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Comparison of artificial maturation of lignite in hydrous and nonhydrous conditions

F. Behar[a,*], M.D. Lewan[b], F. Lorant[a], M. Vandenbroucke[a]

[a]*Geology-Geochemistry Division, IFP, 1-4 Avenue de Bois Préau, 92506 Rueil-Malmaison Cedex, France*
[b]*US Geological Survey, Box 25046, MS977, Denver Federal Center, Denver, CO 80225, USA*

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Abstract

The objectives of the study are to compare product compositions and yields generated from lignite artificially matured by open nonhydrous pyrolysis, closed nonhydrous pyrolysis, and hydrous pyrolysis. The pyrolysis products were fractionated into CO_2, H_2O, CH_4, C_2–C_5, C_8–C_{14}, C_{14+} saturates, C_{14+} aromatics and NSOs (resins + asphaltenes). All three methods generated high and similar quantities of water during pyrolysis that ranged between 14.6 and 15.2 wt.% of the original lignite. As a result of this high water content generated by the lignite, the experiments with no added water are referred to as nonhydrous rather than anhydrous. Rock-Eval pyrolysis and elemental analyses were conducted on the recovered lignite after solvent extraction to determine their residual hydrocarbon generation potential and to plot their position in a van Krevelen diagram, respectively. Residual lignite from the closed nonhydrous and hydrous experiments showed relationships between vitrinite reflectance ($\%R_o$) values and atomic H/C ratios that occurred within the fields observed for natural maturation of coal. Although no significant differences in the atomic H/C ratios were observed between closed nonhydrous and hydrous pyrolysis, the vitrinite reflectance values were on the average 0.2% R_o lower in the residual lignite from the nonhydrous experiments. The remaining hydrocarbon generation potential as determined by Rock-Eval pyrolysis of the residual lignite showed that the nonhydrous residuals had on the average 16 mg more hydrocarbon potential per gram of original lignite than the hydrous residuals. This suggests there is a better release of the pyrolysis products from the lignite network in the hydrous experiments once generation occurs. For gas generation, at maximum yields, open nonhydrous pyrolysis generates the most hydrocarbon gas (21.0 mg/g original lignite), which is 20% more than closed nonhydrous pyrolysis and 29% more than hydrous pyrolysis. Closed nonhydrous pyrolysis generates on the average 14% more gas than hydrous pyrolysis, but the proportionality of the generated hydrocarbon gases is essentially the same for both pyrolysis methods. At maximum yields, CO_2 generation is greatest in hydrous pyrolysis (99.5 mg/g original lignite), with yields being 37 percent higher than closed nonhydrous pyrolysis and 26% higher than open nonhydrous pyrolysis. The maximum yields of C_{14+} products are highest and similar for open nonhydrous pyrolysis and hydrous pyrolysis (125.6 and 125.9 mg/g lignite, respectively), and are more than 70% higher than closed nonhydrous pyrolysis. This difference in the maximum yields of C_{14+} products can be explained by differences in the proportionality between either cracking reactions that result in liquid product and char formation or trapping of generated products within the coal network (cross-linking reactions). Maximum yields of C_{14+} aliphatics from hydrous experiments may not have been attained, but the maximums that were observed and their GC traces are similar for the three pyrolysis systems.
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* Corresponding author.
E-mail address: francoise.behar@ifp.fr (F. Behar).

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1. Introduction

Coalification or maturation of Type-III kerogen is a process involving diagenetic and catagenetic alteration of sedimentary organic remains of vascular plants as a result of microbial activity, burial compaction and geothermal heating. As sediments are buried, Type-III kerogen undergoes thermal alteration that leads to oil or gas generation and residual kerogen of higher rank. Understanding the chemistry of such processes has been the objective of countless pyrolysis studies, which presupposes that slow burial and mild heating for long periods of time can be simulated by heating samples at elevated temperatures over shorter durations in the laboratory. Simulation of the overall maturation process circumvents the problem of ensuring genetic commonality and also allows for the detection of all intermediate products formed during maturation, some of which may have been removed from samples influenced by natural maturation or have been lost due to natural migration or sampling.

Many papers have been published on hydrocarbon generation from kerogen and coal using various pyrolysis systems, with various descriptions of the generated products in terms of number of chemical classes and optimization procedures for determining the kinetic parameters (Tissot and Espitalié, 1975; Lewan et al., 1979, 1995; Monthioux et al., 1985; Blazso et al., 1986; Ungerer and Pelet, 1987; Tissot et al., 1987; Horsfield et al., 1989; Burnham and Braun, 1990; Ungerer, 1990; Shan-Tan and Kaplan, 1990; Behar et al., 1991, 1995; Fowler et al., 1991; Noble et al., 1991; Teerman and Hwang, 1991; Lewan, 1993, 1994; Behar and Hatcher, 1995; Mansuy et al, 1995; Mansuy and Landais, 1995; Tang et al., 1996; Welte et al., 1996). These studies use three major pyrolysis methods: open nonhydrous (anhydrous) pyrolysis, closed nonhydrous (anhydrous) pyrolysis, and hydrous (closed) pyrolysis. Results of these studies are difficult to compare because of the use of different pyrolysis methods and the use of different starting materials from different geological formations. Although several studies have compared the differences between closed-nonhydrous and hydrous pyrolysis (Michels and Landais, 1994; Huang, 1996; Artok et al., 1998), closed- and open-nonhydrous pyrolysis (Arneth and Matzigkeit, 1986; Monthioux et al., 1985; Behar et al., 1995), closed nonhydrous and semi-open pyrolysis (Mansuy et al., 1995; Mansuy and Landais, 1995) and open-nonhydrous and hydrous pyrolysis (Qin et al., 1994) of Type-III kerogen, no study has compared all three pyrolysis methods using aliquots of the same coal or lignite.

The objectives of this study are to compare the material-balance yields and chemical compositions of products generated from aliquots of the same sample of lignite by the three different pyrolysis methods: open nonhydrous, closed nonhydrous and hydrous pyrolysis.

2. Sample description

Sample were selected according to the following criteria: (i) the sample must be sufficiently immature to ensure that prior generation of products has not occurred, (ii) sufficient amounts of the sample are available, because comparisons between the three pyrolysis methods requires several kilograms of lignite, and (iii) the sample has a low ash content because decomposition of carbonate minerals and sorption by clay minerals in the ash of a lignite complicate material-balance calculations and product comparisons of the different pyrolysis methods. All these conditions were fulfilled for the sample of lignite used in this study. The sample is from the Calvert Bluff Fm. (Paleocene age) of the Wilcox Group in the Big Brown open-pit mine near Fairfield, Freestone Co., Texas. Petrographic analysis of lignites from this mine have average maceral compositions on a volume basis of 64±5% huminite, 28±7% liptinite, and 8±6% inertinite (Mukhopadayay, 1989, Table 2, pp. 31–43).

The sample, designated as WX-3, was collected from a 25-cm thick interval that had been exposed by mining operations only 1-h prior to sampling. The sample was immediately placed in plastic bags that were then heat-sealed. In the laboratory the sample was crushed and sieved to a size ranging from 0.5 to 2.0 cm. Aliquots of 550 g of the crushed and sized sample were placed in glass quart-size canning jars, which were placed open in a vacuum oven at a pressure of 25 in Hg and a temperature of 40 °C for 24 h. The warm jars were removed from the oven and immediately closed with their rubber-gasket metal lids. The warm temperature of the jar and sample at the time of sealing resulted in a vacuum seal that ensured an airtight closure during storage.

The extremely low thermal maturity of this sample is reflected in its solvent extract, Rock-Eval data, elemental analysis, and vitrinite reflectance. Extraction of the sample with dichloromethane (DCM) yielded only 12.2 mg of C_{14+} extract per g of lignite. Saturated hydrocarbons only accounted for 7.4 wt.% of this extract (i.e., 0.9 mg/g) and no pristane was observed in its gas chromatogram. The geochemical characteristics of sample WX-3 are given in Table 1.

3. Experimental

3.1. Open-system pyrolysis

Open system pyrolysis was performed both on the original lignite and on residual lignites resulting from

Table 1
Geochemical characteristics of the original WX-3 lignite

Coal maceral analysis (vol.%)[a]					
Huminite (vol%)	Inertinite (vol%)	Liptinite (vol%)	Minerals (vol%)		
63.0	5.5	30.4	1.1		
C14+ extract analyses					
EOM (mg/gRock)	Saturates (mg/gEOM)	Aromatics (mg/gEOM)	NSOs (mg/gEOM)		
12.2	0.9	1.9	9.4		
Vitrinite reflectance (%R_o)					
Mean	S.D.	Min	Max	Counts	
0.34	0.02	0.28	0.40	35	
Elemental composition					
C (wt.%)	H (wt.%)	O (wt.%)	Ash (wt.%)	Atomic H/C	Atomic O/C
61.53	5.37	25.66	4.68	1.05	0.31
Rock-Eval pyrolysis					
S_1	S_2	HI	OI	T_{max}	
1	172	261	118	422	

[a] Analysis conducted by Mukhopadayay (1989).

Table 2
Pyrolysis conditions (X) used in comparison of closed nonhydrous and hydrous experiments

Time (h)[a]	Temperature (°C)				
	280	300	315	330	350
12	–	–	–	–	X
24	–	X	–	–	X
48	X	–	–	–	–
72	–	X	X	X	–
96	–	–	–	–	X
108	–	–	–	X	–
144	–	X	–	–	–

[a] 'Time' represents the time at which the experiment is at designated temperature.

some hydrous and nonhydrous closed system experiments. The total mass balance of pyrolysis products between 200 and 600 °C with a heating rate of 25 °C/min (classical open system pyrolysis) was done on the original lignite for comparison with closed system balances and with some parameters obtained by Rock-Eval analysis. Other open-system pyrolysis methods were performed on the original lignite with the same temperature program, but stopping heating either at 400 °C or 450 °C, in order to follow the absolute production of some specific GC-amenable alkanes and alkenes in the C_{7+} aliphatic fraction. Finally the classical open system pyrolysis was also performed on residual lignites from hydrous and nonhydrous experiments at 300, 315, 330 and 350 °C during 72 h, in order to follow absolute amounts of the same specific alkanes and alkenes (as above) still remaining to be produced.

Analytical procedures were already described in previous papers and summarized in Behar et al. (1997a). Briefly, two different systems were used: 1) compositional Rock-Eval pyrolysis and 2) preparative pyrolysis. Compositional Rock-Eval pyrolysis is used for quantification of the C_1 and the C_2–C_5 fractions (Espitalié et al., 1988). Typically, pyrolysis was carried out on 50 mg of coal. The pyrolysis chamber was connected to two detectors: a flame ionization detector (FID) and an infra-red detector (IRD), which enabled the specific quantification of methane. During pyrolysis, two traps containing respectively 3 and 10 Å molecular sieves were maintained at 50 °C in order to retain the C_{6+} compounds. The total fraction C_1–C_5, which was not trapped, was split: one aliquot was quantified by the FID, the other one was analyzed with the IRD for the specific methane quantification. By subtracting the two signals, the separate quantification of the C_1 and the C_2–C_5 fraction was obtained.

Preparative pyrolysis was used for the quantification of the C_7–C_{14} hydrocarbons and the C_{14+} fractions with subsequent fractionation of the latter into saturates, aromatics and NSOs (Behar and Pelet, 1985; Behar et al., 1989). About 60–80 mg of coal loaded on a gold rod was introduced into the pyrolysis chamber under an argon flow. After a preliminary heating at 300 °C for 3 min, the temperature was increased to 600 °C, unless mentioned otherwise, at a rate of 25 °C/min, with a temperature program similar to that of classical Rock-Eval pyrolysis. Vaporized products in the chamber were swept away and condensed, along with the carrier gas, into a trap cooled with liquid nitrogen. After pyrolysis completion, the pyrolysate was recovered by addition of solvent at room temperature in the trap, resulting in argon elimination and loss of C_1–C_5 products. The pyrolysate was recovered with *n*-pentane and fractionated without any solvent evaporation by liquid chromatography on silica into C_{7+} saturates + unsaturates (aliphatics), C_{7+} aromatics (ARO) according to the procedure of Behar et al. (1989). A second pyrolysis experiment was performed and effluents were diluted with DCM instead of *n*-pentane in order to get a quantitative recovery of the NSOs. After solvent evaporation, the pyrolysate (C_{14+}) was fractionated into aliphatics and aromatics. The NSOs were calculated by difference (Behar et al., 1989).

The C_{7+} aliphatic and aromatic fractions were injected into a gas chromatograph equipped with a cryogenic system and an auto sampler. The C_7–C_{14} fractions were estimated by integrating the corresponding area with blank subtraction, using a calibration curve. It was not possible to integrate the C_6 area because of its elution on the solvent tail. Individual *n*-alkane/*n*-alkene pairs and pristene were quantified using the same calibration curve.

3.2. Closed-system pyrolysis

3.2.1. Autoclaves and pyrolysis conditions

Detailed description of the autoclaves and experimental conditions were already published by Lewan (1997). The hydrous and nonhydrous experiments were conducted in stainless steel 316 or Hasteloy C-276 reactors with carburized surfaces. Table 2 gives the time and temperature conditions of the experiments used in this study. For the hydrous experiments, 250 g of lignite were introduced into a one-liter reactor. After the reactors were sealed, they were first filled with approximately 7 MPa of He and checked for leaks with a thermal-conductivity detector. The sealed reactor with coal chips was then evacuated and 350 g of distilled/deionized water was injected into the evacuated reactor to ensure complete penetration and contact of the added water with the lignite chips. The headspace of the water charged reactor was refilled with 1–2 MPa of He and vented down to a final pressure of 241 kPa (~46 mmol). The nonhydrous experiments were prepared in the same manner with the exceptions that the mass of lignite chips was reduced to 125 g, the retained He pressure in the reactor after leak checking was reduced to 103 kPa (~40 mmol), and no water was added. Temperatures were monitored with type J thermocouples calibrated against national standards at 300, 330 and 360 °C. Hydrous experiments reached designated temperatures within 50–70 min and maintained designated temperatures within a standard deviation of ±0.2 °C. Nonhydrous experiments reached designated temperatures within 30–60 min and maintained designated temperatures within a standard deviation of ±1.7 °C.

After the hydrous-pyrolysis autoclaves were cooled to room temperature, pressure and temperature were recorded and a sample of headspace gas was collected in an evacuated 30-cm^3 stainless-steel cylinder (Fig. 1a). The generated expelled oil that accumulates on the water surface in the hydrous experiments was collected in three steps. First, the majority of the expelled oil was collected from the surface of the water in the reactor with a spatula instead of a Pasteur pipette because at room temperatures the oil occurred as a solid brown wax. The amount of collected oil was weighed and an aliquot diluted in DCM. After a filtration step through a 0.45 µm polytetrafluoroethylene (PTFE) filter in order to eliminate any residual water or coal dust, an aliquot of this extract was taken for quantification and fractionation by liquid chromatography into saturates, aromatics and NSOs.

Second, the water and minor amounts of oil not recovered in the first step, were concentrated and collected in a separatory funnel. Third, the thin film of oil on the reactor walls, separatory funnel and spatula were rinsed with DCM at room temperature. The oil and the rinse diluted in DCM were filtered through a 0.45 µm PTFE filter. In accordance with Lewan (1997), the free oil collected directly off the water surface and the free oil rinsed from the reactor walls, funnel, and spatula are collectively referred to as expelled oil.

The wet chips were recovered and weighed. An aliquot of lignite chips (25–30 g of unpulverized lignite) was extracted with DCM at room temperature for 5–6 h and referred to as extraction 1 (Ext 1), then filtered through the PTFE filter. The extracted chips were dried overnight at 50 °C, then pulverized and extracted again in a Soxtherm apparatus for 1 h and referred to as extraction 2 (Ext 2). During this procedure (drying and crushing) most of the light hydrocarbons which could not have been extracted in the extract 1 were lost. Consequently, only the C_{14+} fraction was quantified in extract 2 for both hydrous and nonhydrous conditions. The remaining extracted residue is referred to here as residual lignite. The oil, rinse, extract 1 and extract 2 solutions were stored as such in weighed vials.

For nonhydrous experiments, gases were recovered using the same analytical procedure as that for the hydrous experiments (Fig. 1b). It is important to mention that even in nonhydrous experiments, due to the high oxygen content of the initial immature coal, undersaturated water vapor was present during pyrolysis as noted by Lewan (1997). Typically, the volume of water generated by the 125 g of coal chips corresponds to 10–15 cm^3. Due to this presence of water, the total amount of coal chips were rinsed for 2 min with 100 ml of cold (i.e. room temperature) DCM, which was filtered through a 0.45 µm PTFE filter and referred to as extract 1 (Ext 1). An aliquot of the residual coal was taken for drying and submitted to a second DCM extraction using the Soxtherm extraction technique and was referred to as extract 2 (Ext 2).

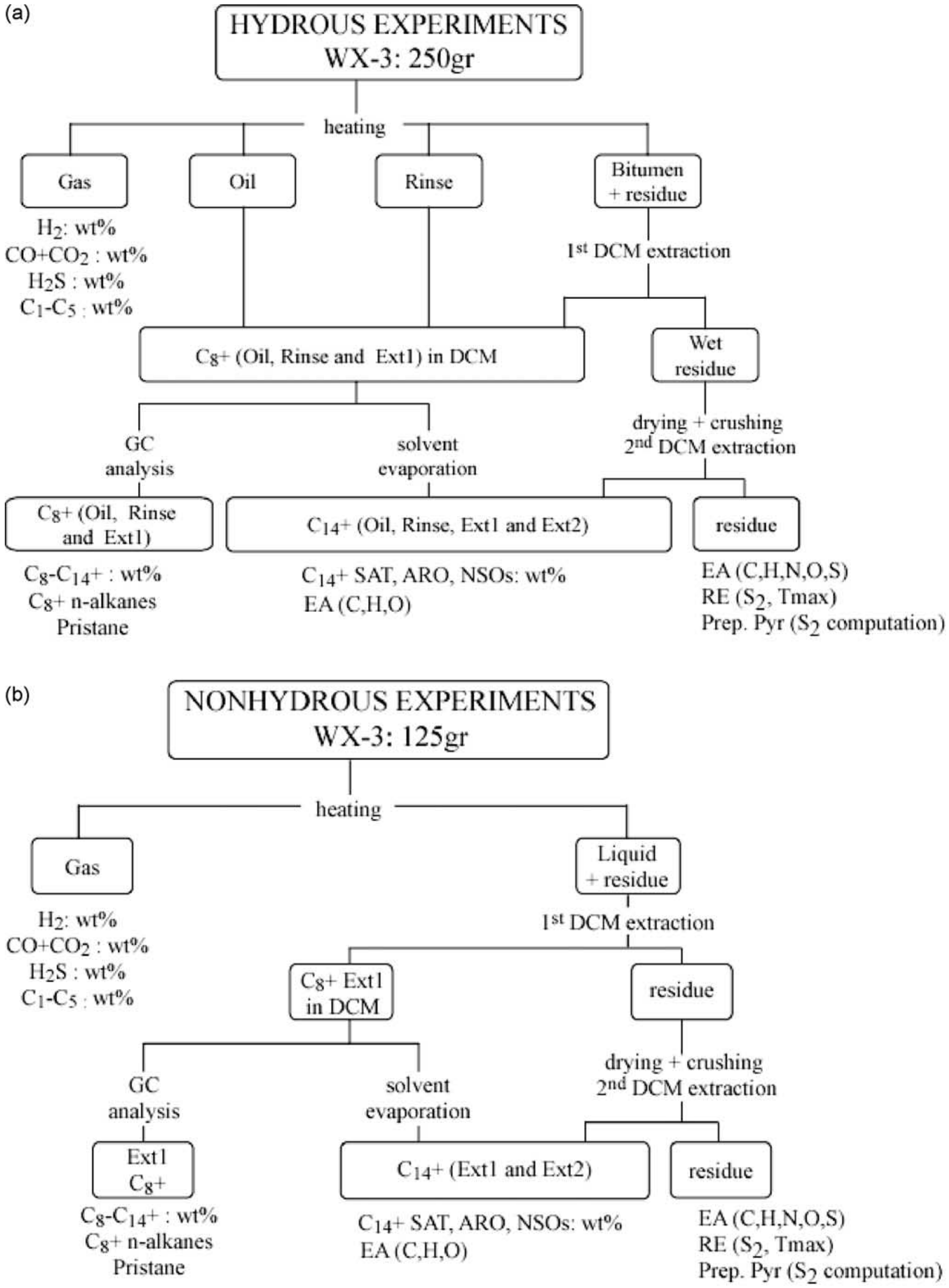

Fig. 1. Flow charts for analysis of products from (a) hydrous pyrolysis experiments and (b) closed nonhydrous pyrolysis experiments.

Although the generation of expelled oil in hydrous pyrolysis is a distinct advantage of this method in simulating natural oil generation (Lewan, 1993, 1997), the lack of a corresponding liquid product in the other pyrolysis methods makes comparisons difficult. Therefore, this study will only compare the total liquid products generated by each of the three pyrolysis methods. The total liquid product for hydrous pyrolysis will include the C_{8+} sum of expelled oil (floating plus rinse), extract 1, and extract 2. The total liquid product for the nonhydrous closed pyrolysis will include the C_{8+} sum of extract 1 and extract 2. However, the GC traces of the C_{8+} hydrocarbons were obtained on individual, and not recombined, fractions for comparisons. As previously noted, the total liquid product for open nonhydrous pyrolysis consists of the C_{7+} products.

3.2.2. *Pyrolysate analyses*

The analytical procedures for the hydrous and nonhydrous experiments are summarized on Fig. 1a and b. Gas composition was determined by gas chromatography and the absolute amounts of H_2, CO, CO_2, H_2S, and hydrocarbons through C_5 (methane, ethane, ethene, propane, propene, *n*-butane, *i*-butane, butenes and pentanes) were calculated by assuming ideal gas behavior at room temperature. The original 39–50 mmol of He retained in the headspace at the beginning of the experiments was also determined for the purpose of quality assurance. Moles of measured He were typically within 0.04% of the original introduced He. For hydrous experiments, the amounts of CO_2, H_2S, C_1 and C_2, dissolved in the water were calculated from Henry's law constants at measured room temperatures and added to the amount measured in the gas phase.

The C_{8+} extract 1 from hydrous experiments and nonhydrous experiments was split into three aliquots. The first one was used for a direct GC analysis, but to prevent damage to the GC column, the heavy and polar compounds were removed by liquid chromatography using a small column filled with 3–4 cm of Florisil. The recovered solution was weighed again and 1 μl was injected into the GC equipped with an auto sampler but not with a cryogenic system. Thus, the initial temperature of the column was 40 °C and only the C_8–C_{14} fraction was quantified instead of the C_7–C_{13} as determined for the open system experiments.

A second aliquot of C_{8+} extract 1 and a first aliquot of C_{14+} extract 2 from both hydrous and nonhydrous experiments were concentrated by evaporation of DCM and the C_{14+} fraction weighed. The NSOs were removed as previously described by liquid chromatography on alumina. The resulting maltene solution was put on the top of a small silica column. Aliphatics were eluted with *n*-pentane and the aromatics with a mixture of *n*-C_5/DCM (65/35 v/v). In this procedure for the extracts, the NSOs were quantified as the difference between the total C_{14+} extract minus the weight of the recovered aliphatics and aromatics (Behar et al., 1989). The DCM was chosen for extraction in order to obtain a good recovery of the NSOs. However, this solvent is not appropriate for the efficient dissolution of heavy waxes. As mentioned above, the expelled oil seemed waxy, thus, it is likely that a part of waxes, if any, should not be dissolved into DCM. Nevertheless, as the same analytical procedure was applied to all the fractions (C_{7+}, C_{8+} and C_{14+}), the data are consistent for comparisons, although the aliphatic content may be underestimated.

A third aliquot of C_{8+} extract 1 and a second aliquot of C_{14+} extract 2 from both hydrous and nonhydrous experiments was evaporated and submitted to elemental analysis as described in the next paragraph for C, H, and O measurements.

The residual lignite recovered in both hydrous and nonhydrous experiments after the DCM extractions (Ext 1 and Ext 2) was submitted to Rock-Eval pyrolysis, preparative open-system pyrolysis, elemental analyses, and vitrinite reflectance. Rock-Eval pyrolysis was used to determine S_2 and $T_{\max}$ of the extracted recovered samples. Preparative open-system pyrolysis was used for the recovery of the C_{7+} pyrolysate in order to quantify the residual hydrocarbon potential as described previously (C_{7+} *n*-alkanes, pristane and pristene).

Elemental analyses were carried out for C, H, N, S, and O, but Fe was not quantified because there is no pyrite in the initial sample. All determinations were run in duplicate or triplicate to establish reproducibility criteria. C, H and N were determined on one aliquot of each sample by thermal conductivity detection of gases resulting from combustion at 1000 °C. O was measured on another aliquot by pyrolyzing the sample under a nitrogen flow, reducing pyrolysis gases on carbon into carbon monoxide, then after transformation into carbon dioxide, quantification by coulometry. Total S was obtained by oxidation of a third aliquot and quantitative coulometry of sulfur dioxide. Vitrinite reflectance ($\%R_o$) values were determined on the original and residual coals. Analyses were carried out under oil on crushed residual coal that was mounted and polished in a plastic plug. The reported mean values are based on 25 counts per sample.

3.2.3. *Mass and atomic balances for hydrous and nonhydrous conditions*

A mass balance for the hydrous and nonhydrous experiments was conducted on a carbon basis. This involved the carbon determinations on the generated gas, C_8–C_{14} fraction, C_{14+} fraction and residue coal (C_r). The absolute amount of residual coal (m_r in mg/g of initial coal) was determined from the carbon balance:

$$m_i C_i = m_g C_g + m_l C_l + m_r C_r \tag{1}$$

where m_i is the mass and C_i is the carbon content of the initial coal, m_g is the mass and C_g is the carbon content of the recovered gas as determined from GC analysis of the total gas fraction, m_l is the mass and C_l is the carbon content of the recovered C_8–C_{14} and C_{14+} fractions, which is determined from elemental analysis on the latter and assumed to be 80 wt.% for the former.

Similarly, the mass of water (m_w) was determined in each experiment by the oxygen balance:

$$m_i O_i = m_g O_g + m_l O_l + m_r O_r + m_w O_w \tag{2}$$

where O_g is the oxygen content for the sum $CO + CO_2$ and O_w that of water. Assuming that the C_8–C_{14} fraction does not contain oxygen, the total oxygen content of the C_{8+} effluents was that given by elemental analysis of the C_{14+} fraction.

It is worth noting that Eqs. (1) and (2) are independent of each other since water does not contain carbon. Consequently, by summing all the fractions measured (gas and C_{8+} products) and calculated (residue and water), it is possible to determine the mass balance and the corresponding total recovery yield. For the two sets of experiments performed in hydrous and nonhydrous systems, the range of total recovery yields are respectively 98.7–103.6 and 98.0–101.7 wt.%.

Additional mass balances were done for the S_2 and total hydrocarbon potential in mg/g: knowing the amount of generated hydrocarbons (ΣHC) and the fraction m_r of residual coal relative to the initial amount of coal, it is possible to calculate the total S_2 (ΣS_2) in each experiment carried out in closed system:

$$\Sigma S_2 = \Sigma \mathrm{HC} + S_{2_r} \text{ with } S_{2_r} = m_r S_2 \tag{3}$$

where S_2 is the generated-hydrocarbon peak measured by Rock-Eval on the residual coal in mg/g of residual coal, m_r is the weight of residual coal from 1 g of initial coal, and

$$\Sigma HC = [C_1 \text{ to } C_5] + [C_8 \text{ to } C_{14}] + C_{14+} \tag{4}$$

C_8—C_{14} = total (saturates + aromatics); C_{14+} = total (saturates + aromatics + NSOs).

4. Results

4.1. Open-system pyrolysis

The mass balance of pyrolysis products including the CO_2, C_1–C_5, C_7–C_{14}, C_{14+} fractions, residual lignite, and water obtained between 200 °C and 600 °C with a heating rate at 25 °C/min in open system pyrolysis is given in Table 3. The total mass balance is equal to 1031 mg/g and not 1000 mg/g because the amount of residual lignite was calculated by the carbon balance [Eq. (1)] and independently of that of water which was determined by the oxygen balance [Eq. (2)].

Table 3
Product compositional fractions and yields from open nonhydrous pyrolysis of WX-3 lignite between 200 and 600 °C at a heating rate of 25 °C/min

Product fractions	Product yield			
	(mg/g lignite)	(wt.% volatiles)	(wt.% ΣHC[a])	(wt.% tot. C_{14+})
CO + CO_2	79.1	20.0	–	–
H_2O	148.0	37.5	–	–
C_1 to C_5	21.0	5.3	12.5	–
C_7 to C_{13}	20.9	5.3	12.5	–
Total C_{14+}	125.6	31.8	75.0	–
C_{14+} sat. + unsat.	28.2	7.1	16.8	22.4
C_{14+} aro.	22.1	5.6	13.2	17.6
C_{14+} NSOs.	75.3	19.1	45.0	60.0
Residual lignite	636.4	–	–	–

[a] ΣHC = [C_1–C_5] + [C_7–C_{13}] + [total C_{14+}] = 167.5 mg/g.

The total hydrocarbon balance obtained by combining preparative pyrolysis and compositional Rock-Eval yield a S_2 value of 167.5 mg/g, which is similar to the 172 mg/g S_2 value measured directly by Rock-Eval pyrolysis.

Nonhydrocarbons (i.e., CO, CO_2, and H_2O) comprise 57.5 wt.% of the volatile products and C_{14+} hydrocarbons comprise only 31.8 wt.% of the volatile products generated by open-system pyrolysis (Table 3). Water accounts for most of the non-hydrocarbon gas and is notably high compared to the non-gaseous hydrocarbons, which constitutes 14.7 wt.% of the lignite. Although this value of 14.7 wt.% for H_2O may appear large, high water production during open system pyrolysis is consistent with previous observations on other very immature coals, for example 144 mg water/g Morwell coal (Behar et al, 1995).

C_{14+} hydrocarbons comprise only 31.8 wt.% of the volatile products generated by open-system pyrolysis (Table 2) and of this percentage, 60 wt.% consists of NSOs, which by some definitions are not considered hydrocarbons (Tissot and Welte, 1984, p. 180; Hunt, 1996, p. 33). The C_{14+} aliphatic (saturates + unsaturates) fraction comprises only 16.8 wt.% of the total generated hydrocarbons i.e. ΣHC (Table 3). However, the amount of generated C_{14+} aliphatics is significantly higher (28.2 mg/g) than that measured in the initial-coal DCM extract (0.9 mg/g). The amounts of generated hydrocarbon gases and C_7–C_{14} hydrocarbons are in the same order of magnitude as that of the C_{14+} saturates and aromatics (i.e. less than 45 mg/g of the initial lignite).

The gas chromatogram (GC) of the aliphatic (saturates + unsaturates) fraction generated at 600 °C in Fig. 2 shows the distribution of C_{7+} hydrocarbons. Additional GCs of aliphatic fractions are also presented in Fig. 2 for pyrolysates recovered at 400 °C and 450 °C. The absolute yields of (prist-1-ene + prist-2-ene) and Σ1 (n-C_{14} + n-C_{16} + n-C_{18}) are given in Table 4 with their respective ratios with n-C_{18} and Σ2 (n-C_{25} + n-C_{27} + n-C_{29}). At 400 °C, the Pr/n-C_{18} ratio of 27.3 decreases to 5.35 at 450 °C and to 1.63 at 600 °C. This ratio decrease and the measured increase in absolute pristene concentrations indicate that pristene is generated at lower thermal maturity levels than n-C_{18}. Similarly, the Σ2/Σ1 ratio of 4.77 at 400 °C decreases to 2.73 at 450 °C and to 0.97 at 600 °C. The measured increase in absolute Σ1 concentrations indicates that higher carbon-number n-alkanes (n-C_{25} + n-C_{27} + n-C_{29}) are generated at lower thermal maturity levels than lower carbon-number

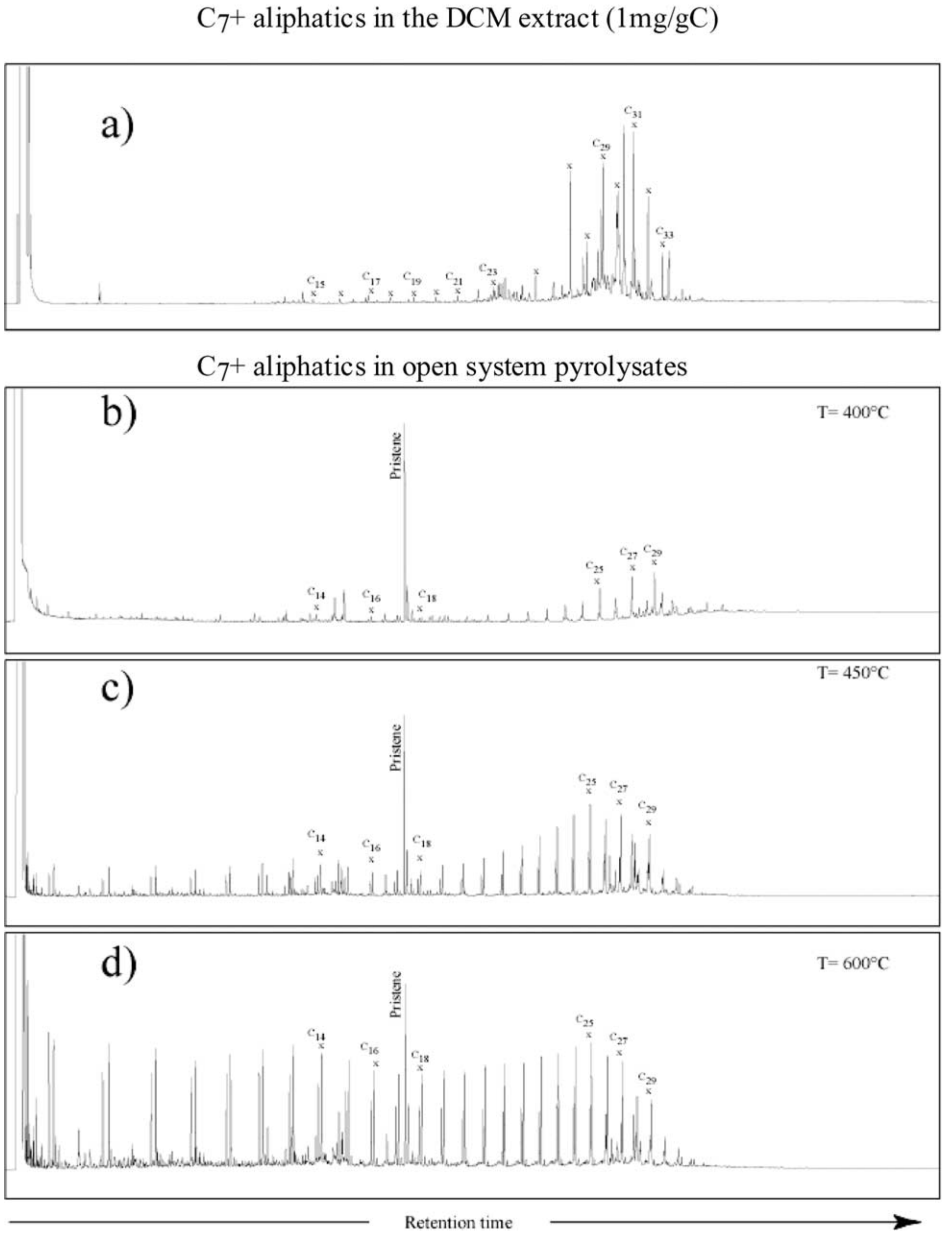

Fig. 2. Gas chromatograms of (a) C_{7+} aliphatics in the DCM extract and pyrolysates from open nonhydrous experiments at (b) 400 °C, (c) 450 °C and (d) 600 °C for the original Wilcox lignite.

n-alkanes (n-C_{14}+n-C_{16}+n-C_{18}). These results are in agreement with previous observations by Behar et al. (1997a,b) and demonstrate that the changes of *n*-alkane carbon distributions with increasing maturity in Type III aliphatics are due to low molecular weight product generation before a possible cracking of high molecular weight *n*-alkanes.

Concentrations of specific GC-amenable alkanes and alkenes released from the residual lignites of hydrous and nonhydrous experiments by preparative open pyrolysis are given in Table 4. Proportions of the high- to low-molecular-weight groupings of *n*-alkanes (Σ_2/Σ_1) and pristenes to n-C_{18} ratios decrease in essentially the same proportion with increasing thermal maturity in closed nonhydrous and hydrous experiments. Measured absolute amounts also decrease with increasing thermal maturity of the residual lignite in closed nonhydrous and hydrous experiments. However, at the same experimental conditions, absolute amounts generated by residual lignites from hydrous pyrolysis are consistently lower than

Table 4
Absolute concentrations of several *n*-alkanes and pristenes generated by open nonhydrous pyrolysis of original lignite (unheated) and residual lignites recovered after hydrous and closed nonhydrous experiments at various temperature/time conditions (°C/h)

Specific hydrocarbons (μg/g orig. lignite)	Open pyrolysis final temperature (°C)						
	400	450	600	600	600	600	600
	Closed pyrolysis conditions (°C/h)						
	Orig. lignite	Orig. lignite	Orig. lignite	300/72	315/72	330/72	350/96
$\Sigma 1 (n\text{-}C_{14}+n\text{-}C_{16}+n\text{-}C_{18})$							
Orig. lignite	12	376	1433				
Resid. lignite hydrous				1036	1004	835	185
Resid. lignite honhydrous				1281	1157	881	214
$\Sigma 2\ (n\text{-}C_{25}+n\text{-}C_{27}+n\text{-}C_{29})$							
Orig. lignite	57	1028	1384				
Resid. lignite hydrous				844	791	467	12
Resid. lignite nonhydrous				1167	823	385	38
$\Sigma 2/\Sigma 1$							
Orig. lignite	4.77	2.73	0.97				
Resid. lignite hydrous				0.82	0.79	0.56	0.07
Resid. lignite nonhydrous				0.91	0.71	0.44	0.18
Pristenes (1+2)							
Orig. lignite	121	695	714				
Resid. lignite hydrous				107	56	18	0
Resid. lignite nonhydrous				150	66	18	0
$n\text{-}C_{18}$							
Orig. lignite	4	130	438				
Resid. lignite hydrous				334	329	257	0
Resid. lignite nonhydrous				405	367	257	0
Pristenes (1+2)/$n\text{-}C_{18}$							
Orig. lignite	27.28	5.34	1.63				
Resid. lignite hydrous				0.32	0.17	0.07	0.00
Resid. lignite nonhydrous				0.37	0.18	0.07	0.00

those generated by residual lignites from closed nonhydrous pyrolysis (Table 4).

4.2. Closed-system pyrolysis

4.2.1. Recovered lignite analyses

DCM extracted residual lignites from closed pyrolysis experiments were submitted to the following analyses: vitrinite reflectance, elemental analysis and Rock-Eval pyrolysis. The amount of recovered residue was also measured to allow comparison of residual hydrocarbon potentials on a same weight basis. The resulting analyses are compared for the same time/temperature conditions in hydrous and nonhydrous systems in Table 5.

The irregularity of time and temperature combinations employed in these experiments make it difficult to align these experimental conditions in order of increasing thermal maturity. Based on the various maturity parameters measured on the residual lignite, random mean vitrinite reflectance (%R_o) of the hydrous experiments was first considered the most robust parameter to denote overall thermal maturity level in comparisons of the closed nonhydrous and hydrous experiments (Table 5). Indeed, vitrinite reflectance is the most commonly employed maturity parameter to evaluate coal rank. However, changes in vitrinite reflectance induced by laboratory pyrolysis are typically not in accordance with stages of oil generation for oil-prone kerogen as

Table 5
Analytical results on residual (i.e., DCM extracted) lignite recovered from hydrous and closed nonhydrous pyrolysis

Analytical parameters	Experimental conditions (°C/h) and maturity parameter ranking (in italics)										Mean difference[a]
	280/48	300/24	300/72	300/144	315/72	330/72	330/108	350/12	350/24	350/96	
Mean % vitrinite R_o											
Hydrous	0.72 *1*	0.90 *2*	0.95 *3*	0.98 *4*	1.10 *5*	1.29 *6*	1.30 *7*	1.34 *8*	1.45 *9*	1.78 *10*	
Nonhydrous	0.65 *1*	0.70 *2*	0.83 *3*	0.89 *4*	0.99 *5*	1.16 *8*	1.22 *9*	1.12 *7*	1.04 *6*	1.51 *10*	0.17
Atomic H/C ratio[b]											
Hydrous	0.880 *1*	0.847 *2*	0.811 *3*	0.767 *4*	0.732 *5*	0.703 *8*	0.708 *7*	0.724 *6*	0.684 *9*	0.616 *10*	
Nonhydrous	0.872 *2*	0.876 *1*	0.812 *4*	0.815 *3*	0.762 *5*	0.720 *6*	0.715 *7*	0.711 *8*	0.706 *9*	0.639 *10*	−0.016
Atomic O/C ratio[b]											
Hydrous	0.166 *1*	0.157 *2*	0.146 *3*	0.128 *4*	0.101 *7*	0.102 *6*	0.099 *8*	0.111 *5*	0.098 *9*	0.087 *10*	
Nonhydrous	0.177 *2*	0.180 *1*	0.138 *3*	0.134 *4*	0.115 *5*	0.106 *8*	0.109 *7*	0.110 *6*	0.103 *9*	0.095 *10*	−0.007
S_2 *(mg/g rec. lignite)*[c]											
Hydrous	118 *1*	106 *2*	100 *3*	99 *4*	91 *5*	76 *6*	76 *7*	68 *8*	60 *9*	39 *10*	
Nonhydrous	142 *1*	126 *3*	131 *2*	116 *4*	98 *5*	94 *6*	76 *8*	92 *7*	74 *9*	49 *10*	−13.5
S_{2_r} *(mg/g orig. lignite)*[d]											
Hydrous	93	80	74	73	62	49	48	45	37	24	
Nonhydrous	117	102	100	88	69	67	53	66	51	34	−16.2
m_r *(mg/g)*[e]											
Hydrous	789 *1*	751 *2*	740 *3*	735 *4*	680 *5*	650 *7*	632 *8*	664 *6*	617 *9*	611 *10*	
Nonhydrous	825 *1*	807 *2*	765 *3*	762 *4*	704 *7*	709 *6*	700 *8*	721 *5*	689 *9*	684 *10*	−49.7
Experiment ranking	1.2	1.9	3.0	3.9	5.4	6.7	7.6	6.6	8.7	10.0	

[a] Mean difference between hydrous and nonhydrous experiments.
[b] Elemental analyses conducted on DCM-extracted recovered lignite.
[c] mg of hydrocarbon generated by Rock Eval per g of recovered lignite.
[d] mg of hydrocarbon generated by Rock Eval per g of original lignite as calculated with Eq. (3).
[e] mg of recovered lignite per g of original lignite as calculated from Eq. (1).

observed in nature due to differences in reaction kinetics (Lewan, 1985). Thus, it is better to consider all the maturity parameters collectively without any bias on their ability to predict maturity. Therefore, the various maturity parameters measured on residual lignites of hydrous and nonhydrous experiments were given a rank from 1 to 10, 1 being the lower maturity (Table 5), and the mean rank value for all the maturity parameters was used for sorting the experimental conditions in the order of their increasing maturity. S_{2_r} was not considered since it results from a calculation using S_2 and m_r. In comparison with the previous ranking based only on vitrinite reflectance of hydrous residues, the experiment at 350 °C/12 h is now at a lower maturity than the experiments at 330 °C/72 h and 330 °C/108 h. Although some inconsistencies are still apparent in the maturity parameters of some experiments, the general maturity trend is better followed on residues as well as on total gaseous and liquid products formed during lignite transformation, as will be shown below.

Atomic H/C and O/C ratios determined from the elemental analyses of residual lignite are given in Table 5 for the hydrous and nonhydrous experiments. Although both hydrous and nonhydrous experiments follow the natural coalification trend (Fig. 3), residual lignite from nonhydrous experiments typically have slightly higher ratios than hydrous experiments (Table 5). This observation is also supported by the mean random vitrinite-reflectance values of the residual lignite. As shown in Table 5, the mean values are consistently higher for residual lignite from hydrous pyrolysis than nonhydrous pyrolysis. Attainment of a slightly higher thermal maturity of lignite under hydrous than nonhydrous pyrolysis is best demonstrated by the relationship between mean random vitrinite reflectance (%R_o) and atomic H/C ratio of the residual lignite (Fig. 4). Although the hydrous and nonhydrous trends are slightly offset, they have similar slopes and both occur within published natural-coalification limits. The difference noticed previously between absolute amounts of specific hydrocarbons generated by open system pyrolysis of residual lignites from hydrous and nonhydrous pyrolysis (Table 4) can be correlated to the calculated S_{2_r} of the residual lignite in both systems (Table 5): although the quantity of residual lignite [Eq. (1), m_r] is higher in hydrous conditions, the S_2 and S_{2_r} values from Rock-Eval analysis of the residual (DCM extracted) lignite were consistently higher in the nonhydrous experiments than in the hydrous experiments (Table 5). This means that there is a slight delay in petroleum generation between nonhydrous and hydrous conditions. This conclusion is supported by R_o data: values determined on residual lignites are lower in nonhydrous conditions (Table 5).

4.3. Generated gas and water

Table 6 gives the types and amounts of gas generated by the hydrous and nonhydrous experiments, and Fig. 5 presents the results graphically. Generated hydrocarbon gases do not exceed 20 mg/g of original lignite at the highest thermal maturities of the hydrous and nonhydrous experiments (Table 5). Although the amounts of hydrocarbon gases are similar in the hydrous and nonhydrous experiments, hydrocarbon gases generated in the latter show a slight increase with increasing maturity relative to those generated in the former (Fig. 5).

The absolute amount of recovered H_2 was always lower than 0.15 mg/g and for H_2S it was always lower than 2.5 mg. However, the amount of H_2 is consistently higher in the nonhydrous experiments than in the hydrous experiments (Fig. 5). Amounts of H_2 increase with maturation for hydrous and nonhydrous pyrolysis but there is a greater increase in the latter than in the former. Conversely, the amount of H_2S is consistently and significantly lower in the nonhydrous experiments than in the hydrous experiments (Fig. 5). Amounts of H_2S increase with maturation for hydrous and nonhydrous pyrolysis but there is a greater increase in the former than in the latter. These observations are in agreement with those of previous comparative studies involving Type-II kerogen (Lewan, 1997).

Among the gaseous compounds, CO_2 is the most abundant constituent. Its maximum yield is 99.5 mg/g of lignite at 350 °C/96 h in hydrous pyrolysis and it exceeds the value observed in open nonhydrous pyrolysis (79.1

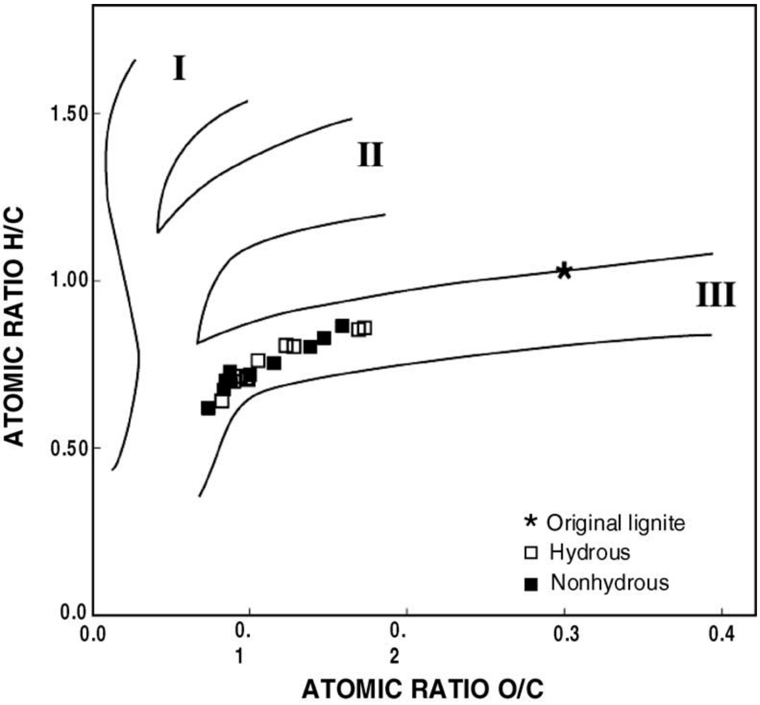

Fig. 3. Elemental analyses of original DCM extracted lignite (*) and residual lignites recovered from hydrous (□) and closed nonhydrous (■) experiments plotted as atomic ratios on a Van Krevelen diagram.

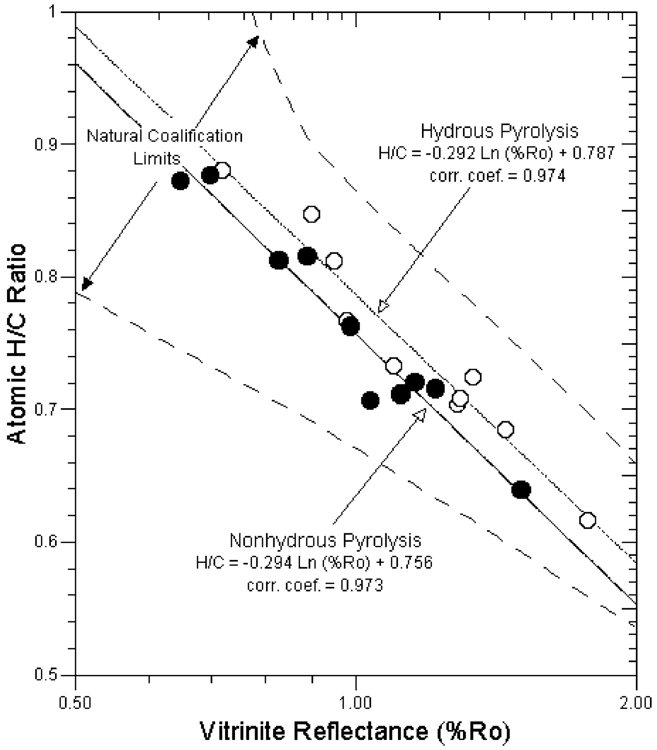

Fig. 4. Atomic H/C ratios of residual lignites recovered from hydrous (○) and closed nonhydrous (●) experiments plotted against mean random vitrinite reflectance (%R_o). Natural coalification limits are from Teichmüller (1971).

mg/g lignite; Table 3), whereas in closed nonhydrous pyrolysis, the maximum yield only reaches 72.5 mg/g of lignite (Table 6). Such an excess of CO_2 under hydrous conditions relative to nonhydrous conditions has previously been reported by Lewan (1997) for Type-II kerogen in the Woodford Shale. As a consequence, the calculated residue using the carbon balance [Eq. (1)] is expected to be lower in hydrous than in nonhydrous experiments for similar pyrolysis conditions (Table 5).

In closed pyrolysis, as well as in open pyrolysis, the maximum amount of generated water (152 mg/g) is very similar for hydrous and nonhydrous experiments and is almost twice that of CO_2. These data are in good agreement with those published in the literature (Behar et al., 1995) on another immature coal with an atomic ratio O/C of 0.34, pyrolysed either in open system at 600 °C (145 mg/g) or in nohydrous closed system (150 mg/g). It is worth noting that more than 10 wt.% of this water is generated at low thermal maturity levels, and therefore, more than 12.5 g of water is present with the 125 g of coal in all the nonhydrous experiments. It was observed, after the closed nonhydrous experiments that sufficient water droplets occurred on the lignite chips and the reactor walls to allow their collection in part with a pipette. These quantities of water at all of the nonhydrous temperatures (280–350 °C) would occur as under-saturated steam with vapor pressures between 30 and 55% of saturated-steam pressures as calculated from the ASTM Steam Tables (Meyer et al., 1992). Lewan (1992) suggested that pyrolysis experiments with water vapor at steam pressures greater than 20% of saturated-steam pressures be referred to as steam pyrolysis. This definition makes the nonhydrous experiments of this study steam-pyrolysis experiments. However, the original definition by Lewan (1992) was based on source rocks containing organic matter that does not commonly generate sufficient water to generate vapor pressures in excess of 20% of saturated-steam pressures (Lewan, 1997). In light of these experiments with lignite, it may be more appropriate to raise the limit for steam pyrolysis to 50% of saturated-steam pressures. Regardless of what these lignite experiments without added water are called (nonhydrous, anhydrous, or steam pyrolysis), it is important to realize that steam is present in these experiments at partial pressures between 30 and 55% of saturated-steam pressures.

4.4. Liquid products

4.4.1. Amounts of generated fractions

The sum of expelled oil, extract 1, and extract 2 are given in Table 7 for the hydrous and nonhydrous experiments. Extracts 1 and 2 constitute the total C_{8+}

Table 6
Yields of gases and water generated by hydrous and closed nonhydrous experiments

Components (mg/g orig. lignite)	Experimental conditions (°C/h)										Mean % difference[a]
	280/48	300/24	300/72	300/144	315/72	350/12	330/72	330/108	350/24	350/96	
Methane											
Hydrous	0.64	0.98	1.38	1.68	2.03	2.42	2.83	3.56	3.42	5.67	
Nonhydrous	0.62	0.91	1.38	2.03	2.69	3.83	3.28	4.26	3.18	6.59	−14.7
Ethane											
Hydrous	0.15	0.28	0.48	0.66	0.90	1.26	1.53	1.99	2.00	3.42	
Nonhydrous	0.13	0.21	0.48	0.75	1.20	2.03	1.78	2.49	1.56	4.34	−10.9
Propane											
Hydrous	0.22	0.36	0.61	0.81	1.00	1.18	1.53	1.90	2.11	2.70	
Nonhydrous	0.20	0.32	0.80	0.95	1.43	2.10	1.93	2.63	1.63	4.09	−24.5
Butanes											
Hydrous	0.10	0.17	0.31	0.45	0.52	0.57	0.85	1.08	1.73	1.30	
Nonhydrous	0.06	0.11	0.32	0.50	0.74	1.00	0.99	1.35	0.78	2.08	−10.1
Pentanes											
Hydrous	0.03	0.05	0.09	0.13	0.14	0.17	0.25	0.37	0.42	0.35	
Nonhydrous	0.02	0.04	0.00	0.15	0.11	0.17	0.16	0.21	0.13	0.34	31.1
Total HC gas											
Hydrous	1.15	1.84	2.87	3.74	4.58	5.60	7.00	8.91	9.68	13.44	
Nonhydrous	1.03	1.58	2.97	4.39	6.17	9.13	8.14	10.95	7.29	17.44	−13.9
H_2S											
Hydrous	0.23	0.57	0.65	0.23	0.98	1.24	1.42	1.85	1.81	2.49	
Nonhydrous	0.00	0.00	0.24	0.01	0.55	0.14	0.01	0.76	0.01	0.86	81.7
CO_2											
Hydrous	44.12	56.50	66.34	67.76	78.09	72.93	84.14	85.67	82.96	99.45	
Nonhydrous	34.66	38.45	48.96	57.66	71.06	58.19	63.87	66.99	65.33	72.48	22.4
H_2											
Hydrous	0.02	0.01	0.02	0.03	0.02	0.04	0.03	0.03	0.04	0.04	
Nonhydrous	0.01	0.01	0.03	0.05	0.04	0.07	0.10	0.10	0.08	0.15	−116.5
H_2O[b]											
Hydrous	117.6	120.8	119.2	124.6	150.5	141.8	146.3	151.6	145.1	151.6	
Nonhydrous	106.8	101.4	129.0	124.3	151.9	140.0	147.4	142.0	145.4	145.6	2.7

[a] Mean % difference is the mean of difference between hydrous and nonhydrous values divided by the hydrous value and multiplied by 100.

[b] Water mass was calculated with Eq. (2).

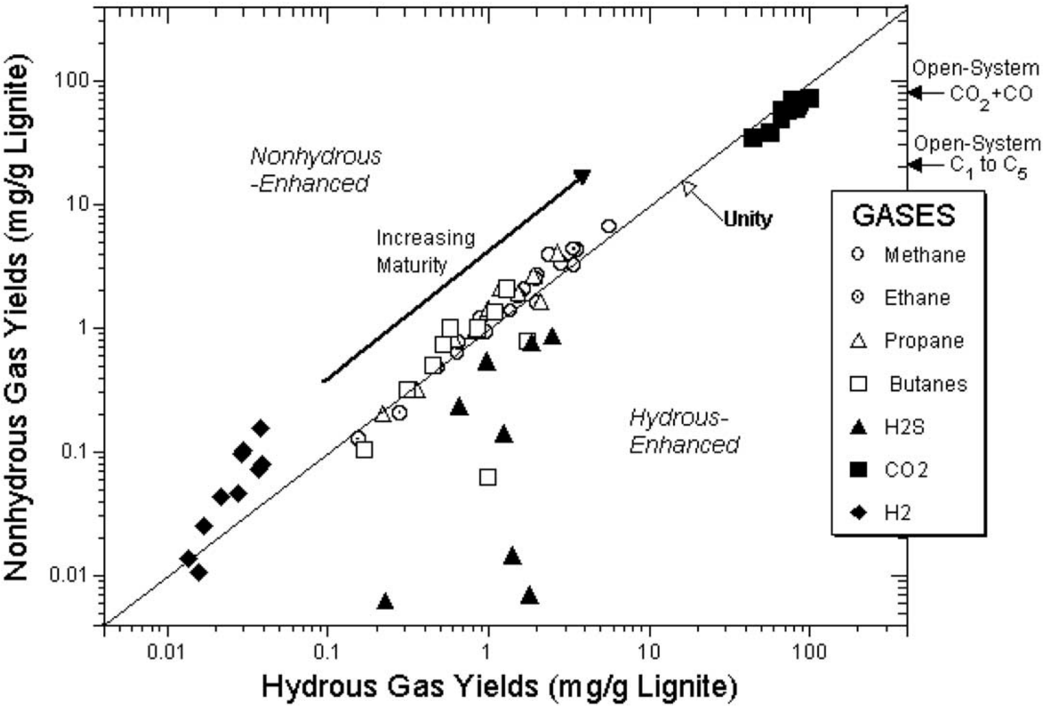

Fig. 5. Plot of gas yields (mg/g original lignite) generated by closed nonhydrous pyrolysis against those generated by hydrous pyrolysis. Gas yields from open nonhydrous pyrolysis are plotted on the right axis.

product for the nonhydrous experiments, and these extracts plus expelled oil constitute the total C_{8+} product for the hydrous experiments. As discussed previously, given the difference in analytical procedures for recovery of the total liquid products of the hydrous and nonhydrous experiments, only the total amounts of C_8–C_{14}, C_{14+} or total C_{8+} (Fig. 6) can be plotted for comparing the different pyrolysis methods.

The C_8–C_{14} shows a systematic increase with thermal maturity (Fig. 6) with the exception of the hydrous experiment conducted at the highest thermal maturity (i.e., 350 °C/96 h) in which a decrease is observed. This decrease is probably due to an incomplete recovery of these compounds in extract 1. Although the C_8–C_{14} amounts increase with thermal maturity in hydrous as well as in nonhydrous experiments, it is observed in Fig. 6 that hydrous pyrolysis experiments consistently have higher yields than nonhydrous experiments. In addition, C_{8+} liquid products from the hydrous experiments continue to increase at thermal maturities greater than 315 °C/72 h and the C_{8+} liquid product from the nonhydrous experiments do not. The C_{14+} fraction is by far the major component of the liquid products generated in both pyrolysis systems (Table 7). Since the C_{14+} fraction always represents more than 80% of the total C_{8+} liquids, the evolution of both fractions with increasing maturity are similar (Fig. 6c). It can, however, be observed that the proportion of C_{14+} compounds in the total C_{8+} liquids is always higher in hydrous than in nonhydrous experiments (Table 7).

Gas chromatograms of extracts 1 and 2 from the hydrous and nonhydrous experiments are similar to those of the expelled oil generated in the hydrous experiments (Fig. 7). At the highest thermal maturity, all of the chromatograms show a waxy *n*-alkane distribution with an odd-carbon predominance between *n*-C_{24} and *n*-C_{30}. Extract 1 and expelled oil from the hydrous experiments are the most similar with respect to the overall *n*-alkane distribution and the relative abundance of isoprenoids (Fig. 7). Relative to the expelled oil and extracts from the hydrous experiment, the nonhydrous extracts have relatively lower abundances of *n*-C_{15}–*n*-C_{24} alkanes and *i*-C_{15}–*i*-C_{21} isoprenoids. The overall similarity of these gas chromatograms is particularly interesting because the saturate-aromatic-NSO proportionality is significantly different for these liquid products (Table 8), and indicates that the prevalent compounds amenable to gas chromatography (*n*-alkanes) are not a complete representation of the liquid products. This is not surprising when one considers that *n*-alkanes between C_1 and C_{40} only constitute 15 to 20 wt.% of most crude oils (Tissot and Welte, 1984, p. 384). Unfortunately, this comparison cannot be extended to that of the C_{8+} saturates recovered in the Ext 2 because this fraction was recovered after drying and crushing of the residual lignite, so the C_{14}-hydrocarbons were lost.

Table 7
Yields of liquid products generated by hydrous and closed nonhydrous pyrolysis

Liquid organic products (mg/g orig. lignite)	Experimental conditions (°C/h)									
	280/48	300/24	300/72	300/144	315/72	350/12	330/72	330/108	350/24	350/96
Total liquid C_8–C_{14}										
Hydrous	1.7	4.7	4.6	5.7	9.2	12.8	14.4	18.5	21.1	15.5
Nonhydrous	0.9	1.7	3.5	4.5	7.2	7.3	6.0	11.6	9.3	13.0
C_{14+}										
Hydrous	46.4	64.9	68.3	63.6	79.8	102.1	108.0	105.2	125.9	109.7
Nonhydrous	30.5	45.6	46.7	45.4	68.6	59.8	63.2	63.9	63.9	61.6
Total C_{8+}										
Hydrous	48.1	69.6	72.9	69.3	89.0	114.9	122.4	123.7	147.0	125.2
Nonhydrous	31.4	47.4	50.1	49.9	75.8	67.1	69.1	75.5	73.2	74.6
C_8–C_{14} of total C_{8+}										
Hydrous	*3.6*	*6.8*	*6.4*	*8.2*	*10.3*	*11.2*	*11.8*	*15.0*	*14.4*	*12.4*
Nonhydrous	*2.9*	*3.7*	*6.9*	*9.0*	*9.5*	*10.8*	*8.7*	*15.3*	*12.7*	*17.4*
C_{14+} of total C_{8+}										
Hydrous	*96.4*	*93.2*	*93.6*	*91.8*	*89.7*	*88.8*	*88.2*	*85.0*	*85.6*	*87.6*
Nonhydrous	*97.1*	*96.3*	*93.1*	*91.0*	*90.5*	*89.2*	*91.3*	*84.7*	*87.3*	*82.6*

4.4.2. SARA analysis

With the exception of the experiments at 350 °C/24 h, the yield of saturates of the C_{14+} fraction of the total liquid product increases with thermal maturity in the hydrous and nonhydrous experiments (Fig. 8). Maximum saturate contents of 24.4 and 24.1 mg/g original lignite occur at the highest thermal maturity (350 °C/96 h) for both hydrous and nonhydrous experiments, respectively (Fig. 8). The open-system maximum for this fraction occurs slighter higher than these maximums with a value of 28.2 mg/g original lignite (Table 3). The aromatic content of the C_{14+} fraction of the total liquid products from hydrous and nonhydrous experiments is essentially the same and increases with thermal maturity to 315 °C/72 h (Table 8 and Fig. 8). At higher thermal maturities, the aromatic contents remain constant with the hydrous experiments having higher abundances (Table 8 and Fig. 8). Maximum aromatic abundances are 20.9 mg/g original lignite at 330 °C/72 h for the hydrous experiments and 13.8 mg/g original lignite at 315 °C/72 h for the nonhydrous experiments (Table 8). The former is closer to the C_{14+} aromatic abundances generated by the open-system pyrolysis (i.e., 22.1 mg/g original lignite; Table 3). Collectively, the maximum total hydrocarbon (i.e., saturates plus aromatics) yield for hydrous pyrolysis (45.3 mg/g) is 20 wt.% higher than that for closed nonhydrous pyrolysis (37.9 mg/g).

The NSOs constitute most of the total extract and do show some similarity to the two incremental increases noted in the total C_{14+} extract (Figs. 6 and 8): their maximum abundance occurs at 350 °C/24 h for the hydrous experiments with a value of 88.3 mg/g, and at 315 °C/72 h for closed experiments, with a value of 39.4 mg/g original lignite. Similar to the aromatic component, the maximum NSO for the hydrous experiments is in closer agreement to that of the open-system pyrolysis (i.e., 75.3 mg/g original lignite; Table 2) than to that of the nonhydrous experiments.

Proportionality of the saturate-aromatic-NSO components for the C_{14+} fraction of the total liquid product is shown in Fig. 9 and in Table 8. Although the hydrous experiments generate similar saturates as the nonhydrous experiments (Table 8), the cogeneration of proportionally more aromatic and NSO components results in a proportionally lower saturate percentage in the hydrous experiments than in the nonhydrous experiments (Table 8). As shown in Fig. 9, the proportionality of the C_{14+} fraction generated by open-system pyrolysis occurs in approximately the middle of the nonhydrous experiments and in the upper half of the hydrous experiments.

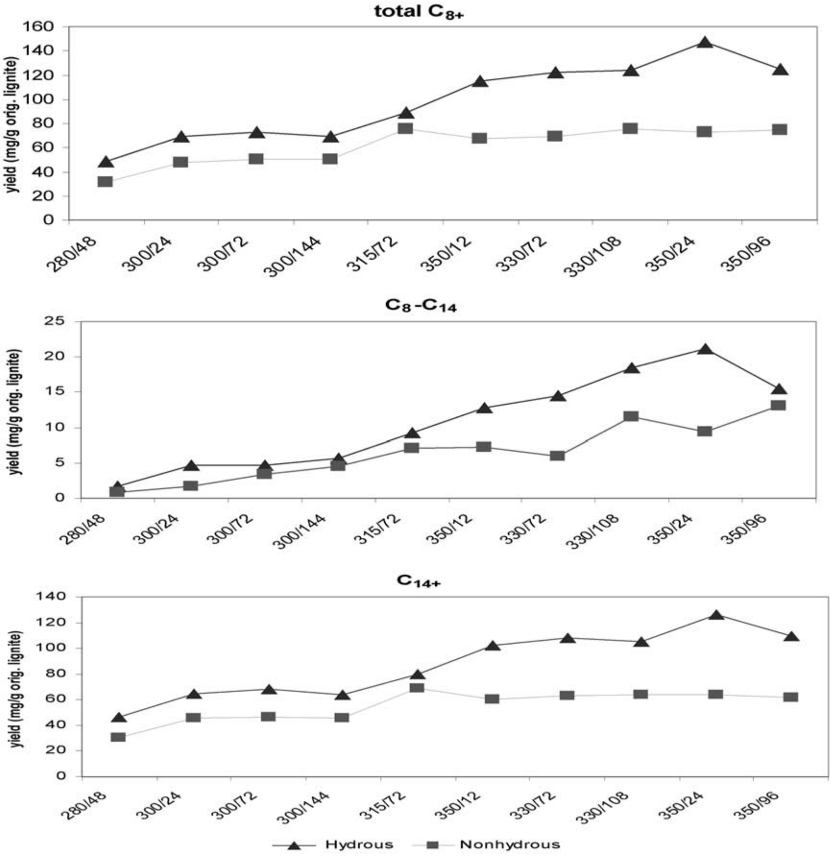

Fig. 6. Yields of liquid products generated by hydrous pyrolysis (▲) and closed nonhydrous pyrolysis (■) plotted against increasing experimental thermal maturity: (a) total C_{8+} products; (b) total C_8–C_{14} products and (c) total C_{14+} products.

Table 9 gives a summary of the maximum yields of the different products generated during artificial maturation of the original lignite in the three pyrolysis systems.

5. Discussion

Table 10 gives a nominal comparison of the different pyrolysis methods used on rocks containing Type-III kerogen. Among the published results and those of this study, comparisons of closed- and open-nonhydrous pyrolysis are the most consistent, with most product characterization parameters being dissimilar (CNP vs. ONP, Table 10). The only exceptions are the similar gas chromatograms of the C_{8+} products, maximum amounts of water, and hydrocarbon gases for both pyrolysis methods observed in this study. Similarly, most of the product characterization parameters are dissimilar between open-nonhydrous and hydrous pyrolysis in the published study by Qin et al. (1994) and this study (HP vs. ONP, Table 10). The only inconsistency between these two studies is in the comparison of the proportionalities of saturate, aromatic, and NSO fractions. Qin et al. (1994) report liquid products with greater saturate percentages from hydrous pyrolysis than from open-nonhydrous pyrolysis, and this study shows there is not a significant difference.

In terms of atomic H/C and O/C ratios (i.e., elemental analyses, Table 5), slight differences are observed between closed nonhydrous- and hydrous-pyrolysis: however the general maturity trends, as reported in a van Krevelen diagram, are very similar and mimic natural maturation. The same is true for $\%R_o$ values. The similar response observed by Teerman and Hwang (1991) and Michels and Landais (1994) and the dissimilar response observed by Huang (1996) and this study of vitrinite reflectance in the hydrous and nonhydrous experiments may be explained by the presence of liquid H_2O generated by the coal in the former confined nonhydrous experiments, thus making them hydrous experiments. This condition is demonstrated in part by several ancillary experiments conducted by Huang (1996). The nonhydrous experiments conducted by Huang (1996) were conducted at 350 °C in unsealed gold capsules that were open to the externally applied

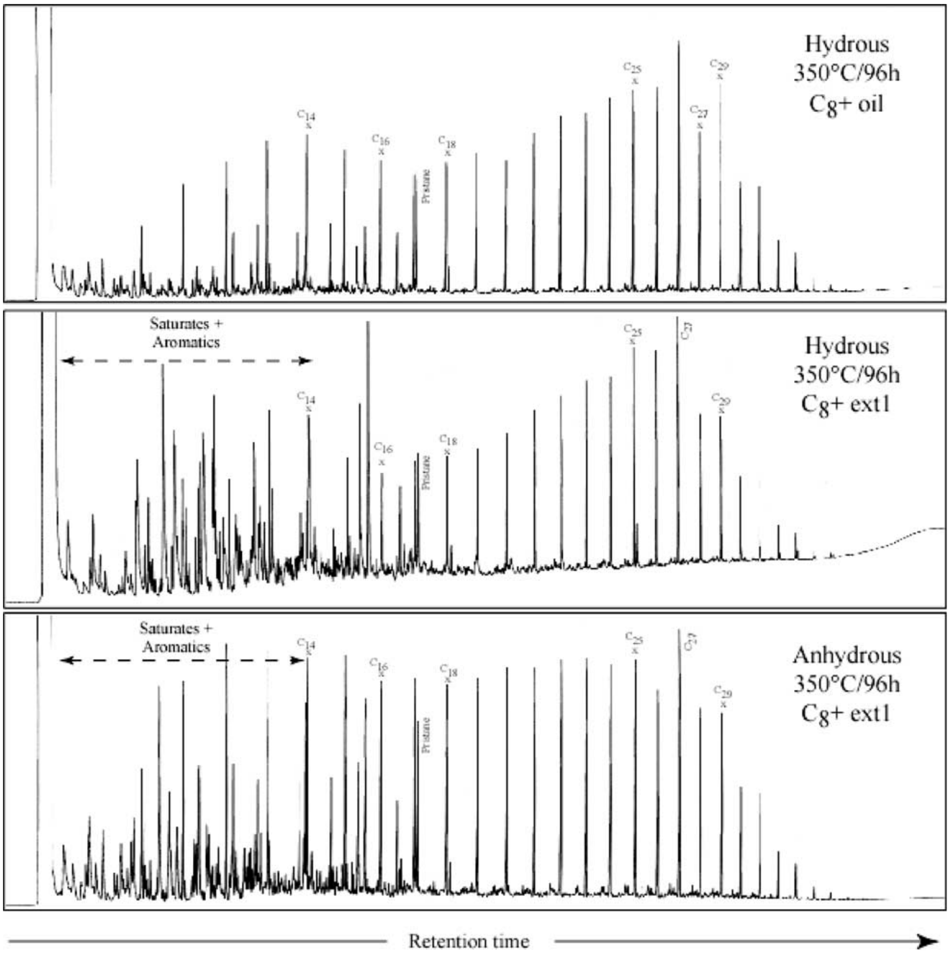

Fig. 7. Gas chromatograms of C_{8+} fractions of pyrolysates generated at 350 °C for 96 h: (a) hydrous pyrolysis expelled oil, (b) hydrous pyrolysis extract 1 and (c) closed nonhydrous pyrolysis extract 1.

Table 8

Column chromatographic fractions of C_{14+} liquid products from hydrous and closed nonhydrous pyrolysis: amounts (mg/g original lignite and fraction composition in italics (wt.%)

Liquid organic products (mg/g orig. lignite) (%)	Experimental conditions (°C/h)																			
	280/48		300/24		300/72		300/144		315/72		350/12		330/72		330/108		350/24		350/96	
Total C_{14+} liquid products																				
Saturates																				
Hydrous	nd	*nd*	5.2	*8*	8.2	*12*	9.4	*15*	12.5	*16*	13.5	*13*	19.2	*18*	20.6	*20*	17.9	*14*	24.4	22
Nonhydrous	3.5	*11*	5.7	*13*	7.2	*15*	9.2	*20*	15.4	*22*	14.9	*25*	16.2	*26*	21.4	*33*	18.5	*29*	24.1	*39*
Aromatics																				
Hydrous	nd	*nd*	9.3	*14*	11.0	*16*	11.1	*17*	13.6	*17*	15.3	*15*	20.9	*19*	17.1	*16*	19.7	*16*	19.0	*17*
Nonhydrous	5.7	*19*	9.0	*20*	9.6	*21*	11.6	*26*	13.8	*20*	12.3	*20*	12.4	20	13.4	*21*	13.2	*21*	10.7	17
NSOs																				
Hydrous	nd	*nd*	50.5	*78*	49.1	*72*	43.2	*68*	53.7	*67*	73.4	*72*	67.9	*63*	67.6	*64*	88.3	*70*	66.3	*60*
Nonhydrous	21.3	*70*	30.8	*68*	29.9	*64*	24.7	*54*	39.4	*57*	32.7	*55*	34.6	*55*	29.1	*46*	32.1	*50*	26.9	*44*

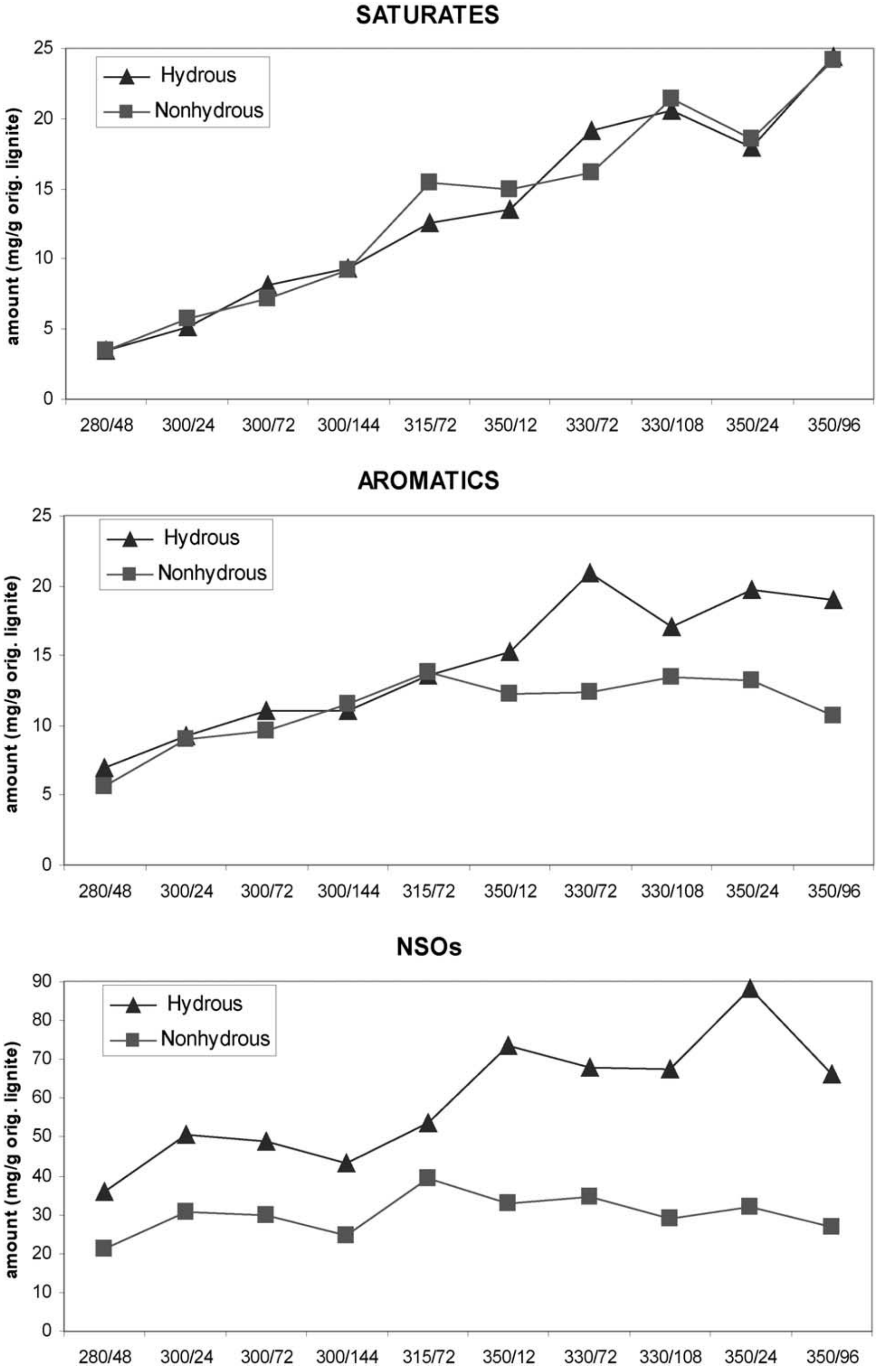

Fig. 8. Yield of column-chromatographic fractions of the total C_{14+} products generated by hydrous pyrolysis and closed nonhydrous pyrolysis plotted against increasing experimental thermal maturity: (a) C_{14+} saturates, (b) total C_{14+}, (c) total C_{14+} NSOs.

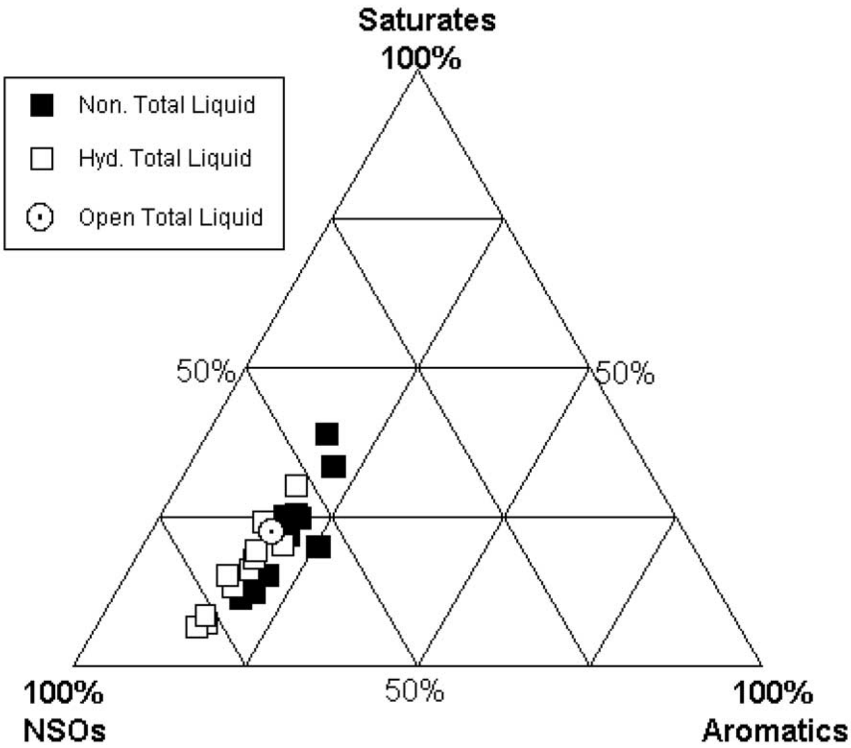

Fig. 9. Ternary plots of saturate, aromatic, and NSO (resins + asphaltenes) components of C_{14+} liquid products generated by hydrous pyrolysis (□), closed nonhydrous pyrolysis (■) and open nonhydrous pyrolysis (⊙).

Table 9
Comparison of the maximum yields of products generated from the original WX-3 lignite by different pyrolysis methods

Product characterization parameter (mg/g)	HP	CNP	ONP
$CO_2 + CO$	100	73	79
H_2O	152	146	148
C_1–C_5	13	17	21
C_8–C_{14}	21	13	13
C_{14+}			
Total	126	69	126
Aliphatics	24	24	28
Aromatics	21	14	22
NSOs	88	39	75
% Sat/Aro/NSOs	22/17/60	39/17/44	22/17/59
ΣHC	157	86	168
ΣS_2	194	153	168

HP = hydrous pyrolysis, CNP = closed nonhydrous pyrolysis, and ONP = open nonhydrous pyrolysis.

51.3 MPa of argon pressure. Under these conditions, H_2O generated from the coal would occur as disseminated vapor in the openness of the external argon-pressurized reactor, thus resulting in nonhydrous experiments. However, Huang (1996) also conducted experiments in sealed gold capsules under the same temperature and pressure conditions. Under these conditions, H_2O generated from the coal occurs as liquid in the confined volume of the compressed capsule, resulting in hydrous experiments. These experiments yielded the same vitrinite reflectance values as the hydrous experiments.

It appears from these comparisons that it is not important whether hydrous pyrolysis experiments are a result of added water at the start of an experiment or confined water generated during the early stages of an experiment. The critical issue is that liquid H_2O is maintained in and around the coal during pyrolysis, which is the situation during natural maturation of coals in the subsurface. The main similarities between closed nonhydrous and hydrous pyrolysis of lignite are the maximum amounts of generated hydrocarbon gases, water, C_{14+} saturates, and gas chromatographic signatures (HP vs. CNP, Table 9 and Figs. 7 and 8). Although closed nonhydrous- and hydrous-pyrolysis generates similar quantities of hydrocarbon gases, the former generates on average 15 wt.% more methane than the latter (Table 6). This difference is significantly less than the 52–76% increases reported for nonhydrous pyrolysis relative to hydrous pyrolysis of source rocks with Type-II kerogen (Lewan, 1997, Table 6). The significantly lower steam pressures in the nonhydrous py-

Table 10
Nominal comparison of similarities and dissimilarities of products generated from Type-III kerogen by different pyrolysis methods

Product characterization parameter	HP versus CNP		HP versus ONP		CNP versus ONP	
	Similar	Dissimilar	Similar	Dissimilar	Similar	Dissimilar
Hydrocarbon gases						
Quantity generated	[a,b]	–	–	[a,c]	–	[a,d,e]
Molecular composition	[a]	–	–	[c]	–	[d,e]
Nonhydrocarbon gases						
Quantity generated	–	[a,b]	–	[a,c]	–	[a,d,e]
Molecular composition	–	[a,b]	–	[c]	–	[d]
Liquid pyrolysate						
Quantity generated	[f]	[a,b]	–	[a,c]	–	[a,d,e]
sat-aro-NSO fractions	[a,f]	–	[a]	[c]	[a]	–
Gas chromatogram	[a,f]	–	[a]	–	[a]	–
Residual lignite						
Elemental analyses	[a,f]	[b]	–	[c]	–	[d,g]
Vitrinite reflectance	[f]	[a,h]	–	–	–	[d]

HP = hydrous pyrolysis, CNP = closed nonhydrous pyrolysis, and ONP = open nonhydrous pyrolysis. Entries with boxed outlines signify inconsistent comparisons among studies.

[a] Reported in this study.

[b] Reported in Artok et al. (1998).

[c] Reported in Qin et al. (1994).

[d] Reported in Behar et al. (1995).

[e] Reported in Arneth and Matzigkeit (1986).

[f] Reported in Michels and Landais (1994).

[g] Reported in Monthioux et al. (1985).

[h] Reported in Huang (1996, open capsule).

rolysis of the Type-II bearing source rock compared to the high steam pressures attained in the nonhydrous pyrolysis of this study may explain this difference. As reported by Lewan (1997, Table 9), elevated steam pressures during nonhydrous pyrolysis can produce hydrocarbon gas yields intermediate to those obtained in low-steam pressure nonhydrous (a.k.a., anhydrous) experiments and hydrous experiments.

Similar gas chromatograms (GC) of liquid products from closed nonhydrous and hydrous pyrolysis in this study have also been observed in comparative pyrolysis studies of source rocks bearing Type-II kerogen (Lewan, 1997, Fig. 1). With the exception of the generation of alkenes, gas chromatograms obtained from open-nonhydrous pyrolysis typically have a similar character to those obtained from closed nonhydrous pyrolysis, as shown in this study for lignite and previous studies involving Type-II kerogen at temperatures less than 500 °C (Dieckmann et al., 2000, Fig. 2). Characterizing gas chromatograms is typically based on the distribution of *n*-alkanes and to a lesser extent the proportionality of several acyclic isoprenoids (i.e., pristine and phytane). These GC-amenable compounds only comprise 15–20 wt.% of natural crude oils (Tissot and Welte, 1984, p. 384) and approximately one half of this range (i.e., ~7.5–10 wt.%) occurs in total pyrolysates as a result of significantly higher NSO fractions (Tissot and Welte, 1984, p. 333). Therefore, care should be taken when interpreting the overall similarities of different pyrolysis methods and the reaction pathways by which they generate pyrolysates simply on the basis of these familiar but minor GC-amenable constituents.

Likewise, comparable proportionalities of saturate, aromatic, and NSO fractions of the C_{15+} total pyrolysates generated by open-nonhydrous, closed nonhydrous, and hydrous pyrolysis (Fig. 9 and Table 8) are not unequivocal confirmation of overall similarity in the mechanisms and reaction pathways. This caution becomes most apparent when comparing the quantities of the fractions generated by each of the pyrolysis methods. At the maximum C_{14+} total yield for closed nonhydrous- and hydrous-pyrolysis, the latter generates 56% more aromatics, and 2.5 times more NSOs (Table 8, 350 °C/24 h). Lewan (1997) has reported similar differences between hydrous and closed nonhydrous experiments conducted on source rocks containing Type-II kerogen. He explains this difference as a result of more water-derived hydrogen being available in the hydrous pyrolysis to minimize cross-linking reactions and enhance the liquid product yield.

While a few cross-linking bonds can render significant portions of organic matter insoluble to non-polar organic solvents (Charlesby, 1954), they may not be sufficient to render significant portions of organic matter thermally inert to open-system pyrolysis. This would explain why the open nonhydrous pyrolysate generated from the residual (i.e., DCM-extracted) lignite (S_{2_r}) of the closed nonhydrous experiments is higher than that from the hydrous experiments. As shown in Fig. 10, addition of this residual pyrolysis yield (S_{2_r}) to the total extract yield (ΣHC) brings the total yields (ΣS_2) of the two pyrolysis methods into closer agreement. This explanation is consistent with the observation that a significant portion of the higher yield in the hydrous experiments is in the NSO components.

These observations can also be compared to those done on two coals already studied in a previous work (Behar et al., 1997a). In their study, two coals with higher initial maturities of 0.57 and 0.62% R_o were subjected to closed nonhydrous pyrolysis. To quantify the maximum amount of generated products, the recovered coals were first extracted with DCM and then subjected to an acid treatment similar to that used for kerogen isolation (Durand and Nicaise, 1980). This procedure breaks down weak bonds and opens the coal network (Behar and Vandenbroucke, 1988). Although the C_{14+} fraction recovery by this procedure was better than with a single DCM extraction, the maximum ΣS_2 was only around 85% of the initial S_2 peak for the two coals. It is clear that this procedure was not necessary in this study because the maximum ΣS_2 of the nonhydrous experiments (157 mg/g) is similar as the initial S_2 from Rock-Eval pyrolysis (172 mg/g). This difference is expected because of some cracking of the NSOs. The better recovery is likely due to the early generated water inside the initially immature lignite preventing a rapid closure of the organic network. Consequently, (i) for similar pyrolysis conditions, TR values calculated on the basis of the S_2 measured on the residual lignite lead to higher values for hydrous experiments, and (ii) the recovered lignite is calculated by difference, so its estimations are lower in hydrous conditions.

Although there is some compensation between free and residual compounds for the generated products, it is clear that the maximum ΣS_2 is both higher (194 vs 153 mg/g initial coal) and more delayed (350 °C/24 h vs 315 °C/72 h) under hydrous than closed nonhydrous conditions. These results confirm the conclusions of Lewan (1997) on a possible delay of secondary cracking reactions in hydrous system compared to anhydrous conditions. Actually, when examining the evolution of ΣS_2 with increasing maturation in both systems (Fig. 10c), it can be seen that the total yield of generated products and residual potential is higher for low maturity in nonhydrous conditions, the reverse being true for high maturity. Although the amount of generated products is higher in hydrous than in nonhydrous conditions, it is possible that this amount is underestimated due to dissolution of a part of the generated polar compounds in water. However, it was previously observed (Lewan and Fisher, 1994: Table 4) that some compounds such as carboxylic acids and phenols were dissolved in the water added in hydrous experiments in a concentration not exceeding 30 mg/g original lignite. Thus, the maximum ΣS_2 should not exceed 224 mg/g.

Fig. 10 also shows that the balance becomes similar in both systems for intermediate maturities, then in experiments at higher maturities ($>$330 °C) the difference increases sharply due to a high production of the C_{14+} fraction in the hydrous experiments. This means that the observed delay for secondary cracking reactions in the hydrous experiments might be also due to a supplementary production of C_{14+} compounds by interaction between water and coal. In previous papers (Siskin et al., 1990; Lewan, 1997), several possible mechanisms were suggested involving hydrocarbons (saturates and aromatics), linked in the coal network and released by bound hydrolysis. Some of them lead to CO_2 production, which is in excess in this type of artificial maturation as indeed reported in the present study. Unfortunately, the set of experiments performed for the present paper do not discriminate between the two possible mechanisms, i.e. (i) a similar production of the C_{14+} pyrolysate, but a delay in its secondary cracking and (ii) a higher production of this fraction by a specific chemical reaction with water. In fact, the experiments were carried out on the coal itself and thus, the resulting mass balance is the sum between primary and secondary reactions.

A remaining question is whether the high NSOs generated by hydrous pyrolysis can decompose into more saturate and aromatic components at higher thermal maturities. Ruble et al. (2001) have shown that lacustrine source rocks can generate saturate and aromatic components from the degradation of NSO components under hydrous pyrolysis conditions at thermal maturities as high as 360 °C/96 h. This experimental condition is 10 °C higher than the highest thermal maturity experiment used in this study (350 °C/96 h). The observation that crude oils are more thermally stable when

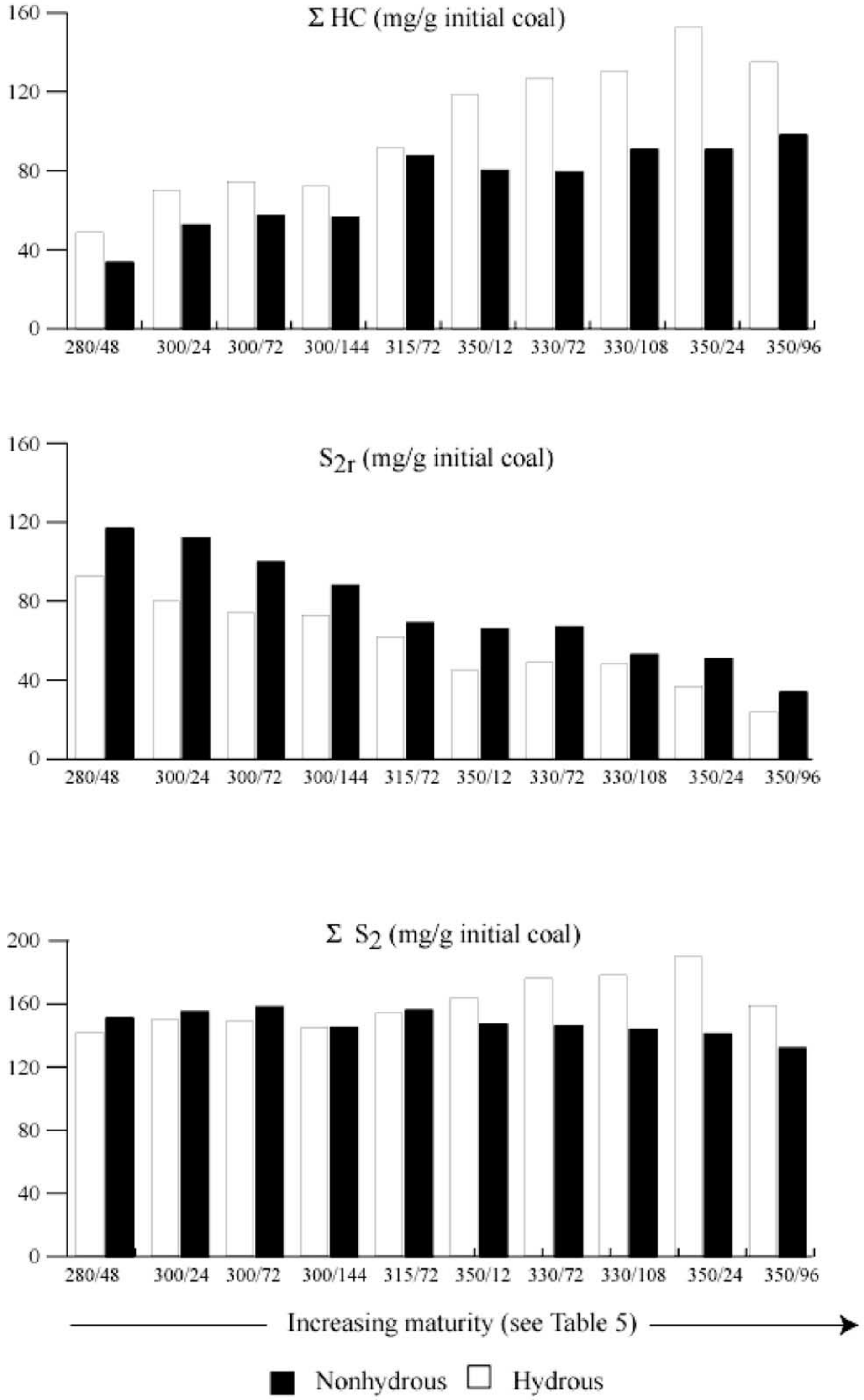

Fig. 10. Comparison of (a) ΣHC (total liquid product), (b) S_{2_r} (Rock-Eval S_2 on residual lignite and corrected for original lignite), and (c) ΣS_2 (sum of ΣHC and S_{2_r}) for hydrous pyrolysis and closed nonhydrous pyrolysis plotted against increasing experimental thermal maturity (Table 5).

heated in the presence of water (Hesp and Rigby, 1973), suggest that higher saturate and aromatic components may be generated at the expense of NSO components under hydrous pyrolysis at thermal maturities higher than those used in this study. Therefore, the full potential for generation of saturate and aromatic components from lignite by hydrous pyrolysis may not have been realized in this study.

Overall, the differences among the pyrolysis methods for Type-III kerogen used in this study are not as significant as those observed for Type-II kerogen (Lewan, 1997; Andresen et al., 1993). This may be the result of differences in the chemical structure of these kerogen types or the high water content generated by Type-III kerogen. If decomposition of the aliphatic portions of kerogen is more influenced by the presence or absence of water, then greater differences between anhydrous and hydrous conditions would be expected from pyrolysis of the more aliphatic-rich Type-II kerogen than the more aromatic-rich Type-III kerogen. Extension of this hypothesis suggests that product differences between hydrous and anhydrous conditions would be greater for highly aliphatic-rich Type-I kerogen than for Type-II kerogen. Furthermore, the amount of water generated during nonhydrous pyrolysis of a kerogen may minimize product differences between hydrous and anhydrous conditions as a result of the presence of a reactive water vapor (Lewan, 1997; Hayashi et al., 1999). The significance of this water vapor would be determined by the amount of water generated and the reactor gas volume in closed-system pyrolysis or water-release rate and carrier-gas flow rate in open-system pyrolysis.

Unfortunately, a set of naturally matured samples of Wilcox lignite in the Gulf Coast was not available for this study. Therefore, determining which pyrolysis method best simulates natural maturation is not possible. It is clear that the similarities in kerogen elemental composition, chromatographic character of liquid products, and molecular composition of generated gases will not be definitive in making this determination. Future studies of stable carbon isotopes and biomarker content of the products may be more helpful in making this determination. With concerns about existing kinetic parameters for oil generation from Type-III kerogen (Burnham et al., 1995; Barth et al., 1996), future kinetic studies based on the different pyrolysis methods may also help determine which pyrolysis method best simulates Nature. Another concern is whether oils can be expelled from coals (e.g., Katz, 1994). In this respect, hydrous pyrolysis is unique in that it generates an expelled waxy oil from the Wilcox lignite. If future studies show this expelled waxy oil is comparable to natural waxy oils generated from source rocks bearing Type-III kerogen, considerable advances may be made in resolving the issue of coals as source rocks and the mechanisms by which oil is expelled.

6. Conclusions

This study is the first to compare yields and compositions of products generated by open nonhydrous, closed nonhydrous, and closed hydrous-pyrolysis of aliquots of the same sample of lignite. All three methods generated high and similar quantities of water during pyrolysis that ranged between 14.8 and 15.2 wt.% of the original lignite. More than 70% of this water is generated during the initial stages of pyrolysis at low thermal stress levels ($\%R_o < 0.7$). This quantity of generated water results in water vapor pressures between 30 and 55% of saturated steam pressures in the closed nonhydrous pyrolysis experiments. As shown by Lewan (1997), high water-vapor pressures results in liquid-product yields intermediate to the low yields from closed anhydrous pyrolysis and the high yields from hydrous pyrolysis of source rock with Type-II kerogen. Therefore, it is important when comparing nonhydrous to hydrous pyrolysis to know the amount of water generated from a sample and the phases it occurs at during nonhydrous pyrolysis experiments. This consideration is especially important in confined pyrolysis experiments with coal because generated water could completely fill intergranular voids in the confined coal, making it a hydrous experiment rather than an intended nonhydrous experiment.

Residual lignite from the closed nonhydrous and hydrous experiments showed relationships between vitrinite reflectance ($\%R_o$) values and atomic H/C ratios that occurred within the fields observed for natural maturation of coal. Therefore, it appears that both closed pyrolysis methods simulate natural maturation of the solid lignite conversion to higher rank coal. Although no significant differences in the atomic H/C ratios were observed between closed nonhydrous and hydrous pyrolysis, the vitrinite reflectance values were on average 0.2% R_o lower in the residual lignite from the nonhydrous experiments. The remaining hydrocarbon-generation potential as determined by Rock-Eval pyrolysis of the residual lignite showed that the nonhydrous residuals had on average 16 more mg of hydrocarbon potential per gram of original lignite than the hydrous residuals. This suggests there is a better release of the pyrolysis products from the coal network in the hydrous experiments once generation occurs.

For gas generation, at maximum yields, open nonhydrous pyrolysis generates the most hydrocarbon gas (21.0 mg/g original lignite)—which is 20% more than closed nonhydrous pyrolysis and 29% more than hydrous pyrolysis. Behar et al. (1995) have shown that hydrocarbon gases generated by open nonhydrous pyrolysis of coal are extremely enriched in C_{2+} hydrocarbons relative to closed nonhydrous pyrolysis. Closed nonhydrous pyrolysis generates on the average 14% more gas than hydrous pyrolysis, but the proportionality of the generated hydrocarbon gases is essentially the same for both pyrolysis methods. At maximum yields, CO_2 generation is greatest in hydrous pyrolysis (99.5 mg/g original lignite), with yields being 37% higher than closed nonhydrous pyrolysis and 26% higher than open nonhydrous pyrolysis. This may be explained by water selectively oxidizing specific functional groups within the lignite, as suggested by Lewan (1997) to explain even greater differences in CO_2 generation between closed anhydrous and hydrous pyrolysis of Type-II kerogen.

Liquid product quantities represent the greatest difference between closed nonhydrous pyrolysis and the open nonhydrous and hydrous pyrolysis. The maximum yields of high-molecular-weight liquid products (C_{14+}) are highest and similar for open nonhydrous pyrolysis and hydrous pyrolysis (125.6 and 125.9 mg/g lignite, respectively), which are more than 70 wt.% higher than closed nonhydrous pyrolysis. These differences in the maximum yields of liquid products are directly related to the greater production of aromatics and NSOs. It is always higher under hydrous conditions, whereas a slow increase followed by a slow decrease is observed under nonhydrous. This can be explained by competition between generation and thermal decomposition of these NSOs, leading on one hand to liquid products and on the other hand to char formation through cross-linking reactions. A remaining question is whether the high NSOs generated by hydrous pyrolysis can decompose into more saturate and aromatic components at higher thermal maturities. However, very similar maximum yields and corresponding GC traces are obtained for the C_{14+} aliphatics in the three pyrolysis systems.

The lack of a comparable set of naturally matured coals and related gases and oils prevents any definitive conclusion on which pyrolysis method best simulates petroleum generation from coals. Additional studies on the stable carbon isotopes and biomarker composition of the products may provide a more definitive conclusion on which pyrolysis method best simulates Nature. Kinetic studies using the different pyrolysis methods to determine kinetic parameters for oil formation may also help make this determination. Furthermore, compositional studies of the expelled waxy oils generated from hydrous pyrolysis of the Wilcox lignite and comparisons with natural waxy oils thought to be generated by Type-III kerogen may resolve issues concerning the mechanisms responsible for oil expulsion from coals.

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