

## Oil from Type III organic matter: resinite revisited\*

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**Abstract**—For coal or terrestrial (Type III) organic matter to act as a source rock for petroleum, two separate criteria must be met. The coal must be capable of (1) generating hydrocarbons in response to thermal stress (catagenesis) and (2) releasing those hydrocarbons to a porous migration conduit or reservoir (expulsion or primary migration). While there is little doubt that coal is an effective source for methane, liquid hydrocarbons (oil) have been only rarely attributed to a coal source. This is in spite of the observation that virtually every high volatile bituminous coal (i.e. in the oil window) contains significant amounts of solvent extractable hydrocarbons, typically up to 24,000 ppm or 30 mg hydrocarbons/g organic carbon (assuming a carbon content of 80%). Thus one is left to conclude that the limiting factor is not the ability to generate hydrocarbons, but rather primary migration out of the rock. In order to be an effective source, the organic matter in a rock must have chemical properties such that it can produce a quantity of bitumen that exceeds the expulsion threshold. Empirical evidence suggests that inertinite (or fusinite) falls well below 30 mg/g and vitrinite typically yields values that are up to this limit but rare above it. Liptinitic macerals such as resinite and sporinite are enriched in hydrogen and have a higher capacity to generate hydrocarbons. As a result, coals that are rich in liptinites will exceed the bitumen saturation threshold at maturity and be capable of expelling liquid hydrocarbons if a physical migration route is available.

**Key words**—coal, Type III organic matter, source rock, migration

### INTRODUCTION

In order for coal (massively deposited) or coaly (dispersed, Type III) organic matter (OM) to function as an effective source for petroleum, two separate processes must occur: (1) bitumen must be generated from the organic matrix within the coal or rock, and (2) this bitumen or the hydrocarbon (HC) portion of it must be expelled from the source (primary migration) into a relatively more permeable, secondary migration pathway. While there are almost certainly differences in the chemical composition of massively bedded coal and dispersed coaly material which result from their different depositional and diagenetic histories, the controls on hydrocarbon generation and expulsion are the same.

Empirical evidence (documented crude oil and source rock pairs; Powell, 1978 and references therein) suggests that before expulsion occurs, the organic carbon (TOC) normalized hydrocarbon concentrations (yield) must exceed a threshold value. The empirical observations are that documented effective source rocks have HC yields of > 50 mg HC/g TOC while coals and coaly samples (which are rarely interpreted as being source rocks) almost always have HC yields that are < 30 mg HC/g TOC (Fig. 1). Thus, solvent extract data indicate that, while Type III OM does yield petroleum hydrocarbons in response

to thermal stress, the quantities are usually not sufficient to overcome the expulsion threshold. In general, Type III OM at levels of maturity within the oil window (0.7%  $R_o$  – 1.2%  $R_o$ ) have given rise to and still contain less than the critical 30–50 mg HC/g TOC. Hence this type of rock would not be expected to have overcome the expulsion threshold and thus would not normally be considered as a potential petroleum source rock.

Hydrocarbon yields are based on the gravimetric analysis of solvent extracts and as such typically represent only the  $C_{13+}$  (liquid) components. Thus the above noted empirical criteria for source rock potential are only valid for consideration as a potential source rock for oil. Source rocks which yield large

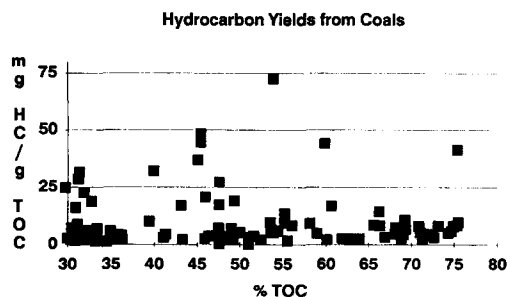


Fig. 1. %TOC vs hydrocarbon yields (mg HC/g TOC) for a number of coals and clastic rock samples dominated by Type III OM from a wide range of thermal maturities. The %TOC is partially a function of the ash (mineral) content and partially the result of catagenesis.

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amounts of hydrocarbons in the  $C_8$ – $C_{12}$  range would be poorly characterized by solvent extraction and fractionation techniques because these materials are typically lost during solvent removal. Hydrocarbons below about  $C_8$  are lost during air drying of the rock sample prior to extraction. Thus while the extractable hydrocarbon yield criteria for source potential may be partially valid for light oils or condensates (by using a threshold value of 30 mg HC/g TOC rather than the 50 mg HC/g TOC which is appropriate for Type II OM), they cannot be used for determining the source potential for gas.

In order to overcome the expulsion threshold for liquid hydrocarbons (oil), a coal or coaly sample must have a higher than normal capacity to generate hydrocarbons in response to catagenetic stress. This can be achieved if the overall hydrogen content of the coal is elevated by the incorporation of a significant amount of hydrogen rich macerals into the coal or coaly material. Cutinite, alginite, resinite, suberinite, desmocollinite and sporinite are all enriched in hydrogen relative to vitrinite and inertinite (the dominant macerals in most coals). Thus if a coal contains some minimum amount of liptinite (for example), then it will generate sufficient hydrocarbons to overcome the expulsion threshold and hence qualify as a potential source rock.

#### *Elements of the resinite source rock model*

Resinite is a common coal maceral typically present in concentrations of about 5% of the organic matrix of any given coal but occasionally occurring in much higher concentrations, notably in Cretaceous/Tertiary samples from S.E. Asia and Gippsland Basin, Australia. It has been considered to have contributed sufficient source potential to Type III dominated OM in the Beaufort–Mackenzie basin (Snowdon, 1980, 1984, 1987; Snowdon and Powell, 1982) to yield several large deposits of oil and condensate. Resinite or its polymerized form amber, is composed of various types of compounds (Langenheim, 1990; Grimalt *et al.*, 1988) including monoterpenes ( $C_{10}$ ), sesquiterpenes ( $C_{15}$ ), diterpenes ( $C_{20}$ ), and triterpenes ( $C_{30}$ ) as well as lipid compounds (waxes and essential oils) and phenolic derivatives. Different resinite materials thus have quite variable chemical compositions and hence would be expected to respond quite differently to thermal stress (Meuzelaar *et al.*, 1990; Crelling *et al.*, 1991). Diterpenoid based resinite appears to be the most common and it is apparently more reactive than sesquiterpenoid base resinite, at least that from the Utah coal (Meuzelaar *et al.*, 1990). Diterpenoid resinite is thus of more significance from the petroleum generation and expulsion standpoint and the following discussion will be restricted to that type of material.

Abietic and isopimaric acids are typical tricyclic diterpenoid resin acids with an atomic H/C ratio of 1.5 ( $C_{30}H_{30}O_2$ ). Reduction of the terpene double bonds, in early diagenesis, will increase the proportion

of hydrogen and measured H/C values of immature resin from the Canadian arctic averaged 1.58 (Snowdon, 1980). Thus the incorporation of these materials into Type III OM will tend to increase their hydrogen content. These compounds undergo complete transformation to volatile hydrocarbon products during pyrolysis and so they increase the hydrocarbon yield and total bitumen yield of Type III OM to an even greater extent than would be expected on the basis of the increase in hydrogen content.

Diterpenoid resinite is also thermally labile. Open system pyrolysis (TGA and Rock-Eval) indicates that resinite reacts at lower temperatures than most other types of OM (Snowdon and Powell, 1982; Fowler, 1991). While questions may arise regarding the absolute kinetic parameters derived from open system pyrolysis, it is quite clear that the experimental results indicate that diterpenoid resinite is *relatively* more reactive than other macerals. Furthermore, the absolute kinetic parameters (or distribution thereof) have been found to yield empirically useful simulations of oil generation (Tissot and Welte, 1984; Tissot *et al.*, 1987). Other types of evidence such as petrographic (Khavari-Khorasani and Murchison, 1988) and field observations (H. Williams, personal communication) corroborate these experimental results, in that resinite is commonly no longer visible as a massive phase in coals or sedimentary rocks at levels of thermal maturity beyond about 0.7%  $R_o$ . Similarly, extract data from samples which have experienced geological heating rates, times and magnitudes show that resinite-related biomarker compounds are no longer present above 0.7%  $R_o$  (Hollerbach and Hagemann, 1981).

The kinetic control of hydrocarbon generation from liptinitic macerals in coal is important to the type and quantity of the products which may ultimately be expelled. Low energy reactions would yield sufficient oil for expulsion whereas moderate to high energy reactions would result in delayed generation. Later generation of liquid hydrocarbons would correspond to higher sorptive capacity of the coal matrix (Fassett, 1989) (i.e. higher expulsion threshold) and also to reduction in liquid concentration through cracking to gas. This process is proceeding simultaneously with bitumen (and hence hydrocarbon) production and with an effective activation energy similar to that of much of the initial potential of Type III OM (239 kJ mol<sup>-1</sup>, Ungerer and Pelet, 1987). Thus, coals with either low concentrations of, or slow reacting, liptinite would never reach the expulsion threshold for liquid hydrocarbons and would thus only be expected to be effective sources for late catagenesis products, i.e. gas.

The resinite hypothesis (Snowdon and Powell, 1982) evolved as a means of explaining a number of phenomena observed in the Tertiary deltaic sediments of the Beaufort–Mackenzie Basin (Snowdon, 1978, 1980; Snowdon and Powell, 1982). These observations included the following:

- (1) the occurrence of crude oils and condensates with low maturity chemical properties including biomarker ratios, odd/even *n*-alkane predominance, high pristane/*n*C<sub>17</sub> ratios, and low gasoline range maturity ratios;
- (2) crude oils which contained very low amounts of wax (*n*-alkanes with 22 or more carbon atoms) but significant amounts of discrete tricyclic diterpenoid compounds and unresolved hydrocarbons chromatographically eluting in the *n*C<sub>13</sub> to *n*C<sub>20</sub> range (sesquiterpane and diterpane humps) and indicators of a terrestrial source including the sterane distribution and specific terpane compounds such as oleanane and lupanes;
- (3) a lower gas/oil ratio for discoveries than is typically observed for other Tertiary deltas;
- (4) up to 10 km of Tertiary, clastic, deltaic sediments which contain essentially only terrestrial (Type III or higher land plant) organic debris;
- (5) unusually low maturation gradients and commensurate low absolute maturity (0.7% *VR*<sub>0</sub>) at depths down to 5 km throughout the near shore and offshore sections.

The resinite hypothesis provides a mechanism for obtaining liquid hydrocarbons, both oil and condensate, from terrestrial OM at low levels of thermal maturity. The consistency with low levels of thermal stress was inferred from open system pyrolysis experiments. That is, pyrolysis experiments on resinitic material yielded hydrocarbon products at lower temperatures than did other types of OM under the same operating conditions.

#### RECENT LITERATURE

##### Kinetics

Hydrous pyrolysis experiments on resinite (Lewan and Williams, 1987; Hwang and Teerman, 1988) have yielded very different kinetic results from those noted above. That is resinite has been determined to react at about the same or a slightly slower rate than most other types of kerogen. These slower kinetic results are consistent with the open system (Curie Point) pyrolysis experiments of Crelling *et al.* (1991) and Meuzelaar *et al.* (1990). However, these latter authors also concluded that the Hiawatha "B" coal seam, the source of their samples, was somewhat unusual in that the resinite was dominated by sesquiterpenoid derivatives rather than the more normal diterpenoid or triterpenoid compounds. Furthermore, the rank of the Hiawatha "B" seam was estimated to be 0.58% *VR*<sub>0</sub>, a rank that is high enough to have resulted in significant alteration of diterpenoid resinates if they had been present in the original coal and also high enough to contain secondary macerals such as exsudatinite. Thus it is not clear that these results are directly applicable to the determination of

the kinetic behaviour of most resinite-rich kerogens, or coals. Langenheim (1990) draws attention to the difference in behaviour of different plant resins with respect to polymerization to the massive, fossil form of amber. It is quite possible that polymerized resin (amber) has quite different kinetic properties from resinite. Langenheim also points out that abietic acid does not polymerize and thus it is quite possible that plants exuding resins, rich in this and other non-polymerizing diterpenoids, will yield a more thermally labile resin (and hence resinite rather than amber) than plants with communic acid or other polymerizable compound based resin. An additional consideration is that the slow kinetic determined by Lewan and Williams (1987) may in part be an artifact of the particular products used to monitor the reaction during or after the hydrous pyrolysis experiment. Fowler *et al.* (1991) tracked not only the products but also the nature of the starting coal, and post-pyrolysis residue, and concluded that resinite reacts in response to hydrous pyrolysis at lower temperatures than classical Type II or Type III OM.

Monthioux *et al.* (1985) and Monthioux and Landais (1989) concluded that confined pyrolysis better approximates natural catagenesis than open system pyrolysis and further than hydrous pyrolysis systems may not actually represent confined pyrolysis. This would be especially true for experiments carried out on small samples in typical hydrous pyrolysis bombs. Evidence for this may be seen in the occurrence of increased amounts of *n*-alkenes along with the *n*-alkanes for hydrous pyrolysis experiments in which the quantity of starting material (kerogen, asphaltene, rock) is unusually small. Not only are *n*-alkenes present but also the proportion of aromatics is increased even more than that observed for "normal" hydrous pyrolysis experiments. Monthioux and Landais (1987) have also presented a considerable amount of evidence documenting the presence of "free but trapped" hydrocarbon in coals. These hydrocarbons comprise products which have been generated but not expelled. This observation is consistent with the expulsion threshold model in that concentrations have not reached the saturation level in response to catagenesis or, if expulsion has occurred, the residual bitumen content corresponds to the threshold saturation level.

Khavari-Khorasani (1987) and Khavari-Khorasani and Murchison (1988) have drawn attention to the occurrence of oil prone coals which result from the presence of hydrogen rich liptinites and also perhydrous vitrinite. Resinites have been divided into terpene resinite (as discussed above) and lipid resinite (a high molecular weight, waxy maceral which is thermally less reactive than alginite). They also draw attention to the little reported but apparently not uncommon maceral, suberinite. This maceral may be very significant in the early generation of oil from coal because it is even more reactive than terpene resinite.

Horsfield *et al.* (1988) have suggested that resinite-derived hydrocarbons may be sufficient to overcome the saturation or expulsion threshold for Type III OM. As a result, the products reflect not only the terpenoid chemistry of the resinite, but also that of modest amounts of early generated hydrocarbons from other macerals, including *n*-alkanes and non-resinite triterpanes. This mixed chemical character was considered by Lewan and Williams (1987) to be evidence against the importance of resinite for early hydrocarbon generation from coal or coaly OM.

#### Mass balance considerations

Lewan and Williams (1987) have also drawn attention to the limited quantitative significance of resinite as a potential source material for petroleum on a world wide scale. This limitation of the restricted volumetric occurrence of resinite rich material is only exacerbated by the apparent distribution of different types of resinite with markedly different thermal properties. That is, not only is resinite present in limited quantities on a worldwide basis, but at least some of this resinite is apparently not particularly reactive. This limitation is consistent with, and may be a valid explanation for, the relatively small deposits (~50 million barrels) of apparently low maturity oils such as those at the Koakoak and Adgo structures in the Beaufort-Mackenzie basin (see, for example, Dixon *et al.*, 1988). Similarly, the rapid increase in maturity predicted (Issler and Snowdon, 1990) for Amauligak (~500 million barrels) would be consistent with a more conventional, albeit Type III, source rock and larger volumes of petroleum.

A mass balance consideration on a much smaller scale involves the impact on the theoretical source potential of substituting relatively small amounts of hydrogen rich (liptinitic) macerals for vitrinite/inertinite in a coal or Type III OM source rock. Table 1 shows that the results of a 10% substitution of Type II OM (liptinite, such as sporinite or cutinite) or Type I OM (resinite) is that the predicted hydrocarbon yield is raised from below the expulsion

threshold (25 mg HC/g TOC) to values high enough to yield liquid hydrocarbons (50–68 mg HC/g TOC in the examples shown). The assumption has been made that thermal maturation is at the 50% transformation ratio in both enriched cases (i.e. 60% total convertibility for the Type II OM and 100% convertibility for resinite). This does not carry any necessary implication for the relative level of thermal maturity for the examples shown and thus does not rely on any particular kinetic behaviour of the starting materials.

#### CONCLUSIONS

In order for coal and Type III OM to function as a source rock for liquid hydrocarbons (oil and condensate), the organic hydrogen content must be enriched to the extent that sufficient bitumen can be generated to overcome the expulsion threshold of about 30–50 mg HC/g TOC. This enrichment would normally be derived from liptinitic macerals such as sporinite and cutinite and especially resinite. As little as 10% hydrogen-rich maceral would be sufficient to raise the bitumen yield to that required for oil expulsion from a Type III source rock. The kinetics of oil generation from diterpenoid resinite appear to be faster than normal Type II OM, yielding sufficient bitumen for expulsion at lower than normal levels of thermal maturity.

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Table 1. Mass balance calculations showing the impact of enriching a "typical" coal with 10% resinite or 10% other liptinite

	TOC(g)	% converted to C <sub>13+</sub> HC	HC mass (mg)	Yield (mg HC/ g TOC)
Base case	2	2.5	50	25
10% liptinite replacement	1.82	2.5	45.5	
	0.18	30	54	
	2		99.5	50
10% resinite replacement	1.82	2.5	45.5	
	0.18	50	90.0	
	2		135.5	68

Resinite is indicated to undergo 50% conversion to liquid hydrocarbons while sporinite or cutinite is shown with 30% conversion to hydrocarbons. These numbers are chosen as about half of the total convertibility for the two types of OM. The HC yields predicted will occur at different levels of thermal maturity as function of the relative reactivity (kinetics) of the various materials. Figure 1 indicates that coal or coaly material rarely exceeds yields of 25 mg HC/g TOC at any level of thermal maturity.

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