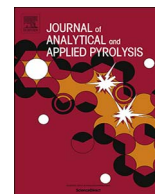




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Investigation of the evolution of sulphur during the thermal degradation of different oil shales

Birgit Maaten*, Lauri Loo, Alar Konist, Tõnu Pihu, Andres Siirde

Department of Energy Technology, Tallinn University of Technology, Ehitajate tee 5, Tallinn, 19086, Estonia

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ABSTRACT

This paper presents the results of the pyrolytic decomposition of six different oil shale samples with different sulphur contents from Estonia, USA and China using non-isothermal thermogravimetry coupled with a mass spectrometer (TGA-MS). Mass spectrometry (MS) was used to analyse the evaporating gases. The results showed a major difference in the evolution of sulphur containing substances. The sulphur behaviour was found to be in excellent correlation with the composition of the sample. H₂S and SO₂, the problematic components forming during the pyrolysis process, both exhibited evaporation in two peaks. The kinetic distribution supported the findings of MS – samples with a higher sulphur content exhibited more parallel reactions that had similar weight percentages. SO₂ evolution intensifies above 500 °C. H₂S is released in the temperature range of 350–500 °C, depending on the sample. The samples Kentucky, Green River, Estonia and Chinese 2 also have an additional peak at 500–570 °C. This is in good accordance with the aforementioned samples having a relatively high amount of sulphur in the forms of organics and sulphides. Based on the results, an important conclusion is that changing the pyrolysis temperature can reduce the sulphur content of the oil produced. The experimental curves obtained were used to calculate the kinetic parameters using a distributed activation energy model. The obtained activation energy values were in the range of 134–276 kJ/mol with the frequency factors ranging from 1.89E10¹² to 1.20E10¹⁴ s⁻¹. In order to validate the obtained kinetic parameters, the decomposition curves were compared to modelled ones. The dependence of total conversion on reaction time was calculated at isothermal conditions to show the effect of pyrolysis temperature.

1. Introduction

Oil shale is an unconventional fossil fuel, often described as a complex material consisting of an organic part (called kerogen) and an inorganic part, which consists of a wide range of minerals [1–4]. When oil shale particles are heated to a certain critical temperature, the organic part starts to decompose and vaporize, leading to the production of gas, oil and residual carbon [5]. In addition to being an energy source, the exploitation of oil shale in, for example, China represents a valuable source of liquid hydrocarbons. The pyrolysis process of oil shale involves complex reactions and its end products are dependent on numerous factors like heating rate, final temperature, etc. [6]. Therefore, in order to maximize the potential, the conversion process of oil shale to oil should be studied and optimized [7].

There are several different devices and methods to conduct studies about kinetics, but thermogravimetry is the most used technique [8]. Since the decomposition of oil shale is complex and consists of a large number of parallel and series reactions, thermal analysis describes the

overall weight loss due to these reactions instead of describing individual reactions [9]. The factors that are considered to influence the thermal behaviour of oil shale have been widely discussed in the literature [2,5,6,10–13]. Non-isothermal methods are usually preferred to isothermal ones due to not having a thermal induction period and permitting a more rapid scan of the whole temperature range [2,7,14]. As an additional advantage, using a non-isothermal approach helps to more closely simulate the conditions of a large-scale retorting process [3]. Using different models to analyse the devolatilization process can help predict the burnout of a particle, the heating value of pyrolysis products and the overall process efficiency [15]. Additionally, one can calculate the time a particle should be in a retort in order to obtain complete decomposition, which is useful in industry.

Another big advantage of thermal analysis is the possibility to couple it with other analytical devices, for example FTIR, GC or MS. Thermal analysis helps to understand the process of oil shale pyrolysis process, but understanding the mechanism is still tricky due to the potential effect of various minerals and without additional analysis, it is

* Corresponding author.

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quite often hypothetical. For example, MS data enables us to study gas evolution [16], molecular characterization [17], the kinetics of hydrocarbon generation [18], etc. Pan, et al. has used TG-MS to investigate the effect of mineral matter on the thermal decomposition of Jimsar oil shale [10] – using MS they showed that pyrites can react with organic matter to form H₂S and SO₂ in the temperature range of 510–650 °C. Lan, et al. found that the content of sulphur-containing gases in non-condensable gases changes when increasing the retorting temperature [19]. They found that H₂S is the primary component in non-condensable gases and the release of this gas begins even at low temperatures. Therefore, MS offers valuable information regarding the evolution of gases and the behaviour of the components in the samples.

There are numerous methods to calculate and analyse the experimental data in order to calculate the kinetic parameters of different processes. Their advantages and disadvantages have been critically evaluated by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee, with the most important principle being that methods that use only a single heating rate should not be used. The choice of a good method is important, since good kinetic data is essential to accurately model various processes, which in the case of oil shale pyrolysis is the oil-evolution step [14].

As opposed to the considerable research that has been devoted to publishing single sample results or articles comparing several samples [18,20–24], the objective of this paper is to describe the decomposition of samples from all over the world using simultaneous thermogravimetric analysis and mass spectrometry (MS). Sulphur behaviour and evolution is investigated in light of potential benefits to oil plants. In Estonia oil is produced at temperatures of 450–500 °C [25]. The solid heat carrier technology utilizes lower temperatures than the gaseous heat carrier technology making it the preferred technology [26]. Since this directly influences emissions, sulphur behaviour was analysed in order to see whether the sulphur content in the oil could be reduced for oil shales of other origins. It is necessary to investigate the limits of the sulphur release to determine the optimal temperature for the pyrolysis process. To overcome the shortcomings of previous research [27], this study offers the calculation of kinetic parameters based on experiments with different heating rates, analyses the decomposition products and their profiles and also focuses on modelling. The effect of sulphur and heating rate on the pyrolysis kinetics and evolved products of different oil shales is studied.

2. Experimental

2.1. Materials

Six oil shale samples from the USA, China and Estonia were investigated. The samples exhibited different sulphur concentrations (0.81–2.16%), both in the mineral and organic part. The samples were chosen due to China and USA having the largest resources (1600 and 354 million barrels, respectively [28]) and Estonia being highly dependent on oil shale for power production (about 90% of electricity is produced from oil shale [29,30]). The sampling locations are as follows: Estonia – from an underground mine called “Estonia” in Estonia; Colorado – from Green River shale formation, Colorado, USA; Green River – from the Uinta basin of the Green River shale formation, Utah, USA; Kentucky – from the New Albany shale formation, Kentucky, USA; Chinese 1 and Chinese 2—from the Maoming mine, Guangdong Province, Southwest China with the local classifications of C and A, respectively. All oil shale samples used in pyrolysis tests were previously dried and crushed to less than 1 mm. The elemental analysis results can be seen in Table 1 and the proximate analysis in Table 2. As sulphur in oil shale exists in the form of sulphide, sulphate and organic sulphur the organic sulphur content has been calculated by difference (from the total sulphur content and sulphide and sulphate forms) [31,32].

Table 1
Ultimate analysis results (wt%, dry base) and characteristics of the tested oil shale samples.

Sample	N	C	H	S ^{total}	S _{sulphide}	S _{sulphate}	S _{organic}
Estonian	0.1	27.3	2.7	1.46	0.96	0.07	0.43
Colorado	0.9	27.7	3.2	1.39	0.67	0.30	0.42
Green River	0.4	17.2	1.7	0.81	0.20	0.03	0.58
Kentucky	0.5	15.4	1.7	1.76	0.76	0.33	0.67
Chinese 1	0.9	23.3	2.4	2.16	1.17	0.30	0.69
Chinese 2	0.9	23.0	3.0	1.96	1.26	0.23	0.47

Table 2
Proximate analysis results, presented on an as received basis.

	Estonian	Colorado	Green River	Kentucky	Chinese 1	Chinese 2
Ash (wt%)	51.3	61.9	66.8	76.6	56.1	61.0
Moisture (wt%)	0.5	1.9	0.3	0.9	0.6	1.2
Volatile matter (wt%)	47.5	26.9	33.2	14.9	42.8	28.9
Fixed carbon (wt%)	1.3	11.2	0.0	8.6	1.2	10.1
Higher heating value (MJ/kg)	9.85	11.34	5.51	6.41	11.40	10.14

2.2. Experimental setup and methods

The samples were analysed using a NETZSCH STA 449 F3 Jupiter[®] TG-DSC apparatus coupled with a NETZSCH QMS Aëolos[®] mass spectrometer. The samples were heated in a pure nitrogen atmosphere from 200 °C to 650 °C using constant heating rates set to 2, 5, 10, 20 and 35 °C/min. For comparison of the MS data, the measurements with a heating rate of 5 °C/min were chosen to ensure that there were no overlaps between the peaks. In order to correctly interpret the results it was checked that the ratio of the mass-to-charge-ratio (m/z) at 34 to that at 33 is 2.38 to ensure that the compound is indeed H₂S. m/z 34 was selected for comparison due to its higher intensity. For the analysis of SO₂ m/z 64 was investigated and m/z 48 was also checked. The data was normalized starting from 200 °C to remove background noise and smoothed with a 5 point moving average. The results of kerogen decomposition with a heating rate of 20 °C/min can be seen on Fig. 1. A protective gas flow of 50 mL/min of high purity nitrogen was used. In order to eliminate buoyancy effects during the furnace heat-up cycle, background mass data were recorded during empty crucible experiments and subtracted from the each of the oil shale measurement data set. The temperature calibration of the apparatus was done using In, Sn, Zn, Al and Au standards. Excellent reproducibility (temperature differences less than 2 °C and mass change differences less than 0.7% for parallel measurements) was observed for the mass loss curves. All the reported results are the average values of the conducted repeated measurements.

2.3. Kinetic computations

Due to the complexity of oil shale composition [17,33,34], a distributed reactivity model was used to calculate the activation energy values. The reactivity distribution corresponds to a set of independent and parallel reactions and an activation energy value and a frequency factor are calculated for each of them [35]. As a further validation, the reactions are described with a single frequency factor, thereby representing the reactivity distribution by a continuous distribution of activation energy values. The calculations and recreation of the curves were done using Kinetics2015. Although the earliest model of sequential decomposition of kerogen to bitumen and then bitumen to oil and gas is still the most cited one, an alternate pathway is believed to be

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