

PYROLYSIS KINETICS OF OIL SHALE FROM ULUKIŞLA, TURKEY

H. SÜTCÜ^{(a)*}, S. PİŞKİN^(b)

^(a) Zonguldak Karaelmas University, Chemistry Department
Zonguldak, Turkey

^(b) Yıldız Technical University, Chemical Engineering Department
Istanbul, Turkey

Ulukışla oil shale in Turkey was pyrolysed at varying heating rates by thermogravimetric analysis. Kinetic analysis was undertaken at the decomposition steps of pyrolysis using the Coats & Redfern kinetic method. In addition, activation energies and reaction orders of the steps were calculated. Moreover, structural analysis of the oil shale sample was carried out by FTIR spectrometry, X-Ray diffractometry and XRF spectrometry.

Introduction

Oil shale is a sedimentary rock containing organic matter which, when heated, can change into liquid compounds. It cannot be dissolved in oil-derived solvents efficiently [1]. Much work has been done on pyrolysis of oil shales and their pyrolysis kinetics by thermogravimetric analysis. Williams and Ahmad pyrolyzed Pakistani oil shales at heating rates of 5, 10, 20 and 40 °C/min under isothermal conditions and studied process kinetics using the Arrhenius and Coats & Redfern kinetic model [2]. Bhargava et al [3] carried out characterization of Australian oil shales by thermogravimetric analysis, DRIFT and X-Ray diffractometry. Kök and Pamir [4] conducted non-isothermal thermogravimetric pyrolysis of Turkish oil shales and investigated their decomposition kinetics. Li and Yue [5] studied pyrolysis kinetics of oil shales using different models. Değirmenci and Durusoy [6] pyrolyzed Göynük (Turkey) oil shale by varying particle size and heating rates. Williams and Ahmad [7] performed pyrolysis of Pakistani oil shales at varying heating rates. Jaber and Probert [8] carried out thermogravimetric analysis of Jordanian oil shales and investigated their decomposition kinetics. Toronto and Galan [9] undertook thermogravimetric analysis of Spanish oil shales under isothermal and non-isothermal conditions at varying

* Corresponding author: e-mail halesutcu@hotmail.com

heating rates using different kinetic methods. Aboulkas and El Harfi [10] studied thermal decomposition kinetics of Tafraya (Morocco) oil shale and kerogen.

Considering the fact that fuel consumption in Turkey for energy consumption has increased from 53 million tonnes to 77 million tonnes, the existing energy sources should be utilized in the best possible way. Of these sources, oil shale is the second-ranking fossil fuel in Turkey [11]. The reason why Ulukışla oil shale was chosen for this study is that not much work has been carried out on it. The oil shale sample was obtained from the Ulukışla township of Niğde Province, Turkey (Fig. 1). The oil shale reserves of this area are about 130 million tonnes [12].



Fig. 1. A geological map of Turkey showing the locations of oil shale reserves [13].

The purpose of the present study is to demonstrate that Ulukışla oil shale can be utilized as an alternative energy source. To this end, pyrolysis of Ulukışla oil shale was investigated by thermogravimetric analysis. Also, its pyrolysis kinetics was analyzed using the Coats & Redfern method, and the reaction orders of decomposition reactions during pyrolysis were calculated.

Experimental

Material and Analyses

The proximate analysis of the Ulukışla oil shale ground $<250\ \mu\text{m}$ was conducted in accordance with ASTM D3172-07a using a LECO CHN-600 carbon-hydrogen-nitrogen analyzer and LECO SC-132 sulfur analyzer. Calorific value was determined by means of IKA-Calorimeter C400. The results obtained are given in Tables 1 and 2.

Table 1. The results of the proximate and ultimate analyses of Ulukışla oil shale

Ash ^a	Volatile matter ^a	Fixed carbon ^a	C ^b	H ^b	N ^b	S ^b	kJ/kg ^b
29.45	45.73	24.82	57.81	4.19	0.96	5.60	22.31

^a dry basis, %^b dry and ash free basis, %**Table 2. The ash content of Ulukışla oil shale (dry basis, %)**

SiO ₂	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	SrO	TiO ₂
11.12	42.90	6.20	5.44	8.54	24.76	0.43	0.33

The pyrolysis experiments were performed using a Perkin Elmer Pyris Diamond DTA/TG apparatus at heating rates of 2, 5, 10, 15, 30 and 60 °C/min under a nitrogen flow rate of 100 ml/min from ambient temperature up to 1000 °C.

The X-Ray diffraction analysis of the oil shale sample was carried out in a Philips Panalytical X'Pert PRO Model diffractometer using CuK α radiation (40 kV and 40 mV) at a diffraction angle of 0°-70°.

The SEM picture was taken by means of a Jeol JSM model 5410 LV scanning electron microscope.

The FTIR spectrum was taken using a Perkin Elmer Spectrum One FTIR spectrometer.

The ash analysis was performed in a PANalytical MiniPal4 Energy Dispersive XRF spectrometer.

Kinetic approach

The kinetic parameters for pyrolysis reactions were calculated using the Coats & Redfern kinetic model [14]. The Coats & Redfern equation employed for calculations based on the reaction order is

$$\text{(for } n \neq 1) \quad \ln \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2 (1-n)} \right] = \ln \frac{AR}{aE} - \frac{E}{RT},$$

where E is activation energy, α fraction decomposed, T temperature, A pre-exponential factor, R ideal gas constant, a heating rate and n reaction order. The curve of a line drawn from the left-hand side of the equation to $\frac{1}{T}$ yields E and the point of intersection A . To achieve this, the n value was varied between 0.5 and 2.0, and the n value which gave the highest correlation value was assumed to be the order of that reaction.

Results and discussion

Analysis of the chemical structure

Figure 2 gives the FTIR spectrum of Ulukışla oil shale. The broad band at $3600\text{--}3200\text{ cm}^{-1}$ is attributable to hydroxyl groups in water and phenolic compounds. The bands at 2920 cm^{-1} and 2850 cm^{-1} (C–H stretching symmetric and asymmetric vibration) are indicative of aliphatic structures. The band at $1600\text{--}1400\text{ cm}^{-1}$ can be assigned to the C=C aromatic stretching. The bands 1150 cm^{-1} and 1035 cm^{-1} correspond to the aliphatic ether C–O band having an aromatic structure. The peaks at $900\text{--}450\text{ cm}^{-1}$ indicate the presence of mineral groups.

It has been established from the X-Ray diffraction analysis and SEM graph of Ulukışla oil shale (Figures 3 and 4) that it contains mainly carbonate minerals (calcium carbonate, calcite and dolomite), quartz and pyrite.

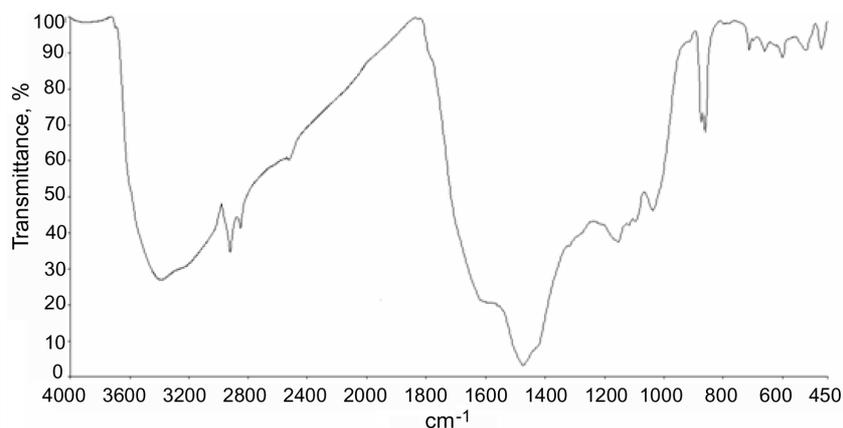


Fig. 2. FTIR spectrum of Ulukışla oil shale.

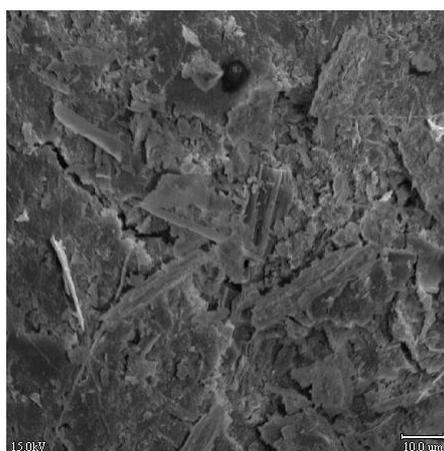


Fig. 3. SEM micrograph of Ulukışla oil shale (1000 X).

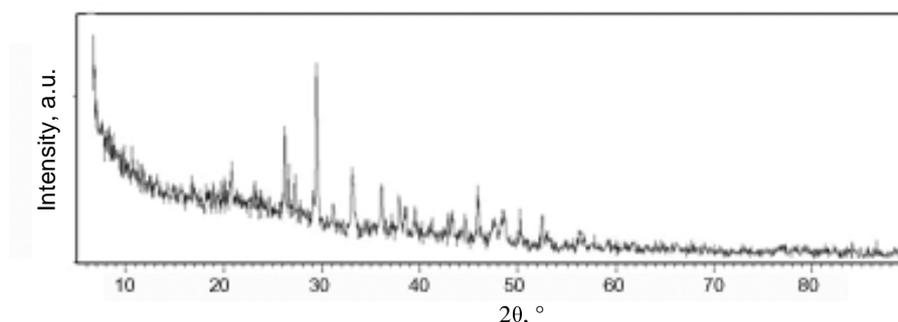


Fig. 4. XRD pattern of Ulukışla oil shale.

Pyrolysis

The TG-DTG graphs for pyrolysis of Ulukışla oil shale at six different heating rates are given in Fig. 5. Table 3 gives data obtained through interpretation of these graphs.

Pyrolysis of Ulukışla oil shale took place in three stages. The first stage up to 180 °C is characterized by the loss of moisture in the structure. The second stage which occurs in the temperature range of 180–600 °C results in breaking down of the organic matter. The last stage involves decomposition of the mineral matter containing carbonate, which takes place in the temperature range of 600–850 °C.

As the heating rate increased, so did the initial, maximum and final temperatures of each stage. Accordingly, there was also an increase in the maximum decomposition rate at each stage.

As increasing the heating rate affects the rate of heat transfer, it causes temperatures at which reactions occur to be reached in a shorter period of time, and the reaction to occur in a shorter time [9, 15, 16]. However, at

Table 3. Data for decomposition stages of pyrolysis at heating rates of 2, 5, 10, 15, 30 and 60 °C/min

Heating rate, °C/min	Step	T _{initial} , °C	T _{max} , °C	T _{final} , °C	Max decomposition rate, %/min
2	II	180	358	537	0.27
	III	616	668	692	0.43
5	II	183	396	545	0.47
	III	624	676	704	0.94
10	II	202	409	567	0.94
	III	662	716	747	2.04
15	II	222	419	579	1.38
	III	664	716	749	2.87
30	II	227	434	595	2.57
	III	680	747	804	5.27
60	II	232	437	600	5.50
	III	716	780	847	9.30

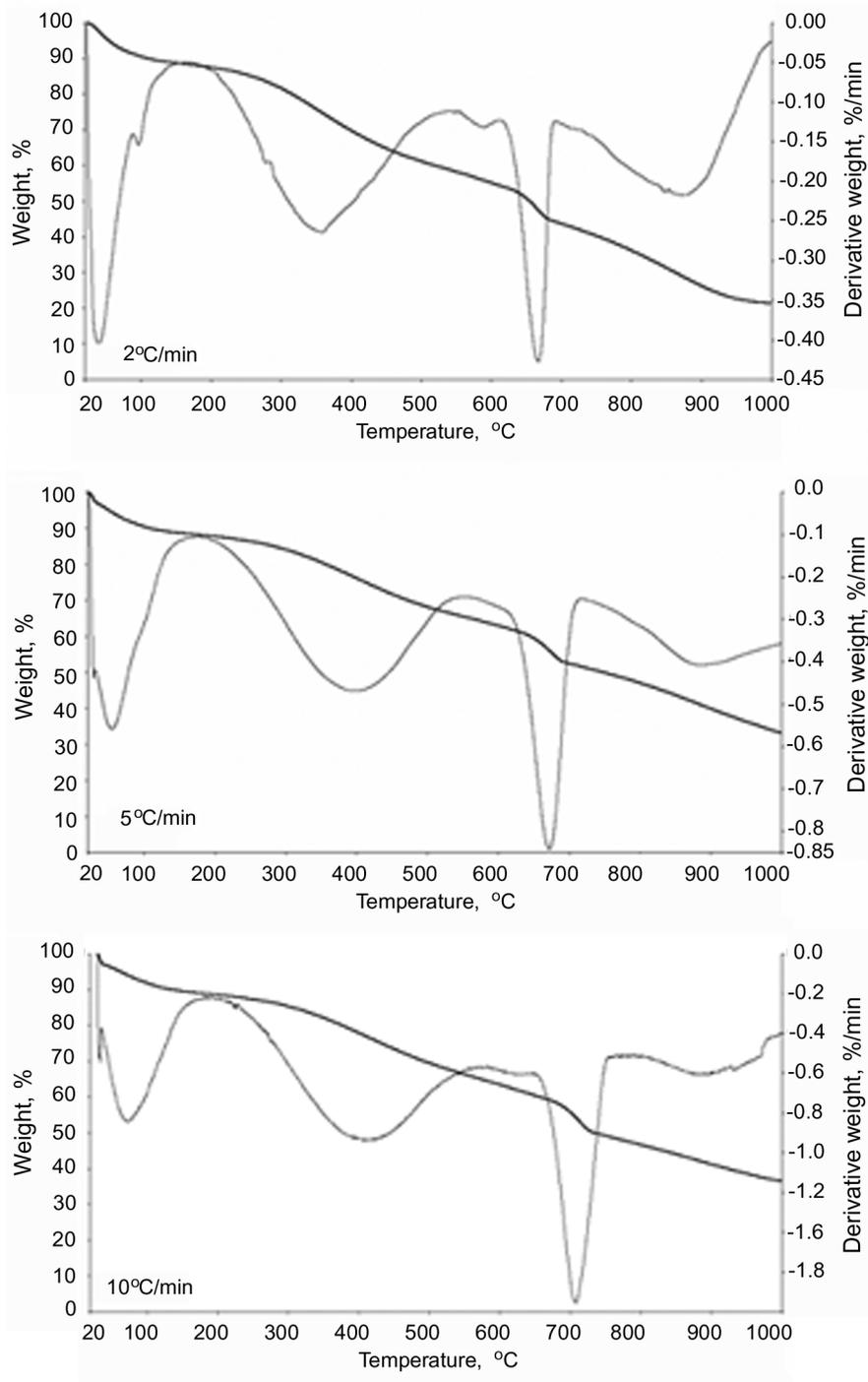


Fig. 5. TG-DTG curves for pyrolysis of Ulukışla oil shale.

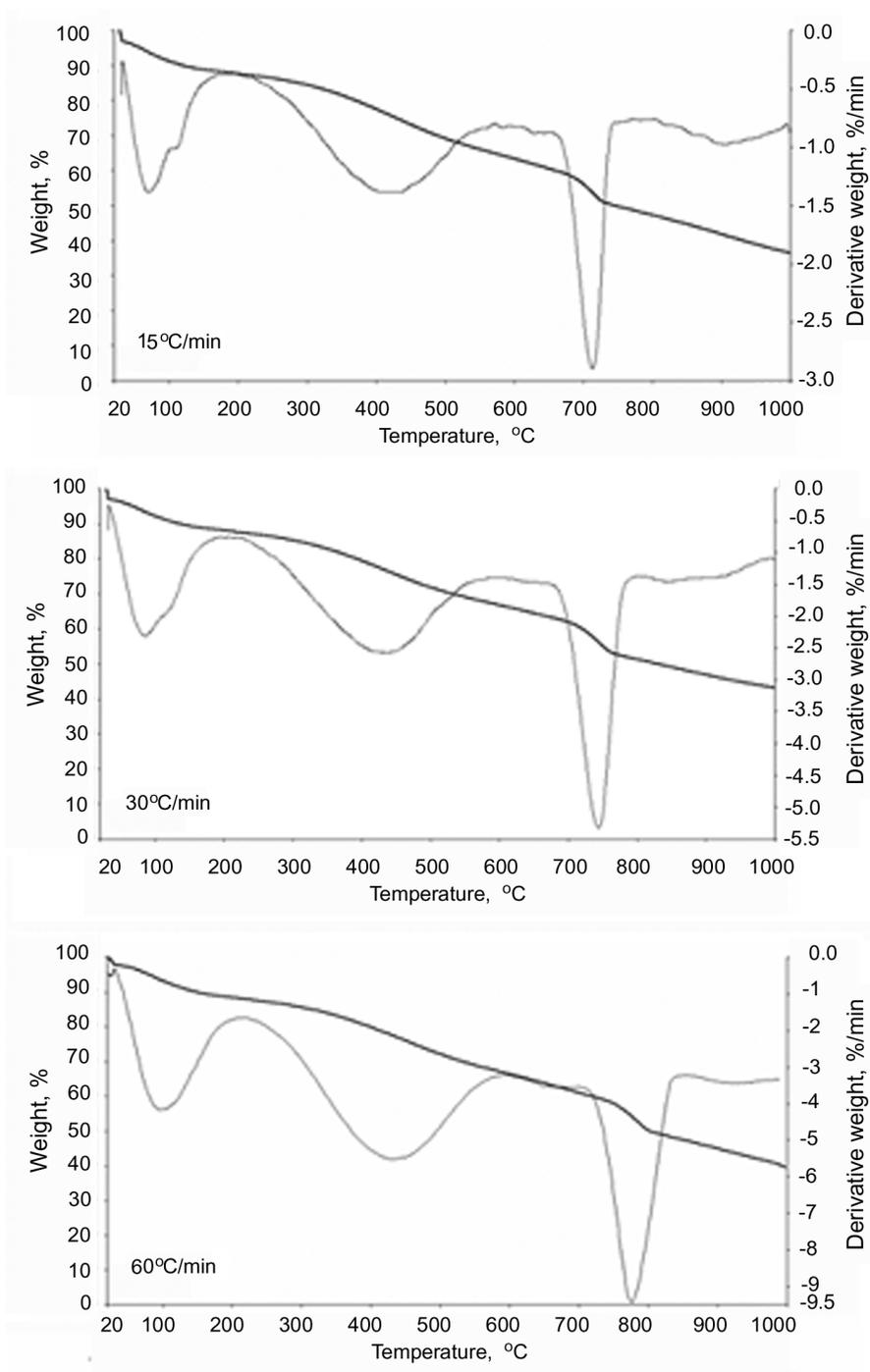


Fig. 5. Continued.

lower heating rates reactions take place gradually and heat transfer becomes more efficient, thus allowing even secondary reactions [6, 10].

Kinetics

Pyrolysis of Ulukışla oil shale occurred in three stages. However, as the first stage involved removal of moisture, it was overlooked in the kinetic study of this stage. Table 4 gives the kinetic parameters for the second and third stages of pyrolysis which were calculated using the Coats & Redfern kinetic model.

Heating rate has a negligible effect on reaction orders and activation energies.

As the heating rate was increased from 2 °C/min to 5 °C/min and from 5 °C/min to 10 °C/min, there was an increase in the activation energy values for the second stage. The heating rate did not have any effect above 15 °C/min.

When the heating rate was increased from 2 °C/min to 5 °C/min, from 5 °C/min to 10 °C/min and from 10 °C/min to 15 °C/min progressively, the activation energies of the third stage were found to increase. Above 15 °C/min the activation energy became independent of the heating rate.

The activation energies values for the second stage were established to be lower than those for the third stage.

It was found that heating rate did not have any effect on the reaction order.

Table 4. Kinetic parameters calculated based on the Coats & Redfern kinetic model

Heating rate, °C/min	Step	<i>n</i>	<i>E</i> , kJ/mol	<i>A</i> , l/min	<i>R</i> ²
2	II	1.69	120	4.63·10⁷	0.9678
	III	1.49	789	6.43·10 ⁴²	0.9867
5	II	1.66	192	1.10·10¹³	0.9669
	III	1.69	809	8.96·10 ⁴³	0.9700
10	II	1.73	198	3.35·10¹³	0.9665
	III	1.53	886	6.40·10 ⁴⁵	0.9979
15	II	1.50	92	7.58·10⁴	0.9764
	III	1.63	904	7.04·10 ⁴⁷	0.9987
30	II	1.45	84	1.05·10⁴	0.9929
	III	1.65	672	5.70·10 ³¹	0.9902
60	II	1.55	99	1.88·10⁵	0.9846
	III	1.59	723	7.81·10 ³²	0.9931

Conclusions

It has been established that pyrolysis of Ulukışla oil shale at six different heating rates occurs in three stages.

The activation energies and reaction orders calculated using the Coats & Redfern kinetic model have little relationship to heating rate. The activation energy values for the second stage were found to range between 84 kJ/mol and 198 kJ/mol and the reaction orders between 1.45 and 1.73. As for the third stage, the activation energy values and reaction orders were found to vary from 672 kJ/mol to 904 kJ/mol and from 1.49 to 1.69, respectively.

REFERENCES

1. United States Congress Office of Technology Assessment. An Assessment of Oil Shale Technologies. 1980. Vol. I, 517 pp.
2. Williams, P. T., Ahmad, N. Investigation of oil-shale pyrolysis processing conditions using thermogravimetric analysis // *Appl. Energy*. 2000. Vol. 66, No. 2. P. 113–133.
3. Bhargava, S., Awaja, F., Subasinghe, N. D. Characterisation of some Australian oil shale using thermal, X-ray and IR techniques // *Fuel*. 2005. Vol. 84, No. 6. P. 707–715.
4. Kök, M. V., Pamir, M. R. Comparative pyrolysis and combustion kinetics of oil shales // *J. Anal. Appl. Pyrol.* 2000. Vol. 55, No. 2. P. 185–194.
5. Li, S., Yue, C. Study of different kinetics models for oil shale pyrolysis // *Fuel Process. Technol.* 2003. Vol. 85, No. 1. P. 51–61.
6. Değirmenci, L., Durusoy, T. Effect of heating rate and particle size on the pyrolysis of Göynük oil shale // *Energy Sources*. 2005. Vol. 27, No. 9. P. 787–795.
7. Williams, P. T., Ahmad, N. Influence of process conditions on the pyrolysis Pakistani oil shales // *Fuel*. 1999. Vol. 78, No. 6. P. 653–662.
8. Jaber, J. O., Probert, S. D. Non-isothermal thermogravimetry and decomposition kinetics of two Jordanian oil shales under different processing conditions // *Fuel Process. Technol.* 2000. Vol. 63, No. 1. P. 57–70.
9. Torrente, M. C., Galan, M. A. Kinetics of the thermal decomposition of oil shale from Puertollano (Spain) // *Fuel*. 2001. Vol. 80, No. 3. P. 327–334.
10. Aboulkas, A., El Harfi, K. Study of the kinetics and mechanisms of thermal decomposition of Moroccan Tarfaya oil shale and its kerogen // *Oil Shale*. 2008. Vol. 25, No. 4. P. 426–443.
11. Kök, M. V. Oil shale resources in Turkey // *Oil Shale*. 2006. Vol. 23, No. 3. P. 209–210.
12. State Planning Organization (DPT), 2001. Energy, Eighth five-year development plan, Special impression commission report, Ankara [in Turkish].
13. <http://www.mta.gov.tr/madenler/turmaden/bitumluseyl.htm> [in Turkish].
14. Coats, A. W., Redfern, J. P. Kinetic parameters from thermogravimetric data // *Nature*. 1964. Vol. 201. P. 68–69.
15. Jaber, J. O., Probert, S. D. Pyrolysis and gasification kinetics of Jordanian oil-shales // *Appl. Energy*. 1999. Vol. 63, No. 4. P. 269–286.
16. Barkia, H., Belkbir, L., Jayaweera, S. A. A. Thermal analysis studies of oil shale residual carbon // *J. Therm. Analys. Cal.* 2004. Vol. 76, No. 2. P. 615–622.

Presented by J. Kann

Received March 19, 2009