Available online at www.sciencedirect.com
ScienceDirect
International Journal of Coal Geology 71 (2007) 85–102
International Journal of COAL GEOLOGY
www.elsevier.com/locate/ijcoalgeo

Comparison of generative capacities for bitumen and gas between Carboniferous coals from Donets Basin (Ukraine) and a Cretaceous coal from Sabinas–Piedras Negras Basin (Mexico) during artificial maturation in confined pyrolysis system

D. Alsaab [a], I. Suarez-Ruiz [b], M. Elie [a,*], A. Izart [a], L. Martinez [a]

[a] *UMR CNRS 7566-G2R Université H. Poincaré, BP-239, 54506 Vandoeuvre-lès-Nancy, Cedex, France*
[b] *Instituto Nacional del Carbón - (INCAR) - CSIC. Ap.Co., 73, 33080-Oviedo, Spain*

Received 6 January 2006; received in revised form 17 September 2006; accepted 19 September 2006
Available online 17 November 2006

Abstract

The goal of this work is to study the ability of two immature Carboniferous coals from Donets Basin (Ukraine) to act as source for oil. Heating experiments in confined medium were performed to compare the thermal behavior of these coals, 1l1 Dim (%R_r=0.55; H/C at.=0.79) and 2c10YD (%R_r=0.65; H/C at.=0.80), relative to a mature Cretaceous coal from Sabinas Basin (Olmos, %R_r=0.92, H/C at.=0.77). Macerals analysis carried out on starting materials showed that Olmos is exhausted in liptinite contrary to 2c10YD (20 vol.%) and 1l1Dim (6 vol.%). The vitrinite content is lower for 2c10YD (59 vol.%) than for Olmos (84 vol.%) and 1l1Dim (80 vol.%). Solid bitumen occurs often dispersed in the raw coals. Both petrographic and geochemical analyses on starting materials revealed that the selected Carboniferous Donets coals have better potentialities for bitumen generation than the Cretaceous Sabinas coal. The presence of long chain *n*-alkanes (>*n*-C_8) in the pyrolysis-GC chromatograms indicates that the two raw Carboniferous coals from Donets Basin can yield non-volatile hydrocarbons under further thermal maturation. It is speculated that some vitrinite macerals present in hydrogen-rich Carboniferous coals from Donets Basin can act as source rocks for oil. As a matter of fact, results showed that the 'oil window' occurs between ~1.0%R_r and ~2.0%R_r for both Cretaceous Sabinas and Carboniferous Donets coals during confined pyrolysis. As expected from geochemical and petrographic analyses of starting samples, the Carboniferous Donets coals yielded more bitumen and hydrocarbons than Cretaceous Sabinas coal during artificial maturation. Low proportions of solid bitumen (<12 vol.%) are also formed between 1.1%R_r and 1.5%R_r during confined pyrolysis of coals. Two solid bitumen groups have been identified, which correspond to distinct phases of neo-formation. The drop in the solid bitumen content at higher ranks indicates that it contributes to generation of gas during experimental simulation. Moreover, their morphology and porosity change with the level of maturity. The porosity of the vitrinite matrix increases as well as the pore size with increasing maturity. A relationship has been observed between the porosity and the weight loss: the higher pore content of Carboniferous Donets coals is correlated with a higher generation of gas compared to Cretaceous Sabinas coal.

Keywords: Artificial maturation; Carboniferous coals; Cretaceous coals; Oil potential; Sabinas Basin; Donets Basin

* Corresponding author.
E-mail address: marcel.elie@g2r.uhp-nancy.fr (M. Elie).

0166-5162/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.coal.2006.09.006

1. Introduction

Under the influence of time and temperature due to increasing burial, sedimentary organic matter undergoes thermal alteration that leads to oil or gas generation and residual organic solid of higher rank. It is generally accepted that type-II kerogen is oil-prone. There is, however, no consensus concerning the assessment of humic coals as sources for oil. Oil-source rock correlation attempts and basin modeling attributed to coals from Jurassic to Tertiary age range high oil-generative capacities (Wilkins and George, 2002 and references therein; Pedersen et al., 2006). Because most of field observations did not indicate Carboniferous coals-sourced oil accumulations, these coals are generally considered as sources for gas and condensates (Petersen, 2006). Floral evolution through the geologic time is suspected to be the main factor controlling the ability of post-Paleozoic coals to generate non-volatile hydrocarbons (Petersen and Nytoft, 2006). However, the occurrence of oilfields derived from pre-Jurassic coals has been reported. Suggate (2002) suggested that humic coals in the Carboniferous Nottinghamshire–Yorkshire Coalfield in England contributed to the East Midlands hydrocarbon fields. Durand and Parratte (1982) and Bertrand (1984) believed that the near absence of Carboniferous coals associated with oilfields result from a probable loss of oils by migration over the very long period of geological time.

The ability of coals to generate hydrocarbons strongly depends on their macerals composition, and as a general rule liptinite-rich coals are oil-prone while vitrinite-rich coals are gas-prone. However, hydrogen-rich New Zealand coals poor in liptinite and containing more than 80% of vitrinite have high potentialities of generation for oil (Powell et al., 1991; Killops et al., 1998). In addition, Isaksen et al. (1998) did not observe any clear relationship between the liptinite content and capability of Middle Jurassic humic coals of the Norwegian North Sea for oil generation. So, some vitrinite group macerals, such as desmocollinite, are more and more recognized to have the potential for oil generation (Bertrand, 1984; Killops et al., 1994, 2001; Suggate, 2002; Wilkins and George, 2002 and references therein).

Combining to maceral analysis, the pyrolytic methods offer the possibility of qualitatively and quantitatively assessing the oil-generative potential of both coals and maceral concentrates. Open pyrolysis systems, including Rock-Eval pyrolysis (Espitalié et al., 1977; Verheyen et al., 1984; Sykes and Snowdon, 2002), but also pyrolysis-gas chromatography (Schenck et al., 1983; Katz et al., 1991; Isaksen et al., 1998), have been extensively used for these purposes. However, olefins rarely found in crude oils are generated during heating experiments in open-pyrolysis systems (Behar et al., 2003) So, closed-pyrolysis systems using different type of reactors including glass (Saxby et al., 1986; Horsfield et al., 1989; Lu and Kaplan, 1990; Boreham et al., 1999), stainless steel (Brooks and Smith, 1969; Lewan and Williams, 1987; Kholi et al., 1994; Mishra et al., 1996; Petersen, 2002; Kotarba and Lewan, 2004) and gold tubes (Monthioux et al., 1985; Monthioux and Landais, 1988; Behar and Hatcher, 1995; Huang, 1996; Xiong et al., 2004; Su et al., 2006) have been developed for reproducing the natural coalification. Excess of liquid water during heating experiments in stainless steel tubes is unequivocal essential to obtain pyrolysis products similar to those found in nature. Brooks and Smith (1969) detected only small amounts of alkenes when 5 wt.% of water is added during heating experiments of brown coals. Geochemical and isotopic investigations have indicated that liquid water is a source of hydrogen for the newly formed hydrocarbons during thermal maturation (Lewan, 1997 and references therein; Schimmelmann et al., 1999; 2001). However, several studies have shown that it is also possible to yield oil-like pyrolysis products in absence of water when using the others types of reactor. The quality of simulation strongly depends on experimental conditions and reacting medium (Saxby et al., 1986; Horsfield et al., 1989; Mansuy et al., 1995; Michels et al., 2000). Saxby et al. (1986) did not observe olefins in pyrolyzates during six years of anhydrous pyrolysis of torbanite and brown coal in glass tubes. Using sealed glass capillary tubes (micro-scale sealed vessel MSSV pyrolysis) to reduce free volume, Horsfield et al. (1989) greatly improve the quality of simulation compared to classical glass tubes. The addition of excess water is not needed in confined-medium pyrolysis (Monthioux et al., 1985; Huang, 1996; Su et al., 2006). Experimental data clearly indicate that water generated by organic matter is sufficient for the formation of hydrocarbons in a confined environment (Landais et al., 1994; Michels et al., 1994). Some papers have been published concerning the ability of these pyrolysis systems to simulate the natural coalification (Monthioux et al., 1985; Monthioux and Landais, 1988; Michels and Landais, 1994; Behar et al., 1997a, 2003). We think that each of these pyrolysis systems must be viewed as additional and not as a replacement. Open pyrolysis enables us to simulate the primary cracking while the closed pyrolysis takes into account the secondary cracking. However, primary and secondary cracking are overlapped in the latter. The

need to add water in closed-system pyrolysis to improve the quality of simulation still remains matter of debate. Hydrous pyrolysis presents a major advantage for expelling of oil. However, this technique needs to add an excess of water in the reacting medium (100 to 250 wt.%). Despite its ubiquity in the geological medium, the proportion of water, however, progressively decreases with the coal rank (Hildenbrand et al., 2006). So, as already pointed out by Saxby et al. (1986), there may well be cases in which liquid water is not in intimate contact with organic material at the time of generation. Monthioux (1988) thought that the natural-reaction system should be considered as 'quasi confined' in the case of coals on account of their physical and chemical properties. In this case, the non-hydrous closed-systems pyrolysis using glass tubes (Horsfield et al., 1989) or gold cells (Monthioux et al., 1985) can be appropriated to simulate natural coalification. Experimental data clearly show that the addition of water in excess is not needed to obtain products closed to crude oils. We agree that the involved mechanisms are not the same in absence or in presence of water. Lewan (1997) experimentally demonstrated that the presence of water in excess inhibits the transformation of bitumen into solid bitumen during artificial maturation of marine sediments. However, the amount of solid bitumen is low or nil for type III kerogen during non-hydrous confined pyrolysis, thus indicating that its formation also depends on the nature of organic material (Behar et al., 1991). In the same way, the addition of water in excess dramatically retards the thermal evolution of residual kerogen (Michels and Landais, 1994). This may have important implications for estimating of the coalbed gas.

However, the purpose of this study is not to compare hydrous pyrolysis and confined pyrolysis. A relevant comparison should be needed to heat the same sample using these two pyrolysis techniques (Behar et al., 2003). Here, we prefer to provide additional information to better understand the transformations occurring in the coal during artificial maturation in confined medium. As a matter of fact, till now, only geochemical and molecular analyses were performed to demonstrate that confined pyrolysis satisfactorily duplicates the transformations of organic matter during the natural coalification (Monthioux et al., 1985; Monthioux and Landais, 1989a,b). Petrographic examinations were limited to vitrinite reflectance measurements while the changes occurring in the maceral composition and the relationship between porosity/solid bitumen formation and gas generation during confined pyrolysis have never been studied before. In addition, most of experimental simulations using confined pyrolysis were carried out on lignite and immature coals (Michels and Landais, 1994; Behar and Hatcher, 1995; Behar et al., 1995, 2003). Only some studies dealing with Paleozoic coals or comparing thermal behavior of coals different in age during confined pyrolysis are reported in the literature (Landais et al., 1989; 1991; Landais, 1991; Piedad-Sánchez et al., 2005). This study deals with the characterization and the thermal reactivity of three coals: a mature Cretaceous coal from Sabinas Basin depleted in liptinite and whose both petrographic and geochemical parameters indicate that peak of oil generation has been reached during natural coalification and two immature coals from Donets Basin that lie at the beginning of oil window and have different maceral compositions. This study is targeted at the following objectives:

1. comparison of thermal behavior of one Cretaceous coal from Sabinas–Piedras Negras (Mexico) and two Carboniferous coals from Donets (Ukraine) during artificial maturation,
2. changes in maceral composition with increasing maturity in confined pyrolysis,
3. role plays by vitrinite on the generation of oil, especially in the case of Carboniferous coals,
4. relationships between solid bitumen content/extract yield and between porosity/gas yield.

Following a general characterization of starting materials, coals were subjected to pyrolysis experiments under confined conditions. Unextracted pyrolysates were analyzed by optical microscopy whereas Rock-Eval pyrolysis and elemental analysis were performed on extracted raw samples and solid residues. The amounts of bitumen and gas generated during confined pyrolysis were measured. Saturates and aromatic hydrocarbons were analyzed by gas chromatography-mass spectrometry.

2. Geological settings and sampling

2.1. Sabinas–Piedras Negras Basin

The Sabinas Basin encompasses an area of about 37,000 km^2. The Sabinas basin initially developed on the margin of the North American craton during the early Mesozoic opening of the Gulf of Mexico with a preferential direction NW–SE (transtensional or extensional phase), and then it folded during the Laramide orogen (compressional phase) (Cserna, 1960; Longoria, 1984; Santamaría-Orozco, 1990). The most important source rocks in this basin correspond to the following formations: Olmos (Maastrichtian), Eagle Ford (Late

Cretaceous), la Peña (Early Cretaceous), la Virgen (Early Cretaceous), and la Casita (Late Jurassic) (Eguiluz de Antuñano, 2001). A vitrinite-rich coal from Olmos (Maastrichtian) of the Mimosa coal mine was selected for this study.

2.2. Donets Basin (Donbas)

The Donets Basin is located in the south-eastern part of Ukraine, extending into the territory of Russia. Geologically, the Donets Basin represents a large bending flexure that covers an area of approximately 60,000 km^2 (Triplett et al., 2000; Sachsenhofer et al., 2003). There are over 330 identified Carboniferous coal seams to a depth of 1800 m. However, only a hundred seams are considered mineable due to either thin seam thickness or depth constraints (Privalov et al., 1998). Two vitrinite-rich coals from Donets Basin were studied: 2c10YD from the Serpukhovian seams of the Yuzhno Donbasskaya #1 coal mine and 111Dim from the Moscovian seams of the Dimitrova coal mine.

3. Methodology

3.1. Confined-system pyrolysis

Three coal samples from Donets (2 coals) and Sabinas (1 coal) basins were selected for the experimental artificial maturation. The starting materials are vitrinite-rich coals with a reflectance of 0.92% for Sabinas coal and 0.55–0.65% for Donets coals. Artificial maturation was performed by confined-system pyrolysis on unextracted coals. About 1 g of coal powdered and sieved (<250 μm) was placed inside a gold cell (L=5 cm, i.d.=1 cm). The loaded gold tubes were evacuated and purged with Ar twice over to minimize the pre-exiting gas, and were then welded under an Ar atmosphere. The sealed gold cells were placed into the high-pressure autoclaves and isothermally heated at 330, 360 and 400 °C for different periods of times (1, 5 and 30 days) and under an external hydrostatic pressure of 700 bars. Temperature was controlled by an internal thermocouple in contact with the gold cells (accuracy ±1 °C). After the pyrolysis runs, the gold cells were recovered and carefully cleaned, then pierced and kept at ambient temperature for 2 h to measure the weight loss.

3.2. Geochemical analysis of organic effluents

The raw and heated samples were extracted using a Dionex ASE 200 instrument (Dionex, CA, USA) at 100 °C with dichloromethane as solvent following the conditions: 5-min heat up time, 8-min static time, 60% flush, 200 s purge with nitrogen and pressure 130 bars. About 1 g of powdered sample (sieve <250 μm) was placed inside an 11 ml stainless steel extraction cell for each raw coal. Heated coals were also powdered (sieve <250 μm) before solvent extraction. Coals have the ability to trap the bitumen generated during the natural coalification (Littke and Leythaeuser, 1993). On the other hand, in confined-system pyrolysis the coal network and pore structures are altered by high temperatures, facilitating the solvent extraction of generated bitumen (Monthioux and Landais, 1987). Monthioux (1988) recommended extracting several times natural coals grounded to compare natural and artificial series. Two coals, Olmos and 2c10YD, were extracted four times. Each organic extract was recovered in a vial, concentrated by evaporation under nitrogen using Turbo Vap 500 and then weighted to calculate the cumulative extract yield. The trends observed in Fig. 1 reveal that bitumen remains trapped even if the coals are extracted four times. However, a major part of extractable organic material seems to be recovered after two successive extractions by using a Dionex ASE 200 with dichloromethane as solvent. 111Dim was extracted two times and the heated samples one time according to the analytical procedure described above.

The extractable fractions were deasphaltened with *n*-heptane. The maltene fractions were then fractionated into saturated and aromatic hydrocarbons, and resins by means of liquid chromatography on alumina and silica columns. These fractions were gently dried under nitrogen and then weighted.

Saturated and aromatic hydrocarbons were analyzed by gas chromatography-mass spectrometry. The gas chromatograph was a Hewlett-Packard 5890 Series II

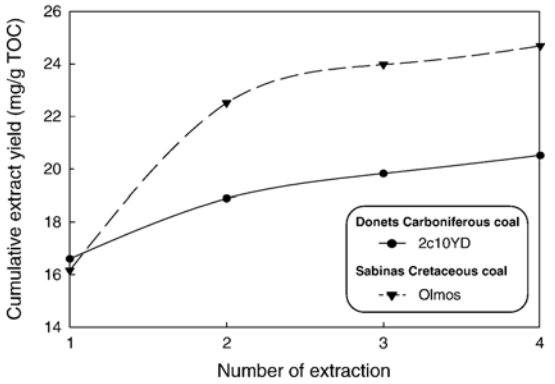

Fig. 1. Cumulative extract yield in mg/g TOC as a functifon of the number of extraction for the unheated coals: 2c10YD and Olmos from Donets and Sabinas Basins, respectively.

instrument equipped with a split/splitless injector (used in the splitless mode) heated at 300 °C and a J & W DB-5 capillary column (60 m × 0.25 mm i.d. × 0.1 μm film thickness). The oven temperature was programmed as follows: 70–130 °C at 15 °C/min, then at 3 °C/min to 315 °C and held at that temperature for 10 min. Helium was used as the carrier gas at a constant flow of 1 ml/min. The detector was a HP 5971 mass selective detector with an ionizing voltage of 70 eV. It was operated first in full scan mode and alternatively in multiple ion monitoring mode for the detection of biomarkers.

3.3. Petrographic and geochemical analysis of kerogen

Aliquots of unheated and heated coals were prepared for petrographic analysis. Maceral and porosity analysis, and mean random vitrinite reflectance measurements were carried out with a MPV-Combi Leitz microscope. On both unheated and heated coals. The new maceral classifications for the vitrinite macerals (ICCP, 1998) and the inertinite group (ICCP, 2001) were used in this study. In addition, solid bitumen in the coals was also counted following a similar procedure as for maceral analysis, and its reflectivity was measured.

Raw and heated coals were analyzed using a Vinci Rock-Eval 6 instrument at ISTO (Orléans, France) to determine total organic carbon (TOC), T_{max} (°C) and petroleum potential HI (mg HC/g TOC). The C, H, and O contents were determined by using a CHNS-932 Leco microanalyzer.

Flash pyrolysis of extracted raw coals was performed with a CDS 2000 pyroprobe. Samples were loaded into quartz tubes and heated at 620 °C for 15 s. The characteristics of the GC were the same as described above. After cryofocusing, the GC oven was temperature programmed from 40 to 300 °C at 5 °C/min. As the products eluted from the GC column, they were analyzed by MS using a HP 5972 spectrometer.

4. Results and discussion

4.1. Starting materials

Table 1 shows that the three starting coals have a high volatile bituminous rank with maturation levels increasing in the order 2c10YD < 111Dim < Olmos. Vitrinite reflectance measurements indicate that the starting coal from Sabinas basin (%R_r = 0.92) has reached the peak of oil generation during the natural coalification whereas the two Donets coals fall into the onset of the 'oil window' (Petersen, 2002). The maceral composition changes with the maturity level of coal. The low liptinite content of Sabinas coal compared to Donets coals can be accounted by its higher rank (Table 1). With higher liptinite contents (6–20% of the total volume), Carboniferous Donets coals are expected to have better capabilities for generating liquid hydrocarbons compared to Olmos.

Elemental data and vitrinite reflectance are coincidental in assessing of ranks since both indicate that all samples are high volatile bituminous coals (Alpern and Lemos de Sousa, 2002). Moreover, the order of maturation based on elemental analysis is similar to that given by reflectance vitrinite measurements i.e. Olmos > 111Dim > 2c10YD. The two Carboniferous coals from Donets Basin have higher atomic H/C ratios, which is consistent with their higher liptinite contents. Vitrinite is by far the most abundant of macerals in coals (more than 59% of the total volume). Its hydrogen content may be assumed to be similar to that of the whole coal. A previous study showed that vitrodetrinite and desmocollinite are the dominating vitrinite macerals, and that sporinite and liptodetrinite are the most abundant liptinite macerals in the two Carboniferous Donets coals analyzed in this study (Sachsenhofer et al., 2003).

Table 1
Geochemical and petrographic characterizations for two Carboniferous coals from Donets Basin (1l1 Dim & 2c10YD) and one Cretaceous coal from Sabinas Basin (Olmos)

Basin	Sabinas	Donets	
Coal mines	Mimosa	Dimitrova	Yuzhno–Donbasskaya #1
Samples	Olmos	1l1 Dim	2c10 YD
Rock-Eval parameters			
TOC (wt.%)	66	82	84
T_{max} (°C)	454	438	430
HI (mg HC/g TOC)	167	256	275
OI (mg CO_2/g TOC)	3	4	5
Elemental analysis			
% C	67.42	80.4	67.42
% O	6.50	7.88	9.57
% H	4.33	5.29	4.33
H/C at.	0.77	0.79	0.80
O/C at.	0.07	0.07	0.09
Petrographic analysis			
Vitrinite (vol.%)	84	80	59
Inertinite (vol.%)	8	7	12
Liptinite (vol.%)	0	6	20
Porosity (vol.%)	6	4	5
Pyrobitumen I (vol.%)	1	2	3
Pyrobitumen II (vol.%)	1	1	1.5
Vitrinite reflectance (%)	0.92	0.65	0.55

Reviewing the hydrogen indices (HI, mg HC/g TOC), the Carboniferous Donets coals have better abilities to yield liquid hydrocarbons than the Cretaceous Sabinas coal (Table 1). The hydrogen index is more important for 2c10YD than for 111Dim, indicating that the former has a better generative potential. Rock-Eval T_{max} values also show that the Sabinas coal is more mature than the Donets coals. With a T_{max} of 460 °C, the Cretaceous Sabinas coal has already generated massive amounts of bitumen during the natural coalification, in agreement with the vitrinite reflectance value (Espitalié et al., 1985). On the other hand, T_{max} values of Carboniferous Donets coals indicate that their oil generative capacity is intact.

Pyrolysis-gas chromatography analyses show that the pyrolysates of the Sabinas and Donets coals have low aliphatic and high aromatic contents (Fig. 2). However, the abundance of aliphatic groups relative to aromatic is higher for Carboniferous Donets coals than for Cretaceous Sabinas coal. The pyrolysis-GC chromatograms of Carboniferous Donets coals show long-chain aliphatic groups ($>n$-C_8), thus providing additional evidence of their capability of generating non-volatile oils (Fig. 2).

4.2. Optic microscopy examination of unextracted solid residues

4.2.1. Vitrinite reflectance and macerals composition

Table 2 shows that the reflectance of vitrinite increases during thermal maturation in confined-system pyrolysis. The maturity ranged from high volatile bituminous coal to semi-anthracite, which corresponds to changes from early mature oil stage to main zone of gas generation. Table 2 also reveals that the modifications in the structure of artificially heated kerogen depend on both time and temperature. The increase in vitrinite reflectance is more pronounced for the sample 2c10YD, especially for 30 days of experiments.

Thermal stability of maceral groups have been studied both on natural and artificial series. In natural series the degradation of vitrinite takes place earlier compare to liptinite macerals (Price and Barker, 1985; Cook and Struckmeyer, 1986; Murchison, 1987; Han et al., 1993). Landais et al. (1991) showed that the peak of generation occurs later (at ~375 °C) for exinite (liptinite) during confined pyrolysis of individual macerals separated of Carboniferous coal (Lorraine Basin, France). However, the vitrinite is present whereas the proportion of liptinite is often very low or nil at medium volatile bituminous rank corresponding to vitrinite reflectance of 1.1–1.4% in a suite of coals (Alpern and Lemos de Sousa, 2002; Izart et al., 2006). As an example, the liptinite is absent in Donets Basin coals having vitrinite reflectance values higher than 1.0% (Sachsenhofer et al., 2003). Kinetic models show that vitrinite has a broader range of activation energies than liptinite, explaining the presence of the former at high temperatures.

Our simulation on whole coals indicates that the liptinite content is exhausted at 330 °C for 1 day, a time-temperature condition for which the R_r values are higher than 1.0% (Table 3). Comparing to the raw sample, the vitrinite content in 111Dim significantly decreases from the beginning of heating treatment (i.e. 330 °C/1 day or 330 °C/5 days) and then does not show any significant evolution with further thermal maturation (Table 3). Changes in vitrinite content for 2c10YD are comparable to those observed for 111Dim. The drop is however much less pronounced at 330 °C for the former because the original material is poorer in vitrinite. On the other hand, the rate of evolution of vitrinite content is lower for Sabinas Cretaceous coal, likely due to differences in the structural chemistry and macerals composition of vitrinite relative to Carboniferous Donets Basin coals. The degradation of inertinite occurs later, consistent with its highly condensed structure (Sun et al., 2003). Variations in the macerals composition, and especially decreasing in the vitrinite content, are associated with changes in the porosity of the matrix and solid bitumen content during artificial maturation as evidenced below.

4.2.2. Solid bitumen occurrence and alteration

In source rocks having reached high levels of maturation, all macerals of the liptinites group become increasingly difficult to observe because their original structure is modified during the significant loss of mass accompanying the generation of bitumen. The generated bitumen is trapped in the fine porosity of coals. If any expulsion occurs, it is then converted to gas and solid bitumen under increasing thermal stress. The occurrence of solid bitumen finely dispersed in the rock has been noted in natural series (Behar et al., 1991; Huc et al., 2000) and in a deep sample from the Møre Basin at maturities as high as 1.3%R_r (Erdmann, 1999).

In a confined-system pyrolysis, the bitumen is not removed from the environment of generation, and its subsequent degradation with increasing temperature is accompanied by the production of solid bitumen and gas (Behar et al., 1992; Hill et al., 2003). Schlepp et al. (2001) showed that the production of solid bitumen starts at 330 °C for 72 h and then increases up to a maximum value with temperature. The formation of solid macromolecular material likely results of recombination reactions of first formed high molecular weight compounds during artificial maturation in closed system (Erdmann and Horsfield, 2006). Behar et al. (1992)

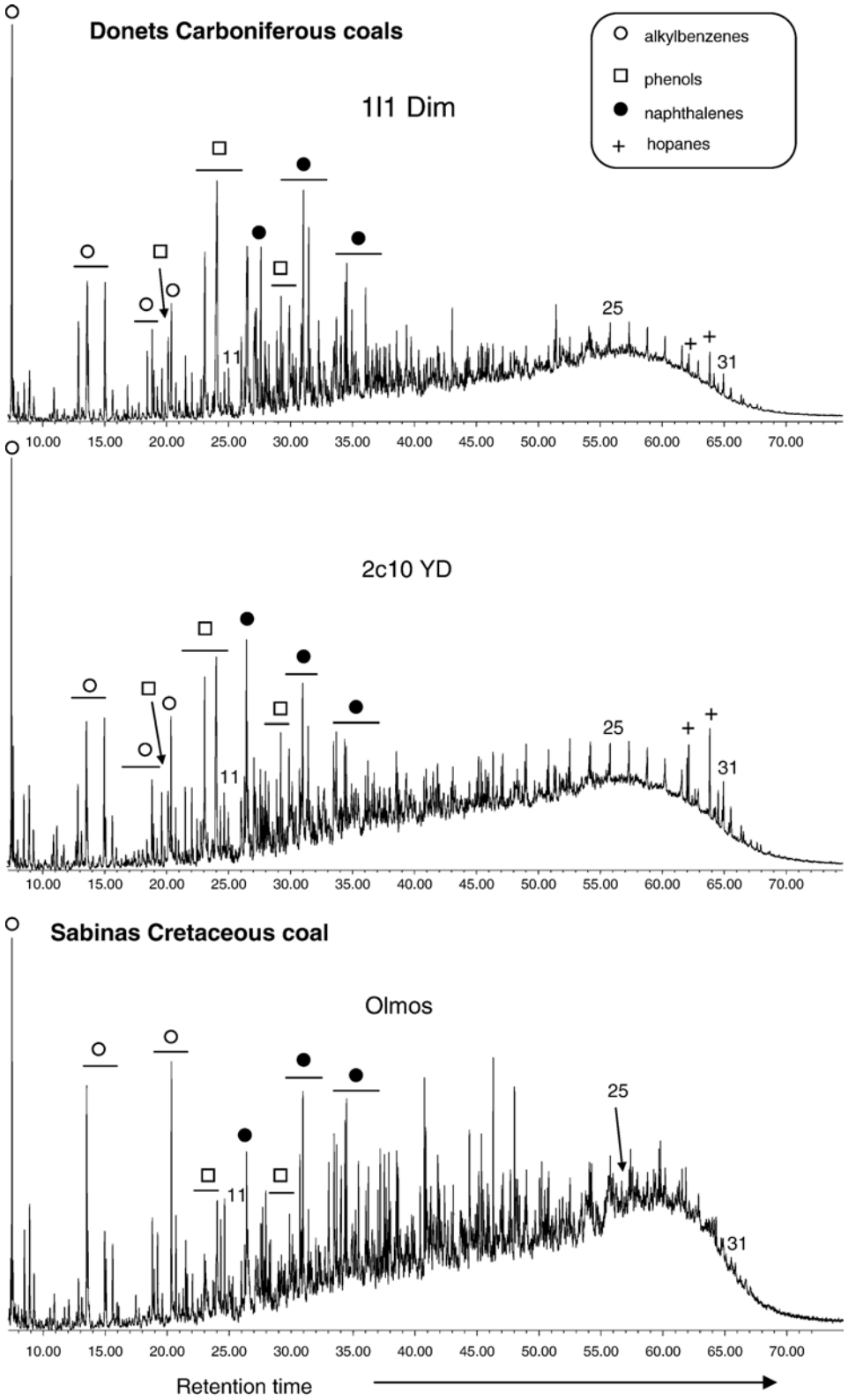

Fig. 2. Pyrolysis-GC chromatograms of unheated Carboniferous (1l1 Dim & 2c10YD) and Cretaceous (Olmos) coals from Donets and Sabinas Basins, respectively. The numbers refer to the chain length of aliphatic groups.

Table 2
Evolution of vitrinite reflectance values for the two Carboniferous coals from Donets Basin (1l1 Dim & 2c10YD) and the Cretaceous coal from Sabinas Basin (Olmos) with time/temperature conditions during artificial maturation in confined medium

T (°C)	Time (day)	Olmos	1l1 Dim	2c10 YD
		%R_r		
330	1	1.05	1.07	1.09
360	1	1.37	1.56	1.65
400	1	2.13	2.11	2.16
330	5	1.20	1.44	1.49
360	5	1.87	1.94	2.07
400	5	2.24	2.30	2.23
330	30	1.59	1.90	1.98
360	30	2.27	2.28	2.51
400	30	2.65	2.57	2.78

showed that the amount of solid bitumen formed during artificial maturation in closed-systems is lower for type III kerogen than for type II kerogen.

Fig. 3 shows two groups of solid bitumen (they are distinct by their reflectance and their morphology), which likely correspond to distinct phases of occurrence. The first generated solid bitumens (group I) display the highest reflectance values (>2.8%). They are degraded with increasing maturity, for producing not only gas but also more mature solid bitumens (group II) whose reflectance values range between 1.8 and 2.5%. The proportions of solid bitumen groups (I and II) are shown in Table 3 and Fig. 4. Solid residues in Sabinas and Donets coals are richer in group I than in group II. The amounts of both solid bitumens I and II are very low at the ultimate maturity stages.

In addition, the content of first generated solid bitumens (group I) shows two peaks during thermal maturation in confined system, especially in the case of Donets Carboniferous coals (Fig. 4). The first occurs at maturity levels ranging between 1.0 and 1.5%R_r whereas the second is observed around 2.0%R_r. It is probable that the mechanisms involved in the generation of first solid bitumens are different during confined pyrolysis of Donets coals (Figs. 3B and 4). The thermal cracking of recombination residues is postulated to occur at vitrinite reflectance higher than 2.0% (Erdmann and Horsfield, 2006). The relative abundance of solid bitumens drops with increasing maturity levels, suggesting that they crack to contribute to the generation of gaseous hydrocarbons (Erdmann and Horsfield, 2006). Their shape progressively becomes more irregular and porous with increasing temperatures (Fig. 3).

The petrological examination also indicates that the amount of solid bitumen formed during confined pyrolysis strongly depends on the liptinite content and maturity level of starting coals (Fig. 4, Table 1). The solid bitumen is a thermal degradation product of bitumen yielded by H-rich

Table 3
Trends in the vitrinite, inertinite, liptinite, solid bitumen and porosity contents (vol.%), and in the vitrinite reflectance (%) for the Carboniferous coals from Donets Basin (1l1 Dim & 2c10YD) and the Cretaceous coal from Sabinas Basin (Olmos) with time/temperature conditions during artificial maturation in confined medium

Basin	Sample	Temperature	Time	Solid bitumen I	Solid bitumen II	Vitrinite	Inertinite	Liptinite	Porosity	SUM	R_r
		(°C)	(day)	(vol.%)							(%)
Sabinas	Olmos	330	1	2	6.4	75.6	7.2	0	8.8	100	1.05
		330	5	1.6	6	69.6	5.6	0	17.2	100	1.20
		360	1	1.2	5.2	58.8	5.2	0	29.6	100	1.37
		400	1	0.8	3.6	59.6	5.2	0	30.8	100	2.13
		400	5	0.4	2	56.8	5.6	0	35.2	100	2.24
		360	30	0.4	1.6	59.6	5.2	0	33.2	100	2.27
Donets	1l1Dim	330	1	2.4	9.6	58	6.4	2.8	20.8	100	1.07
		330	5	3.6	10.8	54.4	7.6	0	23.6	100	1.44
		360	1	2.4	7.6	54	7.2	0	28.8	100	1.56
		360	5	1.2	3.6	59.2	4.4	0	31.6	100	1.94
		400	1	0.8	5.6	55.2	4.8	0	33.6	100	2.11
		360	30	0.4	2	56	4	0	37.6	100	2.28
		400	5	0	3.2	56.8	5.6	0	34.4	100	2.30
	2c10YD	330	1	4	8.4	48.4	6.8	4	28.4	100	1.09
		360	1	1.2	3.6	51.2	10	0	34	100	1.65
		360	5	0.4	2.4	52.8	6.8	0	37.6	100	2.07
		400	5	0.8	2.8	49.4	4.6	0	42.4	100	2.23
		360	30	0	1.2	49.6	3.6	0	45.6	100	2.51

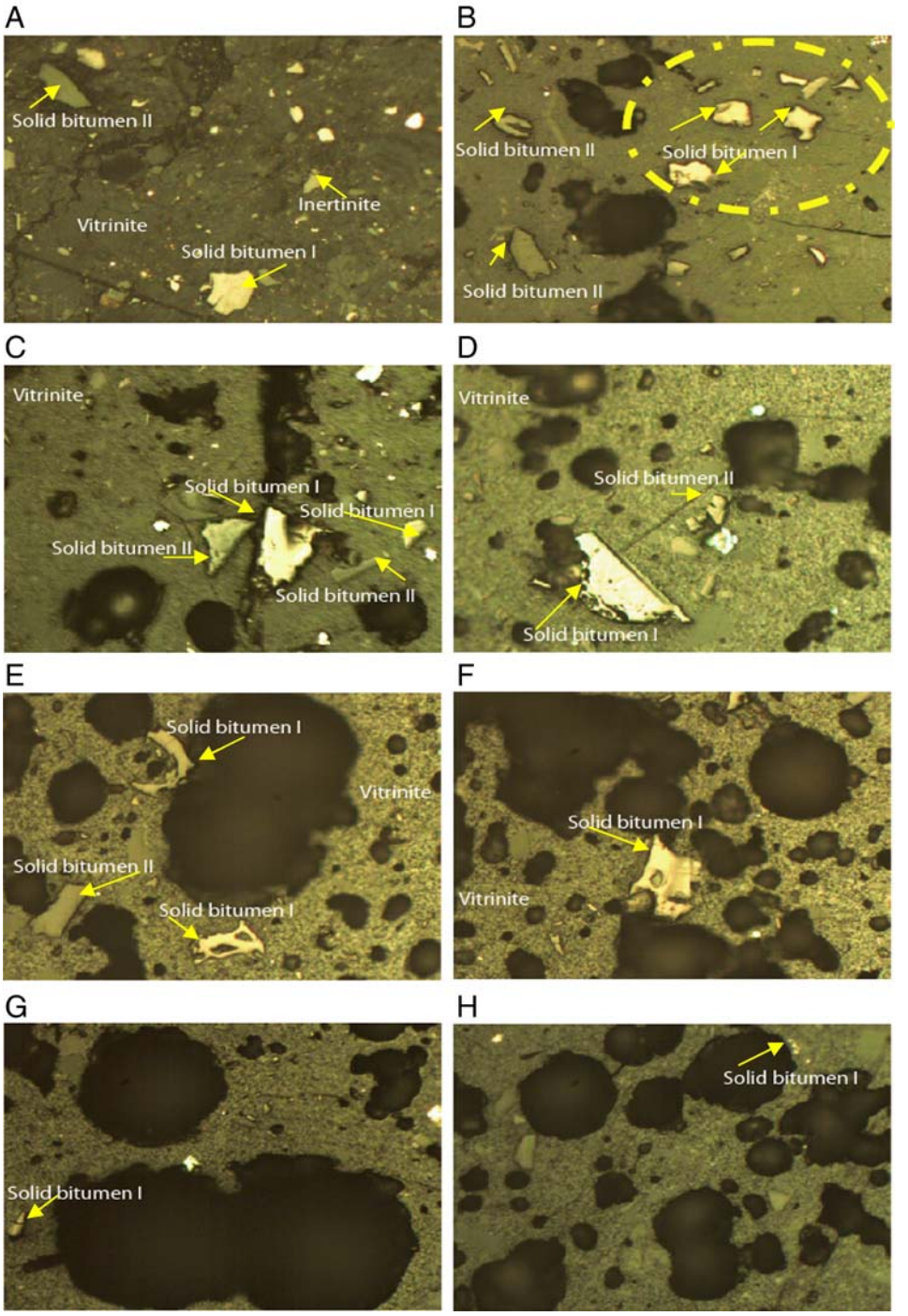

Fig. 3. Maceral analysis of 111Dim from Donets Basin unheated and artificially maturated in confined pyrolysis. A) Raw coal (R_r=0.65%), B) 330 °C for 1 day (R_r=1.07%), C) 330 °C for 5 days (R_r=1.44%), D) 360 °C for 1 day (R_r=1.56%), E) 360 °C for 5 day (R_r=1.94%), F) 400 °C for 1 day (R_r=2.11%), G) 360 °C for 30 days (R_r=2.28%), and H) 400 °C for 5 days (R_r=2.30%). (R_r: random reflectance, picture width of 130 mm along the long axis).

macerals (mainly liptinites) during the bituminous stage (at the lower limit of the oil window with a vitrinite reflectance of about 0.5–0.6%). This corresponds to the first coalification jump in the liptinites and vitrinites, initiating the liptinite transformation with oil generation (Stach et al., 1982; Taylor et al., 1998). As expected, the amounts of

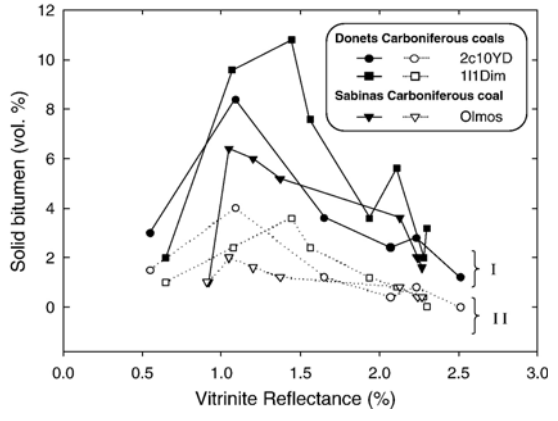

Fig. 4. Evolution of pyrobitumen contents (vol.%) during thermal maturation in confined medium for two Carboniferous coals (1l1 Dim & 2c10YD) from Donets Basin and one Cretaceous coal from Sabinas Basin (Olmos).

solid bitumen are higher in liptinite-rich Donets coals than in Sabinas coal (Table 3, Figs. 3 and 4).

4.2.3. Porosity evolution

Fig. 5 shows the evolution of the porosity *vs.* R_r values in raw samples and solid residues after pyrolysis for Sabinas and Donets coals. The porosity increases from bituminous to anthracite stages. Its increase is slow with respect to that of starting material at the first stages of pyrolysis (330–360 °C) on account of the generation of both gas and liquid hydrocarbons. At the ultimate stage of thermal maturation (400 °C), the rapid increase of R_r and the development of a highly porous structure in the kerogen are the most significant features. In this study, the porosity reaches a maximum for the 360 °C–30 days pair, where the pores are completely round and often stuck together (Fig. 5). A massive production of gas is expected to occur due to secondary cracking of hydrocarbons and primary cracking of kerogen itself at this maturity level (Behar et al., 1995). It is important to keep in mind that the pore size is smaller in Sabinas coal than in Donets coal samples (Fig. 5).

The optical microscopy observations also show major changes in textural and microtextural properties associated with the corresponding structural modifications undergone by the coal samples during thermal stress. At the last stages of pyrolysis (i.e. 400 °C), the vitrinite matrix develops a texture of fine mosaic, which can be explained by the cracking of bitumen occupying the microporosity. One can observe that the development of the significant network of large vacuoles in the kerogen coincides with the increase of the pore volume.

4.3. Rock-Eval pyrolysis of extracted solid residues

In the plot $\%R_r$ *vs.* T_{max} in Fig. 6, the shaded zone shows the natural trend as proposed by Espitalié et al. (1985). Fig. 6 reveals that the T_{max} values increase linearly with increasing vitrinite reflectance for Donets and Sabinas coals (Teichmüller and Durand, 1983; Espitalié et al., 1985). Fig. 6 also shows that the artificial maturation paths of our three coal samples point out similar trends to the natural evolution of the type III kerogen reported by Espitalié et al. (1985).

Fig. 7 shows the variations of HI (mg HC/g TOC) *vs.* T_{max} for the three coals. The horizontal dashed lines represent the three-fold classification of kerogen according to Peters et al. (2005): (i) oil prone (HI>300 mg HC/g TOC) (ii) gas and oil prone (HI of 200–300 mg HC/g TOC), and (iii) gas prone (HI of 50–200 mg HC/g TOC). Samples from Donets basins can be classified as oil- and gas-prone coals and the Sabinas

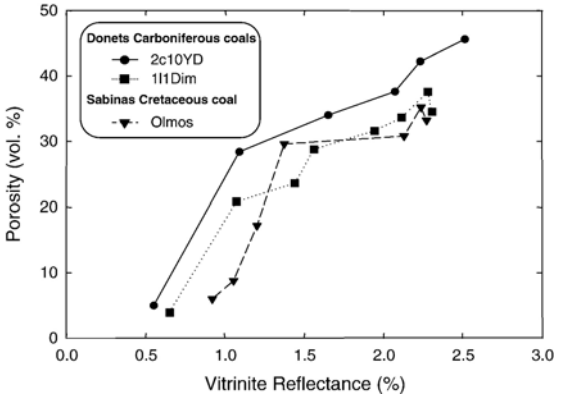

Fig. 5. Evolution of the porosity (vol.%) during artificial maturation in confined pyrolysis for two Carboniferous coals from Donets Basin (1l1 Dim & 2c10YD) and one Cretaceous coal from Sabinas Basin (Olmos).

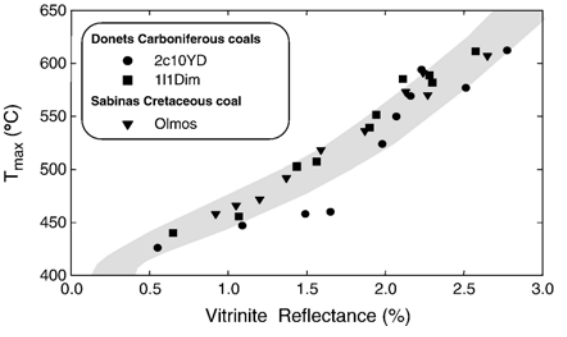

Fig. 6. Vitrinite reflectance (%) *vs.* T_{max} (°C) for the two Carboniferous coals (1l1 Dim & 2c10YD) from Donets Basin and the Cretaceous coal (Olmos) from Sabinas Basin during artificial maturation confined pyrolysis. Shaded field represents the natural coalification pathway as reported by Espitalié et al. (1985).

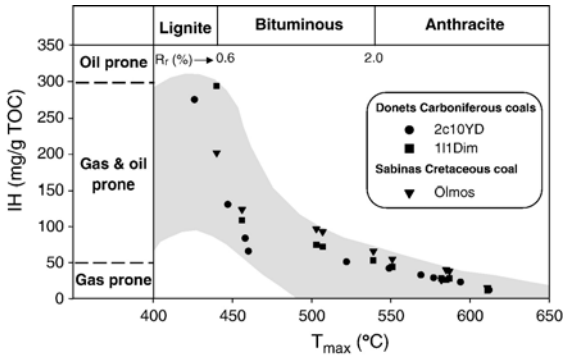

Fig. 7. Hydrogen index (HI, mg HC/g TOC) *vs.* T_{max} (°C) for the two Carboniferous coals (1l1 Dim & 2c10YD) from Donets Basin and the Cretaceous coal (Olmos) from Sabinas Basin during artificial maturation confined pyrolysis. Shaded field represents the natural coalification pathway as reported by Espitalié et al. (1985).

sample as a gas-prone coal. Donets coals lost a massive part of their initial petroleum potentialities from the beginning of experimental maturation. Sabinas coal differs mainly by a lower decrease in its hydrogen index. A clear correlation between HI and T_{max} can be observed for the three coals despite a large variability of their maceral composition. The plot HI *vs.* T_{max} shows that the artificial maturation pathways of three coals are inside the envelope of natural coalification of type III kerogen (Espitalié et al., 1985).

4.4. Solvent-extractable organic matter

4.4.1. Yields and compositions

The organic extract yields show typical trends to those observed during artificial maturation of coals: an increase up to a maximum value followed by a decline (Fig. 8). The 'oil window' occurs between R_r ~1.0% and ~2.0% for both Cretaceous Sabinas and Carboniferous Donets coals (Fig. 8). As expected from maceral analysis, the liptinite-rich Donets coals yields more organic extract than Cretaceous Sabinas coal during the heating treatment (Fig. 8). However, the liptinite content cannot explain all. Indeed, although containing less liptinite, 1l1Dim generates more extractable organic material than 2c10YD (216 mg/g TOC compared to 189 mg/g TOC) at R_r ~1.6. As a comparison, the sample no. 32362 (Monthioux et al., 1985) from Tertiary Mahakam coals (Indonesia) that have been associated with oilfields (Burrus et al., 1992; Peters et al., 2000), yielded 233 mg of organic extract per gram TOC when it was artificially heated and extracted by using a Dionex ASE 200 extractor (Li et al., 2002). Although its liptinite content is nil, the Cretaceous Sabinas coal also yields organic extract during artificial maturation. Thus, these results indicate that, in addition to liptinite, vitrinite can play a role in the generation of bitumen during confined pyrolysis of the whole coal. The most important point is that the two Carboniferous Donets coals (1l1 Dim and 2c10YD) analyzed in this study can be considered as sources for oil.

Table 4 shows that the chemical composition of bitumen recovered from raw coals is dominated by resins and asphaltenes (more than 70 wt.%). Their proportion progressively decreases whereas that of hydrocarbons increases with increasing temperature. Despite the absence of liptinite, the Cretaceous Sabinas coal also generates hydrocarbons during thermal maturation. As expected from elemental and Rock-Eval analyses, the Carboniferous Donets coals yield more hydrocarbons than the Cretaceous Sabinas coals.

4.4.2. Saturated hydrocarbons

For the most immature coals, the GC-MS fingerprints of saturated hydrocarbons are dominated by high molecular weight *n*-alkanes that typify terrestrial inputs. A typical evolution of *n*-alkanes distribution during thermal maturation in a closed pyrolysis system is exemplified by sample 2c10YD for one day heating experiment (Fig. 9). It shows that it is progressively shifted toward low molecular compounds with increasing temperature. Kinetic studies indicate that *n*-alkanes derived mainly from thermal cracking of kerogen in a temperatures range corresponding to the zone of bitumen production; the heavy compounds being generated much faster than low molecular weight *n*-alkanes from type III kerogen (Behar et al., 1997b). However, in our case, heating experiments at temperatures below 330 °C are needed to better evaluate the contribution of kerogen in the *n*-alkanes

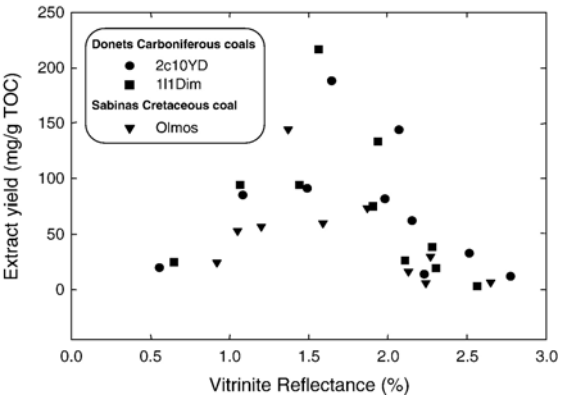

Fig. 8. Evolution of extractable organic material yields (mg/g TOC) *vs.* vitrinite reflectance (%) for the Cretaceous coal (Olmos) from Sabinas Basin and the Carboniferous coals (2c10YD and 1l1Dim) from Donets Basin during confined pyrolysis.

Table 4
Evolution of (i) the yields of aliphatics, aromatics and polars, (ii) molecular parameters C_{17-19}/total (A), C_{20-24}/total (B), C_{25-34}/total (C), Pr/C_{18} and Pr/Ph calculated from the *n*-alkanes distribution (*m/z* 57), and (iii) MPI-1 values calculated from the phenanthrenes distribution (*m/z* 178; 192) for the Carboniferous Donets coals (1l1 Dim & 2c10YD) and the Cretaceous Sabinas coal (Olmos) with time/temperature conditions during thermal maturation in confined medium

Basin	Sample	Temperature	Time	Aliphatics	Aromatics	Polars	C_{17-19}/total (A)	C_{20-24}/total (B)	C_{25-34}/total (C)	Pr/C18	Pr/Ph	MPI-1
		(°C)	(day)	(mg/g TOC)			(%)					
Sabinas	Olmos	Raw		0.6	4.7	19.4						
		330	1	3.8	10.4	41.2	21.79	37.71	40.50	0.55	3.18	1.04
		330	5	5.8	17.1	37.7	25.05	40.51	34.4	0.28	2.73	1.11
		330	30	8.2	21.0	34.1	28.81	41.55	29.6	0.19	1.60	1.23
		360	1	6.1	24.4	113.1	20.01	36.42	34.6	0.14	3.81	1.16
		360	5	9.2	22.6	44.8	31.16	40.95	27.9	0.13	1.62	1.33
		360	30	5.4	9.8	14.0	45.80	40.32	13.87	0.02	n.d.	1.33
		400	1	2.2	7.1	8.3	38.42	41.99	19.58	0.03	0.71	1.53
Donets	1l1Dim	Raw		0.62	3.90	16	20.97	35.11	43.92	0.75	4.75	0.33
		330	1	3.85	31.79	49.7	18.79	39.66	41.55	0.41	3.59	0.42
		330	5	5.83	32.59	52.61	21.31	39.97	38.73	0.23	2.77	0.51
		330	30	8.21	31.47	41.63	24.87	40.73	34.40	0.19	1.54	0.74
		360	1	6.05	39.92	143.22	23.62	39.33	37.06	0.14	3.90	0.55
		360	5	9.21	50.64	84.01	26.54	40.62	32.84	0.17	1.85	0.88
		360	30	5.40	12.79	15.37	43.85	40.89	15.26	n.d.	n.d.	0.99
		400	1	2.17	20.53	39.33	35.24	41.88	22.88	0.04	1.08	0.83
	2c10YD	Raw		0.73	3.81	19.93	n.d.	23.6	66.7	0.9	5.2	0.3
		330	1	3.39	22.70	68.01	17.5	34.6	48.0	0.5	3.7	0.4
		330	5	4.06	29.44	60.76	20.3	37.2	42.6	0.3	2.7	0.5
		330	30	4.41	29.60	40.66	23.4	37.8	38.8	0.3	1.9	0.8
		360	1	10.17	53.22	153.18	23.1	35.1	41.8	0.2	4.5	0.5
		360	5	11.48	43.80	78.25	25.5	39.2	35.2	0.1	3.7	0.8
		360	30	6.75	13.49	17.88	42.6	41.4	16.0	0.0	n.d.	0.9
		400	1	1.04	10.28	15.38	34.9	43.2	21.9	0.0	0.8	0.8

generation. For higher temperatures, there is an overlap between the generation from macromolecular materials and the cracking of formed heavy *n*-alkanes. Fig. 9 suggests that it occurs between 330 and 360 °C for one day of experimentation in confined pyrolysis. At high pressure, as used in this study (700 bars), the thermal decomposition of C_{15+} hydrocarbons occurs in liquid phase. Experimental results show that low molecular weight alkanes are the main products formed during liquid-phase thermal decomposition of hexadecane, eventhough high molecular weight alkanes were also found (Ford, 1986). At an elevated temperature the hydrocarbons-generative potential of kerogen is totally depleted and the cracking of *n*-alkanes becomes the predominant mechanism responsible for a major enrichment in light compounds. This is verified by the *m/z* 57 mass chromatogram at 400 °C for one day heating in Fig. 9.

Changes in the *n*-alkanes fingerprints can be visualized by calculating their relative abundances in the C_{17-19}, C_{20-24} and C_{25-34} ranges. The percentages drastically change at 330 °C for 30 days: the relative abundance of *n*-alkanes in the C_{25-34} range declines whereas that of the C_{17-19} range increases (Table 4). Variations with increasing temperatures are steadier for one and five days. Reviewing the data in Table 4, it is apparent that the displacement of the hydrocarbons distribution toward low molecular weight compounds occurs more intensively for Olmos followed by 1l1Dim and 2c10YD. Maturity indicators can be calculated from the *n*-alkane fingerprints. Amongst them, the Carbon Preference Index [$CPI = 0.5 \times \sum_n C_{2n+1} \times (1/\sum_n C_{2n} + 1/\sum_n C_{2n+2})$ where $n = 12$ to 16] allows us to follow the evolution of the odd predominance of *n*-alkanes in the C_{24-35} range with maturation. CPI in the C_{24-35} hydrocarbons range is high in immature coals, reflecting the contribution of wax-derived *n*-alkanes to the bitumen present at the end of diagenesis. With maturity it steadily decreases for approaching values closed to one within the oil generation window for type III kerogen, indicating a progressive disappearance of the odd predominance. Calculations carried out for the three starting coals reveal that the *n*-alkanes have almost lost their odd predominance during the natural coalification (CPI < 1.3), thus CPI has a limited applicability in this study. The relative abundance of pristane (Pr) to phytane (Ph), two isoprenoids having several organic precursors (Blumer et al., 1963; Goossens

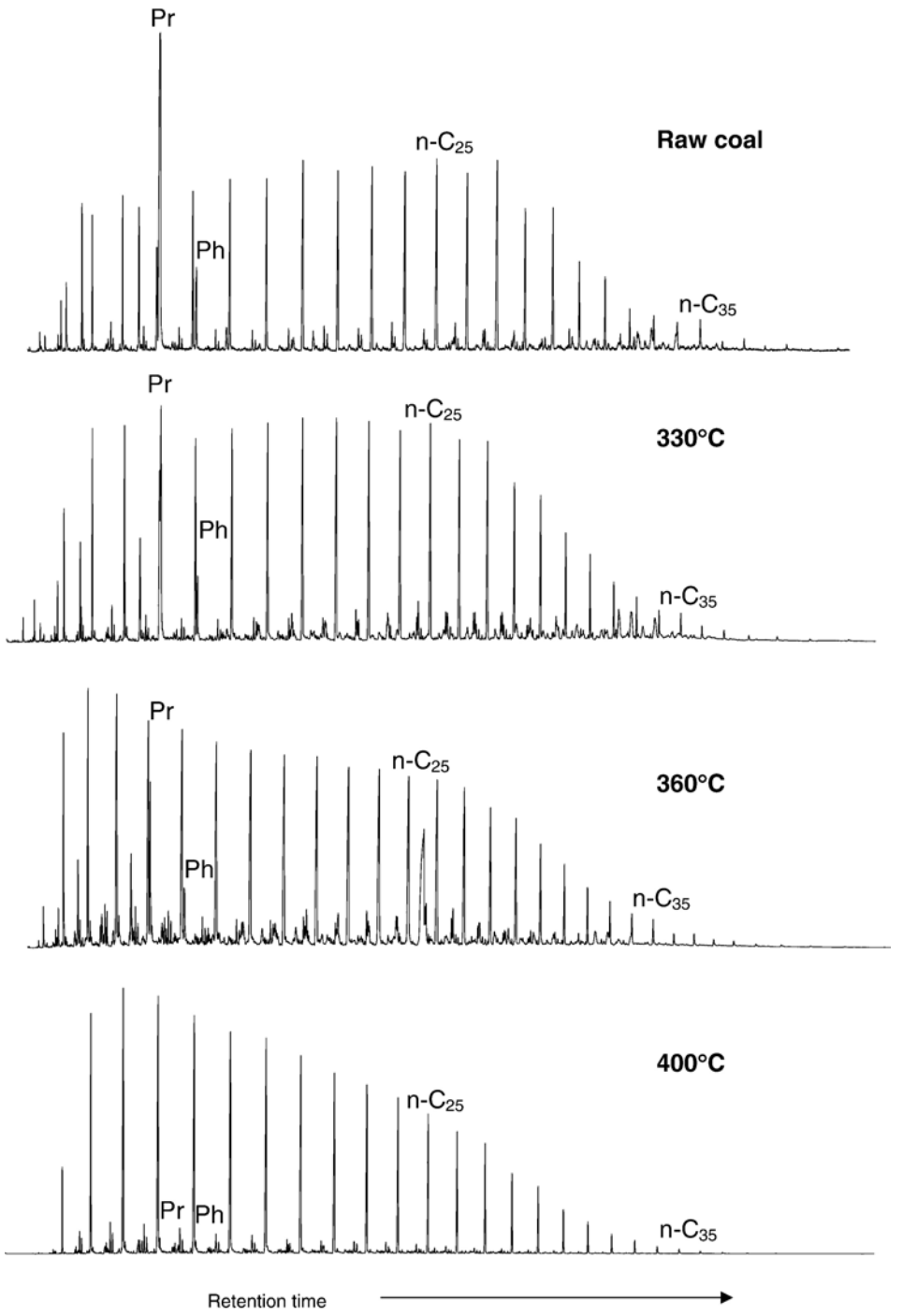

Fig. 9. Changes in the *n*-alkanes distribution (*m/z* 57) for the Carboniferous coal (2c10YD) from Donets Basin with temperature for 1 day during confined pyrolysis.

et al., 1984; Rowland, 1990; Navale, 1994), is also commonly used as maturity parameter. It has been demonstrated that the Pr/Ph ratio first increases up to around 300–350 °C, but then decreases at higher levels of maturity during confined pyrolysis of a lignite from Mahakam delta (Monthioux and Landais, 1989a; Piedad-Sánchez et al., 2005). Koopmans et al. (1999) experimentally demonstrated that the rising results from higher

amounts of precursors for Pr compared to Ph rather than different timings of generation. Radke et al. (1980) interpreted the drop as a result of a major change in involved reaction types i.e. a shift from predominantly generation to predominantly degradation reactions as the coal rank increases. Table 4 shows that the Sabinas coal is more mature than Donets coals, consistent with the vitrinite reflectance values and Rock-Eval parameters. The Pr/Ph ratios drop in the artificially maturated coals compared to starting materials, probably due to a preferential degradation of pristane relative to phytane at the time-temperature pairs selected in this study (Radke et al., 1980). The Pr/Ph ratio remains lower for Sabinas coal than Donets coals at 330 °C — 1 day. On the other hand, no significant difference can be noticed at higher temperatures and experiment duration between the three coals. No differences are also observed regarding trends and values of Ph/C_{18} ratios with the time-temperature conditions (Table 4).

4.4.3. Aromatic hydrocarbons

Phenanthrene (P) and methyl-phenanthrenes (1, 2, 3 and 9-MP) were identified (*m/z* 178 and 192, respectively) from aromatic hydrocarbons then integrated to calculate the MPI-1 (MPI-1 = 1.5 × (2-MP + 3-MP)/(P + 1-MP + 9-MP). The development of this index was based on the assumption that the stables isomers (2 and 3 methyl-phenanthrenes) are derived not only from 1 and 9-methyl-phenanthrenes by rearrangement, but also phenanthrene through methylation reactions. The MPI-1 increases then declines from vitrinite reflectance of 1.3% in a suite of coals (Radke et al., 1986). However, the vitrinite reflectance value at which the reversal is observed depends on the heating rate. Studying igneous intrusions, Raymond and Murchison (1992) showed that the applicability of MPI-1 can be extended up to vitrinite reflectance of ~2.00% for rapidly heated coals. The calculated MPI-1 values confirm the higher rank of original Sabinas coal compared to Donets coals. MPI-1 displays a relatively strong correlation with vitrinite reflectance during thermal stress in confined pyrolysis for all the studied coals up to the reversal. It is attained at vitrinite reflectance approximately 0.5% lower for the Sabinas coal (Fig. 10). Our result reveals that the applicability of MPI-1 can be extended up to 2.5% for Carboniferous coals heated in confined system. The reversed trend in MPI-1 may be interpreted as a result of change in the predominating reactions from methylation and rearrangement to demethylation (Radke et al., 1982). The shift toward higher values of vitrinite reflectance for Donets coals is probably due to difference in the chemical composition and macromolecular structure because the coal-forming plants changed significantly from Carboniferous to Cretaceous. This difference in the chemical composition of coals may explain why the MPI-1 values are always lower for the Carboniferous Donets coals and never exceed 1.5, even at the ultimate stage of thermal stress in confined medium. As a comparison, Piedad-Sánchez et al. (2005) obtained a maximum MPI-1 value of 1.2 during confined pyrolysis of the Carboniferous Asturian coal.

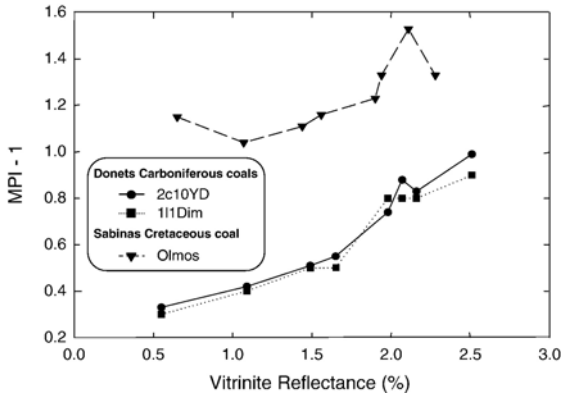

Fig. 10. Evolution of the MPI-1 *vs.* vitrinite reflectance (%R_r) for the Cretaceous coal (Olmos) from Sabinas Basin and the two Carboniferous coals (2c10YD and 1l1Dim) from Donets Basin during confined pyrolysis.

4.5. Weight loss

Gas yield is one of the most important parameters monitored during the artificial maturation experiments conducted on coals. These gases include methane and other light hydrocarbons, as well as CO_2 and H_2O. Gaseous hydrocarbons originate from cracking of kerogen, liquid organic effluents and solid bitumen in the reacting medium during heating experiments in a closed system (Erdmann and Horsfield, 2006). The thermal cracking of type III kerogen is mainly responsible for a massive production of gaseous hydrocarbons. Methane is mainly generated at high temperatures due to desalkylation reactions of coals during confined pyrolysis (Behar et al., 1995). A detailed analysis of the gas phase in our samples is in progress. Below we describe results for bulk gas evolution in Donets and Sabinas coals.

A common trend in the gas yields is observed for the three coal samples i.e. a steadily increase with increasing maturity (Fig. 11). However, the Donets coals generated significantly more gas than the Sabinas coal with increasing maturity. As a consequence, the matrix of Carboniferous Donets kerogens is more intensively affected by high temperatures than that of Cretaceous

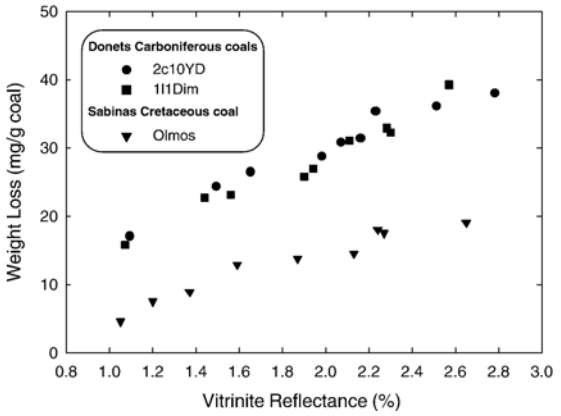

Fig. 11. Gas weight loss (mg/g of coal) *vs.* vitrinite reflectance (%R_r) for the Cretaceous coal (Olmos) from Sabinas Basin and the two Carboniferous coals (2c10YD and 1l1Dim) from Donets Basin during confined pyrolysis.

Sabinas kerogen (Fig. 5). Compared to the matrix kerogen, the bitumen contributes at a much less extent to the gas generation during thermal maturation of type III kerogen in a closed pyrolysis system. However, it is transformed in solid bitumen which degrades to give gas at very high temperatures (Erdmann and Horsfield, 2006). The more gas-prone nature of Donets during thermal maturation in confined pyrolysis, compared to Sabinas coal, may be explained by the more intense alteration of matrix kerogen combined with the higher generation of organic extract and solid bitumen in the former. This is consistent with field data (Triplett et al., 2000; Eguiluz de Antuñano, 2001).

5. Conclusion

General characterization of starting coals based on both optical microscopy and Rock-Eval pyrolysis has revealed that the Sabinas coal lies around the peak of oil generation while the Donets coals fall at the beginning of 'oil window'. Sabinas coal has a low petroleum potential and is depleted in liptinite. Contrary, elemental analysis shows that the Carboniferous coals from Donets Basin are hydrogen-rich coals containing 6–20 vol.% of liptinite with hydrogen indices higher than 250 mg HC/g TOC. Pyrolysis-GC chromatograms evidence that the two Carboniferous coals from Donets Basin selected in this study can generate non-volatile oils under further maturation.

The confined-system pyrolysis was used to estimate the generative potential for oil of Cretaceous coal (Olmos) from Sabinas Basin and Carboniferous coals (1l1 Dim & 2c10YD) from Donets Basin. Petrographic analyses evidence that the coals range from high volatile bituminous rank to semi-anthracite or anthracite (% R_r=2.5–3) with increasing temperature during confined pyrolysis. As in geological medium, liptinite is completely exhausted at a maturity stage corresponding to vitrinite reflectance values higher than 1.0%. A strong correlation is observed between Rock-Eval parameters and vitrinite reflectance during thermal maturation in confined-system pyrolysis. Plots T_{max} *vs.* %R_r and HI *vs.* %R_r show that the artificial maturation paths for the three coal samples point out similar trends to the natural evolution of the type III kerogen. Here, it is found that the changes in the physical and chemical properties of coals induced by heating experiments under confining satisfactorily reproduce the natural transformations of type III kerogen.

Data also show that Olmos (Cretaceous coal) yields little amounts of bitumen when artificially maturated in confined pyrolysis because it has already lost a major part of its petroleum potential during natural coalification. The selected Carboniferous coals (1l1 Dim & 2c10YD) from Donets coals generate more bitumen than the Cretaceous Sabinas coal, which is in line with the presence of liptinite in the former. As a comparison, the two Carboniferous coals from Donets Basin yield amounts of bitumen comparable to Tertiary Mahakam coals, which have been associated with oilfields. Whatever the studied coals in the present work, the 'oil window' occurs between 1.0%R_r and 2.0%R_r during confined pyrolysis. Cretaceous coal from Sabinas Basin can also generate hydrocarbons under further maturation. As expected, the two Carboniferous coals from Donets Basin (1l1 Dim & 2c10YD) produce more hydrocarbons that Cretaceous Sabinas coal (Olmos). Hydrocarbons are dominated by aromatics in the pyrolyzates yielded by the three coals artificially maturated in confined pyrolysis.

Increasing thermal stress induces the cracking of bitumen (secondary cracking) to form low molecular weight compounds and solid bitumen (solid bitumen). The solid bitumen content increases soon the first stage of thermal maturation, suggesting an overlap of primary and secondary cracking during confined pyrolysis of coals. A correlation can be observed between the solid bitumen content and the amounts of generated bitumen. The proportion of solid bitumen decreases in the order 1l1Dim > 2c10YD > Olmos.

The hydrocarbons occupied the porosity of coals since they are not removed from the environment of generation in a confined medium only because no water is used to separate oil from source rock. At elevated temperature, one of the reasons explaining changes in porosity during pyrolysis might be linked to the

formation of volatile decomposition products. Gas generated at the ultimate stage of thermal maturation probably induces a growth of the pores. Our results show a correlation between the porosity and the gas yields: Carboniferous Donets coals producing more gas have a higher porosity than Cretaceous Sabinas coal.

Acknowledgements

The authors wish to acknowledge the PEMEX (Mexico) for Sabinas coal samples, V.A. Privalov (Donetsk University, Ukraine) for Donets coal samples, the Instituto Nacional del Carbon (INCAR-CSIC, Spain) for all petrographic studies, Didier Kéravis for Rock-Eval analysis (ISTO Orléans, France), the CREGU (France) and the Syria Government for there financial support and Noé Piedad-Sanchez for his help. This research was also supported by a CSIC-CNRS (Spain-France) By-Lateral Agreement (Collaboration Cooperation Accord CNRS/CSIS Project Conjoint 16226). We are indebted to three anonymous reviewers for their constructive reviews and suggestions which led to considerable improvement to the manuscript.

References

Alpern, B., Lemos de Sousa, M.J., 2002. Documented international enquiry on solid sedimentary fossil fuels; coal: definition, classification, reserve-resources, and energy potential. International Journal of Coal Geology 50, 3–41.

Behar, F., Hatcher, P.G., 1995. Artificial coalification of a fossil wood from brown coal by confined system pyrolysis. Energy & Fuel 9, 984–994.

Behar, F., Ungerer, P., Kressman, S., Rudkiewicz, J.L., 1991. Thermal evolution of crude oils in sedimentary basins: experimental simulation in a confined system and kinetic modeling. Revue de l'Institut Français du Pétrole 46, 151–181.

Behar, F., Kressmann, S., Rudkiewicz, J.L., Vandenbroucke, M., 1992. Experimental simulation in a confined system and kinetic modelling of kerogen and oil cracking. Organic Geochemistry 19, 173–189.

Behar, F., Vandenbroucke, M., Teermann, S.C., Hatcher, P.G., Leblond, C., Lerat, O., 1995. Experimental simulation of gas generation from coals and a marine kerogen. Chemical Geology 126, 247–260.

Behar, F., Vandenbroucke, M., Tang, Y., Marquis, F., Espitalié, J., 1997a. Thermal cracking of kerogen in open and closed systems: determination of kinetic parameters and stoichiometric coefficients for oil and gas generation. Organic Geochemistry 26, 321–339.

Behar, F., Tang, Y., Liu, J., 1997b. Comparison of rate constants for some molecular tracers generated during artificial maturation of kerogens: influence of kerogen type. Organic Geochemistry 26, 281–287.

Behar, F., Lewan, M.D., Lorant, F., Vandenbroucke, M., 2003. Comparison of artificial maturation of lignite in hydrous and nonhydrous conditions. Organic Geochemistry 34, 575–600.

Bertrand, P., 1984. Geochemical and petrographic characterization of humic coals considered as possible oil source rocks. Organic Geochemistry 6, 481–488.

Blumer, M., Mullin, M.M., Thomas, D.W., 1963. Pristane in zooplankton. Science 140, 974.

Boreham, C.J., Horfield, B., Schenk, H.J., 1999. Predicting the quantities of oil and gas generated from Australian Permian coals, Bowen Basin using pyrolytic methods. Marine and Petroleum Geology 16, 165–188.

Brooks, J.D., Smith, J.W., 1969. The diagenesis of plant lipids during the formation of coal, petroleum and natural gas-II. Coalification and the formation of oil and gas in the Gippsland Basin. Geochimica et Cosmochimica Acta 33, 1183–1194.

Burrus, J., Brosse, E., de Janvry, G.C., Grosjean, Y., Oudin, J.L., 1992. Basin modelling in the Mahakam Delta based on the intergrated 2D model Temispack. Proceedings of the Indonesian Petroleum Association, 21 st Annual Convention, Jakarta, 92-11.04, pp. 23–43.

Cook, A.C., Struckmeyer, H., 1986. The role of coal as a source rock for oil. In: Glenie, R.C. (Ed.), Second South-Eastern Australia Oil Exploration Symposium, pp. 419–432.

Cserna, Z., 1960. Orogenesis in time and space in Mexico. Geologishe Rundschau 50, 67–88.

Durand, B., Parratte, M., 1982. Oil potential of coals: a geochemical approach. Symposium of Petroleum Geochemistry Exploration in Europe, Glasgow, September 1982.

Eguiluz de Antuñano, S., 2001. Geologic evolution and gas resources of the Sabinas in northeastern Mexico. In: Bartolini, C., Buffler, R.T., Cantú-Chapa, A. (Eds.), The western Gulf of Mexico Basin: tectonics, sedimentary basins and petroleum systems. AAPG (American Association of Petroleum Geology) Memoir, vol. 75, pp. 241–270.

Erdmann, M., 1999. Gas generation from overmature Upper Jurassic source rocks, northern Viking Graben. Berichte des Forschungszentrums Jülich; 3700. Dissertation RWTH Aachen.

Erdmann, M., Horsfield, B., 2006. Enhanced late gas generation potential of petroleum source rocks via recombination reactions: Evidence from the Norwegian North Sea. Geochimica et Cosmochimica Acta 70, 3943–3956.

Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Poulet, J., Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mères de leur potentiel pétrolier et de leur degré d'évolution. Revue de l'Institut Français du Pétrole 32, 32–42.

Espitalié, J., Deroo, G., Marquis, F., 1985. La pyrolyse Rock-Eval et ses applications. Revue de l'Institut Français du Pétrole 40, 755–784.

Ford, T.J., 1986. Thermal decomposition of hexadecane: reaction mechanism. Industrial Engineering and Chemical Research 25, 240–243.

Goossens, H., de Leeuw, J.W., Schenck, P.A., Brassell, S.C., 1984. Tocopherols as likely precursors of pristane in ancient sediments and crude oils. Nature 312, 440–442.

Han, Z., Crelling, J.C., Zhou, Y., 1993. Fluorescence intensity and alteration of coal macerals and their relation to coalification. Organic Geochemistry 20, 677–685.

Hildenbrand, A., Krooss, B.M., Busch, A., Gaschnitz, R., 2006. Evolution of methane sorption capacity of coal seams as a function of burial history — a case study from the Campine Basin, NE Belgium. International Journal of Coal Geology 66, 179–203.

Hill, R.J., Tang, Y., Kaplan, I.R., 2003. Insights into oil cracking based on laboratory experiments. Organic Geochemistry 34, 1651–1672.

Horsfield, B., Disko, U., Leistner, F., 1989. The micro-scale simulation of maturation: outline of a new technique and its potential applications. Geologische Rundschau 78, 361–374.

Huang, W.L., 1996. Experimental study of vitrinite maturation: effects of temperature, time, pressure, water, and hydrogen index. Organic Geochemistry 24, 233–241.

Huc, A.Y., Nederlof, P., Debarre, R., Carpentier, B., Boussafir, M., Laggoun-Défarge, F., Lenail-Chouteau, A., Bordas-Le Floch, N., 2000. Pyrobitumen occurrence and formation in a Cambro–Ordovician sandstone reservoir, Fahud Salt Basin, North Oman. Chemical Geology 168, 99–112.

International Committee for Coal and Organic Petrology (ICCP), 1998. The new vitrinite classification (ICCP System 1994) International Committee for Coal and Organic Petrology. Fuel 77, 349–358.

International Committee for Coal and Organic Petrology (ICCP), 2001. The new inertinite classification (ICCP System 1994), International Committee for Coal and Organic Petrology. Fuel 80, 459–471.

Isaksen, G.H., Curry, D.J., Yeakel, J.D., Jenssen, A.I., 1998. Controls on the oil and gas potential of humic coals. Organic Geochemistry 29, 23–44.

Izart, A., Sachsenhofer, R.F., Privalov, V.A., Elie, M., Panova, E.A., Antsiferov, V.A., Alsaab, D., Rainer, T., Sotirov, A., Zdravkov, A., Zhykalyak, M.V., 2006. Stratigraphic distribution of macerals and biomarkers in the Donets Basin: Implications for paleoecology, paleoclimatology and eustacy. International Journal of Coal Geology 66, 69–107.

Katz, B.J., Kelley, P.A., Royle, R.A., Jorjorian, T., 1991. Hydrocarbon products of coals as revealed by pyrolysis-gas chromatography. Organic Geochemistry 17, 711–722.

Kholi, K.B., Thomas, N.J., Prabhu, B.N., Misra, K., 1994. Simulated petroleum generation studies by hydrous pyrolysis of a Tertiary coal from Northern Cambay Basin of India. Organic Geochemistry 21, 323–332.

Killops, S.D., Woolhouse, A.D., Weston, R.J., Cook, R.A., 1994. A geochemical appraisal of oil generation in the Taranaki Basin, New Zealand. American Association of Petroleum Geology Bulletin 78, 1560–1585.

Killops, S.D., Funnell, R.H., Suggate, R.P., Sykes, R., Peters, K.E., Walters, C., Woolhouse, A.D., Weston, R.J., Boudou, J.-P., 1998. Predicting generation and expulsion of paraffinic oil from vitrinite-rich coals. Organic Geochemistry 29, 1–21.

Killops, S., Walker, P., Wavrek, D., 2001. Maturity-related variations in the bitumen compositions of coals from Tara-1 and Toko-1 wells. New Zealand Journal of Geology and Geophysics 44, 157–169.

Koopmans, M.P., Rijpstra, W.I.C., Klapwijk, M.M., de Leeuw, J.W., Lewan, M.D., Sinninghe Damsté, J.S., 1999. A thermal and chemical degradation approach to decipher pristane and phytane precursors in sedimentary organic matter. Organic Geochemistry 30, 1089–1104.

Kotarba, M.J., Lewan, M.D., 2004. Characterizing thermogenic coalbed gas from Polish coals of different ranks by hydrous pyrolysis. Organic Geochemistry 35, 615–646.

Landais, P., 1991. Assessment of coal potential evolution by experimental simulation of natural coalification. Organic Geochemistry 17, 705–710.

Landais, P., Muller, J.-F., Michels, R., Oudin, J.-L., Zaugg, P., 1989. Comparative behaviour of coal and maceral concentrates during artificial coalification. Fuel 68, 1616–1619.

Landais, P., Zaugg, P., Monin, J.-C., Kister, J., Muller, J.-L., 1991. Experimental simulation of the natural coalification of coal maceral concentrates. Bulletin de la Société Géologique de France 162, 211–217.

Landais, P., Michels, R., Elie, M., 1994. Are temperature and time the only constraints to the simulation of organic matter maturation. Organic Geochemistry 22, 617–630.

Lewan, M.D., 1997. Experiments on the role of water in petroleum formation. Geochimica et Cosmochimica Acta 61, 3691–3723.

Lewan, M.D., Williams, J.A., 1987. Evaluation of petroleum generation from resinites by hydrous pyrolysis. American Association of Petroleum Geologists Bulletin 71, 207–214.

Li, Y., Michels, R., Mansuy, L., Fleck, S., Faure, P., 2002. Comparison of pressurized liquid extraction with classical solvent extraction and microwave-assisted extraction–application to the investigation of the artificial maturation of Mahakam coal. Fuel 81, 747–755.

Littke, R., Leythaeuser, D., 1993. Migration of oil and gas in coals. In: Law, B.E., Rice, D.D. (Eds.), Hydrocarbons from coal. Studies in Geology, vol. 38. American Association of Petroleum Geologists, pp. 219–236.

Longoria, F.J., 1984. Stratigraphic studies in the Jurassic of northern Mexico: Evidence for the origin of Sabinas basin, in the Jurassic of the Gulf Rim: Gulf Coast Section, Society for Sedimentary Geology (SEPM) Foundation. Third Annual Research Conference Proceeding, pp. 171–193.

Lu, S.-T., Kaplan, I.R., 1990. Hydrocarbon-generation potential of humic coal from dry pyrolysis. American Association of Petroleum Geologists Bulletin 74, 163–173.

Mansuy, L., Landais, P., Ruau, O., 1995. Importance of the reacting medium in artificial maturation of a coal by confined pyrolysis. 1. Hydrocarbons and polar compounds. Energy & Fuel 9, 691–703.

Michels, R., Landais, P., 1994. Artificial coalification: comparison of confined pyrolysis and hydrous pyrolysis. Fuel 73, 1691–1696.

Michels, R., Landais, P., Elie, M., 1994. Expected hydrogen-transfer reactions during organic matter maturation in confined and hydrous pyrolysis systems. American Chemical Society, Division of Petroleum Chemistry Preprints 39 (3), 348–352.

Michels, R., Burkle, V., Mansuy, L., Langlois, E., Ruau, O., Landais, P., 2000. Role of polar compounds as source of hydrocarbons and reactive medium during the artificial maturation of Mahakam coal. Energy & Fuel 14, 1059–1071.

Mishra, C.S., Samanta, U., Gupta, A., Thomas, N.J., Misra, K.N., 1996. Hydrous pyrolysis of a Type III source: fractionation effects during primary migration in natural and artificially maturated samples. Organic Geochemistry 25, 489–505.

Monthioux, M., 1988. Expected mechanism in nature and in confined-system pyrolysis. Fuel 67, 843–847.

Monthioux, M., Landais, P., 1987. Evidence of free but trapped hydrocarbons in coals. Fuel 67, 843–847.

Monthioux, M., Landais, P., 1988. Natural and artificial maturations of a coal series: infrared spectroscopy study. Energy & Fuels 2, 794–801.

Monthioux, M., Landais, P., 1989a. Natural and artificial maturation of coal: non-hopanoid biomarkers. Chemical Geology 77, 71–85.

Monthioux, M., Landais, P., 1989b. Natural and artificial maturation of coal: hopanoid biomarkers. Chemical Geology 75, 209–226.

Monthioux, M., Landais, P., Monin, J.C., 1985. Comparison between natural and artificial series of humic coals from the Mahakam delta, Indonesia. Organic Geochemistry 8, 275–292.

Murchison, D.G., 1987. Recent advances in organic petrology and organic geochemistry: an overview with some reference to 'oil from coal'. In: Scott, A.C. (Ed.), Coal and coal-bearing strata: Boston, Blackwell Scientific Publications, Geological Society Special Publication 32, pp. 257–302.

Navale, V., 1994. Comparative study of low and high temperature hydrous pyrolysis products of monoglyceryl diether lipid from archaebacteria. Journal of Analytical and Applied Pyrolysis 29, 33–43.

Pedersen, G.K., Andersen, L.A., Lundsteen, E.B., Petersen, H.I., Bojesen-Koefoed, J.A., Nytoft, H.P., 2006. Depositional environments, organic maturity and petroleum potential of the Cretaceous coal-bearing Atane formation at Qullissat, Nuussuaq Basin, West Greenland. Journal of Petroleum Geology 29, 3–26.

Peters, K.E., Snedden, J.W., Sulaeman, A., Sarg, J.E., Enrico, R.J., 2000. A new geochemical-sequence stratigraphic model for the Mahakam Delta and Makassar Slope, Kalimantan, Indonesia. American Association of Petroleum Geologists Bulletin 84, 12–44.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The biomarker Guide-2- Biomarkers in petroleum systems and Earth history. Cambridge University Press, p. 680.

Petersen, H.I., 2002. A re-consideration of the "oil window" for humic coal and kerogen type III source rocks. Journal of Petroleum Geology 25, 407–432.

Petersen, H.I., 2006. The petroleum generation potential and effective oil window of humic coals related to coal composition and age. International Journal of Coal Geology 67, 221–248.

Petersen, H.I., Nytoft, H.P., 2006. Oil generation capacity of coals as a function of coal age and aliphatic structure. Organic Geochemistry 37, 558–583.

Piedad-Sánchez, N., Martínez, L., Izart, A., Suárez-Ruiz, I., Elie, M., Ménétrier, C., 2005. Artificial maturation of a high volatile bituminous coal from Asturias (NW Spain) in a confined pyrolysis system — Part I. Petrographic, geochemical and molecular studies. Journal of Analytical and Applied Pyrolysis 74, 61–76.

Powell, T.G., Boreham, C.J., Smyth, M., Russell, N., Cook, A.C., 1991. Petroleum source rock assessment in non-marine sequences: pyrolysis and petrographic analysis of Australian coals and carbonaceous shales. Organic Geochemistry 17, 375–394.

Price, L.C., Barker, C.E., 1985. Supression of vitrinite reflectance in amorphous rich kerogen — a major unrecognised problem. Journal of Petroleum Geology 8, 59–84.

Privalov, V.A., Panova, E.A., Azarov, N.Ya., 1998. Tectonic events in the Donets Basin: spatial, temporal, and dynamic aspects. Geologiya i Geochimiya Goruchykh Kopalin Geology and Geochemistry Fossil Fuels 4, 11–18 (in Russian).

Radke, M., Welte, D.H., Willsch, H., 1982. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. Geochimica et Cosmochimica Acta 46, 1–10.

Radke, M., Schaeffer, R.G., Leythaeuser, D., 1980. Composition of soluble organic matter in coals: relation to rank and liptinite fluorescence. Geochimica et Cosmochimica Acta 44, 1787–1800.

Radke, M., Welte, D.H., Willsch, H., 1986. Maturity parameters based on aromatic hydrocarbons: influence of the organic matter type. In: Leythaeuser, D., Rullkötter, J. (Eds.), Advances in Organic Geochemistry 1985. Organic Geochemistry, vol. 10, pp. 51–63.

Raymond, A.C., Murchison, D.G., 1992. Effect of igneous activity on molecular-maturation indices in different types of organic matter. Organic Geochemistry 18, 725–735.

Rowland, S.J., 1990. Production of acyclic isoprenoid hydrocarbons by laboratory maturation of methanogenic bacteria. Organic Geochemistry 15, 9–16.

Sachsenhofer, R.F., Privalov, V.A., Izart, A., Elie, M., Kortensky, J., Panova, E.A., Sotirov, A., Zhykalyak, M.V., 2003. Petrography and geochemistry of Carboniferous coal seams in the Donets Basin (Ukraine): implications for paleoecology. International Journal of Coal Geology 55, 225–259.

Santamaría-Orozco, D.M., 1990. Ambientes sedimentarios de las rocas del Cretácico Superior en la Cuenca Carbonífera de Sabinas, Estado de Coahuila, México. Master Thesis. Facultad de Ingeniería. Universidad Nacional Autónoma de México. 72 p.

Saxby, J.D., Bennet, A.J.R., Corcoran, J.F., Lambert, D.E., Riley, K.W., 1986. Petroleum generation: simulation over six years of hydrocarbon formation from torbanite and brown coal in a subsiding basin. Organic Geochemistry 9, 69–81.

Schenck, P.A., de Leeuw, J.W., Viets, T.C., Haverkamp, J., 1983. Pyrolysis-mass spectrometry in coal chemistry: a study of the coalification of vitrites and the typification of Australian brown coals. In: Brooks, J. (Ed.), Petroleum Geochemistry and Exploration of Europe. Geological Society Special Publication, vol. 12. Blackwell Scientific Publications, Oxford, pp. 255–265.

Schimmelmann, A., Lewan, M.D., Wintsch, R.P., 1999. D/H isotope ratios of kerogen, bitumen, oil, and water in hydrous pyrolysis of source rocks containing kerogen types I, II, IIS, and III. Geochimica et Cosmochimica Acta 63, 3751–3766.

Schimmelmann, A., Boudou, J.-P., Lewan, M.D., Wintsch, R.P., 2001. Experimental controls on D/H and $^{13}C/^{12}C$ ratios of kerogen, bitumen and oil during hydrous pyrolysis. Organic Geochemistry 32, 1009–1018.

Schlepp, L., Elie, M., Landais, P., Romero, M.-A., 2001. Pyrolysis of asphalt in the presence and absence of water. Fuel Processing Technology 74, 107–123.

Stach, E., Mackowsky, M.-T., Teichmüller, M., Taylor, G.H., Chandra, D., Teichmüller, R., 1982. Stach's Textbook of Coal Petrology, 3rd ed. Gebrüder Borntraeger, Berlin.

Su, K.H., Shen, J.C., Chang, Y.J., Huang, W.L., 2006. Generation of hydrocarbon gases and CO_2 from a humic coal: experimental study on the effect of water, minerals and transition metals. Organic Geochemistry 37, 437–453.

Suggate, R.P., 2002. Application of Rank (Sr), a maturity index based on chemical analyses of coals Application of Rank (Sr), a maturity index based on chemical analyses of coals. Marine and Petroleum Geology 19, 929–950.

Sun, Q., Li, W., Chen, H., Li, B., 2003. The variation of structural characteristics of macerals during pyrolysis. Fuel 82, 669–676.

Sykes, R., Snowdon, L.R., 2002. Guidelines for assessing the petroleum potential of coaly source rocks using Rock-Eval pyrolysis. Organic Geochemistry 33, 1441–1455.

Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R., Report, P., 1998. Organic Petrology. Gebrüder Borntraeger, Berlin.

Teichmüller, M., Durand, B., 1983. Fluorescence microscopical rank studies on liptinites and vitrinites in peat and coals, and comparison with results of the Rock-Eval pyrolysis. International Journal of Coal Geology 2, 197–230.

Triplett, J., Filippov, A., Pisarenko, A., 2000. Coal mine methane in Ukraine: opportunities for production and investment in the Donets coal basin. Report is available online at http://www.peer.org.ua/Handbook/Hand_E.pdf.

Verheyen, T.V., Johns, R.B., Espitalié, J., 1984. An evaluation of Rock-Eval pyrolysis for the study of Australian coals including their kerogen and humic acid fractions. Geochimica et Cosmochimica Acta 48, 63–70.

Wilkins, R.W.T., George, S.C., 2002. Coal as a source rock for oil: a review. International Journal of Coal Geology 50, 317–361.

Xiong, Y., Geng, A., Liu, J., 2004. Kinetic-simulating experiment combined with GC-IRMS analysis: application to identification and assessment of coal-derived methane from Zhongba Gas Field (Sichuan Basin, China). Chemical Geology 213, 325–338.