

COMPETITION BETWEEN THE ORGANIC MATTER AND WATER IN THE HYDROGEN TRANSFER REACTIONS DURING ARTIFICIAL MATURATION.

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INTRODUCTION

The quantity, quality and timing of oil generation from source rock is directly dependant upon the type of organic present in the sediment. Type II are considered as oil prone, while type III is rather considered as gas prone, although some coals are sources of economic oil fields. The initial nature of the kerogen being significantly different in type II and III kerogens, it is important to study the similarities or differences of the chemical reactions taking place in both during maturation. Water is considered as an important parameter in the generation of hydrocarbons and is suspected to act as a source of hydrogen. However, coals are known to contain significant amounts of hydronaphthalenics able to efficiently provide hydrogen to organic reactions. Also, type III kerogens are richer in aromatics than type II kerogens and undergo more readily aromatization reactions which provide abundant hydrogen to the surrounding medium.

The following experiments compare the role of the free hydrocarbons, polars and water in the maturation and oil generation capabilities of type II kerogen (Woodford) and type III coal (Mahakam). The aim of the study is to identify the interactions between organic moieties (residual kerogen, polars, free hydrocarbons) and of these moieties with water. It is suspected that the dominant hydrogen sources and transfer mechanisms are different depending on the availability of specific hydrogen sources and on the stages of maturation of each kerogen type.

EXPERIMENTAL AND ANALYTICAL

The samples used are Woodford kerogen (Devonian Type II, Anadarko basin, Oklahoma, USA; T_{max}=422°C, HI=534mgHC/gOC) and Mahakam coal (Tertiary Type III, Mahakam delta, Kalimantan, Indonesia; T_{max}=418°C HI=258mgHC/OC). Experiments were performed by confined pyrolysis¹ (250-370°C, 24 and 72 hours, 700 bars). The experiments using successive pyrolysis of a same sample aliquot were adjusted to the reference series using temperatures adjusted by Time Temperature Index calculations². Several experimental series were performed: 1) standard pyrolysis (CP) in which the gold cell is loaded with fresh sample at each maturation stage 2) EC series in which a unique sample aliquot is isothermally heated from 250 to 370°C and chloroform extracted (removal of the bitumen) after each pyrolysis step. 3) EP series using the same procedure as for the previous series, but chloroform is replaced by pentane (removal of the free hydrocarbons and part of the resins after each pyrolysis step). 4) these series were also performed in the presence of 100 weight percent water (ECO and EPO series).

Hot chloroform and pentane extraction were performed on powdered samples during 45 minutes. For the CPEP series, the aliquots of the residual solid obtained after pentane extraction were extracted by chloroform for the quantitation of the asphaltenes. In such experiments, pentane yields values must be cumulated in order to be comparable to the CP and CPEC series, while the values for asphaltenes are not (they are intrinsic cumulative values as far as they remain in the reactor at each maturation step). Therefore, the cumulative pentane extraction yields are summed with the asphaltenes yields obtained at each temperature in order to obtain the cumulative bitumen yields. The residual kerogen (chloroform extracted) were analyzed by Rock-Eval pyrolysis and Py-GCMS (Pyroprobe CDS2000 connected to a HP5980 Series II Plus gas chromatograph coupled with a HP5972A mass spectrometer. The GC was equipped with a 60m DB-5 ms column initially held at 0°C for 5 min, then heated to 300°C at 5°C/min and held at 300°C for 15min).

RESULTS AND DISCUSSION

Figure 1 compares the effect of the removal of the bitumen, of the absence of the resins+free hydrocarbons and of the presence of water on the capacity of the residual kerogen (EC-ECO series) and kerogen+asphaltenes assemblage (EP-EPO series) to generate bitumen. General trends of the behavior for both kerogens appear: the cumulative bitumen yields for the EC and ECO series give values close to the maximum bitumen yield of the reference series. The removal of the resins+free hydrocarbons (EP series) lead to a deficit in the generation of bitumen. However, the effects are stronger for the coal than for the type II kerogen.

The addition of water to the sample in the chloroform extracted series (ECO experiments) does not change much the results for type II kerogen, while the effect is stronger for type III. In the pentane extraction series, the addition of water (EPO series) clearly improves the yields for both kerogens.

The removal of specific organic phases and the addition of water can also be followed through the analyses obtained on the residual kerogen. T_{max} values increase faster with maturation in the EC and EP series (Figure 2). The removal of the resins+hydrocarbons has strongest effect on the coal. For type II kerogen, the fastest T_{max} increase occurs in the EC series. In general, the extraction of the bitumen (EC) or resins+hydrocarbons (EP) has a smoother effect on the type II kerogen than on type III.

The addition of water retards the increase of T_{max} with maturation. With Mahakam coal, the effect is clear in the ECO series while the strongest retardation is noticed with the EPO series. For type II kerogen, the ECO is not much different from the EC series, while the EPO series shows the strongest effect (as for the coal).

The impact of the extractions on the structure of the residual kerogen were followed by PyGCMS (Figure III). For type III, the removal of the bitumen (EC series) or of the resins+hydrocarbons (EP series) leads to the destruction of the hydrocarbon potential (no free hydrocarbons are generated to counter part the loss of hydrocarbons in the coal). The presence of water in the ECO series allows a better preservation of the hydrocarbon potential of the coal. The effect is much stronger in the EPO series (kerogen+asphaltenes assemblage). This potential is also well preserved in the reference series.

For type II kerogen, the removal of the bitumen (EC series) leads to a PyGCMS chromatograms containing less aliphatics than the reference. For the EP series the results are fairly similar to the reference. The addition of water (comparison of the EC and EP chromatograms with the ECO and EPO series) has not much effect on the Py-GCMS chromatograms.

DISCUSSION AND CONCLUSION

In both types of kerogen, the removal of the bitumen does influence the yields, but the effects are rather limited. On the contrary, the removal of the resins+free hydrocarbons strongly decreases the bitumen yields, especially for the coal. The thermostability of the kerogen (T_{max} in the EC series) and the kerogen+asphaltenes (EP series) increases faster than for the reference series. This effect is related to an increasing aromaticity of the residue and a loss of the aliphatic potential of the sample (as followed by Py-GCMS and Mansuy et al.). This effect is however far stronger for the coal than for type II kerogen. These experiments show that the resins+hydrocarbons play a crucial role in the generation of hydrocarbons from kerogen. The kerogen+asphaltenes assemblage needs the presence of the resins+hydrocarbons in order to generate the bitumen. The presence of the resins+hydrocarbons avoids the crosslink of the kerogen+asphaltenes during maturation, which leads to the loss of the hydrocarbons potential in the kerogen^{2,3}

For the coal, the addition of water improves the yields in presence of the kerogen alone (ECO series) and in the presence of the asphaltenes (EPO). At the same moment, the thermostability of the residue (Table I) increases later in the maturation profile while the hydrocarbons potential in the kerogen is better preserved, especially in the EPO series (Figure III). For type II kerogen, water does not modify the behavior of the kerogen alone (EC and ECO series). A clear improvement is however noticed on the bitumen yields in the EPO series. Water also retards the increase of the Rock-Eval T_{max} with maturation (the effect is moderate in the ECO series for type II kerogen, but significant for the EPO series). The PyGCMS chromatograms are however not very conclusive concerning the preservation of the aliphatic potential in the residual kerogen

These data suggest that in the kerogen and especially in the kerogen+asphaltenes assemblage, chemical functions allowing the interaction with water are present. These interactions allow a better preservation of the oil potential in the kerogen and improve the generation of the bitumen from the kerogen+asphaltenes assemblage. It must however be noticed that the addition of water to the kerogen+asphaltenes (EP and EPO series) never totally restores the generation capability of the kerogen (either reference series or EC+ECO series). Therefore, it can be concluded that the full capacity of the organic matter to generate the bitumen needs the presence of the resins, the free hydrocarbons and water. In the reference series, these conditions are reached as far as the sample generates all of these ingredients during confined pyrolysis. The kerogen alone, as shown by the EC and ECO series behave fairly closely to the reference series. This shows that the crucial chemical interactions leading to good conditions of the generation of bitumen avoid crosslink reactions between the asphaltenes and the kerogen and allows a good preservation of the hydrocarbons potential.

The close contact between the kerogen, the asphaltenes, the resins, the hydrocarbons and water are therefore responsible for proper generation of bitumen. Specific oxidation of the polars by water during hydrous pyrolysis could be evidenced on Woodford Shale⁴. These results strongly suggest that water preferentially interacts with the polars (through oxidation-reduction reactions) during maturation. The fact that the addition of water in the EPO series never completely restores the generation capabilities as seen in the reference series suggests that other compounds are acting in the chemical network.

A closer analysis of the polars and kerogen from Mahakam coal (for which the removal of the resins+hydrocarbons has the most drastic effect) lead to identify the presence of significant amounts of hydronaphthalenics. These compounds are known to be very effective in the radical hydrogen transfer reactions during the pyrolysis of coal. Also, the strong abundance of naphthalenes in the aromatics generated by the coal during maturation is a good marker of hydronaphthalenic precursors. The removal of the polars by pentane extraction would remove this source of hydrogen and contribute to the destruction of the hydrocarbon potential in the kerogen by crosslink reactions.

Therefore, two types of hydrogen transfer reactions can be considered prior to aromatization reactions (which occur later in the maturation profile): 1) the polars+water interactions through oxidation-reduction reactions 2) the radical hydrogen transfer between hydronaphthalenics and the organic system.

Both systems are certainly active during maturation and are in competition, one taking advantage of the other depending on the composition of the medium. This composition is dependant either on the maturation stage (as in the reference series) or on the modifications induced by the chemical treatment during the EC, EP, ECO and EPO series.

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TABLES AND FIGURES

TABLE 1: ROCK-EVAL Tmax (°C) for the chloroform extracted residual kerogen obtained after confined pyrolysis of Woodford kerogen and Mahakam coal. CP: reference series EC: chloroform extracted series EP: pentane extracted series ECO: chloroform extracted series with addition of water EPO: pentane extracted series with addition of water.

	WOODFORD KEROGEN					MAHAKAM COAL				
	CP	EC	ECO	EP	EPO	CP	EC	ECO	EP	EPO
Raw	422					418				
260	-	440	440	439	439	-	-	-	-	-
278	432	444	-	441	441	437	439	437	437	437
300	436	449	450	445	445	444	446	445	455	449
323	-	-	-	-	-	451	463	455	544	453
330	445	461	456	455	456	454	538	486	553	455
346	-	564	550	540	464	-	-	-	-	-
350	496	-	560	-	-	457	564	542	574	521
358	-	580	-	560	553	-	-	-	-	-
365	521	-	-	-	-	514	582	556	579	531
375	-	580	585	573	569	561	-	-	-	-
400	541	-	-	-	-	579	-	-	-	-

FIGURE 1: Bitumen yields obtained after confined pyrolysis of Mahakam coal and Woodford kerogen. Pyrolysis series as in Table I. The yields are cumulative for the EC, EP, ECO and EPO series. The yields are not cumulated for the reference series (CP), however, they are intrinsic cumulative values (see text).

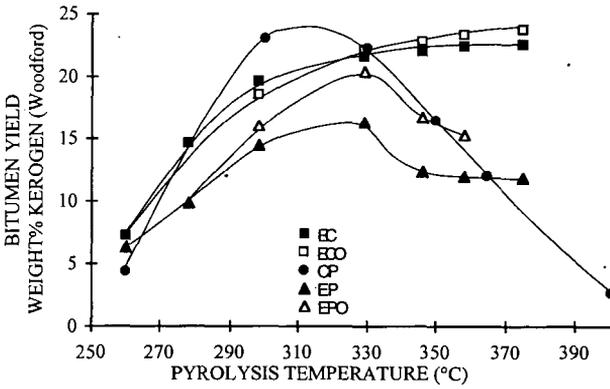
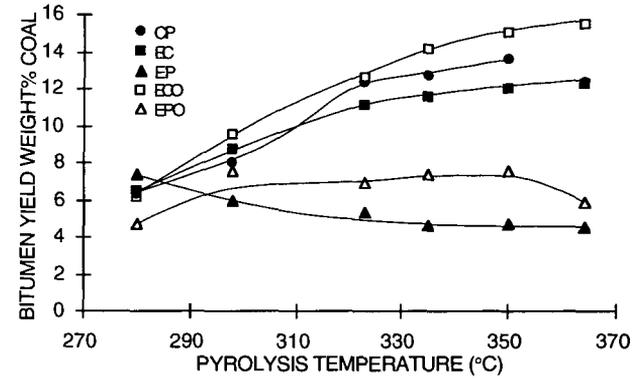


FIGURE II: PyGCMS chromatograms of the chloroform extracted kerogens obtained after confined pyrolysis at 335°C (Mahakam coal) and 330°C (Woodford kerogen). EC, EP, ECO, EPO as in text. IS: internal standard

