Evidence for Hydrocarbon Generation from NSOs: Implication for Modeling of Oil and Gas Generation in Basins*

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Abstract

Understanding the occurrence and generation of gaseous and liquid hydrocarbons in sedimentary basins is often predicated on knowing the processes involved in cracking and expulsion of these hydrocarbons from the kerogen matrix. There are several theories on how cracking of the kerogen occurs to yield hydrocarbons; however, there is little definitive evidence for any of these that is based on a full molecular-level understanding of the proposed pathways. A major theory considers that oil and gas is generated directly by cracking of the kerogen in a series of parallel reactions. Another suggests that successive reactions acting on the main kerogen polymer involve the generation of hydrocarbons by cracking of both the kerogen and the intermediate sub-products. In the successive reaction kinetic scheme presumably, compounds of intermediate molecular weight (NSOs) are formed first from the kerogen and then become the main source of petroleum. Resolving which of these transformation pathways is most important is crucial to our ability to model and predict petroleum formation in sedimentary basins.

To evaluate the feasibility of each of these pathways the present study presents some new molecular-level correlations among NSO fractions and extracted oils from immature kerogen subjected to artificial maturation in sealed gold tubes. A Type I kerogen from the Green River formation was pyrolyzed in a closed system at various temperature/time conditions. The NSO compounds generated during the artificial maturation were collected by successive n-pentane and dichloromethane (DCM) extractions and analyzed using a new ultrahigh resolution mass spectrometric technique involving electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICR-MS) to identify dominant series of compounds. This approach allows us to examine the individual elemental components of polar NSOs by providing ultra-resolution mass spectra whose precise mass assignments provide the requisite information from which elemental compositions are determined.

Discussion

A large variety of up to 75 homologous series of formulas is identified across the entire m/z range of each mass spectrum. Several series of polar CHO-, CHOS-, and CHON-containing compounds between C_{12} and C_{50+} are observed. During artificial maturation, the molecular weights of these C_{12} - C_{50+} compounds tend to decrease with increasing thermal severity. The CHO compounds are dominant in each spectrum.

Within these CHO compounds, more than half are comprised of four series, $C_nH_{2n}O_2$, $C_nH_{2n-2}O_2$, $C_nH_{2n-2}O_4$, $C_nH_{2-10}O_2$, which all correspond to carboxylic acids, mainly fatty acids.
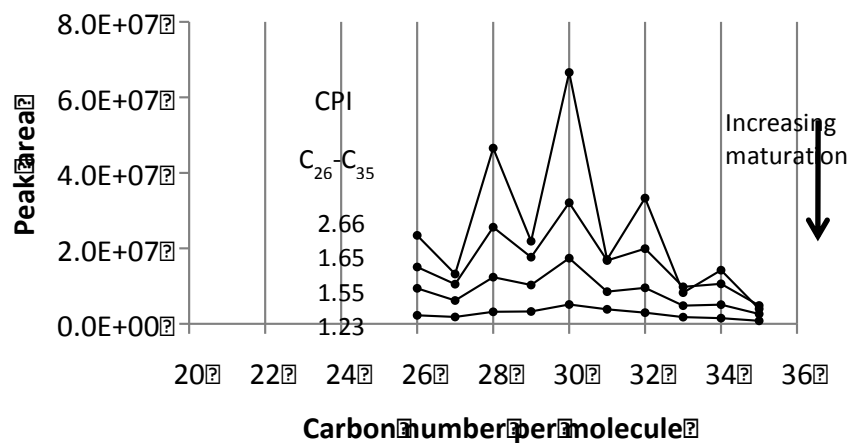
We show that the distribution of these carboxylic acid compounds (Figure 1) detected by ESI-FTICR-MS is directly correlated to the distribution of hydrocarbons using the carbon preference index (CPI). This index is commonly used to characterize oils and source rock extracts and is defined as the predominance of odd over even numbered hydrocarbons. In the case of carboxylic acids, the even-numbered fatty acids predominate over the odd. The correspondence of CPI between saturated hydrocarbons (odd-dominated and displaced by one carbon from fatty acids) and saturated monoacids $C_nH_{2n}O_2$ (even dominated) is suggestive of a genetic link.

We have quantified the amounts of carboxylic acids in NSO fractions and show that the entire distribution of hydrocarbons generated during the artificial maturation can be related to the amounts of carboxylic acid compounds extracted from the kerogen into the NSO fractions. This strongly suggests that decarboxylation of acid compounds from the generated NSO's is the main process for the generation of hydrocarbons. Moreover, there is a strong qualitative and quantitative relationship between the hydrocarbon distributions and the fatty acid distributions. For example, the carbon preference index for hydrocarbons matches exactly that observed for the fatty acids, only displaced by one carbon. Results also show that carboxylic acids that become incorporated into the NSO fractions are produced from initial cracking of the kerogen and then consumed over the course of increased maturation of the kerogen (Figure 2). It is clear that the abundance of long chain carboxylic acids in kerogen can be correlated to the hydrocarbon potential of that kerogen. We are currently investigating Type II and Type III kerogens to see if the same relationships noted for Type I kerogen are observed.
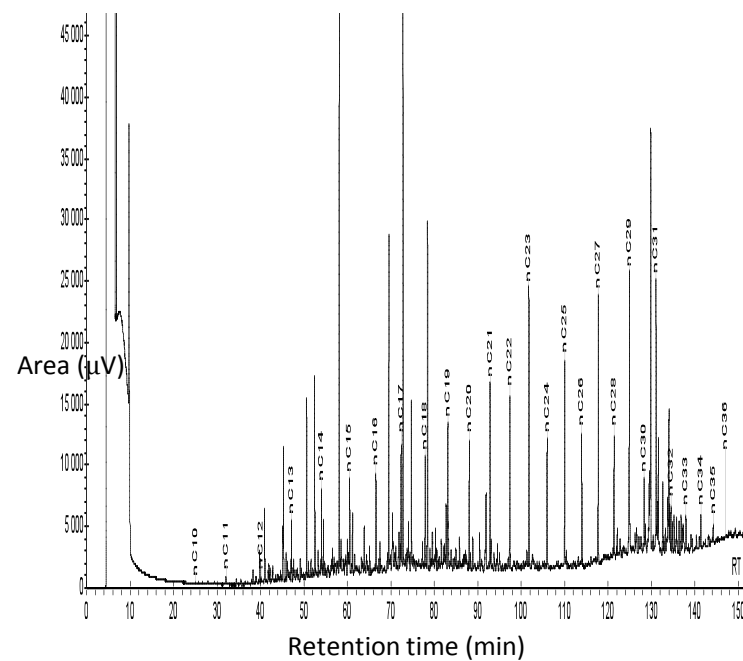
Summary

For a transformation ratio around 50%, the total amount of saturated and unsaturated mono-carboxylic acid reached their maximum value, which is equivalent to approximately 50% of the total hydrocarbons produced. Perhaps more intriguing is the fact that at high transformation ratios, the NSO fractions still harbor significant amounts of fatty acids. These can fuel further cracking at continued high maturation levels at depth or can be a source of fuel for microorganisms in the production of biogenic methane gas in systems that have been uplifted following high maturation. Thus, we may have discovered a new source for "delayed" biogenic methane production, as it is well known that microorganisms can decompose fatty acids to acetate and this acetate can fuel methanogenesis. In addition, the persistence of fatty acids in NSO fractions throughout the maturation window provides a source for microbial metabolites at burial depths extending to the temperature limits for microbial growth and the production of biogenic gas.

A- Carbon distribution of fatty acids, $C_nH_{2n}O_2$

CPI

C_{26}-C_{35}

2.66
1.65
1.55
1.23

Increasing maturation

Peak area

Carbon number per molecule

C- GC trace of saturated hydrocarbons collected at 275°C / 9h

B- Carbon distribution of saturated hydrocarbons

CPI

C_{25}-C_{34}

2.48
2.08
1.97
1.58

Increasing maturation

Area (uV.sec.)

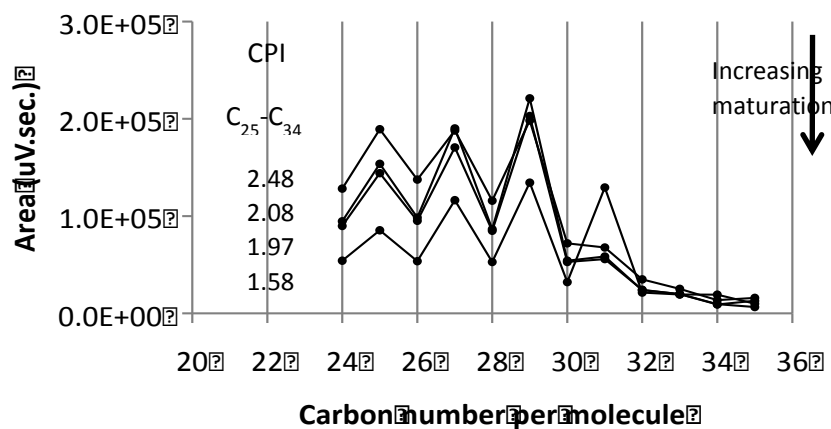**Carbon number per molecule**

Area (µV)

Retention time (min)

Figure 1. Evolution of the distribution of saturated mono-carboxylic acids (A) obtained by negative ESI-FTICR-MS (B) and of saturated hydrocarbons (C) obtained by GC-FID (D) during artificial maturation using a closed system pyrolysis.
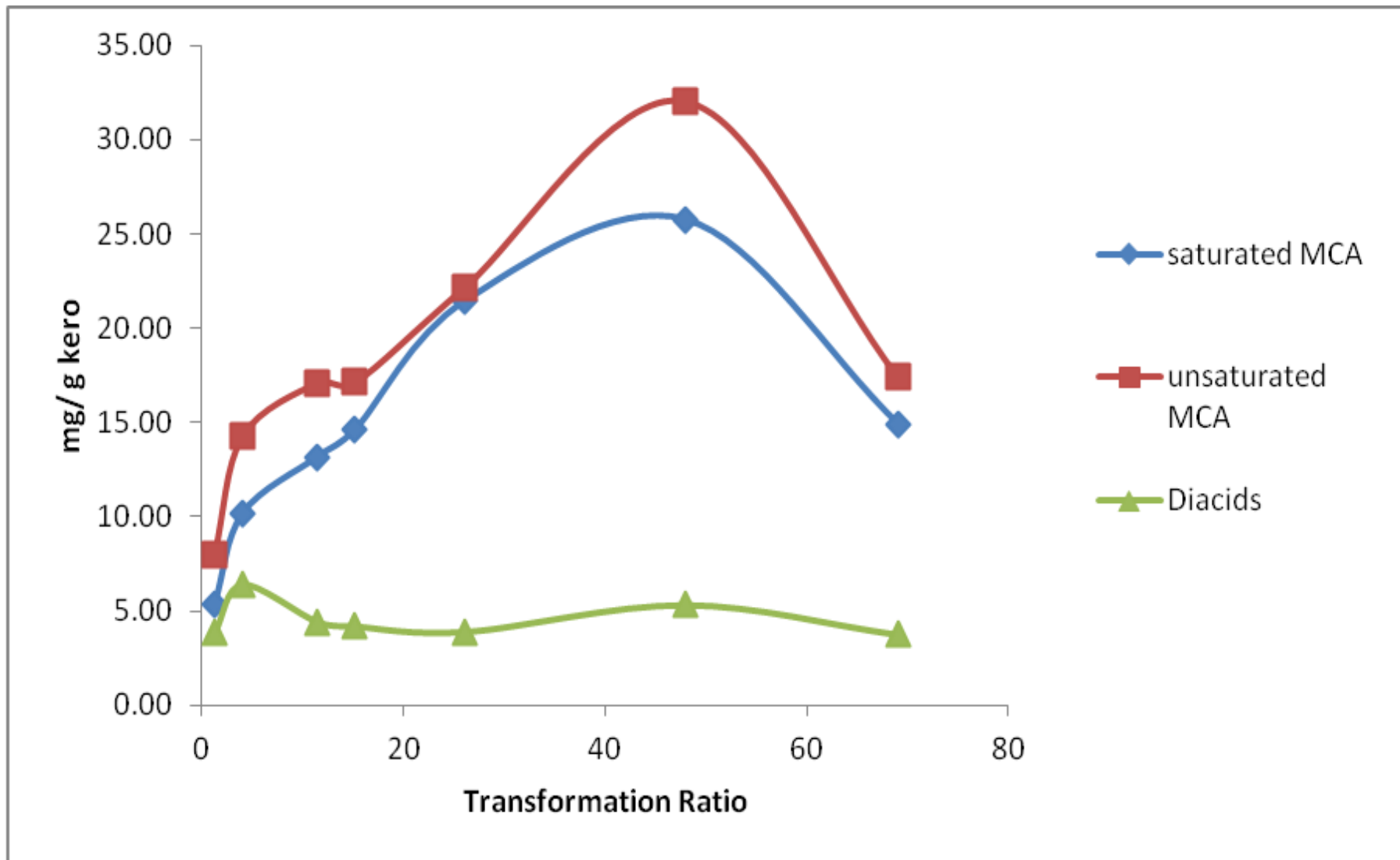
Figure 2. Evolution of total carboxylic acids over the transformation ratio during the maturation of kerogen: saturated MCA: total saturated mono-carboxylic acid, unsaturated MCA: total unsaturated mono-carboxylic acids and Diacids: total di-carboxylic acids. Total implies the addition of n-pentane extracts and DCM extracts.