



A model for lignin alteration—part II: numerical model of natural gas generation and application to the Piceance Basin, Western Colorado

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Abstract

The model presented here simulates a network of parallel and sequential reactions that describe the structural and chemical transformation of lignin-derived sedimentary organic matter (SOM) and the resulting generation of mobile species from shallow burial to approximately low-volatile bituminous rank. The model is calibrated to the Upper Cretaceous Williams Fork Formation coal of the Piceance Basin at the Multi-Well Experiment (MWX) Site, assuming this coal is largely derived from lignin. The model calculates the content of functional groups on the residual molecular species, C, H, and O elemental weight percents of the residual species, and moles of residual molecular species and mobile species (including components of natural gas) through time. The model is generally more sensitive to initial molecular structure of the lignin-derived molecule and the H₂O content of the system than to initial temperature, as the former affect the fundamental reaction paths. The model is used to estimate that a total of 314 trillion cubic feet (tcf) of methane is generated by the Williams Fork coal over the basin history. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Lignin; Structural transformation; Reaction network; Kinetic; Piceance Basin

1. Introduction

This paper presents a numerical model of the transformation of lignin-derived sedimentary organic matter (SOM) and generation of natural gas in the geologic environment and an application of this model to a natural gas resource assessment of the Piceance Basin in western Colorado. The numerical model is based on a chemical–structural–kinetics model of the transformation of lignin-derived SOM as presented in Part I of this contribution (Payne and Ortoleva, 2001). The purposes of this model are to: (1) simulate the generation of natural gas in a way that respects the observed chemical and molecular structure changes that occur to lignin-derived

SOM; and (2) to calculate stoichiometrically and kinetically appropriate quantities of natural gas generated under natural burial conditions. The model introduces a new approach to simulating the maturation of SOM and prediction of hydrocarbon generation.

The chemical structural kinetic model is constructed as follows. A simplified guaiacyl polymer is adopted as the starting molecular structure, assuming that early microbial degradation has not significantly altered the lignin macromolecular structure. Observed transformations that occur over the maturation of lignin-derived sedimentary organic matter are described in terms of reactions. These reactions are placed in sequential order according to estimated thermal conditions during which each transformation occurs and constrained by the availability of reactant species, creating a network of sequential and competing reactions. Rough kinetic parameters for each reaction are assigned by using an estimated thermal range for each transformation. The reaction network is then refined by specifically calibrating the

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kinetic parameters of the network to elemental chemistry of Upper Cretaceous Williams Fork Formation coal from the Multi-Well Experiment (MWX) Site in the Piceance Basin (Fig. 1).

In the Piceance Basin, much of the methane resources are believed to be sourced by Williams Fork Formation coal. A fundamental assumption of this model is that the precursory molecular SOM for the Williams Fork Formation coal can be described as a lignin-derived macromolecule that has not experienced significant biodegradation after burial, aside from the degradation of cellulose. In reality, sedimentary organic matter from

which the Williams Fork Formation coal derives may have been comprised of a variety of precursory molecules, or may have experienced biodegradation after deposition that altered the lignin-derived macromolecules. Our assumption rests on the observation that the Williams Fork Formation coal is comprised of almost 90% vitrinite macerals (Zhang et al., 1997), and that vitrinite has been structurally described by a molecular model for gymnospermous lignin (Hatcher, 1990; Mukhopadhyay and Hatcher, 1993). The data also show that almost 5% of the coal comprises H-rich lipinitite macerals, which could contribute significantly to

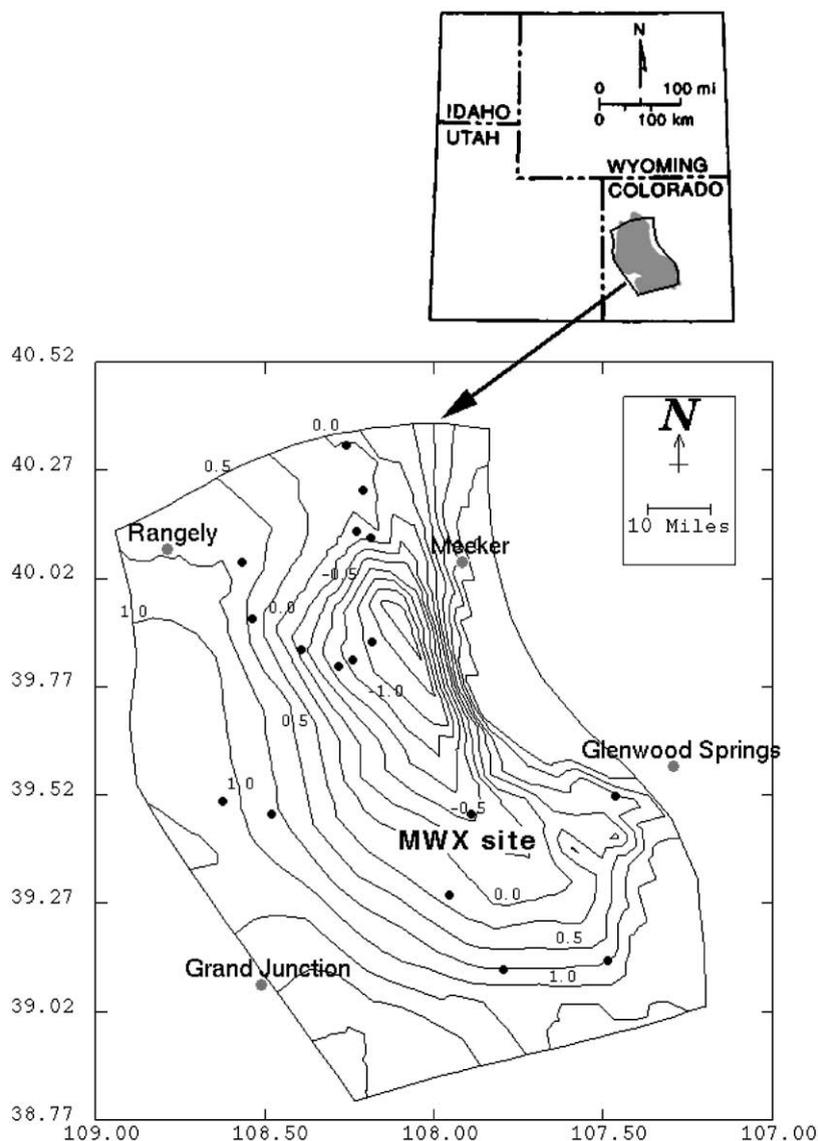


Fig. 1. Location of the Piceance Basin, and the MWX Site. The dots indicate locations of sites for which there is vitrinite reflectance data and burial and thermal histories; the contours indicate present day elevation (in km relative to sea level) to the top of the Rollins sandstone marker unit of the Mesaverde Group. Many of the coal source rock units are in the interval above this marker.

its methane generating potential. The available data for this research, however, do not indicate the nature of the methane source molecular chemistry. Thus for the purpose of demonstrating the model, it is assumed that a significant quantity of the starting material for the Williams Fork Formation coal is lignin-derived, and experiences the transformations that are described in the structural kinetics model presented in Part I of this contribution (Payne and Ortoleva, 2001).

Models, by their very nature, are simplifications of natural systems. As more aspects of these systems are described, models representing them may become more complex. For example, the model presented in this paper could be modified to represent the chemical and structural transformation, and hence natural gas generation, of the H-rich biomacromolecular components of the liptinitic fraction of the Williams Fork Formation SOM. Recognizing the implications of the model's assumptions, our primary intent here is to demonstrate this new approach to modeling natural gas generating systems, which takes advantage of descriptions of chemical structural changes of biomacromolecular components of SOM.

Here, we describe input and output for the model as applied to the MWX Site. Sensitivity of the model to initial land surface temperature, initial lignin chemical structure, and initial H₂O content are tested. Results of the model are used to estimate the amount of methane generated by the Williams Fork Formation coal for the whole Piceance Basin over the history of the basin, and compared with other resource evaluations.

2. Numerical model

Details of model construction are presented in Part I of this contribution (Payne and Ortoleva, 2001).

2.1. Input

Input for the model includes thermal and burial histories, the starting structural composition of the lignin-derived macromolecule (relative abundance of monomers A and B, Fig. 2), and initial H₂O content (a reactant in several of the reactions). The thermal and burial histories were constructed using available published data and thermal modeling (Fig. 3) (Lorenz, 1985; Johnson and Nuccio, 1986, 1993; Nuccio and Johnson, 1989; Comer et al., 1997). The starting lignin composition was assumed to be a two-monomer unit, 50% each of monomers A and B (this has an elemental weight percent of C: 64.3; H: 5.67; O: 30.0, compared with unaltered lignin C: 62.7; H: 5.5; O: 30.4; Hatcher, 1990). Thus 1 mol of the starting molecule comprises 1 mol of monomer A and 1 mol of monomer B. Initial H₂O content was taken to be 0.55 mol of H₂O for every mole

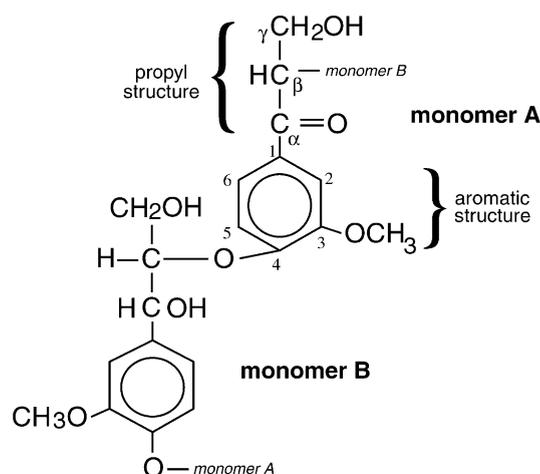


Fig. 2. Simplified model of initial lignin-derived macromolecule structure used in this study; one molecular unit of lignin comprises one monomer each of A and B, except as noted in the lignin composition sensitivity tests.

of starting molecule. This was the minimum required for all the reactions to go to completion (see Sensitivity testing section), yet there is not so much as to simulate a situation in which the precursor or any generated molecules were dissolved in H₂O (probably not a likely scenario).

2.2. Output

The output includes the following: content of functional groups (aromatic methoxyl, α -carbonyl, carboxyl, aromatic and aliphatic hydroxyl groups, and aromaticity); elemental weight percents (C, H and O) of the residual species; atomic O/C and H/C ratios; and moles of all species, mobile and residual, through time. R_0 has been calculated using predicted H/C and O/C ratios after the method of Burnham and Sweeney (1989), serving primarily as a guide to estimate the maturity of the residual molecular species throughout the simulation.

Fig. 4 shows how the structures of the residual molecular species change with time by showing the abundance of specific functional groups. The fraction of C3 aromatic sites occupied by a methoxyl functional group declines over the course of the simulation. The initial value represents the initial lignin-derived macromolecule with one aromatic carbon site occupied by a methoxyl functional group per lignin monomer. This functional group is completely lost by about 37 Ma in the simulation. R_0 calculated using predicted H/C and O/C ratios is approximately 0.45, which roughly corresponds to the sub-bituminous coal rank (Stach et al., 1982) (Fig. 5). This agrees with the observation that this functionality is lost by the sub-bituminous rank (Hatcher, 1990).

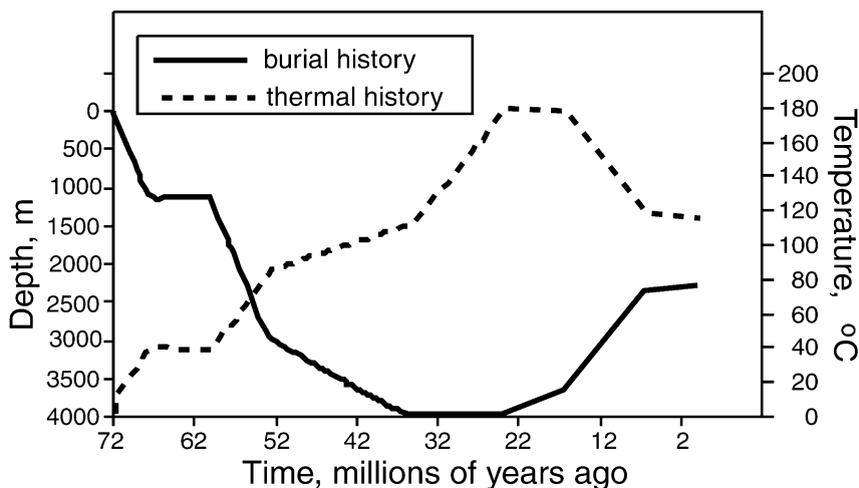


Fig. 3. Burial and thermal histories at the MWX Site in the Piceance Basin, used as input for the simulations. The curves follow the depth and temperature of a source rock-bearing interval at the bottom of the William's Fork Formation over the last 72 millions years.

Fig. 4 shows the fraction of carbon sites occupied by a carbonyl substituent group, which occurs in this network only at the propyl- α site. The loss of these substituent groups corresponds to an increase in carboxyl functional groups, as these sites are oxidized. The carboxyl functional groups are eventually lost by decarboxylation reactions, as indicated by the subsequent decrease in carboxyl groups. This is roughly predicted to occur by the sub-bituminous coal rank (Fig. 5). Observations, however, indicate that small amounts of carboxyl and even carbonyl functional groups remain by the sub-bituminous coal rank (Hatcher, 1990). This suggests that the first-order decarboxylation reaction rates of the model are probably too fast, and that other non-first order processes may be operating during decarboxylation.

Fig. 4 shows the fraction of carbons atoms that are aliphatic and occupied by hydroxyl functional groups. In the adopted initial molecular structure (Fig. 2), these hydroxyl sites are all located at the propyl- γ site, although observations suggest that many of these may be located on the propyl- α site. This shows that these sites are dehydroxylated early in the simulation, by about 57 Ma (approximately brown coal rank, Fig. 5), corresponding to observations of early loss of hydroxyl groups from the γ -site (Hatcher, 1990).

Fig. 4 shows that as aliphatic hydroxyl groups are decreasing, aromatic hydroxyl content increases, and subsequently decreases. This corresponds to the observations of Hatcher (1990). The initial increase in aromatic hydroxyl functional groups corresponds to the cleavage of the β -O-4 bond (Fig. 2), which creates an aromatic hydroxyl functional group (Payne and Ortoleva, 2001). Subsequent increases in aromatic hydroxyl are the result of a demethoxylation reaction, which also

results in substitution with an aromatic hydroxyl functional group. Loss of aromatic hydroxyl groups after about 55 Ma result from dewatering reactions. Aromatic hydroxyl functional groups are entirely lost from the macromolecular structure by about 29 Ma, approximately corresponding to high-volatile bituminous rank (Fig. 5).

Fig. 4 also shows the general increase in aromaticity (or fraction of C atoms in aromatic structures) with time. Three periods of increase in aromaticity increase are associated with demethoxylation, subsequent decarboxylation, and finally late stage demethylation. A final aromaticity of 1.0 may be high compared with observed aromaticity of higher coal ranks (Solum et al., 1989; Hatcher et al., 1992). This is a result of simplifications in the construction of the model lignin structure and the reaction network, as well as the assumption that the initial molecular composition is 100% lignin.

Fig. 6 shows the predicted generation of mobile species in moles per mole of starting lignin over the simulation history. The mobile species include H_2O , CH_3OH , CO_2 , CH_4 , and H^* . The species H^* is the cumulative concentration of reactive hydrogen in an unspecified form. When hydrogen is produced by any of the reactions, it may either react with itself to form H_2 gas, or it may serve as a reactant. Although the former is certainly possible, the latter may be a prerequisite for many of the other reactions to take place. For example, if demethylation of pendant aromatic methyl is written as a balanced reaction, a hydrogen source is necessary:



The importance of determining a hydrogen source is critical and is addressed elsewhere (Hoering, 1984;

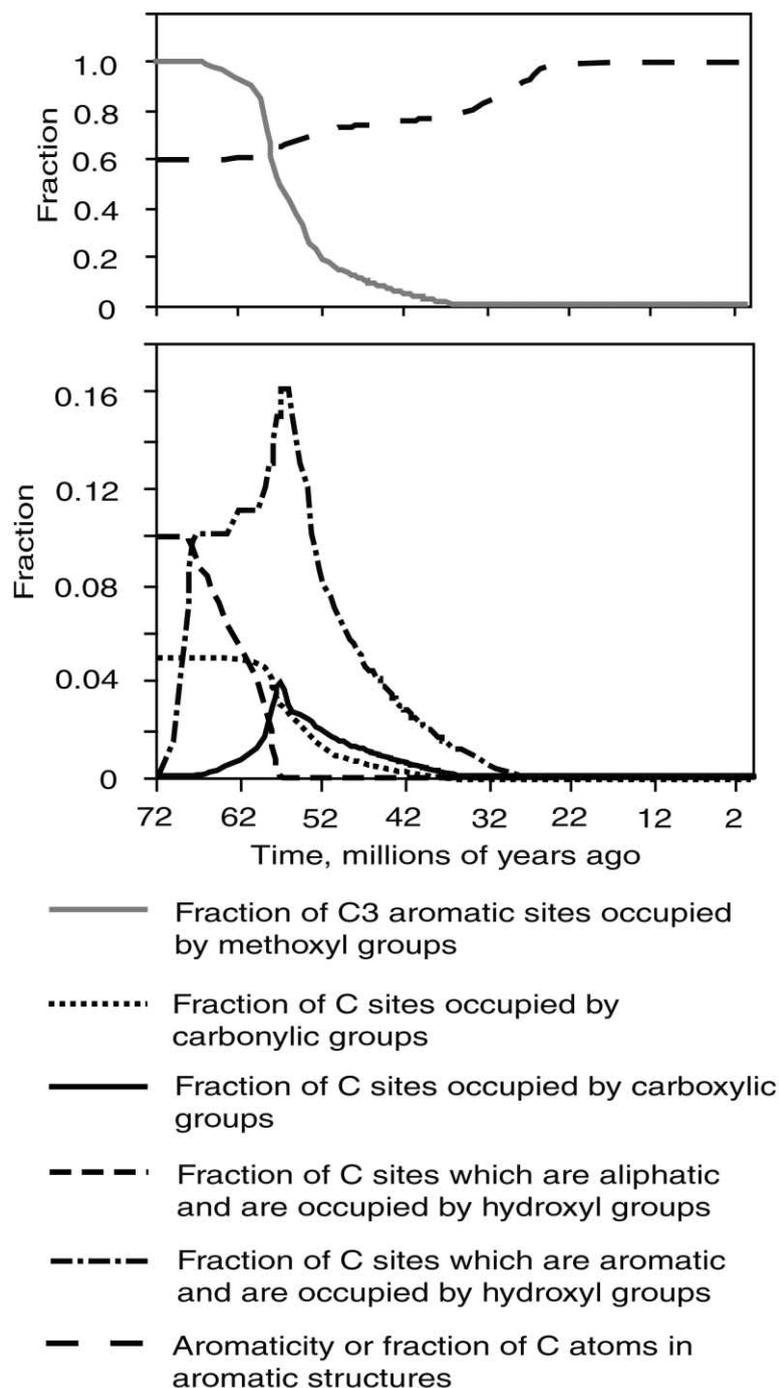


Fig. 4. Fractional changes in functional groups over the course of the simulation.

Monthioux et al., 1985; Mansuy and Landais, 1995; Michels et al., 1995a,b, 1996; Lewan, 1997), but is not the focus of this paper.

H₂O content is initialized as 0.55 mol (Fig. 6). Its concentration decreases after 62 Ma as it is being consumed in several reactions mentioned previously. Until

about 37 Ma, any H₂O produced is being immediately consumed, and thus there is no extra H₂O in the system (its concentration is negligible). After about 37 Ma, the H₂O consuming reactions have ceased, and H₂O producing reactions are still occurring, allowing a build-up of H₂O in the system. Thus there is a net consumption

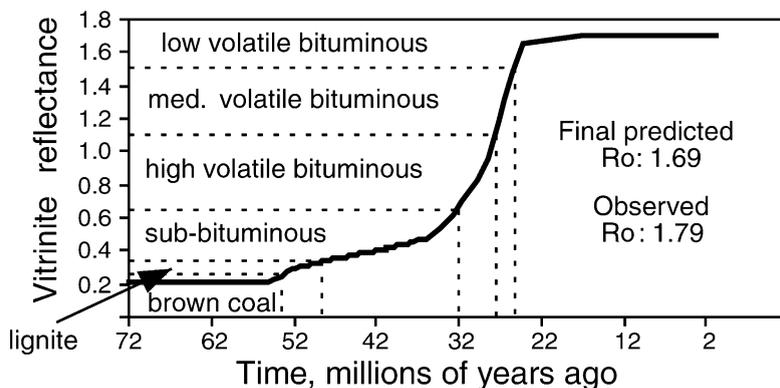


Fig. 5. Predicted vitrinite reflectance and approximate rank classification, and final predicted and observed present-day values.

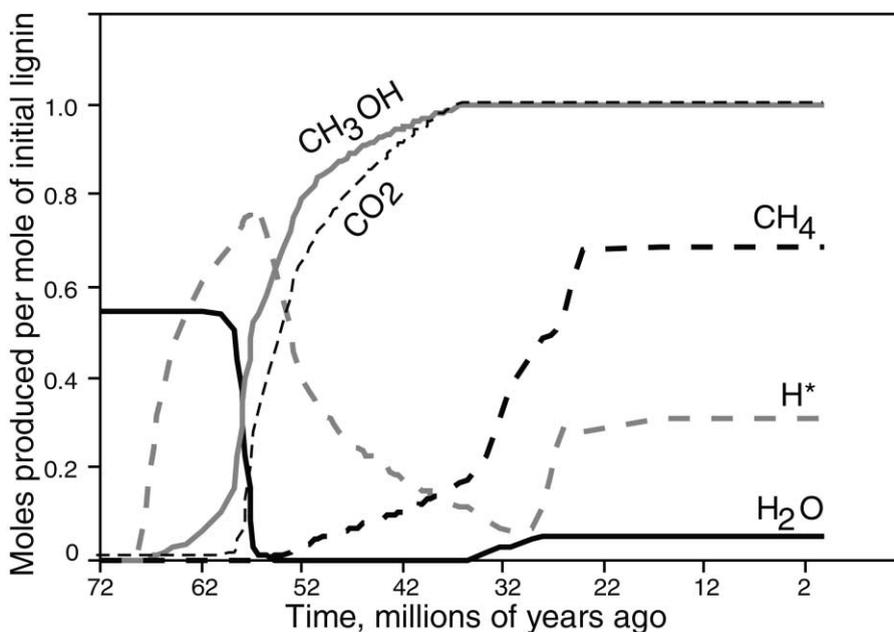


Fig. 6. Total production of mobile species in moles per mole of lignin reacted, over the simulated basin history.

of H_2O in the system over the course of the thermal history.

Similarly, H^* production increases over the first 15 my (57 Ma), then experiences a decline as it is consumed in other reactions (Fig. 6). From about 57 Ma to about 32 Ma, more H^* is consumed than produced by the reactions. After about 30 Ma, H^* consuming reactions cease and H^* producing reactions continue, allowing a build-up of H^* .

CH_3OH , CO_2 , and CH_4 all show increases over the course of the simulation history, which is expected as none of these species is a reactant in the model reaction network (Fig. 6). The different timing of the generation of these species reflects the kinetics of the involved reactions (Table 1 of Payne and Ortoleva, 2001). Demethoxylation

occurs at lowest activation energies; decarboxylation occurs at higher activation energy; and demethylation reactions require still higher activation energies. The methane generation slope is complex, indicative of the different types of reactions invoked for demethylation, each with different kinetics (Payne and Ortoleva, 2001).

The total amount of each of mobile species produced in Fig. 6 reflects the molecular structural configuration of the reactant immobile species. For example, there is one methoxyl functional group per lignin monomer, thus 1 mol of lignin will produce a maximum of 1 mol of methanol by the demethoxylation reaction, assuming this reaction process goes to completion over the simulation history. The total amount of methane produced will vary depending on the kinetics of various reaction

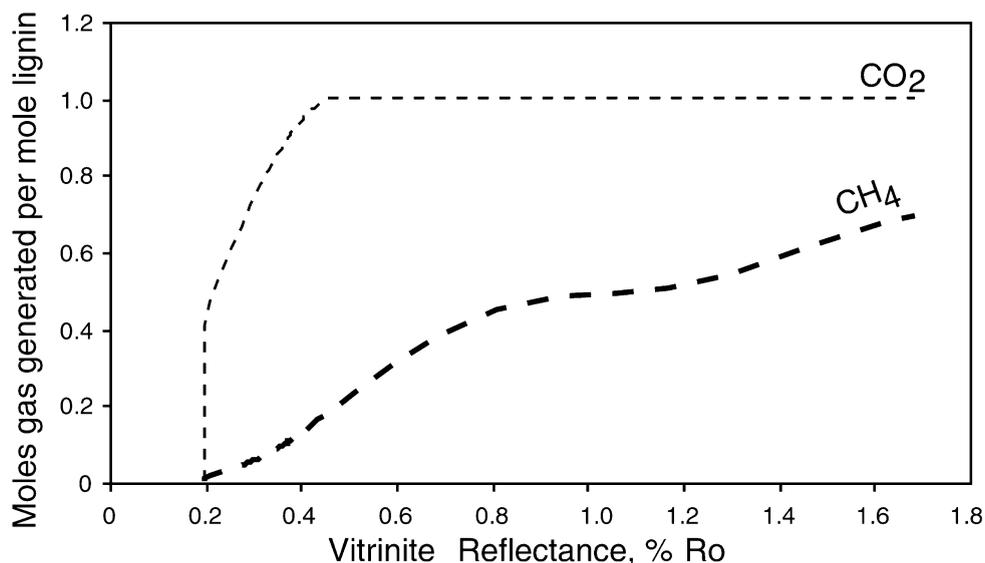


Fig. 7. CO₂ and CH₄ generated per mole of lignin vs. vitrinite reflectance.

pathways. For example, an immobile species may react by demethylation of pendant methyl groups, or by a cross-linking reaction that produces no methane. The relative reaction rates of these two processes will affect the total amount of methane produced. This demonstrates one of the complexities of bifurcating reaction pathways in a reaction network that is composed of neither simple parallel nor sequential reactions.

An interesting correlation occurs when the predicted CO₂ and CH₄ generation are plotted against estimated R_0 : the bulk of CO₂ generation occurs below approximately 0.4% R_0 and a significant quantity of CH₄ is generated below 0.8% R_0 (Fig. 7). This implies lower maturity gas generation than is suggested by Scott (1996), who shows that CO₂ generation does not start until above 0.35% R_0 and CH₄ generation does not start until almost 0.8% R_0 . Similarly, Zhang et al. (1997) suggest that the CH₄ generation does not start until above 0.6% R_0 . Typically, gas generation kinetics are determined from pyrolysis experiments, and thus will have higher activation energies than are determined for this model. If the reaction kinetics used in this model more accurately represent reaction rates under geologic conditions, then more gas may be generated by less mature lignin-derived SOM. This may have implications for natural gas resource assessments, as will be discussed later.

3. Sensitivity testing

3.1. Initial temperature

Because the kinetic transformation of organic matter is temperature dependent, the assumed land surface (or

initial) temperature is an important consideration in thermal modeling. Over the history of a basin, the mean earth surface temperature may have changed before becoming the present day value of approximately 17 °C (Weast, 1986). Sensitivity testing of this model illustrates the effect of initial temperature over a reasonable range for the Mesozoic to present day history of the Earth (Fig. 8).

By the end of the simulation, total predicted amounts of generated CO₂ and CH₄ are the same regardless of the initial temperature, but the initial temperature is an important factor in the timing of gas generation over the course of the basin history (Fig. 8). For example, at an initial temperature of 25 °C, by 10 my into the simulation, considerable CO₂ has been generated, whereas for lower initial temperatures none has been generated yet. This is critical in such processes as overpressuring, in which the relative timing of compaction and compartment seal development with respect to gas generation is important. Early loss of gas before formation of compartment seal will allow less overpressure to develop (Payne et al., 2000). It must be noted that the higher initial temperatures may also affect diagenetic processes and thus the timing of the formation of a compartment seal. Although initial temperature does not affect the total amounts of CO₂ and CH₄ generated by this model, it is potentially important over the course of basin development and in consideration of the relative timing of other basin processes.

3.2. Chemistry of lignin-derived precursor molecule

Sensitivity testing of the model shows that predicted results are influenced by the initial structure and chemistry

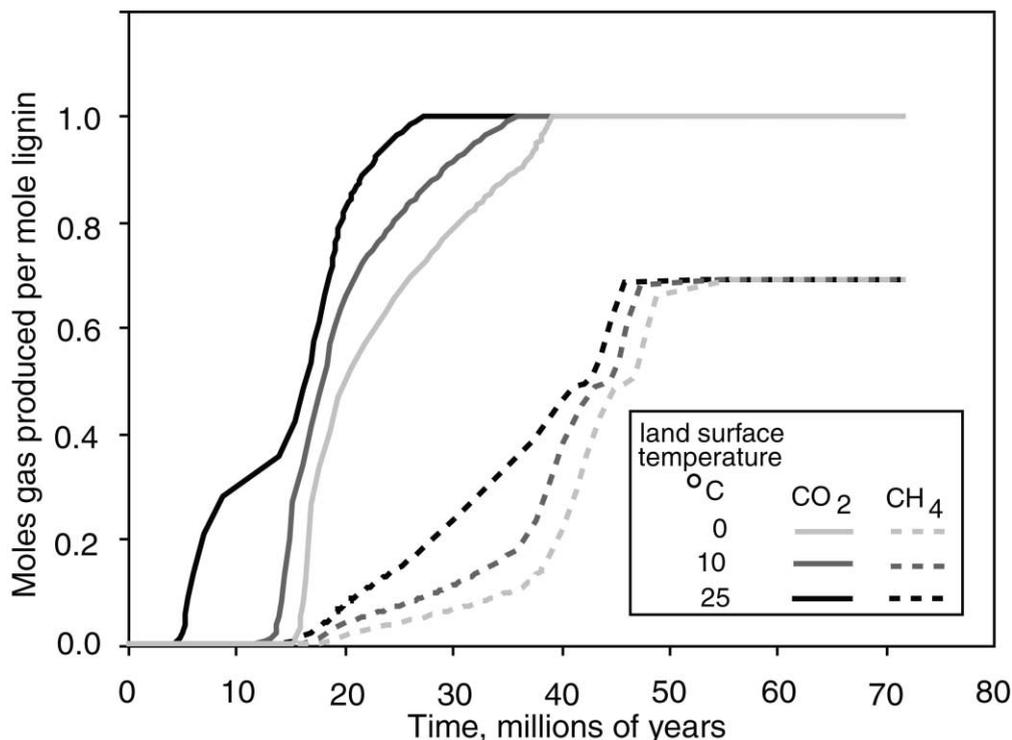


Fig. 8. Results of sensitivity testing for varying assumptions of land surface temperature: predicted total production of CO_2 and CH_4 . All three simulations have the same geothermal gradient history. Hence, the fundamental difference in results is the timing of initiation of reactions.

of the lignin-derived molecule. Lignin is a complex molecule with variable composition, which, for the purpose of modeling, has been simplified to represent a distribution of its major functional groups. Different functional groups will undergo different types of reactions, resulting in different structures and products.

The results of simulations at the MWX site discussed previously are based on a model lignin-derived molecular structure comprising 50% each of monomers A and B (Fig. 2). This would represent a molecule comprised of 67% β -O-4 linkages, 33% α -linkages, one methoxyl group per aromatic ring, 33% of aliphatic carbons with a hydroxyl functional group, 17% of aliphatic carbons with a carbonyl group, and one propyl structure for every aromatic structure. To test the effect of variations in initial molecular structure on the model, simulations were run for monomer fractions ranging from 0.3 to 0.7. Fig. 9a shows that over this compositional range, the initial C, H and O weight percents vary by a few percent. By the end of the simulation, the resultant weight percents may vary by almost 15% for carbon and oxygen, and a few percent for hydrogen (Fig. 9b). These results show that starting chemical composition is not necessarily an indicator of chemical composition at the end of the simulation. For example, if monomer A comprises 30% and monomer B com-

prises 70% initially, this starting composition has the highest carbon weight percent of the tested combinations. However, the highest carbon weight percent predicted at the end of the simulation results from a starting composition of 50% monomers A and B.

The reason for this phenomenon is that the initial lignin structure, not the chemical composition, controls which reactions occur and therefore the resulting chemistry. This is illustrated by examining variations in total predicted CH_4 generation with initial molecular composition (Fig. 10). CH_4 production is maximized with an equal distribution of starting monomers A and B. Monomer A evolves more CH_4 in the reaction network, so more of monomer A results in more total CH_4 production. Monomer B, however, generates much of the H^* required for the CH_4 generating reactions of the monomer A reaction pathway. With less initial monomer B, less reactive H^* is produced, thus less total CH_4 can be produced. Thus CH_4 production is maximized because equal parts of monomers A and B cancel these effects. This figure also shows that production of CO_2 decreases with decreasing initial amounts of monomer A. This is because there are two sites on monomer A that can evolve carboxyl functional groups and subsequently decarboxylate, the propyl- α and the propyl- γ sites. On monomer B, however, the propyl- α site is a

polymer linkage and thus only the propyl- γ can evolve a carboxyl functional group. Clearly, the differences in total gas produced show that in this model dif-

ferent initial molecular composition affects predictions of gas abundance and chemical composition of residual material.

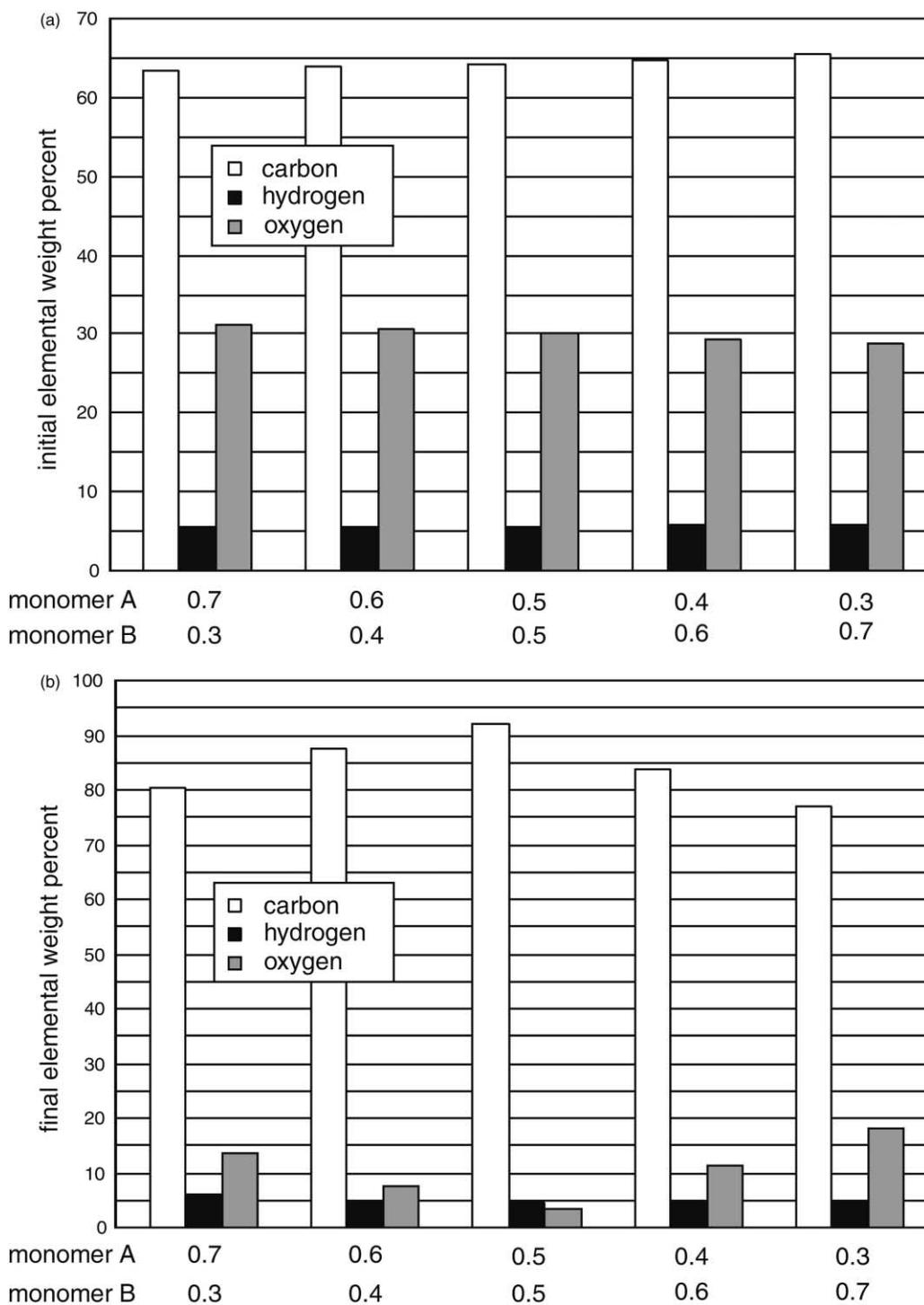


Fig. 9. Results of sensitivity testing for varying ratios of monomers A and B in the model lignin molecular unit: (a) initial elemental weight percents; (b) final elemental weight percents of residual species.

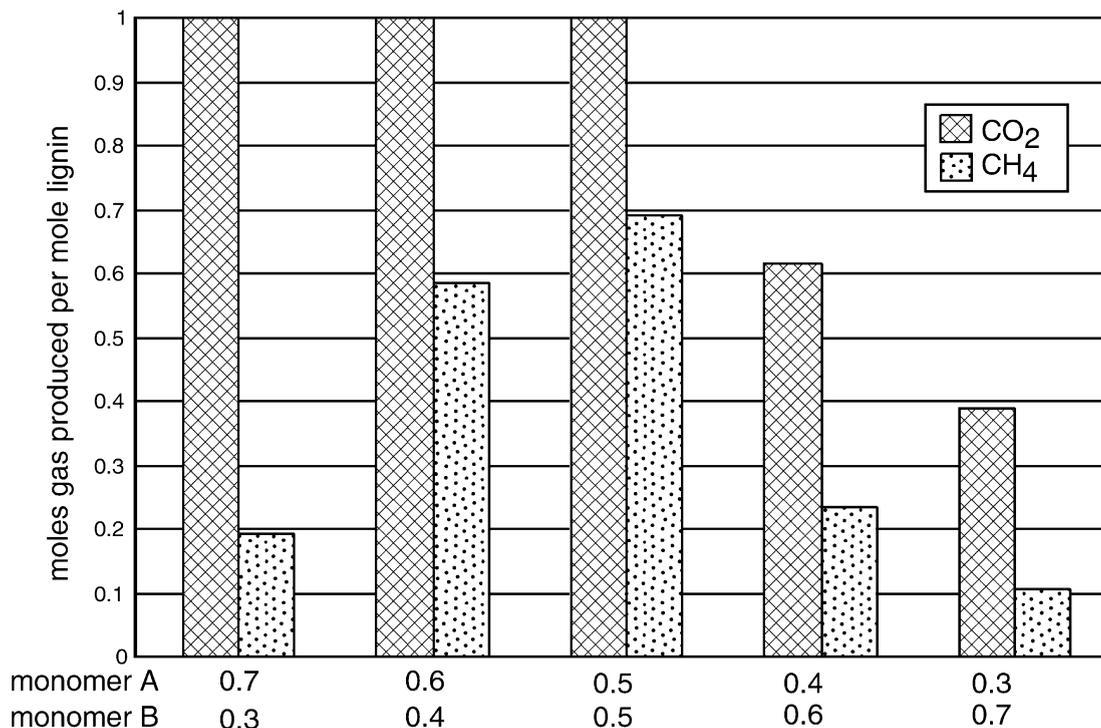


Fig. 10. Results of sensitivity testing for varying ratios of monomers A and B in the model lignin molecular unit: total CO₂ and CH₄ production.

3.3. Initial H₂O content

Several of the early, low-maturity reactions require the addition of H₂O as a reactant, for example demethoxylation, and the oxidation of α -carbonyl to carboxyl functional groups. Although H₂O is generated by some of the reactions, in order for all reactions to go to completion, H₂O is required as an initial input. Availability of H₂O will control to some degree the reaction rates because its concentration is a factor in some non-first-order reaction rates, and by creating a “domino effect” by limiting the production rate of species that behave as reactants in ensuing reactions.

In order to test the effects of varying amounts of initial H₂O in the system, simulations were run with initial input of H₂O ranging from 0.0 to 1.0 mol for every mole of initial lignin-derived molecule (Figs. 11–13). Fig. 11 shows that elemental weight percent distributions of the final residual material vary with initial amounts of H₂O in the system. The results show that final carbon weight percent decreases and oxygen weight percent increases for initial H₂O decreasing below 0.5 mol. This suggests that below this amount, some of the reactions are retarded or inhibited by the lack of H₂O available for reaction. At initial values of 0.55 mol H₂O and above, the resultant elemental weight percents are very close, suggesting that at least 0.55 mol of H₂O per

mole of lignin are needed in this reaction network to allow all reactions to go essentially to completion.

Naturally, it follows that some of the mobile product distribution will be affected by initial H₂O content. Fig. 12 shows that with increasing initial H₂O content up to about 0.5 mol, total production of both CO₂ and CH₄ increase. From 0.55 to 1.0 mol of initial H₂O, CO₂ production remains constant, but CH₄ production decreases slightly. This occurs because as H₂O content increases the rates of reactions that compete with demethylation reaction pathways increase, limiting CH₄ production slightly. Above 0.5 mol of initial H₂O, the total gas produced does not change much, however the timing of gas production varies. In Fig. 13, the total production of CO₂ and CH₄ for initial H₂O contents of 0.5 mol and above are shown through the simulation time. This figure shows the timing of CO₂ production is quite sensitive to initial H₂O content above 0.5 mol, and that of CH₄ production is only slightly sensitive.

4. Application of the model to Piceance Basin resource assessment

The natural application of this kind of model is predicting the estimating Piceance Basin natural gas resources. We present here an estimate for the total

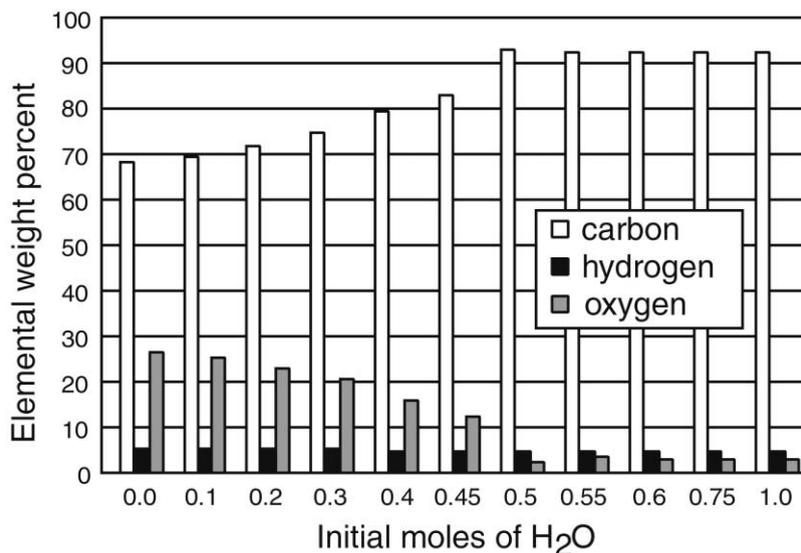


Fig. 11. Results of sensitivity testing for varying initial moles of H₂O per mole of starting lignin: final predicted elemental weight percents of residual species.

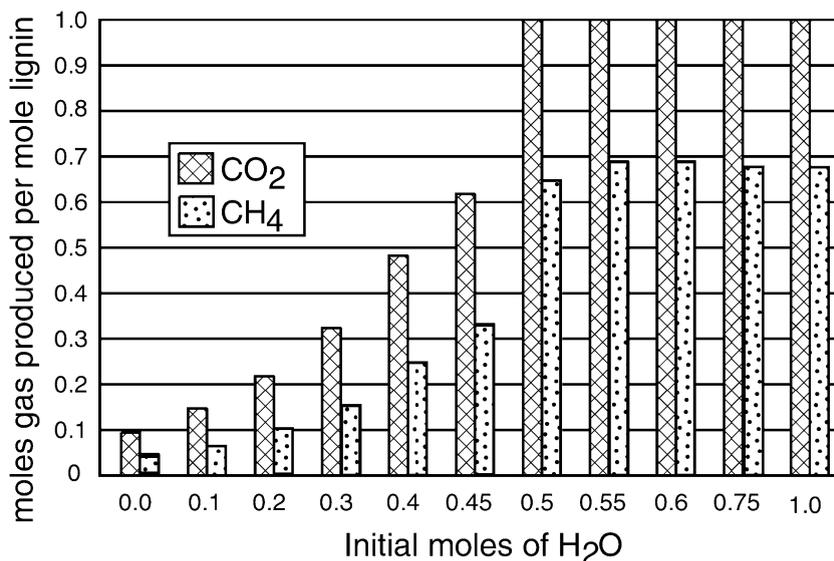


Fig. 12. Results of sensitivity testing for varying initial moles of H₂O per mole of starting lignin: total CO₂ and CH₄ production at the end of the simulation.

methane generated for the entire Piceance Basin over its history, assuming that the Williams Fork Formation coal is wholly lignin-derived and that it represents the majority of the methane source rock. It is possible that the non-vitrinitic component of the coal, though fractionally smaller than the vitrinitic component, may contribute significantly to the generation of methane. In this case, the model may underestimate the total meth-

ane generated. This assessment is not intended to be a complete and detailed assessment of gas in place, but is meant primarily to illustrate an application of the results of this approach to modeling. With further model development to refine the model for lignin-derived SOM, to expand the model to account for other precursory molecular species important in natural gas generation, or to account for effects of different coal or

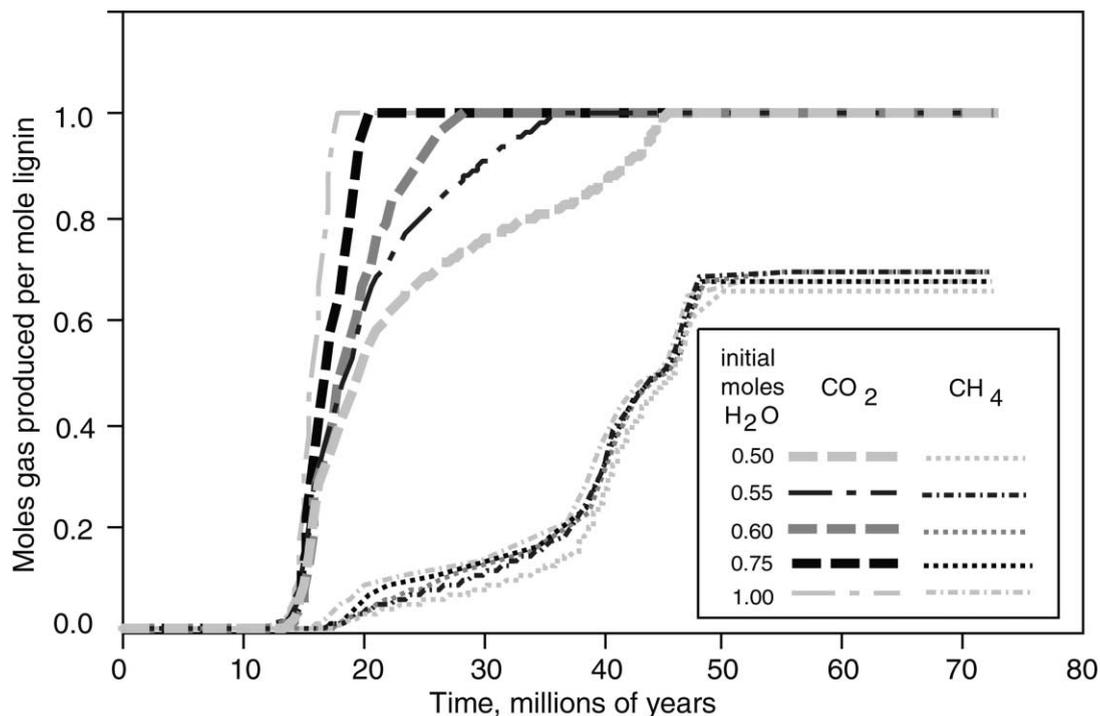


Fig. 13. Results of sensitivity testing for varying initial moles of H₂O per mole of starting lignin: total CO₂ and CH₄ production over time for initial H₂O content of 0.5–1.0 mol per mole of lignin.

kerogen fabrics on the physical release of natural gas, this model may become a useful tool for assessing the quality and quantity of other natural gas resources.

To calculate the total methane generated, first the volume of the Williams Fork Formation coal was estimated for each of several ranges of R_0 using a map of coal thickness (McMurry and Tyler, 1996), and a map of R_0 (Scott, 1996) (Table 1). For each maturity range a total amount of methane generated is calculated as follows:

$$\left(\frac{\text{coal}}{\text{volume}} \right) \times \left(\frac{\text{coal}}{\text{density}} \right) \times \left(\frac{\text{moles CH}_4}{\text{per mole lignin}} \right) \times \left(\frac{\text{molecular}}{\text{weight lignin}} \right)^{-1} = \left(\frac{\text{total CH}_4}{\text{generated}} \right) \text{ moles}$$

The coal density is calculated from the carbon weight percent in the lignin maturation model using an empirical function that is derived from data in Levine (1993). This calculation assumes that 100% of the coal volume is comprised of lignin-derived SOM and that 1 mol of lignin-derived SOM can be described as 1 mol of the molecular unit described in the lignin maturation model (Payne and Ortoleva, 2001). In this case, the Williams

Fork Formation coal comprises approximately 90% vitrinite; in other cases, where vitrinite content is lower, this calculation may also include a factor representing the fraction of vitrinite relative to all macerals. The calculated value was summed for all of the ranges of R_0 to give a total value of CH₄ generated in the Piceance Basin: 3.98×10^{14} mol. This results in an estimated volume of 314 trillion cubic feet (tcf) of methane gas (assuming a gas density of 4.92×10^{-2} ft³/g), part of which is in place as coal-bed methane, part of which has migrated to other reservoirs such as the local Mesaverde sandstones, part of which has migrated out of and lost from the basin, and part of which has been produced.

Although this rough estimate calculates the total amount of methane generated and other estimates calculate the total gas in place, the validity of this estimation can be addressed. Scott et al. (1996) estimate a coal gas resource of 99 tcf, using coal gas analysis data from coals of various rank and from coal volume estimates. This value is expected to be smaller than that calculated here because it comprises only part of the total natural gas generated by the coals over the basin history, yet the order of magnitude suggests that the estimate presented in this paper is reasonable. Similarly, earlier assessments by Rightmire and Choate (1986) estimate a value of 60 tcf of coal bed methane for the whole Piceance Basin, and McFall et al. (1986) estimate a value of 84 tcf. Hence, if it is assumed that 100–200 tcf of gas migrated

Table 1
Coal volume, density, and methane produced for several maturity ranges

Maturity, % R_0	Coal volume (10^{10} m ³)	Coal density (g/cm ³)	CH ₄ generated per mole lignin (mol)	Total CH ₄ generated (10^{13} mol)	Total CH ₄ generated per ton of coal (scf/ton)
< 0.6	9.31	1.35	0.13	4.38	275
0.6–0.8	5.72	1.41	0.39	8.42	826
0.8–1.0	1.76	1.44	0.47	3.19	996
1.0–1.2	1.75	1.45	0.50	3.39	1059
1.2–1.4	1.17	1.47	0.54	2.49	1145
1.4–1.6	2.05	1.48	0.63	5.12	1333
> 1.6	4.64	1.49	0.69	12.8	1463

away from the source coals or has been produced, then the model presented here may provide insight into the whole basin natural gas resources, both those found within coal beds and those found in associated sandstone reservoirs, as suggested by Rightmire and Choate (1986).

5. Summary

The model presented here simulates a network of parallel and sequential reactions that describe the structural and chemical transformations of residual lignin-derived SOM and resulting generation of mobile species from shallow burial to approximately low-volatile bituminous rank. The novelty of the model is that it simulates the generation of natural gas in a way that respects the observed chemical and molecular structure changes that occur to lignin-derived SOM and calculates stoichiometrically and kinetically appropriate quantities of natural gas components generated under natural burial conditions. Assuming that the natural gas generating Upper Cretaceous coals of the Mesaverde Group are primarily lignin-derived, the kinetic parameters of the model are calibrated for the MWX Site in the Piceance Basin. Although it has been noted that there may be a significant fraction of non-lignin derived SOM, the same type of model could be applied to that fraction, if appropriate kinetic reaction network models are developed for other biomacromolecular components comprising such fractions.

Model input includes burial and thermal history for the MWX Site, starting lignin composition, and initial H₂O content. Output includes mole fractions of all species, residual and mobile, functional group fractions, and elemental weight percents. R_0 has been calculated from elemental weight ratios based on the method of Burnham and Sweeney (1989), serving primarily as a guide to estimate the maturity of the residual molecular species throughout the simulation.

We tested sensitivities of the model to initial land surface temperature, initial molecular composition, and

H₂O content. Higher initial land surface temperature results in earlier generation of CO₂ and CH₄ over the course of the basin history, suggesting that it may be an important factor when considering the timing of gas generation relative to compaction and the development of compartment and seals. The model also shows that CH₄ generation is maximized with equal parts of monomers A and B and that CO₂ generation decreases with decreasing initial amounts of monomer A. This is the result of effects of molecular structure on the numbers of relevant functional group sites and on the generation of required reactant species. These results indicate the model is more directly sensitive to the molecular structure than the elemental composition of the reactant material. The model shows that as initial H₂O content increases from 0.0 to 0.55 mol per mole of lignin-derived molecular species, total production of both CO₂ and CH₄ increase; from 0.55 to 1.0 mol of initial H₂O, CO₂ production remains constant, but CH₄ production decreases slightly. This occurs because the presence of H₂O affects competing reaction pathways in the model. As H₂O is a reactant in several of the reactions, its availability will affect the rates of those reactions, and will thus affect the rates of subsequent reactions in the model reaction network.

The model is used to estimate total methane generation of Williams Fork Formation coal using estimated values for coal density and coal volume for several ranges of maturity in the Piceance Basin. The calculated total methane generated for the Piceance Basin is approximately 314 tcf. Assuming that part of this methane is in place as coal-bed methane, part has migrated to other reservoirs such as the local Mesaverde sandstones, part has migrated out of the basin, and part has been produced, this estimate compares reasonably with estimated in-place coal-bed methane reserves which range from 60 to 100 tcf.

This approach to modeling the maturation of natural gas generating molecular species is well suited to predictive basin modeling of natural gas potential. Characterizing specific reactions allows for the bookkeeping of mobile and residual species, accounting for a variety

of reaction pathways depending on molecular input and thermal history. Because the model predicts the speciation of gases, it can be used to estimate the quality and quantity of natural gas generated over the course of a basin history, and therefore may be a useful tool in natural gas resource assessments, complementary to in-place coal-bed methane estimates.

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References

- Burnham, A.K., Sweeney, J.J., 1989. A chemical kinetic model of vitrinite maturation and reflectance. *Geochimica et Cosmochimica Acta* 53, 2649–2657.
- Comer, J.B., Payne, D.F., Sibb, W., 1997. Modeling Burial and Thermal History of the Mesaverde Group, Piceance Basin, Colorado—Implications for Gas Generation from Coals. Abstract, AAPG Annual Meeting, Dallas, p. A22.
- Hatcher P.G., 1990. Chemical structural models for coalified wood (vitrinite) in low rank coal. *Advances in Organic Geochemistry* 1989. *Organic Geochemistry*, 16, 959–968.
- Hatcher, P.G., Faulon, J.-L., Wenzel, K.A., Cody, G.D., 1992. A structural model for lignin-derived vitrinite from high-volatile bituminous coal (coalified wood). *Energy and Fuels* 6, 813–820.
- Hoering, T.C., 1984. Thermal reactions of kerogen with added water, heavy water and pure organic substances. *Organic Geochemistry* 5, 267–278.
- Johnson, R.C., Nuccio, V.F., 1986. Structural and thermal history of the Piceance Creek Basin, Western Colorado, in relation to hydrocarbon occurrence in the Mesaverde Group. In: Spencer, C.W., Mast, R.F. (Eds.), *Geology of Tight Gas Reservoirs*. AAPG Studies in Geology, Vol. 24, pp. 165–205.
- Johnson, R.C., Nuccio, V.F., 1993. Surface vitrinite reflectance study of the Uinta and Piceance Basins and adjacent areas, eastern Utah and western Colorado—implications for the development of Laramide basins and uplifts. *US Geological Survey Bulletin* 1787-DD.
- Levine, J.R., 1993. Coalification: the evolution of coal as source rock and reservoir rock for oil and gas. In: Law, B.E., Rice, D.D. (Eds.), *Hydrocarbons from Coal*. AAPG Studies in Geology, Vol. 38, pp. 39–77.
- Lewan, M.D., 1997. Experiments on the role of water in petroleum formation. *Geochimica et Cosmochimica Acta* 61, 3691–3723.
- Lorenz, J.C., 1985. Tectonic and Stress Histories of the Piceance Creek Basin and the MWX Site, from 75 m.y.a. to Present. Sandia National Laboratories report SAND84-2603, UC-92.
- Mansuy, L., Landais, P., 1995. Importance of the reacting medium in artificial maturation of a coal by confined pyrolysis. 2. Water and polar compounds. *Energy and Fuels* 9, 809–821.
- McFall, K.S., Wicks, D.E., Kuuskraa, V.A., Sedwick, K.B., 1986. A Geologic Assessment of Natural Gas from Coal Seams in the Piceance Basin, Colorado. Gas Research Institute Topical Report, GRI 87/0060.
- McMurry, R.G., Tyler, R., 1996. Genetic stratigraphy and coal deposition of progradational sequences in the Upper Cretaceous Williams Fork Formation, Mesaverde Group, Piceance Basin, Colorado. Geologic and Hydrologic Controls Critical to Coalbed Methane Producibility and Resource Assessment: Williams Fork Formation, Piceance Basin, Northwest Colorado. GRI Topical Report, GRI-95/0532, pp. 112–148.
- Michels, R., Landais, P., Philp, R.P., Torkelson, B.E., 1995. Influence of pressure and the presence of water on the evolution of the residual kerogen during confined, hydrous, and high-pressure hydrous pyrolysis of Woodford Shale. *Energy and Fuels* 9, 204–215.
- Michels, R., Landais, P., Torkelson, B.E., Philp, R.P., 1995. Effects of effluents and water pressure on oil generation during confined pyrolysis and high-pressure hydrous pyrolysis. *Geochimica et Cosmochimica Acta* 59, 1589–1604.
- Michels, R., Langlois, E., Ruau, O., Mansuy, L., Elie, M., Landais, P., 1996. Evolution of Asphaltenes during artificial maturation: a record of the chemical processes. *Energy and Fuels* 10, 39–48.
- Monthieux, M., Landais, P., Monin, J.-C., 1985. Comparison between natural and artificial maturation series of humic coals from the Mahakam delta, Indonesia. *Organic Geochemistry* 8, 275–292.
- Mukhopadhyay, P.K., Hatcher, P.G., 1993. Composition of coal. In: Law, B.E., Rice, D.D. (Eds.), *Hydrocarbons from Coal*. AAPG Studies in Geology, Vol. 38, pp. 79–118.
- Nuccio, V.F., Johnson, R.C., 1989. Variations in vitrinite reflectance values for the Upper Cretaceous Mesaverde Formation, southeastern Piceance Basin, northwestern Colorado—implications for burial history and potential hydrocarbon generation. *US Geological Survey Bulletin* 1787-H.
- Payne, D.F., Ortoleva, P.J., 2001. A model for lignin alteration, part I: a kinetic reaction-network model. *Organic Geochemistry*, this issue.
- Payne, D.F., Tuncay, K., Park, A.J., Comer, J.B., Ortoleva, P.J., 2000. A reaction-transport-mechanical approach to modeling the interrelationships among gas generation, overpressuring, and fracturing: implications for the Upper Cretaceous natural gas reservoirs of the Piceance Basin, Colorado. *AAPG Bulletin* 84, 545–565.
- Rightmire, C.T., Choate, R., 1986. Coal-bed methane and tight gas sands interrelationships. In: Spencer, C.W., Mast, R.F. (Eds.), *Geology of Tight Gas Reservoirs*. AAPG Studies in Geology, Vol. 24, pp. 87–110.
- Scott, A.R., 1996. Coalification, cleat development, coal gas composition and origins, and gas content of Williams Fork

- coals in the Piceance Basin, Colorado. Geologic and Hydrologic Controls Critical to Coalbed Methane Producibility and Resource Assessment: Williams Fork Formation, Piceance Basin, Northwest Colorado. GRI Topical Report, GRI-95/0532, pp. 220–251.
- Scott, A.R., Tyler, R., Kaiser, W.R., McMurry, R.G., Nance, H.S., Tremain, C.M., 1996. Coal and coalbed methane resources and production in the Piceance Basin, Colorado. Geologic and Hydrologic Controls Critical to Coalbed Methane Producibility and Resource Assessment: Williams Fork Formation, Piceance Basin, Northwest Colorado. GRI Topical Report, GRI-95/0532, pp. 269–285.
- Solum, M.S., Pugmire, R.J., Grant, D.M., 1989. ^{13}C solid-state NMR of Argonne premium coals. *Energy and Fuels* 3, 187–193.
- Stach, E., Mackowsky, M.-Th., Teichmuller, M., Taylor, G.H., Chandra, D., Teichmuller, R., 1982. *Stach's Textbook of Coal Petrology*. Gebruder Borntraeger, Berlin.
- Weast, R.C. (Ed.), 1986. *CRC Handbook of Chemistry and physics*, 66th Edition. CRC Press, Boca Raton.
- Zhang, E., Tang, Y., Hill, R., Liu, J., Foss, D.C., Chung, E.Y., 1997. Kinetic and Basin Modeling of Gas Generation from the Cameo Coal, Piceance Basin, Northwest Colorado. Chevron internal report.