Comparison of hydrocarbon gases (C$_1$–C$_5$) production from Carboniferous Donets (Ukraine) and Cretaceous Sabinas (Mexico) coals

D. Alsaab [a], M. Elie [a], A. Izart [a,*], R.F. Sachsenhofer [b],
V.A. Privalov [c], I. Suarez-Ruiz [d], L. Martinez [a]

[a] G2R, Nancy — Université, CNRS, CREGU, BP-239, 54506 Vandoeuvres-lès-Nancy, France
[b] Institut für Geowissenschaften, Montanuniversität Leoben, Peter-Tunner-Strasse 5, A-8700 Leoben, Austria
[c] Donetsk National Technical University, Artem str., 58, UA-83000 Donetsk, Ukraine
[d] Instituto Nacional del Carbón – (INCAR) – CSIC. Ap.Co., 73, 33080-Oviedo, Spain

Abstract

The main purpose of this contribution is to compare the ability of Carboniferous coals from the Donets Basin of the Ukraine and Cretaceous coal from the Sabinas Basin of the Mexico to generate hydrocarbon gases (C$_1$–C$_5$). Two bituminous coals from the Donets Basin (2c10YD and 1l1Dim; 0.55 and 0.65%R_r respectively) and one bituminous coal from the Sabinas Basin (Olmos, 0.92%R_r) were studied using heating experiments in a confined-pyrolysis system. The highest rank reached during the heating experiments corresponds to the anthracite stage (2.78 and 2.57%R_r) for the 2c10YD and 1l1Dim coals and (2.65%R_r) for the Olmos coal. The composition of the generated (C$_1$–C$_5$) gases was evaluated using a thermodesorption-multidimensional gas chromatography. The results show that the Carboniferous Donets coals produced more wet gas and methane during pyrolysis than the Cretaceous Olmos coal. This is probably due to their higher liptinite (6–20%) and collodetrinite content and to the loss of a major part of the petroleum potential of the Olmos coal during natural coalification. C$_2$–C$_5$ compounds are mainly derived from the cracking of liquid hydrocarbons. Ethane is the most stable compound and formed from the cracking of higher hydrocarbon component.

Large amounts of methane (up to 81 mg/g coal for the Donets coals and 50 mg/g coal for the Sabinas coal) were formed at high temperatures by cracking of previously formed heavier hydrocarbons and by dealkylation of the coal matrix. A linear relationship was observed between methane generation and the maturity level of both coal types.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Artificial maturation; Confined pyrolysis; Coal; Methane; Donets Basin; Sabinas Basin

1. Introduction

The Donets Basin in the SE part of Ukraine contains one of the major late Paleozoic coal basins in the world with proven reserves in the order of 60 Gt. Total coal thickness in Carboniferous formations is about 60 m. The Donets coal mines are among the gasiest and the most dangerous in the world (Privalov et al., 1998, 2003; Privalov, 2002). Thermal maturation of coals and dispersed organic matter in the Donets Basin resulted in the formation of an enormous methane

resource of about 278 Tm^3 (Uziyuk et al., 2001; Triplett et al. 2001) estimated the total methane resource in the Donets Basin from coals to be 117 Tm^3 and the methane content in recoverable coal seams at 1400 to be 2500 Gm^3. The high methane content in coal seams in the Donets Basin presents a high potential for coal bed methane recovery (Privalov et al., 2004a; Alsaab et al 2007a). On the other hand it represents a severe mine safety problem, where coal and gas outbursts constitute a major mining hazard and account for many fatalities (Privalov et al., 2004a,b). As well, as an energy resource, CH$_4$ is a greenhouse gas whose atmospheric concentration has been increasing at a rate of about 1% annually (Tyler, 1991). For instance in the Donets Basin only 13% of the total generated methane from coal beds is detected in the degasification system

---

during coal mining activity. Only 30% of that captured methane is used as an energy resource. Thus the emissions of large amounts of methane from Donets coal beds contribute to the gas greenhouse effect (Triplett et al., 2001).

The Sabinas Basin in Mexico contains Upper Cretaceous (Maastrichtian Age) very gassy coals (the Double Seam) in the Olmos Formation, of high to medium volatile bituminous rank (Gentzis et al., 2005). Brunner and Ponce (1999) estimated the presence of 12.2 Gt of coal in the Maastrichtian coals in Coahuila State. Olmos coal is considered as a potential resource of natural gas, with coal seams ranging in thickness from 1.5 to 4 m (Eguiluz de Antuñano, 2001; Gentzis et al., 2005). The average of gas content of Olmos coals is of 8–15 m^3/ton (Eguiluz de Antuñano, 2001). Coal bed methane is mainly methane (98%) (Eguiluz de Antuñano, 2001; Gentzis et al., 2006). The amount of adsorbed methane in Olmos coal formation is still under investigation. Gentzis et al. (2006) estimated this amount to be more than 9 cm^3/g, and that in some mines such as Esmeralda Mine the adsorption capacity at a depth of 300 m is as high as 15 cm^3/g. A report by Minerales Monclova (Santillan-Gonzalez, 2004) indicated an average in-situ content of gas in the coals of Sabinas Basin of 10–14 m^3/ton (98.5% methane) with gas total resource in Coahuila estimated between 1.22×10^{11} m^3 and 2.2×10^{11} m^3.

Previous studies by Law and Rice (1993), Béhar et al. (1995), Taylor et al. (1998), and Petersen (2006) presented coals as being both gas-prone source rocks and reservoir rocks. In accordance with the work of Alsaab et al. (2007b), the Donets and Olmos coals have different abilities to oil generation during heating experiments in a confined system; the Donets coals, which are less mature and richer in liptinite and collodetrinite produce more bitumen than the Olmos coals. Moreover, Alsaab et al. (2007b) observed an increase in the porosity with increasing coal rank for both the Donets and Sabinas coals and attributed that to the cracking of bitumen generated during pyrolysis into solid bitumen and an abundance of light compounds (methane in particular). Given (1984), Derbyshire et al. (1989), and Erdmann and Horsfield (2006) showed that the oil generated by coal tends to be adsorbed in the micropores of vitrinite; eventually this trapped oil is converted to gas as the coal matures under increasing thermal stress. Thus, it is generally accepted that coal can generate an important amount of methane and store a large volume of generated gas, if the entrapment conditions are favourable. Ritter and Grover (2005) related the absorption capacity of generated petroleum (C15+ hydrocarbons) in the coal matrix, the later secondary cracking during subsequent maturation and the generation of light hydrocarbon compounds when cracking becomes more dominant. They revealed that expulsion begins relatively late and that the expelled hydrocarbons consist of C_1 to C_5 hydrocarbons and heavy aromatics.

Prediction of the volume of hydrocarbons (HCs) stored in reservoirs is difficult due to the impossibility of directly quantification of the HCs amounts generated during coalification. Thus, two laboratory methods were proposed. The best known method is heating experiments which allow us to simulate the natural coalification process by applying increased heating temperatures and shortened time (Tissot et al., 1971; Huc and Durand, 1973; Stach et al., 1982). Open, closed, hydrous and confined systems were established to meet this objective. Monthioux (1988) showed that the natural reaction system should be considered as 'quasi confined' in the case of coals because of their physical and chemical properties. In this case, non-hydrous closed pyrolysis system using glass tubes (Horsfield et al., 1989) or gold cells (Monthioux et al., 1985) can be used to simulate natural coalification and estimate HCs generation during basin evolution. Béhar et al. (2003) compared artificial maturation of lignite (Type III) in open non-hydrous, closed non-hydrous and closed hydrous pyrolysis and observed in generally a slight increase in the total HC gas for both non-hydrous pyrolysis with an increase in maturity. Kotarba and Lewan (2004) showed that amounts of thermogenic gases produced by non-hydrous pyrolysis from lignites of Poland are 1.29 times greater than by hydrous pyrolysis. Su et al. (2006) compared artificial maturation of Miocene coal from China (starting 0.35%R_r) with confined hydrous and confined non-hydrous pyrolysis and found 1.6 times more gas generated for non-hydrous than for hydrous pyrolysis. We think that each of these pyrolysis systems must be viewed as additional, not as replacement. An open system pyrolysis experiment enables us to simulate the primary cracking reactions of organic matter, while closed and hydrous pyrolysis systems take into account both primary and secondary cracking. As hydrous pyrolysis is limited by the maximum pyrolysis temperature due to excessive water and its critical point, the complete reaction of gas generation cannot be reached at the end of pyrolysis. Because of the strong adsorption capability, the early generated products (heavy hydrocarbon) will be prevented from expulsion from the coal sample and undergo secondary cracking into gas. Therefore, a dry, confined system pyrolysis was employed in this study to simulate gas generation from coal at three different temperatures (330, 360 and 400 °C).

The second method is through the use of numerical models to estimate the amount of generated HCs by using the changes in major elemental composition (C–H–O) with coal rank. Depending on the elemental data employed, starting rank, and assumptions made about the products, it has been estimated that about 100 to 300 cm^3 CH_4/g can be generated from coals (Jüntgen and Karweil, 1966; Jüntgen and Klein, 1975; Meissner, 1984; Ermakov and Skorobogatov, 1984; Welte et al., 1984; Levine, 1987; Hunt, 1996). Rice (1993) and Clayton (1998) estimated the methane yield by using numerical models method to be in the range of 150–200 cm^3/g, with yield depending strongly on the elemental and maceral composition and also the maturity level of kerogen.

The purpose of this paper is not to compare different pyrolysis methods nor to propose a kinetic study, but to compare the ability of two different coals (Carboniferous and Cretaceous) from two basins (Donets and Sabinas) in order to determine the CBM potential in these basins. This paper is a continuation of the paper (Alsaab et al., 2007b) that concerned the production of oil and pyrobitumen by the same samples under the same artificial maturation by confined-pyrolysis system.

2. Geological settings

2.1. Donets Basin (Donbas)

The Donets Basin, named Donbas by Ukrainian geologists, is located in the southeastern part of Ukraine, extending into Russia (Fig. 1). Geologically, the Donets Basin represents a large bending flexure that covers an area of approximately 60,000 km^2 (Triplett et al., 2001; Sachsenhofer et al., 2002, 2003). Geologically, the Donbas is located between the Dnieper–Donets Depression Basin and the buried Karpinsky Ridge within the limits of continuous Devonian rift system that developed along the margin of the East-European Craton (Chekunov, 1976; Chekunov et al., 1992; Stovba et al., 1996). Among the set of rift structures the Donets Basin is the most anomalous segment: it stands out by its up to 24-km sedimentary column with prominent inversion (Stovba et al., 1996). The thickness of the Carboniferous coal measures in the Donets Basin increases from the basin margins towards the basin centre and in a southeastern direction. Maximum Carboniferous thickness is about 14 km. The coal-bearing strata consist of cyclic successions of marine, continental and transitional facies (Sachsenhofer et al., 2003; Izart et al., 2006). There are over 330 identified Carboniferous coal seams to a depth shallower than 1800 m. However, only a hundred seams are considered mineable due to either thin seam thickness or depth constraints (Privalov et al., 1998). Two high volatile bituminous coals from the Donets Basin (Fig. 1) were selected

for the laboratory experiments: Sample 2c10YD (R_r=0.55%) is from the Serpukhovian c10 seam (Yuzhno Donbasskaya 1 mine). Sample 1l1Dim (R_r=0.65%) is from the Moscovian l1 seam (Dimitrova mine).

2.2. Sabinas Piedras Negras Basin

The Sabinas Basin, Mexico (Fig. 2) 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 Orogeny (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.

3. Methodology

3.1. Confined-system pyrolysis

The unextracted coals were subjected to heating experiments in a confined-pyrolysis system (Monthioux, 1988). About 1 g of powdered and sieved coal (<250 μm) was placed
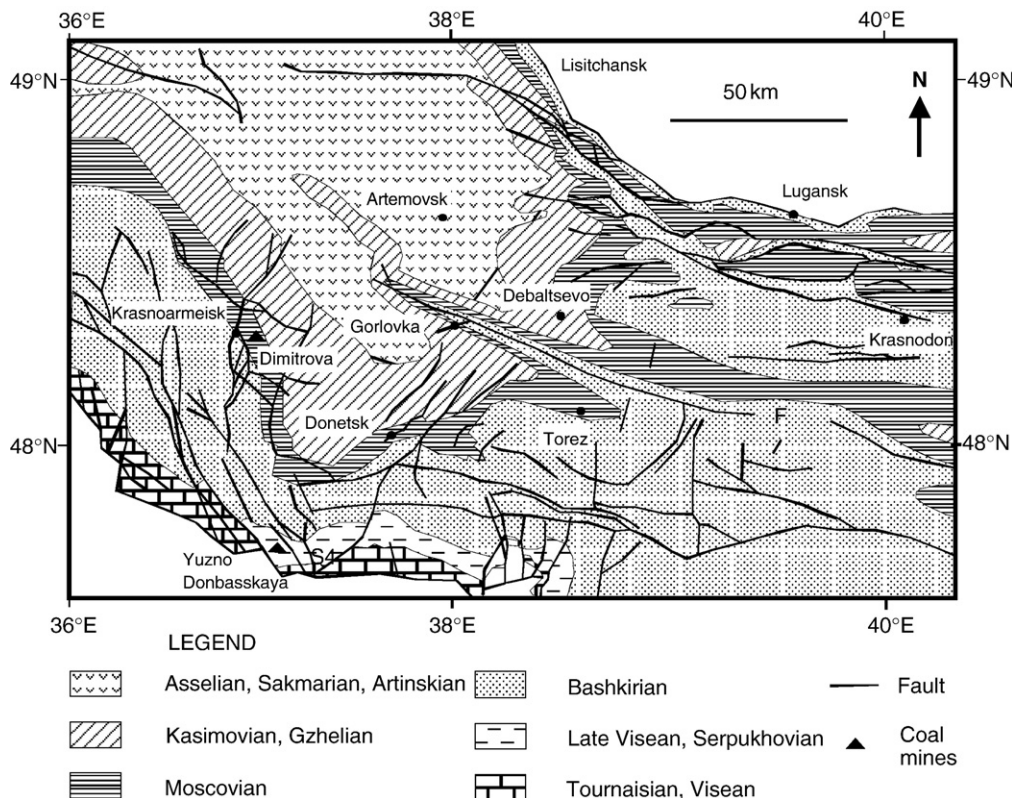

Fig. 1. Map of Donets Basin with location of coal mines (drawn after Makarov, 1990).
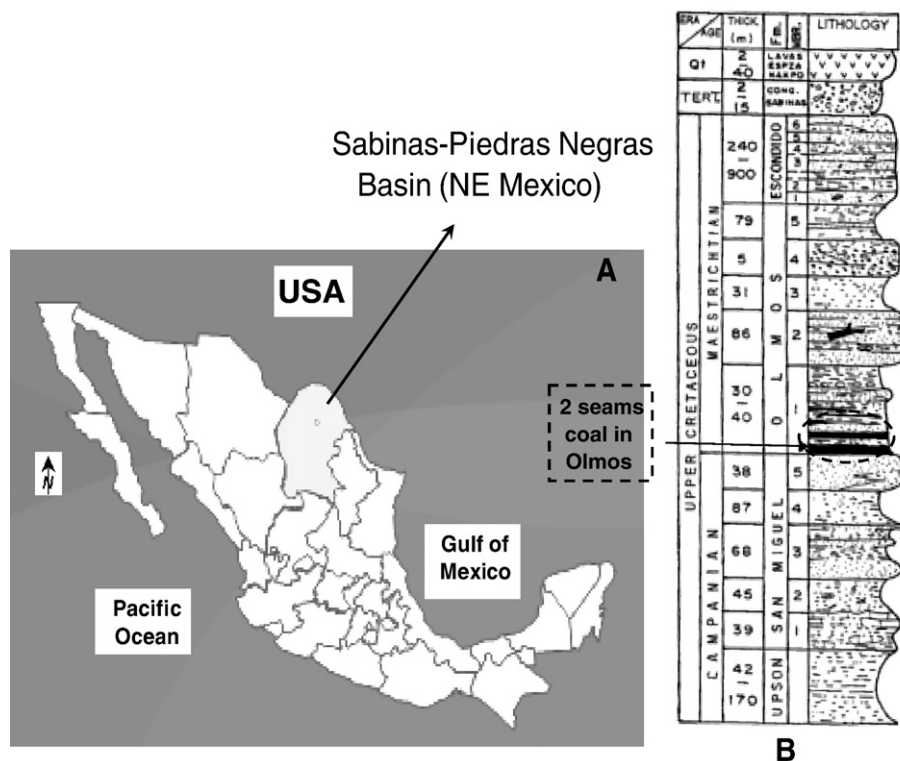
Fig. 2. Map and lithostratigraphic column of Sabinas Basin (drawn after Eguiluz de Antuñano, 2001).

inside a gold cell ($L = 5$ cm, i.d. $= 1$ cm). The loaded gold tubes were evacuated and purged with argon twice to minimize atmospheric gases, and were then welded under an argon atmosphere. The sealed gold cells were placed into 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 bar (70 MPa). Temperature was controlled by an internal thermocouple in contact with the gold cells (accuracy ± 1 °C).

3.2. Geochemical analysis of organic effluents

After the pyrolysis runs, the gold cell was placed in an oven at 250 °C. The system was closed and evacuated before piercing the gold cell. The thermovaporizable content of the gold cell expanded into the system and filled the sample loop of a Valco Valve. After an equilibration time of 30 min and following the measurement of the effluents pressure, an aliquot fraction of 0.5 ml was injected via the Valco valve, without fractionation, into a HP 5890 Series II gas chromatograph with a flame ionisation detector to identify and to quantify the C_1–C_{14} fraction (Gérard et al., 1994). The capillary column used was a DB-5 J&W Scientific (60 m × 0.32 mm i.d. with 0.45-μm film thickness). The temperature program was 0 °C for 3 min followed by a rise to 300 °C at 6 °C/min and finally an isothermal stage at 300 °C for 15 min. Hydrogen was used as a carrier gas (1 ml/min flow rate). The quantitative accuracy of the method is better than 6% (Burklé-Vitzthum et al., 2004).

Then, the gold tubes were opened and extracted using a Dionex extractor ASE 200 with dichloromethane as sol-vent (Alsaab et al., 2007b). The soluble C_{14+} fractions were evaporated, weighed and the asphaltenes were removed with n-heptane.

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

Basin	Sabinas	Donets	
Coal mines	Mimosa	Dimitrova	Yuzno-Donbasskaya #1
Samples	Olmos	1ll 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

3.3. Petrographic and geochemical analyses of kerogen

Unextracted aliquots of raw and heated coals were prepared for petrographic analysis. Random vitrinite reflectance measurements were carried out in accordance with ISO 7405-5 (1994a) on raw coals and solid residues using a MPV-Combi Leitz microscope. Maceral analysis of coals was also performed according to ISO 7404/3 (1994b) norm and the new ICCP system for vitrinite maceral group nomenclature (ICCP, 1998).

Extracted aliquots of raw and heated coals were analyzed using a Vinci Rock-Eval 6 instrument at ISTO (Orléans, France) to determine total organic carbon (TOC), Tmax (°C) and petroleum potential HI (mg HC/g TOC). Their C, H, and O contents were determined by using a CHNS-932 Leco microanalyzer.

The starting coals samples were characterized by using elementary analysis, petrography study and Rock-Eval analysis (Table 1). This table shows that the three starting coals have a high volatile bituminous rank, that Olmos coal reached the peak of oil generation during the natural coalification whereas both Donets coal samples fall into the onset of the 'oil window', not that elementary analysis and petrographic observation ensure this trend of maturation of these three coal samples.

4. Results and interpretation

Table 2 and Fig. 3A, B and C summarize the evolution of the amounts of methane and wet gases (C_2, C_3, iC_4, C_4, iC_5, C_5) produced by pyrolysis in a confined system from 2c10YD, 1l1Dim and Olmos coal samples as a function of coal rank (%R_r). In general terms, the generation of hydrocarbon gas starts at 1.0%R_r. Table 2 and Fig. 3 reveal that:

– During short heating time and at low temperature (1 day, 330 °C), low amounts of methane equal to 2.1–2.5 mg/g coal for the 2c10YD and 1l1Dim samples and 0.24 mg/g coal for the Olmos sample were generated, while the vitrinite reflectance (R_r) increases to ~1.1% for all three coals.
– A quasi-linear increase in methane generation is observed for the three coal samples with the increasing maturity. At relatively long time (30 days) and high temperature (400 °C), methane generation is 72.3 (2c10YD), 80.7 (1l1Dim) and 50 mg/g coal (Olmos). In this experiment R_r values increase to 2.78–2.57% for the 2c10YD and 1l1Dim samples and 2.65 for the Olmos sample. It is clear that the Donets coals have a better ability to generate methane than the Olmos coal.
– The peak of C_3–C_5 generation is attained at a maturity level of ~2.15%R_r for the three coals, with amounts of 41–63 mg/g coal for the 1l1Dim and 2c10YD samples and 14 mg/g coal for the Olmos sample.
– Ethane reached peak of generation at a vitrinite reflectance of 2.24%R_r for the Olmos sample and 2.28–2.51%R_r for the 1l1Dim and 2c10YD samples; the maximum quantity of ethane generated was of 68–71 mg/g coal for the 1l1Dim and 2c10YD samples and of 40 mg/g coal for the Olmos sample.

Alsaab et al. (2007b) observed that the Carboniferous Donets coals can be considered as better source for oil than the Olmos

coal, which can generate only small amounts of oil upon artificial maturation in a confined-pyrolysis system. Alsaab et al. (2007b) noted that the organic extract yields show typical trends to those observed during artificial maturation of coal: an increase up to a maximum value followed by a decline. The peak of bitumen generation (Table 3) occurred at R_r 1.6–1.7% for the 1l1Dim and 2c10YD coals and at 1.4% for the Olmos coal. And they found in using the changes of the organic extract yields that the "oil window" occurred between R_r~1.0% and 2.0% for the Donets and Olmos coals. Similar results were obtained by Petersen (2002), who showed that the "oil window" for humic coals and kerogen type III ranges between R_r=0.85% and 1.8%. We suggest that the range of this window would depend on type of macerals. The 1l1Dim coal generated more oil than the 2c10YD coal despite its poorer liptinite content. Alsaab et al. (2007b) explained this trend by the role of the hydrogen-rich vitrinite ('desmocollinite', collodetrinite according to ICCP (1998)) in the generation of oil. The same explanation applies to the ability of the Olmos coal to generate oil, despite the absence of liptinite in the Olmos unheated coal (Table 1). The pyrolysis gas chromatography of Donets and Olmos coals indicated high relatively capacity for oil generation from the Donets coal, and the abundance of aliphatic groups relative to aromatic groups is higher for the Donets coals that for the Olmos coal (Alsaab et al., 2007b).

All previous observations allow us to suggest that:

– The amount of generated C_3–C_5 hydrocarbons is higher for the two Donets coals than for the Olmos coal (Table 2). This is probably due to: i) the higher liptinite (6–20%) and collodetrinite (60–80%) contents of the Donets coals and ii) the loss of a major part of the Olmos coal petroleum potential during natural maturation as a result of its higher maturation (Table 1). Rice et al. (1989) observed a correlation between the presence of collodetrinite and high C_{2+} compounds produced from coals in the San Juan Basin. In accordance with Bertrand (1984), Killops et al. (1994), Suggate (2002) and Wilkins and George (2002) some vitrinite group macerals (including collodetrinite) have the potential to generate heavy hydrocarbons. Detrovitrinite is the dominate vitrinite maceral subgroup in the c_{10} and l_1 seams in Donets Basin (Sachsenhofer et al., 2003), thus it is not surprising that the Donets coals can generate more non-volatile and wet-gases hydrocarbons than the Olmos coal. The C_3–C_5 compounds are probably derived from the cracking of heavier hydrocarbons (C_{6+}).
– Decreasing abundance of the C_3–C_5 hydrocarbons started at 2.16–2.11%R_r for the 2c10YD and 1l1Dim coals and at 2.13%R_r for the Olmos coal (Fig. 3 and Tables 2 and 3). This can be explained by their degradation or cracking into lighter compounds (C_2 and CH_4). It has expected that the Donets coals would generate more ethane than the Olmos coal. At higher rank (2c10YD: 2.51%R_r; 1l1Dim: 2.28%R_r; Olmos: 2.27%R_r) the ethane is degraded (Fig. 3 and Tables 2 and 3) and transformed to methane. Thus, ethane is more stable than C_3–C_5 compounds during pyrolysis and may originate directly from the coal matrix and/or from the cracking of

Table 2
The amount of HCs gases generated during heating experiences of three coal samples (2c10YD, 1l1Dim and Olmos)

Pyrolysis time (day)	1	5	30	1	5	30	1	5	30
Temperature (C°)	330	330	330	360	360	360	400	400	400
Pressure (bar)	700	700	700	700	700	700	700	700	700
Sample	Olmos			Olmos			Olmos		
%R_r	1.05	1.2	1.59	1.37	1.87	2.27	2.13	2.24	2.65
mg CH4/g coal	0.244	2.14	9.25	7.33	16.91	40.21	27.15	33.02	49.96
mg C2H6/g coal	0.05	0.40	2.47	1.44	2.88	9.00	3.58	5.37	2.303
mg C3/g coal	0.276	2.36	4.76	3.12	5.62	3.14	7.24	4.92	0
mg iC4/g coal	0.067	0.63	1.18	0.64	1.47	1.06	1.69	1.32	0.55
mg C4/g coal	0.123	1.21	2.42	1.37	2.89	1.42	3.12	1.82	0.37
mg iC5/g coal	0.029	0.35	0.63	0.62	0.80	0.08	0.85	0.30	0.01
mg C5/g coal	0.04	0.43	0.85	0.71	1.03	0.13	1.17	0.38	0
% CH4	29.46	28.43	29.89	48.03	53.49	73.03	60.61	70.05	93.92
% C2H6	6.07	5.33	14.09	9.49	9.12	16.35	7.98	11.4	4.33
% C3	33.27	31.4	27.1	20.49	17.79	5.7	16.16	10.44	0
% iC4	8.08	8.41	6.72	4.21	4.67	1.93	3.77	2.81	1.04
% C4	14.86	16.06	13.78	9.01	9.15	2.59	6.96	3.85	0.69
% iC5	3.48	4.64	3.58	4.07	2.53	0.15	1.9	0.63	0.02
% C5	4.78	5.72	4.85	4.7	3.25	0.25	2.61	0.81	0
CH4 m³/t	0.378	3.31	8.14	11.35	26.18	62.27	42.04	51.14	77.38
Sample	Donets 1l1Dim			Donets 1l1Dim			Donets 1l1Dim		
%R_r	1.07	1.44	1.9	1.56	1.94	2.28	2.11	2.3	2.57
mg CH4/g coal	2.47	5.72	29	22.65	44.63	68.06	48.38	69.45	80.74
mg C2H6/g coal	0.69	1.18	11.48	12.92	18.88	22.35	10.6	5.81	5.82
mg C3/g coal	3.03	6.45	12.15	10.47	14.47	10.17	19.02	11.03	0
mg iC4/g coal	0.85	1.53	3.6	1.88	2.71	2.77	5.32	2.75	0.8
mg C4/g coal	1.68	3.66	4.81	4.99	5.87	5.32	9.9	3.86	0.63
mg iC5/g coal	0.62	1.02	1.96	1.95	2.75	2.25	3.17	0.63	0.02
mg C5/g coal	0.65	1.4	2.39	2.57	3.01	2.32	4.03	0.8	0.01
% CH4	24.72	27.27	50.91	39.44	48.35	58.05	46.56	72.46	91.73
% C2H6	6.95	5.62	4.44	22.49	20.45	19.07	9.22	6.43	6.61
% C3	30.28	30.79	21.41	18.24	15.67	12.09	21.86	12.22	0
% iC4	8.48	7.31	4.79	3.28	2.94	2.37	5.25	3.04	0.91
% C4	16.79	17.47	11.4	8.69	6.36	4.54	10.8	4.27	0.72
% iC5	6.25	4.86	2.87	3.39	2.98	1.92	2.63	0.69	0.02
% C5	6.52	6.68	4.17	4.48	3.26	1.98	3.68	0.89	0.01
CH4 m³/t	3.83	8.85	12.26	35.08	69.12	105.4	59.44	101.36	125.04
Sample	Donets 2c10YD			Donets 2c10YD			Donets 2c10YD		
%R_r	1.09	1.49	1.98	1.65	2.07	2.51	2.16	2.23	2.78
mg CH4/g coal	2.08	4.38	ND	19	37.27	71.43	47.42	60.06	72.26
mg C2H6/g coal	0.43	0.82	ND	11.26	18.43	23.47	13.33	22.11	1.44
mg C3/g coal	2.78	5.57	ND	10.38	16.59	12.59	21.58	18.28	0.72
mg iC4/g coal	0.61	1.15	ND	1.74	2.85	1.63	9.6	4.07	1.29
mg C4/g coal	1.63	3.56	ND	5.63	8.61	1.16	15.68	8.53	0.93
mg iC5/g coal	0.37	0.72	ND	1.85	2.85	0.27	5.74	3.81	0.04
mg C5/g coal	0	0	ND	3.5	4.92	0.37	11.17	5.73	0.03
% CH4	26.28	27.04	ND	35.61	40.72	48.99	38.08	92.85	89.53
% C2H6	5.42	5.07	ND	21.11	20.14	18.04	10.71	0.62	6.74
% C3	35.2	34.36	ND	19.46	18.13	14.91	17.33	3.37	0.89
% iC4	7.68	7.1	ND	3.25	3.12	3.32	7.71	0.82	1.6
% C4	20.65	21.97	ND	10.56	9.41	6.96	12.59	1.51	1.16
% iC5	4.74	4.45	ND	3.46	3.12	3.11	4.61	0.35	0.04
% C5	0.04	0.02	ND	6.55	5.38	4.67	8.97	0.48	0.04
CH4 m³/t	3.22	6.78	ND	29.43	57.72	93.01	73.44	110.63	111.91

ND: not determined.

heavier hydrocarbons (oil and C$_3$–C$_5$). Similar results were obtained by Béhar et al. (1995) during closed system pyrolysis of Morwell and Mahakam coals, where the peak C$_2$–C$_5$ generation occurred at 2.04 to 2.23%R_r (Morwell coal) and 2.0 to 2.1%R_r (Mahakam coal). Béhar et al. (1992) showed that ethane is more stable than C$_3$–C$_5$ compounds and that it can be derived from the cracking of heavier components. Piedad-Sanchez et al. (2005)
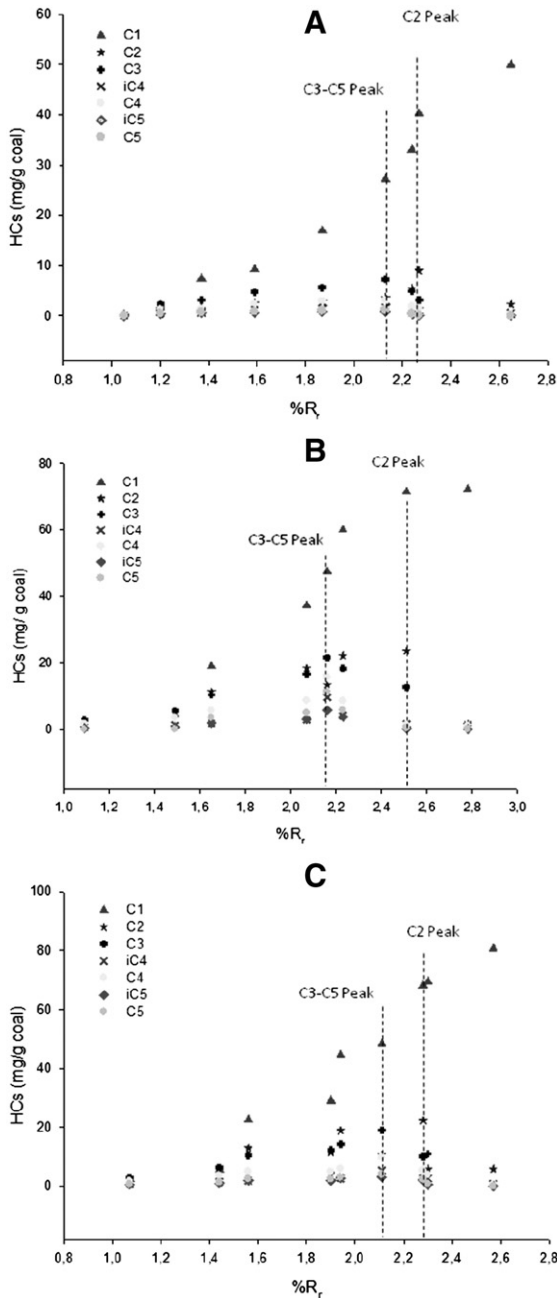
Fig. 3. Hydrocarbon gases (C_1, C_2, C_3, iC_4, C_4, iC_5 and C_5) production vs. Vitrinite reflectance of coals heated by pyrolysis in confined system (a for Olmos, b for 2c10YD and c for 1l1Dim).

obtained a peak of C_2–C_5 generation at vitrinite reflectance of 2.24%R_r for a bituminous Carboniferous coal sample from the Asturias Basin (Spain) pyrolysed in a confined-pyrolysis system.

– Within the oil window (located between $R_r \sim 1.0\%$ and 2.0%; Alsaab et al., 2007b) the methane generated ranges from 2–44.6 mg/g coal for the Donets coals and from 0.24–16 mg/g coal for the Olmos coal. In the ultimate maturation stage (at 400 °C and 30 days corresponding to 2.6 to 2.8%R_r) this amount reaches ~72–80 mg/g coal for the Donets coals and ~49 mg/g coal for the Olmos coal (Fig. 3 and Table 2). Moreover, Alsaab et al. (2007b) observed that the Donets

Table 3
Vitrinite reflectances (%R_r) corresponding to maximum of oil generation, pyrobitumen I, C_3–C_5 and C_2 and increase of pyrobitumen II (from Alsaab et al., 2007b)

Sample	%R_r of oil maximum	%R_r of bitumen I maximum	%R_r of bitumen II increase	%R_r of C_3–C_5 maximum	%R_r of C_2 maximum
Olmos	1.9	1.37		2.13	2.27
2c10YD	1.6	1.44	2.23	2.16	2.51
1l1Dim	1.6	1.65	2.11	2.11	2.28

and Olmos coals can produce low molecular weight compounds and two groups of solid bitumen (Table 3). The first generated solid bitumens (group I) are degraded with increasing maturity, for producing not only gas but also more mature solid bitumens (group II) as demonstrated by an increase of solid bitumens from group II (Table 3) that is observed at 2.1 to 2.2%R_r only for Donets coals. The degradation of solid bitumen at high maturity level can participate in the methane generation.

Fig. 4 shows a slight increase in the yield of methane relative to wet gases within the first part of oil window (between 1.0–1.5%R_r) in terms of [$C_1/(C_1+C_2+C_3)$] ratios. Gas dryness increases intensely after the occurrence of the peak of oil generation for both the Donets and Sabinas coals. This increase can be explained by the high amount of methane generated after 1.5%R_r by the cracking of heavier hydrocarbon compounds (bitumen in particular) and probably by the demethylation of the coal matrix (Su et al., 2006). Michels et al. (2002) showed that methane can be generated directly from the cracking of kerogen and hydrocarbon liquids (polars and C_{6+}) in successive closed pyrolysis experiments using Mahakam coal. They found that [$C_1/(C_1+C_2+C_3)$] ratios increased during maturation when pyrolysis temperatures increased from 340 °C to 470 °C. Thus, at the lowest maturity level the methane is produced directly from demethylation of the coal matrix (primary cracking) and from both primary and secondary cracking of all oil, solid bitumen and C_2–C_5 compounds at the highest maturity stage. Our results are in agreement with the findings of Béhar et al.
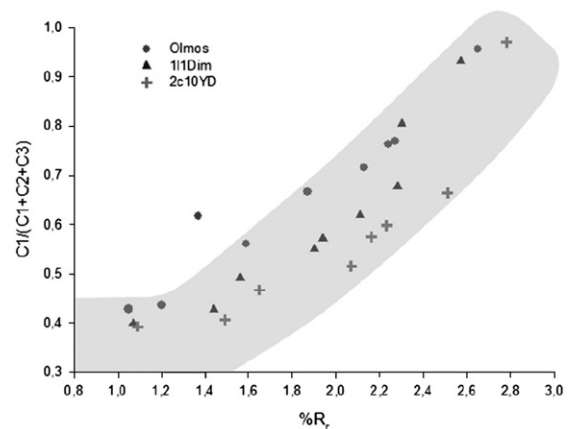

Fig. 4. The [$C_1/(C_1+C_2+C_3)$] ratio evolution during increasing thermal stress in confined system of three coals (1l1Dim and 2c10YD) from Donets Basin and Olmos from Sabinas Basin.

(1992). Methane is generated at high temperatures under very severe thermal conduction from C_2–C_5 compounds. Relatively more bitumen, wet gas, solid bitumen and methane were observed during pyrolysis of the Carboniferous Donets coals versus the Cretaceous Olmos coal.

5. Conclusion

The generation of hydrocarbon gases from two high volatile bituminous coals from the Donets Basin in Ukraine and one bituminous coal from the Sabinas Basin in Mexico has been studied using pyrolysis experiments in a confined system. The highest rank reached during the heating experiments corresponds to the anthracite stage (2.65–2.78%R_r). The results show that:

– More oil, wet gas, solid bitumen and even methane were produced during the pyrolysis of the Carboniferous Donets coals than from the Cretaceous Olmos coal. This is probably due to the higher liptinite (6–20%) and collodetrinite contents of the Donets coals. The loss of a major part of the Olmos coal petroleum potential during coalification, because of its higher maturity, reduces its capacity for gas generation.
– Ethane is more stable than C_3–C_5 compounds during pyrolysis evolution. It can be produced directly from the coal matrix and/or from the cracking of heavier hydrocarbons (bitumen and C_3–C_5).
– During the first maturity stage, methane is produced directly from the demethylation of the coal matrix (primary cracking), and from both primary and secondary cracking of all oil; solid bitumen and C_2–C_5 contribute during the highest maturity stage.
– A linear relationship was observed between methane generation and maturity level (%R_r) for both the Donets and Olmos coals.

Acknowledgements

References

Alsaab, D., Izart, A., Elie, M., Sachsenhofer, R.F., Privalov, V.A., 2007a. 2D Modelling of coalification history, hydrocarbons (oil & gas) generation, expulsion and migration in Donets Basin (Ukraine). Abstract, AAPG Hedberg Research Conference. Basin Modelling Perspectives: Innovative Developments and Novel Applications. May 2007, 3 pp.

Alsaab, D., Suarez-Ruiz, I., Elie, M., Izart, A., Martinez, L., 2007b. 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. International Journal of Coal Geology 71, 85–102.

Béhar, 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.

Béhar, 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.

Béhar, 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.

Brunner, D.J., Ponce, J.R., 1999. Methane drainage at the Minerales Monclova Mines in Sabinas Coal Basin, Coahuila, Mexico. Proceeding of the 18th US Ventilation Symposium, June 11–17, 1999, Rolla, Missouri, pp. 123–129.

Burklé-Vitzthum, V., Michels, M., Scacchi, G., Marquaire, P.-M., Dessort, D., Pradier, B., Olivier Brevart, O., 2004. Kinetic effect of alkylaromatics on the thermal stability of hydrocarbons under geological conditions. Organic Geochemistry 35, 3–31.

Chekunov, A.V., 1976. On spreading and rotation of blocks during the formation of the Dnieper–Donets aulacogen (in Ukrainian). Geological Journal 1, 119–123.

Chekunov, A.V., Garvish, V.K., Kutas, R.I., Ryabchun, L.I., 1992. Dnieper–Donets palaeorift. Tectonophysics 208, 257–272.

Clayton, J.L., 1998. Geochemistry of coalbed gas — a review. In: Flores, R.M. (Ed.), Coalbed methane: from coal-mine outbursts to a gas resource. International Journal of Coal Geology, vol. 35, pp. 159–173.

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

Derbyshire, F., Marzec, A., Schulten, H.R., Wilson, M.A., Davis, A., Tekely, P., Delpuech, J.J., Jurkiewicz, A., Bronnimann, C.E., Wind, R.A., Maciel, G.E., Narayan, R., Bartle, K., Snape, C., 1989. Molecular structure of coals: a debate. Fuel 68, 1091–1106.

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 Memoir, vol. 75, pp. 241–270.

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.

Ermakov, V.I., Skorobogatov, V.A., 1984. Formation of hydrocarbon gases in coal-bearing and subcoal-bearing (in Russian). Nedra Publ., Moscow. 205 pp.

Gentzis, T., Murray, K., Klinger, R.L., 2005. Coalbed methane potential in the Sabinas Basin, Mexico. Gussow Geoscience Conference on Coalbed-Methane, March 09–11, 2005. Alberta, Canada.

Gentzis, T., Murray, K., Klinger, R.L., Santillan, M., 2006. Horizontal degasification and characterization of coals in the Sabinas Sub-basin, Mexico: implications for CBM production. Bulletin of Canadian Petroleum Geology 54, 221–237.

Gérard, L., Elie, M., Landais, P., 1994. Analysis of confined pyrolysis effluents by thermodesorption-multidimensional gas chromatography. Journal Analytical and Applied Pyrolysis 29, 137–152.

Given, P., 1984. An essay on the organic geochemistry of coal. Coal Science 3, 65–252.

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.

Huc, A.Y., Durand, B.M., 1973. Etudes des acides humiques et de l'humine des sédiments récents considérés comme précurseurs des kérogènes. In: Tissot, B.P., Bienner, F. (Eds.), Advances in Organic Geochemistry, Technip, Paris. 53–72 pp.

Hunt, J.M., 1996. Petroleum geochemistry and geology, 2nd ed. W.H. Freeman and Company, New York. 743 pp.

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 Organization for Standardization, ISO 7404-5, 1994a. Methods for the Petrographic Analysis of Bituminous Coal and Anthracite — Part 5: Methods determining microscopically the reflectance of Vitrinite. ISO 7404-5. Geneva, Switzerland. 11 pp.

International Organization for Standardization, ISO 7404-3, 1994b. Methods for the Petrographic Analysis of Bituminous Coal and Anthracite — Part 3: Methods determining maceral group composition. ISO 7404-3. Geneva, Switzerland. 4 pp.

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.

Jüntgen, H., Karweil, J., 1966. Gasbildung und Gasspeicherung in Steinkohlenflozen, Part I and II. Erdöl und Kohle-Erdgas-Petrochemie 19 (251–258), 339–344.

Jüntgen, H., Klein, J., 1975. Entstehung von Erdgas aus kohligen Sedimenten. Erdöl und Kohle-Erdgas-Petrochemie 28, 52–69.

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. AAPG Bulletin 78, 1560–1585.

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

Law, B.E., Rice, D.D., 1993. Hydrocarbons from coal. AAPG Studies in Geology 38 Tulsa, 400 pp.

Levine, J.R., 1987. Influence of coal composition on the generation and retention of coalbed natural gas. Proceedings of 1987 Coalbed Methane Symposium, pp. 15–18.

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.

Makarov, I.A., 1990. Geological map of Donbas (1/300,000). Ukrainian Geological Ministry, PGO Donbas Geology, Artemovsk GPE.

Meissner, F.F., 1984. Cretaceous and lower Tertiary coals as sources for gas accumulations in the Rocky Mountain area. In: Woodward, J., Meissner, F.F., Clayton, J.L. (Eds.), Hydrocarbon source rocks of the greater Rocky Mountain region. Rocky Mountain Association of Geologists, pp. 401–431.

Michels, R., Enjelvin-Raoult, N., Elie, M., Mansuy, L., Faure, P., Oudin, J.L., 2002. Understanding of reservoir gas compositions in a natural case using stepwise semi-open artificial maturation. Marine and Petroleum Geology 19, 589–599.

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

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

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.

Piedad-Sanchez, N., Martinez, L., Izart, A., Suarez-Ruiz, I., Elie, M., Menetrier, C., Lannuzel, F., 2005. Artificial maturation of a high volatile bituminous coal from Asturias (NW Spain). Part II. Gas production during pyrolysis and numerical simulation. Journal Analytical and Applied Pyrolysis 74, 77–87.

Privalov, V.A., 2002. Methane in coals from Donbas (in Russian). Geologiya i Geohimiya Goryutchikh Kopalin 2, 65–83.

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

Privalov, V.A., Zhykaliak, M.V., Panova, E.A., 2003. Geologic controls on coalbed occurrences in the Donets Basin (Ukraine). Abstract, 3ed International Methane & Nitrous oxide Mitigation conference "coal Section", November 2003, Beijing China.

Privalov, V.A., Sachsenhofer, R.F., Panova, E.A., Antsiferov, V.A., 2004a. Coal geology of the Donets Basin (Ukraine/Russia). An overview. BHM 149 (6), 212–222.

Privalov, V.A., Izart, A., Sachsenhofer, R.F., Panova, E.A., Zhykaliak, M.V., Antsiferov, V.A., Alsaab, D., 2004b. Coalbed methane in Donbas (Ukraine), relationships with methane exploitation and mining outbursts. Abstract, International Science and Technology Conference, "Rock Geology, Rock Mechanics and Mine Surveying", November 2004, Donetsk, Ukraine. 8 pp.

Rice, D.D., 1993. Composition and origins of coalbed gas. In: Law, B.E., Rice, D.D. (Eds.), Hydrocarbons from coal. AAPG Studies in Geology, vol. 38, pp. 159–184.

Rice, D.D., Clayton, J.L., Pawlewicz, M.J., 1989. Characterization of coal-derived hydrocarbons and source rock potential of coal beds, San Juan basin, New Mexico and Colorado, USA. International Journal of Coal Geology 13, 597–626.

Ritter, U., Grover, A., 2005. Adsorption of petroleum compounds in vitrinite: implications for petroleum expulsion from coal. International Journal of Coal Geology 62, 183–191.

Sachsenhofer, R.F., Privalov, V.A., Zhykalyak, M.V., Bueker, C., Panova, E., Rainer, T., Shymanovskyy, V.A., Stephenson, R., 2002. The Donets Basin (Ukraine/Russia): coalification and thermal history. International Journal of Coal Geology 49, 33–55.

Sachsenhofer, R.F., Privalov, V.A., Izart, A., Elie, M., Kortensky, J., Panova, E.F., 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., 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 pp.

Santillan-Gonzalez, M.A., 2004. Potencial uso del gas Metano del carbón como Energía. Draft Report International Minerales Monclova.

Stach, E., Mackowsky, M.-Th., Teichmüller, M., Taylor, G.H., Chandra, D., Teichmüller, R., 1982. Stach's textbook of coal petrology. Gebrüder Borntraeger, Berlin. 535 pp.

Stovba, S.M., Stephenson, R.A., Kivshik, M., 1996. Structural features and evolution of the Dniepr–Donets Basin, Ukraine, from regional seismic reflection profiles. Tectonophysics 268, 127–147.

Su, K.-H., Shen, J.-C., Chang, Y.-J., Huang, W.-L., 2006. Generation of hydrocarbon gases and CO2 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. Marine and Petroleum Geology 19, 929–950.

Taylor, G.H., Teichmüller, M., Davus, A., Diessel, C.F.K., Littke, R., Robert, P., 1998. Organic Petrology. Borntraeger Berlin, Stuttgart. 704 pp.

Tissot, B.P., Califet-Debyser, Y., Deroo, G., Oudin, J.L., 1971. Origin and evolution of hydrocarbons in Early Toarcian shales. American Association Petroleum Geology 55, 2177–2193.

Triplett, T., Filipov, A., Pisarenko, A., 2001. Coal Mine methane in Ukraine: opportunities for production and investment in the Donetsk coal Basin. U.S. EPA Report, 131pp. This report is available online at http://www.peer.org.ua/Handbook/Hand_E.pdf.

Tyler, S.C., 1991. The global methane budget. In: Rogers, J.E., Whitman, W.B. (Eds.), Microbial production and consumption of greenhouse gases: methane, nitrogen oxides and halomethanes. American Society for Microbiology, Washington, D.C., pp. 7–38.

Uziyuk, V.I., Byk, S.I., Ilcthishin, A.V., 2001. Gas generation potential of Carboniferous basins of the Ukraine (in Ukrainian). Geologiya i geohimiya goryutchikh kopalin (Geology and geochemistry of fossil fuels) 2, 110–121.

Welte, D.H., Schaefer, R.G., Stoessinger, W., Radke, M., 1984. Gas generation and migration in the Deep basin of western Canada. American Association of Petroleum Geologists Memoir 38, 35–47.

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.