

Utilization of Desulfurized Heavy Liquid Fuel Blends in Domestic Boiler

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ABSTRACT

One way to cut down the consumption of diesel fuel in domestic heating in Jordan is to blend it with shale oil, which may be extracted from oil shale. This leads to a cut down in the national fuel bill in Jordan. Unfortunately, shale oil contains significant amounts of sulfur as impurities and upon burning sulfur oxides are emitted causing a negative environmental impact, and hence desulfurization of such fuel blends is essential. This may be achieved by adding activated carbon to the fluids. The process of removing sulfur from shale oil is crucial for safeguarding the environment, human well-being, and equipment, as well as meeting regulatory requirements and creating superior-quality goods. In this study, a domestic boiler was utilized to evaluate the degree of desulfurization process of blends of diesel and shale oil fuels upon their burning in a domestic boiler, to achieve this, blends of both fuels were prepared with varying amounts of shale oil (10%, 20%, 30%, and 40%) and various amounts of activated carbon were added to the prepared mixtures of diesel fuel and shale oil. The assessment of performance included examining the environmental impact, specifically by analyzing exhaust gases to measure the concentration of Sulfur Oxide (SO₂). It was found that an increase in the concentration of shale oil in the mixture led to an increase in the concentration of SO₂. However, adding more activated carbon to the mixture from the fuels resulted in a decrease in the SO₂ concentration. The lowest SO₂ concentration was observed when 1g of activated carbon was added per liter of the fuel mixture at a 20% concentration of shale oil, and 0.6g of activated carbon per liter of the fuel mixture at a 40% concentration of oil shale.

Keywords: shale oil; domestic boiler; activated carbon; diesel, sulfur oxide.

INTRODUCTION

Fossil fuels are energy sources that come from the remains of plants and animals that existed millions of years ago. The three main types of fossil fuels are coal, crude oil derivatives, and oil shale. These fuels are not renewable, which

means they are limited and will eventually run out. Unfortunately, burning these fossil fuels results in the release of various pollutants, such as carbon, sulfur, nitrogen oxides, and particulate matter (PM) (Hamdan and Almomani, 2015; Kebede et al., 2022; Breeze 2019; Alahmer et al., 2023). These pollutants can negatively impact

human health and the environment. Consequently, research work was conducted on the desulfurization of diesel fuel using several methods.

Shale oil has been promoted as an alternative to traditional petroleum for a while (Smith et al., 1952). It is a liquid fuel generated through the pyrolysis of solid oil shale (Lee 1990; Oja and Suuberg, 2012) and there are projections that indicate known deposits could produce at least 4.7 trillion barrels of oil (World Energy Council 2013). Nonetheless, the economic viability of shale oil production has been hampered by technical and environmental obstacles. Despite this, shale oil is presently being industrially manufactured in Brazil, China, and Estonia (World Energy Council 2013), and its potential remains appealing due to the vast resources available, particularly when petroleum prices are elevated.

Shale oil is a type of conventional oil extracted from shale rock formations through hydraulic fracturing, or “fracking” (Zhang et al., 2015). The combustion of shale oil releases energy in the form of heat and light but also generates a range of air pollutants, including carbon dioxide (CO_2), nitrogen oxides (NO_x), sulfur dioxide (SO_2), and particulate matter (PM) (Zhang et al., 2015). These pollutants can have negative impacts on human health and the environment. Thiophenes, benzothiophenes, dibenzothiophenes, thioesters, and thiols are among the sulfur compounds that are frequently discovered in shale oil, along with the possibility of some disulfides (Derenne et al., 1990; Andersson et al., 1995; Zehua et al., 1988; Zelenin et al., 1968; Dijkmans et al., 2015; Al-Harashsheh et al., 2005). To comply with existing environmental regulations, a substantial improvement is necessary to eliminate the significant amounts of sulfur, nitrogen, and oxygen that are typically present in oil (Landau 1997). Given the significance of eliminating these heteroatoms, it is necessary to take action.

Hydrotreatment has been the most widely used technology for eliminating heteroatoms from shale oil (Smith 1952; Zehua et al., 1988; Hüsse 1930; Koern 1930; Landau et al., 1997; Harvey et al., 1986; Souza et al., 1992; Luik et al., 1999a; Luik et al., 1999b; Luik et al., 2000a; Luik et al., 2000b). It typically produces high-quality oil and a large yield and can reduce the concentrations of heteroatoms in the oil to very low levels. However, achieving these low levels necessitates severe hydrotreating conditions that may be costly. In order to make the upgrading process more

cost-effective, it has often been suggested to combine hydrotreatment with other techniques (such as coking or extraction) or use it to the extent that the oil can be used as a feedstock for a traditional refinery (Curtin et al., 1978; Sullivan and Stangeland, 1979; Sullivan and Stangeland, 1978).

Coking is advantageous when utilized with shale oil because the solid or metal residue is retained in the residue of the coking process, which simplifies the refining of the remaining liquid fuel (Sullivan and Stangeland, 1978). Egloff et al. (1951) also conducted coking experiments around the same time. Additionally, Sullivan and Stangeland (1979), looked into using coking as the initial step in upgrading shale oil and reported a $\text{C}_5 +$ liquid yield of 77.9% and a coke yield of 18.3%.

Hydrodesulfurization is believed to be the most commonly used desulfurization method in refineries, but it necessitates harsh conditions such as high temperatures, pressure, and large catalyst volumes (Prajapati and Verma, 2017). As a result, adsorptive desulfurization is viewed as an alternative and a promising technique due to its mild operating conditions, high selectivity to thiophene compounds, and the potential to achieve 100% sulfur removal with an appropriate adsorbent. Ahmed and Jung (2014), Activated carbon is utilized to remove sulfur compounds from shale oil in the desulfurization process, and it acts by adsorbing the sulfur compounds onto its surface, which can then be readily removed from the crude oil.

Activated carbon is a highly porous form of carbon often used to reduce emissions of sulfur oxides (SO_x), a group of air pollutants that consist of sulfur dioxide (SO_2) and other sulfur compounds. When SO_x emissions are released into the air, they can react with other substances to form small particles and harmful gases that can have serious health and environmental impacts. Activated carbon can be used to capture and remove SO_x emissions from flue gas, which is the gas emitted from burning fossil fuels in power plants and other industrial facilities. When SO_x particles come into contact with the surface of the activated carbon, they are adsorbed, or attracted and held, by the carbon’s surface. This helps reduce the amount of SO_x released into the air, improving air quality and protecting public health (Heidarinejad et al., 2020).

There are several advantages to using activated carbon for the desulfurization of oil shale, as it has a large surface area and a high degree of porosity, which allows it to adsorb a large number of

sulfur compounds per unit of mass. Also activated carbon is a relatively low-cost material, which makes it an attractive option for large-scale industrial applications. It is also readily available and can be easily sourced from a variety of suppliers. Finally, the use of activated carbon for desulfurization is a relatively simple process that requires minimal equipment and can be easily integrated into existing refining and processing facilities.

Triantafyllidis and Deliyanni (2014) carried out research in 2014 on the adsorption of 4,6-dimethyl dibenzothiophene (4,6-DMDBT) in hexadecane solutions using three different commercial activated carbons that had either microporous or combined micro/mesoporous structures, as well as their oxidized versions. The results showed that the removal capacity of 4,6-DMDBT increased when the volume of pores with a similar size to the 4,6-DMDBT molecule, which is approximately 6 Å, increased. The presence of functional groups on the surface of larger pores contributed to the adsorption through polar interactions.

Hamdan et al. (2021) conducted a study on the emission of SO₂ while burning desulfurized diesel fuel that had been treated with activated carbon using three types of Artificial Neural Networks, specifically Elman, NARX, and Feedforward. The study was based on previous research on the desulfurization of diesel fuel using activated carbon. They collected metrological data, including temperature, humidity, wind speed, pressure, particulate matter concentration, and solar radiation, from February 1, 2020, to December 30, 2020. The results indicated that the NARX model was

the most precise in predicting SO₂ emissions, followed by the Elman model, and the feedforward model was the least accurate.

In this study, activated carbon will be used to desulfurize blends of diesel and shale oil fuels during the combustion process in a domestic boiler. These blends are characterized by substantial sulfur content (shale oil in particular). The amounts of added activated carbon to each blend will vary such that the optimum amount will be estimated experimentally, and the quantity of emitted sulfur oxides will be determined. Hence, the degree of the desulfurization process will be measured by flue gas analysis for sulfur oxide.

EXPERIMENT SETUP

A comprehensive illustration of the equipment used and its configuration in the experiment is presented in Figure 1.

As shown, the experimental setup consists of the followings:

1. BiasiB-10 boiler (as shown in Figure 2), has a maximum heating capacity of 75 kW and an efficiency range of 85.8% to 87.2%. It has a water content of 3.7 gallons.
2. ST120 burner has a fuel consumption range of 2–5 kg/h and an output power range of 24–60 kW. It has a recommended pump pressure of 10 bar and a viscosity range of 1.3–12 mm²/s.
3. The Wilo Circulation pump, identified by the model number Star-RS 25/4, is capable of pumping up to a height of 4 meters and can

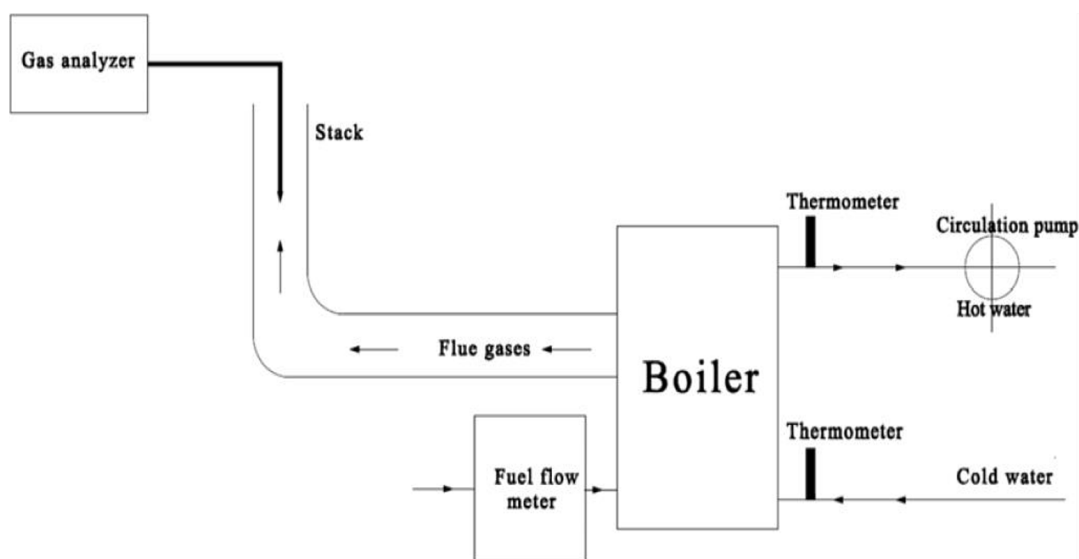


Figure 1. Experimental setup (Hamdan and Almomani, 2015)

handle a flow rate of up to 3.5 cubic meters per hour like the RG device. It operates at a frequency of 50 Hz and has a pipe connection diameter of 1 inch.

4. NOVApplus gas analyzer is a compact flue gas measuring instrument with a wireless Remote-Control Unit for industrial applications. It can measure exhaust emissions of NO, NO₂, NO_x, SO₂, CO₂, and hydrocarbons.
5. Two type K Thermocouples were used to measure the inlet and outlet water temperatures.

The proposed work is achieved as follows:

1. A mixture of diesel and shale oil at different concentrations was prepared.



Figure 2. The burner used in this work

2. Activated carbon derived from oil shale was prepared following the procedure outlined in detail by Hamdan et al. (2023).
3. Desulfurization of the prepared mixture (diesel and shale oil) was obtained as each fuel blend will be mixed with a certain amount of the activated carbon.
4. Each desulfurized fuel blend was used to operate a domestic boiler.
5. The hourly outlet and inlet water temperatures were recorded. The outlet temperature is used as an indication of the combustion temperature.
6. Exhaust gas samples were withdrawn for pollutants concentration measurements (mainly sulfur oxides).
7. The effect of desulfurization of the fuel blends was estimated as the sulfur oxides emitted from the boiler will compare to those emitted when the boiler is powered by shale oil.

RESULTS AND DISCUSSION

The effect of temperature on the emitted concentration of sulfur dioxide from diesel fuel shale oil blends was first investigated without the addition of activated carbon.

Figure 3, shows the effect of outlet water (and hence the combustion temperature) on amounts of SO₂ gas released during the burning of these blends. As indicated the emitted concentration of SO₂ increases with the temperature, this is due to the fact the rate of formation of SO₂ increases with temperature. Furthermore, the

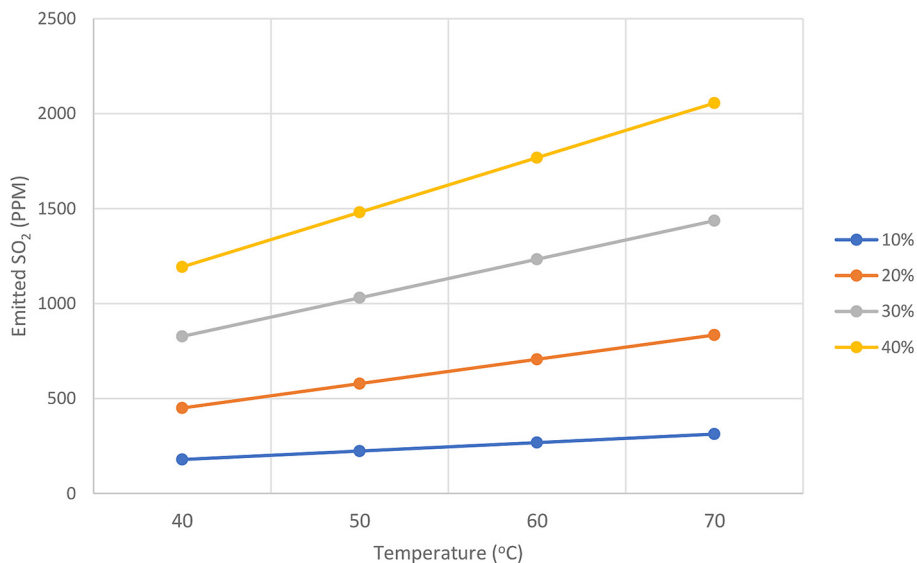


Figure 3. Temperature effect on the emitted SO₂

concentration of SO₂ increases with the amount of shale oil in the combustible mixture due to the increase in the sulfur contents in the shale oil. It is to be noted that the maximum percentage of shale oil in the fuel such that the combustion process of the fuel blend proceeds smoothly was 40%. However, to obtain smooth and continuous boiler operation, it was decided to use a mixture of 20% shale oil and 80% diesel fuel throughout the experimental work.

Figure 4, shows the emitted amounts of SO₂ gas from burning mixtures of diesel and different concentrations of oil shale oil. As indicated the SO₂ concentration increases with the concentration of shale oil. This is due to the fact that shale oil, is characterized by sulfur compounds often found in shale oil including thiophenes, benzothiophenes, dibenzothiophenes, thioesters, and thiols (Derenne et al., 1990; Andersson et al.,

1995; Zehua et al., 1988; Zelenin et al., 1968; Dijkmans et al., 2015; Al-Harashseh et al., 2005). Some disulfides may also be present (Zelenin et al., 1968), Such sulfur compounds and upon combustion of shale oil lead to the increase of emitted SO₂ in the presence of oxygen and under high-temperature conditions. This is clearly indicated in Figure 4.

Figure 5, shows the emitted amounts of SO₂ gas during the burning mixture of diesel and oil shale fuels with a 20% concentration of oil shale at various water outlet temperatures when different amounts of activated carbon are added to this mixture, (0, 0.6, 0.8, 1 and 1.2 g/l). As shown in this figure, the emitted amount of SO₂ decreases when activated carbon was added at any amount compared with that emitted without any activated carbon added. Furthermore, at any specified water outlet temperature from the boiler, the emitted

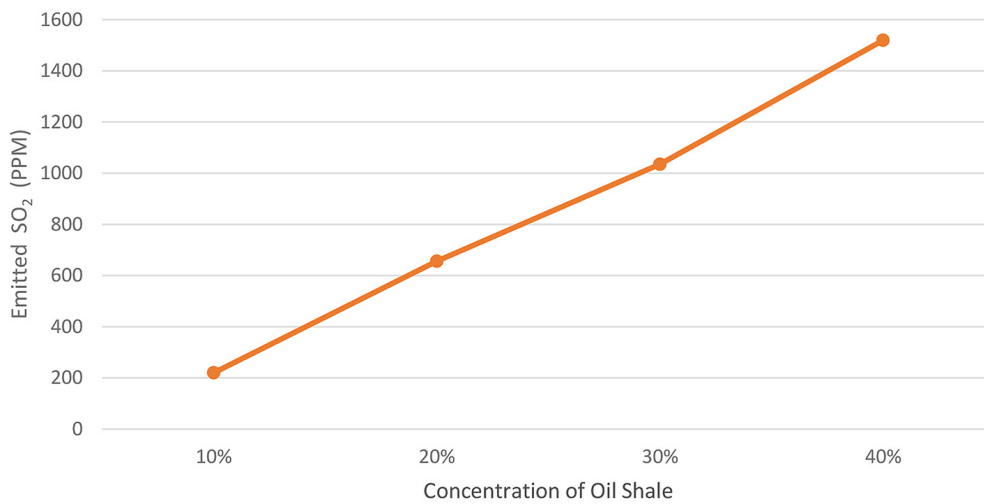


Figure 4. Emitted SO₂ at different concentrations of oil shale

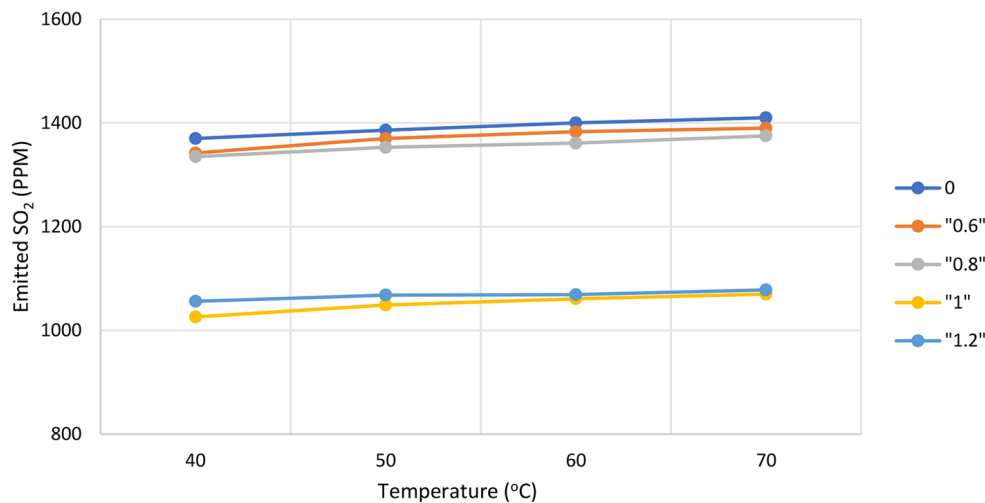


Figure 5. Emitted SO₂ at 20% concentration of oil shale at different activated carbon weights

amount increases with the amount of activated carbon up to the value of 1.0 g/l, beyond which the concentration decreases.

The chemical mechanism of shale oil desulfurization using activated carbon is primarily based on the adsorption of sulfur-containing compounds onto the surface of the activated carbon. Activated carbon is a highly porous material with a large surface area, which provides ample sites for sulfur compounds to bind to. The sulfur compounds, which are typically present in shale oil in the form of thiols, sulfides, and disulfides, are attracted to the activated carbon surface through weak van der Waals forces and hydrogen bonding. As the oil flows through the bed of activated carbon, the sulfur compounds are adsorbed onto the carbon surface, effectively removing them from the oil. The efficiency of the adsorption process depends on various factors, such as the pore

size distribution, surface area, and surface chemistry of the activated carbon.

The variation of the emitted amounts of SO₂ during the burying of a blend containing 20% of shale and 80% of diesel fuel with the amount of added activated carbon at a constant water outlet temperature is presented in Figure 6. As it is seen in this figure, the emitted concentration decreases to 1430PPM without the addition of activated carbon to a minimum emitted concentration of 1020 PPM, then it increases again with further addition of activated carbon.

Figure 7 shows the variation of the emitted concentration of SO₂ gas during the burning of a blend made up of 60% diesel fuel and 40% with water outlet temperature with the added activated carbon to this blend. As indicated in the figure, the SO₂ emitted concentration increases with temperature at any amount of added activated carbon.

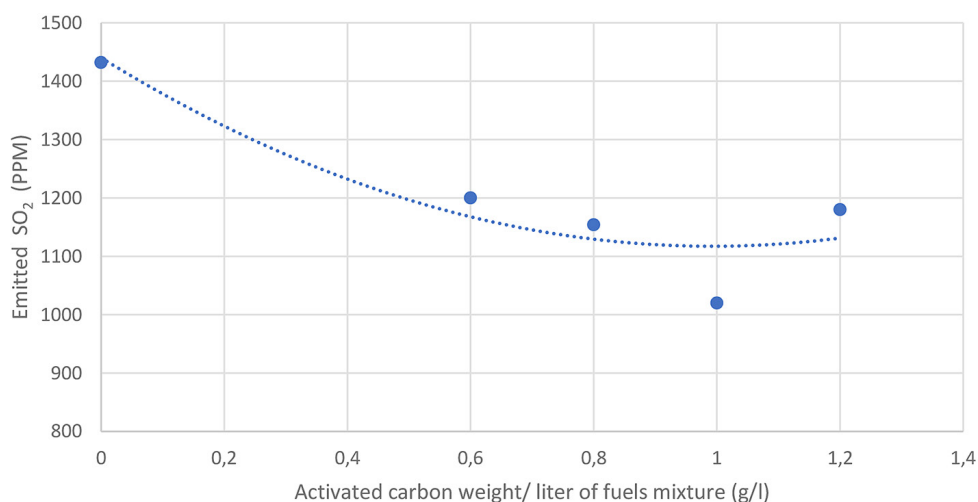


Figure 6. Emitted SO₂ at 20% concentration of oil shale

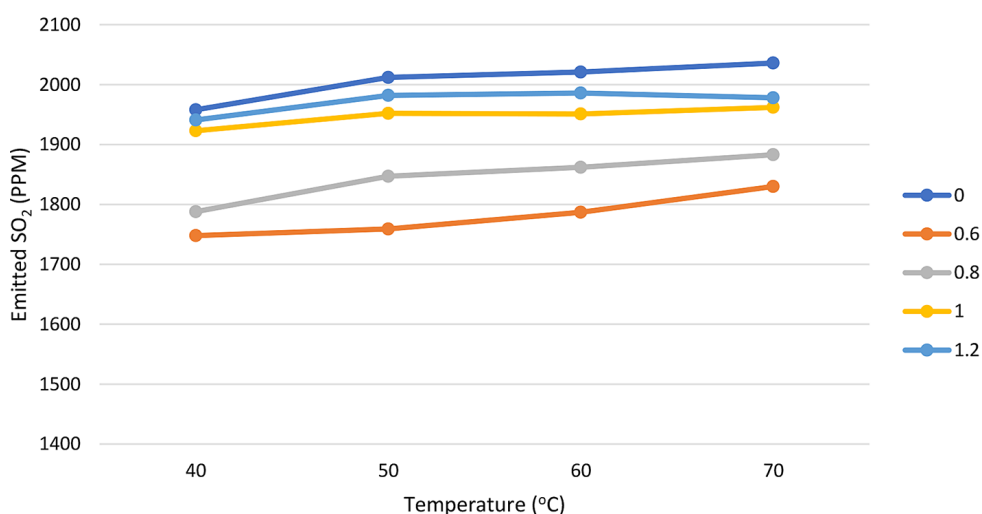


Figure 7. Emitted SO₂ at 40% concentration of oil shale at different activated carbon weights

However, it decreases with the amount of added activated carbon up to the value of 0.6 g/l and then increases to a concentration value of PPM when 1.2 g/l is added to activated carbon. It is to be noted that the concentration of emitted SO_2 increased by almost 80% compared with it the case when 20% of shale oil was used as indicated in Figure 5.

Figure 8, shows the emitted amounts of SO_2 from the burning of a mixture of diesel fuel and oil shale at 40% concentration of oil shale when various amounts of activated carbon were added to the mixture. As illustrated, the emitted concentration decreases from 2010 PPM (no activated carbon was added) to 1780 PPM with the amount of added activated carbon increasing up to almost 0.6 g/l, then it increases again with further addition of activated carbon. The reason for this could be that when the activated carbon gets filled up with sulfur compounds, it is possible to restore its effectiveness by heating it with an oxidizing agent like air or steam. This process causes the sulfur compounds to get oxidized and expelled from the surface of the carbon, making it possible to reuse the activated carbon in the desulfurization process.

In general, and comparing the present work, it may be stated that activated carbon is not commonly used as the primary method for desulfurizing shale oil due to its limited effectiveness in removing sulfur compounds compared to other methods. Other methods such as hydrotreating, oxidation, and adsorption with metal oxides or zeolites are typically more effective in reducing the sulfur content of shale oil. This might be due to the fact that activated carbon can be effective in removing certain sulfur compounds, such as thiophenes and mercaptans, but it may not be as effective in removing larger sulfur compounds

like dibenzothiophenes. In addition, activated carbon can become quickly saturated with sulfur compounds and require frequent regeneration or replacement, which can be costly. However, activated carbon is an appealing choice for large-scale industrial applications due to its relatively low cost. It is also widely accessible and can be obtained from various suppliers with ease. Additionally, the use of activated carbon for desulfurization is a simple process that doesn't require much equipment and can be conveniently incorporated into existing refining and processing facilities.

CONCLUSIONS

The main objective of this study was to desulfurize blends of heavy liquid fuels (diesel and shale oil) that are used to power a domestic boiler that is used for domestic heating. This was achieved by activated carbon that is produced from Jordanian oil shale. The emitted sulfur dioxide during the combustion process of the blends was measured to indicate the potential of the desulfurization process. From this study, the following may be concluded. The boiler operates smoothly with continuous combustion with a maximum shale oil percentage of 40%. The measured concentrations of the emitted SO_2 indicated that the desulfurization process was successfully achieved. The optimum amount of activated carbon used to minimize the emitted concentration of SO_2 were 1.0 and 0.6 gm/lit when 20 and 40% of shale oil were used, respectively. A decrease in SO_2 of 29 % when 20% of shale oil was in the blend, while it was 12% when 40% of shale oil was used.

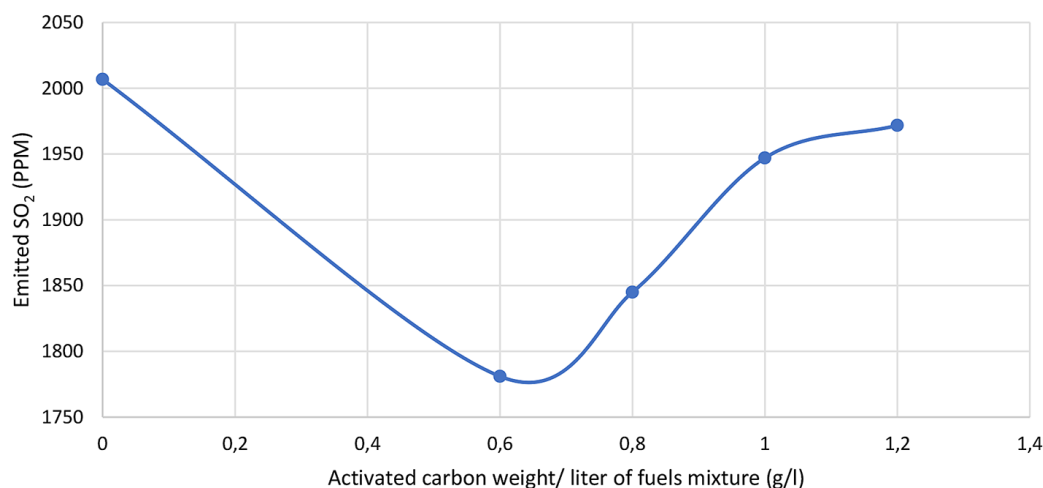


Figure 8. Emitted SO_2 at 40% concentration of oil shale

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