

COMBUSTION KINETICS OF OIL SHALES BY REACTION CELL EXPERIMENTS

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In this study, kinetics parameters of combustion reaction of Seyitömer and Beypazarı oil shales were determined using Weijdema's model of reaction kinetics. The analysis of reaction kinetics experiments showed two different reaction regions at combustion of Beypazarı oil shale sample. Only one reaction region was observed at combustion of Seyitömer oil shale. CO₂/CO ratios increased gradually at low and medium temperatures and stabilized at high temperatures, especially after complete combustion. A decrease in the H/C ratio with the increasing temperature was observed. No relationship between activation energies of different oil shale types was observed.

Introduction

Oil shale can be defined as a sedimentary rock of ash content exceeding 33% and containing organic matter that yields oil when destructively distilled, but not in appreciable amounts when extracted with ordinary solvents. Organic matter content of an oil shale should be approximately 5.5 wt.%, just to provide the calorific requirements necessary to heat the rock to 500 °C in order to produce shale oil by thermal decomposition of organic matter. Thermal methods providing information about net results of mass loss and calculation of kinetic parameters are based on simplifying assumptions, which do not correspond to the complex of chemical reactions occurring at thermal degradation of oil shale. The study of combustion kinetics is essential for understanding the mechanisms and modeling of combustion process, which may lead to improved techniques for oil shale conversion, and the related kinetic parameters derived from thermal analysis data can also be used for oil shale characterization.

Weijdema [1] studied quantitative data concerning oxidation kinetics of oils in retained sands. He identified at least three successive stages of oxida-

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tion of hydrocarbon oil: at lower temperatures oxygen is taken up by oil molecules, at increased temperatures oxidative cracking occurs leaving a coke residue, and at still higher temperatures the coke is burnt. Dabbous and Fulton [2] studied the kinetics of low-temperature oxidation (LTO) of crude oils in porous media. Analysis of LTO kinetics data indicated that the order of the overall LTO reaction with respect to oxygen was between half and the first order. At temperatures below 500 °F (260 °C), most of the oxygen was utilized in hydrogen and hydrocarbon oxidation reactions rather than in carbon atom oxidation to carbon oxides. Fassihi *et al.* [3] found that combustion of crude oil in porous media proceeds according to several consecutive reactions analysing the produced gases emitted from a small packed reactor. They grouped the reactions into three categories, namely LTO reactions, middle-temperature reactions and high-temperature ones. They also found that distillation as well as clay content of shale profoundly affect reaction front temperature. Meyers *et al.* [4] presented the results of a laboratory study on low-temperature oxidation of four oils. LTO was shown to increase both oil viscosity and density. Moreover, LTO significantly increased the asphaltene content of the oxidized oils. Besides, the results of simulated distillation demonstrated that LTO did not significantly affect the volatility or carbon number distributions of either light or heavy oils. Abu-Khamisin *et al.* [5] observed that pyrolysis of crude oil in porous media went through three overlapping stages: distillation, visbreaking and coking. During distillation, the oil lost most of its light fraction and part of its medium-gravity fraction. During visbreaking, the oil mildly cracked into a slightly different product. At high temperatures, the oil remaining in the porous medium cracked into a semi-solid residue rich in carbon. Another important result was the ascertainment of catalytic effect of clay minerals on cracking reactions, especially on coking. Adegbesan [6] provided LTO reaction models that would be suitable for the use in numerical simulators of *in-situ* combustion for bitumen and heavy oil reservoirs. Two main types of reaction models were proposed: a non-steady-state kinetic model representing the overall rate of oxygen consumption, and four non-steady-state multi-response kinetic models representing oxidation reactions of the liquid-phase components. Greaves *et al.* [7] found that the addition of very finely ground clay mineral (kaolin) to the hot sand matrix contributed a catalytic effect to the carbon deposition reaction, but carbon combustion reaction was unaffected. Verkoczy and Jha [8] highlighted the importance of mineral matter present in the core, which has a profound effect on coke yield. Arrhenius parameters were dependent on the oil and rock composition of the core indicating that each system should be investigated to generate such data. When carrying out the TGA and DSC studies on Canadian heavy-oil cores, they found that the surface area seemed to be the most important factor contributing to the fuel lay-down mechanism. Pure quartz enhanced, while, on the other hand, mixed-layer clay tended to inhibit, coke formation. Fassihi *et al.* [9] presented results of a laboratory study on thermal alteration of two biodegraded crudes and one immature heavy oil over a

temperature range from 25 to 416 °C at reaction times up to 350 hours. The results indicated that up to a 1000-fold reduction of viscosity could occur. It was shown that the viscosity and density of the reacted oil could be predicted from the net change in the carbon number distribution determined by simulated distillation. Urban and Udell [10] stated the effects of steam on combustion of oil and sand. Oxidation of crude oil deposited on sand was studied, using catalysis by dissolved ionic compounds and reservoir sand materials, and considering changes in the reaction mechanism caused by the presence of steam. In the presence of steam, LTO exothermicity was similar to the dry case, but oxygen consumption was reduced, and unlike the dry case, all consumed oxygen appeared in the effluent carbon oxides. Shallcross *et al.* [11] performed experiments to study the effects of various additives on oxidation kinetics of Californian and Venezuelan oils. Aqueous solutions of ten metallic salts were mixed with sand and Huntington Beach (CA) oil. Iron and tin salts were found to enhance fuel formation, while copper, nickel and cadmium salts had no significant effects. Mamora and Brigham [12] studied the effect of LTO on the fuel and produced oil during *in-situ* combustion. Combustion tube experiments of 10.2° API crude oil were performed with three matrix types: sand, sand and clay, and sand and sand fines. LTO was observed in the run where the matrix consisted of sand only. High-temperature oxidation (HTO) was observed in runs where either clay or sand fines formed a part of the matrix. Ignition was not obtained in the LTO run, which had a reaction front temperature of only 350 °C compared to a combustion front temperature of 500 °C for the HTO runs. Moore *et al.* [13] explored combustion-oxidation behavior of Athabasca oil sands bitumen. They concluded that the key operating parameter controlling the transition from temperatures corresponding to an oxidation zone (maximum temperature below 355 °C) to those corresponding to a combustion zone (peak temperature over 550 °C) was the oxygen flux. At low oxygen fluxes, the negative temperature gradient region acts as a barrier to achieving the high-temperature combustion mode. Kok *et al.* [14–21] studied the factors influencing kinetic data, such as sample order geometry, heating rate and atmosphere, of oil shales under non-isothermal conditions. It was observed that the products obtained through pyrolysis and combustion depend on oil shale composition and conditional variables, such as temperature, time, and rate of heating, pressure, and gaseous environment.

Experimental

In this research, oil shale samples from Seyitömer and Beypazarı fields were used considering their high grades, reserves and exploitability. The oil shale samples (particle size <60 mesh) were prepared according to ASTM standards. Results of proximate and ultimate analysis [22] of the samples are given in Table 1a.

Table 1a. Proximate and ultimate analysis of studied oil shales

Oil shale	Calorific value, cal/g	H ₂ O, %	Ash, %	C, %	H, %	O, N, %	S, %
Seyitömer	1006	2.8	70.9	8.58	1.4	4.39	0.19
Beypazari	850	2.4	65.2	8.4	1.6	4.55	0.21

Table 1b. Fisher Assay results of oil shales from the two main oil shale reserves of Turkey [23]

Oil shale	Oil, wt.%	Gas, wt.%	Residue, wt.%
Seyitömer	2.41	1.51	88.67
Beypazari	39.16	9.02	41.87

The experimental set-up used in reaction kinetics studies consists of four basic parts: fluid injection system, reaction kinetics cell, gas analysis system, and automatic control and data recording system (Fig. 1). The fluid injection system is designed to inject air and nitrogen into the reaction kinetics cell. Its principle parts involve cylinders for high-pressure air or nitrogen, air filter, flow transducer, motorized control valve, pressure gauges and pressure transducers. The reaction kinetics cell is constructed from a stainless steel tube, and its dimensions are as follows: length 130.2 mm, outside diameter 34.2 mm and wall thickness 1.1 mm. An iron-constantan thermocouple is inserted into the reaction kinetics cell to measure the temperature at the center of the reaction cell. Another thermocouple is used to control and measure the temperature of the heater which is used to heat the cell according to a given temperature program. To analyze the composition of the produced gases emitted from the combustion tube, a gas chromatograph is used. Gas sampling ports are installed at different points of the combustion tube as the combustion front passes through these sections. Also, during reaction kinetics experiments, the amounts of CO₂, CO, and O₂ in the produced gas stream are measured by using a continuous gas analyzer. A non-isothermal temperature program was applied to the reaction kinetics cell at a constant heating rate in order to determine reaction rate data. During the experiments, the initial temperature of the reaction cell was set at around 20 °C after which the cell temperature was raised to 100 °C at a 5 °C/min heating rate and retained for 30 minutes at 100 °C in order to reach thermal equilibrium in the reaction cell. After thermal equilibrium had been achieved, the reaction kinetics cell temperature was increased at a constant heating rate (1 °C/min). After this point, throughout the heating of the reaction kinetics cell, air was injected into the cell at a constant rate. The air injection rate and pressure were also recorded throughout the runs (Table 2). The operational procedure was terminated when it was sure that there was no fuel left in the sample. To guarantee the consistency and repeatability, experiments were performed twice. Fischer Assay oil yields of the studied oil shales [23] are given in Table 1b.

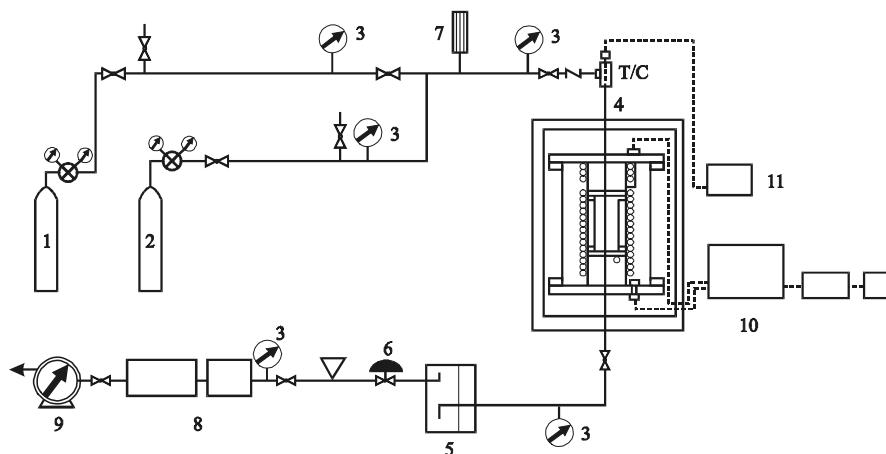


Fig. 1. Schematic diagram of the combustion reaction kinetics apparatus.

1 – high-pressure cylinder of air; 2 – high-pressure cylinder of nitrogen; 3 – pressure gauges; 4 – reaction kinetics cell; 5 – condenser; 6 – back pressure regulator; 7 – rotameter; 8 – continuous gas analyzer; 9 – wet test meter; 10 – temperature programmer control unit; 11 – digital read-out of temperature.

Table 2. Experimental conditions of reaction kinetics experiments

Oil shale	Pressure, psi	Partial pressure of O ₂ , psi	Air injection rate, l/min
Seyitömer-1	25	5.2	2.50
Seyitömer-2	50	10.4	2.50
Seyitömer-3	75	15.6	1.80
Beypazarı-1	25	5.2	1.50
Beypazarı-2	50	10.4	1.80
Beypazarı-3	75	15.6	1.80

Results and discussion

The reaction between fuel and oxygen in the combustion process is a heterogeneous reaction. For combustion to proceed, it is necessary for the injected oxidant gas to pass through the burning zone. The burning zone moves as the reacting fuel is removed from sand grains by oxidation. Within the burning zone, a number of known transport processes occur:: oxygen diffuses from the bulk gas stream to the fuel interface; oxygen is adsorbed and it reacts with the fuel; thereafter combustion products are desorbed and the products are finally transferred into the bulk stream.

Monitoring of the consumption of produced CO₂, CO, O₂, and of temperature as a function of time was an important part of the study. To achieve this goal, data on produced gases and temperature were continuously recorded. Two different peaks were established at different times in the case of Beypazarı oil shale sample (Fig. 2). The first slight peak is considered to

belong to the low-temperature oxidation while the second greater peak represents the fuel combustion period. Between the two peaks there is a zone of linearly increasing temperature. This zone is called fuel deposition region in which organic matter is coked and deposited as a fuel for the combustion process. However, Seyitömer oil shale shows only one peak, which corresponds to fuel combustion region, and no low-temperature zone exists (Fig. 3).

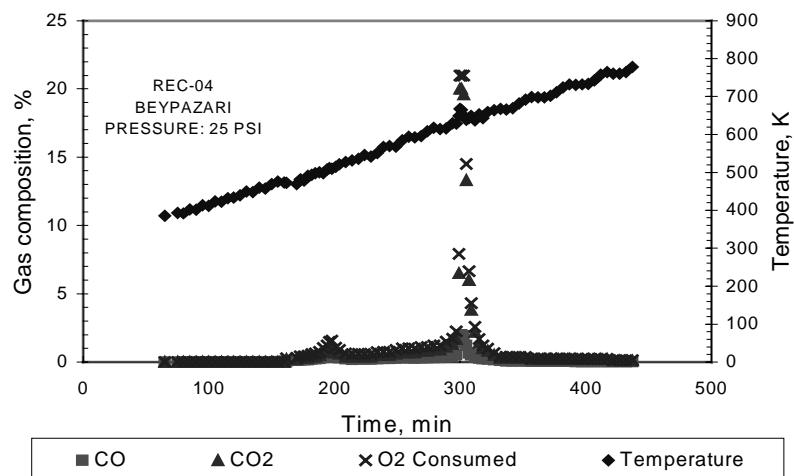


Fig. 2. Gas composition and temperature vs. time for Beypazarı oil shale.

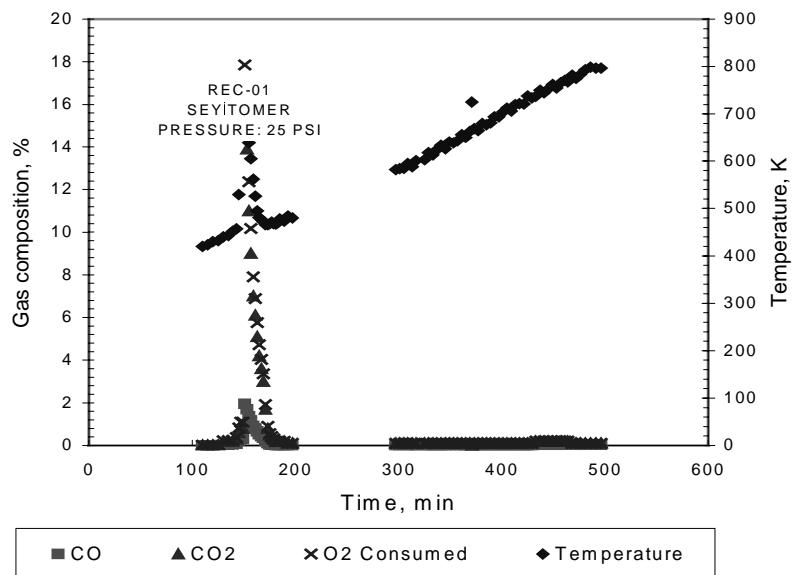


Fig. 3. Gas composition and temperature vs. time for Seyitömer oil shale.

Consumed oxygen can be calculated as the difference between the amount of oxygen in the injected air and that of the unreacted oxygen in the exhaust gases [1–3]. Moreover, although the air injection rate was kept constant, there have been variations in exhaust gas production. At high temperatures, the amount of consumed O₂ is comparable with the amount of produced CO₂ and CO. However, in low-temperature regions, the amount of consumed oxygen exceeds that of produced CO₂ and CO.

When oxygen reacts with organic matter in oil shale, CO₂ and CO are released as gaseous products. When the temperature increases, there is also an increase in the CO₂/CO ratio. This phenomenon indicates the conversion of CO into CO₂. At higher temperatures the CO₂/CO values have a tendency to stabilize. This stabilization means that formation of carbon oxides becomes stable. Molar CO₂/CO values have a tendency to stabilize at low and moderate temperatures. Molar CO₂/CO values for each experiment were calculated by taking arithmetic means of the values after the stabilization of formation of carbon oxides (Table 3).

Atomic H/C ratio of the fuel consumed was calculated from the analysis of produced gases for each combustion experiment as a function of temperature. Figures 4 and 5 illustrate the semi-log relationship between temperature and atomic H/C ratio for each run. One important assumption for calculations was that all the oxygen not observed in the emitted gas had reacted to form water. The relationship between produced gases and H/C ratio was defined as [3]

$$(H/C) = 4 [(W_i/V_i) V_o - CO_2 - 1/2 CO - W_o] / (CO_2 + CO), \quad (1)$$

where

W_i = concentration of injected oxygen, mole %

W_o = concentration of produced oxygen, mole %

V_i = concentration of injected nitrogen, mole %

V_o = concentration of produced nitrogen, mole %

After plotting the data as a function of temperature, a negative trend line was obtained for each run. Each trend line followed the relationship [1–3]:

$$\ln (H/C) = a + bT, \quad (2)$$

where *a* and *b* are constants for this correlation (Table 4).

Table 3. Molar CO₂/CO ratios

Oil shale	Molar CO ₂ /CO ratios
Seyitömer, 25 psi	8.9
Seyitömer, 50 psi	17.5
Seyitömer, 75 psi	8.8
Beypazarı, 25 psi	3.3
Beypazarı, 50 psi	11.3
Beypazarı, 75 psi	6.1

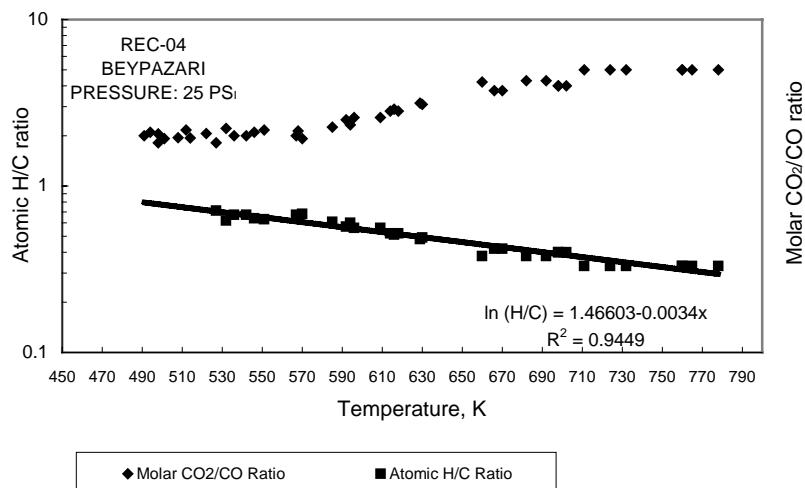


Fig. 4. Atomic H/C ratio and molar CO₂/CO ratio vs. temperature for Beypazari oil shale.

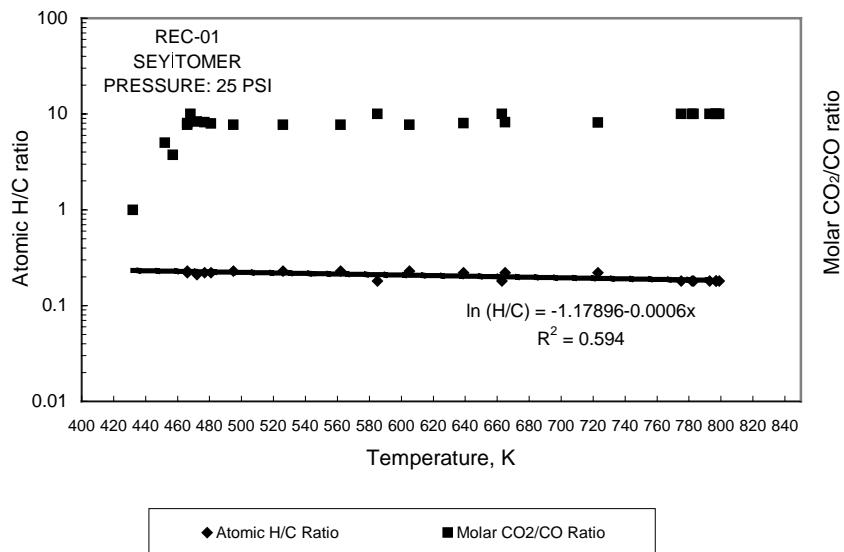


Fig. 5. Atomic H/C ratio and molar CO₂/CO ratio vs. temperature for Seyitömer oil shale.

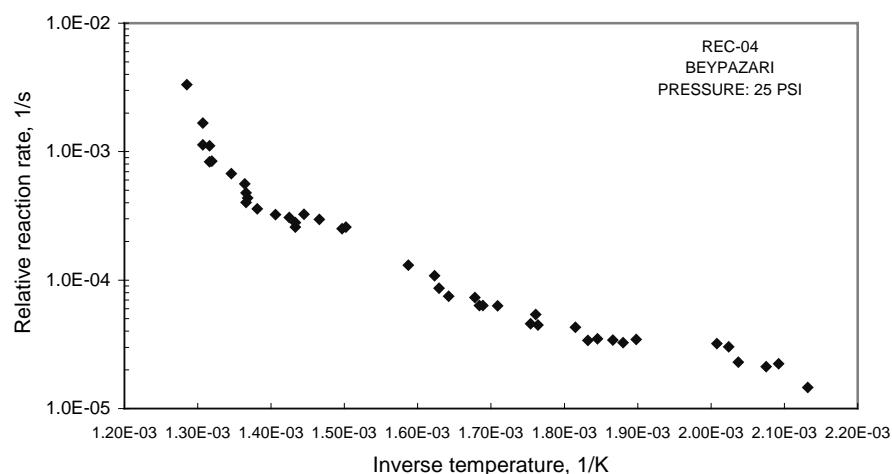
Table 4. Correlation constants, $\ln(H/C) = a + bT$

Oil shale	<i>a</i>	<i>b</i>
Seyitömer, 25 psi	-1.17896	-0.0006
Seyitömer, 50 psi	-1.65078	-0.0008
Seyitömer, 75 psi	-0.64493	-0.0014
Beypazari, 25 psi	1.46603	-0.0034
Beypazari, 50 psi	0.59922	-0.0022
Beypazari, 75 psi	3.14953	-0.0070

Weijdema [1] proposed the kinetic model, and Fassihi *et al.* [3] modified the model for the use of non-isothermal runs. Figures 6 and 7 show the semi-log plot of inverse temperature against relative reaction rate for each experiment. Relative reaction rate values were calculated by graphical integration of the area under the oxygen consumption curve, $y = f(t)$. It was hard to separate the fuel deposition peak from the fuel combustion peak, and no low-temperature oxidation region was distinctive in performed runs. A straight line was obtained for each data set. Activation energies were calculated from the slopes and tabulated (Table 5).

Table 5. Activation energy values, kJ/mol

Oil shale	Activation energy
Seyitömer, 25 psi	16.3
Seyitömer, 50 psi	13.5
Seyitömer, 75 psi	22.6
Beypazari, 25 psi	35.2
Beypazari, 50 psi	32.5
Beypazari, 75 psi	32.9

**Fig. 6. Relative reaction rate vs. inverse temperature for Beypazari oil shale.**

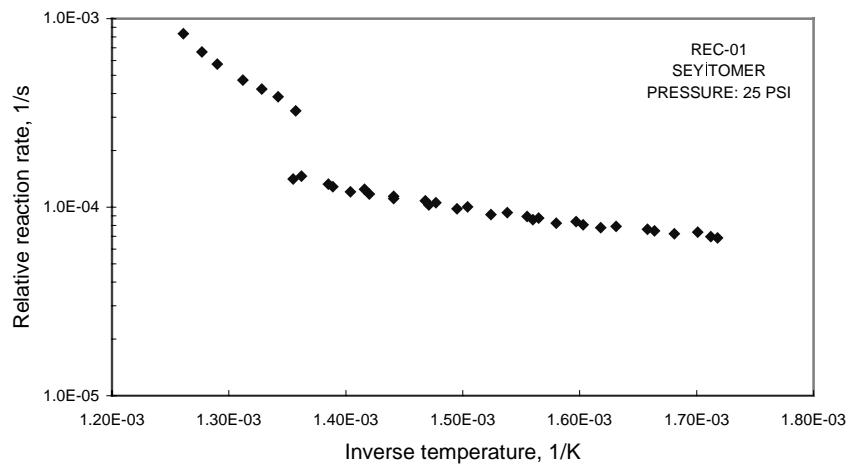


Fig. 7. Relative reaction rate vs. inverse temperature for Seyitömer oil shale.

Conclusions

As a result of experiments on combustion reaction kinetics of oil shale samples the following conclusions were drawn:

- Time versus gas compositions graph shows two different peaks for the Beypazarı oil shale sample. The first peak, which is small is concluded to be the low-temperature oxidation peak, whereas the second, greater one, is the fuel combustion peak. Between these two peaks there exists a region of linearly increasing temperature, which is called fuel deposition zone. Only one peak – fuel combustion peak – is observed in the case of Seyitömer oil shale.
- Molar CO_2/CO ratios increasing gradually at low and medium temperatures stabilize at high temperatures, especially after complete combustion. This phenomenon is explained as stabilization of conversion of CO into CO_2 .
- All experiments showed a decrease in H/C ratio with increasing temperature. The following relationship was established for all runs: $\ln(\text{H/C}) = a + bT$.
- Activation energies for each run were determined. No correlation between activation energies of combustion of different oil shales was observed.

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