THERMAL AND MICROBIAL GAS GENERATION, ACCUMULATION AND DISSIPATION IN COAL BASINS:

ROLE OF SORPTIVE STORAGE CAPACITY EVOLUTION

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Summary

The regional variation of chemical and isotopic composition of coal gases has been investigated in the Upper Silesian Coal Basin (USCB), Czech Republic, and the Paraná Basin, Brazil.

The field studies were complemented by laboratory experiments on selected samples to elucidate the effects of sorption/desorption processes on the chemical and isotopic composition of coal gases. Non-isothermal open system pyrolysis (Py-GC) was used to assess the gas generation potential and kinetics for the reconstruction of gas generation history in the study areas. The experimental results were integrated into a conceptual dynamic model of gas generation and storage in coal seams during structural and thermal basin evolution.

Coal gases in the southern part of the USCB have a thermogenic isotope signature, while gases in the northern part have isotope signatures typical for microbial CO_2 reduction and mixed thermogenic/microbial origin. Chemical and isotopic compositions of gas samples from canister desorption of coal cores showed larger variations, but were generally in agreement with those of samples taken from cross-measure boreholes. Canister desorption did not cause any systematic isotope fractionation effects. Trends in geochemical composition of thermogenic gases suggest a contribution of gas from deeper parts underlying the Carpathian overthrust.

Coals from the two principal coal-bearing sequences of the USCB (paralic Ostrava Fm. and limnic Karviná Fm.) are vitrinite-rich, of high- to low-volatile bituminous rank and have mostly reached the stage of gas generation and expulsion. Using mass balance calculations the volumes of gas generated up to this coalification stage were estimated at 201 m^3 per ton of Total Organic Carbon (TOC) for methane and 138 m^3/t TOC for carbon dioxide. Cumulative pyrolytic methane yields ranged between 52 and 79 m^3/t TOC. Based on the reaction-kinetic parameters obtained from these tests thermogenic gas generation at a geologic heating rate of 10^{-11} K/min was predicted to reach a maximum between 208 and 246°C. A 1D basin model of the subsidence and thermal history of the study area indicated that major gas generation occurred at maximum burial between 319 and 285 Ma b.p. and that no significant methane generation was associated with reburial in the Miocene.

Excess sorption isotherms (up to 27 MPa) for methane and carbon dioxide under different experimental conditions showed that gas sorption capacity is mainly controlled by pressure, moisture content and temperature, whereas organic matter content and maturity have a lesser impact. The average methane sorption capacity of USCB coals of 15 m^3/t was significantly higher than the present-day gas contents in the study area (< 2 - 10 m^3/t). Correlations between sorption capacity, coal rank and temperature were derived from sorption experiments and used in combination with geological pressure and temperature data.

A static model assuming present-day pressure and temperature gradients predicts an increase in sorption capacity with increasing depth towards a maximum value between 600 and 1000 m, followed by a decrease due to increasing temperature.

Results from 1D burial history and temperature history modeling were integrated with experimental results to reconstruct the dynamic evolution of sorption capacity during basin history in relation to thermal gas generation. These computations revealed that the sorption capacity of the coals at maximum burial depth was significantly lower than estimated based on present-day pressure and temperature gradients. At the time of maximum gas generation, the amount of generated gas exceeded the sorption capacity of coals and the excess gas was expelled. Uplift started at the Carboniferous/Permian transition and the concomitant temperature decrease resulted in the presently observed under-saturation of the coal seams. From the end of the Permian uplift phase until present, coal seams of the Karviná formation were at temperatures below 80°C and thus amenable to microbial methane generation. In contrast, temperatures of coal seams of the Ostrava formation were significantly higher in the post-uplift phase and microbial methane generation from these coals was unlikely.

Coal from the Santa Terezinha coalfield in the southern Paraná Basin, Brazil had a significantly lower residual gas generation potential than USCB coals. Gas contents and average gas sorption capacities were also lower. Methane and carbon dioxide sorption capacities of coals and shales correlated with the TOC. For CO_2 the linear regression showed a non-zero intercept, indicating a significant sorption capacity of the mineral matter. The present-day gas content of coals from the Santa Terezinha coalfield amounts to 13 – 38% of the methane sorption capacity. Assuming sorption capacities at reservoir conditions theoretically an amount of up to 15.4 Gt CO_2 could be stored in the Santa Terezinha coal seams, if all methane were produced prior to CO_2 injection.

Zusammenfassung

Regionale Unterschiede in der chemischen und isotopischen Zusammensetzung von Flözgasen wurden im Oberschlesischen Becken (USCB) in Tschechien und im Santa Terezinha Kohlefeld (STC) des Paraná Beckens in Brasilien untersucht.

Geländestudien wurden durch Laborexperimente an ausgewählten Proben ergänzt um den Einfluss von Sorptions- und Desorptionsprozessen auf die chemische und isotopische Zusammensetzung von Flözgas zu untersuchen. Unter Einsatz von nicht-isothermer, offener Pyrolyse (Py-GC) wurden Gasbildungspotenzial und Kinetik zur Rekonstruktion der Gasbildungsgeschichte ermittelt. Experimentelle Ergebnisse wurden in ein konzeptionelles dynamisches Modell zur Bildung und Speicherung von Gas in Kohlenflözen während der strukturellen und thermischen Beckenentwicklung integriert.

Flözgas aus dem südlichen USCB weist eine thermogene Isotopensignatur auf, während die Signatur im nördlichen Bereich auf mikrobielle CO_2 Reduktion und eine Mischung von Gasen thermogenen und mikrobiellen Ursprungs hindeutet. Die chemische und isotopische Zusammensetzung von Gasen die während der Kanisterdesorption beprobt wurden, war stark Variabel aber grundsätzlich ähnlich der Zusammenstzung von Gasen aus Flözentgasungsbohrungen. Während der Kanisterdesorption wurden keine eindeutigen Isotopenfraktionierungseffekte beobachtet. Trends in der geochemischen Zusammensetzung thermogener Gase im USCB lassen einen Beitrag von Gas aus tieferen Bereichen unterhalb der Karpathenüberschiebung vermuten.

Kohlen der zwei hauptflözführenden Formationen im USCB (paralische Ostrava Fm. und limnische Karviná Fm.) sind Vitrinit-reiche Gasflamm- bis Esskohlen die überwiegend das Stadium der Gasbildung und Gasfreisetzung erreicht haben. Aus Massenbilanzrechnungen konnte ein während der Inkohlung gebildetes Methanvolumen von 201 m^3/t organischen Kohlenstoffs (TOC) und ein CO_2-Volumen von 138 m^3/t TOC abgeschätzt werden. Die kumulative im Pyrolyseexperiment freigesetzte Methanmenge lag zwischen 52 und 79 m^3/t TOC. Aus experimentell bestimmten reaktionskinetischen Parametern wurde ermittelt dass die thermogene Gasbildung bei einer geologischen Aufheizrate von 10^{-11} K/min in einem Temperaturbereich zwischen 208 und 246°C ihr Maximum findet. Ein 1D Beckenmodell der Subsidenz- und Temperaturgeschichte des USCB deutet darauf hin dass die Hauptgasbildung während der maximalen Versenkung zwischen 319 und 285 Ma b.p. stattfand und es zu keiner signifikante Gasbildung im Zusammenhang mit der Wiederversenkung im Miozän kam.

Exzess Sorptionsisothermen (bis zu 27 MPa) für Methan und CO_2 unter verschiedenen experimentellen Bedingungen zeigten dass die sorptive Speicherkapazität hauptsächlich von Druck, Wassergehalt und Temperatur abhängt und in geringerem Maße von TOC und Reife beeinflusst wird. Die mittlere Sorptionskapazität im USCB (15 m^3/t) liegt deutlich über dem heutigen Gasgehalt der Kohlen (<2 – 10 m^3/t). Korrelationen zwischen Sorptionskapazität, Inkohlungsgrad und Temperatur wurden experimentell ermittelt und mit geologischen Druck- und Temperaturdaten kombiniert. Bei Annahme heutiger Druck- und Temperaturgradienten ergibt ein statisches Modell dass die Sorptionskapazität mit zunehmender Teufe bis zu einem Maximum zwischen 600 und 1000 m ansteigt und anschließend aufgrund steigender Temperaturen wieder absinkt.

Resultate einer 1D Modellierung der Versenkungs- und Temperaturgeschichte wurden mit experimentellen Ergebnissen integriert um die Entwicklung der Sorptionskapazität zusammen mit der thermischen Gasbildung während der Beckengeschichte zu rekonstruieren. Diese Berechnungen zeigten dass die Sorptionskapazität der Kohlen bei maximaler Versenkungstiefe deutlich niedriger lag, als die mit heutigen Druck- und Temperaturgradienten berechnete. Während der maximalen Gasbildung überstieg die gebildete Gasmenge die Speicherkapazität der Kohlen und überschüssiges Gas entwich. Die am Karbon-Perm Übergang einsetzende Hebung und die daraus resultierende Abkühlung bewirkte die heutige Gas-Untersättigung der Flöze. Seit dem Ende der Permischen Hebungsphase lagen Flöze der Karviná Fm. in einem

Temperaturbereich der mikrobielle Gasbildung ermöglichte (<80°C). Im Gegensatz hierzu lagen die Temperaturen der Ostrava Fm. nach der Hebungsphase deutlich höher und mikrobielle Gasbildung war unwahrscheinlich.

Kohlen aus dem Santa Terezinha Kohlefeld weisen ein deutlich niedrigeres Gasbildungspotenzial auf als Kohlen aus dem USCB. Gasgehalt und Sorptionskapazität sind ebenfalls niedriger. Die Korrelation der Methan und CO_2 Sorptionskapazität brasilianischer Kohlen und Brandschiefer mit dem TOC-Gehalt deutet auf eine signifikante CO_2 Sorptionskapazität der Mineralsubstanz hin. Heutige Gasgehalte im STC liegen zwischen 13 und 38% der Methan Sorptionskapazität. Bei Annahme der Sorptionskapazität unter Reservoirbedingungen lässt sich eine theoretische Menge von bis zu 15.4 Gt CO_2 in Flözen des STC speichern, wenn vor der CO_2 Injektion das gesamte Flözgas gefördert wird.

Symbols and Abbreviations

A	pre-exponential factor
A	area (chapter 5)
α_{a-b}	isotopic fractionation factor *e.g.* $((\delta^{13}C_a + 10^3) / (\delta^{13}C_b + 10^3))$
AMM	abandoned mine methane
ASTM	American Society for Testing and Materials
BI	bitumen index [mg HC/g TOC]
b.p.	before present
C_{2+}	gaseous hydrocarbons with more than two carbon atoms
C	concentration
C	completion factor (chapter 5)
CBM	coalbed methane
CCS	carbon capture and storage
CHP	combined heat and power
CMM	coal mine methane
CSG	coal seam gas
δD	stable hydrogen isotopic composition (‰)
$\delta^{13}C$	stable carbon isotopic composition (‰)
Δ	isotopic difference, isotopic separation (*e.g.* $\delta^{13}C_a - \delta^{13}C_b$) (‰)
daf	dry, ash-free
DIN	Deutsche Industrie Norm
E_a	activation energy
ECBM	enhanced coalbed methane production
EOS	equation of state
ER	exchange ratio
ESG	enhanced shale gas production
FID	flame ionization detector
GC	gas content
GIP	gas in place
HC	hydrocarbons

HI	hydrogen index [mg HC/g TOC]
ICCP	International Committee for Coal and Organic Petrology
IGIP	initial gas in place
IUPAC	International Union of Pure and Applied Chemistry
k	reaction rate constant
mBtu	million British thermal units
n	molar amount
n_{ads}	molar amount of adsorbed gas
n_{max}	maximum measured sorption
n_L	Langmuir sorption capacity
OI	oxygen index [mg HC/g TOC]
OKC	Ostrava – Karviná Coalfield
P	pressure
P_L	Langmuir pressure
PGIP	producible gas in place
ppm	parts per million
Py-GC	pyrolysis coupled to gas chromatography
QI	quality index [mg HC/g TOC]
q_{st}	isosteric heat of adsorption
R	universal gas constant = 8.3145 $m^3 \cdot Pa/(mol \cdot K)$
RF	recovery factor
RS	Rio Grande do Sul
$\rho_{adsorbed}$	density of adsorbed phase
ρ_{gas}	gas density
scf	standard cubic feet
SCO_2	storage capacity for CO_2
T	temperature
T_{max}	temperature of maximum hydrocarbon generation rate
t	time
$\tau_{1/2}$	half-life

TCD	thermal conductivity detector
TCF	trillion cubic feet
TFRR	thermal oxidation by flow reversal reactor
TH	thickness (m)
TIC	total inorganic carbon (wt. %)
TOC	total organic carbon (wt. %)
TST	transition state theory
TVD	true vertical depth (m)
TR	transformation ratio
USCB	Upper Silesian Coal Basin
V_{CH4}	volume of methane
VM	volatile matter yield (wt. %)
VMM	ventilation mine methane
VPDB	Vienna Pee Dee Belemnite (stable carbon isotope standard)
VR	vitrinite reflectance (%)
VRc	calculated vitrinite reflectance (%)
VRr	vitrinite reflectance measured in random mode (%)

Units and Conversions

J	Joule ; 1 kJ = 4.184 kcal
°C	degrees Celsius
K	Kelvin ; 0°C = 273.15 K
ft^3	cubic foot ; 1 ft^3 = 0.028 m^3
Pa	Pascal ; 100kPa = 1 bar
psi	pound per square inch ; 1 psi = 6.894 kPa
t	metric ton ; 1 t = 10^6 g
scf/t	standard cubic feet per ton

IUPAC standard conditions T = 273.15 K (0 °C); P= 100000 Pa

1 mmol/g = 22.71 std. m^3/t = 802.03 scf/t (using IUPAC standard conditions)

1 mmol/g = 23.69 std. m^3/t (using T = 15.56°C = 60°F and P = 101.325 kPa)

1mmol/g = 922.16 scf/t_s

(using T = 15.56°C = 60°F; P = 101325 Pa and short ton (t_s), 1 t_s = 907185 g)

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1. Introduction

The past two decades have seen significant changes in the global energy supply from fossil fuels. While many, if not all, oil producing countries passed peak production rates, oil and gas prices have increased drastically. This led to increased exploration and production activities for unconventional resources, such as coalbed methane (CBM) and more recently, shale gas. On the one hand, technological improvements enabled production of these resources, which often occur in deep and low-permeable reservoirs, *e.g.* by reservoir stimulation techniques, such as hydraulic fracturing. On the other hand, these unconventional resources are characterized by a more evenly global distribution as compared to conventional oil and gas reserves, of which more than 50% are located in the Middle East alone. Increased production of unconventional gas has led to significant changes in gas supply for some countries. For the United States, proven CBM resources of 19 trillion cubic feet (TCF) and estimated resources of 158 TCF (EIA, 2007) and even larger shale gas resources (687 TCF, OPEC, 2011) are reported. Production of these unconventional gas resources increased significantly during the last 10 years and now accounts for 30% of US gas production, resulting in a decrease in gas price from 13$/ million British thermal units (mBtu) in 2006 to less than 4$/mBtu in 2011 (OPEC, 2011). These developments and an increasing global energy demand led to predictions that the role of gas (conventional and unconventional) for the global primary energy supply will see a steady increase within the next decades (BP, 2011; OPEC, 2011). Some organizations even predict that the world might face a "golden era for gas" (IEA, 2010). However, unconventional gas resources are associated with significant geologic and technical uncertainty regarding their reserve assessment. Production of coalbed methane has been successful in the US, Canada, Australia and China and other countries, whereas in European coal basins, economic production of CBM has not been possible until now. Low or highly variable gas contents, low permeability of coal seams and also compositional variation of the coal related gas are some of the reasons why CBM exploration and production was problematic and less successful in Europe and other countries. This led to an increasing scientific interest in methane and its role in geologic and biologic processes influencing generation, migration and accumulation of coal related gas. Scientific interest is also driven by environmental concerns, raised by increasing greenhouse gas emissions that are associated with coal basins and coal mining. Methane (CH_4), water vapour and carbon dioxide (CO_2) are the most abundant greenhouse gases and affect the global climate change. Several case studies have proven that methane and CO_2 are often genetically linked in the subsurface due to microbial activity, which modifies the chemical and isotopic signature of the natural gases. Differentiation among the various sources of emissions related to coal seam gas, oil and gas fields, microbial CO_2 reduction, and methane oxidation requires additional research (Thielemann et al., 2000, 2001, 2004; IPCC, 2005). Comprehension of geochemical and microbiological processes involved in natural gas habitats and compositions within the geosphere provides the key to understanding atmospheric CH_4 change (Whiticar 1990).

The present work presents results of a bilateral research project that was aimed to improve the understanding of generation, migration and dissipation of coal-related gas in the course of the geological history of sedimentary basins, with special consideration of the influence of sorption and desorption processes on the compositional and isotopic signature. The main study area of this project was the SW Upper Silesian Basin in Czech Republic, which was chosen as a 'natural laboratory'. In this basin the occurrence of gases of both, thermal and microbial origin has been documented in previous studies (Buzek et al. 1999a, b; Franců et al., 2007). Additionally, a coal field from the Paraná Basin, Brazil was studied, where CBM and shale gas resources and potential carbon dioxide sequestration in unminable coal seams are currently under evaluation.

1.1. Coal related gas

Methane is formed either during thermal maturation of coals and kerogen in deeper zones of sedimentary basins or due to microbial activity in soils and at depth up to several hundred meters and temperature up to 75-85 °C (Schoell, 1980; Tissot and Welte 1984; Schoell, 1983, 1988 and Whiticar, 1990, 1996). About 6% of global methane emissions originate from coal mining activities (USEPA, 2006). Additionally, considerable methane flux to the atmosphere occurs from agriculture, mainly flooded rice fields and ruminant manure (Thielemann, 2004; IPCC, 2005). Different genetic types of methane are distinguished from one another by isotopic composition of carbon and hydrogen in combination with the molecular composition (Schoell, 1988; Whiticar, 1990, 1996). In general, thermogenic gas is isotopically heavy and wet (rich in C_{2+} hydrocarbons), when associated with oil, or dry, i.e. poor in C_{2+} hydrocarbons, when generated from highly mature coals. Bacterial gas is isotopically very light and contains almost no C_{2+} hydrocarbons. The deuterium content (δD) is used to distinguish between methane formed by acetate fermentation, *e.g.* in liquid manure, and by bacterial CO_2 reduction.

Coal related gases are classified into:

1. *Coalbed methane* (CBM) (termed coal seam gas (CSG) in Australia), produced from boreholes in unworked and hydrodynamically fractured coal beds

2. *Coal mine methane* (CMM) released in active collieries

3. *Abandoned mine methane* (AMM) which escapes or is extracted from abandoned mines.

Coalbed methane

Coalbed methane is often found in significant quantities, either within coal seams itself, but also in the surrounding rock formations. CBM is trapped underground as free gas in the pore space and as adsorbed gas on the micropore surface of coal, which is rank dependant and often in the range of several hundred square meters per gram. The amount of adsorbed gas in coal is approximately 28 times the volume of coal at standard pressure and temperature (Cervik, 1969). Coalbed methane is generally not released into the atmosphere until it is liberated, *e.g.* by mining activities. Depending on the depth of the seams and the petrophysical properties of the coal (porosity, permeability, water-saturation) this gas can be produced economically, however, production often requires reservoir stimulation, such as hydraulic fracturing, to improve permeability.

Coalmine methane

Historically, coal mine methane has been considered as a nuisance rather than a resource. During coal mining activities, methane contained in coal seams is released into the coalmine itself. This poses a potential safety hazard because methane concentrations between ca. 4 and 16% in air form explosive mixtures and above 16% the oxygen-deficient atmosphere may cause suffocation. While modern coal mines are equipped with ventilation systems ensuring that methane concentrations in the workings are kept below 1%, firedamp explosions during underground coal mining activities remain a major hazard causing significant casualties, especially in China but also in other countries. In coal mines where gas-rich coal is produced, additional pre-mining gas extraction is used to reduce the methane concentration. Methane concentrations from such a mineface extraction are often high enough for energy production, *e.g.* by gas power plants or smaller combined heat and power (CHP) units. The ventilation mine methane (VMM) is mostly vented into the atmosphere, but recent technologies emerged, such as thermal oxidation using a flow-reversal reactor (TFRR), which enable conversion of methane to CO_2 in order to reduce greenhouse gas emissions (Somers and Schulz, 2008). By integrating CMM capture into the mining strategy it is now possible to utilize >90% of the coalmine methane for energy production (Stöttner, 2003)

Abandoned mine methane

The decline in coal-mining activities in Western and Central Europe during the past decades has resulted in a large number of abandoned mines. From these mines considerable amounts of methane may leak to the atmosphere over extended periods of time. The intensity and duration of this leakage process depends on the rate at which the mines are flooded by inflowing groundwater. One example of hazardous AMM leakage occurred in Czech Republic in the early 1990s. During a period of mine closure in the Ostrava-Karviná Coalfield (Upper Silesian Coal Basin) that followed the collapse of the communist regime in former Czechoslovakia, uncontrollable methane emissions to the surface occurred, caused by the termination of mine ventilation and water pumping (Martinec and Schejbalova, 2004). Where methane emissions penetrated buildings in the Ostrava area, gas explosions took place, causing fatal injuries. Currently, AMM is utilized in several European countries for thermal or electrical energy production, partly under emission-reduction schemes.

1.2. Upper Silesian Coal Basin (USCB)

An overview of geology, structural evolution, and coal resources of the study area has been given by Dopita et al. (1997). Methane is reported to occur in three major structural zones: 1) primary source zone, 2) degassed zone in the upper part of the Carboniferous, and 3) secondary accumulations of methane gas in the weathered crust of the Carboniferous and in overlying Miocene reservoirs (Martinec, 1999).

In previous geochemical studies a substantial amount of analytical data has been compiled on the chemical and isotopic composition of coal-related gases in the study area (Buzek et al. 1999a, b; Francŭ et al., 2007).

It is evident from these previous studies that both, microbial and thermal gas is encountered in the Czech part of the Upper Silesian Basin. While methane with microbial isotope signature occurs mainly in the northern section of the study area, the southern area is characterised by thermogenic methane. The distribution of the methane types follows neither stratigraphy, nor the thermal maturity of the coal seams. More systematic research is necessary to elucidate the influence of hydrology, isolation by impermeable seals in the overburden, human activities such as coal mining, and mine ventilation on the microbial coal oxidation, CO_2 reduction, and methane oxidation.

1.3. Chapter 2: Geochemical and stable carbon isotopic composition of coal related gases from the SW Upper Silesian Coal Basin, Czech Republic

Chapter 2 presents results of gas analyses carried out to investigate composition and origin of coal related gas in the Czech part of the Upper Silesian Coal Basin. In the course of these studies, a range of gas samples from mine face extraction in different underground coal mines were analyzed. Additionally, gas samples obtained during canister desorption experiments, which are routinely performed by coal mines in the OKC to determine gas contents, were analyzed. Most of these gas analyses were performed by the Czech Geological Survey. Results of chapter 2 were presented at the international meeting on organic geochemistry (IMOG 2011) and are published in Organic Geochemistry by Weniger et al. (2012).

1.4. Chapter 3: Gas generation from bituminous coals of the Upper Silesian Coal Basin, Czech Republic and the Paraná Basin, Brazil

Chapter 3 presents results of non-isothermal open system pyrolysis experiments that were performed to evaluate the hydrocarbon generation potential of coals from the USCB. Analysis comprised Rock-Eval pyrolysis measurements for 30 coal samples from coal seams of different stratigraphic units in the USCB. Additionally, temperature-programmed open system pyrolysis coupled to gas chromatography (Py-GC) was carried out on 6 selected coal samples from the UCSB and one coal sample from the Paraná Basin, Brazil. These pyrolysis experiments were performed to determine reaction kinetic parameters, which were used to extrapolate laboratory gas generation to geologic conditions in order to estimate the thermogenic gas generation during basin evolution of the USCB. Results of Rock-Eval pyrolyses presented in chapter 3 were published in proceedings to the annual meeting of the German Society for Petroleum and Coal Science and Technology (DGMK) (Weniger et al., 2011a). Results of pyrolysis experiments of the Brazilian coal are part of a publication submitted to AAPG Bulletin (Kalkreuth et al., submitted). Parts of the results of Py-GC of coal from USCB are published in the International Journal of Coal Geology by Heim et al. (2012).

1.5. Chapters 4 and 5: Investigations on the methane and carbon dioxide sorption capacity of coals from the SW Upper Silesian Coal Basin, Czech Republic and the Paraná Basin, Brazil

Chapter 4 and 5 presents results of high-pressure methane sorption experiments carried out to determine the sorptive storage capacity of coal samples from the Upper Silesian Coal Basin (Czech Republic) and the Paraná Basin (Brazil). Additional sorption experiments were performed using carbon dioxide to evaluate the potential for carbon dioxide sequestration in unmined coal seams (CCS) and CO_2 enhanced coalbed methane production (CO_2-CBM). The aim of these sorption studies was to evaluate influence and controls of different reservoir parameters (pressure, temperature, water saturation) and coal properties (coal rank, petrographic composition, amount and composition of mineral matter) on the gas storage capacity.

Upper Silesian Coal Basin, Czech Republic

Chapter 4 presents results from extensive sorption tests on 30 coal samples from different coal mines in the Ostrava-Karviná Coal District, covering almost the entire stratigraphic range of Carboniferous coal seams in the Czech part of the USCB. Samples from one mine (ČSM) were selected because they are of similar rank but differed in age and maceral composition and thus allowed evaluation of these factors. Other samples covered a wide range in coal rank and were used to evaluate rank dependence of gas sorption.

This chapter represents a manuscript by Weniger et al. (2012), published in the International Journal of Coal Geology in 2012.

Paraná Basin, Brazil

Chapter 5 presents results from methane and carbon dioxide sorption experiments carried out on coal samples from the Santa Terezinha coalfield, located in the SW Paraná Basin, Brazil. This work was performed to analyse the influence of different controlling factors on sorption capacities and to evaluate the methane and carbon dioxide storage capacity of coals from the Santa Terezinha coalfield. One aim of this study was to evaluate controls on sorption capacity for coals of different geologic age, formed under significantly different paleoenvironmental conditions as compared to coals from the USCB. This study also includes an evaluation of CO_2 storage in the Santa Terezinha coalfield, which is currently under investigation by different research groups and petroleum companies in Brazil.

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2. Geochemical and stable carbon isotopic composition of coal related gases from the SW Upper Silesian Coal Basin, Czech Republic

Geochemical and stable carbon isotopic composition of coal-related gases from the SW Upper Silesian Coal Basin, Czech Republic

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2.1. Abstract

Gas associated with Carboniferous coal seams and younger Miocene sediments in the SW Upper Silesian Basin in Czech Republic shows wide compositional variation. Coal-related gas extracted from cross-measure degassing boreholes, as well as gas released during canister desorption of coal samples from three different mines was analyzed to evaluate the genetic origin and the influence of sorption / desorption processes on the gas composition. Analyses comprised the compositional and stable carbon and isotope composition of coal-related gases. The isotopic composition of gas from cross-measure boreholes indicates thermogenic origin in the southern part of the basin and microbial CO_2 reduction and mixed type origin in the northern part. Gas from canister desorption shows similar origins, but larger compositional and isotopic variation. No consistent isotopic fractionation due to desorption could be observed. Differences in geochemical composition of thermogenic gases could indicate a contribution of gas migrated from deeper parts below the Carpathian overthrust.

2.2. Introduction

Worldwide coal deposits are associated with the occurrence of gas, which is most commonly composed of variable amounts of methane, carbon dioxide and nitrogen. Methane is primarily generated during coalification, but also through anaerobic microbial activity in coal seams (Rice, 1993). Microbial coalbed methane has been found in major coal basins in the U.S., Europe, Asia and Australia (Strapoc et al., 2006, 2011). Especially in underground mines methane represents a major safety hazard and its concentration has to be controlled by ventilation. Coal mine methane (CMM) is released during underground and surface mining operations as well as during post-mining activities and from abandoned mines. It can also migrate from unmined coal seams to the surface by diffusion or transport through natural faults. When released to the atmosphere, methane acts as a potent greenhouse gas. About 6% of global methane emissions originate from coal mining activities (USEPA, 2006). Methane represents an important energy source when extracted during coal mining as mine gas or gob gas, as well as during post-mining activities from abandoned mines. Coalbed methane (CBM) from unmined coal seams also represents an unconventional hydrocarbon source, if efficient extraction is possible. Carbon dioxide, which also acts as a greenhouse gas in the atmosphere, has been observed in certain coal seams. It can be of magmatic origin but may also be produced by chemical or microbial oxidation in active and abandoned coal mines, where oxygen is

present. Knowledge of the genetic origin of coal-related gas is important for the correlation of surface emissions with potential gas sources and the understanding of gas migration pathways.

2.2.1. Study area

The Upper Silesian Coal Basin (USCB) is one of Europe's major hard coal basins. It is located at the eastern edge of the Variscan Bohemian Massif, representing the eastern extension of the Moravo-Silesian Basin (*Fig. 2.1*). The NW part of the USCB is covered by the Miocene Carpathian Foredeep. The SE part is buried below nappes of the Carpathian overthrust belt (Silesian and Subsilesian units). The USCB occupies a known area of more than 7000 km^2, of which more than two thirds are located in Poland, whereas the southern part of the basin, the Ostrava-Karviná coalfield (OKC), with a known area of 1550 km^2, is situated in NE Czech Republic (Sivek et al., 2003). In this region coal mining has been carried out for more than 200 years. Economically important coal reserves occur within Upper Carboniferous siliciclastic, molasse-type sediments of the Ostrava Formation (Namurian A, paralic facies) and Karviná Formation (Namurian B, C and Westphalian, limnic facies). Most coal bearing strata of the OKC are of Namurian A-C age (Fig. 2.2). More than 250 coal seams with a cumulative thickness of 150 m were identified at depth between 480 and 1200 m. Thermogenic gas generation from these coal seams took place during and after Late Carboniferous burial. Laboratory pyrolysis of Carboniferous coals of the German Ruhr Basin yielded methane volumes in excess of 38 m^3 per ton of coal (Jüntgen and Karweil, 1966; Krooss et al., 1995). Mass balance approaches predict even larger volumes (180-200 m^3/t coal). Similar results were obtained for coals of the OKC (Weniger et al., unpublished results). Present day gas contents of coals in the OKC indicate that during the post-Carboniferous period of erosion and the lack of an effective seal, a significant part of the thermogenic gas was lost due to migration to the surface. The emplacement of Carpathian nappes in the southern OKC as well as deposition of sediments of the outer Carpathian foredeep 12-15 million years ago and deposition of Quarternary sediments formed a seal, below which hydrocarbon gases accumulated (Martinec and Schejbalová, 2004). Low maturities of coal seams, found Below the Carpathian nappes, render a new onset of the coalification process and associated secondary thermogenic gas generation unlikely (Kotarba, 2001). A simplified map of Carboniferous geology of the OKC is given in *Fig. 2.1* and a stratigraphic overview is shown in *Fig. 2.2*.
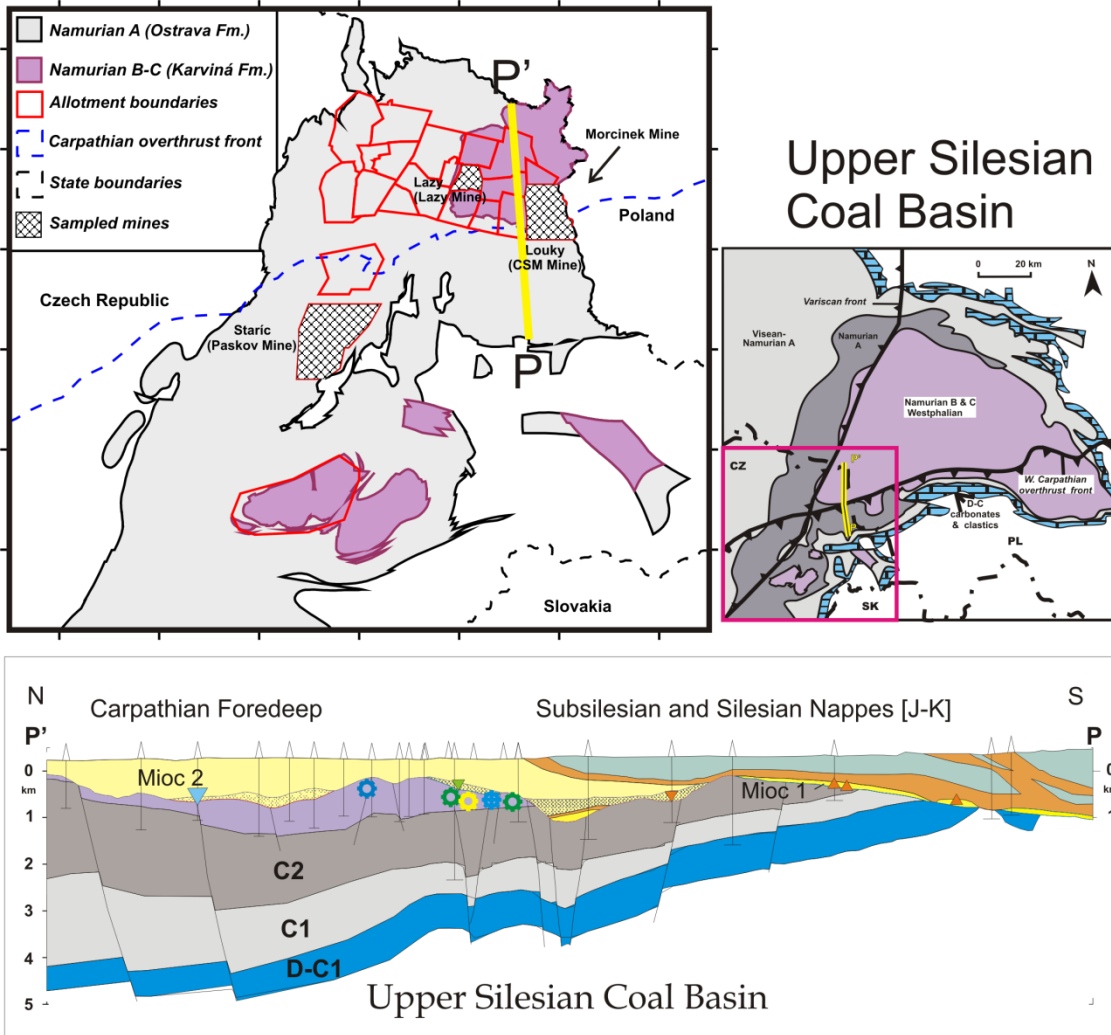
Fig. 2.1 Location of the study area in the SW Upper Silesian Basin, Czech Republic (adapted from Sivek et al., 2003) and PP' section (adapted from Menčík et al. 1983).

					Czech Republic			Samples
								mineface ⊖
								desorbed ⊕

Pennsylvanian	Bashkirian	Westphalian				Czech Republic		Samples
		Westphalian **B** 311.7 Ma				Eroded		
		A 316.5 Ma		Upper	Karviná Formation	Doubrava Member — Seam 962 — Seam 702		
		C	**G**	Lower		Suchá Member — Seam 686 — Seam 605		⊖
		B 318.1 Ma	**R**			Saddle Member — Seam 564 — (Prokop) Seam 504		⊕⊕⊕⊕ ⊖
Mississippian	Serpukhovian	Namurian	**H**			Hiatus		
		A	**E₂**	Upper	Ostrava Formation	Poruba Member — Seam 499 — Seam 403		⊕
						Jaklovec Member — Seam 385 — Seam 301		
			E₁	Lower		Hrušov Member — Seam 255 Upper — Seam 201 — Seam 169 Lower — Seam 102		
		326.5 Ma				Petřkovice Member — Seam 099 — Seam 009		⊖ ⊕⊕

Fig. 2.2 Stratigraphic overview of the Ostrava Karviná Coalfield (modified from Sivek et al., 2003).

2.2.2. Coal-related methane in the OKC

The gas content of coal-bearing sequences in the Czech part of the USCB mostly ranges between 2 m^3/t and 10 m^3/t and shows an overall decline with increasing depth (Hemza et al., 2009). The occurrence of methane in the OKC is related to the Carboniferous paleotopography, coal rank and permeability of overlying sediments as well as zones of intense faulting (Martinec and Schejbalová, 2004). To reduce the hazard of explosive methane-air mixtures in coal mines the methane is emitted by controlled mine ventilation and also extracted by controlled gas drainage for methane utilization. Between 1965 and 1997, 20 x 10^9 m^3 have been produced

during coal mining. More than two thirds of this gas was emitted through mine air systems (Martinec and Schejbalová, 2004). During the last decade utilization of coal-related methane has been intensified and today extracted coal mine methane (CMM) from five active mines supplies combined heat and power (CHP) units. Abandoned mine methane (AMM) is produced from abandoned shafts and wells. During the 1990s the potential for coalbed methane production (CBM) from virgin coal seams has been evaluated. CBM resources from coal seams deeper than 1200 m were estimated to range between 50-370 x 10^9 m^3 (USEPA, 2005). However, CBM production tests in the OKC did not prove to be economic.

2.2.3. Previous studies on the origin of hydrocarbon gases in the OKC

Possible source for gases in the OKC include humic, type III organic matter of the Ostrava and Karviná Formations, but also the Menilite Formation of the deeper Carpathian Flysch Belt, which is also the main source rock for oil in the NE Czech Republic and in Poland (Franců et al., 1996; Krejčí et al., 1996; Köster et al., 1998). Miocene sediments of the Carpathian Foredeep are immature and did not generate hydrocarbons in significant amounts. Oil and gas reservoirs are located at different stratigraphic levels.

Several studies have been carried out by the Czech Geological Survey (CGS) to evaluate the origin of hydrocarbon gases in the OKC. These studies comprised analyses of gas samples from numerous boreholes, *e.g.* in Micoene sediments of the Carpathian Foredeep (Badenian, Karpatian), Devonian and Carboniferous sediments (Culm and Devonian to Carboniferous carbonates), sediments of the Carpathian overthrust, as well as the crystalline basement. Additionally, gas from active and abandoned coal mines was analyzed (Bůzek et al., 1999; Franců et al., 2007).

Based on the results of these studies the USCB was divided into the following gas-geochemical systems: (1) Upper Carboniferous coal-bearing strata in front of and below the Carpathian overthrust, (2) abandoned workings in coal mines of the OKC and (3) Lower and Middle Miocene sediments and Carpathian overthrust. Geochemical and stable isotope analyses showed evidence of the co-occurrence of several different gases in the OKC. Microbial gas (^{13}C depleted, dry gas (δ^{13}C-CH$_4$ from -80‰ to -50‰) is associated with coal seams of the Karviná Formation, where infiltration of freshwater occurred as deep as 500 m. Microbial gas also occurs in Middle Miocene sediments (Badenian), where it is probably related to CO$_2$ reduction.

Thermogenic gas (less ^{13}C depleted, wet gas (δ^{13}C-CH$_4$ -49‰ to -33‰) occurs in coal beds of the Ostrava Formation and Lower Miocene sediments (Karpatian) sealed by Silesian and Subsilesian nappes. Oxidized microbial and thermogenic gases occur in the abandoned and active mine workings.

The absence of a relationship between gas composition and stratigraphy or thermal maturity of associated coal beds suggests that the gases do not represent the original coalification pattern in the USCB and that the coal seams are rather reservoirs than source rocks. Kotarba (2001) made similar observations in the Polish part of the USCB. Kandarachevová et al. (2009) report that the occurrence of gas accumulations found in Carboniferous rocks and overburden strata in the OKC is spatially related to zones of elevated thermal maturity.

Thermal modelling suggests that the recent hydrocarbon generation and migration from below the deeper parts of the Carpathian Flysch Belt is possible. Miocene thrusting, burial and heating may have affected the coal sorption properties and induced local sorbed gas redistribution (Krejčí et al., 1996; Franců et al., 1999, 2002).

2.3. Samples

For this study gas samples were collected by GreenGas DPB from three different coal mines (ČSM, Lazy and Paskov-Staříč) in the SW USCB in Czech Republic between 2006 and 2008. From each coal mine, coal-related gas was sampled from cross-measure boreholes, as well as during canister desorption of coal samples from exploration wells.

Gas samples were collected from three subhorizontal cross-measure degassing boreholes drilled for safety reasons prior and during coal extraction. Six samples were collected during 28 days of gas extraction at Paskov mine, three in 12 days at ČSM South, and seven samples in 25 days at ČSM North (*Appendix I, Table 1*).

During exploration drilling operations by GreenGas DPB in areas of active mines in the Ostrava-Karviná coal district, the gas content of coal cores was evaluated by canister desorption. Desorbed gas was collected for periods of up to 35 days. For each canister between 1 and 4 gas samples (average of 3) were obtained at different intervals. A total of 49 gas samples from individual desorption experiments of coals from 15 different wells were analyzed. A list of all analyzed desorbed gas samples is given in *Appendix I, Table 2*.

2.4. Methods and experimental procedures

Canister desorption experiments were performed by GreenGas DPB, Paskov following recommended procedures of the US Bureau of Mines (USBM) (Kiessell et al., 1973) and Gas Research Institute (GRI) (McLennan et al., 1995). Lost gas was estimated using the USBM "straight line" method. Desorbed gas was measured after placing coal samples into desorption canisters at reservoir temperature and atmospheric pressure. Residual gas contents were measured after crushing of coal samples in an air-tight ball mill. The total gas content was calculated as the sum of lost gas, desorbed gas and residual gas. Gas contents were converted to volumes at standard conditions (273 K, 101.325 kPa) and reported as m^3/t "as-received" coal in this study.

The molecular composition of desorbed and extracted gas was determined at CGS, Brno by conventional gas chromatography (GC). The detection limits were 0.2 ppm for hydrocarbon gases, 10 ppm for helium, 20 ppm for hydrogen and 100 ppm for CO, CO_2, N_2 and O_2. The chemical gas composition is given in volume % or ppm on an air-free basis.

The stable carbon isotopic composition of CH_4 and CO_2 was determined at the CGS laboratory in Prague using a Finnigan MAT 251 mass spectrometer following on-line combustion. Carbon isotope data are given relative to the VPDB standard as $\delta^{13}C = (R_{sample}/R_{standard} - 1000)$. Reproducibility of $\delta^{13}C$ determinations was better than ±0.3‰. The isotopic difference is given as $\Delta = \delta^{13}C_e - \delta^{13}C_s$, with e = end of desorption and s = start of desorption. Carbon isotopic fractionation factors are given as $\alpha_{a-b} = (\delta^{13}C_a + 10^3)/(\delta^{13}C_b + 10^3)$, with a = CH_4 and b = CO_2.

2.5. Results

2.5.1. Gas from cross-measure safety degassing

2.5.1.1. Molecular gas composition

Gas sampled from boreholes during cross-measure degassing contained significant amounts of air. Since it is very unlikely that coal gases contain large amounts of free oxygen, the gas composition was calculated to the air-free basis by setting the oxygen content to zero and

subtracting the amount of nitrogen (atmospheric N_2/O_2 ratio = 3.72). For some samples this correction yielded negative N_2 values most likely due to measurement uncertainties (*Appendix I, Table 1*). These samples were excluded from further evaluations with regard to chemical and isotopic composition. Methane contents showed large variation of 7-92%. At ČSM South, the methane content gradually increased during degassing, whereas it showed no systematic variation at Paskov and ČSM North. Gas extracted at Paskov mine contained significantly larger amounts of higher molecular mass hydrocarbon gases (C_{2+}) than ČSM gases. The amount of CO_2 was generally higher in ČSM gases (1-8%) than in Paskov gases (0.4-3%). Argon concentrations were higher at ČSM North (1.2-3.6%), than at ČSM South (0.6-0.7%) and showed large variation at Paskov mine (0.7-2.9%). Since argon was not taken into account when normalizing to the air-free basis, the high concentrations can also reflect contamination. Helium and hydrogen were below the detection limits (10 ppm and 20 ppm respectively) for ČSM gases, while some Paskov gases contained up to 45 ppm helium and up to 101 ppm hydrogen (H_2).

2.5.1.2. Stable carbon isotopic composition

Stable carbon isotopic composition of methane in cross-measure borehole gas from Paskov mine ranged from -24‰ to -39‰ (average -34‰), whereas gases from the ČSM mine showed significantly lower abundance of the ^{13}C carbon isotope ($\delta^{13}C$-CH_4 from -60‰ to -68‰; average -64‰). The variation of $\delta^{13}C$-CH_4 values was higher for Paskov gas than for ČSM gas. No significant difference in methane $\delta^{13}C$ values was observed between gas from ČSM North and ČSM South. During gas extraction at ČSM South, $\delta^{13}C$-CH_4 showed a slight increase, whereas no systematic variation was observed for gas extracted from Paskov and ČSM North mine (*Fig. 2.3*).

Carbon dioxide of gas collected from cross-measure boreholes at ČSM South was depleted in ^{13}C ($\delta^{13}C$-CO_2 from -22‰ to -24‰), whereas CO_2 of cross-measure gas from ČSM North and Paskov mine was less depleted in ^{13}C ($\delta^{13}C$-CO_2 from -9‰ to -16‰ and +3‰ to -14‰, respectively). At ČSM North, $\delta^{13}C$ of CO_2 decreased during gas extraction (*Fig. 2.3*). The isotopic fractionation (α) between $\delta^{13}C$-CO_2 and $\delta^{13}C$-CH_4 of gas collected from cross-measure boreholes ranged from 0.96-0.99 for samples from Paskov mine and from 0.94-0.96 for gas from ČSM mine. Results of geochemical and stable carbon isotope analysis of cross-measure degassing samples are listed in *Appendix I Table 1*.
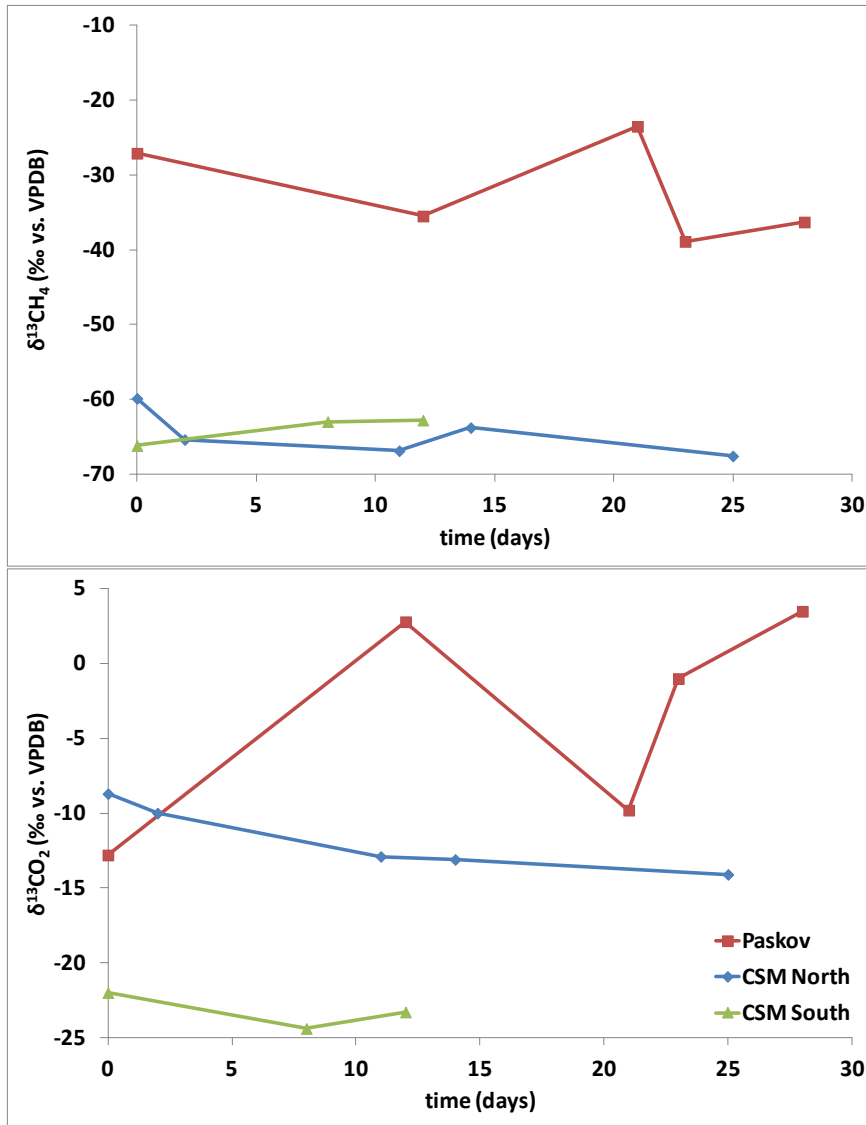
Fig. 2.3 Variation of stable isotope composition of CH₄ (top) and CO₂ (bottom) of gas extracted from cross-measure degassing boreholes.

2.5.2. Canister desorption experiments

2.5.2.1. Gas contents

Gas contents determined in 15 canister desorption experiments were generally low (<5 m^3/t). Lowest gas contents were measured for ČSM coals, ranging from 0.4-2.3 m^3/t (average 1.3 m^3/t). Higher gas contents were measured for the four samples from Paskov mine (1.9 to 3.9 m^3/t) and the five Lazy coal samples (0.9- 4.8 m^3/t). The total gas content was made up of 0.2-4% of lost gas (average 1.3%), 45-88% desorbed gas (average 71%) and 10-54% of residual gas (average 27%). Gas contents ČSM coals from different seams decrease with increasing well depth, whereas they increase with depth at the Paskov and Lazy mines. However, since only well depth data were available, no systematic change of gas contents with true vertical depth (TVD) could be evaluated. Results of gas content measurements are shown in *Fig. 2.4*.
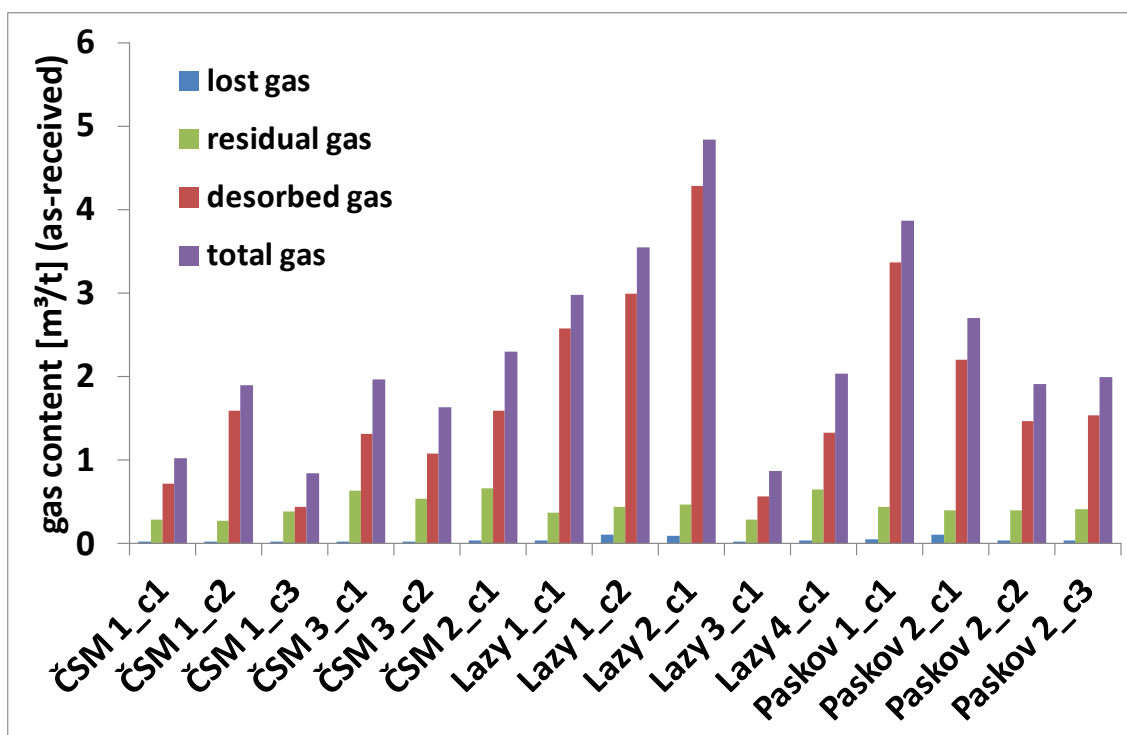
Fig. 2.4 Gas content determined by canister desorption of coals from Paskov, Lazy and ČSM mine on "as-received" basis.

2.5.2.2. Molecular gas composition

Multiple analyses were performed to determine the chemical composition of the gases collected during the 15 canister desorption tests. Results of the geochemical analyses (49 gas samples) are listed in *Appendix I Table 2.*

Desorption canisters were not filled with water or inert gas before they were sealed and therefore the first gas samples in each desorption test contained significant amounts of oxygen (1.8-17.8%). In most cases the amount of oxygen and nitrogen decreased in the course of desorption. In some instances desorbed gases with significantly elevated oxygen concentrations were observed, which might indicate contamination by atmospheric air during gas sampling or leaking desorption containers. Similar to cross-measure degassing samples, the desorbed gas values were normalized to an air-free basis. Samples yielding negative nitrogen values upon this correction were excluded from further evaluations with respect to molecular and isotopic composition.

Desorbed gases were dominated by nitrogen and methane. Both gases show a large variation between 0 and 91% (nitrogen) and <1% to >99% for methane. Highest amounts of nitrogen were measured in desorbed gases from ČSM North well 1. C_{2+} hydrocarbon gases were generally less abundant in ČSM wells (C_2H_6 < 800 ppm), variable in Lazy wells (C_2H_6 ranging from 4-7870 ppm) and highest in Paskov wells (C_2H_6 up to 4.4%). Besides a general increase in ethane contents between the first two desorption steps, no significant change was observed.

CO_2 contents were generally <10%, ranging from 0.03-8.9%. Highest CO_2 contents were measured in desorbed gas from ČSM well 1.

Argon contents ranged from 0-3.1% and again, highest amounts were measured in gases from ČSM well 1, where they generally decreased with increasing desorption time.

Most desorbed gases did not contain any helium, with the exception of three canisters from well 1 at ČSM North. These gases contained up to 1225 ppm of helium and showed a

general increase with increasing well depth and decrease with increasing desorption time (*Fig. 2.5*). Only three desorbed gas samples contained significant amounts of hydrogen, ranging from 300-580 ppm. This amount of molecular hydrogen could be the product of fermentation processes in the desorption canister. In the presence of oxygen the molecular hydrogen can not be utilized by microbial methenogenesis.
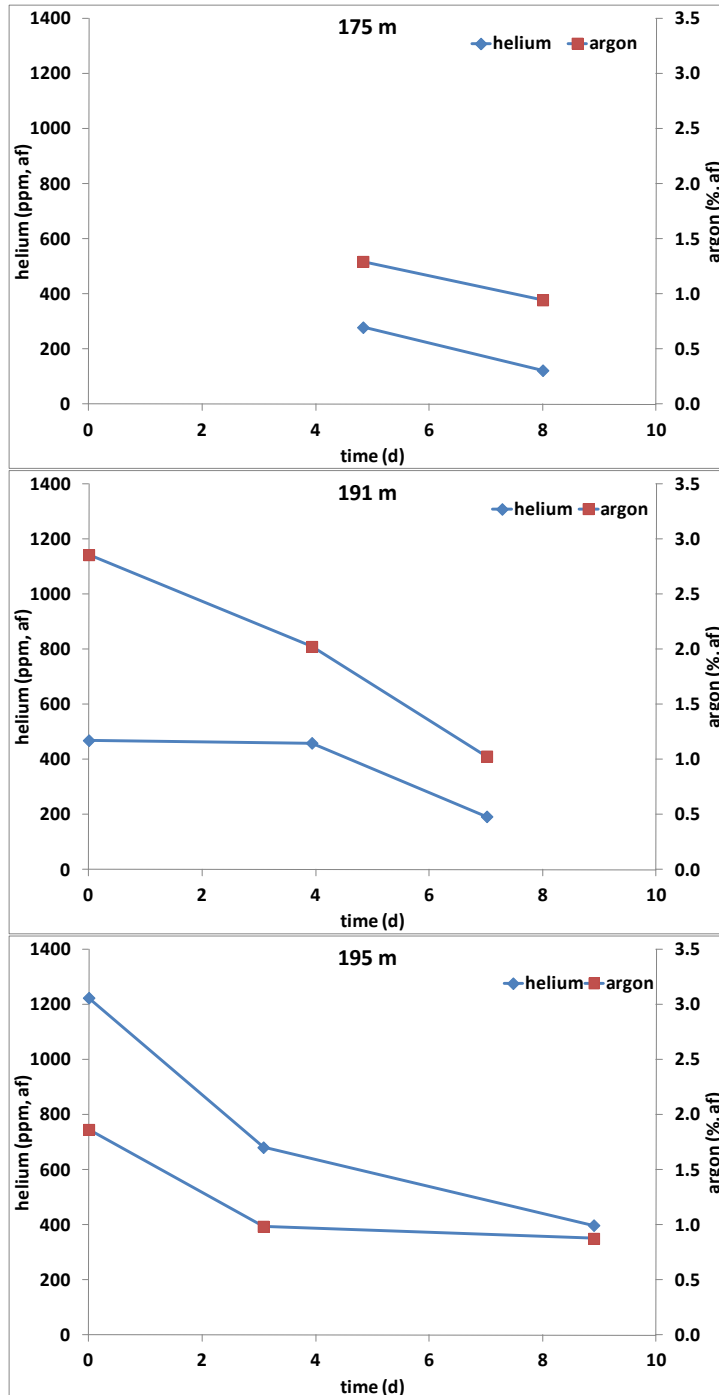
Fig. 2.5 Variation of helium and argon concentrations during canister desorption of samples from different depth of ČSM well 1.

2.5.2.3. Stable carbon isotopic composition

The isotopic composition of methane and CO_2 collected during canister desorption tests from all three mines is highly variable. Methane $\delta^{13}C$ values range from -72‰ to -35‰ with an average of -54‰. Strong depletion in ^{13}C is observed for methane desorbed from coal at ČSM North mine (average $\delta^{13}C$-CH_4 -71.6‰) with little variation, whereas the $\delta^{13}C$-CH_4 from ČSM South and Lazy range from -44‰ to -71‰ (average -58‰). Methane desorbed from coals from the Paskov mine are significantly less depleted in ^{13}C, ranging from -46‰ to -35‰ (average -42‰). The carbon isotopic composition of methane and CO_2 measured at different times during canister desorption was also highly variable (*Fig. 2.6*). The isotopic difference between methane desorbed at the start and at the end of desorption ($\Delta CH_4 = \delta^{13}C_{CH4e} - \delta^{13}C_{CH4s}$) varies from +3‰ to -2‰ with an average of -0.6‰. For carbon dioxide the isotopic difference shows even larger variation, ranging from +8‰ to -9‰ (average of -0.7‰).

The isotopic fractionation factor α between CO_2 and CH_4 ($\alpha = \delta^{13}C$-$CH_4 + 10^3/\delta^{13}C$-$CO_2 + 10^3$) ranged from 0.94-1.01 (average of 0.96). The largest fractionation was observed for gases from ČSM and Lazy mine.
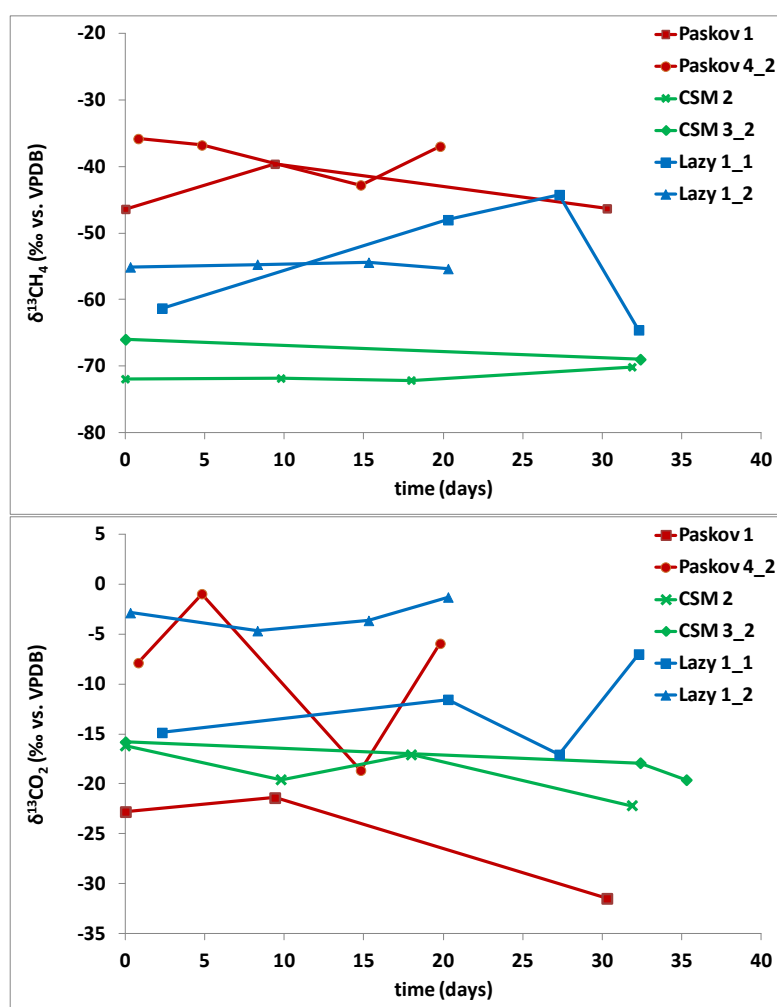
Fig. 2.6 Variation of stable carbon isotope composition of methane (top) and CO_2 (bottom) during canister desorption of coals from Paskov, Lazy and ČSM mine.

2.6. Discussion

2.6.1. Origin of CO_2

The carbon dioxide encountered in natural gases may be of organic origin (*e.g.* acetate fermentation or decarboxylation) or of inorganic origin. CO_2 of organic origin has usually low $\delta^{13}C$ values (<-10‰) and concentrations are mostly <10%, while CO_2 of inorganic origin is enriched in ^{13}C (0‰ to +10‰) often forms CO_2 rich reservoirs (>15%; Wycherley et al., 1999 and references therein). However, the isotopic signatures of CO_2 of different origins are highly variable and overlap. Thus, $\delta^{13}C$ values of CO_2 from biogenic decay can range from +15‰ to -30‰ (Schoell, 1983; Whiticar, 1994) and therefore the origin of CO_2 cannot be deduced from $\delta^{13}C$ alone. A combination of stable carbon isotope data from CO_2 with the stable isotope composition from associated noble gases (Ar, He, Ne) could significantly improve the identification of CO_2 sources (Sherwood-Lollar et al., 1997).

Generally, gas samples from the SW USCB have low CO_2 concentrations with stable carbon isotopic signature mostly < -15‰, indicating a purely organic origin. The large variation in isotopic composition most likely reflects different degrees of organic decomposition or oxidation of organic matter. The coals from Paskov well 3 contain low concentrations (<2%) of isotopically heavy CO_2 (average $\delta^{13}C$ -7‰), which is probably related to oxidation of the isotopically heavy methane or coal components, rather than derived from a mantle source or metamorphism.

2.6.2. Origin of methane and higher hydrocarbons

Methane generated by thermal cracking during coalification is characterized by high $\delta^{13}C$ values (> -55‰) (Cramer et al., 1998; Gaschnitz et al., 2001). This thermogenic gas usually contains significant amounts of higher molecular weight hydrocarbons (C_2 – C_5). For some coals, thermogenic methane with $\delta^{13}C$ values as low as -61‰ has been reported (Whiticar, 1996). The isotopic composition of thermogenic methane depends on the type of the source organic matter. Gas generated from vitrinite rich coal, where cracking of aromatic structures is the dominant process, is isotopically heavier than gas generated from liptinite rich coals, where cracking of aliphatic hydrocarbons is dominant (Galimov, 1988). Similarly, gas generated from bitumen cracking will be more depleted in ^{13}C than gas from kerogen cracking. The isotopic fractionation during thermogenic gas generation also depends on the degree of depletion of molecular structures that can easily be cracked to form hydrocarbon gases (Galimov, 2006).

Microbial methane can be generated during diagenesis or during late stage secondary processes and involves groups of fermentive bacteria that are syntrophically associated with methanogenic archaea (Thauer, 1990; Strapoc et al., 2011). Microbial methane is more depleted in ^{13}C than thermogenic methane (Rice, 1993). The two most common processes of microbial methanogenesis are the reduction of CO_2, occurring predominantly in marine environments, and the fermentation of acetate, prevailing in young terrigenous freshwater environments. Microbial CO_2 reduction is associated with methane $\delta^{13}C$ values between -55‰ and -110‰ (carbon isotopic fractionation factors $\alpha_{CH4-CO2}$ between 0.94 and 0.92) (Jenden and Kaplan, 1986).

The hydrogen isotopic composition of methane generated by CO_2 reduction depends on the hydrogen source. If hydrogen is derived from direct utilization of water hydrogen, it shows a close relationship to the isotopic composition of formation waters $\delta D_{CH4} = \delta D_{water}$ -180‰ (Whiticar, 1999; Galimov, 2006).

Methane generated during acetate fermentation is characterized by $\delta^{13}C$ values between -40‰ and -70‰ (carbon isotopic fractionation factors $\alpha_{CH4-CO2}$ between 0.96 and 0.94) (Jenden

and Kaplan, 1986) and δD values closer to the isotopic composition of the precursor acetate ($\delta D_{CH4} = 0.4 \cdot \delta D_{water} -323‰$) (Whiticar, 1999; Galimov, 2006).

Bernard et al. (1976) used a combination of the stable carbon isotopic composition and the molecular gas composition ($C_1/(C_2+C_3)$) to discriminate between thermogenic and microbial gas. A plot of gas data from cross-measure degassing and desorbed gases analyzed in the present study classifies gas in coals from Paskov mine (paralic Ostrava Formation) as thermogenic, whereas cross-measure gas from the ČSM mine shows a microbial signature (*Fig. 2.7*). Gas samples collected during canister desorption show a similar microbial signature for ČSM and Lazy mine gas and a thermogenic signature for Paskov mine gas. Additionally, desorbed gases show larger variation in isotopic and molecular composition and exhibit significant influence of oxidation or mixing of thermogenic and microbial gas. These results are in good agreement with those previously obtained by Kotarba (2001) who analyzed coal gases from the USCB in Poland and also one sample from Paskov mine. The purely thermogenic signature of gas from Paskov coals indicates that in mature coals below impermeable layers of the Carpathian overthrust, no secondary biogenic gas generation took place. It is also possible that gas generated from organic-rich sediments in deeper parts below the Carpathian overthrust, *e.g.* the Oligocene Menilite Formation, migrated upwards and was adsorbed by Carboniferous coals. The Menilite kerogen slightly depleted in ^{13}C ($\delta^{13}C\text{-}CH_4 = -26‰$ to $-28‰$) compared to the one of coal ($\delta^{13}C\text{-}CH_4 = -24‰$). A contribution of migrated gas is difficult to identify based on carbon isotopes alone and would rather lead to increased ^{13}C depletion of methane (Köster et al., 1998; Kotarba, 2001; Cornford, 2011).
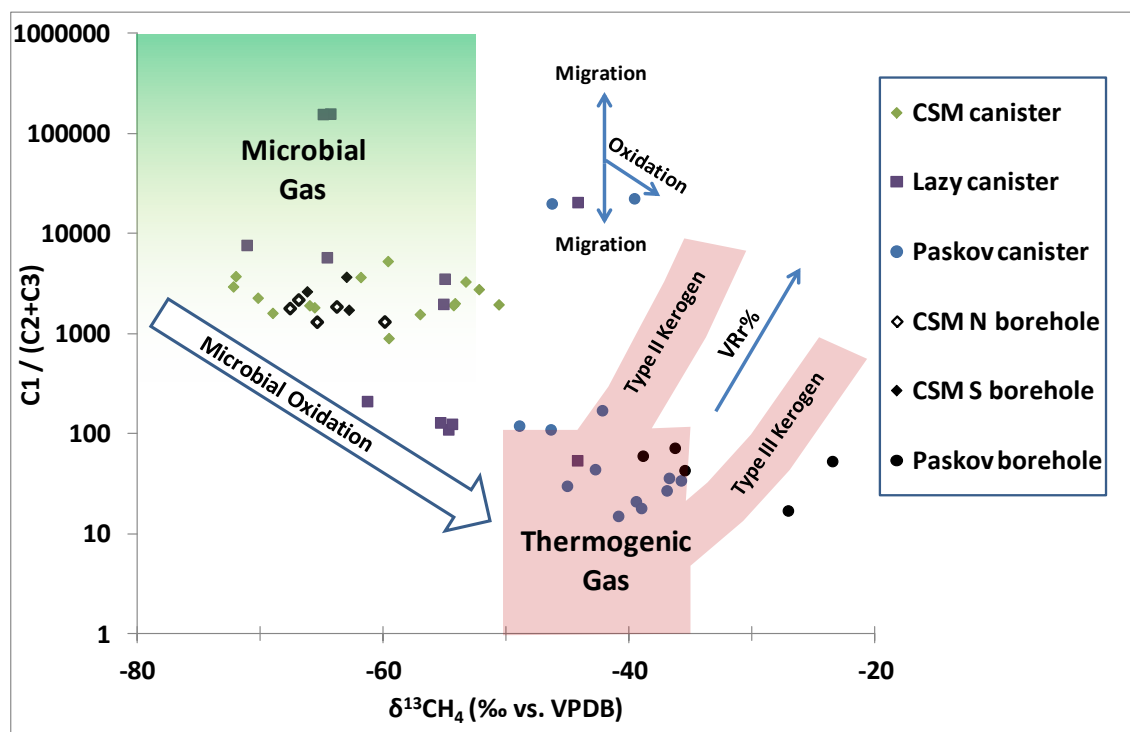
Fig. 2.7 Bernard plot combining molecular and isotopic composition of coal related gas from cross-measure boreholes and canister desorption (after Bernard et al., 1976 with interpretations after Whiticar, 1999).

Fig. 2.8 shows a plot of $\delta^{13}C\text{-}CH_4$ versus $\delta^{13}C\text{-}CO_2$ for coal-related gas analyzed in the present study. The interpretational fields indicate the range for acetate fermentation between $\alpha =0.96$ and $\alpha = 0.94$ and the range for CO_2 reduction between $\alpha = 0.94$ and $\alpha= 0.92$ (Jenden and Kaplan, 1986). Additionally, diagnostic fields for microbial gas and methane oxidation by Whiticar et al. (1986) and for thermogenic gases by Smith and Palasser (1996) are plotted.

Dashed lines represent lines of equal carbon isotopic fractionation $\alpha_{CH4-CO2}$. This plot confirms a thermogenic origin of gases from Paskov mine and also indicates influence of methane oxidation. Coals from ČSM and Lazy mine (limnic Karviná Formation) show a microbial origin from CO_2 reduction and acetate fermentation and also a possible alteration by migration or oxidation of methane. More detailed differentiation between these methanogenic processes requires combining δD and $δ^{13}C$ of methane (Whiticar, 1986, 1999; Schimmelmann et al., 2006).

Preliminary hydrogen isotopic composition of methane from a cross-measure degassing borehole in the ČSM mine (Francǔ et al., unpublished results) indicate that these gases result from microbial CO_2 reduction, rather than acetate fermentation. This is in good agreement with results of stable carbon and hydrogen isotope analyses by Kotarba (2001) and Kotarba and Pluta (2009) of gas from coals in the Morzinek mine, which is located in the Polish part of the USCB, a few kilometers NE from the ČSM mine (*Fig. 2.1*). Analysis of formation waters in the SW USCB provide evidence of infiltration of meteoric waters between late Permian and the Miocene transgression (Kotarba and Pluta, 2009 and references therein). These meteoric waters could have introduced methanogenic microbes and nutrients into coal-bearing Carboniferous strata. The isotopic information from $δ^{13}C$-CO_2 and $δ^{13}C$-CH_4 of the majority of gas samples from canister desorption is most likely the result of a mixture of thermogenic gas with gas from CO_2 reduction or of alteration during canister desorption, rather than the result from different microbial methanogenic pathways.
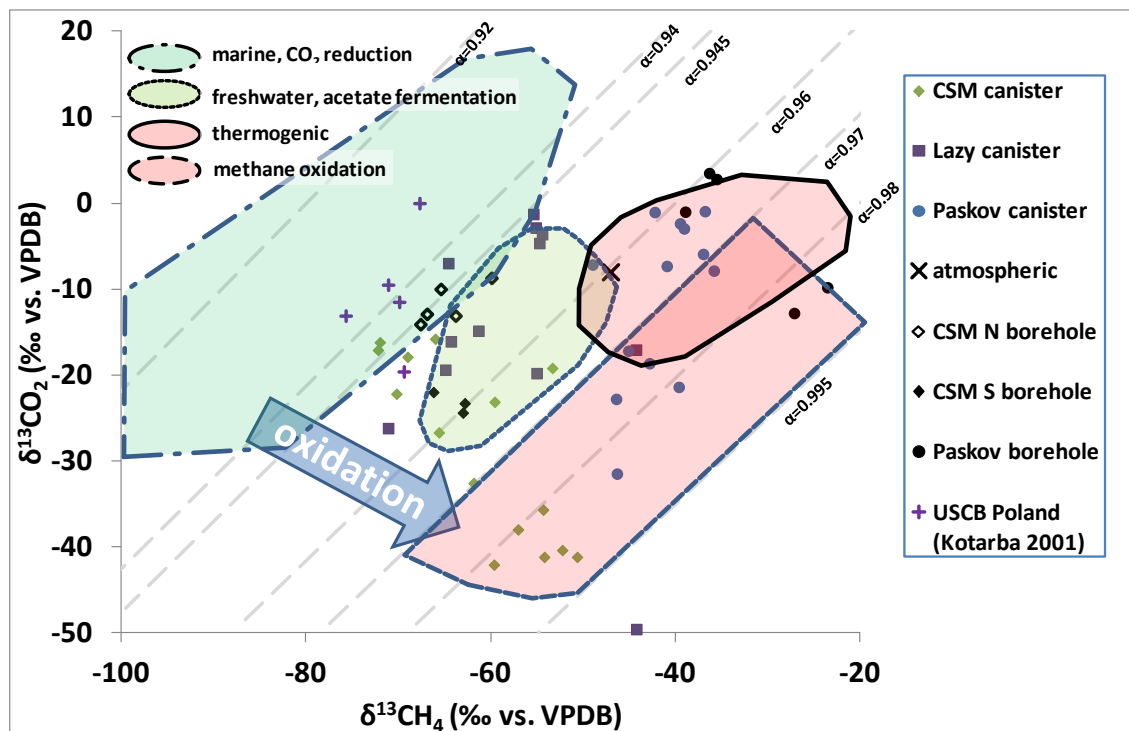
Fig. 2.8 Variation of $δ^{13}C$ of CH_4 and CO_2 in gas from cross-measure boreholes and canister desorption. Diagram after Jenden and Kaplan (1986) with diagnostic fields from Smith and Palasser (1996) and Whiticar (1999). Isotope fractionation lines according to $\alpha = (δ^{13}CH_4 + 10^3)/(δ^{13}CO_2 + 10^3)$.

2.6.3. Influence of thermal maturity on the carbon isotopic composition of thermogenic methane

Differences in binding energies of carbon-carbon bonds for ^{13}C and ^{12}C result in kinetic isotope fractionation during thermal maturation. During the early stage of thermal maturation,

methane depleted in the ^{13}C isotope will be generated, whereas methane generated from high rank coals will be enriched in ^{13}C. This relationship between the maturity of type III kerogens (*e.g.* humic coals) and the stable carbon isotopic composition of generated methane has been studied by Stahl (1977) and later Faber (1987) for Carboniferous coals from Germany. The relationship has been described by the following functions:

$\delta^{13}C$-CH_4 = 8.6 log VR -28 (‰) (Stahl, 1977)

$\delta^{13}C$-CH_4 = 13.4 log VR -27.7 (‰) (Faber, 1987)

VR is the vitrinite reflectance of the coal in %.

Later Berner and Faber (1996) calculated a linear relationship between kerogen maturity and methane isotopic composition from pyrolysis experiments:

$\delta^{13}C$-CH_4=3.6848VR-31.292 (Berner and Faber, 1996).

A comparison of $\delta^{13}C$-CH_4 values measured for the USCB gases with these maturity $\delta^{13}C$ relationships indicates that thermogenic gas from Paskov mine is significantly more depleted in ^{13}C than predicted based on coal rank (*Fig. 2.9*). This could indicate that coal gas from Paskov coals represents a mixture of primary thermogenic gas ^{13}C depleted methane, either from secondary microbial generation or methane generated from a different source that migrated into the coal seams. One potential source could be kerogen of the Oligocene Menilite Formation, which is more depleted in ^{13}C than the carboniferous coals (Köster et al., 1998). Molecular partitioning during migration could explain the 'dry' character of such migrated gas.
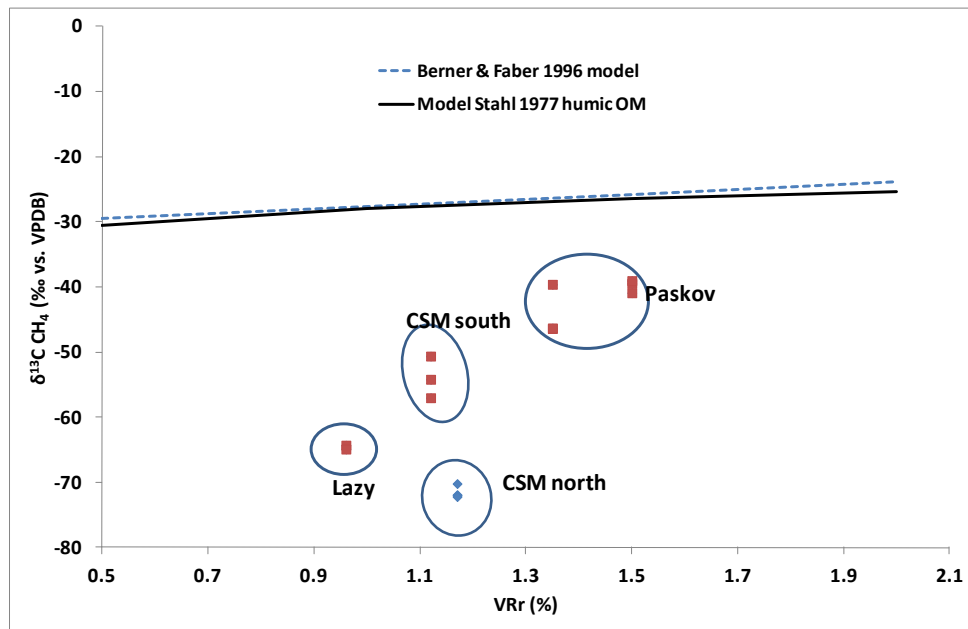
Fig. 2.9 Variation of $\delta^{13}C$-CH_4 with coal rank for desorbed gases from different mines. For comparison, maturity $\delta^{13}C$ trends for thermogenic methane, calculated after relationships reported by Stahl 1977 and Berner and Faber, 1996, were added.

2.6.4. Occurrence and genetic origin of coal-related gas

Coal-related methane in Carboniferous basins has long been known to exhibit a wide variation in $\delta^{13}C$ (Colombo et al., 1966; Teichmüller et al., 1970). These studies report $\delta^{13}C$-CH_4 values ranging from >-20‰ to <-70‰. It was found that ^{13}C depleted methane (<-40‰) is associated with shallow coal seams and that $\delta^{13}C$-CH_4 significantly increases (-30‰ to >-20‰) for gases below a certain depth (desorption zone). The depth of this desorption zone can be highly variable and is controlled by regional tectonics, permeability and the position of seals. It

ranges from -300 m to -800 m in German coal basins. From these early studies Colombo et al. (1966) and Teichmüller et al. (1970) concluded that indigenous methane from the desorption zone was lost to the atmosphere due to a lack of sealing formations after coalification was completed. Furthermore they propose that gas currently present the coals migrated from deeper coal seams into the desorption zone and, due to fractionation during desorption and migration, became depleted in ^{13}C and lost most of the heavier hydrocarbons on the way. Gas in the primary zone below this desorption zone represents the indigenous methane that is enriched in ^{13}C and heavier hydrocarbons. Later studies on coal-related gas found evidence that the process of secondary microbial gas generation can play a significant role in coal basins and that kinetic isotope effects associated with microbial processes have a much larger impact on gas isotopic composition than isotope effects associated with thermogenic gas generation (Stahl, 1977; Rice and Claypool, 1981; Whiticar et al., 1986; Schoell, 1988; Rice, 1993; Smith and Pallasser, 1996). Additionally, early field studies and experimental results showed that the isotopic fractionation associated with diffusion in a CH_4-water-solution system is only small (0.3‰) (Zhang and Krooss, 2001; Galimov, 2006 and references therein).

Accumulations of coal related gas in the USCB show variations in methane concentrations with depth, which mainly depend on the depth of the Carboniferous paleosurface and on the permeability of overlying sediments. Sivek et al. (2003) distinguished three different zones of methane accumulations (*Fig. 2.10*). Zone I represents accumulations of indigenous thermogenic methane. This zone occurs at depth >1250 m if an impermeable cover is present and below ~ 1050 m if covering sediments are of higher permeability. Zone II is characterized by significantly lower methane concentrations (<10^{-3} m^3/t). This zone is located near the top of the Carboniferous paleorelief, where most of the methane is desorbed and lost. Zone III represents secondary methane accumulations at the top of the Carboniferous paleorelief, where impermeable sediments *e.g.* shales of the Carpathian overthrust represent an effective seal. This zone occurs between ~ 750 m and 1000 m depth. Similar observations are also reported from the Polish USCB, *e.g.* by Kotarba and Pluta (2009) and Kedzior (2009). The large variability of gas content at similar depth (*Fig. 2.10*) indicates that depth is not the primary control of gas content.

(A) impermeable cover

CH$_4$ (m³/t coal, daf)

2 4 6 8 10 12 14 16

depth (m)

250
500
750
1000
1250
1500
1750
2000

Zone III
Zone II
Zone I

(B) permeable cover

CH$_4$ (m³/t coal, daf)

2 4 6 8 10 12 14 16

depth (m)

250
500
750
1000
1250
1500
1750
2000

Zone II
Zone I
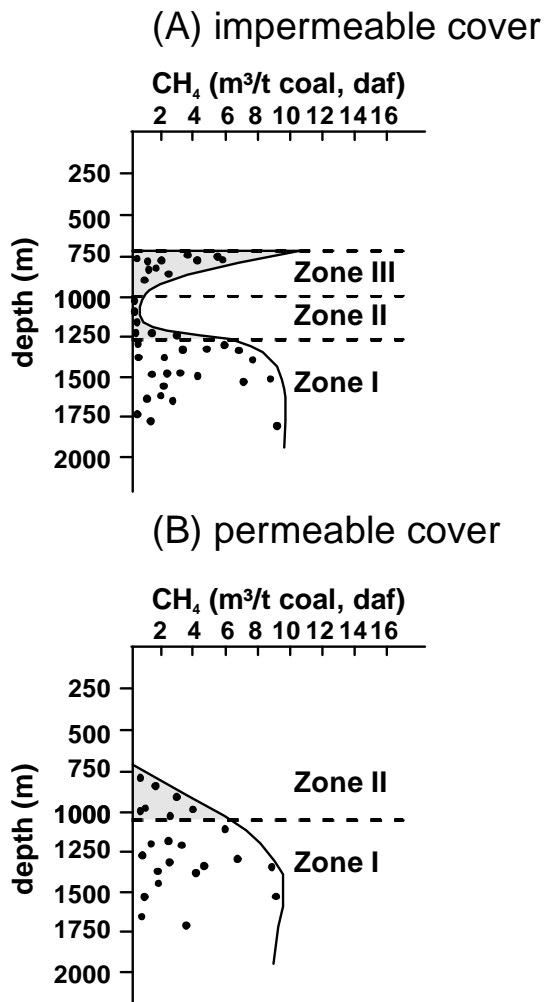
Fig. 2.10 Distribution of coal-related gas in the Czech USCB below impermeable cover (Carpathian nappes) (A) and below permeable cover (B). Redrawn after Sivek et al. (2003).

A direct correlation of gas contents determined in the present study with the zones of gas occurrence described by Sivek et al. (2003) is not possible because no information on the true vertical depth of the samples was available. Gas samples collected from coal seams at the Paskov mine, which is located in an area covered by low permeable sediments of the Carpathian overthrust, are more likely to represent primary thermogenic gas. A reconstruction of the thermogenic gas generation history of coal seams in the OKC indicates that gas generation was completed in the early Permian and that no significant thermogenic gas generation resulted from re-burial upon the overthrust of Carpathian nappes (see chapter 6). The temperature history of coal-bearing formations of the OKC indicates that reservoir temperatures of coal seams of the Ostrava Formation were not favourable for microbial gas generation (>80°C) for most of the basin history, whereas conditions were much more favourable for coal seams of the younger Karviná Formation (*Fig. 2.11*). A reconstruction of the evolution of the sorptive gas storage capacity of coal seams during basin history in the OKC showed that the uplift of coal-bearing formations was associated with an increase in storage capacity (Weniger et al., 2012; see also chapter 5). This increase can explain the gas undersaturation (present day gas content smaller than sorptive gas storage capacity) that is observed for coal seams in the OKC. On the other hand, the "free" sorptive storage capacity could accomodate gas from migration or secondary microbial generation. The average isotope fractionation of <1‰ observed during desorption and the evaluation of the basin history suggest that the large variation of the chemical and isotopic composition observed in coal-related gases of the OKC is related to

differences in the geologic history and different gas origin, rather than bein a result of fractionation processes associated with sorption and migration.
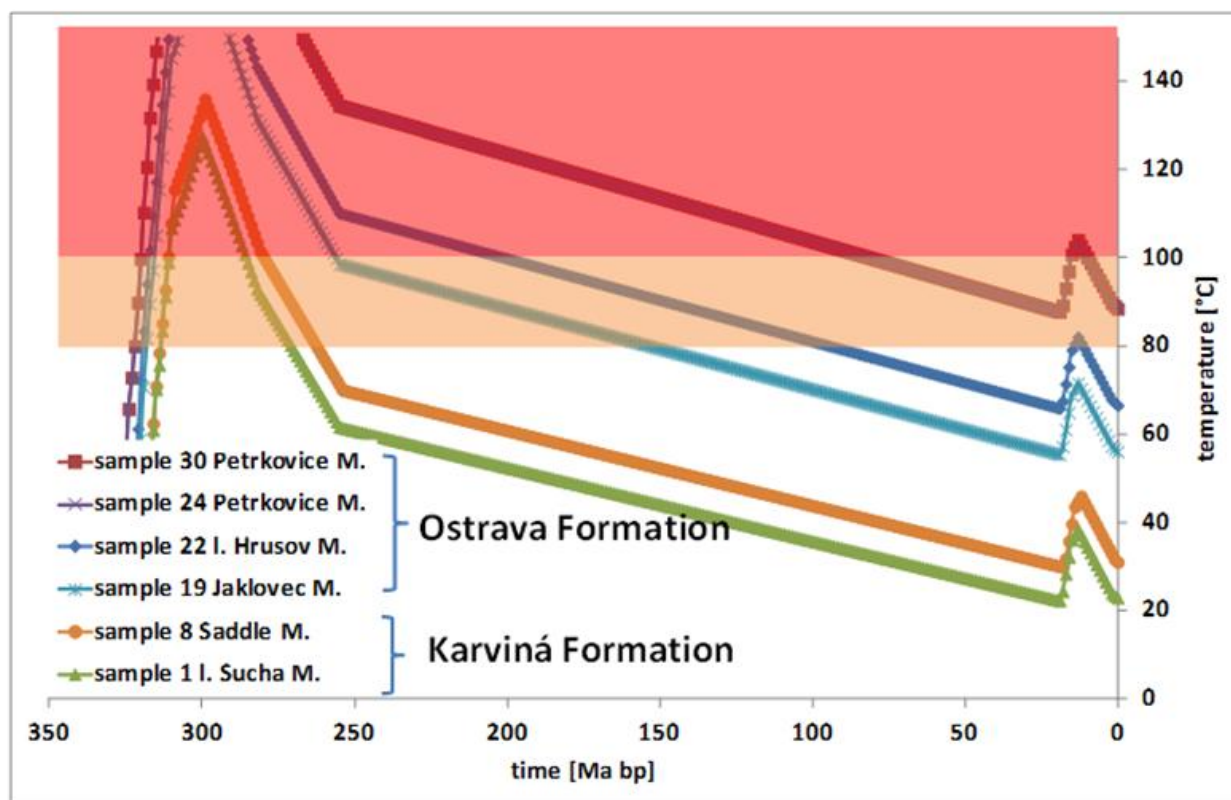
Fig. 2.11 Reconstructed temperature history of coal-bearing formations in the OKC, based on a 1-D basin model.

2.7. Conclusions

Experimental results of the geochemical and stable carbon isotopic composition of coal-related gas in the Czech part of the Upper Silesian Basin revealed a wide range of $\delta^{13}C$ of methane, indicating multiple genetic origins.

Gas of thermogenic origin is associated with coal seams in the southern part of the basin, where Carboniferous and Miocene sediments are covered by impermeable nappes of the Carpathian Flysch Belt. Composition of gas from coal seams in the NE part of the basin, where permeable Miocene molasse sediments overlie Carboniferous formations and infiltration of meteoric waters occurred, indicate a microbial and mixed type origin.

These compositions of coal gases are similar to results of gases from overlying Miocene sediments, analyzed in previous studies.

Coal-related gas from cross-measure extraction shows a similar composition as gas released from coal samples during canister desorption.

Stable carbon isotope composition of methane and carbon dioxide indicates in some cases microbial oxidation of methane during canister desorption, resulting in a coeval shift in the isotopic values.

No consistent isotopic fractionation related to desorption is observed. Low abundance of higher molecular mass hydrocarbons (C_{2+}) in some of the thermogenic gases indicates possible C_{2+} loss during migration. Thus mixture of coal gases and migrated gas, *e.g.* from source rocks below the Carpathian overthrust is conceivable.

Conditions for secondary microbial gas generation were more favourable in coal seams of the Karviná Formation, where temperatures after maximum burial were lower than in the Ostrava Formation and no impermeable cover of Carpathian overthrust nappes exists.

Microbial methane could be stored in the free storage capacity of coal seams that resulted from the uplift of these sediments.

Further studies are required to evaluate the influence of migrated gas and associated fractionation processes.

2.8. Acknowledgements

3. **Gas generation from bituminous coals of the Upper Silesian Coal Basin, Czech Republic and the Paraná Basin, Brazil**

3.1. Introduction

Thermal maturation of coal is associated with the generation of methane and carbon dioxide. Gas generation results from thermal decomposition of complex kerogen molecular structures during geologic times. For type III kerogen, such as humic coals, effective gas generation is believed to begin at a rank of >0.8% VR and reaches a maximum around 1.1% VR (Schimmelmann, 2006).

Several approaches have been proposed to estimate the amount of gas that can be generated from coal. Correlations based upon the volatile matter yield of coals were used in several studies to evaluate potential gas generation (Karweil, 1969; Meissner, 1984; Ryan, 1992).

Mass balance calculations based upon the intrinsic changes of the elemental composition of coal during generation of methane, carbon dioxide and water were used in early studies, *e.g.* by Jüntgen and Karweil (1966) and have been applied in numerous following studies.

Early observations of products generated in coal pyrolysis experiments showed that the composition of gas generated in the laboratory is remarkably similar to the gas present in coal seams (Hanbaba and Jüntgen, 1969). These observations led to the assumption that thermogenic gas generation that occurs during coalification can be simulated by open system pyrolysis experiments. While it is not possible to simulate gas generation under geological conditions, pyrolysis experiments with coal have been used to estimate the amount of gas generated during coalification by extrapolation of experimentally derived reaction kinetic parameters to geological heating rates (Hanbaba and Jüntgen, 1969; Ungerer and Pelet, 1997; Schenk et al., 1997 and references therein) and also to estimate the stable isotope composition of generated gas (Tang et al., 2000; Cramer et al., 2001; Gaschnitz et al., 2001).

3.2. Estimation of gas generation from volatile matter yield

An early approach to evaluate gas generation from coal based upon the change of volatile matter yield between high volatile bituminous and anthracite rank was introduced by Karweil to estimate gas generation from German coals with volatile matter yield less than 37.8% (ca. 0.8% VR). His equation was later used by Meissner (1984) and Ryan (1992) to evaluate gas generation from US coals and Canadian coals respectively:

$VCH_4 = -325.6 \cdot \log (VM/37.8)$ (Ryan, 1992 and references therein)

Here VCH_4 is the volume of generated methane and VM is the volatile matter yield in wt. % (daf).

Applying this approach to coals from the USCB analyzed in the present study a maximum volume of 120 m^3 of methane per ton of dry, ash-free coal, can potentially be generated. This indicates that the amount of gas that can be generated from coal is significantly higher than the amount of gas that can be stored in coal by sorption processes. However, this equation does not take into account any gas that has been generated during early catagenesis (<0.8% VR) and it is also not based upon correlations for coal from the USCB.

3.3. Mass balance calculation

The amount of gas that theoretically can be generated through thermal decomposition of organic matter can be estimated by mass balance calculations, based upon intrinsic changes of the elemental composition during gas generation (van Krevelen, 1961). Jüntgen and Karweil (1966) used this stoichiometric mass balance approach to estimate the amount of gas generated from coal seams of the German Ruhr Basin. It was subsequently applied in several other studies (Littke et al., 1989, 1995; Krooss et al., 1995; Thielemann, 2000 and Gaschnitz, 2001).
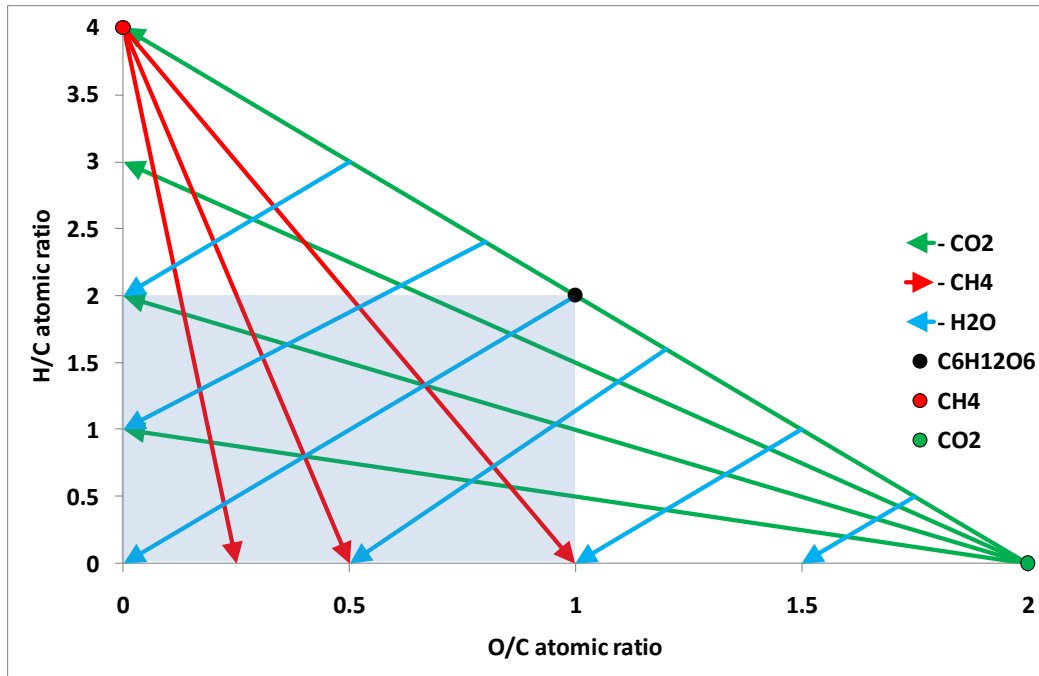
Fig. 3.1 Influence of removal of methane, carbon dioxide and water during thermal decomposition on the elemental composition of organic matter. For comparison, the composition of glucose and the end members CH_4 and CO_2 are plotted. The shaded area represents the range of elemental composition of sedimentary organic matter.

Mass balance calculation based upon changes of the atomic H/C and O/C ratios can be used to estimate the amount of gas (CO_2 and CH_4) generated during coalification (*Fig. 3.1*).

For these calculations, the relationship between elemental composition (CHNO) and coal rank, derived from numerous elemental analyses of coals is used. Martinec et al. (2005) report the following correlations for coals from the Upper Silesian Coal Basin:

$$C = -0.0004 \cdot VM^3 + 0.0169 \cdot VM^2 - 0.395 \cdot VM + 94 \qquad (1)$$

$$H = 0.001 \cdot VM^2 + 0.0927 \cdot VM + 3.3 \qquad (2)$$

$$N = 0.0035 \cdot VM + 1.3241 \qquad (3)$$

VM = volatile matter yield (wt. %, dry, ash-free)

The amount of oxygen was calculated by difference:

O = 100 - (C + H + N) (4)

Volatile matter yield was converted to vitrinite reflectance (VRc) using the following relationship reported by Martinec et al. (2005):

$$VRc = 3.04 - 0.1 \cdot VM + 0.001 \cdot VM^2 \qquad (5)$$

The mass balance calculation was performed using the following assumptions:

- only the two primary products methane (CH_4) and carbon dioxide (CO_2) are generated during coalification

- the generation of H_2O during coalification is not taken into account. Jüntgen and Karweil (1966) estimated from mass balance calculations that below a carbon content of 94% (anthracite rank) no significant generation of water ocurs during coalification. Loss of water during coalification would decrease the H/C and O/C ratios and reduce the generation of CO_2

and CH_4. Thus, the present mass balance calculation represents an estimation of the maximum amount of generated gases.

For the mass balance the molar elemental composition was used. The initial molar amounts are defined as: n_C^0; n_H^0; n_O^0

The molar amounts of the product are defined as: n_C^1; n_H^1; n_O^1

The initial molar ratios are: $R_{O/C}^0 = \frac{n_O^0}{n_C^0}$; $R_{H/C}^0 = \frac{n_H^0}{n_C^0}$

The molar ratios of the product are: $R_{O/C}^1 = \frac{n_O^1}{n_C^1}$; $R_{H/C}^1 = \frac{n_H^1}{n_C^1}$

The molar amounts of produced gases are: ΔnCO_2; ΔnCH_4

Changes of the initial molar composition of carbon, oxygen and hydrogen during coalification can be described by the following mass balance equations:

$$n_C^1 = n_C^0 - \Delta nCO_2 - \Delta nCH_4 \tag{6}$$

$$n_O^1 = n_O^0 - 2\Delta nCO_2 \tag{7}$$

$$n_H^1 = n_H^0 - 4\Delta nCH_4 \tag{8}$$

Substitution of molar ratios and rearrangement yields an expression for the amount of substance of carbon dioxide formed:

$$\Delta nCO_2 \cdot \left(\frac{2}{R_{O/C}^1} - \frac{R_{H/C}^1}{2R_{O/C}^1} - 1 \right) = \left(\frac{\frac{R_O^0}{C} \cdot n_C^0}{R_{O/C}^1} \right) \cdot \left(1 - \frac{R_{H/C}^1}{4} \right) - n_C^0 \cdot \left(1 - \frac{R_{H/C}^0}{4} \right) \tag{9}$$

$$\frac{\Delta nCO_2}{n_C^0} \cdot \left(2 - \frac{R_{H/C}^1}{2} - R_{O/C}^1 \right) = R_{O/C}^0 \cdot \left(1 - \frac{R_{H/C}^1}{4} \right) - R_{O/C}^1 \cdot \left(1 - \frac{R_{H/C}^0}{4} \right) \tag{10}$$

$$\frac{\Delta nCO_2}{n_C^0} = \frac{R_{O/C}^0 \cdot \left(1 - \frac{R_{H/C}^1}{4} \right) - R_{O/C}^1 \cdot \left(1 - \frac{R_{H/C}^0}{4} \right)}{\left(2 - \frac{R_{H/C}^1}{2} - R_{O/C}^1 \right)} \tag{11}$$

This equation allows for the calculation of generated CO_2 relative to the initial amount of carbon from the initial and final molar ratios. The calculation of generated methane can be performed in a similar way:

$$R_{O/C}^1 \cdot n_C^1 = R_{O/C}^0 \cdot n_C^0 - 4\Delta nCO_2 \tag{12}$$

$$\Delta nCO_2 = \frac{R_{O/C}^0 \cdot n_C^0 - R_{O/C}^1 \cdot n_C^1}{2} \tag{13}$$

$$R_{H/C}^1 \cdot n_C^1 = R_{H/C}^0 \cdot n_C^0 - 4\Delta nCH_4 \tag{14}$$

$$n_C^1 = \frac{R_{H/C}^0 \cdot n_C^0 - 4\Delta nCH_4}{R_{H/C}^1} \tag{15}$$

$$n_C^1 = n_C^0 - \frac{\left(R_{O/C}^0 \cdot n_C^0 - R_{O/C}^1 \cdot n_C^1 \right)}{2} - \Delta nCH_4 \tag{16}$$

$$\left(\frac{R_{H/C}^0 \cdot n_C^0 - 4\Delta nCH_4}{R_{H/C}^1} \right) \cdot \left(1 - \frac{R_{O/C}^1}{2} \right) = n_C^0 - \frac{\left(R_{O/C}^0 \cdot n_C^0 \right)}{2} - \Delta nCH_4 \tag{17}$$

$$\left(\frac{R_{H/C}^0 \cdot n_C^0 - 4\Delta nCH_4}{n_C^0} \right) \cdot \left(1 - \frac{R_{O/C}^1}{2} \right) = R_{H/C}^1 - \frac{R_{H/C}^1 \cdot R_{O/C}^0}{2} - \frac{\Delta nCH_4}{n_C^0} \cdot R_{H/C}^1 \tag{18}$$

$$R_{H/C}^0 \cdot \left(1 - \frac{R_{O/C}^1}{2} \right) = R_{H/C}^1 \cdot \left(1 - \frac{R_{O/C}^0}{2} \right) + \left(\frac{\Delta nCH_4}{n_C^0} \right) \cdot \left(4 - 2 \cdot R_{O/C}^1 - R_{H/C}^1 \right) \tag{19}$$

$$\frac{\Delta nCH_4}{n_C^0} = \frac{R_{H/C}^1 \cdot \left(1 - \frac{R_{O/C}^1}{2}\right) - R_{H/C}^1 \cdot \left(1 - \frac{R_{O/C}^0}{2}\right)}{4 - 2 \cdot R_{O/C}^1 - R_{H/C}^1} \qquad (20)$$

Equations (11) and (20) were used in the mass balance calculation to estimate the maximum amount of gas that can be generated from coal for CO_2 and methane, respectively. The calculation was performed for coals in a rank range starting at VRc = 0.57% up to a rank of VRc = 2.57%. Any gas that has been generated at an earlier maturation stage (< VRc = 0.57%) is not taken into account. Molar amounts of generated gas were converted to volumes using standard conditions (100kPa, 0°C). Results of the mass balance calculation are given in *Appendix II Table 1*. For the rank range considered here, a total cumulative volume of 201 m^3methane per ton of TOC was calculated for coal from the Upper Silesian Coal Basin. For carbon dioxide a total cumulative volume of 138 m^3/t TOC was calculated. Results of the mass balance calculation for coals from the Upper Silesian Coal Basin were compared with calculations based upon elemental analysis data for coals from the German Ruhr Basin, by Gaschnitz (2001) (*Fig. 3.2*).
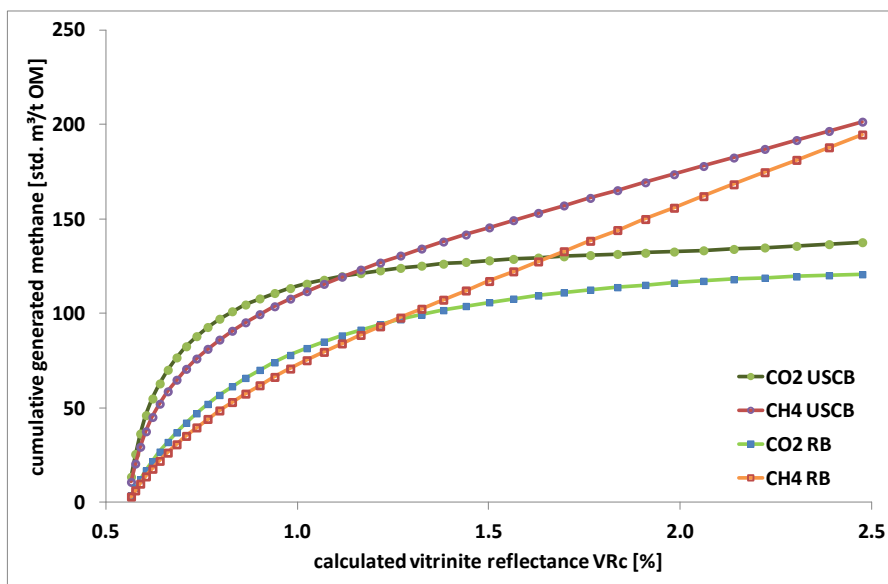
Fig. 3.2 Comparison of cumulative methane and carbon dioxide generation from mass blanace calculations for coals from the German Ruhr Basin (RB) and Upper Silesian Coal Basin (USCB) for a maturity range between 0.6 and 2.6 VRc %. Data for RB calculations from Gaschnitz (2001).

The comparison shows that for both coal basins the amount of methane that theoretically can be generated from coal is slightly higher for USCB coals at low coal rank, but the total cumulative amount at semi-anthracite rank range is similar for both basins. These results are in good agreement with mass balance results from previous studies (*Table 3.1*).

Table 3.1 Comparison of mass balance calculations for methane generation from coals

	Coal basin	Rank range %VR	Generated methane m^3/t OM
Jüntgen and Karweil (1966)	Ruhr Basin	0.75 – 3	250 (200 m^3/t coal)
Krooss et al. (1995)	Ruhr Basin	0.75 – 3.2	181
Gaschnitz (2001)	Ruhr Basin	0.65 – 2.7	230
This study	USCB	0.57 – 2.57	201

3.4. Rock-Eval pyrolysis

Rock-Eval pyrolysis is based upon a method developed by Espitalié et al. (1977) to determine the degree of maturity of organic matter and to detect the petroleum potential of source rocks. While Rock-Eval pyrolysis can also be used to experimentally determine reaction kinetic parameters for bulk hydrocarbon generation, it was applied in the present study only as a first "screening" method to assess the maturity and hydrocarbon generation potential of coals. For detailed evaluation of the reaction kinetics of gas generation, open system non-isothermal pyrolysis coupled to gas chromatography (Py-GC) was applied (see chapter 3.5).

3.4.1. Method

Analyses were carried out on a Rock-Eval II system (Delsi-Nermag, France) in duplicate measurements. A standard was measured three times every 10 samples. To avoid the problem of coal swelling, caking and incomplete reaction of high-rank coal during Rock-Eval pyrolysis (Bostick and Daws, 1994), 9-10 mg of each coal sample were blended with 90 mg quarz sand. During pyrolysis, samples were heated under inert atmosphere (helium) using the following temperature program: Rapid heating to 300°C; holding this temperature for 3 minutes; heating to 550°C with a rate of 25°C/min. At 300°C free hydrocarbons are vaporized and detected by a flame ionization detector (FID) as S1-peak [mg HC/g coal]. Between 300°C and 600°C heavy hydrocarbons (>C40) and unextractable organic matter (kerogen) are thermally cracked and expelled. These hydrocarbons are detected by the FID as S2-peak [mg HC/g coal]. The temperature at which S2 reaches its maximum is recorded as T_{max} [°C]. After heating, trapped carbon dioxide, which was released during pyrolysis, is detected by a thermal conductivity detector (TCD) as S3-peak [mg CO_2/g coal]. From measured peaks for S1, S2 and S3 and the amount of TOC, the following indices are calculated (Tissot and Welte, 1984):

Hydrogen Index	HI = $100 \cdot$ S2/TOC [mg HC/g TOC]	(21)
Oxygen Index	OI = $100 \cdot$ S3/TOC [mg CO_2/g TOC]	(22)
Transformation Ratio	TR = S1/(S1+S2)	(23)
Bitumen Index	BI = S1/TOC (Killops et al., 1998) [mg HC/g TOC]	(24)
Quality Index	QI = (S1 + S2)/TOC [mg HC/g TOC]	(25)
	(Pepper and Corvi, 1995)	

3.4.2. Results and discussion

All coal samples studied here are within the effective oil window for type III kerogen (VR_r 0.85-1.8%) and most of them have reached the peak of thermogenic gas generation (VR_r ~1.1%) (Schimmelmann et al., 2006). For humic organic matter the end of the oil window is suggested to correspond to a vitrinite reflectance of 1.8% (Petersen, 2002).

The amount of "free" bitumen (S1 peak) in coal samples from the limnic Karviná Formation (ČSM mine) is very low (<2 mg HC/g), whereas coal samples from the paralic Ostrava Formation (Paskov and Lazy mine) released more "free" bitumen (1.5 – 11 mg HC/g) during pyrolysis. For samples from the Paskov mine, S1 values are lower than 4 mg HC/g, with one exception (approx. 10 mg HC/g). This sample has the lowest thermal maturity (highest volatile matter yield) among the Paskov samples. Coal samples from the Lazy mine show a larger variation in S1 (4.5 to 11 mg HC/g). Low amounts of "free" bitumen (S1) have previously been reported for different coals from the U.S., England and Poland (Teichmüller and Durand, 1983; Bostick and Daws, 1994; Kotarba et al., 2002).

The amounts of hydrocarbons released during thermal cracking of organic matter (S2 peak) vary between 47 and 103 mg/g for Paskov samples, between 89 and 118 mg/g for ČSM samples and between 106 and 252 mg/g for Lazy samples. The liptinite-rich sample from Prokop seam has the highest S2 yield of 252 mg/g.

The Hydrogen Index (HI) is used to assess the kerogen type as well as the hydrocarbon potential. As expected for humic coals, essentially all samples plot in the type III kerogen field (HI < 300). The temperatures of maximum hydrocarbon generation rate during Rock-Eval pyrolysis, T_{max}, range between 456 and 483°C for coal samples from the Paskov and ČSM mines and from 443 to 465°C for coals from the Lazy mine. Such high T_{max} values are typically found in mature and overmature type III kerogens (Taylor et al., 1998). The T_{max} values show a good correlation with vitrinite reflectance for the Paskov coals, whereas the correlation for the ČSM and Lazy coals is very weak. Kotarba et al. (2002) have previously reported a good correlation between T_{max} and VRr% for coals from the Polish part of the USCB.

Hydrogen Index (HI) decreases with increasing coal rank (VRr %, T_{max}), reflecting the loss of hydrocarbon generation potential during thermal maturation (Bertrand, 1984). Boreham et al. (1999) observed a maximum of HI at T_{max} ~440°C for Permian coals from Australia, which was followed by a continuous decrease of HI with increasing coal rank, reflecting active petroleum generation and expulsion. For coals from the USCB the decrease of HI is well expressed for samples from the Paskov mine and also for coals from the Polish part of the USB (Kotarba et al., 2002), whereas it is not obvious for coals from ČSM and Lazy mines. This is due to the narrow maturity range of ČSM coal samples and the large variation in petrographic properties of the Lazy samples. The Rock-Eval data can provide insight into the thermal maturation process of coals and the thresholds of hydrocarbon generation and expulsion. Thus, the Bitumen Index, as defined by Killops et al. (1998), may be used to identify the onset of oil and gas generation (Sykes and Snowdon, 2002). For coals from New Zealand and other regions, an increase of BI with increasing maturity around T_{max} 430°C, followed by a peak around T_{max} 450°C is interpreted to represent the onset of oil generation and gas generation, respectively (Sykes and Snowdon, 2002 and references therein). A cross-plot of BI with T_{max} for coals from the USB shows that almost all coals from the Czech part have reached the stage of gas generation (*Fig. 3.3*). In Poland, coals from the south-eastern part of the USCB, where thermal maturity is lower (T_{max} ~430°C, VR_r<1%), are at the onset of petroleum generation, whereas coals of higher maturity (T_{max} 460-470°C, VR_r>1.2%) from the south-western part have passed the stage of gas generation (Kotarba et al., 2002). The quality index (QI = (S1+S2)/TOC)) indicates the decrease in total generation potential per unit mass of organic carbon (Sykes and Snowdon, 2002). For New Zealand coals QI increases with increasing maturity to a maximum around T_{max} 440°C, followed by a continuous decrease, which can be interpreted as the onset of petroleum expulsion (Sykes and Snowdon, 2002). A cross-plot of QI vs. T_{max} for coals from the USB shows that all coals are beyond this onset of petroleum expulsion. Coal samples from Paskov mine show a clear decline of QI with increasing maturity, whereas this trend is not well expressed for the other samples (*Fig. 3.3*). Some coals from the south-eastern part of the USB in Poland did not reach the stage of petroleum expulsion, whereas coals from the western part plot close to samples from the upper Ostrava and lower Karviná Formation (ČSM and Lazy mine) analyzed in this study. The Rock-Eval S3 values for all samples are very low, resulting in oxygen index (OI) values less then 5 for most samples. A decrease of OI with increasing rank is observed, indicating that most original organic oxygen is lost. Samples with high inertinite contents tend to show higher OI values compared to samples with low amounts of inertinite.
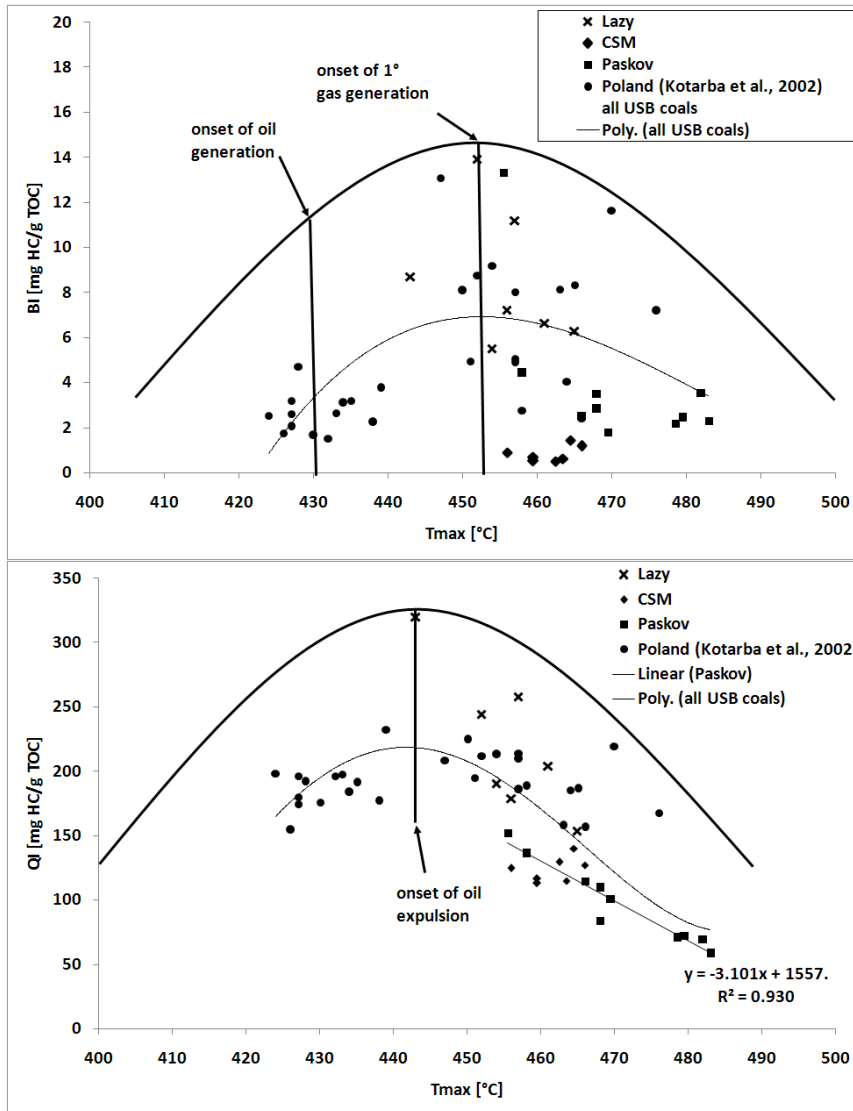
Fig. 3.3 Bitumen Index (BI) and Quality Index (QI) versus maturity (T_{max}) for coal samples from the USCB including interpretation according to Sykes and Snowdon (2002).

3.5. Open system non-isothermal pyrolysis

This approach is based on the concept that gas generation measured in laboratory experiments at high temperatures (up to 1200°C) and high heating rates (0.1 – 10 K/min) can be extrapolated to geologic conditions (<200°C, heating rates of ca. 10^{-11} K/min) to estimate gas generation during coalification (Hanbaba and Jüntgen, 1969).

3.5.1. Method of Pyrolysis Experiments

A non-isothermal open system pyrolysis unit coupled to a gas chromatograph (Py-GC) according to Krooss et al. (1995, 2005) was used to evaluate methane (CH_4) and nitrogen (N_2) generation from powdered coal samples. The pyrolytic gas generation reflects successive liberation of both components during artificial thermal maturation. The experimental set-up consists of a pyrolysis oven, a gas chromatograph (HP 5890), a flow controller for the furnace gas (He) current and an automated 6-port sampling valve (Valco). The pyrolysis gases evolving from the sample (0.14 – 0.3 g) during programmed heating are continuously flushed out of the

tubular furnace by a constant helium stream of known flow-rate (12 ml/min). Every 5 minutes, aliquots of the pyrolysis gas current are transferred to a 5 ml sample loop and injected into the carrier gas stream of the GC system by the automated sampling valve. With a programmed heating rate of 0.5 °K/min, the pyrolysis gas is analyzed at 2.5 °C temperature intervals throughout the experiment. The amounts of pyrolysis gases in these aliquots are quantified by a thermal conductivity detector (TCD).

Before each experiment, the furnace is purged with helium for several hours to remove atmospheric oxygen and nitrogen. When the background N_2 and O_2 signals have declined to an acceptable level, the heating program is started at room temperature with a constant heating rate of 0.5 K/min until the final temperature of 1200 C is reached. Before and after each pyroylsis run the GC/TCD is calibrated with a certified gas mixture containing known concentrations of CH_4.

Generation rates in terms of mass (mg) of gas per unit mass (g) of original substance and unit time (s) are computed, based on original sample mass, flow rate of helium through the furnace, sample loop volume and integrated TCD signal after conversion to mass units (mg).

A total of 6 coals from the Upper Silesian Basin (Czech Republic) and one coal from the Paraná Basin (Brazil) were pyrolysed at a heating rate of 0.5 K/min.

Additionally sample 8 from the USCB (Prokop seam) was pyrolysed at higher heating rates (1 K/min and 2 K/min), to evaluate kinetic parameters of pyrolytic gas generation. Furthermore, the bitumen of sample 8 was extracted for 48h using a Soxhlet extraction system and an azeotropic solvent mixture of chloroform, acetone and methanol (47/30/23 v/v/v). After solvent extraction, the residue was air-dried and pyrolyzed using a heating rate of 0.5 K/min.

Gas generation rates were normalized to mass of organic matter and, using the constant heating rate, converted to ((mg gas / g TOC) / K) for better comparison. Generation rates and cumulative amounts of gas generation were also converted to volumes ((m^3gas / t TOC) / K) using IUPAC standard conditions (0°C, 100kPa). For better comparison with literature data, activation energies are given in kcal/mol (1 J = $2.39 \cdot 10^{-4}$ kcal).

3.5.2. Results and discussion

During temperature-programmed open-system pyrolysis (0.5 K/min heating rate) the onset of methane generation occurred between 280 and 326°C. Generation rates increased until a maximum was reached between 467 and 503 °C was reached.At the same heating rate the temperature of maximum methane generation shifts towards higher values with increasing coal rank. Maximum measured methane generation rates ranged from 0.23 to 0.37 (mg/gTOC)/K for coals from USCB whereas a significantly lower generation rate was observed for the coal sample from Brazil (0.14 (mg/gTOC)/K). Generation rates for most coals exhibit a characteristic 'shoulder' or, in case of sample 8, even a second maximum at higher temperatures between 650 and 900°C (*Fig. 3.4*).
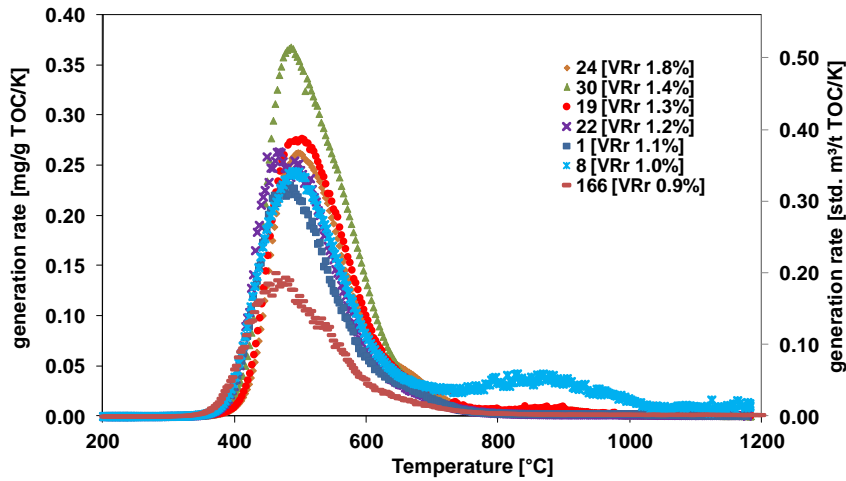
Fig. 3.4 Methane generation rates during temperature-programmed (0.5 K/min) open system pyrolysis

Similar features have been reported in previous studies for coals of different rank (Krooss et al., 2005; Heim et al., 2012). This observed methane generation at higher temperatures indicates additional late gas generation from a thermally more stable portion of the kerogen. A cumulative methane yield of up to 79 m^3/tTOC was determined from pyrolysis experiments for coal from the USCB. The cumulative methane yield for the coal sample from Brazil was significantly lower (32 m^3/tTOC) (*Fig. 3.5*).
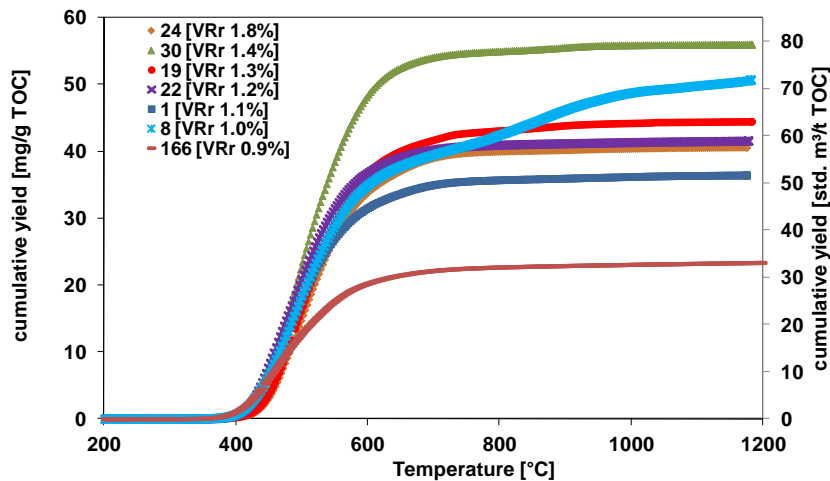
Fig. 3.5 Cumulative methane yield from temperature-programmed (0.5 K/min) open system pyrolysis. (166 = Coal sample from Brazil)

The methane generation shows a general increase with increasing coal rank towards a maximum, roughly coinciding with the peak of effective hydrocarbon generation for type III kerogen (ca. 1.35% VR) (Schimmelmann et al., 2006), followed by a decrease at higher coal ranks (*Fig. 3.6*).
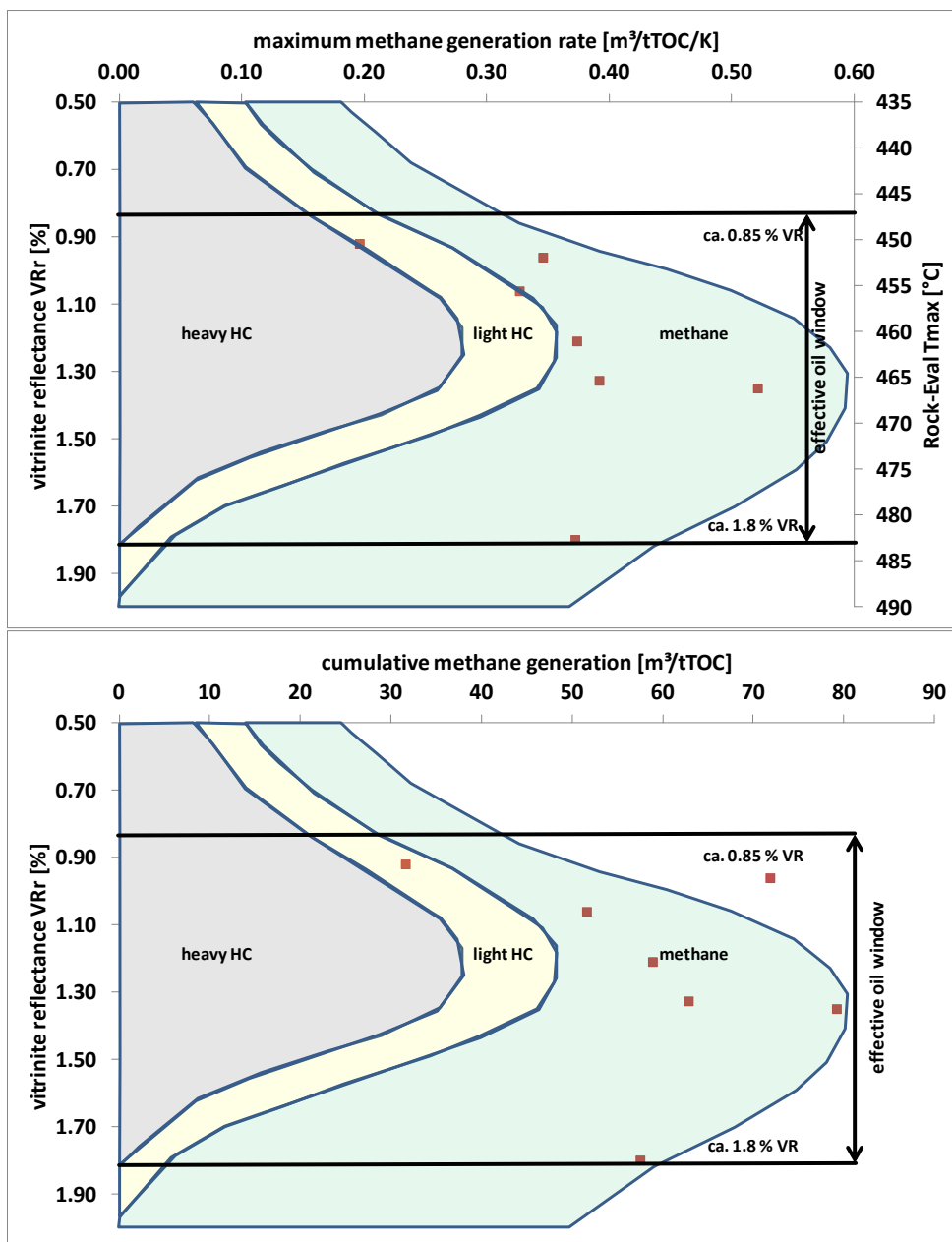
Fig. 3.6 Maximum measured generation rate (top) and cumulative generation (bottom) versus maturity. For comparison, estimated hydrocarbon generation fields for type III kerogen modified from Schimmelmann et al. (2006) have been added (not to scale with pyrolysis methane generation).

Pyrolytic release of nitrogen was significantly lower than methane and began at significantly higher temperatures (>600°C). Nitrogen generation rate curves exhibit a bimodal shape, showing a first small maximum around 700°C and a second, larger maximum at very high temperatures around 1100°C (*Fig. 3.7*). For coals from the USCB, the generation maxima shift towards higher temperatures with increasing coal rank. The coal from Brazil shows significantly lower nitrogen generation than coal from the USCB of similar rank. Additionally, nitrogen generation for the Brazilian coal started at higher temperatures and the second generation maximum is much less expressed. This indicates that not only maturity, but also the composition of coal plays a controlling role for nitrogen generation. The high ash yield of the

Brazilian coal also indicates that inorganic matter does not significantly contribute to the pyrolytic generation nitrogen.
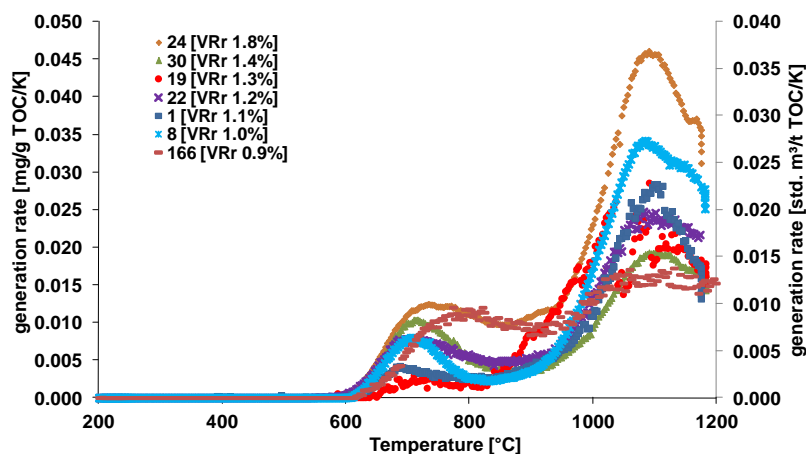
Fig. 3.7 Nitrogen generation rates during temperature-programmed (0.5 K/min) open system pyrolysis

The cumulative nitrogen yield is much smaller compared to methane, varying between 4 and 9 m^3/tTOC (Fig. *3.8*). The highest nitrogen yield was observed for the highest rank coal. However, no clear correlation between nitrogen generation and coal rank was observed.
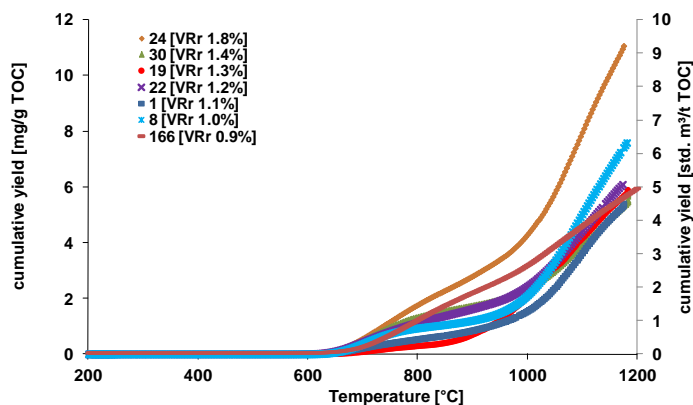
Fig. 3.8 Cumulative nitrogen yield from temperature-programmed (0.5 K/min) open system pyrolysis

Observations from pyrolysis experiments of the present study are in good agreement with results reported in previous studies, *e.g.* by Krooss et al. (1995) and Heim et al. (2012). To evaluate the influence of the bitumen fraction on the pyrolytical methane generation, one coal (sample 8) was pyrolyzed after solvent extraction. Methane generation from the extraction residue was lower than from the unextracted coal and the cumulative methane yield decreased by 28% (*Fig. 3.9*). Results of temperature-programmed open system pyrolyses are given in *Table 3.2* and *Appendix II*.
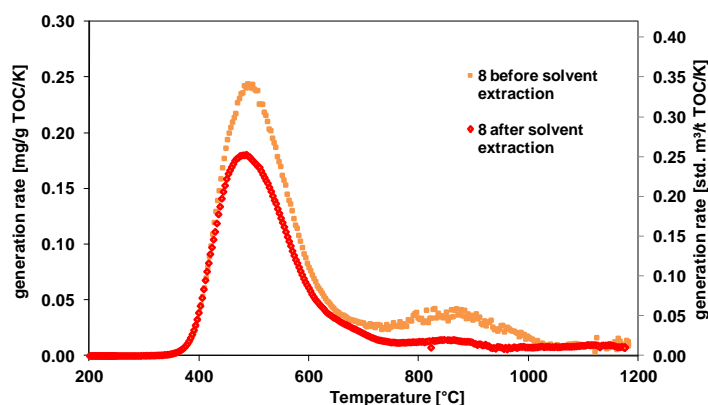
Fig. 3.9 Comparison of methane generation of sample 8 before and after solvent extraction.

Table 3.2 Results of temperature-programmed open system pyrolysis (heating rate = 0.5K/min)

sample #	max pyrolysis temp [°C]	CH₄ onset temp. [°C]	CH₄ max generation temp. [°C]	CH₄ yield [mg/g coal]	CH₄ yield [m³/t coal]	CH₄ yield [mg/g TOC]	CH₄ yield [m³/t TOC]	N₂ yield [mg/g coal]	N₂ yield [m³/t coal]	N₂ yield [mg/g TOC]	N₂ yield [m³/t TOC]
1	1175	302	483	31.79	45.00	36.45	51.60	4.62	3.75	5.66	4.30
8	1182	291	488	41.11	58.20	50.75	71.85	6.21	5.04	7.91	6.22
8 *	1174	272	489	35.91	50.84	44.34	62.77	5.01	4.06	6.93	4.78
8 +	1177	283	506	24.63	34.87	30.41	43.05	2.75	2.23	3.39	2.75
8 #	1175	295	486	30.91	43.75	36.36	51.47	5.43	4.40	6.38	5.17
19	1183	326	502	21.94	31.07	44.39	62.84	2.88	2.34	5.84	4.73
22	1178	294	467	29.63	41.95	41.59	58.88	4.69	3.81	1.54	5.29
24	1182	310	503	36.35	51.46	40.62	57.50	10.18	8.26	11.38	9.23
30	1183	280	485	43.84	62.06	55.94	79.19	4.31	3.49	5.50	4.46
07_166	1209	301	477	9.80	13.87	22.31	31.59	2.65	2.15	6.04	4.90

heating rate: *=(1K/min); +=(2K/min); #= after solvent extraction

3.5.3. Evaluation of the kinetic parameters of methane generation

Chemical reactions such as those involved in thermal gas generation result in changes of the concentration (C) of the involved components over time (t). These changes are described by rate equations. The most commonly used rate equation in petroleum system analysis is the first-order rate equation which relates the decay rate (-dC_i/dt) of a (precursor, reactant) substance i to the concentration C_i present at time t.

1. order reaction: $-\frac{dC}{dt} = k \cdot C$; $(k = const.)$ $\rightarrow$ $C = C_0 \cdot \exp(-k \cdot t)$

Here k is a temperature-dependant reaction rate constant (k(T)).

For constant temperature (T) the first-order rate equation can be readily integrated and yields the remaining precursor concentration $C_i(t)$.

The temperature dependence of chemical reactions was described in earlier studies by a simplified assumption that upon a 10°C temperature increase, the reaction rate is doubled (Waples, 1980).

A more realistic approach to the temperature dependence of reaction rates is provided by the Transition State Theory (TST) or Absolute Rate Theory, which describes elemental reactions of activated complexes that require overcoming of potential barriers (activation energies) (Lasaga, 1981). The Arrhenius equation is a semi-empirical form that is widely used to describe the temperature dependence of the reaction rate of petroleum generation (Ungerer, 1990; Schenk et al., 1997 and references therein).

Integration of the rate equation allows for the calculation of the cumulative yield of generated gas:

$$k(T) = A \cdot exp^{\left(-\frac{E_a}{R \cdot T}\right)} \tag{26}$$

$$\frac{dC}{C} = -k\big(T(t)\big) \cdot C(t)dt \tag{27}$$

$$d\,ln(C) = -k\big(T(t)\big) \cdot dt \tag{28}$$

$$ln\left(\frac{C}{C_0}\right) = \int_0^t -k\big(T(t)\big) \cdot dt \tag{29}$$

$$C = C_0 \cdot exp\left(-\int_0^t k\big(T(t)\big) \cdot dt\right) \tag{30}$$

$$C = C_0 \cdot exp\left(-A \cdot \int_0^t exp\left(-\frac{E_a}{R \cdot T}\right) \cdot dt\right) \tag{31}$$

Here A is a pre-exponential factor, Ea is the activation energy, R is the universal gas constant and T is the temperature. The pre-exponential factor has the dimension of a frequency (s^{-1}) for first order reactions. For reactions of the form A -> B + C that occur during thermal decomposition of a larger molecule (A) into two smaller ones (B and C), the pre-exponential factor describes the frequency of intra-molecular vibration (Polanyi and Wigner, 1928). The vibrational frequency of molecular bonds in organic molecules lies within the range of infrared light ($\sim 10^{12}$-10^{14}). Consequently, the vibrational frequency to break these bonds will be higher, *e.g.* in the range of ultraviolet light ($\sim 10^{14}$-10^{17}). The pre-exponential factor is also temperature dependent; however, as discussed by Hanbaba and Jüntgen (1969), the influence of this temperature dependence is several magnitudes lower than the overall temperature dependence of the reaction rate constant (Hanbaba and Jüntgen, 1969). The activation energy of thermal cracking reactions depends on the kerogen composition and covers a range from <50 kcal/mol to >80 kcal/mol. For type I and II kerogens a normal (Gaussian) distribution of activation energies was found, with a maximum between 40 and 60 kcal/mol, whereas for type III kerogen a discrete (asymmetrical) distribution of activation energies with higher mean values was found (Ungerer, 1990 and references therein). Different ranges of activation energies have been used in previous studies to describe pyrolytic methane generation from coal and type III kerogen; *e.g.* 40 - 60 kcal/mol (Hanbaba and Jüntgen, 1969), 47 - 60 kcal/mol (Ungerer, 1990), 40 - 80 kcal/mol (Krooss et al., 1995), 30 - 94 kcal/mol (Schaefer et al., 1999), 40 - 80 kcal/mol (Schenk et al., 1997). The same applies for the pre-exponential factor derived from pyrolysis experiments. It ranged from low values of 3.18^9 s^{-1} (Krooss et al., 1995) to significantly higher values > 10^{16} s^{-1} (Ungerer, 1990; Schenk et al., 1997). Detailed information on the individual cracking reactions occurring during coal pyrolysis and also during natural coalification can not be derived from laboratory bulk pyrolysis experiments. To evaluate the influence of the kinetic parameters activation energy (Ea) and the pre-exponential factor (A) on methane generation rates, especially with regard to an extrapolation to geologic conditions, half-life values ($\tau_{1/2}$) for methane generation were calculated:

$$\tau \frac{1}{2} = \frac{ln(2)}{k} \quad [Ma] \tag{32}$$

The half-life represents the time required to transform 50% of the substrate (coal). Half-life calculations were performed for a range of activation energies between 10 and 100 kcal/mol and pre-exponential factors of 10^{16} s^{-1} and 10^{12} s^{-1} (*Fig. 3.10*). The calculation shows that the half-life of reactions that require energies >80 kcal/mol is larger than 10 Ma for a frequency factor of 10^{16} s^{-1} and even higher for larger frequncy factors. Contribution of these reactions to the overall methane generation under geologic conditions (T<250°C) will be minor compared to reactions of lower activation energy. Smaller pre-exponential factors result in a shift towards grater half-life values. Consequently, gas generation at geologic temperatures for the same time interval will be significantly lower if a smaller pre-exponential factor is used.
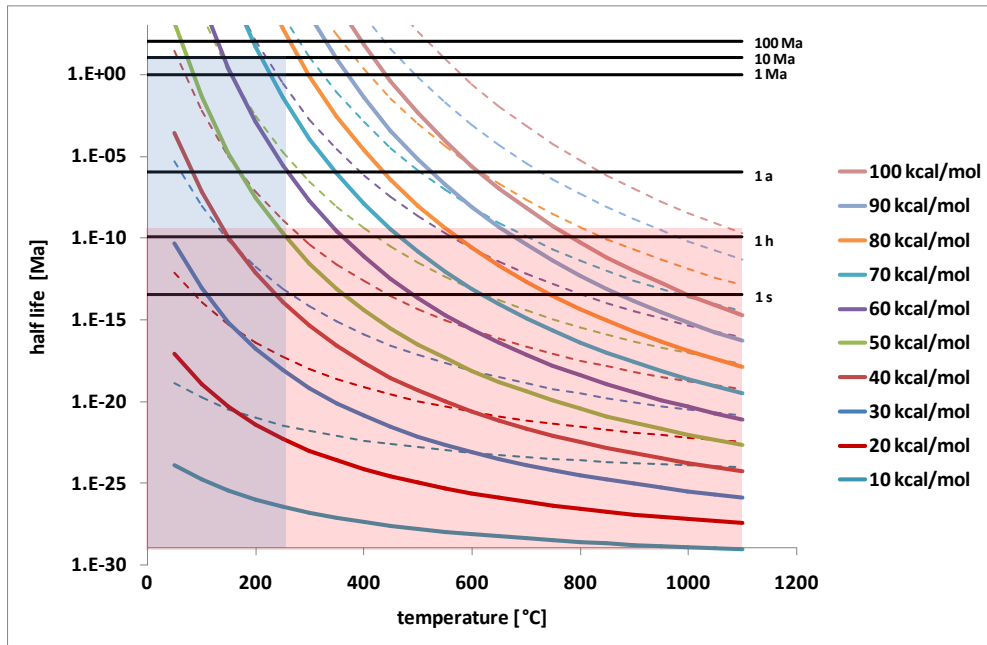
Fig. 3.10 Half-life values calculated using activation energies between 10 and 100 kcal/mol and a pre-exponential factor of 10^{16} s^{-1} (solid lines) and 10^{12} s^{-1} (dashed lines). The time and temperature range of laboratory experiments is represented by the red area, the blue area represents conditions during 'natural' coalification.

During coalification (catagenesis) the complex kerogen structure of coal is thermally decomposed by different chemical reactions that result in the formation of gaseous products (Jüntgen and Klein, 1975). The chemical reactions occurring during coal pyrolysis and also during natural coalification are very complex and not known in great detail. Thus, thermal decomposition is commonly described by a series of parallel first order reactions with different activation energies. To obtain kinetic parameters for methane generation, pyrolytically measured methane generation rates were approximated by generation rates calculated for a set of first order reactions. Experimental data were fitted with calculated reaction rates by a least squares method using the Arrhenius function and a range of activation energies from 35 to 100 kcal/mol. Similar to kinetic evaluations reported by Ungerer (1990) and Krooss et al. (1995), a single pre-exponential factor was used for reaction rate calculations in order to decrease the number of adjustable parameters. Since experimentally measured generation rate curves exhibit an asymmetric shape, a discrete distribution of activation energies was calculated, rather than assuming a Gaussian distribution. A pre-exponential factor of $8.7 \cdot 10^{16}$ s^{-1} was derived from the shift of the generation maximum between pyrolysis measurements at three different heating rates, as described by van Heek and Jüntgen (1968), was used (*Fig. 3.11, 3.12*).

However, the correlation was only weak (R^2 = 0.77), which is attributed to uncertainties in the determination of the pyrolysis maxima. To evaluate the influence of different pre-exponential factors, additional reaction rate calculations were performed using a pre-exponential factor of 10^{15} s^{-1}. Finally, a narrower set of 10 activation energies between 46 and 78 kcal/mol and a pre-exponential factor of $4.3 \cdot 10^{13}$, similar to parameters used by Krooss et al. (1993) for coals of the German Ruhr Basin, was used for comparison. Results of these kinetic models are given in *Table 3.3*.
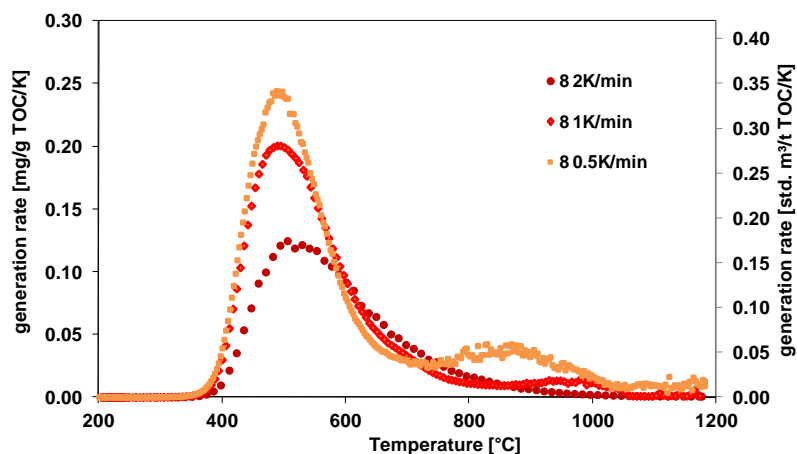
Fig. 3.11 Comparison of methane generation at different heating rates for sample 8.
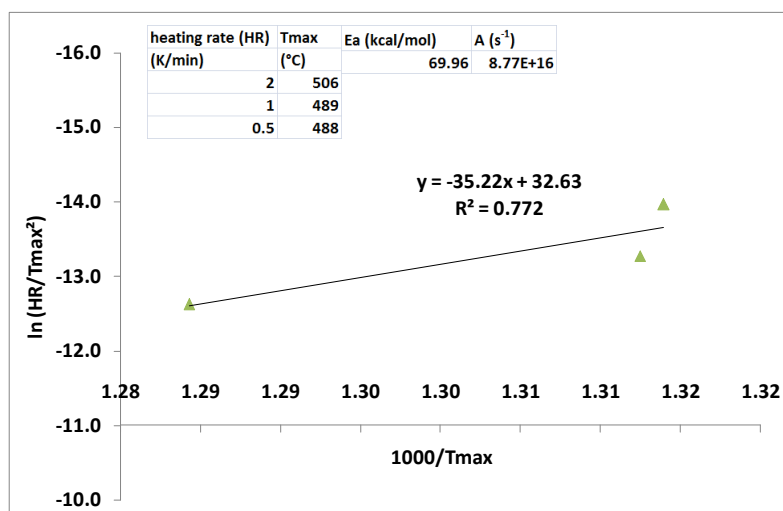
Fig. 3.12 Calculation of the pre-exponential factor (A) from the shift of the temperature of maximum methane generation (T_{max}) between pyrolysis experiments on sample 8 using three different heating rates.

The approximation of the experimental data by different kinetic parameter sets yielded similar results for samples that did not show significant methane generation at high temperatures (>700°C) (*Fig. 3.13* bottom).

Table 3.3 Results of kinetic modelling for coal samples from the USCB
(A = pre-exponential factor [s^{-1}]

cumulative CH$_4$ yield

sample #	stratigraphy	stratigraphy	[m^3/tTOC] Pyrolysis experiment	[m^3/t TOC] A=10^{15}	[m^3/t TOC] A=8·10^{16}	[m^3/t TOC] A=4.3·10^{13} Krooss et al., 1993	[m^3/t TOC] A=8·10^{16} geol. Rate 10^{-11} K/min
1	L. Sucha M.		51.59	50.63	50.65	50.07	48.00
8	Saddle M.	Karviná	71.84	66.76	61.29	57.73	59.42
19	Jaklovec M.		62.86	61.20	61.04	60.17	57.73
22	L. Hrušov M.		58.85	58.04	57.35	57.94	54.96
24	Petrkovice M	Ostrava	57.46	56.81	56.66	56.10	51.62
30	Petrkovice M		79.26	78.34	77.94	77.22	73.33

In contrast, the approximation of pyrolysis data for sample 8, which showed significant methane generation above 700°C, yielded better results with a wide range of activation energies and a frequency factor of 10^{15} s^{-1}, whereas approximation with a higher frequency factor (8.7 · 10^{16} s^{-1}) could only fit 85% of the experimental data. For this sample, the approximation using a narrow range of activation energies was less satisfactory in describing gas generation at high temperatures and only 80% of experimental data were represented (*Fig. 3.13*).
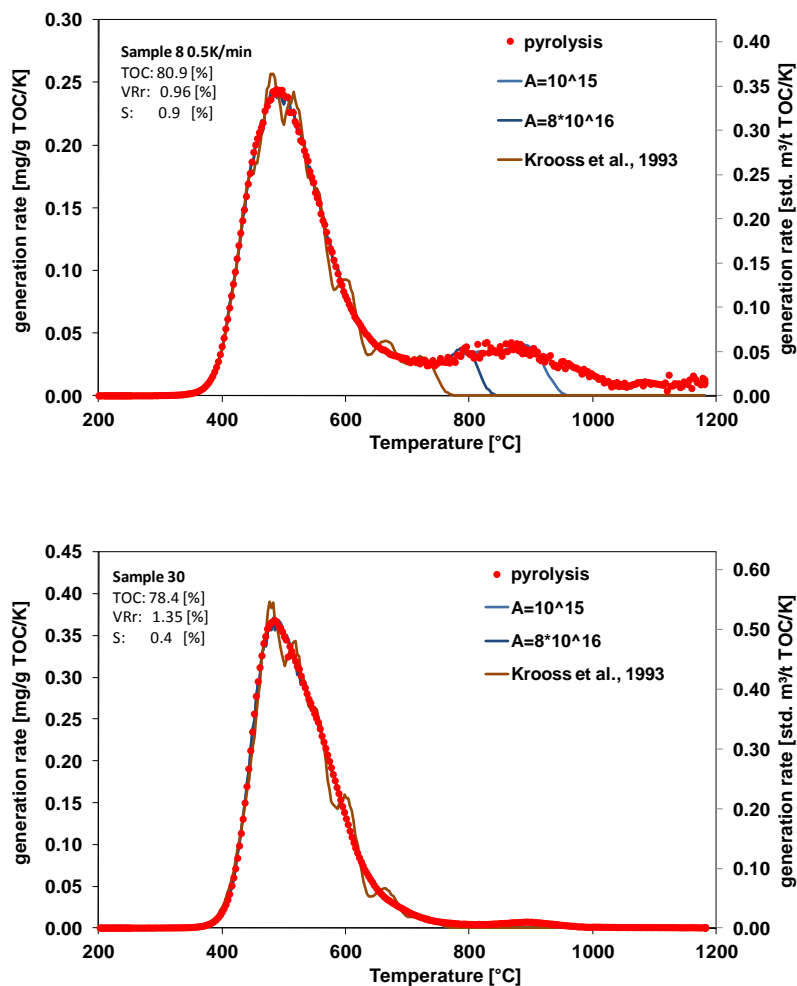
Fig. 3.13 Approximations of experimental pyrolysis data for two coal samples using different kinetic sets. Sample 8 shows significant methane generation at high temperatures (top) while sample 30 generates only small amounts of methane at high temperatures (bottom).

The activation energy distribution obtained from the different kinetic models showed no significant contribution of reactions with activation energies lower than 55 kcal/mol. The model using the experimentally derived frequency factor of $8.7 \cdot 10^{16}$ s^{-1} resulted in an activation energy distribution with a maximum between 70 and 75 kcal/mol. Activation energies obtained from modeling using a lower frequency factor of 10^{15} s^{-1} showed a maximum between 60 and 70 kcal/mol and were generally lower than those generated using the higher frequency factor (*Fig. 3.14*).
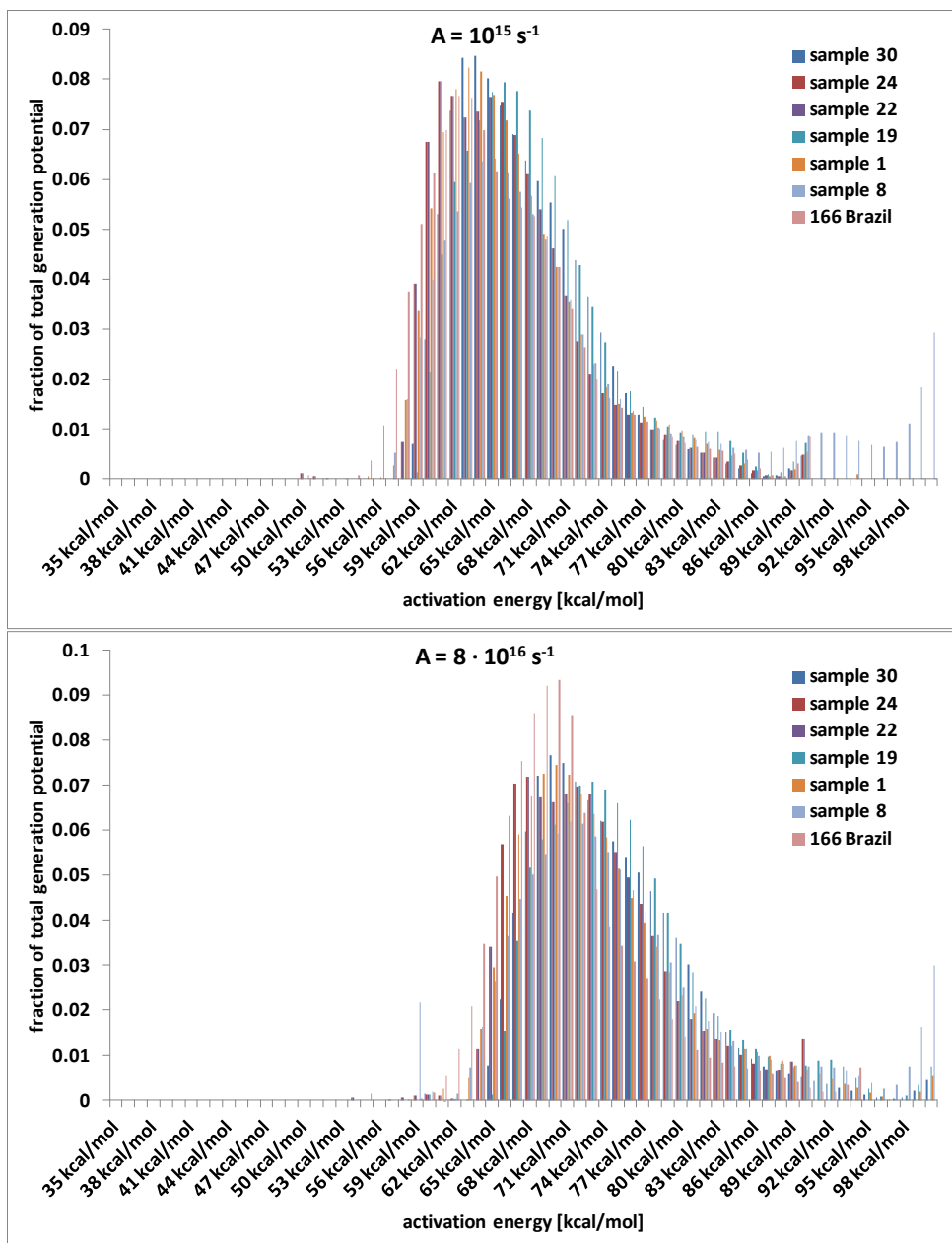
Fig. 3.14 Comparison of activation energy distributions obtained from least-square fits of experimental data using different frequency factors.

The kinetic model used by Krooss et al. (1993) to for coal from the German Ruhr Basin yields higher activation energies for coal from the Upper Silesian Coal Basin in the present study (*Fig. 3.15*). This indicates that the kerogen of coal samples from USCB is thermally more stable than coal from the Ruhr Basin. The differences in activation energy distributions are therefore due to the higher rank of the Czech coals (VRr 1.4%) as compared to the German coal (VRr 0.7%).
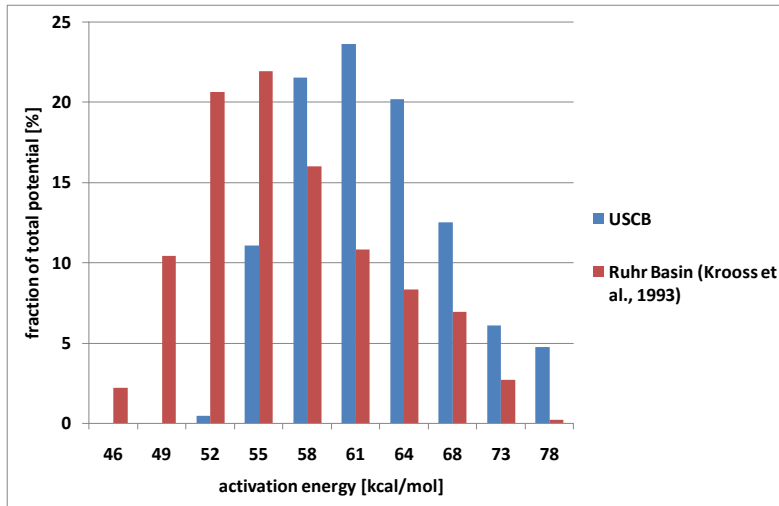
Fig. 3.15 Comparison of activation energy distribution obtained for coal from the Ruhr Basin (D) (Krooss et al., 1993) and for coal (sample 19) from the Upper Silesian Coal Basin (CR). Both kinetic parameter sets use a single pre-exponential factor (A= 4.33^{13} s^{-1}).

To evaluate the methane generation during coalification on the geologic scale, a constant heating rate of 10^{-11} K/min may be assumed (Schenk et al., 1997). Extrapolation of methane generation to the geologic heating rate was performed using the same activation energy distribution obtained from approximation of experimental data using a frequency factor of 8 · 10^{16} s^{-1}. Results of the extrapolation show a shift of methane generation rates towards lower temperature and a relative increase in generation rates (*Fig. 3.16*). The maximum of methane generation for the geologic conditions occurred between 208 and 246 °C.
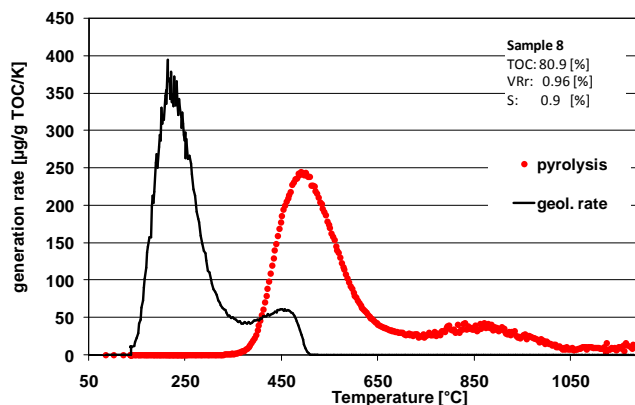
Fig. 3.16 Experimental methane generation curve measured at a laboratory heating rate of 0.5 K/min (red), and extrapolation to a constant geologic heating rate of 10^{-11} K/min (black).

Cumulative methane generation for the geologic heating rate ranged from 48 to 73 m^3/tTOC for coals from the USCB. The onset (> 0.0001 mg/gTOC/K) of methane generation at geologic heating rates occurred between 93 and 136 °C.

Combining the temperature history from basin modelling with gas generation kinetics gives information on the timing of gas generation in the USCB. For these calculations the temperature history data from PetroMod were converted to 1Ma temperature steps and kinetic parameters for a constant frequency factor (10^{15} s^{-1}) were used.

Since these calculations are based upon pyrolysis data from coal samples of medium- to high rank that have already generated gas during the earlier basin history, the extrapolation of these data to geologic times can only be used to estimate the timing of gas generation during the basin evolution. However, such estimation is based upon the assumption that the activation energy distribution derived from laboratory experiments is similar to the activation energy distribution of processes occurring during natural coalification, which might not be the case. To evaluate the amount of gas generated in the geologic past from coals in the USCB, pyrolysis of low rank coals that did not generate significant amounts of gas would be required. Such low rank samples were not available for the present study. Gas generation reported here represents the residual gas generation potential of present-day coals from the USCB (*Table 3.4*). Maximum gas generation occurred earlier in coal seams from the Ostrava Formation, resulting in higher methane generation yields than from coal seams of the younger Karviná Formation. These Methane yields are based on experimental kinetic parameters derived from coals of a rank interval between 1.0 and 1.8% VRr and thus are significantly lower than the theoretical methane yield obtained from mass balance calculations for the rank interval from 0.6 to 2.6% VRc. Accordingliy, the amount of gas that was generated during the basin history could not be assesse from coal samples available fort he present study.

Results of the extrapolation of kinetic parameters to the temperature history of the USCB show that gas generation started between 319 and 306 Ma b.p. and that no significant generation took place from 285 Ma b.p. until present day (*Fig. 3.17*). Coal from the Hrusov Formation shows a bimodal generation rate, with a small generation phase between 319 and 316 Ma b.p. and the major gas generation between 314 and 286 Ma b.p.. Coal seams from the Ostrava Formation (Jaklovec M., Hrussov M.) showed the highest gas generation compared to coal from the Karviná Formation (Saddle M., Sucha M.). The maximum gas generation rate was reached at 310 Ma for the Ostrava Formation and 10 million years later for coals from the Karviná Formation.

Table 3.4 Gas generation calculated for a linear geologic heating rate (10⁻¹¹ K/min) and for the temperature history obtained from 1D basin modelling. These values are derived from mature coals and do not reflect the entire gas generation during the basin history.

sample #	stratigraphy	stratigraphy	geologic heating rate (10⁻¹¹ K/min)		Temperature history from 1D basin model		
			temperature at max. generation rate [°C]	temperature at onset of gas generation (> 0.001 µg/gTOC/K) [°C]	Time of gas generation (> 1e-4 mg/gTOC/Ma) [Ma]	Gas generation rate. [m³/t TOC Ma]	Cumulative CH₄ yield [m³/t TOC]
1	L. Sucha M.		225	113	306 - 293	0.001	0.46
8	Saddle M.	Karviná	231	122	310 - 290	0.005	1.89
19	Jaklovec M.		246	130	312 - 286	0.019	9.78
22	L. Hrušov M.		208	93	319 - 316; 314 - 286	0.054	24.49
24	Petrkovice M	Ostrava	242	132	318 - 285	0.072	32.02
30	Petrkovice M		235	136	317 - 285	0.106	46.39
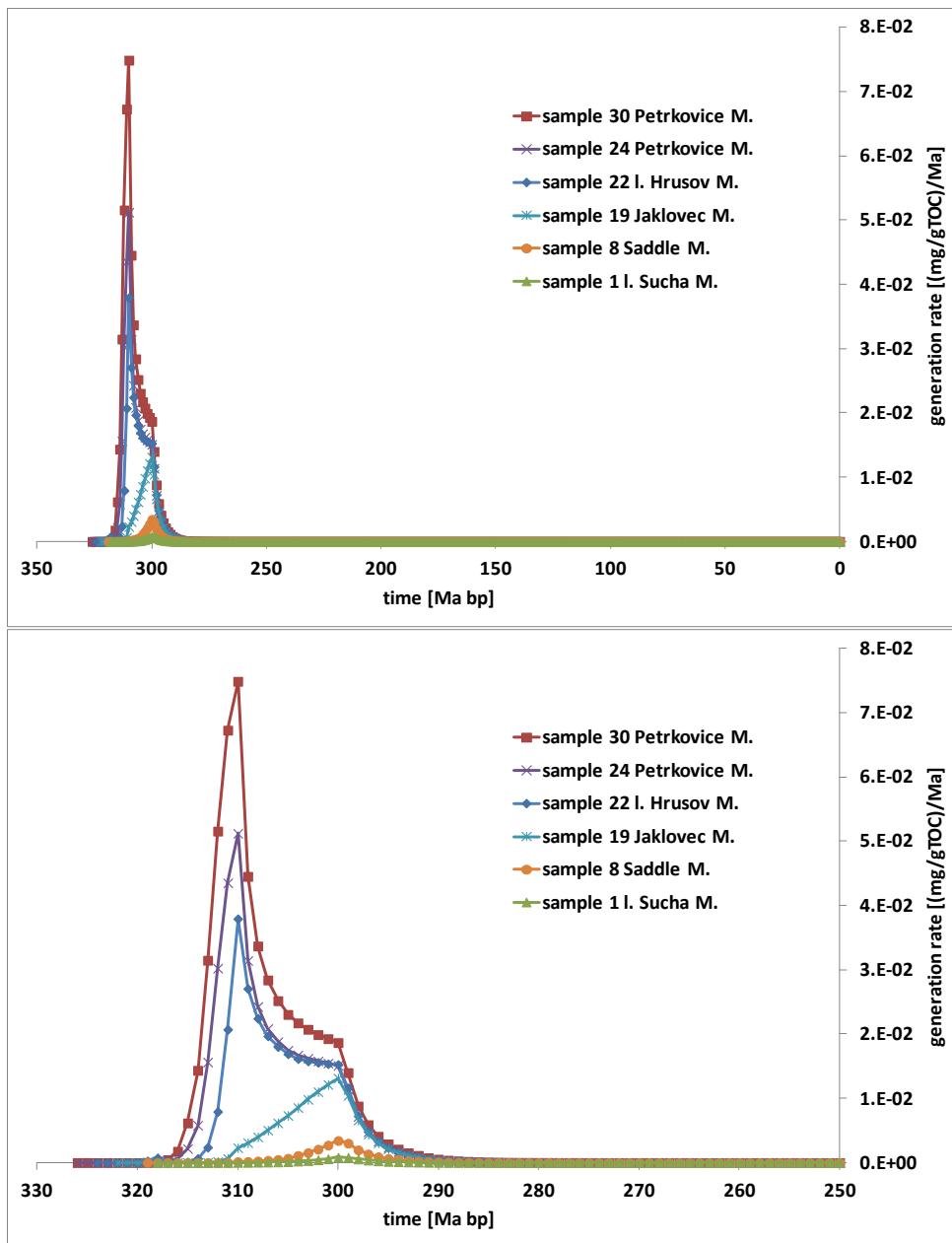
Fig. 3.17 Gas generation during basin history of the USCB for coal from the principal coal bearing formations, showing that major gas generation was complete by the Carboniferous – Permian transition (290 Ma b.p.).

The reburial of coal bearing sequences during the Carpathian overthrust in the Miocene and the associated temperature increase was too small to reinitiate significant gas generation in the study area (*Fig. 3.18*).
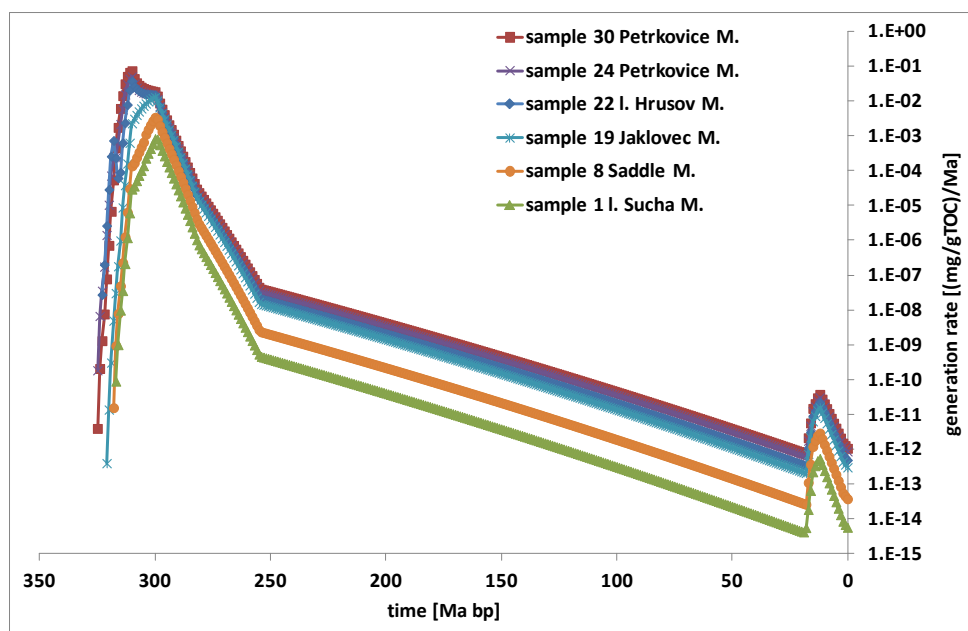
Fig. 3.18 Gas generation during the basin history of the USCB for coal samples from the principle coal-bearing formations on a logarithmic scale showing the influence of the Carpathian overthrust during Miocene.

3.6. Conclusions

Estimation of the theoretical gas generation potential of coals from the Upper Silesian Coal Basin by mass balance calculation showed that a cumulative amount of 201 m³/tTOC of methane and 138 m³/tTOC of CO_2 could be generated during coalification from 0.6% to 2.6% vitrinite reflectance.

Maturity information from Rock-Eval pyrolysis (T_{max}) of coals from the USCB analysed in this study showed that coals are of high-volatile bituminous A to low-volatile bituminous rank. Comparison of different maturity parameters (Rock-Eval T_{max}, VRr, VM) showed good correlations. Results of this bulk pyrolysis indicate that all of the analysed coals have reached the stage of effective thermogenic gas generation and expelled hydrocarbons during catagenesis.

During temperature-programmed open system pyrolysis experiments (Py-GC) at a constant heating rate of 0.5 K/min, gas generation from coals started around 300°C and reached maximum generation rates around 500°C. Methane generation showed a single peak for most samples; in some instances methane generation at higher temperatures (>700°C) was observed. The cumulative methane yield measured from Py-GC experiments of coals from the USCB ranged from 52 to 79 m³/tTOC, while for a coal sample from the Brazilian Paraná Basin a significantly lower methane yield of 32 m³/tTOC was measured. Pyrolysis experiments performed on one sample at different heating rates showed a shift of the methane generation maximum towards higher temperatures with increasing heating rate. From this shift a pre-exponential factor of $8.7 \cdot 10^{16}$ s⁻¹ was derived. Furthermore, pyrolysis of a sample from the USCB before and after solvent extraction indicated a contribution of the bitumen fraction to the overall residual methane yield of 28%.

Calculations of the half-life of gas generation for different kinetic parameters showed that activation energies >80 kcal/mol do not contribute significantly to methane generation at geologic times (pre-exponetial factor = 10^{16} s⁻¹).

Approximation of experimental gas generation data by kinetic models using different combinations of activation energies and pre-exponential factor show good fits for coals with a single generation peak. Coals that exhibit additional methane generation at high temperatures (>700°C) require higher activation energies for a good approximation of experimental data.

Activation energy distributions from kinetic analysis of the experimental data showed a maximum between 70 and 75 kcal/mol for the determined pre-exponential factor of $8.7 \cdot 10^{16}$ s^{-1}, whereas calculations using a lower pre-exponential factor (10^{15} s^{-1}) result in a shift towards lower activation energies (60 – 70 kcal/mol).

Extrapolation of methane generation to geologic conditions represented by a constant heating rate of 10^{-11} K/min results in a shift of generation maxima to lower temperatures between 208 and 246°C. The residual cumulative methane yields at these geologic conditions are lower than the methane yields measured in pyrolysis experiments under laboratory conditions. Calculation of methane generation using time and temperature information from 1D basin modelling showed that major gas generation in the SW USCB took place between 319 and 285 Ma b.p.. The maximum gas generation occurred earlier in coal seams from the Ostrava Formation, resulting in higher residual methane generationpotentilas than for coal seams of the younger Karviná Formation. These residual methane generation potentials represent less than 25% of the theoretical methane yield that was estimated from mass balance calculations.

Methane generation associated with the Carpathian overthrust during Miocene did not yield significant amounts of gas.

4. Investigations on the methane and carbon dioxide sorption capacity of coals from the SW Upper Silesian Coal Basin, Czech Republic

Investigations on the methane and carbon dioxide sorption capacity of coals from the SW Upper Silesian Coal Basin, Czech Republic

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4.1. Abstract

High-pressure sorption experiments with methane (CH_4) and carbon dioxide (CO_2) were performed on coals from different mines in the SW Upper Silesian Basin in Czech Republic. The coals were of high- to low-volatile bituminous rank, representing the late stage of catagenesis. The influence of different factors on the sorption capacity of these coals was evaluated by varying the experimental conditions. Excess sorption capacities of moisture equilibrated coals ranged from 0.3 to 0.8 mmol/g daf for CH_4 and from 0.8 to 1.2 mmol/g, daf for CO_2. Excess sorption capacities of as-received (air dried) coals were on average 34% higher for CH_4 and 17% higher for CO_2 as compared to the moisture equilibrated state. Sorption capacity shows a weak positive correlation with coal rank and a negative correlation with temperature. The CO_2/CH_4 sorption capacity ratio is larger for moisture-equilibrated coal, while it decreases with increasing pressure as well as increasing coal rank. From the experimental data correlations were derived between sorption capacity, and coal rank and temperature. These correlations were used to estimate the 'static' variation of sorption capacity with coal seam depth. Estimated sorption capacities increase towards a maximum value between 600 and 1000 m depth, followed by a decrease due to the predominance of the temperature effect. Temperature and pressure data derived from the reconstructed (1D) burial history were used to calculate the 'dynamic' variation of sorption capacity during basin evolution. These computations show that initial sorption capacity was significantly higher compared to the one estimated from present day pressure and temperature gradients. Uplift of coal seams resulted in under-saturation of the coal.

4.2. Introduction

Methane is the most common gas associated with bituminous coal seams worldwide (Rice, 1993). It is primarily generated during coalification, but also through anaerobic microbial activity in coal seams. Coal mine methane (CMM) is released during underground and surface mining operations as well as during post mining activities and from abandoned mines. Especially in underground mines it represents a major safety hazard and its concentration has to be controlled by ventilation. When released to the atmosphere, methane acts as a potent greenhouse gas. It is estimated that about 6% of global methane emissions originate from coal mining activities (USEPA, 2006). On the other hand methane represents an important energy source when extracted during coal mining as mine gas or gob gas. Coalbed methane (CBM) from unmined coal seams also represents an unconventional hydrocarbon source, if efficient extraction is possible.

Carbon dioxide, as a greenhouse gas in the atmosphere, has also been observed commonly in coal seams. It can be of geologic origin but may also be produced by chemical or

microbial oxidation of methane and other organic substances in active and abandoned coal mines, where oxygen is present. The sequestration of carbon dioxide in unmined coal seams has been evaluated as a means to reduce industrial CO_2 emissions (*e.g.* from power plants) and to enhance coalbed methane recovery (ECBM) (White et al., 2005). Consequently, there is growing demand for a better understanding of occurrence, transport and reactivity of coalbed methane and coalbed carbon dioxide.

To improve knowledge of the influence of adsorption/desorption processes on the amount and composition of coal-related gas, the work presented in this paper was focused on the determination of the methane and carbon dioxide sorption capacity of bituminous coals, as well as the characterization of coal maturity and composition, which can have an effect on the sorption capacity. The Upper Silesian Coal Basin (USCB) in Czech Republic was chosen as a 'natural laboratory' for this study. Samples from three different underground coal mines in the Ostrava-Karviná coalfield (OKC) in the SE USCB were analyzed. Based on the experimental results, a simple model was developed to estimate the in situ methane sorption capacity of coals as a function of inherent coal properties such as ash yield and rank as well as pressure, temperature and moisture content.

4.3. Study area and previous work

4.3.1. Geological setting

The Upper Silesian Coal Basin is one of Europe's major hard coal basins. It is located at the eastern edge of the Variscan Bohemian Massif, representing the eastern extension of the Moravo-Silesian Basin (*Fig. 4.1*). The USCB occupies a known area of more than 7000 km^2, of which more than two thirds are located in Poland, whereas the southern part of the basin, the Ostrava-Karvina coalfield (OKC), with a known area of 1550 km^2, is situated in NE Czech Republic (Sivek et al., 2003). Most coal bearing strata of the OKC are of Namurian A-C age. A simplified map of Carboniferous geology of the OKC is given in *Fig. 4.1* and a stratigraphic overview is shown in *Fig. 4.2*.

Economically important coal reserves of the OKC occur within the Upper Carboniferous Ostrava and Karviná formations.

The paralic Ostrava Formation (Upper Mississippian) contains 168 coal seams with an average thickness of 0.73 m. The most important unit is the Petrkovice Member, which contains more than 60% of the coal reserves of the Ostrava Formation (Dopita and Kumpera, 1993).

The coal content of the limnic Karviná Formation (Lower Pennsylvanian) is up to four times higher than that of the paralic Ostrava Formation. The largest coal reserves of the basin are found in the Saddle and Sucha Member of the Karvina Formation, which contains a total of 87 seams with an average thickness of 1.76 m. The most important seam is the Prokop (504) seam of the Saddle Member, which alone contains about 14% of all coal reserves. With a thickness of more than 10 m it is the thickest coal seam of the OKC (Dopita and Kumpera, 1993).
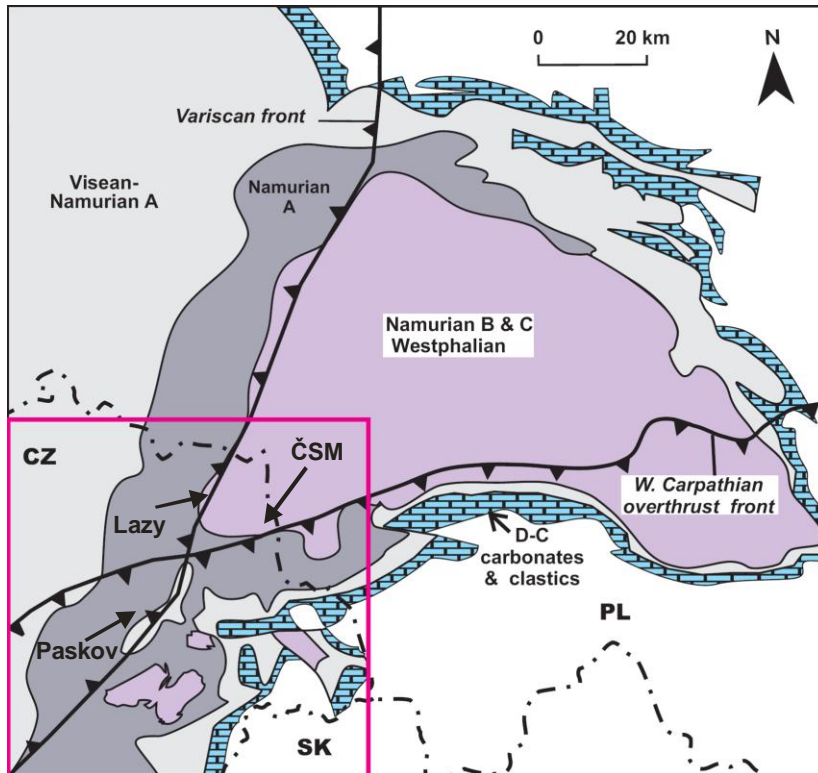
Fig. 4.1 Location of the study area in the Southern Upper Silesian Coal Basin, Czech Republic (adapted from Sivek et al,. 2003).

The gas content of coal-bearing sequences in the Czech part of the USCB mostly ranges between 2 and 10 m^3/t and shows an overall decline with increasing depth (Hemza et al., 2009). Geochemical and carbon isotopic investigations of coal related gas provide evidence of co-occurrence of thermogenic and microbial gas in the Ostrava-Karviná Coalfield, showing no clear relationship between gas composition and stratigraphy or thermal maturity of associated coal beds (Franců et al., 2007; Weniger et al., 2011b submitted). Similar observations were made in the Polish part of the USCB by Kotarba (2001). Kandarachevová et al. (2009) report that the occurrence of gas deposits found in Carboniferous rocks and overburden strata in the OKC is spatially related to zones of elevated thermal maturity.

Czech Republic				Poland		
				Western Part	**Eastern Part**	
Pennsylvanian / Bashkirian / Westphalian — 311.7 Ma — B		Eroded		Siltstone Series — Orzesze Beds (Seam 301 ... Seam 326)	Seam 301 ... Seam 326	Limnic Series
A — 316.5 Ma	Karviná Formation / Upper	Doubrava Member (Seam 962 ... Seam 702)		Zalęźe Beds	Seam 327 / Seam 364 / Seam 401 / Seam 406	
C — G	Lower	Suchá Member (Seam 686 ... Seam 605)		Upper Silesian Sandstone Series — Ruda Beds	Seam 407 ... Seam 420	
B — R		Saddle Member ((Prokop) Seam 504) Seam 564		Saddle/Zabrze Beds	Seam 501 ... Seam 510	
318.1 Ma — H		Hiatus		Jejkowice Beds	Hiatus	
Mississippian / Serpukhovian / Namurian — E₂	Ostrava Formation / Upper	Poruba Member (Seam 499 ... Seam 403)	Upper	Poręba Beds (Seam 601 ... Seam 630)	Grodziec Beds	Paralic Series
A		Jaklovec Member (Seam 385 ... Seam 301)		Jaklowiec Beds (Seam 701 ... Seam 723)		
E₁	Lower	Hrušov Member — Upper (Seam 255, Seam 201), Lower (Seam 169, Seam 102)	Lower	Gruszów Beds (Seam 801 ... Seam 848)	Flora Beds	
326.5 Ma		Petřkovice Member (Seam 099 ... Seam 009)		Pietrzkowice Beds (Seam 901 ... Seam 915)	Sarnów Beds	

Fig. 4.2 Stratigraphic overview of the Ostrava Karviná Coalfield (modified from Sivek et al,. 2003).

McCants et al. (2001) observed a zone of 'gassy coal' below ca. 1000 m during CBM exploration in the Polish part of the USCB. They found a link between the occurrence of gas rich coal seams and changes in the local depth/rank gradient and emphasized the importance of coal rank information for CBM exploration.

4.3.2. Thermal maturity of coal from the Ostrava-Karviná Coalfield

In the Czech part of the Upper Silesian Basin, intense exploration for coal was conducted in the course of the 20th century. During this exploration phase, maturity was primarily determined based on volatile matter yield (VM, daf). Only recently, during the final stage of exploration, vitrinite reflectance (VRr) measurements have been used for thermal maturity assessment (Sivek et al., 2003; Sivek et al., 2008; Hemza et al., 2009). Coals in the Czech part of the USB are mostly of bituminous rank and show the highest thermal maturity in the WNW part of the OKC, where Variscan orogenic processes were most intense and coals locally reach anthracite rank. The degree of coalification decreases towards the ESE and S to SSW (Kandarachevová et al., 2009; Sivek et al., 2003). Sivek et al. (2008) report a good correlation of thermal maturity (VM, daf) with increasing depth, showing slightly different trends in different parts of the basin.

4.4. Samples

A total of thirty coal, carbonaceous shale and coal-bearing rock samples, from different mines of the Ostrava-Karviná Coalfield were analyzed in this study. These samples cover almost the entire stratigraphic range of coal-bearing sequences in the study area. The set comprised ten channel samples from the Paskov mine near Staric, representing coal seams of the lower Ostrava Formation, and seven channel samples from the ČSM mine near Stonava, representing coal seams from the Karviná Formation. Additionally, thirteen samples from two exploration wells (Lazy D-75/08, Lazy D-76/08), drilled in the Karviná mine (Lazy Business Unit), representing coal seams from the upper Ostrava and Karviná Formations were analysed in this study. The Prokop seam of the Lazy D-76/08 well was split into two sub-samples (8.1 and 8.2). All seventeen channel samples, as well as nine samples from exploration wells, were subjected to high pressure sorption experiments. Locations of sampled coal mines are given in *Fig. 4.1*. A list of all analyzed samples is given in *Table 4.1*.

Table 4.1 Overview of samples from the Ostrava-Karviná coalfield

Sample #	Mine	Seam Code	Lithology	Litostrati-graphy	Formation	Age	Depth (m)
1	ČSM	648	coal	l. Suchá M.	Karviná	Namurian C	714
2	ČSM	634	coal	l. Suchá M.	Karviná	Namurian C	700
3	ČSM	624	coal	l. Suchá M.	Karviná	Namurian C	700
4	ČSM	608	coal	l. Suchá M.	Karviná	Namurian C	638
5	ČSM	546	coal	Saddle M.	Karviná	Namurian B	694
6	ČSM	530	coal	Saddle M.	Karviná	Namurian B	743
7	ČSM	504	coal	Saddle M.	Karviná	Namurian B	558
8.1	Karviná (Lazy)	504	coal	Poruba M.	Karviná	Namurian B	460
8.2	Karviná (Lazy)	504	coal	Poruba M.	Karviná	Namurian B	460
9	Karviná (Lazy)		ss+coal	Poruba M.	u. Ostrava	Namurian A E2	467
10	Karviná (Lazy)	446	coal	Poruba M.	u. Ostrava	Namurian A E2	804
11	Karviná (Lazy)	440	coal	Poruba M.	u. Ostrava	Namurian A E2	831
12	Karviná (Lazy)	444	si+coal	Poruba M.	u. Ostrava	Namurian A E2	832
13	Karviná (Lazy)	436	coal	Poruba M.	u. Ostrava	Namurian A E2	866
14	Karviná (Lazy)	432	laminit	Poruba M.	u. Ostrava	Namurian A E2	862
15	Karviná (Lazy)	424	coal	Poruba M.	u. Ostrava	Namurian A E2	951
16	Karviná (Lazy)	420	ss-si	Poruba M.	u. Ostrava	Namurian A E2	948
17	Karviná (Lazy)	410	laminite	Poruba M.	u. Ostrava	Namurian A E2	1009
18	Karviná (Lazy)	409	coal	Poruba M.	u. Ostrava	Namurian A E2	1060
19	Karviná (Lazy)		volc, ss	Jaklovec M.	u. Ostrava	Namurian A E2	1142
20	Karviná (Lazy)	386	ss	Jaklovec M.	u. Ostrava	Namurian A E2	1152
21	Paskov	112	coal	l. Hrušov M.	l. Ostrava	Namurian A E1	550
22	Paskov	112	coal	l. Hrušov M.	l. Ostrava	Namurian A E1	599
23	Paskov	84	coal	Petřkovice M.	l. Ostrava	Namurian A E1	855
24	Paskov	82	coal	Petřkovice M	l. Ostrava	Namurian A E1	840
25	Paskov	82	coal	Petřkovice M	l. Ostrava	Namurian A E1	815
26	Paskov	80	coal	Petřkovice M	l. Ostrava	Namurian A E1	800
27	Paskov	76	coal	Petřkovice M	l. Ostrava	Namurian A E1	749
28	Paskov	63	coal	Petřkovice M	l. Ostrava	Namurian A E1	707
29	Paskov	63	coal	Petřkovice M	l. Ostrava	Namurian A E1	600
30	Paskov	41	coal	Petřkovice M	l. Ostrava	Namurian A E1	505

ss= sandstone; si= siltstone; volc= volcaniclastics

4.5. Methods and experimental procedures

4.5.1. Proximate analysis

Proximate analyses of coal samples according to DIN 51700 comprised of the determination of "as received" (hygroscopic) moisture content, ash yield and volatile matter yield. All analyses were performed in triplicate on powdered sub-samples (1 g, grain size <0.2 mm).

4.5.2. Determination of equilibrium moisture content

The equilibrium moisture content was determined according to the ASTM 1412 standard method in an atmosphere of 97% relative humidity (saturated K_2SO_4 solution at 30°C). All measurements were performed in triplicate on coal samples from ČSM and Paskov mines.

4.5.3. Coal petrography

Petrographic analyses were performed following recommendations by the International Committee for Coal and Organic Petrology (ICCP) (Taylor et al., 1997). For petrographic analyses polished particulate mounts were prepared from representative subsamples. Optical petrographic characterization comprised maceral group analysis on a H-Pl-Pol microscope (Zeiss, Germany) by point counting (500 counts) and determination of vitrinite reflectance on an Axioplan microscope (Zeiss, Germany) using DISKUS Fossil software (Hilgers, Germany) in random mode (100 measurements).

4.5.4. TOC analysis

The total organic carbon (TOC) contents were determined in triplicate measurements on a multiphase carbon analyzer RC-412 (LECO, USA) using 50 mg of powdered samples (grain size <0.2 mm).

4.5.5. High-pressure sorption experiments

4.5.5.1. Experimental set-up

Methane and carbon dioxide excess sorption isotherms were determined using the manometric method described by Krooss et al. (2002), Busch et al. (2004), Siemons and Busch (2007) and Gensterblum et al. (2009, 2010). The experimental set-up consists of a stainless-steel sample cell (~14 cm^3 for CH4, ~8.5 cm^3 for CO_2), a set of actuator-driven valves, and a pressure transducer (max. pressure 17 MPa for CH_4 and 25 MPa for CO_2), with a precision of 0.05% of the full-scale value. The volume of the reference cell and the void volume in the sample cell were determined by helium (He) expansion in a calibration run. The stainless-steel sample cell is equipped with a 2-μm filter to prevent coal or mineral particles from entering the valves. The entire experimental device is placed in a temperature-controlled oven to ensure constant temperature (±0.1°C) throughout the experiments. Helium density of samples was calculated from sample mass and void volume (determined by helium expansion) for each measurement / isotherm.

The procedure of sorption measurements on moisture-equilibrated coal was as follows:

- Moisture equilibration

- Transfer of moist samples to sample cell and weight measurement

- Transfer of sample cell to the sorption apparatus

- Leak test (100 bar helium for ca. 2 h until temperature, pressure equilibration)
- Evacuation (10^{-3} Pa, 15 minutes)
- Void volume measurement (helium, stepwise pressure increase until 100 bar)
- Evacuation (10^{-3} Pa, 15 minutes)
- Sorption measurement (CH_4 or CO_2)

4.5.5.2. Determination of multiple isotherms

In order to avoid moisture loss from previously moisture-equilibrated samples during depressurization and evacuation between successive sorption experiments, multiple isotherms were recorded in a single run by varying the system temperature during each pressure step. A defined quantity of gas was charged into the system through the reference cell at 45°C. After pressure equilibration, the temperature was raised to 55°C and 65°C. At each temperature the system was equilibrated for two hours and the pressures recorded. Finally, the temperature was set back to 45°C and the resulting equilibrium pressure was compared with the initial equilibrium pressure at 45°C to check for consistency and absence of leaks. This procedure was repeated at all pressure steps. Based on the known quantities of gas introduced into the system at each pressure step, the equilibrium pressures at each temperature and the equations of state of the gases the excess sorption isotherms were calculated for the three temperatures.

4.5.5.3. Parameterization of experimental sorption isotherms

The experimental methane sorption isotherms were fitted by the Langmuir function:

$$n_{ads} = n_L \cdot \frac{p}{P_L + p}$$

(1)

The Langmuir function is based on the implicit assumption that the adsorbed phase has a negligible volume i.e. that its density is much higher than the density of the free gas phase. This assumption is not valid any longer for CO_2 at high pressures. Therefore the density of the adsorbed phase is explicitly taken into account in the extended formulation of the Langmuir sorption capacity function for CO_2:

$$n_{ads} = n_L \cdot \frac{p}{P_L + p} \cdot \left(1 - \frac{\rho_{free}}{\rho_{adsorbed}}\right)$$

(2)

Here Here the density of the adsorbed phase ($\rho_{adsorbed}$) represents an adjustable parameter, in addition to the Langmuir parameters n_L and P_L.

The equations of state (EOS) for CO_2 and CH_4 by Span and Wagner (1996) and Setzman and Wagner (1991), respectively, were used in the evaluation of the manometric sorption experiments. Helium densities used for the assessment of the void volume of the measuring cell were calculated by a van der Waals equation of state after Michels and Wouters (1941).

The total experimental error for adsorption measurements is less than 10% n_{ads} for carbon dioxide isotherms and less than 3% n_{ads} for methane isotherms at the final experimental pressure. Further information on the accuracy of the manometric sorption setup used for this

study, as well as a thorough evaluation of possible experimental errors and pitfalls has been published recently by Li et al. (2010) and Gensterblum et al. (2009, 2010).

4.6. Results

4.6.1. Coal Petrography

Results of the maceral group analysis and random vitrinite reflectance measurements are listed in *Appendix III, Table 1*. The maceral group composition is reported on a mineral matter free (mmf) basis.

4.6.2. Maceral composition

Coals from all three locations are dominated by vitrinite (*Fig. 4.3*). Coals from Paskov mine have vitrinite contents from 78 to 92%, whereas inertinite varies between 8% and 22% and liptinite is generally less abundant (<2.5%) or absent. The limnic coals from the ČSM mine have a higher abundance of liptinite group macerals (1-11%), dominated by sporinite. Vitrinite contents range from 52% to 84%, i.e. lower than those of the paralic Paskov coals, and inertinite contents vary between 5% and 39%. The maceral composition of coals from Lazy mine have a higher variability, with vitrinite ranging from 49 to 98%, inertinite between 2 and 51% and liptinite up to 23%.
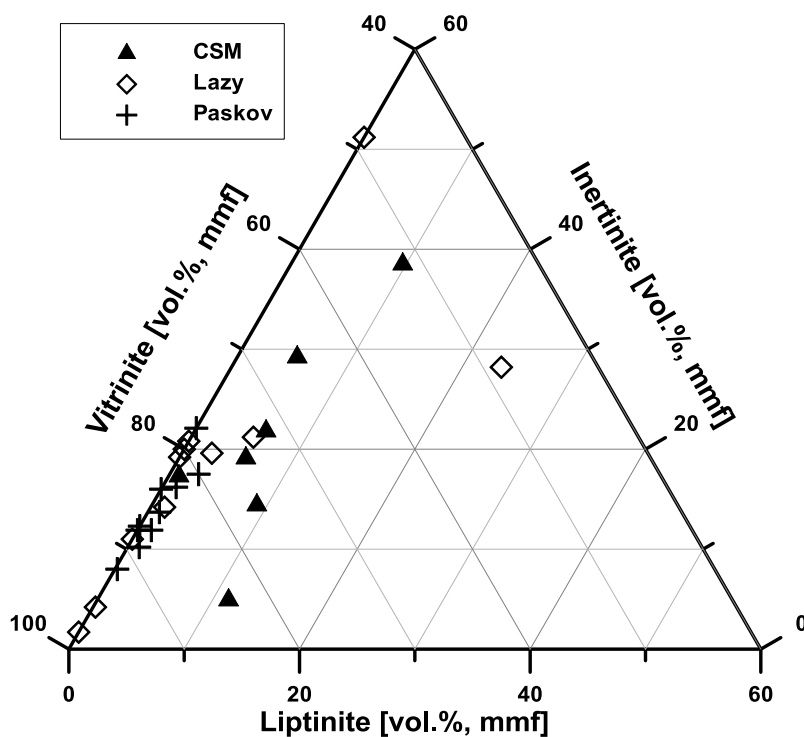
Fig. 4.3 Maceral group composition of the coals from the three sampling locations.

4.6.3. Vitrinite Reflectance

Vitrinite reflectance (VRr) values of coal samples used in this study range from 1.0 to 1.8%. Coals from Paskov mine cover a range from medium volatile to low volatile bituminous

rank, whereas coal samples from ČSM mine are of medium volatile bituminous rank (VRr 1.1 – 1.2%) and coals from Lazy mine are of high volatile bituminous A and medium volatile bituminous rank. Vitrinite reflectance values increase with depth. This rank vs. depth trend is steeper for coals from Paskov mine (0.18% VRr / 100 m) than for coals from Lazy mine (0.05% VRr / 100 m) (*Fig. 4.4*).

Fig. 4.4 Maturity vs. depth plot showing different trends for coals from Paskov and Lazy mine.

4.6.4. Proximate analysis and moisture equilibration

Results of proximate analysis ("as-received" moisture content, ash yield, volatile matter yield and amount of fixed carbon) and equilibrium moisture of all samples analyzed in this study are summarized in *Appendix III, Table 1*.

4.6.5. Hygroscopic moisture and equilibrium moisture

Hygroscopic moisture contents range from 0.3 up to 1.7 wt.% and show a decreasing trend with increasing thermal maturity. The highest values (0.6 to 1.7 wt.%) were measured for high volatile bituminous coals from the ČSM mine, while carbonaceous shale and rock samples from the Lazy mine show the lowest hygroscopic moisture contents, ranging from 0.3 to 1 wt.%.

4.6.6. Equilibrium moisture

Equilibrium moisture ranged between 1.6 and 2.5 wt.% for coal from ČSM mine and between 1.0 and 1.6 wt.% for Paskov mine coal. The moisture content increased during moisture equilibration by 19 to 185% relative to the "as received" moisture. The variation of equilibrium moisture with coal rank shows a similar trend to the one observed for the hygroscopic moisture.

4.6.7. Volatile matter yield

The volatile matter (VM) yield has been used predominantly to classify coal rank in the Czech part of the Upper Silesian Basin. Due to the lack of vitrinite reflectance data for most of the coal deposits in the OKC, it is the main parameter for thermal maturity ranking of these coals. However, low-rank coals with volatile matter yields in excess of 31 wt.% (daf) are difficult to classify by this parameter (van Krevelen, 1993). It is also known that maceral composition as well as amount and type of mineral matter, especially carbonates and clay minerals, can affect the volatile matter yield, thus compromising the applicability of VM for rank classification (Alpern et al., 2002). Therefore, in this study VM yields were not determined for samples with ash yields higher than 80 wt.% and samples with ash yields significantly higher than 10 wt.% were not used for correlation of volatile matter with other maturity parameters (VRr, T_{max}).

For coals from the ČSM mine the volatile matter yield ranged from 23 to 26 wt.%, indicating medium volatile bituminous rank. Coal samples from Paskov mine show a larger variation in VM, ranging from 16 to 28 wt.%, corresponding to a range from medium volatile bituminous to low volatile bituminous rank. Coal samples from the Lazy mine wells cover the largest maturity range with VM yields between 22 and 35 wt.%. The highest volatile matter yield of 35 wt.% was found for a coal from the Prokop seam, which also had the highest liptinite (sporinite) content of 23%. However, the correlation between liptinite content and volatile matter yield is very weak (r^2=0.3).

4.6.8. Total Organic Carbon (TOC)

The amount of total organic carbon (TOC) measured for all coal samples ranged between 70% and 85%.

The amount of total inorganic carbon (TIC) ranged between 0.3% and 3.8%. TOC values are given in *Appendix III, Table 1*.

4.6.9. High-pressure gas sorption

Results of the methane and carbon dioxide sorption tests as well as sample densities calculated from sample mass and void volume (helium expansion) for each measurement are summarized in *Appendix III Tables 3 through 9*. All measured isotherms as well all measured isotherm data are listed in *Appendix III*.

Variations in calculated density for the same sample were observed and are attributed to changes in sample volume and / or weight during sample handling (evacuation). While additional water (adsorbed or in pore space) would cause a decrease in the overall sample density, we observe slightly higher densities for moist coals. While errors in sample weight are very unlikely, one explanation could be that coal samples lost water during sample transfer or during evacuation after the leak test. Because sample weight was only determined before the leak test, the density would be overestimated if water was lost during evacuation and thus the 'real' sample mass would have been lower.

If water was lost during evacuation, this would also mean that the observed effect of moisture on sorption is underestimated.

Another factor could be alteration effects such as oxidation of coal samples during storage between the different measurements, which could cause an increase in ash yield

(Mastalerz et al., 2009). However, this would be more likely for low-rank coal and the amount of oxygen uptake required explaining the higher density would be very high.

4.6.9.1. Methane sorption isotherms

To allow for good comparison of sorption isotherms on different coal samples, all sorption measurements were carried out at 45°C. Since sorption capacity decreases with increasing temperature, sorption capacities determined at 45°C represent minimum capacities for the coal samples analyzed in this study.

Methane excess sorption isotherms were determined on all samples in the "as-received" state. Furthermore, sorption isotherms were determined at 20°C on three "as-received" samples from the Paskov mine and at 55°C and 65°C on one moisture-equilibrated coal from Lazy mine. Results of the methane sorption tests are summarized in Appendix II, Tables 4 through 10. Apart from the measured maximum value of excess sorption (n_{max}) isotherms, these Tables list the Langmuir pressures (P_L) and the maximum sorption capacities (n_L), obtained from a least-squares fit of the Langmuir function to the experimental results. All parameters are reported on the "raw" and "dry, ash-free" basis.

Results from sorption isotherms measured at different temperatures were used to construct isosteres (plots of ln(P) vs. reciprocal temperature 1/T) for measured constant sorbate loadings (nm) between 0.15 - 0.3 mmol/g. From the slope of each of these isosteres, the isosteric heat of adsorption (qst) was calculated using the Clausius Clapeyron equation (Sircar, 1985;, Shen and Bülow, 2000):

$$qst = -R[dlnP/(1/T)]nm \qquad [kJ/mol] \qquad\qquad (3)$$

It should be noted that this approach is strictly only valid for an ideal gas. Since the isosteres used for the calculation are derived from isotherms measured at pressures between 1 and 6 MPa, calculated heats of adsorption should be viewed with caution and were only used to confirm that the observed process was physisorption rather than chemisorption.

To evaluate the effect of moisture content on gas sorption, isotherms for all Paskov and ČSM samples, as well as for one sample from the Lazy mine, were also measured in the moisture equilibrated state according to ASTM 1412. Plots of methane sorption isotherms measured on "as-received" and moisture-equilibrated coal at 45°C are given in *Fig. 4.5* and *Appendix III Fig. 1*. For two of the Paskov samples isotherms were also measured after drying them in the sample cell (evacuation and heating to 105°C for approximately 1.5 h). After the end of the measurements it was found that the samples still had moisture contents of 0.2 – 0.8%.
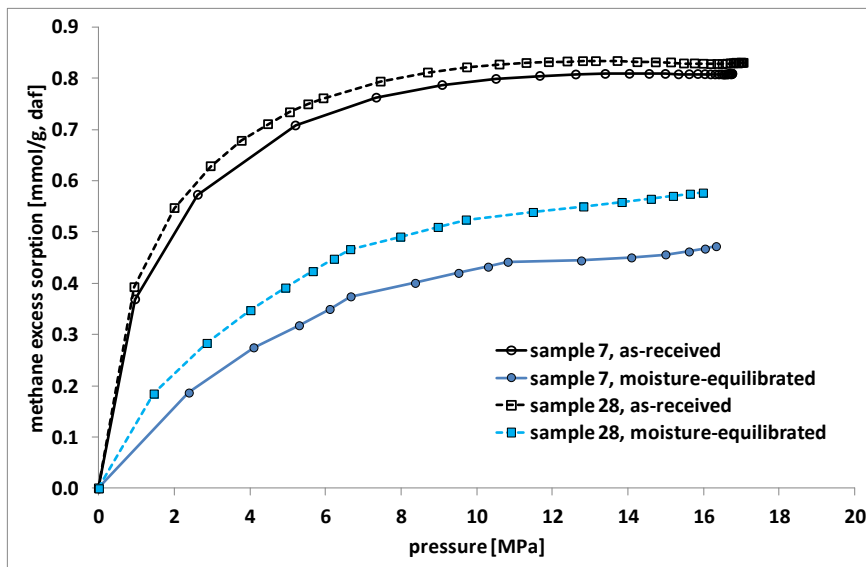
Fig. 4.5 Methane sorption isotherms for "as-received" (open symbols) and moisture-equilibrated (solid symbols) coal from Paskov mine (squares) and ČSM mine (circles).

Maximum methane excess sorption capacities measured on "as-received" coal at 45°C range from 0.49 to 0.99 mmol/g of dry ash-free coal. The calculated Langmuir sorption capacities (n_L) range from 0.57 to 1.1 mmol/g, daf. Moisture-equilibration causes a significant reduction of excess sorption capacity ranging from 0.30 to 0.78 mmol/g, daf. The corresponding Langmuir sorption capacities range from 0.40 to 1.08 mmol/g, daf, which corresponds to a reduction in sorption capacity between 4 and 47% (average 24%).

Isotherms measured at 20°C show maximum excess sorption and sorption capacities very similar to the 45°C isotherms. However, the excess sorption in the low- to intermediate-pressure region (<10MPa) is significantly higher at 20°C. In the high-pressure region above ~12MPa, methane sorption isotherms measured at 20°C converge with isotherms measured at 45°C for two of the three compared coals (*Fig. 4.6*). On a dry, ash-free basis, a temperature increase of 25°C, from 20°C to 45°C, is accompanied by a decrease in sorption capacity by 7 – 13% at a pressure of 3 MPa. However, in the high-pressure range (15 – 17 MPa) temperature variation does not result in a significant change in maximum excess sorption (<5%).

Maximum excess sorption measured on a moisture-equilibrated coal from the Lazy mine decreased with increasing temperature from 0.44 mmol/g, daf at 45°C to 0.39 mmol/g, daf at 65°C (nL 0.54 – 0.45 mmol/g, daf).
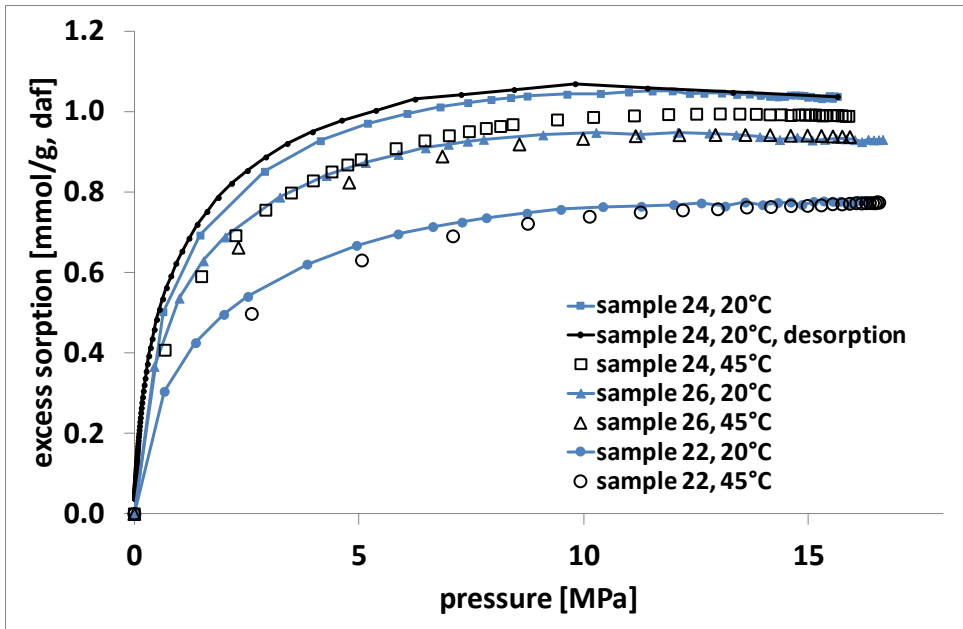
Fig. 4.6 Methane isotherms for three "as received" coals from Paskov mine measured at 20°C and 45°C.

4.6.9.2. Carbon dioxide sorption isotherms

High-pressure carbon dioxide sorption isotherms were measured at 45°C on "as-received" coal samples from the Paskov and ČSM mines, as well as on one sample from Lazy mine. In addition, carbon dioxide sorption measurements were performed after moisture equilibration on four coals from Paskov mine, one coal from ČSM mine and one coal from Lazy mine (*Fig. 4.7, Appendix III Fig. 2*). Analogue to methane sorption experiments, additional sorption measurements were performed at 20°C and on one sample at 55°C and 65°C. To avoid condensation of carbon dioxide in the sorption apparatus, CO_2 sorption measurements at 20°C were only performed up to 5.5 MPa. All measured CO_2 isotherms were approximated by the excess sorption function given in equation (3). Maximum excess sorption as well as the three parameters n_L, P_L and $\rho_{adsorbed}$, adjusted by a least-squares optimization procedure, for the individual isotherms are listed in *Appendix III Tables 4 through 8*.
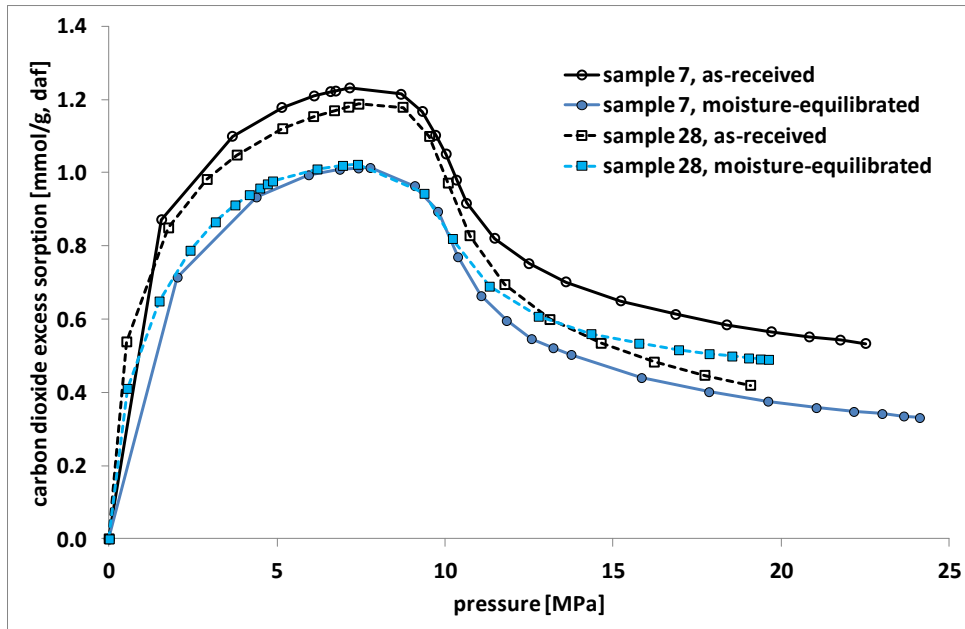
Fig. 4.7 CO₂ sorption isotherms for "as-received" (open symbols) and moisture-equilibrated (solid symbols) coal from Paskov mine (squares) and ČSM mine (circles).

All high-pressure CO_2 excess sorption isotherms measured at 45°C exhibit a maximum in the 6 to 10 MPa pressure range, followed by a continuous decline. This maximum is due to the steep increase in the specific density of supercritical CO_2 in this pressure range (cf. Gensterblum et al., 2009, Bae and Bhatia, 2006).

Maximum excess sorption (n_{max}) values measured on "as-received" coals range from 0.96 to 1.41 mmol/g, daf. CO_2 sorption capacities (n_L) obtained from approximation of the experimental data range from 1.38 to 2.42 mmol/g, daf.

CO_2 sorption on moisture-equilibrated coals is generally lower as compared to "as-received" samples. Maximum CO_2 excess sorption values measured on moisture equilibrated coals range from 0.80 to 1.16 mmol/g, daf, which represents a reduction between 14 and 28% (average 18%) relative to "as-received" samples. CO_2 sorption capacities, derived from approximation of experimental data using equation (3), range from 1.53 to 1.96 mmol/g, daf, corresponding to a reduction between 2 and 31% (average 12%) relative to "as-received" samples.

Parameterisation of experimental data using equation (3) yields approximate values for the density of the sorbed phase. Alternatively, the density of sorbed CO_2 can be estimated by plotting the measured excess sorption data versus the density of the gas CO_2 phase. Extrapolation of the linear part of this plot in the high density (high pressure) region to the x-intercept yields the sorbed phase density (Sudibandriyo et al., 2003; Gensterblum et al., 2009). At this (extrapolated) intercept the free (supercritical) CO_2 phase and the sorbed phase have the same density so that they cannot be distinguished any more. In consequence, the excess sorption at this pressure is zero. Estimations of the sorbed phase density by both methods were compared and show good agreement (*Appendix III Table 4 – 8*). The estimated sorbed phase density differs among the analyzed samples and ranges from 940 g/cm³ to 1490 g/cm³. Comparison of CO_2 sorbed phase densities with ash yield of coal samples seems to indicate that CO_2 is more densely sorbed on organic surfaces as compared to inorganic surfaces, *e.g.* of clay minerals (*Fig. 4.8*). This is in agreement with results from CO_2 sorption experiments on shales and clay minerals performed in our laboratory. However, additional research is needed to

investigate whether the sorbed phase density is similar to the density of liquid CO_2 at the boiling point or if and how it is controlled by the adsorbent composition.
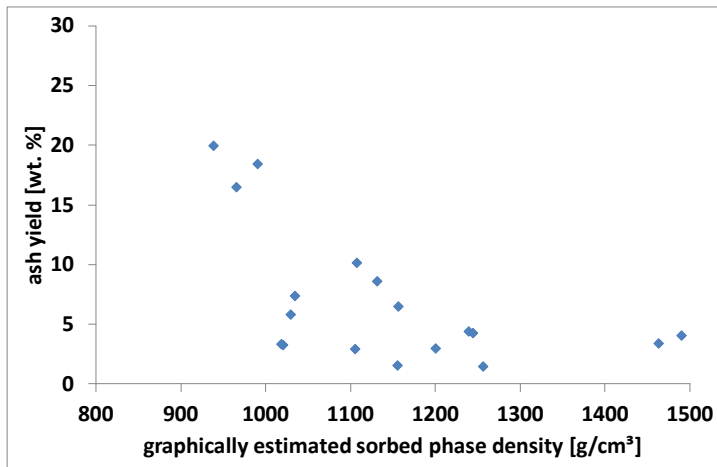
Fig. 4.8 Relationship between the estimated density of the adsorbed CO_2 phase and ash yield of coal samples.

Maximum excess sorption values measured at 20°C range from 1.07 to 1.36 mmol/g, daf. Sorption capacities derived from approximation of experimental data by the Langmuir function range from 1.99 to 2.48 mmol/g, daf. These isotherms exhibit a maximum in the 2 to 4 MPa pressure region, exceeding those of the 45°C isotherms. At higher pressures between 4 and 5 MPa the 20°C isotherms decrease until they cross the 45°C isotherms. A 25°C temperature increase results in a decrease of sorption capacity between 27 and 59% at a pressure of 3 MPa, whereas the maximum measured excess sorption is only reduced by up to 8%, which might indicate inaccuracies of the parameterization of experimental data by the extended Langmuir function.

4.7. Discussion

4.7.1. Correlations between maturity parameters

For the entire set of coal samples, the volatile matter yield shows good correlation with other maturity parameters, such as vitrinite reflectance or T_{max} (*Fig. 4.9*). These correlations may thus be used to relate archived data of volatile matter yields of coals from the study area to vitrinite reflectance. The best correlations are observed for coal samples from the Paskov mine which cover a maturity range from 1.0 – 1.8 % VRr. This is in good agreement with previous results for Upper Silesian Basin coals (Kotarba et al., 2002; Martinec, 2005).

Because T_{max} is influenced by the petrographic composition of coal (Teichmüller and Durand, 1983) and volatile matter yield is a valid rank parameter only in the mvb to semi-anthracite range (1.2 – 2.5% VRr; cf. Teichmüller and Teichmüller, 1979), we chose to use vitrinite reflectance as the parameter for rank correlation of sorption characteristics.
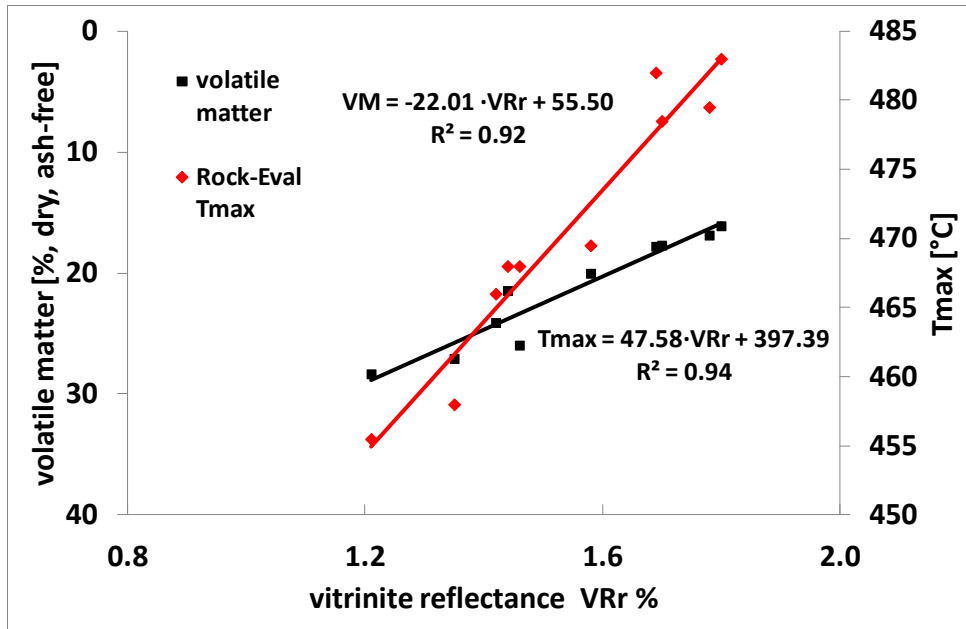
Fig. 4.9 Relationship between vitrinite reflectance (VRr%) volatile matter yield and the Rock-Eval T_{max} value for coal samples from Paskov mine.

4.7.2. Influence of coal properties and reservoir parameter on sorption capacity

The in-situ sorption capacity of coal seams is not only influenced by pressure and temperature, but also in-situ moisture content and inherent coal properties such as mineral matter content, coal rank and maceral composition. However, these parameters affect the sorption capacity to different degrees. Knowledge of the influence of each parameter is necessary to evaluate the distribution of sorption capacity of individual coal seams throughout a basin. Previous studies *e.g.* by Hildenbrand et al. (2006) have derived algorithms to evaluate the sorption capacity distribution in a certain coal basin, based upon literature data from different basins (Ruhr Basin, Campine Basin) and different sample types (lithotypes, sapropel, humic coals). In the present study the sorption capacity distribution is derived based upon experimental data for coal seams of the same basin.

4.7.3. Influence of moisture content on sorption capacity

The presence of moisture reduces the sorptive gas storage capacity of coals. In low-pressure sorption experiments on dry and moisture-equilibrated coal Ettinger et al. (1958) observed a linear decrease of sorption capacity with increasing moisture content which he described by the empirical formula:

$$Vd/Vw = C0 \cdot m + 1 \qquad (4)$$

Where Vd and Vw are the methane sorption capacity of dry and moist coal, m is the moisture content in wt. % and C0 is a pressure-dependent constant for which Ettinger et al. (1958) found a value of 0.31 (ca. 1 bar) and later Joubert et al. found values between 0.27 (10 bar) and 0.19 (60 bar) (Joubert et al., 1973, 1974 and references therein). The negative effect of moisture on gas sorption has been studied in several subsequent studies (Smith and Williams, 1987, Yee et al., 1993; Levy et al., 1997; Bustin and Clarkson, 1998; Clarkson and Bustin, 2000;

Crosdale et al., 2008; Day et al., 2008a,b; Ozdemir and Schroeder, 2009). Beyond a critical moisture content, no further reduction in sorption capacity occurs (Joubert et al., 1973, 1974; Gaschnitz, 2001; Day et al., 2008a). Day et al. (2008a) report that this critical moisture content is slightly higher for CO_2 sorption as compared to CH_4 and that it is equivalent to equilibrium moisture achieved between 40 and 80% relative humidity.

Results from sorption isotherm measurements in this study on "as-received" and moisture-equilibrated coals show an average reduction of CH_4 sorption capacity of 23% for ČSM samples and 27% for Paskov samples, which is similar to observations reported in previous studies. For example Krooss et al. (2002) observed a reduction of 20 - 25% between dry and moisture-equilibrated Carboniferous coal from Netherlands. The sensitivity of sorption capacity to moisture decreases with increasing rank, as reported by Kim (1977) for US coals.

Experimental results from the present study indicate a higher degree of reduction of CH_4 (average 24%) sorption capacity as compared to CO_2 (average 12%), which is in agreement with results by Day et al. (2008a). These observations can be interpreted as a result of the competition between water and gas molecules for specific sorption sites, which also influences the selectivity between CO_2 and CH_4 sorption (Bustin and Clarkson, 1998; Clarkson and Bustin, 2000; Busch and Gensterblum, 2011).

To evaluate the effect of moisture on sorption, we compare the methane sorption capacity at different moisture states m (m= moisture of "as-received" or partially dried coal) relative to the moisture equilibrated state em. Taking the equilibrium moisture as reference state, the distance d of the "as-received" or partially dried moisture to the equilibrium moisture is defined as:

$$d = m/em. \tag{5}$$

For d a value of 1 represents equilibrium moisture and 0 represents dry samples. Correlations between Langmuir sorption capacity and distance from moisture equilibrium were calculated for individual samples for two different moisture states and for three samples additionally for the partially dried or dry state.

From the slope of the observed correlation for these three samples we derive the following linear equation:

$$n_{CH4} = -0.19 \cdot d + 0.86 \tag{6}$$

For all coal samples an average correlation is derived:

$$n_{CH4} = -0.43 \cdot d + 1.13 \tag{7}$$

However, this average correlation shows a strong variation between -0.1 and -1.5 with a standard deviation of 0.3. The y-axis intercept represents the average CH_4 sorption capacity of dry coal. This estimated sorption capacity of dry coal increases with increasing coal rank.

4.7.4. Effect of temperature on sorption capacity

Adsorption of gas molecules results in entropy reduction and thus it is an invariably exothermic process. Consequently, a negative correlation between sorption capacity of coals and temperature exists, which has been reported in previous studies for a wide temperature range (Ruppel et al., 1974; Yee et al., 1993; Levy et al., 1997; Bustin and Clarkson, 1998; Gaschnitz, 2001; Krooss et al., 2002). From CH_4 sorption experiments on moisture-equilibrated

coal Levy et al. (1997) calculated a linear reduction of sorption capacity (at 5 MPa) between 10°C and 70°C of 0.12 cm^3/g per 1K temperature increase. Other studies report that sorption capacity decreases more slowly at temperatures above 30 to 60°C (Ruppel et al., 1974; Krooss et al., 2002; Crosdale et al., 2008). These authors also observed a decreasing influence of temperature in the high pressure region (above ca. 10 MPa).

Isotherms measured in this study show the expected reduction of excess sorption with higher temperature. Methane Langmuir sorption capacities for the moisture-equilibrated sample 8 decrease linearly with increasing temperature (*Fig. 4.10*). A 1K increase in temperature reduces the sorption capacity by 0.11 cm^3/g, which is similar to the reduction calculated by Levy et al. (1997). Isosteric heats of adsorption calculated from this set of isotherms range from 10 to 21 kJ/mol and show a linear increase with increasing adsorbate loading (*Fig. 4.11*). At low loading, the values lie within the range of 1 – 1.5 times the heat of evaporation (8.2 kJ/mol for methane), corresponding to the range of physisorption (Ruthven, 2008). For comparison, Day et al. (2008a) report net heats of adsorption between 8 and 12 kJ/mol for methane on moist coal from Australia, showing a decrease with increasing moisture content from 0 to 7 wt.%.
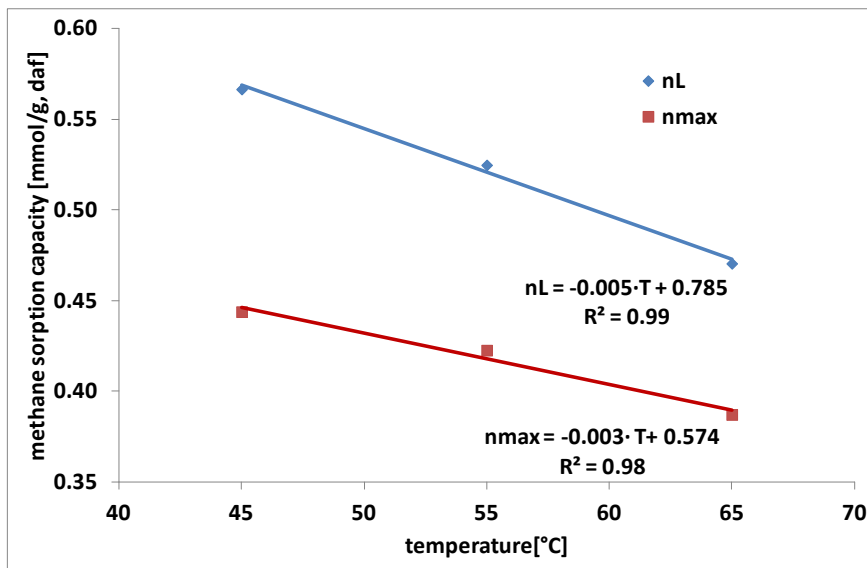
Fig. 4.10 Relationship between methane sorption capacity and experimental temperature for moisture equilibrated coal sample 8. n_{max} = maximum excess sorption, n_L = Langmuir sorption capacity.
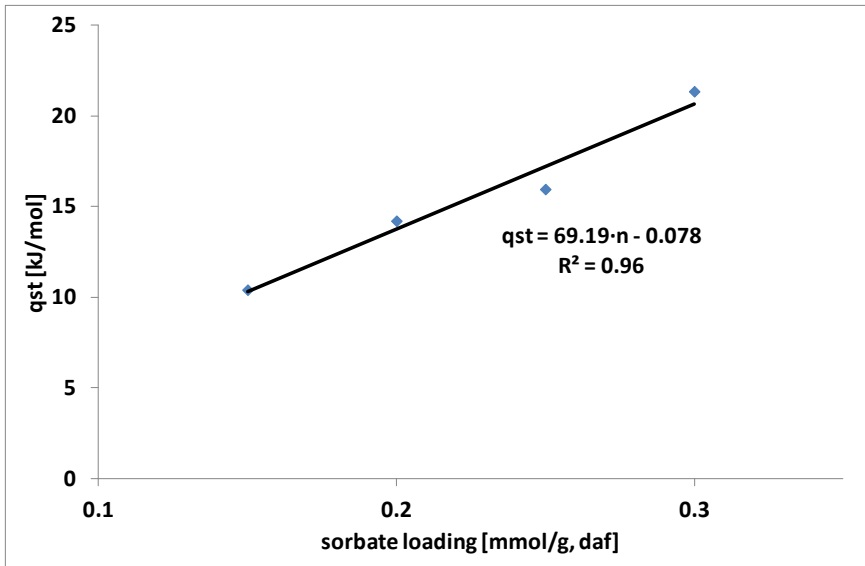
Fig. 4.11 Isosteric heat of adsorption for different sorbate loadings determined from methane isotherms measured on moisture-equilibrated sample 8.

For some methane sorption isotherms measured on "as-received" coal at 20°C and 45°C a temperature dependence is no longer observed at higher pressures (between 10 MPa and 12 MPa). Similar observations were reported by Krooss et al. (2002) for isotherms measured on moisture-equilibrated coal at 40°C and 60°C.

At 20°C CO_2 is in the subcritical state and isotherms were only measured up to a pressure of 5 MPa to avoid condensation. Comparison of the 20°C and the 45°C isotherms is difficult because for the 45°C isotherm only a few data points were recorded below 5 MPa. The 20°C excess sorption isotherms initially lie above the 45°C isotherms, but the difference decreases with increasing pressure and a cross-over occurs between 4 MPa and 5 MPa as the 20°C excess isotherms decline due to the onset of condensation (*Fig. 4.12*).
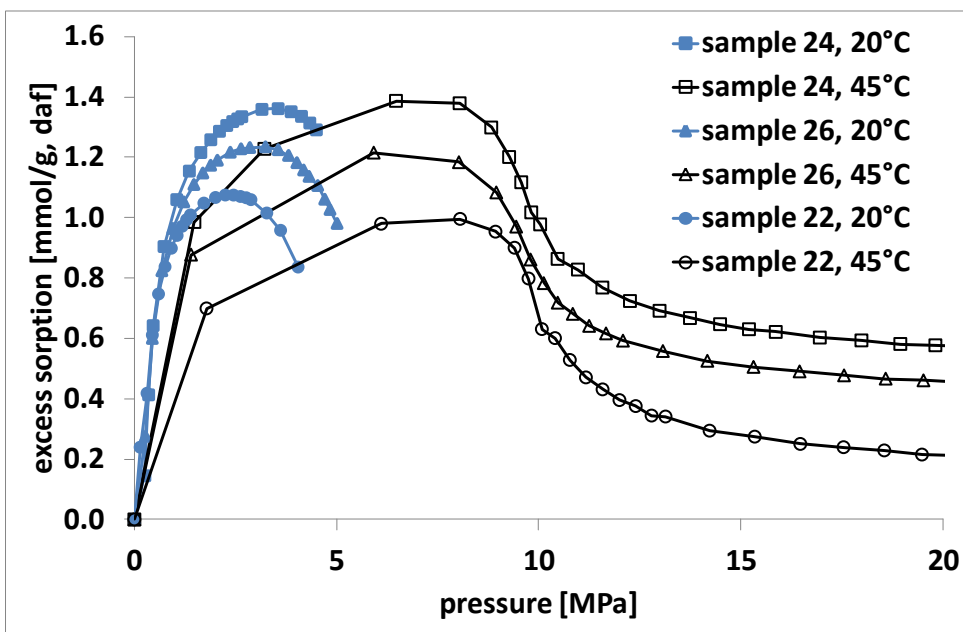
Fig. 4.12 CO_2 isotherms for "as received" coals from the Paskov mine measured at 20°C (open symbols) and 45°C (solid symbols).

Comparison of CO_2 sorption isotherms measured at 45°C and 55°C on the moisture-equilibrated sample 8 shows that in the pressure region below 8 MPa, the 45°C isotherm has higher excess sorption capacities, while at higher pressures (>8.5 MPa) the excess sorption values of the 55°C isotherm are higher. Such behaviour has also been reported by Krooss et al. (2002), but the pressure at which the crossover occurs seems to vary from sample to sample. The decline of CO_2 isotherms results from the steep increase of CO_2 gas density in the pressure region close to the critical point (8-10 MPa). At higher temperatures this density increase is less dramatic and the decline in excess sorption decreases. Thus, for carbon dioxide, the influence of temperature on gas density is larger than the direct influence on the adsorption process.

4.7.5. Effect of thermal maturity

In previous studies, no global correlation was found between coal rank and methane sorption (Bustin and Clarkson, 1998). However, for moisture-equilibrated coal from individual coal basins, methane sorption showed a linear increase of sorption capacity with increasing coal rank (Joubert et al., 1973, 1974; Kim, 1977, Ryan, 1992, Laxminarayana and Crosdale, 2002; Reeves et al., 2005; Chalmers and Bustin, 2007). This relationship could allegedly be applied to estimate the coal-bed methane potential in the US and Canada (Kim, 1977; Ryan, 1992). For methane sorption (Levy et al., 1997 (5 MPa, 30°C); Laxminarayana and Crosdale, 1999 (9 MPa, 23.5°C); Laxminarayana and Crosdale, 2002 (9 MPa, 23.5°C); Faiz et al., 2007 (5 MPa, 27°C)) and low-pressure (<0.13 MPa to 4 MPa; 0°C to 22°C) CO_2 sorption (Levy et al., 1997; Bustin and Clarkson, 1998; Prinz and Littke, 2005; Ozdemir and Schroeder, 2009) on "as received" and dry coals, a 'U'-shaped or polynomial correlation between coal rank and sorption capacity has been reported, which exhibits a minimum similar to the correlation between moisture and sorption. For high pressure CO_2 sorption on the other hand, no or only weak correlation with coal rank was found (Krooss et al., 2002; Mastalerz et al., 2004; Reeves et al., 2005; Day et al., 2008a). Structural changes during coalification or plugging of pores by low-boiling hydrocarbons, generated during coalification are believed to cause this 'U-shaped' correlation (Levine, 1993; Prinz and Littke, 2005; Chalmers and Bustin, 2007).

A decrease of Langmuir pressure with increasing coal rank has also been reported and was attributed to the homogenization of the pore space during coalification (Laxminarayana and Crosdale (1999).

Methane sorption capacities measured on coal samples in the present study show a general increase with increasing coal rank (*Fig. 4.13*). For medium- to low-volatile bituminous coal from the Paskov mine, a similar correlation is observed for CH_4 and CO_2 sorption on "as-received" coal, as well as for CH_4 sorption on moist coal. CO_2 sorption capacity on moisture-equilibrated coal shows a steeper increase with coal rank and a much better correlation (*Fig. 4.14*). However, this correlation is only based on four measurements and thus has to be viewed with caution. Apart from the general correlation between sorption capacity and maturity, the influence of moisture content on sorption capacity, as well as the molar ratio of CO_2 and CH_4 sorption capacity, shows a dependence coal rank.
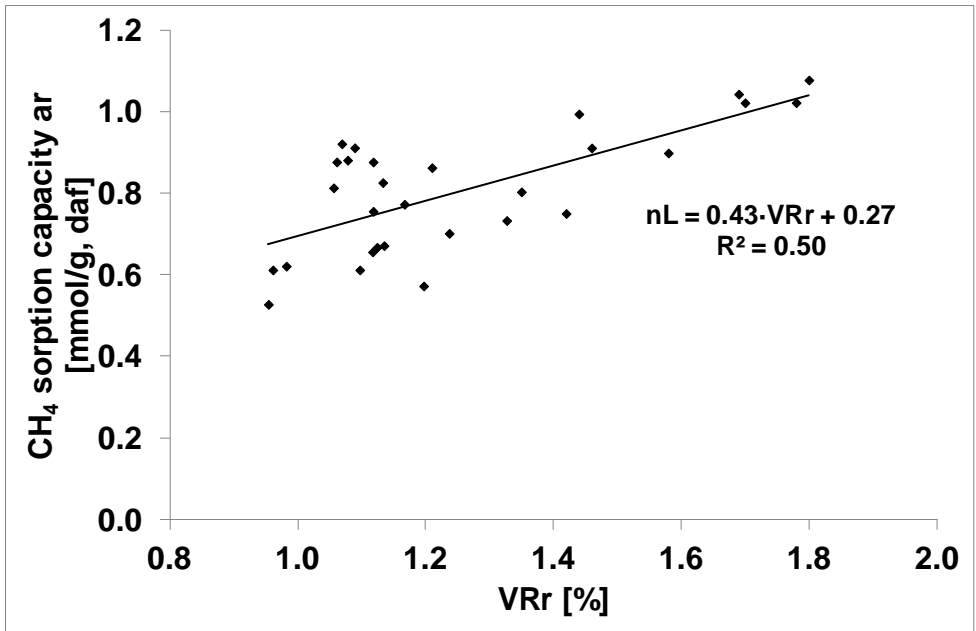
Fig. 4.13 Relationship between methane sorption capacity and coal rank ("as-received", 45°C).
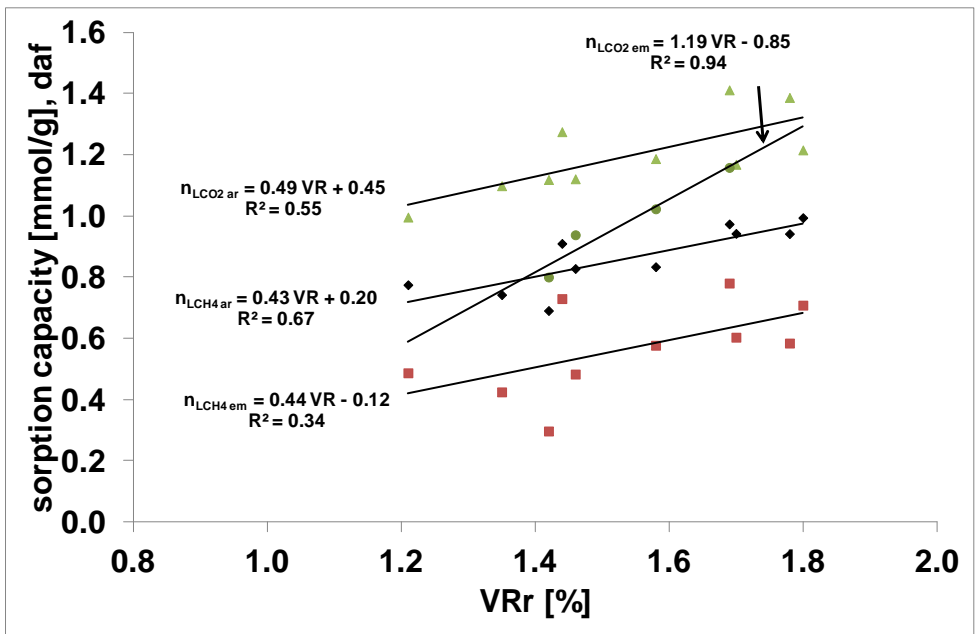
Fig. 4.14 Relationship between rank and sorption capacities measured for CH_4 and CO_2 on "as received" and moisture equilibrated coal from Paskov mine.

4.7.6. Effect of mineral matter content (ash yield)

Coal samples from the Lazy mine exploration well exhibit the largest variation in ash yield. On a 'raw' basis, these samples show a linear decrease in sorption capacity with increasing ash yield and decreasing TOC content (*Fig. 4.15*). A 1% increase in ash yield decreases the sorption capacity by 0.16 cm^3/g. The observed trend is in agreement with results from previous studies reporting a linear decrease in methane sorption capacity with increasing mineral matter content (ash yield) (Barker-Read and Radchenko, 1989; Laxminarayana and Crosdale, 1999;

Clarkson and Bustin, 2000; Laxminarayana and Crosdale, 2002; Weniger et al., 2010). No correlation between ash yield and CH_4 or CO_2 sorption is observed for coal samples from Paskov mine and ČSM mine, which are dominantly high-grade coals. These results support that organic matter plays a dominant role in methane sorption in coals and carbonaceous sediments, whereas mineral matter has a diluting effect on methane sorption.
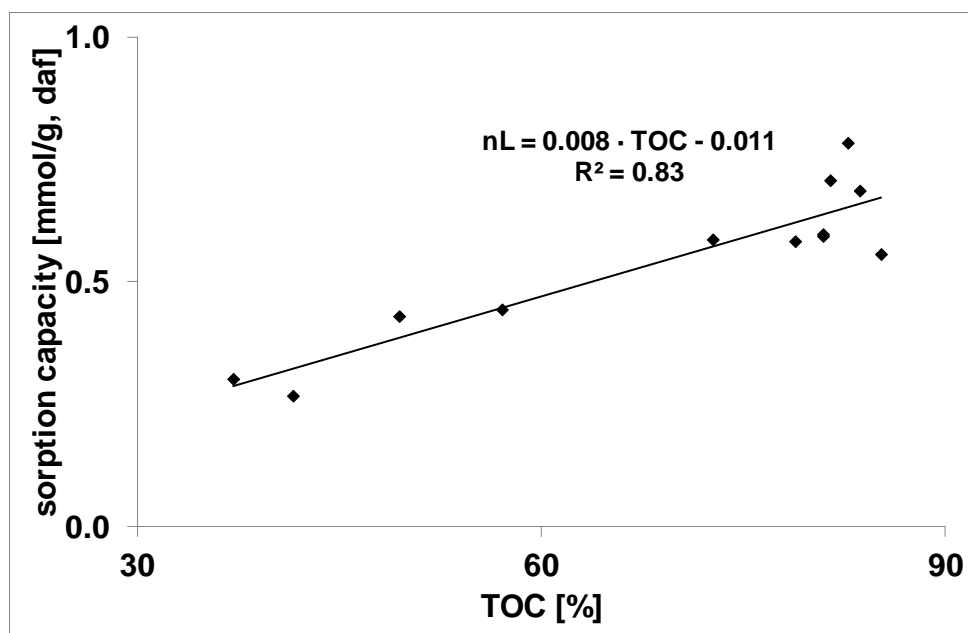
Fig. 4.15 Correlation between methane sorption capacity and TOC content for samples from Lazy cores ("as- received", 45°C).

4.7.7. Effect of maceral composition

Petrographic composition can influence the sorption capacity of coal, but, no consistent global correlation has been reported. Some studies showed a positive correlation between vitrinite content and sorption capacity, which are attributed to higher microporosity of vitrinite (Lamberson and Bustin, 1993; Bustin and Clarkson, 1998; Laxminarayana and Crosdale, 1999; Clarkson and Bustin, 2000; Chalmers and Bustin, 2007). Other studies did not observe any correlation between sorption capacity and maceral composition (Laxminarayana and Crosdale, 2002; Mastalerz et al., 2004; Faiz et al., 2007; Weniger et al., 2010). Different sorption capacities of inertinite group macerals could explain why no consistent influences of maceral group composition on sorption is observed. For instance Faiz et al. (2007) report that Permian coals from Australia contain more inertinite, which is dominated by semi-fusinite, compared to Carboniferous coals from the northern hemisphere, which are dominated by fusinite. The higher microporosity of semi-fusinite compared to fusinite could explain why negative correlations between inertinite and sorption capacity are mostly reported for coals from the northern hemisphere. Some studies report an influence of liptinite on sorption capacity but no consistent corelation appears to exist (Mastalerz et al., 2004; Chalmers and Bustin, 2007).

Of all samples analyzed in this study, coals from the ČSM mine extend over the smallest maturity range. Therefore they are suitable for studying the dependence of sorption capacity on petrographic composition. No clear correlation between sorption capacity of "as received" or moisture equilibrated coal and maceral composition was observed. Furthermore, the liptinite-rich coal from Prokop seam (sample 8) did not show a higher sorption capacity as compared to coal samples of similar rank. Vitrinite was the dominant maceral in all coals analyzed in this

study, and for this rank range, the influence of maceral composition on sorption capacity seems to be minor.

4.7.8. Comparison of CH_4 and CO_2 sorption – implications for CO_2 enhanced methane recovery (CO_2-ECBM)

The ratio of the Langmuir sorption capacities (n_LCO_2/n_LCH_4) derived from the single-component sorption isotherms is consistently >1, reflecting the preferential sorption of CO_2 as compared to CH_4. The degree of preferential sorption of CO_2 is reduced with moisture content. Clarkson and Bustin (2000) used single gas sorption isotherms of methane and carbon dioxide measured on dry and moisture equilibrated coal to model the sorption capacity of CO_2 - CH_4 gas mixtures. They found that the selectivity for carbon dioxide sorption decreases in the presence of moisture and concluded that water competes with gas for sorption sites, especially higher energetic sites that would be occupied by CO_2 molecules in the dry state.

A decrease of the CO_2/CH_4 sorption ratio with increasing pressure has also been observed in previous studies from single gas isotherms (Krooss et al., 2002, Mastalerz et al., 2004, Reeves et al., 2005), whereas Clarkson and Bustin (2000) report increasing carbon dioxide selectivity with increasing pressure. Further, Mastalerz et al. (2004) report a slight increase of CO_2/CH_4 sorption ratio with increasing rank for sub-bituminous coals, whereas Krooss et al. (2002) and Reeves et al. (2005) report a decrease in CO_2/CH_4 ratio with increasing rank.

In the present study, CO_2/CH_4 sorption ratios were found to be lower (1.5 – 2.7) for "as-received" coals, as compared to moisture-equilibrated coals (1.3 – 4.3). For most "as-received" coals the n_LCO_2/n_LCH_4 ratio increases with increasing pressure, whereas for moisture-equilibrated coals it decreases. However, for some "as-received" coals this ratio decreased or showed little change with increasing pressure, and for one moisture-equilibrated coal it remained constant with increasing pressure. Sorption measurements on coal samples from the Paskov mine indicate a rank-dependence of the preferential sorption of CO_2, similar to the one observed by Krooss et al. (2002) and Reeves et al. (2005). For moisture-equilibrated coals, the reduction of the CO_2/CH_4 sorption ratio with increasing rank is more significant (*Fig. 4.16*).
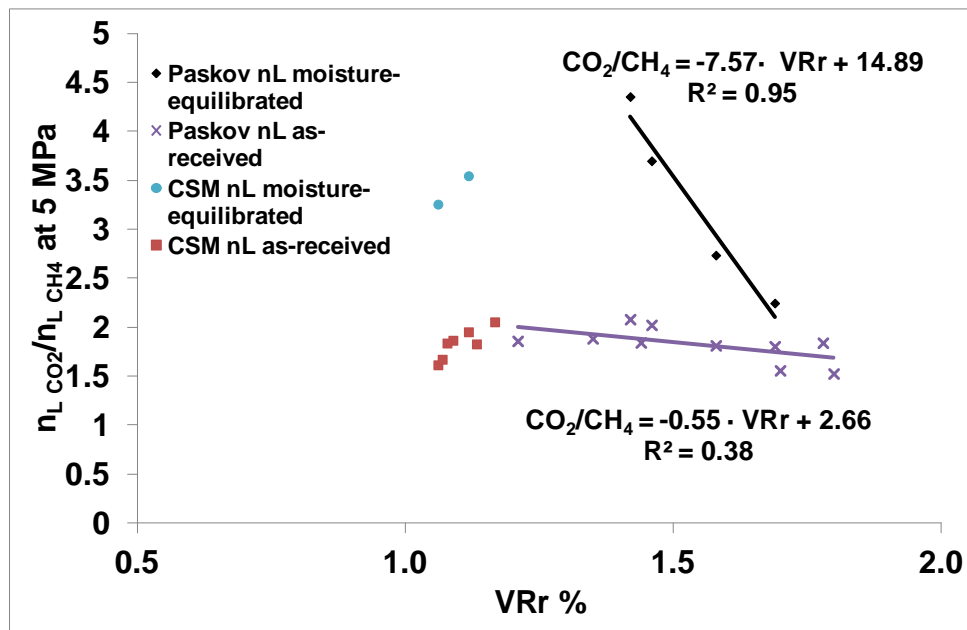
Fig. 4.16 Rank dependence of the preferential sorption capacity between CO_2 and CH_4 at 5MPa.

4.7.9. Calculated variation of sorption capacity with depth

The observed relationships between temperature, pressure and sorption capacity can be used to estimate the sorption capacity of a coal seam at a certain depth, if the local pressure and temperature gradients are known. Vertical movements of coal seams during geological basin history, such as burial and uplift, result in changes of reservoir pressure and temperature conditions, which influence the sorption capacity. During burial, the (hydrostatic) reservoir pressure increases and more gas can be stored in the coal, while the increase in temperature during burial will reduce the sorption capacity. On the other hand, uplift is accompanied by a decrease in reservoir pressure, which reduces the sorption capacity while the concomitant decrease in temperature enhances sorption capacity. The interplay of these opposing effects determines whether gas will be desorbed from coal and migrate, or if coals will gain sorption capacity and either become undersaturated or adsorb available gas, migrated from deeper seams or produced during secondary generation.

Gaschnitz (2001) measured methane sorption isotherms on dry and moist sapropelic coal and a vitrain from the Ruhr Basin in a temperature range from 35 to 150°C up to 20 MPa. He used logarithmic functions to describe the variation of the Langmuir parameters n_L and P_L with increasing temperature and estimated sorption capacities for burial depths down to 6000 m, using different pressure and temperature gradients. Hildenbrand et al. (2006) used results from sorption experiments on coals from the German Ruhr Basin (Denneberg, 1997, Gaschnitz, 2001) and the Belgian Campine Basin (Arets et al., 1962, Coppens 1967), to model the evolution of methane sorption capacity for coal seams. Bustin and Bustin (2008) measured methane isotherms for three U.S. coals of different coal rank at different temperatures. They found that the influence of depth variations (pressure and temperature) on the sorption capacity differs at different rank.

A "static" calculation was used to estimate the sorption capacity of a coal of a given rank as a function of depth in a time-invariant pressure and temperature field. To estimate the sorption capacity of coals from the USCB, the linear relationship between Langmuir sorption capacity and temperature for moisture equilibrated coal was used to recalculate sorption isotherms for pressures and temperatures for a depth interval down to 2000 m (*Fig. 4.17a-f*). Sorption measurements on this coal at different temperatures did not reveal a relationship between the Langmuir pressure P_L and temperature. Parameter used for these calculations are listed in *Table 4.2*. These calculations show, that, assuming present-day maturity, the sorption capacity of moisture-equilibrated coal from Prokop seam would increase with depth (10.1 MPa/km, 35K/km) until it reaches a maximum of 0.35 mmol/g (daf) at 1090 m depth, followed by a constant decline to 0.18 mmol/g (daf) at 2000 m. For moisture contents less than equilibrium moisture, the maximum would be higher and reached at shallower depth (0.49 mmol/g at 940 m for average hygroscopic moisture, 0.68 mmol/g at 660 m for dry coal). At low temperature gradients, the influence of the increasing pressure is the dominant factor on sorption capacity, and thus, higher temperature gradients result in a stronger decline of sorption capacity at depth >1000 m and also shift the maximum towards shallower depth.

A significantly higher pressure gradient of 15.1 MPa/km would increases the overall sorption capacity compared to a more realistic gradient of 10.1 MPa/km. At the higher pressure gradient, the maximum in sorption capacity (0.39 mmol/g, daf at 950 m) is reached at a shallower depth than with the lower pressure gradient (0.35 mmol/g, daf at 1090 m) (*Fig. 4.17c*).

The effect of rank was tentatively taken into account by assuming that the maturity increases with the trend observed for coal from Paskov mine ($n_L = 0.2289 \cdot VR + 0.3674$). Then the sorption capacity at 0.6% VRr would be 7% lower than the sorption capacity at 0.96% (coal from Prokop seam used in the present measurements) and the sorption capacity at 2% VR and

3% VR would be 34% and 48% higher, respectively (*Fig. 4.17e*). The calculation of the sorption capacity trends with increasing depth provides an estimate of the range of sorption capacities that could be encountered in the USCB for coals of different rank. Assuming that the present coal rank was obtained in response to thermal stress at maximum burial of the coal seams, the uplift (erosion during Permian and Mesozoic times), caused an increase in sorption capacity until a depth shallower than 800 – 950 m was reached. This increase in sorption capacity would have resulted in undersaturation of coals, if no refilling of the sorptive storage capacity by gas from secondary generation or migration occurred. Further uplift above the depth of maximum sorption capacity would have caused a subsequent loss in sorption capacity. The calculated maximum of sorption capacity at a depth between 600 and 1000 m can be used to identify suitable coal seams for gas storage, such as carbon dioxide sequestration in coal seams.

Table 4.2 Parameter for 'static' estimation of sorption capacity (n_L) vs. depth trends

Pressure gradient	10.1 MPa/km, 15.1 MPa/km
Temperature gradient	15K/km - 35K/km
Temperature correlation	$n_L = -0.004 \cdot T + 0.752$ (T = 45°C – 65°C)
Moisture correlation	$n_L = -0.43 \cdot d + 1.13$ *
	$P_L = 4.2066 \cdot d + 1.4637$
Rank correlation	$n_L = 0.2289 \cdot VR + 0.3674$

* d=1 for moisture-equilibrated coal, d=0 for dry coal and d=0.53 ± 0.14 for "as received" coal

The calculated trends for the SW USCB were compared to results from the Ruhr Basin (RB) by Gaschnitz (2001). The sorption capacity trend calculated for a temperature gradient of 35K/km and a pressure gradient of 10.1 MPa/km for moisture-equilibrated coal was compared to the trend calculated from isotherm data of Gaschnitz (2001) on a vitrain sample (dry and moisture-equilibrated, VR 0.89%), using the same pressure and temperature gradients (*Fig. 4.17f*). Even though a direct comparison of sorption capacity trends derived from coal and isolated macerals might strictly not be valid, it shows that different sorption trends exist for different basins that are not only influenced by local p, T gradients and coal rank, but also depend on maceral composition and related differences in microporosity.
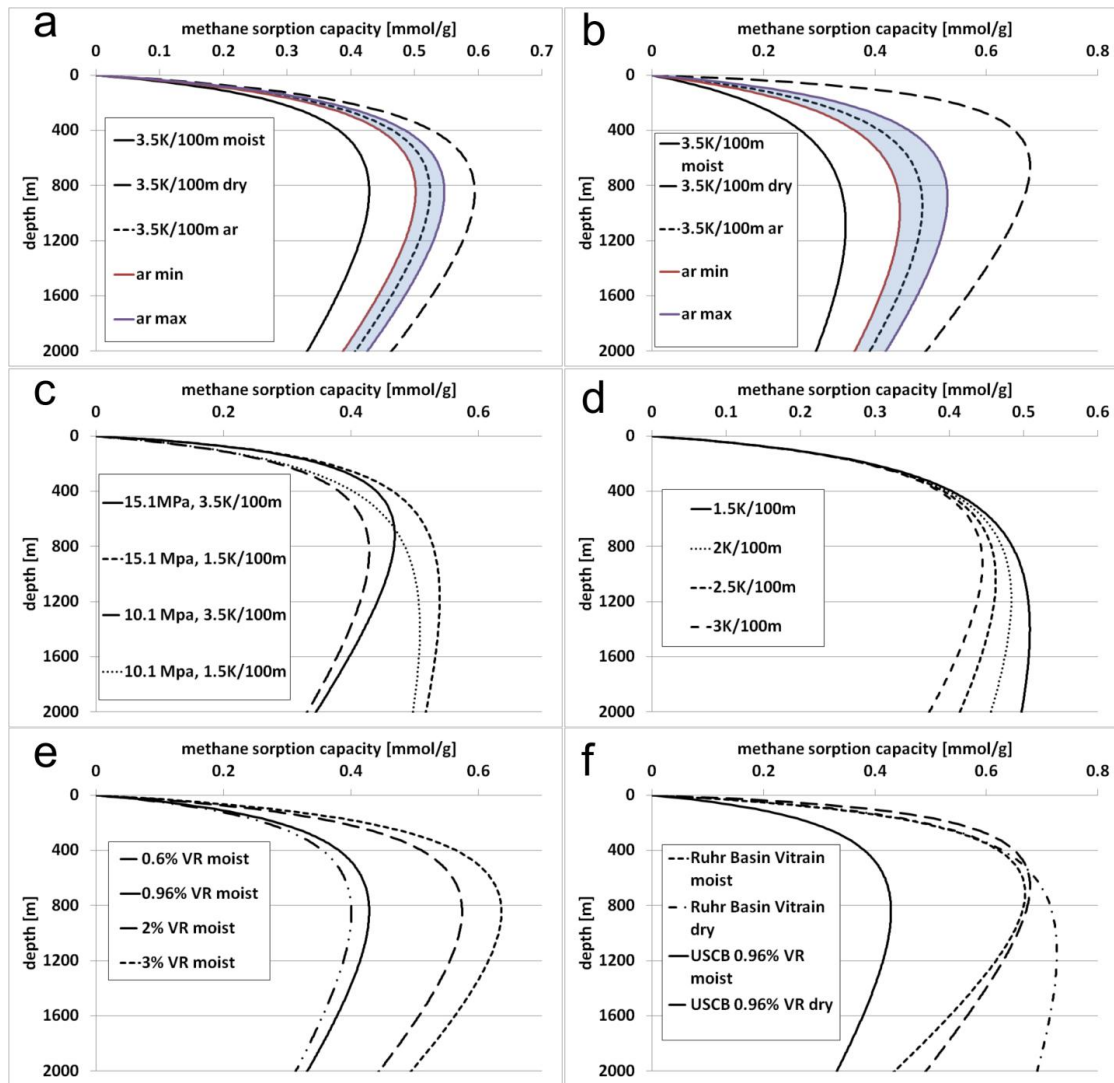
Fig. 4.17 Influence of different parameters on calculated sorption capacity depth trends.
a: different moisture states with constant Langmuir pressure (VRr 0.96%, 35K/km, 10.1 MPa/km).
b: different moisture states with Langmir pressures calculated from weak correlation for all
samples (R² = 0.2) (VRr 0.96%, 35K/km, 10.1 MPa/km).
c: different pressure and temperature gradients (VR 0.96%, moisture equilibrated).
d: different temperature gradients (VR 0.96%, moisture equilibrated, 10.1 MPa/km).
e: different coal ranks (35K/km, 10.1 MPa/km, moisture equilibrated).
f: comparison of sorption capacity-depth trends for coal from USCB with trends calculated by
Gaschnitz (2001) for vitrain isolated from German Ruhr Basin coal (VR 0.89%).

A "Dynamic model" was developed to follow the simultaneous evolution of rank, pressure and temperature throughout the entire burial history. In this model the sorption capacity was calculated for three of the main coal-bearing stratigraphic units (Poruba M., Saddle M. and Sucha M.) using depth information derived from the burial history of these units. A simplified burial history was assumed by Francŭ et al. (1999) for the USCB. Based upon this approach, a 1-D model, calibrated on maturity and lithostratigraphic information from the Lazy 76 well was developed using PetroMod 11 software (Schlumberger, IES) (*Fig. 4.18*). The sorption capacity of coal for each formation was calculated using correlations derived in this study, as well as pore pressure, temperature and maturity (Easy%Ro) from the 1-D model. Additionally, sorption capacities were calculated for the same maturity, but with present-day pressure and temperature gradients of 10.1 MPa/km and 35K/km respectively. A comparison of

the 'dynamic' sorption capacity model with 'static' sorption capacity-depth calculations using correlations for different coal ranks and temperatures derived from sorption measurements of this study are given in *Fig. 4.19*.
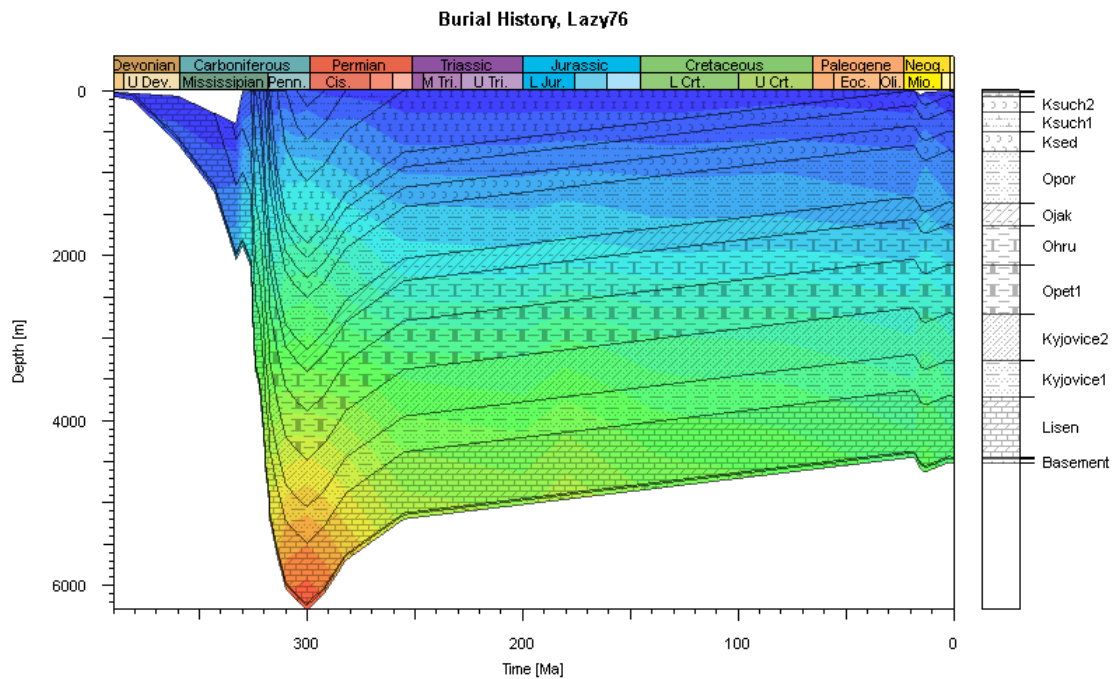
Fig. 4.18 Simplified burial history and 1-D model calibrated on data from Lazy 76 well.

This comparison shows that in the geologic past, when coal seams were at greater depth, the initial sorption capacity was significantly lower as if they would be buried to the same depth today. *Figure 4.19* shows trajectories of the 'dynamic' paleo sorption capacity during uplift for three different coal bearing formations. These trajectories approach the sorption capacity that would be estimated from 'static' present-day pressure and temperature gradients in the late stage of uplift. The difference can be explained by higher paleo temperatures (higher paleo heat flow) (*Fig. 4.20*). Scatter in these paleo sorption capacity trajectories might be attributed to uncertainties in the simplified burial history. It should be noted that this simple model assumes a long period of erosion from early Permian to the Tertiary, which might not reflect the 'true' uplift history. However, detailed information on the uplift history of the basin was not available. Even though no re-initialization of the coalification process took place, uplift or re-burial events could have influenced the gas content of coal seams in the basin.
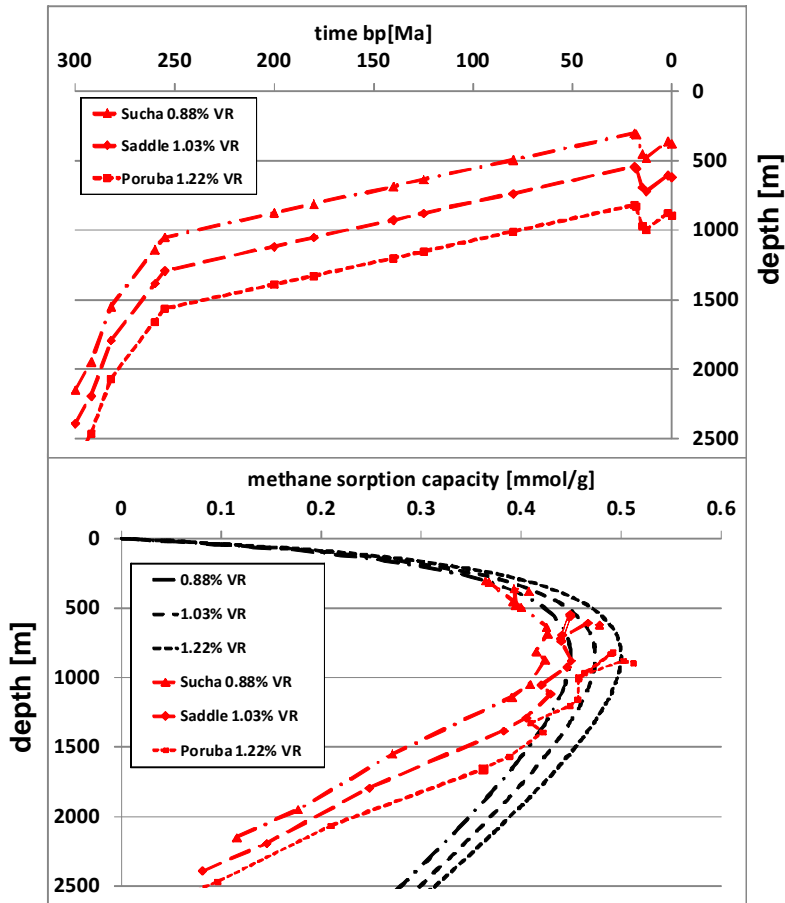
Fig. 4.19 Comparison of calculated sorption capacity depth trends for different stratigraphic units using depth data from burial history (top) data and pore pressure and temperature information from a 1-D model (Petromod). Black lines represent calculated trends using linear pressure (10.1 MPa/km) and temperature (35K/km) trends and depth information from the burial history. Red lines represent trajectories of sorption capacity during basin evolution (uplift).
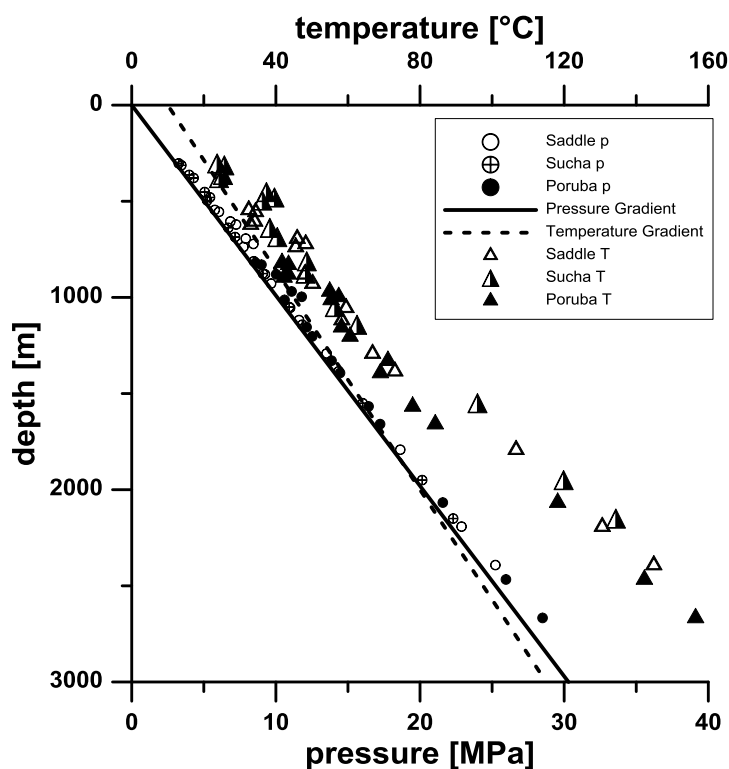
Fig. 4.20 Comparison of linear present-day pressure (p) (10.1 MPa/km) and temperature (T) (35K/km) gradients with paleo- pressure and temperature data from 1-D basin model.

4.8. Conclusions

In the Czech part of the Upper Silesian Basin, coal seams of bituminous rank (low volatile to high volatile bituminous) predominate. Different maturity parameter such as volatile matter yield, vitrinite reflectance and Rock-Eval T_{max} show good correlation, indicating that coal seams cover the mid to late oil window for type III kerogen (~1 to 1.8% VRr).

Methane sorption capacities of moisture-equilibrated coal are up to 47% lower as compared to sorption of "as-received" samples.

Comparison of methane sorption capacity (0.4 to 1 mmol/g) and present day gas contents (< 0.4 mmol/g) shows that most coal seams are undersaturated.

Methane sorption capacity shows a weak relation to coal rank and no significant correlation to maceral composition.

Methane sorption isotherms measured on a moisture-equilibrated coal at different temperatures (45, 55, 65°C), without changing the sample, revealed a linear decrease of sorption capacity of 0.1 cm^3/g for every 1K temperature increase.

Carbon dioxide sorption capacity of coals is generally higher compared to methane sorption capacity. The average CO_2/CH_4 sorption ratio is higher for moisture-equilibrated coal and decreases with increasing coal rank and also with increasing experimental pressure.

Calculation of the 'static' methane sorption capacity variation with increasing depth, assuming a constant hydrostatic pressure gradient and a constant temperature gradient shows

that sorption capacity increases to a maximum value between 600 and 1000 m depth, followed by a constant decrease.

Relationships from experimental data and pressure and temperature information derived from a 1-D basin model can be used to model the 'dynamic' evolution of sorption capacity. During the basin history the initial sorption capacity of coal seams was significantly lower compared to the sorption capacity that would be estimated from 'static' present-day pressure and temperature gradients. Significant deviations for the earlier uplift stage result from higher paleo temperature gradients during basin evolution. To improve the applicability of sorption capacity – depth estimations, experimental data are required for temperatures > 70°C. The increase of sorption capacity during uplift alone is not sufficient to explain the gas undersaturation of most coal seams, indicating that a significant amount of gas, generated during coalification, was lost during times of uplift and erosion.

4.9. Acknowledgements

5. **High-pressure methane and carbon dioxide sorption on coal and shale samples from the Paraná Basin, Brazil**

High-pressure methane and carbon dioxide sorption on coal and shale samples from the Paraná Basin, Brazil

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5.1. Abstract

An experimental study has been conducted to assess the potential for coalbed methane production and carbon dioxide storage in coals, carbonaceous shales and source rocks in the Paraná Basin in Brazil. High pressure sorption tests with methane and carbon dioxide were performed on coal and carbonaceous shales from the Santa Terezinha Coalfield and samples from two principal petroleum source rocks. Measured excess sorption capacities ranged from 0.03 to 0.47 mmol/g for methane and 0.14 to 0.81 mmol/g for carbon dioxide, showing a decrease with decreasing organic matter content. Linear regression lines for methane sorption capacity vs. TOC extrapolated to approximately zero, whereas for carbon dioxide the intercept of the regression line indicated a residual sorption capacity of ~0.2 mmol/g on the mineral matter. Present-day gas contents of coals collected from the first CBM well in the Santa Terezinha Coalfield correspond to 13–38% of the measured maximum sorption capacities. Carbon dioxide sorption capacities exceed methane sorption capacities by a factor of 1.9 to 6.9 for these coals. Free sorption capacities of the under-saturated coals in combination with preferential sorption of carbon dioxide could favour CO_2-enhanced methane recovery and CO_2 storage in coals and shales of the study area. Based upon the calculated coal reserves, gas contents and measured sorption capacities, a total storage potential of 15.4 Gt CO_2 was estimated for an area of 20×40 km2 in the Santa Terezinha coal field, assuming a combined CO_2 enhanced coalbed methane (ECBM) production and CO_2 storage operation. To fully evaluate the potential for carbon dioxide storage and coalbed methane production, further studies are required to assess producibility of methane and efficiency of long term CO_2 storage in the study area.

5.2. Introduction

Worldwide coalbed methane (CBM) resources are estimated to range between 2976 and $12649 \cdot 10^{12}$ scf (84.2–358.2 $\cdot 10^{12}$ m³) (Murray, 1996). Conventional proven gas resources are in the order of $6533 \cdot 10^{12}$ scf ($185 \cdot 10^{12}$ m³) (BP, 2009). Thus, CBM resources would correspond to 46% (minimum estimate) up to 193% (maximum estimate) of conventional gas resources (Holz et al., 2010). Presently CBM is being produced or under exploration in the USA, Canada, China, Australia, Germany and other countries. In Brazil the principal coal resources occur in the southern part of the Paraná Basin, associated with the Permian age Rio Bonito Formation. Earlier studies (Kalkreuth and Holz, 2000; Kalkreuth et al., 2003) have identified the Santa Terezinha Coalfield (Fig. 5.1), Rio Grande do Sul (RS), as the prime candidate for coalbed methane exploration in Brazil, based on coal distribution (coal thickness and lateral continuity of coal beds), size and depth of coal beds and coal rank, estimating a CBM gas in place (GIP) volume of $672 \cdot 109$ scf ($19 \cdot 109$ m³) for this coalfield. In 2007 the first Brazilian CBM test well

(CBM-001-ST-RS) was drilled in the Santa Terezinha Coalfield (*Fig. 5.1*). Samples from 12 coal seams and carbonaceous shales were collected from a depth interval of 605 to 638 m using wire line core retrieval techniques, followed by canister desorption tests and coal quality analyses on 24 samples (Kalkreuth et al., 2008a,b). Total gas contents (desorbed gas, lost gas, and estimated residual gas) were found to range from 0.34 to 2.18 m^3/t with an average value of 1 m^3/t. Gas composition was determined on nine samples, indicating that methane constitutes >94 vol. % in all samples (Kalkreuth et al., 2008b), with minor contributions of hydrocarbon homologues (ethane, propane and butane), CO_2 and N_2. Stable carbon isotope values indicate a mixed (thermal/biogenic) origin of the methane (Kalkreuth et al., 2008b). Based on the average total desorbed gas volumes, and 3D modelling of the coal volume in a 20×40 km^2 area (Kalkreuth et al., 2008b), the total gas in place (GIP) associated with the coals and carbonaceous shales was estimated to amount to 194·109 scf (5.5·109 m^3) CH_4. Only few studies have been published on the evaluation of the gas storage capacity of Brazilian coals. Soares et al. (2007) performed sorption experiments on dry coals from Santa Catarina State at sub-atmospheric pressures (<1 bar) and at a temperature of 30 °C. They report CO_2 storage capacities ranging between 0.089 and 0.186 mmol/g. In the present study, high-pressure sorption isotherms for methane (CH_4) and carbon dioxide (CO_2) were measured on seven samples (coals and carbonaceous shales) from the CBM-001-ST-RS well (*Table 5.1*) to evaluate the potential for coalbed methane (CBM) production, enhanced CBM recovery (CO_2–ECBM) and CO_2 sequestration in the Santa Terezinha Coalfield.

Fig. 5.1 Location of the Santa Terezinha coal field, state of Rio Grande do Sul, Brazil (Kalkreuth et al., 2008b).

It is known from earlier studies that moisture substantially reduces the sorption capacity of coals for methane (Joubert et al., 1973) and carbon dioxide (Krooss et al., 2002; Day et al., 2008b; Crosdale et al., 2008; Ozdemir and Schroeder, 2009). To evaluate the effect of moisture content on the sorption properties of Brazilian coals, methane and carbon dioxide sorption isotherms were measured on one selected coal (sample 07_166) first in the "as received" and then in the moisture-equilibrated state. In addition, this study includes measurements on five shale samples (*Table 5.1*) considered to be the principal petroleum source rocks of the Paraná Basin (Ponta Grossa Fm., Devonian; Irati Fm., Permian).

5.3. Geological setting

The Paraná Basin is a large intra-cratonic basin, located in southern Brazil, Paraguay, Uruguay and Argentina and covering an area of more than 1,400,000 km². Sediments and volcanic rocks of the basin range in age from Ordovician to Cretaceous (Zalán et al., 1990, 1991; Milani et al., 2007), with a cumulative thickness in excess of 7000 m in the depocentre. The samples analysed in this study come from the Permian Irati and Rio Bonito formations and from the Devonian Ponta Grossa Formation.

5.3.1. Irati Formation

According to Milani (1997) the Permo-Carboniferous sequence of the Paraná Basin was deposited during maximum flooding of the basin. The organic-rich bituminous shales, siltstones, sandstones and carbonates of the Permian Irati Formation occurs basinwide from the state of Rio Gande do Sul in the south, to the state of Mato Grosso in the north (a distance of approximately 2500 km). The Irati Formation varies in thickness from 10 to 50 m, with major bituminous shale development in Rio Grande do Sul (Padula, 1969), where cumulative shale thickness reaches up to 13.5 m. The bituminous shales of the Irati Formation are considered the principal petroleum source rocks of the basin (Milani and Zalán, 1999), with TOC contents between 8 and 13 wt.%, and TOC peaks in excess of 20 wt.%. Level of preservation of the organic matter (kerogen type I/II) was controlled by variations in the redox potential during deposition (Araújo et al., 2004).

5.3.2. Rio Bonito Formation

Coal deposits occur in the southern part of the Paraná basin in the Permian age Rio Bonito Formation, a fluvial to marine sand- and shale prone lithostratigraphic unit (Holz, 1998), where peat accumulated in coastal mires that formed in a back barrier/strand plain depositional system (Holz et al., 2000; Holz and Kalkreuth, 2004). In the Santa Terezinha Coalfield the cumulative coal thickness increases towards the north-east from ca. 4 m to more than 10 m, with individual coal seam thicknesses of up to 3 m (Kalkreuth and Holz, 2000). Coal rank, based on vitrinite reflectance values, also increases towards the north-east, from sub-bituminous to high volatile A bituminous. Local diabase intrusions have increased locally the thermal maturity of the coals to semi-anthracite and anthracite rank, with vitrinite reflectances of up to 5.46% VRr (Kalkreuth and Holz, 2000; Kalkreuth et al., 2008a,b).

Table 5.1 Sample list and results of proximate and petrographic analyses. For stratigraphic position of canister samples, see Fig. 5.2.

Sample #	Formation	Geol. Age	Sample Type	Seam interval, (Canister #)	Depth [m]	Total Gas Content [m³/t coal]*	V.M. [%] (V.M. % daf)	Ash Yield [wt.%]	TOC [wt.%]	VRr [%]	Moisture Content [wt.%, a.r.]	VIT, mmf [Vol%]	LIP, mmf [Vol%]	IN, mmf [Vol%]
08-154	Irati	Permian	shale	n.d.	n.d.	n.d.	n.d.	n.d.	1.62	n.d.	0.92	n.d.	n.d.	n.d.
08-168	Irati	Permian	shale	n.d.	n.d.	n.d.	n.d.	n.d.	24.21	n.d.	1.65	n.d.	n.d.	n.d.
08-170	Irati	Permian	shale	n.d.	n.d.	n.d.	n.d.	n.d.	11.66	n.d.	1.20	n.d.	n.d.	n.d.
07-114/	Rio Bonito	Permian	carb sh	L1, (2)	609.10	0.38	5.00 (79.37)	93.11	1.73	2.61	1.38	10.0	0.0	90.0
07-117-118/	Rio Bonito	Permian	carb sh	L2, (3)	610.30	1.04	9.94 (39.99)	67.21	21.09	1.51	1.33	42.0	0.5	57.5
07-153/	Rio Bonito	Permian	coal	C, (7)	618.24	1.69	19.73 (37.88)	35.8	n.d.	0.82	0.98	46.0	6.0	48.0
07-166/	Rio Bonito	Permian	coal	D, (11)	620.80	2.18	21.26 (43.19)	41.99	43.9	0.92	0.93	53.0	9.0	38.0
07-177/	Rio Bonito	Permian	carb sh	G, (20)	630.35	0.68	15.20 (42.26)	61.1	n.d.	1.62	0.89	20.0	6.0	74.0
07-186/	Rio Bonito	Permian	coal	H, (22)	636.47	1.03	22.72 (43.17)	44.9	n.d.	0.88	0.59	61.0	0.0	39.0
07-181/	Rio Bonito	Permian	carb sh	I, (24)	637.86	0.31	10.10 (52.80)	81.69	11.13	1.05	0.82	17.0	4.0	79.0
08-100	Ponta Grossa	Devonian	shale	n.d.	n.d.	n.d.	n.d.	n.d.	1.29	n.d.	3.26	n.d.	n.d.	n.d.
08-101	Ponta Grossa	Devonian	shale	n.d.	n.d.	n.d.	n.d.	n.d.	0.70	n.d.	1.01	n.d.	n.d.	n.d.

V.M. = volatile matter yield; TOC=total organic carbon; VRr[%]=mean vitrinite reflectance value, determined in random mode; a.r. = as received; daf=dry, ash-free; VIT=vitrinite; LIP=liptinite; IN=inertinite; mmf=mineral matter-free basis; Carb sh=carbonaceous shale, n.d. = not determined. a Includes measured desorbed gas, lost gas and estimated rest gas, from Kalkreuth et al (2008b).

Petrographic analysis of coal seams from the Santa Terezinha Coalfield indicated high inertinite contents, often exceeding 50%, and also high mineral matter contents (Araújo et al;, 1995; Kalkreuth et al., 2006; Kalkreuth et al., 2008a,b) grading coal seams into carbonaceous shale. Recent sequence stratigraphic analysis (Kalkreuth et al., 2008a,b) identified five coal-bearing sequences (parasequences) in the Santa Terezinha Coalfield, with major coal development in parasequence 2.

5.3.3. Ponta Grossa Formation

Marine shale and sandstones of the Devonian Ponta Grossa Formation are widespread in the Paraná Basin (Zalán et al., 1990, 1991), reaching a maximum thickness of about 600 m (Neto, 1995). Black shales developed in the São Domingo Member of the Ponta Grossa Formation (Candido and Rostirolla, 2007) are considered important source rocks in the Paraná Basin (Milani and Zalán, 1999), with TOC contents ranging between 1.5 and 2.5 wt.%, occasionally reaching more than 4 wt.%. The organic matter is of kerogen type II and accumulated paleogeographically in an epicontinental sea depositional environment.

5.4. Samples

Seven coal and carbonaceous shale samples (*Table 5.1*) were obtained from the CBM pilot well CBM-001-ST-RS, drilled in early 2007 in the Santa Terezinha Coalfield, State of Rio Grande do Sul (RS), Brazil. The samples were collected from a depth interval between 605 and 638 m, using a wireline core retrieval technique. A stratigraphic overview of the CBM well as well as locations of sampled seam intervals is shown in (*Fig. 5.2*). Additionally, three oil shale samples of the Permian Irati Formation and two Devonian source rock samples of the Ponta Grossa Formation were investigated in this study. Excess sorption isotherms for CH4 and CO_2 were measured in the "as received" moisture state, *i.e.* without drying. To assess the effect of moisture on sorption isotherms, methane and carbon dioxide sorption isotherms were measured both in the "as received" state and after moisture equilibration on one coal (sample 07_166).

5.4.1. Sample preparation

The grain size of coals controls gas diffusion (diffusivity) and sorption kinetics. On smaller particles, gas can diffuse faster to micropore sorption sites and the equilibration time will be shorter compared to larger particles. For sorption experiments coal samples are commonly pulverized to reduce the equilibration time. Grinding of coal and size fractionation (sieving) may cause compositional changes (Cloke et al., 2002). Mineral matter tends to be enriched in the smaller size fractions (Spears and Booth, 2002) and maceral composition will also differ from the smallest fraction (inertinite enriched) to larger fractions (vitrinite enriched) (Cloke et al., 2002). These compositional changes can also cause differences in sorption capacity (Busch et al., 2004). To avoid any compositional fractionation, the entire sample material was powdered to <0.2 mm. Proximate analysis and sorption measurements were carried out on sub-samples, acquired using a sample divider (homogenizer) from the powdered samples. The equilibrium moisture content was established according to ASTM D1412 (1999) with the exception that instead of –16 mesh sieve fractions, pulverized samples (<0.2 mm) were used and samples were moisture-equilibrated under vacuum.

5.5. Methods and experimental procedures

5.5.1. Coal characterisation

Proximate analyses of the coal samples were carried out according to DIN 51700: "Testing of solid fuels". The analysis comprised thermo-gravimetric determination of the "as received" (hygroscopic) moisture content (DIN 51718) and ash yield (DIN 51719). All analyses were performed in triplicate on powdered sub-samples (1 g, <0.2 mm grain size). Optical petrographic characterization was performed on grain mounts and polished blocks according to common petrographical procedures (*e.g.* Bustin et al., 1989) at the Instituto de Geociencias Laboratories, Porto Alegre, Brazil. The characterization comprised vitrinite reflectance measurements (VRr%) and maceral group analysis (point counting). Total organic carbon (TOC) contents were determined in duplicate with a multiphase carbon analyser RC-412 (LECO, USA). Sample quantities of the carbonaceous shale were in the range of 50 mg, with grain sizes <0.2 mm.
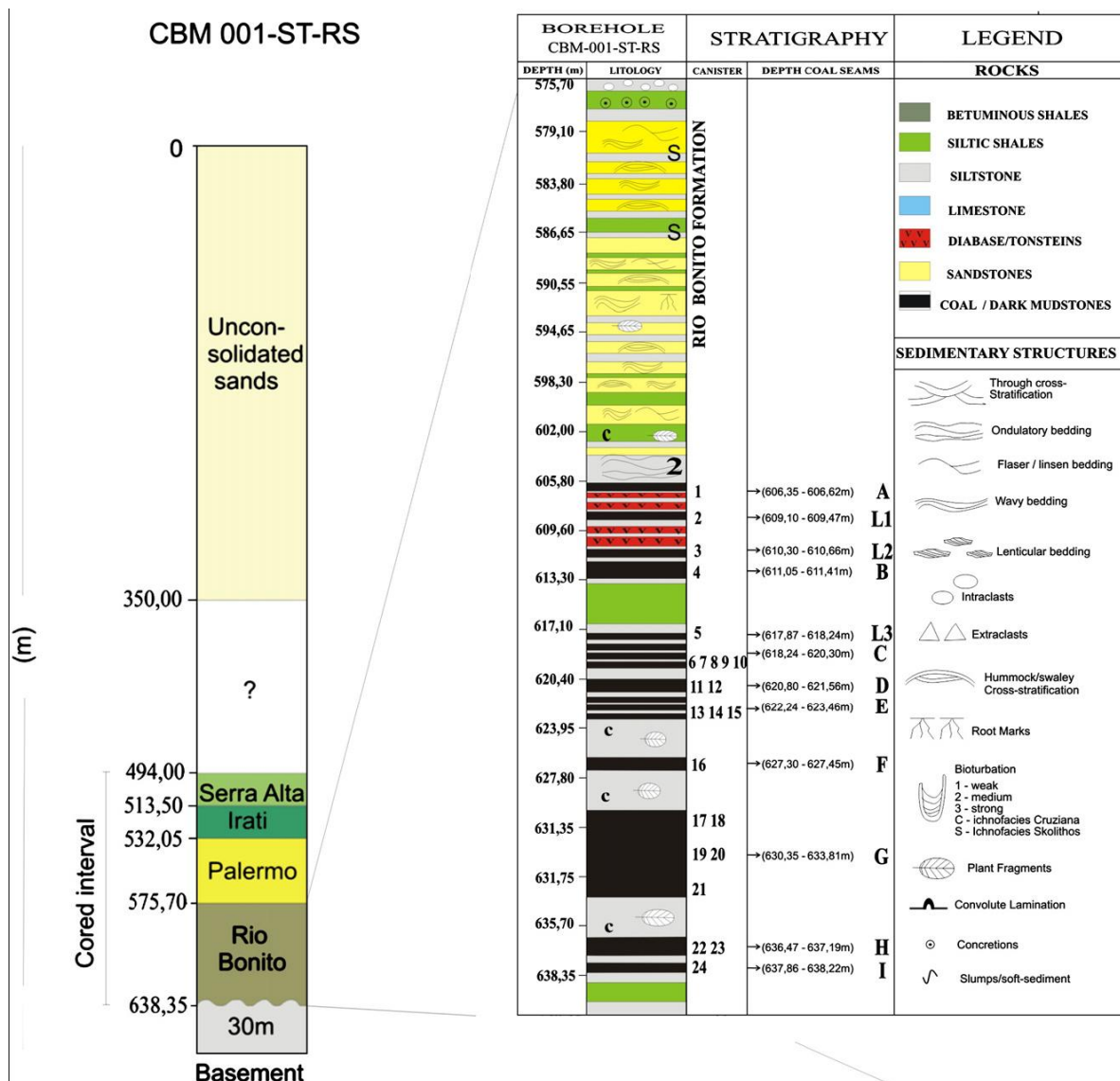
Fig. 5.2 Stratigraphic profile of the CBM-001-ST-RS well and position of canister samples analysed by Kalkreuth et al. (2008b). Sorption experiments of the present study were carried out on samples from canisters 2, 3, 7, 11, 20, 22 and 24.

5.5.2. High-pressure sorption isotherms

5.5.2.1. Experimental setup and conduction of sorption experiments

Methane and carbon dioxide excess sorption isotherms were determined using the manometric method described by Krooss et al. (2002), Busch et al. (2004), Siemons and Busch (2007) and Gensterblum et al. (2009). The experimental setup (*Fig. 5.3*) consists of a stainless-steel sample cell ($\sim$14 cm^3 for CH4 and $\sim$8.5 cm^3 for CO_2), a set of actuator-driven valves, and a pressure transducer (max. pressure 17 MPa for CH_4 and 25 MPa for CO_2), with a precision of 0.05% of the full-scale value. The volume between valve 1 and valve 2, including the void volume of the pressure transducer, is used as reference volume ($\sim$2 cm^3 for CH_4 and $\sim$1.1 for CO_2) and determined by helium (He) expansion in a calibration run. The sample cells are equipped with 2-μm filters to prevent coal or mineral particles from entering the valves. The

entire experimental device is placed in a temperature-controlled oven. Sorption measurements in this study were conducted by the following procedure:

1. Samples were degassed by evacuation for 15 min at 1 mPa.

2. After moisture equilibration, samples were transferred immediately into the sorption cell. The evacuation time was reduced to 5– 10 min to avoid moisture loss.

3. Leak test was conducted using He at 10 MPa for 2 h to assure thermal equilibration of samples and a helium leakage rate of less than 5 mbar/h (<500 Pa/h).

4. Void volume determination by helium expansion. Void volume was calculated using the average value of 10 pressure steps ranging from 1 to 10 MPa with a standard deviation <0.05%. In addition the void volume determination provided the sample volume, which was used to calculate sample skeletal density.

5. Sorption measurement with CH_4 and CO_2 up to 17 and 25 MPa, respectively.
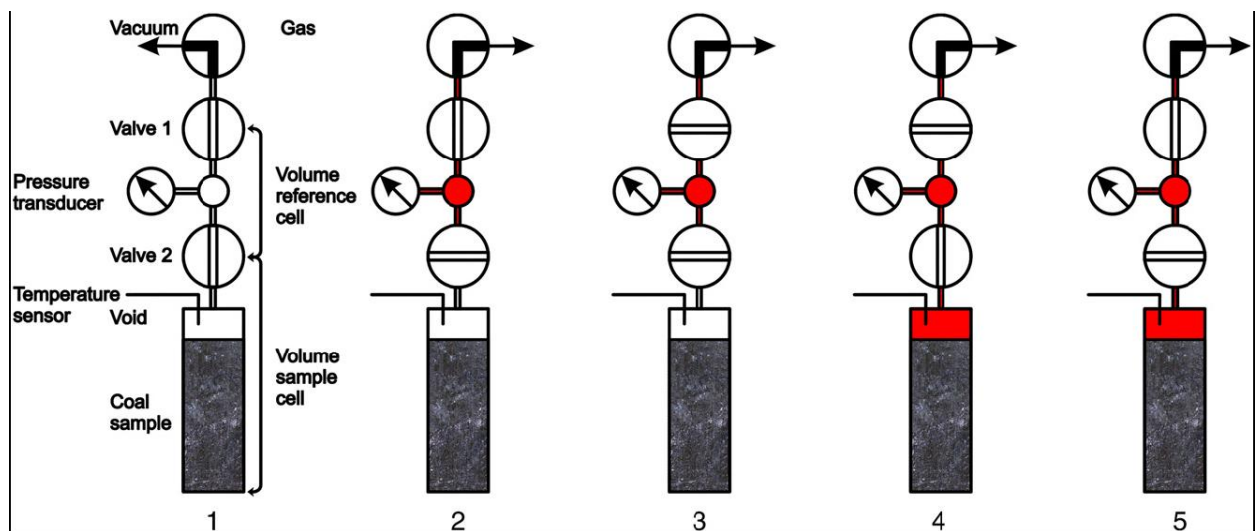
Fig. 5.3 Schematic flow diagram for the manometric method for gas sorption measurements: (1) evacuation of the whole system (2) filling of the reference cell (3) closure of valve 1 and thermal equilibration, (4) valve 2 is opened and gas transferred into the sample cell; start of the sorption process (5) after pressure equilibration, closure of valve 2 and refilling of the reference cell. Steps 3 to 5 are repeated until the maximum system pressure is reached (after Siemons and Busch, 2007).

5.5.2.2.   Parameterization of experimental sorption isotherms

The experimental methane sorption isotherms as well as carbon dioxide sorption isotherms measured at 35 °C were fitted by the (2- parameter) Langmuir function (1):

$$n_{ads} = n_L \cdot p \, / \, (P_L + p) \tag{1}$$

Here n_{ads} (mmol/g) denotes the adsorbed amount of substance at pressure p (MPa). P_L (MPa) is the Langmuir pressure, corresponding to the pressure at which half of the ("monolayer") sorption sites are occupied and n_L (mmol/g) is the "Langmuir amount of substance" (corresponding to the "Langmuir volume"), denoting the amount adsorbed at full occupation of the Langmuir monolayer. Because the Langmuir sorption model is a limiting model for low pressures, its application to high-pressure sorption isotherms is strictly not justified. In many instances it represents, however, a reasonable approximation of the measured excess sorption isotherms and can thus be used as a fitting function. Some of the sorption isotherms reported here have characteristic features that cannot be represented by the simple Langmuir model. Here a modified Langmuir model, taking explicitly into account the volume of the adsorbed phase was used to approximate the measured data. This function is given by (2):

$$n_{ads} = n_L \cdot p / (P_L + p) \cdot (1 - (\rho_{free}/\rho_{adsorbed}))$$ (2)

It contains an additional adjustable parameter, the density of the adsorbed phase ($\rho_{adsorbed}$). Carbon dioxide isotherms were approximated by *Eq. (2)* by adjusting n_L, P_L and $\rho_{adsorbed}$ in a least-squares fit. For comparison of CO_2 and CH_4 isotherms, methane isotherms were also approximated by *Eq. (2)*, using a sorbed phase density value of 421 kg/m^3 (Arri et al., 1992) and adjusting n_L and P_L. However, approximation of methane isotherms using *Eq. (1)* usually yields a better fit of experimental data compared to approximation using *Eq. (2)*, which might indicate that the 'real' sorbed phase density differs from the assumed sorbed phase density.

5.5.2.3. Evaluation of sorption experiments

The equations of state (EOS) for CO_2 and CH_4 developed by Span and Wagner (1996) and Setzmann and Wagner (1991), respectively, were used in the evaluation of the manometric sorption experiments. The EOS provided the specific density of the free gas phase under the experimental pressure and temperature conditions. The amount of gas transferred from the reference to the sample cell was calculated from the density of the gas phase and the corresponding void volumes. Helium densities used for the assessment of the void volume of the measuring cell were calculated by a van der Waals equation of state after Michels and Wouters (1941). The total experimental error for adsorption measurements is less than 10% n_{ads} for carbon dioxide isotherms and less than 3% n_{ads} for methane isotherms at the final experimental pressure. Further information on the accuracy of the manometric sorption setup used for this study, as well as a thorough evaluation of possible errors and pitfalls has been published recently by Li et al. (2010) and Gensterblum et al. (2009).

5.6. Results and discussion

5.6.1. Proximate analysis

The results of the proximate analyses ("as received" moisture content and ash yield) are summarized in *Table 5.1*. Moisture contents of coal and carbonaceous shale samples from the CBM well range between 0.6% and 1.4%, and from 0.9% to 3.3% for the shale samples from the Irati and Ponta Grossa formations. Comparison of moisture contents measured in Brazil, shortly after retrieval of samples from the CBM well, with "as received" moisture contents measured ca. 1.5 years later in the RWTH laboratory, Aachen, revealed an average moisture loss of 0.3 wt.% (*Fig. 5.4*). Ash yields for the CBM well samples, reported on a dry basis, are generally high, ranging from 36% to more than 90%. This indicates that coal seams are grading into carbonaceous shales. A comparison of ash yields determined at Universidade Federal do Rio Grande do Sul, (UFRGS) and at RWTH Aachen University, revealed no significant differences.

5.6.2. TOC contents

TOC values for the two samples from Ponta Grossa Formation were 0.7% and 1.3% while the Irati oil shale had TOC contents extending from 2.3 to 26.3%. The TOC values of the samples from the Rio Bonito Formation ranged from 1.7% to 43.9%.
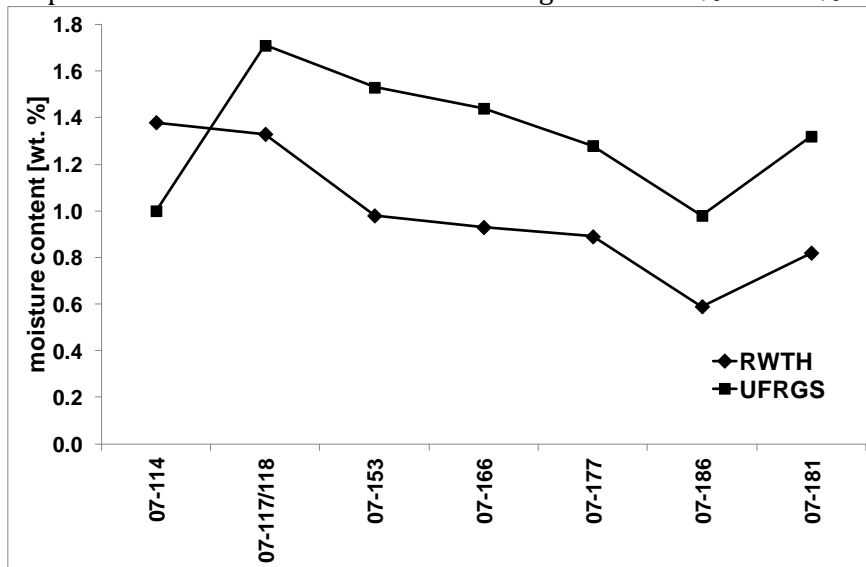
Fig. 5.4 Comparison of moisture content determined after sample acquisition in Brazil (UFRGS) and later before sorption tests in Germany (RWTH) indicating drying of powdered coal samples.
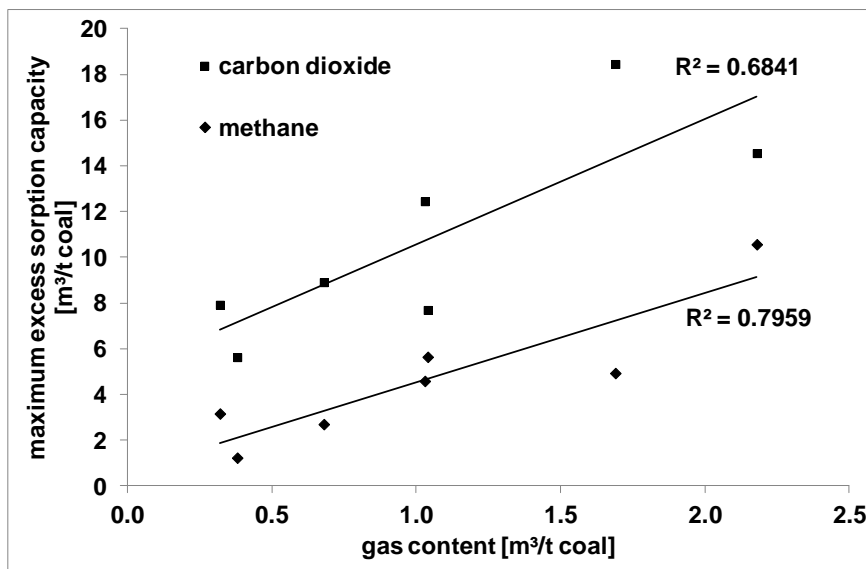
Fig. 5.5 Correlation of excess sorption capacity with gas content of coal and carbonaceous shale from CBM-001-ST-RS well.

5.6.3. Coal petrography

5.6.3.1. Vitrinite reflectance

Coals from the Rio Bonito Formation in the Santa Terezinha Coalfield are of high volatile bituminous rank (Kalkreuth et al., 2003) and have reached anthracite rank locally, where the

coal seams were thermally altered by diabase intrusions. The measured vitrinite reflectance values for the coals and carbonaceous shales from the CBM well range between 0.8% and 2.6%, with coals in contact with igneous intrusions (intervals L and G) showing the highest vitrinite reflectance.

5.6.3.2. Maceral group analysis

The maceral compositions of the Rio Bonito samples show large variations (*Table 5.1*). Inertinite contents are generally high and range from 38% to 90% with an average value of 61%. Most coals with high vitrinite reflectance (>1%) also show high inertinite contents (>50%). Liptinite is absent in coal seams from intervals L and H and reaches its highest value of 9% in interval D. Vitrinite content varies between 10% in interval L1 and 61% in interval H.

5.6.4. Gas contents

The coalbed gas contents of different intervals of the Rio Bonito CBM well have been reported previously by Kalkreuth et al. (2008b), based on temperature and pressure controlled gas (canister) desorption values. Gas contents range between 0.3 and 2.1m^3/t coal with the highest values in intervals C and D at a depth of ~620 m. Coal samples with less than 1% vitrinite reflectance show the highest gas contents. However, no clear correlation of gas content with maturity is observed. A slight correlation of gas content with increasing sorption capacity was observed for methane. This trend is less expressed for carbon dioxide (*Fig. 5.5*).

5.6.5. Results of gas sorption experiments

Most gas sorption isotherms in this study were measured at 45 °C up to pressures of 17 MPa for methane and up to 25 MPa for carbon dioxide. For three samples (07_153, 07_177, and 07_186) isotherms were measured at 35 °C. This temperature is only slightly above the critical temperature of CO_2 (31.1 °C) where the CO_2 density is very sensitive to temperature variations. Sorption isotherms for CO_2 in this temperature range therefore carry an inherent risk of inaccuracy due to even slight errors in temperature measurements. Maximum values of the measured excess sorption capacities and the Langmuir parameters (n_L and P_L for CH_4 and n_L, P_L and $\rho_{adsorbed}$ for CO_2), obtained from approximation of the experimental data are listed in *Table 5.2*. Results of sorption measurements are reported in units of mmol/g, and in mmol/g dry, ash-free coal (daf). Conversion of the adsorbed amount of substance to gas volumes (Std. m^3/t coal, daf) was performed using the standard conditions for gases (IUPAC, 1997).

5.6.5.1. Methane sorption isotherms

The methane sorption isotherms, measured on coal and carbonaceous shale samples from the Rio Bonito Formation of the CBM-001-ST-RS well are shown in *Fig. 5.6* (45 °C isotherms) and *Fig. 5.7* (35 °C isotherms). Sorption capacities for these samples range between 0.07 and 0.57 mmol/g (0.38 to 1.02 mmol/g coal, daf). Normalization of sorption isotherms to the dry ash-free basis shows that the first three samples have a significantly lower sorption capacity. This is unexpected because these isotherms were measured at a lower temperature (35 °C) than the other samples (45 °C). The reason for the lower sorption capacity is most likely a difference in moisture content. As described in chapter 5.1, coal samples lost a significant amount of water before sorption tests. It is very likely that samples measured at 45 °C lost additional moisture until they were measured. However, because most sample material was consumed, isotherms measured at 35 °C could not be re-measured at 45 °C and the moisture loss could not be quantified. For better comparison, isotherms measured at 35 °C have been excluded in the further data interpretation. The experimental isotherms were fitted by the Langmuir function (*Eq. (1)*) and the 3-parameter function (*Eq. (2)*), shown in the diagrams. The Langmuir parameters n_L and P_L for the individual sorption isotherms are listed in *Appendix IV*,

Table 2. Methane sorption isotherms, measured on the Permian and Devonian carbonaceous shales are shown in *Fig. 5.8*. As expected, the shale samples show lower methane sorption capacities (between 0.04 and 0.37 mmol/g) than coals. Normalized to TOC content, sorption capacities of the shale samples are, however, significantly higher than those of the coal samples on a daf basis (1.5 to 11.5 mmol/g, TOC). For shale samples with low TOC contents (<3%) (*e.g.* samples 08_100, 08_101 and 08_154), the bulk excess sorption values are also low and bear a relatively large error. Uncertainties in the assessment of low TOC values increase the experimental error. In consequence, the TOC-normalization of the sorption isotherms is likely to overestimate the methane sorption capacity of these samples (values in brackets in *Table 2*). The gas contents of coals from the CBM-001-ST-RS well are lower than their CH_4 sorption capacity (excess sorption), i.e. the coals are under-saturated in methane. Assuming a hydrostatic pressure gradient of 10MPa/km, the reservoir pressure in the depth interval under consideration should range between 6.1 and 6.4 MPa. Sorption capacities for the mean reservoir pressure (6.25 MPa) calculated from the Langmuir fits range between 7.7 and 16.5 m³/t coal. The actual methane contents of the coal seams, determined by canister desorption, thus represent between 13% and 38% of the sorption capacity.

5.6.5.2. Carbon dioxide sorption isotherms

Carbon dioxide excess sorption isotherms measured at 45 °C on coal and carbonaceous shale samples from well CBM-001-ST-RS are shown in *Fig. 5.9*, and another set of isotherms measured at 35 °C in *Fig. 5.10*. While the 45 °C isotherms were determined up to pressures of more than 20 MPa, the 35 °C isotherms were recorded only up to a pressure of ~7 MPa. *Fig. 5.11* shows 45 °C CO_2 sorption isotherms measured for the Permian (Irati) and Devonian (Ponta Grossa) shales. The CO_2 isotherms at 45 °C typically exhibit a maximum in the 8 to 10 MPa pressure range and then show a continuous decline. The maximum is related to the steep increase in the specific density of supercritical CO_2 in the corresponding pressure range (cf. Gensterblum et al., 2009). Maximum excess sorption capacities for CO_2, measured in this pressure interval, range from 0.25 - 0.81 mmol/g (5.6 - 18.5 m³/t) for coals and carbonaceous shales and from 0.14 - 0.54 mmol/g (3.2 - 12.2 m³/t) for the shales from the Irati and Ponta Grossa formations. The measured CO_2 isotherms were approximated by the excess sorption function given in *Eq. (2)*. The three parameters n_L, P_L and $\rho_{adsorbed}$, adjusted by a least-squares optimization procedure, for the individual isotherms are listed in *Table 2*. Some of the CO_2 isotherms for the shale samples (*Fig. 5.11*) show a pronounced maximum with a steep decline in the pressure range between 9 and 11 MPa. These isotherms could not be satisfactorily approximated by the 3-parameter fitting function. Isotherms with similar shapes were obtained by Busch et al. (2008) for CO_2 sorption on the Australian Muderong shale and on pure clay minerals, such as illite, montmorillionite and kaolinite.

5.6.6. Effect of mineral matter content (ash yield) on gas sorption

Coal seamsfromthe Santa Terezinha Coalfield areknownto have high mineralmatter and inertinite contents as reported by Araújo et al. (1995) and more recently by Kalkreuth et al. (2006, 2008a,b). It has been suggested that the high-ash yields of coals from the Rio Bonito Formation are related to the occurrence of diamictites (Begossi and Della Fávera, 2002). X-ray diffraction analysis on coal samples from the CBM-001-STRS well revealed that the mineral matter is mostly composed of quartz, kaolinite and mica, with minor contributions of pyrite, ankerite, calcite, dolomite, albite and alunite (Kalkreuth et al., 2008b). Using the ash yield as a proxy for the mineral matter content, *Fig. 5.12* shows an essentially linear decrease of the maximum sorption capacity of methane and carbon dioxide with increasing mineral matter content for the coals and carbonaceous shales from the CBM-001-ST-RS well. The regression line for methane indicates that the sorption capacity is close to zero for ash yields approaching 100%, i.e. an organic matter content of zero. This supports the predominant role of organic matter in methane sorption in coals and carbonaceous sediments and is in agreement with

findings reported, for instance, for Australian Bowen Basin coals (Laxminarayana and Crosdale, 1999) and coals from British Columbia (Clarkson and Bustin, 2000). According to the regression in *Fig. 5.12*, the maximum sorption capacity for methane in the CBM-001- ST-RS well samples decreases by 0.009 mmol/g for each 1% increase in ash yield. This is somewhat lower than the value of 0.38 cm^3/g (0.017 mmol/g) reported by Laxminarayana and Crosdale (1999), which is likely to reflect differences in the type (maceral composition) and maturity of the organic matter.
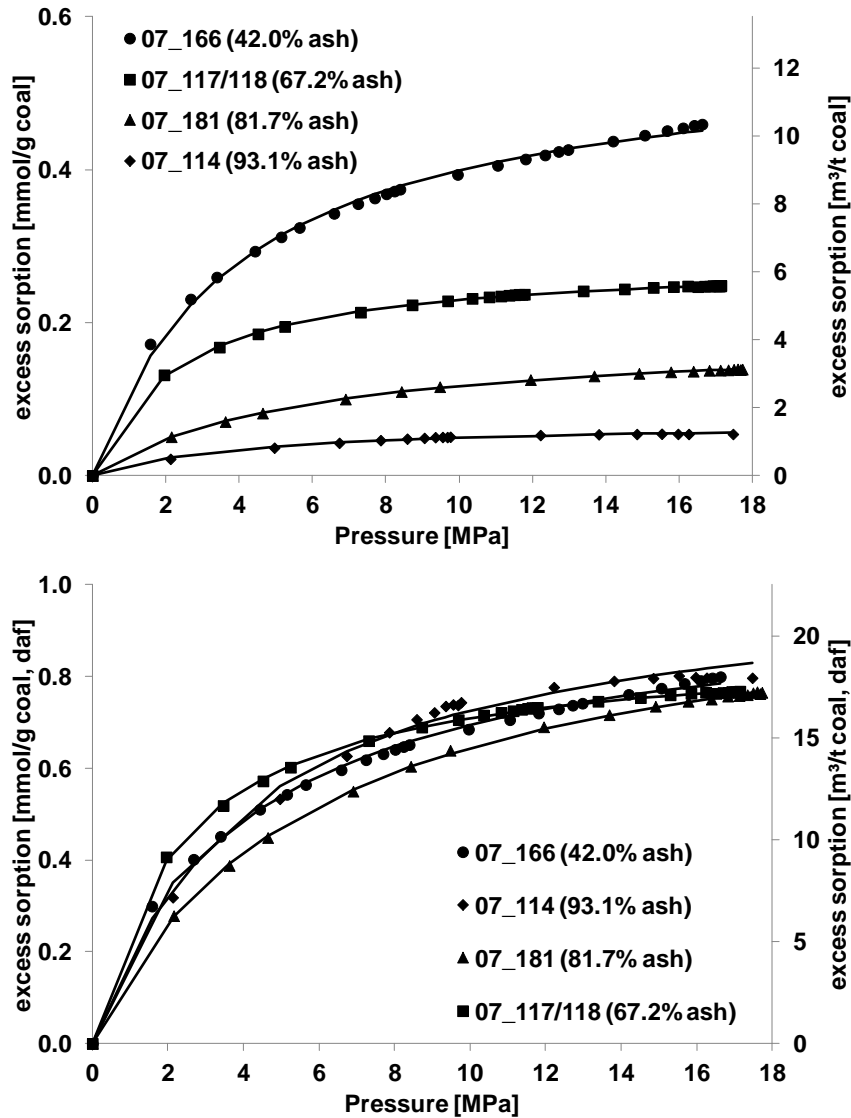
Fig. 5.6 Methane sorption isotherms (45 °C) with Langmuir approximations (solid lines) for coal and carbonaceous shale samples from the Permian Rio Bonito Formation of CBM well 001-ST-RS on a raw basis (top) and dry, ash-free basis (bottom).

The maximum sorption capacity of carbon dioxide for the CBM- 001-ST-RS well samples decreases by 0.008 mmol/g for each 1% increase in ash yield. The regression shows that at ash yields approaching 100%, i.e. organic carbon contents approaching zero, the samples still exhibit a considerable CO_2 sorption capacity (approximately 0.183 mmol/g) which can be attributed to the mineral matter. *Fig. 5.13* shows maximum excess sorption capacities of methane and carbon dioxide for coal and shale samples from the CBM-001-ST-RS well and

Permian (Irati) and Devonian (Ponta Grossa) formations as a function of organic carbon contents (TOC). The following linear regression functions were obtained:

$CH_4(mmol/g) = 0.009 \cdot TOC(\%) + 0.026$

$CO_2(mmol/g) = 0.008 \cdot TOC(\%) + 0.183$

As stated above, the regression function for CO_2 indicates that the mineral matter exhibits a significant sorption capacity (0.183 mmol/g) for this gas. This finding is in general agreement with results reported by Nuttall et al. (2005), who evaluated the potential for carbon dioxide sequestration and enhanced natural gas production of Devonian black shales in Kentucky. These workers find a linear increase of CO_2 sorption capacity at 400 psia (2.75 MPa) with TOC content described by the regression function:

$CO_2 (scf/ton) = 7.9 \cdot TOC (\%) + 20.7$ (CO_2 pressure = 400psia)

Expressed in metric units and amounts of substance this yields:

$CO_2 (mmol/g) = 0.009 \cdot TOC (\%) + 0.025$ (CO_2 pressure = 2:75MPa)

This regression was obtained for a much lower CO_2 pressure than the pressure levels corresponding to the maximum excess sorption (8– 10 MPa) considered in the present study. However, even when taking this into account, the mineral matter in the Devonian black shales of Kentucky appears to have a significantly lower CO_2 sorption capacity than the sample sequences from the Paraná Basin investigated here. The difference in CO_2 sorption capacity is most likely related to differences in mineralogical composition. *Table 3 (Appendix IV)* shows a comparison of X-ray diffraction mineralogy for Santa Terezinha coal samples reported by Kalkreuth et al. (2006) and for Ohio shale samples (Huron Formation) reported by Nuttall et al. (2005).
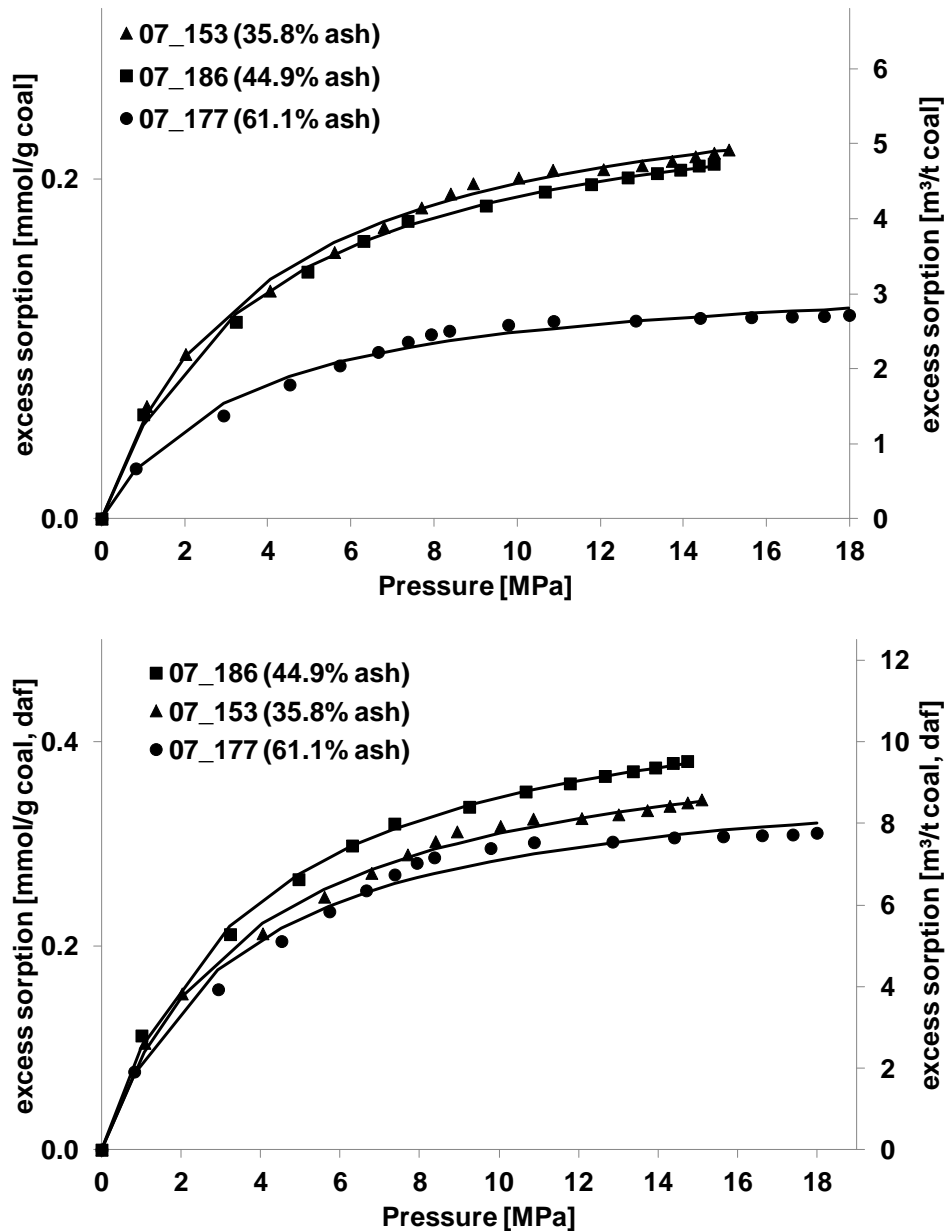
Fig. 5.7 Methane sorption isotherms (35 °C) with Langmuir approximations (solid lines) for coal and carbonaceous shale samples from the Permian Rio Bonito Formation of CBM-001- ST-RS well on a raw basis (top) and dry, ash-free basis (bottom).

Evidently, shales and some pure clay minerals exhibit a significant sorption capacity for CO_2. Busch et al. (2008) reported CO_2 sorption capacities for the Muderong shale and pure clay minerals (kaolinite, montmorillonite and illite), ranging from 0.1 mmol/g to 1.2 mmol/g for "as received" samples. The higher kaolinite and carbonate (calcite, ankerite and siderite) contents of coal samples explain the larger CO_2 sorption capacity of Brazilian coal samples. The Ohio shale has larger illite and mica contents as well as higher amounts of chlorite, plagioclase pyrite and quartz. Illite is reported to have a higher CO_2 sorption capacity compared to kaolinite (Busch et al., 2008). However, the sum of kaolinite and illite content is higher for the coal samples as compared to the Ohio shale. The higher carbonate content of the coals could also contribute to higher CO_2 sorption capacities through carbonate dissolution. However, this assumption is based on few literature data of coal samples. To better understand the variation of CO_2 sorption capacity of mineral matter, a more thorough mineralogical characterization of Santa Terezinha coal samples and shale samples in combination with isotherm measurements is

required. Particularly for high-ash coals and carbonaceous shales carbon dioxide adsorption on the mineral matter cannot be neglected and therefore normalization to a dry, ash-free basis is not appropriate.

5.6.7. Effect of moisture on sorption isotherms

It is well known that the moisture content of a coal significantly influences its methane sorption capacity (Joubert et al., 1973; Yalcin and Durucan, 1991; Crosdale et al., 2008; Day et al., 2008a). To investigate the effect of moisture, in addition to the measurements on the "as received" sample, methane and CO_2 sorption isotherms were measured on one coal (sample 07_166) in the moisture-equilibrated state (*Figs. 5.14 and 5.15*). The equilibrium moisture content of this sample was 2.44 wt.%, while the hygroscopic ("as-received") moisture content was 0.98 wt.%. The methane sorption capacity of the moisture-equilibrated coal sample is significantly lower (0.30 mmol/g; 0.53 mmol/g, daf) than the sorption capacity of the "as received" sample (0.57 mmol/g; 0.99 mmol/g, daf). This corresponds to a reduction by 45%. For carbon dioxide the maximum excess sorption of the moisture equilibrated sample was 0.28 mmol/g, which is 56% lower than for the "as received" coal (0.64 mmol/g). This indicates a stronger competition for sorption sites (*e.g.* with functional oxygen groups) between water and CO_2 than for methane, which is in contrast to observations by Day et al. (2008a), who found that water saturation caused a stronger reduction of sorption capacity for methane than for carbon dioxide for a high volatile bituminous Australian coal (Hunter Valley, Australia, VR_{max}=0.8%). The authors suspect that clusters of water molecules attach to pore-surfaces with polar sites, which then can become inaccessible for other adsorbates. CO_2 is considered to be able to adsorb on top of the polar water clusters, whereas CH_4 is limited to hydrophobic sorption sites and thus, the reduction of methane sorption capacity would be greater than the reduction of CO_2 sorption capacity. This effect diminished for a high rank coal (Illawara, Australia, Rmax=1.4%) with fewer polar sorption sites. Day et al. (2008a) also argue that the smaller kinetic diameter of CO_2, compared to CH_4would allow carbon dioxide to enter some of the blocked pores, which methane could not access. The observation in the present study, that moisture equilibration results in a stronger reduction of CO_2 sorption capacity as compared to methane is based on only one sample; further investigations are needed to examine this effect in more detail.
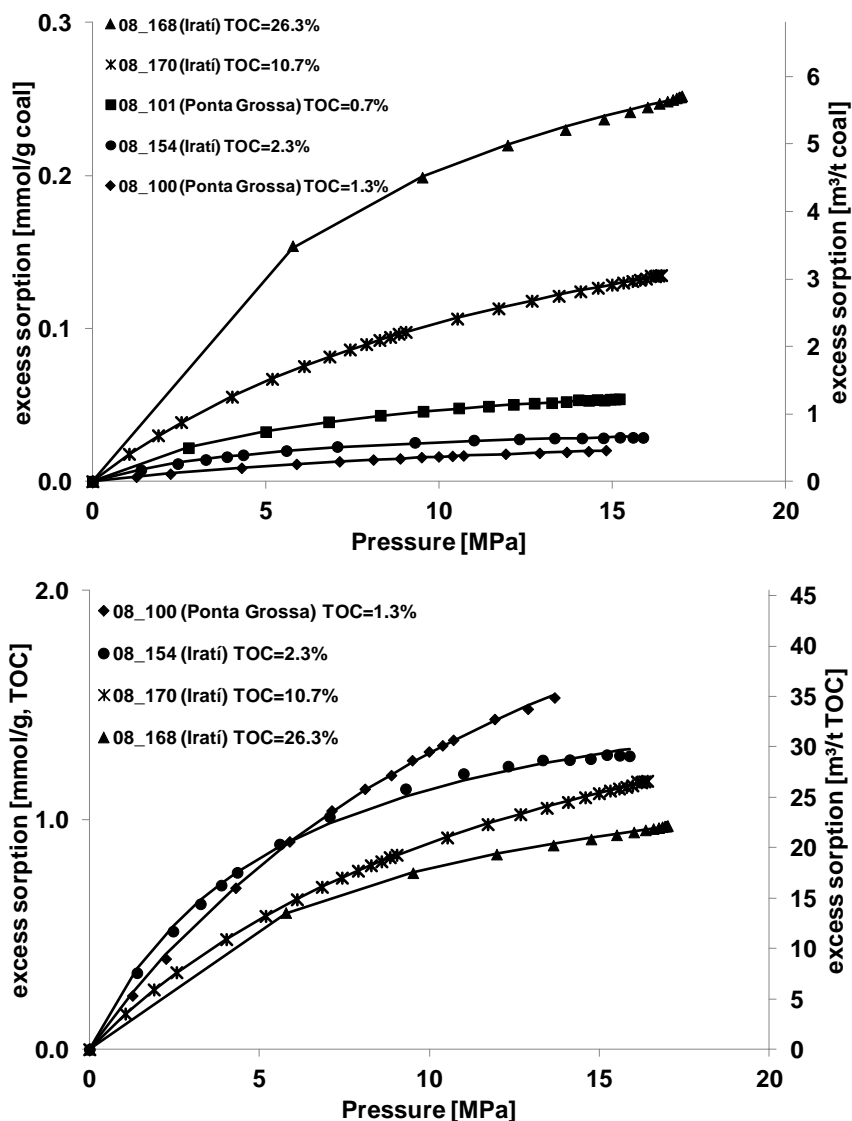
Fig. 5.8 Methane sorption isotherms with Langmuir approximations (solid lines) for Permian (Irati) and Devonian (Ponta Grossa) shale samples on a raw basis (top) and TOC basis (bottom, sample 08_101 with TOC<1% not included).

5.6.8. Effect of coal maceral composition on sorption isotherms

The effect of maceral composition on methane and carbon dioxide sorption on coals is attributed to differences in microporosity of the macerals. Vitrinite is predominantly microporous, whereas inertinite is rather meso- to macroporous (Lamberson and Bustin, 1993). Some authors report a significant influence of maceral composition on sorption capacities (*e.g.* Lamberson and Bustin, 1993; Mastalerz et al., 2004; Chalmers and Bustin, 2007), whereas others could not observe such a relationship (*e.g.* Krooss et al., 2002; Faiz et al., 2007; Day et al., 2008b). To compare the effect of coal composition on sorption, isotherms have to be normalized to a dry ash-free basis. Lamberson and Bustin (1993) report increasing methane sorption with increasing vitrinite content on medium-volatile coals from British Columbia. Chalmers and Bustin (2007) report higher methane sorption capacity for liptinite-rich coals with low microporosity, where methane is held as solution gas. Mastalerz et al. (2004) observed a relationship between maceral composition of coals from Indiana (high volatile bituminous C) and CO_2 sorption capacity, measured at 2.8 MPa (400 psi) and 17 °C (62 °F). They found increasing CO_2 sorption capacities for coals with higher vitrinite content and suggest that

telocollinite content may be of greatest influence on CO_2 sorption capacity of all macerals. Coals with higher liptinite content showed lower CO_2 sorption capacities. No correlation between methane or carbon dioxide sorption capacity and petrographic composition of coal was observed for coals and carbonaceous shale samples analysed in the present study (*Fig. 5.16*). As mentioned in section 5.6, the normalization of carbon dioxide sorption isotherms, measured on high-ash coals, to the dry, ash-free basis is prone to overestimation of sorption capacity, which could mask a correlation of CO_2 sorption capacity with maceral composition. Laxminarayana and Crosdale (1999) found that the influence of maceral composition on gas adsorption decreases with increasing rank. The high rank of some coals analysed in this study (high volatile A bituminous–anthracite) might explain why no correlation with maceral composition was observed.

5.6.1. Effect of maturity on sorption isotherms

Previous studies report that methane sorption capacity decreases with increasing rank to a minimum in the medium-volatile bituminous range, followed by an increase with increasing rank (Yalcin and Durucan, 1991; Faiz et al., 2007). This effect has also been observed for carbon dioxide sorption capacity (Busch et al., 2003; Day et al., 2008b). With increasing thermal maturity from mediumvolatile bituminous to anthracite rank, the microporosity of coal increases (Bustin and Clarkson, 1998; Prinz and Littke, 2005; Chalmers and Bustin, 2007). Since most of the physical adsorption takes place in the micropore structure of coal (Yalcin and Durucan, 1991), the increase in microporosity with increasing rank is also considered to cause an increase in sorption capacity from medium volatile bituminous coal to anthracite. In the present study no correlation was found between methane or carbon dioxide sorption and maturity (*Fig. 5.17*).
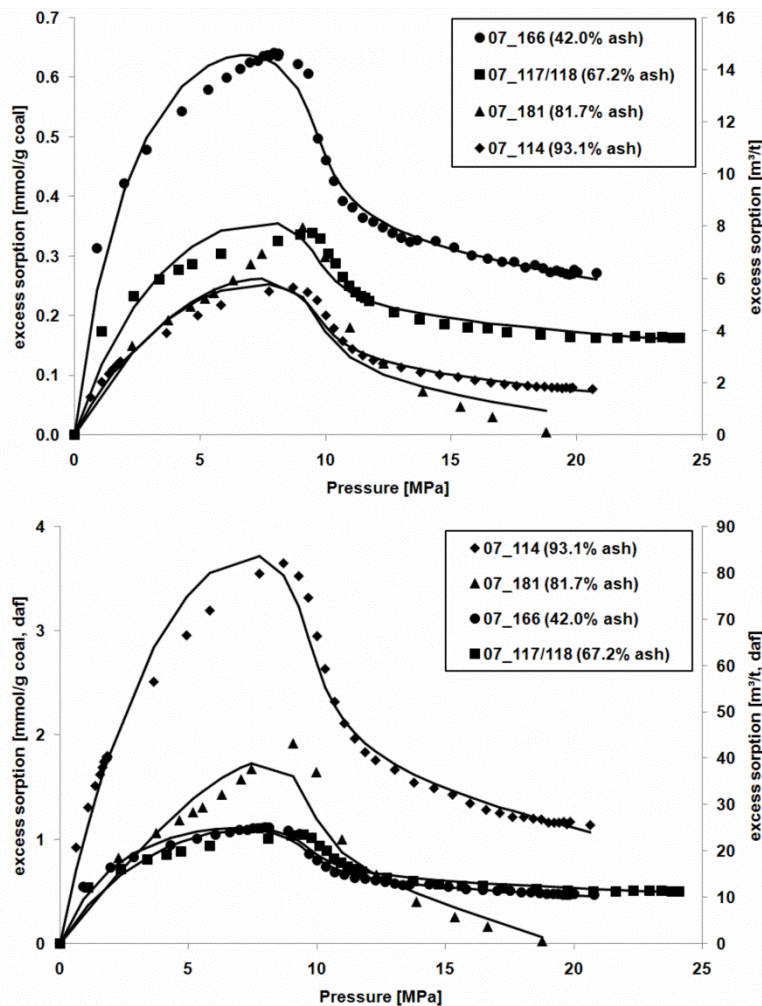
Fig. 5.9 Carbon dioxide sorption isotherms for coal and carbonaceous shale samples from well CBM-001-ST-RS on a raw basis (top) and dry, ash-free basis (bottom), measured at 45 °C.

5.6.2. Evaluation of potential for carbon dioxide sequestration and enhanced coalbed methane (CO_2–ECBM) and shale gas recovery (CO_2–ESG)

Sorption capacities for CO_2 on coals and shales are generally higher than for CH_4. Sorption capacities of samples from the CBM-001-ST-RS well (^1n_L) for an average reservoir pressure of 6.25 MPa, range between 0.29 and 0.73 mmol/g (6.66–16.63 m^3/t) for carbon dioxide and between 0.04 and 0.34 mmol/g (0.95–7.72 m^3/t) for methane. The sorption capacity ratios (V_LCO_2/V_LCH_4 at 6.25 MPa) range between 2.0 and 7.0 (average 3.6). Ratios of maximum excess sorption amounts ($n_{max}CO_2/n_{max}CH_4$) range between 1.4 and 4.6 for the coal and carbonaceous shale samples from the CBM well. For the Permian (Irati) and Devonian (Ponta Grossa) shales these ratios range between 2.1 and 10. Results from the present study suggest that coal seams in the Santa Terezinha Coalfield are generally under-saturated in methane, which means that the current gas content is lower than the measured sorption capacity. The free sorption capacity, not occupied by methane, could possibly be used for storage of carbon dioxide. Depending on the economical and market situation the methane present in the coals could be produced prior to CO_2 injection. Simultaneous injection of CO_2 for ECBM is considered less promising because the produced gas would have a low calorific value due to co-production of injected CO_2 (cf. van Bergen et al., 2008, 2009). In a first approach to estimate the effective CO_2 storage capacity of a CBM reservoir, a calculation similar to the

assessment of producible gas in place (PGIP) from initial gas in place (IGIP) (*Eq. 3*) can be applied (van Bergen et al., 2001):

PGIP = RF·C·IGIP (3)

Here the producible part of the gas in place is estimated using a recovery factor (RF) and estimating a completion factor (C). The recovery factor represents the amount of gas that can technically be produced by reducing the reservoir pressure through water production. The completion factor (C) represents an estimation of the part of coal seams that can be accessed by drilling operations.[1]
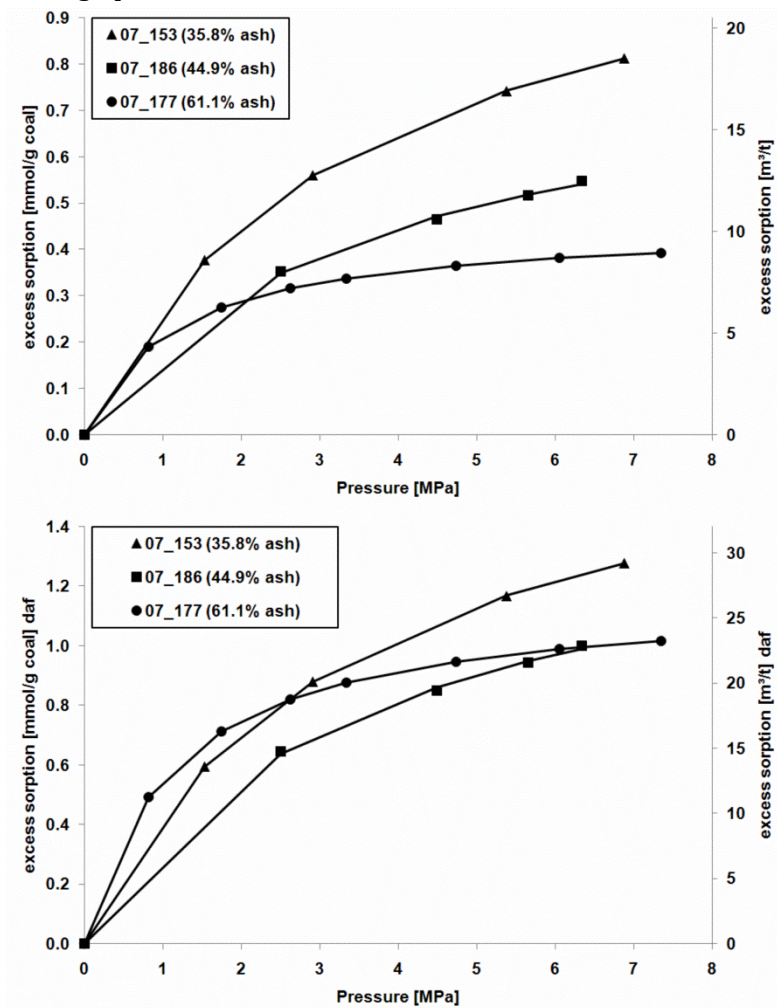
Fig. 5.10 Carbon dioxide sorption isotherms for coal and carbonaceous shale samples from CBM well 001-ST-RS on a raw basis (top) and dry, ash-free basis (bottom), measured at 35 °C. Solid lines represent Langmuir fit.

Hendriks et al. (2004) estimated the global carbon dioxide storage potential in various underground reservoirs. For the CO_2 storage capacity (SCO_2) in coal basins during ECBM operations they used the following equation:

SCO_2 = PGIP·ER·ρCO_2 (4)

PGIP = producible gas in place (standard conditions) [m^3]

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[1] In mmol/g rock; not daf-normalized

ER = exchange ratio [−]

ρCO_2 = CO$_2$ density at standard conditions [1.977 kg/m^3].

The amount of producible gas in place (PGIP) is estimated according to:

$$PGIP = A \cdot TH \cdot \rho_{coal} \cdot GC \cdot RF \cdot CF \tag{5}$$

A = area of the coal basin [m^2]

TH = cumulative thickness of coal seams [m]

$\rho coal$ = coal density [t/m^3]

GC = gas content [m^3/t]

RF = recovery factor [−]

CF = completion factor [−].

In *Eq. (5)* the initial gas in place is calculated by multiplying the total mass of coal (A·TH·ρ_{coal}) by the average gas content (GC). Hendriks et al. (2004) conservatively assumed that only 10% of the total area of a coal basin can be used for CO$_2$ storage and thus they used a completion factor of 0.1. The recovery factor usually ranges between 20% and 60% (van Bergen et al., 2001). For the case of CO$_2$ sequestration, the recovery factor represents the storage efficiency. It was conservatively assumed to be 40% by Hendriks et al. (2004).
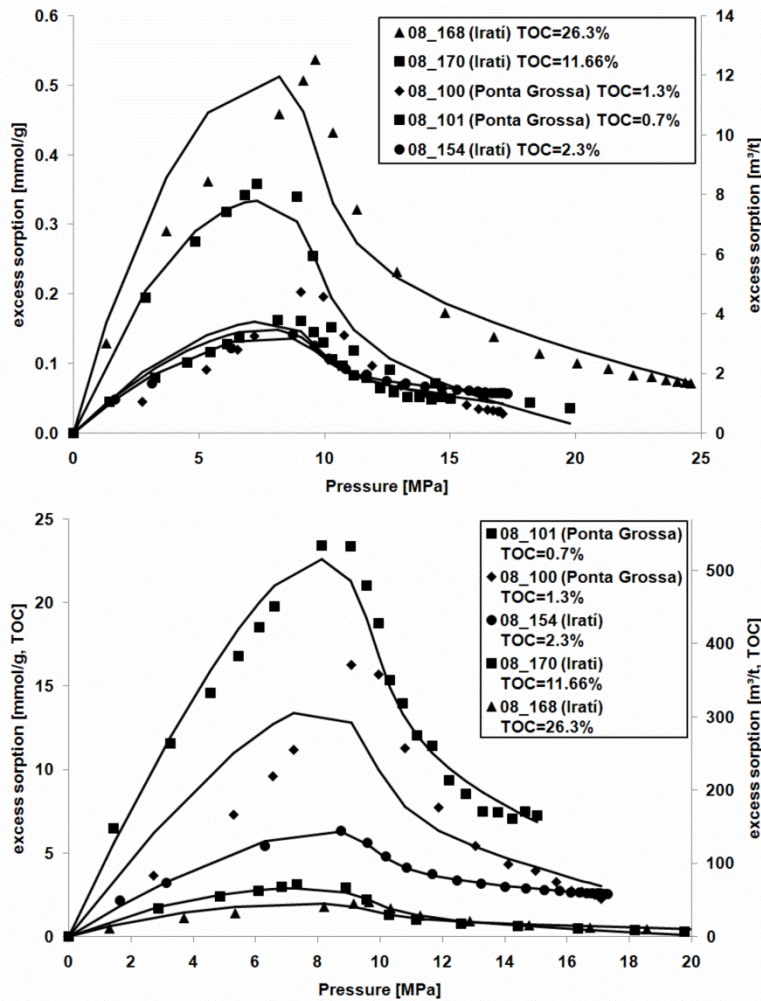
Fig. 5.11 Carbon dioxide sorption isotherms for Permian (Irati) and Devonian (Ponta Grossa) shale samples on a raw basis (top) and TOC basis (bottom), measured at 45 °C.

To estimate the CO$_2$ storage capacity of the study area in the Santa Terezinha Coalfield, we used *Eq. (5)*, assuming the same recovery factor and completion factor used by Hendriks et

al. (2004). Based upon 3D geological modelling for a study area of approx. 20×40 km in the Santa Terezinha Coalfield, Kalkreuth et al. (2008b) calculated the total mass of coal in the coal-bearing sequence to be in the order of $5.46 \cdot 109$ t. The average gas content of this area is 1 m³/t (Kalkreuth et al., 2008b). From sorption isotherm measurements for CO_2 and CH_4, an average exchange ratio of 3.6 was calculated.
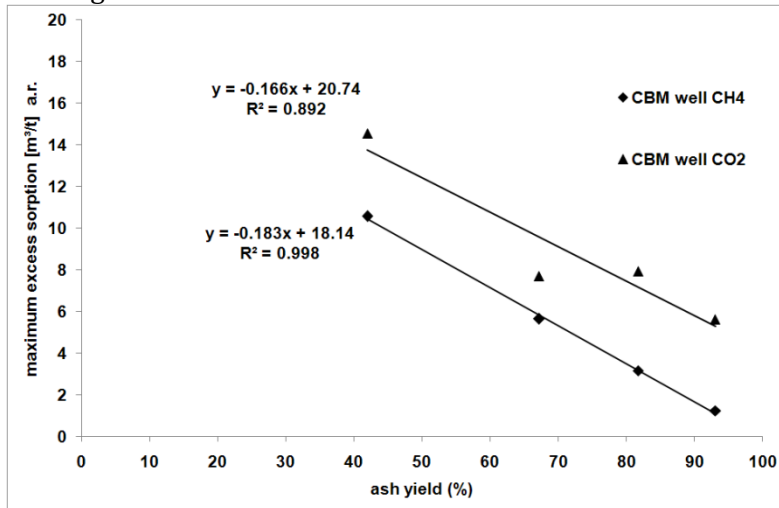
Fig. 5.12 Maximum excess sorption capacities (45 °C) of methane and carbon dioxide as a function of ash yield for coals and carbonaceous shales from CBM well 001-ST-RS.
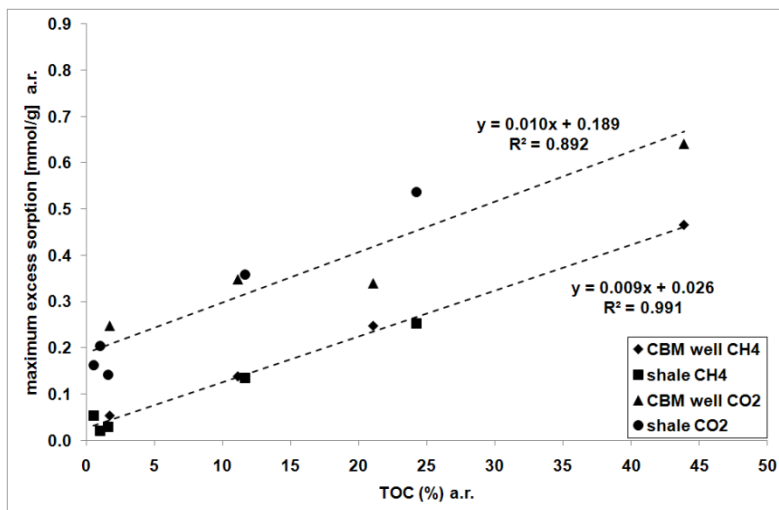
Fig. 5.13 Maximum excess sorption capacities for methane and carbon dioxide (8–12 MPa pressure range, 45 °C) vs. TOC contents of coal and shale samples from CBM-001-ST-RS well and Permian (Irati) and Devonian (Ponta Grossa) shale samples.

The CO_2 storage capacity for a 20×40 km² area in the Santa Terezinha Coalfield has been estimated using *Eq. (5)*. For the case of replacing sorbed methane by CO_2 injection, the storage potential of the study area would then amount to 1.55 Gt. For a mean reservoir pressure of 6.25 MPa, the average sorptive storage capacity for CO_2 is 0.43 mmol/g (9.86 m³/t). Considering carbon dioxide sequestration only, *e.g.* keeping the gas currently stored in the coal (1 m³/t) in place, the remaining "free" CO_2 sorption capacity of 8.86 m³/t could be used for CO_2 storage. Assuming a recovery factor of 40%, the above calculation then yields a total CO_2 storage capacity of 13.8 Gt in the coals of the study area. In a combined CBM production and CO_2 storage operation, a mass of 15.4 Gt CO_2 could theoretically be stored in the study area of the Santa Terezinha Coalfield as defined by Kalkreuth et al. (2008b). To refine this very simplistic calculation of the CO_2 storage potential of the Santa Terezinha Coalfield, additional factors

affecting CBM production (*e.g.* water saturation), injection (*e.g.* permeability) and storage (presence and integrity of sealing formations) as well as potential environmental safety and health problems associated with CO_2–ECBM need to be considered (Bachu, 2007; White et al., 2005).

5.7. Conclusions

To evaluate the sorptive storage capacity of the Paraná Basin in Brazil, methane and carbon dioxide sorption experiments were performed on coal and carbonaceous shale samples from a CBM test well, drilled in 2007 in the Santa Terezinha Coalfield. Additionally, storage capacities were determined on samples of the two major petroleum source rocks of the basin: the Devonian Ponta Grossa Formation and the Permian Irati Formation. Experiments were performed on powdered samples at pressures up to 25 MPa and temperatures of 35 °C and 45 °C. The present study reports the first comprehensive set of high-pressure sorption data for methane and carbon dioxide for coals, carbonaceous shales and petroleum source rocks of the Paraná Basin, Brazil. On a raw mass basis ("as received", i.e. not dry, ash-free normalized), the Langmuir sorption capacities of methane on coal and carbonaceous shale from the CBM well ranged between 0.05 and 0.47 mmol/g. For the shale source rocks they were lower, ranging between 0.04 and 0.37 mmol/g. For carbon dioxide the maximum excess sorption, reached in the 8–12 MPa interval, ranged between 0.25 and 0.81 mmol/g for coal and carbonaceous shale samples, and between 0.14 and 0.54 mmol/g for shale source rocks. Normalized to dry, ash-free mass, methane sorption capacities of shales exceeded those of coal and carbonaceous shale. Methane and carbon dioxide sorption capacities of coal and shales correlated with the organic carbon content (TOC). For carbon dioxide the linear regression showed a non-zero intercept, indicating a significant sorption capacity of the mineral matter. This was not the case for methane.
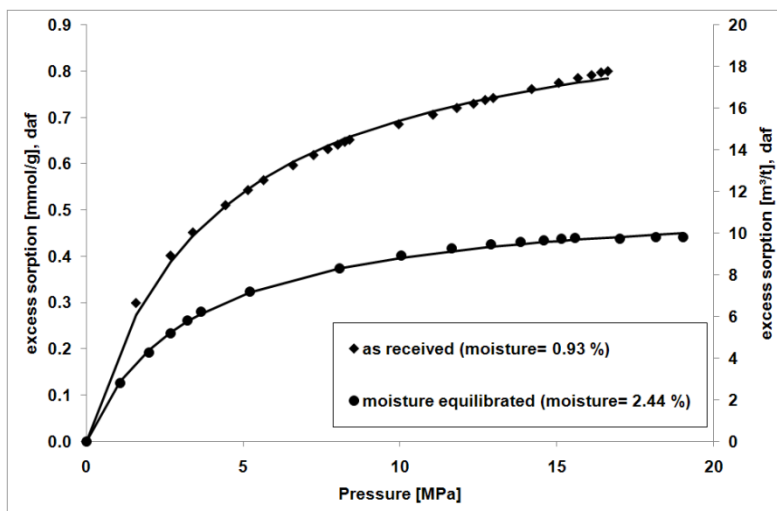
Fig. 5.14 Effect of moisture on methane sorption for coal sample 07_166. At equilibrium moisture (2.44%) the sorption capacity is 45% lower as compared to the "as received" coal (moisture content: 0.93%). Solid lines represent Langmuir fit.
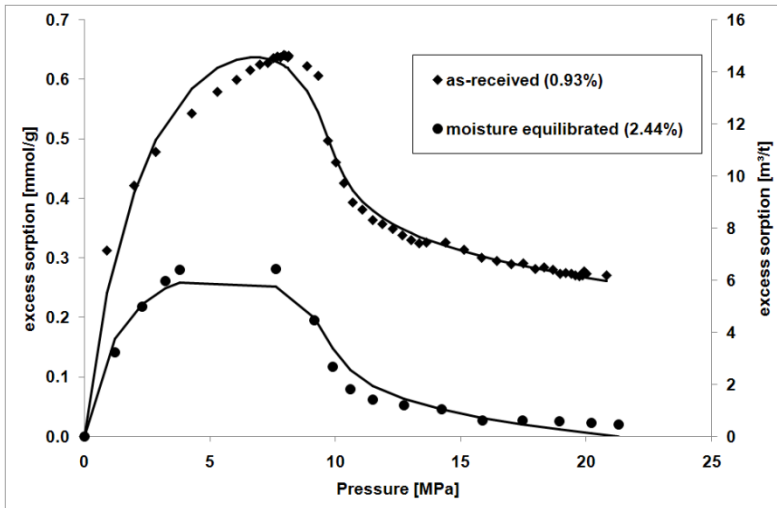
Fig. 5.15 Effect of moisture on carbon dioxide sorption for coal sample 07_166 from CBM well ST-RS-001. At equilibrium moisture (2.44%) the sorption capacity is 56% lower as compared to the "as received" coal (moisture content: 0.93%). Solid lines represent 3-parameter fit.
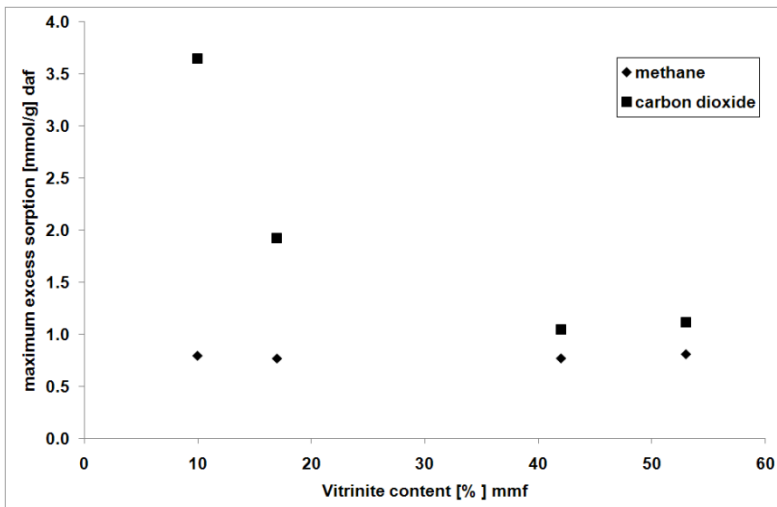
Fig. 5.16 Maximum excess sorption of capacity of methane and carbon dioxide vs. vitrinite content for coal samples from well CBM-001-ST-RS.
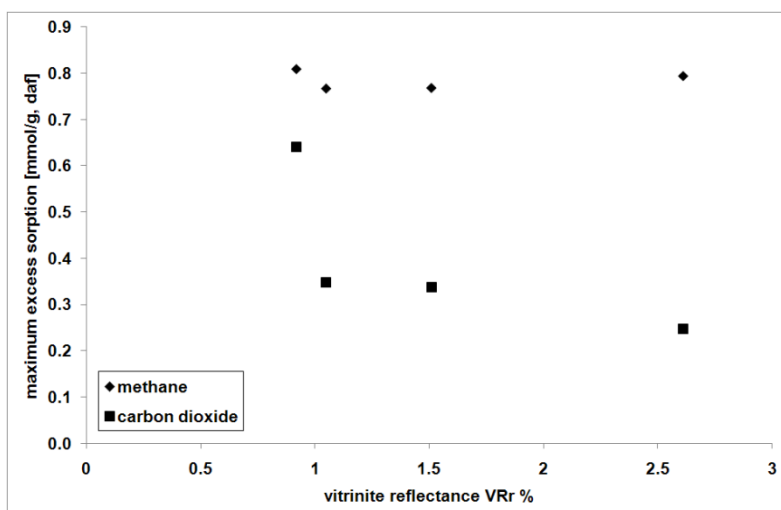
Fig. 5.17 Maximum excess sorption of capacity of methane and carbon dioxide vs. vitrinite reflectance for coals from well CBM-001-ST-RS.

The present-day gas content of coals analysed from the first CBM well in the Santa Terezinha Coalfield, as determined from canister desorption, amounts to 13–38% of the methane sorption capacity measured on "as-received" samples. Experiments on one coal sample from seam interval D (collected from a depth of 620.8 m) after moisture equilibration showed that its sorption capacity was reduced by 46% for methane and by 56% for CO_2 as compared to the "as received" state. No correlation between sorption capacity and coal composition or thermal maturity was observed. Carbon dioxide sorption capacity was higher than methane sorption capacity for all samples. The CO_2/CH_4 sorption capacity ratio was larger for coal and carbonaceous shales (1.9–6.9) than for source rock shale samples (1.4–4.5). Sorption capacities calculated for reservoir conditions indicated that theoretically an amount of 13.8 Gt carbon dioxide can be stored in coal seams of the study area. This amount would increase to 15.4 Gt, if all methane were produced from coal seams prior to carbon dioxide injection. In a further step, geological factors such as permeability, presence and integrity of sealing formations and economic factors such as depth and number of wells, costs for transport and injection of CO_2, that influence carbon dioxide storage, need to be evaluated to provide a more realistic view on the feasibility of carbon dioxide storage in the Santa Terezinha Coalfield.

5.8. Acknowledgements

6. Final Discussion and Outlook

6.1. Origin and composition of coal-related gas

Numerous gas samples from mine faces as well as desorbed from coals of the Upper Silesian Coal Basin were analyzed during the present study. Results of chapter 2 showed that microbial gas is associated with coal seams of the Pennsylvanian Karviná Formation, whereas thermogenic gas is associated with coal seams of the Mississipian Ostrava Formation, confirming results from earlier studies in the USCB. Apart from this general pattern, no correlation between gas composition and stratigraphy or coal rank was observed. Analyses of gas samples taken during desorption experiments, did not reveal any influence of sorption / desorption processes on gas composition. The composition of coal-related gases desorbed from drilling cores of a CBM well in the Santa Terezinha coalfield, Brazil, indicates a mixture of gases from thermogenic and microbial sources (*Fig. 6.1*).
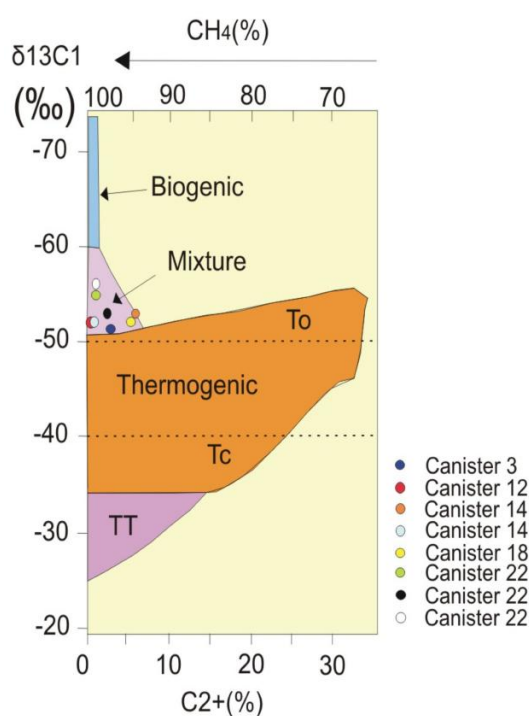
Fig. 6.1 Composition of gas from canister desorption of samples from the CBM well, drilled in the Santa Terezinha coalfield, Brazil (from Kalkreuth et al., 2011 (submitted); modified from Schoell, 1983). To = gas associated with oil, Tc = condensate, TT = dry gas.

Difficulties associated with the sampling procedure that arose during the study of coal-related gas in the USCB showed that additional measurements using an improved method are required to confirm that sorption / desorption processes do not significantly alter the geochemical and stable isotopic signature of coal related gases.

For effective microbial gas generation, temperatures lower than 80 – 100°C are required and consequently, microbial methanogenesis could only start after coal seams were uplifted and reservoir temperatures finally dropped below this temperature threshold. For the Karviná Formation, paleotemperatures ultimately dropped below 100°C in early Permian, while reservoir temperatures of coal seams of the Ostrava Formation were less favourable (*Fig. 6.2*). Coal from the Petrkovice and lower Hrusov Member reached temperatures > 80 – 90°C during

Miocene (Carpathian overthrust), resulting in paleopasteurization. Thermogenic gas generation, however, was not reinititated during this reburial.
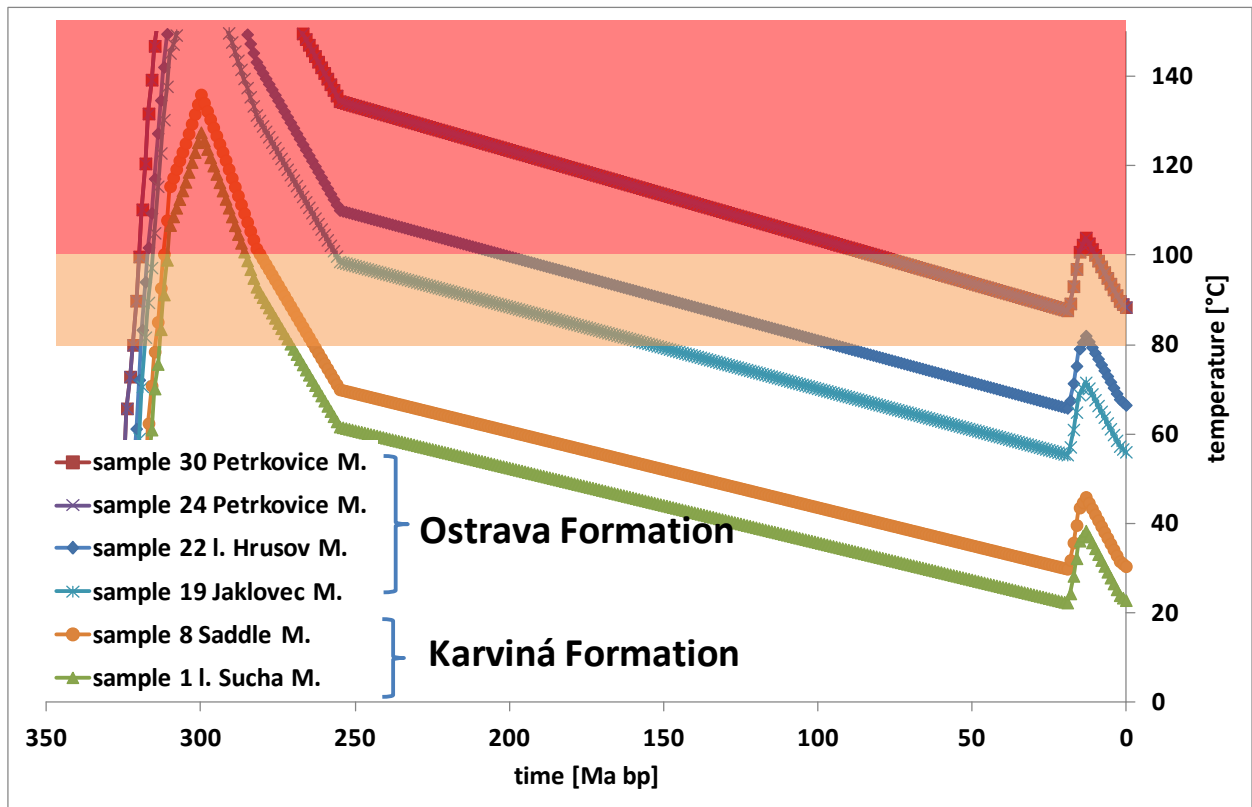
Fig. 6.2 Temperature history of coal-bearing formations in the USCB showing that temperature conditions in the Ostrava Formations were less favourable for microbial methanogensis than for sediments of the Karviná Foramtion.

From this information it can be concluded that, while all coal seams still have enough gas generation potential, temperature conditions were more favourable for microbial gas generation in coals of the Karviná Formation than for the Ostrava Formation.

Recent studies on microbial gas generation in coal seams in Poland (Kotarba and Pluta, 2009) and the Illinois Basin, USA (Strapoc et al., 2007) linked the timing of meteoric water percolation into coal-bearing sediments to microbial gas generation. On the one hand, meteoric waters dilute basinal brines and introduce nutrients for microbial activity and on the other hand, methanogenic microbes can be transported with percolating meteoric waters into coal beds. Kotarba and Pluta (2009) discuss that meteoric waters percolated into coal bearing sediments in the USCB during early Jurassic and until the Miocene. These waters might have introduced microbes and nutrients enabling microbial gas generation until the marine transgression during the Miocene, and the associated increase in salinity impeded microbial activity. This is most likely also the case for coal bearing sediments of the Karviná Formation in the Czech part of the basin. Without detailed hydrogeologic information, *e.g.* composition of formation waters and occurrence and timing of meteoric water percolation, the exact origin and timing of microbial gas generation remains speculative. Differences in overburden sediments, *e.g.* permeable molasse sediments above the Karviná Formation compared to lower permeable flysch nappes of the Carpathian overthrust above parts of the Ostrava Formation might have favored percolation of meteoric water and microbial gas generation in the Karviná Formation.

Results from this study demonstrate that integration of experimental data on reaction kinetics and sorptive storage capacity into numerical basin modelling provides a useful tool for the reconstruction of gas generation history and the evolution of gas storage capacity. This information can improve the understanding of the distribution of different gases and gas mixtures in sedimentary basins.

6.2. Gas generation

Results of pyrolysis experiments and reaction kinetic modelling in the present study showed that coal seams of the USCB have generated significant amounts of thermogenic gas during late Carboniferous between 320 and 290 Ma at temperatures <210°C. At the time of gas generation the amount of generated gas exceeded the sorption capacity, *e.g.* 0.15 mmol/g (3.4 m^3/t) at 292 Ma for coal from the Saddle Member. At present day, coals still have significant methane generation potential and also 'free' sorptive storage capacity. On the one hand, this remaining generation capacity can allow microbial gas generation from the coal organic matter, if the required conditions (temperature, nutrients) are met and methanogens are present in these sediments. The 'free' sorption capacity of these coals on the other hand would allow storage of a significant amount of microbially generated gas before expulsion and migration to the surface would occur.

6.3. Gas storage capacity

A large number of high-pressure sorption isotherms for methane and CO_2 on coal samples from the USCB was recorded under controlled temperature conditions and defined moisture state. These were used to establish functions that, in combination with pressure and temperature information from a 1-D basin model, could be used to model the dynamic evolution of the sorption capacity of coal seams in the study area over geologic time. These algorithms are useful complements to the reconstruction of gas generation history based on reaction kinetics and migration modelling. To improve the applicability of these calculations, experimental isotherms are required for temperatures >70°C. The increase of sorption capacity during uplift alone is not sufficient to explain the gas under-saturation of most coal seams, indicating that a significant amount of gas, generated during coalification, was lost during times of uplift and erosion.

Investigations of the sorption capacity and its controlling factors reported in chapters 4 and 5 indicate a significant correlation between coal rank and sorption capacity. Combination of these results with information from numerous analyses of coals from other European coal basins that were performed in our laboratory supports the control of coal rank on methane sorption capacity (*Fig. 6.3*).
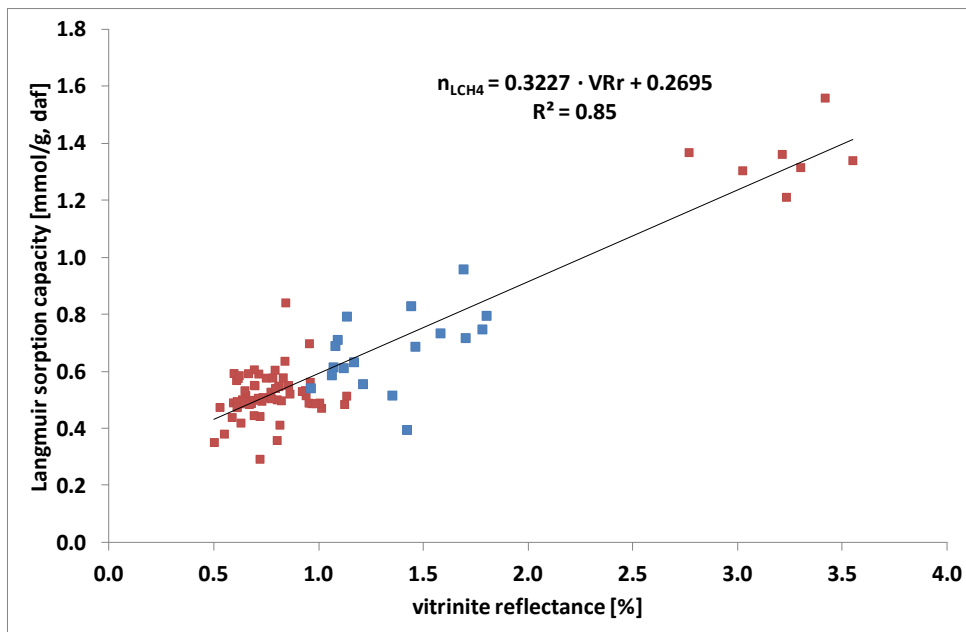
Fig. 6.3 Relationship between methane sorption capacity (n_L) and coal rank for Carboniferous coals from different Europena basins (blue squares represent samples from the USCB analysed in the present study).

Especially the variation of hygroscopic moisture and equilibrium moisture with increasing coal rank becomes more obvious, when considering a large rank interval from sub-bituminous coal to anthracite stage (*Fig. 6.4*). The hygroscopic moisture decreases with increasing coal rank between sub-bituminous and high volatile bituminous rank. With further increase in coal rank, the hygroscopic moisture shows a small increase, but generally stays below 4 wt.%. The equilibrium moisture of coal (moisture holding capacity), is reported to correlate with the 'in-situ' bed moisture of coal seams (Alpern et al., 1989). In contrast to the hygroscopic moisture, the equilibrium moisture shows a more significant increase in the high rank range (*Fig. 6.4*). These observations are in line with results from previous studies (Teichmüller and Teichmüller, 1979; Prinz et al., 2004; Levy et al., 1997; Day et al., 2008a).

The change in moisture content with increasing coal rank is believed to be related to the amount of functional oxygen groups and the formation of water clusters (Joubert et al., 1974; Prinz and Littke, 2005; Day et al., 2008a). The loss of oxygen groups and changes in the pore space during coalification result in a decrease in porosity and micropore volume towards medium volatile bituminous rank. Structural changes above 1.5% VRr lead to an increase in microporosity and micropore volume accessible for water, which results in a gradual increase of moisture in the high-rank range (Prinz and Littke, 2005).
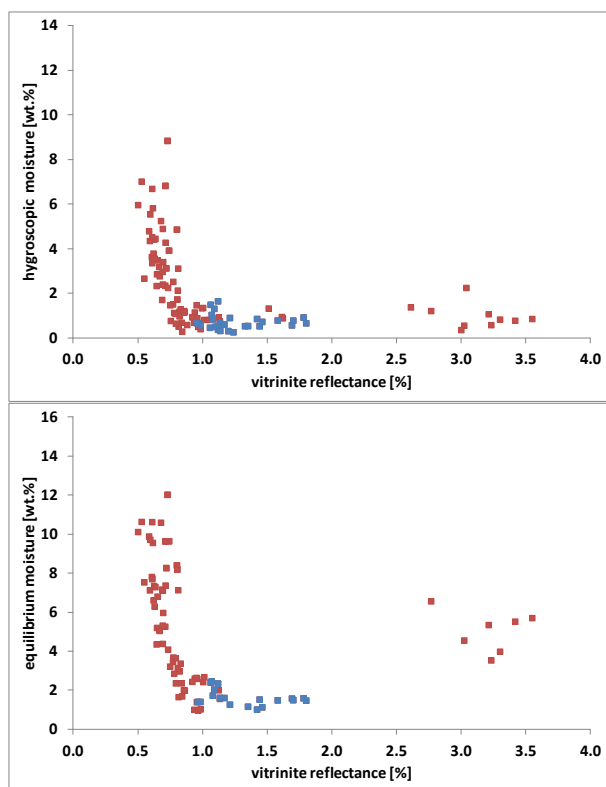
Fig. 6.4 Variation of "as-received" (hygroscopic) moisture (left) and equilibrium moisture (right) with coal rank for Carboniferous coals from different Europena basins (blue squares represent samples from the USCB analysed in the present study).

6.4. Comparison of sorption capacity of coals from the Upper Silesian Coal Basin and the Paraná Basin

The Permian Paraná Basin coals were deposited under different paleoenvironmental conditions than the Central European Carboniferous coals. Carboniferous coals of the northern hemisphere (Euramerica), such as those from the USCB, were deposited in a paralic environment under tropical conditions, whereas Permian coals of the southern hemisphere (Gondwana) were deposited under different (colder) paleoclimatic and depositional conditions (Diessel, 1992; DiMichele et al., 2009). The differences in plant organic matter affect the maceral composition and the geochemistry of such coals, *e.g.* liptinite from Gondwana coal can be different from liptinite from Euramerican coal. However, the geochemical composition of coal organic matter was not analyzed in detail in the present study. Despite a likely difference in organic matter composition, no correlation was observed between maceral composition and sorption capacity for coal from the USCB and the Paraná Basin. Both coals show a similar negative correlation between sortion capacity and ash yield (mineral matter content), indicating that the diluting effect of inorganic matter is the controlling factor for sorption capacity. Comparison of the rank dependence observed for coal from the USCB with results from the Paraná Basin shows that no or only a weak rank correlation exists for the Brazilian coal (*Fig. 6.5*). This could be related to differences in the coalification process for these coals. While coalification for the European coals was controlled by slow heating during burial (T < 300°C), the high rank of some of the Brazilian coals was induced by volcanic activity and thus by exposure to high temperatures for a relatively short period of time. The increasing sorption capacity of bituminous coals with increasing coal rank is related to an increase in micropore volume, associated with changes during coalifications (Prinz et al., 2005). The lack of correlation between coal rank and sorption capacity for Brazilian coals could indicate that the coalification

process for these coals did not increase the micropore volume, or that micropores are 'plugged', *e.g.* by generated bitumen. Further investigations are required to create a statistically more significant dataset and to improve the understanding of different coalification processes on gas sorption capacity.
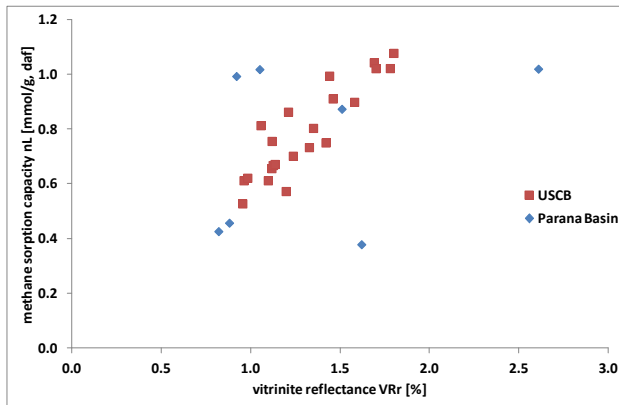
Fig. 6.5 Comparison of the influence of coal rank (vitrinite reflectance) on methane sorption capacity for coal from the Upper Silesian Coal Basin with coal from the Paraná Basin.

6.5. Outlook and Recommendation

In the present study a wide range of analyses were performed to investigate the gas composition, gas generation processes as well as the gas storage potential and influence factors of coal and reservoir properties on gas storage. Results of these investigations showed that some questions still remain open. The main questions that are still not satisfactorily answered are:

1. To what extent was the isotopic composition of coal related gas influenced by migration processes? Can light methane be the result of migration rather than of a different generation process?
2. What is the amount of gas generated by present day microbial gas generation from coal seams and what are the generation rates? Can microbial gas generated from coal seams be considered as a "regenerative energy source"?
3. How exactly did basin evolution influence the gas storage capacity of coal seams in the USCB? When and for how long was gas expelled from coal seams and lost to the atmosphere during the period of erosion and uplift?
4. How does the influence of coal rank on sorption capacity of gas or water change over the entire coalification range in the USCB?
5. Is the influence of coal rank and coal composition on gas sorption capacity different for Gondwana coals than for Euramerican coals?
6. What is the shale gas potential of organic-rich shales in the Upper Silesian Coal Basin in Czech Republic?
7. What is the environmental impact of exploration and production of coalbed methane and shale gas?

These principal questions are now briefly discussed and additional studies or measures to improve the understanding of these issues are recommended.

6.6. Gas composition and generation

Geochemical and stable isotopic analyses performed in the present study showed, that sampling procedures need to be improved in order to assess the influence of sorption/desorption processes on gas composition. Recent studies recommend purging coal samples with inert gas (Argon) during sampling, to avoid contamination with air that may result in oxidation and alteration of the gas composition during canister desorption experiments (Jin et al., 2010). Additional analyses and canister desorption experients using such an improved method are required to evaluate the influence of sorption/desorption processes on the gas composition. Stable isotope analyses of coal-related gas can significantly be improved by including hydrogen isotope composition, especially to differentiate between different processes of microbial gas generation, as shown in recent studies on gas generated from coal and organic rich shales (Golding et al., 2010; Osborne and McIntosh, 2010; Strapoc et al., 2007, 2008, 2010). Additionally, the analysis of gas associated with the Oligocene Menilite Formation is required to evaluate whether thermogenic gas in coal seams of the USCB is mixed with gas from this source

6.7. Microbial gas

While several recent studies found evidence of active microbial gas generation in coal seams and abandoned coal mines (Hendry, 2006; Krüger et al., 2008; Faiz and Hendry, 2009; Penner et al., 2010), a quantative assessment of microbial gas generation rates is still missing. Such a quantitative assessment of methanogenesis has been performed recently in laboratory experiments using methanogens extracted from recent lake sediments and peat swamps (Metje and Frenzel, 2007, Metje, 2006; Schwarz et al., 2008; Schwarz, 2007). Until the amount and the rate of microbial gas generation in present day coal seams is known, it remains speculative, whether microbial gas in coals seams represents a regenerative energy source. A possible enhancement of microbial gas generation from coal, *e.g.* by addition of nutrients or injection of more efficient microbial communities into coal seams is subject of current research projects, *e.g.* by CSIRO, Australia. Results of this research might show whether present day microbial gas generation in coal seams can yield commercial amounts of methane.

6.8. Basin history of the USCB

Pyrolysis experiments of coals of the Upper Silesian Coal Basin in the present study allowed estimation of the residual thermogenic gas generation potential of coals seams at a rank range between 1.0 and 1.7% VRr. To evaluate the amount of gas that was generated during the basin history, pyrolysis experiments of low-rank coals (<0.6% VRr) are required. Additionally, information on the basin evolution of the USCB, especially for the uplift phase between Permian and Tertiary, has to be improved. Apatite fission-track analysis provides information on timing and amount of uplift, which may be used to improve the econstruction of the uplift history of a basin. Fission-track analysis has been successfully applied to reconstruct the uplift history of the northern Ruhr Basin (Karg et al., 2005) and could also be applied to improve basin history reconstruction of the USCB.

6.9. Influence of coal rank on sorptive gas storage capacity

From analyses of a large set of coal samples in the present study, correlations between coal properties and gas storage capacity could be derived. However, not the entire range of coalification in the study area could be covered. Additional measurements on low-rank coals (<1% VRr) as well as on coals of semi-anthracite and anthracite rank are required to improve

the assessment of gas storage capacity of coals for the entire basin. The influence of changes associated with coalification on gas and water sorption capacity could further be studied by characterization of the microporosity of coals, *e.g.* by low temperature adsorption of CO_2 or nitrogen (BET).

6.10. Comparison of European coals and Gondwana coals

The comparison of coal from the USCB and the Brazilian Paraná basin indicates differences in the influence of controlling parameters, such as coal rank, on gas storage capacity and gas generation potential. However, in the present study only few coals from Brazil were analyzed and studies on the CBM potential of coal in the Paraná basin are rare. Results from CBM exploration activities that are currently under way in southern Brazil could shed more light on controlling factors for CBM generation and storage, allowing a better comparison with other coal basins.

6.11. Shale gas

It has long been known that bituminous shales, *e.g.* from the Upper Carboniferous of the Ruhr Basin in Germany, have a significant potential as source rocks for thermogenic methane (Teichmüller et al., 1970). Even though shales contain a lower percentage of organic matter than coal, the significantly higher thickness and extension of shale formations may result in comparable or even higher yields of thermogenic gas. Recent technological developments have improved the production of shale gas and, as a consequence, exploration activities for shale gas or combined CBM and shale gas exploration are now under way in European basins. The analytical and experimental methods developed and applied in the present study for the evaluation of the potential for CBM in the USCB and in Brazil can also be adopted for the characterization of organic-rich shales to evaluate the shale gas potential of sediments in the USCB.

6.12. Environmental impact of coalbed methane and shale gas exploration

Recent studies investigated and discussed the environmental impact of shale gas and CBM exploration and production in the US. Especially a potential influence of reservoir stimulation techniques, such as hydraulic fracturing, on ground water quality is under debate (USEPA, 2004). A recent study by Osborn et al. (2011) reports that shale gas production in Pennsylvania and New York was associated with a significant increase in methane concentrations in drinking water. Contamination of drinking water and methane emissions to the surface that could reach explosive concentrations can pose a serious threat to the environment and the population. As a consequence of environmental concerns associated with unconventional gas exploration and production, several European countries put a moratorium on shale gas and CBM drilling and the use of hydraulic fracturing. Whether shale gas and CBM exploration and production activities in Europe are associated with environmental pollution remains speculative. Furthermore, the background emission of methane from unconventional reservoirs into aquifers and / or the atmosphere is only poorly understood. Detailed and independent monitoring studies of background methane concentrations and methane emissions, as well as water quality, before and during gas exploration and production activities are required to ensure the safety and sustainability of gas production from these unconventional resources. Furthermore, these studies should result in guidelines for the regulation and monitoring of gas drilling activities and finally improve the public acceptance and confidence in this technology.

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Appendix I Geochemical and stable carbon isotopic composition of coal related gases from the SW Upper Silesian Coal Basin, Czech Republic

Table 1 gas samples from cross-measure boreholes

mine	seam	stratigraphy	time	$\delta^{13}O_2$	$\delta^{13}CH_4$	$^1O_2$	$^1N_2$	He	H_2	CO_2	Ar	N_2	CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	C_4H_{10}	2-m-C_4H_{10}	C_5H_{12}	sum i-C_6H_{14}	C_6H_{14}	C_7H_{16}	C1/(C2+C3)	C1/(C2+)
			days	‰ vs VPDB	‰ vs VPDB	%	%	ppm	ppm	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm			
Paskov	84	Petrkovice M	0	-12.8	-27.1	16.2	60.23	0	0	0.8	3.1	0	90.8	49450	3117	142	126	11	7	4	21	4	17	17
Paskov	84	Petrkovice M	12	2.8	-35.5	0.72	7.55	40	101	0.4	0.1	5.06	92.29	19692	1060	47	41	4	2	1	4	1	43	43
Paskov	84	Petrkovice M	21	-9.8	-23.5	15.72	61.91	0	0	3.2	2.9	12.98	79.38	3667	682	43	38	6	3	2	9	2	53	53
Paskov	84	Petrkovice M	23	-1	-38.9	7.29	35.15	45	31	3.3	0.7	12.19	82.48	8580	591	31	27	4	2	1	5	1	60	60
Paskov	84	Petrkovice M	28	3.5	-36.3	12	46.41	0	0	1.7	1.3	3.86	91.76	5278	584	26	25	2	2	1	5	1	72	71
ČSM S	504	Saddle M	0	-22	-66.2	5.37	43.88	13	0	5.5	0.7	31.99	61.78	173	2	1	1	1	0	0	3	0	2640	2568
ČSM S	504	Saddle M	8	-24.4	-63	4.21	38.94	0	0	2.7	0.6	29.02	67.63	145	2	1	0	1	0	0	4	1	3692	3560
ČSM S	504	Saddle M	12	-23.3	-62.8	3.81	37.05	0	0	1.2	0.6	27.88	70.31	285	59	7	7	2	1	0	2	0	1729	1644
ČSM N	643	Sucha M	0	-8.7	-59.9	7.35	71.59	0	0	8.2	1.4	67.72	22.64	110	4	1	2	0	0	0	0	0	1319	1297
ČSM N	643	Sucha M	2	-10	-65.4	6.3	67.95	0	0	7.5	1.2	63.33	27.95	146	5	1	3	1	1	0	0	0	1313	1277
ČSM N	643	Sucha M	11	-12.9	-66.9	13.88	67.09	0	0	7.4	2.4	44.66	45.52	70	4	0	3	1	1	0	0	0	2188	2125
ČSM N	643	Sucha M	14	-13.1	-63.8	15.94	70.99	0	0	6.2	3.6	46.97	43.19	56	4	1	3	2	3	7	8	3	1865	1659
ČSM N	643	Sucha M	25	-14.1	-67.6	10.67	64.37	0	0	7.2	1.6	49.63	41.49	112	5	1	4	1	1	0	0	0	1797	1736

Table 2 gas samples from canister desorption

mine_well_canister_sample	stratigraphy	Desorption time	Seam #	VRr	depth min	depth max	lost gas	des. gas	res. gas	total gas	δ13C-CO2	δ13C-CH4	O2	N2	He	H2	N2	CO2	Ar	CH4	C2H6	C3H8	i+n-C4H10	C1/(C2+C3)	C1/(C2+)
		d		%	m	m	m³/t	m³/t	m³/t	m³/t	‰ vs VPDB	‰ vs VPDB	%	%	ppm	ppm	%	%	%	%	ppm	ppm	ppm		
ČSM_S1c1_2	Saddle	4.8	522	n.d.	175.4	175.85					-32.6	-61.84	7.51	63.9	279	0	56	1.97	1.3	41.06	111	1	0	3672	3672
ČSM_S1c1_3	Saddle	8	522	n.d.	175.4	175.85	0.02	0.72	0.28	1.02	-42.1	-59.63	0.46	69.1	123	0	69	3.5	0.95	26.64	50	0	0	5304	5304
ČSM_S1c2_2	Saddle	3.9	507	n.d.	190.5	191					-19.2	-53.31	12.42	59.9	460	0	33	2.3	2.03	62.67	188	1	0	3311	3304
ČSM_S1c2_3	Saddle	7	507	n.d.	190.5	191	0.03	1.59	0.28	1.9	-40.4	-52.23	0.3	71.4	193	304	71	4.28	1.03	23.33	83	1	0	2778	2771
ČSM_S1c3_1	Saddle	0	504	1.12	194	194.5					-41.2	-50.62	9.42	79	1225	0	79	8.09	1.87	10.86	55	1	2	1957	1884
ČSM_S1c3_2	Saddle	3.1	504	1.12	194	194.5					-38	-57.02	4.09	58.2	682	0	53	7	0.99	38.67	245	2	9	1563	1505
ČSM_S1c3_3	Saddle	8.9	504	1.12	194	194.5	0.02	0.44	0.39	0.85	-41.2	-54.18	1.51	60.7	399	0	59	3.32	0.88	36.41	180	1	3	2010	1974
ČSM_N2c1_1	Saddle	0	532	1.17	156.3	157					-16.2	-72	1.85	39.1	0	0	35	3.17	0	61.55	164	0	0	3747	3747
ČSM_N2c1_2	Saddle	9.8	532	1.17	156.3	157					-19.6	-71.9	0.36	1.63	0	0	0	0.03	0	99.63	133	0	0	7467	7467
ČSM_N2c1_3	Saddle	18	532	1.17	156.3	157					-17.1	-72.2	4.36	58.9	0	0	54	12.73	0	33.52	113	0	0	2956	2956
ČSM_N2c1_4	Saddle	31.9	532	1.17	156.3	157	0.04	1.59	0.67	2.3	-22.2	-70.2	2.14	24.7	0	0	19	2.66	0	78.69	345	0	0	2281	2281
ČSM_S3c1_1	Saddle	0	559	n.d.	85.55	86					-35.7	-54.3	10.2	51	0	0	25	2.43	0	72.44	377	0	0	1923	1923
ČSM_S3c1_2	Saddle	11.1	559	n.d.	85.55	86					-26.7	-55.6	3.25	44.2	0	0	38	1.57	0	60.49	331	0	0	1829	1829
ČSM_S3c2_1	Saddle	0	559	n.d.	163.5	164					-15.8	-66	5.63	57	0	0	49	3.96	0	46.97	245	0	0	1917	1917
ČSM_S3c2_2	Saddle	32.4	559	n.d.	163.5	164					-17.9	-69	4.84	53.2	0	0	46	2.33	0	52.08	324	0	0	1608	1608
ČSM_S3c2_3	Saddle	35.3	559	n.d.	163.5	164	0.02	1.08	0.53	1.63	-19.6		9.27	57.7	0	0	41	2.69	0	56.07	285	0	0	1969	1969
ČSM_S4c1_1	-	-	-	n.d.	167.8	168.65					-23.14	-59.56	16.4	67.28	0	0	27	1.29	3.11	68.18	734	23	0	900	900
Lazy_1c1_1	Poruba	2.3	465	n.d.	73.85	74.55					-14.86	-61.31	12.4	54.44	0	0	20	0.85	1.39	77.54	3350	318	46	211	209
Lazy_1c1_2	Poruba	20.3	465	n.d.	73.85	74.55					-11.54	-48.01	16.19	54.24	0	0	0	0.23	0	98.94	8107	169	0	120	120
Lazy_1c1_3	Poruba	27.3	465	n.d.	73.85	74.55					-17.06	-44.23	11.94	47.6	0	0	7	0.66	0	90.52	16743	115	0	54	54
Lazy_1c1_4	Poruba	32.3	465	n.d.	73.85	74.55	0.04	2.57	0.37	2.98	-6.99	-64.58	7.03	34.93	0	0	13	0.21	0	86.69	75	75	0	5790	5790
Lazy_1c2_1	Poruba	0.3	465	n.d.	255.88	256.75					-2.84	-55.11	16.39	63.82	0	0	12	0.02	0	87.82	222	222	0	1979	1979
Lazy_1c2_2	Poruba	8.3	465	n.d.	255.88	256.75					-4.65	-54.71	8.77	39.41	0	0	12	0.07	0	87.63	7870	85	0	110	110
Lazy_1c2_3	Poruba	15.3	465	n.d.	255.88	256.75					-3.62	-54.41	4.86	24.89	0	0	9	0.05	0	90.43	7187	65	0	125	125
Lazy_1c2_4	Poruba	20.3	465	n.d.	255.88	256.75	0.11	3	0.44	3.54	-1.27	-55.36	3.73	22.39	0	0	10	0	0	89	6813	61	0	129	129
Lazy_2c1_3	Saddle	5.8	504	n.d.	55	55.5	0.02	0.56	0.29	0.87	-26.2	-71.1	13.7	66.7	0	0	44	1.32	2.4	51.91	66	1	0	7685	7685
Lazy_3c1_1	Saddle	0	504	0.96	56.65	57.15					-16.1	-64.3	5.25	46.5	0	0	36	1	0	63.15	4	0	0	158333	158333
Lazy_3c1_2	Saddle	14.5	504	0.96	56.65	57.15	0.04	1.33	0.66	2.03	-19.4	-64.9	n.d.	n.d.	0	0	0	2	0	98.37	6	0	0	156667	156667
Lazy_4c1_1	Saddle	0	504	n.d.	51	51.5					-19.8	-55.01	14.52	67.3	0	0	42	1.12	2.7	54.16	153	1	1	3533	3518
Lazy_4c1_2	Saddle	10.4	504	n.d.	51	51.5	0.02	0.74	0.41	1.17	-49.6	-44.2	11.9	60.7	0	0	37	1.46	0	61.2	30	0	0	20615	20615
Paskov_1c1_1	Petrko.	0	41	1.35	180.61	181.05					-22.8	-46.39	1.82	39.9	0	0	36	1.03	0.58	61.6	5547	38	4	110	110
Paskov_1c1_2	Petrko.	9.4	41	1.35	180.61	181.05					-21.4	-39.6	9.59	47.6	0	0	22	0.9	0	77.4	34	0	0	22500	22500
Paskov_1c1_3	Petrko.	30.3	41	1.35	180.61	181.05	0.06	3.37	0.44	3.86	-31.5	-46.3	n.d.	n.d.	0	0	0	1.18	0	98.82	49	0	0	20000	20000
Paskov_2c1_1	-	-	-	n.d.	178.75	188					-17.19	-45.06	12.8	51.97	0	435	11	0.37	1.53	84.42	26482	1463	257	30	30
Paskov_3c1_1	-	3.4	-	n.d.	17.2	18.2					-1.04	-42.21	4.02	15.98	0	0	1	1.39	0.23	96.55	5467	168	63	171	169
Paskov_3c1_3	-	33.4	-	n.d.	17.2	18.2					-7.15	-48.95	6.32	29.39	0	0	8	0.1	0	90.8	7511	71	0	120	120
Paskov_4c1_1	Petrko.	2.2	47	1.5	127.7	128.4					-7.32	-40.9	4	34.2	26	578	24	1	0.43	69.96	43863	3054	570	15	15
Paskov_4c1_2	Petrko.	17.2	47	1.5	127.7	128.42					-2.36	-39.46	10.18	33.74	0	0	0	0.72	0	94.76	42678	2222	362	21	21
Paskov_4c1_3	Petrko.	32.2	47	1.5	127.7	128.42	0.04	1.47	0.41	1.92	-2.95	-39.03	4.24	24.43	0	0	11	1.61	0	82.9	44281	2350	331	18	18
Paskov_4c2_1	-	0.8	-	n.d.	269	270					-7.86	-35.8	8.98	48.08	0	0	25	0.41	0	72.08	20820	129	0	34	34
Paskov_4c2_2	-	4.8	-	n.d.	269	270					-0.94	-36.77	6.08	28.2	0	0	8	0.58	0	89.16	24487	215	0	36	36
Paskov_4c2_3	-	14.8	-	n.d.	269	270					-18.65	-42.78	4.02	23.34	0	0	10	0.89	0	86.79	19749	198	0	44	44
Paskov_4c2_4	-	19.8	-	n.d.	269	270	0.04	1.53	0.42	1.99	-5.92	-36.96	4.21	25.12	0	0	12	1.06	0	84.05	30674	719	0	27	27

Appendix II Pyrolytic gas generation from bituminous coals of the Upper Silesian Coal Basin, Czech Republic and the Paraná Basin, Brazil

Appendix II Table 1 Results from Rock-Eval pyrolysis

sample	mine	formation	TOC [%]	S1 [mg/g]	S2 [mg/g]	S3 [mg/g]	Tmax [°C]	HI	OI	BI [mg HC/g TOC]	QI [mg HC/g TOC]	TR
1	ČSM	Karviná	84.7	0.4	109.2	3.3	463	129	0.5	0	1.3	0
2	ČSM	Karviná	80.8	0.4	90.8	3.4	460	112	0.5	0.01	1.1	0
3	ČSM	Karviná	78	0.5	90.3	5.9	460	116	0.7	0.01	1.2	0.01
4	ČSM	Karviná	84.1	0.8	104.2	4.2	456	124	0.9	0.01	1.2	0.01
5	ČSM	Karviná	70.4	0.8	88.8	10.6	466	126	1.2	0.01	1.3	0.01
6	ČSM	Karviná	85.3	1.2	118	3	465	138	1.4	0.01	1.4	0.01
7	ČSM	Karviná	84.3	0.5	96.4	0.3	464	114	0.6	0.01	1.1	0.01
8.1	Lazy	Karviná	80.9	9.2	192.7	7.9	444	238	11.4	0.11	2.5	0.05
8.2	Lazy	Karviná	80.9	7	251.8	1.2	443	311	8.7	0.09	3.2	0.03
9	Lazy	u. Ostrava	41.6	4	77.8	1.2	452	187	9.5	0.1	2	0.05
10	Lazy	u. Ostrava	57.1	8.7	102.5	n.d.	459	180	15.2	0.15	1.9	0.08
11	Lazy	u. Ostrava	81.5	5.4	160.6	1.9	461	197	6.6	0.07	2	0.03
12	Lazy	u. Ostrava	78.9	11	181.3	0.1	452	230	13.9	0.14	2.4	0.06
13	Lazy	u. Ostrava	82.8	4.6	152.7	4.8	454	184	5.5	0.05	1.9	0.03
14	Lazy	u. Ostrava	37.1	3.4	44.8	1	474	121	9	0.09	1.3	0.07
15	Lazy	u. Ostrava	72.7	4.6	106.8	1.8	465	147	6.3	0.06	1.5	0.04
16	Lazy	u. Ostrava	85.2	9.5	209.8	4.6	457	246	11.2	0.11	2.6	0.04
17	Lazy	u. Ostrava	83.7	6	143.3	1.9	456	171	7.2	0.07	1.8	0.04
18	Lazy	u. Ostrava	5.8	1	6.7	1.7	465	114	17.8	0.18	1.3	0.14
19	Lazy	u. Ostrava	49.4	4.1	49.3	2.3	475	100	8.3	0.08	1.1	0.08
20	Lazy	u. Ostrava	12.1	1.6	9	0.6	468	74	13.2	0.13	0.9	0.15
21	Pskov	l. Ostrava	82.8	2.9	87.8	2.6	468	106	3.5	0.04	1.1	0.03
22	Pskov	l. Ostrava	73.1	9.8	101.5	3.3	456	139	13.3	0.13	1.5	0.09
23	Pskov	l. Ostrava	79	2.8	52.2	0.3	482	66	3.6	0.04	0.7	0.05
24	Pskov	l. Ostrava	83.5	1.9	47	3.4	483	56	2.3	0.02	0.6	0.04
25	Pskov	l. Ostrava	85.4	1.9	58.5	0.7	479	69	2.2	0.02	0.7	0.03
26	Pskov	l. Ostrava	83.5	2	58.4	1.8	480	70	2.4	0.02	0.7	0.03
27	Pskov	l. Ostrava	81.6	2.1	91.5	2.2	466	112	2.6	0.03	1.1	0.02
28	Pskov	l. Ostrava	83.3	1.5	82.9	1.6	470	100	1.8	0.02	1	0.02
29	Pskov	l. Ostrava	70.3	2	57.3	2.6	468	81	2.8	0.03	0.8	0.03
30	Pskov	l. Ostrava	78.4	3.5	103.3	3.3	458	132	4.4	0.04	1.4	0.03

Appendix II Table 2 Results of mass balance calculations

VRc	VM	C	O	H	N	C	O	H	H/C	O/C	ΔCH4/nc0	ΔCO2/nc0
%	wt. %	wt. %	wt. %	wt. %	wt. %	mol	mol	mol			m³CH4/tTOC	m³CO2/tTOC
0.57	45	74.00	19.07	5.45	1.48	6.16	1.19	5.40	0.88	0.19		
0.58	44	75.26	17.81	5.44	1.48	6.27	1.11	5.40	0.86	0.18	10.62	13.37
0.59	43	76.46	16.63	5.44	1.47	6.37	1.04	5.39	0.85	0.16	20.32	25.39
0.60	42	77.59	15.51	5.43	1.47	6.46	0.97	5.39	0.83	0.15	29.22	36.21
0.62	41	78.65	14.47	5.42	1.47	6.55	0.90	5.38	0.82	0.14	37.41	45.97
0.64	40	79.64	13.49	5.41	1.46	6.63	0.84	5.37	0.81	0.13	44.99	54.80
0.66	39	80.57	12.57	5.39	1.46	6.71	0.79	5.35	0.80	0.12	52.03	62.78
0.68	38	81.44	11.72	5.38	1.46	6.78	0.73	5.34	0.79	0.11	58.59	70.00
0.71	37	82.26	10.93	5.36	1.45	6.85	0.68	5.32	0.78	0.10	64.73	76.53
0.74	36	83.02	10.19	5.34	1.45	6.91	0.64	5.30	0.77	0.09	70.50	82.45
0.77	35	83.73	9.51	5.32	1.45	6.97	0.59	5.28	0.76	0.09	75.94	87.81
0.80	34	84.38	8.88	5.30	1.44	7.03	0.55	5.25	0.75	0.08	81.09	92.65
0.83	33	84.99	8.30	5.27	1.44	7.08	0.52	5.23	0.74	0.07	85.99	97.04
0.86	32	85.56	7.76	5.24	1.44	7.12	0.49	5.20	0.73	0.07	90.67	100.99
0.90	31	86.08	7.28	5.21	1.43	7.17	0.45	5.17	0.72	0.06	95.15	104.56
0.94	30	86.56	6.83	5.18	1.43	7.21	0.43	5.14	0.71	0.06	99.46	107.78
0.98	29	87.00	6.42	5.15	1.43	7.24	0.40	5.11	0.70	0.06	103.63	110.67
1.02	28	87.41	6.06	5.11	1.42	7.28	0.38	5.07	0.70	0.05	107.68	113.27
1.07	27	87.78	5.73	5.07	1.42	7.31	0.36	5.03	0.69	0.05	111.63	115.59
1.12	26	88.12	5.43	5.03	1.42	7.34	0.34	4.99	0.68	0.05	115.50	117.67
1.17	25	88.44	5.16	4.99	1.41	7.36	0.32	4.95	0.67	0.04	119.30	119.53
1.22	24	88.72	4.92	4.95	1.41	7.39	0.31	4.91	0.66	0.04	123.06	121.19
1.27	23	88.99	4.70	4.90	1.40	7.41	0.29	4.86	0.66	0.04	126.79	122.66
1.32	22	89.23	4.51	4.86	1.40	7.43	0.28	4.82	0.65	0.04	130.49	123.97
1.38	21	89.45	4.34	4.81	1.40	7.45	0.27	4.77	0.64	0.04	134.20	125.14
1.44	20	89.66	4.19	4.75	1.39	7.47	0.26	4.72	0.63	0.04	137.91	126.18
1.50	19	89.85	4.06	4.70	1.39	7.48	0.25	4.66	0.62	0.03	141.65	127.12
1.56	18	90.03	3.94	4.64	1.39	7.50	0.25	4.61	0.61	0.03	145.42	127.96
1.63	17	90.20	3.83	4.59	1.38	7.51	0.24	4.55	0.61	0.03	149.23	128.73
1.70	16	90.37	3.72	4.53	1.38	7.52	0.23	4.49	0.60	0.03	153.10	129.43
1.77	15	90.53	3.63	4.47	1.38	7.54	0.23	4.43	0.59	0.03	157.03	130.10
1.84	14	90.68	3.54	4.40	1.37	7.55	0.22	4.37	0.58	0.03	161.04	130.73
1.91	13	90.84	3.45	4.34	1.37	7.56	0.22	4.30	0.57	0.03	165.12	131.35
1.98	12	91.00	3.36	4.27	1.37	7.58	0.21	4.23	0.56	0.03	169.30	131.98
2.06	11	91.17	3.27	4.20	1.36	7.59	0.20	4.17	0.55	0.03	173.56	132.62
2.14	10	91.34	3.17	4.13	1.36	7.60	0.20	4.09	0.54	0.03	177.93	133.29
2.22	9	91.52	3.07	4.05	1.36	7.62	0.19	4.02	0.53	0.03	182.40	134.00
2.30	8	91.72	2.95	3.98	1.35	7.64	0.18	3.95	0.52	0.02	186.98	134.77
2.39	7	91.93	2.83	3.90	1.35	7.65	0.18	3.87	0.51	0.02	191.68	135.62
2.48	6	92.15	2.68	3.82	1.35	7.67	0.17	3.79	0.49	0.02	196.49	136.55

Sample 166
TOC: 43.9 [%]
VRr: 0.92 [%]
S: 0.7 [%]

N₂/g TOC

CH₄/g TOC

mg CH4/g TOC

A=10^15

A=8*10^16

Krooss et al., 1993

– 166 [VRr 0.9%]

pyrolysis

geol. rate

Sample 8
extracted
TOC: 80.9 [%]
VRr: 0.96 [%]
S: 0.9 [%]

N₂/g TOC
CH₄/g TOC

8 extracted [VRr 1.0%]

Sample 8
extracted
TOC: 80.9 [%]
VRr: 0.96 [%]
S: 0.9 [%]

mg CH4/g TOC
A=10^15
A=8*10^16
Krooss et al., 1993

Sample 8
extracted

pyrolysis
geol. rate

Sample 22
TOC: 73.1 [%]
VRr: 1.21 [%]
S: 0.4 [%]

▲ mg N2/g TOC
● mg CH4/g TOC

Sample 22
TOC: 73.1 [%]
VRr: 1.21 [%]
S: 0.4 [%]

● mg CH4/g TOC
— A=10^15
— A=8*10^16
— Krooss et al. 1993

Sample 22
TOC: 73.1 [%]
VRr: 1.21 [%]
S: 0.4 [%]

● pyrolysis
— geol. rate

■ 22 [VRr 1.2%]

Sample 30
TOC: 78.4 [%]
VRr: 1.35 [%]
S: 0.4 [%]

N₂/g TOC
CH₄/g TOC

Sample 30
TOC: 78.4 [%]
VRr: 1.35 [%]
S: 0.4 [%]

pyrolysis
A=10^15
A=8*10^16
Krooss et al., 1993

Sample 30
TOC: 78.4 [%]
VRr: 1.35 [%]
S: 0.4 [%]

pyrolysis
geol. rate

30 [VRr 1.4%]

Appendix II Table 3 Temperature and maturity values derived from 1D basin modeling (PetroMod11) for different formations of the USCB. EASY%Ro values calculated after Sweeney and Burnham (1987). Sample number indicates coal samples that were analyzed from the respective geologic formation.

sample: 1 — seam: 648 — Formation: L. Sucha M.

Time [Ma]	Temperature [°C]	EASY%Ro [%Ro]
318	33	0.24
317	44	0.28
314	76	0.43
310	107	0.63
305	116	0.71
300	128	0.80
292	113	0.80
282	93	0.80
255	62	0.80
19	22	0.80
18	24	0.80
15	36	0.80
13	38	0.80
2	24	0.80
0	23	0.80

sample: 8 — seam: 504 — Formation: Saddle M.

Time [Ma]	Temperature [°C]	EASY%Ro [%Ro]
319	33	0.24
318	47	0.30
317	56	0.32
314	85	0.48
310	115	0.69
305	125	0.77
300	136	0.88
292	121	0.89
282	102	0.89
255	70	0.89
19	30	0.89
18	32	0.89
15	44	0.89
13	46	0.89
2	32	0.89
0	30	0.89

sample: 19 — seam: 386 — Formation: Jaklovec M.

Time [Ma]	Temperature [°C]	EASY%Ro [%Ro]
322	34	0.25
320	59	0.33
319	71	0.38
318	82	0.43
317	89	0.46
314	115	0.68
310	145	0.98
305	155	1.18
300	166	1.38
292	152	1.40
282	131	1.40
255	99	1.40
19	55	1.40
18	57	1.40
15	69	1.40
13	72	1.40
2	57	1.40
0	56	1.40

sample: 22 — seam: 112 — Formation: L. Hrušov M.

Time [Ma]	Temperature [°C]	EASY%Ro [%Ro]
324	34	0.24
322	50	0.32
320	72	0.38
319	83	0.44
318	94	0.49
317	101	0.53
314	127	0.77
310	157	1.17
305	167	1.40
300	178	1.64
292	164	1.66
282	143	1.66
255	110	1.66
19	66	1.66
18	68	1.66
15	79	1.66
13	82	1.66
2	68	1.66
0	67	1.66

sample: 24 — seam: 82 — Formation: Petrkovice M. | sample: 30 — seam: 41 — Formation: Petrkovice M.

Time [Ma]	Temperature [°C]	EASY%Ro [%Ro]
326	35	0.25
325	51	0.31
324	66	0.36
322	80	0.44
320	100	0.54
319	110	0.60
318	121	0.68
317	127	0.71
314	153	1.08
310	183	1.67
305	193	2.00
300	204	2.31
292	190	2.34
282	169	2.35
255	135	2.35
19	88	2.35
18	89	2.35
15	101	2.35
13	104	2.35
2	90	2.35
0	88	2.35

Appendix II Table 4 Results of temperature-programmed open system pyrolysis

Sample	166			Sample	1			Sample	8			Sample	8			Sample	8		
Heating Rate	0.5K/min	CH4	N2	Heating Rate	0.5K/min	CH4	N2	Heating Rate	0.5K/min	CH4	N2	Heating Rate	1K/min	CH4	N2	Heating Rate	2K/min	CH4	N2
Time [min]	Temperature (°C)	Generation Rate [mg/g/min]	Generation Rate [mg/g/min]	Time [min]	Temperature (°C)	Generation Rate [mg/g/min]	Generation Rate [mg/g/min]	Time [min]	Temperature (°C)	Generation Rate [mg/g/min]	Generation Rate [mg/g/min]	Time [min]	Temperature (°C)	Generation Rate [mg/g/min]	Generation Rate [mg/g/min]	Time [min]	Temperature (°C)	Generation Rate [mg/g/min]	Generation Rate [mg/g/min]
0.0	23.8	0.0000	0.0003	0.0	23.7	0.0000	0.0000	0.0	23.3	0.0000	0.0000	0.0	23.2	0.0000	0.0000	0.0	23.1	0.0000	0.0000
6.2	27.2	0.0000	0.0005	6.2	23.7	0.0000	0.0000	6.2	85.1	0.0000	0.0000	6.2	30.4	0.0000	0.0000	6.2	67.8	0.0000	0.0000
12.4	87.5	0.0000	0.0004	12.4	71.6	0.0000	0.0000	12.4	101.6	0.0000	0.0000	12.4	76.1	0.0000	0.0000	12.4	89.7	0.0000	0.0000
18.6	104.4	0.0000	0.0000	18.6	90.3	0.0000	0.0000	18.6	121.8	0.0000	0.0000	18.6	96.4	0.0000	0.0000	18.6	106.8	0.0000	0.0000
24.8	118.9	0.0000	0.0004	24.8	112.8	0.0000	0.0000	24.8	137.4	0.0000	0.0000	24.8	114.8	0.0000	0.0000	24.8	123.6	0.0000	0.0000
31.0	130.3	0.0000	0.0000	31.0	125.6	0.0000	0.0000	31.0	137.7	0.0000	0.0000	31.0	128.9	0.0000	0.0000	31.0	131.4	0.0000	0.0000
37.2	128.9	0.0000	0.0000	37.2	132.5	0.0000	0.0000	37.2	137.3	0.0000	0.0000	37.2	131.7	0.0000	0.0000	37.2	128.8	0.0000	0.0000
43.4	129.5	0.0000	0.0000	43.4	130.9	0.0000	0.0000	43.4	137.1	0.0000	0.0000	43.4	133.1	0.0000	0.0000	43.4	130.6	0.0000	0.0000
49.6	130.2	0.0000	0.0004	49.6	130.6	0.0000	0.0000	49.6	137.3	0.0000	0.0000	49.6	131.9	0.0000	0.0000	49.6	129.2	0.0000	0.0000
55.8	128.6	0.0000	0.0000	55.8	131.8	0.0000	0.0000	55.8	136.2	0.0000	0.0000	55.8	133.3	0.0000	0.0000	55.8	131.9	0.0000	0.0000
62.0	131.0	0.0000	0.0002	62.0	131.4	0.0000	0.0000	62.0	137.4	0.0000	0.0000	62.0	130.7	0.0000	0.0000	62.0	129.3	0.0000	0.0000
68.2	130.1	0.0000	0.0000	68.2	132.0	0.0000	0.0000	68.2	136.0	0.0000	0.0000	68.2	132.7	0.0000	0.0000	68.2	130.0	0.0000	0.0000
74.4	130.0	0.0000	0.0002	74.4	132.3	0.0000	0.0000	74.4	137.3	0.0000	0.0000	74.4	131.3	0.0000	0.0000	74.4	130.3	0.0000	0.0000
80.6	129.8	0.0000	0.0002	80.6	131.4	0.0000	0.0000	80.6	135.9	0.0000	0.0000	80.6	133.6	0.0000	0.0000	80.6	133.6	0.0000	0.0000
86.8	131.7	0.0000	0.0000	86.8	131.8	0.0000	0.0000	86.8	137.7	0.0000	0.0000	86.8	131.4	0.0000	0.0000	86.8	128.9	0.0000	0.0000
93.0	131.2	0.0000	0.0000	93.0	132.5	0.0000	0.0000	93.0	139.7	0.0000	0.0000	93.0	133.5	0.0000	0.0000	93.0	140.9	0.0000	0.0000
99.2	134.9	0.0000	0.0002	99.2	133.3	0.0000	0.0000	99.2	143.4	0.0000	0.0000	99.2	139.4	0.0000	0.0000	99.2	151.7	0.0000	0.0000
105.4	136.9	0.0000	0.0000	105.4	136.8	0.0000	0.0000	105.4	145.9	0.0000	0.0000	105.3	144.3	0.0000	0.0000	105.4	160.7	0.0000	0.0000
111.6	139.2	0.0000	0.0000	111.6	140.7	0.0000	0.0000	111.6	148.6	0.0000	0.0000	111.5	149.4	0.0000	0.0000	111.6	169.3	0.0000	0.0000
117.8	142.7	0.0000	0.0000	117.8	142.9	0.0000	0.0000	117.8	152.4	0.0000	0.0000	117.8	154.5	0.0000	0.0000	117.8	177.3	0.0000	0.0000
124.0	144.8	0.0000	0.0001	124.0	145.1	0.0000	0.0000	124.0	153.7	0.0000	0.0000	123.9	159.3	0.0000	0.0000	124.0	185.2	0.0000	0.0000
130.2	147.6	0.0000	0.0001	130.2	147.6	0.0000	0.0000	130.2	156.8	0.0000	0.0000	130.1	163.9	0.0000	0.0000	130.2	193.3	0.0000	0.0000
136.4	150.1	0.0000	0.0003	136.4	150.3	0.0000	0.0000	136.4	158.8	0.0000	0.0000	136.3	168.4	0.0000	0.0000	136.4	199.2	0.0000	0.0000
142.6	151.7	0.0000	0.0000	142.6	152.2	0.0000	0.0000	142.6	161.9	0.0000	0.0000	142.5	172.8	0.0000	0.0000	142.6	206.3	0.0000	0.0000
148.8	154.8	0.0000	0.0002	148.8	155.2	0.0000	0.0000	148.8	164.3	0.0000	0.0000	148.7	176.5	0.0000	0.0000	148.8	212.6	0.0000	0.0000
155.0	156.7	0.0000	0.0001	155.0	157.5	0.0000	0.0000	155.0	166.3	0.0000	0.0000	154.9	182.3	0.0000	0.0000	155.0	219.3	0.0000	0.0000
161.2	158.8	0.0000	0.0001	161.2	159.7	0.0000	0.0000	161.2	169.4	0.0000	0.0000	161.1	185.0	0.0000	0.0000	161.2	223.8	0.0000	0.0000
167.4	160.9	0.0000	0.0000	167.4	161.8	0.0000	0.0000	167.4	170.4	0.0000	0.0000	167.3	189.4	0.0000	0.0000	167.4	228.8	0.0000	0.0000
173.7	163.4	0.0000	0.0000	173.6	164.5	0.0000	0.0000	173.6	172.9	0.0000	0.0000	173.5	193.1	0.0000	0.0000	173.6	234.5	0.0000	0.0000
179.8	165.7	0.0000	0.0001	179.8	166.3	0.0000	0.0000	179.8	174.7	0.0000	0.0000	179.7	197.8	0.0000	0.0000	179.8	239.7	0.0000	0.0000
186.0	167.6	0.0000	0.0000	186.0	168.8	0.0000	0.0000	186.0	178.1	0.0000	0.0000	185.9	199.5	0.0000	0.0000	186.0	247.9	0.0000	0.0000
192.3	170.4	0.0000	0.0001	192.2	171.0	0.0000	0.0000	192.2	180.3	0.0000	0.0000	192.1	203.6	0.0000	0.0000	192.2	259.8	0.0000	0.0000
198.4	172.2	0.0000	0.0001	198.4	172.9	0.0000	0.0000	198.4	182.2	0.0000	0.0000	198.3	207.3	0.0000	0.0000	198.4	271.3	0.0000	0.0000
204.6	174.3	0.0000	0.0001	204.6	175.3	0.0000	0.0000	204.6	184.1	0.0000	0.0000	204.5	211.1	0.0000	0.0000	204.6	282.8	0.0001	0.0000
210.9	175.9	0.0000	0.0000	210.8	177.1	0.0000	0.0000	210.8	186.3	0.0000	0.0000	210.7	213.2	0.0000	0.0000	210.8	293.4	0.0001	0.0000
217.0	177.7	0.0000	0.0000	216.9	180.4	0.0000	0.0000	217.0	188.5	0.0000	0.0000	216.9	216.3	0.0000	0.0000	217.0	305.1	0.0001	0.0000
223.3	180.2	0.0000	0.0000	223.1	182.6	0.0000	0.0000	223.2	190.5	0.0000	0.0000	223.1	218.7	0.0000	0.0000	223.2	316.7	0.0002	0.0000
229.5	182.1	0.0000	0.0000	229.3	183.1	0.0000	0.0000	229.4	192.0	0.0000	0.0000	229.3	221.7	0.0000	0.0000	229.4	327.9	0.0003	0.0000
235.7	183.8	0.0000	0.0000	235.5	185.0	0.0000	0.0000	235.6	194.8	0.0000	0.0000	235.5	225.5	0.0000	0.0000	235.6	339.8	0.0005	0.0000
241.9	185.6	0.0000	0.0000	241.7	188.6	0.0000	0.0000	241.8	196.7	0.0000	0.0000	241.7	227.6	0.0000	0.0000	241.8	351.0	0.0009	0.0000
248.1	187.9	0.0000	0.0001	247.9	189.1	0.0000	0.0000	248.0	198.8	0.0000	0.0000	247.9	230.7	0.0000	0.0000	248.0	362.8	0.0018	0.0000
254.3	189.2	0.0000	0.0000	254.1	192.4	0.0000	0.0000	254.2	200.5	0.0000	0.0000	254.1	233.5	0.0000	0.0000	254.2	374.3	0.0037	0.0000
260.5	191.1	0.0000	0.0000	260.3	193.6	0.0000	0.0000	260.4	202.0	0.0000	0.0000	260.3	235.9	0.0000	0.0000	260.4	385.8	0.0078	0.0000
266.7	192.9	0.0000	0.0000	266.5	195.4	0.0000	0.0000	266.6	203.9	0.0000	0.0000	266.5	238.9	0.0000	0.0000	266.6	397.5	0.0156	0.0000
272.9	194.9	0.0000	0.0000	272.7	197.2	0.0000	0.0000	272.8	205.1	0.0000	0.0000	272.7	240.9	0.0000	0.0000	272.8	411.4	0.0347	0.0000
279.1	196.2	0.0000	0.0000	278.9	199.2	0.0000	0.0000	279.0	208.7	0.0000	0.0000	278.9	244.1	0.0000	0.0000	279.0	423.1	0.0571	0.0000
285.3	198.2	0.0000	0.0000	285.1	200.5	0.0000	0.0000	285.2	210.4	0.0000	0.0000	285.1	248.8	0.0000	0.0000	285.2	434.8	0.0867	0.0000
291.5	199.9	0.0000	0.0000	291.3	202.0	0.0000	0.0000	291.4	210.9	0.0000	0.0000	291.3	254.6	0.0000	0.0000	291.4	446.8	0.1150	0.0000
297.7	201.4	0.0000	0.0000	297.5	203.6	0.0000	0.0000	297.6	213.0	0.0000	0.0000	297.5	260.3	0.0000	0.0000	297.6	458.5	0.1471	0.0000
303.9	204.0	0.0000	0.0000	303.7	206.6	0.0000	0.0000	303.8	214.1	0.0000	0.0000	303.7	266.0	0.0000	0.0000	303.8	470.5	0.1615	0.0000
310.1	204.8	0.0000	0.0000	309.9	206.7	0.0000	0.0000	310.0	216.2	0.0000	0.0000	309.9	271.8	0.0000	0.0000	310.0	482.0	0.1815	0.0000
316.3	206.1	0.0000	0.0000	316.1	208.1	0.0000	0.0000	316.2	217.8	0.0000	0.0000	316.1	277.3	0.0001	0.0000	316.2	493.8	0.1959	0.0000
322.5	208.9	0.0000	0.0000	322.3	210.4	0.0000	0.0000	322.3	218.7	0.0000	0.0000	322.3	283.3	0.0001	0.0000	322.4	505.7	0.2018	0.0000
328.7	209.7	0.0000	0.0000	328.5	211.6	0.0000	0.0000	328.6	220.4	0.0000	0.0000	328.5	289.0	0.0001	0.0000	328.6	517.4	0.1923	0.0000
334.9	211.7	0.0000	0.0000	334.7	213.0	0.0000	0.0000	334.7	222.0	0.0000	0.0000	334.7	294.7	0.0001	0.0000	334.8	529.3	0.1968	0.0000
341.1	213.0	0.0000	0.0000	340.9	214.5	0.0000	0.0000	340.9	223.9	0.0000	0.0000	340.9	299.9	0.0001	0.0000	341.0	541.0	0.1922	0.0000
347.3	214.2	0.0000	0.0000	347.1	217.1	0.0000	0.0000	347.1	224.9	0.0000	0.0000	347.1	305.7	0.0001	0.0000	347.2	553.0	0.1891	0.0000
353.5	215.9	0.0000	0.0000	353.3	218.4	0.0000	0.0000	353.3	226.5	0.0000	0.0000	353.3	311.8	0.0001	0.0000	353.4	565.1	0.1765	0.0000
359.7	217.7	0.0000	0.0000	359.5	219.6	0.0000	0.0000	359.5	228.2	0.0000	0.0000	359.5	317.8	0.0002	0.0000	359.6	577.1	0.1690	0.0000
365.9	218.9	0.0000	0.0000	365.7	221.0	0.0000	0.0000	365.7	229.9	0.0000	0.0000	365.7	323.6	0.0003	0.0000	365.8	588.9	0.1591	0.0000
372.1	220.5	0.0000	0.0000	371.9	222.7	0.0000	0.0000	371.9	230.8	0.0000	0.0000	371.9	329.4	0.0003	0.0000	372.0	600.6	0.1483	0.0001
378.3	222.4	0.0000	0.0000	378.1	224.2	0.0000	0.0000	378.1	232.3	0.0000	0.0000	378.1	335.3	0.0005	0.0000	378.2	612.8	0.1379	0.0002
384.5	223.2	0.0000	0.0000	384.3	224.9	0.0000	0.0000	384.3	234.1	0.0000	0.0000	384.3	341.1	0.0007	0.0000	384.4	625.2	0.1183	0.0003
390.8	224.3	0.0000	0.0000	390.5	227.3	0.0000	0.0000	390.5	235.3	0.0000	0.0000	390.4	347.1	0.0009	0.0000	390.6	637.0	0.1088	0.0007
397.0	226.1	0.0000	0.0000	396.7	228.3	0.0000	0.0000	396.7	236.7	0.0000	0.0000	396.6	353.0	0.0013	0.0000	396.8	649.2	0.1040	0.0013
403.1	227.8	0.0000	0.0000	402.9	229.9	0.0000	0.0000	402.9	238.1	0.0000	0.0000	402.9	358.7	0.0019	0.0000	403.0	661.3	0.0937	0.0021
409.4	229.0	0.0000	0.0000	409.1	230.5	0.0000	0.0000	409.1	239.6	0.0000	0.0000	409.0	364.6	0.0028	0.0000	409.2	673.2	0.0814	0.0029
415.6	231.3	0.0000	0.0000	415.3	232.0	0.0000	0.0000	415.3	241.2	0.0000	0.0000	415.2	370.4	0.0040	0.0000	415.4	685.4	0.0765	0.0041
421.7	231.8	0.0000	0.0000	421.5	234.1	0.0000	0.0000	421.5	242.3	0.0000	0.0000	421.4	376.2	0.0059	0.0000	421.6	697.5	0.0677	0.0051
428.0	233.0	0.0000	0.0000	427.7	235.5	0.0000	0.0000	427.7	243.6	0.0000	0.0000	427.6	382.1	0.0086	0.0000	427.8	709.6	0.0629	0.0062
434.2	234.2	0.0000	0.0000	433.9	236.6	0.0000	0.0000	433.9	245.1	0.0000	0.0000	433.8	388.1	0.0125	0.0000	434.0	721.7	0.0567	0.0070
440.4	235.5	0.0000	0.0000	440.1	237.8	0.0000	0.0000	440.1	246.8	0.0000	0.0000	440.0	393.9	0.0180	0.0000	440.2	733.9	0.0488	0.0072
446.6	236.5	0.0000	0.0000	446.3	238.4	0.0000	0.0000	446.3	248.0	0.0000	0.0000	446.2	399.8	0.0254	0.0000	446.4	746.2	0.0455	0.0077
452.8	238.1	0.0000	0.0000	452.5	240.2	0.0000	0.0000	452.5	249.9	0.0000	0.0000	452.4	405.7	0.0351	0.0000	452.6	758.4	0.0397	0.0074
459.0	239.1	0.0000	0.0000	458.7	241.4	0.0000	0.0000	458.7	251.0	0.0000	0.0000	458.6	411.5	0.0467	0.0000	458.8	771.1	0.0343	0.0069
465.2	240.6	0.0000	0.0000	464.8	242.4	0.0000	0.0000	464.9	252.7	0.0000	0.0000	464.8	417.5	0.0599	0.0000	464.9	783.2	0.0314	0.0068
471.4	242.5	0.0000	0.0000	471.0	244.3	0.0000	0.0000	471.1	255.2	0.0000	0.0000	471.0	423.4	0.0735	0.0000	471.1	795.4	0.0275	0.0064
477.6	245.2	0.0000	0.0000	477.2	246.6	0.0000	0.0000	477.3	258.3	0.0000	0.0000	477.2	429.3	0.0878	0.0000	477.4	807.6	0.0259	0.0064
483.8	247.8	0.0000	0.0000	483.4	249.1	0.0000	0.0000	483.5	261.4	0.0000	0.0000	483.4	435.1	0.1026	0.0000	483.5	819.8	0.0232	0.0061
490.0	250.8	0.0000	0.0000	489.6	252.1	0.0000	0.0000	489.7	264.0	0.0000	0.0000	489.6	441.2	0.1168	0.0000	489.7	832.0	0.0206	0.0057
496.2	253.3	0.0000	0.0000	495.8	254.7	0.0000	0.0000	495.9	267.4	0.0000	0.0000	495.8	447.2	0.1296	0.0000	496.0	844.6	0.0180	0.0054
502.4	256.2	0.0000	0.0000	502.0	257.6	0.0000	0.0000	502.1	270.3	0.0000	0.0000	502.0	453.2	0.1420	0.0000	502.1	856.6	0.0155	0.0050
508.6	258.6	0.0000	0.0000	508.2	260.4	0.0000	0.0000	508.3	273.3	0.0000	0.0000	508.2	459.0	0.1513	0.0000	508.3	871.6	0.0136	0.0048
514.8	261.5	0.0000	0.0000	514.4	263.2	0.0000	0.0000	514.5	276.4	0.0000	0.0000	514.4	464.9	0.1579	0.0000	514.6	883.7	0.0114	0.0046
521.0	264.3	0.0000	0.0000	520.6	266.1	0.0000	0.0000	520.7	279.3	0.0000	0.0000	520.6	470.8	0.1640	0.0000	520.7	895.9	0.0108	0.0050
527.2	266.9	0.0000	0.0000	526.8	269.1	0.0000	0.0000	526.9	282.2	0.0000	0.0000	526.8	476.8	0.1675	0.0000	526.9	908.5	0.0095	0.0051
533.4	269.7	0.0000	0.0000	533.0	271.9	0.0000	0.0000	533.1	285.2	0.0000	0.0000	533.0	482.9	0.1693	0.0000	533.2	921.1	0.0079	0.0049
539.6	272.7	0.0000	0.0000	539.2	275.0	0.0000	0.0000	539.3	288.2	0.0000	0.0000	539.2	488.9	0.1704	0.0000	539.3	933.4	0.0070	0.0052
545.8	275.3	0.0000	0.0000	545.4	277.9	0.0000	0.0000	545.5	291.3	0.0001	0.0000	545.4	494.6	0.1703	0.0000	545.5	945.8	0.0060	0.0054
552.0	278.1	0.0000	0.0000	551.6	281.0	0.0000	0.0000	551.7	294.2	0.0000	0.0000	551.6	500.6	0.1692	0.0000	551.7	957.9	0.0052	0.0056
558.2	281.0	0.0000	0.0000	557.8	283.7	0.0000	0.0000	557.9	297.2	0.0001	0.0000	557.8	506.5	0.1676	0.0000	557.9	970.6	0.0045	0.0060
564.4	283.7	0.0000	0.0000	564.0	286.4	0.0000	0.0000	564.1	299.9	0.0001	0.0000	563.9	512.4	0.1648	0.0000	564.1	983.1	0.0040	0.0067
570.6	286.7	0.0000	0.0000	570.2	289.3	0.0000	0.0000	570.3	303.3	0.0001	0.0000	570.1	518.8	0.1620	0.0000	570.3	995.4	0.0035	0.0076
576.8	289.6	0.0000	0.0000	576.4	292.6	0.0000	0.0000	576.5	306.0	0.0001	0.0000	576.4	524.1	0.1590	0.0000	576.5	1007.9	0.0031	0.0083
583.0	292.2	0.0000	0.0000	582.6	295.5	0.0000	0.0000	582.7	309.3	0.0001	0.0000	582.5	531.2	0.1540	0.0000	582.7	1020.5	0.0027	0.0095
589.2	295.6	0.0000	0.0000	588.8	299.7	0.0000	0.0000	588.9	312.3	0.0001	0.0000	588.7	537.1	0.1498	0.0000	588.9	1033.3	0.0024	0.0109
595.4	298.3	0.0000	0.0000	595.0	302.0	0.0001	0.0000	595.1	315.2	0.0001	0.0000	594.9	543.1	0.1424	0.0000	595.1	1046.1	0.0022	0.0129
601.6	301.1	0.0000	0.0000	601.2	303.6	0.0001	0.0000	601.3	318.1	0.0002	0.0000	601.1	549.1	0.1351	0.0000	601.3	1058.6	0.0019	0.0141
607.8	304.4	0.0001	0.0000	607.4	306.6	0.0001	0.0000	607.4	321.8	0.0002	0.0000	607.3	554.9	0.1282	0.0000	607.5	1071.1	0.0017	0.0165

Table 4 Results of temperature-programmed open system pyrolysis (continued)

614.0	306.9	0.0001	0.0000	613.6	309.5	0.0001	0.0000	613.7	324.3	0.0002	0.0000	613.5	560.9	0.1212	0.0000	613.7	1083.8	0.0015	0.0191
620.2	309.7	0.0001	0.0000	619.8	312.6	0.0001	0.0000	619.9	326.7	0.0002	0.0000	619.7	567.1	0.1149	0.0000	619.9	1096.4	0.0014	0.0204
626.4	312.8	0.0001	0.0000	626.0	315.5	0.0001	0.0000	626.0	329.9	0.0002	0.0000	625.9	572.7	0.1078	0.0000	626.1	1109.0	0.0013	0.0225
632.6	315.5	0.0001	0.0000	632.2	318.5	0.0002	0.0000	632.3	333.0	0.0003	0.0000	632.1	578.9	0.1008	0.0000	632.3	1121.9	0.0013	0.0238
638.8	318.2	0.0001	0.0000	638.4	321.3	0.0002	0.0000	638.5	336.0	0.0003	0.0000	638.3	584.8	0.0948	0.0000	638.5	1134.4	0.0013	0.0238
645.0	321.3	0.0001	0.0000	644.6	324.2	0.0002	0.0000	644.6	339.2	0.0004	0.0000	644.5	590.5	0.0887	0.0000	644.7	1147.1	0.0013	0.0246
651.2	324.1	0.0001	0.0000	650.8	327.1	0.0002	0.0000	650.9	342.2	0.0005	0.0000	650.7	596.7	0.0827	0.0000	650.9	1159.3	0.0012	0.0264
657.4	326.9	0.0002	0.0000	657.0	329.9	0.0003	0.0000	657.1	345.2	0.0007	0.0000	656.9	602.6	0.0771	0.0001	657.1	1172.0	0.0012	0.0253
663.6	329.9	0.0002	0.0000	663.2	332.9	0.0003	0.0000	663.3	348.3	0.0006	0.0000	663.1	608.6	0.0717	0.0002	663.3	1176.6	0.0012	0.0244
669.8	332.9	0.0003	0.0000	669.4	335.7	0.0003	0.0000	669.5	351.4	0.0007	0.0000	669.3	614.4	0.0665	0.0003				
676.0	335.7	0.0003	0.0000	675.6	338.9	0.0004	0.0000	675.7	355.0	0.0010	0.0000	675.5	620.4	0.0619	0.0005				
682.2	338.5	0.0004	0.0000	681.8	341.7	0.0004	0.0000	681.9	357.8	0.0011	0.0000	681.7	626.4	0.0581	0.0007				
688.4	341.3	0.0005	0.0000	687.9	344.5	0.0005	0.0000	688.1	360.9	0.0013	0.0000	687.9	632.5	0.0543	0.0010				
694.6	344.3	0.0005	0.0000	694.2	347.5	0.0006	0.0000	694.3	363.8	0.0016	0.0000	694.1	638.2	0.0502	0.0013				
700.8	347.1	0.0006	0.0000	700.4	350.3	0.0006	0.0000	700.5	366.7	0.0020	0.0000	700.3	644.2	0.0472	0.0017				
707.0	350.1	0.0007	0.0000	706.5	353.3	0.0008	0.0000	706.7	369.8	0.0023	0.0000	706.5	650.5	0.0444	0.0021				
713.2	352.9	0.0008	0.0000	712.7	356.2	0.0010	0.0000	712.9	372.9	0.0030	0.0000	712.7	656.4	0.0417	0.0027				
719.4	356.1	0.0010	0.0000	718.9	359.2	0.0011	0.0000	719.1	375.8	0.0036	0.0000	718.9	662.3	0.0393	0.0031				
725.6	358.8	0.0012	0.0000	725.1	362.1	0.0014	0.0000	725.3	378.9	0.0043	0.0000	725.1	668.3	0.0369	0.0037				
731.8	361.7	0.0013	0.0000	731.3	365.1	0.0017	0.0000	731.5	381.9	0.0053	0.0000	731.3	674.4	0.0353	0.0043				
738.0	364.6	0.0018	0.0000	737.5	367.9	0.0019	0.0000	737.7	384.9	0.0063	0.0000	737.5	680.3	0.0336	0.0049				
744.2	367.6	0.0019	0.0000	743.7	371.0	0.0024	0.0000	743.9	388.0	0.0077	0.0000	743.6	686.2	0.0318	0.0055				
750.4	370.2	0.0023	0.0000	749.9	373.7	0.0029	0.0000	750.1	391.0	0.0092	0.0000	749.8	692.2	0.0303	0.0060				
756.6	373.4	0.0027	0.0000	756.1	376.6	0.0034	0.0000	756.3	394.0	0.0110	0.0000	756.1	698.2	0.0284	0.0064				
762.8	376.3	0.0031	0.0000	762.3	379.7	0.0042	0.0000	762.5	397.1	0.0133	0.0000	762.2	704.4	0.0266	0.0068				
769.0	379.1	0.0039	0.0000	768.5	382.5	0.0050	0.0000	768.7	400.0	0.0159	0.0000	768.4	710.4	0.0250	0.0070				
775.2	382.2	0.0047	0.0000	774.7	385.5	0.0062	0.0000	774.9	403.2	0.0186	0.0000	774.7	716.4	0.0235	0.0073				
781.4	385.1	0.0056	0.0000	780.9	389.1	0.0076	0.0000	781.1	406.0	0.0216	0.0000	780.8	722.6	0.0216	0.0071				
787.6	388.0	0.0064	0.0000	787.1	392.1	0.0093	0.0001	787.3	409.1	0.0247	0.0000	787.0	728.3	0.0200	0.0071				
793.8	390.9	0.0068	0.0000	793.3	395.0	0.0107	0.0001	793.5	412.4	0.0284	0.0000	793.2	734.4	0.0183	0.0069				
800.0	393.8	0.0078	0.0000	799.5	397.9	0.0126	0.0000	799.7	415.3	0.0322	0.0000	799.4	740.3	0.0170	0.0067				
806.2	396.6	0.0086	0.0000	805.7	400.7	0.0156	0.0000	805.9	418.3	0.0360	0.0000	805.6	746.4	0.0157	0.0064				
812.4	399.7	0.0103	0.0000	811.9	403.9	0.0178	0.0000	812.1	421.3	0.0400	0.0000	811.8	752.6	0.0146	0.0061				
818.6	402.5	0.0111	0.0000	818.1	406.7	0.0219	0.0000	818.3	424.3	0.0443	0.0000	818.0	758.4	0.0135	0.0058				
824.8	405.5	0.0129	0.0000	824.3	410.0	0.0242	0.0000	824.5	427.2	0.0485	0.0000	824.2	766.0	0.0123	0.0054				
831.0	409.0	0.0142	0.0000	830.5	412.9	0.0277	0.0001	830.7	430.1	0.0525	0.0000	830.4	771.6	0.0118	0.0052				
837.2	411.9	0.0149	0.0000	836.7	415.6	0.0343	0.0000	836.9	433.3	0.0565	0.0000	836.6	777.9	0.0112	0.0049				
843.4	414.9	0.0153	0.0000	842.9	418.8	0.0350	0.0000	843.1	436.1	0.0600	0.0000	842.8	783.8	0.0106	0.0046				
849.6	417.9	0.0178	0.0000	849.1	421.5	0.0393	0.0000	849.3	439.3	0.0644	0.0000	849.0	790.1	0.0103	0.0044				
855.8	421.2	0.0206	0.0000	855.3	424.5	0.0465	0.0000	855.5	442.3	0.0684	0.0000	855.2	796.0	0.0095	0.0042				
862.0	423.7	0.0207	0.0000	861.5	427.3	0.0520	0.0000	861.7	445.4	0.0718	0.0000	861.4	801.8	0.0093	0.0041				
868.2	426.6	0.0210	0.0000	867.7	430.4	0.0569	0.0000	867.9	448.4	0.0755	0.0000	867.6	808.2	0.0093	0.0039				
874.4	429.7	0.0228	0.0000	873.9	433.4	0.0590	0.0000	874.1	451.2	0.0786	0.0000	873.8	814.0	0.0088	0.0036				
880.6	432.6	0.0245	0.0000	880.1	436.3	0.0652	0.0000	880.3	454.3	0.0810	0.0000	880.0	820.4	0.0087	0.0035				
886.8	435.5	0.0249	0.0000	886.3	439.3	0.0668	0.0000	886.5	457.3	0.0831	0.0000	886.2	826.3	0.0084	0.0034				
893.0	438.4	0.0254	0.0000	892.5	442.4	0.0756	0.0000	892.7	460.4	0.0850	0.0000	892.4	832.6	0.0083	0.0033				
905.4	444.3	0.0272	0.0000	898.7	445.2	0.0772	0.0000	898.9	463.5	0.0866	0.0000	898.6	838.4	0.0084	0.0032				
911.6	447.3	0.0273	0.0000	904.9	448.1	0.0813	0.0000	905.1	466.3	0.0881	0.0000	904.8	844.7	0.0079	0.0032				
917.8	450.2	0.0291	0.0000	911.1	451.2	0.0877	0.0000	911.3	469.5	0.0920	0.0000	911.0	850.6	0.0079	0.0031				
924.0	453.2	0.0289	0.0000	917.3	454.1	0.0895	0.0000	917.5	473.1	0.0935	0.0000	917.2	856.8	0.0079	0.0031				
930.2	456.2	0.0265	0.0000	923.5	457.1	0.0948	0.0000	923.7	476.0	0.0953	0.0000	923.4	862.6	0.0081	0.0031				
936.4	459.1	0.0278	0.0000	929.7	460.2	0.0961	0.0000	929.9	479.0	0.0956	0.0000	929.6	869.0	0.0085	0.0032				
942.6	462.2	0.0314	0.0000	935.9	463.0	0.0927	0.0000	936.1	482.1	0.0982	0.0000	935.8	875.2	0.0088	0.0031				
948.8	465.2	0.0298	0.0000	942.1	466.3	0.0952	0.0000	942.3	485.1	0.0974	0.0000	942.0	880.9	0.0085	0.0032				
955.0	467.9	0.0285	0.0000	948.3	469.3	0.1001	0.0000	948.5	488.1	0.0989	0.0000	948.2	887.0	0.0090	0.0032				
961.2	470.8	0.0291	0.0000	954.5	471.9	0.0986	0.0000	954.7	491.1	0.0986	0.0000	954.4	892.9	0.0099	0.0033				
967.4	473.9	0.0289	0.0000	960.7	474.9	0.0993	0.0000	960.9	494.2	0.0974	0.0000	960.6	899.1	0.0093	0.0033				
973.6	476.9	0.0304	0.0000	966.9	477.6	0.0959	0.0000	967.1	497.0	0.0987	0.0000	966.8	905.3	0.0098	0.0035				
979.8	479.8	0.0289	0.0000	973.1	481.0	0.0965	0.0000	973.3	499.8	0.0970	0.0000	973.0	912.1	0.0096	0.0036				
986.0	482.9	0.0298	0.0000	979.3	483.7	0.1006	0.0000	979.5	503.1	0.0964	0.0000	979.2	917.1	0.0100	0.0037				
992.2	486.0	0.0278	0.0000	985.5	486.6	0.0989	0.0000	985.7	506.2	0.0964	0.0000	985.4	923.4	0.0105	0.0038				
998.4	488.8	0.0277	0.0000	991.7	489.7	0.0992	0.0000	991.9	509.2	0.0915	0.0000	991.6	929.4	0.0116	0.0041				
1004.6	492.0	0.0253	0.0000	997.9	492.4	0.0965	0.0000	998.1	512.2	0.0915	0.0000	997.8	935.6	0.0109	0.0043				
1010.8	495.0	0.0248	0.0000	1004.1	495.5	0.0954	0.0001	1004.3	515.3	0.0914	0.0000	1004.0	941.7	0.0113	0.0045				
1017.0	498.1	0.0264	0.0000	1010.3	498.4	0.0938	0.0000	1010.5	518.1	0.0886	0.0000	1010.2	947.7	0.0113	0.0047				
1023.2	500.9	0.0241	0.0000	1016.5	501.9	0.0935	0.0000	1016.7	521.1	0.0874	0.0000	1016.4	953.8	0.0108	0.0050				
1029.4	503.8	0.0252	0.0000	1022.7	504.7	0.0896	0.0000	1022.9	524.1	0.0852	0.0000	1022.6	959.7	0.0095	0.0052				
1035.6	506.9	0.0232	0.0000	1028.9	507.9	0.0896	0.0000	1029.1	527.2	0.0824	0.0000	1028.8	966.1	0.0106	0.0056				
1041.8	510.0	0.0235	0.0000	1035.1	510.9	0.0878	0.0000	1035.3	530.2	0.0819	0.0000	1035.0	972.0	0.0101	0.0059				
1048.0	513.1	0.0224	0.0000	1041.3	514.0	0.0829	0.0000	1041.5	533.4	0.0791	0.0000	1041.2	978.5	0.0119	0.0063				
1054.2	516.1	0.0231	0.0000	1047.5	517.1	0.0848	0.0000	1047.7	536.1	0.0775	0.0000	1047.4	984.1	0.0121	0.0067				
1060.4	519.1	0.0206	0.0000	1053.7	519.6	0.0815	0.0000	1053.9	539.1	0.0758	0.0000	1053.6	990.1	0.0084	0.0071				
1066.6	522.1	0.0216	0.0000	1059.9	522.9	0.0801	0.0000	1060.1	542.2	0.0724	0.0000	1059.8	997.6	0.0099	0.0079				
1072.8	525.2	0.0195	0.0000	1066.1	525.8	0.0750	0.0000	1066.3	545.1	0.0706	0.0000	1066.0	1003.5	0.0098	0.0086				
1079.0	528.1	0.0205	0.0000	1072.3	528.8	0.0756	0.0000	1072.5	548.2	0.0689	0.0000	1072.2	1009.8	0.0082	0.0100				
1085.2	531.2	0.0215	0.0000	1078.5	531.7	0.0717	0.0000	1078.6	551.0	0.0656	0.0000	1078.4	1015.8	0.0079	0.0100				
1091.4	534.3	0.0194	0.0000	1084.7	534.9	0.0652	0.0001	1084.9	554.0	0.0639	0.0000	1084.6	1022.0	0.0072	0.0108				
1097.6	537.1	0.0202	0.0000	1090.9	537.7	0.0676	0.0000	1091.1	557.2	0.0621	0.0000	1090.8	1028.1	0.0065	0.0117				
1103.8	540.2	0.0190	0.0000	1097.1	540.6	0.0637	0.0000	1097.2	560.0	0.0588	0.0000	1097.0	1034.3	0.0063	0.0126				
1110.0	543.3	0.0196	0.0000	1103.3	543.7	0.0595	0.0000	1103.5	563.3	0.0566	0.0000	1103.2	1040.9	0.0060	0.0134				
1116.2	546.5	0.0178	0.0000	1109.5	546.7	0.0579	0.0000	1109.7	566.2	0.0552	0.0000	1109.4	1046.7	0.0058	0.0144				
1122.4	549.5	0.0166	0.0000	1115.7	549.5	0.0546	0.0000	1115.8	569.0	0.0528	0.0000	1115.6	1052.5	0.0037	0.0149				
1128.6	552.3	0.0152	0.0000	1121.9	552.5	0.0537	0.0000	1122.1	572.2	0.0499	0.0000	1121.8	1059.0	0.0012	0.0167				
1134.8	555.5	0.0158	0.0000	1128.1	555.7	0.0508	0.0000	1128.3	575.3	0.0475	0.0000	1128.0	1064.9	0.0009	0.0171				
1141.0	558.5	0.0158	0.0000	1134.3	558.4	0.0495	0.0000	1134.4	578.1	0.0464	0.0000	1134.2	1071.2	0.0008	0.0181				
1147.2	561.7	0.0146	0.0000	1140.5	561.4	0.0462	0.0000	1140.7	581.1	0.0438	0.0000	1140.4	1077.5	0.0008	0.0190				
1153.4	564.6	0.0139	0.0000	1146.7	564.8	0.0474	0.0000	1146.9	584.1	0.0417	0.0000	1146.6	1083.5	0.0009	0.0199				
1159.6	567.7	0.0136	0.0000	1152.9	567.3	0.0432	0.0000	1153.0	587.8	0.0394	0.0000	1152.8	1090.3	0.0007	0.0209				
1165.8	570.7	0.0124	0.0000	1159.1	570.3	0.0427	0.0000	1159.3	590.7	0.0371	0.0000	1159.0	1096.4	0.0008	0.0225				
1172.0	573.7	0.0120	0.0000	1165.3	573.6	0.0399	0.0000	1165.5	593.8	0.0357	0.0000	1165.2	1102.8	0.0013	0.0228				
1178.2	576.7	0.0113	0.0000	1171.5	576.4	0.0386	0.0000	1171.6	596.8	0.0336	0.0000	1171.4	1108.6	0.0032	0.0227				
1184.4	579.9	0.0106	0.0000	1177.7	579.4	0.0369	0.0000	1177.9	599.8	0.0322	0.0000	1177.6	1115.0	0.0014	0.0231				
1190.6	583.0	0.0099	0.0000	1183.9	582.2	0.0329	0.0000	1184.1	602.7	0.0310	0.0000	1183.8	1121.3	0.0009	0.0229				
1196.8	586.1	0.0094	0.0000	1190.1	585.2	0.0327	0.0000	1190.2	605.8	0.0294	0.0000	1190.0	1127.6	0.0011	0.0229				
1203.0	589.1	0.0087	0.0000	1196.3	588.1	0.0296	0.0000	1196.5	608.8	0.0281	0.0000	1196.2	1134.0	0.0013	0.0231				
1209.2	592.0	0.0086	0.0000	1202.5	591.2	0.0274	0.0000	1202.7	612.0	0.0270	0.0001	1202.4	1139.8	0.0026	0.0227				
1215.4	595.3	0.0083	0.0000	1208.7	594.1	0.0285	0.0000	1208.8	614.8	0.0254	0.0002	1208.6	1145.9	0.0010	0.0222				
1221.6	598.5	0.0081	0.0000	1214.9	597.3	0.0260	0.0001	1215.1	617.7	0.0246	0.0002	1214.8	1152.2	0.0009	0.0220				
1227.8	601.4	0.0072	0.0000	1221.1	600.0	0.0263	0.0001	1221.3	620.9	0.0238	0.0003	1221.0	1158.8	0.0024	0.0222				
1234.0	605.0	0.0067	0.0000	1227.3	603.4	0.0243	0.0001	1227.4	623.9	0.0228	0.0004	1227.2	1165.0	0.0050	0.0218				
1240.2	607.7	0.0068	0.0000	1233.5	606.4	0.0231	0.0001	1233.7	626.8	0.0218	0.0004	1233.4	1170.3	0.0013	0.0210				
1246.4	610.8	0.0064	0.0000	1239.8	609.2	0.0232	0.0002	1239.9	629.9	0.0209	0.0005	1239.6	1173.4	0.0012	0.0204				
1252.6	613.8	0.0058	0.0000	1245.9	612.2	0.0205	0.0001	1246.0	632.9	0.0199	0.0006								
1258.8	616.8	0.0058	0.0000	1252.1	615.3	0.0207	0.0001	1252.3	635.8	0.0195	0.0008								
1265.0	619.9	0.0058	0.0001	1258.4	618.7	0.0195	0.0002	1258.5	638.9	0.0187	0.0008								
1271.2	623.4	0.0056	0.0001	1264.6	621.8	0.0186	0.0002	1264.7	641.8	0.0179	0.0010								
1277.4	626.2	0.0050	0.0001	1270.7	624.8	0.0190	0.0003	1270.9	644.9	0.0173	0.0011								
1283.6	629.4	0.0054	0.0002	1277.0	627.6	0.0173	0.0003	1277.1	647.8	0.0166	0.0012								
1289.8	632.6	0.0052	0.0002	1283.2	630.6	0.0177	0.0004	1283.3	650.9	0.0161	0.0013								
1296.0	635.5	0.0049	0.0002	1289.3	633.7	0.0163	0.0004	1289.5	653.9	0.0158	0.0015								
1302.2	638.7	0.0045	0.0002	1295.6	636.6	0.0161	0.0005	1295.7	657.2	0.0151	0.0016								
1308.4	641.6	0.0043	0.0003	1301.8	639.8	0.0160	0.0006	1301.9	660.0	0.0148	0.0017								
1314.6	644.8	0.0045	0.0004	1307.9	642.8	0.0151	0.0006	1308.1	663.0	0.0148	0.0019								

Table 4 Results of temperature-programmed open system pyrolysis (continued)

1320.8	647.8	0.0040	0.0003	1314.2	645.8	0.0144	0.0007	1314.3	665.9	0.0144	0.0021
1327.0	650.9	0.0040	0.0004	1320.4	649.1	0.0148	0.0008	1320.5	668.9	0.0139	0.0022
1333.2	654.2	0.0039	0.0004	1326.5	651.8	0.0140	0.0008	1326.7	672.0	0.0134	0.0023
1339.4	657.2	0.0036	0.0004	1332.8	654.8	0.0145	0.0011	1332.9	675.1	0.0132	0.0024
1345.6	660.4	0.0036	0.0005	1339.0	657.7	0.0137	0.0011	1339.1	678.0	0.0130	0.0026
1351.8	663.4	0.0037	0.0006	1345.1	660.7	0.0131	0.0012	1345.3	680.9	0.0130	0.0026
1358.0	666.7	0.0033	0.0006	1351.4	663.8	0.0124	0.0012	1351.5	684.1	0.0126	0.0027
1364.2	669.7	0.0034	0.0007	1357.6	666.4	0.0124	0.0014	1357.7	687.1	0.0126	0.0028
1370.4	672.9	0.0031	0.0007	1363.8	669.9	0.0114	0.0014	1363.9	690.0	0.0120	0.0030
1376.6	675.8	0.0027	0.0007	1370.0	673.1	0.0110	0.0014	1370.1	693.1	0.0123	0.0030
1382.8	679.0	0.0028	0.0008	1376.2	675.7	0.0109	0.0016	1376.3	696.2	0.0119	0.0031
1389.0	682.2	0.0027	0.0009	1382.4	679.0	0.0101	0.0016	1382.4	699.1	0.0120	0.0031
1395.2	685.3	0.0029	0.0009	1388.6	681.7	0.0105	0.0018	1388.7	702.2	0.0112	0.0032
1401.4	688.6	0.0024	0.0009	1394.8	684.6	0.0097	0.0017	1394.9	705.2	0.0107	0.0032
1407.6	691.6	0.0025	0.0011	1401.0	687.6	0.0098	0.0018	1401.0	708.2	0.0111	0.0032
1413.8	694.8	0.0024	0.0012	1407.2	690.9	0.0088	0.0018	1407.3	711.2	0.0117	0.0032
1420.0	697.9	0.0023	0.0013	1413.4	693.8	0.0084	0.0017	1413.5	714.3	0.0108	0.0031
1426.2	701.0	0.0022	0.0014	1419.6	697.0	0.0076	0.0017	1419.6	717.2	0.0113	0.0031
1432.4	704.1	0.0020	0.0014	1425.8	699.9	0.0075	0.0017	1425.9	720.4	0.0103	0.0030
1438.6	707.4	0.0021	0.0016	1432.0	703.0	0.0070	0.0016	1432.1	723.3	0.0114	0.0030
1444.9	710.4	0.0018	0.0015	1438.2	706.3	0.0068	0.0017	1438.2	726.2	0.0114	0.0029
1451.1	713.5	0.0017	0.0017	1444.4	709.0	0.0065	0.0017	1444.5	729.3	0.0112	0.0029
1457.2	716.7	0.0017	0.0018	1450.6	711.9	0.0058	0.0016	1450.7	732.2	0.0097	0.0028
1463.5	719.8	0.0017	0.0018	1456.8	714.8	0.0057	0.0016	1456.9	735.3	0.0099	0.0030
1469.7	723.1	0.0016	0.0019	1463.0	718.2	0.0051	0.0015	1463.1	738.3	0.0103	0.0027
1475.8	726.2	0.0015	0.0020	1469.2	721.1	0.0048	0.0014	1469.3	741.3	0.0114	0.0026
1482.1	729.4	0.0014	0.0020	1475.4	724.1	0.0047	0.0014	1475.4	744.3	0.0097	0.0025
1488.3	732.6	0.0014	0.0020	1481.6	727.4	0.0046	0.0015	1481.7	747.4	0.0103	0.0023
1494.4	735.7	0.0013	0.0021	1487.8	730.3	0.0043	0.0015	1487.9	750.5	0.0107	0.0023
1500.7	738.9	0.0012	0.0021	1494.0	733.8	0.0037	0.0014	1494.0	753.6	0.0121	0.0021
1506.9	742.2	0.0012	0.0022	1500.2	736.9	0.0033	0.0014	1500.3	756.5	0.0109	0.0020
1513.0	745.3	0.0011	0.0022	1506.4	740.1	0.0030	0.0012	1506.5	759.5	0.0110	0.0021
1519.3	748.4	0.0010	0.0021	1512.6	743.0	0.0028	0.0012	1512.7	762.4	0.0108	0.0018
1525.5	751.6	0.0010	0.0023	1518.8	746.0	0.0029	0.0014	1518.9	765.5	0.0124	0.0018
1531.6	754.8	0.0011	0.0023	1525.0	749.0	0.0027	0.0013	1525.1	768.5	0.0106	0.0017
1537.9	757.9	0.0010	0.0023	1531.2	752.1	0.0025	0.0013	1531.3	771.7	0.0116	0.0016
1544.1	760.9	0.0010	0.0024	1537.4	755.2	0.0025	0.0014	1537.5	774.6	0.0113	0.0015
1550.3	764.2	0.0009	0.0022	1543.6	758.2	0.0022	0.0013	1543.7	777.5	0.0108	0.0015
1556.5	767.5	0.0009	0.0024	1549.8	760.9	0.0020	0.0012	1549.9	780.7	0.0132	0.0014
1562.7	770.6	0.0009	0.0024	1556.0	764.2	0.0019	0.0012	1556.1	783.6	0.0129	0.0014
1568.8	773.9	0.0008	0.0026	1562.2	767.1	0.0019	0.0012	1562.3	786.6	0.0127	0.0013
1575.1	776.9	0.0008	0.0023	1568.4	770.1	0.0018	0.0012	1568.5	789.7	0.0147	0.0013
1581.3	780.0	0.0008	0.0025	1574.6	773.2	0.0018	0.0013	1574.7	792.6	0.0154	0.0011
1587.5	783.3	0.0007	0.0024	1580.8	776.1	0.0017	0.0013	1580.9	795.6	0.0158	0.0011
1593.7	786.7	0.0007	0.0024	1587.0	779.3	0.0016	0.0012	1587.1	798.6	0.0138	0.0010
1599.9	789.7	0.0007	0.0023	1593.2	782.4	0.0015	0.0012	1593.3	801.8	0.0133	0.0010
1606.0	793.0	0.0007	0.0026	1599.4	785.4	0.0015	0.0012	1599.5	804.6	0.0137	0.0011
1612.3	796.2	0.0007	0.0024	1605.6	788.5	0.0014	0.0011	1605.7	807.8	0.0121	0.0010
1618.5	799.2	0.0007	0.0026	1611.8	791.3	0.0013	0.0011	1611.9	810.8	0.0127	0.0010
1624.6	802.6	0.0007	0.0026	1618.0	794.3	0.0013	0.0011	1618.1	813.8	0.0166	0.0010
1630.9	805.7	0.0006	0.0024	1624.2	797.3	0.0014	0.0012	1624.3	817.0	0.0122	0.0010
1637.1	809.0	0.0007	0.0025	1630.4	800.6	0.0013	0.0012	1630.5	819.9	0.0137	0.0010
1643.2	812.2	0.0006	0.0025	1636.6	803.5	0.0013	0.0012	1636.7	822.8	0.0137	0.0009
1649.5	815.3	0.0006	0.0023	1642.8	806.6	0.0013	0.0012	1642.9	825.9	0.0169	0.0009
1655.7	818.6	0.0006	0.0025	1649.0	809.6	0.0013	0.0012	1649.1	828.9	0.0172	0.0009
1661.8	821.7	0.0006	0.0026	1655.2	812.7	0.0012	0.0012	1655.3	832.0	0.0138	0.0009
1668.1	824.9	0.0006	0.0025	1661.4	815.6	0.0012	0.0011	1661.5	835.1	0.0155	0.0009
1674.3	828.1	0.0005	0.0023	1667.6	818.8	0.0012	0.0013	1667.7	838.0	0.0143	0.0009
1680.4	831.1	0.0005	0.0023	1673.8	821.9	0.0010	0.0011	1673.9	841.1	0.0146	0.0010
1686.6	834.5	0.0005	0.0021	1680.0	824.9	0.0011	0.0012	1680.1	844.1	0.0139	0.0009
1692.8	837.6	0.0006	0.0023	1686.2	828.1	0.0011	0.0012	1686.3	847.1	0.0140	0.0010
1699.0	841.0	0.0005	0.0022	1692.4	831.0	0.0011	0.0012	1692.5	850.2	0.0159	0.0010
1705.2	844.1	0.0005	0.0023	1698.6	834.2	0.0010	0.0011	1698.7	853.2	0.0128	0.0010
1711.4	847.2	0.0005	0.0023	1704.8	837.0	0.0010	0.0011	1704.9	855.9	0.0140	0.0011
1717.6	850.3	0.0005	0.0021	1711.0	840.1	0.0010	0.0011	1711.1	859.4	0.0168	0.0011
1723.8	853.5	0.0005	0.0021	1717.2	842.9	0.0010	0.0012	1717.3	862.2	0.0143	0.0011
1730.0	856.9	0.0005	0.0020	1723.4	846.5	0.0010	0.0012	1723.5	865.2	0.0166	0.0011
1736.2	860.0	0.0005	0.0021	1735.8	852.9	0.0011	0.0013	1729.7	868.2	0.0172	0.0011
1742.4	863.2	0.0004	0.0023	1742.0	855.8	0.0010	0.0013	1735.9	871.3	0.0149	0.0011
1748.6	866.5	0.0004	0.0021	1748.2	859.1	0.0010	0.0013	1742.1	874.2	0.0152	0.0012
1754.8	869.8	0.0004	0.0021	1754.4	861.7	0.0011	0.0014	1748.3	877.2	0.0168	0.0012
1761.0	872.9	0.0005	0.0022	1760.6	865.2	0.0010	0.0014	1754.5	880.2	0.0145	0.0012
1767.2	876.4	0.0005	0.0020	1766.8	867.9	0.0010	0.0014	1760.7	883.3	0.0166	0.0012
1773.4	879.5	0.0005	0.0022	1773.0	871.1	0.0010	0.0014	1767.0	886.3	0.0136	0.0013
1779.6	882.7	0.0004	0.0022	1779.2	874.2	0.0011	0.0016	1773.1	889.4	0.0153	0.0014
1785.8	886.0	0.0005	0.0022	1785.4	877.2	0.0010	0.0016	1779.4	892.4	0.0137	0.0013
1792.0	889.3	0.0004	0.0020	1791.6	880.2	0.0010	0.0016	1785.6	895.4	0.0147	0.0014
1798.2	892.4	0.0005	0.0020	1797.8	883.3	0.0010	0.0016	1791.7	898.3	0.0131	0.0014
1804.4	895.6	0.0004	0.0022	1804.0	886.3	0.0010	0.0016	1798.0	901.4	0.0138	0.0014
1810.6	899.0	0.0003	0.0018	1810.2	889.6	0.0010	0.0016	1804.2	904.5	0.0153	0.0015
1816.8	902.2	0.0004	0.0020	1816.4	892.3	0.0010	0.0018	1810.4	907.4	0.0135	0.0016
1823.0	905.6	0.0004	0.0019	1822.6	895.6	0.0011	0.0018	1816.6	910.6	0.0141	0.0016
1829.2	908.7	0.0005	0.0021	1828.8	898.4	0.0011	0.0018	1822.8	913.5	0.0118	0.0017
1835.4	912.0	0.0005	0.0022	1835.0	901.4	0.0011	0.0019	1829.0	916.3	0.0114	0.0017
1841.6	915.2	0.0004	0.0021	1841.2	904.7	0.0010	0.0018	1835.2	919.6	0.0127	0.0018
1847.8	918.5	0.0004	0.0018	1847.4	907.7	0.0011	0.0021	1841.4	922.5	0.0109	0.0020
1854.0	921.7	0.0004	0.0020	1853.6	910.5	0.0010	0.0020	1847.6	925.5	0.0123	0.0020
1860.2	925.0	0.0004	0.0019	1859.8	913.8	0.0010	0.0020	1853.8	928.5	0.0123	0.0021
1866.4	927.9	0.0004	0.0022	1866.0	916.9	0.0010	0.0020	1860.0	931.5	0.0130	0.0022
1872.6	931.4	0.0004	0.0019	1872.2	919.8	0.0010	0.0022	1866.2	934.5	0.0105	0.0023
1878.8	934.8	0.0004	0.0019	1878.4	923.0	0.0011	0.0023	1872.4	937.6	0.0096	0.0024
1885.0	937.7	0.0004	0.0022	1884.6	925.9	0.0011	0.0022	1878.6	940.6	0.0098	0.0026
1891.2	941.2	0.0004	0.0022	1890.8	929.1	0.0012	0.0024	1884.8	943.6	0.0090	0.0028
1897.4	944.6	0.0004	0.0021	1897.0	932.5	0.0010	0.0023	1891.0	946.7	0.0097	0.0029
1903.6	947.6	0.0004	0.0024	1903.2	935.0	0.0010	0.0023	1897.2	949.7	0.0110	0.0031
1909.8	950.9	0.0004	0.0020	1909.4	938.2	0.0010	0.0024	1903.4	952.7	0.0111	0.0032
1916.0	954.3	0.0004	0.0020	1915.6	941.2	0.0010	0.0025	1909.6	955.8	0.0087	0.0034
1922.2	957.6	0.0004	0.0022	1921.8	944.1	0.0011	0.0026	1915.8	958.8	0.0103	0.0036
1928.4	960.7	0.0004	0.0025	1928.0	947.3	0.0010	0.0028	1922.0	961.7	0.0104	0.0038
1934.6	964.0	0.0004	0.0022	1934.2	950.0	0.0011	0.0028	1928.2	964.7	0.0098	0.0041
1940.8	967.1	0.0004	0.0021	1940.4	953.1	0.0011	0.0028	1934.4	967.7	0.0093	0.0042
1947.0	970.5	0.0004	0.0025	1946.6	956.5	0.0010	0.0030	1940.6	970.7	0.0090	0.0043
1953.2	973.8	0.0003	0.0023	1952.8	959.5	0.0010	0.0029	1946.8	973.7	0.0090	0.0046
1959.4	977.0	0.0004	0.0024	1959.0	962.4	0.0010	0.0031	1953.0	976.9	0.0085	0.0047
1965.6	980.3	0.0004	0.0024	1965.2	965.6	0.0010	0.0032	1959.2	979.6	0.0083	0.0051
1971.8	983.5	0.0004	0.0028	1971.4	969.3	0.0011	0.0034	1965.4	982.8	0.0070	0.0054
1978.1	987.0	0.0004	0.0027	1977.6	972.4	0.0010	0.0036	1971.6	985.8	0.0086	0.0056
1984.3	990.0	0.0004	0.0025	1983.8	975.5	0.0011	0.0037	1977.8	988.7	0.0075	0.0059
1990.5	993.5	0.0004	0.0030	1990.0	978.7	0.0012	0.0039	1984.0	991.8	0.0078	0.0061
1996.7	996.7	0.0004	0.0029	2002.4	984.6	0.0011	0.0043	1990.2	994.7	0.0061	0.0065
2002.9	1000.0	0.0004	0.0027	2008.6	987.4	0.0011	0.0043	1996.4	997.8	0.0072	0.0067
2009.1	1003.2	0.0004	0.0028	2014.8	990.9	0.0010	0.0040	2002.6	1000.8	0.0067	0.0071
2015.3	1006.7	0.0004	0.0031	2021.0	993.7	0.0010	0.0040	2008.8	1003.8	0.0062	0.0073

Table 4 Results of temperature-programmed open system pyrolysis (continued)

2021.5	1009.9	0.0004	0.0029	2027.2	997.0	0.0011	0.0048	2015.0	1006.8	0.0061	0.0076
2027.7	1013.3	0.0004	0.0032	2033.4	999.8	0.0010	0.0047	2021.2	1009.8	0.0053	0.0080
2033.9	1016.4	0.0004	0.0030	2039.6	1002.8	0.0010	0.0051	2027.4	1013.0	0.0054	0.0082
2040.1	1019.8	0.0004	0.0035	2045.8	1006.2	0.0010	0.0050	2033.6	1015.8	0.0056	0.0085
2046.3	1023.0	0.0004	0.0032	2052.0	1009.0	0.0011	0.0057	2039.9	1018.7	0.0041	0.0087
2052.5	1026.3	0.0003	0.0033	2058.2	1012.2	0.0012	0.0061	2046.0	1021.6	0.0045	0.0090
2058.7	1029.6	0.0004	0.0032	2064.4	1015.0	0.0010	0.0063	2052.2	1025.0	0.0046	0.0094
2064.9	1033.0	0.0004	0.0035	2070.6	1017.9	0.0010	0.0070	2058.5	1027.7	0.0041	0.0097
2071.1	1036.3	0.0004	0.0035	2076.8	1021.2	0.0009	0.0068	2064.7	1030.8	0.0028	0.0099
2077.3	1039.8	0.0004	0.0036	2083.0	1024.7	0.0009	0.0068	2070.8	1034.1	0.0040	0.0103
2083.5	1042.8	0.0003	0.0032	2089.2	1027.5	0.0008	0.0070	2077.1	1037.0	0.0032	0.0107
2089.7	1046.4	0.0004	0.0036	2095.4	1030.5	0.0008	0.0073	2083.3	1039.7	0.0043	0.0110
2095.9	1049.7	0.0003	0.0033	2101.6	1033.6	0.0008	0.0076	2089.4	1042.9	0.0030	0.0113
2102.1	1052.9	0.0003	0.0031	2107.8	1036.8	0.0008	0.0081	2095.7	1046.1	0.0036	0.0116
2108.3	1056.1	0.0004	0.0036	2114.0	1040.1	0.0008	0.0088	2101.9	1049.1	0.0030	0.0119
2114.5	1059.6	0.0004	0.0037	2120.2	1043.0	0.0008	0.0092	2108.1	1051.7	0.0041	0.0121
2120.7	1063.1	0.0004	0.0035	2126.4	1046.1	0.0007	0.0093	2114.3	1055.1	0.0027	0.0124
2126.9	1066.7	0.0004	0.0036	2132.6	1049.3	0.0007	0.0095	2120.5	1057.8	0.0032	0.0126
2133.1	1069.9	0.0003	0.0034	2138.8	1053.2	0.0007	0.0094	2126.7	1061.3	0.0031	0.0128
2139.4	1073.2	0.0004	0.0033	2145.0	1055.6	0.0006	0.0096	2132.9	1063.6	0.0035	0.0132
2145.5	1076.5	0.0004	0.0035	2151.2	1058.5	0.0007	0.0105	2139.1	1067.2	0.0037	0.0132
2151.7	1079.7	0.0004	0.0033	2157.4	1061.7	0.0007	0.0113	2145.3	1070.5	0.0038	0.0135
2158.0	1083.6	0.0004	0.0033	2163.6	1064.9	0.0006	0.0110	2151.5	1072.8	0.0042	0.0136
2164.2	1087.1	0.0004	0.0035	2169.8	1067.9	0.0006	0.0104	2157.7	1075.8	0.0042	0.0136
2170.4	1090.1	0.0004	0.0036	2176.0	1071.2	0.0007	0.0108	2163.9	1079.3	0.0043	0.0137
2176.6	1093.4	0.0003	0.0034	2182.2	1074.2	0.0006	0.0110	2170.1	1082.0	0.0032	0.0138
2182.8	1096.8	0.0003	0.0033	2188.4	1077.3	0.0006	0.0110	2176.3	1084.8	0.0045	0.0138
2189.0	1100.3	0.0004	0.0036	2194.6	1080.3	0.0006	0.0115	2182.5	1087.8	0.0042	0.0138
2195.2	1103.8	0.0004	0.0034	2200.8	1083.9	0.0005	0.0119	2188.7	1090.7	0.0043	0.0136
2201.4	1107.0	0.0004	0.0036	2207.0	1086.8	0.0005	0.0116	2194.9	1094.2	0.0037	0.0136
2207.6	1111.3	0.0004	0.0037	2213.2	1090.7	0.0005	0.0119	2201.1	1096.8	0.0041	0.0135
2213.8	1114.2	0.0004	0.0037	2219.4	1093.5	0.0005	0.0119	2207.3	1099.9	0.0039	0.0136
2220.0	1117.5	0.0004	0.0035	2225.6	1096.6	0.0005	0.0122	2213.5	1102.8	0.0038	0.0134
2226.2	1120.8	0.0004	0.0037	2231.8	1100.0	0.0005	0.0124	2219.7	1106.0	0.0037	0.0134
2232.4	1124.1	0.0004	0.0033	2238.0	1103.5	0.0005	0.0124	2225.9	1109.0	0.0036	0.0132
2238.6	1127.8	0.0003	0.0033	2244.2	1106.2	0.0005	0.0121	2232.1	1111.7	0.0035	0.0131
2244.8	1131.4	0.0004	0.0038	2250.4	1109.5	0.0005	0.0118	2238.3	1114.9	0.0034	0.0131
2251.0	1134.4	0.0003	0.0032	2256.6	1112.9	0.0005	0.0123	2244.5	1117.6	0.0042	0.0130
2257.2	1138.0	0.0004	0.0032	2262.8	1116.0	0.0004	0.0109	2250.7	1120.8	0.0015	0.0129
2263.4	1141.3	0.0004	0.0036	2269.0	1118.9	0.0004	0.0106	2256.9	1123.8	0.0067	0.0125
2269.6	1145.8	0.0003	0.0032	2275.2	1121.8	0.0004	0.0106	2263.1	1126.4	0.0031	0.0128
2275.8	1149.5	0.0003	0.0032	2281.4	1124.7	0.0004	0.0104	2269.3	1130.3	0.0032	0.0127
2282.0	1152.7	0.0004	0.0035	2287.6	1128.1	0.0003	0.0108	2275.5	1133.1	0.0039	0.0127
2288.2	1156.2	0.0004	0.0035	2293.8	1131.2	0.0005	0.0103	2281.7	1136.2	0.0036	0.0127
2294.4	1160.4	0.0003	0.0032	2300.0	1134.3	0.0004	0.0099	2287.9	1138.9	0.0039	0.0125
2300.6	1164.2	0.0004	0.0035	2306.2	1137.5	0.0003	0.0101	2294.1	1142.0	0.0026	0.0124
2306.8	1167.5	0.0003	0.0032	2312.4	1140.3	0.0003	0.0097	2300.3	1145.0	0.0029	0.0124
2313.0	1171.2	0.0003	0.0030	2318.6	1143.7	0.0004	0.0097	2306.5	1147.8	0.0045	0.0126
2319.2	1174.6	0.0003	0.0033	2324.8	1146.9	0.0003	0.0091	2312.7	1151.2	0.0042	0.0124
2325.4	1178.3	0.0003	0.0034	2331.0	1149.8	0.0004	0.0091	2318.9	1154.1	0.0037	0.0124
2331.6	1181.8	0.0004	0.0034	2337.2	1152.8	0.0003	0.0087	2325.1	1157.0	0.0051	0.0121
2337.8	1185.3	0.0003	0.0031	2343.4	1155.7	0.0003	0.0082	2331.3	1160.5	0.0024	0.0121
2344.0	1189.1	0.0003	0.0033	2349.6	1159.1	0.0003	0.0085	2337.5	1163.1	0.0064	0.0119
2350.2	1192.6	0.0003	0.0034	2355.8	1162.1	0.0003	0.0080	2343.7	1166.4	0.0054	0.0118
2356.4	1195.9	0.0003	0.0035	2362.0	1164.9	0.0003	0.0080	2349.9	1169.3	0.0043	0.0117
2362.7	1199.4	0.0003	0.0033	2368.2	1168.0	0.0003	0.0078	2362.3	1175.3	0.0035	0.0114
2368.8	1202.9	0.0003	0.0031	2374.4	1171.2	0.0003	0.0077	2368.5	1178.4	0.0057	0.0112
2375.1	1206.4	0.0003	0.0031	2380.6	1173.7	0.0003	0.0076	2374.7	1181.2	0.0050	0.0112
2381.3	1208.8	0.0003	0.0034	2386.8	1175.1	0.0003	0.0075	2380.9	1181.4	0.0052	0.0110
				2393.0	1175.1	0.0002	0.0072	2387.1	1181.2	0.0036	0.0108
				2399.2	1175.1	0.0003	0.0069	2393.3	1181.3	0.0043	0.0105
				2405.4	1175.4	0.0002	0.0063	2399.6	1181.6	0.0041	0.0102
				2411.6	1175.0	0.0002	0.0060				
				2417.8	1175.2	0.0002	0.0057				

Appendix II Table 5 Results of temperature-programmed open system pyrolysis

Sample	8	Extracted		Sample	19			Sample	22			Sample	24			Sample	30		
Heating Rate	0.5K/min	CH4	N2	Heating Rate	0.5K/min	CH4	N2	Heating Rate	0.5K/min	CH4	N2	Heating Rate	0.5K/min	CH4	N2	Heating Rate	0.5K/min	CH4	N2
Time [min]	Temperature (°C)	Generation Rate [mg/g/min]	Generation Rate [mg/g/min]	Time [min]	Temperature (°C)	Generation Rate [mg/g/min]	Generation Rate [mg/g/min]	Time [min]	Temperature (°C)	Generation Rate [mg/g/min]	Generation Rate [mg/g/min]	Time [min]	Temperature (°C)	Generation Rate [mg/g/min]	Generation Rate [mg/g/min]	Time [min]	Temperature (°C)	Generation Rate [mg/g/min]	Generation Rate [mg/g/min]
0.0	21.8	0.0000	0.0000	0.0	23.3	0.0000	0.0000	0.0	24.1	0.0000	0.0000	0.0	24.0	0.0000	0.0000	0.0	83.9	0.0000	0.0000
6.2	21.8	0.0000	0.0000	6.2	48.7	0.0000	0.0000	6.2	31.7	0.0000	0.0000	6.2	55.3	0.0000	0.0000	6.2	101.8	0.0000	0.0000
12.4	42.0	0.0000	0.0000	12.4	94.9	0.0000	0.0000	12.4	93.2	0.0000	0.0000	12.4	81.1	0.0000	0.0000	12.4	119.3	0.0000	0.0000
18.6	87.0	0.0000	0.0000	18.6	115.5	0.0000	0.0000	18.6	109.6	0.0000	0.0000	18.6	100.4	0.0000	0.0000	18.6	136.6	0.0000	0.0000
24.8	106.5	0.0000	0.0000	24.8	129.7	0.0000	0.0000	24.8	126.6	0.0000	0.0000	24.8	119.1	0.0000	0.0000	24.8	136.6	0.0000	0.0000
31.0	122.9	0.0000	0.0000	31.0	136.3	0.0000	0.0000	31.0	130.8	0.0000	0.0000	31.0	132.3	0.0000	0.0000	31.0	136.0	0.0000	0.0000
37.2	134.6	0.0000	0.0000	37.2	138.3	0.0000	0.0000	37.2	130.2	0.0000	0.0000	37.2	131.8	0.0000	0.0000	37.3	136.9	0.0000	0.0000
43.4	132.7	0.0000	0.0000	43.4	136.1	0.0000	0.0000	43.4	130.2	0.0000	0.0000	43.4	131.5	0.0000	0.0000	43.4	136.8	0.0000	0.0000
49.6	134.0	0.0000	0.0000	49.6	138.1	0.0000	0.0000	49.6	131.1	0.0000	0.0000	49.6	132.6	0.0000	0.0000	49.6	136.1	0.0000	0.0000
55.8	133.7	0.0000	0.0000	55.9	136.8	0.0000	0.0000	55.8	131.2	0.0000	0.0000	55.8	131.2	0.0000	0.0000	55.9	136.1	0.0000	0.0000
62.0	134.7	0.0000	0.0000	62.1	136.9	0.0000	0.0000	62.0	131.2	0.0000	0.0000	62.0	131.6	0.0000	0.0000	62.1	137.2	0.0000	0.0000
68.2	133.1	0.0000	0.0000	68.2	136.8	0.0000	0.0000	68.2	131.9	0.0000	0.0000	68.2	132.3	0.0000	0.0000	68.3	136.1	0.0000	0.0000
74.4	134.0	0.0000	0.0000	74.5	136.8	0.0000	0.0000	74.4	130.3	0.0000	0.0000	74.4	132.4	0.0000	0.0000	74.5	136.2	0.0000	0.0000
80.6	134.3	0.0000	0.0000	80.7	136.4	0.0000	0.0000	80.6	132.6	0.0000	0.0000	80.6	131.9	0.0000	0.0000	80.7	137.4	0.0000	0.0000
86.8	132.9	0.0000	0.0000	86.9	137.3	0.0000	0.0000	86.8	130.9	0.0000	0.0000	86.8	133.5	0.0000	0.0000	86.9	140.2	0.0000	0.0000
93.0	134.4	0.0000	0.0000	93.1	141.3	0.0000	0.0000	93.1	135.9	0.0000	0.0000	93.0	133.5	0.0000	0.0000	93.1	143.3	0.0000	0.0000
99.2	134.9	0.0000	0.0000	99.3	142.9	0.0000	0.0000	99.3	136.2	0.0000	0.0000	99.2	136.4	0.0000	0.0000	99.3	145.6	0.0000	0.0000
105.4	138.1	0.0000	0.0000	105.5	143.4	0.0000	0.0000	105.5	138.9	0.0000	0.0000	105.4	139.5	0.0000	0.0000	105.5	148.9	0.0000	0.0000
111.6	142.1	0.0000	0.0000	111.7	148.1	0.0000	0.0000	111.7	141.6	0.0000	0.0000	111.6	142.5	0.0000	0.0000	111.7	151.3	0.0000	0.0000
117.8	143.1	0.0000	0.0000	117.9	150.4	0.0000	0.0000	117.9	144.1	0.0000	0.0000	117.8	145.0	0.0000	0.0000	117.9	154.7	0.0000	0.0000
124.0	146.1	0.0000	0.0000	124.1	152.7	0.0000	0.0000	124.1	146.8	0.0000	0.0000	124.0	147.9	0.0000	0.0000	124.1	156.7	0.0000	0.0000
130.2	149.0	0.0000	0.0000	130.3	156.0	0.0000	0.0000	130.3	149.9	0.0000	0.0000	130.2	149.2	0.0000	0.0000	130.3	159.6	0.0000	0.0000
136.4	152.2	0.0000	0.0000	136.5	157.7	0.0000	0.0000	136.5	151.5	0.0000	0.0000	136.4	152.6	0.0000	0.0000	136.5	161.7	0.0000	0.0000
142.6	154.1	0.0000	0.0000	142.7	160.8	0.0000	0.0000	142.7	154.0	0.0000	0.0000	142.6	154.5	0.0000	0.0000	142.7	165.0	0.0000	0.0000
148.8	156.6	0.0000	0.0000	148.9	162.8	0.0000	0.0000	148.9	156.4	0.0000	0.0000	148.8	157.1	0.0000	0.0000	148.9	167.5	0.0000	0.0000
155.0	159.0	0.0000	0.0000	155.1	165.0	0.0000	0.0000	155.0	158.7	0.0000	0.0000	155.0	159.5	0.0000	0.0000	155.1	169.7	0.0000	0.0000
161.2	161.6	0.0000	0.0000	161.3	167.6	0.0000	0.0000	161.2	160.8	0.0000	0.0000	161.2	162.0	0.0000	0.0000	161.3	172.5	0.0000	0.0000
167.3	164.2	0.0001	0.0001	167.5	170.3	0.0000	0.0000	167.4	163.3	0.0000	0.0000	167.4	164.4	0.0000	0.0000	167.5	175.1	0.0000	0.0000
173.6	166.4	0.0000	0.0000	173.7	172.8	0.0000	0.0000	173.6	165.5	0.0000	0.0000	173.6	165.8	0.0000	0.0000	173.7	175.8	0.0000	0.0000
179.7	168.4	0.0000	0.0000	179.9	175.7	0.0000	0.0000	179.8	168.0	0.0000	0.0000	179.8	168.7	0.0000	0.0000	179.9	178.6	0.0000	0.0000
185.9	171.0	0.0000	0.0000	186.2	177.7	0.0000	0.0000	186.0	169.5	0.0000	0.0000	186.0	171.3	0.0000	0.0000	186.1	180.5	0.0000	0.0000
192.2	173.0	0.0000	0.0000	192.4	180.0	0.0000	0.0000	192.2	171.6	0.0000	0.0000	192.2	173.2	0.0000	0.0000	192.4	183.0	0.0000	0.0000
198.3	175.1	0.0000	0.0000	198.5	182.0	0.0000	0.0000	198.4	174.0	0.0000	0.0000	198.4	174.9	0.0000	0.0000	198.6	185.7	0.0000	0.0000
204.5	177.7	0.0000	0.0000	204.8	184.6	0.0000	0.0000	204.6	176.2	0.0000	0.0000	204.6	177.4	0.0000	0.0000	204.8	188.2	0.0000	0.0000
210.7	179.9	0.0000	0.0000	211.0	186.3	0.0000	0.0000	210.8	178.6	0.0000	0.0000	210.8	179.7	0.0000	0.0000	211.0	189.6	0.0000	0.0000
216.9	182.0	0.0000	0.0000	217.2	190.2	0.0000	0.0000	217.0	180.5	0.0000	0.0000	217.0	181.2	0.0000	0.0000	217.2	191.1	0.0000	0.0000
223.1	183.4	0.0000	0.0000	223.4	190.8	0.0000	0.0000	223.2	182.2	0.0000	0.0000	223.2	183.5	0.0000	0.0000	223.4	194.3	0.0000	0.0000
229.3	185.9	0.0000	0.0000	229.6	192.4	0.0000	0.0000	229.4	184.4	0.0000	0.0000	229.4	184.4	0.0000	0.0000	229.6	194.2	0.0000	0.0000
235.5	187.5	0.0000	0.0000	235.8	194.7	0.0000	0.0000	235.6	186.2	0.0000	0.0000	235.6	187.5	0.0000	0.0000	235.8	196.5	0.0000	0.0000
241.7	189.4	0.0000	0.0000	242.0	196.5	0.0000	0.0000	241.8	187.8	0.0000	0.0000	241.8	188.8	0.0000	0.0000	242.0	198.2	0.0000	0.0000
247.9	192.1	0.0000	0.0000	248.2	198.4	0.0000	0.0000	248.0	190.0	0.0000	0.0000	248.0	190.2	0.0000	0.0000	248.2	199.8	0.0000	0.0000
254.1	193.6	0.0000	0.0000	254.4	201.0	0.0000	0.0000	254.2	191.7	0.0000	0.0000	254.2	192.3	0.0000	0.0000	254.4	202.6	0.0000	0.0000
260.3	195.3	0.0000	0.0000	260.6	201.9	0.0000	0.0000	260.4	193.6	0.0000	0.0000	260.4	193.4	0.0000	0.0000	260.6	203.2	0.0000	0.0000
266.5	196.3	0.0000	0.0000	266.8	204.4	0.0000	0.0000	266.6	195.3	0.0000	0.0000	266.6	196.0	0.0000	0.0000	266.8	204.8	0.0000	0.0000
272.7	198.8	0.0000	0.0000	273.0	206.3	0.0000	0.0000	272.8	197.1	0.0000	0.0000	272.8	197.8	0.0000	0.0000	273.0	206.4	0.0000	0.0000
278.9	200.3	0.0000	0.0000	279.2	207.6	0.0000	0.0000	279.0	199.0	0.0000	0.0000	279.0	199.6	0.0000	0.0000	279.2	208.1	0.0000	0.0000
285.1	202.4	0.0000	0.0000	285.4	209.3	0.0000	0.0000	285.2	201.2	0.0000	0.0000	285.2	201.5	0.0000	0.0000	285.4	209.9	0.0000	0.0000
291.3	204.1	0.0000	0.0000	291.6	211.4	0.0000	0.0000	291.4	202.2	0.0000	0.0000	291.4	203.5	0.0000	0.0000	291.6	211.7	0.0000	0.0000
297.5	205.9	0.0000	0.0000	297.8	212.5	0.0000	0.0000	297.6	204.4	0.0000	0.0000	297.6	204.9	0.0000	0.0000	297.8	213.4	0.0000	0.0000
303.7	207.8	0.0000	0.0000	304.0	213.9	0.0000	0.0000	303.8	207.1	0.0000	0.0000	303.8	206.8	0.0000	0.0000	304.0	214.6	0.0000	0.0000
309.9	208.9	0.0000	0.0000	310.3	217.3	0.0000	0.0000	310.0	207.6	0.0000	0.0000	310.0	208.3	0.0000	0.0000	310.2	216.3	0.0000	0.0000
316.1	210.7	0.0000	0.0000	316.5	216.8	0.0000	0.0000	316.2	209.0	0.0000	0.0000	316.2	210.0	0.0000	0.0000	316.4	218.1	0.0000	0.0000
322.3	212.3	0.0000	0.0000	322.6	219.4	0.0000	0.0000	322.4	210.7	0.0000	0.0000	322.4	211.4	0.0000	0.0000	322.6	219.8	0.0000	0.0000
328.5	213.9	0.0000	0.0000	328.9	220.7	0.0000	0.0000	328.6	212.7	0.0000	0.0000	328.6	213.0	0.0000	0.0000	328.9	221.5	0.0000	0.0000
334.7	215.8	0.0000	0.0000	335.1	223.3	0.0000	0.0000	334.8	213.4	0.0000	0.0000	334.8	214.3	0.0000	0.0000	335.1	222.9	0.0000	0.0000
340.8	217.0	0.0000	0.0000	341.3	223.0	0.0000	0.0000	341.0	215.5	0.0000	0.0000	341.0	215.8	0.0000	0.0000	341.3	224.2	0.0000	0.0000
347.1	218.9	0.0000	0.0000	347.5	225.3	0.0000	0.0000	347.2	216.3	0.0000	0.0000	347.2	217.6	0.0000	0.0000	347.5	225.9	0.0000	0.0000
353.2	220.3	0.0000	0.0000	353.7	226.1	0.0000	0.0000	353.4	218.5	0.0000	0.0000	353.4	219.0	0.0000	0.0000	353.7	227.2	0.0000	0.0000
359.4	221.9	0.0000	0.0000	359.9	227.8	0.0000	0.0000	359.6	219.2	0.0000	0.0000	359.6	220.5	0.0000	0.0000	359.9	228.9	0.0000	0.0000
365.6	223.4	0.0000	0.0000	366.1	228.7	0.0000	0.0000	365.8	221.4	0.0000	0.0000	365.8	222.1	0.0000	0.0000	366.1	230.3	0.0000	0.0000
371.8	224.8	0.0000	0.0000	372.3	230.4	0.0000	0.0000	372.0	222.3	0.0000	0.0000	372.0	223.6	0.0000	0.0000	372.3	231.8	0.0000	0.0000
378.0	226.0	0.0000	0.0000	378.5	231.8	0.0000	0.0000	378.2	223.9	0.0000	0.0000	378.2	224.8	0.0000	0.0000	378.5	233.5	0.0000	0.0000
384.2	227.4	0.0000	0.0000	384.7	233.2	0.0000	0.0000	384.4	225.7	0.0000	0.0000	384.4	226.4	0.0000	0.0000	384.7	234.7	0.0000	0.0000
390.4	229.5	0.0000	0.0000	390.9	234.8	0.0000	0.0000	390.6	227.0	0.0000	0.0000	390.6	227.8	0.0000	0.0000	390.9	235.9	0.0000	0.0000
396.6	230.5	0.0000	0.0000	397.1	236.4	0.0000	0.0000	396.8	228.7	0.0000	0.0000	396.8	229.1	0.0000	0.0000	397.1	237.4	0.0000	0.0000
402.8	232.7	0.0000	0.0000	403.3	238.2	0.0000	0.0000	403.0	229.8	0.0000	0.0000	403.0	230.4	0.0000	0.0000	403.3	239.3	0.0000	0.0000
409.0	233.4	0.0000	0.0000	409.5	239.7	0.0000	0.0000	409.2	231.0	0.0000	0.0000	409.2	232.3	0.0000	0.0000	409.5	241.0	0.0000	0.0000
415.2	235.1	0.0000	0.0000	415.7	240.8	0.0000	0.0000	415.4	231.9	0.0000	0.0000	415.4	233.5	0.0000	0.0000	415.7	242.4	0.0000	0.0000
421.4	236.4	0.0000	0.0000	421.9	242.1	0.0000	0.0000	421.6	233.7	0.0000	0.0000	421.6	234.8	0.0000	0.0000	421.9	243.7	0.0000	0.0000
427.6	237.4	0.0000	0.0000	428.1	243.7	0.0000	0.0000	427.8	235.5	0.0000	0.0000	427.8	236.2	0.0000	0.0000	428.1	244.8	0.0000	0.0000
433.8	239.3	0.0000	0.0000	434.3	245.5	0.0000	0.0000	434.0	236.6	0.0000	0.0000	434.0	237.6	0.0000	0.0000	434.3	246.6	0.0000	0.0000
440.1	240.4	0.0000	0.0000	440.5	246.3	0.0000	0.0000	440.2	237.9	0.0000	0.0000	440.2	238.6	0.0000	0.0000	440.6	247.3	0.0000	0.0000
446.2	241.6	0.0000	0.0000	446.7	248.0	0.0000	0.0000	446.4	238.9	0.0000	0.0000	446.4	240.1	0.0000	0.0000	446.7	249.0	0.0000	0.0000
452.4	242.7	0.0000	0.0000	452.9	249.0	0.0000	0.0000	452.6	240.9	0.0000	0.0000	452.6	241.6	0.0000	0.0000	453.0	250.1	0.0000	0.0000
458.6	244.2	0.0000	0.0000	459.2	250.1	0.0000	0.0000	458.8	242.0	0.0000	0.0000	458.8	242.4	0.0000	0.0000	459.2	252.3	0.0000	0.0000
464.8	245.9	0.0000	0.0000	465.4	252.1	0.0000	0.0000	465.0	243.0	0.0000	0.0000	465.0	244.0	0.0000	0.0000	465.4	254.8	0.0000	0.0000
471.0	247.0	0.0000	0.0000	471.5	254.4	0.0000	0.0000	471.2	245.7	0.0000	0.0000	471.2	245.8	0.0000	0.0000	471.6	257.9	0.0000	0.0000
477.2	248.9	0.0000	0.0000	477.8	257.2	0.0000	0.0000	477.4	248.1	0.0000	0.0000	477.4	248.1	0.0000	0.0000	477.8	260.9	0.0000	0.0000
483.4	251.3	0.0000	0.0000	484.0	260.3	0.0000	0.0000	483.6	251.2	0.0000	0.0000	483.6	251.4	0.0000	0.0000	484.0	264.0	0.0000	0.0000
489.6	254.2	0.0000	0.0000	490.2	263.5	0.0000	0.0000	489.8	253.8	0.0000	0.0000	489.7	254.1	0.0000	0.0000	490.2	266.9	0.0000	0.0000
495.8	257.3	0.0000	0.0000	496.4	266.3	0.0000	0.0000	496.0	256.7	0.0000	0.0000	496.0	256.8	0.0000	0.0000	496.4	269.9	0.0000	0.0000
502.0	260.0	0.0000	0.0000	502.6	269.1	0.0000	0.0000	502.2	259.3	0.0000	0.0000	502.2	259.7	0.0000	0.0000	502.6	273.1	0.0000	0.0000
508.2	263.0	0.0000	0.0000	508.8	272.2	0.0000	0.0000	508.4	262.2	0.0000	0.0000	508.3	262.4	0.0000	0.0000	508.8	276.0	0.0000	0.0000
514.4	265.8	0.0000	0.0000	515.0	275.1	0.0000	0.0000	514.6	265.0	0.0000	0.0000	514.5	266.0	0.0000	0.0000	515.0	279.7	0.0000	0.0000
520.6	268.8	0.0000	0.0000	521.2	278.3	0.0000	0.0000	520.8	267.8	0.0000	0.0000	520.7	268.7	0.0000	0.0000	521.2	282.0	0.0000	0.0000
526.8	271.7	0.0000	0.0000	527.4	281.3	0.0000	0.0000	527.0	270.7	0.0000	0.0000	526.9	271.7	0.0000	0.0000	527.4	285.1	0.0000	0.0000
533.0	274.7	0.0000	0.0000	533.6	284.0	0.0000	0.0000	533.2	273.5	0.0000	0.0000	533.1	274.6	0.0000	0.0000	533.6	287.7	0.0000	0.0000
539.2	277.6	0.0000	0.0000	539.8	287.2	0.0000	0.0000	539.4	276.4	0.0000	0.0000	539.3	277.4	0.0000	0.0000	539.8	290.8	0.0000	0.0000
545.4	280.5	0.0000	0.0000	546.0	290.2	0.0000	0.0000	545.5	279.6	0.0000	0.0000	545.5	280.3	0.0000	0.0000	546.0	293.6	0.0000	0.0000
551.6	283.4	0.0000	0.0000	552.2	293.1	0.0000	0.0000	551.7	282.1	0.0000	0.0000	551.7	283.1	0.0000	0.0000	552.2	296.7	0.0000	0.0000
557.8	286.3	0.0000	0.0000	558.4	296.0	0.0000	0.0000	557.9	284.4	0.0000	0.0000	557.9	286.1	0.0000	0.0000	558.4	300.8	0.0000	0.0000
564.0	289.6	0.0000	0.0000	564.6	299.1	0.0000	0.0000	564.1	287.8	0.0000	0.0000	564.1	288.8	0.0000	0.0000	564.6	303.1	0.0000	0.0000
570.2	292.8	0.0000	0.0000	570.8	302.3	0.0000	0.0000	570.3	290.9	0.0000	0.0000	570.3	291.8	0.0000	0.0000	570.9	306.5	0.0001	0.0000
576.4	295.0	0.0001	0.0000	577.0	305.7	0.0000	0.0000	576.5	293.6	0.0000	0.0000	576.5	295.4	0.0000	0.0000	577.1	309.5	0.0001	0.0000
582.5	298.6	0.0001	0.0000	583.2	307.7	0.0000	0.0000	582.7	296.7	0.0001	0.0000	582.7	298.2	0.0000	0.0000	583.3	313.1	0.0001	0.0000
588.7	301.5	0.0001	0.0000	589.4	310.9	0.0000	0.0000	588.9	299.1	0.0001	0.0000	588.9	301.2	0.0000	0.0000	589.5	315.3	0.0001	0.0000
594.9	303.6	0.0001	0.0000	595.6	313.8	0.0000	0.0000	595.1	302.2	0.0001	0.0000	595.1	302.9	0.0001	0.0000	595.7	318.5	0.0001	0.0000
601.1	306.8	0.0001	0.0000	601.8	316.6	0.0000	0.0000	601.3	305.0	0.0001	0.0000	601.3	306.1	0.0000	0.0000	601.9	321.5	0.0001	0.0000
607.3	309.9	0.0001	0.0000	608.1	320.0	0.0000	0.0000	607.5	307.9	0.0001	0.0000	607.5	309.1	0.0000	0.0000	608.1	324.5	0.0001	0.0000
613.6	312.8	0.0001	0.0000	614.3	323.0	0.0000	0.0000	613.7	310.2	0.0001	0.0000	613.7	312.1	0.0001	0.0000	614.3	327.5	0.0001	0.0000
619.8	315.9	0.0001	0.0000	620.4	325.9	0.0001	0.0000	619.9	313.3	0.0001	0.0000	619.9	314.9	0.0001	0.0000	620.5	330.6	0.0001	0.0000

Table 5 Results of temperature-programmed open system pyrolysis (continued)

626.0	318.8	0.0001	0.0000	626.7	329.1	0.0000	0.0000	626.1	316.7	0.0001	0.0000	626.1	317.8	0.0001	0.0000	626.7	333.7	0.0001	0.0000
632.2	321.7	0.0002	0.0000	632.9	332.1	0.0001	0.0000	632.3	319.4	0.0001	0.0000	632.3	320.9	0.0001	0.0000	632.9	336.7	0.0001	0.0000
638.4	324.8	0.0002	0.0000	639.1	335.0	0.0001	0.0000	638.5	322.3	0.0001	0.0000	638.5	323.6	0.0001	0.0000	639.1	339.5	0.0002	0.0000
644.6	327.7	0.0002	0.0000	645.3	338.7	0.0001	0.0000	644.7	325.1	0.0001	0.0000	644.7	326.7	0.0001	0.0000	645.3	342.8	0.0002	0.0000
650.8	330.6	0.0003	0.0000	651.5	341.8	0.0001	0.0000	650.9	328.2	0.0002	0.0000	650.9	329.5	0.0001	0.0000	651.5	345.6	0.0002	0.0000
657.0	333.5	0.0002	0.0000	657.7	344.7	0.0001	0.0000	657.1	331.0	0.0002	0.0000	657.1	332.5	0.0001	0.0000	657.7	348.7	0.0002	0.0000
663.2	336.7	0.0004	0.0000	663.9	347.7	0.0002	0.0000	663.3	333.9	0.0002	0.0000	663.3	335.4	0.0001	0.0000	663.9	351.8	0.0003	0.0000
669.4	339.6	0.0004	0.0000	670.1	350.8	0.0002	0.0000	669.5	336.9	0.0002	0.0000	669.5	338.3	0.0002	0.0000	670.1	354.7	0.0003	0.0000
675.6	342.5	0.0005	0.0000	676.3	353.8	0.0002	0.0000	675.7	339.5	0.0002	0.0000	675.7	341.3	0.0002	0.0000	676.3	357.8	0.0004	0.0000
681.8	345.4	0.0005	0.0000	682.5	356.9	0.0002	0.0000	681.9	342.5	0.0003	0.0000	681.9	344.3	0.0002	0.0000	682.6	360.7	0.0005	0.0000
688.0	348.6	0.0007	0.0000	688.7	359.9	0.0002	0.0000	688.1	345.5	0.0004	0.0000	688.1	347.1	0.0003	0.0000	688.8	363.9	0.0006	0.0000
694.2	351.4	0.0008	0.0000	694.9	363.0	0.0003	0.0000	694.3	349.0	0.0005	0.0000	694.3	350.1	0.0003	0.0000	695.0	366.9	0.0008	0.0000
700.3	354.4	0.0010	0.0000	701.1	365.8	0.0004	0.0000	700.5	351.8	0.0006	0.0000	700.5	353.0	0.0003	0.0000	701.2	369.9	0.0009	0.0000
706.5	357.3	0.0012	0.0000	707.3	368.8	0.0004	0.0000	706.7	355.0	0.0006	0.0000	706.7	355.9	0.0004	0.0000	707.4	372.9	0.0011	0.0000
712.7	360.4	0.0014	0.0000	713.5	371.7	0.0004	0.0000	712.9	357.6	0.0008	0.0000	712.9	358.6	0.0004	0.0000	713.6	375.9	0.0014	0.0000
718.9	363.3	0.0018	0.0000	719.7	374.7	0.0006	0.0000	719.1	360.7	0.0010	0.0000	719.1	361.9	0.0005	0.0000	719.8	379.0	0.0017	0.0000
725.1	366.3	0.0022	0.0000	725.9	377.8	0.0006	0.0000	725.3	363.6	0.0011	0.0000	725.3	364.8	0.0006	0.0000	726.0	381.9	0.0021	0.0000
731.4	369.3	0.0026	0.0000	732.1	380.7	0.0007	0.0000	731.5	366.5	0.0014	0.0000	731.5	367.8	0.0007	0.0000	732.2	385.2	0.0027	0.0000
737.5	372.1	0.0031	0.0000	738.3	384.1	0.0009	0.0000	737.7	369.4	0.0017	0.0000	737.7	370.6	0.0007	0.0000	738.4	388.1	0.0033	0.0000
743.7	375.2	0.0038	0.0000	744.5	387.0	0.0011	0.0000	743.9	372.3	0.0021	0.0000	743.9	373.5	0.0009	0.0000	744.6	390.9	0.0039	0.0000
749.9	378.3	0.0046	0.0000	750.7	389.8	0.0012	0.0000	750.1	375.1	0.0025	0.0000	750.1	377.1	0.0011	0.0000	750.8	394.1	0.0049	0.0000
756.1	381.2	0.0056	0.0000	757.0	393.1	0.0017	0.0000	756.3	378.2	0.0031	0.0000	756.3	380.1	0.0012	0.0000	757.0	397.2	0.0060	0.0000
762.3	384.1	0.0068	0.0000	763.1	396.0	0.0018	0.0000	762.5	380.8	0.0037	0.0000	762.5	383.0	0.0015	0.0000	763.2	400.1	0.0074	0.0000
768.5	387.2	0.0082	0.0000	769.4	399.1	0.0022	0.0000	768.7	384.2	0.0044	0.0000	768.7	385.9	0.0017	0.0000	769.4	403.1	0.0090	0.0000
774.7	390.2	0.0098	0.0000	775.6	402.3	0.0028	0.0000	774.9	387.0	0.0054	0.0000	774.9	388.9	0.0021	0.0000	775.6	406.3	0.0109	0.0000
780.9	393.1	0.0117	0.0000	781.8	405.1	0.0033	0.0000	781.1	389.8	0.0062	0.0000	781.1	391.9	0.0025	0.0000	781.8	409.4	0.0131	0.0000
787.1	396.1	0.0139	0.0000	788.0	408.1	0.0040	0.0000	787.3	393.0	0.0078	0.0000	787.3	394.8	0.0029	0.0000	788.0	412.3	0.0158	0.0000
793.3	399.1	0.0164	0.0000	794.2	411.1	0.0049	0.0000	793.5	395.8	0.0094	0.0000	793.5	397.8	0.0035	0.0000	794.2	416.0	0.0197	0.0000
799.5	402.1	0.0190	0.0000	800.4	414.1	0.0061	0.0000	799.7	398.8	0.0108	0.0000	799.7	400.7	0.0042	0.0000	800.5	418.9	0.0235	0.0000
805.7	405.3	0.0221	0.0000	806.6	417.3	0.0074	0.0000	805.9	401.7	0.0134	0.0000	805.9	403.7	0.0050	0.0000	806.7	422.0	0.0278	0.0000
811.9	408.2	0.0254	0.0000	812.8	420.1	0.0089	0.0000	812.1	404.6	0.0163	0.0000	812.1	406.7	0.0059	0.0000	812.9	425.3	0.0327	0.0000
818.1	411.2	0.0288	0.0000	819.0	423.1	0.0106	0.0000	818.3	407.7	0.0182	0.0000	818.3	409.8	0.0070	0.0000	819.1	428.1	0.0385	0.0000
824.3	414.1	0.0321	0.0000	825.2	426.3	0.0127	0.0000	824.5	410.5	0.0228	0.0000	824.5	412.7	0.0085	0.0000	825.3	431.1	0.0443	0.0000
830.5	417.2	0.0354	0.0000	831.4	429.3	0.0152	0.0000	830.7	413.3	0.0254	0.0000	830.7	415.5	0.0102	0.0000	831.5	434.0	0.0510	0.0000
836.7	420.0	0.0388	0.0000	837.6	432.3	0.0179	0.0000	836.9	416.5	0.0323	0.0000	836.9	418.4	0.0121	0.0000	837.7	437.2	0.0586	0.0000
842.9	423.1	0.0413	0.0000	843.8	435.2	0.0210	0.0000	843.0	419.2	0.0353	0.0000	843.1	421.6	0.0144	0.0000	843.9	440.2	0.0663	0.0000
849.1	425.9	0.0443	0.0000	850.0	438.2	0.0242	0.0000	849.2	422.3	0.0373	0.0000	849.3	424.4	0.0172	0.0000	850.1	443.1	0.0746	0.0000
855.3	428.9	0.0473	0.0000	856.2	441.4	0.0277	0.0000	855.4	425.2	0.0460	0.0000	855.5	427.4	0.0204	0.0000	856.3	446.3	0.0831	0.0000
861.5	432.1	0.0505	0.0000	862.4	444.3	0.0317	0.0000	861.6	428.2	0.0509	0.0000	861.7	430.3	0.0242	0.0000	862.5	449.3	0.0919	0.0000
867.7	434.9	0.0540	0.0000	868.6	447.5	0.0358	0.0000	867.8	431.1	0.0595	0.0000	867.9	433.4	0.0285	0.0000	868.7	452.2	0.1003	0.0000
873.9	437.9	0.0569	0.0000	874.8	450.4	0.0396	0.0000	874.0	434.0	0.0661	0.0000	874.1	436.3	0.0336	0.0000	875.0	455.3	0.1086	0.0000
880.1	441.0	0.0600	0.0000	881.0	454.0	0.0444	0.0000	880.2	437.0	0.0686	0.0000	880.3	439.2	0.0389	0.0000	881.1	458.4	0.1155	0.0000
886.4	443.9	0.0626	0.0000	887.3	456.8	0.0482	0.0000	886.4	440.0	0.0758	0.0000	886.5	442.4	0.0449	0.0000	887.4	461.3	0.1221	0.0000
892.5	446.9	0.0649	0.0000	893.4	459.8	0.0519	0.0000	892.6	443.0	0.0787	0.0000	892.7	445.1	0.0516	0.0000	893.6	464.5	0.1276	0.0000
898.7	449.9	0.0675	0.0000	899.7	462.9	0.0552	0.0000	898.8	445.9	0.0811	0.0000	898.9	448.0	0.0580	0.0000	899.8	467.5	0.1333	0.0000
904.9	453.1	0.0694	0.0000	905.9	466.1	0.0579	0.0000	905.0	448.8	0.0932	0.0000	905.1	451.1	0.0650	0.0000	906.0	470.5	0.1366	0.0000
911.1	456.0	0.0707	0.0000	912.1	469.0	0.0604	0.0000	911.2	451.8	0.0840	0.0000	911.3	454.0	0.0720	0.0000	912.2	473.5	0.1402	0.0000
917.3	459.0	0.0720	0.0000	918.3	472.1	0.0629	0.0000	917.4	454.7	0.0891	0.0000	917.5	457.0	0.0785	0.0000	918.4	476.7	0.1420	0.0000
923.5	462.0	0.0732	0.0000	924.5	475.1	0.0644	0.0000	923.6	457.6	0.0890	0.0000	923.7	460.0	0.0845	0.0000	924.6	479.5	0.1431	0.0000
929.7	465.0	0.0744	0.0000	936.9	481.1	0.0668	0.0000	929.8	461.3	0.0917	0.0000	929.9	463.0	0.0905	0.0000	930.8	482.7	0.1437	0.0000
935.9	468.1	0.0752	0.0000	943.1	484.1	0.0675	0.0000	936.0	464.2	0.0948	0.0000	936.1	466.1	0.0960	0.0000	937.0	485.3	0.1442	0.0000
942.1	470.9	0.0754	0.0000	955.5	490.3	0.0677	0.0000	942.2	467.2	0.0950	0.0000	942.3	468.7	0.0998	0.0000	943.2	488.5	0.1436	0.0000
948.3	474.0	0.0762	0.0000	961.7	493.3	0.0681	0.0000	948.4	470.0	0.0946	0.0000	948.5	471.7	0.1045	0.0000	949.4	491.6	0.1415	0.0000
954.6	476.9	0.0763	0.0000	967.9	496.1	0.0676	0.0000	954.6	473.1	0.0914	0.0000	954.7	474.7	0.1074	0.0000	955.6	494.7	0.1404	0.0000
960.7	480.0	0.0765	0.0000	974.1	499.2	0.0680	0.0000	960.8	476.3	0.0892	0.0000	960.9	477.8	0.1094	0.0000	961.8	497.8	0.1388	0.0000
966.9	483.0	0.0765	0.0000	980.3	502.3	0.0684	0.0000	967.0	478.9	0.0889	0.0000	967.1	480.7	0.1113	0.0000	968.0	500.7	0.1366	0.0000
973.1	486.0	0.0767	0.0000	986.5	505.2	0.0681	0.0000	973.2	481.9	0.0871	0.0000	973.3	483.7	0.1129	0.0000	974.2	503.8	0.1350	0.0000
979.3	488.9	0.0762	0.0000	992.7	508.2	0.0674	0.0000	979.4	484.9	0.0858	0.0000	979.5	486.6	0.1151	0.0000	980.4	506.8	0.1271	0.0000
985.5	491.9	0.0758	0.0000	998.9	511.3	0.0673	0.0000	985.6	487.7	0.0873	0.0000	985.7	489.6	0.1160	0.0000	986.6	509.8	0.1320	0.0000
991.7	494.8	0.0750	0.0000	1005.1	514.3	0.0657	0.0000	991.8	490.9	0.0917	0.0000	991.9	493.0	0.1172	0.0000	992.9	512.9	0.1296	0.0000
997.9	497.9	0.0744	0.0000	1011.4	517.3	0.0662	0.0000	998.0	493.8	0.0904	0.0000	998.1	496.0	0.1176	0.0000	999.1	515.9	0.1273	0.0000
1004.1	500.9	0.0736	0.0000	1017.6	520.2	0.0653	0.0000	1004.2	496.7	0.0906	0.0000	1004.3	499.0	0.1174	0.0000	1005.3	519.1	0.1249	0.0000
1010.3	503.9	0.0731	0.0000	1023.8	523.3	0.0641	0.0000	1010.4	499.6	0.0883	0.0000	1010.5	502.1	0.1167	0.0000	1011.5	521.9	0.1225	0.0000
1016.5	506.9	0.0722	0.0000	1030.0	526.4	0.0627	0.0000	1016.6	502.5	0.0869	0.0000	1016.7	504.9	0.1153	0.0000	1017.7	525.0	0.1213	0.0000
1022.7	510.0	0.0718	0.0000	1036.2	529.3	0.0614	0.0000	1022.8	505.5	0.0837	0.0000	1022.9	508.3	0.1143	0.0000	1023.9	528.0	0.1181	0.0000
1028.9	512.9	0.0705	0.0000	1042.4	532.4	0.0600	0.0000	1029.0	508.5	0.0841	0.0000	1029.1	510.9	0.1135	0.0000	1030.1	531.1	0.1148	0.0000
1035.1	516.0	0.0692	0.0000	1048.6	535.3	0.0590	0.0000	1035.2	511.5	0.0832	0.0000	1035.3	514.0	0.1129	0.0000	1036.3	534.6	0.1126	0.0000
1041.3	519.0	0.0680	0.0000	1054.8	538.3	0.0572	0.0000	1041.4	514.6	0.0853	0.0000	1041.5	517.0	0.1113	0.0000	1042.5	537.6	0.1098	0.0000
1047.5	521.8	0.0668	0.0000	1061.0	541.4	0.0549	0.0000	1047.6	517.4	0.0815	0.0000	1047.7	519.9	0.1099	0.0000	1048.7	540.6	0.1072	0.0000
1053.7	524.9	0.0658	0.0000	1067.2	544.4	0.0548	0.0000	1053.8	520.3	0.0786	0.0000	1053.9	522.9	0.1081	0.0000	1054.9	543.7	0.1054	0.0000
1059.9	527.7	0.0642	0.0000	1073.4	547.4	0.0530	0.0000	1060.0	523.4	0.0770	0.0000	1060.1	525.9	0.1067	0.0000	1061.1	546.7	0.1027	0.0000
1066.1	531.0	0.0627	0.0000	1079.6	550.2	0.0510	0.0000	1066.2	526.3	0.0739	0.0000	1066.3	528.8	0.1049	0.0000	1067.3	549.8	0.1004	0.0000
1072.3	534.0	0.0610	0.0000	1085.8	553.4	0.0502	0.0000	1072.4	529.3	0.0721	0.0000	1072.5	532.0	0.1021	0.0000	1073.5	552.8	0.0983	0.0000
1078.5	537.0	0.0593	0.0000	1092.0	556.4	0.0491	0.0000	1078.6	532.3	0.0679	0.0000	1078.7	534.9	0.0998	0.0000	1079.7	555.8	0.0964	0.0000
1084.7	539.9	0.0580	0.0000	1098.2	559.4	0.0466	0.0000	1084.8	535.5	0.0648	0.0000	1084.9	537.8	0.0975	0.0000	1085.9	558.9	0.0933	0.0000
1090.9	542.8	0.0561	0.0000	1104.4	562.2	0.0446	0.0000	1091.0	538.3	0.0655	0.0000	1091.1	540.7	0.0951	0.0000	1092.2	561.8	0.0900	0.0000
1097.1	545.9	0.0543	0.0000	1110.6	565.4	0.0431	0.0000	1097.2	541.3	0.0611	0.0000	1097.3	543.7	0.0918	0.0000	1098.3	564.9	0.0871	0.0000
1103.3	548.9	0.0525	0.0000	1116.8	568.4	0.0413	0.0000	1103.4	544.1	0.0595	0.0000	1103.5	546.8	0.0886	0.0000	1104.5	568.0	0.0842	0.0000
1109.5	551.8	0.0508	0.0000	1123.1	571.8	0.0393	0.0000	1109.6	547.2	0.0581	0.0000	1109.7	549.8	0.0860	0.0000	1110.8	570.8	0.0811	0.0000
1115.7	554.9	0.0491	0.0000	1129.2	575.0	0.0379	0.0000	1115.8	550.2	0.0562	0.0000	1115.9	552.7	0.0824	0.0000	1117.0	574.0	0.0781	0.0000
1121.9	557.8	0.0473	0.0000	1135.5	578.1	0.0360	0.0000	1122.0	553.1	0.0527	0.0000	1122.1	555.9	0.0794	0.0000	1123.2	577.0	0.0751	0.0000
1128.1	560.8	0.0454	0.0000	1141.7	580.9	0.0339	0.0000	1128.2	556.1	0.0514	0.0000	1128.3	558.7	0.0761	0.0000	1129.4	580.0	0.0719	0.0000
1134.3	563.7	0.0437	0.0000	1147.8	583.9	0.0329	0.0000	1134.4	559.1	0.0507	0.0000	1134.5	561.6	0.0717	0.0000	1135.6	583.1	0.0690	0.0000
1140.5	566.7	0.0419	0.0000	1154.1	587.1	0.0312	0.0001	1140.6	562.0	0.0470	0.0000	1140.7	564.7	0.0691	0.0000	1141.8	586.0	0.0659	0.0000
1146.7	569.7	0.0400	0.0000	1160.3	590.0	0.0292	0.0000	1146.8	565.0	0.0449	0.0000	1146.9	567.6	0.0651	0.0000	1148.0	589.1	0.0630	0.0001
1152.9	572.8	0.0383	0.0000	1166.4	593.0	0.0279	0.0000	1153.0	568.2	0.0430	0.0000	1153.1	570.9	0.0626	0.0000	1154.2	592.1	0.0600	0.0000
1159.1	575.9	0.0366	0.0000	1172.7	595.9	0.0263	0.0000	1159.2	571.1	0.0398	0.0000	1159.3	573.6	0.0600	0.0000	1160.4	595.1	0.0570	0.0001
1165.3	578.8	0.0353	0.0000	1178.9	599.1	0.0249	0.0000	1165.4	574.2	0.0379	0.0000	1165.5	576.6	0.0566	0.0001	1166.6	598.2	0.0542	0.0001
1171.5	581.7	0.0338	0.0000	1185.0	602.2	0.0236	0.0000	1171.6	577.7	0.0370	0.0001	1171.7	579.6	0.0536	0.0001	1172.8	601.1	0.0512	0.0001
1177.7	584.5	0.0323	0.0000	1191.3	605.1	0.0221	0.0000	1177.8	580.6	0.0339	0.0001	1177.9	582.6	0.0517	0.0001	1179.0	604.2	0.0484	0.0001
1183.9	587.4	0.0309	0.0000	1197.5	608.2	0.0211	0.0000	1184.1	583.7	0.0321	0.0001	1184.1	585.5	0.0493	0.0001	1185.2	607.2	0.0454	0.0000
1190.1	590.6	0.0294	0.0000	1203.6	611.2	0.0193	0.0000	1190.2	586.7	0.0303	0.0001	1190.3	588.6	0.0470	0.0001	1191.4	610.3	0.0426	0.0003
1196.3	593.4	0.0281	0.0000	1209.9	614.1	0.0186	0.0000	1196.4	589.6	0.0280	0.0001	1196.5	591.4	0.0446	0.0002	1197.6	613.4	0.0400	0.0003
1202.5	596.5	0.0270	0.0000	1216.1	617.3	0.0177	0.0000	1202.6	592.6	0.0263	0.0001	1202.7	594.8	0.0425	0.0002	1203.8	616.2	0.0375	0.0005
1208.7	599.6	0.0259	0.0001	1222.3	620.3	0.0169	0.0000	1208.8	595.6	0.0236	0.0001	1208.9	597.5	0.0407	0.0003	1210.0	619.4	0.0351	0.0005
1214.9	602.5	0.0247	0.0001	1228.5	623.4	0.0162	0.0000	1215.0	598.7	0.0233	0.0002	1215.1	600.7	0.0384	0.0003	1216.2	622.3	0.0330	0.0004
1221.1	605.3	0.0235	0.0001	1234.7	626.3	0.0148	0.0000	1221.2	601.8	0.0223	0.0002	1221.3	603.4	0.0364	0.0003	1222.4	625.4	0.0311	0.0006
1227.3	608.4	0.0225	0.0002	1240.9	629.2	0.0143	0.0000	1227.4	604.7	0.0220	0.0002	1227.5	606.9	0.0347	0.0004	1228.7	628.3	0.0291	0.0007
1233.5	611.5	0.0215	0.0002	1247.1	632.4	0.0138	0.0000	1233.6	607.7	0.0204	0.0002	1233.7	610.2	0.0331	0.0004	1234.9	631.4	0.0271	0.0008
1239.7	614.5	0.0208	0.0003	1253.3	635.4	0.0131	0.0000	1239.8	610.7	0.0198	0.0003	1239.9	613.0	0.0320	0.0005	1241.1	634.4	0.0257	0.0010
1245.9	617.4	0.0201	0.0003	1259.5	638.5	0.0127	0.0000	1246.0	613.7	0.0189	0.0003	1246.1	616.0	0.0307	0.0006	1247.3	637.4	0.0242	0.0010
1252.1	620.6	0.0192	0.0004	1265.7	641.3	0.0121	0.0002	1252.2	616.7	0.0187	0.0004	1252.3	619.0	0.0298	0.0007	1253.5	640.5	0.0227	0.0012
1258.3	623.5	0.0186	0.0005	1271.9	644.3	0.0118	0.0001	1258.4	619.5	0.0174	0.0004	1258.5	622.1	0.0287	0.0007	1259.7	643.5	0.0215	0.0013
1264.5	626.6	0.0180	0.0006	1278.1	647.1	0.0111	0.0001	1264.6	622.6	0.0170	0.0006	1264.7	625.1	0.0276	0.0009	1265.9	646.4	0.0200	0.0014
1270.7	629.4	0.0171	0.0006	1284.3	650.3	0.0105	0.0000	1270.8	625.7	0.0158	0.0006	1270.9	628.0	0.0269	0.0010	1272.1	650.1	0.0186	0.0016
1276.9	632.5	0.0165	0.0007	1290.5	653.5	0.0102	0.0001	1277.0	628.7	0.0152	0.0007	1277.1	631.1	0.0261	0.0011	1278.3	653.0	0.0174	0.0018
1283.1	635.6	0.0160	0.0008	1296.7	656.3	0.0096	0.0002	1283.2	631.7	0.0147	0.0008	1283.3	634.1	0.0257	0.0013	1284.5	656.1	0.0165	0.0019
1289.3	638.7	0.0155	0.0010	1302.9	659.3	0.0097	0.0002	1289.4	634.6	0.0136	0.0008	1289.5	637.1	0.0250	0.0014	1290.7	659.0	0.0156	0.0021
1295.5	641.4	0.0152	0.0011	1309.1	662.3	0.0092	0.0003	1295.6	637.7	0.0133	0.0009	1295.7	640.1	0.0242	0.0015	1296.9	662.1	0.0146	0.0022
1301.7	644.4	0.0146	0.0012	1315.3	665.6	0.0086	0.0003	1301.8	641.0	0.0130	0.0011	1301.9	643.0	0.0237	0.0017	1303.1	665.2	0.0139	0.0024
1307.9	647.3	0.0144	0.0013	1321.5	668.4	0.0085	0.0004	1307.9	643.7	0.0123	0.0011	1308.1	646.1	0.0231	0.0019	1309.3	668.0	0.0133	0.0025
1314.1	650.4	0.0139	0.0015	1327.7	671.3	0.0080	0.0002	1314.1	646.6	0.0121	0.0013	1314.3	649.2	0.0225	0.0020	1315.5	671.1	0.0127	0.0026
1320.3	653.5	0.0135	0.0016	1333.9	674.3	0.0080	0.0003	1320.3	649.8	0.0115	0.0014	1320.5	652.2	0.0220	0.0023	1321.7	674.1	0.0121	0.0029

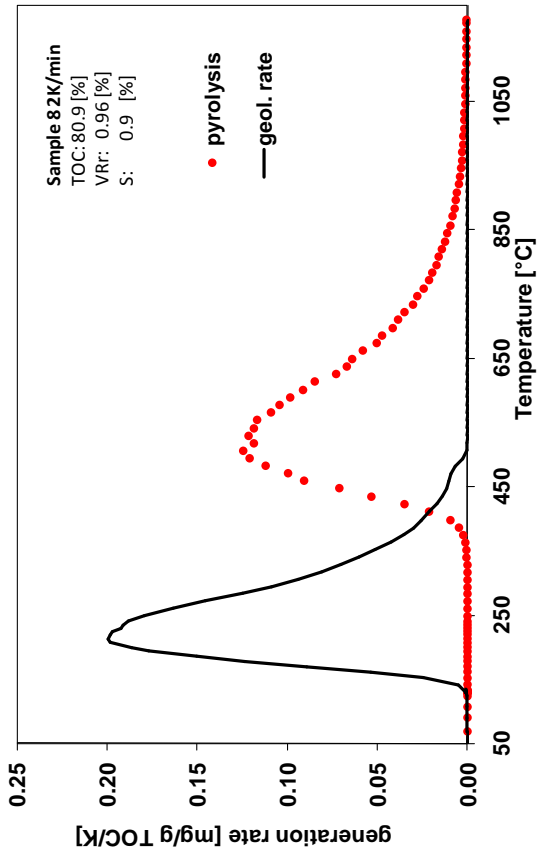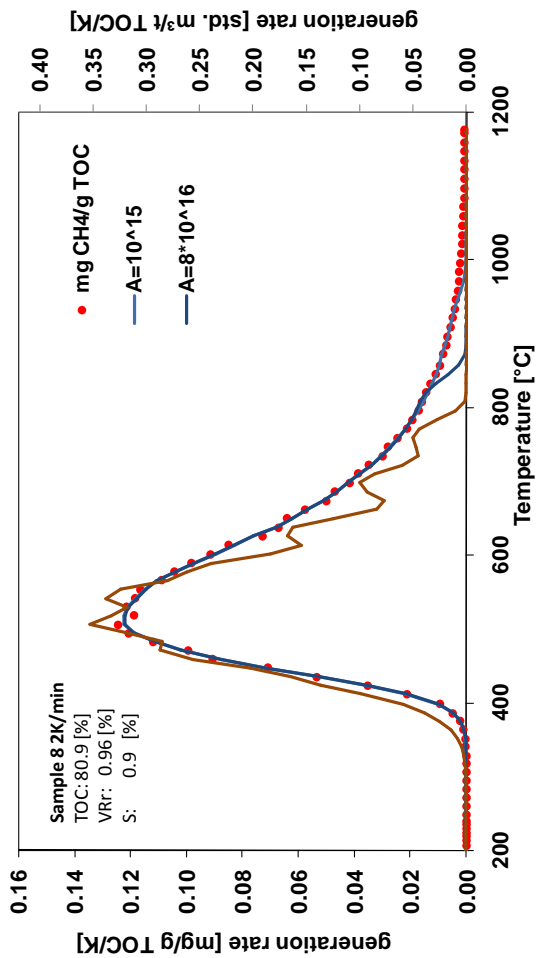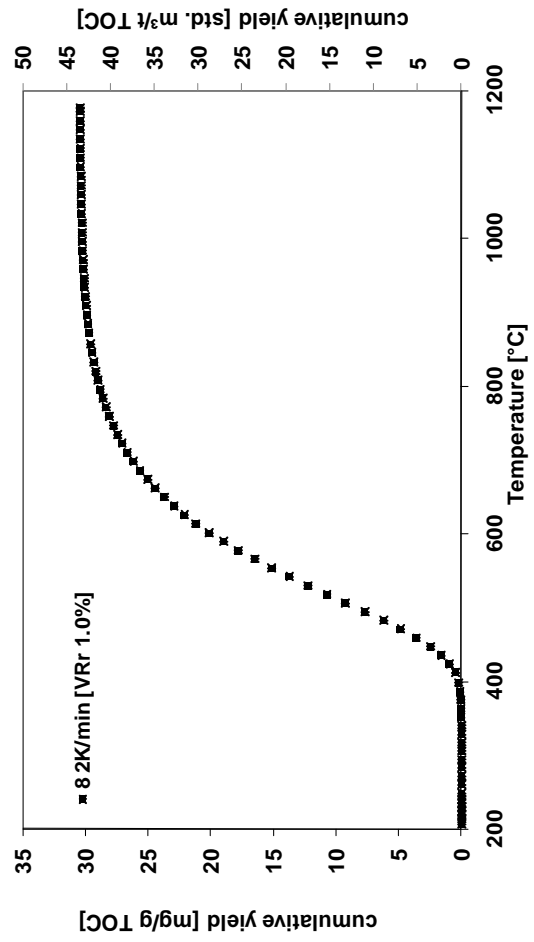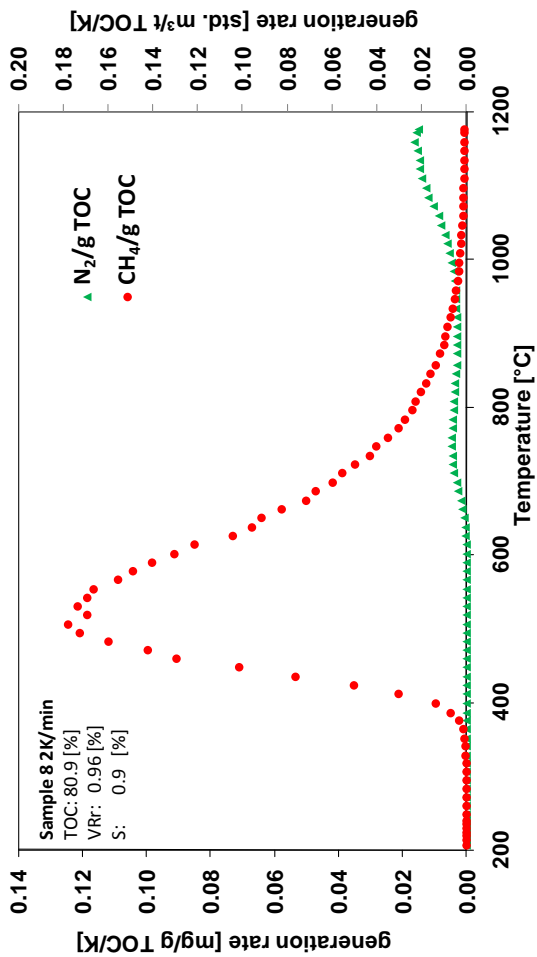|																			
1326.5	656.5	0.0131	0.0017	1340.1	677.6	0.0081	0.0003	1326.5	652.7	0.0113	0.0016	1326.7	655.1	0.0214	0.0024	1327.9	677.1	0.0115	0.0030
1332.7	659.5	0.0127	0.0019	1346.3	680.2	0.0074	0.0003	1332.7	655.8	0.0112	0.0017	1332.9	658.1	0.0209	0.0026	1334.1	680.1	0.0111	0.0032
1338.9	662.4	0.0124	0.0020	1352.5	683.3	0.0074	0.0006	1338.9	658.8	0.0103	0.0017	1339.1	661.0	0.0202	0.0028	1340.3	683.2	0.0104	0.0033
1345.1	665.5	0.0120	0.0022	1358.7	686.9	0.0074	0.0006	1345.1	661.8	0.0099	0.0018	1345.3	664.1	0.0197	0.0030	1346.6	686.2	0.0100	0.0034
1351.3	668.4	0.0118	0.0023	1364.9	690.0	0.0071	0.0005	1351.3	664.9	0.0094	0.0019	1351.5	667.1	0.0192	0.0033	1352.7	689.2	0.0095	0.0035
1357.5	671.4	0.0115	0.0024	1371.1	693.0	0.0068	0.0004	1357.5	668.0	0.0090	0.0020	1357.7	670.3	0.0185	0.0034	1359.0	692.2	0.0091	0.0037
1363.7	674.4	0.0112	0.0026	1377.3	696.0	0.0066	0.0005	1363.7	671.0	0.0093	0.0023	1363.9	673.2	0.0178	0.0036	1365.2	695.1	0.0086	0.0037
1369.9	677.3	0.0108	0.0027	1383.5	699.1	0.0069	0.0004	1369.9	673.7	0.0086	0.0023	1370.1	676.2	0.0172	0.0038	1371.4	698.2	0.0081	0.0039
1376.1	680.4	0.0104	0.0027	1389.7	701.9	0.0065	0.0005	1376.1	676.8	0.0084	0.0025	1376.3	679.4	0.0164	0.0040	1377.6	701.2	0.0076	0.0039
1382.3	683.4	0.0102	0.0029	1395.9	704.9	0.0065	0.0005	1382.3	679.8	0.0080	0.0026	1382.5	682.4	0.0156	0.0041	1383.8	704.1	0.0071	0.0039
1388.5	686.6	0.0099	0.0029	1402.1	707.8	0.0062	0.0006	1388.5	683.1	0.0078	0.0027	1388.7	685.2	0.0149	0.0043	1390.0	707.2	0.0067	0.0039
1394.7	689.5	0.0095	0.0029	1408.3	710.9	0.0070	0.0007	1394.7	685.9	0.0075	0.0028	1394.9	688.3	0.0139	0.0044	1396.2	710.2	0.0063	0.0041
1400.9	692.6	0.0093	0.0030	1414.5	714.1	0.0063	0.0005	1400.9	688.8	0.0067	0.0026	1401.1	691.3	0.0132	0.0045	1402.4	713.1	0.0059	0.0040
1407.1	695.6	0.0089	0.0030	1420.7	716.9	0.0065	0.0005	1407.1	692.6	0.0064	0.0027	1407.3	694.3	0.0125	0.0047	1408.6	716.2	0.0056	0.0041
1413.3	698.5	0.0086	0.0030	1426.9	720.1	0.0065	0.0005	1413.3	695.7	0.0059	0.0026	1413.5	697.3	0.0119	0.0049	1414.8	719.3	0.0053	0.0040
1419.4	701.6	0.0082	0.0030	1433.1	723.1	0.0064	0.0006	1419.5	698.6	0.0058	0.0028	1419.7	700.3	0.0112	0.0050	1421.0	722.2	0.0049	0.0039
1425.6	704.6	0.0079	0.0030	1439.3	726.1	0.0064	0.0006	1425.7	701.5	0.0055	0.0028	1425.9	703.5	0.0107	0.0051	1427.2	725.2	0.0047	0.0040
1431.9	707.6	0.0077	0.0030	1445.5	729.2	0.0063	0.0006	1431.9	704.8	0.0052	0.0028	1432.1	706.5	0.0102	0.0052	1433.4	728.3	0.0043	0.0039
1438.0	710.5	0.0074	0.0029	1451.7	732.0	0.0034	0.0003	1438.1	707.8	0.0048	0.0028	1438.3	709.5	0.0095	0.0052	1439.6	731.4	0.0040	0.0038
1444.2	713.8	0.0070	0.0028	1457.9	735.1	0.0035	0.0006	1444.3	710.5	0.0046	0.0028	1444.5	712.5	0.0088	0.0052	1445.8	734.2	0.0038	0.0038
1450.4	716.5	0.0068	0.0028	1464.1	738.2	0.0031	0.0007	1450.5	713.5	0.0044	0.0027	1450.7	715.4	0.0083	0.0052	1452.0	737.3	0.0036	0.0037
1456.6	719.7	0.0065	0.0027	1470.3	741.0	0.0025	0.0006	1456.7	716.8	0.0041	0.0027	1456.9	718.5	0.0079	0.0054	1458.2	740.3	0.0035	0.0037
1462.8	722.6	0.0063	0.0027	1476.5	744.1	0.0025	0.0005	1462.9	719.8	0.0040	0.0028	1463.1	721.6	0.0073	0.0054	1464.4	743.4	0.0032	0.0036
1469.0	725.7	0.0061	0.0026	1482.7	747.1	0.0027	0.0006	1469.1	722.9	0.0037	0.0027	1469.3	725.2	0.0067	0.0054	1470.6	746.4	0.0031	0.0036
1475.2	728.8	0.0060	0.0026	1488.9	750.2	0.0024	0.0006	1475.4	725.8	0.0035	0.0028	1475.5	728.1	0.0062	0.0055	1476.8	749.3	0.0030	0.0035
1481.4	731.7	0.0058	0.0024	1495.2	753.3	0.0020	0.0004	1481.6	728.9	0.0033	0.0027	1481.7	731.3	0.0058	0.0055	1483.0	752.3	0.0028	0.0034
1487.6	734.6	0.0057	0.0024	1501.3	756.2	0.0022	0.0006	1487.8	732.0	0.0032	0.0027	1487.9	734.1	0.0053	0.0056	1489.2	755.4	0.0027	0.0034
1493.8	737.8	0.0056	0.0023	1507.6	759.1	0.0021	0.0006	1494.0	735.0	0.0029	0.0026	1494.1	737.4	0.0049	0.0055	1495.5	758.5	0.0026	0.0033
1500.0	740.7	0.0055	0.0023	1513.8	762.2	0.0017	0.0004	1500.2	738.0	0.0028	0.0026	1500.3	740.2	0.0045	0.0055	1501.6	761.4	0.0025	0.0032
1506.2	743.8	0.0054	0.0022	1519.9	765.3	0.0019	0.0004	1506.4	741.2	0.0026	0.0026	1506.5	743.1	0.0043	0.0055	1507.8	764.5	0.0024	0.0031
1512.4	746.8	0.0053	0.0022	1526.2	768.2	0.0017	0.0004	1512.6	743.9	0.0025	0.0025	1512.7	746.4	0.0038	0.0054	1514.1	768.1	0.0024	0.0030
1518.6	749.8	0.0051	0.0021	1532.4	771.0	0.0019	0.0004	1518.8	747.2	0.0024	0.0026	1518.9	749.4	0.0035	0.0054	1520.3	771.3	0.0023	0.0029
1524.8	752.7	0.0052	0.0021	1538.5	774.1	0.0017	0.0004	1525.0	750.3	0.0022	0.0025	1525.1	752.5	0.0033	0.0054	1526.5	774.1	0.0021	0.0030
1531.0	756.0	0.0051	0.0020	1544.8	777.3	0.0017	0.0004	1531.2	753.3	0.0022	0.0025	1531.3	755.4	0.0031	0.0054	1532.7	777.2	0.0021	0.0028
1537.2	758.9	0.0050	0.0020	1551.0	780.2	0.0018	0.0004	1537.4	756.3	0.0021	0.0025	1537.5	758.3	0.0029	0.0054	1538.9	780.2	0.0020	0.0028
1543.4	761.9	0.0050	0.0020	1557.1	783.1	0.0017	0.0005	1543.6	759.4	0.0020	0.0024	1543.7	761.5	0.0027	0.0054	1545.1	783.2	0.0020	0.0026
1549.6	765.0	0.0049	0.0020	1563.4	786.0	0.0017	0.0003	1549.8	762.5	0.0017	0.0022	1549.9	764.4	0.0025	0.0054	1551.3	786.2	0.0017	0.0022
1555.8	767.9	0.0050	0.0020	1569.6	789.2	0.0018	0.0005	1556.0	765.4	0.0016	0.0021	1556.1	767.3	0.0023	0.0054	1557.5	789.1	0.0018	0.0023
1562.0	771.1	0.0051	0.0019	1575.8	792.4	0.0018	0.0004	1562.2	768.6	0.0017	0.0023	1562.3	770.6	0.0023	0.0055	1563.7	792.1	0.0019	0.0024
1568.2	773.8	0.0050	0.0019	1582.0	795.1	0.0018	0.0005	1568.4	771.4	0.0016	0.0024	1568.5	773.7	0.0020	0.0053	1569.9	795.2	0.0018	0.0022
1574.4	777.0	0.0050	0.0019	1588.2	798.2	0.0019	0.0005	1574.6	774.3	0.0016	0.0023	1574.7	776.7	0.0019	0.0054	1576.1	798.1	0.0017	0.0020
1580.6	780.0	0.0052	0.0019	1594.4	801.3	0.0017	0.0005	1580.8	777.7	0.0014	0.0022	1580.9	779.8	0.0017	0.0052	1582.3	801.2	0.0017	0.0019
1586.8	783.1	0.0052	0.0020	1600.6	804.9	0.0014	0.0004	1587.0	780.7	0.0013	0.0021	1587.1	782.8	0.0016	0.0052	1588.5	804.2	0.0017	0.0020
1593.0	786.1	0.0051	0.0019	1606.8	807.8	0.0014	0.0004	1593.2	783.9	0.0013	0.0021	1593.3	785.7	0.0016	0.0052	1594.7	807.2	0.0017	0.0019
1599.2	789.0	0.0053	0.0019	1613.0	810.9	0.0015	0.0004	1599.4	786.8	0.0013	0.0021	1599.5	788.8	0.0015	0.0052	1600.9	810.1	0.0017	0.0019
1605.4	792.1	0.0052	0.0019	1619.2	813.8	0.0014	0.0003	1605.6	789.8	0.0012	0.0020	1605.7	791.8	0.0013	0.0050	1607.1	813.0	0.0017	0.0018
1611.6	795.2	0.0052	0.0018	1625.4	816.8	0.0016	0.0004	1611.8	793.1	0.0011	0.0020	1611.9	794.9	0.0012	0.0050	1613.3	816.2	0.0018	0.0019
1617.8	798.1	0.0053	0.0018	1631.6	819.8	0.0016	0.0003	1618.0	796.0	0.0012	0.0020	1618.1	798.0	0.0012	0.0050	1619.5	819.1	0.0016	0.0017
1624.0	801.1	0.0055	0.0018	1637.8	822.8	0.0014	0.0004	1624.2	798.9	0.0011	0.0021	1624.3	801.2	0.0012	0.0049	1625.7	822.3	0.0017	0.0017
1630.2	804.2	0.0053	0.0017	1644.0	826.0	0.0017	0.0005	1630.4	801.9	0.0010	0.0020	1630.5	804.1	0.0011	0.0049	1631.9	825.3	0.0017	0.0016
1636.4	807.2	0.0054	0.0018	1650.2	828.9	0.0015	0.0004	1636.6	805.2	0.0011	0.0019	1636.7	806.9	0.0011	0.0049	1638.1	828.0	0.0016	0.0016
1642.6	810.2	0.0052	0.0018	1656.4	831.9	0.0017	0.0005	1642.8	808.2	0.0010	0.0019	1642.9	810.0	0.0011	0.0049	1644.3	831.3	0.0017	0.0016
1648.8	813.1	0.0054	0.0017	1662.6	834.9	0.0018	0.0006	1649.0	812.0	0.0010	0.0019	1649.1	813.2	0.0010	0.0048	1650.6	834.3	0.0018	0.0016
1655.0	816.1	0.0055	0.0018	1668.8	837.9	0.0017	0.0006	1655.2	815.0	0.0009	0.0018	1655.3	816.0	0.0010	0.0047	1656.8	837.2	0.0018	0.0016
1661.2	819.0	0.0057	0.0018	1675.0	840.7	0.0025	0.0009	1661.4	818.0	0.0009	0.0018	1661.5	819.3	0.0009	0.0046	1663.0	840.2	0.0019	0.0017
1667.4	822.2	0.0031	0.0015	1681.2	843.9	0.0018	0.0007	1667.6	820.9	0.0009	0.0018	1667.7	822.4	0.0009	0.0046	1669.2	843.3	0.0019	0.0015
1673.5	825.2	0.0058	0.0018	1687.4	847.0	0.0019	0.0007	1673.8	824.0	0.0009	0.0018	1673.9	825.3	0.0009	0.0045	1675.4	846.3	0.0019	0.0015
1679.8	827.9	0.0057	0.0017	1693.6	849.8	0.0019	0.0008	1680.0	827.2	0.0009	0.0018	1680.1	828.4	0.0009	0.0045	1681.6	849.1	0.0021	0.0016
1685.9	830.9	0.0058	0.0017	1699.8	853.1	0.0019	0.0008	1686.2	830.3	0.0009	0.0018	1686.3	831.4	0.0010	0.0045	1687.8	852.2	0.0022	0.0016
1692.1	834.1	0.0058	0.0018	1706.0	856.0	0.0021	0.0010	1692.4	833.3	0.0009	0.0017	1692.5	834.6	0.0009	0.0044	1694.0	855.2	0.0021	0.0014
1698.4	837.2	0.0060	0.0018	1712.2	859.0	0.0020	0.0009	1698.6	836.2	0.0008	0.0017	1698.7	837.3	0.0009	0.0044	1700.2	858.3	0.0022	0.0016
1704.5	840.2	0.0061	0.0018	1718.4	861.9	0.0020	0.0010	1704.8	839.2	0.0008	0.0016	1704.9	841.1	0.0008	0.0044	1706.4	861.3	0.0022	0.0014
1710.7	843.4	0.0060	0.0018	1724.6	865.0	0.0020	0.0011	1711.0	842.2	0.0008	0.0017	1711.1	844.3	0.0008	0.0044	1712.6	864.3	0.0023	0.0014
1716.9	846.3	0.0061	0.0018	1730.9	867.9	0.0021	0.0011	1717.2	845.5	0.0008	0.0017	1717.3	847.0	0.0009	0.0044	1718.8	867.3	0.0024	0.0015
1729.3	852.1	0.0060	0.0019	1737.1	870.9	0.0022	0.0013	1723.4	848.6	0.0007	0.0017	1723.5	850.1	0.0009	0.0044	1725.0	870.3	0.0025	0.0014
1735.5	855.4	0.0060	0.0018	1743.2	874.0	0.0024	0.0014	1729.6	851.7	0.0008	0.0018	1729.7	853.3	0.0009	0.0043	1731.2	873.3	0.0025	0.0015
1741.7	858.4	0.0059	0.0019	1749.5	877.1	0.0018	0.0013	1735.8	854.6	0.0007	0.0018	1735.9	856.5	0.0009	0.0044	1737.4	876.3	0.0025	0.0014
1747.9	861.6	0.0060	0.0020	1755.7	880.0	0.0018	0.0014	1742.0	857.7	0.0008	0.0018	1742.1	859.4	0.0008	0.0043	1743.6	879.3	0.0026	0.0015
1754.1	864.3	0.0061	0.0020	1761.8	882.8	0.0018	0.0015	1748.2	861.1	0.0007	0.0018	1748.3	862.4	0.0010	0.0044	1749.8	883.0	0.0026	0.0013
1760.3	867.4	0.0059	0.0020	1768.1	886.1	0.0020	0.0017	1754.4	863.7	0.0007	0.0017	1754.5	865.5	0.0010	0.0044	1756.0	886.0	0.0026	0.0015
1766.5	870.5	0.0058	0.0021	1774.3	889.1	0.0019	0.0018	1760.6	867.0	0.0007	0.0017	1760.7	868.5	0.0009	0.0044	1762.2	889.0	0.0028	0.0015
1772.7	873.6	0.0057	0.0020	1780.5	892.2	0.0021	0.0019	1766.8	869.9	0.0007	0.0017	1766.9	871.4	0.0009	0.0044	1768.4	891.9	0.0028	0.0015
1778.9	876.8	0.0056	0.0021	1786.7	895.1	0.0022	0.0020	1773.0	873.1	0.0007	0.0017	1773.1	874.9	0.0010	0.0044	1774.6	894.9	0.0028	0.0016
1785.1	879.4	0.0055	0.0021	1792.9	898.3	0.0024	0.0021	1779.2	876.3	0.0007	0.0018	1779.3	877.8	0.0010	0.0045	1780.8	897.9	0.0027	0.0013
1791.3	882.6	0.0055	0.0021	1799.1	901.2	0.0019	0.0021	1785.5	879.3	0.0007	0.0017	1785.5	880.7	0.0009	0.0045	1787.1	900.9	0.0028	0.0015
1797.5	885.6	0.0054	0.0021	1805.3	904.2	0.0013	0.0020	1791.7	882.4	0.0007	0.0018	1791.7	883.6	0.0010	0.0046	1793.2	903.9	0.0026	0.0015
1803.7	888.4	0.0054	0.0023	1811.5	907.3	0.0014	0.0021	1797.9	885.6	0.0007	0.0018	1797.9	886.9	0.0010	0.0046	1799.4	906.7	0.0025	0.0014
1809.9	891.5	0.0054	0.0023	1817.7	910.4	0.0014	0.0022	1804.1	888.6	0.0006	0.0018	1804.1	889.8	0.0010	0.0047	1805.7	909.9	0.0025	0.0015
1816.1	894.6	0.0053	0.0023	1823.9	913.1	0.0014	0.0023	1810.3	891.7	0.0006	0.0019	1810.3	892.9	0.0010	0.0048	1811.9	912.7	0.0024	0.0014
1822.3	897.7	0.0051	0.0023	1830.1	916.2	0.0013	0.0022	1816.5	894.7	0.0006	0.0019	1816.5	896.0	0.0010	0.0048	1818.1	915.9	0.0024	0.0015
1828.5	900.6	0.0047	0.0024	1836.3	919.8	0.0013	0.0022	1822.7	897.9	0.0006	0.0019	1822.7	899.2	0.0010	0.0048	1824.3	918.8	0.0022	0.0016
1834.7	903.7	0.0046	0.0025	1842.5	922.8	0.0011	0.0023	1828.9	900.9	0.0006	0.0019	1828.9	902.1	0.0010	0.0049	1830.5	921.8	0.0022	0.0016
1840.9	906.6	0.0041	0.0029	1848.7	925.8	0.0011	0.0025	1835.1	904.2	0.0006	0.0019	1835.1	905.1	0.0011	0.0049	1836.7	924.8	0.0021	0.0016
1847.1	909.6	0.0045	0.0026	1854.9	928.8	0.0011	0.0026	1841.3	907.1	0.0007	0.0020	1841.3	908.1	0.0010	0.0050	1842.9	927.7	0.0020	0.0017
1853.3	912.4	0.0044	0.0026	1861.1	931.9	0.0010	0.0027	1847.5	910.3	0.0007	0.0021	1847.5	911.0	0.0011	0.0051	1849.1	930.7	0.0019	0.0017
1859.5	915.5	0.0040	0.0026	1867.3	935.0	0.0011	0.0028	1853.7	913.2	0.0006	0.0020	1853.7	914.4	0.0011	0.0051	1855.3	933.9	0.0019	0.0017
1865.7	918.5	0.0040	0.0027	1873.5	937.9	0.0009	0.0028	1859.9	916.1	0.0006	0.0020	1859.9	917.3	0.0011	0.0051	1861.5	936.7	0.0018	0.0019
1871.9	921.7	0.0043	0.0027	1879.7	941.1	0.0008	0.0028	1866.1	919.6	0.0006	0.0020	1866.1	920.3	0.0011	0.0051	1867.7	939.7	0.0016	0.0019
1878.1	924.5	0.0038	0.0028	1885.9	944.0	0.0007	0.0028	1872.3	922.4	0.0006	0.0021	1872.3	923.2	0.0012	0.0052	1873.9	942.7	0.0016	0.0020
1884.3	927.7	0.0038	0.0029	1892.1	947.0	0.0008	0.0030	1878.5	925.5	0.0007	0.0021	1878.5	926.5	0.0012	0.0052	1880.1	945.8	0.0014	0.0021
1890.5	930.5	0.0031	0.0029	1898.3	950.0	0.0007	0.0033	1884.7	929.2	0.0006	0.0020	1884.7	929.6	0.0012	0.0052	1886.3	948.7	0.0013	0.0021
1896.6	933.8	0.0029	0.0030	1904.5	953.1	0.0007	0.0033	1890.9	932.1	0.0006	0.0022	1890.9	932.5	0.0012	0.0053	1892.5	951.8	0.0013	0.0022
1902.8	936.7	0.0031	0.0030	1910.7	956.0	0.0008	0.0035	1897.1	935.2	0.0007	0.0022	1897.1	935.7	0.0012	0.0053	1898.7	954.8	0.0011	0.0023
1909.1	940.0	0.0027	0.0030	1916.9	959.2	0.0008	0.0035	1903.3	938.3	0.0006	0.0024	1903.3	938.5	0.0012	0.0054	1904.9	957.7	0.0011	0.0024
1915.2	942.9	0.0034	0.0031	1923.1	962.2	0.0008	0.0037	1909.5	941.4	0.0006	0.0022	1909.5	941.6	0.0011	0.0054	1911.1	960.8	0.0010	0.0024
1921.4	945.6	0.0034	0.0031	1929.3	964.8	0.0007	0.0038	1915.7	944.4	0.0006	0.0023	1915.7	944.6	0.0010	0.0055	1917.3	963.7	0.0010	0.0025
1927.7	948.9	0.0033	0.0032	1935.6	968.3	0.0006	0.0038	1921.9	947.7	0.0006	0.0026	1921.9	947.5	0.0011	0.0057	1923.5	966.6	0.0008	0.0026
1933.8	951.7	0.0031	0.0033	1941.8	971.0	0.0006	0.0038	1928.1	950.7	0.0006	0.0026	1928.1	950.5	0.0010	0.0058	1929.7	969.8	0.0008	0.0027
1940.0	955.0	0.0026	0.0032	1947.9	974.1	0.0009	0.0042	1934.3	953.7	0.0006	0.0025	1934.3	953.8	0.0010	0.0060	1935.9	972.7	0.0007	0.0028
1946.3	957.9	0.0032	0.0036	1954.2	977.1	0.0009	0.0043	1940.5	956.9	0.0006	0.0027	1940.5	956.9	0.0008	0.0062	1942.1	975.7	0.0006	0.0028
1952.6	961.0	0.0025	0.0036	1960.4	980.1	0.0004	0.0038	1946.7	959.8	0.0006	0.0028	1946.7	960.3	0.0009	0.0065	1948.3	978.7	0.0005	0.0028
1958.6	964.0	0.0033	0.0038	1966.6	983.1	0.0004	0.0037	1952.9	962.8	0.0007	0.0031	1952.9	963.5	0.0008	0.0067	1954.5	981.7	0.0006	0.0030
1964.8	967.1	0.0029	0.0039	1972.8	986.0	0.0004	0.0039	1959.1	966.0	0.0007	0.0032	1959.1	966.4	0.0009	0.0070	1960.7	984.8	0.0005	0.0031
1971.0	970.1	0.0030	0.0040	1979.0	989.0	0.0004	0.0042	1965.3	969.0	0.0006	0.0033	1965.3	969.7	0.0009	0.0072	1967.0	987.8	0.0004	0.0031
1977.2	973.2	0.0033	0.0041	1985.2	992.0	0.0004	0.0042	1971.5	972.3	0.0007	0.0035	1971.5	972.6	0.0009	0.0075	1973.2	990.7	0.0004	0.0032
1983.4	976.1	0.0032	0.0043	1991.4	995.2	0.0004	0.0044	1977.7	975.1	0.0007	0.0037	1977.7	975.5	0.0009	0.0077	1979.4	993.7	0.0004	0.0033
1989.6	979.1	0.0030	0.0045	1997.6	998.0	0.0003	0.0042	1983.9	978.4	0.0006	0.0037	1983.9	978.5	0.0008	0.0080	1985.6	996.7	0.0003	0.0000
1995.8	982.0	0.0033	0.0050	2003.8	1001.2	0.0004	0.0045	1990.1	981.4	0.0007	0.0039	1990.1	981.6	0.0008	0.0083	1991.8	1000.2	0.0004	0.0036
2002.0	985.2	0.0035	0.0048	2010.0	1004.0	0.0005	0.0050	1996.3	984.5	0.0006	0.0041	1996.3	984.9	0.0009	0.0086	1998.0	1003.0	0.0005	0.0038
2008.2	988.0	0.0034	0.0050	2016.2	1007.0	0.0004	0.0048	2002.5	987.6	0.0005	0.0039	2002.5	987.9	0.0008	0.0089	2004.2	1006.1	0.0004	0.0040
2014.4	991.2	0.0035	0.0050	2022.4	1010.0	0.0004	0.0052	2008.7	990.8	0.0006	0.0041	2008.7	990.8	0.0008	0.0092	2010.4	1009.1	0.0004	0.0042
2020.6	994.2	0.0032	0.0052	2028.6	1012.9	0.0004	0.0051	2014.9	993.7	0.0006	0.0045	2014.9	994.0	0.0008	0.0096	2016.6	1012.1	0.0004	0.0044
2026.8	997.4	0.0032	0.0055	2034.8	1016.0	0.0004	0.0054	2021.1	996.7	0.0006	0.0047	2021.1	996.9	0.0009	0.0100	2022.8	1015.1	0.0004	0.0045

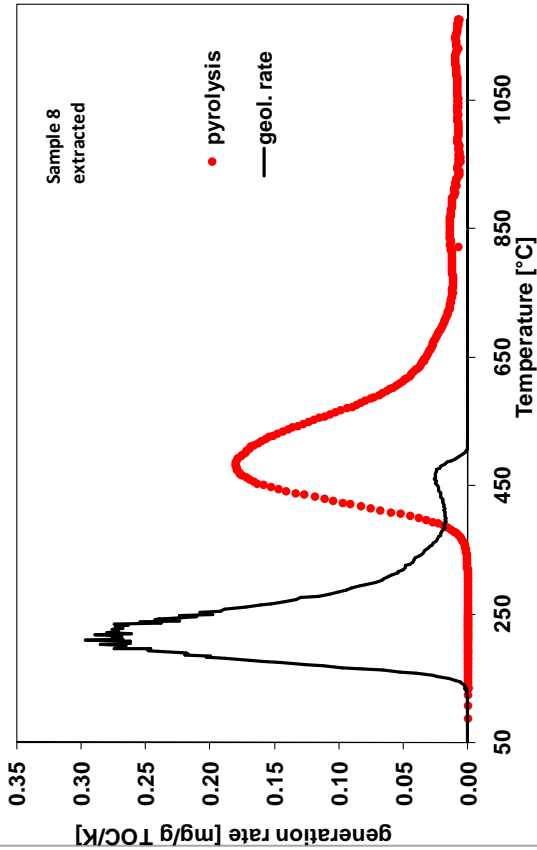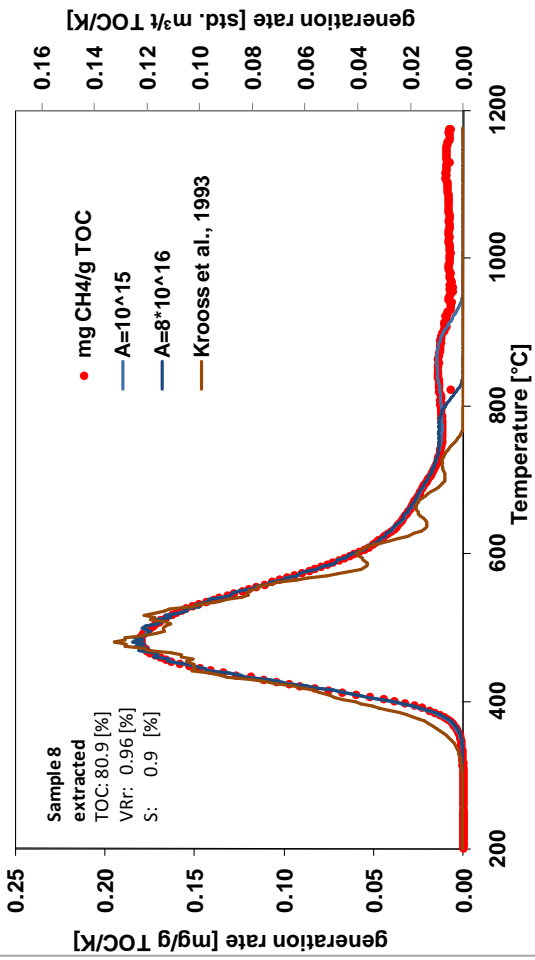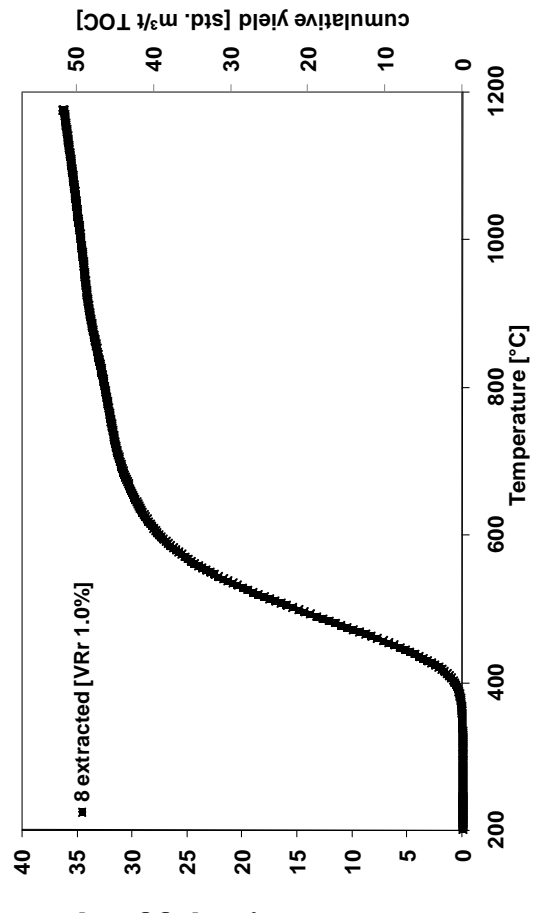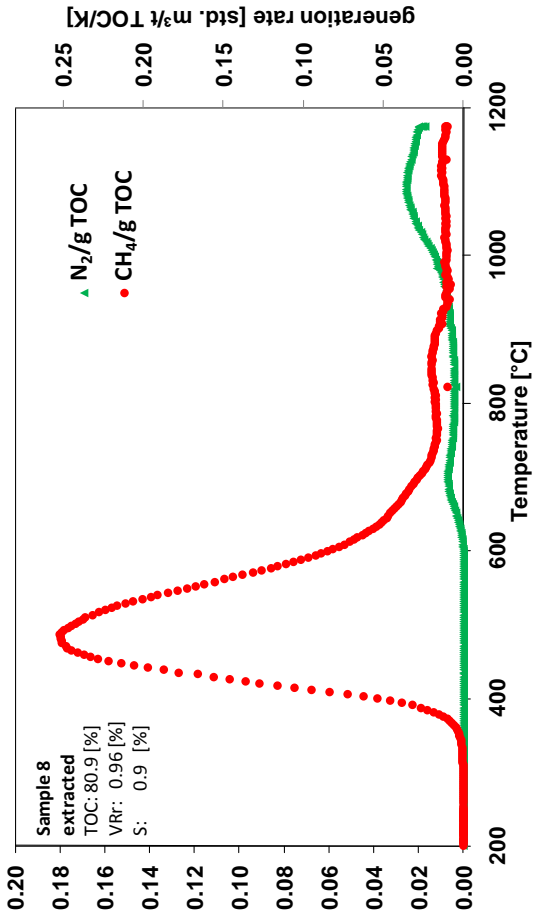Table 5 Results of temperature-programmed open system pyrolysis (continued)

2033.0	1000.4	0.0032	0.0057	2041.0	1019.2	0.0005	0.0057	2027.3	999.9	0.0006	0.0049	2027.3	1000.0	0.0008	0.0103	2029.0	1018.1	0.0005	0.0046				
2039.2	1003.4	0.0032	0.0059	2047.2	1021.9	0.0010	0.0059	2033.5	1003.1	0.0006	0.0050	2033.5	1003.1	0.0008	0.0106	2035.2	1021.2	0.0010	0.0047				
2045.4	1006.6	0.0031	0.0061	2053.4	1025.1	0.0010	0.0060	2039.7	1006.1	0.0006	0.0051	2039.7	1006.1	0.0009	0.0111	2041.4	1024.2	0.0010	0.0049				
2051.6	1009.6	0.0032	0.0064	2059.6	1028.1	0.0013	0.0061	2045.9	1009.2	0.0006	0.0052	2045.9	1009.3	0.0007	0.0114	2047.6	1027.1	0.0013	0.0051				
2057.8	1012.5	0.0033	0.0066	2065.8	1031.1	0.0005	0.0060	2052.1	1012.2	0.0006	0.0056	2052.1	1012.5	0.0008	0.0118	2053.8	1030.1	0.0005	0.0052				
2064.0	1015.5	0.0033	0.0069	2072.0	1034.1	0.0014	0.0062	2058.3	1015.5	0.0005	0.0056	2058.3	1015.5	0.0007	0.0122	2060.0	1033.2	0.0014	0.0054				
2070.2	1018.4	0.0034	0.0071	2078.2	1037.6	0.0026	0.0064	2064.5	1018.4	0.0006	0.0060	2064.5	1018.5	0.0007	0.0125	2066.2	1036.3	0.0026	0.0056				
2076.4	1021.5	0.0035	0.0074	2084.4	1040.5	0.0002	0.0037	2070.7	1021.6	0.0005	0.0062	2070.7	1021.5	0.0003	0.0077	2072.5	1039.3	0.0002	0.0056				
2082.6	1024.7	0.0036	0.0078	2090.6	1043.6	0.0002	0.0038	2076.9	1024.6	0.0005	0.0062	2076.9	1024.5	0.0006	0.0134	2078.7	1042.3	0.0002	0.0059				
2088.8	1027.8	0.0033	0.0079	2096.8	1046.7	0.0002	0.0041	2083.1	1027.9	0.0005	0.0066	2083.1	1027.8	0.0006	0.0139	2084.9	1045.5	0.0002	0.0060				
2095.0	1030.7	0.0034	0.0081	2103.0	1049.6	0.0001	0.0034	2089.3	1031.0	0.0005	0.0064	2089.3	1031.2	0.0007	0.0145	2091.1	1048.4	0.0001	0.0061				
2101.2	1034.1	0.0035	0.0084	2109.2	1052.8	0.0001	0.0036	2095.5	1034.0	0.0005	0.0070	2095.5	1034.0	0.0007	0.0149	2097.3	1051.5	0.0001	0.0063				
2107.4	1036.9	0.0035	0.0086	2115.4	1055.4	0.0001	0.0037	2101.7	1037.4	0.0005	0.0070	2101.7	1037.1	0.0007	0.0154	2103.5	1054.5	0.0001	0.0065				
2113.6	1040.0	0.0033	0.0087	2121.6	1058.4	0.0001	0.0037	2108.0	1040.4	0.0005	0.0069	2107.9	1040.4	0.0006	0.0158	2109.7	1057.5	0.0001	0.0066				
2119.8	1043.2	0.0034	0.0090	2127.8	1061.7	0.0001	0.0039	2114.2	1043.6	0.0005	0.0072	2114.1	1043.4	0.0004	0.0151	2115.9	1060.5	0.0001	0.0067				
2126.0	1046.1	0.0033	0.0091	2134.0	1064.6	0.0002	0.0048	2120.4	1046.6	0.0004	0.0070	2120.3	1046.6	0.0006	0.0168	2122.1	1063.7	0.0002	0.0068				
2132.2	1049.4	0.0035	0.0094	2140.3	1067.9	0.0002	0.0052	2126.6	1050.6	0.0005	0.0080	2126.5	1049.6	0.0006	0.0173	2128.3	1066.8	0.0002	0.0070				
2138.4	1052.5	0.0033	0.0095	2146.4	1070.9	0.0003	0.0060	2132.8	1053.6	0.0005	0.0079	2132.7	1052.6	0.0005	0.0177	2134.5	1069.8	0.0003	0.0070				
2144.6	1055.6	0.0034	0.0096	2152.7	1073.5	0.0002	0.0058	2139.0	1056.6	0.0004	0.0081	2138.9	1055.9	0.0006	0.0180	2140.7	1073.0	0.0002	0.0070				
2150.8	1058.5	0.0034	0.0097	2158.9	1076.6	0.0002	0.0053	2145.2	1059.9	0.0005	0.0083	2145.1	1059.2	0.0006	0.0185	2146.9	1076.0	0.0002	0.0073				
2157.0	1061.4	0.0035	0.0100	2165.1	1079.9	0.0002	0.0055	2151.4	1063.1	0.0004	0.0085	2151.3	1062.3	0.0006	0.0190	2153.1	1078.9	0.0002	0.0073				
2163.2	1064.9	0.0035	0.0101	2171.3	1082.7	0.0002	0.0059	2157.6	1066.1	0.0005	0.0085	2157.5	1065.1	0.0005	0.0192	2159.3	1082.1	0.0002	0.0074				
2169.4	1068.0	0.0035	0.0103	2177.5	1085.8	0.0002	0.0054	2163.8	1069.4	0.0004	0.0081	2163.7	1068.2	0.0006	0.0194	2165.5	1085.1	0.0002	0.0075				
2175.6	1071.2	0.0035	0.0104	2183.7	1088.7	0.0002	0.0056	2170.0	1072.5	0.0004	0.0081	2169.9	1071.3	0.0005	0.0199	2171.7	1088.2	0.0002	0.0075				
2181.8	1074.2	0.0035	0.0105	2189.9	1091.7	0.0004	0.0070	2176.2	1076.0	0.0004	0.0086	2176.1	1074.5	0.0005	0.0202	2177.9	1091.1	0.0004	0.0076				
2188.0	1077.4	0.0034	0.0106	2196.1	1095.0	0.0001	0.0046	2182.4	1079.4	0.0004	0.0088	2182.3	1077.8	0.0005	0.0201	2184.1	1094.4	0.0001	0.0075				
2194.2	1080.0	0.0036	0.0107	2202.3	1097.8	0.0001	0.0044	2188.6	1082.1	0.0004	0.0089	2188.5	1081.0	0.0005	0.0203	2190.4	1097.5	0.0001	0.0075				
2200.4	1083.4	0.0036	0.0108	2208.5	1100.6	0.0001	0.0045	2194.8	1085.5	0.0004	0.0088	2194.7	1084.1	0.0004	0.0205	2196.5	1100.5	0.0001	0.0075				
2206.6	1086.6	0.0036	0.0109	2214.7	1103.7	0.0002	0.0045	2201.0	1088.6	0.0004	0.0083	2200.9	1087.1	0.0005	0.0204	2202.7	1103.4	0.0002	0.0075				
2212.8	1089.6	0.0037	0.0109	2220.9	1106.5	0.0002	0.0049	2207.2	1091.8	0.0004	0.0085	2207.1	1090.8	0.0005	0.0206	2208.9	1106.7	0.0002	0.0075				
2219.0	1092.8	0.0037	0.0109	2227.1	1109.5	0.0002	0.0049	2213.4	1095.0	0.0004	0.0088	2213.3	1093.5	0.0004	0.0204	2215.1	1109.8	0.0002	0.0075				
2225.2	1096.1	0.0039	0.0108	2233.3	1112.6	0.0002	0.0053	2219.6	1098.3	0.0004	0.0085	2219.5	1096.7	0.0005	0.0204	2221.4	1112.9	0.0002	0.0074				
2231.4	1099.2	0.0039	0.0109	2239.5	1115.8	0.0002	0.0049	2225.8	1101.2	0.0004	0.0089	2225.7	1099.9	0.0004	0.0204	2227.6	1116.5	0.0002	0.0075				
2237.6	1102.5	0.0038	0.0107	2245.7	1118.6	0.0002	0.0051	2232.0	1104.3	0.0004	0.0085	2231.9	1103.1	0.0004	0.0204	2233.8	1119.5	0.0002	0.0074				
2243.7	1105.4	0.0041	0.0107	2251.9	1121.7	0.0001	0.0049	2238.2	1107.6	0.0004	0.0085	2238.1	1106.1	0.0004	0.0204	2240.0	1122.8	0.0001	0.0074				
2249.9	1108.5	0.0042	0.0107	2258.1	1124.5	0.0003	0.0058	2244.4	1110.7	0.0004	0.0082	2244.3	1109.0	0.0005	0.0201	2246.2	1125.7	0.0003	0.0074				
2256.2	1111.6	0.0041	0.0107	2264.3	1127.8	0.0002	0.0053	2250.6	1113.8	0.0004	0.0084	2250.5	1112.3	0.0004	0.0198	2252.4	1128.6	0.0002	0.0072				
2262.3	1114.6	0.0042	0.0106	2270.5	1130.8	0.0002	0.0049	2256.8	1117.1	0.0004	0.0084	2256.7	1115.6	0.0004	0.0198	2258.6	1131.6	0.0002	0.0072				
2268.5	1117.5	0.0041	0.0104	2276.7	1133.8	0.0003	0.0054	2263.0	1120.3	0.0004	0.0084	2262.9	1118.3	0.0004	0.0195	2264.8	1134.7	0.0003	0.0072				
2274.8	1120.9	0.0042	0.0103	2282.9	1137.1	0.0002	0.0048	2269.2	1123.3	0.0004	0.0086	2269.1	1121.6	0.0004	0.0193	2271.0	1137.8	0.0002	0.0071				
2280.9	1123.9	0.0040	0.0102	2289.1	1139.0	0.0002	0.0049	2275.4	1126.4	0.0004	0.0083	2275.3	1124.5	0.0003	0.0190	2277.2	1140.7	0.0002	0.0069				
2287.1	1126.5	0.0040	0.0101	2295.3	1142.0	0.0002	0.0049	2281.6	1129.5	0.0004	0.0084	2281.5	1127.8	0.0004	0.0188	2283.4	1143.8	0.0002	0.0068				
2293.3	1129.9	0.0032	0.0098	2301.5	1144.9	0.0002	0.0049	2287.8	1132.9	0.0004	0.0085	2287.7	1130.8	0.0004	0.0186	2289.6	1146.7	0.0002	0.0068				
2299.5	1133.3	0.0040	0.0098	2307.7	1148.2	0.0002	0.0049	2294.0	1136.1	0.0004	0.0083	2293.9	1134.1	0.0003	0.0181	2295.8	1149.6	0.0002	0.0068				
2305.7	1136.3	0.0040	0.0098	2313.9	1151.2	0.0002	0.0049	2306.4	1142.0	0.0004	0.0082	2300.1	1136.9	0.0004	0.0180	2302.0	1152.6	0.0002	0.0067				
2311.9	1139.7	0.0040	0.0095	2320.1	1154.5	0.0002	0.0046	2312.6	1145.3	0.0004	0.0080	2306.3	1140.0	0.0004	0.0177	2308.2	1155.4	0.0002	0.0067				
2318.1	1142.4	0.0040	0.0095	2326.3	1157.7	0.0002	0.0047	2318.8	1148.5	0.0004	0.0082	2312.5	1143.3	0.0004	0.0175	2314.4	1158.4	0.0002	0.0067				
2324.3	1145.6	0.0041	0.0094	2332.5	1160.8	0.0002	0.0045	2325.0	1151.9	0.0004	0.0081	2318.7	1146.3	0.0004	0.0171	2320.6	1161.3	0.0002	0.0067				
2330.5	1148.3	0.0041	0.0094	2338.7	1164.0	0.0002	0.0044	2331.2	1154.4	0.0004	0.0082	2324.9	1149.4	0.0004	0.0168	2326.8	1164.2	0.0002	0.0066				
2336.7	1151.4	0.0039	0.0092	2344.9	1166.8	0.0002	0.0044	2337.4	1157.6	0.0004	0.0079	2331.1	1152.3	0.0003	0.0166	2333.0	1167.1	0.0002	0.0066				
2342.9	1154.5	0.0039	0.0091	2351.1	1169.9	0.0002	0.0042	2343.6	1160.7	0.0004	0.0079	2337.3	1155.2	0.0003	0.0164	2339.2	1170.1	0.0002	0.0066				
2349.1	1157.5	0.0037	0.0091	2357.3	1173.0	0.0002	0.0042	2349.8	1163.5	0.0004	0.0078	2343.5	1158.4	0.0004	0.0165	2345.4	1172.9	0.0002	0.0065				
2355.3	1160.6	0.0034	0.0090	2363.6	1175.7	0.0002	0.0045	2356.0	1166.6	0.0004	0.0078	2349.7	1161.2	0.0004	0.0165	2351.6	1175.7	0.0002	0.0064				
2361.5	1163.6	0.0034	0.0089	2369.7	1178.8	0.0002	0.0043	2362.2	1170.2	0.0003	0.0077	2355.9	1164.3	0.0004	0.0165	2357.8	1178.8	0.0002	0.0064				
2367.7	1166.5	0.0033	0.0088	2376.0	1182.0	0.0002	0.0043	2368.4	1173.5	0.0004	0.0078	2362.1	1167.6	0.0004	0.0166	2364.0	1181.4	0.0002	0.0065				
2373.9	1169.8	0.0035	0.0087	2382.2	1183.3	0.0002	0.0044	2374.6	1176.7	0.0004	0.0079	2368.3	1170.3	0.0004	0.0164	2370.2	1182.9	0.0002	0.0064				
2380.1	1172.5	0.0033	0.0086	2388.3	1183.2	0.0003	0.0043	2380.8	1177.5	0.0003	0.0079	2374.5	1173.2	0.0004	0.0161	2376.5	1182.9	0.0003	0.0063				
2386.3	1175.2	0.0033	0.0085	2394.6	1183.2	0.0002	0.0040	2387.0	1177.4	0.0003	0.0071	2380.7	1175.4	0.0004	0.0159	2394.6	1182.7	0.0002	0.0062				
2392.5	1175.0	0.0032	0.0082	2400.8	1183.2	0.0002	0.0041	2393.2	1177.6	0.0003	0.0069	2386.9	1175.4	0.0004	0.0156	2400.8	1182.7	0.0002	0.0060				
2398.7	1175.1	0.0033	0.0079	2407.0	1183.2	0.0002	0.0040	2399.4	1177.7	0.0003	0.0066	2393.1	1175.2	0.0004	0.0151	2407.0	1182.7	0.0002	0.0059				
2404.9	1175.0	0.0032	0.0076	2413.2	1183.5	0.0002	0.0038	2405.6	1177.7	0.0003	0.0063	2399.3	1175.4	0.0004	0.0146	2413.2	1182.7	0.0002	0.0057				
2411.1	1175.0	0.0030	0.0072	2419.4	1183.1	0.0002	0.0037	2411.8	1177.7	0.0003	0.0065	2399.3	1175.4	0.0004	0.0139	2419.4	1182.7	0.0002	0.0056				

Appendix III Investigations on the methane and carbon dioxide sorption capacity of coals from the SW Upper Silesian Coal Basin, Czech Republic

Appendix III Fig. 1 Methane sorption isotherms measured at 45°C.

Appendix III Fig. 2 Carbon dioxide sorption isotherms measured at 45°C.

Appendix III Table 1 Results of proximate and petrographic analysis

Sample #	Hygr. moisture [wt.%]	Equil. moisture [wt.%]	Ash [wt.%, dry]	Vol. matter [wt.%, daf]	Fixed carbon [wt.%, daf]	VRr [%]	Vitr. [vol.%, mmf]	Lipt. [vol.%, mmf]	Inert. [vol.%, mmf]	TOC [wt. %]	Rock-Eval T_{max} [°C]
1	1.5	2.4	1.5	26.0	74.0	1.1	72.0	6.2	21.7	84.7	463
2	1.3	2.0	7.4	25.8	74.2	1.1	65.6	5.2	29.2	80.8	460
3	1.0	2.5	10.2	25.4	74.6	1.1	51.8	9.7	38.5	78.0	460
4	0.8	1.7	4.1	25.2	74.8	1.1	83.7	11.4	4.8	84.1	456
5	0.7	1.6	18.5	25.8	74.2	1.1	81.8	0.9	17.3	70.4	466
6	0.6	1.6	3.4	23.3	76.7	1.2	76.5	9.1	14.4	85.3	465
7	1.7	2.4	3.0	25.1	74.9	1.1	75.1	5.8	19.1	84.3	464
8.1	0.7	1.4	2.9	32.2	67.8	1.0	n.d.	n.d.	n.d.	n.d.	n.d.
8.2	0.6	n.d.	3.3	35.3	64.7	1.0	48.4	23.4	28.2	80.9	443
9	0.7	n.d.	49.0	(37.1)	62.9	1.0	80.0	0.0	20.0	41.6	452
10	0.5	n.d.	32.0	29.3	70.7	1.1	89.0	0.0	11.0	57.1	459
11	0.4	n.d.	6.0	25.7	74.3	1.1	79.2	0.0	20.8	81.5	461
12	0.5	n.d.	4.2	27.9	72.1	1.1	77.8	2.6	19.6	78.9	452
13	0.5	n.d.	3.1	27.2	72.8	1.1	84.6	1.2	14.2	82.8	454
14	0.5	n.d.	54.6	(31.8)	68.2	1.1	98.3	0.0	1.7	37.1	474
15	0.3	n.d.	12.3	28.3	71.7	1.1	48.8	0.0	51.2	72.7	465
16	0.3	n.d.	2.4	25.0	75.0	1.2	95.6	0.2	4.2	85.2	457
17	0.3	n.d.	1.9	22.0	78.0	1.2	73.4	5.4	21.2	83.7	456
18	1.0	n.d.	89.8	(68.0)	32.0	1.2	n.d.	n.d.	n.d.	n.d.	n.d.
19	0.5	n.d.	41.1	26.3	73.7	1.3	80.8	0.0	19.2	49.4	475
20	0.3	n.d.	85.2	(38.6)	61.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
21	0.5	1.5	2.9	21.5	78.5	1.4	88.8	1.0	10.1	82.8	468
22	0.9	1.3	20.0	28.3	71.7	1.2	80.0	2.5	17.5	73.1	456
23	0.6	1.6	8.6	17.8	82.2	1.7	88.1	0.0	11.9	79.0	482
24	0.7	1.5	4.4	16.1	83.9	1.8	84.0	0.0	16.0	83.5	483
25	0.8	1.5	1.6	17.7	82.3	1.7	87.7	0.0	12.3	85.4	479
26	0.9	1.6	4.3	16.9	83.1	1.8	77.9	0.0	22.1	83.5	480
27	0.9	1.0	5.8	24.1	75.9	1.4	91.8	0.2	8.0	81.6	466
28	0.8	1.5	3.4	20.0	80.0	1.6	86.9	1.2	11.9	83.3	470
29	0.7	1.1	16.5	26.0	74.0	1.5	85.3	1.0	13.6	70.3	468
30	0.5	1.2	6.5	27.1	72.9	1.4	82.6	1.2	16.2	78.4	458

VRr=mean vitrinite reflectance (random); TOC=total organic carbon; ; n.d.= not determined; daf=dry, ash-free; mmf=mineral matter free; volatile matter values in brackets are from 'high-ash' samples

Appendix III Table 2 Results of high-pressure methane sorption experiments on "as received" coal samples at 45°C.

Sample #	n_{max} raw [mmol/g]	P at n_{max} [MPa]	n_L raw [mmol/g]	n_{max} daf [mmol/g]	n_L daf [mmol/g]	P_L daf [MPa]	He density [g/cm³]	V_{max} daf [m³/t]	V_L daf [m³/t]
1	0.77	16.36	0.85	0.80	0.88	1.39	1.21	18.14	19.90
2	0.76	14.05	0.83	0.84	0.91	1.27	1.25	18.98	20.69
3	0.76	15.70	0.82	0.85	0.92	1.18	1.30	19.39	20.91
4	0.76	17.14	0.84	0.80	0.88	1.63	1.22	18.15	20.00
5	0.64	13.13	0.67	0.79	0.83	0.80	1.43	17.95	18.75
6	0.67	15.77	0.74	0.70	0.77	1.62	1.22	15.79	17.54
7	0.77	14.04	0.84	0.81	0.88	1.29	1.22	18.36	19.90
8.1	0.50	15.78	0.59	0.52	0.61	2.65	1.29	11.75	13.89
8.2	0.52	16.00	0.60	0.55	0.62	2.11	1.32	12.39	14.10
11	0.63	14.89	0.71	0.67	0.76	1.67	1.35	15.30	17.15
12	0.50	16.62	0.58	0.53	0.61	2.73	1.32	11.93	13.89
13	0.71	15.78	0.78	0.73	0.81	1.58	1.32	16.65	18.46
14	0.27	16.75	0.30	0.59	0.67	2.07	1.85	13.48	15.15
15	0.53	15.75	0.59	0.60	0.67	1.59	1.48	13.67	15.24
16	0.47	15.39	0.56	0.49	0.57	2.71	1.31	11.06	13.00
17	0.61	15.39	0.69	0.62	0.70	1.75	1.33	14.15	15.93
19	0.38	14.30	0.43	0.64	0.73	1.90	1.71	14.64	16.64
21	0.88	14.57	0.96	0.91	0.99	1.33	1.21	20.66	22.57
22	0.61	16.55	0.68	0.77	0.86	1.85	1.29	19.58	19.58
23	0.88	17.30	0.95	0.97	1.04	1.10	1.28	22.10	23.68
24	0.94	13.05	1.02	0.99	1.08	1.17	1.26	22.57	24.46
25	0.92	13.68	1.00	0.94	1.02	1.19	1.23	21.40	23.19
26	0.89	12.94	0.97	0.94	1.02	1.17	1.26	21.38	23.20
27	0.64	16.68	0.70	0.69	0.75	1.33	1.23	15.68	17.03
28	0.80	13.73	0.86	0.83	0.90	1.19	1.23	18.93	20.40
29	0.69	14.95	0.75	0.83	0.91	1.40	1.35	18.80	20.68
30	0.69	15.29	0.75	0.74	0.80	1.17	1.26	16.86	18.24

daf= dry, ash-free; n_{max}=maximum measured excess sorption; n_L=Langmuir sorption capacity; P_L=Langmuir pressure; V_{max}= volume of maximum measured excess sorption; V_L=volume of Langmuir sorption capacity

Appendix III Table 3 Results of high-pressure carbon dioxide sorption experiments on "as received" coal samples at 45°C.

Sample #	n_{max} raw [mmol/g]	P at n_{max} [MPa]	n_L (Eq.3) raw [mmol/g]	n_{max} daf [mmol/g]	n_L (Eq.3) daf [mmol/g]	P_L (Eq.3) daf [MPa]	Density SP (Eq.3) [g/cm³]	Density SP graph. [g/cm³]	He density [g/cm³]	V_{max} daf [m³/t]	V_L (Eq.3) daf [m³/t]
1	1.01	6.15	1.34	1.04	1.38	1.23	1213	1256	1.44	23.64	31.28
2	1.11	7.56	2.09	1.21	2.29	3.44	1026	1034	1.25	27.49	51.93
3	0.95	7.85	1.43	1.07	1.60	1.44	1134	1107	1.47	24.31	36.42
4	1.13	7.21	1.50	1.19	1.58	1.48	1303	1490	1.34	26.98	35.92
5	0.97	7.27	1.59	1.20	1.96	2.55	1018	990	1.46	27.17	44.61
6	1.07	6.81	1.52	1.11	1.58	1.66	1551	1463	1.20	25.30	35.89
7	1.17	7.16	1.90	1.23	1.99	2.32	1218	1200	1.35	27.97	45.23
8.2	0.92	8.04	1.96	0.96	2.04	4.18	1018	1020	1.44	21.71	46.33
21	1.23	7.11	2.07	1.27	2.14	2.40	1094	1105	1.34	28.95	48.66
22	0.79	8.06	1.45	1.00	1.83	2.81	936	938	1.56	22.61	41.51
23	1.28	6.43	1.81	1.41	2.00	1.47	1223	1131	1.40	32.06	45.31
24	1.15	5.92	1.55	1.22	1.64	1.15	1150	1239	1.49	27.60	37.19
25	1.14	6.80	1.58	1.17	1.61	1.29	1146	1155	1.50	26.53	36.66
26	1.31	6.47	1.56	1.39	1.99	1.54	1179	1244	1.19	31.49	45.24
27	1.04	7.27	1.63	1.12	1.76	2.15	931	1029	1.20	25.40	40.01
28	1.14	7.43	1.77	1.19	1.84	2.01	1137	1018	1.35	26.95	41.90
29	0.93	9.70	2.01	1.12	2.42	3.41	968	965	1.50	25.46	54.99
30	1.02	8.79	1.73	1.10	1.86	2.57	1295	1156	1.39	24.94	42.16

daf= dry, ash-free; n_{max}=maximum measured excess sorption; n_L=Langmuir sorption capacity; P_L=Langmuir pressure; V_{max}= volume of maximum measured excess sorption; V_L=volume of Langmuir sorption capacity;Eq.3 = calculated from equation 3; SP=sorbed phase; graph=graphical estimation; P=pressure

Appendix III Table 4 Results of high-pressure methane sorption experiments on moisture equilibrated coal samples.

Sample #	n_{max} raw [mmol/g]	P at n_{max} [MPa]	n_L raw [mmol/g]	n_{max} daf [mmol/g]	n_L daf [mmol/g]	P_L daf [MPa]	He density [g/cm³]	V_{max} daf [m³/t]	V_L daf [m³/t]
1	0.47	16.81	0.58	0.49	0.59	3.58	1.33	11.19	13.34
2	0.33	14.61	0.50	0.36	0.60	8.66	1.38	8.17	13.52
3	0.46	11.49	0.54	0.53	0.62	2.37	1.47	11.98	13.98
4	0.52	16.15	0.65	0.55	0.69	4.26	1.35	12.60	15.68
5	0.50	14.96	0.64	0.63	0.79	4.12	1.47	14.21	18.02
6	0.46	15.88	0.60	0.48	0.63	4.61	1.35	10.98	14.39
7	0.45	16.33	0.58	0.47	0.61	4.72	1.32	10.73	13.91
8.1	0.43	15.15	0.52	0.44	0.54	2.75	1.28	10.11	12.31
21	0.70	16.58	0.80	0.73	0.83	2.16	1.34	16.56	18.85
22	0.38	13.12	0.44	0.49	0.56	2.56	1.41	11.05	12.64
23	0.70	16.82	0.88	0.78	0.96	3.19	1.41	17.72	21.78
24	0.67	10.59	0.75	0.71	0.80	1.47	1.34	16.08	18.09
25	0.58	16.76	0.70	0.60	0.72	3.03	1.34	13.70	16.31
26	0.69	16.47	1.01	0.74	1.08	8.02	1.43	16.73	24.61
27	0.28	15.20	0.37	0.30	0.40	4.83	1.33	6.74	8.99
28	0.55	15.99	0.70	0.58	0.73	4.20	1.29	13.10	16.68
29	0.40	15.74	0.57	0.48	0.69	7.11	1.52	10.96	15.62
30	0.39	16.15	0.48	0.42	0.52	6.04	1.43	9.64	11.73

daf= dry, ash-free; n_{max}=maximum measured excess sorption; n_L=Langmuir sorption capacity; P_L=Langmuir pressure; V_{max}= volume of maximum measured excess sorption; V_L=volume of Langmuir sorption capacity; P=pressure

Appendix III Table 5 Results of high-pressure and carbon dioxide sorption experiments on moisture equilibrated coal samples.

Sample #	n_{max} raw [mmol/g]	P at n_{max} [MPa]	n_L (Eq.3) raw [mmol/g]	n_{max} daf [mmol/g]	n_L (Eq.3) daf [mmol/g]	P_L (Eq.3) daf [MPa]	Density SP (Eq.3) [g/cm³]	density SP graph. [g/cm³]	He density [g/cm³]	V_{max} daf [m³/t]	V_L (Eq.3) daf [m³/t]
1	0.95	8.31	1.79	0.99	1.86	3.34	1104	945	1.34	22.46	42.21
7	0.96	7.76	1.87	1.01	1.96	3.77	1066	1106	1.35	23.03	44.53
23	1.05	9.64	1.59	1.16	1.75	1.64	1475	1319	1.43	26.30	39.63
27	0.78	9.34	1.67	0.80	1.70	5.20	1350	1469	1.36	18.16	38.71
28	0.98	7.39	1.46	1.02	1.53	1.99	1272	1190	1.35	23.23	34.68
29	0.77	6.04	1.38	0.94	1.67	2.96	1170	1015	1.54	21.30	37.98

daf= dry, ash-free; n_{max}=maximum measured excess sorption; n_L=Langmuir sorption capacity; P_L=Langmuir pressure; V_{max}= volume of maximum measured excess sorption; V_L=volume of Langmuir sorption capacity; Eq.3 = calculated from equation 3; SP=sorbed phase; graph=graphical estimation; P=pressure

Appendix III Table 6 Results of methane sorption experiments on "as received" coal samples at 20°C.

Sample #	n_{max} raw [mmol/g]	P at n_{max} [MPa]	n_L raw [mmol/g]	n_{max} daf [mmol/g]	n_L daf [mmol/g]	P_L daf [MPa]	He density [g/cm³]	V_{max} daf [m³/t]	V_L daf [m³/t]
22	0.62	16.20	0.67	0.78	0.85	1.31	1.45	17.70	19.22
24	1.00	11.98	1.05	1.05	1.10	0.77	1.40	23.88	25.06
26	0.90	12.09	0.97	0.95	0.99	0.80	1.39	21.54	22.58

daf= dry, ash-free; n_{max}=maximum measured excess sorption; n_L=Langmuir sorption capacity; P_L=Langmuir pressure; V_{max}= volume of maximum measured excess sorption; V_L=volume of Langmuir sorption capacity; P=pressure

Appendix III Table 7 of carbon dioxide sorption experiments on "as received" coal samples at 20°C.

Sample #	n_{max} raw [mmol/g]	P at n_{max} [MPa]	n_L (Eq.3) raw [mmol/g]	n_{max} daf [mmol/g]	n_L (Eq.3) daf [mmol/g]	P_L (Eq.3) daf [MPa]	Density SP (Eq.3)	He density [g/cm³]	V_{max} daf [m³/t]	V_L (Eq.3) daf [m³/t]
22	0.85	2.25	1.66	1.07	1.99	0.98	214	1.45	24.41	45.23
24	1.29	3.56	2.36	1.36	2.48	1.45	369	1.40	30.91	56.37
26	1.17	3.24	2.06	1.23	2.18	1.17	325	1.51	28.04	49.40

daf= dry, ash-free; n_{max}=maximum measured excess sorption; n_L=Langmuir sorption capacity; P_L=Langmuir pressure; V_{max}= volume of maximum measured excess sorption; V_L=volume of Langmuir sorption capacity; Eq.3 = calculated from equation 3; SP=sorbed phase; graph=graphical estimation; P=pressure

Appendix III Table 8 Results of high pressure methane sorption experiments on moisture equilibrated coal samples 8 at different temperatures

Temperature (°C)	n_{max} raw [mmol/g]	P at n_{max} [MPa]	n_L raw [mmol/g]	n_{max} daf [mmol/g]	n_L daf [mmol/g]	P_L daf [MPa]	He density [g/cm³]	V_{max} daf [m³/t]	V_L daf [m³/t]
45	0.43	15.15	0.52	0.44	0.54	2.75	1.28	10.11	12.31
55	0.40	15.28	0.48	0.42	0.50	2.66	1.28	9.60	11.31
65	0.37	17.54	0.43	0.39	0.45	2.84	1.28	8.79	10.19

daf= dry, ash-free; n_{max}=maximum measured excess sorption; n_L=Langmuir sorption capacity; P_L=Langmuir pressure; V_{max}= volume of maximum measured excess sorption; V_L=volume of Langmuir sorption capacity; P=pressure

Appendix III Table 9 Experimental data (pressure, excess sorption) for high-pressure sorption isotherms.

Sample: 1 — Moisture: a.r. — Gas: CH4 — T (°C): 44.56

P [MPa]	n_{ads} [mmol/g]
0	0
0.98	0.349
2.12	0.5
3.16	0.58
4.03	0.628
4.76	0.658
5.36	0.679
5.85	0.693
6.25	0.704
6.58	0.712
6.85	0.718
8.76	0.748
10.3	0.762
11.56	0.769
12.59	0.772
13.42	0.774
14.1	0.774
14.66	0.775
15.11	0.774
15.48	0.774
15.77	0.775
16.02	0.773
16.21	0.774
16.36	0.775
16.49	0.774
16.59	0.774

Sample: 1 — Moisture: e.m. — Gas: CH4 — T (°C): 45.4

P [MPa]	n_{ads} [mmol/g]
0	0
1.01	0.071
1.77	0.143
2.34	0.213
2.86	0.259
3.29	0.293
3.64	0.318
5.04	0.368
6.13	0.4
8.58	0.431
10.47	0.445
11.92	0.452
13.06	0.455
13.94	0.458
14.63	0.46
15.15	0.463
15.54	0.464
15.84	0.466
16.08	0.467
16.26	0.469
16.41	0.469
16.53	0.471
16.62	0.471
16.69	0.471
16.73	0.472
16.77	0.473
16.79	0.473
16.81	0.474

Sample: 1 — Moisture: a.r. — Gas: CO2 — T (°C): 46.09

P [MPa]	n_{ads} [mmol/g]
0	0
1.6	0.732
6.15	1.01
8.18	0.98
9.05	0.902
9.52	0.815
9.88	0.716
10.23	0.658
10.59	0.629
10.99	0.593
11.42	0.563
11.86	0.545
12.3	0.522
12.7	0.521
13.82	0.487
15	0.47
16.2	0.45
17.36	0.44
18.45	0.44
19.44	0.43
20.33	0.43
21.12	0.42
21.8	0.42
22.38	0.42
22.88	0.42
23.3	0.42
23.66	0.42
23.96	0.42
24.21	0.42

Sample: 1 — Moisture: e.m. — Gas: CO2 — T (°C): 45.02

P [MPa]	n_{ads} [mmol/g]
0	0
0.86	0.44
2.13	0.69
3.27	0.82
4.1	0.88
4.69	0.91
5.1	0.93
5.38	0.94
8.31	0.95
9.26	0.91
9.73	0.87
10.47	0.73
11.45	0.62
12.7	0.55
14.05	0.5
15.34	0.47
16.48	0.44
17.41	0.43
18.15	0.42
18.73	0.41
19.15	0.4
19.47	0.4
19.7	0.4
19.88	0.4
20.01	0.4
20.11	0.4
20.17	0.4
20.2	0.4

Sample: 1 — Moisture: p.d. — Gas: CH4 — T (°C): 45.5

P [MPa]	n_{ads} [mmol/g]
0	0
0.65	0.18
2.29	0.35
5.17	0.48
7.52	0.53
9.38	0.56
10.87	0.57
12.07	0.58
13.03	0.58
13.8	0.58
14.42	0.59
14.93	0.59
15.33	0.59

Sample: 2 — Moisture: a.r. — Gas: CH4 — T (°C): 44.68

P [MPa]	n_{ads} [mmol/g]
0	0
0.94	0.349
2.92	0.564
4.67	0.651
6.13	0.696
7.34	0.721
8.33	0.736
9.16	0.745
9.83	0.751
10.39	0.756
10.85	0.758
11.89	0.762
12.75	0.764
13.46	0.764
14.05	0.764
14.54	0.764
14.95	0.763
15.28	0.762
15.56	0.762
15.79	0.762
15.98	0.762
16.14	0.761
16.27	0.761
16.37	0.761
16.46	0.761

Sample: 2 — Moisture: e.m. — Gas: CH4 — T (°C): 45.41

P [MPa]	n_{ads} [mmol/g]
0	0
1.16	0.038
2.7	0.099
3.86	0.153
4.78	0.189
5.51	0.216
6.07	0.236
6.51	0.251
6.85	0.264
7.12	0.274
7.33	0.283
7.49	0.29
7.62	0.296
7.72	0.302
7.8	0.306
7.86	0.31
7.92	0.314
7.96	0.317
9.66	0.309
10.92	0.305
11.87	0.304
12.99	0.322
13.92	0.321
14.61	0.326
15.19	0.32

Sample: 2 — Moisture: e.m. (2) — Gas: CH4 — T (°C): 45.41

P [MPa]	n_{ads} [mmol/g]
0	0
0.92	0.09
1.68	0.15
2.32	0.2
2.84	0.24
3.25	0.27
3.59	0.29
4.97	0.34
6.05	0.36
8.43	0.4
10.25	0.42
11.66	0.44
12.77	0.46
13.65	0.47
14.34	0.48
14.88	0.49
15.32	0.5
15.65	0.5
15.92	0.5

Sample: 2 — Moisture: a.r. — Gas: CO2 — T (°C): 45.02

P [MPa]	n_{ads} [mmol/g]
0	0
1.74	0.784
3.84	0.985
5.29	1.054
6.23	1.081
6.85	1.094
7.27	1.101
7.56	1.106
8.75	1.078
9.34	1.044
9.72	0.961
10.04	0.885
10.61	0.753
11.39	0.654
12.38	0.572
13.47	0.516
14.56	0.47
15.58	0.44
16.49	0.42
17.28	0.4
18.74	0.38
20.03	0.35
21.09	0.34
21.99	0.33
22.7	0.32
23.25	0.31
23.68	0.31
24.04	0.31
24.32	0.3

Sample: 3 — Moisture: a.r. — Gas: CH4 — T (°C): 44.55

P [MPa]	n_{ads} [mmol/g]
0	0
0.84	0.356
1.82	0.489
2.7	0.558
3.45	0.601
4.09	0.628
4.63	0.648
5.07	0.662
5.45	0.672
5.76	0.68
6.02	0.686
7.02	0.704
7.85	0.717
8.54	0.725
9.11	0.731
9.59	0.735
9.99	0.738
10.32	0.741
10.59	0.743
10.82	0.745
11.01	0.745
11.17	0.747
11.3	0.748
11.42	0.748
11.51	0.75
11.59	0.75
11.66	0.75
12.52	0.753
13.25	0.753
13.85	0.755
14.36	0.757
14.79	0.757
15.15	0.756
15.45	0.756
15.7	0.759

Sample: 3 — Moisture: e.m. — Gas: CH4 — T (°C): 45.51

P [MPa]	n_ads [mmol/g]
0	0
1.49	0.153
2.73	0.263
3.81	0.327
4.7	0.366
5.43	0.392
6	0.409
6.46	0.421
7.72	0.436
8.69	0.446
9.44	0.451
10.02	0.455
10.47	0.458
10.83	0.46
11.1	0.462
11.32	0.463
11.49	0.464
12.71	0.461
13.67	0.459
14.4	0.458
14.98	0.458
15.43	0.458
15.77	0.458
16.04	0.459
16.25	0.459
16.42	0.46
16.55	0.46
16.66	0.46
16.74	0.461
16.8	0.462
16.85	0.462
16.89	0.462

Sample: 3 — Moisture: a.r. — Gas: CO2 — T (°C): 45.02

P [MPa]	n_ads [mmol/g]
0	0
0.72	0.518
3.11	0.845
7.85	0.952
9.41	0.85
10.18	0.717
11.21	0.593
12.68	0.513
14.51	0.449
16.4	0.413
18.17	0.389
19.71	0.372
20.98	0.36
21.99	0.352
22.79	0.345
23.38	0.342
23.85	0.34
24.18	0.34
24.45	0.33
24.62	0.33
24.77	0.33

Sample: 4 — Moisture: a.r. — Gas: CH4 — T (°C): 44.53

P [MPa]	n_ads [mmol/g]
0	0
1.01	0.33
2.14	0.467
3.14	0.54
4.69	0.615
5.98	0.657
7.59	0.695
8.91	0.716
9.98	0.729
10.87	0.737
11.59	0.743
12.19	0.746
12.68	0.749
13.08	0.751
13.41	0.752
13.68	0.754
13.91	0.754
14.49	0.755
14.98	0.756
15.38	0.756
15.7	0.758
15.98	0.757
16.2	0.758
16.39	0.759
16.55	0.759
16.68	0.757
16.79	0.759
16.88	0.758
16.95	0.759
17.01	0.758
17.06	0.759
17.1	0.759
17.14	0.76

Sample: 4 — Moisture: e.m. — Gas: CH4 — T (°C): 45.52

P [MPa]	n_ads [mmol/g]
0	0
0.92	0.722
1.71	0.972
2.35	1.071
2.89	1.11
3.32	1.124
3.67	1.13
3.95	1.052
5.33	0.981
6.38	0.864
7.19	0.756
9.42	0.7
11.12	0.672
12.42	0.662
13.44	0.678
14.22	0.659
14.82	0.64
15.29	0.63
15.65	0.61
15.93	0.6
16.15	0.58

Sample: 4 — Moisture: a.r. — Gas: CO2 — T (°C): 45.01

P [MPa]	n_ads [mmol/g]
0	0
1.44	0.722
3.38	0.972
4.95	1.071
6.03	1.11
6.74	1.124
7.21	1.13
8.62	1.052
9.12	0.981
9.47	0.864
9.75	0.756
10.02	0.7
10.3	0.672
10.63	0.662
11	0.678
11.9	0.659
12.6	0.64
13.42	0.63
14.37	0.61
15.42	0.6
16.54	0.58
17.68	0.57
18.83	0.56
19.95	0.54
21.01	0.53
21.9	0.53
22.64	0.52
23.23	0.51
23.68	0.51
24.04	0.51
24.32	0.51

Sample: 5 — Moisture: a.r. — Gas: CH4 — T (°C): 44.12

P [MPa]	n_ads [mmol/g]
0	0
5.02	0.566
8.81	0.626
11.37	0.638
13.13	0.64
14.35	0.639
15.2	0.637
15.79	0.635
16.2	0.634
16.48	0.634
16.68	0.633
16.82	0.632
16.92	0.627
11.68	0.635
8.2	0.613
5.77	0.575
4.07	0.527
2.88	0.472
2.06	0.417
1.48	0.364
1.08	0.315
0.8	0.27
0.6	0.23
0.46	0.195
0.36	0.165
0.28	0.138
0.22	0.116
0.18	0.096
0.15	0.08
0.12	0.065

Sample: 5 — Moisture: e.m. — Gas: CH4 — T (°C): 45.02

P [MPa]	n_ads [mmol/g]
0	0
0.92	0.112
1.72	0.181
2.4	0.23
2.94	0.266
3.38	0.293
3.73	0.314
5.12	0.356
6.21	0.384
8.6	0.421
10.45	0.445
11.82	0.462
12.94	0.492
13.79	0.495
14.45	0.499
14.96	0.502

Sample: 5 — Moisture: a.r. — Gas: CO2 — T (°C): 45.02

P [MPa]	n_ads [mmol/g]
0	0
0.3	0.312
1.67	0.645
2.99	0.778
4.09	0.847
4.97	0.886
5.72	0.911
6.32	0.929
7.27	0.969
8.9	0.905
9.56	0.815
10.12	0.691
10.77	0.585
11.6	0.502
12.58	0.44
14.05	0.379
15.62	0.33
17.17	0.3
18.58	0.28
19.84	0.26

Sample: 5 — Moisture: e.m. — Gas: CO2 — T (°C): 45.01

P [MPa]	n_ads [mmol/g]
0	0
1.77	0.14
3.99	0.22
5.56	0.26
6.56	0.28
8.68	0.28
9.65	0.2
10.19	0.12
10.56	0.08
11.36	0.06
12.31	0.05
13.43	0.05
14.62	0.03
15.74	0.03
17.54	0.03
19.2	0.02
20.62	0.02
21.75	0.02
22.64	0.02

Sample: 6 — Moisture: a.r. — Gas: CH4 — T (°C): 44.55

P [MPa]	n_ads [mmol/g]
0	0
0.9	0.271
1.89	0.394
2.79	0.462
3.54	0.504
4.17	0.531
5.51	0.576
6.6	0.602
8.58	0.634
10.17	0.65
11.46	0.658
12.51	0.662
13.37	0.665
14.07	0.666
14.64	0.666
15.1	0.666
15.47	0.667
15.77	0.667
16.02	0.667
16.22	0.667
16.38	0.667

Sample: 6 — Moisture: e.m. — Gas: CH4 — T (°C): 45.53

P [MPa]	n_ads [mmol/g]
0	0
1.56	0.141
2.95	0.22
4.08	0.273
4.97	0.31
5.67	0.336
6.22	0.355
6.65	0.37
7.93	0.39
8.9	0.405
9.63	0.417
11.35	0.43
12.67	0.439
13.68	0.446
14.46	0.451
15.06	0.455
15.52	0.458
15.88	0.459

Sample: 6 — Moisture: a.r. — Gas: CO2 — T (°C): 45.16

P [MPa]	n_ads [mmol/g]
0	0
1.61	0.764
3.37	0.954
4.7	1.026
5.64	1.056
6.32	1.069
6.81	1.07
7.18	1.068
7.45	1.068
8.56	1.047
9.14	0.999
9.49	0.996
9.75	0.968
9.99	0.954
10.21	0.898
10.43	0.872
10.65	0.84
10.86	0.82
11.05	0.8
11.23	0.79
11.4	0.79
11.55	0.77
11.68	0.77
11.79	0.77
12.42	0.73
13.04	0.72
13.66	0.72
14.26	0.7
14.81	0.69
15.32	0.68
15.77	0.68
16.17	0.67
16.51	0.67
16.81	0.67
17.07	0.67

Sample: 7 — Moisture: a.r. — Gas: CH4 — T (°C): 44.6

P [MPa]	n_ads [mmol/g]
0	0
0.96	0.352
2.62	0.546
5.2	0.675
7.34	0.727
9.09	0.75
10.51	0.762
11.67	0.767
12.62	0.77
13.4	0.771
14.04	0.771
14.57	0.771
14.99	0.771
15.34	0.77
15.63	0.771
15.85	0.771
16.04	0.771
16.19	0.77
16.31	0.77
16.41	0.77
16.49	0.77
16.55	0.77
16.6	0.77
16.64	0.77
16.67	0.771
16.7	0.771
16.72	0.771
16.74	0.77
16.75	0.771
16.76	0.771
16.76	0.772
16.76	0.771

Sample: 7 — Moisture: e.m. — Gas: CH4 — T (°C): 46.09

P [MPa]	n_ads [mmol/g]
0	0
1.98	0.086
3.35	0.19
4.45	0.257
5.31	0.301
5.99	0.331
6.5	0.353
6.9	0.369
8.23	0.382
9.21	0.391
9.94	0.399
11.73	0.392
13.07	0.389
14.1	0.389
14.83	0.391
15.4	0.395
15.8	0.398
16.11	0.397

Sample: 7 — Moisture: e.m. (2) — Gas: CH4 — T (°C): 46.09

P [MPa]	n_ads [mmol/g]
0	0
2.38	0.18
4.09	0.26
5.3	0.3
6.11	0.33
6.66	0.35
8.37	0.38
9.52	0.4
10.3	0.41
10.82	0.42
12.76	0.42
14.09	0.43
14.99	0.43
15.61	0.44
16.04	0.44
16.33	0.45

Sample: 7 — Moisture: p.d. — Gas: CH4 — T (°C): 45.12

P [MPa]	n_ads [mmol/g]
0	0
0.97	0.36
2.18	0.5
3.27	0.58
4.19	0.63
5.35	0.67
6.67	0.7
7.73	0.72
8.58	0.73
9.27	0.74
9.81	0.74
10.25	0.75
10.6	0.75
10.88	0.75
11.11	0.76
11.3	0.76
11.45	0.76
11.57	0.76
11.66	0.76
12.7	0.76
13.55	0.75
14.22	0.75
14.76	0.75
15.2	0.75
15.55	0.75
15.83	0.75
16.06	0.75
16.24	0.75
16.38	0.75
16.5	0.75

Sample: 7 — Moisture: e.m. — Gas: CO2 — T (°C): 45.03

P [MPa]	n_ads [mmol/g]
0	0
2.02	0.68
4.37	0.89
5.93	0.94
6.86	0.96
7.41	0.96
7.76	0.96
9.09	0.92
9.78	0.85
10.37	0.73
11.07	0.63
11.82	0.57
12.57	0.52
13.21	0.5
13.75	0.48
15.84	0.42
17.85	0.38
19.61	0.36
21.04	0.34
22.16	0.33
23	0.32
23.65	0.32
24.12	0.31

Sample: 7 — Moisture: a.r. — Gas: CO2 — T (°C): 45.02

P [MPa]	n_ads [mmol/g]
0	0
1.56	0.831
3.67	1.049
5.14	1.124
6.11	1.154
6.59	1.165
6.75	1.166
7.16	1.175
8.69	1.158
9.33	1.113
9.72	1.051
10.03	1.003
10.34	0.934
10.64	0.874
11.48	0.783
12.5	0.717
13.6	0.67
15.23	0.62
16.87	0.58
18.39	0.56
19.72	0.54
20.85	0.53
21.77	0.52
22.52	0.51

Sample: 7 — Moisture: p.d. — Gas: CO2 — T (°C): 45.12

P [MPa]	n_ads [mmol/g]
0	0
1.27	0.82
3.2	1.08
4.69	1.18
7.54	1.22
8.9	1.06
9.52	0.84
9.94	0.71
10.34	0.63
10.85	0.59
11.43	0.55
12.06	0.53
12.72	0.51
13.37	0.5
13.97	0.49
14.52	0.48
15	0.47
15.41	0.47
15.77	0.46
16.07	0.46
16.31	0.45
16.51	0.45
16.68	0.45
16.81	0.45

Sample: 8.1 — Moisture: a.r. — Gas: CH4 — T (°C): 45.52

P [MPa]	n_ads [mmol/g]
0	0
1.43	0.21
2.83	0.3
4	0.35
4.93	0.38
5.65	0.4
6.22	0.42
7.59	0.44
8.63	0.46
9.43	0.47
10.05	0.47
10.53	0.48
10.89	0.48
12.31	0.49
13.39	0.49
14.24	0.5
14.89	0.5
15.39	0.5
15.78	0.5

Sample: 8.1 — Moisture: p.d. — Gas: CH4 — T (°C): 45.52

P [MPa]	n_{ads} [mmol/g]
0	0
1.75	0.3
3	0.41
4.07	0.47
4.93	0.5
6.53	0.54
7.77	0.56
8.73	0.57
10.56	0.59
11.98	0.6
13.09	0.61
13.96	0.61
14.65	0.61
15.18	0.61
15.6	0.61
15.92	0.61
16.17	0.61

Sample: 8.1 — Moisture: e.m. — Gas: CH4 — T (°C): 45.52

P [MPa]	n_{ads} [mmol/g]
0	0
1.48	0.169
2.83	0.253
3.97	0.301
5.8	0.347
7.16	0.395
8.29	0.404
9.13	0.415
9.74	0.425
11.24	0.425
12.29	0.431
13.14	0.422
13.9	0.424
14.62	0.42
15.15	0.426
15.55	0.424

Sample: 8.1 — Moisture: e.m. — Gas: CH4 — T (°C): 55.82

P [MPa]	n_{ads} [mmol/g]
0	0
1.58	0.168
3.01	0.247
4.21	0.284
6.11	0.332
7.58	0.364
8.74	0.374
9.61	0.384
10.26	0.394
11.81	0.403
12.95	0.402
13.63	0.401
14.5	0.397
15.28	0.404
15.94	0.386
16.38	0.384

Sample: 8.1 — Moisture: e.m. — Gas: CH4 — T (°C): 66.03

P [MPa]	n_{ads} [mmol/g]
0	0
1.69	0.153
3.19	0.224
4.43	0.259
6.43	0.298
7.88	0.326
9.19	0.332
10.09	0.344
10.77	0.352
12.44	0.353
13.83	0.35
14.78	0.346
15.63	0.356
16.46	0.359
17.07	0.37
17.54	0.37

Sample: 8.1 — Moisture: dry — Gas: CH4 — T (°C): 65.02

P [MPa]	n_{ads} [mmol/g]
0	0
1.13	0.31
2.68	0.41
3.93	0.46
4.85	0.49
5.51	0.5
6.99	0.52
7.94	0.53
8.58	0.54
9.02	0.56
9.33	0.57
11.36	0.58
12.92	0.58
14.22	0.6
15.5	0.61
16.76	0.62
18.72	0.62
20.71	0.62
22.55	0.62
24.19	0.62
25.58	0.63

Sample: 8.1 — Moisture: e.m. — Gas: CO2 — T (°C): 45.03

P [MPa]	n_{ads} [mmol/g]
0	0
1.11	0.29
2.46	0.42
3.56	0.47
4.37	0.5
4.95	0.52
6.19	0.53
6.94	0.53
7.43	0.52
7.74	0.51
7.96	0.51
9.13	0.36
9.78	0.21
10.27	0.2
10.78	0.23
11.35	0.25
12.36	0.26
13.51	0.25
14.68	0.25
15.76	0.24
16.71	0.24
17.51	0.24
18.18	0.23
19.65	0.23
20.89	0.22
21.9	0.22
22.72	0.22
23.33	0.22
23.82	0.21

Sample: 8.1 — Moisture: e.m. — Gas: CO2 — T (°C): 55.05

P [MPa]	n_{ads} [mmol/g]
0	0
1.2	0.28
2.64	0.39
3.81	0.43
4.67	0.45
5.29	0.46
6.65	0.47
7.49	0.47
8.06	0.46
8.44	0.46
8.7	0.45
10.31	0.37
11.41	0.32
12.29	0.33
13.18	0.34
14.1	0.34
15.59	0.34
17.17	0.34
18.68	0.33
20.06	0.33
21.23	0.33

Sample: 8.2 — Moisture: a.r. — Gas: CH4 — T (°C): 45.42

P [MPa]	n_{ads} [mmol/g]
0	0
0.69	0.162
1.44	0.246
2.11	0.297
2.68	0.33
3.15	0.353
3.54	0.369
3.85	0.381
4.1	0.39
4.29	0.397
4.45	0.402
5.18	0.422
5.76	0.437
6.23	0.447
6.6	0.454
6.9	0.46
7.14	0.464
7.33	0.468
7.48	0.47
7.59	0.472
9.51	0.494
11.02	0.505
12.23	0.512
13.19	0.516
13.97	0.518
14.58	0.521
15.07	0.522
15.46	0.522
15.77	0.523
16	0.525

Sample: 8.2 — Moisture: a.r. — Gas: CO2 — T (°C): 45.42

P [MPa]	n_{ads} [mmol/g]
0	0
0.8	0.394
5.49	0.864
8.04	0.919
9.13	0.916
9.71	0.876
10.31	0.761
11.23	0.608
12.5	0.51
14.05	0.437
15.71	0.387
17.33	0.352
18.79	0.331
20.09	0.311
21.15	0.303
22.04	0.294
22.76	0.286
23.32	0.281

Sample: 10 — Moisture: a.r. — Gas: CH4 — T (°C): 45.02

P [MPa]	n_{ads} [mmol/g]
0	0
1.54	0.187
2.97	0.255
4.12	0.291
5.93	0.328
7.33	0.348
8.4	0.36
10.53	0.374
12.18	0.382
13.46	0.385
14.87	0.386
15.99	0.387
16.87	0.386
17.56	0.386
18.1	0.385
18.53	0.385
18.86	0.385
19.12	0.385
19.31	0.385
21.06	0.378
22.48	0.373
23.63	0.368
24.56	0.364

Sample: 11 — Moisture: a.r. — Gas: CH4 — T (°C): 45.02

P [MPa]	n_{ads} [mmol/g]
0	0
0.67	0.216
1.44	0.327
2.16	0.392
2.75	0.432
3.23	0.459
3.61	0.478
5	0.527
6.11	0.556
6.95	0.574
7.61	0.586
8.12	0.594
8.51	0.599
10.33	0.615
11.75	0.623
12.84	0.627
13.68	0.63
14.36	0.63
14.89	0.631
15.31	0.631
15.65	0.631

Sample: 12 — Moisture: a.r. — Gas: CH4 — T (°C): 45.40

P [MPa]	n_{ads} [mmol/g]
0	0
0.77	0.135
1.51	0.212
2.15	0.258
2.68	0.288
3.12	0.309
3.48	0.324
4.76	0.366
5.8	0.393
6.63	0.411
7.3	0.423
7.83	0.432
8.26	0.438
8.61	0.443
8.89	0.447
9.11	0.45
10.65	0.465
11.87	0.475
12.85	0.482
13.64	0.486
14.27	0.489
14.77	0.492
15.18	0.494
15.5	0.496
15.76	0.497
15.97	0.498
16.15	0.5
16.28	0.5
16.4	0.5
16.49	0.5
16.56	0.5
16.62	0.5

Sample: 13 — Moisture: a.r. — Gas: CH4 — T (°C): 45.40

P [MPa]	n_{ads} [mmol/g]
0	0
0.54	0.221
1.19	0.342
1.81	0.414
2.36	0.461
2.82	0.494
3.22	0.517
4.46	0.573
5.49	0.607
6.33	0.629
7.01	0.644
7.56	0.654
8.01	0.662
9.66	0.681
11	0.692
12.08	0.698
12.97	0.701
13.7	0.704
14.3	0.704
14.78	0.705
15.18	0.706
15.51	0.706
15.78	0.707

Sample: 14 — Moisture: a.r. — Gas: CH4 — T (°C): 45.41

P [MPa]	n_{ads} [mmol/g]
0	0
0.78	0.09
1.55	0.129
2.76	0.169
3.77	0.191
4.59	0.205
5.26	0.215
5.8	0.221
6.23	0.226
6.58	0.23
6.87	0.232
7.85	0.24
8.64	0.245
9.27	0.249
9.78	0.251
11.12	0.257
12.21	0.26
13.09	0.262
13.81	0.263
14.4	0.264
14.88	0.265
15.27	0.265
15.59	0.266
15.84	0.266
16.04	0.267
16.21	0.267
16.34	0.268
16.46	0.267
16.55	0.267
16.63	0.267
16.7	0.267
16.75	0.268

Sample: 15 — Moisture: a.r. — Gas: CH4 — T (°C): 45.38

P [MPa]	n_{ads} [mmol/g]
0	0
0.6	0.175
1.29	0.263
1.93	0.316
2.48	0.35
2.94	0.373
3.33	0.39
4.21	0.42
4.93	0.44
5.51	0.454
5.97	0.463
6.35	0.471
6.66	0.476
6.91	0.48
7.13	0.483
7.3	0.486
7.44	0.488
8.31	0.497
8.44	0.499
9.11	0.505
9.65	0.509
10.09	0.511
10.45	0.514
11.66	0.519
12.66	0.521
13.47	0.523
14.13	0.524
14.67	0.525
15.1	0.526
15.46	0.526
15.75	0.526
15.99	0.526

Sample: 16 — Moisture: a.r. — Gas: CH4 — T (°C): 45.40

P [MPa]	n_{ads} [mmol/g]
0	0
0.76	0.131
1.49	0.202
2.12	0.246
2.66	0.275
3.11	0.295
3.88	0.323
5.06	0.358
6.01	0.38
6.77	0.396
7.39	0.406
7.89	0.414
8.29	0.42
8.61	0.424
10.23	0.441
11.5	0.452
12.53	0.459
13.36	0.465
14.04	0.467
14.59	0.47
15.03	0.472
15.39	0.474

Sample: 17 — Moisture: a.r. — Gas: CH4 — T (°C): 45.03

P [MPa]	n_{ads} [mmol/g]
0	0
0.7	0.209
1.48	0.314
2.18	0.375
2.77	0.414
3.24	0.44
3.62	0.457
5	0.506
6.08	0.535
6.92	0.552
7.58	0.564
8.1	0.572
8.5	0.578
8.81	0.582
10.69	0.596
12.01	0.602
13.05	0.605
13.86	0.607
14.49	0.608
15	0.609
15.39	0.61
15.71	0.609

Sample: 19 — Moisture: a.r. — Gas: CH4 — T (°C): 45.02

P [MPa]	n_{ads} [mmol/g]
0	0
0.85	0.139
2.34	0.233
3.59	0.277
4.58	0.302
5.35	0.317
5.96	0.328
8.43	0.354
10.33	0.366
11.8	0.372
12.95	0.375
13.84	0.377
14.55	0.378
14.3	0.378
13.23	0.377
11.93	0.374
10.63	0.369
9.42	0.362
8.32	0.353
7.34	0.344

Sample: 21 — Moisture: a.r. — Gas: CH4 — T (°C): 44.75

P [MPa]	n_{ads} [mmol/g]
0	0
2.39	0.601
4.81	0.752
6.89	0.817
8.6	0.848
10.01	0.863
11.17	0.872
12.13	0.875
12.92	0.877
13.58	0.878
14.12	0.878
14.57	0.878
14.94	0.878
15.24	0.877
15.49	0.876
15.7	0.876
15.86	0.876
16	0.876
16.11	0.877
16.2	0.876

Sample: 21 — Moisture: e.m. — Gas: CH4 — T (°C): 44.75

P [MPa]	n_{ads} [mmol/g]
0	0
0.74	0.194
1.53	0.314
2.25	0.392
2.86	0.445
3.35	0.482
3.74	0.506
5.26	0.565
6.43	0.601
7.31	0.625
9.68	0.658
11.45	0.674
12.79	0.683
13.79	0.688
14.55	0.691
15.12	0.693
15.55	0.694
15.87	0.694
16.12	0.695
16.31	0.696
16.46	0.696
16.58	0.697
16.67	0.697
16.74	0.697

Sample: 21 — Moisture: a.r. — Gas: CO2 — T (°C): 45.02

P [MPa]	nads [mmol/g]
0	0
0.73	0.626
1.88	0.888
3.78	1.09
5.15	1.168
6.06	1.201
6.68	1.221
7.11	1.231
8.6	1.215
9.25	1.2
9.83	1.105
10.4	0.961
11.12	0.82
12	0.738
13.01	0.66
14.06	0.605
15.05	0.57
15.96	0.55
16.77	0.52
17.45	0.51
18.01	0.5
19.32	0.47
20.45	0.45
21.39	0.44
22.17	0.43
22.8	0.42
23.31	0.41
23.72	0.41
24.04	0.41
24.3	0.4
24.51	0.4
24.65	0.4
24.77	0.4
24.87	0.4
24.93	0.4

Sample: 22 — Moisture: a.r. — Gas: CH4 — T (°C): 44.84

P [MPa]	nads [mmol/g]
0	0
2.62	0.394
5.07	0.499
7.1	0.547
8.77	0.572
10.14	0.586
11.28	0.594
12.22	0.598
13	0.6
13.64	0.604
14.18	0.605
14.62	0.606
14.99	0.607
15.3	0.608
15.55	0.61
15.76	0.61
15.93	0.611
16.08	0.612
16.2	0.612
16.3	0.612
16.38	0.612
16.45	0.612
16.51	0.612
16.55	0.614
16.59	0.613

Sample: 22 — Moisture: e.m. — Gas: CH4 — T (°C): 46.12

P [MPa]	nads [mmol/g]
0	0
6.25	0.289
9.29	0.361
11.51	0.38
13.12	0.385
14.27	0.384
15.09	0.382
15.66	0.381
16.07	0.379
16.36	0.378
16.56	0.378
16.7	0.378
16.81	0.378
16.88	0.377
16.94	0.377
16.97	0.376
16.99	0.377
17.02	0.377
17.03	0.377
17.04	0.377

Sample: 22 — Moisture: a.r. — Gas: CH4 — T (°C): 19.54

P [MPa]	nads [mmol/g]
0	0
0.66	0.24
1.36	0.34
1.99	0.39
2.52	0.43
3.84	0.49
4.95	0.53
5.87	0.55
6.64	0.57
7.29	0.58
7.84	0.58
8.74	0.59
9.49	0.6
10.43	0.61
11.28	0.61
12.01	0.61
12.62	0.61
13.15	0.61
13.6	0.61
13.99	0.61
14.33	0.61
14.61	0.61
14.87	0.61
15.12	0.62
15.35	0.62
15.55	0.62
15.72	0.62
15.87	0.61
15.99	0.62
16.1	0.62
16.2	0.62
16.28	0.62

Sample: 22 — Moisture: a.r. — Gas: CO2 — T (°C): 19.42

P [MPa]	nads [mmol/g]
0	0
0.14	0.19
0.31	0.33
0.44	0.48
0.6	0.59
0.76	0.66
0.91	0.71
1.06	0.75
1.18	0.77
1.29	0.79
1.39	0.8
1.72	0.83
2.01	0.85
2.25	0.85
2.45	0.85
2.62	0.85
2.77	0.85
2.88	0.84
3.28	0.8
3.62	0.76
4.05	0.66

Sample: 22 — Moisture: a.r. — Gas: CO2 — T (°C): 44.85

P [MPa]	nads [mmol/g]
0	0
1.79	0.554
6.11	0.777
8.06	0.79
8.94	0.756
9.41	0.714
9.75	0.633
10.08	0.5
10.41	0.476
10.78	0.419
11.17	0.373
11.59	0.342
12	0.314
12.41	0.298
12.8	0.273
13.14	0.27
14.23	0.23
15.35	0.22
16.48	0.2
17.55	0.19
18.56	0.18
19.49	0.17
20.31	0.17
21.05	0.16
21.69	0.16
22.26	0.16
22.74	0.16
23.15	0.15
23.51	0.15
23.8	0.15

Sample: 23 — Moisture: a.r. — Gas: CH4 — T (°C): 44.68

P [MPa]	nads [mmol/g]
0	0
0.86	0.404
1.87	0.574
3.99	0.741
5.82	0.812
7.33	0.848
8.58	0.867
9.62	0.877
10.48	0.883
11.2	0.886
12.21	0.888
13.04	0.889
13.75	0.886
14.34	0.886
14.83	0.885
15.24	0.884
15.58	0.883
15.87	0.881
16.11	0.881
16.31	0.88
16.48	0.881
16.62	0.88
16.74	0.88
16.83	0.882
16.92	0.88
16.98	0.881
17.04	0.881
17.09	0.882
17.13	0.881
17.17	0.882
17.2	0.881
17.23	0.882
17.25	0.881
17.27	0.882
17.28	0.883
17.29	0.883
17.3	0.884

Sample: 23 — Moisture: e.m. — Gas: CH4 — T (°C): 45.43

P [MPa]	nads [mmol/g]
0	0
0.74	0.141
1.46	0.24
2.09	0.313
2.63	0.368
3.08	0.41
3.46	0.442
3.77	0.468
4.02	0.488
5.35	0.536
6.38	0.57
7.18	0.595
7.81	0.615
8.3	0.629
8.68	0.641
8.98	0.65
9.22	0.657
9.41	0.663
9.55	0.668
9.65	0.671
9.73	0.674
9.8	0.677
9.84	0.679
9.88	0.68
9.91	0.682
9.94	0.683
9.96	0.684
11.57	0.689
12.81	0.69
13.76	0.692
14.5	0.694
15.06	0.696
15.49	0.696
15.83	0.698
16.09	0.699
16.3	0.7
16.45	0.7
16.58	0.701

Sample: 23 — Moisture: p.d. — Gas: CH4 — T (°C): 45.43

P [MPa]	nads [mmol/g]
0	0
0.69	0.228
1.39	0.404
2.19	0.501
2.93	0.558
4.86	0.645
6.45	0.683
7.7	0.701
8.69	0.709
9.45	0.713
11.14	0.715
12.45	0.713
13.46	0.71
14.24	0.706
14.85	0.703
15.32	0.7
15.68	0.698
15.97	0.696
16.2	0.695
16.37	0.693
16.5	0.692
16.61	0.692
16.69	0.691
16.76	0.691
16.81	0.691
16.85	0.691
16.87	0.691
16.89	0.691

Sample: 23 — Moisture: a.r. — Gas: CO2 — T (°C): 45.02

P [MPa]	nads [mmol/g]
0	0
0.65	0.661
1.67	0.926
2.63	1.053
3.42	1.119
6.43	1.282
8.43	1.241
9.24	1.144
9.7	1.026
10.07	0.97
10.49	0.871
10.94	0.816
11.43	0.769
11.95	0.731
12.47	0.701
13.19	0.658

Sample: 23 — Moisture: e.m. — Gas: CO2 — T (°C): 45.5

P [MPa]	nads [mmol/g]
0	0
0.52	0.446
1.54	0.708
7.03	1.027
8.92	1.047
9.64	1.052
10.18	0.988
10.83	0.883
11.6	0.811
12.45	0.764
13.28	0.732
14.06	0.71
14.74	0.693
15.29	0.685
15.76	0.677
16.12	0.672

Sample: 24 — Moisture: a.r. — Gas: CH4 — T (°C): 44.66

P [MPa]	nads [mmol/g]
0	0
0.69	0.386
1.5	0.56
2.26	0.656
2.93	0.717
3.5	0.757
3.99	0.786
4.4	0.807
4.75	0.823
5.05	0.835
5.83	0.862
6.47	0.88
7.01	0.892
7.46	0.902
7.84	0.909
8.16	0.914
8.43	0.918
9.42	0.929
10.23	0.935
11.14	0.939
11.9	0.942
12.52	0.943
13.05	0.944
13.48	0.943
13.85	0.943
14.15	0.941
14.41	0.942
14.62	0.94
14.8	0.941
14.94	0.941
15.06	0.941
15.17	0.941
15.26	0.94
15.33	0.939
15.4	0.94
15.56	0.94
15.67	0.94
15.76	0.939
15.84	0.938

Sample: 24 — Moisture: e.m. — Gas: CH4 — T (°C): 45.63

P [MPa]	nads [mmol/g]
0	0
1.16	0.252
2.23	0.415
3.2	0.503
4.06	0.554
4.78	0.586
5.38	0.607
5.87	0.621
6.28	0.63
6.61	0.637
6.88	0.642
7.11	0.646
7.29	0.649
7.44	0.651
7.57	0.653
7.68	0.654
7.77	0.655
7.84	0.656
7.91	0.657
8.68	0.661
9.31	0.664
9.83	0.665
10.25	0.666
10.59	0.667
10.88	0.666
11.11	0.666
11.3	0.667
11.46	0.666
11.59	0.666
12.22	0.665
12.74	0.664
13.17	0.664
13.52	0.663
13.81	0.663
14.05	0.662
14.25	0.663
14.41	0.662
14.54	0.662
14.64	0.663

Sample: 24 — Moisture: a.r. — Gas: CH4 — T (°C): 19.54

P [MPa]	nads [mmol/g]
0	0
0.64	0.48
1.46	0.66
2.9	0.81
4.14	0.88
5.19	0.92
6.07	0.94
6.81	0.96
7.42	0.97
7.94	0.98
8.38	0.98
8.75	0.99
9.63	0.99
10.38	0.99
11	1
11.53	1
11.98	1
12.36	0.99
12.68	0.99
13.08	0.99
13.41	0.99
13.69	0.99
13.94	0.99
14.15	0.99
14.32	0.98
14.48	0.99
14.61	0.99
14.73	0.99
14.83	0.99
14.91	0.99
14.99	0.98
15.06	0.99
15.19	0.98
15.3	0.98
15.4	0.98
15.47	0.99
15.55	0.98
15.6	0.99
15.65	0.98

Sample: 24 — Moisture: a.r. — Gas: CO2 — T (°C): 44.97

P [MPa]	nads [mmol/g]
0	0
1.4	0.833
5.92	1.154
8.03	1.124
8.96	1.029
9.45	0.921
9.8	0.817
10.13	0.743
10.48	0.682
10.85	0.647
11.25	0.609
11.67	0.585
12.09	0.562
13.08	0.53
14.18	0.499
15.32	0.48
16.46	0.47
17.56	0.45
18.59	0.44
19.53	0.44
20.37	0.43
21.12	0.43
21.76	0.43
22.33	0.42
22.81	0.42
23.22	0.42
23.57	0.42
23.87	0.42
24.12	0.42
24.33	0.42

Sample: 24 — Moisture: a.r. — Gas: CO2 — T (°C): 19.54

P [MPa]	nads [mmol/g]
0	0
0.26	0.14
0.35	0.39
0.46	0.61
0.73	0.86
1.05	1.01
1.36	1.1
1.64	1.15
1.89	1.19
2.11	1.22
2.29	1.24
2.43	1.25
2.56	1.26
2.66	1.27
3.16	1.29
3.56	1.29
3.88	1.28
4.14	1.27
4.34	1.25
4.5	1.23

Sample: 25 — Moisture: a.r. — Gas: CH4 — T (°C): 44.84

P [MPa]	nads [mmol/g]
0	0
2.21	0.629
4.62	0.792
6.66	0.859
8.34	0.891
9.72	0.907
10.85	0.915
11.78	0.919
12.54	0.92
13.17	0.92
13.68	0.92
14.11	0.919
14.46	0.919
14.75	0.919
14.98	0.919
15.18	0.919
15.34	0.918
15.46	0.918
15.57	0.918
15.65	0.918
15.71	0.918
15.76	0.919
15.79	0.919
15.82	0.919

Sample: 25 — Moisture: e.m. — Gas: CH4 — T (°C): 43.94

P [MPa]	nads [mmol/g]
0	0
2.59	0.268
4.46	0.384
5.7	0.452
6.52	0.496
7.06	0.528
7.42	0.552
7.65	0.571
9.23	0.595
10.23	0.613
10.88	0.628
13.05	0.638

Sample: 25 — Moisture: e.m.2 — Gas: CH4 — T (°C): 46.08

P [MPa]	nads [mmol/g]
0	0
2.2	0.26
3.94	0.37
5.17	0.43
6.02	0.47
6.62	0.49
7.04	0.51
7.34	0.53
8.98	0.54
10.07	0.55
11.16	0.55
12.15	0.56
12.83	0.56
14.1	0.57
14.99	0.57
15.6	0.57
16.03	0.57
16.32	0.58
16.53	0.58
16.67	0.58
16.76	0.58

Sample: 25 — Moisture: a.r. — Gas: CO2 — T (°C): 44.94

P [MPa]	nads [mmol/g]
0	0
0.52	0.553
1.43	0.805
2.32	0.929
3.08	1
3.7	1.04
6.8	1.141
8.25	1.119
8.96	1.048
9.37	0.95
9.66	0.866
9.9	0.807
10.12	0.768
10.34	0.715
10.54	0.687
10.74	0.649
10.92	0.66
11.09	0.64
11.24	0.63
11.83	0.6
12.56	0.57
13.37	0.53
14.49	0.52
15.69	0.48
16.84	0.47
17.94	0.46
18.93	0.45
19.85	0.44
20.62	0.45
21.31	0.45

Sample: 26 — Moisture: a.r. — Gas: CH4 — T (°C): 19.39

P [MPa]	nads [mmol/g]
0	0
0.44	0.35
1	0.51
1.54	0.6
2.02	0.65
3.24	0.75
4.27	0.8
5.14	0.83
5.87	0.85
6.48	0.86
6.99	0.87
7.42	0.88
7.77	0.88
9.1	0.89
10.28	0.9
11.27	0.89
12.09	0.9
12.79	0.9
13.4	0.89
13.92	0.89
14.37	0.88
14.76	0.89
15.09	0.88
15.37	0.88
15.62	0.88
15.84	0.88
16.04	0.88
16.2	0.88
16.34	0.88
16.46	0.88
16.57	0.88
16.66	0.88

Sample: 26 — Moisture: a.r. — Gas: CH4 — T (°C): 44.85

P [MPa]	nads [mmol/g]
0	0
2.32	0.627
4.78	0.781
6.86	0.842
8.58	0.871
9.99	0.884
11.17	0.89
12.14	0.892
12.94	0.893
13.61	0.893
14.16	0.893
14.62	0.891
14.99	0.891
15.3	0.891
15.56	0.89
15.77	0.889
15.94	0.888

Sample: 26 — Moisture: e.m. — Gas: CH4 — T (°C): 46.08

P [MPa]	nads [mmol/g]
0	0
1.77	0.174
3.15	0.302
4.27	0.38
5.16	0.432
5.84	0.468
6.37	0.495
6.77	0.516
8.1	0.53
9.09	0.542
9.82	0.553
11.62	0.546
12.95	0.544
13.95	0.544
14.71	0.546
15.27	0.549
15.71	0.55

Sample: 26 — Moisture: p.d. — Gas: CH4 — T (°C): 45.12

P [MPa]	nads [mmol/g]
0	0
0.86	0.372
2.06	0.558
3.21	0.652
4.21	0.703
5.01	0.734
6.53	0.773
7.73	0.793
9.75	0.812
11.32	0.818
12.56	0.819
13.52	0.819
14.28	0.816
14.88	0.814
15.34	0.812
15.71	0.811
15.99	0.81
16.22	0.808

Sample: 26 — Moisture: a.r. — Gas: CO2 — T (°C): 19.42

P [MPa]	nads [mmol/g]
0	0
0.27	0.26
0.44	0.57
0.68	0.78
0.95	0.91
1.22	1
1.47	1.05
1.69	1.09
1.89	1.11
2.05	1.13
2.37	1.15
2.64	1.16
2.86	1.17
3.24	1.17
3.56	1.16
3.81	1.14
4.02	1.12
4.19	1.1
4.32	1.08
4.54	1.05
4.71	1.01
4.84	0.97
5.02	0.93

Sample: 26 — Moisture: a.r. — Gas: CO2 — T (°C): 45.02

P [MPa]	nads [mmol/g]
0	0
1.49	0.934
3.22	1.164
6.47	1.315
8.05	1.307
8.83	1.231
9.27	1.139
9.57	1.059
9.82	0.965
10.04	0.927
10.47	0.818
10.98	0.785
11.58	0.728
12.26	0.686
13	0.655
13.75	0.633
14.49	0.61
15.21	0.6
15.87	0.59
16.96	0.57
17.99	0.56
18.95	0.55
19.82	0.55
20.6	0.54
21.29	0.54
21.9	0.53
22.42	0.53
22.84	0.54
23.23	0.54
23.56	0.54
23.84	0.54
24.09	0.53

Sample: 27 — Moisture: a.r. — Gas: CH4 — T (°C): 44.7

P [MPa]	nads [mmol/g]
0	0
0.9	0.286
1.89	0.399
3.22	0.485
4.35	0.532
5.3	0.56
6.09	0.578
6.74	0.59
7.28	0.6
7.74	0.606
8.11	0.61
8.42	0.615
9.51	0.624
10.42	0.63
11.17	0.634
11.79	0.636
12.32	0.637
12.75	0.638
13.12	0.639
13.42	0.64
13.67	0.641
13.88	0.641
14.42	0.642
14.86	0.641
15.24	0.641
15.55	0.641
15.81	0.641
16.02	0.641
16.2	0.641
16.36	0.641
16.48	0.642
16.59	0.643
16.68	0.644
16.75	0.643
16.82	0.643

Sample: 27 — Moisture: e.m. — Gas: CH4 — T (°C): 45.37

P [MPa]	nads [mmol/g]
0	0
1.85	0.09
3.3	0.143
4.42	0.175
5.29	0.198
5.94	0.215
9.87	0.263
11.61	0.262
12.91	0.264
13.89	0.268
14.63	0.272
15.2	0.276

Sample: 27 — Moisture: a.r. — Gas: CO2 — T (°C): 44.83

P [MPa]	nads [mmol/g]
0	0
1.7	0.723
3.45	0.907
4.73	0.987
7.27	1.044
8.47	0.987
9.07	0.877
9.44	0.754
9.71	0.646
9.94	0.601
10.16	0.56
10.38	0.538
10.59	0.515
10.8	0.449
11	0.437
11.18	0.424
11.34	0.41
11.49	0.41
11.61	0.41
12.02	0.39
12.42	0.38
13.19	0.35
13.97	0.33
14.73	0.31
15.45	0.3
16.11	0.29
16.71	0.29
17.24	0.28

Sample: 27 — Moisture: e.m. — Gas: CO2 — T (°C): 45.02

P [MPa]	nads [mmol/g]
0	0
2.29	0.49
7.9	0.75
9.34	0.78
10.03	0.75
10.8	0.68
11.78	0.63
12.89	0.6
14.87	0.56
16.91	0.54
18.76	0.53
20.33	0.52
21.59	0.51
22.58	0.51
23.32	0.5
23.85	0.5
24.25	0.5
24.54	0.5
24.77	0.5

Sample: 28 — Moisture: a.r. — Gas: CH4 — T (°C): 44.67

P [MPa]	n_{ads} [mmol/g]
0	0
0.94	0.376
2	0.524
2.96	0.602
3.78	0.65
4.48	0.681
5.06	0.703
5.54	0.718
5.94	0.729
7.46	0.761
8.71	0.778
9.74	0.787
10.6	0.793
11.32	0.795
11.91	0.797
12.4	0.798
12.81	0.799
13.15	0.799
13.73	0.799
14.25	0.797
14.74	0.797
15.14	0.796
15.48	0.795
15.77	0.795
16	0.794
16.2	0.793
16.37	0.794
16.51	0.793
16.62	0.794
16.72	0.795
16.8	0.795
16.86	0.796
16.92	0.795
16.96	0.796
17	0.796

Sample: 28 — Moisture: e.m. — Gas: CH4 — T (°C): 45.39

P [MPa]	n_{ads} [mmol/g]
0	0
1.45	0.176
2.85	0.27
4.01	0.331
4.94	0.373
5.66	0.403
6.22	0.426
6.65	0.444
7.98	0.467
8.97	0.485
9.71	0.499
11.49	0.513
12.82	0.523
13.83	0.532
14.61	0.538
15.19	0.543
15.64	0.547
15.99	0.549

Sample: 28 — Moisture: a.r. — Gas: CO2 — T (°C): 45.02

P [MPa]	n_{ads} [mmol/g]
0	0
0.52	0.516
1.77	0.814
2.92	0.941
3.81	1.005
5.17	1.074
6.09	1.105
6.71	1.121
7.14	1.13
7.43	1.138
8.75	1.13
9.54	1.054
10.1	0.931
10.74	0.794
11.78	0.666
13.12	0.574
14.65	0.51
16.23	0.46
17.74	0.43
19.1	0.4

Sample: 28 — Moisture: e.m. — Gas: CO2 — T (°C): 46.08

P [MPa]	n_{ads} [mmol/g]
0	0
0.54	0.39
1.49	0.62
2.41	0.76
3.16	0.83
3.74	0.87
4.17	0.9
4.48	0.92
4.71	0.93
4.86	0.94
6.19	0.97
6.95	0.98
7.39	0.98
9.37	0.9
10.22	0.79
11.31	0.66
12.77	0.58
14.34	0.54
15.77	0.51
16.95	0.5
17.86	0.48
18.54	0.48
19.03	0.47
19.39	0.47
19.63	0.47

Sample: 29 — Moisture: a.r. — Gas: CH4 — T (°C): 44.74

P [MPa]	n_{ads} [mmol/g]
0	0
2.41	0.469
4.83	0.585
6.84	0.634
8.5	0.658
9.86	0.671
10.98	0.678
11.92	0.682
12.69	0.683
13.32	0.684
13.85	0.685
14.29	0.685
14.65	0.685
14.95	0.686
15.19	0.686
15.4	0.686
15.56	0.685
15.7	0.687

Sample: 29 — Moisture: e.m. — Gas: CH4 — T (°C): 45.57

P [MPa]	n_{ads} [mmol/g]
0	0
1.56	0.13
3.25	0.19
6.17	0.252
8.34	0.289
9.96	0.316
11.19	0.336
12.11	0.352
12.81	0.363
13.34	0.373
13.75	0.381
14.07	0.386
14.79	0.391
15.33	0.395
15.74	0.398

Sample: 29 — Moisture: a.r. — Gas: CO2 — T (°C): 45.02

P [MPa]	n_{ads} [mmol/g]
0	0
0.8	0.479
5.42	0.923
7.98	0.969
9.11	0.971
9.7	0.932
10.21	0.816
10.85	0.664
11.65	0.549
12.57	0.478
13.56	0.422
14.54	0.388
15.46	0.359
16.3	0.337
17.04	0.315
17.66	0.304
18.19	0.3
18.62	0.29
18.98	0.28
19.26	0.28
19.5	0.27
19.68	0.27
19.84	0.26
19.94	0.26
20.04	0.26

Sample: 29 — Moisture: e.m. — Gas: CO2 — T (°C): 45.03

P [MPa]	n_{ads} [mmol/g]
0	0
2.12	0.59
4.54	0.74
6.04	0.77
8.96	0.75
9.82	0.71
10.65	0.57
11.81	0.47
13.21	0.4

Sample: 30 — Moisture: a.r. — Gas: CH4 — T (°C): 44.68

P [MPa]	n_{ads} [mmol/g]
0	0
4.4	0.581
7.71	0.658
10	0.679
11.61	0.687
12.75	0.689
13.57	0.69
14.14	0.69
14.56	0.689
14.84	0.69
15.05	0.69
15.19	0.69
15.29	0.69
15.36	0.688
15.41	0.687

Sample: 30 — Moisture: e.m. — Gas: CH4 — T (°C): 45.4

P [MPa]	n_{ads} [mmol/g]
0	0
0.98	0.083
1.74	0.155
2.39	0.208
2.92	0.245
4.58	0.29
5.84	0.321
6.81	0.341
7.55	0.356
8.12	0.366
8.56	0.374
10.55	0.379
12.04	0.382
13.18	0.385
14.04	0.387
14.71	0.389
15.22	0.391
15.62	0.392
15.92	0.392
16.15	0.392
16.36	0.392

Sample: 30 — Moisture: a.r. — Gas: CO2 — T (°C): 45.02

P [MPa]	n_{ads} [mmol/g]
0	0
0.71	0.509
2.14	0.755
3.39	0.861
4.35	0.913
7.47	0.987
8.28	1.005
8.79	1.021
9.15	1.013
9.43	1.012
9.67	0.975
9.88	0.956
10.12	0.904
10.38	0.85
10.69	0.804
11.04	0.755
11.44	0.733
11.91	0.697
12.41	0.672
12.98	0.642
13.56	0.627
14.31	0.599
15.75	0.566
17.21	0.534

Appendix IV High-pressure methane and carbon dioxide sorption on coal and shale samples from the Paraná Basin, Brazil

Appendix IV Table 1 Results of high-pressure methane and carbon dioxide sorption experiments measured at 45 °C.

	CH$_4$ isotherms			Langmuir parameter				
sample number	n$_{max}$ CH$_4$ [mmol/g]	n$_{max}$ CH$_4$ [mmol/g, daf]	V$_{max}$ CH$_4$ [m³/t, daf]	n$_L$ CH$_4$ [mmol/g]	n$_L$ CH$_4$ [mmol/g] daf	P$_L$ [MPa]	V$_L$ [m³/t] at 6.25 MPa (reservoir pressure)	helium density [g/cm³]
07_114	0.05	0.79	17.94	0.07	1.02	4.09	0.95	2.32
07_117/118	0.25	0.77	17.49	0.28	0.87	2.31	4.68	2.29
07_153[a]	0.22	0.34	7.72	0.27	0.43	3.73	3.85	1.84
07_166	0.47	0.81	18.4	0.57	0.99	4.23	7.72	1.66
07_166[b]	0.25	0.44	9.99	0.3	0.53	3.35	4.06	1.7
07_177[a]	0.12	0.31	7.04	0.15	0.38	3.34	2.15	2.07
07_186[a]	0.2	0.37	8.4	0.25	0.46	3.47	3.65	1.83
07_181	0.14	0.77	17.49	0.18	1.02	5.79	2.18	2.04
08_100	0.02	1.63[c]	-36.98	0.04	3.37[c]	16.09	n.d.	2.59
08_101	0.05	7.78[c]	-194.79	0.08	11.45[c]	7.09	n.d.	2.46
08_168	0.25	1.02[c]	5.73	0.37	1.52[c]	8.39	n.d.	1.9
08_170	0.13	1.27[c]	-26.58	0.25	2.36[c]	14.16	n.d.	2.25
08_154	0.03	1.28[c]	-33.55	0.04	1.77[c]	5.65	n.d.	2.72

sample number	CO₂ isotherms						Langmuir parameter			
	n_{max} CO₂ [mmol/g]	Pressure at nmax [MPa]	V_{max} CO₂ [m³/t]	n_{max}CO₂ / n_{max}CH₄	n_L CO₂ [mmol/g]	P_L CO₂ [MPa]	$\rho_{sorbate}$ [g/cm³]	V_L [m³/t] at 6.25 MPa (reservoir pressure)	V_{LCO2}/ V_{LCH4} at 6.25 MPa	helium density [g/cm³]
07_114	0.25	8.7	5.63	4.58	0.69	8.43	960	6.66	7	2.81
07_117/118	0.34	9.47	7.69	1.36	0.8	6.19	1133	9.14	2	2.46
07_153[a]	0.81	6.88	18.45	3.4	1.91	3.4	n.d.	n.d.	n.d.	1.72
07_166	0.64	7.94	14.56	1.38	1.11	3.18	1129	16.63	2.2	1.88
07_166[b]	0.28	7.65	6.38	1.12	0.43	1.87	825	6.47	1.59	1.69
07_177[a]	0.39	7.35	8.91	3.3	1.18	1.14	n.d.	n.d.	n.d.	1.93
07_186[a]	0.55	6.34	12.45	2.71	1.54	3.56	n.d.	n.d.	n.d.	1.66
07_181	0.35	9.08	7.92	2.51	0.9	12.01	862	6.99	3.2	2.02
08_100	0.2	9.083	4.62	10.01	0.78	20	882	n.d.	n.d.	2.23
08_101	0.16	8.13	3.68	3	0.69	19.03	902	n.d.	n.d.	2.71
08_168	0.54	9.63	12.21	2.13	2.02	15	907	n.d.	n.d.	1.88
08_170	0.359	7.32	8.15	2.76	1.25	13.43	823	n.d.	n.d.	2.27
08_154	0.14	8.73	3.22	4.93	0.65	19.9	960	n.d.	n.d.	2.72

[a] Measured at 35 °C. [b] Moisture equilibrated. [c] [mmol/g TOC]; n_L=Langmuir sorption; P_L=Langmuir pressure; n_{max}=maximum excess sorption; n.d. = not determined.

Appendix IV Table 2 Semi-quantitative and quantitative X-ray mineralogy.

Santa Terezinha Coal Kalkreuth et al., (2006)			
seaminterval	I	D	G
Quartz	40%	45%	30%
Kaolinite	30%	T	60%
Siderite	15%	R	R
Calcite	T	15%	n.d.
Ankerite	n.d.	15%	n.d.
Illite	M	M	10%
Pyrite	n.d.	M	n.d.
Feldspar	T	T	T
Dolomite	n.d.	T	n.d.
Sphalerite	T	R	R
Bassanite	n.d.	T	T
Apatite	T	R	T
Rutile	R	n.d.	T
Hematite	T	R	n.d.

Ohio Shale Nuttall et al., (2005)			
formation	Lower Huron	Middle Huron	Upper Huron
Quartz	48%	47%	51%
Kaolinite	1.30%	2.50%	2.30%
Barite	1.10%	0.60%	0.70%
Calcite	0.30%	1.10%	0.30%
Gypsum	0.30%	0.30%	0.50%
Illite+Mica	25%	29%	25%
Pyrite	8.60%	6.20%	5.40%
Feldspar (Plagioclase)	5.40%	7.00%	7.50%
Fe-Dolomite	5.40%	1.30%	4.40%
Chlorite	4.10%	5.00%	3.10%

T=trace amount≤5%, M=minor amount N5≤10%, R=rejected, n.d. =not detected.

Appendix IV Table 3 Experimental data for methane sorption isotherms

sample	166	sample	166	sample	181	sample	117-118	sample	114
moisture state	a.r.	moisture state	e.m.	moisture state	a.r.	moisture state	a.r.	moisture state	a.r.
gas	CH4	gas	CH4	gas	CH4	gas	CH4	gas	CH4
temperature	43.92	temperature	45.02	temperature	45.02	temperature	44.60	temperature	45.02
pressure [Mpa]	excess sorption [mmol/g]	pressure [MPa]	excess sorption [mmol/g]	pressure [MPa]	excess sorption [mmol/g]	pressure [MPa]	excess sorption [mmol/g]	pressure [MPa]	excess sorption [mmol/g]
0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000
1.58	0.172	1.08	0.072	2.15	0.051	1.96	0.132	2.13	0.022
2.68	0.231	1.98	0.109	3.62	0.070	3.46	0.168	4.96	0.036
3.39	0.259	2.68	0.132	4.64	0.082	4.52	0.185	6.73	0.043
4.43	0.293	3.22	0.147	6.90	0.100	5.25	0.195	7.86	0.046
5.15	0.312	3.65	0.158	8.43	0.110	7.31	0.214	8.58	0.048
5.65	0.324	5.21	0.183	9.47	0.116	8.72	0.223	9.05	0.049
6.59	0.343	8.05	0.212	11.95	0.125	9.69	0.228	9.35	0.050
7.24	0.355	10.03	0.227	13.68	0.130	10.36	0.232	9.55	0.050
7.70	0.363	11.64	0.236	14.91	0.134	10.82	0.233	9.68	0.050
8.01	0.368	12.88	0.241	15.77	0.135	11.14	0.235	9.76	0.051
8.24	0.372	13.83	0.243	16.39	0.136	11.36	0.236	12.22	0.053
8.39	0.374	14.56	0.246	16.82	0.137	11.52	0.236	13.81	0.054
9.96	0.394	15.13	0.248	17.12	0.138	11.64	0.237	14.85	0.054
11.05	0.406	15.57	0.249	17.34	0.138	11.72	0.237	15.53	0.054
11.81	0.414	17.01	0.248	17.49	0.139	11.78	0.237	15.97	0.054
12.34	0.419	18.13	0.250	17.60	0.139	13.39	0.241	16.26	0.054
12.71	0.424	19.01	0.250	17.67	0.138	14.51	0.244	17.47	0.054
12.97	0.426	20.33	0.249	17.73	0.139	15.30	0.246		
14.20	0.437	21.36	0.248			15.85	0.247		
15.06	0.445	22.17	0.248			16.23	0.248		
15.67	0.451	22.80	0.248			16.51	0.247		
16.11	0.455	23.29	0.248			16.70	0.248		
16.41	0.458	23.66	0.247			16.83	0.248		
16.63	0.459	23.95	0.248			16.93	0.248		
		24.17	0.247			17.00	0.248		
						17.05	0.248		
						17.09	0.248		
						17.11	0.248		
						17.13	0.248		
						17.14	0.248		

Curriculum vitae

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Title of mapping thesis: "Stratigraphie und Strukturgeologie der variszischen Überschiebungsfront südöstlich von Aachen".

Title of Diplom (MSc) thesis: "Organic geochemical and compound specific stable carbon isotope analysis of saturated carboxylic acids, extracted from Late Paleozoic coals".

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PhD thesis:

„Thermal and microbial gas generation, accumulation and dissipation in coal basins: role of sorptive storage capacity evolution"

Research exchange:

July 2006: Electron microscopy and XRD analysis on fly ash and soil samples at IGME Athens, Greece as part of the IKYDA program. Investigation of fly-ash related soil pollution in the Ptolemaida Basin, Greece.

October 2009: Development and application of experimental methods (mercury porosimetry, helium pycnometry, true triaxial stress permeameter) to evaluate compressibility and permeability of bituminous coals at the University of Queensland, Brisbane, Australia. Go8 / DAAD project: „New experimental methods for the investigation of gas sorption and transport processes in coal seams".

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