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APPENDIX B

"Polymethylenes"

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POLYMETHYLENES

Polymethylenes in Coals - In a series of papers, Calkins and coworkers (1984a,b,c) did one of the most thorough studies on the occurrence of polymethylenes in coals. Calkins et al. (1984a) studied the pyrolysis of several coals in a fluidized bed reactor over a series of temperatures from 400 to 1000°C. The gases produced from pyrolysis were analyzed by GC. The results indicated that the yields of ethylene, propylene and butadiene were related, suggesting that these gases had a common precursor. The methane and benzene yields were not related to the ethylene yield, which indicates that these gases were derived from other components in the coal.

The coals were also analyzed by ¹³C-NMR. A good correlation was found with the ethylene yield and the resonance peak for long chain paraffinic carbons, which suggests that these (polymethylenes) are the likely precursors for ethylene, propylene and butadiene. These gases are known decomposition products of pure aliphatic materials.

Calkins and Tyler (1984b) confirmed that the paraffinic compounds were present in the tar itself by a combination of analytical techniques and pyrolysis experiments. Examination of some of the tar fractions indicated olefin/paraffin pairs from C₁₇ to C₂₄. They note that the form of the polymethylene compounds in the coal itself is not known. They could derive from aryl alkyl compounds, fatty acids, alcohols or other structures. Only a relatively small fraction are solvent extractable (Vahrman, 1970; Bartle et al., 1975,1979; Deno et al., 1981).

In a later paper, Calkins (1984c) reports a method for analysis of polymethylenes in coals based on liquefaction of the coal in tetrahydroquinoline with subsequent ¹H-NMR analysis of the liquefaction products in CDCl₃. This analysis was run on approximately 140 coals of a wide range of ranks. It was found that the polymethylene content was very low or absent in high rank coals (medium volatile bituminous, low volatile bituminous, anthracite) could be either high or low for medium rank coals (high volatile bituminous or subbituminous) and was consistently high for lignites.

The conclusion is that the polymethylenes are apparently destroyed or lost during the coalification process. The wide variation in low rank coals is apparently due to differences in geological origin or conditions. Cannel coals contain the largest amounts of $(CH_2)_n$, up to 18 wt.% or more, while lignites and subbituminous coals may contain as much as 10 wt.%.

In the final paper of this series, Calkins et al. (1984d) studied individual macerals from a wide range of coals. Both microliquefaction experiments and pyrolysis experiments were done to assess the $(CH_2)_n$ content. It was found that the exinite macerals were all high in $(CH_2)_n$, followed by vitrinite and then inertinite. It was also found that the $(CH_2)_n$ content was lower at higher vitrinite reflectance, supporting the idea that these are lost during the coalification process.

The work of Calkins and coworkers established in a systematic way that polymethylenes were present in coals but did not address the form in which they were present. This was the objective of Nelson (1987) who analyzed tars which had been produced by flash pyrolysis of three Australian coals using high resolution gas chromatography to determine n-alkane and n-alkene contents. They also analyzed liquids which had been produced from catalytic hydrotreatment of these tars. The objective of this work was to provide a quantitative estimate of the proportion of n-alkyl groups which are chemically bound to other structures in the parent coals.

The n-alkane and n-alkene contents were roughly equal for the subbituminous coal tar, while the alkenes predominate in the brown coal tar and the alkanes predominate in the bituminous coal tar. The tars from the first two coals were upgraded in the hydrotreatment process. For both coals, the n-alkane yield increased with the extent of hydrotreatment, even though the two stages of hydrotreatment were accompanied by significant gas formation.

The results of Nelson provided strong evidence that most of the n-alkyl groups are chemically bound to other structures in the coal. Nelson notes that these structures are not necessarily part of the polymeric framework of the coal but may be bonded to single ring aromatic compounds which comprise the "guest" material in coals.

Freihaut and Seery (1981) investigated the variation in the tar yield with the H/C and O/C ratio in the parent coal. The tar yield increases from high rank coals to medium rank coals as the H/C ratio increases (with little change in O/C ratio) and reaches a maximum for the Pittsburgh Seam bituminous coal. The tar yield then declines with the further increases in the O/C ratio as rank decreases (while the H/C ratio is fairly constant), which has been attributed to competition for donatable hydrogen from oxygen groups and/or crosslinking as a result of oxygen groups. A contributing factor may be the larger percentage of polymethylenes in low rank coals which implies that the aliphatic hydrogen is not as well distributed throughout the coal structure.

In a more recent paper, Freihaut et al. (1988) studied the chemical characteristics of tars produced in a novel, low severity, entrained flow reactor. The entrainment gas temperatures were kept below the wall temperatures to minimize the extra-particle gas phase reactions of tars. A set of samples from a wide range of ranks was studied. It was found that as the rank of coal increased, the elemental compositions of the tars became more like the parent coal, but that there was a wide disparity for low rank coals. This dissimilarity was primarily related to the aliphatic to aromatic hydrogen ratio and the oxygen-sulfur heteroatom content of the tars relative to the parent coals. The former was higher while the latter was lower for low rank coals. The higher aliphatic hydrogen concentration in the tars was shown to correlate with a polymethylene peak in the parent coals measured with FT-IR spectroscopy.

The Occurrence of Polymethylenes in Extracts - Studies on extracts are often cited in discussions of tar structure or properties. It is necessary to be cautious when relating the structure of extracts to tars or to raw coals. The temperature of extract formation is very important in determining whether these relationships are valid. This issue was addressed in a recent paper by Given et al. (1986). This paper contained a debate over the concept of a mobile phase trapped in the macromolecular structure of coal. The focus of the debate was the experimental ¹H-NMR data which indicates a population of relatively mobile protons in coals. The question was raised as to whether this material is the same as that extracted from the coal at low temperatures even though the amounts of extracts are usually not large enough to account for all the mobile protons. Given favors the view that this material is extractable, but that some of it is trapped or clathrated inside the coal. One piece of evidence is the

interaction of coal with solvent vapors, like toluene. After the coal is allowed to come to equilibrium with toluene over a period of seven days, upon evacuation of the sample one-half of the toluene is lost rather rapidly, while the rest was very difficult to remove. In the same paper, Marzec concurred with Given's view on the mobile phase and noted that the difficulty in extracting some components arises from the strength of their binding to the network by secondary interactions and partly by trapping of molecules within cages. It is likely that the former mechanism would be important for aromatic and heteroatom species while the latter would be important for the long chain polymethylenes.

In the same paper, Barton and Lynch took the opposite view, suggesting that parts of the macromolecular structure could become sufficiently flexible in the presence of solvents to contribute to the mobile proton signal. This view was also supported by Gerstein in the same article. All of the authors recognized that a major obstacle in settling the debate was the difficulty in carrying out the appropriate extraction experiment: one that would remove the tightly bound molecules in a reasonable amount of time while not disrupting the macromolecular framework of the coal.

At temperatures below 300°C, extraction of coal proceeds very slowly and occurs primarily by dissolution of molecules which are physically adsorbed in the pore structure of the coal or chemically bound to the macromolecular structure by very weak bonds (i.e., hydrogen bonds). The average composition of the extract does not usually reflect the major part of the coal although it may contain compounds which do. These points have been made by Vahrman and his co-workers in a series of papers, discussed below.

The above observations would explain the results of Gavalas and Oka (1978), who extracted coal by refluxing with THF at room temperature and at 66°C. At both temperatures, the composition of products was similar, although the yields were higher at the elevated temperature, up to 8.0 wt.% for a bituminous coal. The extracts were compared to the tars produced by pyrolyzing the same coal in vacuum at 500°C for 30 s, and also with the raw coal. It was found that tars were much closer in elemental composition to the raw coals, given that the extracts had a significantly lower oxygen content. Gavalas and Oka concluded that the difference was based on crosslinking of phenolic-OH. However, a simpler and more likely explanation was that the extraction temperature was too low to

cause a significant breakdown of the main coal structure and that only loosely bound molecules were extracted. These "loose" molecules are primarily aromatic and aliphatic hydrocarbons, including polymethylenes, which have a higher H/C ratio than the primary coal structure. At low temperatures, the rate of dissolution is controlled by physical transport of the molecules into the bulk solution. This is consistent with the low activation energy (3kJ/mole) for coal dissolution in the range from 200 to 320°C that was found by Słomka and Rutkowski (1982).

At temperatures above (approximately) 350°C, pyrolysis of coal becomes the dominant mode of product generation. The kinetic rates of ordinary pyrolysis and dissolution are very similar in this range (Wiser, 1986; Wiser et al., 1971), although the total yield of product is generally higher in the latter. This is especially true if a hydrogen-donor solvent is present. The donor solvent can provide hydrogen to stabilize reactive fragments, which are likely to repolymerize in ordinary pyrolysis due to the low inventory of hydrogen in the coal. Extracts produced at these elevated temperatures are generally representative of the "average" coal structure, since they are produced by depolymerization of the coal in the same manner as the primary pyrolysis tars. They are usually of higher molecular weight than the tars since it is easier for a large fragment to go into solution than to evaporate without decomposing. In this sense, extracts produced at pyrolysis temperatures can be more "primary" than the primary tars.

Vahrman and his colleagues produced a classic series of papers which revealed the similarities between low-temperature tars and extracts (Vahrman, 1970; Spence and Vahrman, 1970; Rahman and Vahrman, 1971; Palmer and Vahrman, 1972a,b; Vahrman and Watts, 1972a,b). In the first paper, Vahrman (1970) noted that extracts and primary tars contained two broad groups of substances which he called H-compounds and O-compounds. The first group was made up of hydrocarbons (aromatic and aliphatic) and smaller quantities of neutral, oxygen-containing compounds (mainly heterocyclic), of molecular weights up to about 550 which are soluble in light petroleum. This group includes the polymethylene compounds. The second group of compounds contained a series of alkylated, hydroxyl-substituted aromatic compounds, insoluble in light petroleum, with molecular weights up to about 1000. In the terminology developed for petroleum, the H-compounds would be considered "oils" while the "O" compounds would be

divided into asphaltenes (benzene-soluble) and preasphaltenes (benzene-insoluble). The preasphaltenes are also referred to as asphatols in some papers.

In all the studies done by Vahrman and his colleagues, the extraction temperature was 300°C or less. Consequently, one can assume that "true" extracts were being formed rather than pyrolytic extracts. This is supported by the work of Rahman and Vahrman (1971). They found little evidence of the complex O-compounds (benzene-insolubles or preasphaltenes) in the extracts although they did occur in low-temperature tar. The preasphaltenes are considered to be the most primary fragments from the decomposition of the main part of the coal structure.

However, Rahman and Vahrman did find that the amounts of H-compounds in the low-temperature tar and extract agreed quite well if a thorough extraction was performed by using high pressure, long extraction times, and/or relatively high temperatures (300°C). The composition of the polymethylenes portion (C₁₂-C₃₈) of the H-compounds was also similar for the tars and extracts. The major difference was the presence in the tars of terminal mono-olefins, in amounts which varied depending on the thermal history of the coal and its volatile products. This indicated that polymethylenes in the tar had undergone mild thermal cracking. In the extracts, the ratio of 1-alkenes to n-alkanes was small and consistent with their being derived from the original plant hydrocarbon wax.

In another study, Spence and Vahrman (1970) performed stepwise Soxhlet extractions using benzene/ethanol, of a weakly-caking bituminous coal at atmospheric pressure. It was found that under mild conditions most of the hydrocarbons (H-compounds) were extracted with difficulty and the order of extraction was governed by their molecular size and structure. For these reasons, the hydrocarbons were postulated to exist primarily as adsorbed molecules in the microporous structure of the coal.

In a later study of pyrolysis of thin beds of weakly-caking coal, heated in stages to 500°C, Vahrman and Watts (1972) found that evolution of aliphatics below 250°C and of aromatics from 250-300°C could be correlated with the boiling range of the materials released, indicating adsorption in macropores. There was no such correlation above these temperatures, as each fraction had a much wider boiling range than the interval of its release, as shown in Fig. B-1. A tendency

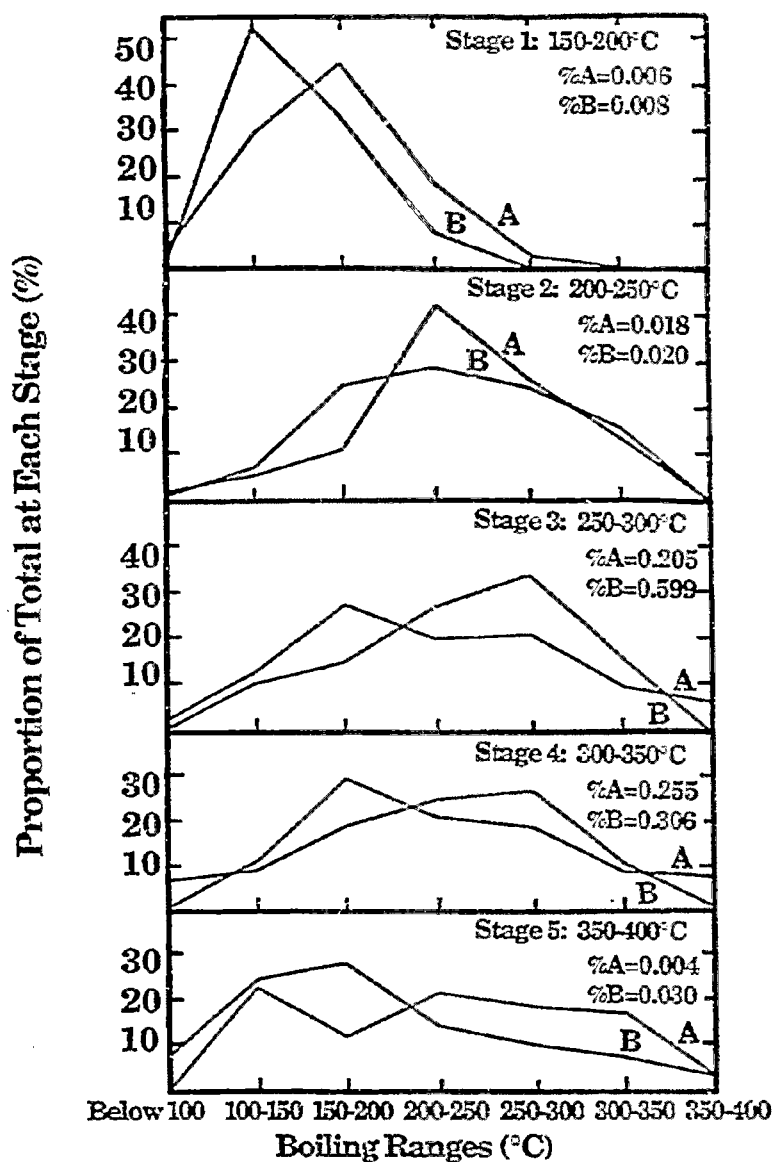


Figure B-1. Aliphatic and Aromatic Hydrocarbons of Different Boiling Ranges Liberated in Five 50°C Stages when Heating Coal between 150 and 400°C Proportions of the Totals at Each Stage. A-Aliphatic Hydrocarbons, B-Aromatic Hydrocarbons % A and B for Each Stage Above is on dmmf Basis (Vahrman and Watts, 1972).

was observed, though not as clearly as in the case of extraction, for molecules to emerge in order of diminishing molecular size, indicating that the material was adsorbed in micropores and that molecular sieve processes were operating. Since most of the hydrocarbon (H-compound) evolution could be accomplished at temperature less than 400°C, below the decomposition temperature of the main part of the coal, the evolution of these species by physical transport processes appears to be a reasonable explanation, as in the case of extraction.

Another conclusion that can be reached from an examination of Fig. B-1 is that the low temperature tars contain almost equal amounts of aliphatic and aromatic material. Above 350°C, where the network decomposition has begun, the aromatics predominate.

Snape et al. (1985) studied the distribution of aliphatic groups in supercritical gas extracts, hydrogen-donor solvent extracts, pyrolysis tars and hydrolysis tars using an NMR based structural analysis method which identifies hydroaromatic, methyl, and long alkyl ($\geq C_6$) groups. The results indicated that, in lignites, methyl and other alkyls account for about one-half of the aliphatic carbon. The long alkyl chains (polymethylenes) accounted for about 35% while short chains accounted for 10% of the aliphatic carbons in lignites. The evidence suggested that some of the long alkyl chains were joined to aromatic structures. For bituminous coals, the long chains represented only 10% of the aliphatic carbons, while short chains represented 20%.

Evolution Kinetics of Polymethylenes - Burnham et al. (1989) report results for the Argonne coals from a pyrolysis experiment interfaced to a triple-quadrupole mass spectrometer (TQMS). The samples were heated at 4°C/min in a gas-swept, annular stainless steel reactor. They also report results from Rock-Eval analysis of the same coals at heating rates of 5, 16, 25 and 59°C/min.

In the standard Rock Eval experiment, the sample is heated at 300°C for three minutes to evolve all free hydrocarbons. These results are compared to the amount of pyridine extractables determined for the same set of coals in Fig. B-2. It can be seen that the quantities are only roughly correlated since solubility and volatility are affected differently by such factors as molecular weight and functional group composition.

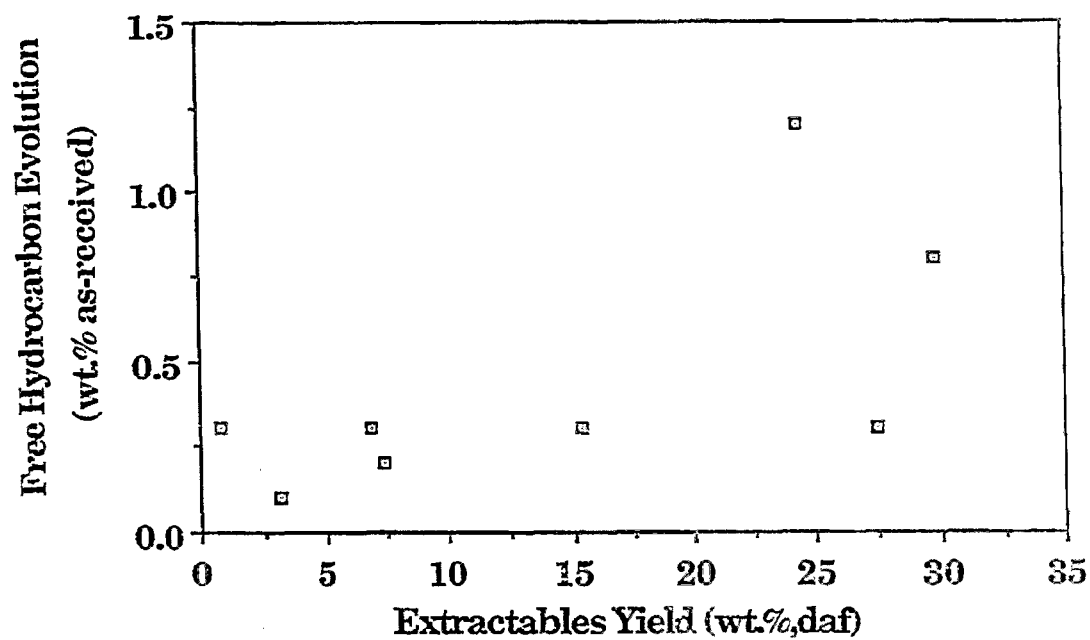


Figure B-2. The Evolution of "Free Hydrocarbons" from Rock Eval Analysis of the Argonne Premium Coal Samples (Data of Burnham et al., 1989) Compared to the Pyridine Extract Yields (Data of M. Lee, Brigham Young University).

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Burnham et al. found that in the TQMS experiments, where the sample was not preheated, the tar evolution profile had two peaks. The low temperature (-350°C) peak was relatively small and appeared to be obscured by the larger peak for low rank coals. It is most pronounced for the Upper Freeport coal and the Pittsburgh Seam bituminous coal.

The evolution of hydrocarbons (both peaks) are coincident with CO₂ evolution peaks below 500°C. This suggests that, in both cases, hydrocarbon evolution is related to the decomposition of coal carboxylic acids, salts, or esters.

Burnham et al. examined the mass spectrum of the two hydrocarbon peaks for the Upper Freeport coal. The masses characteristic of polymethylenes and alkylthiophenes are relatively more abundant in the lower temperature peak (355°C at 4°C/min) while the masses characteristic of alkylbenzenes and phenols are more abundant in the high temperature peak. A similar bimodal tar peak was observed for the Pittsburgh Seam and Utah Blind Canyon coals.

Burnham et al. found that the evolution profiles of aromatic compounds are generally broader than those of aliphatic compounds. The latter can generally be described by a single first order reaction with a small value of σ . The σ increases as rank decreases. In addition, the values of T_{max} are less rank dependent for aliphatic compounds.

Oforu-Asante et al. (1989) studied the pathways for the decomposition of linear paraffinic materials during coal pyrolysis. They prepared Illinois No. 6 coals with covalent incorporation of 1-pentadecyl, 1-octadecyl, and 1-octadecyl-d₃₇ fragments. The modified coals were heated at 1000°C/s to 700-850°C in a helium atmosphere at 0.02 MPa. The gaseous product distribution was examined in order to define the principal reaction pathways for the decomposition of the paraffinic constituents. The modified coals were analyzed by FT-IR to confirm that the polymethylene fragments had been successfully covalently bonded to the oxygen atoms of the phenolic groups of the coal samples. The degree of alkylation was approximately 1.0 mole of alkyl group per one hundred mole carbon atoms for the unlabelled alkyl groups. The yields of char were significantly reduced and the yields of tar significantly increased for the modified coals. This was believed to be due to an increased amount of donatable hydrogen

available to stabilize free radicals produced during the thermal decomposition of the coal which diverted the intermediates from retrogressive char formation pathways into pathways which lead to lower molecular weight volatile tars.

The yields of ethylene, propylene and butadiene were significantly enhanced in the alkylated coals. This is consistent with the conclusion of Calkins and coworkers (1984a) that the polymethylenes are precursors for these gases. The results on the labelled substituents also confirmed that the linear paraffins are not the precursors of methane, benzene, or other volatile aromatic compounds. This same conclusion was also reached by Calkins and coworkers (1984a).

It should be noted that the evidence supplied by Ofosu-Asante et al. was for attached alkyl fragments and may not apply to those which are physically bound in the coal.

Summary - There is present in coals varying amounts (typically 0-9%, but in some cases as high as 18%) of long-chain aliphatics (polymethylenes). These have recently been reported in pyrolysis products by Nelson (1987) and by Calkins and coworkers (1984a,b,c,d) and references quoted therein. The chains appear alone and attached to aromatic nuclei. During devolatilization, the smaller molecules may be released without bond breaking and the heavier molecules with bond breaking to contribute to the tar. The presence of these polymethylenes makes the tar more aliphatic than the parent coal. Further cracking of this material under more severe devolatilization conditions produces ethylene, propylene, and butadiene from which the concentration of polymethylenes may be determined (Calkins, 1984c). Presently, the polymethylenes are included in the FG model as part of the aliphatic functional group pool, which is assumed to decompose to produce gas products, not tar (Serio et al., 1987). This leads to an error in determining the H/C ratio in the tar which can be important for low rank coals (Freihaut et al., 1988). If the amount of heavy polymethylenes is determined, these can be computed as a separate functional group pool with an appropriate release rate and added to the tar. However, strictly speaking, the polymethylenes should also be included as a type of oligomer so that the smaller species can vaporize directly, without bond breaking. This would also allow the polymethylenes to be included in the extractable species.

The problem of vaporizing the small polymethylenes and including them in the extract yield are related. For most coals, there is a low temperature tar peak which is polymethylene-rich but also includes aromatic tars. Currently, the FG-DVC model uses an interactive procedure at the beginning of a simulation which adjusts the oligomer length to match the experimental pyridine extract yield with the molecular configuration in the computer. The model considers extract to be those molecules which are less than 3000 in molecular weight. However, this does not produce tar molecules which are light enough to vaporize at low temperatures. A possible route to achieving the desired bimodal tar molecular weight distribution is to start out with a large oligomer length and allow the coal to undergo pre-pyrolysis using geological time-temperature profile. A second possibility is to use a distribution of oligomer sizes.

The information in this appendix can be summarized as follows:

1. Polymethylenes, $(CH_2)_n$, are present in coals at a level of 0 - 18 wt.% depending on rank.
2. Very high rank coals (anthracites) contain very little $(CH_2)_n$ while low rank coals (lignites) generally contain at least 10 wt.%. The amounts for coals of intermediate rank are highly variable and depend on geochemical factors.
3. Exinite macerals are high in polymethylenes, followed by vinitrite and then inertinite.
4. A significant fraction of the $(CH_2)_n$ are attached to aromatic structures in the coal and are not readily extractable.
5. The $(CH_2)_n$ are the precursors for the ethylene, propylene, and butadiene produced from high temperature pyrolysis of coal. They are not precursors for methane, benzene or other light aromatic compounds.
6. The $(CH_2)_n$ appear to play an important role in donating hydrogen to stabilize the reactive aromatic fragments.

7. The $(CH_2)_n$ appear to decompose by a free radical chain reaction which is different than that observed for pure $(CH_2)_n$ in the gas phase. They also decompose differently than the main coal structure.
8. Some of the $(CH_2)_n$ are light enough to vaporize directly without bond breaking. The low temperature tars which evolve prior to the main decomposition peak and the low temperature extracts from coal are enriched in $(CH_2)_n$.
9. The vaporization laws which apply to $(CH_2)_n$ will be different than those which apply to the aromatic tars. For a given molecular weight, aliphatic compounds are more volatile than aromatic compounds.
10. The $(CH_2)_n$ will not participate in crosslinking reactions in the same way as the rest of the (aromatic) tar molecules.

All of these factors must be addressed to correctly deal with the occurrence of polymethylenes. However, some can be neglected in the first generation model.