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The petroleum generation potential and effective oil window of humic coals related to coal composition and age

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Abstract

A worldwide data set of more than 500 humic coals from the major coal-forming geological periods has been used to analyse the evolution in the remaining (Hydrogen Index, HI) and total (Quality Index, QI) generation potentials with increasing thermal maturity and the 'effective oil window' ('oil expulsion window'). All samples describe HI and QI bands that are broad at low maturities and that gradually narrow with increasing maturity. The oil generation potential is completely exhausted at a vitrinite reflectance of 2.0–2.2%R_o or T_{max} of 500–510 °C. The initial large variation in the generation potential is related to the original depositional conditions, particularly the degree of marine influence and the formation of hydrogen-enriched vitrinite, as suggested by increased sulphur and hydrogen contents. During initial thermal maturation the HI increases to a maximum value, HI_{max}. Similarly, QI increases to a maximum value, QI_{max}. This increase in HI and QI is related to the formation of an additional generation potential in the coal structure. The decline in QI with further maturation is indicating onset of initial oil expulsion, which precedes efficient expulsion. Liquid petroleum generation from humic coals is thus a complex, three-phase process: (i) onset of petroleum generation, (ii) petroleum build-up in the coal, and (iii) initial oil expulsion followed by efficient oil expulsion (corresponding to the effective oil window). Efficient oil expulsion is indicated by a decline in the Bitumen Index (BI) when plotted against vitrinite reflectance or T_{max}. This means that in humic coals the vitrinite reflectance or T_{max} values at which onset of petroleum generation occurs cannot be used to establish the start of the effective oil window. The start of the effective oil window occurs within the vitrinite reflectance range 0.85–1.05%R_o or T_{max} range 440–455 °C and the oil window extends to 1.5–2.0%R_o or 470–510 °C. For general use, an effective oil window is proposed to occur from 0.85 to 1.7%R_o or from 440 to 490 °C. Specific ranges for HI_{max} and the effective oil window can be defined for Cenozoic, Jurassic, Permian, and Carboniferous coals. Cenozoic coals reach the highest HI_{max} values (220–370 mg HC/g TOC), and for the most oil-prone Cenozoic coals the effective oil window may possibly range from 0.65 to 2.0%R_o or 430 to 510 °C. In contrast, the most oil-prone Jurassic, Permian and Carboniferous coals reach the expulsion threshold at a vitrinite reflectance of 0.85–0.9%R_o or T_{max} of 440–445 °C.

Keywords: Humic coals; Depositional conditions; Generation potential; Hydrogen index; Quality index; Bitumen index; Oil window

1. Introduction

The oil window refers to the depth or maturity range within which a source rock generates and expels liquid petroleum. In a petroleum exploration situation, the establishment of the oil window in a basin is critical in order to assess the prospectivity of the area. It was recognised early on that the depth to the oil window and the duration of oil generation are mainly dependant on the basin temperature (Philippi, 1965), i.e. the heat flow

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history. A vitrinite reflectance (VR) range from 0.5–0.55%R_o to 1.3%R_o for the oil window was proposed by Teichmüller (1973) and Vassoevich et al. (1974), and generally in petroleum geology the oil window is considered to span the VR range 0.5–0.6%R_o to 1.3–1.35%R_o (Hunt, 1996; Mukhopadhyay, 1994; Peters and Cassa, 1994; Pittion and Gouadain, 1985; Taylor et al., 1998; Teichmüller, 1987; Tissot et al., 1987). Different generation characteristics, however, of marine, lacustrine and coaly source rocks are indicated from the distribution of activation energies of the various kerogen types and from artificial maturation experiments by hydrous pyrolysis (e.g. Jarvie, 1991; Lewan, 1994; Petersen and Rosenberg, 2000; Petersen et al., 2001, 2002; Tegelaar and Noble, 1994; Tissot et al., 1987; Ungerer, 1990). Powell and Snowdon (1983) suggested a composite petroleum generation model for different kerogen types. Since then, several studies have confirmed not only a variation in generation potential among different macerals but also that they generate oil at different thermal maturities (Khavari Khorasani and Michelsen, 1999; Khavari Khorasani and Murchison, 1988; Lewan and Williams, 1987; Michelsen and Khavari Khorasani, 1990, 1995; Murchison, 1987; Teichmüller and Durand, 1983; Tegelaar and Noble, 1994; Waples and Marzi, 1998). Although the petroleum generation range overlaps among the different macerals or kerogen types it seems evident that a single oil window representing all source rock types in many cases will be inadequate in describing the generation history of source rocks dominated by different kerogen types.

Humic coal source rocks dominated by vitrinite are particularly complex due to the heterogeneous composition of the organic matter. However, the increasing recognition of the ability of humic coal and Type III kerogen source rocks to generate and expel liquid petroleum has stimulated research, which has provided considerable new insights into the petroleum generative potential and generation and expulsion characteristics of these source rocks (for a thorough review, see Wilkins and George, 2002). Several studies have demonstrated that the depositional conditions influence not only the overall organic composition of coals, but also the chemical composition of the huminite/vitrinite, for example, by enhancing the hydrogen content in humic organic matter deposited in marine-influenced mires (Diessel, 1992; George et al., 1994; Petersen and Rosenberg, 1998; Petersen et al., 1996, 1998a,b; Sykes, 2001).

Activation energy distributions for bulk petroleum generation from vitrinite and humic coals are broad (Petersen and Rosenberg, 1998, 2000; Schenk and Horsfield, 1998; Ungerer and Pelet, 1987), indicating gradual petroleum generation over a wide temperature range (Petersen, 2002; Petersen et al., 2001; Tissot et al., 1987). As a consequence of the gradual liquid petroleum generation, and in contrast to marine and lacustrine source rocks, the maturity at which oil generation starts does not correspond to the maturity at which oil expulsion commences for humic coal source rocks (Petersen, 2002; Price, 1989a; Sykes, 2001; Sykes and Snowdon, 2002). This results in a three-phase petroleum generation model consisting of (i) onset of petroleum generation, (ii) petroleum build-up in the source rock, and (iii) the *effective oil window* or *oil expulsion window* (Petersen, 2002). The start of the effective oil window thus coincides with the start of efficient oil expulsion; this definition of the oil window is in agreement with that of Hunt (1996). The start of the effective oil window corresponds to the maturity at which the Bitumen Index (BI, Killops et al., 1998; Rock-Eval-derived S_1 yields normalised to total organic carbon, TOC) begin to decrease during maturation as the decrease is taken to indicate efficient oil expulsion. The arguments for interpreting a decrease in S_1 yields as an indication of oil expulsion rather than oil-to-gas cracking are thoroughly discussed in Price (1989a) and Petersen (2002). The method was used by Price (1989a, 1991, 1993) who initially considered a revision of the oil window for humic coals and Type III kerogen source rocks. Petersen (2002) defined a general effective oil window for these source rock types between a VR of 0.85–1.8%R_o. At a VR of 1.8%R_o S_1 yields are very low and the remaining generation potential determined by the Hydrogen Index (HI) have stabilised at low values. The onset of petroleum generation was determined to start at a VR of about 0.5–0.6%R_o and liquid petroleum build-up thus occurs from approximately 0.5–0.85%R_o. In addition, several studies have recognised the initial increase in HI up to a maximum value (HI_{max}) with increasing maturity (e.g. Huc et al., 1986; Teichmüller and Durand, 1983; Sykes, 2001; Sykes and Snowdon, 2002). HI_{max} corresponds to the effective HI (HI′) according to Sykes (2001) and Sykes and Snowdon (2002).

The coal database of the present study allows a detailed and comprehensive investigation of petroleum generation from humic coals. The aims are to (i) investigate the influence of the depositional conditions on the petroleum generative potential; (ii) investigate the evolution in generation potential with increasing maturity; (iii) estimate the range in HI_{max} for humic coals in general, and for coals from the major coal-forming periods: Carboniferous, Permian, Jurassic, and Cenozoic; (iv) refine the general effective oil window for humic coals proposed by Petersen (2002), and (v) present individual effective oil windows for Carboniferous, Permian, Jurassic, and Cenozoic coals.

2. Database

The worldwide data set of the present study consists of 509 Carboniferous, Permian, Jurassic, Cretaceous and Cenozoic humic coals, and some coals of unknown age (Table 1). The coals are from 37 different countries and represent all continents except for Antarctica. More than 250 of the coal samples are from the coal database of the Geological Survey of Denmark and Greenland (GEUS). In order to strengthen this data set, it has been supplemented with data from over 250 coal samples from the literature (Table 1). Cenozoic, Jurassic, Permian, and Carboniferous coals constitute the main body of the samples, and focus has been put on these four major coal-forming geological periods. All samples represent humic coals, i.e. they are principally dominated by huminite/vitrinite. Inertinite may be dominant, in particular in the Permian Gondwana coals. The liptinite maceral group is subordinate with maximum contents generally <15 vol.%, but commonly the liptinite content does not exceed 10 vol.%. Such low contents of liptinite should eliminate liptinite-induced suppression of vitrinite reflectance in the used coals (e.g. Carr, 2000; Hutton and Cook, 1980; Kalkreuth, 1982; Petersen and Vosgerau, 1999). The rank ranges from lignite to anthracite, with VR values ranging from 0.32%R_o to 3.60%R_o. All VR values are mean random, but the VR values from Curry et al. (1994) and Norgate et al. (1997) (Table 1) were presented as maximum VR values. These %R_{max} values have been recalculated here to %R_{random} by using the equation %R_{max} = 1.07%R_{random} − 0.01, from Diessel and McHugh (1986).

Table 1
Composition of coal database (total number of coals: 509)

Period	Region	Number
Carboniferous	Canada, Denmark, England, France [a], Germany [b], Ireland, Netherlands [c], Norway [d], Poland [e], Ukraine [f], USA, Wales	105
Permian	Australia [g], Brazil, China, Russia, South Africa, Tanzania [h]	96
Jurassic	Canada, China [i], Denmark, Egypt [j], Greenland, Mongolia [k], North Sea, Russia, Scotland, Sweden	112
Cretaceous	Canada, Germany, Greenland, Mexico [a], Mongolia [k], New Zealand, Nigeria [l], USA [m]	22
Cenozoic	Canada [n], Colombia, Faeroe Islands, Germany, Greece [o], Hungary [p], India [q], Indonesia [r], Italy [a], Japan [a], Malaysia [s], New Zealand [t], Pakistan [a], Thailand, USA, Venezuela [u], Vietnam	140
Unknown + 1 Triassic sample [v]	–	34

Notes to Table 1:
[a] 2 French Carboniferous coals, 1 Mexican Cretaceous coal, and 1 Italian, 1 Japanese and 1 Pakistani Cenozoic coal from Bertrand et al. (1986) [no S_1 and S_2 data].
[b] German coals include 10 Ruhr Basin samples from Littke and ten Haven (1989) [no T_{max} data].
[c] 31 Dutch coals from Veld et al. (1993) [no S_1 and S_2 data].
[d] 1 Norwegian coal, Bjørnøya, from Bjorøy et al. (1983).
[e] Polish coals include 10 Lower and Upper Silesian Coal basins samples from Hanak and Pozzi (1999) and Kotarba and Lewan (2004) [in Kotarba and Lewan, no S_1 and S_2 data].
[f] 20 Ukrainian coals from Sachsenhofer et al. (2003) [S_2 calculated from their HI and TOC data].
[g] Australian coals include 17 Bowen Basin samples from Boreham et al. (1999).
[h] 9 Tanzanian coals from the Ruhuhu and Rukwa basins and Southern coalfields from Kagya et al. (1991) and Mpanju et al. (1991) [no S_1 and S_2 data].
[i] Chinese coals include 19 Junggar Basin and Tarim Basin samples from Ding et al. (2003) and Hendrix et al. (1995).
[j] 2 Egyptian Western Desert coals from Bagge and Keeley (1994).
[k] 6 Mongolian Jurassic coals from the Jargalant, Chandaman and Dzint basins and 2 Cretaceous coals from the Ulaan Bataar Basin from Johnson et al. (2003).
[l] 7 Nigerian coals from the Anambra Basin, Middle Benue Trough, and Upper Benue Trough from Obaje et al. (2004).
[m] US coals include 1 Greater Green River Basin sample from Garcia-Gonzlez et al. (1997).
[n] 16 Canadian Eureka Sound Group coals from Kalkreuth et al. (1996).
[o] 2 Greek coals from Fowler et al. (1991).
[p] 7 Hungarian coals from Sajgó et al. (2003).
[q] 1 Indian coal (Cambay Basin) from Kohli et al. (1994).
[r] Indonesian coals include 3 Adjuna Basin samples from Noble et al. (1991) [no T_{max} data], 2 Kutei Basin samples from Peters et al. (2000), 6 Kutei Basin, 3 NW Java Basin and 1 Sunda Basin samples from Thompson et al. (1985) [no S_1 and S_2 data], and 3 samples from Bertrand et al. (1986) [no S_1 and S_2 data].
[s] Malaysian coals include 2 Batu Arang samples from Wan Hasiah and Abolins (1998).
[t] New Zealand coals include 15 Buller Coalfield samples from Norgate et al. (1997, 1999) and 12 Taranaki Basin samples from Curry et al. (1994).
[u] Venezuelan coals include 12 Falcón and Maracaibo basins samples from Canónico et al. (2004).
[v] 17 of the samples are US coals, presumably of Carboniferous age, but this cannot be confirmed. 1 Triassic sample is from Sweden.

3. Methods

The coal data in GEUS' database have been acquired over several years, and accordingly some variation in the analytical instruments used is unavoidable. All analyses have, however, been carried out following international standards and procedures. The VR data, including new ones acquired during this study, have all been carried out on polished blocks by means of a Leitz MPV-SP system, which was calibrated against appropriate standards (0.515%R_o, 0.893%R_o, or 1.677%R_o). It was attempted to determine 100 measurements in each sample on eu-ulminite or collotelinite. Rock-Eval screening data were derived on Rock-Eval II, 5, and 6 instruments, and TOC contents were determined on Leco IR-212 or CS-200 induction furnaces. Since 1999, TOC has only been determined on the CS-200 analyser, and Rock-Eval screening data has been principally on the Rock-Eval 6 instrument. Although the Rock-Eval 6 instrument has an oxidation temperature of 850 °C, incomplete combustion of the refractory coal constituents may lead to too low TOC determinations; this problem is overcome with the CS-200 analyser which has an about twice as high oxidation temperature. The interpretation and pitfalls of Rock-Eval data have among others been discussed by Bordenave et al. (1993), Bostick and Daws (1994), Peters (1986) and Sykes and Snowdon (2002). Pitfalls may include interference by the mineral matrix, underestimation of the S_2 signal, influence by retained petroleum, and overloading of the detector. Mineral matrix effects can be neglected in coals due to their high organic content, but retained petroleum in the coal structure may increase the HI values (Killops et al., 1998). HI values obtained from non-extracted Carboniferous coal samples were upon solvent extraction on average reduced by 30% (GEUS, unpublished data). In order to avoid overloading of the Rock-Eval FID a sample amount of 9–11 mg coal diluted by 39–41 mg decarbonated, pyrolysed, and dichloromethane-extracted sand was used. Elemental data (C, H, N, S, O), measured on 26 coals, were determined on dry samples by means of a Carlo Erba EA1108 analyser (C, H, N) and an Eltra CS 500 analyser (S). The oxygen contents were calculated by difference. Water contents were determined by drying the samples for 2 h at 105 °C in a nitrogen atmosphere, and the ash contents by heating the samples at 815 °C for 3 h. The elemental data are recalculated to a dry ash-free basis (d.a.f.).

4. Results and discussion

4.1. Worldwide coal data set: evolution in the generation potential and the effective oil window

4.1.1. Influence of depositional conditions on the generation potential

HI refers to the remaining generation potential of the coals. The evolution in HI with increasing VR for 509 coals is shown in Fig. 1a, and the evolution in HI with increasing T_{max} for 494 coals in Fig. 1b. An envelope can be drawn around the vast majority of the samples. The HI band is broadest (up to ~290 mg HC/g TOC broad) below a VR of approximately 0.6–0.65%R_o, beyond which it gradually narrows to a band width of 25 mg HC/g TOC or less at a VR of about 2.2%R_o. Above this VR value, the HI does not show any change with increasing maturity. A similar evolution in the remaining generation potential is shown by Fig. 1b. The HI band is broadest (up to ~330 mg HC/g TOC) below a T_{max} of about 430–435 °C, which, according to the relationship between T_{max} and VR, corresponds to 0.65–0.73%R_o (Fig. 2). Between 0.7%R_o and 1.3%R_o the present correlation deviates with ≤2 °C from the correlation in Petersen (2002), and <1.6%R_o the deviation does not exceed 4 °C. With increasing maturity the HI band narrows to ~50 mg HC/g TOC or less at a T_{max} above 500 °C (=approximately 1.8%R_o, cf. Fig. 2). The broad bands up to a VR of about 0.6–0.75%R_o and about 430–435 °C reflect a pronounced variation in petroleum generation capacity of humic coals of similar maturity. This is caused by the heterogeneous chemical composition of the organic matter before increasing maturation results in structural reorganisation of the organic material, realisation of the source potential, and finally in homogenisation of the organo-chemical composition. The initial organic heterogeneity can be related to different depositional conditions and vegetation in the original mires.

For humic coals the difference in source potential at similar maturity can be attributed to a difference in the hydrogen content of the vitrinite, with the highest HI values related to the coals with the more hydrogen-rich (per-hydrous) vitrinite (e.g. Sykes, 2001). It has been proposed that coals should contain a certain minimum proportion of liptinite macerals, generally >15 vol.%, to be oil-prone (Hunt, 1991; Mukhopadhyay and Hatcher, 1993). However, in oil-prone humic coal source rocks with a low content of liptinitic organic matter, e.g. <10 vol.% (Bertrand, 1989), the significant oil-generating component is vitrinite, in particular hydrogen-enriched vitrinite (Newman et al., 1997; Norgate et al., 1997; Petersen et al., 1996, 1998a, 2000; Petersen and Rosenberg, 1998, 2000; Sykes, 2001). For a worldwide humic coal data set, Petersen and Rosenberg (2000) were able to explain 85% of the variance in the remaining source potential (HI) by the petrographic composition of the coals. The study showed that the source potential was principally related to the liptinite maceral group as a whole, liptodetrinite, and the vitrinite-rich components. Hydrogen-enriched vitrinite

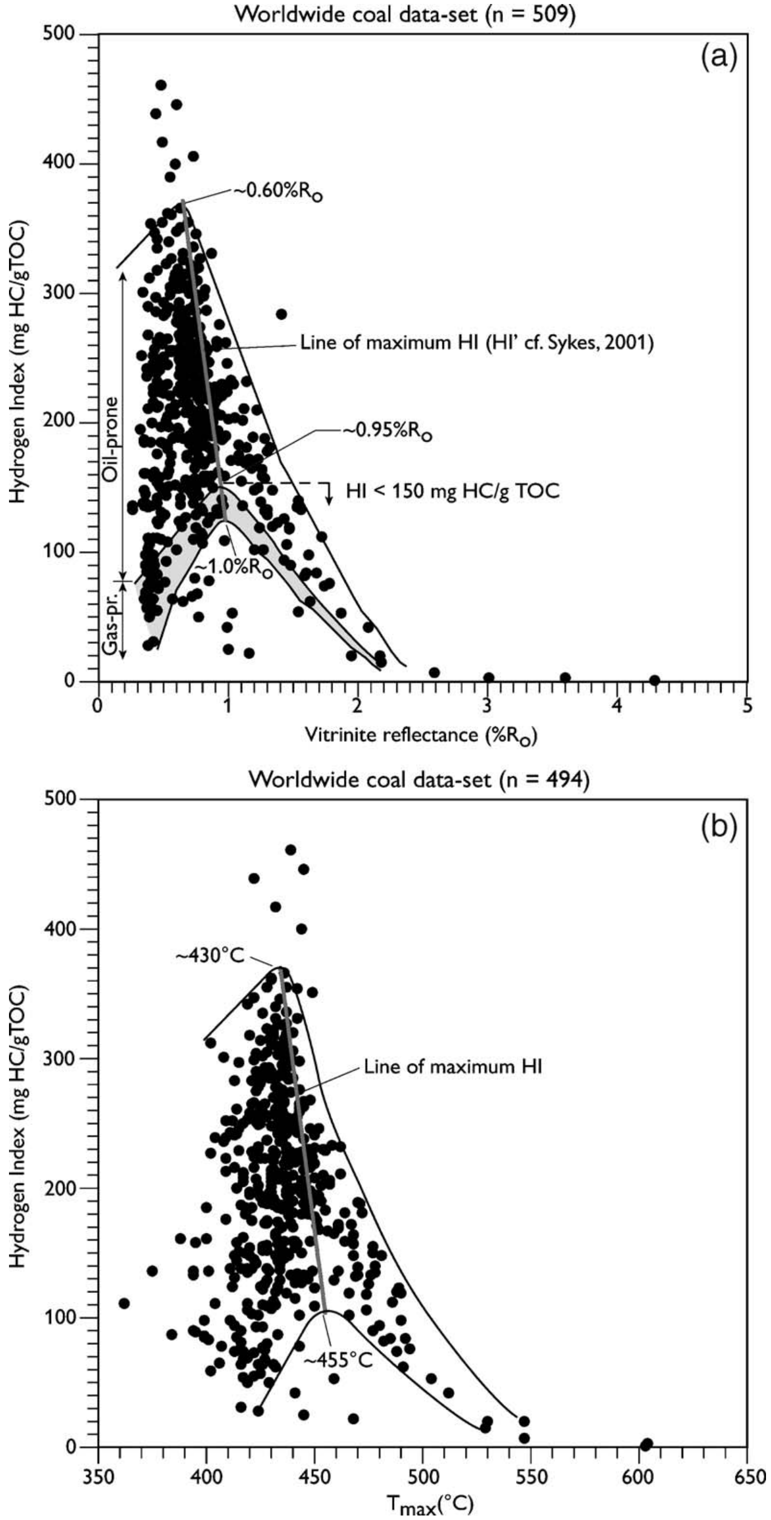

Fig. 1. The evolution in the remaining generation potential (HI) with increasing thermal maturity for a large worldwide humic coal data set: (a) HI vs. $\%R_o$; (b) HI vs. T_{max}. The coals define an HI band that narrows with increasing maturity. A line of maximum HI can be defined from ~0.6 to 1.0$\%R_o$ or from ~430 to 455 °C. Coals with an HI_{max} < 150 mg HC/g TOC are considered mainly gas-prone (shaded area).

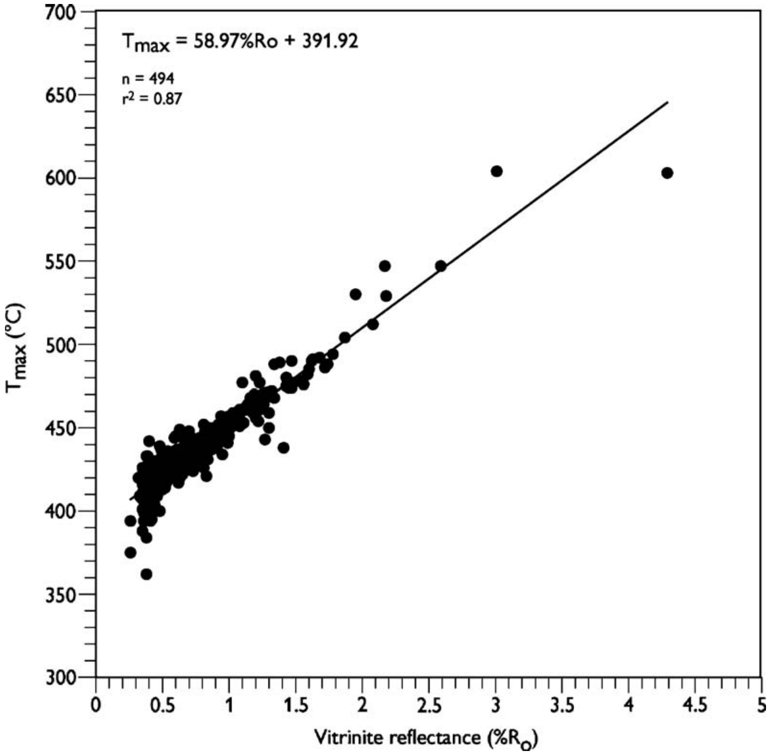

Fig. 2. Correlation between $\%R_o$ and T_{max} based on 494 worldwide humic coals.

is commonly associated with marine-influenced coals and therefore also increased sulphur contents (e.g. Diessel, 1992; Diessel and Gammidge, 1998; George et al., 1994). Sykes (2001) has convincingly demonstrated this relationship for Late Cretaceous–Cenozoic coaly sediments in the Taranaki Basin, New Zealand. Enhanced source potential of per-hydrous vitrinite has been related to a higher content of aliphatic compounds in the vitrinitic material (Mastalerz et al., 1993). The elemental data of 26 of the worldwide coal sample set in the present study (Table 2) is in good agreement with these results. Fig. 3 shows some correlation between high HI values and increased sulphur content in the coals and as shown this correlation is independent of coal age. A plot of HI vs. atomic hydrogen content shows a rough proportionality (Fig. 4), and also a tendency to a relationship between hydrogen-enrichment and increased sulphur content. This supports a correlation between increased hydrogen content and marine influence during peat formation; therefore, high HI values are associated with increased sulphur content (Fig. 3). Hence, marine influence during peat accumulation seems to result in the formation of vitrinite with a higher than normal hydrogen content, which is also demonstrated by the samples plotted in the simplified Seylers chart (Seyler, 1931) (Fig. 5). The band in the chart is the 'bright coal band' and most coals plot within the limits of this band. Most of the sulphur-poor coals in this study plot below the band (sub-hydrous), whereas the more sulphur-rich coals plot towards the upper limit of the band or above (per-hydrous). Diessel (1992) has likewise shown that coals formed during marine transgressions plot towards or above the upper limit of the bright coal band in the Seylers chart. The elemental data in the present study are derived from bulk humic coals, but Petersen and Rosenberg (1998) studied handpicked vitrinite concentrates. The concentrates of per-hydrous vitrinite from thermally mature petroleum-generating Middle Jurassic coals in the Danish North Sea plotted close to or above the bright coal band and showed an average increase of ~22% in HI compared to the concentrates of 'normal' vitrinite. The per-hydrous vitrinites also had suppressed vitrinite reflectance values.

4.1.2. Development of generation potential with increasing maturity

The HI band shows an initial increase with increasing maturity (Fig. 1). The upper limit of the HI band reaches a maximum HI of about 370 mg HC/g TOC at a VR of

Table 2
Elemental data of selected coal samples listed according to age and vitrinite reflectance

Age	Sample	Country	$\%R_o$	C	H	N	S	O	H/C	O/C
				(wt.%, d.a.f.)					atomic ratio	
Carboniferous	9586	Poland	0.73	81.11	5.12	1.42	0.78	11.57	0.76	0.11
	9587	USA	0.73	81.59	5.74	1.52	3.57	7.58	0.84	0.07
	9584	UK	0.81	79.96	5.30	1.81	1.92	11.01	0.80	0.10
	9583	Germany	0.82	80.11	5.26	1.58	1.68	11.37	0.79	0.11
	9582	Danish North Sea	0.86	77.46	5.09	1.06	9.27	7.12	0.79	0.07
	9585	Germany	0.97	78.28	5.43	1.58	3.50	11.21	0.83	0.11
Permian	9606	China	0.67	82.73	5.37	1.56	0.60	9.74	0.78	0.09
	9603	Australia	0.71	81.39	5.67	1.84	0.61	10.49	0.84	0.10
	9604	South Africa	0.75	83.40	4.81	1.91	0.38	9.50	0.69	0.09
	9605	Russia	0.78	81.05	4.85	1.89	0.34	11.87	0.72	0.11
	9607	Australia	1.11	87.55	4.83	1.57	0.40	5.65	0.66	0.05
Jurassic	9597	Norwegian North Sea	0.80	84.37	5.58	1.28	0.55	8.22	0.79	0.07
	9598	Danish North Sea	0.82	83.99	5.45	1.42	0.60	8.54	0.78	0.08
	9599	Danish North Sea	0.83	83.38	5.26	1.22	0.50	9.64	0.76	0.09
	9600	Danish North Sea	0.86	83.26	5.13	1.19	0.88	9.53	0.74	0.09
	9602	Danish North Sea	0.87	82.82	5.55	1.25	0.86	9.52	0.80	0.09
	9601	Danish North Sea	0.88	82.16	5.53	1.12	0.95	10.24	0.81	0.09
Cenozoic	9591	Thailand	0.38	70.65	6.45	1.93	2.27	18.70	1.10	0.20
	9592	Germany	0.41	73.54	4.85	0.30	0.27	21.04	0.79	0.21
	9590	Malaysia	0.42	68.17	5.01	1.28	0.16	25.38	0.88	0.28
	9589	Malaysia	0.44	76.86	6.63	1.47	3.65	11.39	1.04	0.11
	9594	Vietnam	0.45	71.98	6.95	1.65	0.85	18.57	1.16	0.19
	9595	Indonesia	0.50	75.24	5.58	1.69	0.96	16.53	0.89	0.16
	9596	Indonesia	0.55	77.23	5.70	1.62	0.72	14.73	0.89	0.14
	9588	New Zealand	0.61	78.37	5.55	1.04	4.44	10.60	0.85	0.10
	9593	Venezuela	0.66	81.48	5.64	1.54	0.80	10.54	0.83	0.10

~0.6%R_o or a T_{max} of ~430 °C whereas the lower limit, i.e. the coals with the lowest initial generation potential, reaches a maximum HI of about 110–120 mg HC/g TOC at a VR of ~1.0%R_o or a T_{max} of ~ 455 °C (Table 3). The line defined by the VR values 0.6%R_o and 1.0%R_o and the T_{max} values 430 °C and 455 °C represents the line of HI_{max} (effective HI [HI′], cf. Sykes, 2001), and the slope of the line suggests that the coals with the highest generation potential reach their HI_{max} at lowest maturity. Pepper and Corvi (1995) state that kerogen needs an HI > 200 mg HC/g TOC before oil expulsion can occur, and Hunt (1996) notes that source rocks with an HI < 150–200 mg HC/g TOC are considered to be mainly gas-prone. Therefore, the coals with an HI_{max} lower than ~150 mg HC/g TOC may principally be regarded as gas-prone (grey shading in the HI band; Fig. 1a). The line of HI_{max} for the oil-prone coals thus spans the VR range 0.6–0.95%R_o (Fig. 1a). As demonstrated by Sykes and Snowdon (2002), HI values of immature coals or of mature coals that have passed beyond the line of HI_{max}, can be translated along their maturation pathways to their HI_{max} values in order to estimate the true generation potential of the coals. The true remaining generation potential of immature coals may without adjustment of the HI be underestimated by up to approximately 90 mg HC/g TOC (Fig. 1a). Sykes and Snowdon (2002) showed that the HI of New Zealand coals may be underestimated with as much as 150 mg HC/g TOC.

The effect of the gradual exhaustion of the generation potential is evident from the narrowing of the HI band with increasing maturity. However, humic coals may still possess generative potential at a VR of 1.3–1.35%R_o (HI up to ~190 mg HC/g TOC) which is the end of the traditional oil window (Fig. 1a). Depending on the initial source potential of the coals,

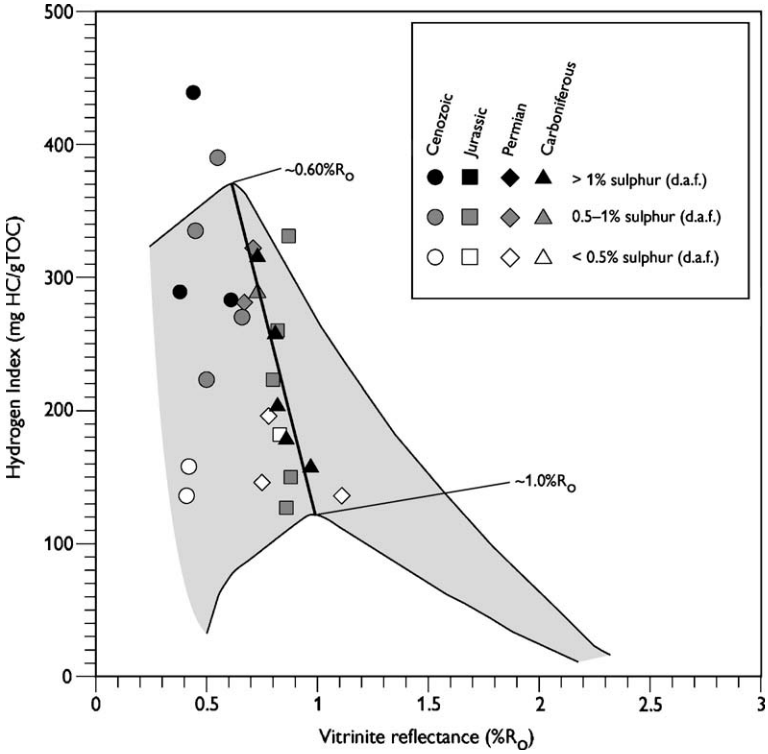

Fig. 3. Coals of different age and with different sulphur content (wt.%, d.a.f.) plotted on the HI band defined by the worldwide coal data set (see Fig. 1a). A moderate relationship between high HI values and increased sulphur contents is shown. The relationship is independent of coal age.

their remaining generation potential will during maturation pass below the 150 mg HC/g TOC limit between 1.0%R_o and 1.55%R_o or 450 °C and 485 °C (Fig. 1), indicating a reduced ability to generate liquid petroleum. The T_{max} values are according to the VR–T_{max} relationship in Fig. 2 in very good agreement with the VR values derived from Fig. 1a. The HI shows that the generation potential for liquid petroleum of humic coals is exhausted at a VR of approximately 2.0–2.2%R_o or T_{max} of 500–510 °C.

The increase in HI has been shown by several coal data sets (e.g. Huc et al., 1986; Petersen, 2002; Sykes, 2001; Sykes and Snowdon, 2002; Teichmüller and Durand, 1983). This increase in generation capacity is considered to result from the formation of additional source potential in the early stages of maturation, although other explanations have been suggested. Huc et al. (1986) interpreted the increase in HI to be caused by an absolute decrease in TOC due to CO_2 loss. The increase in the HI may, alternatively, be considered to be caused by initial underestimation of the HI (i.e. the S_2 signal) by the Rock-Eval instrument due to the abundance of oxygen groups (such as carboxyl and hydroxyl) in immature to early mature coals (Boudou et al., 1994). The gradual decrease of oxygen-bearing compounds in the pyrolysates would result in an increase in the detected S_2 yields due to a relative enrichment of hydrogen-rich compounds (Levine, 1993). Chemical removal of the oxygen groups resulted in an increase in the HI (Boudou et al., 1994). However, Killops et al. (1998) concluded that although oxygen group removal could explain a variation in HI, correction for the oxygen groups was not able to reproduce the expected evolution of HI in a suite of coals from the Taranaki and Great South basins, New Zealand. They suggested that re-combination of thermally cleaved compounds and the solid organic matter could create new petroleum generative compounds. Boreham et al. (1999) have similarly suggested that re-incorporation of bitumen into the coal structure creates new oil-prone components, and Schenk and Horsfield (1998) showed that the increase in generation potential could reflect the formation of additional source potential by re-organisation of the coal matrix via solid state aromatisation and condensation processes. The formation of new generation potential during maturation of humic coals results in unexpected negative values of the transformation ratio

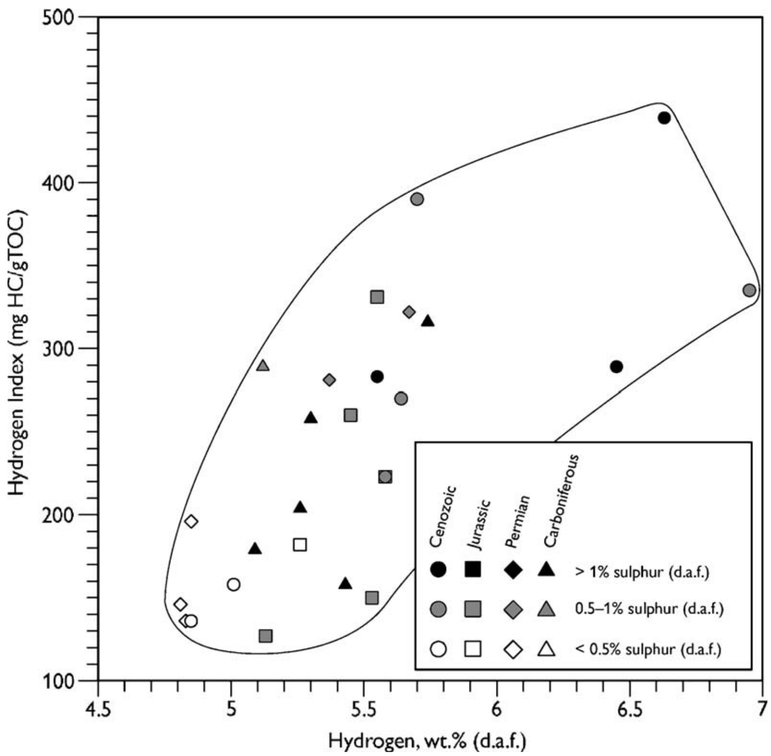

Fig. 4. The coals show a rough relationship between HI and the hydrogen content (wt.%, d.a.f.). In addition, a moderate relationship between hydrogen-enrichment and increased sulphur content is evident.

(TR) calculated from the relationships (I: Bordenave et al., 1993, II: Espitalié et al., 1985; Pelet, 1985)

$$TR_z = \frac{(HI_i - HI_z(TOC_z/TOC_i))}{HI_i} \quad (I)$$

$$TR_z = \frac{1200(HI_i - HI_z)}{(HI_i(1200 - HI_z))} \quad (II)$$

where 'i' indicates the initial value of the immature sample and 'z' the value at burial depth z. The evolution of TR of a number of samples approximately having similar maturation pathway defined by HI has been determined (Figs. 6 and 7). An immature sample (VR = 0.58%R_o) with a TOC content of 68 wt.% and an HI of 299 mg HC/g TOC was chosen as the initial sample. Ideally, the same sample at different maturity levels should be used to calculate TR. This is practically impossible to fulfil and, as an approximation, different samples considered to have almost the same maturation pathway were used. The TR will normally develop from TR = 0, when none of the generation potential has been realised (immaturity), towards TR = 1 when all generation capacity is exhausted. This well-known evolution in TR is illustrated by the TR-curve of the Type I kerogen dominated lacustrine mudstone in Fig. 8. In contrast, the TR-curve of the humic coals yields negative values up to a VR of about 0.9%R_o as a consequence of the maturity-related increase in HI (i.e. the initial $HI_i < HI_z$ up to nearly 1%R_o) (Fig. 7).

Several studies have pointed out that water may constitute a significant and abundant source of hydrogen in hydrocarbon formation, which is then not limited by the available hydrogen in the organic matter (Mastalerz and Schimmelmann, 2002; Schimmelmann et al., 2001; Seewald, 1994, 2003). It is anticipated that incorporation of water-derived hydrogen retards thermal decomposition of hydrocarbons and C–C condensation of the organic matter by hydrogen termination of cleaved free radical fragments (Lewan, 1997), a process which will enhance the generation capacity of source rocks and extend the thermal stability of oil (extend the oil window, see below) (Price, 1994). Hydrous pyrolysis experiments have shown that from 1/3 to 2/3 of the hydrogen in expelled oil is water-derived hydrogen, and with regard to kerogen type, bitumen, and expelled oil the influence of water-derived hydrogen seems to

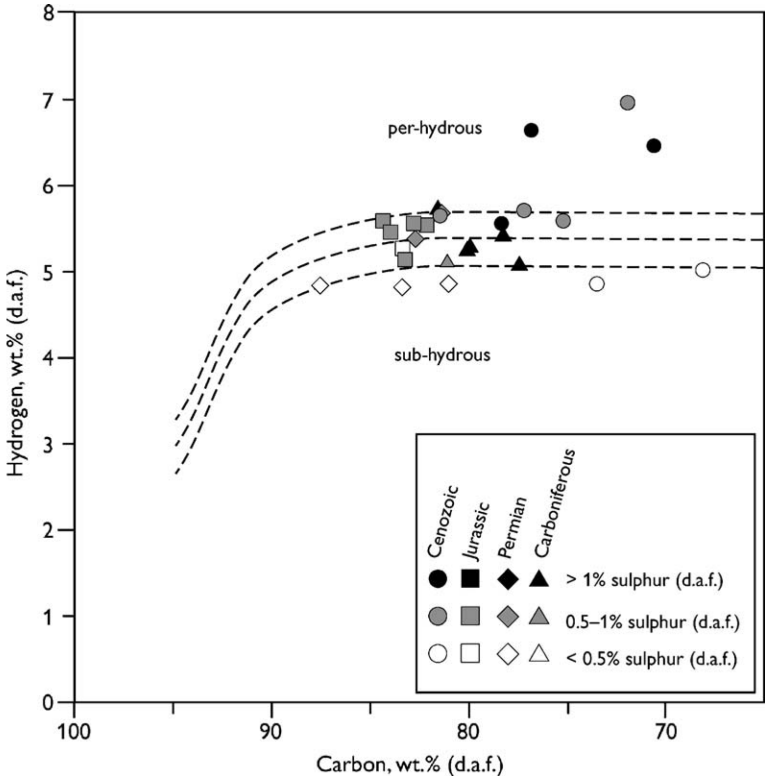

Fig. 5. Simplified Seylers chart with the 'bright coal band' indicated by the dashed lines. The sulphur-poor coals (see also Figs. 3 and 4) plot below this band in the area of sub-hydrous coals, whereas the more sulphur-rich coals plot towards or above the upper limit of the bright coal band in the area of per-hydrous coals.

decrease in the order IIS > II ≈ III > I (Schimmelmann et al., 1999). This means that Type I kerogen is least affected by water-derived hydrogen, which may explain why the TR does not attain negative values (Fig. 8).

4.1.3. The effective oil window

In contrast to HI, which shows the remaining generation potential, the so-called Quality Index (QI = (S_1+S_2)/TOC) used by Pepper and Corvi (1995) represents the total generation potential. The evolution in QI is shown in Fig. 9. A line of maximum QI (QI_{max}) can be defined between ~0.70%R_o and ~1.0%R_o or ~435 °C and ~455 °C (corresponding to 0.73%R_o and 1.07%R_o, see Fig. 2). The decline in QI has been interpreted to indicate the onset of initial oil expulsion (Sykes and Snowdon, 2002).

Killops et al. (1998) named S_1/TOC the Bitumen Index (BI). A cross-plot of BI vs. %R_o shows that the majority of the coal samples form a BI band (Fig. 10a). Most of the samples with very high BI values above the upper limit of the band are of Cenozoic age. A possible minimum in the upper limit of the BI band may occur at about 0.5%R_o (Fig. 10a). This would be in accordance with Suggate and Boudou (1993) who interpreted the higher S_1 yields recorded at low maturities (<0.4%R_o) to be an effect of the original biogenic compounds in the plant material. BI plotted against T_{max}, however, does not show this minimum (Fig. 10b). The upper limit of the BI band shows a rapid increase from ~12–14 mg HC/g TOC at about a VR of 0.5%R_o to ~26 mg HC/g TOC at a VR of 0.85%R_o. Similarly BI vs. T_{max} shows an increase in BI from ~420 °C to above 30 mg HC/g TOC at 440 °C (Fig. 10b), which, according to the VR–

Table 3
General range of maximum HI for humic coals of different age

	VR (%R_o)	HI_{max} (VR)[a]	T_{max} (°C)	HI_{max} (T_{max})[b]
Worldwide coal data set	~0.6–1.0	~120–370	~430–455	~105–370
Cenozoic	~0.6–0.8	~250–370	~430–445	~220–370
Jurassic	~0.75–0.95	~130–290	~440–455	~105–280
Permian	~0.75–1.0	~120–290	~440–450	~120–290
Carboniferous	~0.7–0.95	~150–320	~440–455	~120–320

[a] HI_{max} range defined from VR.
[b] HI_{max} range defined from T_{max}.

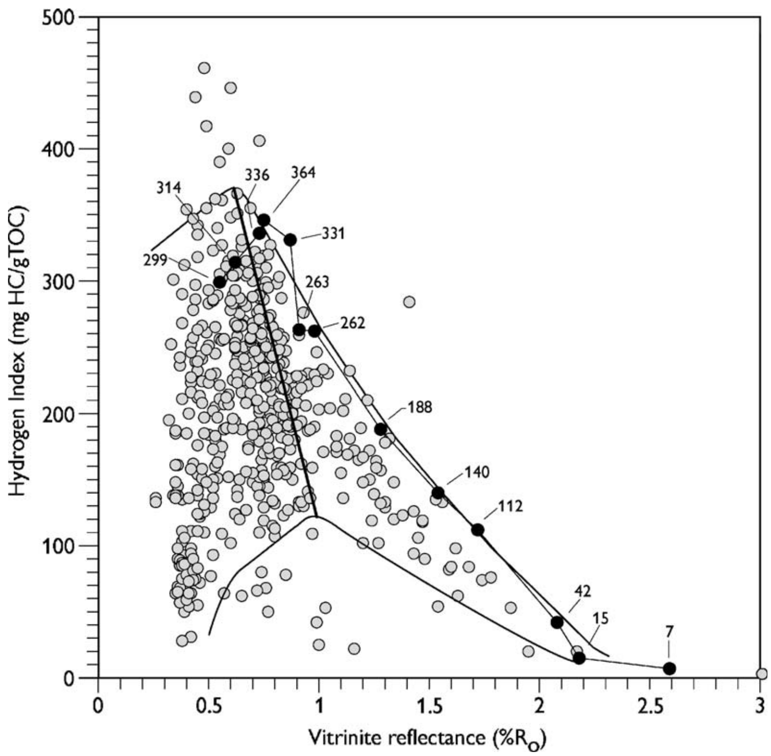

Fig. 6. HI vs. %R_o for the worldwide coal data set. Samples approximately following the same maturation pathway have been chosen to calculate the transformation ratio (TR; see Fig. 7). As the samples lie on the same maturation pathway, they are considered to be initially chemically similar; the samples have thus been used to simulate the thermal maturation of the immature sample with HI = 299 mg HC/g TOC.

T_{max} relationship in Fig. 2, corresponds to 0.82%R_o. Above 0.85%R_o or 440 °C, the upper limit of the BI band decreases to very low yields at approximately 1.8–2.0%R_o or 500–510 °C.

The lower limit of the BI band shows low values up to a VR of 0.8–0.9%R_o or T_{max} of 440–445 °C. The maximum of the lower limit of the BI band may tentatively be set at a VR of 1.05%R_o or T_{max} of 455 °C after which the lower limit decreases to very low values around 1.5%R_o or 470 °C. T_{max} = 470 °C corresponds to 1.32%R_o according to the VR–T_{max} relationship in Fig. 2; this discrepancy between VR and T_{max} is a consequence of the uncertain drawing of the lower limit of the BI band (Fig. 10).

The sharp increase in BI at a VR of 0.5–0.6%R_o or T_{max} of ~420 °C is taken to mark onset of petroleum generation (Petersen, 2002; Sykes, 2001; Sykes and Snowdon, 2002). The early generated compounds are presumed to be bitumen or heavy petroleum, that at higher maturity forms oil by partial decomposition (Lewan, 1994, 1997). The early generated bitumen fills the coal pore system (Fig. 11), which may enhance the expulsion efficiency of saturated hydrocarbons as the generated hydrophobic oil will be separated from the water-saturated bitumen. Early generated bitumen/heavy petroleum are recognised on activation energy distributions as an apron of low activation energy values, that partly can be removed by extraction (Petersen et al., 2001, 2002).

The onset of petroleum expulsion is preceded by petroleum build-up to a maximum BI. The reappraisal of the conventional oil window by Petersen (2002) showed that the effective oil window for humic coals starts at a VR of 0.85%R_o. The present worldwide coal data set shows that 0.85%R_o corresponds to the upper limit of the BI band, while the lower limit of the band reaches a maximum at approximately 1.05%R_o or 455 °C (Fig. 10). In accordance with the principle of Sykes (2001) and Sykes and Snowdon (2002), the line between these two maxima (i.e. 0.85–1.05%R_o; 440–455 °C) defines the line for *efficient* liquid petroleum expulsion (which Sykes (2001) associated with onset of primary gas generation). The maximum BI line thus corresponds to the maturity range within which the start of the effective oil window generally occurs for this worldwide coal data set. However, as mentioned in Section 4.1.2, coals with an HI_{max} < 150 mg HC/g TOC can

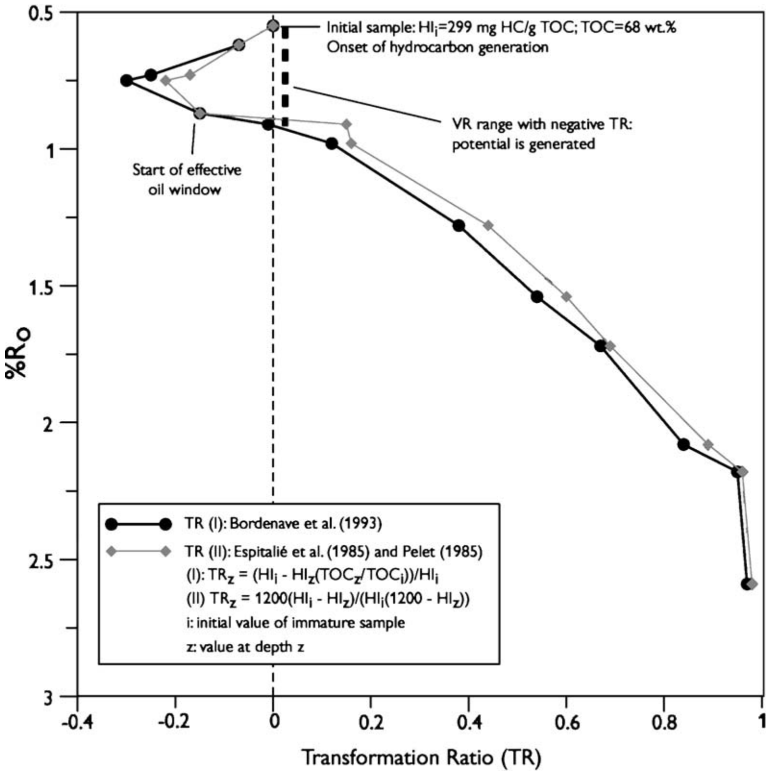

Fig. 7. The evolution in TR with increasing maturity for the samples indicated in Fig. 6. The initial increase in HI results in negative TR. Up to a reflectance of about 0.9%R_o the remaining source potential is consequently higher than the initial potential of the immature sample.

mainly be considered gas-prone, and the present data set suggests that this corresponds to a BI value of <12 mg HC/g TOC. The line of the start of the effective window (expulsion line) shows that coals with a capacity to generate >12 mg HC/g TOC occur from 0.85 to 1.0%R_o or from 440 to 450 °C (Fig. 10). Coals with a maximum BI value of less than ~12 mg HC/g TOC may have a limited expulsion efficiency. This may tentatively be explained by a restricted ability to saturate the coal matrix.

The range in maturity for the start of the effective oil window is related to variations in the chemistry of the coals, i.e. a high vs. a low content of aliphatics, with the aliphatic-rich coals (high HI) expelling liquid petroleum at lower maturity (e.g. Sykes, 2001). The 0.85–1.05%R_o VR range for the start of the effective oil window is in agreement with the 0.81–1.1%R_o range for oil expulsion indicated for coals and Type III kerogen in a number of studies (García-Gonzlez et al., 1997; Newman et al., 1997; Norgate et al., 1997; Price, 1989a). In this VR range, extracts from coals subjected to hydrous pyrolysis also show a significant increase in the proportion of saturated hydrocarbons, and the *n*-alkanes attain a distribution very similar to coal-sourced oils (Petersen, 2002). In particular, the generation of long chain *n*-alkanes with a carbon number >15 is considered of fundamental importance for efficient expulsion of oil (Isaksen et al., 1998).

Carr and Williamson (1990) detected significant structural changes in vitrinite, which among other things resulted in the onset of petroleum formation and a more rapid increase in VR, at a VR of ~0.7%R_o. Although the aromaticity of the vitrinite increases with increasing maturity below ~0.7%R_o, the VR increases slowly due to lack of, or only restricted, polyaromatisation. Also, approximately in the maturity range 0.6–1.0%R_o, which to a large extent coincides with the range for the start of the effective oil window, Suggate (1998) observed a rapid increase in VR. These observations may be evaluated in the context of the petroleum generation model. Generation of petroleum in the build-up phase up to the start of the effective oil window increases the aromaticity by release of aliphatics (free hydrocarbons) from the coal structure. Polyaromatisation of the aromatic rings is hindered by the free hydrocarbons in the coal. However, as soon as efficient liquid petroleum expulsion begins at the start of the effective oil window, polycondensation of the aromatic rings is possible and

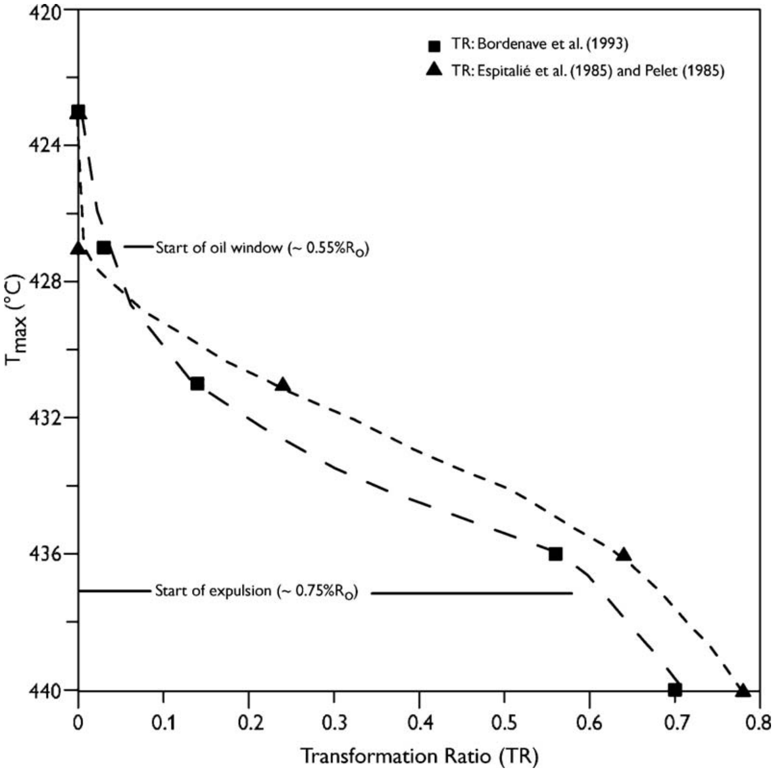

Fig. 8. In contrast to the TR of the coals in Fig. 7, the lacustrine mudstones with Type I kerogen show the expected development in TR from TR = 0 at immaturity to TR approaching 1 with increasing maturity and the realisation of the source potential.

VR increases rapidly. The increase in aromaticity slows down as petroleum generation (cracking of aliphatics) gradually decreases with increasing maturity, although expulsion continues as does the polyaromatisation. Other physical parameters observed in coals provide further support for the determined VR range for the start of the effective oil window. The internal surface area of coals reaches a minimum approximately in the VR range 0.8–1.0%R_o (Levine, 1993), which can be explained by the gradual petroleum build-up in the coal pore system before expulsion commences at the start of the effective oil window. Similarly, the secondary fluorescence intensity from vitrinite, which has been related to petroleum formation, reaches a maximum at a VR of about 0.85–0.9%R_o (Lin et al., 1987; Taylor et al., 1998), and the decrease in secondary fluorescence intensity is thus coinciding with the onset of expulsion. Loss of visible fluorescence at a VR of 1.8%R_o (Teichmüller and Durand, 1983; Lin et al., 1987) is in good agreement with the end of the effective oil window (see below).

Low liquid petroleum yields are recorded in the VR range 1.5 to 1.8–2.0%R_o or T_{max} range 470 °C to 500–510 °C (Fig. 10). Combined with the complete exhaustion of the liquid source potential at about 2.0%R_o or 510 °C as described above (Fig. 1), the VR range 1.5–1.8%R_o or T_{max} range 470–500 °C is considered to define the end of the effective oil window. This means that an optimistic and a conservative range of the effective oil window can be postulated, depending on whether the VR thresholds for the upper or the lower band limits are used: 0.85–1.8%R_o or 440–500 °C for hydrogen-rich coals, and 1.05–1.5%R_o or 455–470 °C for hydrogen-poor coals (Fig. 12). The effective oil window range for hydrogen-poor coals is the weakest defined due to the uncertain position of the lower limit of the BI band.

As shown below, the start of the effective oil window for Cenozoic coals occurs at even lower maturity (possibly from 0.65%R_o) and may extend to 2.0%R_o (see discussion below). Hence, 0.85–1.7%R_o is recommended as a good general approximation of the oil window for humic coals instead of the conventional oil window from 0.5–0.6%R_o to 1.3–1.35%R_o.

Depending on the initial generation potential of the coals, they reach ~12 mg HC/g TOC (defined as the minimum value for onset of efficient expulsion) somewhere between 1.0%R_o and 1.4%R_o or between

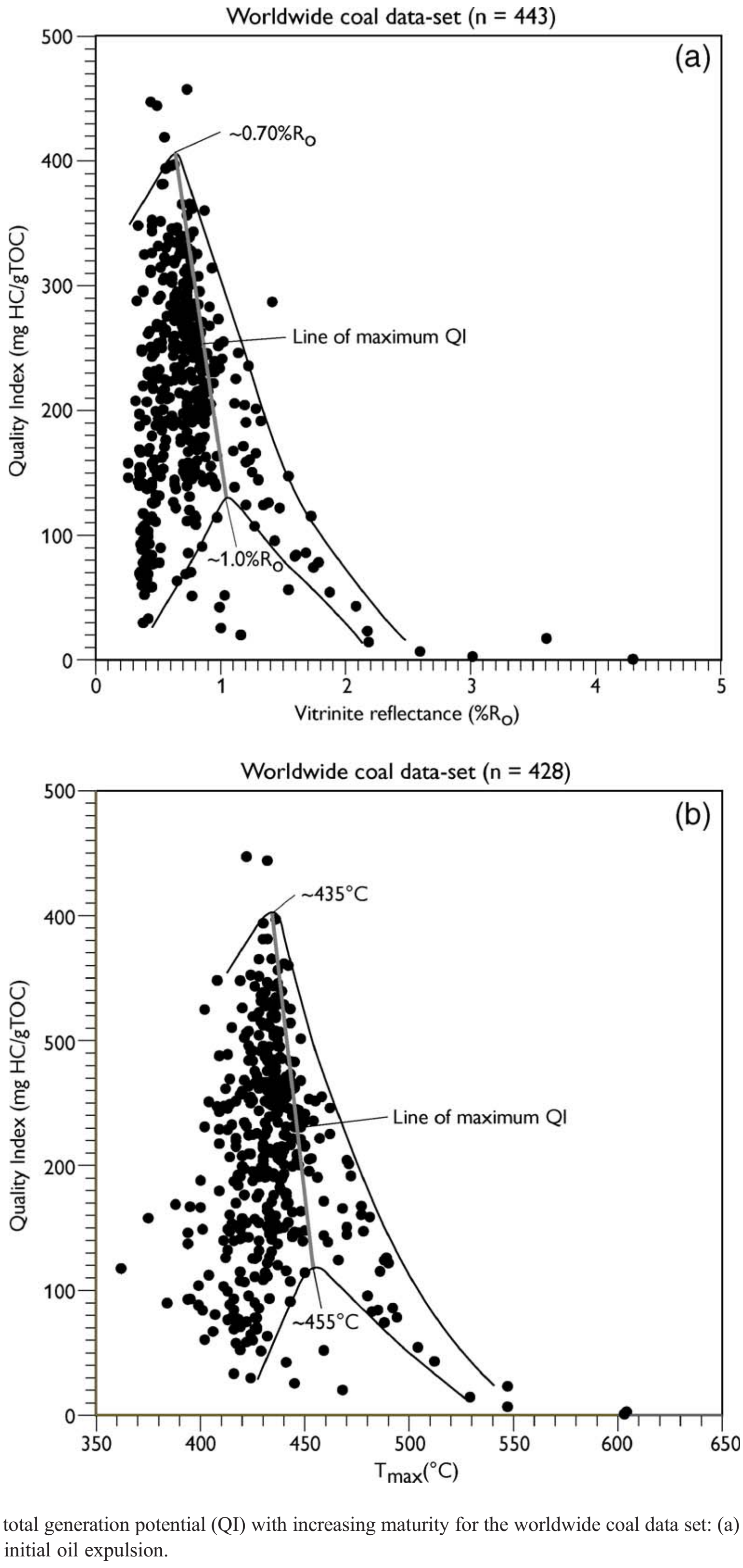

Fig. 9. The evolution in the total generation potential (QI) with increasing maturity for the worldwide coal data set: (a) QI vs. %R_o; (b) QI vs. T_{max}. The decline in QI indicates initial oil expulsion.

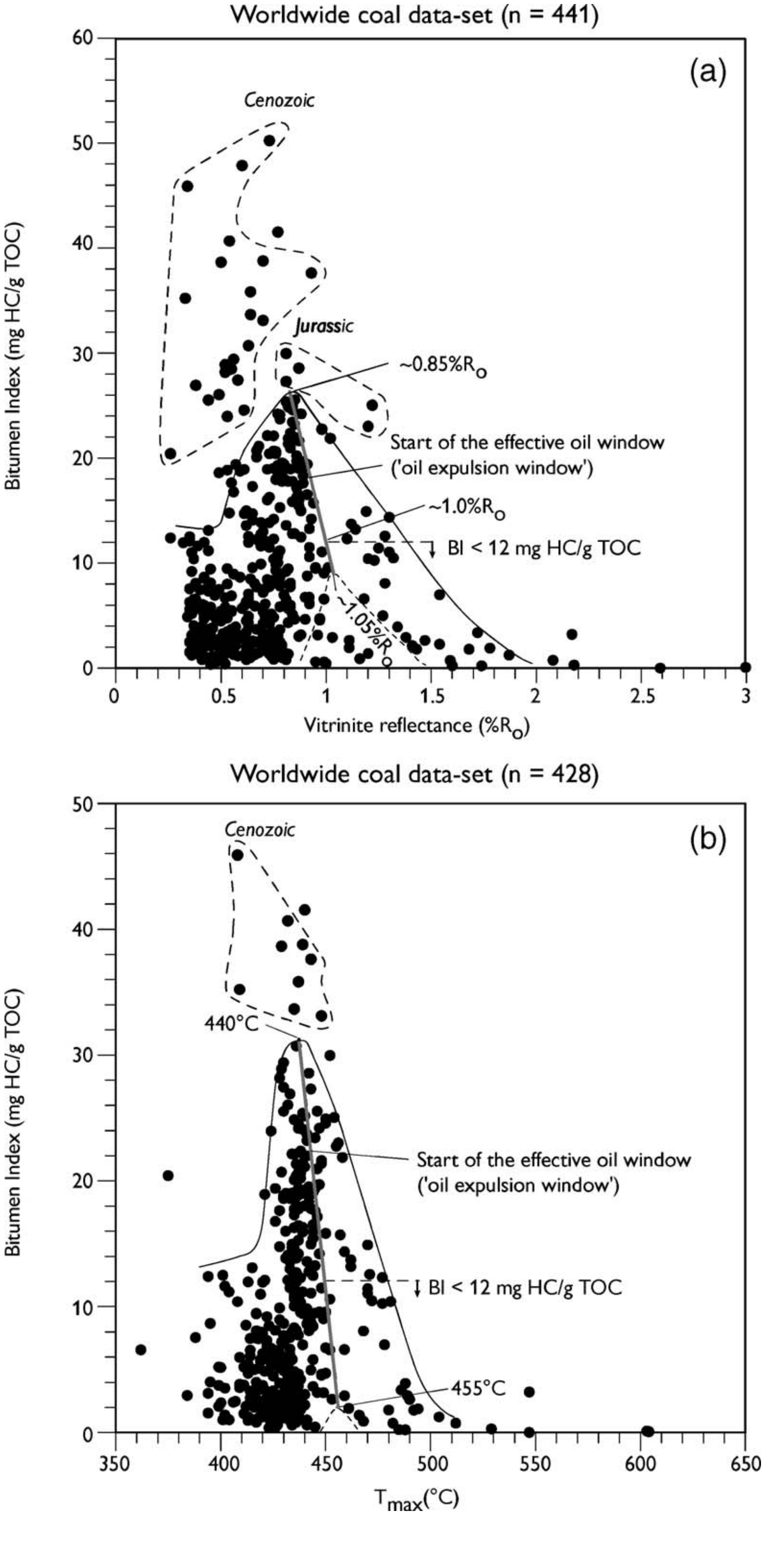

Fig. 10. (a) BI vs. $\%R_o$ and (b) BI vs. T_{max} for the worldwide coal data set. The majority of the samples define a BI band that illustrates the three-phase petroleum generation process from humic coals: (i) onset of petroleum generation, (ii) liquid petroleum build-up to a maximum value, and (iii) efficient oil expulsion in the 'effective oil window'. The line between ~0.85 and $1.05\%R_o$ or 440 and 455 °C defines the start of the effective oil window ('oil expulsion window').

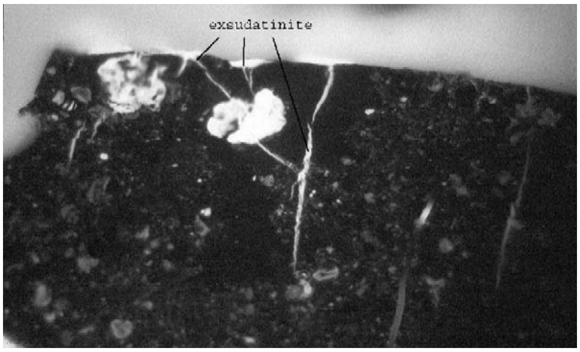

Fig. 11. Photomicrograph of early generated petroleum (exsudatinite) intruded into cleats in the huminite in an Oligocene low rank coal (VR = 0.4%R_o) from Vietnam (reflected blue light, oil immersion).

450 °C and 480 °C during maturation (Fig. 10). From this maturity it could be argued that the expulsion efficiency of oil decreases. However, it is tentatively suggested that increasing gas-generation may facilitate continued oil expulsion by "squeezing" out the oil, or by migration of oil in gas solution (Price, 1989b). Nevertheless, expulsion mechanisms of liquid petroleum are probably the least understood part of 'oil from coals'. Efficient expulsion seems to be a function of various parameters such as: coal seam thickness, the distribution of source potential within the coal seams, the ability to generate long-chain aliphatics, restricted retention of generated petroleum due to a continuous transformation (breakdown) of the coal matrix, coal compaction, the pore size distribution of the coal matrix, and development of a natural fracture system (e.g. Bojesen-Koefoed et al., 1996; Isaksen et al., 1998; Law, 1991; Petersen et al., 2000; Ritter, 2004). Natural cleat density is highest within the VR range corresponding to the effective oil window, and importantly Close (1993) showed for the Fruitland coals of the San Juan Basin, USA, that the cleats may have a high degree of effective connectivity.

The effective oil window implies that both oil generation and stability extends into the conventional (i.e. at temperatures > 160 °C and VR > 1.3–1.35%R_o; Hunt, 1996) late gas generation zone. In the late part of the effective oil window (VR ~1.5%R_o) late gas generation, which initially is composed of wet and dry gas, accelerates, and above 1.8–2.0%R_o late dry gas dominates (Fig. 12). A pure gas window (related to coal source rocks) will then start at the end of the effective oil window (Fig. 12). The dry gas is derived directly from primary cracking of the coal or kerogen and from the start of oil-to-gas cracking. This is in agreement with the observed higher thermal stability of oil due to the retardation of thermal cracking and cross-linking reactions caused by quenching of free radical sites by water-derived hydrogen (Price, 1993; Lewan, 1997; see also discussion in Section 4.1.2). It is further supported by published activation energies and temperatures for late gas generation and oil-to-gas cracking (Table 4) (see also discussion in Petersen, 2002). According to Hill et al. (2003), C_{15+} hydrocarbons are completely depleted at

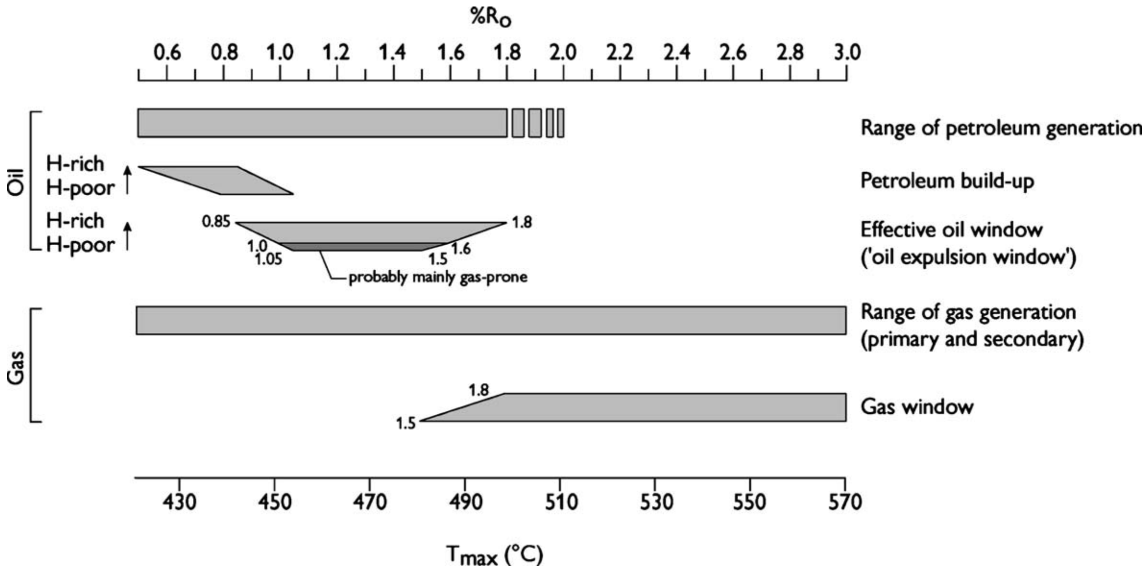

Fig. 12. General schematic representation of the maturity ranges for oil and gas generation from humic coals. Gas generation ranges are based on the literature (see references in text).

Table 4
Late gas generation and thermal cracking of nC_{15+} hydrocarbons to gas

E_a (kcal/mol)	A (s^{-1})	Temperature (°C)	Vitrinite reflectance (% R_o)	References
66–70	1.1×10^{16}	>165	>1.5 [a]	Horsfield et al. (1992)
–	–	–	1.5–3.0	Levine (1993) Behar et al. (1995) Taylor et al. (1998)
>82.6	–	–	–	Price (1993)
>60, max at ~66	3.0×10^{15}	–	–	Behar et al. (1997)
>68.2 (for nC_{25})	6.1×10^{17}	>170	>1.5 [a]	
>71–72	3.42×10^{19} – 4.99×10^{19}	>180	>1.7 [a]	Schenk et al. (1997)
		225 (peak)	3.0 [a]	
62–66	1.12×10^{16}	>170	>1.5 [a]	Seewald et al. (1998)
59 (mean)	$10^{14.25}$	>184	>1.8 [a]	Waples (2000)
–	–	230–240	3.2–3.6 [a]	Domine et al. (2001)
–	–	190	1.9 [a]	Shuichang et al. (2004)

[a] Determined from the correlation between burial peak temperature and vitrinite reflectance established by Barker and Pawlewicz (1994).

a VR of ~1.7% R_o due to cracking to C_{6-14}, C_{1-5} hydrocarbons, and pyrobitumen, but the processes of secondary cracking may overlap significantly with the processes of primary petroleum formation. In addition to late gas generation, early methane generation occurs contemporaneously with oil generation from humic coals and Type III kerogen throughout the maturation process (Behar et al., 1995; Monnier et al., 1983; Price, 1989b; Seewald et al., 1998). The proportion of primary gas generated from a coal and the maturity at which this generation maximises is dependent on the coal composition (Khavari Khorasani and Michelsen, 1999). Kotarba and Lewan (2004) reported for Polish Carboniferous coals that about 75% of the maximum primary methane generation has been realised at a VR of about 1.7% R_o.

4.2. Evolution in HI and the effective oil window of Cenozoic, Jurassic, Permian, and Carboniferous coals

4.2.1. Evolution in HI related to coal age

From the worldwide coal data set, four subsets composed of Carboniferous, Permian, Jurassic, and Cenozoic coals were extracted. The evolution of HI with increasing maturity for these age-specific coal data sets was studied within the band limits defined by the worldwide coal data set (Figs. 1, 13, and 14). Translation of the Cenozoic samples on the HI vs. VR plot to the HI_{max} line indicates that the main cluster of coals have a HI_{max} between approximately 250–370 mg HC/g TOC, which is attained between a VR of 0.6–0.8% R_o (Fig. 13a; Table 3). The HI vs. T_{max} yields a slightly lower HI_{max} value of 220 mg HC/g TOC (Fig. 14a). HI_{max} is attained from 430 to 445 °C, which corresponds to a VR range from 0.65 to 0.9% R_o according to the VR–T_{max} correlation in Fig. 2. Some samples are located above the upper limit of the HI band, and they reach HI_{max} values of >400 mg HC/g TOC at VR values as low as ~0.5% R_o. The increase in the HI during maturation seems to be more pronounced than for coals of Carboniferous, Permian, and Jurassic age (Figs. 13 and 14). The HI band is thus steeper than the HI band defined for the worldwide coal data set. The significant increase in HI to values generally >220 mg HC/g TOC suggests that the Cenozoic coals are oil-prone. This agrees with the fact that Cenozoic coals and Type III kerogen-dominated shales constitute significant oil source rocks in SE Asia (e.g. Adjuna Basin and Kutei Basin, Indonesia; offshore Brunei; Nam Con Son Basin, Vietnam), New Zealand (Taranaki Basin), and Nigeria (Niger Delta) (Curiale et al., 2000; Eneogwe and Ekundayo, 2003; Killops et al., 1994; MacGregor, 1994; Noble et al., 1991; Peters et al., 2000; Todd et al., 1997). A differentiation of the Cenozoic coals into Paleocene/Eocene, Oligocene, and Miocene periods based on HI is not obvious (Fig. 15a). The HI of the Oligocene coals are high, but the number of samples is small and in addition the samples are restricted to only two countries (Vietnam and Indonesia), which render any conclusions speculative.

HI values for the Jurassic coals indicate that evolution of HI during maturation follow the evolution as defined by the worldwide coal data set (Figs. 13b and 14b). The majority of the samples have an HI_{max} approximately in the range 105–290 mg HC/g TOC, which is reached within the VR range 0.75–0.95% R_o or 440–455% R_o (corresponding to 0.82–1.07% R_o) (Table 3). T_{max} thus yields a slightly higher maturity range for HI_{max}. Overall the Jurassic coals posses a poorer

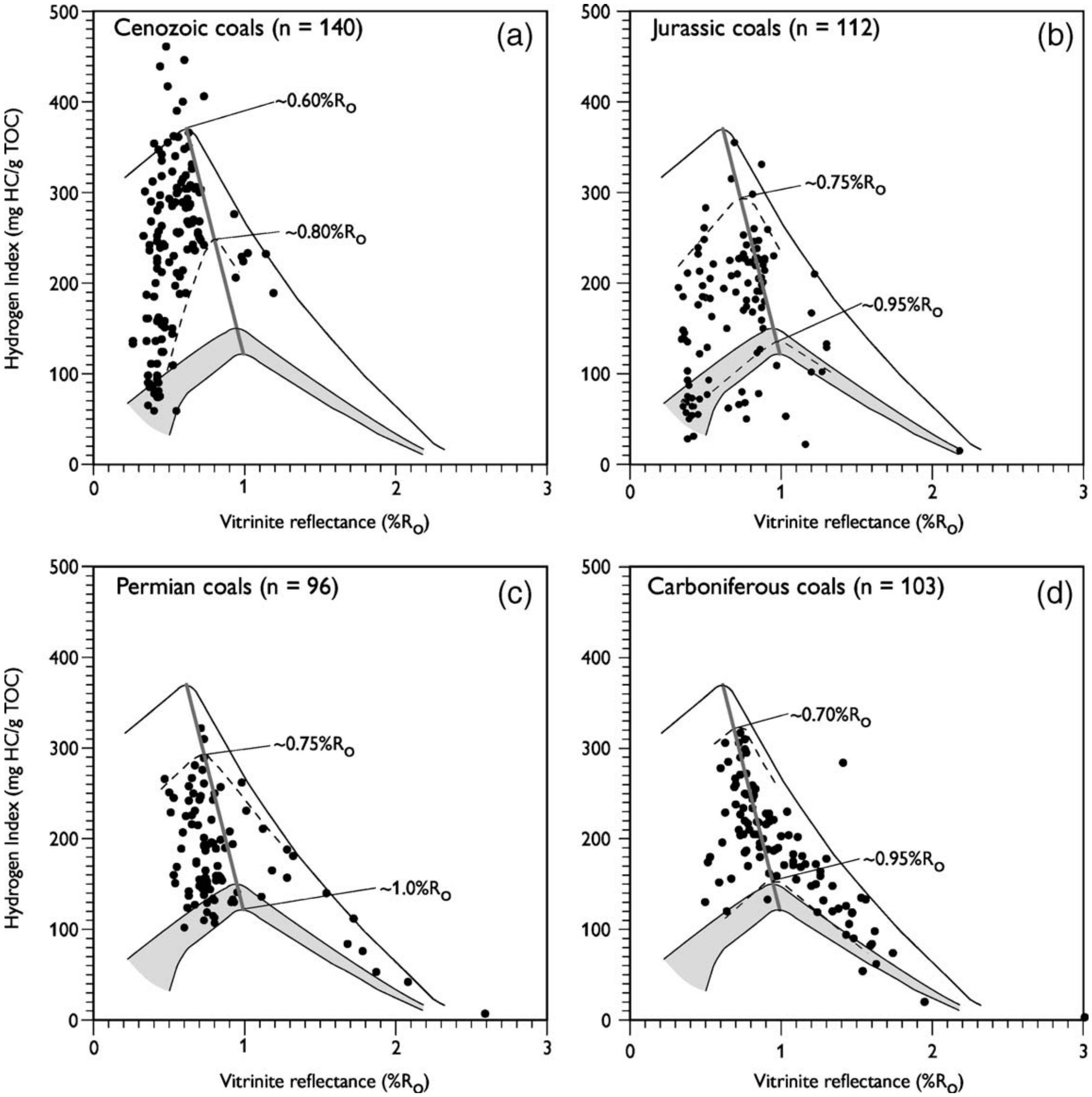

Fig. 13. HI vs. $\%R_o$ for (a) Cenozoic, (b) Jurassic, (c) Permian, and (d) Carboniferous coals. The vitrinite reflectance ranges for HI_{max} are shown. The shaded band indicates mainly gas-prone coals.

generative potential than the Cenozoic coals, but oil accumulations sourced or partly sourced from Jurassic coal and Type III kerogen source rocks are known from Australia (Eromanga Basin), China (Turpan Basin) and the Danish North Sea (Søgne Basin) (Carr and Petersen, 2004; Murchison, 1987; Petersen et al., 2000; Sun et al., 2000; Thomas, 1982).

The HI values of the Permian coals form a main group within the HI_{max} range 120–290 mg HC/g TOC, which is attained in the VR range 0.75–1.0%R_o or the T_{max} range 440–450 °C (corresponding to 0.82–0.98% R_o, cf. Fig. 2) (Figs. 13c and 14c; Table 3). T_{max} thus suggests a slightly higher maturity for the lower HI_{max} value. This is practically the same HI_{max} range as shown by the Jurassic coals, and implies a similar ability to generate liquid petroleum. Many Permian Gondwana coals are dominated by inertinite which inherently is non-generative due to its polyaromatic and carbon-rich structure. However, the source potential of these highly inertinite-rich coals may be increased by the presence of sub-microscopic algal and algae-like material (Liu and Taylor, 1991), and oils in the Australian Cooper and Surat/Bowen basins are believed to have been sourced from Permian coals and Type III kerogen (Thomas, 1982; Murchison, 1987; Boreham et al., 1999). Overall, the ability to saturate the coals to the expulsion threshold may be a critical parameter for the Permian coals (see Section 4.2.2).

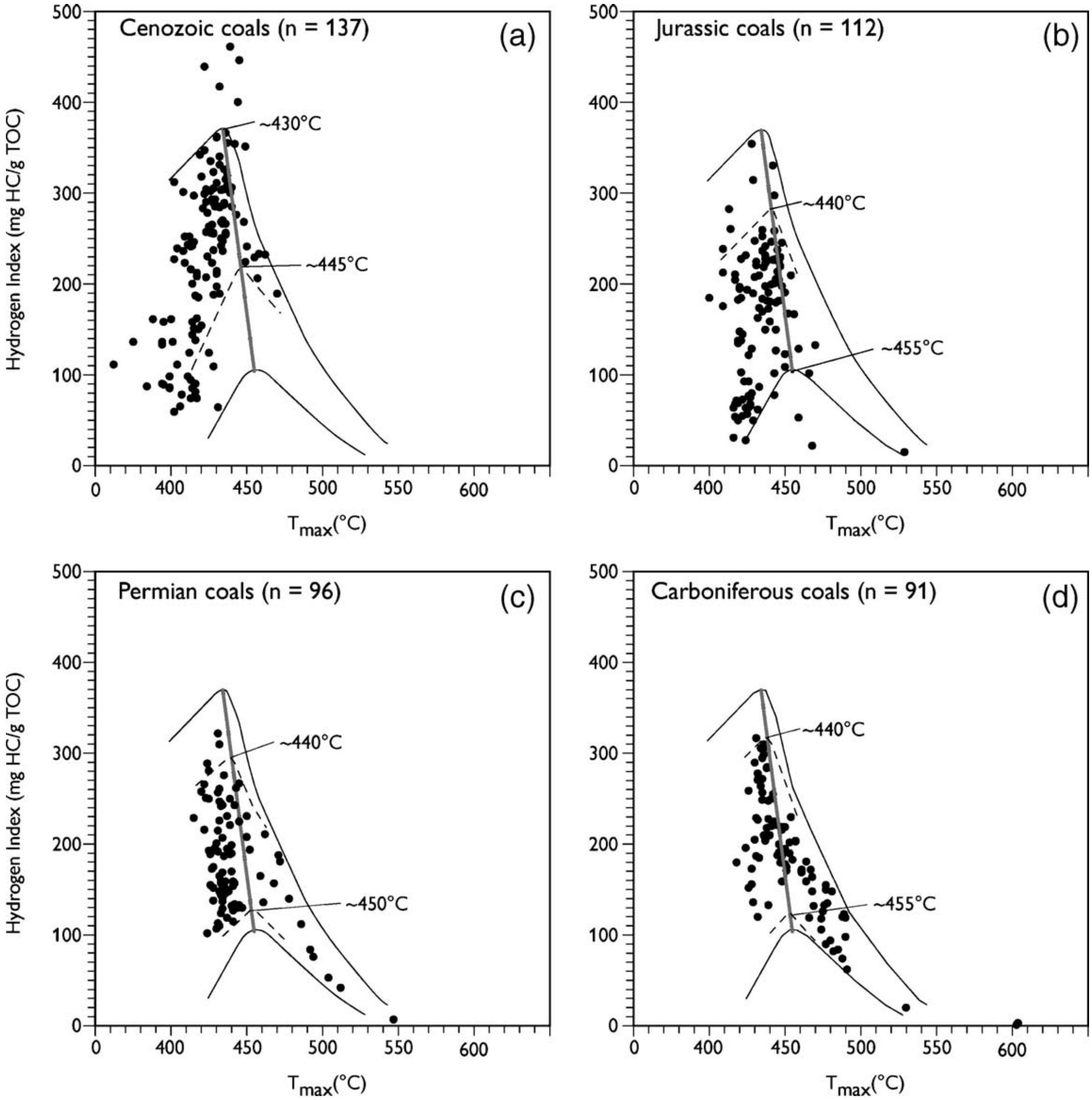

Fig. 14. HI vs. T_{max} for (a) Cenezoic, (b) Jurassic, (c) Permian, and (d) Carboniferous coals. The T_{max} ranges for HI_{max} are shown.

The HI values of the Carboniferous coals define an HI_{max} range from 120 to 320 mg HC/g TOC, implying a considerable generative potential for these coals, which is reached between a VR range of 0.7–0.95%R_o or T_{max} range of 440–455 °C (corresponding to 0.82–1.07%R_o) (Figs. 13d and 14d; Table 3). The maturity range for HI_{max} is thus higher if based on T_{max}. However, despite the high HI_{max} values, no oil accumulations considered to have been sourced from Carboniferous coals have been reported. Small amounts of condensate in the Chinese Hetianhe gasfield, Tarim Basin, are considered to have been generated from Carboniferous coals (Zhiming et al., 2004). In contrast, Carboniferous coals are associated with significant gas accumulations, for example in NW Europe (Anglo-Dutch Basin and Northwest German Basin; Gautier, 2003). The reason for this is not well understood, but a limited ability of the coals to generate long-chain aliphatic hydrocarbons may offer an explanation. Terrestrial-sourced oils are highly aliphatic with a considerable proportion of long-chain *n*-alkanes, and the coals ability to generate in particular nC_{15+} *n*-alkanes may be essential for oil expulsion (Isaksen et al., 1998). Killops et al. (1994) suggested that a coal's aliphatic oil potential is important and therefore concluded that the HI is not suited for a direct measurement of the oil potential. If the Carboniferous coals have a limited ability to generate long-chain aliphatics compared to younger coals derived from more

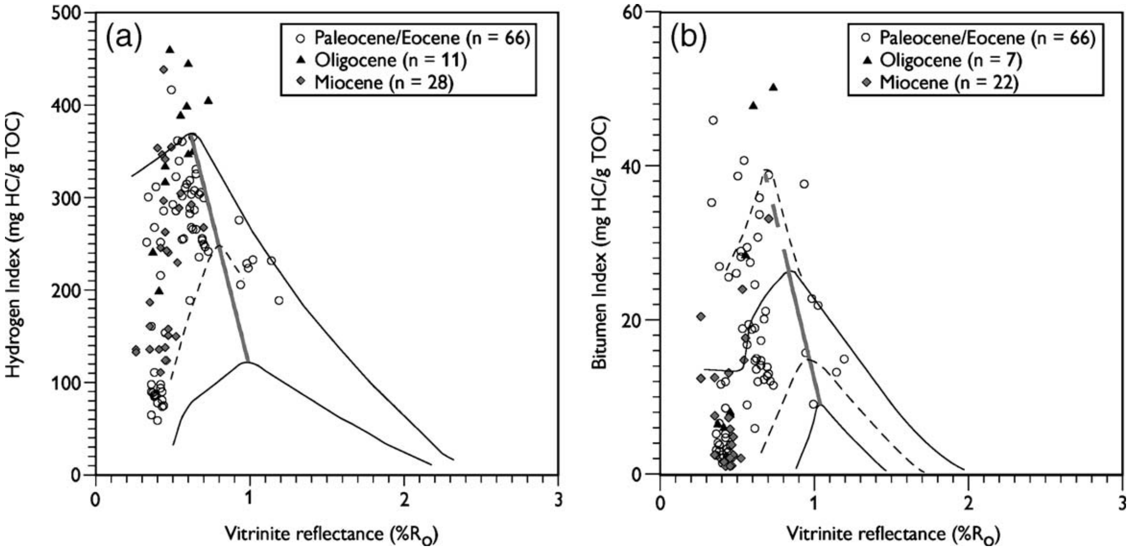

Fig. 15. (a) HI vs. $\%R_o$ and (b) BI vs. $\%R_o$ for the Cenozoic coals differentiated into Paleocene/Eocene, Oligocene, and Miocene periods. The Paleocene/Eocene coals show a tendency to generate a larger amount of petroleum and to expel at lower maturity than the Miocene coals.

diversified plant communities, this may reflect an overall vegetational control on the source potential. This aspect is presently under detailed investigation by the author, and preliminary results from Fourier Transform Infrared Spectroscopy (FTIR) and rhuthenium tetroxide-catalysed oxidation of a number of coals from the major coal-forming periods indicate such a relationship.

4.2.2. The effective oil window of coals of different age

The BI band defined by the worldwide coal data set and the line defining the start of the effective oil window have been related to coals of the major coal-forming periods (Figs. 10, 16, and 17)). For the Cenozoic coals, the upper limit of the BI band defined by the worldwide coal data set may be inappropriate. Most of the coals above this limit are of Cenozoic age, and the majority of these coals suggest that the line defining the start of the effective oil window must be extended to a VR of about $0.65\%R_o$ or T_{max} of 430 °C (Figs. 16a and 17a). The start of the effective oil window for a few coals may occur at even lower maturity.

In Section 4.1.1, the relationship between marin influence, hydrogen enrichment, and HI was discussed. Hence, the extraordinary high HI values may potentially be related to hydrogen-enriched vitrinite in the coals. The low content of liptinite in the coals in this study precludes that the high HI values are caused by a significant increase in liptinitic components (at least microscopic visible liptinite). Hydrogen-enrichment may be associated with suppression of vitrinite reflectance (George et al., 1994; Hao Fang and Chen Jianyu, 1992; Petersen and Rosenberg, 1998), and it is thus possible that the low thresholds for oil expulsion are due to suppressed VR values. George et al. (1994) recorded suppression of up to $0.25\%R_o$ in the Permian marine-influenced Greta seam, Sydney Basin. If a similar magnitude of suppression is present in the Cenozoic coals with very high HI values the expulsion thresholds (start of the effective oil window) would in reality be comparable to the expulsion thresholds of the Jurassic, Permian, and Carboniferous coals. FTIR and rhuthenium tetroxide-catalysed oxidation of a number of coals demonstrates, however, a significantly higher proportion of long-chain aliphatics in Cenozoic coals than in the older coals (GEUS, unpublished data). This indicates a considerably higher ability to generate liquid hydrocarbons, which may result in a lower maturity for expulsion.

The lower limit of the BI band defined by the Cenozoic coals reaches a maximum at a VR of 0.95% R_o or T_{max} of 450 °C (Figs. 16a and 17a). Most of the Cenozoic coals may thus start to expel oil within the VR range 0.65–0.95$\%R_o$ or 430–450 °C, whereas the effective oil window ends approximately within the VR range 1.7–2.0$\%R_o$ or T_{max} range 490–510 (Figs. 16a, 17a and 18). If the Cenozoic coals are differentiated into Paleocene/Eocene, Oligocene, and Miocene periods, the Paleocene/Eocene coals seem to have the capacity to generate larger quantities of petroleum than the Miocene coals (Fig. 15b). Therefore, the Paleocene/Eocene coals may also expel oil at lower maturity. Similarly, for Cenozoic Indonesian coals, Davis et al.

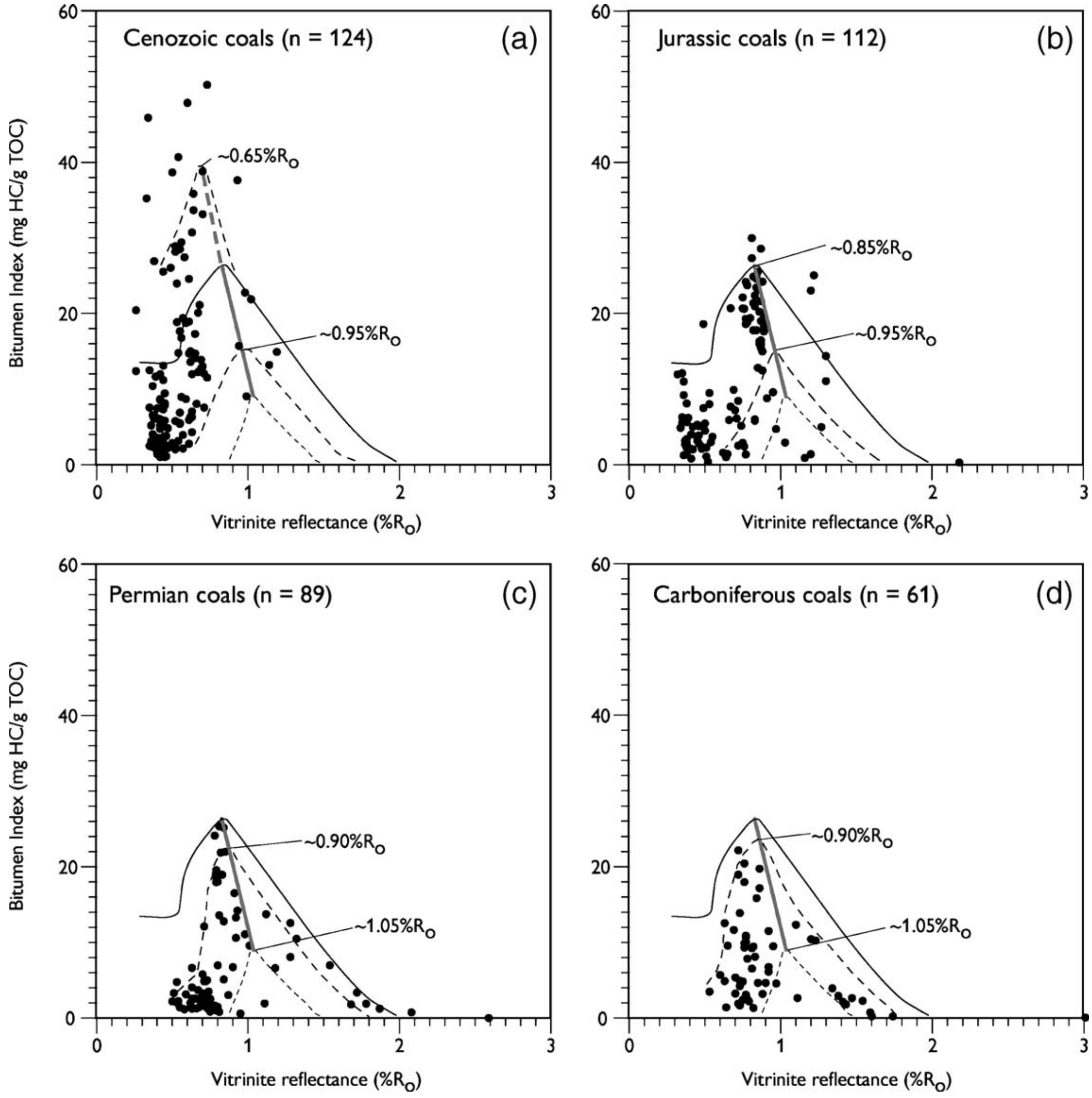

Fig. 16. BI vs. $\%R_o$ for (a) Cenozoic, (b) Jurassic, (c) Permian, and (d) Carboniferous coals. The line (reflectance range) for the start of the effective oil window for the worldwide coal data set is shown (see Fig. 10a); for Cenozoic coals, the line may be extended to lower maturities. The specific vitrinite reflectance range for the start of the effective oil window for each of the four coal-forming periods is indicated.

(2004) observed that the Palaeogene coals are generally more hydrogen-rich and will expel oil at lower maturity than the Neogene coals. The difference was related to specific coal sub-facies, which are a product of both the peat-forming vegetation and the depositional conditions.

The vast majority of the Jurassic coals display a start of the effective oil window from 0.85 to $0.95\%R_o$ or from 440 to 450 °C, and the effective oil window extends to $1.7–1.9\%R_o$ or 485–510 °C (Figs. 16b, 17b and 18). These results are in excellent agreement with the results of kinetic modelling of the Middle Jurassic Brent coal, North Sea (pers. comm. 2004, S. Hansen, DONG): onset of oil generation occurs at $0.8\%R_o$, but is first significant at $0.95\%R_o$ (8 mg HC/g TOC); oil generation ends at $2.13\%R_o$, but decreases considerably at $1.81\%R_o$. About 90% of the oil is generated from 0.95 to $1.81\%R_o$. As for the Cenozoic coals, the Jurassic coals are considered to be able to expel liquid petroleum efficiently.

The Permian coals generally seem to need a higher maturity before expulsion of oil is possible, as most of the samples define a start of the oil window from 0.9 to $1.05\%R_o$ or from 445 to 455 °C (Figs. 16c, 17c and 18). This may tentatively be explained by the generally higher proportion of non-generative inertinite in the coals. The lower proportion of petroleum generating

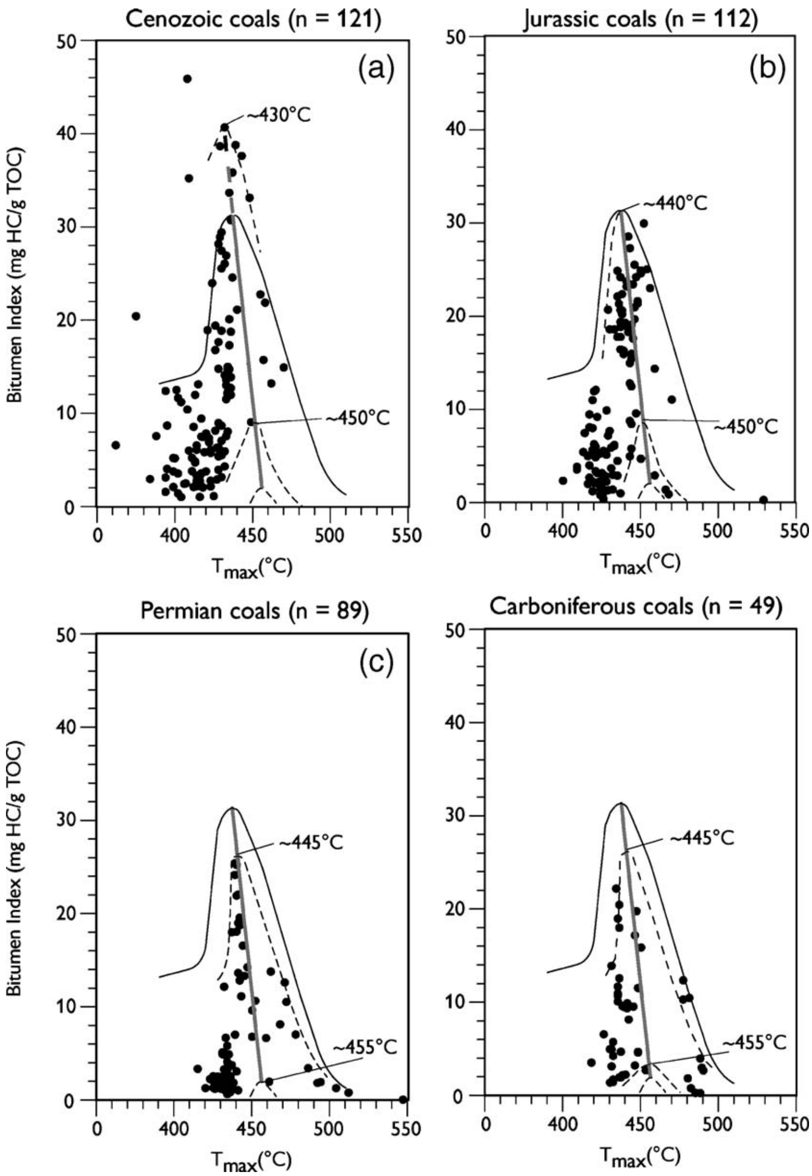

Fig. 17. BI vs. T_{max} for (a) Cenozoic, (b) Jurassic, (c) Permian, and (d) Carboniferous coals. The line (T_{max} range) for the start of the effective oil window for the worldwide coal data set is shown (see Fig. 10b). The specific T_{max} range for the start of the effective oil window for each of the four coal-forming periods is indicated.

organic matter still has to saturate the coal matrix, which may be achieved at higher maturities due to an overall lower bulk source potential. The start of the effective oil window from 0.9%R_o is in agreement with the expulsion threshold for Permian Cooper Basin coals, Australia, where significant expulsion of oil and condensate occurs around 0.9%R_o, in association with increasing gas expulsion (personal communication 2004, S. Taylor, Santos Ltd.). The effective oil window for Permian coal source rocks ends at 1.5–1.8%R_o or 470–500 °C. However, several of the Permian coals may possess a limited expulsion efficiency due to their restricted ability to saturate the coal, and overall the Permian coals are considered to be limited effective oil source rocks.

The effective oil window defined by the Carboniferous coals is very similar to that defined by the Permian coals (Figs. 16d, 17d and 18). Similarly, some of the Carboniferous coals also show a poor ability to generate sufficient quantities of liquid petroleum to saturate the coal matrix. In addition, as mentioned in the previous section, Carboniferous coals may not be able to generate

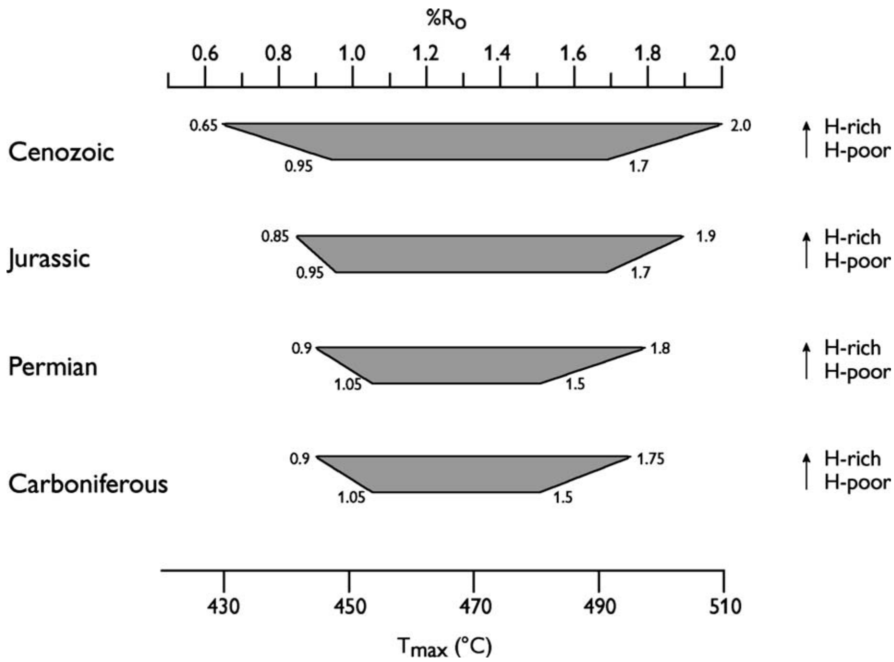

Fig. 18. Effective oil windows for Cenozoic, Jurassic, Permian, and Carboniferous coals. Cenozoic coals may possess the broadest maturity range for the effective oil window.

and expel commercial quantities of oil due to a restricted ability to form long chain aliphatics (GEUS, unpublished data). The S_1 peak has been found to consist of C_{1-33} hydrocarbons (Bordenave et al., 1993), although in practice the proportion of hydrocarbons with a carbon number less than about 10 will be limited. The S_1 peak derived from the Carboniferous coals may therefore be composed of shorter chain hydrocarbons. Preliminary FTIR and rhuthenium tetroxide-catalysed oxidation investigations by the author of the aliphatic components in Carboniferous coals close to their HI_{max} suggest that the coal structure principally contains aliphatic chains $<C_{18}$. Carboniferous coals thus seem to be very poor effective oil source rocks, and further investigations may show that the effective oil window for the Carboniferous coals in reality is an effective condensate/gas window.

5. Conclusions

The evaluation of a large worldwide coal data set permits the following conclusions to be made:

(1) The evolution of HI for all samples with increasing maturity can be described by a band that is broad (up to ~290 mg HC/g TOC) below a VR of about 0.6–0.65%R_o or below a T_{max} of approximately 430–435 °C (up to ~330 mg HC/g TOC). The HI band gradually narrows to a band width of c. 25–50 mg HC/g TOC or less with increasing maturity. The liquid petroleum potential is completely exhausted and stabilises at a very low value above a VR of c. 2.0%R_o or T_{max} of 510 °C.

(2) The variation in HI at a specific maturity is to some extent related to the depositional conditions, such as marine influence and the formation of H-enriched vitrinite. In addition, an overall vegetational control is exerted on the coal's generation potential. Generally the best coal source rocks were developed in Cenozoic times when a diverse angiospermous vegetation was widespread.

(3) The remaining generation potential shows an initial increase to a maximum. The upper limit of the HI band increases to a maximum of about 370 mg HC/g TOC at a VR of ~0.6%R_o or T_{max} of ~430 °C whereas the lower limit reaches a maximum of approximately 105–120 mg HC/g TOC at a VR of ~1.0%R_o or T_{max} of ~455 °C. The line from 0.6 to 1.0%R_o or from 430 to 455 °C defines the line of HI_{max}, which by translation of the samples can be universally used to derive the HI_{max} of immature coal source rocks or to reconstruct HI_{max} of matured samples. The initial increase in HI with increasing maturity yields negative TR values in the early stages of maturation.

(4) Liquid petroleum generation and expulsion from humic coals are highly complex mechanisms. The process of oil generation and expulsion from humic coals can be divided into three phases:
   (i) Onset of liquid petroleum generation, which occurs at a considerably lower maturity than the maturities at which oil expulsion begins.
   (ii) A phase of petroleum build-up in the coal source rock. The critical point is the start of the effective oil window, i.e. the maturity at which efficient oil expulsion begins. The VR or T_{max} values at which this maturity threshold is reached is dependent on the coal composition, including the chemistry of the vitrinite, and to some extent the age of the coal source rocks in question.
   (iii) Oil expulsion phase, corresponding to the effective oil window (oil expulsion window). The range of the effective oil window is dependent on the initial source potential and to some extent coal age. Initial oil expulsion for the worldwide coal data set can be defined by a line of maximum QI from approximately 0.7–1.0%R_o or 435–455 °C. Initial expulsion thus occurs at slightly higher maturity than the maturity at which HI_{max} is reached, but at a lower maturity than onset of efficient expulsion (start of the effective oil window). Efficient oil expulsion is defined by a decline in the BI. The BI-line from 0.85 to 1.05%R_o or from 440 to 455 °C defines the VR-range or T_{max}-range of the start of the effective oil window.

(5) The upper limit of the BI band decreases to very low values at a VR of about 1.8–2.0%R_o or T_{max} of about 500–510 °C whereas the lower limit decreases to very low values at a VR of ~1.5%R_o or T_{max} of ~470 °C.

(6) The worldwide coal data set defines two 'end-member' effective oil window ranges represented by the upper and lower limits of the BI band: an 'optimistic' range from 0.85 to 1.8%R_o or from 440 to 500 °C for hydrogen-rich coals and a more 'pessimistic' range from 1.05 to 1.5%R_o or from 455 to 470 °C for hydrogen-poor coals. For general use, in particular if the coal source is poorly known, it is recommended to use the VR range 0.85–1.7%R_o.

(7) Coals from the major coal-forming periods suggest that:
   (i) Cenozoic coals principally have HI_{max} values from 250 to 370 mg HC/g TOC, and in general the effective oil window ranges from 0.65–0.95%R_o to 1.7–2.0%R_o or 430–450 °C to 490–510 °C. Suppression of vitrinite reflectance may potentially be responsible for the low expulsion thresholds which thus in reality would be similar to the other coals. However, a relatively high proportion of long-chain aliphatics in the organic structure of Cenozoic coals suggests a considerable ability to generate oil which may result in expulsion at lower maturities.
   (ii) Jurassic coals principally have HI_{max} values from 105 to 290 mg HC/g TOC, and in general the effective oil window ranges from 0.85–0.95%R_o to 1.7–1.9%R_o or 440–450 °C to 485–510 °C.
   (iii) Permian coals principally have HI_{max} values from 120 to 290 mg HC/g TOC, and in general the effective oil window ranges from 0.9–1.05%R_o to 1.5–1.8%R_o or 445–455 °C to 470–500 °C.
   (iv) Carboniferous coals principally have HI_{max} values from 120 to 320 mg HC/g TOC, and in general the effective oil window ranges from 0.9–1.05%R_o to 1.5–1.75%R_o or 445–455 °C to 480–500 °C.

The Carboniferous and Permian coals are the poorest effective oil source rocks, and preliminary studies suggest that the effective oil window of Carboniferous coals in reality is an effective condensate/gas window. Overall, the ranges for the effective oil windows defined by VR and T_{max} are in good agreement, but due to the uncertain definition of the lower limit of the BI band, the largest deviations between VR and T_{max} exist for these values.

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