Fixed Bed Pyrolysis and Hydropyrolysis of an Immature Type I Turkish Oil Shale

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A number of different pyrolysis procedures were investigated in order to achieve higher oil yields from an immature type I oil shale than obtained under static retorting conditions. Both nitrogen and steam gases increased yields as anticipated: Steam achieving comparable yields to nitrogen but at much lower gas velocities. The composition of the tars varied considerably, steam increasing the concentration of alkenes. In coprocessing the oil shale with a Turkish lignite in the Heinze retort, oil yields were higher than predicted principally due to extraction of the lignite by pyrobitumens obtained from the oil shale. Fixed bed hydropyrolysis of the shale at 15 MPa resulted in oil yields of 75% daf shale. The use of a dispersed sulphided molybdenum catalyst increased the oil yield to over of 80%.

Introduction

The Göynük region of North Eastern Turkey contains one of the country's largest deposits of oil shale (10^9 tones), much of this shale generally contains less than 30% mineral matter content and it has been classified as an immature type I kerogen. It has been previously shown that moderately high oil yields ($\approx$ 30-40 % daf shale) can be obtained from Göynük shale by pyrolysis in a Heinze retort at $550°C$[1,2]. It is however well known that Heinze retort oil yields are mass transfer limited especially in the absence of a sweep gas[3-5]. In this paper a number of pyrolysis procedures were investigated with the aim of producing shale oil in considerably higher yields than can be obtained in the Heinze retort under static retorting conditions[1]. In addition, variations in shale oil composition were determined.

Experimental

Proximate and ultimate analysis of Göynük oil shale and a neighboring lignite (Yatağan) are listed in Table 1.

Table 1. Proximate and ultimate analyses of Göynük oil shale and Yatağan lignite (wt %)

	Göynük Oil Shale	Yatağan Lignite
Moisture	4.8	22.1
Ash	21.5	22.2
Volatile matter	61.6	30.6
Fixed carbon	13.6	25.1
C	49.9	36.3
H	6.4	3.4
S	3.3	1.2
N	1.1	1.2
H/C (daf basis)	1.5	1.1

Heinze Retort Pyrolysis Reactor

In the Heinze retort[1,2], the influence of pyrolysis atmosphere (self-generated, nitrogen and steam atmospheres) and co-processing with the Göynük oil shale-Yatağan lignite (mass ratio of oil shale to lignite 1:2, 1:1, 2:1) were studied.

In all the experimental runs, the retort was heated at 5°C/min to 550°C (hold time of 30 min). The first series of experiments were carried out in a self-generated (static) atmosphere during pyrolysis. Experiments were carried out in a flowing nitrogen atmosphere (sweep velocity 3.3 cm/s). Finally, superheated water vapour was injected continuously during the course of the heating period at different flow rates (sweep velocity 0.7, 1.3, 3.3 cm/s). The effect of different blends of Göynük oil shale and Yatagan lignite (using 1:2, 1:1 and 2:1 mass ratios) on the oil yield was also investigated. The aqueous liquor was separated from the pyrolysis oil, which was dissolved in n-hexane and the n- hexane solubles were fractionated by silica gel adsorption chromatography into aliphatics, aromatics and polars using a modified form of silica gel ASTM 2549[6].

Fixed-bed Pyrolysis Reactor

To compare the effect of reator geometry on oil yields, Göynük oil shale was pyrolysed in the fixed bed reactor used for hydropyrolysis (Figure 1). The same heating rate regime as in the Heinze retort was used for retorting in the lncoloy reactor tube 5°C/min to 550°C (hold time of 30 min). Experiments were carried out in both self- generated atmosphere and in a flowing nitrogen atmosphere (sweep velocity 22 cm/s at N.T.P.).

Fluidised-bed Pyrolysis Reactor

The semicontinuous bench-scale fluidised bed retort[7] (quartz, 30 mm id., 300 mm length), in which the sample (30 g) was slowly heated (5°C/min) from ambient temperature with a superficial gas velocity of 6 cm/s corresponding to twice the minimum fluidising velocity, was designed to provide information on the ultimate yields and characteristics of pyrolysis products.

The temperature of the fluidised bed was controlled to within ±1°C by an electric heater tube furnace around the bottom section of the retort that contained the bed. The bed temperature was measured by a thermocouple inserted through the lid of the reactor.

The volatiles were swept from the reactor by the fluidising gas and condensables were collected in two tar traps which were cooled by dry ice.
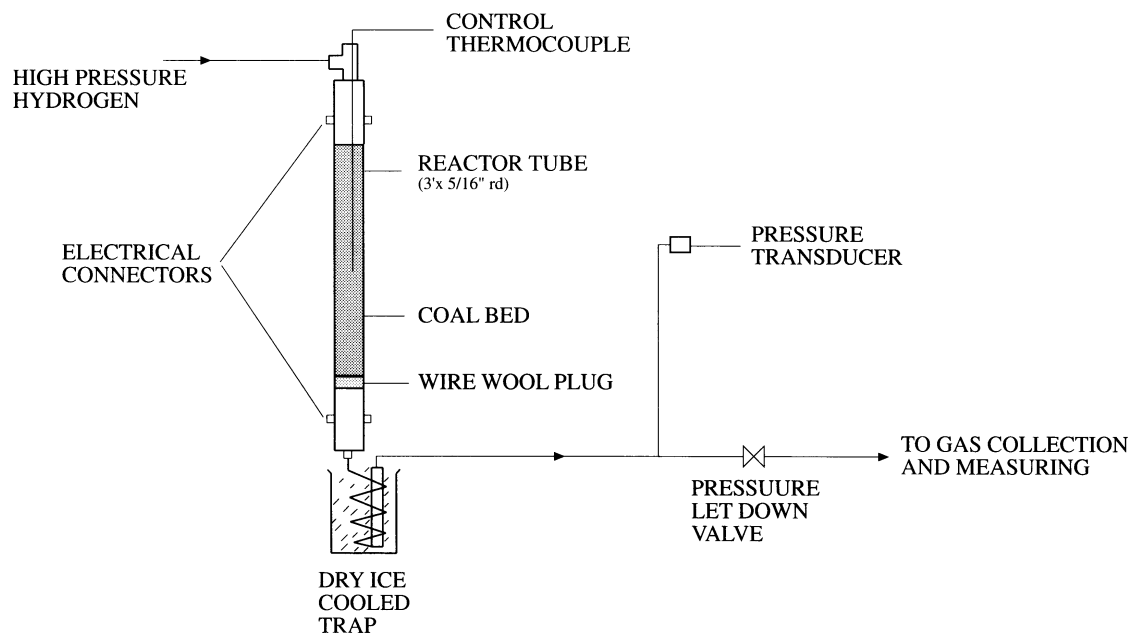

Figure 1. Schematic arrangement of fixed-bed hydropyrolysis reactor

Fixed-bed Hydropyrolysis Reactor

Figure 1 shows a schematic diagram of the hydropyrolysis unit. Hydropyrolysis experiments were conducted at 520° C and 15 MPa hydrogen pressure, and a heating rate of 5° C/sec and a hydrogen flow of 10 lt/min measured by atmospheric pressure. Hydropyrolysis tests were conducted both with and without a sulphided molybdenum (Mo) catalyst (1% daf shale) which was prepared by impregnation of the shale with an aqueous solution of ammonium dithiodioxy molybdate which thermally decomposes at 350° C in a reducing atmosphere to form MoS_2 in a highly dispersed form across the substrate surface[8-10]. 15 g of neat shale or 5g of shale mixed with 10g of sand was used in all of the pyrolysis and hydropyrolysis experiments, respectively. Char yields were determined from the weight loss of the reactor tube. Liquid yields were measured by the mass increase of the cold trap and the total gas was collected and analysed by gas chromatography (GC) for $C_1 - C_4$ hydrocarbons.

Prior to each hydropyrolysis run, the masses of the reactor, cold trap and coal charge were recorded. The coal bed was held in place by a preweighed steel wool plug ($\cong$ 1.5 g) inserted in the bottom of the reactor. After the run, the reactor and cold trap were re-weighed. Overall coal conversion was calculated from the weight loss from the reactor, and tar yield from the weight increase of the cold trap. The cold trap was cooled using dry ice, which was found to be more effective than ice and brine in condensing out water formed during pyrolysis. The use of liquid nitrogen to cool the trap resulted in the collection of all the water but it also caused the condensation of C_2 and greater hydrocarbon gases, giving rise to erroneous gas analysis and the resulting mass balance. Prior to tar analysis the contents of the cold trap was extracted using dichloromethane and passed through phase separation paper to remove water. For the experiments where water yield was to be accurately measured, the trap was extracted with toluene and the water content measured by the Dean-Stark method.

After removal of the asphaltenes, the n-hexane solubles were fractionated into paraffins, aromatics and polars by silica gel adsorption chromatography[6]. The fractions were subjected to elemental, IR, ^{1}H and

^{13}C NMR and GC analysis where appropriate. The distribution of biomarker compounds in the paraffins was determined by gas chromatography- mass spectrometry (GC-MS).

Results and Discussion

Mass Balance for Pyrolysis Experiments

Normally yields are expressed on a dry ash free (daf) basis to reflect the conversion of organic matter in oil shales.

All the pyrolysis experiments were carried out in duplicate, typical repeatability being 2% of the total organic matter for both char and oil.

Atmospheric Pressure Pyrolysis

Table 2 compares the oil and char yields obtained from Göynük oil shale in the different procedures investigated with steam and nitrogen. Although gas yields were not determined for the modified Heinze retort, it is expected that these will be similar to the figure of $\sim$ 9 wt % daf shale obtained in the fixed-bed reactor with nitrogen (Table 2). As expected, the use of a sweep gas increased the oil yield considerably, and the total conversion (100-wt % char) in the region of 80 %, achieved using fixed-bed reactor with a relatively high superficial gas velocity or by using a fluidised-bed reactor, are close to the volatile matter content of the shale (Tables 1 and 2). Steam is much more effective than nitrogen at low sweep gas velocities in the Heinze retort. The use of steam as a sweep gas resulted in higher overall conversions[2,7]. It can be determined from Table 2 that the oil yield from a steam sweep velocity of 3.3 cm/s is only slightly lower than the yield of nitrogen at a sweep velocity of 22 cm/s.

Table 2. Pyrolysis yields from Göynük oil shale under different pyrolysis regimes at low pressure (wt % daf shale)

Regime	Conversion	Oil	Char
Heinze Retort			
Static	45	33	55
Steam 0.7 cm/s	54	40	46
Steam 1.3 cm/s	60	44	40
Steam 3.3 cm/s	75	55	25
Nitrogen 3.3 cm/s	53	39	47
Fixed Bed			
Static	52	38	48
Nitrogen 22 cm/s*	77	61	23
Fluidised Bed Reactor			
Nitrogen 6 cm/s	85	74	15

* Total hydrocarbon gas yield 2.8 wt% comprising 0.9 wt% methane, 0.8 wt% ethane and 0.4 wt% ethene

The composition of the Göynük shale oils from the Heinze retort are determined in Figure 2, which indicates that, compared with static retorting, the alkanes and aromatics increase markedly and polars decrease slightly, using either nitrogen or steam as sweep gas.
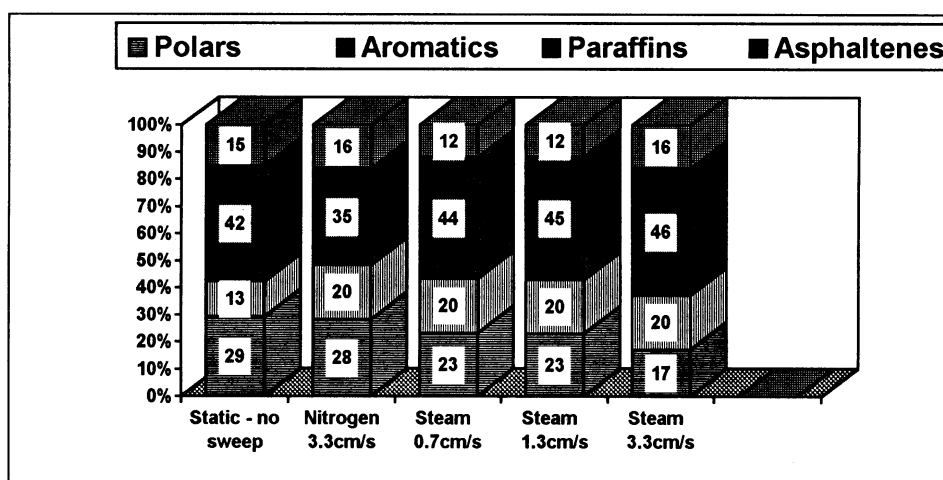
Figure 2. Composition of Göynük Shale oils prepared in Heinze Retort

Characteristic carboxyl peaks are prominent features in the IR spectra of the aromatic and polar fractions indicating that esters and carboxylic acids, respectively, are present in significant concentrations[11]. A number of long chain acids and esthers have already been identified by GC-MS. The carboxyl containing compounds must therefore escape at relatively low temperatures ($< 450°$ C) to avoid thermolysis. Indeed, thermal gravimetric analysis indicates that volatile release starts to commence at $\sim 350°$ C. However, the effect is more pronounced with steam, indicating that alkanes must be involved in retrogressive reactions leading to char formation, probably via dehydrogenation to alkenes and subsequent cyclization. Significant differences are also evidenced in the n-alkane distributions. For steam pyrolysis, the proportions of low molecular mass (MM) n-alkanes were higher compared to the nitrogen and more so to the self-generated atmosphere experiments (Figure 3).
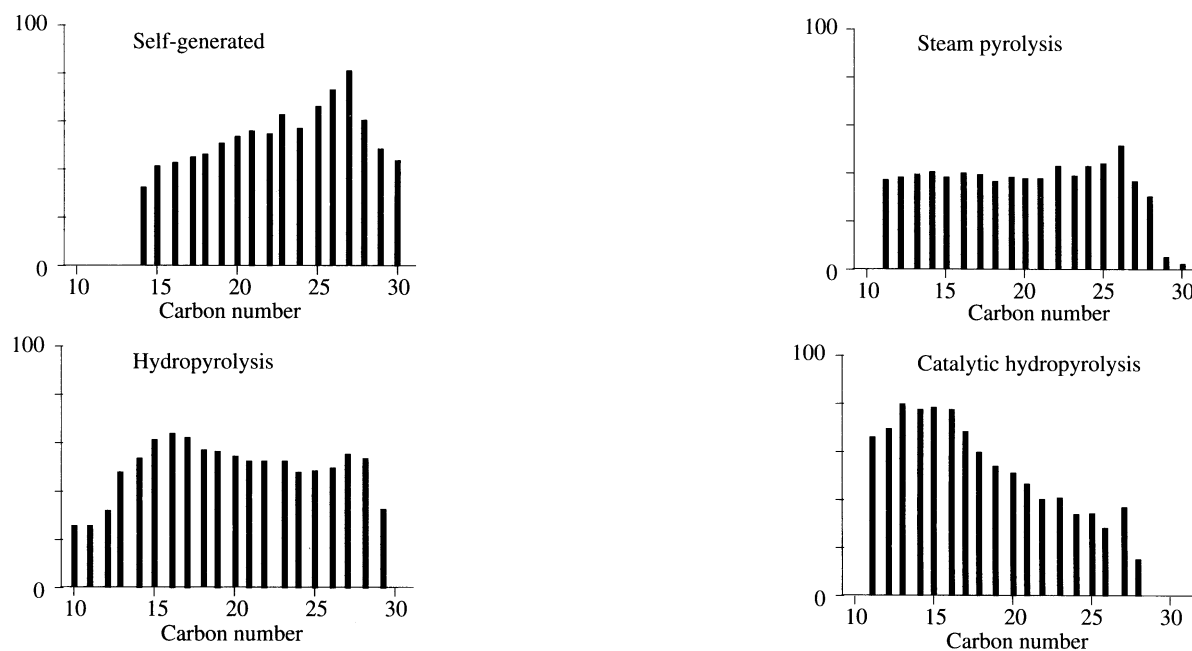

Figure 3. Composition of n-alkane Separated from Göynük oils

The n-alkane distribution starts at C_{10} for steam pyrolysis compared to C_{15} with nitrogen. Moreover, the Carbon Preference Index (CPI=ratio of odd to even n-alkanes chain length) decreased with increasing steam

velocity from 1.06 to 0.75. However, the general characteristics of type I kerogen, i.e. high MM n-alkanes $(C_{20} - C_{30})$ still persisted. This is consistent with a study on Kentucky oil shales where yields of light oils obtained with steam were twice those obtained in a nitrogen atmosphere[12].

Indeed, gas chromatography analysis of the alkane fraction and ^{1}H NMR analysis of the aromatics qualitatively indicated that the alkene concentration broadly increases with increasing steam velocity. For example in a self-generated atmosphere the rotio of n-alkenes to n-alkanes was found to be 0.23 compared to 0.44 with steam for the highest sweep velocity. Thus, either the steam is actually promoting bond cleavage reactions, creating a greater demand for transferable hydrogen, or is merely providing a more protective environment, limiting the extent of cyclization and aromatization of the alkenes by passivating the acidic clay minerals[13]. Evidence that the steam may actually promote bond cleavage was provided by Minkova et al [14,15], who found that the sulpur contents of the oils obtained with steam were lower.

Like the results obtained in this study higher oil yields were reported for steam pyrolyis compared to inert gas pyrolysis[12,15]. However, the mechanism forwarded for the explanation of the performance difference is also different. On the one hand it is claimed that the difference in oil yields between steam and inert carrier gas is significant. The difference is mainly due to the trapping of light oil which captures lower MM products which causes the compositional changes. Steam gives more olefins as qualitatively and quantitatively determined in this study. This can be explained in terms of cyclisation reactions catalysed by MM that are curtailed by steam. This fact is substantiated by n-hexadecane experiments which have shown cyclisation[16]. It is believed that steam does not have a chemical effect on organic matter conversion. Carter and Taulbee[17] carried out gas compositional determinations from which they concluded that the compositions are virtually similar for steam and nitrogen carrier gas. Also the same authors found similar n-alkane/n-alkene ratios for C_2 to C_5 products of steam and nitrogen in fluidised bed pyrolysis of eastern oil shales. This was interpreted as steam and nitrogen having similar gas formation mechanisms.

In their fixed bed experiments Minkova et al. found 20-50% higher oil yield for steam pyrolysis over Fischer Assay. The effect of steam on yield constitutes the second school of thought on this issue. It is believed that steam is a vehicle in accelerating the emission of volatiles to prevent further cracking and cooking which is also shared by the results obtained on eastern oil shales. Also, it is believed that donor-acceptor interaction and desorption of hydrophobically retained low MM products from the cavity of cross-linked molecules. This means the involvement of steam as a chemical mediator in direct interaction of the radicals produced by the destruction of solid fuel with steam or hydrogen. This is substantiated by the measurements of reduced CO and increased H_2, CO_2 concentrations in the gas and the increased content of paraffinic-naphthenic hydrocarbons and polar compounds in the oils.

The modified Heinze retort char of Göynük oil shale was subject to BET-N_2 specific surface area measurements. 7 m^2/g specific surface area was determined. Steam pyrolysed char resulted in a BET-N_2 specific surface area of 130 m^2/g. An extensive increase in porosity was reported for fixed bed steam pyrolysis of oil shales[18]. Göynük oil shale retorted in a nitrogen swept fixed bed was found to have a BET-N_2 specific surface area of 8.7 m^2/g. This porosity was mainly macro (>20 nm) and meso (< 20nm, >0.2 nm) pore size. The char obtained from fixed bed was further processed at 800m^2/g in the presence of steam for half an hour and the specific surface area was found to increase to 170m^2/g. The nature of the new pore formation was in the micro range. All these findings indicate that the porosity related characteristics of shale matrix is greatly enhanced during steam treatment.

Co-Processing of Lignite and Oil Shale

Figure 4 represents the actual and predicted oil yields from the Heinze retort experiments with the Göynük oil shale-Yatağan lignite mixtures, the predicted yields were simply deduced from those of the separate components. The mass ratio of lignite to oil shale was varied between 1:3 and 3:1. The actual oil yields for the mixtures are consistently higher than those predicted. For the oil shale-lignite mixtures, the increase in oil yield is highest for 3:1 mass ratio of oil shale to lignite and would broadly appear to increase with increasing oil shale content. Thus the oil shale is reasonably effective in partly preventing retrogressive char-forming reactions for the lignite. However, relatively large amounts of oil shale are probably required, because compatibility between the shale and lignite is relatively poor. It has been found that the shale oils are highly aliphatic in character[2,7], and during the initial stage of pyrolysis, the pyrobitumen which is the precursor of the shale oil is expected to be a relatively poor solvent for the phenolic material from the lignites.
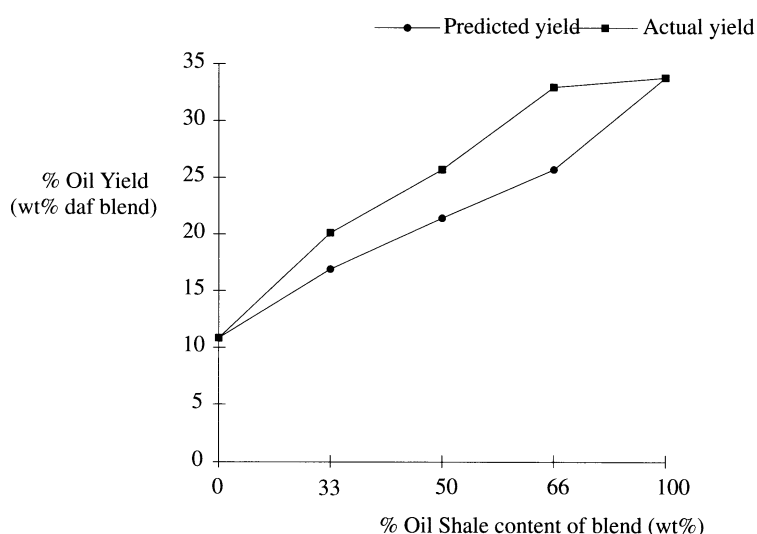

Figure 4. Oil yields obtained from coprocessing of Göynük oil Shale and Yatağan Lignite Mixtures

Hydropyrolysis

Table 3 lists the yields from the hydropyrolysis experiments. At $550°$ C, the temperature used in atmospheric pressure pyrolysis to maximize oil yields, the hydrocarbon gas yield is appreciable. To increase the selectivity to oil (% oil / % hydrocarbon gases), the temperature was reduced to $520°$ C, the same as that used in recent studies on coals[19,20]. Table 3 indicates that the same oil yield was obtained at both temperatures but, as anticipated, the hydrocarbon gas yield was lower at $520°$ C. As discussed previously[21], the beneficial effect of high pressure hydrogen in terms of mediating bond cleavage reactions is offset by the increased mass transfer to volatiles released within the coal bed.

The use of the dispersed Mo catalyst slightly increased the total conversion to $\approx$ 100%, the oil yield increased to 82% daf shale and the hydrocarbon gas yield was reduced by 4% (Table 3). In fact, the gas yield was reduced probably as a consequence of volatile release being shifted to slightly lower temperatures. Despite the total conversion being in excess of 90% daf shale without catalyst, the increase in oil yield is much higher than that typically achieved for low-rank coals[10].

Table 3. Hydropyrolysis yields from Göynük oil shale (wt% daf Shale)

	Pyrolysis Temp. °C	Conversion	Oil	$C_1 - C_4$ Gas
Oil Shale	550	94	72	9
Oil Shale	520	95	73	8
Oil Shale+1% Mo Catalyst	520	100	82	4

Hydropyrolysis conditions:

Heating Rate: 5° C/sec from ambient to 520° C,10 min hold time

Pressure : Hydrogen 15 MPa

Flow: 10 l/min measured at atmospheric pressure

A number of major compositional differences have been found between the hydropyrolysis and atmospheric pressure pyrolysis oils. As discussed previously[4], the beneficial effect of high hydrogen pressure in terms of mediating hydrogenolysis reactions is partly offset by the increased mass transfer within the coal bed to volatiles release. For Göynük oil shale, the hydropyrolysis oils contain fewer asphaltenes and more polars and have lower oxygen and sulphur content (Table 4) due to mass transfer and hydrogenolysis effects, respectively. In addition, the hydropyrolysis oils contain fewer alkene groups and IR has indicated that carboxyl concentrations are lower. The hydropyrolysis oils are much more aromaticy increasing with conversion and hydrogenolysis reactions[7].

Overall aromaticity balances give useful insights into the conversion chemistry, especially for highly aliphatic immature Type I kerogens. Static pyrolysis gave rise to a large net aromaticity increase (Table 4) consistent with earlier studies[22].b Both the use of effective sweep gases and hydrogen at pressure nullify this change and, with catalyst in hydropyrolysis, an overall decrease occurs indicating that hydrogenation has occurred[7].

Table 4. Compositional parameters of the oil and total aromaticities of the products (% as determined)

	C	H	N	S	H_{ar+oE}	F_a
Göynük Shale	49.9	6.4	1.1	3.3	-	36
Heinze Retort (Static)	82.5	11.6	1.3	1.9	1.0	55
Hydropyrolysis	83.9	10.0	1.7	1.5	12.7	34
Hydropyrolysis+Catalyst	85.0	11.3	1.7	0.5	6.7	25

F_a -Total Aromaticity of Products

H_{ar+oE} -% Aromatic and Olefinic Hydrogen

Biomarkers

Oil shale and coal contain a variety of fossilised plant tissues in different stages of preservation. During and after deposition in sedimentary basins, plant remains undergo a sequence of physical, chemical and biochemical changes, i.e. diagenesis and catagenesis, which result in a series of coals of increasing ranks. Extracts of fossil fuels frequently contain compounds (biomarkers) where the structures are related to chemical structures in the original flora in ways that provide information about the deposition and the diagenesis that formed the fuel. Amongst the biomarkers studies are n-alkanes, in particular the ratio of odd/even carbon numbered alkanes, branched paraffins, pristane and phytane; cycloalkanes; alky-benzenes; substituted naphthalenes; hopanes; tetracyclic terpanes; and steranes[23].

For immature sediments, the n-alkane distribution reflects the composition of the biological matter and the depositional environment. The overall distribution of n-alkanes shifts to lower MM due to thermolytic reactions which contribute to significant amounts of additional alkanes from the berakdown of kerogen. These contribute to and change the carbon number distribution[24,25].

The Göynük oil shale overlie coal seams. An invesigation of their geochemistry[1] by single pulse solid state and high resolution nuclear magnetic resonance, infra-red spectroscopy and gas chromatography-mass spectrometry of the extracted bitumen suggests a classification as immature Type I kerogens[11].

The alkanes obtained via hydropyrolysis contain a greater proportion of low molecular mass (MM) compounds than their pyrolysis counterparts (Figure 6). This is probably due to a combination of hydro-cracking of the higher MM alkanes and the additional alkanes released as a consequence of covalent bond cleavage during hydropyrolysis having lower MM distribution. However, it is interesting to note that the distribution of hopanes and steranes in the pyrolysis and hydropyrolysis oils are similar, the only significant difference being the presence of 22, 29, 38 trisnorhop- 17(21-ene in the pyrolysis oil as a result of dehydrogenation reactions.

Otherwise, the hopane distributions are broadly characteristic of a relatively immature type I kerogen, especially the presence of C_{29} $\beta\beta$ norhopane and normoretane and moretane with the stereochemistry of $17\beta(H), 21\alpha(H)$ as opposed to that of $17\alpha(H), 21\beta(H)$ which dominates at thermodynamic equilibrium. Some isomerisation may have occurred during pyrolysis, especially in trisnorhopane where the $17\alpha(H)$ isomer is present in a higher concentration than the less stable $17\beta(H)$ isomer.

The GC-MS spectra of the pyrolysis and the hydropyrolysis oils from the Göynük oil shale are also characteristic of Type I organic matter.

Hydrogen Utilisation

From the yields and compositions of the products obtained from Göynük oil shale at $(520°C)$ and 15 MPa pressure the expression given below was used to estimate that the hydrogen consumption with dispersed MoS_2 was approximately 4.5 % (daf) compared to 2.3% without catalyst.

Most of the increased hydrogen consumption for the catalysed experiments is due to the greater tar production through a combination of heteroatom removal and C-C bond cleavage, the increase in hydrocarbon gas yield only accounted for 0.2% of the extra 2.2% hydrogen consumed.

The results of aromaticity measurements (Table 4 and Figure 5) on each of the products from the different pyrolysis regimes yield important information regarding the reaction mechanisms of the conversion chemistry being investigated.

Pyrolysis using self-generated atmosphere or low sweep gas velocities resulted in a net dehydrogenation of the oil shale as anticipated from earlier studies. These observations are in accordance with results published in other studies on similar materials[26,27].

The use of a hig velocity inert sweep gas or high pressure hydrogen without a sulphided catalyst did not result in any loss of aromatic carbon confirming that retrogressive reactions had been avoided. However when the oil shale was pyrolysed in the presence of a sulphided molybdenum catalyst and high pressure hydrogen the net aromaticity of the system decreased, indicating that hydrogenation of the oil shale had occurred to a significant extent.
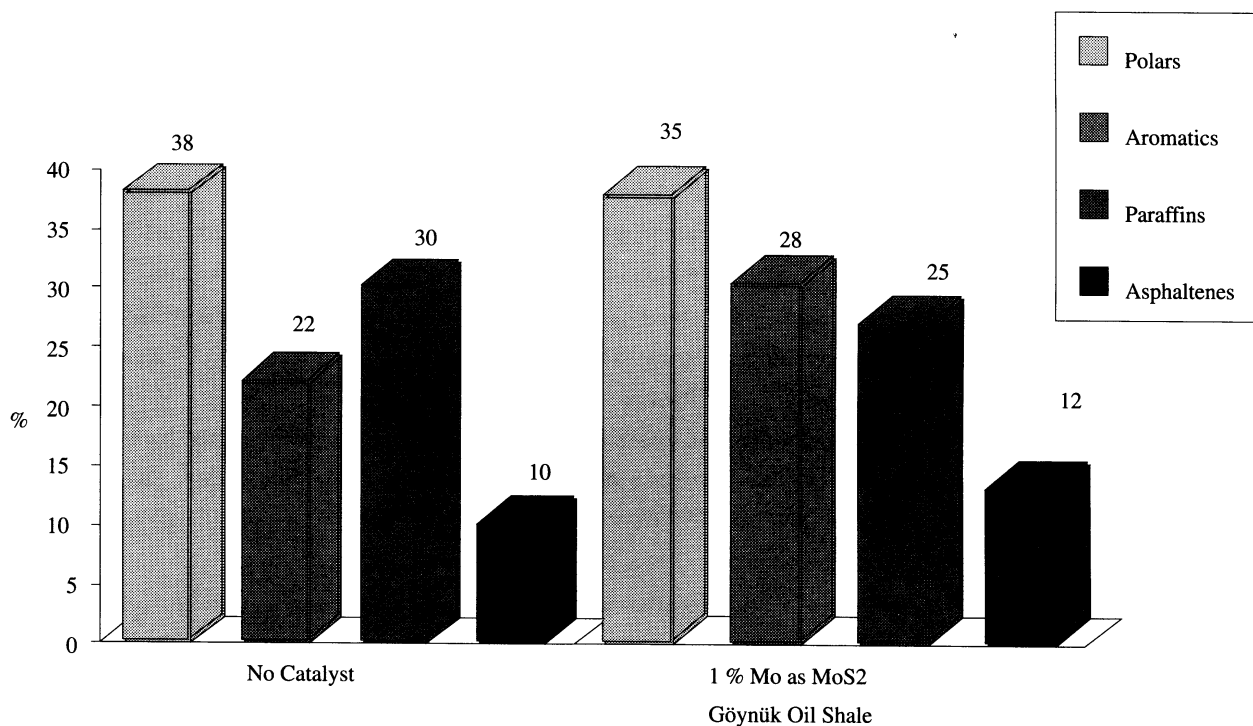
Figure 5. Composition of hydropyrolysis of oils: Effect of catalyst (1% Mo)

The highly aromatic nature of the atmospheric pressure pyrolysis oils agrees well with the hypothesis proposed by Miknis et al [26,27] that it is principally the aliphatic carbons in the oil shale that contributes to pyrolysis oils. Thus, a major advantage of hydropyrolysis is that it enables most of the aromatic carbon to be released from oil shale. The mechanism by which the release occurs is topic for further investigation but it will inevitably involve hydrogenation and subsequent cleavage of resultant weak C-C and C-heteroatomic bond.
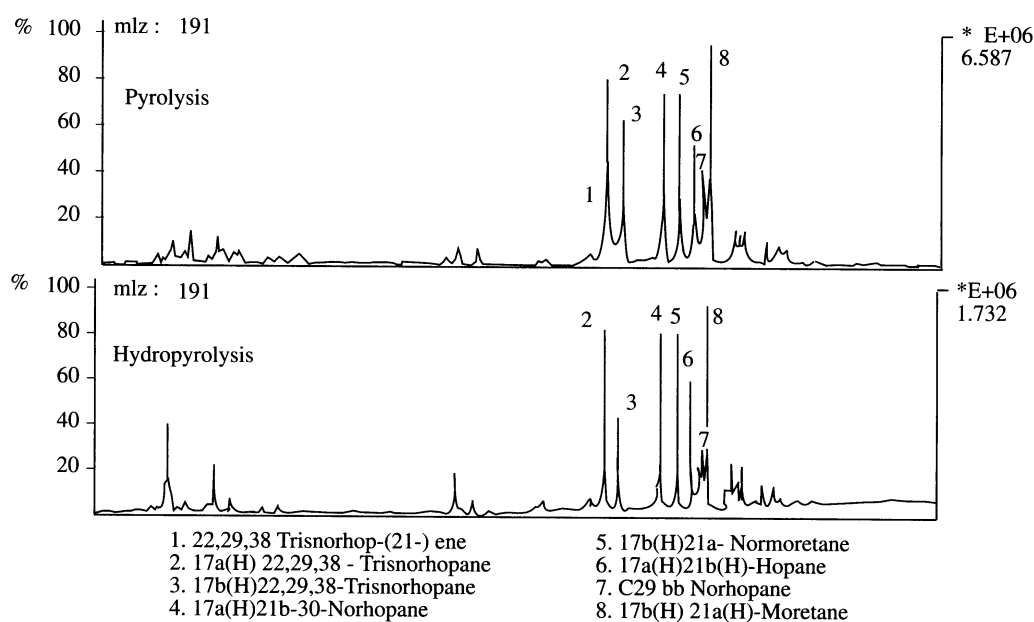

1. 22,29,38 Trisnorhop-(21-) ene
2. 17a(H) 22,29,38 - Trisnorhopane
3. 17b(H)22,29,38-Trisnorhopane
4. 17a(H)21b-30-Norhopane
5. 17b(H)21a- Normoretane
6. 17a(H)21b(H)-Hopane
7. C29 bb Norhopane
8. 17b(H) 21a(H)-Moretane

Figure 6. Paraffinic biomarker distributions

Acknowledgment

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