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Energy Fuels, Just Accepted Manuscript • DOI: 10.1021/acs.energyfuels.8b03164 • Publication Date (Web): 05 Dec 2018

Downloaded from http://pubs.acs.org on December 10, 2018

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Hydrocarbon generation potential of Oligocene oil shale deposit at onshore Penyu Basin, Chenor, Pahang, Malaysia

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Abstract

This is the first study that focuses on the evaluation of a newly-discovered oil shale deposit in the eastern Chenor area in the state of Pahang, Malaysia. Previously, this deposit was reported as carbonaceous/coaly mudstone. However, in this study, organic-rich immature carbonaceous mudstone containing above 15 wt % TOC is evaluated as oil shale, and that below 3.5 wt % TOC is termed mudstone. Oil shale and mudstone, which are significant sedimentary facies for oil and gas exploration, were investigated using organic geochemical and petrological methods, as well as Computed Tomography (Micro- CT), pyrolysis and bulk kinetic techniques, to evaluate their hydrocarbon generation potential.

The vitrinite reflectance values are less than 0.5 %Ro in all of the analyzed samples, indicating low maturity stage. This is corroborated by \(T_{\text{max}}\) values ranging from 383 to 429 °C. However, based on the kinetic simulation model, the average of predicted geological temperature for onset of hydrocarbon generation is 109 °C, while the peak of hydrocarbon generation is 153 °C. The extractable organic matter and hydrocarbon contents results show that the oil shale samples possess excellent petroleum potential compared to very good values for the studied mudstone.
This is consistent with the plots of TOC content versus extractable organic matter, and hydrocarbon yields versus TOC content, commonly used in estimating the hydrocarbon generative potential of source rocks. The TOC of these oil shales are consistent with those of the Tertiary oil shale deposits in China.

The analysed oil shale samples are characterized by a high hydrogen index (HI) of up to 700 mg HC/g TOC (average 517.4 mg HC/g TOC), suggesting oil-prone Type I and Type II kerogens. However, the open pyrolysis-gas chromatography (Py-GC) result of these samples displays a predominance of n-alkene/n-alkane doublets extending to the long range homologous series (C_7-C_{33}) with considerably high aromatic compounds, which indicates Type II/III kerogen (mixed oil and gas) generative potential. Similarly, bulk kinetic analysis of the analysed samples suggest typical petroleum source rocks facies derived from heterogeneous (Type II/III kerogens) organic matter assemblages. Thus, based on the pyrolysis and bulk kinetic result, the studied oil shale can be classified as “cannel coal” derived from terrestrial plants materials. This is supported by organic petrological and Micro-CT studies which revealed that the samples composed mainly of liptinite (sporinite, cutinite, amorphous organic matter and resinite), vitrinite, with varied trace amounts of inertinite.

Keywords: China Tertiary oil shale; cannel coal; organic-rich mudstone; Micro-CT; source rock evaluation
1. Introduction

The study area is located near Kg Pejing, east Chenor, Pahang, Malaysia (Fig. 1), a Oligocene onshore extension of the Penyu Basin [1]. The Penyu Basin is an important petroleum-bearing Cenozoic sedimentary basin in Peninsular Malaysia. It was formed in the early Oligocene period following the regional dextral shear deformation caused by the indentation of India into Eurasia [2]. It was filled with about 8 km of Oligocene to recent sediments [1-2]. The Penyu Basin is separated from the Malay Basin by the Tenggol Arch (Fig. 2); [2-3]. The basin appears to be structurally contiguous with the West Natuna Basin of Indonesia (Fig. 2).

Exploration in the Penyu Basin is still at an early stage. After almost three decades of exploration, only 8 wells have been drilled in the basin. Although good reservoir rocks are present in the basin, no commercial hydrocarbons were found [3]. Out of the 8 wells, only 1 well has oil show, which is Rhu-1/1A at a depth of between 2544m and 2815m from the upper Penyu formation (Fig. 3). The discovered well produced oil with an accumulative production exceeding 6000 BOPD. The discovered oil proves the existence of an existing oil system in the Penyu Basin [2-3].

The structure and stratigraphy of the basin was studied by [4-5]. A detailed structural analysis was done by [3]. Moreover, [6] reported the occurrence of isolated and widely separated Tertiary sedimentary rocks in Peninsular Malaysia (Fig. 4). Examples of such basins are Bukit Arang in Kedah and north Perlis, Kampong Durian Chondong, Lawin, in north Perak, Batu Arang in Selangor, Enggor in central Perak, Layang-Layang and Kluang-Niyor in Johor (Fig. 4). The occurrence of Oligocene sediments of east Chenor, Pahang (e.g. Fig. 5), was not reported by [6] as these sediments were previously mapped as the Tembeling Group with a Late Jurassic-Early Cretaceous age [7]. However, [8] deduced a Tertiary age for the sediments. The Tertiary age for
these sediments is in agreement with the immature nature of the organic matters in the studied samples (see section 5.1).

Previously, these sediments are described as interbedded carbonaceous mudstone, shale and sandstone [7-8]. However, organic-rich immature mudstone containing about 20 wt. % TOC can be evaluated as oil shale [9]. An oil shale is an immature, TOC-rich shale from which the liquid hydrocarbons can be produced by pyrolysis [10-12]. Previous studies by [13] on Tertiary coal-bearing sequence at Batu Arang in Selangor, Malaysia, also reported the presence of an oil shale facies assemblage. Worldwide, Tertiary oil shale deposits are widespread. For example, the Tertiary Green River oil shale deposit of USA is known to be the biggest oil shale resource in the world [14-15]. In China, the Maoming and Fushun, Tertiary oil shales were deposited in lacustrine environments [16-20]. The Hydrocarbon-generative potential of the Fushun oil shales has been described by [19-20]. According to these authors the Fushun oil shale has very high TOC contents (up to 20 wt. %)

Petrographically, oil shale can be divided into lacustrine, terrestrial and marine oil shales. Terrestrial oil shale characterized by liptinite-rich organic matter of vascular terrestrial plants such as resin, cuticles and stems, whereas lacustrine oil shales composed of liptinite-rich organic matter derived from algal that lived in freshwater, and marine oil shales comprised liptinite-rich organic matter derived from marine algal, marine dinoflagellates and acritarchs [21-22]. [22] recognized six specific oil shale types within these three group of oil shales; cannel coal, lamosite, marinite, torbanite, tasmanite, and kukersite. Generally, cannel coal is a brown – black homogeneous oil shale composed of vitrinite, inertinite and liptinite (cutinite, resinite and sporinite derived from terrestrial plants) [22]. Lamosite is composed of lamalginite derived mainly from lacustrine planktonic algal, while marinite is originated from lamalginite and
bituminite derived from marine phytoplankton. Torbanite, tasmanite and kukersite are related to specific kinds of algal from which the organic matter was derived.

This is the first study that focuses on detailed organic geochemical and petrological investigations in the Oligocene oil shale at onshore Penyu Basin (Figs. 5 and 6) to determine the oil-generating potential, as well as the kerogen composition of the oil shale and mudstone. This involves determining the total amount of organic matter present, assessing the type and quality of the organic matter as well as the level of thermal maturity. The hydrocarbon type that would be generated and the temperature of the petroleum generation will be assessed using Py-GC analysis and bulk kinetic models. The outcome of this investigation would enhance the understanding related to the petroleum source potential of the Tertiary basins in Peninsula Malaysia, including the Penyu Basin.

2. Geological setting

The Penyu Basin is one of the three major extensional basins of interior Sundaland (Fig. 2). These basins are believed to have formed as pull-aparts along a major NW-trend shear zone due to the India-Asia collision during the Late Eocene [3]. The exact timing of the basin formation is unknown, but [23] propose that the Penyu Basin was formed during the Late Eocene to Late Oligocene epoch based on analogy with the West Natuna Basin.

As in the neighboring Malay and west Natuna basins (Fig. 2), the Penyu Basin sediments are predominantly siliciclastic, consist of interbedded sandstone, siltstone, shale and coal [3]. The sedimentary strata can be divided into a syn- and a post-rift succession, in age of Oligocene to recent (Fig. 7). The distinction between these sedimentary succession is typical characteristic for basins formed as result of lithospheric extension [24]. The synrift sequence represents Oligocene sedimentation while the postrift sequence represents sedimentation of Miocene to recent. The
synrift sequence occurs as half-graben fills whose thicknesses are determined by the amount of extension along the bounding faults, whereas the postrift sequence has a more uniform thickness across the entire basin as a result of gentle sagging due to non-fault-related subsidence.

Figure 7 shows the stratigraphic subdivision of the Penyu Basin. An informal four-fold seismolithostratigraphic subdivision was established by [3]. Four formations were identified, in ascending order: Penyu, Terengganu, Pari, and Pilong (Figs. 3 and 7). Further subdivision into seismic units (P1 to P7) was proposed by [3] based on seismic features (H1 – H8), including unconformities (Fig. 7). The seismic units are interpreted mainly by aid of palynology, which is also used in deducing the sedimentary environments.

The Penyu Formation basically represents the synrift deposition during the Oligocene. It consists of interbedded sandstone and shale deposited in alluvial and lacustrine environments. By late Oligocene times, the basin was near sea level and was affected by marine incursions. Palynomorph assemblages in the formation indicate that there was increasing marine influence as the basin evolved [3].

The uppermost part of the synrift sequence is marked by the base of Pari Unconformity, which is the result of the basin inversion during the late Oligocene. This inversion event caused some folding and faulting within the synrift sequences in certain parts of the basin. Subsequently, during the Early to Middle Miocene, postrift sequences belonging to the Terengganu and Pari formations were deposited in alluvial and coastal plain environments. Coals are particularly abundant in the Pari Formations at Penyu-1 well [3].

The top of the Pari Formation is marked in places by an erosional unconformity, the Top-Pari Unconformity, which truncates part of the uplifted and folded Pari Formation that overlies inverted half-grabens. The Late Miocene-Pliocene regional unconformity in the Malay and West Natuna basins [25] is probably the result of the same basin inversion event [3].
The Pilong Formation includes sandstone and shale deposited in near-shore to shallow water marine environments following a marine transgression during Late Miocene to Early Pliocene time. The undeformed nature of the post-inversion sequence suggests that the Pliocene was a phase of relative tectonic quiescence [3].

The average heat flow in the Penyu Basin is about 85 mWm\(^{-2}\) [3], which is similar to that of the West Natuna Basin [26]. Such a high heat flow implies the presence of a thermal anomaly beneath the basin that may have been caused by lithospheric thinning. The high heat flow may contribute to the maturation of potential source rocks in the half-grabens [3].

3. Samples and methods

A total of 19 outcrop samples were obtained from the studied locality to investigate their geochemical characteristics such as organic matter source input and thermal maturity. During the course of sampling, a uniform sampling interval to avoid human bias of the evaluation of source potential was considered in determining the sampling interval. Fresh samples were taken after removing weathered surfaces to avoid contaminated and weathered samples. Organic matter is well known to be lost and degraded due to weathering process. In the highly weathered shale profile, most of the total organic carbon, biomarkers and some aromatic compounds are completely removed or their concentration decreased significantly [27]. However, there is no much losses in organic matter within unweathered shale [27-28]. Nevertheless, any organic geochemical data of outcrop samples should be interpreted with caution [29]. In this study, fresh (unweathered) outcrop samples were described, logged (Fig. 6) and subjected to the following analyses.

3.1 Organic geochemical methods

Powdered samples of oil shale, mudstone and sandstone were screened using Weatherford source rock analyser (SRA); (equivalent of Rock-Eval 6) to determine the bulk composition of the
organic matters (S1, S2 and T_{max}). Also, to determine the organic matter richness, about 100 mg of the sedimentary face was analyzed for total organic carbon (TOC) using a Multi N/C 3100 analyzer. Other parameters were computed from the SRA and TOC results (Table 1). These include hydrogen index (HI) and production index (PI) as described by [30] and [31].

To determine the amount of extractable organic matter and hydrocarbon content of the studied organic facies, about 15 g of <75 µm grain size of each sample was subjected to bitumen extraction procedure using Soxhlet apparatus. A mixture of 93% dichloromethane (DCM) and 7% methanol was used for the extraction which lasted 72 hours. The EOM obtained (Table 2) was separated into its different components (saturated, aromatic, NSO and asphaltene) using liquid column chromatography with the aid of solvents of increasing polarity (petroleum ether, dichloromethane and methanol). Pyrolysis gas chromatography (Py-GC) study was carried out to examine the structural features and compositional characteristics of kerogens as well as the hydrocarbon potential of the samples. The S2 Py-GC analysis (at 600°C) was performed using a Frontier Lab Pyrolyser System coupled to a 30 m x 0.25 mm column attached to an Agilent’s gas chromatography system with a flame ionization detector instrument. Pyrolysate of the samples flowing through the GC column were released between 300–600°C (25°C/min). Peaks identification was done manually with reference to standard chromatograms using Agilent ChemStation software as well as comparison to previous literature [32-33]. Table 3 shows the percentage abundance of specified compounds on the Py-GC pyrograms of the studied sedimentary facies. Following Py-GC analysis, representative samples were subjected to open system kinetic pyrolysis analysis. The concentrations of carbon (C), hydrogen (H), nitrogen (N), sulfur (TS) and oxygen (O) in representative samples were determined using a PerkinElmer 2400 Series II CHNS/O machine. From the result of the CHNS/O analysis, atomic ratios of H/C, O/C and S/C were calculated (Table 4). Approximately 10–20 mg of selected samples were analyzed
using programmed heating rates of 1, 5, 10, 25 and 50 °C/minute. The bulk petroleum formation curves measured at five heating rates served as input for the kinetic model. During the process, KINETICS 2000 and KMOD software were used to determine the activation energy distribution (Ea) and frequency factor (A). The strenuous mathematical model used for this kinetic study is suggested by [34].

3.2. Organic petrographical methods.

Organic petrographic studies were carried out on polished blocks to determine kerogen type as well as thermal maturity of the organic matter and to classify oil shale types. The blocks were produced by mounting about 3 mm size of crushed rock samples in a mixture of Serifix resin and resin-hardener. After drying, they were gently polished by fine grades of silicon carbide, followed by alumina powder using distilled water as a lubricant for oil shale samples, while isopropyl alcohol was used for the mudstone and sandstone samples. Microscopic studies were performed using a Leica DM 6000M microscope, and a Leica CTR6000 photometry system equipped with fluorescence illuminators. The microscope is fitted with BP 340–380 excitation filters, a RKP 400 dichromatic mirror, and a LP425 suppression filter. Vitrinite reflectance measurements were performed under oil immersion, using an immersion oil with a refractive index of 1.518 refractive index (ne) at 23°C. Calibration was done with a sapphire glass standard (0.589% reflectance value). Reported vitrinite reflectance (%Ro) are the averages of not less than 50 measurements per sample. UV (ultraviolet) light as well as normal reflected ‘white’ light were used in kerogen and/or maceral identification.

For coal-imaging, the micro-CT (computed tomography) imaging technique was followed as suggested by [35]. This 3D non-destructive micro-CT imaging was carried out using a Zeiss Xradia 520 Versa (helical scanning instrument) with a spatial resolution of 3.2843μ and 7mm field of view to produce 2048 x 2048 Pixel image sizes.
4.0 Results

4.1 Bulk source rock parameters

Table 1, shows the bulk geochemical parameter of the Oligocene sediments of east Chenor. These parameters are used to evaluate their organic matter richness, hydrocarbon potential and degree of thermal maturation. From Table 1, oil shales have slightly high TOC content (average: 22.02 wt. %). The mudrock samples possess lower TOC content (average: 3.25 wt. %) compared to the oil shales samples. The TOC values of the oil shales and mudstones are inclinations of very good to excellent petroleum source rock potential in the Oligocene sediments of the east Chenor. Also, the SRA pyrolysable hydrocarbon yield (S2) of the analyzed oil shales (77.3 to 176 mg HC/g rock) is obviously higher than that of the mudstones (14.8 to 17.6 mg HC/g rock) in the area. These parameters (TOC and S2) resulted into the observed high HI (Table 1) for both the oil shale (up to 772 mg HC/g TOC) and the mudstones (average of 432 mg HC/g TOC). Other bulk geochemical parameters are shown on Table 1.

4.2 Extractable organic matter - EOM

EOM yield (Table 2) gives further information about the organic matter composition (i.e. saturated, aromatic, NSO, and Asphaltenes fractions) of the Oligocene Chenor samples. This is based on results of the Soxhlet extraction procedure and column chromatography carried out on 14 representative samples to establish the extent of source richness and thermal maturity [36-37]. As expected, the oil shales are characterized by high EOM yield (average 26,420 ppm) compared to the mudstones (average 2,646 ppm) in the study area. Table 2 shows the detail composition of EOM in terms of wt. %, the saturated, aromatic, NSO, and Asphaltenes fractions. The hydrocarbon fractions (aromatic + aliphatic) of the oil shales and mudstones account for about 20 – 38% and 60 – 61%, respectively of the EOM in this area. The EOM result also revealed that the NSO and asphaltenes compounds account the highest values specially for the oil shale
samples (Table 2). This is an indication of a high concentration of polar compounds (NSO and asphaltenes) which is typical for immature petroleum source rocks [38].

4.3 CHNSO analysis

Result of CHNSO analysis carried out on the 13 representative samples from the Oligocene Chenor sediments is tabulated in Table 4. The analysis provides information about the relative percentage weight of carbon, hydrogen, oxygen, nitrogen and total sulfur content in study area. Table 4 also shows the computed hydrogen-to-carbon (H/C) versus oxygen-to-carbon (O/C) ratios which were used in characterizing the OM type and identifying the oil shale zone of the studied samples. From the elemental CHNSO analysis, an average of 1.86 and 0.38 for the oil shales and 1.85 and 0.49 for the mudstones were recorded as the atomic H/C and O/C respectively, which tallies with the high HI of the analyzed samples.

4.4 Py-GC data

In this study, Figure 8 shows the Py-GC pyrograms of the analyzed samples. The numbered peaks represent the n-alkene/n-alkane doublet peaks of equivalent carbon number. Cadinene (cad.) is also identified along with aromatic compounds such as toluene (T), m+p-Xylenes (X) and phenol (P); (Table 3). The analyzed oil shale samples show high abundance of n-alkene/n-alkane doublet peaks within the range of C7-C33 as well as a high abundance of aromatic compounds. The pyrograms display noticeable high concentration of < C12 n-alkene/n-alkane doublet compared to moderate amount of n-C12 to especially n-C27 to n-C31 as well as prist-1-ene. This is an indication of mixed oil and gas (Type II/III kerogens) generative potential. The ratios of concentration of cadalene/m(+p)-xylene (cd/xy) alongside with m(+p)-xylene to n-octene are presented on Table 3. These ratios were also used to determine the kerogen type in the study area. It is good to note that, for all the analyzed samples, the xylene compound shows a trend of
high concentration than cadeline. This gives a generally low ratio of cd/xy (0.09-0.2) as computed on Table 3. On the other hand, the “kerogen type index” varies from 0.4 to 1.2 indicating low degree of heterogeneity of organic matter composition.

4.5 Petrographic description

Liptinite, vitrinite and inertinite macerals derived from terrestrial plants are minor (volumetrically) components in all oil shales except cannel coals [21, 39]. In this study, the maceral group analysis performed on the oil shale samples revealed that liptinite > vitrinite > inertinite macerals (Table 5; Fig. 9). The analyzed samples consist of vitrinite (e.g. Fig. 9a), highly fluorescing, well-preserved sporinite, cutinite and amorphous organic matter (AOM); (e.g. Figs 9b-d). Resinite is apparently present as indicated by intense greenish-yellow fluorescence under the UV light excitation (e.g. Fig. 9e). Liptodetrinite and secondary solid bitumen (Fig. 9f) show bright yellow to dull yellow variation in fluorescence intensity. The secondary resinite and solid bitumen maceral, i.e. exsudatinite are commonly associated with early generation of liquid hydrocarbon [e.g. 40-41]. The common occurrence of these macerals groups indicate liptinite-rich cannel coal, derived from terrestrial vascular plants [e.g. 21]. This is in a good agreement with the biological marker (biomarker) studies reported by [3] on the Penyu Formation oil samples which also suggest terrestrial organic matter input. In addition, the darker grey vitrinite maceral observed in all of the analyzed oil shale that are associated with liptinites such as sporinites, cutinites, resinites (derived from terrestrial vascular plants) further support cannel coal classification. Moreover, the presence of liptinite maceral (sporinite, cutinite, AOM, and resinite) of >28 vol. % with vitrinite macerals (>19 Vol. %), indicate strong association with oil-and-gas prone Type II/III kerogens for the studied samples, especially oil shale [e.g. 40-41]. This is in solid agreement with the Py-GC and kinetic results. Hence, it supports the possibility of both oil and gas hydrocarbon within the Chenor area. Similarly, greenish-yellow fluorescing
liptinitic macerals (e.g. spores, liptodetrinite, resinite, solid bitumen, and amorphous organic matter) were also observed in the analyzed mudstone samples.

The inertinite maceral group, on the other hand, display a clear predominance of high reflecting fusinitic detritus mostly associated with sclerotinite and inertodetrinite macerals. Vitrinite reflectance data of the investigated samples are shown in Table 1. Generally, the analyzed Chenor samples have low reflectance values (0.31 to 0.47%). All these point to terrestrial plants source input and potential for oil and gas hydrocarbon within the Chenor area.

4.6 Micro-computed tomography study

The recent development of high resolution multi-scale imaging techniques, such as x-ray computed tomography (CT) and the application of synchrotron in source characterization, offers complementary evaluation tools in petroleum exploration. This method has proven useful in characterizing coal quality, assessment of gas shale/oil shale properties, and in hydrocarbon evolution [42-45]. In principle, density and effective atomic number of a given sample determine the CT number/beam hardening [46]. The density contrast among the macerals groups, pores and minerals can be used for their identification [47]. In this study, the application of Micro-CT imaging was used to determine the nature of void spaces and fractures as well as maceral types in an oil shale sample. It was observed that some of the pore spaces and fractures are filled with liptinitic material that resembles the secondary resinite maceral, i.e., exsudatinite that is commonly associated with early generation of liquid hydrocarbon from coal [40]. When compared to observation under normal reflected white light, the extensive nature of this exsudatinite vein is more discernible using Micro-CT imaging. Examples of the Micro-CT images are shown in Figure 10. In this case, the dark black coloured parts (lower density) on the profile line of the analyzed oil shale samples (e.g. 153H in Fig. 10) represent the pores, the bright
white colours (highest density) are the minerals, while the coal matrix is identified by medium
density, as previously described by [48], based on electron microprobe (EMP) and micro-FTIR
analysis. Amongst the coal macerals, the vitrinite group has a relatively high density (light grey
color) compared to the inertinite group (medium grey color), while the liptinite group has a
distinguishing low density (dark grey color) [e.g. 48]. Based on the petrographic description in
section 4.5 above, the inertinite group accounts for <3%, meaning that the liptinite and vitrinite
maceral groups dominate the maceral composition in the analyzed sample (Figs. 9 & 10). Thus,
it can be inferred that the dark grey areas shown in Figure 10 represent the liptinite group and
constitute about 30% of the analyzed images, whereas the vitrinite group represent about 20%.
This is in agreement with the petrographic observation discussed above (section 4.5).

5.0 Discussion

5.1 Thermal maturity assessment

Thermal maturity is an important parameter in source rock characterization for determining the
extent to which heat-driven reactions have transformed the available quantity of organic matter
to petroleum [36, 49]. Assessment of thermal maturity in this study is mainly based on vitrinite
reflectance, pyrolysis T_{max} data and fluorescence colours. The result was also correlated with
vitrinite reflectance data from [3].

Analyzed Chenor samples have low vitrinite reflectance (< 0.5%), indicating thermally immature
rock (Table 1). This interpretation is in line with the general trend of the pyrolysis T_{max} values
(<435 °C) shown in Figure 11. Petrographic observations in this study show that the fluorescence
colour of liptinites is mostly greenish-yellow. This is typical of thermally immature samples.
Interestingly, vitrinite reflectance data from source rocks within the Penyu Formation of the
Penyu Basin by [3] show a linear trend of early maturity (0.5-0.7% VR_o) at about 2100 meters
depth. If this trend is extrapolated down, the main oil generation window (0.7-1.3 VR_o) and the
mean peak gas window (1.3% VRo) should be at about 3200 meters and 5500 meters, respectively. This hypothesis is supported by the hydrocarbon generation temperature and transformation ratio derived from bulk kinetic analysis. The values of peak hydrocarbon generation temperature and the transformation ratios reveal a significant 60-65% transformation ratio. Therefore, the studied oil shale samples could generate oils at temperatures ranging from 150–155°C, which correspond to calculated vitrinite reflectance values of 0.93-1.07 % Ro (see Section 5.5).

5.2 Organic matter quantity

The TOC content, S2 values and EOM parameters are integrated to evaluate the quantity of organic matter in the Oligocene oil shale deposit at the onshore Penyu Basin. Presence of sufficient organic matter for hydrocarbon generation was established from the high TOC values. These TOC values indicate a trend of very good to excellent petroleum source rock potential for the analyzed mudstone and oil shale samples respectively (Fig. 12). This inference is supported by the pyrolysable hydrocarbon yield (S1+S2) from the SRA analysis as well as the total organic carbon (TOC, wt%) content for the oil shale and mudstone (see Fig.13). This agrees with [3], who indicated that the Penyu Formation shales contain about 1% TOC, and coal layers or seams within the formation possessed higher TOC (10-26 wt. %) with moderate to excellent generative potential. This is also in broad agreement with the findings of [19-20] whom showed similar TOC contents (up to 20 wt. %) in the Fushun Tertiary oil shale, China.

The detailed results of the bitumen extraction and column chromatography carried out on 14 representative samples further establish the extent of source richness and thermal maturity (Table 2). This is obvious from computed extractable organic matter (EOM) yields (ppm) that are higher in the analyzed oil shales (average 26,420 ppm) than the mudstone (average; 2,646 ppm). Similarly, column chromatography results show that the studied oil shale and mudstone facies
show very good to excellent hydrocarbon yields (2000>HC>2400 ppm) as shown in Table 2 (based on classification by [31]). This is consistent with the cross plot of TOC content versus EOM (Fig. 12a) as well as the hydrocarbon yields (ppm) and total organic carbon (TOC) content (Fig. 12b) commonly used in determining the hydrocarbon potential of probable source rocks.

5.3 Organic matter quality

The kerogen type in a sedimentary rock can be determined using the atomic (hydrogen-to-carbon and oxygen-to-carbon) hydrogen index (HI) and Py-GC data [9, 32-33, 50]. This will enhance prediction of the most likely hydrocarbon (oil or gas) to be generated from the source bed.

Table 4 shows the computed hydrogen-to-carbon (H/C) versus oxygen-to-carbon (O/C) ratios further used in characterizing the OM type and identifying the oil shale zone of the studied samples (Fig. 14). Based on the cross plots of hydrogen-to-carbon (H/C) and total organic content (TOC, wt%), the oil shale samples plot perfectly in the oil shale zone and mudstones samples plot in the range of typical oil-prone source rock (Fig. 14). This finding is supported by the high HI (average 517 mg HC/g TOC); (Fig. 15; Table 1).

Generally, source rocks having oil-prone (Type I and Type II kerogens) are known to have high HI (> 400 mg HC/g TOC) with low oxygen index (< 50 mg CO2/g TOC), while gas-prone (Type III kerogen) commonly show low hydrogen index (< 200 mg HC/g TOC) and OI between the range of 5 to 100 mg CO2/g TOC [36]. Type IV kerogen which have no hydrocarbon generation potential is usually characterised by very low hydrogen index (< 50 mg HC/g TOC) [36]. Type I and Type II kerogens are commonly derived from and marine organic matter (e.g. algal and amorphous organic matter), whereas Type III kerogen is composed mainly of higher plant materials (terrestrial plants) [e.g. 40-41]. Mixed Type II-III kerogens related to the greater abundance of liptinite (cutinite, resinite and sporinite derived from terrestrial plants), as compared to pure Type III kerogen which is mostly vitrinite [21].
Table 1 shows that the HI is relatively high for the analyzed oil shale (average 530 mg HC/g TOC) and mudstone (average 432 mg HC/g TOC). Based on this pyrolysis data and modified van Krevelen diagram (HI versus $T_{\text{max}}$) for classifying kerogen (Fig. 15), Type I and II kerogens as well as mixed Type II-III kerogens are dominant for the analyzed oil shale and mudstone samples, indicating that these sediments are capable for generating mainly liquid hydrocarbons.

Nevertheless, SRA data (HI) does not always accurately gives the types of kerogen present and types of hydrocarbons that can be generated during the maturation process [32-33, 50]. This because, mineral matrix in the source rock can influence the SRA data [32-33]. Therefore, the SRA technique can provide accurate assessments of kerogen type when it used in conjunction with Py-GC data [32-33]. In this study, the Py-GC pyrograms of the oil shales (Fig. 8) which are characterized by carbon peaks up to $C_{33}$, significant amount of $< n-C_{12}$, $n-C_{27}$ to $n-C_{31}$ as well as prist-1-ene and aromatic compounds favour mixed oil and gas (Type II/III kerogens) generative potential (Fig. 16). This is in line with the computed kerogen “Type index” ranging from 0.4 to 1.2 (Table 3) suggesting mixed kerogen Type II/III [32]. Considering the TOC, HI and Py-GC data, the analyzed oil shale samples can be classified as cannel coal. This assumption is supported by petrographic studies and kinetic analysis as discussed in the following sections (sections 5.4 and 5.5).

### 5.4 Hydrocarbon potential

The hydrocarbon potential of the analyzed samples was evaluated on the basis of the liptintic maceral composition, pyrolysis (Py-GC & SRA) and EOM composition. This is in line with previous works which emphasise the need to integrate pyrolysis data and petrographic studies in order to have a dependable result [13, 51]. [41] among others suggested that presence of oil associated liptinites maceral (e.g resinite, sporinite) up to certain thresholds as observed in the studied Penyu basin samples give a clear indication of hydrocarbon potential in a source rock.
Apart from the well-preserved sporinite, cutinite and resinites, there are reasonable amount of amorphous organic matter (AOM) within the area. This observation is further strengthened, under the UV light excitation, by intense greenish-yellow fluorescing resinite and solid bitumen (Fig. 9e). From [21, 41] it can be deduced that association of secondary resinite, solid bitumen maceral, i.e., exsudatinite along with other maceral group in the analyzed sample (Fig. 9f) points to potential for liquid hydrocarbon within the liptinite-rich cannel coal. This is confirmed by the Py-GC result discussed in the previous section as well as the high TOC content.

5.5 Bulk kinetics analysis and predictions for hydrocarbon generation

The analyzed oil shales have a wide range of activation energies. Overall, frequency factors range from 1.0668E+15/s to 9.9056E+13/s (Table 5; Fig. 17). These distributions suggest heterogeneous (mixed) organic matter composition for the studied samples [e.g. 52-54]. In addition, the petroleum generation temperature and timing predictions were made based on the derived kinetic parameters.

The relationship between temperature and transformation ratios of the studied oil shale samples are presented in Figure 18, while data for the onset (10% TR) and peak generation (geol. Tmax) temperatures have been tabulated in Table 5. The estimated predictions for the hydrocarbon generation temperature of the studied Oligocene oil shale samples show similar results in terms of onset and peak generation temperatures (Table 5). This is attributed to the significant similarity in the organic matter composition. In the studied oil shale, the onset of the peak oil window is expected at a moderate temperature from 106-112 °C (about 0.61-0.63Ro %). Such moderate generation temperatures are typical of heterogeneous Type II/III kerogens [e.g. 33, 55]. This supports the earlier observations based on pyrolysis data (see section 4.4). It can be inferred from the plot of the peak generation temperature versus the transformation ratios, measured from
the bulk kinetic analysis, the analyzed oil shales attain a reasonable transformation ratio at 60-65%
as shown in Table 5 and Figure 18. Therefore, the analyzed samples could generate sufficient
oils at temperatures ranging from 150–155 °C which correspond to calculated vitrinite
reflectance of 0.93-1.07Ro% (Table 5). This is in broad agreement with the vitrinite reflectance
data presented by [3] discussed in Section 5.3.

6. Conclusions

The Oligocene sediments of east Chenor were characterized using organic petrological and
geochemical methods as well as previous studies to evaluate their petroleum source potential,
origin and thermal maturity. In this study, the organic-rich immature carbonaceous mudstone (as
previously classified) with a relatively higher value of TOC of about 20 wt. % is evaluated as oil
shale and that containing below 3.5 wt. % TOC is termed mudstone. The TOC results are well
correlated with previous data from source rocks within the Penyu Formation of the Penyu Basin
and the Tertiary oil shale of Fushun Basin, China. Additional organic matter richness parameters
(e.g., HI, S1 & S2, EOM and HC s) indicated that these oil shale and mudstone samples have
excellent and a very good source rock potential respectively.

The SRA analysis indicates that the analyzed samples are predominantly oil prone, being
dominated by Type I/II and Type II/III kerogens. In contrast, based on the Py- GC results, the
analyzed oil shale samples display dominant \( n \)-alkene/\( n \)-alkane doublets extending to long-range
homologous series with considerably high aromatic compounds. This is an indication of mixed
oil and gas generating potential. This is supported by organic petrographic studies where the
analyzed oil shales are rich in liptinite and vitrinite macerals derived from terrestrial plants
indicating liptinite-rich cannel coals type of oil shale, strongly associated with oil-and-gas prone.
Previous studies biomarker of the Penyu Formation oil also suggest that, the source rock of the
oil was derived from terrestrial organic matter, deposited in a reducing lacustrine environment [3].

On the basis of the bulk kinetic analysis, the values of peak generation temperature and the transformation ratios reveal a significant 60-65% transformation ratio. Thus, the studied oil shale samples could generate oils at temperatures ranging from 150–155°C, which correspond to calculated vitrinite reflectance values of 0.93-1.07 % Ro. This is in a good agreement with the previous vitrinite reflectance data that show a linear trend of early maturity (0.5-0.7% Ro) at about 2100 m depth within the the Penyu Formation. Thus, the main oil generation window (0.7-1.3% VRo) should be deeper at about 3200 m while the top of the gas generation window (<1.3% VRo) is at 5500 m.

Acknowledgement

The authors gratefully acknowledge the University of Malaya for providing research facilities and grant (FP45-2017A) for this study. Micro-CT imaging was performed using a high-resolution, large-field, helical scanning instrument at the University of Malaya, Kuala Lumpur, Malaysia. We would like to thank Prof. Minghou Xu and all the anonymous reviewers for their helpful comments which greatly improved the manuscript.

References


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from Gombe Formation, Gongola Sub-basin, Northern Benue Trough, NE Nigeria. Int. J. Coal Geol. 173, 212–226.


Figures Captions

**Figure 1**: Regional location map showing the study area.
Figure 2: Location of the Penyu Basin east of Peninsular Malaysia [after 3, 5].
Figure 3: Cross section across the Rhu structures showing the Rhu-1/1A well [after 3].
Figure 4: Quaternary sediments, Tertiary basins and Late Cenozoic rocks in Peninsular Malaysia [after 6].
Figure 5: Outcrop view of the studied samples from the Oligocene strata of Eastern Chenor, Pahang, Malaysia.
Figure 6: Sedimentary logged section of the studied outcrop and samples positions.
Figure 7: Stratigraphic column of the Penyu Basin. The succession consists of synrift (Oligocene) and postrift (Miocene and younger) strata. H1 – H8 are based on seismic features interpretation [after 3].
Figure 8: $S_2$ Pyrolysis GC traces of selected mudstone and oil shale samples showing distribution of $n$-alkenes/$n$-alkanes doublets; $T =$ toluene; $S =$ 2,3-dimethylthiophene; $x =$ (m+p)-Xylenes; $P =$ phenol; cad= cadalene.
Figure 9: Photomicrograph of phytoclast in a mudstone sample under reflected white light (a) and (b) same view as (a) under UV light. Highly fluorescing, well-preserved sporinite (b); cutinite (c); amorphous organic matter (d); greenish-yellow fluorescing resinite (e); associated with sporinite and liptodetrinite (f).
Figure 10: Micro-CT imaging display selected cross-sectional image of center XY slices (a); selected cross-sectional image of center YZ slices (b); selected cross-sectional image of center XZ slices (c); and a 3-D view (d). Darker features are fractures and voids that are filled with secondary resinite (or exsudatinite), grey areas are vitrinitic macerals and white areas are predominantly mineral matter and inertinitic materials in a representative oil shale sample.
Figure 11: Cross-plot of pyrolysis $T_{\text{max}}$ versus vitrinite reflectance ($R_o\%$), which shows all the analyzed samples plot in the immature zone.
Figure 12: (a) Cross plots of total organic carbon (TOC, wt%) versus extracted bitumen (ppm) (b) S2 (mgHC/g rock) versus TOC (wt%) showing the hydrocarbon potential for the analyzed samples.
Figure 13: Relationship between petroleum potential yield (PY) versus total organic carbon (TOC, wt%) content for the analyzed samples.
Figure 14: Cross plots of Hydrogen-to-carbon (H/C) and total organic carbon (TOC, wt%) showing the hydrocarbon potential for the oil shale and mudstone samples (after [31]).
Figure 15: Plot of hydrogen index (HI, mg/gTOC) versus pyrolysis Tmax (°C), showing the quality and thermal maturity of the analyzed samples.
Figure 16: Ternary diagram of 2,3- dimethylthiophene, o-xylene (1,2-dimethylbenzene) and n-non-lene (n-C9:1), and (a) n-octene, (m+p)-xylene and phenol (b), showing the kerogen types (based on Py–GC data) of the studied samples (modified after 56 and 57 respectively).
Figure 17: Activation energy distributions (Ea) and frequency factors (A) for representative oil shale samples, illustrating a wide range of activation energies (in the range of 44-68 kcal/mol), with related frequency factors ranging from $9.9056 \times 10^{13}$/s to $1.0668 \times 10^{15}$/s. This distribution suggests heterogeneous organic matter composition for the studied oil shale samples.
Figure 18: Temperature (°C) versus transformation ratio (TR%) and vitrinite reflectance for representative shale samples, illustrating the onset (10% TR) and peak oil generation (geol. T$_{\text{max}}$) temperatures. In the studied oil shale, the onset of bulk hydrocarbon generation is expected at a moderate temperature from 106-112 °C (about 0.61-0.63R$_{\text{o}}$%).
**Tables Captions**

**Table 1:** Results of TOC (wt. %), pyrolysis data (SRA) analyses and measured vitrinite reflectance values (%Ro) of the studied samples.

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<th>No</th>
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<th>$S_1$ (mg/g)</th>
<th>$S_2$ (mg/g)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>HI</th>
<th>PI</th>
<th>$R_o$ (%)</th>
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<td>0.42</td>
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<td>0.08</td>
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<td>7.6</td>
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<td>Mudstone</td>
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<td>153SH</td>
<td>Mudstone</td>
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<td>3.0</td>
<td>17.6</td>
<td>421</td>
<td>419</td>
<td>0.14</td>
<td>0.36</td>
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</table>

$S_1$: Volatile hydrocarbon (HC) content, mg HC/g rock  
$S_2$: Remaining HC generative potential, mg HC/g rock  
PI: Production Index = $(S_1/(S_1+S_2))$  
HI: Hydrogen Index = $S_2 \times 100 / \text{TOC}$, mg HC/g TOC  
TOC: Total organic carbon, wt. %  
$T_{\text{max}}$: Temperature at maximum of $S_2$ peak  
$R_o$: Vitrinite reflectance (%)
Table 2: Bulk geochemical results of EOM, hydrocarbon yield (saturated + aromatic fractions) and non-hydrocarbon (NSO+asphaltenes) of the extractable organic matter (wt% and ppm) of selected samples.

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<th>No</th>
<th>Samples ID</th>
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<th>TOC (wt. %)</th>
<th>Bitumen yield and chromatographic fractions (ppm of whole rocks)</th>
<th>Chromatographic fractions of Bitumen Extraction (EOM wt%)</th>
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<td>EOM Sat. Aro. NSO Asph. HCs HCs/ EOM Sat. Aro. NSO Asph. HCs NSO + Asph.</td>
<td>Sat. Aro. NSO Asph. HCs</td>
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<td>16.0 22.1 34.9 26.9 38.1 61.8</td>
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<td>29,155 2,970 4,291 12,007 9,875 7,261 0.25</td>
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<td>19.60</td>
<td>24,174 3,402 3,870 6,504 10,315 7,272 0.30</td>
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EOM= Extractable organic matter
Sat= Saturated hydrocarbons
Aro= Aromatic hydrocarbons
NSO= Nitrogen, Sulfur, Oxygen components
HCs= Hydrocarbon fractions (Saturated + Aromatic)
Asph = Asphaltenes
Table 3: Py-GC pyrogram quantitative data. (o)-Xylenes: ortho-xylene/ (m+p)- xylene, cad/xy: cadalene/(o)-xylene, C₈/xy: n-octene/(o)-xylene, Type index: (o)-xylene/n-octene, , nd: not determined.

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<th>Phenol %</th>
<th>n-Octene % (C₈)</th>
<th>cd/xy</th>
<th>C₈/xy</th>
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<td>11.5</td>
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<td>0.18</td>
<td>1.7</td>
<td>0.6</td>
<td>12.2</td>
<td>53.1</td>
<td>38.2</td>
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<td>0.12</td>
<td>1.8</td>
<td>0.6</td>
<td>9.8</td>
<td>55.3</td>
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<td>10.3</td>
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<td>0.9</td>
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</tr>
</tbody>
</table>

(o)-Xylenes: ortho-xylene/ (m+p)- xylene, cd/xy: cadalene/(o)-xylene, C₈/xy: n-octene/(o)-xylene, Type index: (o)-xylene/n-octene
Table 4: TOC content, pyrolysis parameters, vitrinite reflectance data and atomic ratios from CHNS/O analysis of the studied samples.

<table>
<thead>
<tr>
<th>No</th>
<th>Sample ID</th>
<th>Lithology</th>
<th>C (wt. %)</th>
<th>Ultimate Analysis</th>
<th>Atomic Ratio</th>
<th>total CHNSO</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H (wt. %)</td>
<td>O (wt. %)</td>
<td>N (wt. %)</td>
</tr>
<tr>
<td>1</td>
<td>153A</td>
<td>Oil shale</td>
<td>17.2</td>
<td>2.8</td>
<td>79.0</td>
<td>0.81</td>
</tr>
<tr>
<td>2</td>
<td>153B</td>
<td>Oil shale</td>
<td>23.7</td>
<td>3.5</td>
<td>71.4</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>153C</td>
<td>Oil shale</td>
<td>19.6</td>
<td>3.3</td>
<td>76.3</td>
<td>0.72</td>
</tr>
<tr>
<td>4</td>
<td>153C1</td>
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<td>15.7</td>
<td>2.9</td>
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</tr>
<tr>
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<td>Oil shale</td>
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<td>1.13</td>
</tr>
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<td>69.9</td>
<td>0.87</td>
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<tr>
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<td>Oil shale</td>
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<td>2.2</td>
<td>86.2</td>
<td>0.76</td>
</tr>
<tr>
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<td>153F</td>
<td>Oil shale</td>
<td>27.1</td>
<td>3.7</td>
<td>68.0</td>
<td>0.96</td>
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<td>2.6</td>
<td>83.6</td>
<td>0.77</td>
</tr>
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<td>153H</td>
<td>Oil shale</td>
<td>26.7</td>
<td>3.6</td>
<td>68.5</td>
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<tr>
<td>11</td>
<td>153Co</td>
<td>Oil shale</td>
<td>29.6</td>
<td>3.9</td>
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</tr>
<tr>
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<td>153D2</td>
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<td>1.6</td>
<td>95.3</td>
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</tr>
<tr>
<td>13</td>
<td>153 SH</td>
<td>Mudstone</td>
<td>3.0</td>
<td>1.6</td>
<td>94.7</td>
<td>0.63</td>
</tr>
</tbody>
</table>

HI: Hydrogen Index = S₂ x 100 / TOC, mg HC/g TOC
TOC: Total organic Carbon, wt. %
Carbon (C), hydrogen (H), nitrogen (N), sulfur (TS) and oxygen (O)
Table 5: Predicted transformation ratio and peak of hydrocarbon generation temperature, and calculated vitrinite reflectance (Ro%) at a linear rate of 3.3 °C/My and summary of petrological data for the analyzed oil shale samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Activation energy</th>
<th>A[1/S]</th>
<th>HI</th>
<th>Onset (°C)</th>
<th>Peak (°C)</th>
<th>Onset (Ro %)</th>
<th>Peak (Ro %)</th>
<th>Peak (TR%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>153A</td>
<td>42-66</td>
<td>2.1629E+14/sec</td>
<td>474</td>
<td>106</td>
<td>150</td>
<td>0.60</td>
<td>0.98</td>
<td>60</td>
</tr>
<tr>
<td>153B</td>
<td>44-68</td>
<td>6.2545E+14/sec</td>
<td>525</td>
<td>108</td>
<td>152</td>
<td>0.62</td>
<td>1.01</td>
<td>61</td>
</tr>
<tr>
<td>153C</td>
<td>44-68</td>
<td>1.0668E+15/sec</td>
<td>581</td>
<td>110</td>
<td>154</td>
<td>0.63</td>
<td>1.05</td>
<td>62</td>
</tr>
<tr>
<td>153C1</td>
<td>44-68</td>
<td>9.9056E+14/sec</td>
<td>560</td>
<td>108</td>
<td>155</td>
<td>0.62</td>
<td>1.07</td>
<td>65</td>
</tr>
<tr>
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<td>44-68</td>
<td>9.8945E+14/sec</td>
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<td>112</td>
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</tr>
<tr>
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<td>7.6956E+14/sec</td>
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</tr>
<tr>
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<td>9.3220E+14/sec</td>
<td>482</td>
<td>109</td>
<td>155</td>
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<tr>
<td>153G</td>
<td>44-68</td>
<td>1.1514E+15/sec</td>
<td>431</td>
<td>107</td>
<td>155</td>
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<td>44-68</td>
<td>1.1043E+15/sec</td>
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<td>110</td>
<td>155</td>
<td>0.63</td>
<td>1.06</td>
<td>65</td>
</tr>
</tbody>
</table>

A-Pre-exponential factors
HI- Hydrogen Index
Onset (°C)- Onset (TR 10%) temperature
Peak (°C)- Peak generation temperature (geological T_{max}).
Ro%- calculated vitrinite reflectance
Peak (TR): Transformation ratio in the peak generation temperature (geological T_{max}).