

Direct Liquefaction of High-Sulfur Coals: Effects of the Catalyst, the Solvent, and the Mineral Matter

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Received November 13, 2001

Two low-rank coals with high sulfur contents (Gediz subbituminous coal: 7.6 wt % S; dry basis. Çayirhan lignite: 5.7 wt % S; dry basis.) were subjected to hydroliquefaction. Liquefaction conditions included dry or solvent mediated runs under pressurized hydrogen without added catalyst or with the impregnated catalyst precursor ammonium heptamolybdate (AHM). Gediz coal having higher sulfur content gave 90% conversion in the absence of catalyst and solvent. Maximum conversion (98%) and maximum oil + gas yield (70%) from this coal were obtained by impregnating AHM onto coal and carrying out liquefaction in H₂/tetralin system at 450 °C for 30 min. Under the same conditions, Çayirhan lignite gave 85% conversion and 70.5% oil + gas yield. The superior hydrodesulfurization effect of impregnated AHM on the oil fraction when used in the absence of solvent (less than 0.1% S in lignite's oil and less than 1% S in subbituminous coal's oil following one-stage hydrogenation) is a promising finding of this work. AHM was found to be much more effective in liquefaction of Çayirhan lignite and this has been ascribed to the well-dispersion of AHM throughout this lignite's structure via a cation-exchange mechanism through oxygen functionalities. Strong evidence for the catalytic effect of clay minerals in coal structure on char-forming reactions during liquefaction was observed by making use of liquefaction reactions of demineralized coal samples. It was also observed that tetralin had a retarding effect on the condensation and subsequent cross-linking reactions.

Introduction

Coals when subjected to direct liquefaction by catalytic hydrogenation, yield valuable organic products to be utilized as feedstocks in various processes, one of which is the possibility of being used in the preparation of jet fuels of high thermal stability.^{1–4} In direct catalytic hydroliquefaction of coals, the factors which are considered to be important in determining the quality and quantity of liquid fuels which will be produced and in determining the economic feasibility of the process are the type of the coal to be processed, the catalyst, the ratio of the amount of hydrogen gas and solvent to the amount of liquid fuels produced, and of course the temperature and the pressure of the process. In general, most of the covalent bonds in coal structure cleave at temperatures between 375 and 450 °C and therefore direct hydroliquefaction processes use temperatures around these values. One should mention that if the treated coal is in the low rank range having high carboxyl and/or sulfidic type of functional groups, then covalent bond breakage starts at significantly lower

temperatures.^{5–7} The main reactions which take place during liquefaction are thermolysis, hydrogenation, dealkylation, desulfurization, denitrogenation, dehydration, cleaving of cyclic hydrocarbon structures into open-chain hydrocarbons, and condensation reactions. Except the last one, the rest of the reactions have to take place for an effective liquefaction though cleaving of alicyclic structures will also be a disadvantage if the final aim is to obtain an oil appropriate for preparing thermally stable jet fuels. On the other hand, retrogressive reactions taking place when quenching of active radical sites by hydrogen transfer is not fast enough, result in the formation of larger and refractory organic structures.^{8–11}

The coal liquids are also used as solvent in coal liquefaction processes. These liquids in general, have two to four condensed rings and are very effective hydrogen shuttlers.^{12,13} These solvents are generally

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used at temperatures between 200 and 400 °C and are hydrogenated while being recycled to liquefaction reactor.^{14–19} It is now certain that these solvents are effective in quenching active radicals which are formed during thermolysis of various covalent bonds in coal structures, but there is also a debate on solvent's effect in thermolysis reactions as well. While a group of researchers argue that solvent-derived cyclohexadienyl radicals induce cleavage of relatively strong covalent bonds, others find this argument quite debatable especially at short liquefaction times.^{20–27} Solvents also enhance various reactions during coal liquefaction via the solvation effect. The hydrogen donor solvents swell the coal structure so that efficient interactions of coal reactive sites with both hydrogen donating solvents and with catalyst precursors dispersed in the reaction medium are attained.²⁸ It has also been proposed that structures such as quinoline and primary amines in coal solvents not only enhanced swelling, but also took part in cleaving relatively strong bonds.^{29,30}

Hydrogen gas is also an important reactant in direct liquefaction reactions. Together with solvent and catalyst, it plays the major role in direct liquefaction of coal. The main functions of hydrogen gas in coal liquefaction are quenching of active radicals which are formed during thermolysis reactions, enhancing the cleavage of C_{ar}-C,²⁰ C_{ar}-O,³¹ and other similar covalent bonds and hydrogenating the solvent molecules in-situ and while being recycled to the liquefaction reactor.

In some cases, addition of H₂S to the reactor also enhances liquefaction of coals.^{17–19,32–37} It has been proposed that H₂S is also effective in cleaving some strong bonds,³⁸ in removal of nitrogen from coal struc-

tures³⁹ and in improving the catalytic effect of mineral matter in coal by converting iron compounds into iron sulfide forms.^{33,40–43}

Hydroliquefaction catalysts are considered to be effective in hydrocracking reactions, in quenching of active radicals which are formed due to the thermolysis reactions, in removal of heteroatoms in coal structures, in hydrogenating the appropriate sites in coal structures, and in hydrogenating the solvent molecules by activating the molecular hydrogen and/or solvent. They can be classified into two main groups: supported catalysts and dispersed catalysts. The former group has been reviewed by Derbyshire.⁴⁴ A general review on coal liquefaction catalysts was done by Anderson.⁴⁵ The catalytic effect of mineral matter in coals in liquefaction was reviewed by Schobert.⁴⁶ Most of the work on coal liquefaction catalysts up to 1990 were cited in these three reviews. Research on development and use of coal liquefaction catalysts in the past decade were still continuing.^{47–56} The superiority of using water soluble molybdenum compounds in coal liquefaction as catalyst precursors by impregnating onto coal particles has been well documented.^{16–19,35–37,44,57–65} Pilot plant studies have also demonstrated that using dispersed molybdenum catalysts were very efficient in primary liquefaction (dissolution) of coal, particularly of low-rank coals such as subbituminous coals and lignites.^{66–70}

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Turkey's low-rank coal reserves exceed eight billion tons and most of these have high sulfur, high volatile matter and high ash contents.⁷¹ Therefore direct combustion of these solid fuels creates extreme pollution. Direct hydroliquefaction by using appropriate catalysts also reduces sulfur content of oil and other liquefaction products via hydrodesulfurization reactions and therefore is one alternative to obtain relatively clean liquid fuels and feedstocks for various chemical industries. When water soluble (e.g., ammoniumheptamolybdate: AHM) or organic soluble molybdenum compounds are dispersed in coal pores and on surfaces, they will react with the H₂S evolving and/or other forms of sulfur during the heat treatment applied to high-sulfur coal in the presence of hydrogen gas and will eventually be transformed into MoS₂, the high-performance hydrodesulfurization and dissolution catalyst.^{50,51} It has been shown that other molybdenum catalysts such as molybdenum hexacarbonyl and/or molybdenum carbide,⁶³ phosphomolybdic acid and Ni or Co phosphomolybdates^{35–37} and bimetallics of Mo with Co or Ni supported on alumina or carbon^{51,56} following sulfidation also had similar performances. Zhan and Givens stated that the water soluble AHM impregnated coal samples (subbituminous Wyodak Black Thunder) were as active as and much less expensive than the corresponding organic soluble precursor impregnated coal samples during hydroliquefaction.¹⁸

In this study, one sub-bituminous coal and one lignite both having high sulfur contents were directly hydroliquefied. In some of the liquefaction experiments, coal samples impregnated with ammonium heptamolybdate (AHM) as a catalyst precursor were used. The effects of the type of coal, the vehicle solvent, the catalyst, the mineral matter of coal, and the reaction temperature on product distribution and on the fate of organic sulfur were discussed.

Experimental Section

Gediz sub-bituminous coal and Çayirhan lignite were liquefied in this study. Their proximate and ultimate analysis data are given in Table 1. The coals were ground to pass 60 mesh, dried at 50 °C under reduced nitrogen pressure (no air) until moisture contents fell below 3%, sealed in glass ampules under nitrogen gas, and kept at –20 °C until utilization in the liquefaction experiment. All solvents and chemicals were bought from Merck and used as received.

The catalyst precursor, ammoniumheptamolybdate (AHM), (NH₄)₆Mo₇O₂₄•2H₂O (1.0047 g), was dissolved in 30 mL of distilled water and added onto 100 g of dry coal dropwise while the coal was effectively mixed with a spatula. This addition took about 30 min after which the coal was dried at 50 °C under reduced nitrogen pressure until the moisture content fell below 3%. The incipient wetness water value of all coal samples were adjusted between 2 and 3%. A bulk of ground coal was subjected to catalyst precursor impregnation with the above procedure and with the same relative amounts of AHM to coal and the impregnated coal samples after drying under reduced nitrogen pressure, were sealed in many glass ampules

Table 1. Proximate and Ultimate Analytical Data of Coals

	coal	
	Gediz	Çayirhan
calorific value (kJ/kg)	22598	16074
ash (wt % dry)	34.0	38.1
V. M. (wt % dry)	32.8	36.8
Elemental Analysis (wt % Daf ^a)		
C	78.3	70.5
H	6.0	6.8
N	1.1	1.9
S	6.8	2.1
O ^b	7.8	18.7
Forms of Sulfur (wt % Dry)		
total	7.6	5.7
pyritic	2.9	2.6
sulfatic	0.2	1.8
org ^b	4.5	1.3

^a Daf: dry, ash-free. ^b Calculated from difference.

under nitrogen gas so that all catalytic liquefaction experiments would be carried out with the coal samples having identical AHM dispersion and identical incipient wetness.

Samples of demineralized coals were also prepared to be used in liquefaction experiments. Three types of demineralization were applied:

Removing Cationic Components. Fifty grams of ground coal was poured into 100 mL of 5 N HCl and heated at 60–70 °C under nitrogen gas atmosphere for 1 day while being mixed with a magnetic stirrer. The solid coal remaining was filtered and washed with distilled water effectively to remove all residual HCl. Chloride test with silver nitrate solution was applied to filtrates.

Removing Clays and Cationic Components. Same procedure was applied with concentrated HF and then 5 N HCl being added in succession.

Removing Pyritic Components as Well as Clays and Cationic Components. Following sequential application of concentrated HF and 5 N HCl, 5 N nitric acid was applied at the same temperature and duration.

After extensive washing with distilled water, all demineralized samples were dried at 50 °C under reduced nitrogen pressure until moisture contents fell below 3%, sealed into glass ampules under nitrogen gas, and kept at –20 °C until utilization for liquefaction experiments.

Microautoclaves of 25 mL volume were used in liquefaction experiments. In a typical experiment, 2.5 g of coal (AHM impregnated or not) and 5 g of solvent (if solvent had to be used) were charged into the reactor. Following sealing the reactor, air inside the reactor was swept out by successive pressurizing (6.9 MPa cold) and depressurizing twice with nitrogen and twice with hydrogen gases. Finally, the reactor was pressurized with hydrogen gas (6.9 MPa cold) and submerged into an eutectic salt bath after fixing on a horizontally oscillating system. The bath, having a temperature of 5 °C above the desired working temperature, heats the reactor to the desired working temperature in 1–2 min. The horizontally oscillating system shakes the reactor with an amplitude of 2 cm at 400 cycles/min. In all of the liquefaction experiments, the duration of operation was 30 min. All liquefaction experiments were carried out twice. Therefore, various numerical quantitative data relevant to liquefied material were the mean of two corresponding values. When the difference between the two replicate values for the total conversion exceed 2% of the mean value, a third replicate experiment was performed and the two most close values out of three were used for calculations. The yield of oil + gas fractions were calculated by difference. Qualitative and quantitative gas analysis were not done except H₂S. For those experiments where tetralin was used as solvent, no attempt

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Table 2. The Effect of Temperature with Different Solvent/Catalyst Combinations on the Conversion of Coals during Liquefaction^a

system	temperature (°C)	conversion (wt % of daf coal) ^b							
		total ^c		PAS ^c		AS ^c		oil + gas ^d	
		GED	CAY	GED	CAY	GED	CAY	GED	CAY
H ₂	300	21.5	7.7	14.5	2.3	6.6	1.5	<1	3.9
	350	30.6	20.0	18.1	3.2	7.3	3.5	5.2	13.3
	400	89.7	74.2	30.0	20.2	47.5	24.0	12.2	30.0
	450	81.9	73.0	10.1	5.2	22.4	16.5	49.4	51.3
H ₂ /tet	300	34.0	9.2	18.4	3.1	9.9	1.5	5.7	4.6
	350	55.1	28.8	34.2	11.2	14.8	12.9	6.1	4.7
	400	95.0	75.1	32.8	18.7	32.1	20.2	30.1	36.2
	450	97.0	85.1	12.2	9.2	17.5	15.0	67.3	60.9
H ₂ /AHM	300	26.5	8.5	17.2	0.5	9.0	1.0	0.3	7.0
	350	36.0	36.3	19.5	4.5	15.6	5.3	0.9	26.5
	400	93.3	85.4	39.8	9.9	47.9	24.0	5.6	51.5
	450	93.5	83.2	23.8	4.4	28.6	12.2	41.1	66.6
H ₂ /tet/AHM	300	36.8	9.2	10.5	2.2	17.6	1.6	8.7	5.4
	350	65.6	37.6	14.9	4.1	33.5	9.8	17.2	23.7
	400	98.6	88.5	18.4	15.0	45.9	22.5	34.3	51.0
	450	98.3	85.0	10.5	3.4	18.2	11.1	69.6	70.5

^a Single-stage liquefaction, 30 min. ^b Daf: dry, ash-free. ^c GED: Gediz coal. CAY: Çayirhan lignite. AS: asphaltene. PAS: preasphaltene. ^d Calculated from difference.

was made to recover tetralin in order not to remove some other volatile oil products as well, however, the oil + gas yield values in corresponding tables did not include the solvent contributions because they were calculated by difference.

When the liquefaction operation time was over, the reactor was taken out of salt bath and immediately plunged into a cold water bath. The gas in the reactor was bubbled through a cadmium acetate solution so that H₂S reacted with Cd²⁺ and precipitated quantitatively as CdS. Gravimetric analysis of precipitated CdS gave the H₂S yield from liquefaction process. The slurry content of the reactor was taken out by *n*-hexane into an extraction thimble and successively extracted in a Soxhlet apparatus with *n*-hexane, toluene, and tetrahydrofuran; oil, asphaltene (AS), and preasphaltene (PAS) were the material solubilized in these three solvents, respectively. The mass of oil + gas products were calculated by subtracting the total mass of asphaltene + preasphaltene + char (residue) from the mass of original dry coal subjected to liquefaction. Sulfur contents of oil, asphaltene, preasphaltene and char were analyzed by using LECO-SC132 instrument. Oil analysis were carried out by using GC-MSD (HP-5970 MSD coupled to a HP-5980 GC). MSD was equipped with a quadrupole analyzer and operated in electron impact (70 eV) mode. The GC of the GC-MSD system was equipped with a TC-17 50%: 50% phenyl-methyl siloxane column (30m × 0.32 mm i.d.; 0.5 μm film thickness). The column oven temperature program starts at 50 °C (5 min hold) and then increases up to 280 °C with a 4 °C/min ramp. The oven temperature was hold at this final value for 15 min.

Results and Discussion

1. Variation of Processing Temperature in the Presence and Absence of Solvent and Catalyst.

Both coals were subjected to liquefaction with various solvent/catalyst combinations at four different processing temperatures, namely, at 300, 350, 400, and 450 °C. The product distributions and the corresponding total conversions are given in Table 2.

The first observation from Table 2 is that dissolution of coal matrix in Gediz coal starts at comparatively lower temperatures than those of Çayirhan lignite, and at all conditions the total conversion values of Gediz coal are higher than those of Çayirhan lignite.

Asphaltene and preasphaltene fractions dominate when Gediz coal is liquefied at temperatures of 400 °C

or below, indicating that the original coal matrix has comparatively large units interconnected or cross-linked by weak bonds; presumably at least some of them are sulfide type of bonds. On the other hand, transformation of these preasphaltene and asphaltene molecules into smaller molecules (oil) is not easy and significant transformations only occur at 450 °C indicating that weak S-S or S-C type of bonds are no longer present in these asphaltene and preasphaltene molecules.

One other observation regarding liquefaction of Gediz coal is that without any solvent and added catalyst, total conversion is almost 90% at 400 °C, though substantial oil + gas formation occurs at 450 °C. This indicates that some of the mineral matter components together with high sulfur content transform into catalyst type material under processing conditions but still quenching of active radicals formed at this temperature is not fast enough because the total conversion decreased to 81.9% due to the retrogressive reactions.

When Gediz coal is liquefied with AHM in the absence of added solvent, small increases in total conversion are noted, whereas oil + gas yields are decreased compared to no catalyst case. This might be an indication that AHM is not effective enough in transferring sufficient active hydrogen from gas phase to the radicalic fragments cleaved off coal structure and the asphaltene and preasphaltene molecules formed from Gediz coal. On the other hand, when tetralin was used as solvent (no AHM) total conversion value increased to 97 % and oil + gas yield also increased to 67.3 % at 450 °C; i.e., using tetralin, in addition to swelling the coal, was effective in transferring hydrogen and stabilizing small fragments which were cleaved off coal and asphaltene and preasphaltene molecules. This observation is consistent with the previous findings that tetralin behaves as an effective stabilizer in thermally stressed jet fuels via its hydrogen donor property where there is no catalyst.⁷⁴

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Table 3. Sulfur Content of the Product Fractions Obtained from Liquefaction of Coals

system	temperature (°C)	sulfur content (wt % of the fractions except Gas)									
		residue		PAS		AS		oil ^a		gas ^b	
		GED	CAY	GED	CAY	GED	CAY	GED	CAY	GED	CAY
H ₂	300	6.8	5.7	6.4	nd ^c	nd	nd	nd	nd	6.4	3.4
	350	6.4	5.9	5.5	5.2	5.9	nd	15.6	nd	13.1	6.4
	400	6.2	7.3	3.9	2.1	4.4	1.3	8.4	<0.1	28.6	23.0
	450	5.3	6.5	2.7	1.8	2.7	1.5	2.7	0.3	51.3	31.3
H ₂ /tet	300	7.2	5.6	4.9	5.6	4.3	nd	17.3	nd	2.7	<1
	350	6.8	5.8	5.2	3.8	5.7	3.8	29.8	0.1	5.2	6.0
	400	6.2	7.4	3.7	2.4	4.5	2.0	12.7	0.8	15.5	15.9
	450	6.8	7.7	2.7	2.9	4.1	1.1	4.8	0.8	31.4	26.7
H ₂ /AHM	300	8.3	5.9	5.6	nd	nd	nd	nd	nd	5.7	<1
	350	6.3	5.9	5.9	3.5	6.1	4.6	nd	1.6	13.5	8.3
	400	6.5	8.5	3.7	2.8	4.8	1.7	9.0	<0.1	32.8	19.4
	450	7.0	8.7	2.2	2.1	2.8	1.4	<1	0.1	48.0	31.7
H ₂ /tet/AHM	300	7.6	5.9	5.5	4.0	4.9	nd	9.3	nd	2.3	<1
	350	5.9	6.0	5.3	3.4	4.6	3.7	18.5	4.1	6.2	3.4
	400	6.4	8.1	3.5	2.8	nd	2.4	nd	1.8	11.6	4.9
	450	7.6	8.9	2.8	3.8	5.0	2.2	4.7	0.9	21.4	11.0

^a Calculated from difference. ^b wt % of total coal sulfur converted to H₂S during liquefaction (assuming H₂S is the only S containing compound in the gas phase. ^c nd: not determined.

On the other hand, in the present liquefaction system it might be probable that the mineral matter of Gediz coal, which presumably has been transformed into active catalyst forms by sulfidation with its own sulfur forms throughout the liquefaction, would have played an additional role in providing this high conversion because there was hydrogen gas in the reactor.

Çayirhan lignite with its relatively lower total sulfur and organic sulfur contents when compared with Gediz coal, behaves rather differently in hydroliquefaction. In no solvent, no added catalyst case, substantial conversion takes place at and above 400 °C. At all temperatures in this no-solvent, no-added-catalyst case, the most abundant fraction of products is oil + gas indicating that many smaller units are attached to the main structural frame by rather weak bonds. Since the oxygen content of this lignite is much more than that of Gediz coal, one can argue that a significant portion of this oxygen content, besides the carboxyl groups, forms those relatively weak bonds, bridges, and cross links of hydrogen bonded phenolic hydroxyls in the lignite structure. The abundant phenolic compounds in the oil fraction derived from this lignite supports this argument.

Although the mineral matter of Çayirhan lignite is also effective in catalyzing hydroliquefaction reactions, the extent is less than the corresponding effect in Gediz coal. In contrast to Gediz coal's behavior, AHM without added solvent, is effective in Çayirhan lignite increasing both total conversion and oil + gas yield substantially. It was well-known that low-rank coals with their high oxygen functional group concentrations adsorb multi-charged metal cations through an ion exchange mechanism and this property has been used for dispersing metal catalysts across a coal surface prior to liquefaction.^{75,76} Since the oxygen functionalities are abundant in Çayirhan lignite, a more well-dispersion of the catalyst precursor compared to Gediz coal's case should be the main reason for this observation. On the other hand, addition of tetralin helps little in improving liquefaction reactions which is also contrary to Gediz coal's corresponding case.

In a recent study,⁷⁷ Çayirhan lignite (called Beypazari lignite in the relevant publication) was liquefied in tetralin under nitrogen atmosphere. Various catalysts including Mo(CO)₆ were used in the liquefaction. The finely ground lignite and the catalyst were mixed in solid form prior to liquefaction. The maximum processing temperature was 425 °C. In all of the liquefaction experiments, oil + gas yields were less than 50 Wt % of daf coal. When these values are compared with the maximum oil + gas yields of the present study (70.5 Wt % of daf coal) which are substantially higher than the yields achieved in the former study, one can conclude that the well-dispersion of the catalyst due to the impregnation of the catalyst precursor onto the lignite should be the main reason for this discrepancy. Hydrogen gas used in our liquefaction experiments might be an additional factor via regenerating reacted tetralin and also taking a part in hydrogenolysis and hydrogenation reactions.

2. The Distribution of Sulfur in Liquefaction Products. Table 3 summarizes sulfur and H₂S analysis. H₂S formations were abundant in liquefaction of both coals when solvent was not used. In Gediz coal, this amounts to half of the total sulfur in coal, whereas in Çayirhan lignite, the corresponding ratio is roughly one-third. Tetralin decreases H₂S yield in liquefaction of both coals to a certain degree. In the literature, there is also an observation regarding reaction of tetralin with H₂S.⁷⁸ One other observation regarding H₂S formation is the effect of AHM especially when used with tetralin. AHM decreases H₂S yield additionally. This may be attributed to the reaction of AHM with some of the H₂S formed and/or with some sulfur functionalities in coal prone to H₂S formation under applied conditions. The sulfur contents of oils obtained from liquefaction of both coals are very low in H₂/AHM system; i.e., when tetralin is not present. This may be an indication of preferential reaction of AHM with H₂S and/or other sulfur functionalities in liquid-phase rather than with H₂S in the gas phase because H₂S yields in H₂ and H₂/AHM systems are almost equal; for Çayirhan lignite the corresponding

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Table 4. The Conversion of Demineralized Coals during Liquefaction at 400 °C in Single Stage Process (30 min)

demineralization	liquefaction system	total conversion ^a		PAS ^a		AS ^a		oil + gas ^{a,b}		Sg/St % ^c GED
		GED	CAY	GED	CAY	GED	CAY	GED	CAY	
	H ₂	89.7	74.2	30.0	20.2	47.5	24.0	12.2	30.0	28.6
HCl	H ₂	69.1	47.9	21.3	13.9	33.2	20.2	14.6	13.8	34.6
HCl/HF	H ₂	90.9	68.6	22.1	16.2	30.0	14.3	38.8	38.1	31.8
HCl/HF/HNO ₃	H ₂	17.6	10.4	4.3	2.7	3.1	2.2	10.2	5.5	6.5
	H ₂ /tet	95.0	75.1	32.8	18.7	32.1	20.2	30.1	36.2	15.5
HCl	H ₂ /tet	86.4	67.1	23.7	17.3	29.0	18.4	33.7	31.4	22.4
HCl/HF	H ₂ /tet	92.1	72.2	16.9	15.6	36.4	19.6	38.8	37.0	12.8
HCl/HF/HNO ₃	H ₂ /tet	74.5	59.7	22.4	9.2	26.6	8.3	25.5	42.2	4.5

^a wt % (daf). ^b Calculated from difference. ^c wt % of total coal sulfur converted to H₂S.

values are 31.3% and 31.7% and for Gediz coal the corresponding values are 51.3% and 48.0%, respectively (450 °C treatments).

The sulfur contents of oils derived from Gediz coal in the presence of tetralin are rather high; 4.8% in H₂/tet and 4.7% in H₂/tet/AHM systems. On the other hand, tetralin or a similar hydrogen donating solvent is necessary to achieve high oil yields (refer Table 2). Therefore, to obtain high yields of oil with low sulfur contents from Gediz coal, a deep desulfurization should be applied to the oil produced in H₂/tet/AHM system oils obtained from liquefaction of Çayirhan lignite has less sulfur contents when compared with oils from Gediz coal. Again, in the presence of tetralin less H₂S is formed. On the other hand, Çayirhan lignite yielded high oil + gas products with H₂/AHM system (refer Table 2). This lignite can be liquefied in a single stage producing oil of sulfur content less than 1%.

It has been stated that H₂S is a good hydrogen donor and in the presence of H₂ can play an autocatalytic effect in liquefaction reactions.^{7,79,80} Recent research results indicate that a concentration of H₂S in H₂ around 3% (by weight) is optimum for sulfidation of molybdenum to form an active hydrodesulfurization and hydrogenation catalyst during liquefaction of Mo-impregnated coals.^{35,36,63} The amounts of H₂S formed during liquefaction of both Gediz coal and Çayirhan lignite were far more in excess of the amount dictated by the amount of hydrogen gas charged into the reactor. In direct liquefaction of these high sulfur coals, excess H₂S formed can be recycled to be used in the liquefaction process or it can be partially or completely converted into hydrogen gas by an economical photocatalytic process developed recently⁸¹ and then recycled to be used in the liquefaction process.

3. Effect of Mineral Matter on Liquefaction.

When low-rank coals are treated with HCl, exchangeable cations which are mainly attached to carboxylate groups are removed and therefore free carboxylic acid groups are formed. Joseph and Forrai have showed that alkali and earth alkali type of metal cations had retarding effect on liquefaction.⁸² Therefore, removal of such cations may be beneficial for liquefaction. However, there are also observations, mainly from model compound studies, that free carboxylic acid groups may undergo condensation reactions forming anhydride and ester type of linkages throughout heat treatment of coal

which are more prone to take a part in radical reactions at higher temperatures to form cross linkages and such behavior would retard liquefaction reactions.^{83,84}

The product distributions from liquefaction of demineralized Gediz coal and Çayirhan lignite are given in Table 4. In the first group of liquefaction experiments, acid-pretreated coal and lignite samples were treated with hydrogen in the absence of solvent. The overall conversions in hydroliquefaction of HCl-pretreated Gediz coal and Çayirhan lignite were retarded substantially. In Gediz coal this retardation was mainly for dissolution reactions toward forming AS and PAS while there was a slight increase in oil + gas yield presumably due to release of some small trapped coal molecules during HCl treatment and/or increased decarboxylation during the heat treatment in liquefaction. On the other hand, in liquefaction of HCl-pretreated Çayirhan lignite, this retardation was much more pronounced with subsequent decreases in both overall and oil + gas yields. The high oxygen functionalities in this lignite, when converted into free forms following HCl treatment, should be responsible for the condensation and subsequent cross-linking reactions.^{83,84}

Following HF/HCl treatment, total conversion in liquefaction of pretreated Gediz coal remained roughly the same, whereas oil + gas yield increased 3-fold (compared to untreated coal) when no solvent was used. This indicates that HF/HCl treatment either activates those mineral matter in catalyzing hydrocracking reactions in this coal and/or removes some mineral matter which retards liquefaction reactions. Since HF treatment mainly removes clays from coal structure, the observed changes during liquefaction should be attributed to the removal of these material. In the literature, one can find both enhancing⁸⁵ and retarding⁸⁶ observations regarding liquefaction of HF/HCl treated coals. It has been stated that char-forming reactions catalyzed by clays (or acidic sites on coal mineral matter) may limit conversion in some liquefaction processes.⁸⁷ The results obtained in this work strongly support this view. The difference in conversion values (liquefaction) of HCl-pretreated and HCl/HF-pretreated coals indicates the catalytic role of clay minerals in

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condensation and subsequent cross-linking reactions of free oxygen functionalities in the coal structure. The other factors contributing to the enhancement of conversions (compared to the HCl-pretreated case) following HF/HCl treatment of coals might be that new pores or void spaces in the coal are created by the removal of the minerals, and that these new pores improve mass transfer in liquefaction reactions. Also pyrite and other catalytic mineral material would have a higher contact area with coal structures following removal of clay material.

Treatment of coals with HF/HCl/HNO₃ removed pyritic material as well as clays and cationic components. Liquefaction of the treated coals with H₂ only were totally unsuccessful due to the lack of catalytic mineral material.

In the second group of liquefaction experiments performed with acid-pretreated coal samples, tetralin as the solvent was used in addition to hydrogen. In general, the effect of the presence of tetralin is positive with regard to conversion. The differences between the conversion values in liquefaction by using H₂ and H₂/tetralin systems of both HCl-pretreated Gediz coal and Çayirhan lignite were such that roughly 20% more conversion took place in the presence of tetralin for both Gediz coal and Çayirhan lignite. It seems that tetralin is much more effective in quenching radicals and/or retarding condensation reactions leading to cross-linking structures. When one compares the conversions of HF/HCl-pretreated Gediz coal and Çayirhan lignite in H₂ and H₂/tetralin systems, one notes that the corresponding values are almost the same in Gediz coal's case and are very similar in Çayirhan lignite's case; i.e., the presence of tetralin does not contribute any significant enhancement to the conversion values. When this observation is coupled with the corresponding observations obtained in the liquefaction of the HCl-pretreated coals, it is most probable that tetralin is playing an effective retarding role on clay-catalyzed condensation and subsequent cross-linking reactions.

In the presence of tetralin, it is interesting to note that oil + gas yield in liquefaction of HF/HCl/HNO₃-pretreated Çayirhan lignite was even higher than the corresponding yield from untreated lignite. The effect of HNO₃ treatment on Çayirhan lignite might be similar to the respond of an Australian brown coal where the brown coal was completely dissolved in tetrahydrofuran following the treatment with HNO₃.⁸⁸ For the time being, we have no explanation for this observation.

4. Oil Analysis. The total ionization chromatograms (TIC) of the oil fractions obtained from liquefaction of Gediz coal and Çayirhan lignite in H₂/AHM systems (no solvent) are given in Figure 1. Those peaks identified from the corresponding mass spectra are numbered and named. There are many hydrocarbon compounds, such as phenolics, alkanes, cycloalkanes, aromatics, hydroaromatics, and thiophenics in these oil fractions. Sulfur containing compounds are composed of mainly benzothiophene- and methyl-substituted benzothiophenes. Dibenzothiophene and its alkyl-substituted derivatives are also present. The corresponding peaks of most of these thiophenic compounds cannot be seen under numbered labels in the chromatograms due to

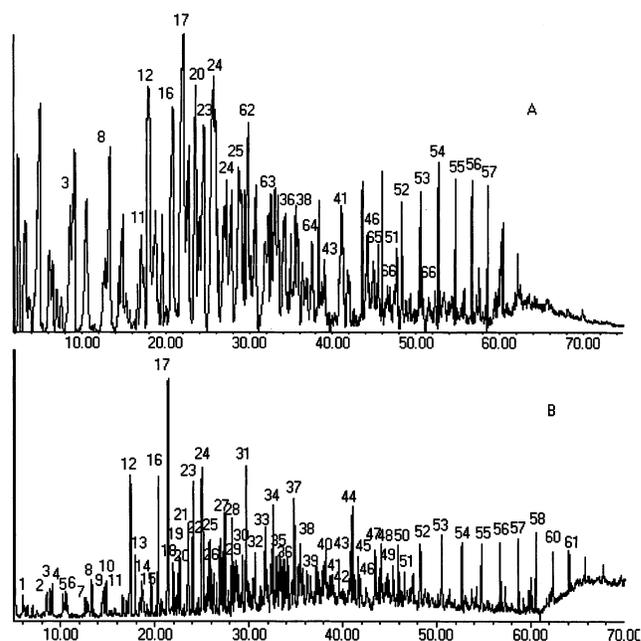


Figure 1. (A) 450 °C H₂/AHM Gediz and (B) 450 °C H₂/AHM Çayirhan oil fractions. (1) undecane, 2,7-dimethyl; (2) cyclohexane, (1-methylethyl), (3) benzene, ethyl; (4) 1,2-dimethyl benzene, (5) Hexadecane, 3-methyl; (6) benzene, 1,4-dimethyl; (7) bicyclo[3.3.1] nonane; (8) 1,2,4-trimethylbenzene, (9) *o*-ethyl toluene; (10) undecane, 4,6-dimethyl; (11) C3-benzene; (12) phenol; (13) benzene, cyclopropyl; (14) undecane; (15) 1H-Indene, 2,3-dihydro-1-methyl; (16) phenol; 2-methyl (*o*-cresol); (17) phenol, 3-methyl (*m*-cresol); (18) 1H-indene, 2,3-dihydro-4-methyl; (19) octadecane; (20) 1H-indene, 2,3-dihydro-1-methyl; (21) 1H-indene, 2,3-dihydro-1,6-methyl; (22) phenol, 2,3-dimethyl; (23) phenol; 2,4-dimethyl; (24) phenol, 4-dimethyl; (25) naphthalene; (26) 1H-indene, 2,3-dihydro-4,6-dimethyl; (27) phenol, 2-ethyl-5-methyl; (28) phenol, 4-propyl; (29) naphthalene, 1,2,3,4-tetrahydro-5-methyl; (30) eicosane, 10-methyl; (31) naphthalene, 1-methyl; (32) phenol, 2-butyl; (33) 1H-indene-5-ol, 2,3-dihydro; (34) 1H-indene-5-ol, 2,3-dihydro; (35) naphthalene, 1-ethyl; (36) naphthalene, 2,6-dimethyl; (37) naphthalene, 1,4-dimethyl; (38) nonadecane; (39) 6-methyl-4-indanol; (40) pentadecane; (41) 1-benzlidene, 2,2,3,3-tetramethylcyclo; (42) naphthalene, 1-(2-propenyl); (43) *n*-nonadecane; (44) naphthalene, 1-(2-propenyl); (45) dibenzofuran, 4-methyl; (46) 1,1'-biphenyl, 2-ethyl; (47) 1-iodo-2-methylundecane; (48) 1,1'-biphenyl, 4,4'-dimethyl; (49) benzene, 1-methyl-2-[(4-methylphenyl)]; (50) pentadecane; (51) anthracene; (52) heptadecane, 9-hexyl; (53) tricosane; (54) tetracosane; (55) heptacosane; (56) triacontane; (57) heptacosane; (58) tricosane; (59) docosane; (60) heneicosane; (61) epoxy-oxopowelline; (62) 7H-benzocycloheptene; (63) 1H-indole; (64) acenaphthene; (65) phenanthrene, 1,2,3,4-tetrahydro; (66) 3,4-dimethyldibenzothiophene.

their very low concentrations. Their presence and the corresponding peaks are determined by using specific ion monitoring. When the composition of oil fractions from both coals are compared, one can note that most of the components exist in both of the oils, but differing in relative quantities. In Çayirhan lignite, phenolics, of course, are much more abundant, whereas thiophenics are in trace levels.

Conclusions

Direct hydroliquefaction of low-rank coals by impregnating the catalyst or the catalyst precursor into the coal is an effective method for obtaining clean liquid feedstocks which can be utilized in various industrial

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processes. Dispersed molybdenum catalysts are effective both in catalyzing dissolution reactions and hydrodesulfurization reactions. Therefore, in this study ammonium heptamolybdate (AHM), which is water soluble, has been chosen as catalyst precursor to be used in direct hydroliquefaction of high-sulfur coals. Since the coals to be liquefied already have high sulfur contents, additional sulfidation of the catalyst has not been done. In this way, it is also expected that the extent of hydrodesulfurization might be more efficient yielding low sulfur content oils.

Total conversions of more than 95% are obtained from liquefaction of Gediz coal even without using added catalyst. Maximum conversion (98%) and maximum oil + gas yield (70%) from this coal were obtained by impregnating AHM onto coal and carrying out liquefaction in H₂/tetralin system at 450 °C for 30 min. Under the same conditions, the other coal, Çayirhan lignite gave 85% conversion and 70.5% oil + gas yield. The impact of impregnated AHM onto coal during liquefaction under hydrogen atmosphere was superior with Çayirhan lignite, whereas with Gediz coal the corresponding effect was not significant. This has been ascribed to the fact that AHM dispersed much more efficiently across Çayirhan lignite's structure due to an efficient ion-exchange mechanism through rich oxygen functionalities. The superior hydrodesulfurization

effect of AHM on the oil fraction when used in the absence of solvent (less than 0.1% S in Çayirhan oil and less than 1% S in Gediz oil following single stage hydrogenation) is a promising finding of this study.

The observations from demineralized coal samples indicated that tetralin retards condensation of oxygen functionalities and subsequent cross-linking reactions during liquefaction. Supporting evidences to the claim that char-forming reactions catalyzed by clays (or acidic sites on coal mineral matter) may limit conversion in some liquefaction processes⁸⁷ were observed.

To obtain high yields of oil with low sulfur contents from these high-sulfur coals, water soluble molybdenum compounds can be impregnated onto them and directly liquefied in the presence of hydrogen gas and a hydrogen donor solvent. Such oils can be deeply desulfurized and an appropriate fraction can be used in the production of high-thermal stability jet fuels.

Acknowledgment. This study has been supported by The Scientific and Technical Research Council of Turkey (TUBITAK) through the project KTCAG-126. We are grateful for the useful comments of Prof. Harold H. Schobert from The Energy Institute of Pennsylvania State University.

EF0102667