Self-heating behavior and ignition of shale rock

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ABSTRACT

The combustion of shale, a porous sedimentary rock, has been reported at times in outcrop deposits and mining piles. However, the initiating event of most of these fires is unknown. It could be that, under the right conditions, shale rock undergoes spontaneous exothermic reactions in the presence of oxygen. This work studies experimentally and for the first time the self-heating behavior of shale rock. Because shale has high inert content, novel diagnostics such as mass loss measurements and visual observation of charring are introduced to detect self-heating ignition in respect to other self-heating materials with lower inter content. Using field samples collected from the outcrop at Kimmeridge Bay (UK) and the Frank-Kamenetskii theory of ignition, we determine the effective kinetic parameters for two particle-size distributions of shale. These parameters are then used to upscale the results to geological deposits and mining piles of different thicknesses. We show that for fine particles, with diameter below 2 mm, spontaneous ignition is possible for deposits of thickness between 10.7 m and 607 m at ambient temperatures between −20°C and 44°C. For the same ambient temperature range, the critical thickness is in excess of 30 km for deposits made of coarse particles with diameter below 17 mm. Our results indicate that shale rock is reactive, with reactivity highly dependent on particle diameter, and that self-ignition is possible for small particles in outcrops, piles or geological deposits accidentally exposed to oxygen.

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1. Introduction

Unconventional oil, as opposed to conventional oil extracted from reservoirs where petroleum can flow naturally, is trapped inside tight porous media that requires enhanced recovering processes like hydraulic fracturing to release oil and gas [1]. Unconventional oil may be trapped in rocks, sands or coal; the most common examples being oil sands, coalbed methane, shale gas and shale oil [1]. Shale oil and shale gas both originate from the same source rock, shale, as shown in Fig. 1. Shale is a general term used to describe a large array of clay rich sedimentary rocks. It is fine grained and is estimated to represent 50% of all the sedimentary rocks deposited on Earth [2]. The thickness of shale rock deposits varies widely with location around the world, but it ranges from 1 m to 600 m [3].

Sedimentary rocks containing significant amount of organic matter are reactive porous media. This includes coal, oil sand and shale. Reactive porous media are materials where small free spaces (pores) are embedded in the solid together with a presence of a carbon-rich component [2], as shown in the sketch on the lower right of Fig. 1. This allows the rock to be permeable to a variety of fluids such as air, water or oil, and greatly increases its surface area making the organic particles reactive because it allows oxidation to take place if O₂ is supplied [2]. Such reactive porous rocks might undergo self-heating. Self-heating is the tendency of certain materials to undergo spontaneous exothermic reactions in oxidative atmospheres at low temperatures [4]. This process starts by slow oxidation at ambient temperature, but the reaction alone is insufficient to raise the material temperature. The temperature rise is determined by the balance between the rate of heat generation and the rate of heat losses [5]. Fire initiated by self-heating ignition is a well-known problem for many types of porous reactive media [6]. Of the reactive porous sedimentary rocks shown in Fig. 1, extensive studies on self-heating ignition behavior have been conducted for coal, both experimentally and computationally [6–13]. Some work is present in the literature on the thermal degradation of shale and kerogens (in environments without oxygen) [14,15]. However, very little work has been done in understanding the behavior of shale rock exposed to an oxidizing environment which might undergo self-heating. Early work was carried out on shale rock ignition 1982, when the US Mining bureau reported initial measurements of the self-heating of shale dust [16]. The report acknowledges that self-heating of shale rock is of importance, and states that in-depth investigation is needed. No studies have been reported in literature since.

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2. Self-heating ignition theory

Frank-Kamenetskii theory is usually employed in the literature to investigate spontaneous ignition [4,24]. The theory allows to calculate ignition conditions from reactive properties like the activation energy and other physical parameters of the material such as the conductivity and the heat of reaction by finding the critical ambient temperature for a given sample size. Total heat production from reactions inside a material sample is proportional to its volume, but heat loss is proportional to its area. This means that as the size of the sample becomes larger, because volume increases with size faster than area, then the critical ambient temperature required for ignition decreases. The theory can therefore be used to predict spontaneous ignition for larger sizes at lower temperatures, provided that the mechanism of heat production is unchanged [4,24]. The heat transfer problem in this study corresponds to the transient heat conduction equation, shown in Eq. (1),

$$\nabla^2 T + \frac{QF(t)e^{-\frac{\Delta}{k}}}{k} = \frac{1}{\alpha} \frac{\partial T}{\partial t}$$

where $T$ is the temperature of the fuel sample, $E$ is the activation energy of the reaction, $k$ is the conductivity of the fuel, $R$ is the universal gas constant, $Q$ is the heat of reaction per fuel mass, $\alpha$ is the thermal diffusivity of the fuel, $t$ is time and $F(t)$ is the mass action law based on concentration of fuel and oxygen at any given time. There is no need to specify the dependency on concentration but an often invoked representation of this law is $[\text{fuel}]^n [\text{O}_2]^m$ [4].

Frank-Kamenetskii theory of ignition assumes that the material has a high reactivity and high activation energy so that a steady-state condition is reached [4,24]. To solve Eq. (1) at steady-state, Frank-Kamenetskii theory defines a dimensionless parameter $\delta$,

$$\delta = \frac{QEFfL^2e^{-\frac{\Delta}{k}}}{kRT_d^2}$$

where $T_d$ is the ambient temperature and $L$ is the characteristic length, half the smallest dimension of the fuel (for a cubic basket $L$ is the side length, and for an infinite slab $L$ is the thickness), $f$ is the value of $F(t)$ at initial time, so based on initial concentrations of fuel and oxygen [24]. Expressing the reaction rate as the Arrhenius law for dependence on temperature, Eq. (1) is solved at steady-state, and the following dependence of critical size and temperature is obtained, as shown in Eq. (3):

$$\ln\left(\frac{\delta_tT_d^2}{L^2}\right) = \ln\left(\frac{QFf}{RK}\right) - \frac{E}{R T_{\text{act}}\alpha c}$$

where $\delta_t$ is the critical value of the dimensionless parameter in Eq. (2), and is used to relate the geometrical shape of the sample to the critical ambient temperature $T_{\text{act}}$, which corresponds to the minimum ambient temperature for which ignition of a given sample will occur. $\delta$ is a non-dimensional representation of the ratio of characteristic heating time to characteristic reaction time, so $\delta$ can be seen as a type of Damköhler number [23]. A solution to Eq. (3) satisfying the boundary condition $T = T_d$ on the wall(s) only exists when the condition $\delta < \delta_t$ is satisfied. Since $\delta_t$ is a function of geometry, this is found by looking up its value for the experiment geometry of interest in the literature [6,23,24]. In our experimental work we used cubic baskets, so $\delta_t = 2.52$ [24], and for geological formations and heaps we assume slab geometry which has $\delta_t = 0.878$ [24]. By plotting the experimental data of $\ln\left(\frac{\delta_tT_d^2}{L^2}\right)$ against $\frac{1}{T_{\text{act}}}$ (Eq. (3)), we obtain a correlation. If the correlation is a straight line, this validates the Frank-Kamenetskii theory. The
slope of the straight line corresponds to \(-\frac{E}{R}\), while the y-intercept is \(\frac{D}{R}\).

### 3. Experimental method

A large shale formation is present in southern England in the Weald Basin near Southampton [25]. The shale for these experiments was collected from the outcrops of this formation on the coastal cliffs of Kimmeridge Bay, shown in Fig. 2, in large blocks to ensure the homogeneity of the samples. The time delay between field collection of all samples and the last experiment conducted was 7 months. This was the shortest possible delay we could manage to complete the series of 37 experiments. We do not expect this delay to have effects on the results because shale samples are chemically stable (fossil matter extracted from the free surface of the formation, and hence already weathered). The shale blocks were all collected from the same area to ensure homogeneity in the rock contents. To ensure further control and minimize loss of water or oxidation, once crushed, the samples were stored in sealed containers.

Elemental analysis was carried out on the samples, measuring the carbon, hydrogen, nitrogen and sulfur contents, and the results are provided in Table 1. The crushed samples have a density of 1200±10 kg/m³. The low carbon content of 13% makes shale a weakly reactive porous media compared to other porous fuels like coal which have much higher carbon contents.

#### Table 1
Basic composition of the shale rock samples collected from Kimmeridge bay.

| Element | C  | H  | N  | S  |
|---------|----|----|----|----|
| Weight% | 13.01 | 1.67 | <0.3 | 2.22 |

Proximate analysis of the shale was carried out and is shown in Table 2 as % of total sample weight. It shows low moisture content, and high ash content.

Thermogravimetric analysis (TGA) of the shale samples was conducted in air with a heating rate of 5 K/min, and is shown in Fig. 3. The error cloud corresponds to 10.9% of the mass measurement based on the worst case found in TGA mass measurements by Grønli et al. [26]. The first peak seen in the mass loss rate (MLR) corresponds to drying. The mass loss resulting in that temperature range matches the measured moisture content from the proximate analysis (Table 1). There are two other peaks in MLR, at 500°C and 730°C. By comparing this TG curve with typical data for coal, we see that the reactivity of shale develops in the same temperature range as coal, with the location of these two MLR peaks at similar temperatures to those of bituminous coal [27]. The large amount of residue mass left at the end of the test shows the high inert content of shale, in agreement with Table 1. The total mass loss from the TGA was found to be 18.6%, which is close to the sum of the moisture (Table 2), C, H and S (Table 1).

Size distribution of particles is important because the reactivity of the material is proportional to the average surface area to volume ratio of the media, A/V, with a decreasing particle size increasing the reactivity. This has been shown for reactive porous media such as coal [28].

When designing the experimental programme, it is important to control for the particle size of the samples as much as possible [28]. However, it is also important to retain as much as possible the field origin of the samples which are extracted from a real formation of porous rock as opposed to being monosize samples produced in the lab. We struck a balance between these two competing scientific aims by crushing the samples in a controlled manner and creating two repeatable sets of shale rocks (fine vs. coarse particle). Coarse particles have a diameter smaller than 17 mm. Fine particles have a diameter smaller than 2 mm. These two sets can test the hypothesis of the particle size effect and also retain much of their natural geological state. The coarse and fine sizes were prepared following fixed weight distribution of particles sizes. The resulting distributions are shown in Table 3.

The laboratory setup to determine the minimum ambient temperature for self-heating \(T_{\text{AC}}\) that leads to ignition was constructed.

#### Table 2
Proximate analysis of the shale rock samples collected from Kimmeridge bay.

| Moisture content | Volatile matter | Ash | Fixed carbon |
|-------------------|-----------------|-----|--------------|
| Weight%           | 2.5             | 16.5| 80.4         | 0.6           |

Fig. 3. Thermogravimetric analysis in air of our shale sample, with a heating rate of 5 K/min. Plots of mass [%] as a function of temperature with error bars (left) and mass loss rate (MLR) as a function of temperature with error bars (right).
Table 3

| Particle diameter range | 2 mm < D < 17 mm | 1 mm < D < 2 mm | D < 1 mm |
|-------------------------|------------------|-----------------|---------|
| Coarse particles        | 57%              | 20%             | 23%     |
| Fine particles          | 0%               | 40%             | 60%     |

Fig. 4. The four cubic shaped baskets used for experiments, with side lengths labeled.

Fig. 5. Experimental setup for self-heating experiments with sample at the center of a thermostatically controlled oven with thermocouples for measuring oven and sample temperatures (left) and sample of shale rock (before crushing) from Kimmeridge Bay used for the experiments (right).

following a similar procedure to that described in the British Standards EN 15,188:2007. The shale was packed into cubic shaped wire mesh baskets of different sizes to study different critical sizes. The baskets were made of 0.5 mm diameter wire mesh with volumes of 131, 442.5, 1048.8, 3539.6 cm³ to ensure a wide range of sizes to obtain experimental data for a large temperature range. The baskets used are shown in Fig. 4, with each cube’s length labeled.

Each basket filled with shale was placed in the middle of a thermostatically controlled laboratory oven with forced air circulation to prevent temperature stratification. The oven was initially preheated to a given uniform temperature. In order to prevent the forced flow affecting the results, a mesh cage was placed inside the oven. The temperature inside the sample was monitored using two thermocouples placed at middle depth in the center of the sample 0.5 cm apart. Oven temperature was also measured by a thermocouple placed several centimeters away from the basket, inside the mesh cage, in the vertical mid plane of the oven. Fig. 5 shows the overall experimental setup on the left, with a sample shale rock on the right.

Supercritical temperature is defined as the temperature for which heat produced by the reactions exceeds the heat dissipated to the environment, causing a thermal runaway to ignition. If the shale failed to reach supercritical temperature the experiment was repeated with a fresh sample at 10°C higher temperature. If the shale reached supercritical temperature and ignited, then the experiment was repeated with a fresh sample at 10°C lower temperature. The repeats were carried out until the minimum ambient temperature $T_{min}$ for ignition was located with a maximum error of 5°C. A summary of the experiments carried out, for each basket size and the two particle size distributions is given in Table 4.

Reactivity of shale can be readily identified because once the baskets are placed in the oven the core reaches a temperature higher than that of the oven. Once the local reactions terminate (burnout) the heat dissipates away from the sample bringing the temperature of that location back to the oven temperature. Fig. 6 shows the temperature evolution at the core of the sample, where the core temperature at the center of a 131 cm³ basket for fine particle samples is compared to the oven reference temperature throughout the duration of an experiment for both an ignition and a no-ignition case. The no-ignition experiment is carried out with an oven temperature of 196°C, while the ignition experiment is carried out with an oven temperature of 244°C. Both temperature curves present very similar characteristics, with the core of the shale sample reaching higher temperatures and in shorter time for the ignition case. In all the experiments, the center of the sample is allowed to cool down to the oven temperature.

Table 4

| Basket length | 5.08 cm | 7.62 cm | 10.16 cm | 15.24 cm |
|---------------|---------|---------|----------|----------|
| Coarse particles, # experiments | 6 | 5 | 5 | 3 |
| Fine particles, # experiments | 8 | 4 | 4 | 2 |

Fig. 6. Temperature measurements at the center of the basket and the oven for ignition and no-ignition 131 cm³ sample experiments. The thermal behavior of both experiments presents similar overall characteristics, with the ignition experiment reaching a higher maximum temperature.

4. Results and discussion

When analyzing results for very reactive media, usually the sharp temperature increase after a critical temperature can be used to identify ignition and criticality [4,6,23,24]. An example of such analysis is shown in Fig. 7, where cases of self-heating ignition, and no-ignition, of a different reactive porous media (much more
reactive than shale), hardwood sawdust, are taken from literature [6]. In the first case there was no-ignition, while in the second case the sample ignited and the sharp temperature increase is evident.

However, as shown in Fig. 6, the shale rock temperature profile is more similar for both the no-ignition and ignition cases. This is due to the low carbon content of the rock, and its very high inert content acting as a heat storage (heat capacity). For shale, the temperature rise is not valid as the only means for identifying ignition. Therefore, two novel diagnostics were introduced to the self-heating ignition criteria: the mass lost (measured after each oven experiment), and the presence of char in the sample. The change in the mass of the shale sample after the experiment exhibited a distinct change in slope for the experiments where ignition took place. This can be seen for the 131 cm$^3$ fine particle size basket experiments on the left of Fig. 8. The best linear fits for the experimental mass loss data of no-ignition and ignition cases are plotted as a function of the oven temperature. The change in slope corresponds to the presence of char in the sample after the experiments (right of Fig. 8). This triple criteria for ignition provides confidence on the identification of critical conditions, even for low-reactive shale.

Analysis of experiments shows the presence of three regions: one where no critical thermal runaway happens and there is no ignition; a transition zone where we are at the critical thermal runaway limit for ignition and therefore have some ignition cases and some no-ignition cases; and a zone for which ignition happens for all the experiments. In the ignition zone char is observed in all of the samples after the experiments. The slopes of the mass loss curves depend on the particle size distribution, and on the basket size. The marked change in slope is observed in all sizes and particle distributions studied.

Using the critical ignition temperatures found in the experiments for the four different basket sizes, we plot the data of $\ln\left(\frac{E_c}{k}\right)$ vs $\frac{1}{T_a}$, and calculate the best linear fit to produce Fig. 9. This shows the typical Frank-Kamenetskii plot for both coarse and fine particle sizes. The linear fits have R-squared values of 0.999 for the coarse particles, and R-squared of 0.984 for the fine particles. The slope is confirmed as strongly linear and the data validates the assumption that the Frank-Kamenetskii theory and Arrhenius reactions assumptions apply.

The impact of particle size is large. We can obtain the effective activation energy from the slope of the two lines in Fig. 9, where $E_c$ and $E_f$ are the coarse particle and fine particle effective
activation energies, and the thermal parameters from the y-axis intercept, as shown in Table 5 [24]. The values are calculated based on the best linear fits from Fig. 9 with the effective activation energy being half for fine particles compared to that of the coarse particles. The error bounds are calculated using the fits that would give the highest and the lowest possible effective activation energies from the experimental data, so they are the worst-case scenario. The kinetic parameters and effect of particle size obtained in this work can be used as parameters for more advanced models of shale self-heating ignition.

5. Upscaling results to the field domain

The activation energies found are used in the Frank-Kamenetskii theory to upscale to geological sizes. A shale formation is usually very wide, up to thousands of kilometers long, but is between 1 m and 600 m thick [3]. Similarly, a heap is typically much wider than thick. They can therefore be modeled as an infinite slab, and determine a critical geological deposit for various temperatures by using Eq. (3) with the critical dimensionless parameter \( \lambda_0 = 0.878 \) [24]. This approach was used for both sets of particle size distributions for a temperature range between -20°C and 44°C, which includes possible ranges of ambient temperature in the natural environment (day and night, winter and summer). It is important to note that this assumes that oxygen is present in the shale for the reactions to occur. Such oxygen supply could be provided at outcrop formations exposed to the atmosphere, as well as by ground perforations providing an accidental route for oxygen ingress from the atmosphere. The upscaled results can be seen in Fig. 10. The error bars are purposefully large, as the fits that would give highest and lowest possible effective reactivity are calculated for the error bars of Table 5. These represent the worst-case scenario.

Results show that the shale rock geological deposit (or mining pile thickness) required for ignition vary dramatically with shale particle size. For the fine particles, with size distribution below 2 mm, at 22°C ignition is possible for a thickness of 35 m. For the coarse particles, which include particles up to 1.7 cm diameter, for the same temperature, a thickness of 358 km is required for ignition. Spontaneous ignition is possible for rock deposits of thickness between 10.7 m and 607 m for the fine particles. These are all shale thickness sizes that can be found in natural geological deposits present throughout the world which are up to 600 m in thickness [3]. For the coarse particles in the same temperature range, the required thickness is between 30 km and 100,000 km, which are all sizes much greater than the natural geological deposits on Earth.

There are some limitations to consider when upsingaling the laboratory results to the field domain. The effect of moisture has not been taken into account but water can affect the heat transfer via evaporation, condensation and changing the thermal diffusivity [24]. The effect of pressure on self-heating ignition has not been studied although shale can be found at higher pressures than atmospheric pressure, it is known that in general pressure has an effect on ignition and that the effects are dependent on the global reaction order and thus vary depending on the fuel and chemistry [29]. Any natural shale formation would have differing carbon contents and different particle size distributions to those present in this study. The effect of these cannot be quantified at the present moment, but this study is the first time self-heating and ignition conditions for shale are studied and should enable future in-depth studies.

6. Conclusions

Shale fires are a common problem in both shale rock outcrop formations and mining heaps throughout the world. The ignition process, which could be due to self-heating of reactive porous shale rock, has not been studied in-depth until now. This study investigates experimentally and for the first time the self-heating and ignition conditions for shale rock at various ambient temperatures and for different particle diameter sizes. Traditional experimental diagnostics for identification of self-heating ignition were enhanced by the addition of two novel diagnostics valuable for samples of high inert content such as in shale. This work contributes to understanding and predicting the onset of shale formation fires, which have been observed in nature. The Frank-Kamenetskii theory of ignition criticality shows that Arrhenius reactions apply, as the effective energy is found to be a constant for the temperature range and particle size distributions studied. Self-ignition conditions depend on shale particle size and ambient temperature. It was shown that particle size has a large effect on reactivity, with fine particles being more reactive than coarse particles and presenting a smaller effective activation energy of 88.79 kJ/mol compared to 179.36 kJ/mol, differing by almost a factor of two. Lab-scale results were upscaled to slab formation thicknesses to model real geological shale formations and find critical thicknesses for self-heating and ignition for a range of ambient temperature conditions. For fine particle size it was shown that a small formation thickness is required for spontaneous ignition at ambient temperature. In nature, this can be in outcrop formations exposed to the environment as well as ground perforations providing an accidental route for oxygen ingress from the environment. The upscaled results highlight a very large reactivity change of shale rock with changes in particle size distributions. This work provides the first experimental study of the self-heating and ignition conditions for shale rocks.

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References

[1] H. Schobert, Chemistry of fossil fuels and biofuels, 126, Cambridge University Press, 2013, pp. 187–189.
[2] F. Dullien, Porous media fluid transport and pore structure, Academic Press, 1979, p. 79.
[3] D.C. Duncan, Geologic setting of oil-shale deposits and world prospects, in: T.F. Yen, G.V. Chilingarian (Eds.), Developments in Petroleum Science, 5, Elsevier, 1976, pp. 13–26.
[4] D. Drysdale, An introduction to fire dynamics, Wiley and Sons, 2011, pp. 228–232, 317–324.
[5] N.N. Semenov, Chain reactions, Goskimizdat. English translation, Oxford, 1935.
[6] P.C. Bowes, Self-heating: evaluating and controlling the hazards, HMSO, London, 1984.
[7] G.B. Stracher, T.P. Taylor, Coal fires burning out of control around the world: thermodynamic recipe for environmental catastrophe, Int. J. Coal Geol. 59 (1) (2004) 7–17.
[8] J.M. Jones, A. Saddawi, B. Dooley, E.J.S. Mitchell, Werner J. D.J. Waldron, S. Weatherstone, A. Williams, Low temperature ignition of biomass, Fuel Proc. Technol. 134 (2015) 372–377.
[9] D. Wu, X. Huang, F. Norman, F. Verplaetse, J. Berghmans, E. Van den Bulck, Experimental investigation on the self-ignition behaviour of coal dust accumulations in oxy-fuel combustion system, Fuel 160 (2015) 245–254.
[10] A. Küçük, Y. Kadoğlu, M.S. Gülaboğlu, A study of spontaneous combustion characteristics of a Turkish lignite: particle size, moisture of coal, humidity of air, Combust. Flame 133 (3) (2003) 255–261.
[11] Z. Song, C. Kuenzer, Coal fires in China over the last decade: a comprehensive review, Int. J. Coal Geol. 133 (2014) 72–99.
[12] A.H Mahmoudi, F. Hoffmann, M. Markovic, B. Peters, G. Brem, Numerical modeling of self-heating and self-ignition in a packed-bed of biomass using XDEM, Combust. Flame (2015).
[13] J Carras, B. Young, Self-heating of coal and related materials: Models, application and test methods, Prog. Energy Combust. Sci. 20 (1) (1994) 1–15.
[14] M.S.K. Youtos, E. Mastroakos, R.S. Cant, Numerical simulation of thermal and reaction fronts for oil shale upgrading, Chem. Eng. Sci. 94 (2013) 200–213.
[15] Alan K. Burnham, Robert L. Braun, Development of a detailed model of petroleum formation, destruction, and expulsion from lacustrine and marine source rocks, Org. Geochem. 16 (1-3) (1990) 27–39.
[16] JK Richmond, M.J Sapko, LF Miller, Fire and explosion properties of oil shales, United States: Bureau of Mines, Pittsburgh, PA, 1982.
[17] PF Hudak, Spontaneous combustion of shale spoils at a sanitary landfill, Waste Manag. 22 (6) (2002) 687–688.
[18] K. Torrance, G. Rein, C. Switzer, R. Carvel, R. Hadden, C.M. Belcher, Smoldering-waste heap in Scotland, in: G.B. Stracher, A. Prakash, E.V. Sokol (Eds.), Coal and Peat Fires: A Global Perspective, Chapter 20, Elsevier, 2013. pp. 395–405.
[19] L. Stromquist, Investigation of an oil shale fire at windfall mountain: an initial assessment of an in-situ formation fire, Report No. NPS/YUC/NERDS—2014/733, US National Park Service, Fort Collins, Colorado, 2014.
[20] R. Arnold, R. Anderson, Metamorphism by combustion of the hydrocarbons in the oil-bearing shale of California, J. Geol. 15 (8) (1907) 750–758.
[21] R. Grapes, Pyrometamorphism, Springer, 2006, pp. 92–112. pp20–28.
[22] Adri Robilant, Venetian navigators: the voyages of the zen brothers to the far north, Faber and Faber, 2011, pp. 169–170.
[23] V. Babrauskas, Ignition handbook, Fire Science Publishers, 2003, pp. 369–411.
[24] B. Gray, Spontaneous combustion and self-heating, in: P.J. DiNenno (Ed.), SFPE Handbook of Fire Protection Engineering, Chapter 10, 3rd Edition, Section 2, 2002, pp. 211–228.
[25] I. Andrews, The jurassic shales of the weald basin: geology and shale oil and shale gas resources estimation, British Geological Survey, Department of Energy and Climate Change, 2014.
[26] M. Grooli, M.J. Antal, G. Várhelyi, A round-robin study of cellulose pyrolysis kinetics by thermogravimetry, Ind. Eng. Chem. Res. 38 (6) (1999) 2238–2244.
[27] J.W. Cummings, J McLaughlin, The thermogravimetric behaviour of coal, Thermochim. Acta 57 (3) (1982) 253–272.
[28] F. Akgün, A. Arisoý, Effect of particle size on the spontaneous heating of a coal stockpile, Combust. Flame 99 (1) (1994) 137–146.
[29] I. Glassman, Combustion, Academic Press, 1997, pp. 336–338.