

TGA and BET characterization of spent oil shale as a catalyst in biomass tar removal applications

Z. Abu El-Rub

German Jordanian University, Pharmaceutical and Chemical Engineering Department, P. O. Box 35247, 11180 Amman, Jordan

Abstract

Oil shale is an abundant-alternative source of energy in Jordan that is yet to be utilized in terms of energy content of the shale oil, and the applications of the spent oil shale. In order to find new applications, a characterization study was made for the spent oil shale to find out the potential of using this material as a catalyst for hot gas catalytic cleaning in biomass chemical conversion processes. The characterization focused mainly on finding industrial catalysts with comparable chemical composition, and the effect of mass loss at different heating rate on the resulted BET surface area and pore size. The chemical composition of the spent oil shale was done through XRF analysis and found comparable to limestones and dolomites, which are applied in industrial catalytic tar removal processes. The key-common components are the high CaO/MgO and iron. Further, the TGA analysis showed a significant and inversely proportional mass loss (20-39 wt.%) at the different heating rates of 10, 50 and 100 °C/min. The higher mass loss was accompanied by a higher surface area (4.44 m²/g) due to the expected smoother evolution of the pore structure when the volatile organic compounds escape from the solid particle. Although the resulted surface areas of the spent oil shale were relatively small due to the microporous nature of the pores, it still worth to be tested in a future work for catalytic tar removal due to its chemical composition and mechanical stability.

Keywords: Spent oil shale, TGA, BET, catalyst, tar

1. Introduction

Jordan is a developing country that suffers from a severe deficiency in energy production. In the year 2017, the country imported 94 % of its energy requirements at high costs [1]. Many alternatives for crude oil have been investigated, while the applications of renewable energy are gradually increasing [2,3]. Biomass is one of the abundant and mostly non-utilized renewable energy resources in Jordan. On the other hand, the oil shale is classified as an alternative energy resource and it is the most abundant in Jordan.

Biomass is any solid waste material from an animal or a plant origin [4]. Wood is considered the largest resource of biomass in addition to the waste produced from different resources such as the municipal solid wastes [5]. This material can be converted to other types of energy through three different processes: thermal, chemical and biochemical [6]. The chemical conversion process is one of the effective ways of utilizing biomass to produce fuels and chemicals. The biomass gasification process is considered one of the promising chemical processes. It partially combusts the biomass and produces carbon monoxide and hydrogen. However, the main problem of this process is the formation of undesirable byproducts such as the tar. Tar is a dark, oily, viscous material, consisting mainly of hydrocarbons heavier than benzene [7]. The production of tar makes it difficult to fully utilize the products of the chemical conversion of biomass in the downstream applications. The tar can be removed physically by filtration, thermal cracking, and catalytic conversion. The latter process enhances the conversion of tars into lighter and useful components and subsequently is more economical.

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Corresponding author. *E-mail address:* ziad.abuelrub@jgu.edu.jo.

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On the other hand, oil shale is an alternative energy source that contains valuable organic materials called kerogen. The oil shale reserves in Jordan are estimated at more than 70 billion tons of proven reserves, covering more than 60% of the country's land, and ranked the sixth in the world [8]. Generally, the oil shale can conventionally be exploited by either retorting to produce oil or by direct combustion to produce electricity [9,10].

Oil shale retorting industry is not commercially mature enough. It still faces several technical challenges that vary from one deposit or country to another. In the retorting process, the oil shale is heated in the absence of oxygen to temperatures around 450 °C. Subsequently, the kerogen in the shale decomposes, releasing shale oil, gas and spent oil shale (alternatively called semi-coke). The spent oil shale can be burned to fully utilize the energy in the remaining carbon content of the spent shale and the solid material is consequently converted to oil shale ash [11].

In order to increase the attractiveness of the oil shale industry and minimize the environmental impact of its waste products, it is important to find new applications for these waste streams [10,12,13]. It is found that the spent oil shale has high calcium oxide and metals content. These components have an influential catalytic activity in catalysts used for the tar removal in biomass gasification and pyrolysis applications. On the other hand, the internal structure of the oil shale is rather complex because it varies in pore sizes (micropore < 2 nm, mesopores = 2-50 nm and macropore > 50 nm), metal content, and total organic carbon [14,15]. Therefore, the spent oil shale may have some catalytic activity and may have the potential to be used as a catalyst for tar removal.

There is no previous research found on spent oil shale as a catalyst in chemical conversion processes of biomass, e.g. in biomass gasification and biomass pyrolysis. However, Link et al. [16] studied the catalytic effect of oil shale ash, resulted from the oil shale combustion, as a catalyst for biomass gasification processes. They found that the oil shale ash enhanced the char reactivity at a low CO₂ partial pressure of 0.09 atm. On the other hand, Bai et al. [17] studied the effect of the final pyrolysis temperature and heating rate on the pore structure of Huadian oil shale. They found that micropores and mesopores were predominant in spent oil shale samples. They also found an inversely proportional relation between the heating rate and the specific surface area and total pore volume.

The aim of this paper is to conduct a characterization study of a Jordanian spent oil shale as a potential catalyst for tar removal downstream gasifiers or as a catalytic fluidizing bed material in biomass gasifiers. The study covers the chemical composition using XRF analysis, thermogravimetric analysis (TGA) at different heating rates, and the BET analysis. In a future study, the activity of the spent oil shale will be tested for tar conversion.

2. Method

Characterizing the potential catalysts is an important step toward predicting the performance of the materials when used as a catalyst for tar elimination. The preliminary characterization was done by studying the chemical composition, surface area and pore structure of the spent oil shale at different heating rates.

2.1. Spent oil shale sample

The spent oil shale sample was sourced out from the labs of the Ministry of Energy and Mineral Resources in Amman, Jordan. The origin of the spent oil shale sample was Attarat Um Ghudran deposit. This deposit is a near surface and commercial deposit located 70 km south of Amman as shown in location 8 in Fig. 1. Further, the deposit has an average thickness of oil shale of 45 m, average thickness of overburden of 53.2 m, an average oil yield of 8%, and 53.2 wt.% ash content [8].

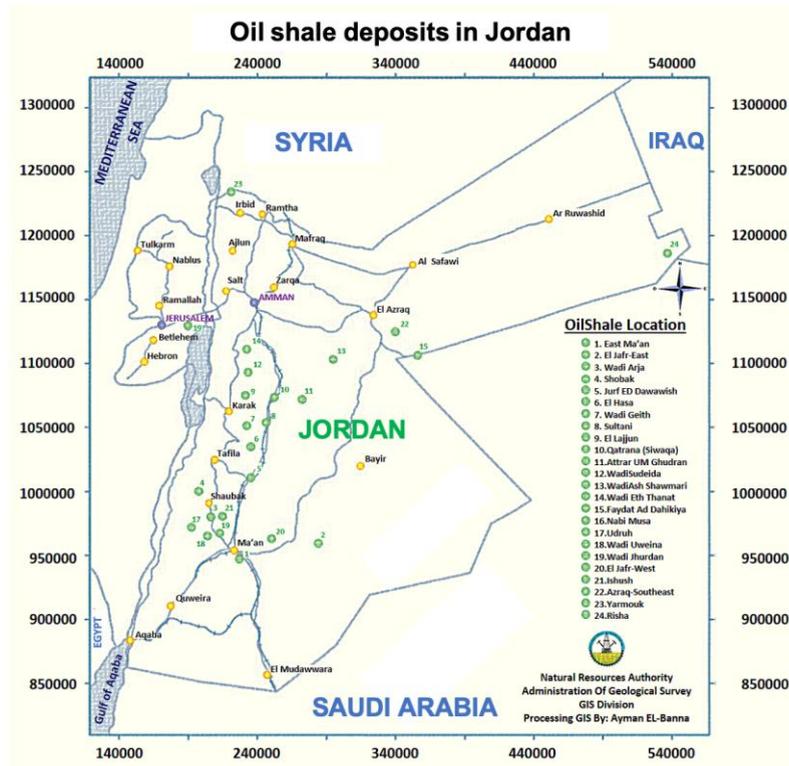


Fig. 1. Map of the major oil shale deposits in Jordan [8].

The spent oil shale sample was crushed and sieved to an average particle size of 0.5 mm. The X-ray fluorescence method was used for determining the chemical composition of the spent oil shale, as given in Table 1. The chemical composition shows that the spent oil shale is mainly composed of calcium oxide (CaO) and silica (SiO₂). Despite the low concentration of some components that contain alkali metals (K, Na) and transition metals (e.g. Fe), they can have an influential catalytic activity.

Table 1. Spent oil shale chemical compositions from the X-ray fluorescence

Component	Wt. %
CaO	43.60
SiO ₂	13.00
P ₂ O ₅	4.26
Al ₂ O ₃	3.47
Fe ₂ O ₃	1.70
MgO	1.18
Na ₂ O	0.266
K ₂ O	0.189
TiO ₂	0.156
MnO	0.010
L.O.I*	32.20

* L.O.I: loss on ignition

2.2. Thermal Gravimetric Analysis (TGA)

Testing the material's stability under pyrolysis conditions was performed using the TG 209 F1 Libra® Thermogravimetric analyzer system. The spent oil shale was heated to a temperature of 900 °C at different heating rates and purged with nitrogen. The heating rates of 10, 50, and 100 °C/min were used. The results were used to give an indication of the surface area of each of the tested minerals. The evaporation of the volatile materials at the different heating rates contributed to the formation of the physical structure of the spent oil shale particles.

2.3. BET analysis

The BET analyzer used was the Autosorb Model AX1C-MP-LP manufactured by Quantachrome Instruments. Physical properties such as surface area and pore size were measured using Brunauer–Emmett–Teller (BET) surface area analysis, which is the most widely accepted method. All samples that were tested by the TGA were stored in a desiccator to prevent any external influence from tampering with the sample. Tested samples on BET go through two stages: degassing and analysis. Degassing was performed by placing the sample up to 0.1 g in a bulb and mounting it to the device. A heating mantle will surround the bulb to heat it to 150 °C and nitrogen will flow at a rate of 50 microns/min through the sample to remove any unwanted vapors and impurities. The degassing process lasted two to three hours. After degassing the sample, it was mounted on the analysis section. The sample was immersed in a liquid nitrogen during this stage to assure that the analysis was performed isothermally at 77.35 K with nitrogen flowing to be adsorbed by the sample [18]. Both adsorption and desorption were selected to be performed while setting up the analysis in order to determine the surface area (adsorption) and pore size (desorption). The results obtained from this analysis will give a prediction of how the catalyst would perform when put into test for tar removal.

3. Results and Discussion

3.1. Chemical composition

The chemical composition of the spent oil shale can be compared to that of calcined rocks that include limestones and dolomites (See Table 2). These materials have been thoroughly investigated, and used in industrial producer gas cleaning. Calcined rocks have high CaO/MgO ratio and their catalytic activity increased as this ratio and the active iron content increases [19]. Calcined dolomites remove tars by catalyzing the reforming reactions above 800 °C. However, these materials have a severe mechanical loss, as they are soft to moderate in hardness, whereas spent oil shale is expected to be mechanically more stable. Consequently, spent oil shale may have the potential to be a suitable catalyst for catalytic tar removal and its catalytic activity for tar removal will be inspected in a future work.

Table 2. Chemical Compositions (wt.%) of the tested Jordanian spent oil shale compared to the calcined rocks [19]

Component	Jordanian Spent shale (this work)	Calcite Morata [19]	Magnesite Navarra [19]	Dolomite Norte [19]
CaO	43.6	53.0	0.7	30.9
MgO	1.18	0.6	47.1	20.9
CO ₂	0.0	41.9	52.0	45.4
SiO ₂	13.0	2.7		1.7
Fe ₂ O ₃	1.7	0.8		0.5
Al ₂ O ₃	3.47	1.0		0.6

3.2. TGA analysis

Three spent oil shale samples were tested. The samples lost a significant percentage of their weight (20- 39 wt.%) with increasing the temperature as shown in Fig. 2. The mass loss occurred in three stages, where each subsequent stage is characterized by a steeper slope of mass loss as a function of temperature. The first stage (from left to right) has the lowest slope covers the moisture removal. The second stage covers the pyrolysis of remaining hydrocarbons in the spent shale. The third stage covers the decomposition of carbonates.

The mass loss increased with decreasing the heating rate. This is due to the slow devolatilization of the volatile components, which can be related to the slow escape of the volatile compounds within the shale. This results in a more organized pore structure that allows more pores that vary in size and volume for the escape of the volatile components, and thus a higher mass loss. The weight percentage under the thermal analysis reached a point where it stopped decreasing only with the heating rate of 10 °C/ min. This is due to the longer time the sample spent under heating compared to the heating of 50 °C/ min and 100 °C/ min. Therefore, the analysis was done under isothermal conditions for extra an 30 min on the TGA analyzer to have a better understanding of the effect of different heating rates on those two samples particularly.

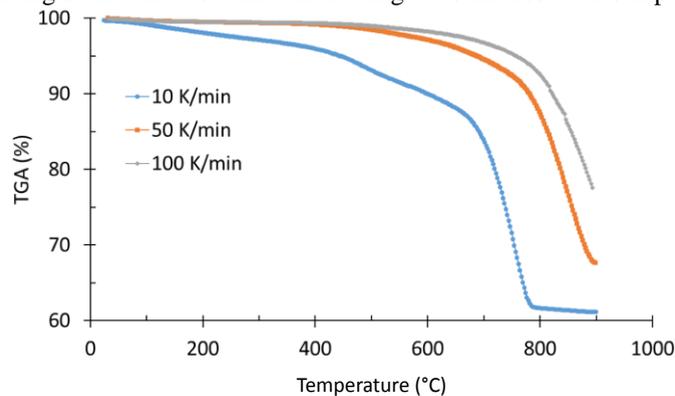


Fig. 2. TGA curves for Jordanian spent oil shale heated at different heating rates, purged with nitrogen

3.3. BET Analysis

The surface area of four spent shale samples were measured. The first sample was tested without any heating, the other three samples were heated at the three heating rates mentioned earlier (10, 50, 100) °C/min, and then the temperature was held at 850 °C for 30 minutes. Fig. 3, Fig. 4, Fig. 5, and Fig. 6 show each sample adsorption and desorption isotherm of nitrogen. It is observed that there are no significant gaps between the adsorption and desorption isotherm and the adsorbed volumes of nitrogen were small.

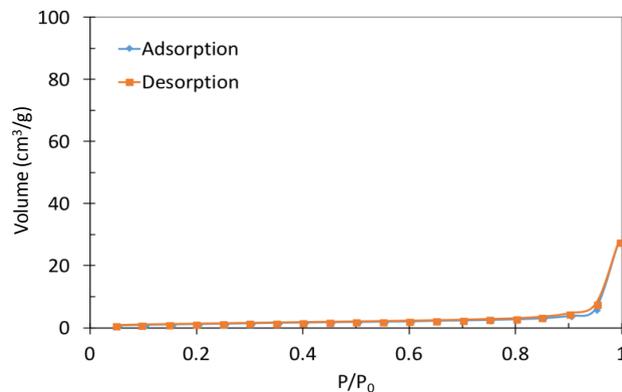


Fig. 3. Produced isotherm of nitrogen for raw spent oil shale sample (no heating)

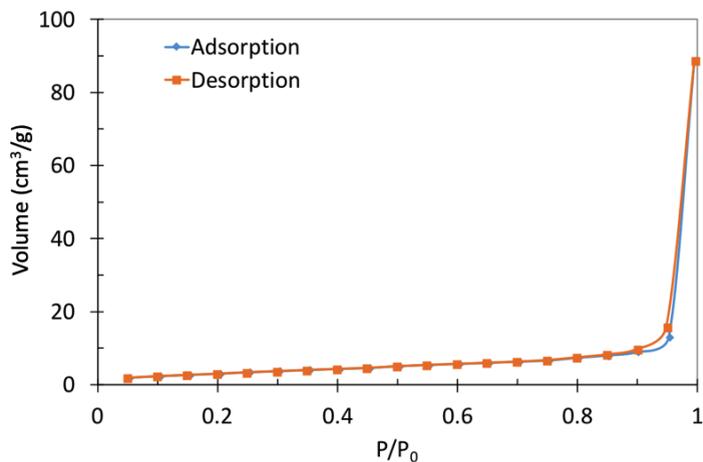


Fig. 4. Produced isotherm of nitrogen for spent oil shale sample (10 °C/min heating)

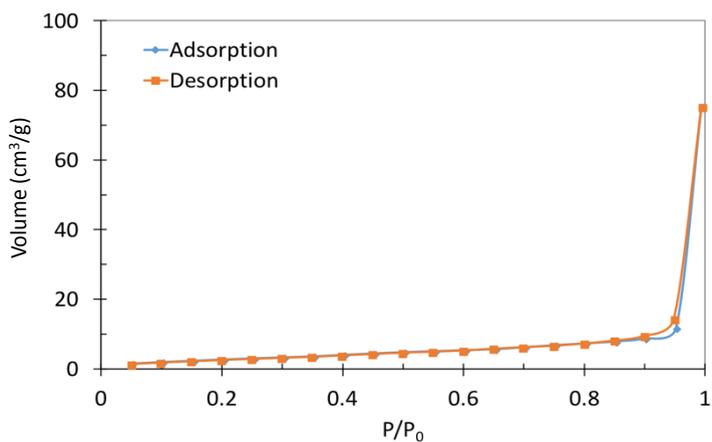


Fig. 5. Produced isotherm of nitrogen for spent oil shale sample (50 °C/min heating)

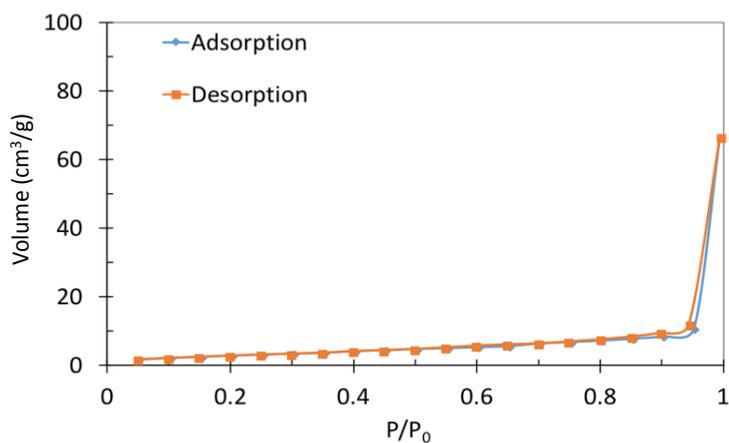


Fig. 6. Produced isotherm of nitrogen for spent oil shale sample (100 °C/min heating)

The effect of the heating rate on the surface area and pore area of the spent oil shale is shown in Fig. 7 and Fig. 8. It is evident that losing a considerable amount of weight when heated to high temperatures at

different heating rates does not necessarily give high surface area as in this case. Further, the low surface and low pore area indicate that the pores of the spent oil shale are microspores. The spent oil shale lost more than 38 wt.% of its weight, while the resulted maximum surface area was found to be relatively small ($4.44 \text{ m}^2/\text{g}$ at $10 \text{ }^\circ\text{C}/\text{min}$). However, the spent oil shale samples heated at a high heating rate ($100 \text{ }^\circ\text{C}/\text{min}$) has a smaller surface area. This can be related to the rapid escape of the volatile compounds within the shale resulting in a deformation and destruction of the catalyst's pore structure resulting in a lower surface area. Further, the heating rate is indirectly proportional to the pore area. This has a trend similar to that of the surface area, which is mainly for the same reason explained earlier.

The BET results show that the surface areas of the testes spent oil shale samples at different heating rates are low. The results are comparable with the found BET results of Kuusik et. al. [20] done on ashes of oil shale. They found the BET of pulverized-fired ashes of oil shale were in the range of $0.36\text{-}1.75 \text{ m}^2/\text{g}$, and the BET of ashes of circulating fluidized bed combustion reached $8.68 \text{ m}^2/\text{g}$.

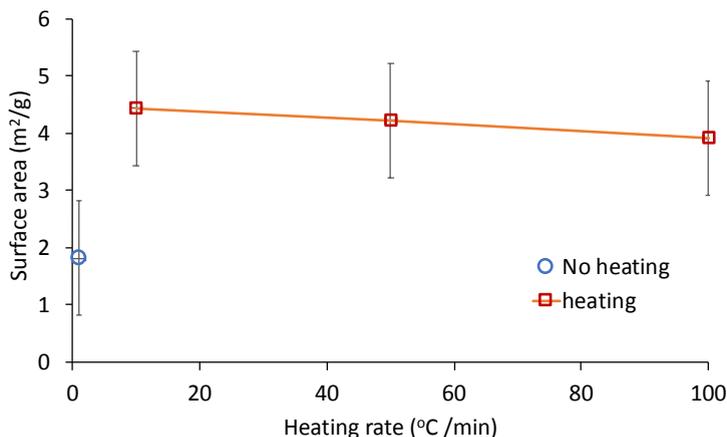


Fig. 7. Effect of the heating rate on spent shale surface area

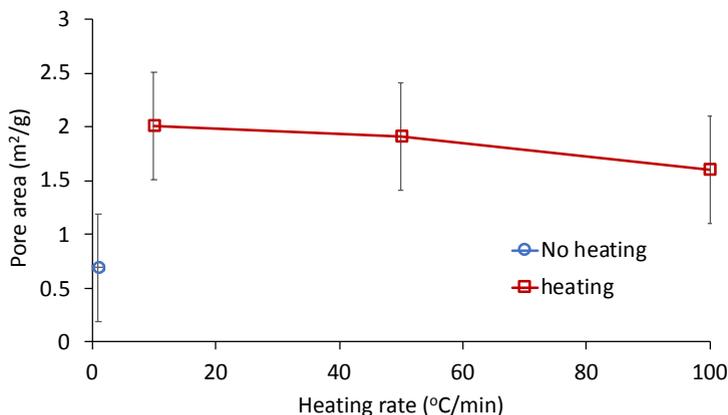


Fig. 8. Effect of the heating rate on spent shale pore area

4. Conclusions

The chemical composition of the spent oil shale can be compared to some known minerals applied industrially in catalytic tar removal. These minerals are calcined rocks, which include limestones and dolomites. The key common components are the high content of CaO/MgO and the influential iron

content. Further, the pores of the spent oil shale were found to be microspores due to the small surface and pore area. Although, the surface area was relatively small (up to 4.44 m²/g) for catalytic applications, it still worth to be tested for catalytic tar removal due to its chemical composition and its expected higher mechanical stability.

In the future work, the catalytic activity of spent oil shale for tar removal in biomass gasification applications will be tested in a packed fixed bed reactor. Further, the kinetics of spent oil shale will be compared with the activity of other active materials used in this field of application.

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