RESEARCH PAPER

Thermochemical investigation of the oil shale from the Early Cretaceous Garau Formation, Lorestan, SW Iran: Preliminary TGA-FTIR results

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Abstract
The oil shale is a prodigious immature kerogen-rich resource, which represent an outstanding potential of oil generation through thermochemical processing at ~350-530°C depending on kerogen peculiarities. Kinetic investigation is one of the fundamental approaches for quantifying and evaluation of this process. The main aim of this study is thermal and kinetic investigation on the Garau oil shale (Early Cretaceous) from Lorestan province of Iran using TGA-DTG analysis (Thermogravimetry Analysis; TGA and Differential Thermogravimetry Analysis; DTG) under three constant 5, 10, 15 °C/min heating rate from 20°C up to 900 °C. The FTIR (Fourier transform infrared spectroscopy) analysis was used to evaluate the evolved gases during thermochemical decomposition of the Garau oil shale. The results show the combustion process of the representative sample from the Garau oil shale involves two main peaks of mass loss, which reveal two main reaction regions. The first reaction region is originated from organic matter (bitumen & kerogen) decomposition and the second reaction region is occurred as the result of calcite thermal breaking down. According to the average activation energy calculated for the organic matter decomposition (~183 kJ/mol), the Garau oil shale corresponds to medium-fast reaction rate kerogens, in consistent with IIS-kerogen reaction rate (144-218 KJ/mol).

Keywords: TGA-FTIR analysis, Kinetic, Oil Shale, Garau Formation, Lorestan, Iran.

Introduction

Oil shale is an immature unconventional oil reservoir and nonrenewable source of energy that represents a huge potential to answer the growing up demand of energy. They often have noticeable solid organic matter (kerogen) content, which has not been subjected and buried to be matured completely to generate conventional petroleum (even oil and/or gas). The only applied method for oil extraction from oil shale is destructive distillation which also known as retorting.

Destructive distillation is a type of thermochemical process that the oil shale raw materials decompose to the lighter hydrocarbons in the vicinity of high thermal flux at high temperature. During the process, following the earlier substances vaporization and/or sublimation, the reaction products are generated. The earlier substances are connate water (moisture), water from dehydration of mineral crystals, minerals dissociation products and products of decrystallization. The hydrocarbon petroleum-like products in addition to volatile gas and residues are generated after exposing the resources to enough heat energy. The whole of these processes can be advanced in-situ or in external retort. Thermogravimetry Analysis (TGA) and

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Differential Thermogravimetry Analysis (DTG) are common tools in order to investigate the characteristics of devolatalization and kinetics of solid materials by accurate measuring of mass change of the samples, which have subjected to temperature program. There are numbers of studies and applications in the investigation of oil shale samples from different resources in the world. TG-DTG analysis is performed to obtain kinetic parameters and analysis of reaction models (Skala et al., 1987; Warne & Dubrawski, 1989; Finucane et al., 1977; Rajeshwar & DuBow, 1982; Burnham et al., 1983; Kök & Pamir, 1995; Williams & Ahmad, 2000; Kök et al., 2001; Johannes & Zaidentsal, 2008; Tiwari & Deo, 2012), devolatalization characteristics (Skala et al., 1987; Campbell et al., 1980; Campbell et al., 1980; Rajeshwar, 1981), effect of heating rate and final process temperature (Rajeshwar, 1981; Williams & Ahmad, 2000; Johannes & Zaidentsal, 2008; Rasouli et al., 2014), evaluation of mineral contents and variation trends (Burnham et al., 1983), time of decomposition (Braun & Rothman, 1975; Johannes & Zaidentsal, 2008; Rasouli et al., 2014;), oil yield (Rosenvold & Rajeshwar, 1982), etc. and the determined results are discussed and compared.

Non-isothermal TG-DTG technique is one of the most advanced methods to investigate the thermal behavior of oil shale deposits. The time-independent single-step experimentation and detection of the entire possible transformation are the main advantages of this method (Vyazovkin & Wight, 1998; Vyazovkin et al., 2011). These advantages come with series of computational difficulties in quantitative analysis of the results, especially in the computation of kinetics parameters. There are many mathematical techniques developed to analyze the non-isothermal TG-DTG records (Brown et al., 2000).

Iso-conversional methodologies are one of the most reliable model-free approaches for determination of complex organic-rich solid reactions kinetic parameters. In this way, instead of reaction mechanism investigation, the simple straightforward reaction is presumed and instead, the kinetic parameters are determined as a function of reaction pathway. By incorporating non-isothermal TG or DTG analyses, the overall reaction can be traced with overall conversion and thus, the kinetic parameters, mainly activation energy can be determined (Qing et al., 2009; Tiwari & Deo, 2012).

Fourier transform infrared spectroscopy (FTIR) has been utilized with success in the identification of gases. The combination of thermogravimetric analysis (TGA) and FTIR techniques permits a complete characterization of materials in terms of thermal stability and decomposition mechanism.

Understanding the overall thermochemical process has been considered for the Garau oil shale deposit in Lorestan province. The non-isothermal TG-DTG analysis in three different heating rates and FTIR analysis was performed to study the thermal behavior, the evolved gases and the effect of different heating rates on the combustion of the Garau oil shale. In addition, Kissinger-Akahira-Sunose (KAS) and Ozawa-Flynn-Wall (OFW) integral iso-conversional methods were scrutinized to identify the behavior of activation energy of influential and reactive compounds either organic matter or minerals (Kissinger, 1957; Ozawa, 1965; Flynn & Wall, 1966).

Material and Methods

Sample

The oil shale samples belong to the Early Cretaceous Garau Formation (Shekarifard et al., 2019; Rasouli et al., 2015). It has been tried to choose the experimentations sample parts from the non-oxidized, non-aerated interior to minimize the ambient effects on the results. In this study, six oil shale samples from three outcrops sections (2 samples from each surface section) of study locality from the Garau oil shale were selected. To obtain a representative oil shale sample for thermal analysis the identical aliquots of oil shale samples were collected from each sample and then they

were crushed, mixed and homogenized (particle size <60 mesh with ASTM D 2013-72 standard). This standard would help to eliminate the effect of temperature distribution and in considering the samples bulk and homogeneous. Table 1 show the results of the proximate and ultimate analyses were performed on the representative sample from the Garau oil shale.

General characterization

To characterize the representative sample from the Garau oil shale the methods of Rock-Eval pyrolysis, Proximate, Ultimate, and (X-ray diffractometer) XRD were used.

Rock-Eval pyrolysis results on the representative sample present a T_{max} of 438 °C, organic carbon content (TOC) of 16.25 wt%, and HI of 526 mg HC/g TOC (Shekarifard et al., 2019). Proximate Analysis means of determining the distribution of products obtained when the oil shale is heated under specified conditions, as defined by ASTM D-121. Ultimate Analysis is defined in ASTM D-3176 as the determination of the carbon and hydrogen in the material, as found in the gaseous products of its complete combustion, the determination of sulfur, nitrogen, and ash in the material as a whole, and the estimation of oxygen by difference.

The results of the Ultimate analysis (Table 1) show some negative and positive factors for the Garau oil shale. For example, the sulfur content of the Garau oil shale is not high, and that low temperature retorting of oil shale is favorable on environmental grounds. In addition, although hydrogen content is not too high, however, low carbon content is favorable for producing high quality shale oil. The oxygen content is high, indicating that the oxygen of oil shale is transferred into gaseous or liquid products during the pyrolysis process. Although this oxygen can be come from organic matter but main part is from calcite decomposition (see next chapters). This indicates high temperature retorting of oil shale is unfavorable due to generation a lot of CO_2 gas.

The mineral phases of the selected samples with X-ray diffractometer (XRD) reveal that calcite is the most dominant phase of minerals in the Garau oil shale samples. Quartz mineral is appeared as minor phase in the oil shales investigated. Table 2 presents the minerals recognized in the Garau oil shales.

Table 1. Characterization of the representative sample from the Garau oil shale (as received base)

Proximate analysis		
	Total Moisture (%)	0.39
	Ash (%)	52.99
	Volatile Matter (%)	29.77
	Fixed Carbon (%)	16.85
	Total Sulfur (%)	2.99
Ultimate analysis		
	C (%)	22.75
	H (%)	1.42
	N (%)	-
	S (%)	1.81
	O (%)	21.03

Table 2. Mineral phases of the Garau oil shales selected

Mineral phase	Mass range (%)	Chemical formula
Calcite	95-97	$CaCO_3$
Quartz	2-5	SiO_2
Dolomite	trace	$CaMg(CO_3)_2$
Sanidine	trace	$Na.56K_3.44Al_4Si_{12}O_{32}$
Muscovite	trace	$KAl_2Si_3AlO_{10}(OH)_2$
Pyrite	trace	FeS_2

TGA-DTG and FTIR analysis

In this study, thermogravimetry analyzer is performed to implement the thermochemical process of the representative sample from the Garau oil shale. The sample is subjected to three constant 5, 10, 15 °C/min heating rate from 20°C up to 900°C and the experiments were preformed twice. This series of non-isothermal measurements helped to have proper calculation of kinetic parameters and better analysis of the outcomes (Vyazovkin et al., 2011). Air atmosphere with 50 ml/min approximate flow rate is performed as the purge gas through the thermochemical process. The in-situ computer has measured the mass change as a function of temperature and also provided the electronic differentiation of mass loss (differential thermogravimetry) in each temperature. Fourier transform infrared spectroscopy (FTIR) was used to determine the decomposition zones and investigate the products evolved during the Garau oil shale combustion. The FTIR spectra of the gases and other organic volatiles were collected in absorbance mode with a wavenumber range of 4000–450 cm^{-1}.

Computer programs

All of the analysis on the records of TG-DTG are obtained performing in-house programmed scripts in MathWorks® MATLAB®. MATLAB's internal numerical and optimization tools are carried out with careful considerations to obtain the reliable results. The program is designed in order to support different aspect of oil shale thermal process analysis, e.g. kinetic analysis in this study. All unit testing, subsystem testing and integration testing prior to final source code evaluation are done during programming development process (programming life cycle).

Results and Discussion

Experimental analysis

TGA-DTG analysis

Based on the TG-DTG experimentations, the mass-loss and derivation of mass per time are acquired as a function of temperature in different heating rates. Figure 1 represents mass- loss and its derivative (TG-DTG) versus temperature curve of the oil shale. The TG-DTG profiles indicate that the reactions are exothermic and occurs in multi-step decomposition.

There are two main mass-loss detected through the entire sample experimentations. The first one is due to organic matter (OM), mainly kerogen decomposition, and the second one is due to breaking down of minerals, mainly calcite. Before 230°C, in the sample subjected to any heating rate, mass-loss is less than 2 %. This phenomenon is related to moisture and interlayer water release and probably, the volatilization of free hydrocarbons, which are less than 2 mg/g rock in average in the Garau oil shale (Shekarifard et al., 2019). This result is corresponded to proximate analyses (Table 1) which have measured maximum total moisture less than 1 % in the whole. Table 3 demonstrates the mass loss and the temperature interval of two main reactions for the representative sample from the Garau oil shale in each heating rate.

Table 3. Thermochemical reaction results of Lorestan Garau oil shale

Heating Rate (°C/min.)	Mass Loss I (wt %)	Reaction I interval (°C)	Mass Loss II (wt %)	Reaction II interval (°C)
5	20,9	233-558	30,2	558-756
10	20,3	237-566	29,9	566-787
15	19,8	242-591	29,8	591-814
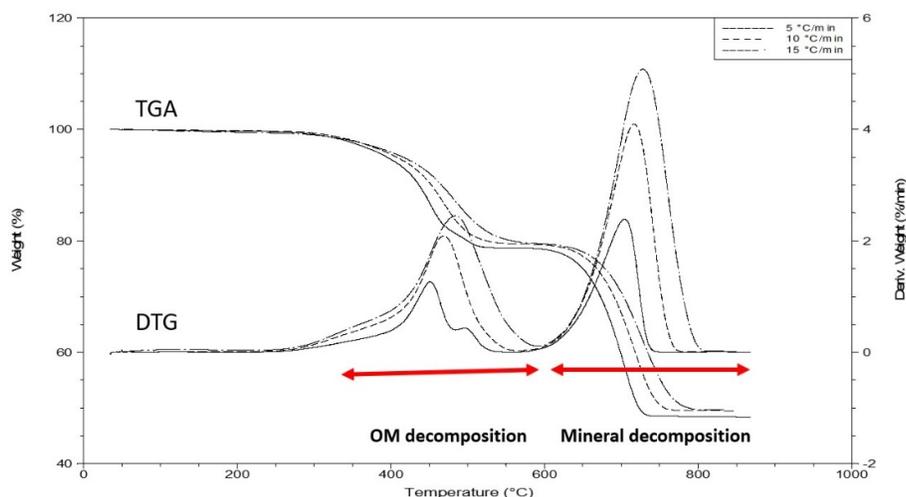
Figure 1. TGA-DTG curves of the representative sample from the Garau oil shale in relation to temperature

The first region of mass change with 20-21 wt % loss is in the range of 230-590 °C. In the sample, DTG curves demonstrate one clear peak, which shows the overall straightforward single-stage dominant organic matter decomposition reaction. By increasing the heating rate, the mass loss fluctuates and the first temperature peak shifts to higher temperature while the reaction transpires in wider temperature interval, especially with higher latter temperature. This phenomenon can justify with theory described kerogen thermal decomposition mechanism, which is in fact involving a series of parallel non-competitive reactions with different activation energy (Behar et al., 2008; Burnham & Happe, 1994; Williams, 1985). The reactions with less activation energy, which mainly produce light-mass gases, react faster in higher temperatures. In this situation, the competitive reactions, i.e. the reactions with relatively higher activation energy that produce heavier products, drop behind. As the former reactions consumed more hydrogen per carbon, the capability of heavy-mass hydrocarbon production would reduce. Instead, the production of non-saturated heavy hydrocarbons would be substituted in the pathway of heavier hydrocarbon generation. As a conclusion, in oil shale organic matter thermochemical processes, the observed fluctuation in the mass changes in different heating rates is due to the change in the quality of the products. Moreover, as the latter reactions with relative higher activation energy perform better in higher temperatures, the overall reaction advance in wider temperature intervals.

The second region of mass change is observed in the range of 600-820 °C with 29-30 wt% loss. As the Garau oil shale is most dominant in calcite mineral (> 95 wt %) with some content of quartz (2 to 5 wt %), the second detected mass loss is mainly due to calcite decomposition. In this case, similar to the first region, increasing heating rate leads to higher reaction temperature peak and respond of reaction in wider temperature interval. When the system is subjected to higher heating rate, it can be concluded that the reactants have less time to decompose and this causes reaction in wider range.

FTIR analysis

Examining the FTIR spectra at different temperatures a comparison with standard spectrograms, and reference to relevant literature, allows for the determination of the gaseous species at corresponding wavenumbers. In this study the FTIR spectra detected during the decomposition of the oil shale at temperatures of ~532 °C and ~760 °C was compared.

The FTIR curve of the Garau oil shale falls under the organic matter decomposition step at

2744 sec. (~532 °C). There are several peaks at 3700-3600, 2400-2330, 2300-2000, 1300-1250, ~1045, ~850, ~745 and 700-650 cm^{-1} . Strong and sharp peak at 2400-2330 with 3700-3600 and 700-650 peaks represent carbon dioxide (CO_2). Adjacent two small peaks at 2300-2000 cm^{-1} demonstrate carbon monoxide (CO) presence. Two strong peaks between 1300-1250 cm^{-1} and the sharp peak at at ~1045 seems to be an indicative of C-O stretch. Small peaks at ~745 cm^{-1} may be an indicative of ortho-disubstituted benzene ring modes. The small peak at ~850 cm^{-1} may be an indicator of para-disubstituted benzene ring modes with decreasing values since most of light components evolved until this point.

Based on the FTIR curve and the evolved gases at 4382 sec. (~760 °C), mineral decomposition has started at this point. 2400-2330 cm^{-1} with 3700-3600 cm^{-1} and 700-650 cm^{-1} peaks representing carbon dioxide have increased absorbance values due to the inorganic decomposition. The main source of the high temperature CO_2 is the calcite minerals in this step. At this temperature carbon monoxide peaks are lost. The CO molecules are reduced since they gain hydrogen. Other groups' bands still can be recognized. There is an increase at ~745 cm^{-1} may be additional C-H rocking bond of alkanes.

Iso-conversional Activation Energy

One of the main objects achieved by carrying out the TG-DTG records is the solid-state decomposition kinetic parameters, especially the activation energy. Therefore, there are several mathematical approaches adopted to calculate the relevant data (Sbirrazzuoli et al., 2009; Sbirrazzuoli, 2007).

In the case of oil shale thermochemical decomposition, which is a type of complex conversion-dependent reaction with relatively high activation energy, each method generates results with large difference. Nevertheless, in this study most of the developed well-known methods, i.e. Ozawa–Flynn–Wall (OFW), and Kissinger–Akahira–Sunose (KAS) methods are performed to determine the reliable ones (Kissinger, 1957; Ozawa, 1965; Flynn & Wall, 1966). Due to its large instability, the value of the frequency factors does not provide meaningful interpretations. Therefore, values of activation energies were treated as superior parameters for the interpretations

The variation of activation energy with related equivalent conversion has been defined by two well-known proposed iso-conversional approaches. Table 4. represents the average values of computed activation energy for the Garau oil shale sample.

The KAS method was also applied as iso-conversional method to analyze the TG-DTG data of oil shale samples. Iso-conversional methods use the certain degree of conversion and a narrow temperature range related to this conversion degree. The final form of the equation is:

$$\ln (\beta / T^2) = \ln (AR/E \, g(\alpha)) - E/RT \qquad\qquad \text{(Eq. 1)}$$

where; α: amount of sample undergoing the reaction; T_p: peak temperature (K); T_o: onset temperature (K); A: pre-exponential factor (sec-1); R: gas constant; E: activation energy (kJ/mol); β is the heating rate (°Cmin^{-1}).

In KAS method, the value of activation energy of the oil shale sample in the range of conversion level (α) 0.1 - 0.9, varied from 121 to 322 kJ/mol for the first reaction region and varied from 201 to 345 kJ/mol for the second reaction region, respectively. The average activation energy values were 181 kJ/mol for the first reaction region and 276 kJ/mol for the second reaction region.

For OFW method, several TG-DTG curves are used simultaneously to determine the activation energy values of biomass samples. The TG-DTG curves move to higher temperatures with increasing heating rates. At the same conversion levels, the following relationship is used where activation energy is obtained from the slope of the plot log (β) vs. 1/T at given conversion levels.

Table 4. Average values of computed activation energy via iso-conversional methods for the Garau oil shale

Method	E_1 (kj/mol)	E_2 (kj/mol)
KAS	181	276
OFW	184	278

$$[d (\log \beta) / d (1/T)] = 0.4565 (E / R) \qquad\qquad (Eq.\ 2)$$

where; E = activation energy in J/mol, R = ideal gas constant = 8.314 Jmol-1K-1, T = temperature in K (Kelvin = °C + 273) corresponding to the measured heating rate at same conversion, β= heating rate in °C/min.

In OFW method, the value of activation energy of the representative sample from the Garau oil shale, in the range of conversion level (α) 0.1 - 0.9, varied from 127 to 316 kJ/mol for the first reaction region and varied from 207 to 342 kJ/mol for the second reaction region, respectively. The average activation energy values were 184 kJ/mol for the first reaction region and 278 kJ/mol for the second reaction region.

The average activation energy calculated for the organic matter decomposition (~183 kJ/mol), confirm the occurrence of medium-fast reaction rate kerogen in the Garau oil shale, in consistent with IIS-kerogen reaction rate (144-218 KJ/mol) (Hunt, 1996).

Conclusion

Thermogravimetry (TG-DTG) analysis was used to study the thermochemical behavior and kinetic of the Garau oil shale from Lorestan, south-west of Iran. These preliminary results show that the combustion of the Garau oil shale take place in two reaction regions. The first reaction region belongs to organic matter (bitumen & kerogen) decomposition and the second one represents calcite decomposition.

Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TGA-FTIR) was used to determine the decomposition zones and investigate the products evolved during the oil shale combustion. Study of the evolved gases showed the presence of C–H stretching, C=C aromatic bending (benzene), C–O, and CO_2.

The experiments show that the peak temperatures and reaction region intervals shifted to higher temperatures, as heating rate is increased. Although the total mass loss during the combustion of the oil shale is almost the same for each heating rate, there is a tendency that at lower heating rates, the mass loss during combustion is slightly higher, possibly due to the better combustion conditions at lower heating rates. It was observed that the reaction intervals during the combustion process depend on the heating rate.

For the Garau oil shale, the average activation energy calculated during the organic matter and mineral decomposition, using the KAS and OFW methods, is 183 kJ/mol and 277 KJ/mol, respectively.

The results of kinetic calculation in consistent with our previous study (Shekarifard et al., 2019) confirm the presence of IIS kerogen in the Garau oil shale.

Acknowledgments

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