

LIQUEFACTION OF NİĞDE-ULUKIŞLA OIL SHALE: THE EFFECTS OF PROCESS PARAMETERS ON THE CONVERSION OF LIQUEFACTION PRODUCTS

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Abstract. In this paper, the direct liquefaction of Turkish Niğde-Ulukışla oil shale in noncatalytic and catalytic conditions was studied. The effects of pressure, tetralin/oil shale ratio, catalyst type and concentration, reaction time and temperature and oil shale/waste paper ratio on the process were investigated. It was found that tetralin/oil shale ratio had no considerable effect on the total and liquefaction products conversions under the non-catalytic conditions. Fe_2O_3 , MoO_3 , $\text{Mo}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$ and zeolite were used as catalysts in catalytic liquefaction. The highest total and liquefaction products conversions were obtained using MoO_3 as catalyst at a concentration of 9% by weight. Reaction temperature of 400 °C and reaction time of 90 minutes were chosen according to obtained liquefaction results. Co-liquefaction experiments were performed using waste paper. Both the total and oil + gas conversions were increased to a considerable extent by the application of the co-liquefaction process. According to gas chromatographic-mass spectrometric (GC-MS) analysis, the liquid product from the liquefaction process of oil shale under catalytic conditions of experiment 22 consisted mainly of naphthalene and its derivatives and polycyclic hydrocarbon such as indene and its derivatives.

Keywords: oil shale liquefaction, total conversion, liquefaction products, Niğde-Ulukışla.

1. Introduction

The world energy demand has increased sharply in recent decades with an ongoing economic growth of community. The fossil fuels currently provide over 80% of the world's energy consumption, but it is expected that their reserves will diminish within this century. As a result, production of

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alternative liquid fuels should be developed to meet global energy demand. Coal liquefaction technology applied either directly or indirectly is considered to be a promising method for the production of liquid fuels, as well as chemical feedstock [1–3]. Similarly to coal liquefaction technology, oil shale can also be converted to liquid fuels and feedstock for the production of chemicals.

Oil shale is a sedimentary rock consisting of organic matter in its mineral matrix. Kerogen is a major organic matter of oil shale and is a cross-linked macromolecule of mainly carbon, hydrogen and oxygen. Shale oil, considered as an alternative fuel for crude oil, is obtained from kerogen [4]. Since total world proven reserves of oil shale are approximately 80 billion tons, it is regarded as an alternative source of liquid fuel [5]. Oil shale has higher atomic H/C ratio than lignite due to its lower rank [6, 7]. Thus, the addition of hydrogen to the reaction medium, which mainly determines the cost of liquefaction processes, could be minimized by use of oil shale in these processes. As a result, much of the research has been focused on the possibility of liquefaction of oil shale by pyrolysis [8–14], co-pyrolysis [15–21], supercritical fluid extraction (SFE) [5, 22–24] and retorting [25–29].

Turkey has 3 to 5 billion tons of estimated oil shale reserves located in the middle and western parts of Anatolia and detailed studies on oil shale potentials of Turkey for production of liquid fuels are reported in literature [30–33]. Since oil shale deposits of Turkey constitute the second largest fossil fuels after lignite, the conversion of oil shale to liquid fuels as an alternative to petroleum becomes an important process. Metecan et al. [34] studied the effect of pyrite catalyst on the hydroliquefaction of Göynük oil shale. The researchers reported that the maximum conversion and yield of extract were observed at 400 °C with and without pyrite catalyst in the presence of toluene. Pyrite catalyst exerted a considerable effect on those below 400 °C and caused an increase of the amount of hydrocarbons in gaseous products and a decrease of the molecular weight of oils at 450 °C. Olukcu et al. [35] examined the liquefaction of Beypazarı oil shale by pyrolysis, one of the oldest liquefaction techniques used, to produce liquid fuels (named as syncrude) from solid fossils and found that in free-falling pyrolysis the maximum conversion was 61.9% at 873 K, whereas in conventional pyrolysis it was 50.5% at 798 K. Compared with free-falling pyrolysis during which the cracking reaction took place to a greater degree, conventional pyrolysis yielded less n-alkenes at the same temperature, 798 K. Balice [36] investigated the effect of the mineral matter of Beypazarı oil shale on the pyrolysis yield and product composition. It is reported that removal of the material soluble in HCl and HNO₃ affected the conversion of organic materials whereas the leaching of pyrites with HNO₃ did not cause a change in the reactivity of the organic material during pyrolysis.

Although a number of studies have been carried on the production of solid, liquid and gaseous products from oil shale, more attention should be

paid to the liquefaction of oil shale due to the dependence of process yield on several factors such as oil shale rank and process parameters. The purpose of this study is to carry out the direct liquefaction of Niğde-Ulukışla oil shale under both noncatalytic and catalytic conditions in a nitrogen gas atmosphere and to investigate the effects of parameters, including tetralin/oil shale ratio, catalyst type and concentration, reaction time and temperature and waste paper amount, on the process. Besides, oils, which are liquid products obtained from the liquefaction process as solubles in hexane, are also analyzed qualitatively to determine their composition.

2. Experimental

Niğde-Ulukışla oil shale and waste paper used in this study were first ground and dried in the laboratory atmosphere. The results of proximate and ultimate analyses of both are given in Table 1.

The liquefaction reactions were carried out in a 500 ml batch autoclave with a motor driven stirrer (PARR Brand Model 4575, USA) in the presence of tetralin used as solvent under both noncatalytic and catalytic conditions in a nitrogen gas atmosphere (Fig. 1).

The reaction temperature was maintained with ± 2 °C accuracy. Commercially available Fe_2O_3 , MoO_3 , $\text{Mo}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$ and zeolite were used without further treatment to compare their catalytic activities in catalytic experiments. Figure 2 shows the flowchart of the experimental procedure.

Table 1. Proximate and ultimate analyses of oil shale and waste paper samples

	Niğde-Ulukışla oil shale	Waste paper
Proximate analysis, wt% as used		
Moisture	4.00	2.60
Ash	69.91	5.88
Volatile matter	17.41	80.00
Fixed carbon ^a	8.68	11.52
Total sulphur	2.13	–
Ultimate analysis, wt% daf		
C	10.04	43.43
H	1.22	5.76
N	–	–
S	0.27	0.09
O ^a	88.47	50.72

^a – by difference; daf – dry ash free

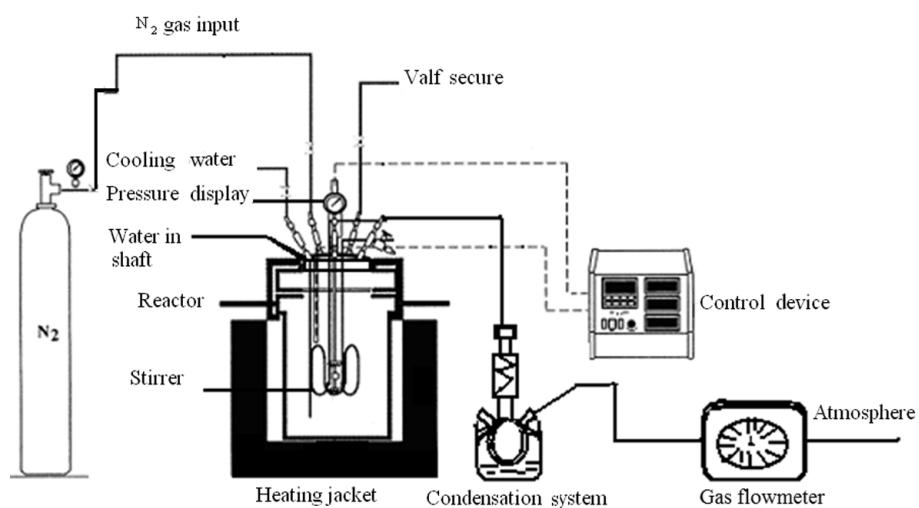


Fig. 1. The experimental set-up.

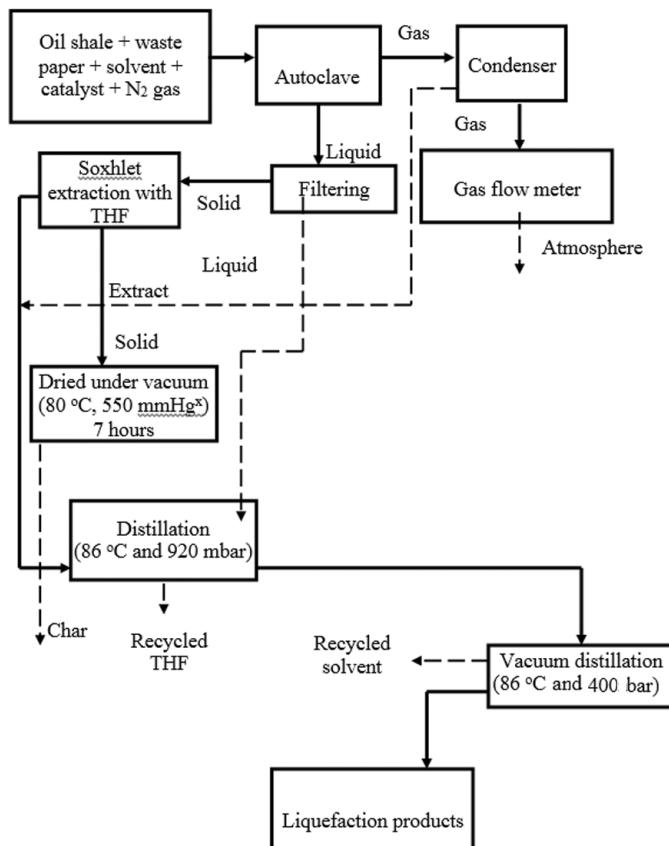


Fig. 2. Flowchart of the experimental procedure.

30 g of oil shale and a prescribed amount of tetralin were charged into the autoclave and then purged and pressurized to 50 bar with a flow of nitrogen at room temperature. In the liquefaction experiments conducted in the presence of catalyst or waste paper the prescribed amounts of both were also added to the autoclave. The content of autoclave was heated to the reaction temperature for about 1 hour with stirring. After each run, the autoclave was immediately cooled. The solid and liquid products were removed from the reactor carefully and solids obtained by filtration were analyzed by successive solvent extraction. The liquid products obtained from the liquefaction process were separated into oils (hexane soluble), asphaltene (toluene soluble but hexane insoluble) and preasphaltene (THF soluble but toluene insoluble), depending on the differences in their solubility. The total conversions were calculated according to char yields, while preasphaltene (PAS), asphaltene (AS) and oil + gas conversions were calculated according to the results of solvent extraction processes. The char yields and conversions were calculated by the use of Equations (1)–(5) given below.

Specifically, char yield was described as follows:

$$\text{Char (daf) \%} = \text{char (daf, g)/sample (daf, g)} \times 100. \quad (1)$$

Equation (2) was used to calculate total conversion (liquefaction products + gas):

$$\text{Total conversion \%} = 100 - \text{char \% (daf)}. \quad (2)$$

The conversion of liquefaction products, preasphaltene and asphaltene, was calculated by Equations (3) and (4), respectively:

$$\text{PAS \%} = \text{PAS (g)/sample (daf, g)} \times 100, \quad (3)$$

$$\text{AS \%} = \text{AS (g)/sample (daf, g)} \times 100. \quad (4)$$

The calculation of conversion of oil + gas was done as follows:

$$(\text{Oil + gas}) \% = \text{total conversion \% (daf)} - \text{PAS \%} - \text{AS \%}. \quad (5)$$

The noncatalytic and catalytic conditions of liquefaction of Niğde-Ulukışla oil shale determined by considering the process parameters such as tetralin/oil shale ratio, catalyst type and concentration, reaction time and temperature and oil shale/waste paper ratio are given in Table 2.

Gas chromatography-mass spectrometry (GC-MS) analysis of oils was carried out by an Agilent 6890 N Network model gas chromatograph equipped with an Agilent 5973 model mass spectrometer. The product distributions were conducted using a DB-1701 capillary column (30 m × 0.25 mm, 0.25 μm film thickness) in the presence of helium as a carrier gas at a flow rate of 5 ml d⁻¹. The column was held at 60 °C for 1 min and then heated to 240 °C at a rate of 4 °C·min⁻¹ and finally held isothermal for 10 min. The injector temperature was 250 °C and injection volume 1 μl.

Table 2. Noncatalytic and catalytic conditions of the liquefaction process (particle size –250, +125 µm, stirring speed 800 rpm)

Exp. No	Pressure, bar	Tetralin/ oil shale	Catalyst type	Catalyst con., wt%	Time, min	Temperature, °C	Oil shale/ waste paper
Effect of pressure							
1	0	3	–	–	60	400	–
2	25	3	–	–	60	400	–
3	50	3	–	–	60	400	–
4	75	3	–	–	60	400	–
Effect of solvent/oil shale ratio							
5	50	1	–	–	60	400	–
3	50	3	–	–	60	400	–
6	50	6	–	–	60	400	–
7	50	9	–	–	60	400	–
Effect of catalyst type							
8	50	3	Fe ₂ O ₃	3	60	400	–
9	50	3	MoO ₃	3	60	400	–
10	50	3	Mo(CO) ₆	3	60	400	–
11	50	3	Cr(CO) ₆	3	60	400	–
12	50	3	Zeolite	3	60	400	–
Effect of catalyst concentration							
13	50	3	–	0	60	400	–
9	50	3	MoO ₃	3	60	400	–
14	50	3	MoO ₃	6	60	400	–
15	50	3	MoO ₃	9	60	400	–
Effect of reaction time							
16	50	3	MoO ₃	9	30	400	–
15	50	3	MoO ₃	9	60	400	–
17	50	3	MoO ₃	9	90	400	–
18	50	3	MoO ₃	9	150	400	–
Effect of reaction temperature							
19	50	3	MoO ₃	9	90	350	–
20	50	3	MoO ₃	9	90	375	–
17	50	3	MoO ₃	9	90	400	–
21	50	3	MoO ₃	9	90	425	–
Effect of oil shale/waste paper ratio							
22	50	3	MoO ₃	9	90	400	1
23	50	3	MoO ₃	9	90	400	2
24	50	3	MoO ₃	9	90	400	3
25	50	3	MoO ₃	9	90	400	4

The abbreviations used: Exp. – Experiment; con. – concentration.

3. Results and discussion

3.1. Effect of pressure

Although hydrogen gas is used to increase the conversion of liquid products in coal liquefaction processes, it can be provided from both the coal and the hydrogen-donor solvent so that coal can be liquefied under nitrogen gas [37]. In this study, the liquefaction of Niğde-Ulukışla oil shale was conducted

under nitrogen gas and as can be seen from Figure 3, the total and oil + gas conversion values increased at pressures between 0 and 50 bar but then they decreased slightly at pressures up to 75 bar. This behavior can be attributed to an effective penetration of the solvent through oil shale pores with pressure. But at higher pressure, the diffusion of liquefaction products formed in the pores can be prevented, as a result, a slight decrease in both conversions was observed and the optimum pressure was determined as 50 bar.

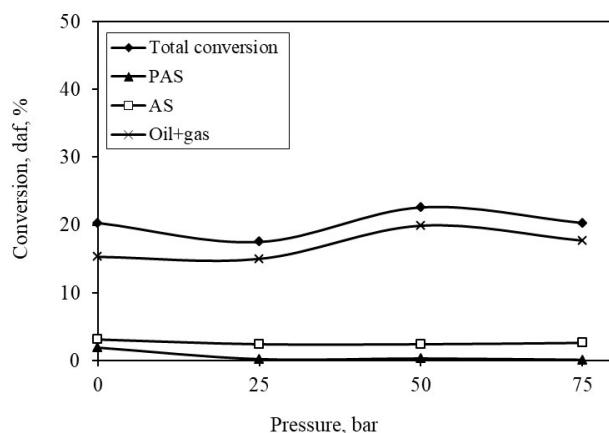


Fig. 3. Effect of initial nitrogen pressure on the liquefaction products conversion in the noncatalytic liquefaction of Niğde-Ulukışla oil shale. (The abbreviation used: daf – dry ash free.)

3.2. Effect of tetralin/oil shale ratio

The ratio of solvent/solid affects both total and liquefaction products conversions, as well as the cost of oil shale liquefaction process, which rises upon increasing this ratio. In recent decades, the cost of a barrel of liquefaction product obtained by coal liquefaction has been calculated to be approximately \$50 and it is noteworthy that this cost mainly depends on solvent/solid ratio. This ratio also determines the hydrogen availability [38]. In this study, tetralin having a hydrogen-donating function was used as solvent and the experiments were conducted by changing the tetralin/oil shale ratio from 1/1 to 9/1. One can see from Figure 4 that there was a slight increase in the total and oil + gas conversions at a tetralin/oil shale ratio of 3/1, while no considerable change took place when this ratio was increased. In catalytic liquefaction processes, a high ratio of solvent/solid was not preferred. This is because the existence of excess tetralin may obscure the effect of the added catalysts as the solvent itself is a strong H-donor [37]. Taking into consideration the volume of the reactor and total conversion values, the optimum corresponding ratio was selected as 3/1.

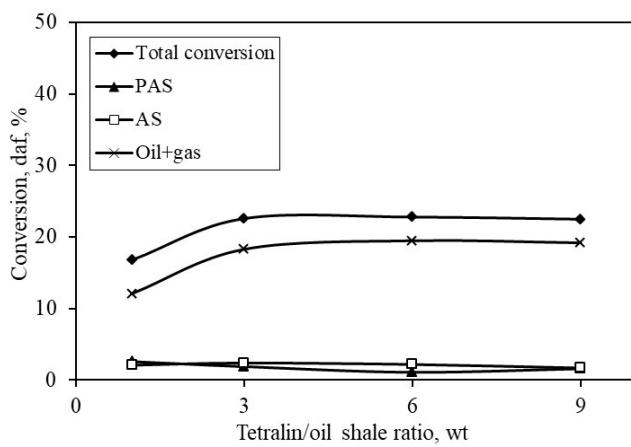


Fig. 4. Effect of tetralin/oil shale ratio on the liquefaction products conversion in the noncatalytic liquefaction of Niğde-Ulukışla oil shale. (The abbreviation used: daf – dry ash free.)

3.3. Effect of catalyst type and concentration

Application of suitable catalysts for direct coal liquefaction appears to improve total conversion and product selectivity by enhancing coal dissolution. A number of catalytic materials have been investigated for their suitability for coal liquefaction [3, 39, 40]. In this study, the catalytic liquefaction of Niğde-Ulukışla oil shale was performed using five different catalysts, namely Fe_2O_3 , MoO_3 , $\text{Mo}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$ and zeolite, to identify a suitable catalyst in terms of cost and environmental aspects. The data shown in Figure 5 indicate that the total conversion of oil shale attained in

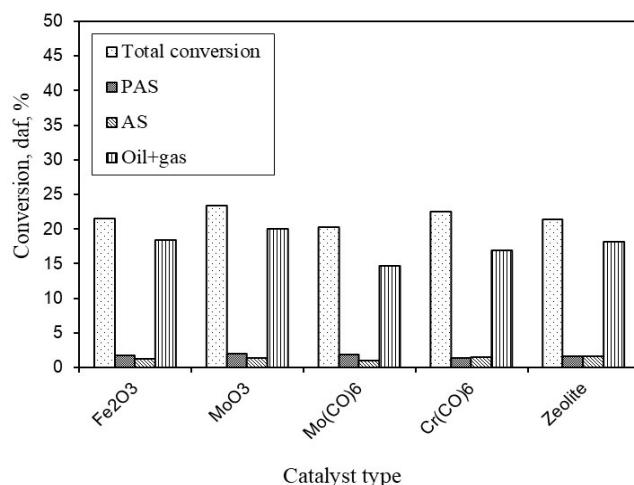


Fig. 5. Effect of catalyst type on the liquefaction products conversion in the catalytic liquefaction of Niğde-Ulukışla oil shale. (The abbreviation used: daf – dry ash free.)

noncatalytic liquefaction was 22.6%, being 23.4% in catalytic liquefaction at a 3% MoO₃ concentration. The order of activity of the tested catalysts for the oil + gas conversion may be given as MoO₃ > Cr(CO)₆ > Fe₂O₃ = zeolite > Mo(CO)₆. As can be seen from Figure 6, an increase in catalyst concentration from 3 to 9% led to a rise in the total and oil + gas conversions from 23.4 to 30.1% and from 20.0 to 26.5%, respectively. Therefore, by considering the conversion values obtained the optimum catalyst concentration was found to be 9%.

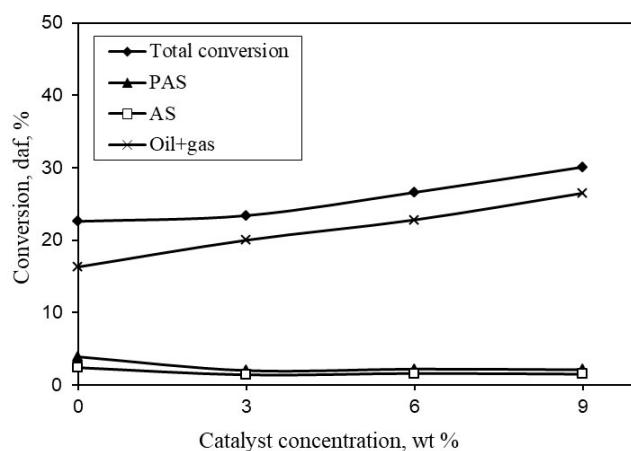


Fig. 6. Effect of catalyst concentration on the liquefaction products conversion in the catalytic liquefaction of Niğde-Ulukışla oil shale. (The abbreviation used: daf – dry ash free.)

3.4. Effect of reaction time

In coal liquefaction process, both the reaction temperature and time are vital parameters. To examine the effect of reaction time ranging from 30 to 150 min, the experiments were carried out in the presence of MoO₃ catalyst at a concentration of 9%. The reactor was heated for about 1 hour to reach the determined reaction temperature, so the formation of radicals by decomposition of oil shale and the transfer of hydrogen to them during this heating-up period would result in the launch of the liquefaction process without attaining the desired reaction temperature. That is why it is impossible to determine the reaction time precisely. As can be seen from Figure 7, the total conversion slightly increased from 28.6 to 31.1 % with an increase in the reaction time from 30 min to 90 min and then remained unchanged. Since a certain amount of time (60–90 min) is necessary for formation of radicals and obtaining a high yield of a light liquid product, i.e. oils, the reaction time was selected to be 90 minutes [1, 37].

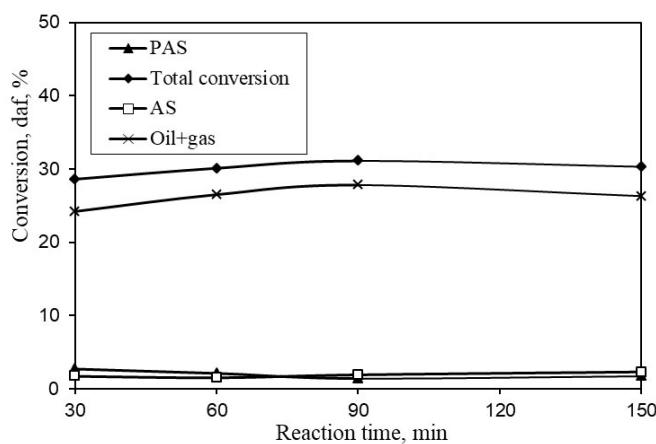


Fig. 7. Effect of reaction time on the liquefaction products conversion in the catalytic liquefaction of Niğde-Ulukışla oil shale. (The abbreviation used: daf – dry ash free.)

3.5. Effect of reaction temperature

In this study, the catalytic liquefaction of Niğde-Ulukışla oil shale in the presence of MoO_3 catalyst at a concentration of 9 % was carried out in the reaction temperature range of 350–425 °C during 90 minutes, to determine its effect on the process. It is accepted that the yield of liquid products should be high and that of gaseous products low to produce fuels alternative to petroleum. It is clearly evident from Figure 8 that as the temperature increased from 350 °C to 400 °C, the total conversion increased from 22.7

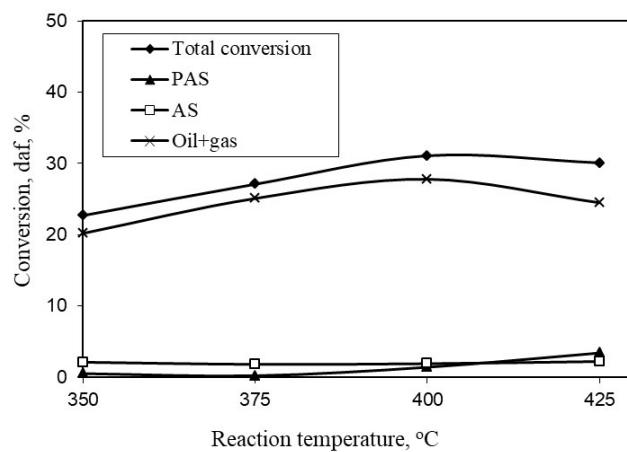


Fig. 8. Effect of reaction temperature on the liquefaction products conversion in the catalytic liquefaction of Niğde-Ulukışla oil shale.

to 31.1 %. However, a further increase in temperature, i.e. from 400 °C to 425 °C, had no considerable effect on the total conversion. Stabilization of radicals formed during liquefaction either by taking hydrogen atoms from reaction medium or combining them with other radicals causes an increase in total conversion. But as temperature increases, formation of radicals decreases and as a result, total conversion does not increase significantly [21, 41]. Besides, as both liquid products and unreacted solid material are oxidized at higher temperatures, the yield of gaseous products is enhanced [42]. Based on these results the effective reaction temperature was selected as 400 °C.

3.6. Effect of oil shale/waste paper ratio

Since biomass from agriculture and wood residues, as well as municipal solid waste and energy crops is found plentifully, it is worthwhile to achieve liquefaction of oil shale with biomass in order to promote the total conversion and production of lighter products and decrease the cost of the liquefaction process [43]. In this study, the co-liquefaction of Niğde-Ulukışla oil shale with waste paper was performed at 400 °C in the presence of MoO₃ catalyst during 90 minutes of reaction time. The contribution of waste paper at different oil shale/waste paper ratios to total conversion in the liquefaction process is shown in Figure 9. It is noteworthy that co-liquefaction was very effective at an oil shale/waste paper ratio of 1/1, providing 80.5% of total conversion as compared with 31.1% attained without using waste paper. It is evident that co-liquefaction of Niğde-Ulukışla oil shale with waste paper enabled an increase of both the total and oil + gas conversions via synergy effect.

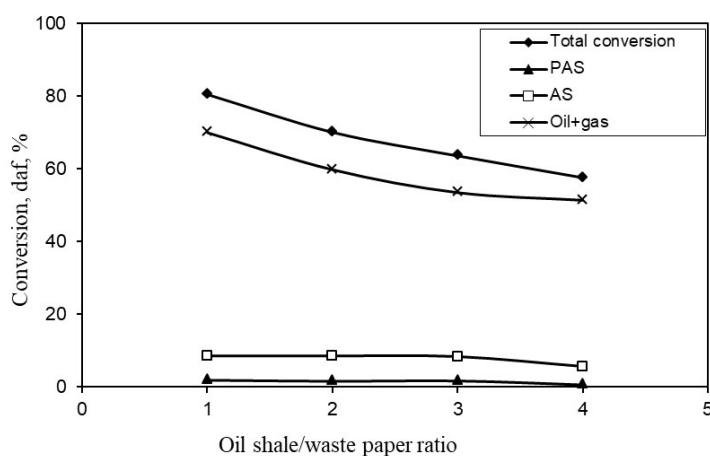


Fig. 9. Effect of oil shale/waste paper ratio on the liquefaction products conversion in the catalytic liquefaction of Niğde-Ulukışla oil shale.

3.7. GC-MS analysis of oils

Figure 10 shows a typical GC-MS chromatogram of oil obtained as a liquid product from the liquefaction process of oil shale under catalytic conditions of experiment 22. This liquid product is soluble in hexane. Table 3 lists compounds attributable to the 18 peaks observed in the GC-MS chromatogram. According to the GC-MS analysis, naphthalene and its derivatives and polycyclic hydrocarbon such as indene and its derivatives as the main components accounted for 50% and approximately 20% of the liquid product, respectively.

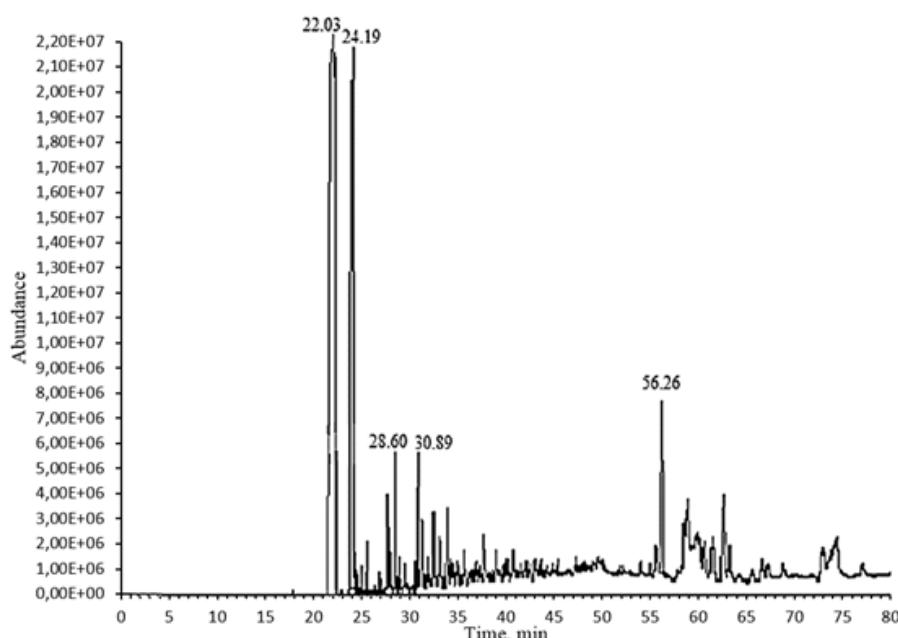


Fig. 10. GC-MS chromatogram of oils (Experiment 22).

Table 3. List of compounds belonging to peaks observed in the GC-MS chromatogram in Figure 10

Peak No.	RT, min	Possible compound	Similarity, %	Amount in total abundance, %
1	22.03	Naphthalene, 1,2,3,4-tetrahydro-Naphthalene	97	53.247
2	22.48	1,4-Dihydronaphthalene, Naphthalene, 1,2-dihydro-Naphthalene, Cycloprop[a]indene, 1,1a,6,6a-tetrahydro- Cycloprop[a]indene	95 94 93	0.764

Table 3 (Continued)

Peak No.	RT, min	Possible compound	Similarity, %	Amount in total abundance, %
3	24.19	Naphthalene, 1H-Indene, 1-methylene- 1H-Indene	97 91	21.397
4	25.68	Naphthalene, 1,2,3,4-tetrahydro-6- methyl-Naphthalene, Naphthalene, 1,2,3,4-tetrahydro-5- methyl-Naphthalene	97 96	0.617
5	27.75	Naphthalene, 1-ethyl-1,2,3,4-tetra hydro- Naphthalene, Naphthalene, 5-ethyl-1,2,3,4-tetra hydro- Naphthalene, 1H-Indene, 1-ethyl-2,3-dihydro-1- methyl-1H-Indene	91 90 78	1.242
6	27.96	Naphthalene, 2-methyl- Naphthalene, 1-methyl-Naphthalene	94 94	0.937 94
7	28.60	Naphthalene, 1-methyl- Naphthalene, Naphthalene, 2-methyl- Naphthalene, 1,4-Methanonaphthalene, 1,4-dihydro- 1,4-Methanonaphthalene	91 91 91	1.774
8	30.74	Naphthalene, 1,2,3,4-tetrahydro-1, 1,6-trimethyl- Naphthalene, 2,3,6-Trifluoroacetophenone, 2',4',5'-Trifluoroacetophenone	70 59 59	0.747
9	30.89	Naphthalene, 1,2,3,4-tetrahydro-1- propyl- Naphthalene, 1-Phenyl-1-hexyn-3-ol, Naphthalene, 5-ethyl-1,2,3,4-tetra hydro- Naphthalene	94 59 53	1.809
10	31.36	Naphthalene, 1-ethyl- Naphthalene, Naphthalene, 2-ethyl- Naphthalene	94 91	1.117
11	32.54	1(2H)-Naphthalenone, 3,4-dihydro- 1(2H)-Naphthalenone	95	1.137
12	33.20	2(1H)-Quinolinone, 1-methyl- 2(1H)-Quinolinone, 4,6-Quinolinediamine, 2-Naphthalenol, 8-amino- 2-Naphthalenol	53 50 47	1.094

Table 3 (Continued)

Peak No.	RT, min	Possible compound	Similarity, %	Amount in total abundance, %
13	33.96	Naphthalene, 1,2,3,4-tetrahydro-1-propyl- Naphthalene, Naphthalene, 5-ethyl-1,2,3,4-tetra hydro- Naphthalene, 1-Hexen-3-one, 5-methyl-1-phenyl-1-Hexen-3-one	81 50 45	1.005
14	37.72	1,1'-Biphenyl, 3-methyl-1,1'-Biphenyl, 1-Isopropenylnaphthalene, 1,1'-Biphenyl, 2-methyl-1,1'-Biphenyl	83 70 64	0.368
15	56.26	5-Chloro-1,3-dimethylpyrazole, 2-Acetoxytetralin, Indole-3-pyruvic acid	47 43 43	5.389 43 43
16	58.58	Naphthalene, 1,2,3,4-tetrahydro-1-octyl- Naphthalene, Naphthalene, 1-ethyl-1,2,3,4-tetra hydro- Naphthalene, 3-Chlorotricyclo[5.2.1.0(4,8)]deca-2,5-diene	53 43 43	1.518
17	58.92	Naphthalene, 1,2,3,4-tetrahydro-1-octyl- Naphthalene, 1H-Indene, 2,3-dihydro-1,6-dimethyl 1H-Indene, Naphthalene, 1-ethyl-1,2,3,4-tetra hydro- Naphthalene	49 38	2.066 38
18	62.62	2,2'-Binaphthalene, 1,1',2,2',3,3',4,4'-octahydro-2,2'-Binaphthalene, Naphthalene-4a,8a-dicarboxylic acid 1,4,4a,5,8,8a-hexahydro-, dimethyl ester, 2-t-Butyl-6-methyl-5-(1-phenylbut-3-enyl)[1,3]dioxan-4-one	96 50 47	3.774

The abbreviation used: RT:- retention time.

4. Conclusions

Based on the results of the study it can be concluded that tetralin/oil shale ratio had no considerable effect on the noncatalytic liquefaction of Niğde-Ulukışla oil shale and the optimum ratio was 3/1, proceeding from total and oil + gas conversions data.

In the catalytic liquefaction of Niğde-Ulukışla oil shale, the highest catalytic activity in terms of total and liquefaction products conversions was obtained with MoO_3 catalyst at a concentration of 9% by weight. As temperature increased from 350 °C to 400 °C, total conversion increased slightly, but a further rise in temperature had no effect on the total conversion during 90 minutes of reaction time.

Since much lower liquefaction conversion of Niğde-Ulukışla oil shale under both noncatalytic and catalytic conditions was attained, its co-liquefaction with waste paper was performed at 400 °C in the presence of MoO_3 catalyst and total and oil + gas conversion values were increased from 31.1 to 80.5 % and from 27.8 to 70.0 %, respectively, at an oil shale/waste paper ratio of 1/1.

Oil obtained as a liquid product from the liquefaction process of oil shale under catalytic conditions of experiment 22 consisted mainly of naphthalene and its derivatives and polycyclic hydrocarbon such as indene and its derivatives.

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