THERMAL BEHAVIOR OF RAW OIL SHALE AND ITS COMPONENTS

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Abstract. *In this study, the thermal behavior of dawsonite, nahcolite, quartz, dolomite, albite, illite, analcime, kerogen and raw oil shale samples is discussed. Thermal Gravimetric Analysis (TGA), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Differential Scanning Calorimetry (DSC) were used to study the thermal properties of the samples. The DSC dynamic experiments were performed in CO_2 and N_2 atmospheres. The influence of purge gases on the thermal decomposition of kerogen, dawsonite and nahcolite was investigated. In the DSC experiments, the heating rate did not change the decomposition mechanism of both dawsonite and nahcolite and the Tp (the sample temperature at which the maximum deflection in the DSC curve is recorded) of dawsonite and nahcolite could be moved to higher temperatures by purging CO_2.*

Keywords: oil shale, TGA, DSC, Tp, ATR-FTIR.

1. Introduction

Energy production is a current global concern as almost all industries depend on different sources of energy in order to operate. New techniques for efficient energy source utilization, the evaluation of potential alternatives, and the exploration of new energy deposits are among the points that must be considered so as to develop an energy policy that can help meet current and future expectations. Hence, hydrocarbon based energy sources such as oil shales are subjected to utilization and concrete investigation. Oil shale is a compact sedimentary rock containing organic matter that yields oil when destructively distilled but not when extracted with ordinary solvents. Therefore pyrolysis is the most convenient method to extract hydrocarbon fuel, such as bitumen, from oil shale [1]. Oil shale contains organic matter mainly as kerogen and slightly as bitumen. Literature reports variable temperature ranges for bitumen formation from kerogen. For example, bitumen formation

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starts at temperatures as low as 200 °C and as high as 400 °C [2]. A variety of thermal reactions, such as emission of gases and water, conversion of kerogen to bitumen, alteration of bitumen, and dissociation of bitumen to oil and gases, have been identified within the above temperature ranges [2]. Hence, studying the thermophysical properties of oil shale and its components is crucial for the efficient process design.

Oil shale is found in many places worldwide. For example, the US has the largest oil shale resources in the world and the estimated amount is 3340 billion tons [3]. If we can extract these vast hydrocarbon deposits, without a doubt future energy crisis will be alleviated, and by far, thermal extraction methods are the most common method to extract hydrocarbon from the oil shale matrix [4]. However, different types of extraction techniques such as ultrasonic and solvent extraction methods can also be seen in the literature [5, 6].

Oil shale formation is known to contain several types of carbonate minerals such as dawsonite and nahcolite. These host minerals in the oil shale matrix significantly complicate the pyrolysis process [2]. The pyrolysis process of kerogen is more complex since the thermal decomposition ranges of several host minerals, such as dawsonite, interfere with the decomposition process of kerogen. Though the molar heat capacity of kerogen is higher than that of dawsonite, a fraction of the supplied energy needed to pyrolyze the system is consumed by dawsonite [7, 8].

The purpose of the present study is twofold: (a) to investigate the thermal decomposition of oil shale host minerals and kerogen and (b) to examine how the partial pressure of CO_2 influences the T_p of dawsonite and nahcolite. DSC and differential thermal analysis (DTA), and TGA are useful thermoanalytical tools which can be used to investigate the thermal behavior of oil shale and its components.

2. Experimental

Mettler-Toledo TGA and PerkinElmer power compensated Diamond DSC were used to study the thermal decomposition of minerals, kerogen and raw oil shale samples. Nitrogen and carbon dioxide were used as purge gases. Purge gas flow rate in the DSC was maintained at 20 ml/min. Both the experimental sample (which contains a non-hermetic pan with the sample of interest) and the reference sample (which contains only a non-hermetic pan) were maintained at the same temperature in the DSC and the difference in the thermal power required to maintain them at the same temperature was measured and plotted as a function of temperature or time. The TGA has the capability of measuring the mass loss either as a function of time or temperature in a varied but controlled atmosphere. The TGA system was calibrated for temperature readings with calcium oxalate monohydrate and

the TGA balance was calibrated with silver in order to overcome the buoyancy effect. N_2 was used as the purge gas for TGA experiments.

A PerkinElmer spectrum 100 ATR-FTIR spectrometer was used for FTIR analysis. The sampling station was equipped with an overhead ATR accessory. The ATR diamond crystal was carefully cleaned with pure *iso*-propanol between measurements. A few milligrams of each sample were carefully placed on the diamond crystal surface and the spectra were recorded as absorbance. The spectra were scanned between 4000 and 650 cm^{-1} at a resolution of 4 cm^{-1}.

Finely ground (approx. 50 μm) dawsonite, nahcolite, quartz, dolomite, albite, illite, analcime, pyrite and kerogen were used to make samples. Quartz, albite and dolomite were not incorporated to prepare samples for the TGA and DSC experiments because the decomposition temperatures of these three minerals are out of our scan range. Synthetic dawsonite, raw oil shale and kerogen were supplied by Shell Company, illite was obtained from Wards Natural Science Inc., and the rest of the minerals were obtained from Alfa Aesar. Sample size was 10 mg for each experiment. Research purity (99.999%) CO_2 and ultra-high purity (99.000%) N_2 were used as purge gases.

3. Results and discussion

Thermal analysis of oil shale samples is a complex multistage process because oil shale contains a mixture of inorganic (mineral) and organic (kerogen) components. All these minerals and kerogens thermally decompose into different chemical species at different temperatures. The TGA experiments were done under nitrogen environment with a 5 °C/min heating rate and a 20 ml/min purge gas flow rate to study the thermal stability of samples. The initial small weight loss up to 150 °C in Figures 1a and 1b can be assigned to the loss of free water or lightweight impurities in the sample. Weight loss above 150 °C in Figure 1b can be assigned to softening and molecular rearrangement due to the release of gases in kerogen prior to its decomposition to bitumen [9]. Nahcolite shows a significant weight loss of about 35% within a 50–160 °C temperature range (Fig. 1a) leading to Na_2CO_3, H_2O and CO_2, and the resultant Na_2CO_3 is very stable at any temperature above 160 °C. Dawsonite shows a 20% weight loss within a 250–360 °C range. The decomposition of dawsonite can be represented by the following chemical reaction [10]:

$$2NaAl(OH)_2CO_3 \longrightarrow Na_2CO_3 + Al_2O_3 + 2H_2O + CO_2. \qquad (1)$$

The ATR-FTIR spectra of dawsonite were recorded before and after the DSC experiments (Fig. 2). The sharp band that is seen around 3260 cm^{-1} before decomposition represents the –OH stretching in the original dawsonite sample. This band disappeared after decomposition due to thermal

decomposition and a broad band appeared at the same wave number. This new broad band represents the free water, –OH, according to Equation 1.
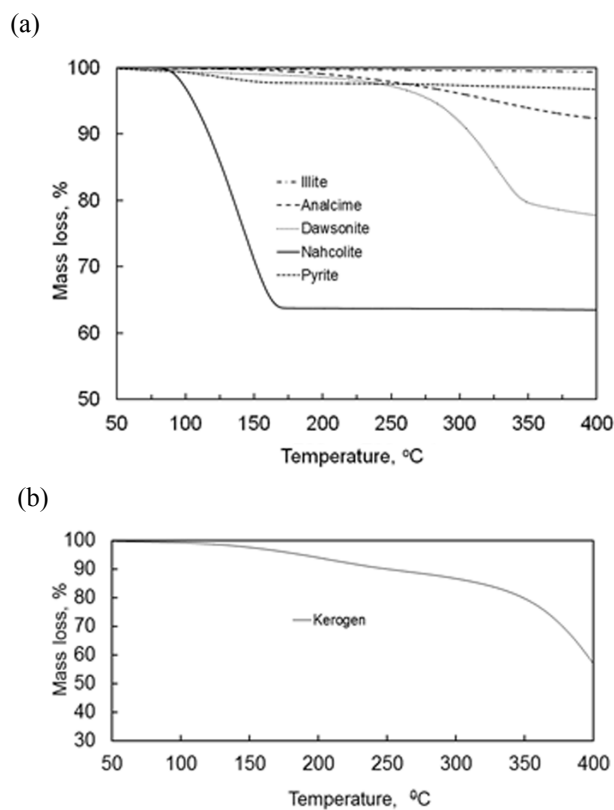
(a)

(b)

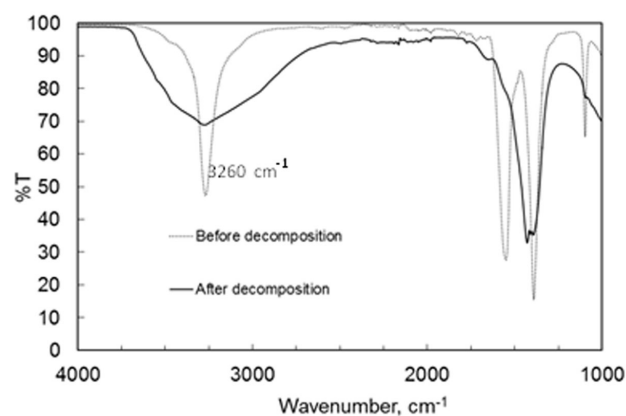Fig. 1. TGA graphs of (a) minerals present in oil shale, (b) kerogen.
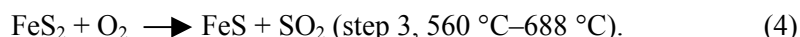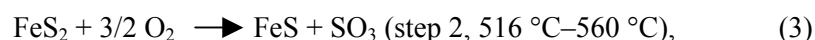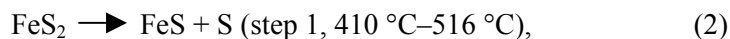

Fig. 2. ATR-FTIR spectra of dawsonite before and after the pyrolysis process.

Pyrite undergoes step-wise thermal decomposition in TGA analysis under nitrogen environment (Fig 1a). Pelovski and Petkova [11] have reported the three-step thermal decomposition in pyrite as seen below:

$$FeS_2 \longrightarrow FeS + S \text{ (step 1, 410 °C–516 °C),} \qquad (2)$$

$$FeS_2 + 3/2 \; O_2 \longrightarrow FeS + SO_3 \text{ (step 2, 516 °C–560 °C),} \qquad (3)$$

$$FeS_2 + O_2 \longrightarrow FeS + SO_2 \text{ (step 3, 560 °C–688 °C).} \qquad (4)$$

We cannot observe two distinct weight losses due to step 2 and step 3 in Figure 1a because our experimental environment is free from O_2.

Analcime clearly shows a small weight loss below 400 °C, which can be assigned to the loss of bound water. Contrastingly, illite is very stable throughout the same temperature range.

CO_2 is the only gaseous product generated by the decomposition of both dawsonite and nahcolite. Strikingly, the endothermic peak position, or point of complete decomposition, of dawsonite and nahcolite was only slightly influenced by the heating rate while under CO_2 environment whereas the heating rate had a significant influence on the endothermic peak position in the N_2 environment (Fig. 3). Kok observed a similar peak displacement under normal air in his Seyitomer oil shale sample [12]. Thermal decomposition is a kinetic event and a function of both time and temperature. The decomposition temperature shifts to a higher temperature with increasing heating rate because the decomposition of the sample is not completed at any specific temperature.

The hump near 300 ºC in Figure 3a and near 350 ºC in Figure 3b can be assigned to the dehydroxylation of gibbsite (γ-Al(OH)$_3$) present in the dawsonite sample [2, 13]. Dawsonite equilibrates with gibbsite according to the equation:

$$NaAl(OH)_2CO_3 + H_2O \longrightarrow Al(OH)_3 + Na^+ + HCO_3^-. \qquad (5)$$

The peak shapes in Figure 3 do not change with the heating rate and this behavior implies that the decomposition mechanism of dawsonite does not change with the given heating rates [14].

Figure 4 shows the influence of partial pressure of CO_2 on the decomposition of dawsonite and nahcolite at a fixed heating rate of 10 ºC/min. It is important to emphasize that the T_p of dawsonite increases with the partial pressure of CO_2. Under complete N_2 environment the T_p of dawsonite is 360 °C but it increases to 381 °C under complete CO_2 environment. The sensitivity of dawsonite T_p to CO_2 partial pressure appears to decrease as the molar fraction of CO_2 increases. However, this trend is not obvious for nahcolite. The influence of CO_2 on the T_p has been reported in the literature for several carbonates [15] but according to our knowledge no one has reported similar observations for dawsonite and nahcolite.
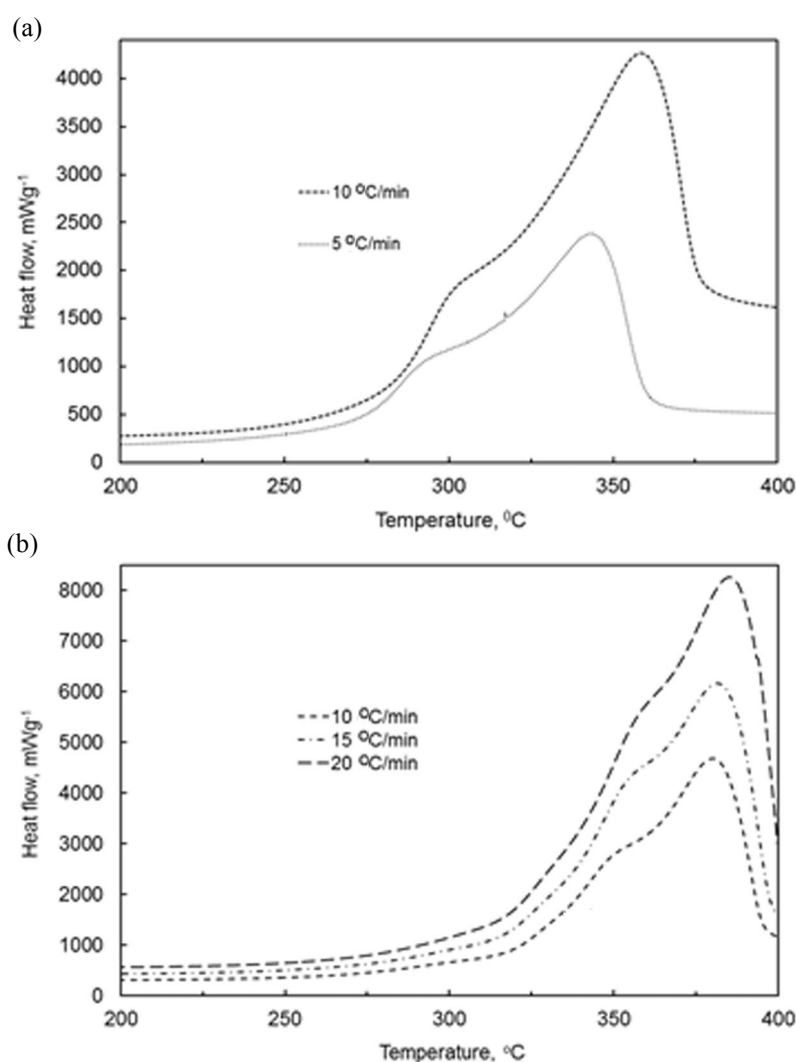
(a)

(b)

Fig. 3. Thermal decomposition of dawsonite under (a) N_2 and (b) CO_2.

Both dawsonite and nahcolite are members of the carbonate family. This peak movement can be explained by considering the reversible nature of carbonate decomposition [16]:

$$MCO_3(s) \iff MO(s) + CO_2(g), \qquad (6)$$

where M symbolizes metal.

Since carbonate decomposition generates CO_2 as a product, addition of CO_2 into the reaction environment will force the reverse reaction. According to Le Chatelier's principle, if a chemical system experiences a change in partial pressure, then the reaction shifts to counteract the imposed change
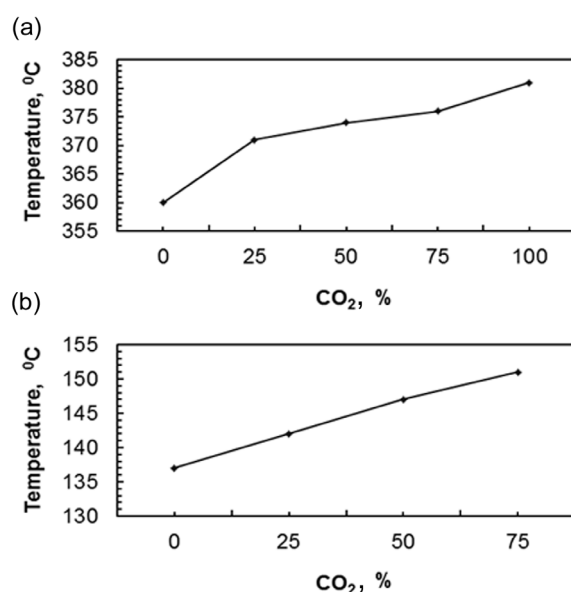
(a)

(b)

Fig. 4. Peak position (Tp) changes on DSC spectra of (a) dawsonite and (b) nahcolite with different CO_2/N_2 gas mixtures (10 °C/min).

and a new equilibrium is established [17]. Hence, the reaction needs more energy to complete thermal decomposition and this phenomenon leads the peak maximum to a higher temperature with higher CO_2 partial pressure.

Kerogen also generates CO_2 by oxidation in the pyrolysis process if O_2 is present in the environment. Since the reaction environment is oxygen-free, the pyrolysis of kerogen does not contribute to generate CO_2. So introduction of CO_2 does not have any influence on the decomposition of kerogen (Fig. 5). The Tp of dawsonite moves toward the high temperature direction of the decomposition window of kerogen by increasing the partial pressure of CO_2 (Fig. 4a).

To investigate the combinatorial effect of the thermal decomposition of minerals and kerogen, raw oil shale samples were studied under N_2 environment. The Table shows the composition of raw oil shale samples. With regard to the ranges of kerogen and mineral contents, our sample analyses show 0–50% kerogen, while mineral contents from XRD (after normalized without kerogen) show the ranges as listed below.

Figure 6 shows the ATR-FTIR spectra of three different raw oil shale samples. All spectra except that of raw oil shale sample #2 show the band around 3226 cm^{-1} and this indicates the presence of dawsonite. The band around 1080 cm^{-1} represents the Si–O stretching band of quartz and the C–O stretching band of carbonate appeared at 1450 cm^{-1} (Fig. 6) [18]. Two small bands near 2929 cm^{-1} indicate that the samples have mainly Type I kerogen which has a high atomic hydrogen–to–carbon (H/C) ratio (ab 1.5) and low atomic oxygen–to–carbon (O/C) ratio (< 0.1) [19].
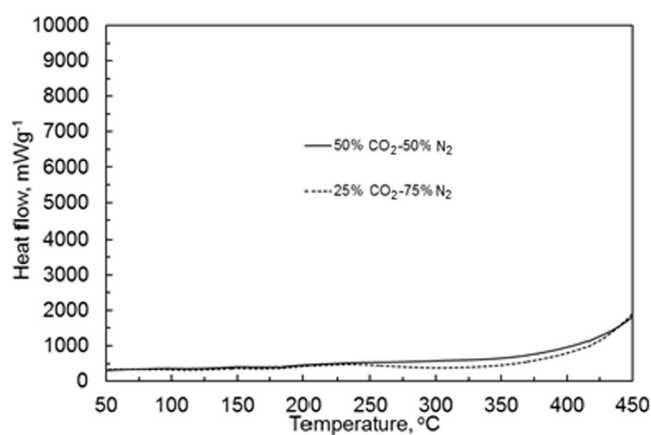
Fig. 5. DSC curves of decomposition of kerogen with different CO_2/N_2 mixtures (10 ºC/min^{-1}).

Table. Mineral composition of raw oil shale samples

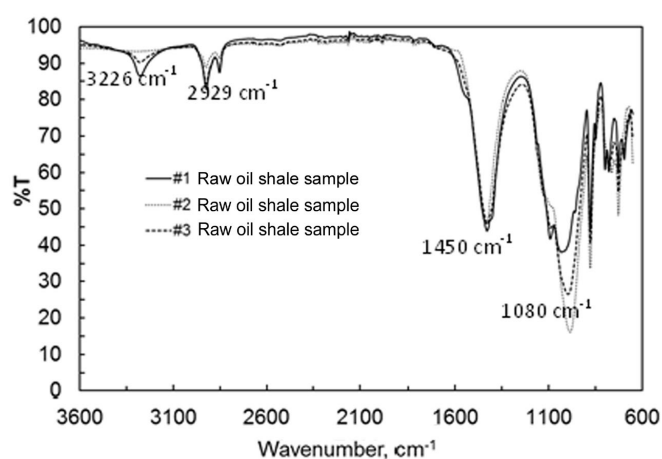| Mineral	Min, wt%	Max, wt%
Illite (K,H$_3$O)	0	14
Calcite (CaCO$_3$)	0	29
Aragonite (CaCO$_3$)	0	21
Dolomite (CaMg·(CO$_3$)$_2$)	2	44
Pyrite (FeS$_2$)	0	16
Analcime (NaAlSi$_2$O$_6$·H$_2$O)	0	33
K-Feldspar (KAlSi$_3$O$_8$)	1	20
Albite (NaAlSi$_3$O$_8$)	0	43
Quartz (SiO$_2$)	2	51
Dawsonite (NaAlCO$_3$(OH)$_2$)	0	15
Nahcolite (NaHCO$_3$)	0	94

Fig. 6. ATR-FTIR spectra of raw oil shale samples.

Within the analysis, we can observe that the above three raw oil shale samples have more than one transition zone and that these zones represent different reactions. Oil shale samples show weight reduction in the drying temperature range (ambient to 250 °C) due to the loss of surface water and interlayer water from clay minerals [9]. We did not observe any thermal transition in the 350–450 °C region for raw oil shale sample #2 in Figures 7a and 7b. This observation indicates that sample #2 does not contain dawsonite. According to Figure 1 dawsonite shows a 20% weight loss but we cannot observe quantitatively a similar weight loss due to dawsonite in raw oil shale samples #1 and #2 because of the influence of other minerals in the sample matrix [9]. Raw oil shale sample #3 in Figure 7b shows a spike around 160 ºC, which is an indication of the presence of nahcolite in the sample. The TGA curves in Figure 7a show a continuous weight reduction in the range of 100–400 °C. Though pure kerogen shows a 70% weight
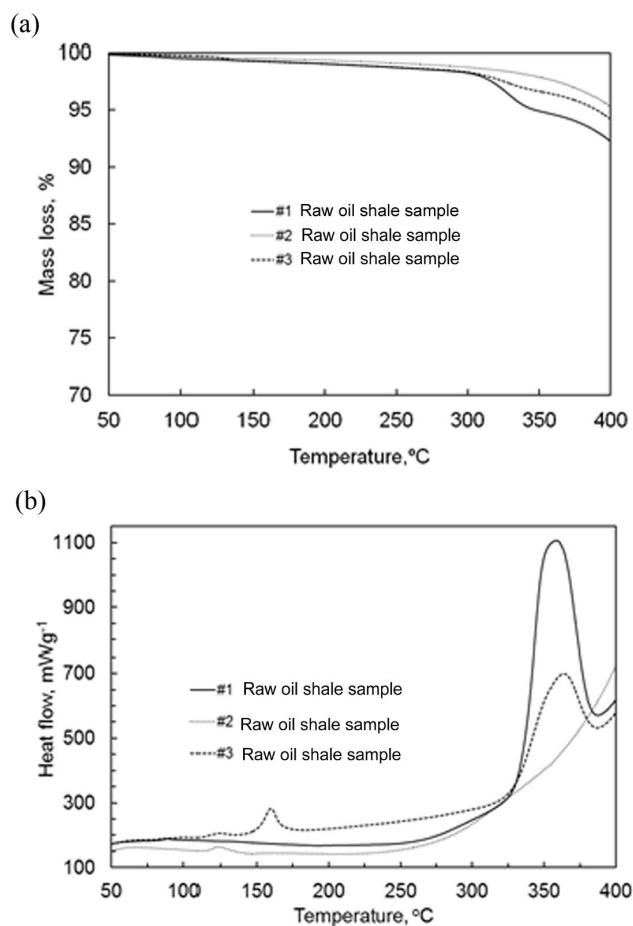
(a)

(b)

Fig. 7. (a) TGA and (b) DSC thermograms of different raw oil shale samples (10 °Cmin^{-1} / N$_2$).

reduction (Fig. 1b) by 450 ºC, we cannot see such a weight reduction for raw oil shale sample because of the influence of host material in the pyrolysis matrix [9, 20].

Figure 8 clearly shows that the Tp of dawsonite and nahcolite has moved from 359 ºC to 381 ºC and from 158 ºC to 161 ºC, respectively, by increasing the partial pressure of CO_2 from 0% to 100%.
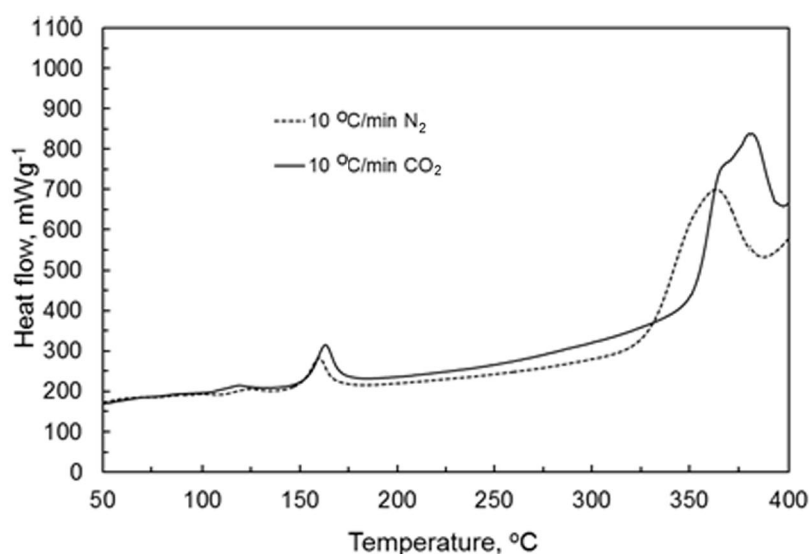

Fig. 8. DSC curves of decomposition of raw oil shale sample #3 under 100% CO_2 and 100% N_2 (10° Cmin^{-1}).

4. Conclusions

A systematic study of the thermal decomposition of minerals, kerogen, and raw oil shale samples was carried out in this work. TGA data shows that all minerals except dawsonite and nahcolite are thermally stable under the scan range. Kerogen is considerably pyrolysed within 200–400 °C. The kerogens contained in the raw oil shale samples studied were of Type I. It was found that the heating rate does not change the decomposition mechanism of dawsonite and nahcolite; however, the Tp of dawsonite and nahcolite can be increased through the introduction of a CO_2 environment. The Tp of dawsonite is less sensitive to the higher partial pressure of CO_2 and the decomposition of kerogen is not influenced by the gaseous environment. Based on our experimental observations we can conclude that oil shale can be pyrolized without substantial interference from dawsonite if the maximum pyrolysis temperature is below 350 °C under a CO_2 environment.

Acknowledgments

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