indicate the maximum value for each steranes parameter (top value) and without using the coelution values (bottom value) to indicate the minimum value for each parameter

hitalics: values for S.Liberty were recalculated based on source related parameter equations (Appendix 2) and for coeluted and non-coeluted values (section 7. 6) in order to be consistent with correlation

ⁱn/a: data not available

JInconclusive: see section 7.4.5 for explanation on why these sterane source biomarker attributes are inconclusive

Inferred Source-rock Environment for Raccoon Bend Field Oils: see text for method of determination

Table 6.5 Maturity-indicating biomarker attributes of the Raccoon Bend (this study), S. Liberty (Banga et al., 2011) and Brazoria oils (Guo, 2004). See appendix 2 for isomers used in biomarker ratios.

Maturity Biomarker Attributes	Published Indicators of	Ro at equilibrium	Raccoon	Bend Oils	South Liberty Oils Banga of	Brazoria Oils Bango of	
	Equilibrium	(%)	UWX4-1	LWX2-1	Values	Values	
22S/(22S+22R) C ₃₁ homohopane	0.57-0.62ª	0.6	0.58	0.59	0.52-0.57	0.53-0.58	
22S/(22S+22R) C ₃₂ homohopane	0.57-0.62ª	0.6	0.56	0.56	0.55-0.66	0.55-0.60	
22S/(22S+22R) C ₃₃ homohopane	0.57-0.62ª	0.6	0.6	0.59	0.56-0.83	0.57-0.59	
22S/(22S+22R) C ₃₄ homohopane	0.57-0.62ª	0.6	0.57	0.62	0.00-0.78	0.56-0.64	
22S/(22S+22R) C ₃₅ homohopane	0.57-0.62ª	0.6	0.49	0.54	0.00-0.67	0.52-0.62	
22S/(22S+22R) C ₃₁₋₃₅ homohopane total	0.57-0.62ª	0.6	0.57	0.58	0.55-0.63	0.56-0.60	
$\beta \alpha$ -mortanes/ $\alpha \beta$ -hopanes and $\beta \beta$ -hopanes	0.05-0.15 [⊾]	0.7	0.27	0.24	0.17-0.21	0.09-0.20	
Tricyclics/(tricyclics+17α(H)-hopanes)	1.00°	1.4	0.09	0.06	0.47-0.57	n/a ^h	
Ts/(Ts+Tm) ^f	1.00°	1.4	0.29	0.27	0.43-0.57	0.45-0.51	
Diasterane/(diasterane+regular sterane)	1.00°	1.4	0.36-0.51 ^f	0.34-0.49 ^f	0.49-0.59	n/a ^h	
20S/(20S+20R) C ₂₉ sterane	0.52-0.55 ^d	0.8	0.51	0.5	0.24-0.45 ^g	0.35-0.40	
$\beta\beta/(\beta\beta+\alpha\alpha)C_{29}$ sterane	0.67-0.71 ^d	0.9	0.49	0.46	0.50-0.63 ^g	0.38-0.51	

a. Seifert and Moldowan (1980) and Zumberge (1987)

b. Seifert and Moldowan (1980) and Grantham (1986)

c. Seifert and Moldowan (1978)

d. Seifert and Moldowan (1986)

e. Ro at equilibrium from Peters and Moldowan, 1993, p.226

f. Ratio is given in range due to coelutions of C27R- α , β , β -cholestane with C29S- β , α -diacholestane and (20R)-24-m ethyl-13 α , 17 β -diacholestane with (20S) 24-m ethyl-13 α , 18 β -diacholestane with (20S) 24-m ethyl-13 α , 18 β -diacholestane with (20S) 24-m ethyl-13

(20S)-24-methyl- 5α , 14β , 17β -cholestane (See Table 6.5 and 7. Results)

g. Italicized values for S, Liberty were recalculated based on source related parameter equations (Appendix 2) in order to be consistent with correlation

h. n/a= not available

i. i at an intermediate ratio of 0.25 Ro = 0.6%

Table 6.6 Group, age, depth, TOC, R _o , TAI, and stable carbon isotope values for two rock cuttings sampled from the middle
Wilcox formation at Raccoon Bend field and for two rock cuttings sampled from the Austin Chalk and Eagle Ford formations

Well Name	API #:	Operator	Field	Group	Age (Mya)	Depth (m)	Sample Type	TOC ^f (wt. %)	R. ⁸ (%)	TAI ^h	δ ¹³ C ⁱ (‰)
UWX1-1ª	4201530968	Sandalwood Oil & Gas	Raccoon Bend	Wilcox (Yoakum Shale)	~54.3°	2073- 2082	cuttings	0.72	0.60	2.4- 2.6	-26.5±.023
UWX1-1ª	4201530968	Sandalwood Oil & Gas	Raccoon Bend	Wilcox (Big Shale)	~56.5°	2271- 2277	cuttings	1.50	0.64	2.4- 2.6	-26.0±.038
E.Sorsby-1 ^b	4237430320	Placid Oil Co.	Wildcat	Austin (Austin Chalk)	~89 ^d	5163- 5182	cuttings	1.07	0.74	2.6- 3.0	-26.4±.044
E.Sorsby-1 ^b	4237430320	Placid Oil Co.	Wildcat	Eagle Ford (upper Eagle Ford)	~94°	5547- 5639 *	cuttings	1.70	0.81	2.6- 3.0	-26.8±.024

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a. UWX1-1 cuttings obtained from well operator

b. E.Sorsby-1 cuttings obtained from Bureau of Economic Geology's Houston Core Center

c. ages from Xue and Galloway (2000) and Haq et al. (1987,1988)

d. age from Grabowski (1981)

e. age from Liro et al. (1994)

f. TOC= total organic carbon content

g. R_o= mean vitrinite reflectance values

h. TAI= thermal alteration index

i. $\delta^{13}C$ = stable carbon isotope ratio ($^{13}C/^{12}C$) compared to standard Pee Dee Belemenite

j. intervals missing due to unavailability for sampling

Table 6.6 Group, Age, depth, TOC, Ro, TAI, and stable carbon isotope values for two rock cuttings sampled from the middle Wilcox formation at Raccoon Bend field and for two rock cuttings sampled from the Austin Chalk and Eagle Ford formations.



Figure 6.3 Vitrinite Reflectance (R_o) histograms for four potential source rock samples. A and b) are from the cuttings of the UWX1-1 well at Raccoon Bend field. C and d) are from a well off the Raccoon Bend field salt dome (E.Sorsby-1) and are also samples from cuttings. For well locations see Figure 5.1. In figure d, the asterisk by the depth interval indicates the interval 5554-5584m was not available for sampling. The light grey values indicate each sample's indigenous population. Dark grey values that are higher than indigenous R_o populations show a significant contribution of reworked organic matter in these samples (Bissada, *personal communication*, 2012; Tissot and Welte, 1984, p.516-519).



Figure 6.4a-d. Kerogen types shown in volume percent for the four cuttings samples.



Figure 6.5. δ^{18} O versus depth plot for Raccoon Bend brine samples (this study) compared to brine samples from the S. Liberty Field (Banga et al., 2002; Banga, 2006) and Brazoria County (Kharaka et al., 1977). The increase in δ^{18} O with depth supports mixing resulting from geopressured brines downdip migrating laterally to Raccoon Bend field and/or brines migrating from below the Wilcox Group at Raccoon Bend vertically through faults. Geopressured brines from Brazoria County are shown in the grey box from Kharaka et al., 1977.

7. DISCUSSION

In the discussion that follows it is shown that the Wilcox-reservoired oils at Raccoon Bend field possess organic geochemical characteristics that provide evidence of entrainment from high-energy lignite-bearing carrier beds of the Wilcox Group. This evidence of entrainment is best seen in whole-oil GC attributes.

Raccoon Bend oils belong to a single genetic family. Three of the samples show evidence of biodegradation ranging from very slightly biodegraded to heavily biodegraded. The Raccoon Bend oils show similar characteristics in their light-end C_7 isomers with S. Liberty field (Banga et al., 2011); however, the Raccoon Bend oils have distinguishably higher pristane values and a strong odd/even predominance of the C_{27} - C_{31} n-paraffins (Figures 7.1, 7.8, 7.9, 7.10). Entrainment from immature coal-rich carrier beds by solubilization has been documented in Gippsland Basin of Australia providing an analogue for this geochemical problem (Grantham, 1986) (see section 7.4 below).

This study interprets biomarkers with caution due to the strong evidence of entrainment because it is unclear if the overprinting affects any or all biomarker parameters for source environment and maturity indicators. Source rock-oil correlations indicate the Wilcox Group at Raccoon Bend is not the source rock of the Raccoon Bend oils. No effective source rock could be identified in source rock-oil correlations; therefore, downdip source rocks as well as deeper source rocks at Raccoon Bend are postulated as potential source rocks for the Raccoon Bend oils.

7.1 Evidence of biodegradation

Aerobic bacteria are the primary cause of biodegradation of reservoired hydrocarbons (Milner et al., 1977; Palmer, 1984). Anaerobes such as sulfate reducers are also know to degrade oil, although more slowly, and are thought to need aerobes to initiate degradation (Jobson et al., 1979). The conditions for biodegradation caused by aerobic bacteria are: 1) access to surface recharge waters containing oxygen, 2) temperatures less than 80°C, 3) petroleum free of H₂S (Peters and Moldowan, 1993, p.252). If these conditions are met, aerobic bacteria will destroy the petroleum in a systematic way and will decrease the API gravity of the oil.

Slight biodegradation is evident in all Raccoon Bend oils shown by the reduction in peak heights below nC₁₀ in all samples indicating a loss of some light-end hydrocarbons (Figure 6.1) (Banga et al., 2011). This is also apparent by the naphthenic nature of these oils indicating some biodegradation has occurred (Tissot and Welte, 1984, p.423) (Figure 7.4a). Further biodegradation is apparent in the GC traces of three of the samples from the Raccoon Bend field (UWX8-1, RGP-45, and RBM3-1) (Figure 6.2). In these samples, the GC fingerprint contains a "hump" that rises significantly from the baseline. This hump is known as an 'unresolved complex mixture', and its poor resolution makes it difficult to correlate the biodegraded oils to the non-biodegraded oils (Milner et al., 1977; Rubinstein et al., 1977; Killops and Al-Juboori, 1990; Peters and Moldowan, 1993, p.253-255). These three biodegraded oils are also characterized by having lower API values which can be attributed to the effects of biodegradation which is known to selectively remove saturates and aromatics (Peters and Moldowan, 1993, p.255). Biodegradation can range from light to severe for oil samples. Wenger et al. (2003) developed a scale for assessing the extent of biodegradation based on the relative abundances of certain hydrocarbon compounds and compound classes. According to the biodegradation scale, RBM3-1 is heavily degraded. Due to its heavy level of biodegradation, RBM3-1 is not included in the group referred to as "Raccoon Bend oils" in the discussion and figures that follows. UWX8-1 is classified as slightly biodegradation and RGP-45 is classified as moderately biodegradation and both are included in the correlation of Raccoon Bend oils as well as comparison with other studies in the basin. δ^{13} C values also agree with these biodegradation levels (Table 6.1); RBM3-1 whole oil has a heavier δ^{13} C value (-26.9‰) than those of UWX8-1 (-27.2‰) and RGP-45 (-27.4‰) consistent with a greater loss of saturate (¹²C enriched) components as a result of biodegradation (Peters and Moldowan, 1993, p.127).

Additional identification of relative amounts of biodegradation in the Raccoon Bend oils was assessed by the C₇ oil-transformation ratio (Figure 7.5) (Halpern, 1995) and toluene/n-heptane ratios relative to n-heptane/methylcyclohexane ratios (Figure 7.6) (Thompson, 1983). From these additional figures, it is clear that RGP-45 is more biodegraded than UWX8-1 and agrees with Wenger et al. (2003)'s biodegradation scale that RGP-45 is more biodegraded than UWX8-1.

 δ^{18} O analyses of water collected from wells RGP-45, RBM3-1, and nonbiodegraded UWX5-1 indicate that a fraction of meteoric water is likely present in all of these reservoirs (Table 6.1 and Figure 6.5), but more so in the shallowest most biodegraded samples (RGP-45 and RBM3-1) as suggested by the lighter δ^{18} O of these samples which is more similar to meteoric water in the area than the deeper sample (UWX5-1) (Figure 6.5). The greater meteoric water component associated with the oils from RBM3-1 and RGP-45 is also supported by the lower dissolved solids contents (TDS) of the water from these wells (2,000 and 20,000 mg/l, respectively, Table 6.1) compared to 95,000 mg/l for water from a well with minimal biodegradation oil (UWX5-1).

Reservoir temperatures indicate that all wells sampled are below the 80°C temperature threshold necessary for biodegradation (Peters and Moldowan, 1993, p.252; Wenger et al., 2003), but the majority of the oils are not biodegraded. The greater salinity (higher TDS of 95,000mg/l, Table 6.1) in the UWX5-1 reservoir than RGP-45 (2,000 mg/l) and RBM3-1 (20,000 mg/l) is the probable reason for only slight biodegradation of UWX5-1. The source of higher salinity is possibly from upwelling of geopressured brines from below (Kharaka et al., 1977; Banga et al., 2002) or halite dissolution from the salt dome (Banga et al., 2002). It is possible that the very slightly biodegraded Wilcox oils at Raccoon Bend (UWX4-1, UWX27-1, UWX5-1, and LWX2-1) are protected from biodegradation due to their high salinity formation water and temperatures (ranging from 66 to 70° C), which are nearing the 80°C threshold (Grassia et al., 1996; Wenger et al., 2003). UWX8-1 differs from the above samples because it is biodegraded compared to the other Wilcox oils at Raccoon Bend, but it has a similar reservoir temperature and depth. UWX8-1 reservoir, however, is disconnected from UWX4-1, UWX5-1, and UWX27-1 identified by a different oil/water contact (Swenson, personal communication, 2012). The different oil/water contact and different migration history are most likely responsible for the different level of biodegradation seen in UWX8-1 compared to the other Wilcox oils at Raccoon Bend.

7.2. Evidence of a single family

All five Wilcox reservoir oils and the Jackson reservoir oil (omitting the oil from RBM3-1 from future discussion because it is too biodegraded for comparison) have very similar molecular characteristics indicating that they belong to a single genetic family. An evident similarity can be seen in the gas chromatographs of the non-biodegraded oil samples shown in Figures 6.1a-d and 7.1a. In these chromatographs, the relative abundances (mole %) of nC_{15+} normal paraffins show harmonic patterns that gradually decrease to the higher end. All of the Wilcox samples, including slightly biodegraded UWX8-1, show this C_{15+} normal paraffin distribution.

Secondly, oil samples were correlated using five lighter hydrocarbon components based on multi-branched C_7 compounds which have been identified as compounds resistant to transformation processes (Halpern, 1995). Transformation processes include biodegradation, water washing, thermal alteration, and evaporation; therefore, biodegraded samples UWX8-1 and RGP-45 could be used in this correlation. All six samples show similar values for these five components (Figure 7.2a), which strongly supports a single genetic family. Further evidence using C_7 alkane isomer distributions is shown in Figures 7.4a and 7.4b. The six oils were plotted relative to their percentages of: normal + iso-alkanes, aromatics, and cyclo-alkanes in Figure 7.4a (oil classification adopted from Tissot and Welte, 1984, p.416-423) and all the oils are clustered together plotting as naphthenic oils, with the most degraded sample RGP-45, as expected, the most naphthenic. In Figure 7.4b, Raccoon Bend oils are plotted relative to their C_7 compound percent of normal-alkanes, iso-alkanes, and cyclo-alkanes, and all the oils again plot next to one another providing more evidence of a single genetic family. Using the C_7 alkane isomer distribution plots (Figures 7.4a and 7.4b) and SARA fractionation groups (Table 6.2), the Raccoon Bend oils fall in the naphthenic class of oils.

A third correlation technique using isoheptane parameters exhibits a linear correlation (after Mango 1990, 1997) that further provides evidence of a single family (Figure 7.3a and 7.3b). A linear correlation suggests that the oils likely generated from the same source rock.

A fourth correlation technique uses the whole-oil δ^{13} C values of the Raccoon Bend wells (Table 6.1). Again omitting the heavily biodegraded sample RBM3-1, all the Raccoon Bend oils have δ^{13} C values that lie within a narrow range -27.2 to -27.6 ‰, with the exception of UWX27-1 with a value of -28.9 ‰. UWX27-1 is more negative compared to the other oils possibly because it has a higher percentage of saturates than the other oils or it could be analytical problems. The standard deviation for UWX27-1 is larger (± 0.282) than that of the other samples by an order of magnitude and although it does not place UWX27-1 in the range of the other samples, it may indicate a low detection signal that contributed to a poor measurement and the δ^{13} C might not be an accurate value for UWX27-1. Excluding UWX27-1 as a possible outlier and RBM3-1 due to biodegradation, the five remaining Raccoon Bend oils support a positive correlation with whole oil δ^{13} C values ranging from -27.3 to -27.6 because they differ by no more than 1‰ (Peters and Moldowan, 1993, p.126).

Lastly, molecular abundances of the terpane (m/z 191) and sterane (m/z 217) biomarkers show similar distributions for UWX4-1 and LWX2-1 showing that these two samples likely belong to the same family (Tables 6.4 and 6.5). Based on the four correlation techniques above and the proximity of all wells sampled, the characteristics of the two wells analyzed for biomarkers, UWX4-1 and LWX2-1, accurately represent the other Wilcox oil samples in this study that were not analyzed for biomarkers. Using the C_{15+} normal paraffins abundance, light hydrocarbon multi-branched C_7 compounds, isoheptane parameters, stable carbon isotope values, and biomarker abundances, all correlations indicate a single genetic family and therefore it is highly likely that all of these oil samples were generated from the same source rock and have the same level of maturity.



Figure 7.1. a) C_{15} + normal paraffin distribution for Raccoon Bend Wilcox oils (this study). There is strong odd/even predominance in the C_{27} - C_{31} range which is characteristic of immature source rocks with significant input of land-plant organic matter (Peters et al., 2005, p.493). b) C_{15} + normal paraffin distribution for S Liberty (Banga et al., 2011) and Brazoria Oils (Guo, 2004, shaded region) showing the harmonic depletion of C_{15} + normal paraffins for S. Liberty oils (from Banga et al., 2011).



Figure 7.2. a) C_7 oil correlation star diagram (Halpern, 1995) for the Raccoon Bend oils (this study). GC correlation parameters are based on compounds resistant to transformation processes. RBM3-1 is not shown because it is heavily degraded and does not contain the shown compounds. Note RGP-45 and UWX8-1 although biodegraded show the same pattern as the other Raccoon Bend samples supporting they are all from the same genetic family and that differences are likely a result of biodegradation. b) C_7 oil correlation star diagram for S Liberty oils (from Banga et al., 2011). The C_7 ratios plot similarly for Raccoon Bend oils and S. Liberty oils suggesting that they belong to the same genetic family (Halpern, 1995).



Figure 7.3 (a and b) C_7 oil correlation of Raccoon Bend oils (this study) based on steady-state kinetic model of light hydrocarbon generation (after Mango, 1987, 1990, 1997). RBM3-1 is not shown because the sample is so severely biodegraded it does not contain the light end compounds used for the above correlations. MH= methylhexane; DMP=di-methylpentane; DMCP= dimethylcyclopentane; P2= 2-MH+3-MH; N2= 1,1-DMCP + 1,3-(cis+trans)-DMCP.



Figure 7.4. a) C_7 alkane isomer distribution of the Raccoon Bend oils (this study) compared to S Liberty oils (Banga et al., 2011). Oil-classification scheme is adapted from Tissot and Welte (1984). b) Comparison of C_7 alkane isomer distribution of Raccoon Bend Oils (this study), S. Liberty Oils (Banga et al., 2011), and Brazoria oils (Guo, 2004). Brazoria oils include samples from Chocolate Bayou, West Columbia, and Algoa-Orchard fields.



Figure 7.5. C₇ oil-transformation ratio (Tr) star diagram (Halpern, 1995) adapted for Raccoon Bend oils.



Figure 7.6_Toluene/n-heptane versus n-heptane/methylcyclohexane plot of the Raccoon Bend oils (this study). The extent of original oil noted by the gray area and the oil-alteration directions are from Thompson (1987).



Figure 7.7. n-heptane/1,1-dimethylcyclopentane ratios for the Raccoon Bend oil samples (this study).

7.3 Interpretation of the source environment

In oil correlation studies, the source environment is inferred from the molecular chemistry of the oils. Oil characteristics such as C_{15} + distribution, Pristane/Phytane (Pr/Ph) ratios, Pr/n- C_{17} versus Ph/n- C_{18} ratios, Pr/Ph versus

dibenzothiophene/phenanthrene (DBT/Phe), and certain saturate biomarkers all have been used to infer organic matter input and source rock depositional environment (Powell and McKirdy, 1975; Shanmugam (1985); Hughes et al., 1995). However, caution must be taken when using these parameters without an understanding of hydrocarbon migration history as many of these characteristics may be the result of solubilization of material along a secondary migration pathway or of the hydrocarbon reservoir causing changes that are unrelated to the migrating oils and therefore would not reflect the source rock environment (Peters and Moldowan, 1993, p.266). Although solubilization of biomarkers is believed to be rare (Peters and Moldowan, 1993, p.268), it has been observed where migration occurs through organic-rich coals such as Australia (Philp and Gilbert, 1982, 1986). The Wilcox Group at Raccoon Bend was deposited in a delta complex consisting of delta sands, muds, and lignites (Fisher and McGowen, 1967) and numerous lignites are seen in the lower Wilcox at Raccoon Bend (Swenson, 2012, *personal communication*); therefore, it is concluded that the Raccoon Bend oils provide evidence of entrainment from high-energy Wilcox lignite beds. Evidence of this entrainment can be seen in GC fingerprints of whole oils at Raccoon Bend (discussed below) and because of this, biomarker analyses are not useful for source rock environment inferences.

7.3.1 C_{15} + distribution

Gas chromatograph fingerprints for the Raccoon Bend oils show a harmonic decrease in C_{15} + distribution (Figures 6.1, 6.2 and 7.1a), which is a known attribute of marine-sourced oils (Bissada, 1993). However, the relative distribution of the C_{15} + nparaffins shows a dominant odd over even normal paraffin distribution in the nC_{27} - nC_{31} range (Figure 7.1a). This is also evident in the odd-to-even preference (OEP) (Peters et al., 2005, p.493) calculated for the five Wilcox-reservoired Raccoon Bend oils, which is 0.42 for all the samples (Table 6.1). OEP values much less than one indicate thermally immature oil (Peters and Moldowan, 1993, p.219). The Raccoon Bend oils are inferred to be thermally mature (see section 7.6 below) and therefore the odd/even predominance of nC_{27} - nC_{31} in Raccoon Bend oils is attributed to entrainment from the immature highenergy lignite beds in the Wilcox.

The odd/even predominance seen in the C_{15} + distribution for Wilcox oils at Raccoon Bend (Figures 7.1a) are most similar to the GC fingerprints reported by Sassen (1990) of hydrocarbons isolated from Wilcox rock. C_{15} + distributions dominated by nC_{27} , nC_{29} , and nC_{31} is a characteristic of immature source rocks with significant input of terrigenous organic matter (Peters et al. 2005, p.493). This suggests that at Raccoon Bend the lignite-bearing Wilcox units that the oils are reservoired in and possibly migrated through are responsible for the odd/even predominance and it is not a true characteristic of the oils from their parent source-rock.

7.3.2 Pristane versus Phytane

Pristane versus phytane analysis is very useful for correlation in geochemical studies. When oil samples are mature, Pr/Ph ratios greater than 3 have an inferred terrigenous organic matter input with a source rock deposited in an oxic environment (Peters and Moldowan, 1993, p.118, 150). Pr/Ph ratios less than 0.6 indicate anoxic, hypersaline source rock depositional environment (Peters and Moldowan, 1993, p.118, 150). Pristane and phytane can be affected by biodegradation. The non-biodegraded Raccoon Bend oils show Pr/Ph ratios between 6.3 and 7.0 (Table 6.1), whereas the two biodegraded Raccoon Bend oils, have lower Pr/Ph ratios of 2.6 (RGP-45) and of 5.0 (UWX8-1). These lower values compared to the non-biodegraded Raccoon Bend oils could be a consequence of biodegradation (Peters and Moldowan, 1993, p.255). Another explanation could be that RGP-45 is not reservoired in the coal-bearing Wilcox Group and possibly did not migrate through the Wilcox Group and therefore may not have the overprinting of high pristane signatures present in the other Raccoon Bend oils, which are reservoired in the Wilcox. The values for non-biodegraded oils (6.3-7.0) suggest the source rock for the oils at Raccoon Bend was deposited in an oxic non-marine setting (Figure 7.9). However, this does not agree with the whole-oil GC fingerprints which support a marine source rock, therefore it is likely that the high Pr/Ph ratios are a result of entrainment, similar to the mechanism suggested above for the odd/even predominance.

7.3.3 Pristane/n- C_{17} versus Phytane/n- C_{18}

Isoprenoid/n-paraffin ratios are used in correlation studies to determine source environment. Pristane/n-C17 and Phytane/n-C18 ratios can be calculated and plotted to determine source environment (Figure 7.8). These ratios are affected by thermal maturation and therefore should be used with caution (Connan and Cassou (1980); Shanmugam (1985)). The Pr/n-C17 v. Ph/n-C18 plot for Raccoon Bend Wilcox oils implies these oils were generated from humic organic matter (peat-swamp source rock environment). The GC fingerprints are inconsistent with these oils being sourced from humic organic matter and therefore the isoprenoid/n-paraffin ratios are also the result of entrainment.

7.3.4 DBT/Phe versus Pr/Ph

The ratio of dibenzothiophene (DBT) to phenanthrene (Phe) can be used with the Pr/Ph ratio to infer the parent source rock environment from crude oils. These compounds can be measured from GCMS from aromatic fractions. A DBT/Phe ratio greater than one is indicative of carbonate source rocks and a ratio less than one supports generation from a shale source rock (Figure 7.10). The DBT/Phe ratio is suggested to indicate the availability of reduced sulfur in the depositional/diagenetic environment that is available to interact with the organic matter (Hughes et al., 1995) and therefore it may not be influenced by source facies like Pr/Ph. The combination allows for a more detailed source paleoenvironment to be identified; however, this source environment indicator can also be affected by entrainment. Raccoon Bend oils plot in Zone 4 which corresponds to a source rock depositional environment composed of fluvial/deltaic shale

and coal providing, rather than marine source rock as evidenced from the whole oil GC data, providing further evidence that these oils contain geochemical characteristics of lignite from Wilcox Group.

7.3.5 Sterane biomarkers (m/z 217)

Sterane biomarker parameters (i) diasteranes/regular steranes (ii) C_{27} - C_{29} sterane distribution and (iii) regular steranes/17 α -hopanes were used to identify the likely environment of deposition for the Wilcox oils' parent source rock. Raccoon Bend oils have two coeluted peaks involving two C_{27} regular steranes (5α , 14 β , 17 β (20S &20R). Because these C_{27} regular steranes are pairs, it is difficult to identify an approximate value for these steranes without being able to compare one to the other. Therefore in this study, sterane biomarker parameters were calculated using the coeluted peak areas for C_{27} steranes and calculated ignoring the coeluted peak areas for C_{27} steranes in order to provide a maximum value and a minimum value for each parameter. By using the maximum and minimum values, inferred source rock depositional environment was only interpreted when both values suggested the same environment (Table 6.4).

(i) Biomarker source parameter calculations involving diasteranes and regular steranes have even more uncertainty because one of the C_{27} regular steranes is coeluted with the C_{29} 13 β , 17 α (20S) diasterane. This creates a problem because it is unknown which coelution compound is the dominant area versus which compound is the less dominant, or what percentage of each comprises the peak area. Calculating the two scenarios (C_{27} sterane dominant and C_{29} diasterane dominant) for the Raccoon Bend oils allows for the discrepancy to

be observed and source-rock depositional environment inferences to be made but no accurate value, only a range, can be given (Table 6.4). Diasteranes/regular steranes ratios greater than 1 suggests clay-rich source rocks and ratios much less than 1 suggests anoxic clay-poor or carbonate source rocks (Mello et al., 1988; Bissada, 1993; Peters and Moldowan, 1993, p.190-192). Wilcox oils at Raccoon Bend have diasteranes/regular steranes ratios that fall between 0.55-1.10 (Table 6.4, Figure 7.11a), which does not support either a clay-poor or clay-rich source rock interpretation.

(ii)

The distribution of C_{27} - C_{29} steranes in crude oils has been used to identify the depositional environment of the parent source rock (Huang and Meinschein, 1979; Shanmugam, 1985; Peters and Moldowan, 1993, p.182-186). The minimum and maximum values for these C_{27} - C_{29} steranes in Raccoon Bend oils is shown in Table 6.4. If the coeluted C_{27} steranes are used in these calculations, the relative percent of each component is C_{27} : 42 and 40%; C₂₈: 23 and 21%; C₂₉: 35 and 39%. Relative percent of each component calculate without coeluted steranes is C₂₇: 16 and 20%; C₂₈: 29 and 32%; C₂₉: 49 and 55%. The coeluted values plot in a different depositional environment than the non-coeluted values (Appendix 3). C_{29}/C_{27} ratios have also been used to infer source rock environment (Bissada et al., 1993). Values including coeluted compounds for Raccoon Bend oils for this ratio are 0.84 and 0.96 and values calculated ignoring the coeluted compounds are 2.47 and 3.36. These calculated values also plot in different depositional environments (Appendix 3). The contradicting inferred source environments from the distribution of

 C_{27} - C_{29} steranes make them unreliable as source biomarker parameters in this study. Moldowan et al. (1985) cautions that using C_{27} - C_{29} distributions can be misleading because these parameters also compete with maturation effects.

(iii) Regular steranes/17 α -hopanes greater than 1 indicate crude oils were generated from marine organic matter with major contributions from planktonic and/or benthic algae (Moldowan et al., 1985; Peters and Moldowan, 1993, p.178-180). Ratios less than 1 indicate the source organic matter is terrigenous and/or microbially reworked organic matter (Tissot and Welte, 1984, p.427-430). Raccoon Bend Wilcox oils regular steranes/17 α -hopanes ratios are 0.34 and 0.15 for calculations using coeluted values and this suggests the source organic matter is likely terrigenous. Ratio calculations without using coeluted values are 0.21 and 0.24 that agrees with the inferred terrigenous source organic matter.

Sterane biomarkers used in this study are interpreted with caution due to two coeluted C_{27} steranes. Regular steranes/17 α -hopanes and diasteranes/regular steranes have similar inferred source rock environments whether coeluted values are used in ratios or not; however, the inferred source environments from these two parameters don't agree because regular steranes/17 α -hopanes suggest terrigenous source rock organic matter and diasteranes/regular steranes ratios do not fall into the much-greater-than-1 category which is a characteristic of clay-rich source rocks which would be a characteristic of terrigenous source rock. Biomarkers are only a small fraction of the whole-oil geochemistry.

Therefore because entrainment is evident in whole-oil geochemistry, biomarker inferences

are suspect as the values could also be the result of overprinting from reactions with the Wilcox lignite.

7.3.6 Triterpane Biomarkers (m/z 191)

Triterpane biomarkers used in this study to evaluate source rock depositional environment are: (i) homohopane index (C_{35}/C_{31-35}), (ii) gammacerane index, (iii) bisnorphane/hopane, and (iv) oleanane/hopane.

- (i) Bissada et al. (1993) and Peters and Moldowan (1991) suggest ratios less than 1 for C_{35} -homohopane relative to total C_{31-35} homohopanes indicates clastic, oxic, low-salinity, non-marine source rock depositional environments. Raccoon Bend values are 0.03 for both samples, suggesting an oxic, lowsalinity, non-marine environment. Figure 7.11b also shows a decreasing ratio from C_{31} to C_{35} This decrease also supports a non-marine, oxic, low-salinity depositional environment (Bissada et al., 1993).
- (ii) The gammacerane index (gammacerane/C₃₀ 17α-hopane) is used to identify hypersaline environments (Peters and Moldowan, 1993, p.159-160).
 Gammacerane index values for Raccoon Bend Wilcox oils are 0.01-0.02 indicating that these oils were mostly likely not derived from source rocks deposited in hypersaline environments.
- (iii) High bisnorphane/hopane ratios indicate highly reducing source rock
 depositional environments, although absence does not exclude an anoxic
 source environment (Peters et al., 2005, p.561-562). Raccoon Bend oils have

low values of 0.17 and 0.14 indicating these oils were probably not generated from source rocks deposited in highly reducing environments.

(iv) Oleanane/hopane ratios (Oleanane Index) are used to identify source rocks from Cretaceous or younger (Peters et al., 2005, p.572-573). Oil with measurable Oleanane is likely Cretaceous or younger and if it has an Oleanane Index greater than 0.20 it is likely Tertiary, although the absence of Oleanane does not confirm the oil sourced from Cretaceous or older rocks. (Moldowan et al., 1985; Peters et al., 2005, p.572-573). The presence of Oleanane, however, is generally an indicator of younger rocks. Raccoon Bend Wilcox oils have oleanane/hopane values of 0.13 and 0.21 which does not differentiate between Tertiary or Cretaceous source rocks due to the fact that one sample is above 0.20 and another is below 0.20 and the oils are highly likely to have been sourced from the same source rock, although as with the other biomarker indicators the Oleanane could have been derived from entrainment from the Tertiary Wilcox host.

All of these triterpane biomarker parameters suggest the source rocks for the Wilcox oils at Raccoon Bend field contained terrestrial organic matter likely deposited in an oxic, low-salinity environment, with variable terrigenous organic matter input. These inferences are again suspect because they contradict the strong evidence of a marine origin provided by the whole oil GC data and because of other biomarkers showing evidence of entrainment from the terrestrial organic material present in the Wilcox beds.



Figure 7.8. Pristane/n-C17 versus phytane/n-C18 plot of the Raccoon Bend oils (this study), Brazoria oils (Guo, 2004) and S. Liberty oils (Banga et al., 2011). Boundaries between different source-rock environments are after Shanmugam (1985) and Bissada (1993).


Figure 7.9 Pristane versus phytane plot for Raccoon Bend oils (this study), S. Liberty oils (Banga et al., 2011) and Brazoria oils (Guo, 2004). The boundaries between different source rock environments are after Powell and McKirdy (1973).



Figure 7.10. DBT/Phe versus Pr/Ph paleoenvironment plot after Hughes et al. (1995). Raccoon Bend oils (this study) plot in Zone 4 which corresponds to a source rock depositional environment composed of fluvial/deltaic shale and coal.



Figure 7.11. a) Suggested source rock depositional environments defined by sterane ratios for the Raccoon Bend (this study), S. Liberty (Banga et al., 2011), and Brazoria (Guo, 2004) oils (figure modified from Banga et al., 2011) (source zones from Bissada et al., 1993). Ratios were calculated using the whole peak area for the coeluted C_{27} steranes and also without using the coeluted peak areas for the C_{27} steranes (see Discussion 7.4.5, Table 6.4). S. Liberty oils calculated ratios were recalculated for Banga et al. (2011) data because these oils show the same coelution (Table 6.4). It is unknown if the oils studied in Guo, 2004 have C_{27} coeluted steranes and therefore the range of values calculated in Banga et al. (2011) are shown without any recalculations. This figure clearly shows that the values chosen for the C_{27} compounds that are coeluted affect the inferred depositional environment (terrestrial versus marine) for the C_{29}/C_{27} biomarker parameter. For the (Dia/Reg)-sterane values, coeluted peak areas for the C_{27} areas were used in the regular steranes denominator when it was also included in the C_{29}/C_{27} ratio and the diasteranes in the numerator gets the coeluted peak area when the C_{27} coeluted steranes are not used (Discussion 7.4.5). Both Raccoon Bend oils plot below 1 for this ratio suggesting that they did not originate from a clay-rich source rock. b) C_{31-35} homohopane distribution for the Raccoon Bend Wilcox oils (this study). Shaded polygon outlines the C_{31-35} homohopanes distribution for both the Brazoria oils (Guo, 2004) and S. Liberty oils (Banga et al., 2011).

7.4 Interpretation of source-rock maturity

Biomarkers are often used in oil correlation studies to identify the likely maturity level of the source rock when the oil was generated and expelled (Peters and Moldowan, 1993, p.221-222). Homohopane isomerization (22S/(22S+22R) is a commonly used parameter to determine the maturation levels of the parent source rocks. Ratios range from 0.57 to 0.62 at equilibrium (Seifert and Moldowan, 1980; Zumberge, 1987a), which is equivalent to an R_0 of 0.6% (Peters et al., 2005, p.612). Raccoon Bend Wilcox oil ratios range from 0.49 to 0.62 (Table 6.5), thus suggesting maturity at least at an R_0 value of 0.6% which correlates with zone II or higher (Figure 5.1) (Bissada, 1982,1983). The tricyclics/(tricyclics+17 α (H)-hopane, Ts/(Ts+Tm) and Diasteranes/ (diasteranes+regular steranes) ratios all have an equilibrium value of 1.0 which correlates with an R_0 of 1.4% (Mackenzie, 1984; Peters et al., 2005, p.612). Raccoon Bend Wilcox oils have values of less than 0.51 for all of these parameters (Table 6.5) supporting maturity of the source was less than an R_0 value of 1.4%.

Sterane isomerization ratios are also used to evaluate the parent source rock maturity. Sterane maturity parameters used include: (i) $20S/(20S+20R) C_{29}$ sterane, and (ii) $\beta\beta/(\beta\beta+\alpha\alpha) C_{29}$ sterane (Figure 7.12a).

- (i) (20S/(20S+20R) C₂₉ sterane ratios reach equilibrium at values of .52 to .55 with corresponding R_o values of ~0.8% (Mackenzie, 1984; Seifert and Moldowan, 1986; Peters et al., 2005, p.612). Wilcox oils at Raccoon Bend have ratios of 0.50 and 0.51 indicating the source has an R_o close to ~0.8%.
- (ii) $\beta\beta/(\beta\beta+\alpha\alpha)$ C₂₉ sterane ratio of 0.25 suggests a thermal maturation level of 0.6% and a ratio of 0.71 suggests a maturation level of at least 0.9% (Mackenzie, 1984; Seifert

and Moldowan, 1986; Peters et al., 2005, p.612 and Peters and Moldowan, 1993, p.226). The ratios for Raccoon Bend oils are 0.46 and 0.49 indicating the source rock maturation is less than an R_0 value of 0.9%.

In summary, of the five sterane isomerization ratios evaluated, three indicate the source rock R_o is less than 1.4, one gives an R_o value close to 0.8 %, and one predicts a value of approximately 0.6%. These sterane isomerization results agree with the non-sterane maturity biomarker parameters and indicate that Raccoon Bend oils have thermal maturities that correlate with R_o values of 0.6% to 0.8%.

Maturation biomarker parameters can be affected by source rock facies (Peters and Moldowan, 1993, p.266-268) as well as relative age of the source rock and therefore may not portray the true source rock maturation levels. Mackenzie and McKenzie (1983) suggested that sterane isomerization ratios for some oils might not be complete due to insufficient amount of time since deposition for the isomerization reactions to proceed to completion. Grantham (1986) confirmed the possibility with Tertiary crude oil samples but also proposed an alternative explanation that blames contamination of the crude oils by immature sediments during migration. In this hypothesis, the Tertiary crude oils obtain incomplete isomerized steranes from the immature sediments through which they migrate and in which they accumulate. For biomarker maturity parameters for overmature rocks ($R_0 > 1.4$) (Table 6.5), Raccoon Bend values are much less than equilibrium values which may indicate entrainment. Biomarker parameters for inferring maturity of the source rock that generated and expelled Raccoon Bend hydrocarbons may be affected by entrainment as well; therefore, they are interpreted with caution.

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Figure 7.12a shows thermal maturation equilibrium values for C_{29} sterane parameters (values from Seifert and Moldowan, 1986). Raccoon Bend Wilcox oils (this study) are plotted with S. Liberty oils (Banga et al., 2011) and Brazoria oils (Guo, 2004) for comparison. Oils from Raccoon Bend do not reach equilibrium values and thus the source rock maturity is less than a R_0 value 0.8%. Both Raccoon Bend oils do have ratios for 20S/(20S+20R) C_{29} greater than 0.25 indicating the source rock thermal maturity has an R_0 value of at least 0.6% (Peters and Moldowan, 1993, p.226; Table 6.5). Figure 7.12b shows estimated expulsion temperatures for the Raccoon Bend oils (128-132°C) compared to S. Liberty oil and Brazoria oil values that are indicated by the shaded region (Banga et al., 2011; Guo, 2004). Calculation of expulsion temperatures is based on BeMent et al. (1994) using C_7 compounds. Both figures are modified from Banga et al., 2011.



Figure 7.13 Paleoenvironment of a middle Wilcox sequence from Xue and Galloway, 1995. The star shows the location of Raccoon Bend field (this study), the triangle shows the location of S. Liberty field (Banga et al., 2011), and the square is located in Brazoria County approximately where many of the fields are from the Guo, 2004 study. Raccoon Bend (this study) is located in the platform delta environment and S.Liberty and Brazoria fields are located in the slope environment.

7.5 Comparison with the S. Liberty and Brazoria oils

Raccoon Bend oils share similar molecular characteristics with S. Liberty oils (Banga et al., 2011) and Brazoria oils (Guo, 2004). However, there are significant differences that can be observed in whole-oil GC fingerprints. The differences are likely the consequence of entrainment from high-energy lignite-bearing Wilcox beds.

Criteria for determining if Raccoon Bend oils belong to the same genetic oil family as S. Liberty and Brazoria oils includes (i) relative abundances of $n-C_{15}+$ normal paraffins, (ii) abundances of the normal, iso, and cyclo-C₇-alkanes, (iii) Pr/n-C₁₇ and Ph/n-C₁₈, and (iv) Pr/Ph ratios and (v) biomarker attributes.

- (i) The relative abundances of n-C₁₅+ normal paraffins for Raccoon Bend oils compared to S. Liberty and Brazoria oils are shown in Figures 7.1a and b. Raccoon Bend oils show a very unusual odd/even predominance in the n-C₂₇ to n-C₃₃ range for Gulf Coast oils. This unusual pattern has been seen in Louisiana Wilcox rocks (Sassen, 1990) and in Wilcox oils and rocks from New Ulm field, southeast Texas Basin (Philippi, 1974). It is possible that at Raccoon Bend the lignite-bearing Wilcox units in which the oils are reservoired could be responsible for the odd/even predominance and therefore the C₁₅+ distribution is not a true characteristic of the oils from their parent source-rock (suggested by Bissada, *personal communication*, 2012).
- (ii) The relative abundances of the normal, iso, and cyclo-C₇-alkanes for Raccoon Bend oils and S.Liberty oils plot very similarly (Figure 7.4a and b). The relative

abundances of these C_7 alkanes classifies Raccoon Bend and S. Liberty oils as naphthenic oils and supports that they are likely from the same genetic family.

- (iii) Pr/n-C₁₇ and Ph/n-C₁₈ values for non-biodegraded Raccoon Bend oils are different from S. Liberty oils and Brazoria oils (Figure 7.8). High pristane values distinguish the non-biodegraded Wilcox oils at Raccoon Bend from S. Liberty oils and Brazoria oils. High pristane values may indicate the Raccoon Bend oils were derived from a more terrestrial-rich facies of the source rock than S. Liberty and Brazoria oils. If this is true, it would be likely, but not necessary, for the Raccoon Bend oils to show higher oleanane/hopane ratios. Oleanane/hopane ratios for the Raccoon Bend oils are 0.13 and 0.21 which are in range of the S.Liberty and Brazoria oils of 0.07-0.19 (Banga et al., 2011; Guo, 2004).
- (iv) The Pr/Ph ratios for the non-biodegraded Wilcox oils from Raccoon Bend (ranging from 6.38 to 7.04) are significantly higher than those from S. Liberty (Banga et al., 2011) and Brazoria oils (Guo, 2004) (ranging from 2.16 to 4.21) (Table 6.1, Figure 7.9 and 7.10). There are two possible explanations for the higher Pr/Ph values of the Raccoon Bend oils. One hypothesis is that they are higher because these oils were possibly derived from a different, more terrestrial deltaic Wilcox source rock that lies up dip from the growth fault zone and possibly oils generated from updip Wilcox facies have significantly more terrigenous input than the downdip Wilcox facies (Fisher and McGowen, 1967, Xue and Galloway, 1995) (Figure 7.13). The different source facies descriptions are explained further below in section 7.8. In this scenario, RGP-45's lower Pr/Ph ratios can only be explained by biodegradation or a different source rock than the Wilcox oils. A

second hypothesis is the high Pr/Ph ratios are a characteristic of the terrigenous organic-rich deltaic Wilcox reservoirs at Raccoon Bend and the oils have picked up the Pr/Ph signature from the reservoir or along the migration path. This hypothesis is supported when comparing Raccoon Bend Pr/Ph ratios to other studies in Texas and Louisiana because no other oil correlation studies have shown Pr/Ph ratios over 4 except the Pr/Ph ratios from other samples from the Wilcox as described for southwestern Louisiana Wilcox rock samples [Pr/Ph= 4.4-6.9] (Sassen, 1990). For this case the lower Pr/Ph values for the more biodegraded RGP-45 is likely a combination of biodegradation as well as a possible different migration and accumulation history. The amount of contact with the Wilcox Group may directly affect the Pr/Ph ratios of these oils. An analogue for this entrainment hypothesis is found in the Gippsland Basin, Australia where abnormally high Pr/Ph ratios are commonly found in oils from Eccene-aged reservoirs characterized by high terrestrial input and major coal intervals (Philp and Gilbert, 1986; 1982) and these Australia oils have been suspected of absorbing geochemical characteristics from these carrier beds (Grantham, 1986).

(v) Biomarker analyses for the three oil fields have similar values for maturity and source parameters (excluding sterane parameters where coelution may result in different calculated values as discussed above) (Tables 6.4 and 6.5). Non-sterane source-indicating biomarkers (homohopane index, gammacerane index, tricyclics/17 α -hopanes, bisnorhopane/hopane, and oleanane/hopane suggest that the Raccoon Bend source rocks were deposited in similar depositional

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environments with similar types of organic matter input compared to the S. Liberty and Brazoria oils (Table 6.4). The homohopane index for Raccoon Bend oils is 0.03 compared to the S. Liberty and Brazoria oils' range of 0.00 to 0.04. The very low homohopane index values suggest the three fields have oils generated from a source rock deposited in an oxic environment (Peters and Moldowan, 1993, p.146). The gammacerane indices for Raccoon Bend oils are 0.01 and 0.02 and the range for S. Liberty oils is 0.00 to 0.003 and Brazoria oils is 0.01 to 0.03. These values are very low suggesting that the three groups of oils were not deposited in a hypersaline environment (Bissada et al., 1993; Peters and Moldowan, 1993, p.160). Tricyclics/17 α -hopanes values for Raccoon Bend oils are 0.01 and 0.06 and S. Liberty oils range from 0.04-0.08 and Brazoria oils 0.02-0.03. These low values indicate these oils were likely generated from terrigenous source rocks (Bissada et al., 1993). Raccoon Bend and S. Liberty oils have low bisnorhopane/hopane ratios; Raccoon Bend oils' are 0.14 and 0.17 and S. Liberty's range is 0.06-0.39. Low bisnorhopane ratios indicate that the parent source rock was not likely deposited in an anoxic environment. Oleanane/hopane ratios for the Raccoon Bend, Brazoria and S. Liberty oils all lie within the range 0.08 to 0.21, supporting that they all have a Cretaceous or younger origin (Peters and Moldowan, 2005, p.572-573). Although biomarker analyses of the Raccoon Bend oils compared to S. Liberty and Brazoria oils suggest a terrigenous source rock, all three groups of oils have whole-oil characteristics that suggest a marine source-rock. Past studies have used biomarker results combined with whole-oil GC results to infer a marine source rock with considerable input from terrigenous

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organic matter (Banga et al., 2011; Guo, 2004). Because entrainment contaminates whole-oil GC results for Raccoon Bend oils, validity of biomarker analyses is in question for this study. Biomarker results may indicate similar genetic families for Raccoon Bend, S. Liberty, and Brazoria oils; however, their ability to distinguish a source-rock depositional environment is not applicable in this study due to the possibility of alteration due to entrainment. Maturity biomarker parameters indicate that Raccoon Bend oils were generated and expelled from mature source rocks (R_0 between 0.6% and 0.8%). S. Liberty oils and Brazoria oils indicate source maturities in this same range (Table 6.5). R_{0} values in this range lead to the conclusion that Raccoon Bend oils were expelled after kerogen had entered the peak oil-generation window. This conclusion was also found for S. Liberty oils and Brazoria oils (Banga et al., 2011). Maturity levels can be compared when oils are inferred to be generated from the same source rock, which is the case for Raccoon Bend oils, S. Liberty oils, and Brazoria oils based on whole oil attributes and biomarker parameters that were used to infer parent source rock attributes. The maturity values confirmed that these oils were generated and expelled from a source rock of similar maturity.

Abundances of the normal, iso, and cyclo- C_7 -alkanes and biomarker attributes suggest that the Raccoon Bend oils belong to the same genetic family as the S. Liberty oils and Brazoria oils. However, whole-oil attributes such as: relative abundances of n- C_{15} + normal paraffins, Pr/n- C_{17} and Ph/n- C_{18} values, and Pr/Ph ratios suggest that the Raccoon Bend oils' organic geochemistry is influenced by entrainment and the values are not characteristics of the oils derived from the parent source rock (Peters et al., 2005, p.964). Therefore, this study concludes that the biomarker attributes are not reliable due to the alteration of Raccoon Bend observed in the whole-oil attributes (relative abundances of $n-C_{15}+$ normal paraffins, $Pr/n-C_{17}$ and $Ph/n-C_{18}$ values, and Pr/Ph ratios). Evidence of entrainment was not seen in the whole-oil attributes for Brazoria and S.Liberty oils. Brazoria and S.Liberty oils may have not experienced entrainment due to the location of these reservoired oils in the Basin. S.Liberty and Brazoria oils are downdip of the Wilcox growth fault zone and therefore likely migrated through a Wilcox Group that do not have thermally immature coal to alter the oils' GC signature.

7.6 Source rock-oil correlation

As discussed below, comparison of analyses of the two Wilcox shales samples (Big Shale and Yoakum Shale) collected from the Raccoon Bend field and with the Raccoon Bend oils indicates that the Wilcox shales sampled are not the source rocks for the analyzed Raccoon Bend oils. However, this does not preclude that the Wilcox shales located off the dome that are buried deeper and subject to higher temperature and thermal stress and thus may be the source rocks for the oils at Raccoon Bend. Analyses of potential Austin Chalk and Eagle Ford source rocks in a nearby well (E.Sorsby-1) suggests that they are currently buried at temperatures and pressures necessary for generating and expelling hydrocarbons. Source rock to reservoired oil correlations in this study were made using (i) δ^{13} C values, (ii) TOC content, and (iii) R_o and TAI.

(i) δ^{13} C values of the Wilcox shale, Austin Chalk, and Eagle Ford shale cuttings (-26.0 to -26.8 ‰. Table 6.6) are less negative than the whole-oil δ^{13} C values of Raccoon Bend oils (-27.2 to -28.9 ‰, Table 6.1). This difference is likely due to fractionation

supporting that a genetic relationship is possible between the Raccoon Bend oils and the source rock samples (Stahl, 1977, 1978). However, the difference in δ^{13} C values is not large, a 3 ‰ difference is usually required and therefore with a larger study of δ^{13} C values in the area, it is possible that the values are close enough that a genetic relationship is not possible with any of these potential source rocks.

- (ii) The total organic carbon content (TOC) of the four rock samples ranges from 0.72 to 1.70% (Table 6.7). According to Bissada et al. (p.124, 1990) potential "source beds must contain at least 1.0% TOC in order to yield significant amounts of hydrocarbons." Thus, the Wilcox Big Shale, Austin Chalk and Eagle Ford shale samples all contain enough organic carbon (ranging from 1.07 to 1.70%) to be a potential source rock. The Yoakum shale has less than 1.0% TOC and thus is not likely to be the source rock for Raccoon Bend oils. However, even the TOC values of the other samples at 1.70% or less are still considered very low for source rocks especially for an oil field that has produced over 110 million barrels of oil (Raccoon Bend production, Swenson, personal communication, 2012; Bissada, personal *communication*, 2012). Also, the vitrinite histograms for these samples (Figure 6.3) show much of the organic carbon content is recycled organic matter which would not generate hydrocarbons. TOC and the relative abundance of recycled organic matter seen in these samples poses serious doubt that any of these samples represent the source rocks for the Raccoon Bend oils.
- (iii) Indigenous vitrinite reflectance (R_o) and thermal alteration index (TAI) values for the rock samples are shown in Table 6.6, Figures 6.3 and 6.4. The values for the Wilcox shale samples, Big Shale and Yoakum shale are similar ($R_o \sim 0.6\%$; TAI~2.4-

2.6) and correlate with Zone II in Figure 5.1. Zone II represents early oil generation but no effective release of hydrocarbons (Bissada et al., 1982). These values indicate the Wilcox shales at Raccoon Bend are not likely the source rocks for the Raccoon Bend oils. However, off the dome, the Big Shale (TOC >1%) is buried at greater depths and subjected to higher temperatures and pressures and could be in Zone III where hydrocarbons are expected to be generated and expulsed from the source rock (Bissada, 1982). The Austin Chalk and Eagle Ford R_o mean values are 0.74 and 0.81 respectively with TAI values of approximately 2.6-3.0. These values fall within the oil window in Zone III 'peak oil generation' (Figure 5.1). However, all vitrinite reflectance histograms for these cuttings show a significant contribution of re-worked organic matter (Figure 6.3). High amounts of re-worked organic matter in combination with relatively low TOC values (less than 2) poses serious doubts that these rocks are the likely source rocks of the Raccoon Bend field oils.

Source rock-oil correlation analysis from this study cannot identify the likely source rock but does rule out the Wilcox shales at Raccoon Bend as likely source rocks for the Raccoon Bend oils.

7.7 Inferred history of hydrocarbon generation and expulsion

From source-rock-oil correlation for Raccoon Bend rocks and oils, it has been determined that the Wilcox shales adjacent to reservoirs hosting the Raccoon Bend oil did not generate the Raccoon Bend oils. This is supported by rock analyses that yielded low R_o values of Wilcox shales (Figure 6.3) and low TOC values (Table 6.6) with a large percent of the organic carbon consisting of reworked organic material as described above

(section 7.6). Thermal maturity of the oils from biomarker analyses also indicates the oils were generated and expelled from a source rock with minimum vitrinite reflectance values between 0.6% and 0.8% which is higher than the thermal maturity of the Wilcox shales at Raccoon Bend. Also, using C₇ compounds, hydrocarbon generation and expulsion temperatures for the Raccoon Bend oils were calculated to be between 129°C and 131°C (Figure 7.15b, calculation based on BeMent et al., 1994) compared to the Wilcox Group reservoir temperatures at Raccoon Bend of 65°-69 °C. Since there has not been substantial uplift of the Wilcox Group in this area (Ewing 1983,1986) the rock was not likely exposed to higher temperatures in the past.

 δ^{18} O values of water collected from the Raccoon Bend oil wells suggest they are a product of mixing of both meteoric water and deeper-sourced fluids from the underlying geopressured formations. This indicates that there is faulting or another pathway that connects the Raccoon Bend reservoirs with geopressured fluids either from below or from downdip Wilcox units. It is likely that hydrocarbon migration to Raccoon Bend reservoirs has occurred along these same pathways inferred for the migrating geopressured fluids.

Therefore, with the Wilcox Group at Raccoon Bend ruled out as a possible source rock, there are two inferred oil histories for the Raccoon Bend oils: (1) Raccoon Bend oils were generated and expelled from downdip Wilcox Group rocks that have been determined to be thermally mature (Banga et al., 2011; Guo, 2004, Sassen et al., 1994) then migrated laterally over 80+ kilometers to Raccoon Bend. The alternate possibility (2) is the Raccoon Bend oils were generated from deeper pre-Tertiary sources near Raccoon Bend and the hydrocarbons migrated to the reservoirs by vertical flow through fault zones and along the edges of the salt diapir (similar to the migration pathway proposed for S. Liberty oil, Banga et al., 2011). This is a commonly accepted migration history for salt domes in the Gulf Coast region (Bissada, 1982; Bissada et al., 1990; Sassen, 1990).

8. CONCLUSIONS

The organic geochemical investigation of Raccoon Bend oils suggests that the oils belong to a single family and they likely generated from the same source rock as oils from S. Liberty field and Brazoria County. The harmonic decrease in C_{15} + distribution is strong evidence of a marine source rock in all these oils. However, the Raccoon Bend oils show evidence of entrainment from the high-energy Wilcox Group that contains lignites. The evidence is most apparent in the GC fingerprints where the C_{15} + normal paraffin distribution shows a harmonic decrease overprinted with dominant odd/even predominance in the C_{27} - C_{31} normal paraffin range. High pristane values are also interpreted to be a result of entrainment (Philp and Gilbert, 1986; 1982; Grantham, 1986).

Three of the Raccoon Bend oil samples are biodegraded. UWX8-1 is very slightly biodegraded and this can be attributed to different migration history than the other Raccoon Bend Wilcox oil samples because the UWX8-1 has a different oil-water contact line. RGP-45 is moderately biodegraded and RBM3-1 is heavily biodegraded, which is attributed to their occurrence in shallower reservoirs with lower temperatures than reservoirs of the Wilcox Group oils sampled.

The inferred source rock depositional environment for Raccoon Bend oils is complex. The strong evidence of entrainment seen in the whole-oil GC fingerprints poses doubts that isoprenoid indicators, such as pristane and phytane, and biomarkers are true indicators of source rock depositional environment. As the biomarkers are only a minor component of the oil as compared to the whole oil GC analyses, thus less reliable. This study concludes that the strongest evidence supports these oils are overprinted and therefore source environment inferences are not applicable to these oils without further study of what geochemical characteristics are affected by entrainment.

Maturation-sensitive biomarker attributes, including C_{31-35} homohopane 22S/(22S+22R), $\beta\beta/(\beta\beta+\alpha\alpha)$ C₂₉ sterane, and 20S/(20S+20R) C₂₉ sterane, indicate that the Raccoon Bend oils were generated in the peak oil-window with R_o values estimated between 0.6% and 0.8%. It is possible the oils were generated from a more mature source rock and these values are lower due to entrainment from immature lignites. However, without an understanding of how entrainment affects biomarkers, the inferred parent source-rock maturity is uncertain.

Source-rock-oil correlation excludes the Wilcox shales (Big Shale and Yoakum Shale) based on low R_o values and relatively low TOC values. Also, the 2,4-DMP/2,3-DMP ratios in the Raccoon Bend oils suggest the generation and expulsion temperatures for Raccoon Bend oils is between 129° and 131°C. The Raccoon Bend Wilcox reservoirs are 65°-69°C and there is not supporting evidence that they have reached these temperatures in their past. Austin Chalk and Eagle Ford samples have low TOC values (less than 2%), but they are currently in the peak oil-window with mean R_o values of 0.74% and 0.81% respectively. High concentration of re-worked organic matter seen in vitrinite reflectance analyses combined with low TOC (<2) suggests that the cuttings sampled may not be adequate source rocks. The Midway Group is a possible source rock

but this study did not obtain a sample for the Midway so there is no evidence for or against its source rock potential.

From this geochemical investigation, I conclude that Raccoon Bend oils were not generated from the Wilcox Group at Raccoon Bend. It also supports alteration of geochemical properties of hydrocarbons in reservoirs that can lead to misinterpretations of source environment. Raccoon Bend oils demonstrate that whole-oil bulk properties can be used for evidence of entrainment and should be assessed before using a small proportion of the geochemistry, such as biomarkers, to infer characteristics of the parent source rock.

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10. APPENDIX

АРІ	Well Name	Operator	Depth	вн т	P (M Pa)	Samp led
ATI	WEITH AME	operator	(■)	(C)	с (ла т <i>а</i>)	ay is and pice
4201530952	UpperWilcox OilUnit 27-1	Sanda Iwood E zqui.	2273	106	27	N
4201530968	UpperWilcox Oil Unit H	Sanda Iwood E zqdi.	2251	106	28	N
4201530992	UpperWilcox Oil Unit 2-1	Sanda Iwood E zgal.	2155	102	27	N
4201530989	UpperWilcox Oil Unit 3-1	Sanda Iwood Expl.	2269	111	28	N
4201530991	UpperWilcox Oil Unit 4-1	Sanda Iwood E zpl.	2085	96	24	Y
4201530998	UpperWikcox Oil Unit 5-1	Sanda Iwood E zpi.	2071	102	26	Y
4201531009	UpperWilcox Oil Unit 6-1	Sanda Iwood E zqal.	2115	106	26	N
4201531021	Upper Wilcox Oil Unit 62	Sanda Iwood E zqdi.	2071	105	26	N
4201531014	Upper Wilcox Oil Unit 7-1	Sanda Iwood E zqdi.	2106	96	26	N
4201531001	Upper Wilcox Oil Unit 8-1	Sanda Iwood E zpl.	2284	119	29	Y
4201531020	LowerWilcoxOilUnit2-1	Sanda Iwood E zpl.	2312	112	29	Y
4201531005	Robent G. Paine No.1	Sanda Iwood E zpl.	2005	102	25	N
4201531016	UpperWilcoxGasUnit10-1	Sanda Iwood E xpl.	1984	111	24	N
4201531015	UpperWilcox Oil Unit 2-2	Sanda Iwood E zpi.	2104	111	24	N
4201530931	Robe at G Paine No.45	EnhancedEnergyPartners	855	28	12	Y
4201530544	Raccom Re. ndM. ioc ene 11 nit 3-1	Koba oce d Koe ov Partners	678	22	NA	Y
4001600272			3135		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	N
4201000373			2110	100	20	N
4201000523		Kussel Magnine	2029	109	<u>v</u>	N
4201500428	KB.W ood eyNo⊥/-f	Hum ble Oil & Kehning Co.	2450	N/A	10 	N
4201531017	Austin Callege #2	Sanda Iwood Bizgal.	2211	101	27	N
4247331215	R_H andy B*#1	Sanda Iwood Bizgal.	2204	110	27	N
4201500146	L.A. Machemehl #IC	Hum ble Oil & Refining Co.	2440	109	30	N
4201500053	R.H. andy #7Y	Hum ble Oil & Refining Co.	2311	92	27	N
4201500440	Diemar#12Y	Hum ble Oil & Refining Co.	2112	95	26	N
4201500044	MaxBa de r#1	Hum ble Oil & Refining Co.	3232	120	396	N
4201531000	Hale#1	Union Gas Operating Co.	2440	115	30	N
4247300244	R.H andy#B-15	Hum ble Oil & Refining Co.	2286	92	28	N
4201500787	J.W. Meckent #1	Hawkins & Hawkins	3279	128	43	N
4201500519	Austin Calle ge #1	PanA mei canProduction Co.	2899	91	35	N
4201500439	A D iem ar#11-Y	Hum ble Oil & Refining Co.	2214	101	29	N
4201500514	Austin Cal lege #16	Hum ble Oil & Refining Co.	2271	85	28	N
4201500511	Austin Col lege #13	Hum ble Oil & Refining Co.	2287	77	28	N
4247300251	EH_Sattain#1	Hum ble Oil & Refining Co.	2290	108	29	N
4247330665	R.H. ardy-29B	Penn Vinginia Oil & Gas	3335	135	40	N
4247300250	EP.M.enkæ #1etal.	Hum ble Oil & Refining Co.	2596	101	31	N
4247300243	R.H andy#B-14	Hum ble Oil & Refining Co.	2287	93	28	N
4201530563	Biene k N a 1	TXO Pundue: tion Co.	3635	137	40	N
4247300249	L.B.S and ers #	Hum ble Oil & Refining Co.	2251	85	27	N
4201500029	WM.Remment Jr#1	Техасо	2896	104	39	N
4247300263	Y oung #1	FalconS eaboard	2351	96	28	N
4247300246	R.H ardy * B* #17B	Hum ble Oil & Refining Co.	3357	118	40	N
4247300022	M.H.Taggatt#1	LD.Fmmch	2491	96	30	N
4201530675	Heam an No.4	Shamroc kO il Co.	2274	103	27	N
4201530726	DiemarN 0.19	Syne sgy Oil & Gas	2335	N/A	28	N
4247300021	Diemar-l	E.J. Gnay & BlackBear Consolidated Mining Co	2899	115	37	N
4201500331	A.A. Sande 15 #9	Hum ble Oil & Refining Co.	2278	94	28	N
4201500230	She mul #Y -16	Hum ble Oil & Refining Co.	3486	137	65	N
4201500066	Hardy #1	Falcon S cabuard	2983	108	38	N
4201500182	L.R.S he mad #18	Hum ble Oil & Refining Co.	2154	88	26	N

Appendix 1. Wells used for temperature and pressure calculations in Methodology 5.1.

Biomarker Ratio	Equation used:				
(C ₃₅ /C ₃₁₋₃₅) homohopane index	C_{35} 17 α , 21 <i>b</i> , 22S+22R/ (C_{31-35} 17 α , 21 <i>b</i> , 22S+22R) p.146-147 ^a				
Gammacerane index	gammacerane/C30 17 α , 21 β p.160 ^a				
Tricycics/17α hopanes	$(C_{28} (S+R) + C_{29} (S+R) \text{ tricyclohexaprenane})/(C_{29} C_{33} 17\alpha \text{-hopanes}), p.174^{a}$				
Regular steranes/17α hopanes	$[C_{27}-C_{29} (5\alpha,14\alpha,17\alpha (S+R) + 5\alpha,14\beta,17\beta (S+R)]/(C_{29}-C_{33} 17\alpha-hopanes) p.178^{b}$				
Bisnorhopane/hopane	28,30-Bisnorhopane/ $(17\alpha$ -hopane (22S+22R)] ^a				
oleanane/C ₃₀ hopane	$(18\alpha \text{ oleanane} + 18\beta \text{ oleanane})/C_{30}17\alpha, 21\beta, p.155^{a}$				
C_{32} (S/S+R) homohopane	$C_{32} [17\alpha\text{-hopane (22S)/ (17\alpha\text{-hopane (22S+22R)}] p.227^{a}]$				
(C / C) homohonane	C_{17a} honome (22S + 22P)/ C34 17a honome (22S + 22P) n 146 147 ^a				
	$C_{35} = 170^{\circ}$ no pane (223+22K) $C_{54} = 170^{\circ}$ no pane (223+22K) $P_{14} = 147^{\circ}$ (138 170 20S+20R)/ $[(50 + 140 + 170 + 20S + 20R) + (50 + 140 + 147) + (50 + 140$				
Diasterane/Regular sterane	(15),170 200 (200),100,170 200 (200) (00,17),17) 200 (200) 101 027 029 , p.170				
(C_{27}/C_{29}) Regular steranes	$[C_{27}(5\alpha, 14\alpha, 17\alpha(S+R) + 5\alpha, 14\beta, 17\beta(S+R)]/C_{29}(5\alpha, 14\alpha, 17\alpha(S+R) + 5\alpha, 14\beta, 17\beta(S+R)] p. 182^{a}$				
(C ₂₉ /C ₂₇) Regular steranes	$[C_{29}(5\alpha, 14\alpha, 17\alpha(S+R) + 5\alpha, 14\beta, 17\beta(S+R)]/C_{27}(5\alpha, 14\alpha, 17\alpha(S+R) + 5\alpha, 14\beta, 17\beta(S+R)] p.182^{a}$				
$C_{27}/(C_{27}-C_{29})$ steranes	$[C_{27}(5\alpha, 14\alpha, 17\alpha(S+R) + 5\alpha, 14\beta, 17\beta(S+R)]/[C_{27}-C_{29}(5\alpha, 14\alpha, 17\alpha(S+R) + 5\alpha, 14\beta, 17\beta(S+R)] p.182^{a}]$				
$C_{28}/(C_{27}-C_{29})$ steranes	$[C_{28}(5\alpha,14\alpha,17\alpha(S+R)+5\alpha,14\beta,17\beta(S+R)]/[C_{27}-C_{29}(5\alpha,14\alpha,17\alpha(S+R)+5\alpha,14\beta,17\beta(S+R)] p.182^{a}]$				
Coo/(Coz-Coo) steranes	$[C_{29}(5\alpha, 14\alpha, 17\alpha(S+R) + 5\alpha, 14\beta, 17\beta(S+R)]/[C_{27}-C_{29}(5\alpha, 14\alpha, 17\alpha(S+R) + 5\alpha, 14\beta, 17\beta(S+R)] p.182^{a}]$				
$C_{30}/(C_{27}-C_{30})$ steranes	$[C_{30}(5\alpha, 14\alpha, 17\alpha(S+R) + 5\alpha, 14\beta, 17\beta(S+R)]/[C_{27}-C_{30}(5\alpha, 14\alpha, 17\alpha(S+R) + 5\alpha, 14\beta, 17\beta(S+R)] p.186^{a}$				
22S/(22S+22R) C ₃₁					
homohopane	$C_{31} [17\alpha-hopane (22S)/(17\alpha-hopane (22S+22R)] p.227^{a}$				
$22S/(22S+22R) C_{32}$	$C_{22} [17\alpha$ -honane (22S)/ (17\alpha-honane (22S+22R)] p 227 ^a				
$22S/(22S+22R) C_{33}$					
homohopane	$C_{33} [17\alpha$ -hopane (22S)/ (17 α -hopane (22S+22R)] p.227 ^a				
$22S/(22S+22R) C_{34}$	C ₃₄ [17α-hopane (22S)/ (17α-hopane (22S+22R)] p.227 ^a				
$\frac{228}{(228+22R)}C_{35}$					
homohopane	C ₃₅ [17α-hopane (22S)/ (17α-hopane (22S+22R)] p.227 ^a				
22S/(22S+22R) C31-35					
homohopane Total	C ₃₁₋₃₅ [17α-hopanes (22S)/ (17α-hopanes (22S+22R) p.227 ^a				
$[\beta a - moretanes/(a(-hopanes + a))] = C$					
$\beta\beta$ -hopanes)] C ₃₀	$(1/\beta, 21\alpha$ -moretanes/ $(1/\alpha, 21\beta$ -hopanes+ $1/\beta, 21\beta$ -hopanes) for C ₃₀ compounds, p.228-230"				
Tricyclics/(Tricyclics+17a(H)- hopanes)	$(C_{28} (S+R) + C_{29} (S+R) tricyclohexaprenane)/ [(C_{28} (S+R) + C_{29} (S+R) tricyclohexaprenane)+(C_{22} C_{22} 17a-hopanes) n 174a$				
	$18\alpha_22 29 30_{\text{trisnorneohonane}/(18\alpha_22 29 30_{\text{trisnorneohonane}+17\alpha_22 29 30_{\text{trisnorhonane}})$				
Ts/(Ts+Tm)	p.233 ^a				
Diasterane/(Diasterane+	$(13\beta,17\alpha 20S+20R)/[(13\beta,17\alpha 20S+20R)+[(5\alpha,14\alpha,17\alpha 20S+20R)+(5\alpha,14\beta,17\beta 20S+20R)]$ for				
Regular sterane)	C ₂₇ -C ₂₉ , p.190 ^a]				
20S/(20S+20R) C ₂₉ sterane	5α,14α,17α(20S)/[5α,14α,17α (20S+20R)] for C ₂₉ sterane, p.237 ^a				
$\frac{\beta\beta/(\beta\beta+\alpha\alpha)}{^{a}}C_{29} \text{ sterane} \qquad 5\alpha,14\beta,17\beta(S+R)/[(5\alpha,14\beta,17\beta(S+R)) + (5\alpha,14\alpha,17\alpha(S+R))] \text{ for } C_{29} \text{ sterane } p.240^{a}$					

[°]Peters and Moldowan, 1993, p.146-240 ^bWaples and Machihara, 1991, p.178

Appendix 2. Biomarker parameter equations used in this study for inferring source environment and maturity with references.



Appendix 3. Ternary diagram of C_{27} - C_{29} sterane distribution for the Raccoon Bend samples UWX4-1 and LWX2-1. The C_{27} regular sterane is coeluted with the C_{29} 13 β , 17 α (20S) diasterane, therefore, values are calculated in this study using the whole coeluted value and without using the coeluted value in order to give a range for the actual value. This diagram illustrates that using the coeluted value or not using the coeluted value to calculate the C_{27} - C_{29} sterane distribution can lead to different inferences on depositional environment of the parent source rock. For this reason, the C_{27} - C_{29} sterane biomarker parameters were not used to identify the depositional environment of the source rock. Values for S. Liberty oils, Frio oils, and Gulf Coast Paleogene oils are also shown for comparison (Banga et al., 2011; Guo, 2004; Kennicutt et al., 1992).



Appendix 4a. UWX1-1 well log at Raccoon Bend field. Cuttings analyzed in this study come from the Yoakum Shale (2073-2082m) and Big Shale (2271-2277m) shown above.



Appendix 4b. E.Sorsby well log. Cuttings analyzed in this study come from the Austin Chalk (5163-5182m) and Eagle Ford (5547-5639m).