

## **H<sub>2</sub>S REMOVAL FROM SOUR LIQUEFIED PETROLEUM GAS USING JORDANIAN OIL SHALE ASH**

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*Oil shale ash was used to adsorb hydrogen sulfide from liquefied petroleum gas (LPG). Fixed mass of ash of particle size 500–710 μm showed a sorption capacity of 30 mg H<sub>2</sub>S per liter of LPG and one gram of ash from 150 ml LPG containing 467 ppm H<sub>2</sub>S. This value increased with increasing the volume of spiked gas and decreasing the particle size of the ash, while it decreased with increasing bed temperature. Ash samples did not adsorb hydrocarbons.*

### **Introduction**

Emission of toxic gases into the atmosphere is a primary source of air pollution. Combustion of heavy oil, coal and oil shale, as well as smelting operation, manufacturing of sulfuric acid and metallurgical processes are the main sources of discharge of these gases into the atmosphere. Once these gases enter the troposphere, they react with the molecules of water and oxygen to form acid rain. The presence of these gases in natural gas is the root for many major problems in the gas-processing industry. Hydrogen sulfide, for example, is certainly a highly hazardous material as it is flammable and poisonous to humans and animals, lethal dosis exceeding 1000 ppm. Therefore, it is required to treat clean sour gases from such pollutants and decrease its concentration in the rain.

Consequently, several attempts were made to diminish the discharge of acidic gases, in general, into the atmosphere. The removal technique most widely used is chemical absorption – treatment of acidic gas with amine solutions (MEA, DEA, MDEA) in absorption towers. Although chemical absorption is the most commonly used separation process in petrochemical industries, this method suffers from numerous problems including: high energy demand, corrosion, and susceptibility to foaming. Alternatively, adsorption process is used effectively. Numerous adsorbents are used to

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remove these toxicants from sour gases. Activated carbon is intensively used in treatment of sulfur dioxide [1–3], carbon dioxide [4–6], and hydrogen sulfide in upstream gases [7–9]. Other adsorbents such as  $\text{Ca}(\text{OH})_2$ -fly ash mixtures [10],  $\text{CuO}/\text{Al}_2\text{O}_3$  catalyst sorbent [11], titanium dioxide [12], clinoptilolite [13] and synthetic and natural zeolite [14–16] are also used. Unlike activated carbon, all the mentioned adsorbents contain either metal oxides or hydroxides.

Oil shale resources in Jordan are large. It is estimated that 50 billion tons of oil shale can be mined in open pits. Thermal treatment of oil shale yields enormous amounts of ash. In this work the feasibility of oil shale ash as adsorbent for cleaning LPG from hydrogen sulfide is studied.

## Experimental

Oil shale samples were brought from El-Lajjun deposit, Jordan. The rock samples were crushed, sieved to different particle sizes and stored in closed containers for further usage. Ashing of oil shale was performed by placing a fixed weight of known size oil shale into a muffle furnace operated at  $950\text{ }^\circ\text{C}$  for 8 h, the ash formed was directly placed into closed containers to prevent hydration. Untreated LPG was brought from Jordan petroleum refinery (JOPETROL). All chemicals were analytical-grade reagents from Scharlau, Spain. All glassware was Pyrex washed several times with soap and deionized water to remove any adhered impurities.

Sorption procedure was carried out by placing 0.3 g oil shale ash of different particle sizes (from  $45\text{ }\mu\text{m}$  to  $1.2\text{ mm}$ ) into a glass tube (0.5 cm ID, 15 cm length). The tube is surrounded by a glass jacket, and controlled-temperature water is circulating through this jacket to maintain isothermal conditions (Fig. 1). Dry air enters the bed from the bottom of the column at

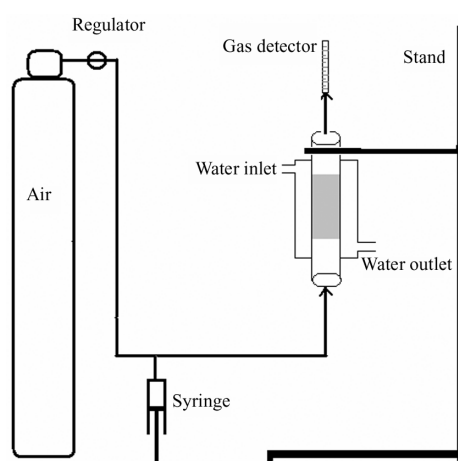


Fig. 1. Fixed-bed adsorption apparatus.

a constant flow rate of 1 L/min, while H<sub>2</sub>S tube detectors (Gastec-4H, Japan) are attached to determine the concentration of H<sub>2</sub>S at the other end of the glass bed. Samples of LPG of known volumes containing fixed concentration of H<sub>2</sub>S were injected into the upstream of the column. The concentration of H<sub>2</sub>S at the entrance and the exit of the column was measured after each injection, and the difference in concentration between the inlet and outlet streams was calculated. Similar procedure was used to determine sorption capacity of ash against hydrocarbons using a Gastec-103 tube detector. All the experiments were repeated at different temperatures of the bed, masses and particle sizes using dry and wet ash.

## Results and discussion

Samples of oil shale were tested in Royal Scientific Society of Jordan for their chemical composition (Table 1). The samples containing much silica, alumina and calcium oxide were ashed at 950 °C for 8 hours to evaporate water and organic matter.

Table 1. Chemical composition of oil shale ash from El-Lajjun area

Component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	CO <sub>3</sub>	S	TiO <sub>2</sub>	Na <sub>2</sub> O
wt. %	19.6	3.4	1.6	2.9	41.6	1.8	26.0	2.6	0.3	0.1

Adsorption of H<sub>2</sub>S was established by introducing a fixed volume of LPG containing hydrogen sulfide into the ash bed. The composition of LPG is shown in Table 2. The untreated gas (mainly propane and butane) contains 467 mg/L H<sub>2</sub>S. The exit stream was attached to the Gastec tube detector to monitor the variation in concentration of H<sub>2</sub>S.

Table 2. Chemical composition of untreated LPG, vol. %

Component	Concentration
Methane	0.0
Ethane	0.0
Propane	0.017
<i>i</i> -Butane .	42.334
<i>n</i> -Butane	27.748
Propylene	13.725
Butene-1	7.709
<i>t</i> -Butene-2	6.716
<i>cis</i> -Butene-2	0.776
<i>i</i> -Pentane	0.935
<i>n</i> -Pentane	0.049
H <sub>2</sub> S, ppm	467

Figure 2 shows the effect of particle size of dry ash on absorption of  $H_2S$ . The smaller are the particles, the more  $H_2S$  is absorbed. However, when particle size approaches  $710 \mu m$ , uptake effectiveness decreases, as shown by comparing the effect of particles of the size  $500\text{--}710 \mu m$  and  $710\text{--}1400 \mu m$ . Increasing sorption capacity with decreasing particle size is attributed to higher surface area of the contact between gas molecules and active sites of ash particles. In general the maximum uptake  $30 \text{ mg}$  per liter of LPG and one gram of ash was achieved treating  $150 \text{ ml}$  LPG with ash particles of the size  $500\text{--}710 \mu m$ .

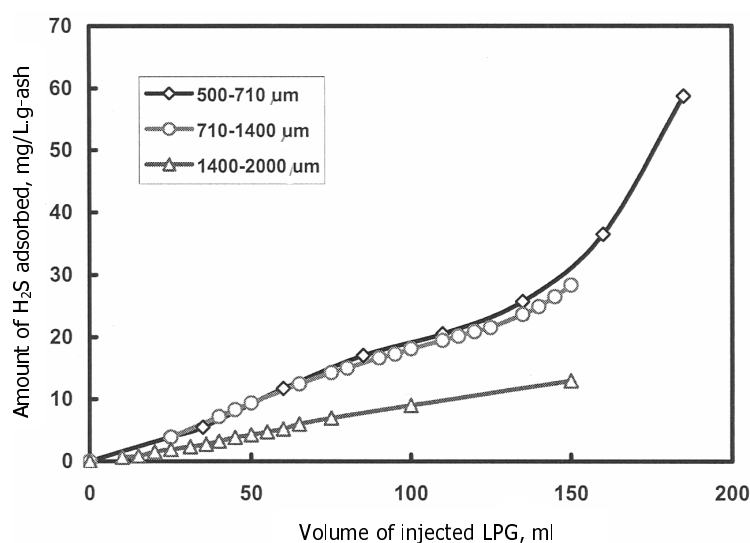


Fig. 2. Effect of particle size of dry ash on adsorption of  $H_2S$  from LPG stream.

The effect of temperature on adsorption of  $H_2S$  was investigated using dry ash (Fig. 3). It is shown that as the temperature of the system decreases, there is a noticeable increase in sorption capacity. This is expected because the higher temperature favors gas-phase interaction with ash due to the T-S entropy term in the free energy expression [17]. Thermodynamics would suggest that the most active sites would be occupied first providing the greatest heat of adsorption. Thus, it is to be expected that the heat evolved per mole of  $H_2S$  at low coverage would be higher than the heat evolved at high coverage.

Effect of wetting of ash was also considered in determination of  $H_2S$  uptake. The obtained results are plotted in Fig. 4. As one can see, the increase in water content of the ash sample noticeably increases the amount of  $H_2S$  uptake. This is due to the fact that wet ash absorbs gas molecules, which facilitate migration of dissolved gas into its microspores. As the

injection volume of H<sub>2</sub>S increases, the difference between uptake by wet and dry ash will also increase. This could be attributed to competition of gas molecules on the ash surface, that increases collision forces between these molecules. As a result, it enhances gas uptake with increasing of spiked amount of LPG.

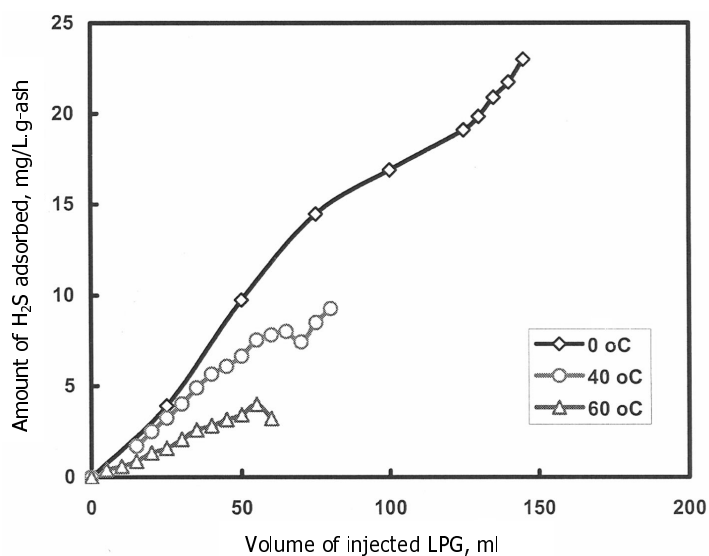


Fig. 3. Effect of bed temperature on adsorption capacity of H<sub>2</sub>S by dry oil shale ash.

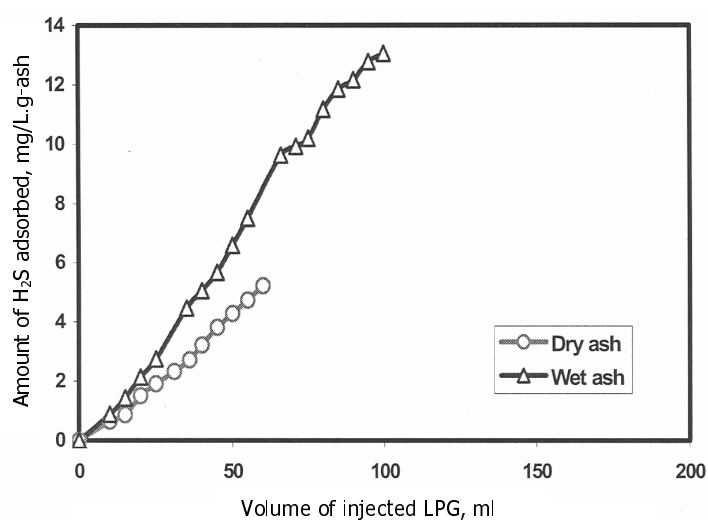


Fig. 4. Effect of wetting of ash on H<sub>2</sub>S uptake.

Figure 5 compares the ability of both wet and dry ash to adsorb hydrocarbon gases from LPG streams. The result indicates that injected hydrocarbons can escape into the detector through the bed without adsorption. This is because of hydrophobic nature of these hydrocarbons compared with that of hydrophilic  $H_2S$ . Moreover, ash itself is hydrophilic as it contains much metal oxides which attract  $H_2S$  and repulse hydrocarbons.

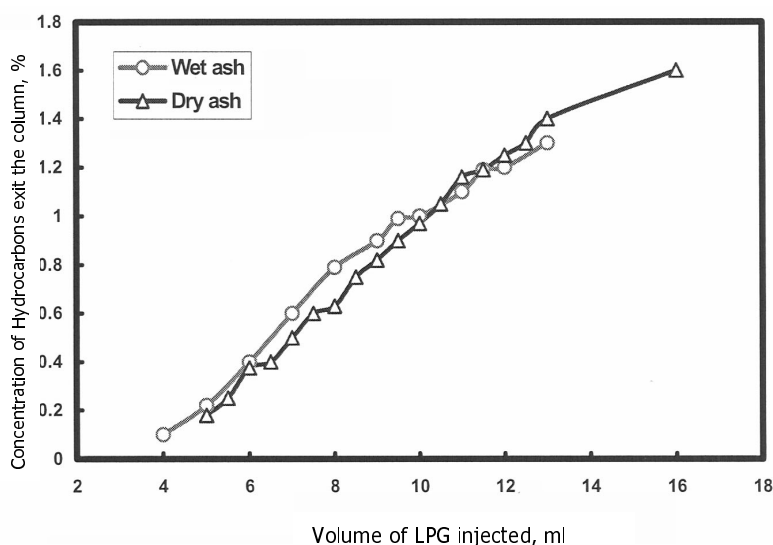


Fig. 5. Adsorption of hydrocarbons by oil shale ash.

## Conclusion

Untreated liquefied petroleum gas containing  $H_2S$  was passed through the bed of oil shale ash. The rate of  $H_2S$  uptake was directly affected by the amount of gas passing through the bed, temperature of the system and particle size of ash. This process is economical, safe and efficient.

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