

THE EFFECT OF SULFUR-PROMOTED RED MUD CATALYSTS ON HYDROLIQUEFACTION OF OIL SHALE

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Göynük oil shale was subjected to supercritical toluene extraction with/without catalyst. The catalysts used were red mud, sulfur-promoted red mud and commercial hydrogenation catalysts. The oils obtained were characterized by gas chromatography and column chromatography. Maximum conversion (~94 %) and extract yield (~64 %) were obtained at 400 °C. At this temperature, catalyst had no effect on conversion whereas it affected the extract yield. In addition, using of catalyst increased the amount of polar and aromatic compounds in the extract. Sulfur-promoted red mud showed the best reactivity to liquefaction of Göynük oil shale at 350 °C. Supercritical toluene extraction at 350 °C without catalyst resulted in a conversion of 34.8 %, but in the presence of sulfur-red mud it was 53–55 %.

Introduction

Oil shales are the second (after lignites) largest solid fuel reserve in Turkey with reserves totalling approximately five billion tonnes [1]. Three of the largest reserves are Göynük-Bolu (2.5 billion tonnes), Beypazari-Ankara (1 billion tonnes) and Seyitömer-Kütahya (1 billion tonnes). Turkish studies have mainly been focused on the Göynük and Seyitömer oil shales. Göynük

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oil shale (GOS) is extremely rich in oil [2] and is composed of liptinite (> 50 vol.%), huminite (20–50 vol%) and inertinite (0–20 vol%) maceral groups [3]. Liptinite and huminite are accompanied by smectite, clinoptilolite and calcite. At present, GOS is occasionally used for domestic purposes. Because of its properties and reserves, it can be considered a valuable potential source of liquid hydrocarbons.

Pyrolysis of GOS has been investigated by several workers [4, 5]. Ballice with co-authors [6] investigated its temperature-programmed pyrolysis. They suggested that thermal decomposition of kerogen in oil shale takes place in two broad reaction steps. The first one occurs at ~440 °C. In this step, kerogen is broken down to bitumen and low-molecular-weight hydrocarbons consisting mainly of methane. Decomposition of bitumen to gas and oil, and formation of heavy fractions take place in the second step. Akat *et al.* [7] observed that the main characteristics of GOS are their high content of alkenes and heterocyclic polar compounds, and higher content of aromatics as compared with crude oil.

Studies under many different conditions have been undertaken to try to increase the yield of oil from GOS [4]. It has been shown that the use of a carrier gas during pyrolysis provides an increase in yield over ordinary pyrolysis.

Usage of water vapor as carrier led to 66-% increase in oil yield. The use of water vapor also affected the oil composition, giving an increased proportion of aliphatic hydrocarbons. In our previous studies [8, 9], GOS was subjected to supercritical water and supercritical toluene extraction. Supercritical water extraction gave the highest liquid yield (75 wt%, dry ash-free basis), but this oil contained a high proportion of asphaltenes and polar compounds, 45.2 and 36.5 % respectively. Experiments carried out in our laboratory have shown that supercritical fluid extraction of GOS with toluene in the presence of catalyst is a potentially useful method.

The major problem concerning catalysts for liquefaction of solid fossils is the difficulty of their reuse because of the difficulties at separation and/or deactivation. Cheap iron-based catalysts, such as red mud, iron ores and natural pyrite have been intensively studied for liquefaction of coal [10–15]. Red mud (RM) is one of the main tailings of the aluminium industry. It consists mainly of Fe_2O_3 , Al_2O_3 and SiO_2 . RM has been widely used in coal liquefaction [16–18]. Although there are many liquefaction studies where RM was used as catalyst, to our knowledge there have been no studies concerning the liquefaction of oil shale with RM.

In this study, hydroliquefaction of GOS with RM and commercial catalysts in the presence of toluene was investigated. In addition, oil shale was subjected to conventional pyrolysis for comparative purposes.

Experimental

Materials

Characteristics of Göynük oil shale used are as follows:

- Proximate and ultimate analysis wt% (air-dry basis): moisture 12.8, ash 20.4, volatile matter 61.2, fixed carbon 18.4, C (total) 55.7, H 8.2, S (total) 4.4, N 1.6, O 9.6;
- Fischer assay, wt%: shale oil 22.8, gas 25.6, water 6.0, residue 45.6.

The oil shale samples were ground to <0.1 mm and dried at 105 °C under nitrogen.

The RM was obtained from the *Seydisehir Aluminium Company*, Turkey. RM received from plant was filtered and dried at 105 °C, then crushed and sieved to <0.1 mm.

The commercial CoMo/Al₂O₃ (UDP S-12) and NiMo/Al₂O₃ (UOP S-16) catalysts were supplied by *Petkim Petrochemical Holding Co.* located in Izmir, Turkey.

Composition of RM and commercial catalysts was analyzed by X-ray fluorescence spectrophotometry, wt%:

- Red mud: SiO₂ 17.25, Fe₂O₃ 37.26, Al₂O₃ 18.12, CaO 4.18, TiO₂ 5.15, P₂O₅ 0.16.
- UDP S-12: CoO 3.62, MoO₃ 27.59, Al₂O₃ 68.79.
- UOP S-16: NiO 2.22, MoO₃ 26.98, Al₂O₃ 70.80.

Procedure

Liquefaction experiments were performed as described in our previous study [9]. 25 g of oil shale sample, 75 g of toluene and 1 g of catalyst were charged into the rotating autoclave. After pressuring with H₂ of 5 MPa, the autoclave content was heated to reaction temperature at a heat rate of 5 °C/min and held at this temperature for 1 h. After the reaction, the reactor was cooled to room temperature by fan. The gases were withdrawn and analyzed by gas chromatograph containing two series columns with a thermal conductivity detector.

The liquid and solid residues in the autoclave were separated by filtration. The solid residue was extracted in a Soxhlet extractor with toluene and tetrahydrofuran (1:1). The Soxhlet extract was combined with the filtrate. Solvent was stripped off by rotary evaporation at <50 °C under vacuum, then the remaining part was weighed as extract. The solid residue remaining from the Soxhlet extraction was dried and weighed as spent shale and its ash content was determined using the ASTM D-3174.

In conventional pyrolysis experiments, oil shale samples (<3 mm) were pyrolyzed in a Jeckner retort. The retort was heated from room temperature to 550 °C at a rate of 5 °C/min under atmospheric pressure and held at this temperature for 2 h.

In pyrolysis experiments, the liquid products condensed in traps were weighed. The residues in the pyrolysis apparatus were weighed as spent shale.

The total conversion of oil shale and extract yield in hydroliquefaction were calculated by using the equations below:

$$\text{Conversion (\%)} = \frac{\text{Oil shale (g, daf basis)} - \text{Insoluble organic parts (g)}}{\text{Oil shale (g, daf basis)}} * 100$$

$$\text{Extract yield (\%)} = \frac{\text{Weight of extract (g)}}{\text{Weight of oil shale (g, dry basis)}} * 100$$

$$\text{Gas + Losses (\%)} = 100 - (\text{Spent shale} + \text{Extract yield})$$

The asphaltenes of the extracts, or liquid product, were precipitated with *n*-hexane and soluble in *n*-hexane portions (oils) were fractionated by column chromatography into aliphatic, aromatic and polar fractions by using hexane, toluene and methanol, respectively [8]. Oils were subjected to gas chromatographic analysis to determine the hydrocarbon distribution using ASTM D 2887 method, and their average molecular weight distribution was determined by a vapor pressure osmometer.

Results and Discussion

The optimum reaction conditions for hydroliquefaction of GOS in the presence of RM were specified by the pre-experiments. They were: initial hydrogen pressure of 5 MPa, reaction time of 60 min, ratio of solvent to solid of 3/1, and RM quantity of 1 wt%. However, under these optimum conditions, usage of RM in hydroliquefaction of GOS at 350 °C slightly increased the conversion and extract yield. To increase the catalytic activity of RM, different types of sulfur compounds were used as promoter.

To investigate the influence of types and amounts of sulfur compound on hydroliquefaction of GOS, a series of experiments with RM + sulfur compounds of different weight ratios of S/RM was carried out at 350 °C. Elemental sulfur, CS₂ and Na₂S were used as sulfur promoter. Table 1 shows the product distribution and the composition of extract and gaseous products obtained from GOS in the presence of RM, and RM with sulfur catalysts.

The addition of sulfur compounds increased the catalytic activity of RM. The conversion and extract yield at 350 °C tended to increase with an increase in sulfur amount. The presence of sulfur compounds had no effect on the gas yield. However, the composition of gaseous products varied with the type of sulfur compounds. The usage of elemental S as promoter led to significant increases in C₂–C₄ amounts, whereas it decreased the formation of CH₄. In contrast, the amount of CH₄ was not significantly changed by addition of Na₂S and CS₂, and also the increase in C₂–C₄ amount was lower than that of using S.

Table 1. Influence of Red Mud/Sulfur Ratios, g/g, on GOS Hydroliquefaction at 350 °C, %

| | Ratio | | | | | | | | |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | – | 1/0 | 1/0.2 | 1/0.4 | 1/0.6 | 1/0.8 | 1/1 | 1/1.5 | 1/2 |
| Red mud/elemental sulfur | | | | | | | | | |
| Conversion | 34.8 | 39.9 | 43.6 | 46.5 | 48.7 | 53.2 | 53.2 | | |
| Gas yield | 10.7 | 9.9 | 10.2 | 9.3 | 9.2 | 9.9 | 10.7 | | |
| Extract yield | 17.0 | 21.9 | 24.2 | 27.7 | 29.6 | 32.5 | 31.6 | | |
| Spent shale | 72.3 | 68.2 | 65.6 | 63.0 | 61.2 | 57.6 | 57.7 | | |
| Composition of extract, wt%: | | | | | | | | | |
| Oil | 51.8 | 44.4 | 46.3 | 44.0 | 46.8 | 47.0 | 45.8 | | |
| Asphaltenes | 48.2 | 55.6 | 53.7 | 56.0 | 53.2 | 53.0 | 54.2 | | |
| Composition of gas, vol%: | | | | | | | | | |
| C ₁ | 30.82 | 28.20 | 29.00 | 27.52 | 21.21 | 15.43 | 12.51 | | |
| C ₂ –C ₄ | <0.10 | 9.50 | 16.00 | 21.65 | 25.36 | 29.13 | 35.09 | | |
| CO | 7.43 | 3.50 | 4.50 | 5.50 | 7.45 | 8.25 | 8.14 | | |
| CO ₂ | 61.65 | 52.50 | 50.50 | 45.33 | 45.98 | 47.09 | 44.26 | | |
| Red mud/Na ₂ S | | | | | | | | | |
| Conversion | | | 43.9 | 47.1 | 52.1 | 55.6 | 53.5 | | |
| Gas yield | | | 10.5 | 10.7 | 11.2 | 10.6 | 15.0 | | |
| Extract yield | | | 24.4 | 26.8 | 30.2 | 33.6 | 31.6 | | |
| Spent shale | | | 65.1 | 62.5 | 58.6 | 55.8 | 53.4 | | |
| Composition of extract, wt%: | | | | | | | | | |
| Oil | | | 46.2 | 46.2 | 49.1 | 49.6 | 44.5 | | |
| Asphaltenes | | | 53.8 | 53.8 | 50.9 | 50.4 | 55.5 | | |
| Composition of gas, vol%: | | | | | | | | | |
| C ₁ | | | 31.75 | 33.10 | 34.78 | 35.28 | 34.40 | | |
| C ₂ –C ₄ | | | 4.84 | 6.76 | 5.19 | 5.70 | 4.70 | | |
| CO | | | 7.71 | 8.22 | 8.85 | 7.80 | 7.20 | | |
| CO ₂ | | | 55.69 | 51.91 | 51.07 | 51.22 | 53.70 | | |
| Red mud/CS ₂ | | | | | | | | | |
| Conversion | | | 43.0 | | 43.9 | | 47.1 | 53.4 | 47.5 |
| Gas yield | | | 9.4 | | 9.3 | | 9.2 | 9.3 | 8.7 |
| Extract yield | | | 25.2 | | 26.4 | | 28.3 | 33.2 | 29.1 |
| Spent shale | | | 65.4 | | 64.3 | | 62.5 | 57.5 | 62.2 |
| Composition of extract, wt%: | | | | | | | | | |
| Oil | | | 55.9 | | 55.7 | | 54.7 | 58.1 | 53.0 |
| Asphaltenes | | | 44.1 | | 44.3 | | 45.3 | 41.9 | 47.0 |
| Composition of gas, vol%: | | | | | | | | | |
| C ₁ | | | 30.49 | | 30.78 | | 31.03 | 31.50 | 32.70 |
| C ₂ –C ₄ | | | 10.56 | | 10.82 | | 10.80 | 11.20 | 11.70 |
| CO | | | 6.50 | | 6.90 | | 7.40 | 7.80 | 8.80 |
| CO ₂ | | | 52.45 | | 52.1 | | 50.77 | 49.50 | 46.80 |

The obtained maximum extract yields and conversion values for all RM + sulfur catalysts were much closer. However, the weight ratios of RM/sulfur compounds which gave the maximum extract yields were different: it was 1/0.8 for elemental S and Na₂S and 1/1.5 for CS₂. In our previous study concerning hydroliquefaction of GOS [9], we obtained a similar product distribution and conversion with pyrite catalyst. This shows that the active sites of the sulfur compounds + Fe₂O₃ (from RM) and FeS₂ catalysts have to be similar in the working state at hydroliquefaction of GOS. It has been reported that sulfur additives promote the formation of iron sulfides which have a higher catalytic activity than that of iron oxides. Under hydroliquefaction conditions, these additives maintain H₂S pressure and convert Fe into pyrrhotite.

The important role played by the SH· radicals and by the *in-situ*-obtained pyrrhotite in the hydrogenation process, and the catalytic effect of these additions has been shown in the literature [10, 19–25]. Moreover, Wang *et al.* [26] have proposed that at hydroliquefaction of coal the active site in the working state of Fe₂O₃ + S catalyst was not Fe_{1-x}S. They suggested that the surface sulfate (SO₄²⁻) on the surface of iron oxide (Fe₂O₃) was formed by oxidation of sulfide and acted as an active site in the hydroliquefaction of coal.

As we did not aim to determine the active site in sulfur-promoted iron oxide catalysts, the surface species of spent catalysts were not investigated. Therefore, we cannot give any explanation on the working state of tested catalysts. However, we can mention that sulfur-promoted iron oxides and FeS₂ catalyst have similar active species at GOS liquefaction.

Table 2. GOS Hydroliquefaction at 400 °C in the Presence of Sulfur-Promoted Red Mud Catalysts, %

| | Catalyst | | | | |
|--------------------------------|----------|------|-------------------------------|-------------------------------|---------------|
| | – | RM | RM/CS ₂ (1/1.5) | RM/Na ₂ S (1/1) | RM/S (1/1) |
| Conversion | 89.1 | 92.3 | 94.0 | 94.3 | 94.6 |
| Gas yield | 19.6 | 20.1 | 20.1 | 11.4 | 12.8 |
| Extract yield | 51.2 | 53.3 | 54.7 | 63.7 | 62.4 |
| Spent shale | 29.2 | 26.6 | 25.2 | 24.9 | 24.8 |
| Composition of gas, vol%: | | | | | |
| C ₁ | 40.4 | 47.7 | 51.7 | 49.3 | 48.7 |
| C ₂ –C ₄ | 12.7 | 7.7 | 14.9 | 20.7 | 16.3 |
| CO | 0.1 | 3.8 | 4.2 | 4.1 | 4.5 |
| CO ₂ | 43.8 | 40.8 | 29.1 | 25.9 | 30.5 |

Table 2 shows the distribution of products formed on hydroliquefaction at 400 °C. A comparison of the results obtained at 350 and 400 °C shows that the temperature has a considerable effect on the dissolution of kerogen. The conversion values were 89 and around 94 % for the thermal run and the cata-

lytic run, respectively. In contrast to experiments at 350 °C, product distribution varied depending on the type of sulfur promoter. Using Na₂S and S led to the formation of extract whereas it decreased the amount of gaseous products. However, the distribution of products formed on hydroliquefaction at 400 °C both in the presence of RM, RM + CS₂ and RM + FeS₂ [9], and in the absence of catalyst was much closer. At higher temperature the Na₂S and S mechanisms seem to be different. As for gaseous products, total yields of CO and CO₂ decreased and C₁–C₄ hydrocarbons increased in the presence of sulfur promoter.

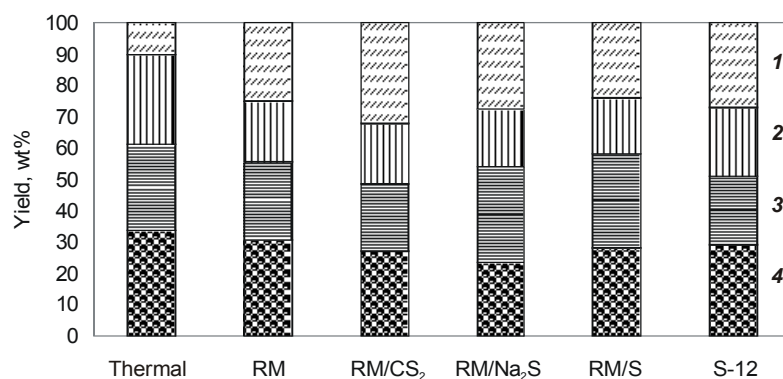
For comparative purposes, hydroliquefaction experiments were carried out at 350 and 400 °C with commercial catalysts (S-12 and S-16) under the same conditions as used for RM (Table 3). At 350 °C, both conversion and extract yields were lower with commercial catalysts than with sulfur-promoted RM. At 400 °C, thermal effect on conversion was pronounced, similarly to that of sulfur-promoted catalysts. However, the CoMo/Al₂O₃ catalyst led to the formation of more extract and less gaseous products than the thermal run. By comparing the results obtained with sulfur-promoted RM and commercial catalysts, the following aspects must be mentioned. First, at lower temperature sulfur-promoted RM catalysts give better conversion and extract yields than commercial catalysts (CoMo/Al₂O₃ and NiMo/Al₂O₃). Second, at higher temperature conversion levels in both thermal and catalytic runs are much closer. However, the extract yields with Na₂S/RM, S/RM and CoMo/Al₂O₃ were greater than those obtained in the thermal run and the catalytic run with RM, CS₂/RM and NiMo/Al₂O₃.

Table 3. GOS Hydroliquefaction with Commercial Catalysts, %

| | Temperature, °C | | | |
|-------------------------|-----------------|------|------|------|
| | 350 | | 400 | |
| | Catalyst | | | |
| | S-12 | S-16 | S-12 | S-16 |
| Conversion | 43.8 | 43.9 | 89.8 | 90.0 |
| Gas | 8.5 | 10.5 | 12.1 | 22.5 |
| Extract | 26.3 | 24.5 | 59.4 | 51.5 |
| Spent shale | 65.2 | 65.0 | 28.5 | 26.0 |
| Composition of extract: | | | | |
| Oil | 70.7 | 70.8 | 72.7 | 77.6 |
| Asphaltenes | 29.3 | 29.2 | 27.3 | 22.4 |

The composition of extracts is given in the Figure, and some properties of the oil fractions from extracts obtained from catalytic and thermal runs at 400 °C – in Table 4. The catalyst had no important effect on boiling-point range of hydrocarbons in the oil fraction. Considering oil composition, the usage of catalyst led to an increase in polar and a decrease in aromatic com-

pounds. In addition, the commercial catalyst led to a slight increase in the molecular weight of oil.



Composition of extracts obtained on catalytic and thermal hydroliquefaction at 400 °C: 1 – polar compounds; 2 – aromatics, 3 – aliphatics; 4 – asphaltenes

Table 4. Some Properties of Oils Obtained on GOS Hydroliquefaction at 400 °C

| | Thermal run | Catalyst | | | | | |
|----------------------------|-------------|----------|-------------------------------|-------------------------------|---------------|------|------|
| | | RM | RM/CS ₂ (1/1.5) | RM/Na ₂ S (1/1) | RM/S (1/1) | S-12 | S-16 |
| Molecular mass M | 370 | 502 | 403 | 411 | 420 | 454 | 470 |
| Initial boiling point, °C | 180 | 179 | 181 | 176 | 182 | 181 | 179 |
| Distillation, vol%, at °C: | | | | | | | |
| 10 | 225 | 223 | 226 | 223 | 245 | 258 | 252 |
| 30 | 310 | 295 | 268 | 286 | 300 | 296 | 320 |
| 50 | 378 | 362 | 323 | 361 | 375 | 348 | 369 |
| 70 | 470 | 450 | 403 | 465 | 460 | 433 | 486 |
| 90 | 560 | 525 | 506 | 550 | 541 | 529 | 541 |
| End point, °C | 680 | 670 | 675 | 665 | 620 | 645 | 610 |

Beside supercritical extraction, GOS was also pyrolyzed at 550 °C by well-known retorting method. The yields and composition of liquid product obtained at GOS conventional pyrolysis are as follows, wt% (dry basis):

- liquid product yield 26.1, spent shale 51.7, gas + loss 22.2,
- composition of liquid product: asphaltenes 12.0, aliphatics 42.8, aromatics 19.1, polar compounds 26.0.

They were markedly different from those obtained by hydroliquefaction. Even if the temperature was higher in the pyrolysis experiments, we obtained less liquid product and more gas and spent shale than at hydroliquefaction. In addition, the liquid product of pyrolysis contained less asphaltenes due to the occurrence of secondary reactions (repolymerizations and further cracking) during pyrolysis.

Higher asphaltene and polar compound content of the extract obtained from hydroliquefaction indicate that supercritical interaction led to dissolution of kerogen fragments. The presence of sulfur-promoted RM enhanced these interactions.

Conclusions

The hydroliquefaction of GOS was carried out by supercritical toluene extraction in the presence of catalysts such as RM, sulfur-promoted RM and commercial metal-supported alumina catalysts. Sulfur-promoted RM showed the best reactivity to liquefaction of GOS at 350 °C, whereas RM itself had a negligible effect. For all tested sulfur-RM catalysts (CS₂/RM, S/RM, Na₂S/RM), the results were much closer. The reactivity of commercial catalysts was better than that of RM but less than sulfur-RM catalysts. Supercritical toluene extraction at 350 °C in the absence of catalyst gave 34.8-% conversion of kerogen, however in the presence of sulfur-RM catalysts, the conversion was around 53–55 %.

Maximum conversion of kerogen (~94 %) was obtained at 400 °C. As the temperature has a greater effect on hydroliquefaction of oil shale than the catalyst, the conversion was not effected by usage of catalyst at this temperature. However, the yield of extract varied with the catalyst type. S/RM, Na₂S/RM and CoMo/Al₂O₃ produced more extract than the thermal run and the catalytic run with RM, RM/CS₂ and NiMo/Al₂O₃. In addition, it was observed that the catalysts increased the amount of polar and of aromatic compounds in the oils at 400 °C.

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