

TURKISH OIL SHALES POTENTIAL FOR SYNTHETIC CRUDE OIL and CARBON MATERIALS PRODUCTION

Ekrem Ekinici

Istanbul Technical University, Department of Chemical Engineering,
Maslak, Istanbul 34469, Turkey
E-mail: ekincie@itu.edu.tr

ABSTRACT

Given the current conditions and gloomy energy future, it is not understood why worldwide research and related activities on solid fuels have almost frozen during the last two decades. This conference, therefore, is most welcome and it is hoped that it will be followed by other international conferences and research activities on solid fuels. In order to make a new start, research work on Turkish oil shales that was done at ITU laboratories with some well-known international laboratories prior to the recent freeze, are reviewed in this work.

Brief information on the oil shale reserves of Turkey is given together with overall quality indicators by (Fischer Assay). Geochemical characterization of Goynuk and Seyitomer oil shales are made by use of van Krevelen diagram. Both of the two reserves were found to be type I kerogens which were substantiated by other analysis methods, such as carbon preference index, NMR and IR.

Proximate and elemental analysis, carbon and hydrogen aromaticities, different H/C ratios and simulated distillation results of Goynuk and Seyitomer oil shales are presented as basis for thermal processing of these minerals.

Thermal processing studies are presented for fixed bed pyrolysis which included self-generated and sweeping atmosphere pyrolysis. In self-generated atmosphere, retort geometry affected the product yield considerably and similarly, sweeping increased the product yield by overcoming the mass transfer limitations. Both the sweeping velocity and the type of sweeping gas, affected both the yield and quality of the liquid products.

Fluidized bed pyrolysis provided a favorable environment to overcome mass transfer limitations and improved the yield compared to self-generated atmosphere.

Hydropyrolysis, catalytic hydropyrolysis studies were conducted to enhance the liquid product yield and results approaching 100% conversion of organic content to liquid and gaseous fuels were observed.

Copyrolysis of oil shales with lignites and waste plastics resulted in synergisms in the liquid product yield or in product distribution, or both. Generally, for the case of copyrolysis, alkane and aromatic fractions increased at the expense of polar fractions.

Carbon adsorbent studies on the Goynuk oil shale showed that compared to commercial carbon it is 50% efficient in NO and NH₃ adsorption but 250% efficient in H₂S adsorption.

Isotropic pitch production studies from Goynuk and Seyitomer oil shales using air-blowing, vacuum distillation and supercritical extraction methods are reviewed. Results of carbon fiber spinning, stabilization and carbonization are given.

In the last section, economics of shale oil are presented.

INTRODUCTION

Oil shale has a wide range of definitions but agreement on these definitions has not been very successful. A very early definition given by (Gavin et.al.,1924) states that, "Oil shale is a compact, laminated rock of sedimentary origin, yielding over 33% of ash and containing organic matter that yields oil when distilled, but not appreciably when extracted with the ordinary solvents for petroleum". One of the more commonly referred to definitions of recent times incorporates economy to this definition: "it is a sedimentary rock that contains organic matter that, when retorted, produces sufficient oil to produce more energy than the energy required to produce the oil initially", (Hutton, 1995). The publication time of the second reference coincides with nearly a freezing out period of oil shale and shale oil studies together with other fossil fuels in the world. Before 1995 there used to be two yearly running conferences in USA ; Eastern US Oil Shale Symposium and Oil Shale Symposium Series, together they enjoyed over 50 continuous annual meetings. There were also Australian and European meetings. What happened to make these two very important symposium series and others be discontinued? Was the energy problem at last solved? Did the world community find a sound alternative to the depleting oil reserves? Was there any rationale behind stopping fossil fuel research?

I cannot find any reasonable answers to these questions. Just the contrary, the solution to the energy problem at present and medium future encompasses fossil fuel utilisation with special emphasis on reduced environmental impact. Oil shale, being a natural solution to crude oil problem, is as designated by the very definition of this mineral.

If the funds spent on military activities to control the depleting crude oil in the Middle East in the last two decades were spent on shale oil from oil shale, or synthetic fuels from coal and renewable sources, we would most probably have solved the medium term oil problem and would be working on long term solutions

Between 1982 and 1995 in Istanbul Technical University (ITU) laboratories, in collaboration with Leeds and Strathclyde Universities, UK and Center for Applied Energy Research,(CAER) University of Kentucky, USA, extensive studies were on

enrichment (Rıdvan), static fixed bed pyrolysis (Citiroglu, 1990 Citiroglu etal, 1991 and 1989, Uzluk, et.al 1990; Yıldırım,1978), nitrogen and steam swept fixed bed pyrolysis (Citiroglu, 1991; Citiroglu, 1993; Ekinci et.al. 1991; Graham et.al., 1992), co-pyrolysis with lignites, asphaltites and plastics (Citiroglu, et.al.,1991; Ekinci, et.al., 1992; Ekinci, et.al.,1995s), fluidised bed retorting with steam and nitrogen (Citiroglu,1993, Ekinci et.al 1995b), Geochemistry (Pütün, et.al.,1988; Pütün, et.al., 1991), Pollution Control (Ekinci et al., 1993), processing conditions (Çitiroğlu M., et.al.,1990; Okutan, H., et.al.1994.) structural investigations (Önen, A., et.al.1992; Okutan,et.al.1993; Okutan, et.al.,1994.) chemical functionalities and chemicals production (Ekinci, et.al.,1994)

OIL SHALE RESERVES of TURKEY

Oil shales constitute the second largest solid fossil fuel reserves of Turkey after lignites. The total reserves are estimated to be about 5 billion tones. Largest of the reserves is the Goynuk-Bolu reserves (2.5 billion tones), followed by Beypazari-Ankara (1.030 tonnes), Seyitomer Kutahya (1.0 billion tonnes), Golpazarı-Bilecik, Ulukısla-Nigde, Bahcecik-Izmit and Burhaniye-Balikesir reserves. Exploration studies for all of these reserves were carried out by the Mineral Research and Exploration Institute (MTAE) of Turkey by 1965 and thereafter attempts were discontinued. This Institute also conducted the initial research work on some of the reserves. For example, synthetic petroleum production studies were conducted on Bolu-Mengen deposits as early as 1928, but were found to be uneconomical mainly due to the low organic content of the samples used. In order to give an indication of the quality of Turkish oil shales as synfuels input, the Fisher Assay results (ASTM-3904-80) of Goynuk and Seyitomer oil shales as determined by (Miknis, 1989) are given in Table 1.

Table 1. Fisher Assay results of the two main oil shale reserves of Turkey (Miknis, 1989)

	Goynuk wt, %	Seyitomer, wt, %
Oil	39.16	2.41
Gas	9.02	1.51
Residue	41.87	88.67

It is obvious that the two main reserves of Turkey have different oil yielding capacities, the former having one of the highest oil yields with comparatively low ash, whereas the latter has a low oil yield and high ash.

GEOCHEMISTRY of TURKISH OIL SHALES

One of the well-established methods of classifying oil shales is done by the plot of H/C and O/C ratios of the kerogen known as Van Krevelen diagram, originally developed for coal classification. This diagram classifies the kerogens into types I, II and III. Kerogens with high H/C and relatively low O/C classify them as type I, while relatively low H/C and high O/C ratio classify them as type III. The broken iso-vitrinite reflectance lines crossing the graph give the thermal maturation history of the kerogen samples.

Turkish Goynuk and Seyitomer samples are plotted on the Van Krevelen diagram in Figure 1, (Putun et.al.,1988)

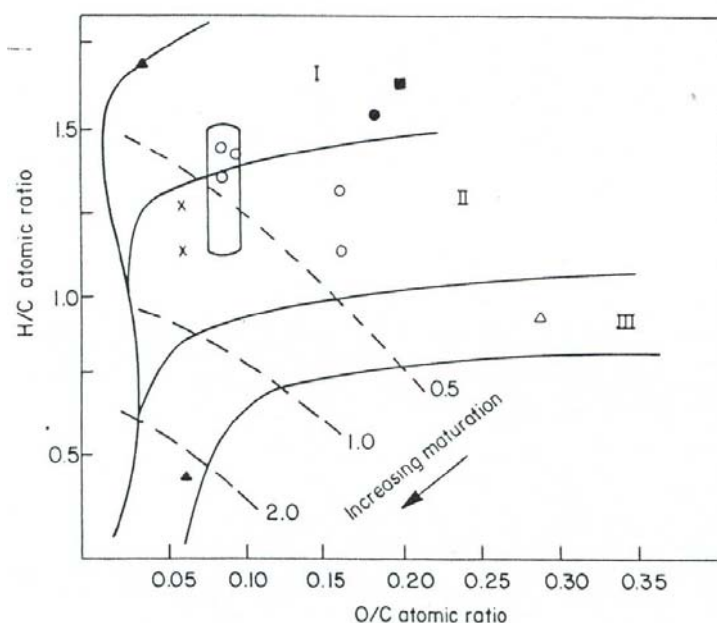


Figure 1. Van Krevelen Plot of Goynuk and Seyitomer Oil Shales of Turkey
(● Goynuk Oil Shale, ■ Seyitomer Oil Shale)

Both Goynuk and Seyitomer oil shales are classified as type I kerogens with low degree of thermal maturation from the van Krevelen diagram.

Another geochemical classification is the comparison of alkane distribution of the pyrolysis generated oils of different kerogens which are known to be representative type I, II and III kerogens. Green River (GRO), and Toarcian Shales and Mahacam Humic Coals are given as representatives of types I, II and III shales. The n-alkane distributions

of both of the oils produced from Seyitomer and Goynuk shales at 520 and 900 °C are bimodal and similar to the distribution obtained from GRO. Our studies on these two Turkish oil shales confirmed them as type I kerogens using carbon preference index (Putun et.al.,1988), NMR and IR(Putun et.al.,1991)

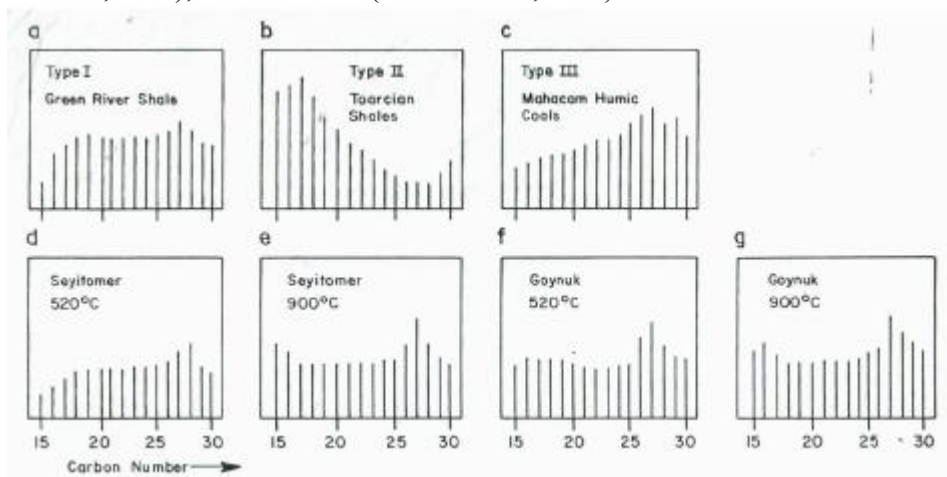


Figure 2 Alkane Distributions for Type I, II and III Kerogens a, b and c respectively (Okutan et.al,1993, Putun et.al.,1988).

Branched alkane are also used to gather information about the maturity of the kerogen. The relatively immature kerogen contains heat sensitive hopanes whereas mature ones depleted in them.

CHARACTERISATION of GOYNUK and SEYITOMER OIL SHALES

Oil shales mainly have inorganic and organic constituents. The inorganic portion is dependent on the input from the environment in which the debris is buried. They certainly had an effect on the evolutionary path of the organic structure. Also, presence of inorganic constituents may play an important role in processing of the oil shale. The proximate analysis of oil shales yields the ratio of organics and inorganics. A typical proximate analysis for Goynuk and Seyitomer oil shales are given in Table 2.

Table 2. Proximate Analysis of Goynuk and Seyitomer Oil Shales

	Goynuk A	Goynuk B	Seyitomer
Moisture, wt %	12	15	3.5
Ash, wt %	17	20	69.0
Vol. Mat. wt %	60.5	55.5	20.1
Fixed C wt %	10	9	7.4

The organic portion of oil shales may also be classified in two general classes; bitumen and kerogen. The bitumen is the soluble portion in petroleum based solvents and kerogen is the complex matrix which is converted into tar, gas and residue (semi-coke) when heated in an oxygen free-lean environment. The elemental analysis and some other chemical and physical analysis of Goynuk and Seyitomer Oil Shales are given in Table 3.

Table 3. Analysis of Goynuk and Seyitomer Oil Shales

	Goynuk	Seyitomer
Carbon, wt %	81.6	85.2
Hydrogen, wt	11.8	12.4
Nitrogen, wt %	1.3	0.9
Sulphur, wt %	1.9	0.6
Carbon Aromaticity, %	33.1	34.6
Hydrogen aromat., %	8.1	9.0
Molecular Weight	300	280
Specific Gravity	0.9301	0.8823
Total H/C	1.74	1.75
Aromatic H/C	0.425	0.454
Aliphatic H/C	2.296	0.8823

The ^{13}C and ^1H NMR spectra are of typical type I kerogen and simulated distillation results of the shale oil are given in Table 4.

Table 4. Simulated distillation of Goynuk and Seyitomer Shale Oils (Putun, et.al.1988, Miknis,1989,)

	Goynuk, % oil	Seyitomer, % oil
Light straight run	-	1
Naphtha	7	14
Kerosene	14.5	21.5
Light Gas Oil	11	14.5
Atmospheric Gas Oil	28	29
Vacuum Distillate	27	18
Residium	14	2

(Okutan et.al.,1993) conducted a study in which effect of process severity on the product distribution by analyzing the alkane distribution. As the product severity increased, the alkane distribution flattened out compared to the bimodal alkanes distribution of typeI.kerogen.

PROCESSING of TURKISH OIL SHALES

Because the organic constituent of oil shale is overwhelmingly kerogen, the liquefaction and solvent extraction does not yield appreciable liquid fuels. Generally speaking, type I kerogens with high C and H content yields synthetic fuel above a certain limit are termed as high quality oil shales and reserves not qualified for this grade may be combusted or utilized with other fuels in blends.

Pyrolysis

In order to have a basis for comparison the Fisher-Assay results for the Goynuk and Seyitomer Oil Shales are given in Table 5 as reported by the Western Research Institute Oil Shale Data Sheet (Miknis, 1980).

Table 5. Fischer-Assay Characterization of Goynuk and Seyitomer Oil Shales

C O N V E R S I O N						
	G O Y N U K			S E Y I T O M E R		
	Fischer As-Say, wt %	Carbon, wt %	C conversion wt %	Fischer As-Say, wt %	Carbon, wt %	C conversion wt %
Oil	39.16	81.6	58	2.41	85.2	39
Gas	9.02	38.6	6	1.51	40.3	11
Residue	41.87	46.7	36	88.67	3.0	50
Raw Shale	100.00	53.4	-	100	5.6	-

The percentage FA yield for the Goynuk and Seyitomer Oil Shales are 100.3 gpt and 7.0 gpt respectively. Oil yields of 10.5 gpt (4 %), 26.7gpt (10.4%), 36.7 gpt (13.8%) and 61.8 gpt (23.6%) classify the shale oils as uneconomical, medium economical, highly economical and very highly economical respectively (Ekinci,1995). Therefore, Goynuk oil shale is classified as very highly economical, whereas Seyitomer oil shale is classified as uneconomical deposit.

Fixed Bed Pyrolysis

Static, Self-Generated Atmosphere

Due to the effect of mineral matter of Goynuk and Seyitomer oil shales, in fixed bed pyrolysis there is mass transfer limitation. As the volatiles are formed, if they are not removed from the surface fast enough, they are catalyzed by the mineral matter to form char. Results of self-generated pyrolysis experiments of some Turkish oil shales are under different conditions and in different retortments are compiled in Table 6.

Table 6. Self-generated Pyrolysis Results of Some of Turkish Oil Shales in Different Retorts.

Oil Shale	Retort	Final T °C	Oil Yield, %	Reference
Goynuk	Heinze	550	33	Citiroglu et al, 1991
Goynuk	Fixed Bed	550	38	Citiroglu et al, 1989
Goynuk	Heinze-m	520	41.3	Putun et al, 1991
Goynuk	Heinze-m	900	43.4	"
Seyitomer	Heinze-m	520	33.4	"
Seyitomer	Heinze-m	900	38.1	"
Seyitomer	Heinze-m	550	28.2	Uzlu, 1990
Seyitomer	Fixed bed	550	28	Citiroglu et al, 1989

It is clear from the results that, under self-generated static conditions, reactor geometry influences the oil yield. Modified Heinze retort performs considerably better than normal Heinze retort.

The limitations experienced in self-generated atmospheres may be overcome by a variety of ways, such as sweeping the volatiles from the surface, de-ashing the oil shale, employing novel retort geometries and addition of hydrogen.

Sweeping the Pyrolysis Atmosphere by Different Gases

In order to overcome the mass transfer limitation of the static conditions, results of a series of experiments in which relatively small sweep velocities employed are presented in Table 6.

Oil Shale	Retort	Gas	Velocity, cm/sec	Max. T °C	Yield, % dafb	Ref
Goynuk	Heinze	Nitrogen	3.3	550	39	Çitiroglu, 1991
Goynuk	Fixed B Tubular	Nitrogen	2.2	550	61	"
Goynuk	Heinze	Steam	0.7	550	40	"
Goynuk	Heinze	Steam	3.3	550	44	"
Seyitomer	Heinze	Steam	4.3	550	38	Ekinci et al 1991
Seyitomer	Heinze	Steam	12.3	550	45	Ekinci et al 1991

It is clear from the fixed bed retort studies that sweeping increases the shale oil yield considerably. Water vapor is a more efficient sweeping environment than nitrogen. Also, change of reactor geometry from Heinze to tubular type of reactor has an important effect on oil yield .

The beneficial effect of steam to oil yield in pyrolysis of oil shales is still an unresolved issue. It is a common observation that both steam and nitrogen sweep affects both the quality and quantity of oil, but the change is more intense for steam. One reported behavior is that, for the increased sweep velocity of steam and nitrogen, the yields of alkanes and aromatics are increased whereas those of poplars are decreased, which is more pronounced for the steam? This is interpreted as alkanes may be involved in retrogressive char-forming reactions via dehydrogenation to alkenes and subsequently cyclisation. ¹ H-NMR studies of the shale oils showed greater aromaticity for steam pyrolysis as compared to static pyrolysis (Citiroglu,1989;Okutan et.al.,1994), one of the well-accepted works conducted by Minkova et.al. 1991, reported measurement of lower CO and CO₂ concentration in the gas for the steam pyrolysis indicating a probable reaction between CO and steam in the presence of Fe catalyst. Minkova et.al,1987;1992) in their continuing studies reported that steam also had a physical effect on the heat transfer, favoring the desorption of low molecular weight products from solid phase surfaces whereby subsequent cracking or coking is avoided. This explanation is in line with the oil yield increase and compositional change.

In order to see the effect of higher velocities on the oil yield, higher sweep velocity of 22 cm/s nitrogen gas is used in an incoloy reactor. The comparative results for the Goynuk and Seyitomer oil shales are presented in Table 7.

Table 7.Effect of Higher Velocity Sweep in an Incoloy Retort on the Oil Yield of Goynuk and Seyitomer Oil Shales, % wt daf / dmmf basis

	Conversion		Tar		Char		Total gas	
	Goyn.	Seyito	Goyn.	Seyito	Goyn.	Seyito	Goyn.	Seyito
Static	52	50	38	33	48	56	14	12
N= 22 cm/s	61	58	51	42	39	48	10	10

Sweeping the environment shortens the residence times of the volatiles, which lessens the chance of char forming reactions and prevents volatiles to contact with hot surfaces for breaking down to smaller gaseous molecules.

Effect of Temperature on Fixed Bed Pyrolysis

Experimental study on the Goynuk A and B samples in a fixed bed reactor with nitrogen sweep and changing final temperatures are shown in Figure 2. In these experiments a

soak time of 35 minutes at the final temperature was used. The results are compiled in Table 8 (Graham et. al,1992).

Table 8. Oil Yields for Goynuk A and B from Nitrogen Swept Fixed Bed

Run temperature, °C	Oil Yield A, %	Oil Yield B, %
400	21.56	12.27
425	28.08	22.61
450	28.93	25.34
500	40.75	37.70
525	41.91	37.50
550	41.26	33.09
575	42.45	31.20
600	41.62	30.10
675	39.88	30.20

With increasing temperature, both Goynuk A and B samples experienced an increase reaching to maximum oil yield, followed by a decrease. At first, as temperature is increased, greater amount of kerogen species are volatilized and stabilized into liquid product. After the maximum temperature, the rate of thermal decomposition of the volatiles as they are formed and their contact with hot surfaces, became greater than condensation to liquid products, thus resulting in decrease in the liquid product.

Fluidized Bed Retorting

Goynuk oil shale was pyrolysed in a 3.81 cm. diameter fluidized bed retort. Helium gas was used as fluidization medium. He was preheated before it entered the bed. Illite particles were used as the bed material. The results of the experiments are compiled in Table 8.

Table 8. Oil Yield for Goynuk A in a Fluidized bed, (Graham et.al.,1992)

Run Number	Temperature °C	Oil Yield,%	Run time, min.
1	550	44.43	44
2	550	45.68	39
3	575	46.71	29
4	575	44.93	49
5	550	46.12	42

Fluidized bed pyrolysis results averaged as 45.59% oil yield. The percentage yield increase compared to fixed bed runs at 550°C was found to be 9.26% higher. In the fluidized bed experiments there was an agglomeration problem related to the spent shale

and even at 50:50 shale to illite mass ratio, agglomeration developed. The run time reported in Table 8 is the time of fluidized operation halted by agglomeration.

Hydropyrolysis and Catalytic Hydropyrolysis of Turkish Oil Shales

From extensive hydropyrolysis coal research work, it is well-known that by radical hydrogen transfer promoting the scission of strong bonds in the macromolecular structure to form moieties of lower molecular weight. This is also applicable to the macromolecular structure of kerogens. In order to investigate effect of hydrogen and molybdenum catalyst hydropyrolysis and catalytic hydropyrolysis experiments were carried out. The results are compiled in Table 9.

Table 9. Hydropyrolysis and Catalytic Hydropyrolysis of Goynuk and Seyitomer Oil Shales, %

Oil Shale	Total conv.	Tar	Char	C ₁ -C ₄ gases	
Goynuk	94	72	6	9	Ekinci et.al.,1991
Goynuk + 1 % Mo	100	82	<2	4	"
Seyitomer	95	77	5	2.5	Citiroglu et.al,1990
Seyitomer +1% Mo	98	80	2	1.9	

In hydropyrolysis a much higher concentration of hydrogen radicals are generated than in normal pyrolysis; these radicals can therefore promote bond cleavage by the radical H-transfer process.

When a catalyst is employed, it is likely that the active molybdenum disulphide increases the level of dissociation of hydrogen molecules and is responsible for hydrogenation of aromatic rings. This then lead to elimination of more oxygen and sulfur because labile aliphatic C-heteroatom bonds are being formed.

From the results it is understood that Mo catalyst has a better effect on Goynuk compared to Seyitomer, which is attributed to the lower ash ratio of the former. The consistent decrease in the char yield is due to hydrogen pressure protecting the oil yield from polymerization and condensation reactions due to the favorable effect of hydrogen as a stabilizing agent for the volatile radicals.

Copyrolysis of Oil Shales

In self-generated fixed bed pyrolysis, due to the effect of mainly clay minerals, there is a mass transfer limitation to the liquid product yield due to retrogressive char forming reactions. One way of preventing this shortage is to use copyrolysis operation in order to

benefit from synergistic effects of different minerals. As an extension of co-processing of coal and heavy oils, copyrolysis of different minerals has received some attention (Saxby et al. , 1990.; Citiroglu et al. 1991, Ekinici et al. 1992) . As a result of copyrolysis, increased aromaticities and decreased molecular weights are reported for Australian oil shale-lignite mixtures. Pyrolysis of two Turkish lignites and oil shale mixtures resulted in increased oil yields. The small but significant synergism was more pronounced for higher concentrations of oil shales in lignites. The synergistic effect of copyrolysis of oil shales and lignites disappeared in fluidized bed pyrolysis where conversions were much higher because of the high fluidization velocity, overcoming the mass transfer limitations.

Turkish oil shale and lignite copyrolysis results are evaluated using N-alkane distribution for 1:1 and 1:2 lignite-oil shale mixtures. The type 1 kerogen distribution was masked with the contributions lignite for the former, but the distribution shifted towards the type 1 kerogen for the latter. The net increase in the yield due to mixture is attributed to the possible effect of water vapor arising from lignite, catalytic effect of inorganic matrix and solvent extraction effect of the oil shale volatiles on the lignite, which may involve hydrogen transfer (Okutan et al. ,1993).

Copyrolysis of Goynuk oil shale and polyethylene did not result in a distinctive synergism for oil yield. However, distinct product modification was observed due to the presence of hydrogen rich polyethylene environment. The alkydienes/ alkene and alkene / alkane ratios indicate that there is possible hydrogen transfer taking place during copyrolysis (Ozdemir et al, 1997)

OIL SHALE to CARBON MATERIALS STUDIES

Carbon Adsorbents

Low ash Goynük oil shale providing considerable porosity, due to volatile release during processing for synthetic oil, has caused interest in it to be considered as a possible activated carbon source. For this purpose, shale chars obtained from pyrolysis were

subjected to steam activation at 880°C and impregnated with ZnCl₂ catalyst before carbonization resulted in BET surface areas in the shale carbon up to 400 m²/g. Characterization of the pore formation with mercury porosimetry indicated meso pore volumes of 9-20% of the total pore volumes of the shale carbons. This result suggested good liquid adsorption capabilities for the developed shale activated carbon.

Application of the derived shale activated carbon for NO, NH₃ and H₂S removal and its comparison with a commercial adsorbent carbon has been made. Comparison of the Goynuk oil shale derived and commercial adsorbent carbon indicate that in NO and NH₃ adsorption developed carbon is about 50% efficient, but it is over 2.5 times more efficient in H₂S adsorption compared to commercial carbon. In liquid phase adsorption

Goynuk carbon has 70% phenol adsorption capacity, whereas Alpha oil shale derived carbon has 60% adsorption capacity of the commercial carbon (Graham et.al.,1993a; Graham et.al,1993b).

Isotropic Pitch and Carbon fiber Production

Carbon fiber industry has been looking into possible alternative precursors to PAN in order to cut the cost of production. Coal tar and shale oil tar pitches have received intense research interest. Direct processing of the tars of these two fossil fuels such as solvent extraction, vacuum distillation, air-blowing and modification by additives gave high softening point pitches for spinning. However, the straightforward processing yielded isotropic pitch which is appropriate for the production of general purpose (environmental) carbon fibers. Comparison of the Goynuk oil shale derived pitches with some other samples from the world is presented in Table 10.

Table 10. Comparison of the Properties of Different Pitches for Fiber Spinning (A-HI-BS, B-Britch bituminous coal, CAER, C-Wyoming sub-bituminous coal, D-Ashland petroleum pitch, E-Goynuk pyrolysis pitch, air-blown, F-Asphaltene fraction of Goynuk air-blown pitch).

Sample	Elemental Analysis			C/H	Spinning T °C	Processing
	C	H	N			
A	80.98	6.64	2.54	1.01	240	Solvent extr.
B	91.52	5.28	1.49	1.44	220	Solvent extr.
C	89.94	6.81	1.23	1.10	167	By-product
D	92.88	4.63	0.31	1.67	304	Pet. Pitch
E	84.35	8.75	1.80	0.80	170±5	Air blowing
F	82.92	6.95	2.46	0.98	170±5	Solvent extr.

Softening point of the Goynuk derived precursors were high enough to spin. Indeed the three samples listed in Table 11 have shown good spin ability.

Table 12. Properties and Spin ability of Selected Goynuk Oil Shale Derived Pitches.

Sample	C	H	N	C/H	Spinning T, °C	Spin ability
GA3	84.00	9.50	1.65	0.74	140±5	Very good
GA6	84.34	8.75	1.80	0.80	170±5	Very good
GA6-S	82.92	6.95	2.46	0.98	205±5	Very good

All these samples resulted in continuously drawn fibers up to more than 1.5 m long. It is important that the spinning temperatures of the three precursors showed a big difference. It is observed that spinning temperature increases with increasing C/H atomic ratio. It was possible to produce general purpose carbon fiber from 550 °C pyrolysis oil by direct air blowing and solvent extraction of Goynuk tar.

In order to produce high performance carbon fibers it is necessary to prepare mesophase pitch from the isotropic pitch that is obtained from pyrolysis oils by solvent extraction, vacuum distillation and air-blowing or combination of these.

OTHER STUDIES

Seyitomer oil shale was subjected to three stage demineralization studies by (Gozogul et.al,1984): oil shale was subjected to HCl, HCl + Zn and HF treatment. The original shale oil had 64.44% ash at the start and it dropped to 63.26%, 13.68% and 6.36% after treatment with HCl, HCl + Zn and HF respectively.

(Berber and Turker,1983) conducted a study on the fluidized bed combustion of Goynuk oil shale. In this study they reported a combustion efficiency between 84.6-92.8%. In 1974 MTAE conducted fluidized bed studies on Bey pazarı oil shale. The calorific value of oil shale was reported to be 850 kcal/kg which sustained bed temperatures between 750-875 °C(envanter)

Davies et.al.,1988) investigated the olefin, saturates and aromatics using HC HPLC/CCGC methods. Polycyclic aromatic hydrocarbons(PAH) in bitumens and pyrolysis oils obtained at 520 °C and 900 °C from Goynuk and Seyitomer oil shales are analysed by (Tolay, et.al.,1987). They reported that bitumens contained up to five ring PAH's and pyrolysis oils had up to four ring PAH's.. The residues of different process (self-generated, steam and nitrogen swept fixed bed) are studied for their organic content (Okutan et.al,1994b)

(Akar et al.) In their study on "Production of chemicals from oil shales" claim that production of various smaller molecular weight alkenes, nitrogen aromatics and value-

added chemicals from heavy aromatic shale oil from fluid bed retorting maybe a more suitable application than production of transportation fuels.

ECONOMICS of SHALE OIL

The main point of interest today is the question, how is the economics of oil shale in replacing the crude oil as the feedstock for petroleum and chemical industries? At the time of the meeting of "Composition, Geochemistry and Conversion of Oil Shale

Symposium, in Akçay Turkey in 1993, a price of \$31-43 per barrel manufacturing cost was quoted for 15% DCF for a plant processing 50 000 bpd (Green,1988, Ekinci,1995). These economical evaluations need to be updated to present day prices and facilities. However, at the time of these studies, the price of petroleum was less than \$30 per barrel and at present it is above \$60 per barrel, and will most probably increase to higher values given the political choices of the influential rulers of the world. Therefore, oil shale research, development and investment should be promoted.

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