

EFFECT OF PRETREATMENT ON LIQUEFACTION BEHAVIOUR OF COAL

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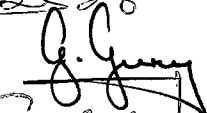
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ABBREVIATIONS

a.d.	: As Analysed
APCS	: Argonne Premium Coal Sample
CRE	: Coal Research Establishment
d.b.	: Dry Basis
daf	: Dry Ash Free Coal
DCM	: Dichloromethane
DCM-conv.	: Dichloromethane Conversion
DCM-insols.	: Dichloromethane Insolubles
GC	: Gas Chromatography
GROS	: Green River Oil Shale
ICCP	: International Committee for Coal Petrology
IUPAC	: International Union of Pure and Applied Chemistry
Pyr-insols.	: Pyridine Insolubles
Pyr-sols.	: Pyridine Solubles
RXOS	: Rundle Ramsay Crossing Oil Shale
SCT	: Short Contact Time
SEM	: Scanning Electron Microscopy
TBAH	: Tetrabutylammoniumhydroxide
Temp.	: Temperature
TG	: Thermogravimetry
TGA	: Thermal Gravimetric Analysis
THF	: Tetrahydrofuran

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EFFECT OF PRETREATMENT ON LIQUEFACTION BEHAVIOUR OF COAL

SUMMARY

Today, our dependency on petrol is continuing to increase since it meets most of our energy requirement and is the basis of most of the raw materials in the industry. However, with the present rates of consumption, petrol reserves dwindle which forces us to find out new sources in the place of petrol. Coal and oil shale should be accepted as the raw materials, which are appropriate technologically, and economically to replace petroleum with artificial petroleum.

There are some technical difficulties faced because of usage of high pressure, high temperature, catalyser and hydrogen in order to increase yield in the liquefaction of solid fuels. Economics of the processes are kept compelling as a result of these difficulties which restricts the artificial petroleum usage. Because of that some methods are needed to increase the yield in the production of artificial petroleum or chemicals from coal and the other solid raw materials. One of these methods is to pretreat coal, which ends up with an increase in the process yield.

The aim of the pretreatment is to reduce mass transfer limitations between the coal and the liquefaction media. The effect of pre-swelling and pre-extracting coals in both polar and non-polar solvents on conversions in direct liquefaction has recently received considerable attention.

Swelling of coals by an appropriate solvent or removal of solvent after swelling, effects the conversion and product quality in the liquefaction. The enhancement depends on to the coal rank and swelling solvent.

It is convenient to divide solvent swelling into two groups; first, coal swelling in non-polar solvents and second with swelling in polar, basic solvents. The differences in swelling efficacies of the solvents may be explained on the basis of their interactions with the various types of effective bridging bonds in coals. They are formed through covalent bonding, ionic bonding, hydrogen bonding and charge transfer complexing. Swelling of coal is caused by disrupting (breaking or extending) one or more of these bonds. The extent of swelling depends on the type of bonds predominant in a coal and the nature of the solvent. Covalent bonds are not likely to be broken by common solvents under ambient conditions. Therefore, only ionic interactions, hydrogen bonding and charge transfer complexing are important as far as swelling is concerned. Ionic and hydrogen bonds are believed to be significant in low rank coals because of the presence of a relatively large number of polar functional groups, such as hydroxyl, carboxyl, and carbonyl. Charge transfer complexing is expected to be predominant only in higher rank coals because of their higher

aromatic content. The maximum swelling possible is limited by the number of covalent cross-links. As the non-covalent cross-links are destroyed by stronger coal-solvent interactions, the swelling will increase.

For instance, pretreating coals, particularly with polar solvents such as tetrahydrofuran, at well below reaction temperature can give rise to significantly improved yields under relatively low-severity liquefaction conditions. However, some organic matter is being removed at the same time that conformational changes may be occurring in the macromolecular structure of coal. Also, in the case of polar solvents and pre-treatments at elevated temperatures, hydrogen bonds are being disrupted. On the other hand, chlorobenzene has the advantage of extracting virtually no organic matter from coals and since it is non-polar hydrogen bonds should be disrupted not significantly at relatively low temperatures (<150 °C). Therefore, in a study made before it was found that the effect of chlorobenzene treatment showed differences depending on coal and liquefaction regime applied.

In this study, the effects of chlorobenzene (CB), tetrahydrofuran (THF) and methanol (MET) treatments on liquefaction behaviour of coal and oil shale were investigated both in thermolysis and in short contact time hydrogen-donor (tetralin) liquefaction experiments. In addition, in order to determine the conformational changes occurred swelling experiments, Thermal Gravimetric Analysis and Scanning Electron Microscopy analysis were done.

Coal samples used for this study were Can and Tuncbilek lignites, and Zonguldak region (Kurtserif and Karadon) bituminous coals and Goynuk (B) oil shale. In addition, in order to make a comparison with an earlier study, Pittsburgh No.8 and Point of Ayr bituminous coals were used.

Coals and oil shale were Soxhlet extracted using chlorobenzene, tetrahydrofuran and methanol which have boiling points of 132, 65 and 66 °C. The extracted coals and oil shale were then dried in vacuo at 50 °C, until the residual solvent content was below 1 % w/w on coal and oil shale.

Thermolysis (400 °C, 60 min.) and hydrogen-donor solvent liquefaction experiments using tetralin (400 °C, 15-60 min.) with a solvent coal weight ratio being 2:1 were carried out. Experiments were done using a stainless steel reactor, which was submerged in a fluidised sandbath and was agitated using a flask shaker.

After extraction, the reactor contents were recovered by filling the microreactor with dichloromethane (DCM) and placing it in an ultrasonic bath. The DCM washings were refluxed, filtered and the amount of DCM-insolubles (DCM-insols.) were determined. DCM-insolubles were then refluxed in pyridine and filtered to determine the yield of pyridine-insolubles (pyr-ins.). The amounts of hydrogen donated to the coals during the tetralin extractions were calculated from the mass ratios of tetralin to naphthalene in the recovered DCM solutions determined by capillary gas chromatography.

The effects of chlorobenzene-treatment were extremely varied and depended both upon the coal and oil shale used. Treatment ended up with an increase in DCM-conversion (DCM-conv.) for Pittsburgh No.8 coal whereas for Karadon and Kurtserif there was not an increase. In short contact time (SCT) tetralin extraction

experiments, the amounts of hydrogen transferred to the untreated and treated Karadon and Kurtserif coals were similar. For Pittsburgh, the amount of hydrogen transferred was almost similar for untreated and chlorobenzene-treated coal, and also the increase in the DCM-conv. together implied that treatment ended up with changes in the conformational structure, which limited char-forming retrogressive reactions. Chlorobenzene-treatment decreased the amount of DCM-conv. for Can and Tuncbilek lignites in thermolysis experiments. In tetralin extraction experiments, DCM-solubles for Can decreased whereas in Tuncbilek there was no change. The amount of hydrogen transferred for untreated and treated Tuncbilek was similar, but, the increase in DCM-solubles was low implying that there was not any significant structural changes. The decrease in the amount of hydrogen transferred for Can implied that there was some structural changes which had an adverse effect to the transfer of hydrogen. For oil shale, there was a little increase in DCM-solubles. In tetralin extraction experiments, when the hydrogen transfer amounts for untreated and treated shales were compared it was noticed that there was a significant increase. It is thought that the reason of this increase was because of conformational changes that result in more bond cleavage.

For tetrahydrofuran and methanol-treated oil shale and Can, similar DCM-conv. results were obtained with chlorobenzene-treated samples. The hydrogen transferred was almost similar for untreated Can. For oil shale as in the case of chlorobenzene-treated shale, there was a significant increase. In Tuncbilek lignite, there was a significant increase in hydrogen transfer amount with a small increase in DCM-conv. with respect to untreated coal. The reason of this increase was probably because of conformational changes ending up with more bond cleavage. Polar solvent treatment decreased the DCM-conv. for Pittsburgh. For Karadon and Kurtserif, there was not significant change. There was a decrease in the amount of hydrogen transferred parallel with DCM-conv. in Pittsburgh. For tetrahydrofuran-treated Karadon and Kurtserif, there was no change in the hydrogen transferred. There was a decrease for methanol-treated Kurtserif.

The pyridine swelling results and per cent carbon (daf) content results of coal and oil shale were given at Table 3. The values of untreated and chlorobenzene-treated Pittsburgh was obtained from an earlier study.

In an earlier study, it was showed that in polar solvents, the swelling degree is almost constant over the range from 65 to 87 per cent (daf) carbon content and decreases suddenly with further increase of rank. This behaviour was also shown by the coals used as seen in Table 3.

The swelling ratios of the coals and oil shale which were given at Table 3 showed an increase or a decrease with respect to untreated samples. Increased swelling indicates covalent bonds or non-covalent bonds have been broken, and a swelling decrease indicates more bonds have been formed.

Table 2. DCM-conversion results of coals and oil shale used from thermolysis and short contact time tetralin extraction experiments.

		% daf		
		Thermolysis	SCT Tetralin Extraction	
		%DCM-conv.*	%DCM-conv.*	%H Transferred
Çan	Untreated	27	42	1.8
	CB-treated	22	38	1.6
	THF-treated	20	39	1.9
	MET-treated	23	43	2
Tunçbilek	Untreated	23	23	1
	CB-treated	15	29	1
	THF-treated	17	32	1.7
	MET-treated	23	33	1.5
Kurtşerif	Untreated	10	25	0.6
	CB-treated	8	27	0.7
	THF-treated	14	25	0.5
	MET-treated	9	10	0.2
Karadon	Untreated	12	14	0.5
	CB-treated	13	22	0.6
	THF-treated	18	22	0.6
Göynük	Untreated	61	74	0.9
	CB-treated	69	78	1.8
	THF-treated	61	81	1.4
	MET-treated	65	81	1.7
Pittsburgh No.8	Untreated	11	32	0.6
	CB-treated	22	47	0.8
	THF-treated	8	24	0.4
	MET-treated	23	28	0.4

*= 100 - %DCM-insolubles, includes DCM-solubles liquid product+gas+water.

Table 3. Pyridine swelling ratios

	%C (daf)	Untreated	CB-treated	THF-treated	MET-treated
Çan	68.77	1.94	1.98	2.04	2.69
Tunçbilek	75.70	2.39	2.51	2.59	2.17
Göynük bitümlü şisti	75.97	1.54	1.72	1.92	1.63
Pittsburgh No.8	84.90	2.74	3.10	2.52	2.11
Karadon	88.46	1.47	1.47	1.48	-
Kurtşerif	88.59	1.57	1.58	1.58	1.31

The swelling results of untreated Can and Tuncbilek lignites were lower than the results of Pittsburgh No.8. In the lignite macromolecule may be covalent cross-links were dominate, and another reason for the low swelling ratio may be the moisture content of the lignite structure.

When pyridine is used as a swelling solvent, the hydrogen bonding mainly occur between hydroxyl in coal and solvent. As the rise of coal rank, the oxygen and hydroxyl content decrease. The cross-links are not hydrogen bonds at high ranks, so the bonds must be van der Waals type or covalent bonds. The charge transfer interaction is one of the important relatively strong interactions in bituminous coal. Some portions of charge transfer complexes in the coal can not be solvated with pyridine. As a result of which the swelling ratio decreases with the increase of coal rank. As mentioned above that there is a decrease in the swelling ratio after 87 per cent carbon (daf) content. In this study, Zonguldak region Karadon and Kurtserif coals' carbon (daf) content were more than 88 per cent. Because of that their swelling ratios did not show significant changes for untreated and treated coals and had the lowest value in between the coals used.

Goynuk (B) oil shale had 75.97 per cent carbon content and had lower swelling ratio then the coal having similar amount of carbon content. This behaviour is attributed to the differences in the organic structure of coal and oil shale. The reason of low swelling ratio was because of having not so much bond that can be disrupted with polar solvent swelling.

When both the liquefaction and swelling results obtained in this study examined together, it was seen that the treatments were not so effective on Goynuk (B) oil shale. In bituminous coals, for the one which has less than 87 per cent carbon (daf) content chlorobenzene treatment was effective whereas tetrahydrofuran and methanol treatments resulted with a decrease in yield. For the ones which have more than the value mentioned above, treatments did not have effect on liquefaction or swelling results. Chlorobenzene-treatment did not show significant improvement on the structure of low-rank coals whereas the effect of the polar solvents used were different according to the coal sample used.

ÖNİŞLEMLERİN KÖMÜRÜN SIVILAŞMA DAVRANIMINA OLAN ETKİSİ

ÖZET

Günümüzde, enerji ihtiyacının büyük bir kısmını karşılaması ve endüstride birçok hammaddenin kaynağının petrol olması, petrole olan bağımlılığı artarak devam ettirmektedir. Ancak ham petrol rezervlerinin mevcut kullanım hızı ile kısa ve orta vadede tükenecek olması, bu kaynağın yerine geçerli alması için ortaya konmasını gerektirmektedir. Ham petrolün yerini alabilecek yapay petrol üretimi için teknolojik ve ekonomik açıdan en uygun hammaddelerin kömür ve bitümlü şistler olduğu kabul edilmelidir.

Katı yakıtların sıvılaştırılmasında düşük verim veya verimi yükseltmek için kullanılması zorunluluğu olabilecek yüksek basınç, yüksek sıcaklık, katalizör ve hidrojen, proseslerin uygulanmasında söz konusu olabilecek bazı teknik engellerdir. Bu engeller prosesin ekonomisini zorlayıcı etkenler olarak yapay petrolün kullanımını baskı altında tutmaktadır. Bu nedenle kömür ve diğer katı hammaddelerden yapay petrol veya kimyasal hammadde üretimi için verimi artırıcı bazı uygulamalara gerek vardır. Bunlardan bir tanesi kömüre ön işlem uygulayarak prosesin verimliliğini artıracak özellikler yaratmaktır.

Genellikle gerçekleştirilen önışlemlerde amaç, kömür ile sıvılaştırma ortamı arasında kütle transferindeki engelleri azaltmaktır. Son yıllarda direkt sıvılaştırmada, dönüşüm esnasında kütle transferindeki engelleri azaltarak ürün artışı sağlanmasından dolayı, kömürün polar olan ve olmayan çözücülerle şişirilmesi ve/veya ekstrakte edilmesi giderek önem kazanmaktadır.

Kömürlerin uygun bir çözücü ile şişirilmesi veya şişirilmesini takiben ortamdan çözücünün uzaklaştırılması, sıvılaştırma işleminde dönüşmeyi ve ürün kalitesini önemli ölçüde etkilemektedir. Bu düzeltme, kömür tenörüne ve şişirmede kullanılan çözücüye bağlıdır.

Çözücü şişmesini sağlayan çözücüler ikiye ayırmak mümkündür. Bunlardan birincisi, kömürün polar olmayan çözücülerle şişirilmesi ve ikincisi de polar, bazik çözücülerde şişirilmesidir. Bu çözücülerin şişme verimleri arasındaki fark, kömürün yapısında bulunan bağlarla etkileşmesine bağlı olarak açıklanabilir. Söz konusu bağlar, kovalent, iyonik, hidrojen bağları ve de yük transfer kompleksinden oluşmaktadır. Kömürün şişmesi bu bağların birinin veya daha fazlasının parçalanması veya genişmesi ile olur. Şişmenin ne dereceye kadar olacağı kömürün yapısında etkin olan bağın cinsi ve de çözücünün doğasına bağlı olarak değişir. Kovalent bağlar, kullanılan çözücüler ile normal şartlar altında kırılmazlar. Şişme gözönüne alındığında iyonik bağlar, hidrojen bağları ve yük transfer kompleksi önemlidir. İyonik ve hidrojen bağları, yapılarında hidroksil, karboksil ve karbonil gibi polar fonksiyonel grupların çok olması nedeni ile düşük tenörlü

kömürlerde önemlidir. Yük transfer kompleksi de, yapılarında daha fazla aromatik yapı bulunan bitümlü kömürler için önemlidir. Mümkün olan maksimum şişme, yapıdaki kovalent çarpaz bağlar ile sınırlandırılmıştır. Kovalent olmayan çarpaz bağlar, kuvvetli kömür çözücü etkileşmesi ile ayrışırken, şişmeyi arttırmaktadır.

Örneğin, polar bir çözücü olan tetrahidrofuran ile yapılan önişlem hafifletilmiş reaksiyon koşullarında ürün artışı sağlamaktadır. Ancak, yapılan önişlem esnasında yapıda bazı değişiklikler meydana gelirken bazı organik maddelerde uzaklaştırılmaktadır. Aynı zamanda, polar çözücü kullanılması, yapıdaki hidrojen bağları etkilemektedir. Diğer yandan, polar olmayan bir çözücü olan klorobenzen kullanılması durumunda, kömürün yapısından organik madde uzaklaştırılmamakta ve (< 150 °C) düşük sıcaklıklarda hidrojen bağlarının fazla ayrışmasına neden olmamaktadır. Bu konuda daha önce gerçekleştirilen bir çalışmada, klorobenzen önişleminin etkisinin kullanılan kömür ve sivilaşma rejimine bağlı olarak farklılıklar gösterdiği belirlenmiştir.

Bu çalışmada, klorobenzen (KB), tetrahidrofuran (THF) ve metanol (MET) önişlemlerinin sivilaşma davranımına olan etkisi termoliz ve tetralin kullanılarak gerçekleştirilen kısa temas süreli (KTS) hidrojen-donor çözücü sivilaştırılması deneylerinde incelenmiştir. Meydana gelen muhtemel yapısal değişikliklerin incelenmesi için şişme deneyleri ve Termal Gravimetrik Analiz ile Scanning Electron Mikroskobu analizleri yapılmıştır.

Bu çalışmada, Çan ve Tunçbilek linyitleri ile Zonguldak bölgesi (Kurtşerif ve Karadon) kömürleri ve Göynük (B) bitümlü şisti kullanılmıştır. Ayrıca daha önce gerçekleştirilen çalışma ile karşılaştırmayı sağlamak için Pittsburgh No.8 ve Point of Ayr bitümlü kömürleri de kullanılmıştır.

Kömürler ve bitümlü şist, kaynama noktaları sırası ile 132, 65 ve 66 °C olan klorobenzen, tetrahidrofuran ve metanol ile soxhlet ekstraksiyonuna tabii tutulmuştur. Ekstrakte edilen kömürler ve bitümlü şist vakum etüvünde 50°C'de, kömür ve bitümlü şist üzerinde kalan çözücü miktarı ağırlık olarak % 1'in altında olacak şekilde kurutulmuştur.

Termoliz (400°C, 60 dak. süre ile) ve hidrojen-donor çözücü sivilaştırılması deneyi tetralin kullanılarak (400°C, 15-60 dak. süre ile) çözücü kömür ağırlık oranı 2:1 olmak üzere yapılmıştır. Deneyler akışkanlaştırılmış kum yatak içerisine daldırılan ve bir sarsıntı cihazı ile hareketi sağlanan paslanmaz çelik reaktör kullanılarak gerçekleştirilmiştir.

Reaktörden ürün diklormetan (DKM) ile yıkanarak alınmış, riflaks yapılarak süzölmüş ve diklormetanda çözünmeyenlerin (DKM-çözünme.) miktarı belirlenmiştir. Elde edilen çözünmeyenlerin bir kısmı piridinle riflaksa tabii tutulmuş, ve süzölerek piridine çözünmeyenlerin (pir-çözünme.) miktarı belirlenmiştir. Tetralin ekstraksiyonu deneylerinde de, kömüre transfer olan hidrojen miktarı, diklormetan çözeltisi içerisinde n-heksan kullanılarak hazırlanan numunenin kapiler kolon gaz kromatografisi sonucundan, tetralinin naftaline olan ağırlık oranından yararlanılarak belirlenmiştir.

Klorobenzen önişleminin etkisi kullanılan kömür ve de bitümlü şiste bağlı olarak farklı olabilmektedir. Pittsburgh No.8 kömüründe DKM-dön. de artışa neden olurken,

Karadon ve Kurtşerif kömürlerinde fazla bir artış olmamıştır. Tetralin ekstraksiyonu deneylerinde, Karadon ve Kurtşerif kömürleri için transfer olan hidrojen miktarının, orijinal ve önışleme uğrayan kömür için aynı olduğu görülmektedir. Pittsburgh kömüründe ise, transfer olan hidrojen miktarı, orijinal ve klorobenzenle önışleme tabii tutulan kömür için hemen hemen aynıdır ve DKM-dön. miktarında da artış gözlenmesi, önışlemin yapıda geri koklaşma reaksiyonlarını engelleyecek bazı yapısal değışiklikler oluşturduğunu düşündürmüştür. Çan ve Tunçbilek linyitlerinde ise klorobenzen önışlemi, termoliz deneylerinde DKM-dön. nün azalmasına neden olmuştur. Tetralin ekstraksiyonu deneylerinde ise Çan'da sıvı ürün miktarında azalma görülürken, Tunçbilek'te fazla bir değışim olmamıştır. Transfer olan hidrojen miktarı Tunçbilek için orijinal ve önışleme uğrayan kömür için benzerdir fakat sıvı ürün miktarında önemli bir yapısal değışiklik olduğunu gösterir fazla bir artış yoktur. Çan'da ise önışlem, transfer olan hidrojen miktarının da düşmesine neden olması, kömürün yapısında hidrojen transferini güçleştirecek bazı değışimlerin olduğunu düşündürmüştür. Bitümlü şistinde ise sıvı ürün miktarında az miktarda bir artış gözlenmiştir. Tetralin ekstraksiyonu deneylerinde de, transfer olan hidrojen miktarı orijinal ve önışlem görmüş bitümlü şist karşılaştırıldığında belirgin bir artış görülmektedir. Bu artışın nedeninin meydana gelen yapısal değışikliklerin daha fazla bağ parçalanması ile sonuçlandığını düşündürmüştür.

Tetrahidrofuran ve metanol önışlemlerine tabii tutulan bitümlü şist ve Çan kömürü için, klorobenzen önışlemi sonucu elde edilen DKM-dönüşümlerine benzer sonuçlar elde edilmiştir. Çan linyitinde transfer olan hidrojen miktarı orijinal kömür ile hemen hemen aynıdır. Bitümlü şiste de, klorobenzen önışleminde olduğu gibi, orijinal şiste göre büyük bir artış vardır. Tunçbilek linyitinde ise, orijinal kömüre göre DKM-dönüşümünde az miktarda artışa paralel olarak, transfer olan hidrojen miktarında belirgin bir artış görülmektedir. Bu görülen artışın nedeni, muhtemelen yapıda meydana gelen değışikliklerin daha fazla bağ parçalanması ile sonuçlanması olarak düşünülmektedir. Pittsburgh No.8 kömüründe, polar çözücü önışlemi, sıvı ürün miktarında düşüşe neden olmuştur. Karadon ve Kurtşerif kömürlerinde ise belirgin artış sözkonusu değildir. Transfer olan hidrojen miktarında, Pittsburgh kömürü için sıvı ürün miktarına paralel olarak bir azalma vardır. THF ile önışleme uğrayan Karadon ve Kurtşerif'te ise hidrojen miktarında da bir değışim yoktur. Sadece, metanol ile önışleme uğrayan Kurtşerif kömüründe azalma sözkonusudur.

Tablo 3'te orijinal ve önışleme tabii tutulan kömür ve bitümlü şistin piridin şişme oranları ve kuru külsüz bazda karbon yüzdesi görülmektedir. Bu Tabloda orijinal ve klorobenzenle önışleme uğramış Pittsburgh değerleri daha önce gerçekleştirilen bir çalışmadan alınmıştır.

Daha önce gerçekleştirilen bir çalışmada, polar çözücülerde, karbon yüzdesi (kbb)'da 65'ten 87'ye kadar olan kömürler için şişme oranının hemen hemen sabit olduğunu ve tenörün artması ile şişme oranının düşüş gösterdiğini göstermişlerdir. Bu durumun bu deneyde kullanılan kömürler için de geçerli olduğu Tablo'dan da görülmektedir.

Tablo 3'te kömür ve bitümlü şist için verilen şişme oranları orijinal örneğe göre artış veya azalma göstermektedir. Artan şişme kovalent olan veya olmayan bağların parçalandığını ve azalan şişme de daha çok bağın oluştuğunu göstermektedir.

Tablo 2. Kullanılan kömürler ile bitümlü şistin termoliz ve KTS tetralin sıvılaştırılmasında elde edilen DKM-dönüşüm değerleri.

		% kkb		
		Termoliz	KTS Tetralin Ekstraksiyonu	
		%DKM-dön.*	%DKM-dön.*	Transfer olan % H
Çan	Orijinal	27	42	1.8
	KB-önişlem	22	38	1.6
	THF-önişlem	20	39	1.9
	MET-önişlem	23	43	2
Tunçbilek	Orijinal	23	23	1
	KB-önişlem	15	29	1
	THF-önişlem	17	32	1.7
	MET-önişlem	23	33	1.5
Kurtşerif	Orijinal	10	25	0.6
	KB-önişlem	8	27	0.7
	THF-önişlem	14	25	0.5
	MET-önişlem	9	10	0.2
Karadon	Orijinal	12	14	0.5
	KB-önişlem	13	22	0.6
	THF-önişlem	18	22	0.6
Göynük	Orijinal	61	74	0.9
	KB-önişlem	69	78	1.8
	THF-önişlem	61	81	1.4
	MET-önişlem	65	81	1.7
Pittsburgh No.8	Orijinal	11	32	0.6
	KB-önişlem	22	47	0.8
	THF-önişlem	8	24	0.4
	MET-önişlem	23	28	0.4

*= 100 - %DKM-çözünmeyenler, DKM-çözünen sıvı ürün+gaz+suyu içermektedir.

Tablo 3. Piridin şişme oranları

	%C (kkb)	Orijinal	KB-önişlem	THF-önişlem	MET-önişlem
Çan	68.77	1.94	1.98	2.04	2.69
Tunçbilek	75.70	2.39	2.51	2.59	2.17
Göynük bitümlü şisti	75.97	1.54	1.72	1.92	1.63
Pittsburgh No.8	84.90	2.74	3.10	2.52	2.11
Karadon	88.46	1.47	1.47	1.48	-
Kurtşerif	88.59	1.57	1.58	1.58	1.31

Tabloda görüldüğü gibi orijinal Çan ve Tunçbilek linyitlerinin şişme oranları, Pittsburgh No.8 kömüründen düşüktür. Linyitlerin makromoleküler yapısında kovalent çarpraz bağlar egemen olabileceği gibi, şişme oranının düşük olmasının bir başka nedeni de, linyitlerin yapısında bulunan nem miktarı olabilir.

Şişme çözücüsü olarak piridin kullanıldığı zaman, çözücü ile kömür arasındaki hidrojen bağı, kömürün yapısında bulunan hidroksil grubu ile çözücü arasında gerçekleşmektedir. Kömür tenörünün artması ile, oksijen ve hidroksil içeriği azalmaktadır. Yüksek tenörlü kömürlerde çarpraz bağlar artık hidrojen bağından değil de van der Waals veya kovalent bağlarından oluşmaktadır. Yük transfer kompleksi de yüksek tenörlü kömürlerin yapısında bulunan önemli bağlardan birisidir, ve bunun bazı kesimlerinin piridin ile etkileşimleyebileceği bildirilmektedir. Bunların sonucu olarak, kömürlerde tenörün artması ile şişme oranı düşer. Yukarıda da belirtildiği gibi (kkb) karbon yüzdesi 87'nin üzerine çıktığı zaman şişme oranı düşmektedir. Bu çalışmada da Zonguldak bölgesinde Karadon ve Kurtşerif kömürlerinin kuru külsüz bazda karbon yüzdesi 88'in üzerindedir. Bu nedenle, şişme oranları, orijinal ve önışleme uğrayan kömürler için fazla bir değişiklik göstermemekte ve kullanılan kömürler içerisinde en düşük değere sahiptir.

Göynük (B) bitümlü şistin'inde kuru külsüz bazda karbon yüzdesi 75.97'dir ve aynı miktarda karbon yüzdesine sahip kömüre göre daha düşük şişme oranına sahiptir. Bu da kömür ile bitümlü şist arasındaki yapısal farklılığı göstermektedir. Şişme oranının düşük olmasının nedeni de, şişme çözücüsü olarak kullanılan piridin'in etki edebileceği bağ olmayışı ile açıklanabilir.

Bu çalışmada elde edilen sıvılaşma ve şişme deneylerinin sonuçları beraberce incelendiği zaman, Göynük (B) bitümlü şisti için yapılan önışlemlerin fazla etkili olmadığı görülmüştür. Bitümlü kömürlerde ise kuru külsüz bazda karbon yüzdesi 87'in altında olanlar için klorobenzen önışlemi etkili iken tetrahidrofuran ve metanol önışlemleri verim düşüklüğüne neden olduğu görülmüştür. Karbon yüzdesi belirtilen değerlerin üzerinde olanlar için ise yapılan önışlemlerin sıvılaşma ve şişme deney sonuçlarına hiçbir etkisi olmadığı belirlenmiştir. Düşük tenörlü kömürlerde, klorobenzen önışleminin yapı üzerinde fazla olumlu bir etki göstermediği ve diğer polar çözücü önışlemlerinin ise kullanılan kömüre göre etkilerinin farklı olabildiği belirlenmiştir.

1. INTRODUCTION

1.1 General Background on Coal and Oil Shale Utilisation

Coal is a sedimentary rock formed over a period of millions of years [1] from consolidated peat [2]. The American Geological Institute defines coal as a readily combustible rock containing more than 50 % by weight and more than 70 % by volume of carbonaceous material including inherent moisture, formed from compaction and induration of variously altered plant remains similar to those in peat. Differences in the kinds of materials (coal type), metamorphism (coal rank) and in the levels of impurities (minerals) are characteristics of coal that are used to grade and classify coal [2].

Oil shales are also potential fossil fuel reserves, which may play an important role in the future. Gavin defined oil shale as 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 [3]. Oil shale is composed of bitumen and kerogen [3,4,5]. Kerogen is divided into types based on elemental composition and maturation path, which are used to classify oil shale [6].

Historically, together with wood and peat, coal was the most important energy source for industry. It has been used as a heat source for centuries [1]. By the middle of the twentieth century, although still the dominant world energy sources, coal had come to be regarded as the product of a traditional industry nearing the end of its useful life cycle. The prospect of cheap and plentiful energy supplies from oil, natural gas and nuclear power promised to make the early decline of the coal industry inevitable [7]. The energy crises in the 1970s revealed the large increase in energy consumption, caused by the growth of the world's population, a rising standard of living and economic growth [1]. Oil price increases and doubts about the planned expansion of nuclear power changed attitudes considerably and led to a widespread recognition that coal had an important and long-term

contribution to make [7]. Besides coals, oil shales comprise a truly enormous and largely untapped fossil fuel resource [3].

Fossil fuels, such as coal and petroleum, are today not only the main source of energy but also the basis of many manufacturing processes (plastics, pharmaceutical products, iron and steel, aluminium and many other materials in daily use). Some of these products are currently manufactured by the use of carbon derived from oil, but there is a reasonable body of opinion to indicate that the production of oil will peak towards the end of the century and then decline sharply, thereby increasing our dependence on coal and oil shale. World petroleum reserves can only be reckoned in decades, at present rates of consumption, while coal and oil shale reserves are likely to be available for centuries [8].

However, coal cannot be used in the same way as in the past [1]. There was a revival of interest in coal technology, particularly in methods of using coal with greater efficiency and environmental acceptability [7]. In newer coal combustion technologies, the attention has been focused on the application of emission control technologies in which the aim is to reduce the effluent emissions, particularly NO_x and SO_2 [9].

There are well proven technologies to substitute crude oil, based on various solid inputs such as coal and oil shale [10]. The production of transport fuels and the generation of a range of chemicals from coal and oil shale by direct and indirect liquefaction, and pyrolysis is essential if large reserves of coal and oil shale are to be substituted for less plentiful fuels [9]. Therefore, it is important to develop those coal and oil shale conversion processes, which have the potential to provide the essential liquids that at present can only be obtained from petroleum. This does not imply that coal/oil shale-based feedstocks will suddenly replace crude oil, but that, as crude oil supplies dwindle, coal and oil shale could gradually take over [8].

The overall conclusions obtained for every coal and oil shale to oil project attempted to date has been that whilst the process is technically feasible, the cost of the resulting product is too high when compared to conventional crude oil derived materials. Comparisons between the costs of coal and oil shale derived synthetic fuels and those obtained from the refining of crude oil are difficult to make, due to

the variability in both price of crude oil and coal/oil shale. As oil reserves decrease and the price of crude oil increases the economics of coal and oil shale derived fuels will become favourable.

1.2 Coal and Oil Shale Resources in Turkey

The known coal reserves of Turkey is around 9.3 billion tones totally [11]. The known deposits of hard coal are very limited, but lignite deposits are found extensively throughout Turkey [12]. Coal seams of the Carboniferous Zonguldak Basin are the only major bituminous coal deposits of Turkey [13]. Lignites constitute the largest solid fuel deposit with reserves of over 8 billion tones [11,12,14]. The lignites are low-grade quality due to their high sulphur, ash, and moisture contents.

Oil shale comprises the second largest solid fuel reserve in Turkey after lignites; reserves totalling approximately 5 billion tones. The largest reserve, Goynuk is situated near Bolu with an estimated 1 billion tones [12].

1.3 Scope of Investigation

Current direct coal liquefaction processes, which operate at relatively high temperatures and pressure, have several drawbacks. These drawbacks include high hydrogen consumption, the occurrence of retrograde reactions producing relatively high molecular mass materials. One way to minimise these drawbacks is by modifying the coal structure by pretreatments prior to liquefaction [15].

Indeed, the effect of pre-swelling and pre-extracting coals in both polar and non-polar solvents on conversions in direct liquefaction has recently received considerable attention [15-21] since it is particularly important to overcome mass transfer limitations to maximise yields [22]. For instance, pre-treating coals, particularly with polar solvents, such as tetrahydrofuran (THF) [16,17], at well below reaction temperatures can give rise to improved yields under relatively low-severity liquefaction condition. However, some organic matter is being removed at the same time that conformational changes may be occurring in the macromolecular

structure of coal. Also, in the case of polar solvents and pre-treatments at elevated temperatures, hydrogen bonds are being disrupted [22].

On the other hand, chlorobenzene has the advantage of extracting virtually no organic matter from coals and since it is non-polar hydrogen bonds should be disrupted not significantly at relatively low temperatures (<150 °C). Therefore, Snape and co-workers have used chlorobenzene in a fundamental study, where the overall aims have been [22]:

- to elucidate the nature and extent of conformational changes induced at low temperatures (<200 °C) in the macromolecular structure of sub-bituminous and bituminous coals by both polar and non-polar solvents.
- to determine the effects of controlled conformational changes on the devolatilisation and liquefaction behaviour of the coals investigated; and
- to investigate the feasibility of using pre-treatments with vehicle (process) solvents to improve yields and throughput in direct liquefaction processes, particularly those using relatively mild thermal regimes for coal dissolution.

In order to ascertain the effects of chlorobenzene treatment, a range of liquefaction and thermolysis experiments were conducted on three bituminous coals, namely Pittsburgh No. 8 Argonne Premium Coal Sample (APCS) and two UK coals (Point of Ayr and Bentinck). Some experiments were also conducted on the Wyodak APCS (sub-bituminous) to show that the solvent-induced effects are fundamentally different for bituminous and low-rank coals [22]. Hydrogen-donor solvent extraction experiments at temperatures close to 400 °C were first of all conducted using tetralin with the relatively short contact time of 15 min. since any conformational effects are likely to be most pronounced during the initial stages of conversion [22].

As a part of the project described above writer made MPhil [23] in which the specific objectives have been:

- to ascertain whether effects of chlorobenzene pretreatment on coal thermolysis and liquefaction are common for other non-polar solvents, such as toluene and chloroform which have lower boiling points than chlorobenzene;
- to ascertain the effects of temperature and residence time on variations in conversion for tetralin extraction of normal and chlorobenzene-treated coals.
- to investigate the feasibility of using a process solvent for coal pretreatment, hydrogenated anthracene oil being selected for the hydrogen-donor liquefaction experiments; and
- to use solvent swelling measurements with pyridine to help ascertain the effects of non-polar solvent pretreatment on the macromolecular structure of coals.

In this study, in order to extend the work to different rank coals and oil shale, a number of coals and an oil shale have been used from Turkey. The specific objectives of this Ph.D. study are :

- to ascertain the effects of chlorobenzene pretreatment on different rank coals and oil shale in thermolysis and liquefaction;
- to ascertain whether effects of chlorobenzene pretreatment on low-rank coal thermolysis and liquefaction are common for other non-polar solvents, such as toluene and chloroform;
- to ascertain the effects of residence time on variations in conversion for tetralin extraction of normal and chlorobenzene-treated coals and oil shale; and
- to ascertain the effects of tetrahydrofuran and methanol pretreatment on different rank coals and oil shale in thermolysis and liquefaction,

- to make solvent swelling measurements with pyridine, tetrahydrofuran, methanol and tetralin to help ascertain the effects of non-polar and polar solvent pretreatment on the macromolecular structure of coals,
- to make Thermal Gravimetric Analysis (TGA) in order to find out the effect of polar and non-polar solvent treatments on coal and oil shale, and
- to use Scanning Electron Microscopy (SEM) analysis to find out the effect of treatment on surface characteristics.



2. LITERATURE SURVEY

2.1 Coal

2.1.1 Coal formation

Coal, comprises a complex organic matrix containing carbon and hydrogen, together with smaller amounts of nitrogen, oxygen and sulphur incorporated with an inorganic matrix. It is a fossil formed mainly by the action of temperature, pressure and other physical and chemical factors on plant debris. The organic matter in coal is associated with varying amounts of moisture and minerals [8]. It comprises visibly distinct regions under an optical microscope, referred to as macerals. The inorganic, non-combustible material comprises mainly of clays, carbonates and sulphides [1,2].

2.1.2 Origin of coal

The origin of coal can be tied closely with the origin and development of plant life on earth [2]. In certain parts of the world, for example during the carboniferous period [24], warm and humid climatic conditions existed, which favoured the growth of huge tropical ferns and giant trees, which grew and died in vast swamp areas [8]. Beginning from these plant materials, the formation of coal has taken place in two stages, which are namely the biochemical (diagenesis) and geochemical (metamorphosis) stages [2,7,24]. It has generally been believed that the formation of peat (diagenesis), occurs by an aerobic decay process which decomposes most of the cellulosic material in preference to more decay-resistant lignins, waxes, and resinous compounds [2].

In the geochemical stage, intermittent subsidence of peat occurs, followed by sedimentation and, often, further cycles of plant growth and peat formation. In the buried layers of peat, biological activity ceases and much slower chemical changes, termed coalification, takes place, transforming peat into coal [7]. Coal will be the end-product of plant type and both physico-chemical and biochemical reactions [25]. The rate of coalification is controlled by increases in temperature, pressure and time that accompany the progressive burial of coal by sediments within a subsiding basin [26].

Not all parts of the original plant material are affected to the same degree by coalification [7]. Differences in the plant material and the extent of its decomposition during diagenesis largely determine the different petrographic types in coals known as macerals. The subsequent action of pressure and heat during the geochemical stage results in the differences in coalification or maturity of coals, usually termed as rank [8]. Rank refers to the stage of coalification that the organic matter has reached [25]. The degree of coalification or rank of coal increases progressively from lignite through sub-bituminous to bituminous coals and then to anthracite [2,8]. The carbon content, dry mineral matter-free basis, increases and the oxygen and hydrogen contents decrease throughout the series, while the reactivity decreases [8,24]. The nitrogen and sulphur content of coal are virtually independent of rank [2].

2.1.3 Macerals

As mentioned before, coal is not homogeneous, but consists of a microscopic mixture of components termed macerals, arising from the decay of different parts of the original plant material [7]. The definition given by the International Committee for Coal Petrology (ICCP) [27] is "Coal macerals evolve from the different organs or tissues of the initial coal-forming plant materials during the course of the first stage of carbonification. However, because of variable but severe alteration, it is not always possible to recognise the starting materials. Macerals are the microscopically recognisable individual constituents of coal and, depending on their

quantitative participation and their association, they mainly determine the chemical, physical and technological properties of a coal of given rank” [6,25].

2.1.3.1 Maceral terminology

Maceral terminology is essentially a classification system developed for the description and classification of organic matter in coal [25,28,29]. There are three maceral groups: vitrinite, inertinite and liptinite (Table 2.1) [26]. A maceral group comprises several macerals, each of which has a set of optically and chemically similar properties [6]. The distinction of macerals within those groups is based upon a combination of morphology, optical properties, botanical affinities and technological properties [26]. Thus, macerals differ in chemical composition and have distinct structural shapes, visible under an optical microscope [1].

2.1.4 Mineral matter and trace elements in coal

The terms ‘mineral matter’, ‘ash’ and ‘inorganic matter’ are often used interchangeably, but each term is clearly distinguishable. Minerals are generally defined as inorganic substances having a consistent and distinctive set of physical properties [2]. Ash is the residue derived from the inorganic and organic matter during combustion of the coal and oil shale [30]. The original mineral matter will be altered during combustion by oxidation and dehydration, so that the chemical form of ash is not the same as the original mineral matter [2].

The material supply and leaching behaviour of different minerals and elements during peat formation and coalification as well as the various plant constituents and regional, depositional and paleoenvironmental conditions are responsible for the most essential changes in the mineral and chemical composition [30,31].

Table 2.1. Hard-coal maceral terminology and origins [26].

Maceral group	Maceral	Origin
Vitrinite	Tellinite	Humified plant remains typically derived from woody, leaf or root tissue with well to poorly preserved cell structures
	Collinite	Humified material showing no trace of cellular structure, probably colloidal in origin
	Vitrodetrinite	Humified attrital or less commonly detrital plant tissue with particles typically being cell fragments
Liptinite (exinite)	Sporinite	Outer casing of spores and pollens
	Cutinite	Outer waxy coating from leaves, roots and some related tissues
	Resinite	Resin filling in cells and ducts in wood; resinous exudations from damaged wood
	Fluorinite	Essential oils in part; some fluorinite may be produced during physico-chemical coalification and represent non-migrated petroleum
	Suberinite	Cork cell and related tissues
	Bituminite	Uncertain but probable algal origin
	Alginite	Some groups of green algae; alginite shows moderate to strong fluorescence
	Exudatinite	Veins of bitumen-related material expelled from organic matter during coalification
	Liptodetrinite	Detrital forms of liptinite that cannot be differentiated
Inertinite	Fusinite	Fusinite originates from wood and leaf tissue oxidation
	Semifusinite	Wood or leaf tissue weakly altered by mouldering or by biochemical alteration
	Inertodetrinite	Similar to fusinite or Semifusinite but occurring as small fragments
	Macrinite	Humic tissue probably first gelified and then oxidized by processes similar to those producing Semifusinite
	Sclerotinite	Moderately reflecting tissue of fungal origin, largely restricted to Tertiary coals
	Micrinite	Largely of secondary origin formed by disproportionation of lipid or lipid-like compounds

Four terms are most often used to describe the mineral matter in coal [2,32,33].

These are:

1. Primary or internal - minerals present in original vegetation.
2. Secondary or external - minerals from sources other than the original vegetation.
 - Syngenetic minerals - those entering the peat and incorporated into the coal matrix during coalification (Table 2.2).
 - Epigenetic minerals - those being deposited, largely by percolation of water into fissures, after coalification has occurred (Table 2.2).

Trace elements can occur in coal basically in either organic or inorganic forms, and most trace elements are probably found in both combination [34]. Virtually, every element in the periodic table occurs in measurable amounts in coal [35,36]. Some of the major trace elements in coal are given at Table 2.3.

Table 2.2 Different types of minerals in coal and their origin [2]

Mineral Group	Syngenetic formation (intimately intergrown)		Epigenetic formation	
	Transported by water or wind	Newly formed	Deposited in fissures and cavities (coarsely intergrown)	Transformation of syngenetic minerals (intimately intergrown)
Clay minerals	Kaolinite, illite, sericite, clay minerals with mixed-layer structure, "Tonstein"			Illite, chlorite
Carbonates		Siderite-ankerite concretions, dolomite, calcite, ankerite Siderite, calcite, ankerite in fusite	Ankerite, calcite, dolomite	
Sulphide ores		Pyrite concretions melnikowite-pyrite, coarse pyrite, (marcasite), Concretions of FeS_2 - CuFeS_2 - ZnS Pyrite in fusite	Pyrite, marcasite, zinc-sulphide(sphalerite), lead sulphide, (galena), copper sulphide, (chalcocopyrite)	Pyrite from the transformation of syngenetic concretions of FeCO_3
Oxide ores		Hematite	Goethite, lepidocrocite, ("needle iron ore")	
Quartz	Quartz grains	Chalcedony and quartz from the weathering of feldspar and mica	Quartz	
Phosphates	Apatite	Phosphorite		
Heavy minerals and accessory minerals	Zircon, rutile, tourmaline, orthoclase, biotite		Chlorides, sulphates, and nitrates	

Table 2.3. Some of the major trace elements in coal [2].

Aluminium	Fluorine
Arsenic	Iron
Beryllium	Lead
Boron	Magnesium
Bromine	Mercury
Cadmium	Molybdenum
Calcium	Nickel
Chlorine	Potassium
Chromium	Sodium
Cobalt	Sulphur
Copper	Zinc

2.1.5 Organic structure of coal

Since coal is the most abundant hydrocarbon resource on earth, its structure needs to be well understood for effective utilisation [37]. In spite of the heterogeneity of coal and the large variety of coal types, many efforts have been made to elucidate the molecular structure of coal [1,8,38]. The aromatic/hydroaromatic model is generally accepted now [1]. In this model, coals are basically composed of aromatic and hydroaromatic building blocks, with heteroatoms substituted mainly in the aromatic ring systems (heterocycles). The aromatic and hydroaromatic building blocks are cross-linked, primarily by methylene, oxygen, and sulphur groups. Figure 2.1 shows the model constructed by Shinn [38]. A variety of aromatics (Figure 2.1a), functional groups (Figure 2.1b), and aliphatics (Figure 2.1c) are joined together to synthesize a predominantly macromolecular structure. However, some molecular entities are shown hydrogen bonded into the structure. These trapped molecules are referred to as the mobile phase and they can be removed from coal by solvent extraction [1,38].

The model structure shown in Figure 2.1 represents high-volatile bituminous coals. However, the structure can be extended to other coals. With increasing coal rank, the relative contribution of aromatics to the coal structure increases, whereas that from functional groups and aliphatics decreases. Also, the average number of

aromatic rings per building block increases. This concept is illustrated in Figure 2.2a, which shows a tentative model structure of a semi-anthracite. In Figure 2.2b a possible structure of a lignite is given [1].

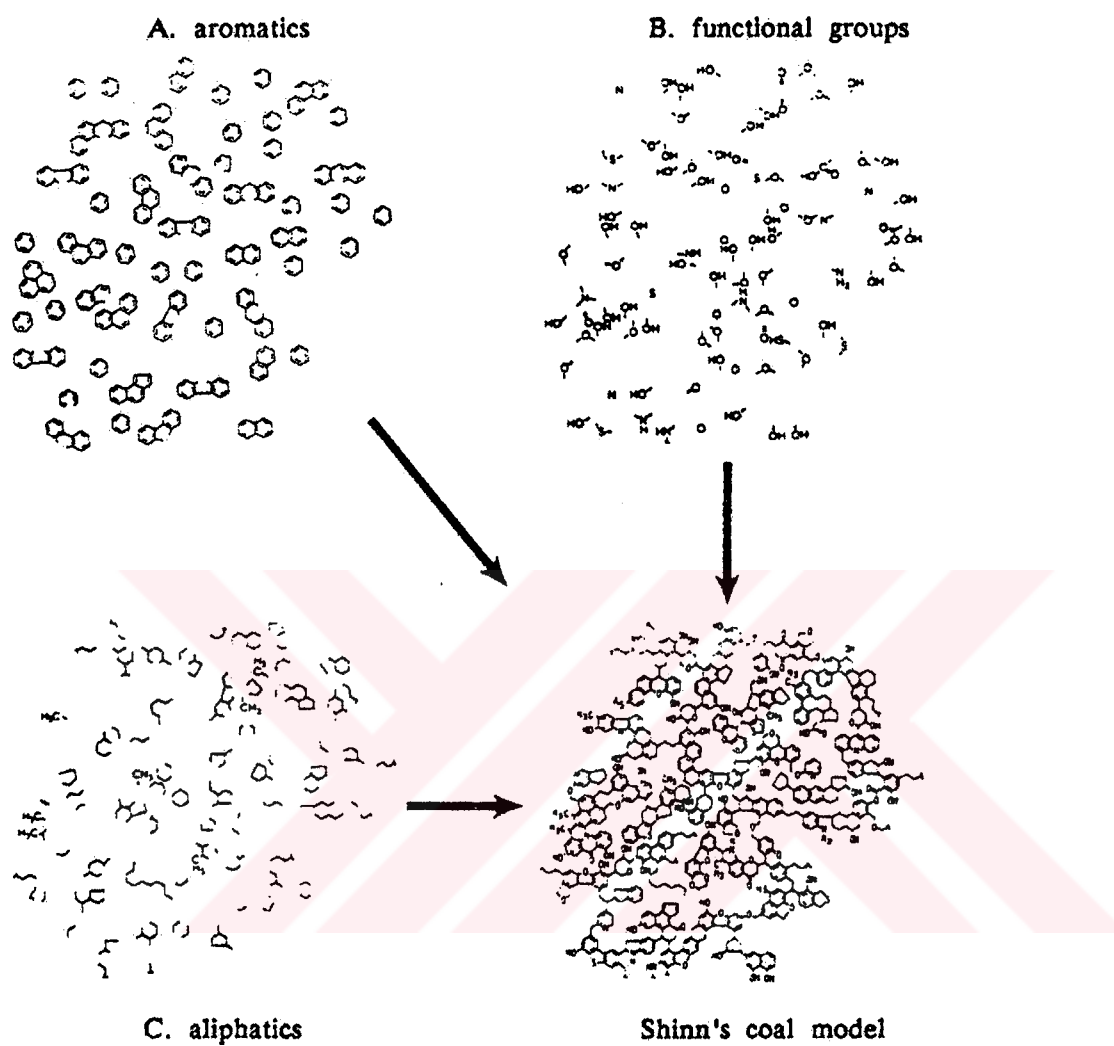


Figure 2.1. Construction of coal model structure for a bituminous coal from a variety of aromatics (a), functional groups (b), and aliphatics (c) [38].

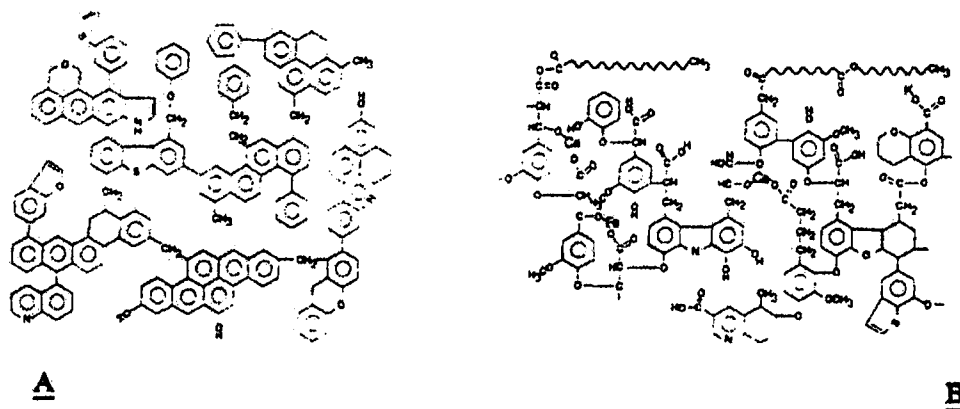


Figure 2.2. Possible structures of a semi-anthracite (a) and of a lignite (b). The aromatic structure of a ring system is indicated by a circle [1].

2.2 Oil Shale

2.2.1 Oil shale formation

Oil shales are fine-grained sedimentary rocks that contain organic matter, which upon heating can be converted to liquid shale oils. Formation of an oil shale requires simultaneous sources of both fine-grained minerals and organics, under conditions where the organics can be preserved [3].

2.2.2 Organic matter in oil shale

There are two fractions of organic matter in oil shale named as bitumen and kerogen [3,4,5]. Bitumen is defined as the organic material, which can be extracted by ordinary organic solvents, such as benzene, toluene, tetrahydrofuran and chloroform or mixtures of solvents, such as benzene-methanol. Kerogen, which comprises the major part of the organic material, is not soluble in such solvent [3].

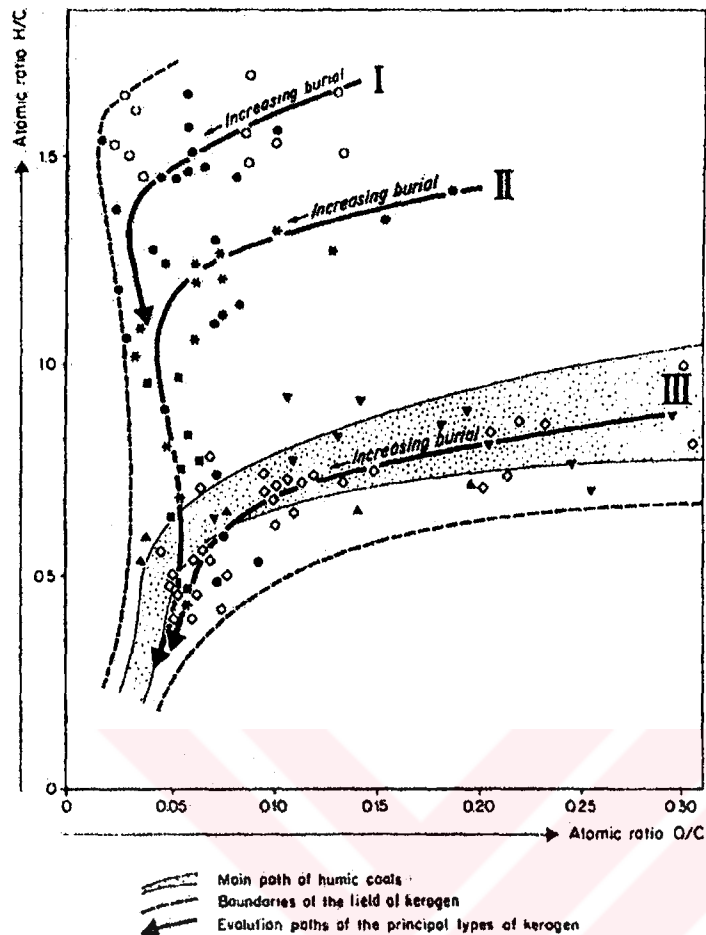
2.2.3 Kerogen types and maturation

The use of the term 'kerogen', originally described as the organic matter in oil shale, has been extended to include all non-soluble solid organic matter in sedimentary rocks. Kerogen is divided into 'types' based on elemental composition and potential maturation path [6].

Kerogen types are determined by the kind of debris that is deposited in the sediment. As initially deposited in a 'recent sediment', each type of sediment has a characteristic range of composition. The preserved organic matter in a sediment undergoes additional changes by the effect of temperature, time, pressure, physical, chemical and biochemical factors. This is the process of kerogen maturation, which is responsible for the generation of crude oil, natural gas, or a mixture of the two [3,39,40]. Maturation involves the loss of hydrogen and oxygen from the kerogen [3].

The Van Krevelen diagram provides a simple way of graphically representing the relationships between kerogen type, composition and maturation (Figure 2.3) for the kerogen derived from demineralised oil shale [3,4]. Based on H/C and O/C ratios, three types of kerogen are recognised: Type I, Type II and Type III. Type I is aliphatic kerogen with high initial H/C (1.5 or more) and the atomic O/C ratio is generally low (0.1 or less). Type II has lower H/C than Type I, and high O/C ratio. Type III kerogen has low H/C ratios (< 1) and O/C ratios generally between 0.1 - 0.3 [3,6].

For instance, Goynuk and Seyitomer oil shales were pyrolyzed using a Heinze retort producing high and medium oil yields, respectively. The oils derived from the kerogen were characterised by Putun et al. [41,42] in order to find out the type of kerogen. The high H/C and low O/C atomic ratios of Goynuk and Seyitomer oil shale kerogens characterise both of them as type I kerogens. The fact that both of these shales overlay lignite deposits giving medium to very high oil yields and increased H/C ratios in the oils, substantiates this classification.



Type	Age and/or formation	Basin, country	
I	Green River shales (Paleocene - Eocene)	Uinta, Utah, U.S.A	●
	Algal kerogens (Botryococcus, etc.), Various oil shales		○
II	Lower Tertiary shales	Paris, France, W. Germany	*
	Silurian shales	Sahara, Algeria and Libya	■
	Various oil shales		●
III	Upper Cretaceous	Douala, Cameroon	○
	Lower Mannville shales	Alberta, Canada	▲
	Lower Mannville shales	Alberta, Canada	▼

Figure 2.3 The Van Krevelen diagram traces the evolution paths of types I, II, III kerogen as a function of increasing burial (increased time-temperature exposure) [3].

As Van Krevelan diagram is originally used for coal, it is noticed that the distribution of Types I, II and III kerogen shows a close relationship between the maceral group distributions and the kerogen type distributions. This is because the kerogen or organic matter in both coal and oil shale is composed of macerals [3,6].

2.2.4 Macerals

Maceral terminology is first developed to describe the organic components of coal and then has been extended to include petroleum source rocks and oil shales [6,25]. As mentioned before [Section 2.1.2 and 2.1.2.1], maceral terminology is based on the direct observation of the morphological and optical properties of the organic matter which ultimately reflects their internal chemistry [6].

The dominant organic matter in oil shale is derived from lipid-rich precursors which, in oil shales, are recognised as liptinite macerals [4]. Thus, vitrinite and inertinite macerals are generally minor components of oil shales [25].

2.2.4.1 Types of oil shales

A petrographic classification of oil shales, which is based on the type, and abundance of liptinite is used mainly. In this system, the primary division of oil shale is based on the source of liptinite whereas secondary sub-divisions are based on the type of liptinite (Figure 2.4). Origins of primary and secondary groups of oil shales are given at Table 2.4 [4].

2.2.5 Mineral matter in oil shale

Mineral matter in oil shale can be classified as detrital, biogenic and authigenic minerals. Detrital minerals typically include quartz, feldspar and clays (including illite, montmorillonite and kaolinite) and sometimes volcanic ash. Biogenic minerals include amorphous silica and calcium carbonate, usually in very minor amounts. Authigenic minerals typically include pyrite and other metal sulphides, carbonates (calcite, dolomite, siderite), and phosphates [3,43].

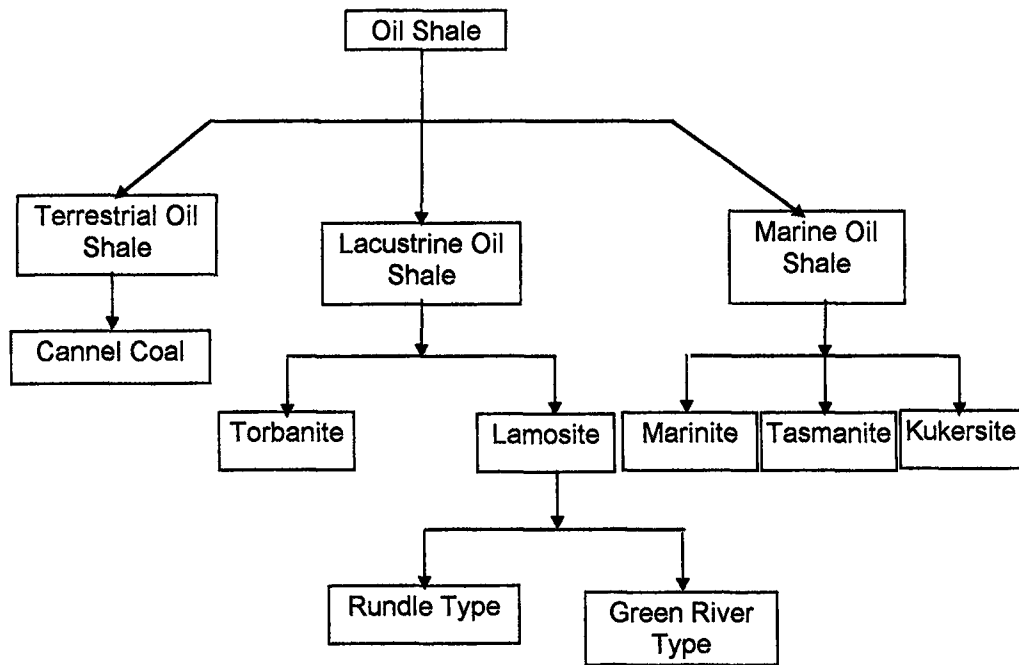


Figure 2.4. Primary and secondary types of oil shales [4].

Table 2.4. Primary and secondary groups of oil shales [4].

Primary Group	Secondary Group	Origin
Terrestrial	Cannel coal	Composed of liptinite(mostly resinite, sporinite, cutinite, liptodetrinite) derived from terrestrial vascular plants with vitrinite and inertinite.
Lacustrine	Torbanite	Liptinite is derived from Botryococcus-related lacustrine algae; sporinite and liptodetrinite are minor components; vitrinite and inertinite occur in variable amounts.
	Lamosite	Liptinite is lamalganite derived from lacustrine algae and phytoplankton; minor components are vitrinite, inertinite, telalginite and bitumen.
Marine	Marinite	Liptinite is lamalginate derived from marine algae, phytoplankton, and/or bituminite derived from marine precursors; vitrinite, inertinite, sporinite, telalginite, bitumen are minor components.
	Tasmanite	Liptinite is telalginite derived from tasmanitids; lamalginate, vitrinite, inertinite, sporinite are minor components.
	Kukersite	Liptinite is telalginite derived from Gloeocapsomorpha prisca.

2.2.6 Organic structure of oil shale

Oil shale organics are largely present as kerogen, an insoluble and non-volatile material, which is finely disseminated in the rock matrix of the shale, and which must be depolymerized in order to recover shale oil from the rock [40,44]. Therefore, there has been intense interest in understanding the molecular structure and chemistry of oil shale kerogens and several research groups have attempted to elucidate the structure of the Green River formation [44].

Green River Kerogen concentrate was subjected to oxidation and the products were analysed by mass spectrometry and gas chromatography. Based upon analysis of these results, a structural model for Green River oil shale organics was proposed (Figure 2.5) [3]. Key features of this model include very large regions of undefined structure containing trapped organics of unknown nature and bearing side chains linked to the main structure by ester linkages [3].

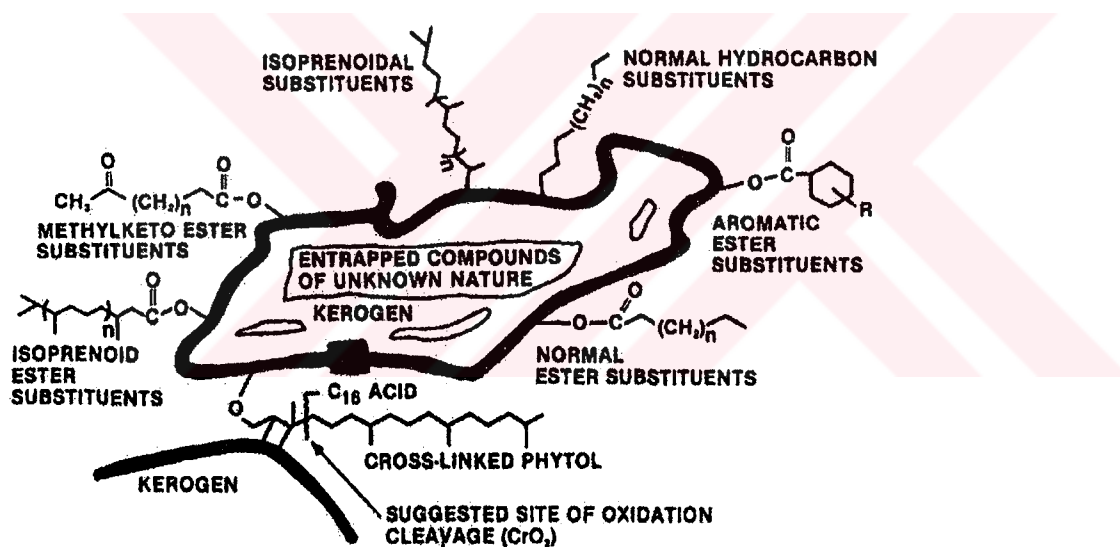


Figure 2.5. Model of Green River oil shale kerogen [3,44,45].

The structure of Green River kerogen was also investigated by a combination of controlled micropyrolysis and mass spectrometry. Based upon the results found, a generalised kerogen structure with alkyl-substituted decalins or tetralins inter-linked

by normal or branched alkane bridges was proposed. In a kerogen matrix the many sub-units are connected by alkane or ether linkages. There are also trapped subunits within the matrix [44].

In addition, based on the results of a study where a wide variety of techniques used, it is concluded that aromaticity is low and that the structure is naphthenic. Also, oxygen is present mostly as esters and ethers, and that ethers serve as cross-links with additional linkages provided by disulphides, nitrogen heterocyclic groups, hydrogen bonding, unsaturated isoprenoid chains, and charge-transfer interactions [3,44].

A comprehensive study is made in order to characterise the organic functionalities in Rundle Ramsay Crossing oil shale (RXOS) from Queensland, Australia. The model is required to accommodate the large range of heteroatom functionalities and long side chains present in RXOS (Figure 2.6). Because carboxylic acids comprise the major part of the RXOS bitumen, all the bitumen in the model was represented as carboxylic acids [3,44].

A comparison with models Figure 2.5 [3,44,45] and 2.6 [3] for Green River oil shale (GROS) kerogen serves to illustrate some of the key features of the RXOS kerogen [3,44,45].

Aliphatic material is the most obvious feature of the RXOS model and RXOS is more aliphatic than typical samples of GROS. Aliphatics in RXOS are longer and more linear than those in GROS and are present both as alkylene bridges and as alkyl side chains. The nitrogen content of RXOS is lower than that of GROS. The major part of the nitrogen in RXOS is present in very stable aromatic nitrogen heterocycles, derivatives of pyridine and pyrrole. The organic oxygen content in RXOS is much higher than that in GROS and present in a variety of functional group types [3].

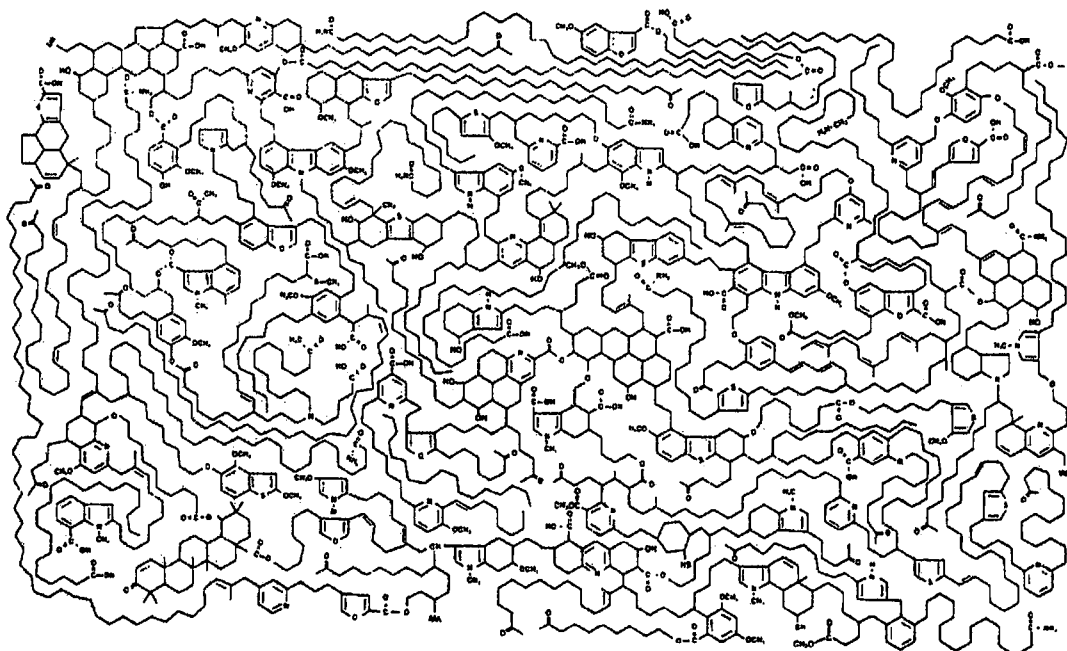


Figure 2.6. Structural model of representative organic material in Rundle Ramsay Crossing oil shale [3].

Most of the organic material is insoluble in kerogen. From oil shales insolubility and swellability, Siskin and co-workers [44] infer the presence within the kerogen of a three dimensional network structure, which must be disrupted prior to dissolution. Accordingly, the models represent one tetrafunctional cross-link in an essentially infinite macromolecular network. The linkages comprising the network may be covalent bonds, bonds between heteroatom functionalities (e.g. carboxylates, amines) and minerals, hydrogen bonds or, physical entanglements. It is believed that most key linkages are covalent bonds between organic moieties [44].

2.3 Solvent Swelling

2.3.1 Introduction

The organic fraction of coal is predominately a three-dimensional macromolecular network structure containing some extractable molecular components as already described [Section 2.1.5,16,46,47]. The coal network swells in some solvents [48-50], leading to the expansion of the micropores present in the structure [17,51-53].

Swelling is known to be a process involving the diffusion of solvent molecules within the coal structure and the solvation of its fragments, followed by a change in conformation [54]. The swelling of coals in liquids [15,16,18,37,46,48,49,51,54-71] and vapours [47,53,60,72,73] is of both scientific and technological importance. Solvent swelling can occur in a number of coal conversion processes, including direct liquefaction [16,46,53,59,74]. The accessibility of the reactive sites in coal micropores to a reagent, particularly in the initial stages of liquefaction, is diffusion limited. In order to overcome this limitation, contact between the reagents and the coal surface should be maximised. Swelling of coal by a solvent helps to increase this contact [15]. When coal is in contact with solvents it presents adsorption of the solvent molecules, dissolution of coal components, swelling of coal, and physicochemical processes including chemical reaction between coal components and the solvent [46,75].

A swollen coal structure can facilitate more complete or rapid penetration of reagents to the active sites and may enhance diffusion of coal fragments from the macromolecular structure, thereby producing more complete reactions or greater product yields. If a highly swollen coal is dried, it retains a distorted structure [53], thus producing greater penetration and diffusion of reagents and products and an enhanced yield [16,46,53,57].

The degree to which coal swells in the presence of a swelling agent is a measure of the solvent-coal compatibility and of the flexibility of the coal structure [47]. Because of this, solvent swelling studies have been used to estimate the average molecular mass between cross-links [76,77] and to understand the bonding between subunits in coals [37,59,64,78] and also the behaviour of coal/solvent system [55]. Organic solvents affect the pore structure of coal, as well as density, mechanical strength, and spectral properties [78,79].

2.3.2 Swelling solvents

Coals are cross-linked macromolecular gels containing particles of minerals and a variety of dissolved organic molecules which can be extracted [Section 2.1.5, 61]. When placed in contact with a solvent for which they have an affinity, the solvent dissolves in the coal, which swells to contain the solvent [61].

Most coals swell in suitable solvents. At constant temperature, the degree of swelling and/or dissolution depends on the basicity and steric properties of the solvent and the nature of the coal rank and macerals, in addition to coal particle size [15,17,18,55,56,62,66,69,77,78,80,81].

Hall et.al. [67] reported a trend of increasing swelling value of coals with increasing basicity of solvent, as defined by PK_b values, until a plateau was reached at $PK_b \sim 8-9$. Further increases in basicity had little effect on swelling [77].

Steric properties of the solvent have significant effects on the swelling ratios of coal solvent swelling [80]. Ndaji et.al. [80] used a high-volatile bituminous coal in order to examine the effects of solvent molecular size on the swelling ratio by using straight-chain amines as a swelling solvent. It is reported that the swelling ratio increases with increase in the solvent molecular size (alkyl chain length) due to the requirement to accommodate the solvent molecules. However, it appears that there is a critical molecular size above which the swelling decreases with increasing molecular size due to limited access of the solvent to the coal structure. The covalent cross-link density of the coal, which prevents the coal structure from swelling further to accommodate larger molecules, determines this limit of solvent swelling. The energy barrier for the solvent swelling process increases with solvent size, as a result of increasing steric effects [80].

The most effective swelling solvents are those containing nitrogen or oxygen atoms with lone pair(s) of electrons available for co-ordination [15,18,49,81]. These solvents are generally organic bases; common examples are pyridine, ethylenediamine and tetrahydrofuran [15,18,49,59,64,80-82].

It is convenient to divide solvent swelling into two groups; first, coal swelling in non-polar solvents and second with swelling in polar, basic solvents [67]. The differences in swelling efficacies of the solvents may be explained on the basis of their interactions with the various types of effective bridging bonds in coals [18,66]. They are formed through (i) covalent bonding, (ii) ionic bonding, (iii) hydrogen bonding and (iv) charge transfer complexing. Swelling of coal is caused by disrupting (breaking or extending) one or more of these bonds. The extent of swelling depends on the type of bonds predominant in a coal and the nature of the solvent. Covalent bonds are not likely to be broken by common solvents under ambient conditions. Therefore, only ionic interactions, hydrogen bonding and charge transfer complexing are important as far as swelling is concerned [18,83]. Ionic and hydrogen bonds are believed to be significant in low rank coals because of the presence of a relatively large number of polar functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (-CO-) [18]. Charge transfer complexing is expected to be predominant only in higher rank coals because of their higher aromatic content than the lower rank coals [18,83-85]. The maximum swelling possible is limited by the number of covalent cross-links. As the non-covalent cross-links are destroyed by stronger coal-solvent interactions, the swelling will increase. The swelling observed with any solvent is a balance between the coal-solvent interactions and coal-coal interaction [56,61].

Owing to the difference in their electronic properties, various solvents react differently with the bridging bonds mentioned above [18]. This behaviour indicates that different solvents will yield chemically different extracts from the coals, depending on which interactions they are able to break. Therefore, different solvents can create substantially different macromolecular structure in the immersed coal [86]. Swelling of coal in non-polar solvents is caused by the dispersion-force interaction between the solvent and the coal macromolecular network [67,77]. Polar solvents form 'coal-solvent' contacts readily by breaking and/or relaxing the

hydrogen bonds in coal [67,77,78,87]. Polar solvents swell the coal significantly more than do the non-polar solvents. This is undoubtedly due to a combination of their greater interaction with the coals and the fact that they disrupt the coal-coal hydrogen bonding leading to a system that effectively has a lower cross-link density [59,77]. Hydrogen bonding is especially important for lower rank coals, but diminishes in importance with rank. Hydrogen bonding is believed to be associated with oxygen functionalities, and the oxygen content of coal decreases with rank. Thus, polar solvents show a lesser ability to swell in higher rank coals. Further, the degree of solvent polarity affects the ability of a solvent to disrupt hydrogen bonds and swell coal. Swellability also decreases with rank for non-polar solvents, probably due to the high covalent cross-link densities in higher rank coals [67,78].

The low-rank coals are highly oxygenated and are much more polar than are bituminous coals. Because of this, their interaction with non-polar solvents is expected to be much less than that with bituminous coals. The character of the non-polar solvents is much more like the chemical character of the bituminous coals and so these will interact better. The greater the oxygen content and the greater the polarity of the low-rank coals, the less the interaction with non-polar solvents compared to coal-coal interactions and therefore the lower the swelling values [59].

It was reported that coals undergo conformational rearrangements when exposed to solvents. Brenner [86] demonstrated that rapid rearrangements occur in coal thin sections swollen with tetrahydrofuran. Hsieh and Duda [88] showed that diffusion rates were sensitive to the previous exposure of coals to solvents. Cody and co-workers [89] observed that the swelling of coals was anisotropic and that the coals rearranged to a new shape when the solvent was removed. It has been argued [90] that extraction with pyridine causes conformational rearrangements in coals, rearrangements, which result in enhanced association through, increased non-covalent interactions between aromatic groups. Evidence has also been presented [82] that warming a coal in chlorobenzene results in similar conformational rearrangements leading to a more highly associated, lower free energy coal [91].

2.3.3 Glasses and rubbers

Coals are glassy, strained, macromolecular solids and cannot relax to an equilibrium conformation as it is removed from the coal seam to ambient conditions of temperature and pressure [55,86,92]. The first clear recognition that coals were glassy solids seems to have been made by Brenner [86]. He associated the optical anisotropy of Illinois No.6 coal viewed in thin section through a polarising microscope with the existence of strain in a glassy system. He showed that this strain could be removed if the coal was swollen with an effective swelling solvent, such as pyridine. Furthermore, exerting pressure on the swollen coal deformed it and re-established optical evidence for strain. Brenner established that untreated coals were strained, solvent swelling could lead to relaxation of strain and that the swollen coals were rubbery [86,92].

Glassy coals and rubbery coals are startlingly different materials [92,93]. In the glassy state, molecular motion is very limited. Diffusion rates are very low because diffusion through the macromolecular solid involves moving portions of the macromolecule around to allow passage of the diffusing molecule. Thermal bond cleavage in a glassy material will leave the fragments close to each other, trapped in a cage which presents them with a very limited set of potential reaction partners, those groups on the inside of their small cage [92]. Rubbery solids are ones, which, after they are stressed, rapidly recover their original configuration when the stress is released [86]. In a rubbery solid, cage effects, while certainly not absent, will be much smaller. In order to reduce diffusional and steric constraints, it is desirable to conduct chemical reactions on coals in the rubbery rather than glassy state [92].

The degree to which coal becomes rubbery is a function of the density of hydrogen bonds disrupted and hence the solvent swelling [94]. Solvent swelling and disruption of polar cross-links reduces the glass transition temperature and provides sufficient mobility of coal segments for the macromolecular network to adjust to a new conformation [55,95]. Swollen samples were found to be substantially more flexible than the untreated or re-dried samples, indicating much greater

macromolecular chain mobility and much lower effective cross-link density, and suggesting that the elasticity of the solvent-swollen coal may be predominantly rubber-like [52,86,92].

2.3.4 Size and shape changes

When thin sections of coal were swollen in three different solvents, namely pyridine, tetrahydrofuran, and chlorobenzene [89], they swelled more in the direction perpendicular to the bedding plane than parallel to it. With pyridine, the linear expansion of the coal is approximately twice as great perpendicular to the bedding plane as parallel to it. Evaporation of the pyridine shrinks the coal thin section to a particle having different dimensions to the original particle. It is thicker i.e. expanded to the perpendicular to the bedding plane and less broad i.e. contracted parallel to the bedding plane. Repeated swellings now return the coal to its original expanded rubbery state and removal of the solvent returns the coal to its new shape. The reversibility indicates that it is the new thicker shape, which is the thermodynamically favoured on formation, and not the original shape [86,92], (Figure 2.7).

Brenner [52,86] observed solvent swelling of thin sections of coal in pyridine, n-propylamine and found that after removal of the solvents, thin sections of coal gave extremely close replicas of the preceding swollen sample. Larsen et. al. [96] tested repetitive swelling of pyridine-extracted Illinois No.6 coal with chlorobenzene, toluene and tetrahydrofuran. The swelling was reproducible for the first and second cycles [97].

An explanation of this behaviour must be consistent with the following facts. The organic structure of the coal is essentially isotropic at the molecular level. The initial swelling of coal to rubbery state followed by solvent removal leads to a change in the coal shape. Subsequent swellings are reversible and the swollen state is the same as that reached in the initial swelling. This can be explained by the fact that the coal, as mined, is strained. The coalification process taking place under great pressure and over a long period deforms the coal, compacting it perpendicular to the bedding plane and expanding it in the bedding plane. Because it is a glassy

solid, these deformations are not reversed when the coal is mined. It is locked into a deformed, high energy state. When the coal is swollen and becomes rubbery, the macromolecules can move about much more freely and the strain is relaxed. As the swelling solvent is removed, the chains still have enough freedom of motion in the slowly contracting material to find their lowest free energy packing arrangement. This involves a different set of interactions than the starting coal and results in a material of lower free energy and different shape [92].

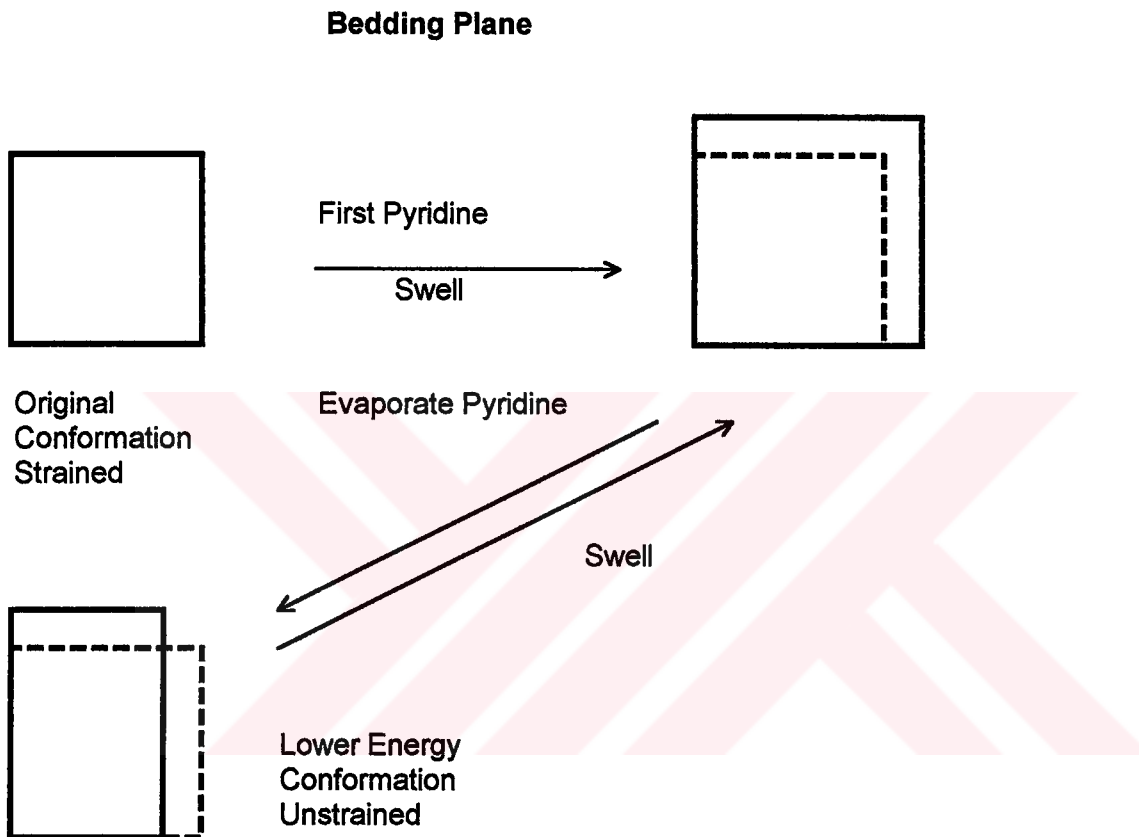


Figure 2.7. Diagram of size and shape changes during coal swelling [86,92].

The observed dimensional changes that occur during this swelling of coals are a consequence of the reorientation of macromolecular chains. As mentioned before, coal is depicted as a gel-like structure [Section 2.3.2] that contains cross-linkages between the various macromolecular strands. In the presence of selected liquids the gel structure of the coal swells substantially, but the cross-linkages prevent dissolution of the structure. The degree of swelling observed indicates that there are a number of flexible (i.e., rotatable) molecular subunits between cross-links in the average chain [53].

Limited structural mobility can be conferred by partial solvent swelling [82,90]. The pyridine extraction of coals results in a conformational isomerisation to a lower free energy state as indicated by solvent swelling and extractability changes. If Illinois No.6 coal is warmed in the poorly swelling solvent, chlorobenzene, it undergoes a transformation as it slowly relaxes to a lower free energy, less conformationally strained state. During this process, both the extent of extractability and solvent swelling decrease. A very limited amount of data has been collected on the reactivity of rearranged coals. Rearranged Illinois No.6 coal gives a significantly reduced conversion to pyridine solubles in low temperature liquefaction [91]. Solvent swelling presumably gives rise to a rearranged, more highly associated structure [91,92].

2.3.4.1 Swelling of macerals

The various microscopic macerals, such as vitrinite, fusinite and liptinite have different swellabilities, hardness and shapes [53]. Shibaoka [81] has reported a microscopic study using reflected light of the swelling of a high-volatile bituminous coal macerals. Vitrinite was reported to swell after exposure to pyridine, while liptinite and inertinite macerals were little affected.

Swelling was reported [53] to be reversible if the solvent was removed early on; however, on prolonged swelling the reversibility was progressively lost in microscopic swelling of coal. The irreversibility was due to fracturing of the coal due to differential swelling, which was suggested to be caused mainly by faster expansion of the outer region of the coal with differential swelling of the macerals [56].

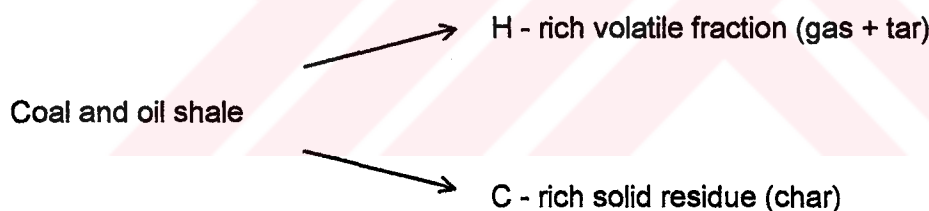
2.4 Pyrolysis Of Coal and Oil Shale

Under oxygen free or deficient conditions when coal and oil shale are subjected to heat they decompose to liquid and gaseous products. This process is called pyrolysis [2]. Pyrolysis is an important aspect of coal behaviour since it is involved in all major coal conversion processes [1,98], such as carbonisation, liquefaction and gasification [7,99]. For coal and oil shale, pyrolysis consists of a very complex

set of reactions during which both chemical and physical changes occur [1,2]. In addition, it is well known that the course and product yields during pyrolysis of coal and oil shale are mainly influenced by factors such as coal rank, kerogen type, maceral composition, particle size, temperature (i.e. temperature-time history), rate of heating, atmosphere, pressure, reactor configuration, residence time, final temperature, catalyst and sweeping [1,2,7,24,99-107]. Thus, practical pyrolysis conditions should be determined by an optimum combination of these parameters [98].

Depending on the type of coal and oil shale conversion process and/or the reactor type pyrolysis can either be slow or rapid (flash) according to the rate at which the coal and oil shale particles are heated. Rapid heating increases instantaneous product formation rate and is used to encourage liquid products to 'explode' out of the coal and to minimise their residence time in bed in order to prevent occurrence of retrogressive reactions [1,100,102,108,109].

Upon pyrolysis, coal and oil shale are divided into a hydrogen-rich volatile fraction, consisting of gases; vapours, tar components, and a carbon-rich solid residue, called char or coke. The overall process can be depicted as follows [1,7,110]:



2.4.1 Reactions and mechanisms

The reactions occurring during coal pyrolysis are summarised in Figure 2.8. When coal is heated from room temperature, first of all the desorption of water and gases takes place up to ~120 °C. The distillation of the mobile phase begins at ~250 °C, giving rise to aliphatic compounds in the tar. With increasing temperature, the formation of aromatic tar and gases begins at 400 °C, and this increasingly is accompanied by the condensation of the aromatic structures to char, which is finally associated with the formation of CO, H₂, CH₄ and N₂ [99].

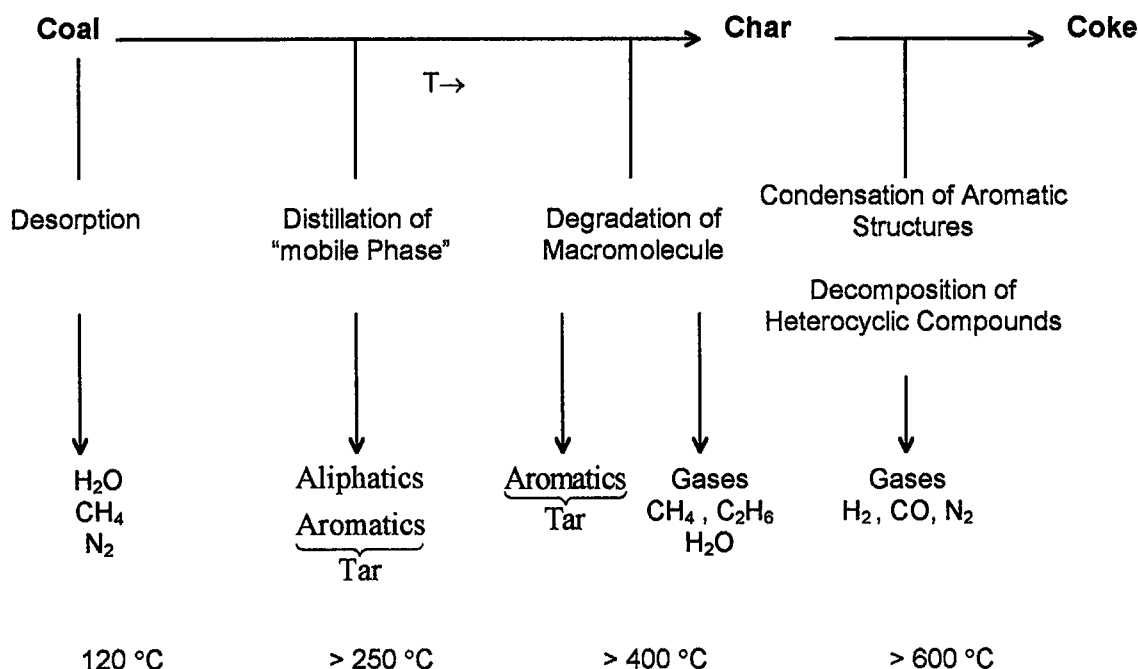


Figure 2.8. Main reactions during pyrolysis [99].

The reactions, which occur upon pyrolysis of coal and oil shale, are illustrated in more detail in Figures 2.9 and 2.10, respectively. The coal and oil shale first decomposes by breaking the least stable bonds within the structure. These bonds are the methylene, oxygen, and sulphur-bridges between the aromatic building blocks [1]. The result is the formation of a large number of radical species, some of which are volatile. These radicals are very reactive and can undergo secondary cracking and rearrangement reactions, both inside and outside the coal particle. Stabilisation of radicals occurs, primarily via hydrogen addition/abstraction, leading to volatile components and prevents undesirable retrogressive reactions [1,24,111]. Condensation reactions, occurring via recombination of both volatile and non-volatile radical components, result in char formation [1,112]. Char is enriched in carbon and is more aromatic compared to the original coal. The volatile products, formed after stabilisation of the radical components, may also undergo secondary gas reactions (both cracking and condensation reactions) due to extended exposure to high temperatures [1].

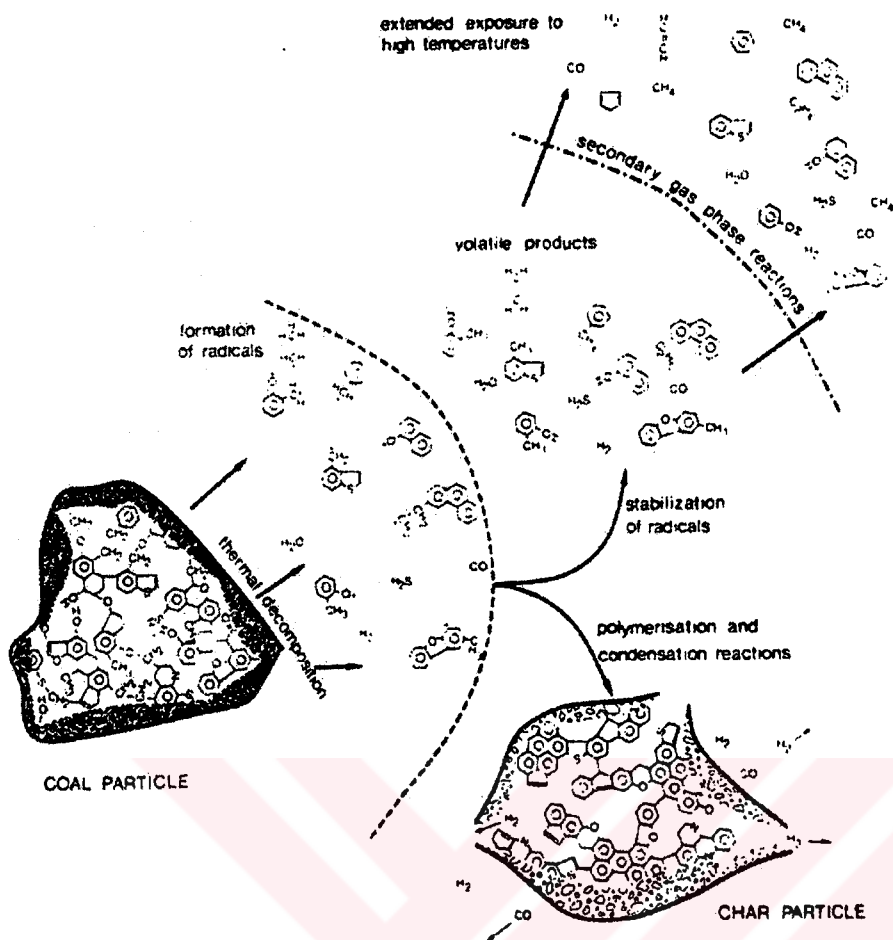


Figure 2.9. Reactions and processes which occur upon pyrolysis of a coal particle [1].

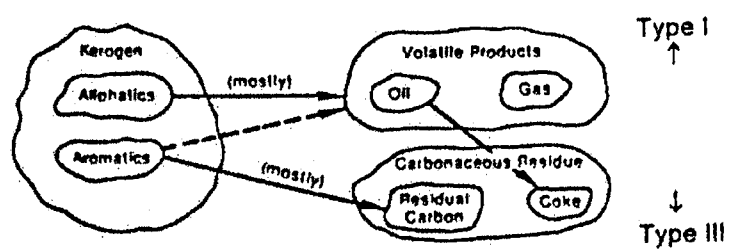


Figure 2.10. A proposed reaction model for oil shale [10].

2.5 Liquefaction Of Coal and Oil Shale

2.5.1 General considerations

Coal, oil shale and oil belong to the family of fossil fuels, which also includes natural gas, oil shales, tar sands and peat. Although all fossil fuels may be broadly regarded as either hydrocarbons as such or as sources of hydrocarbons, there are significant chemical differences which are reflected in the possible approaches to coal liquefaction. To convert coal into synthetic liquid fuels, four inter-related changes must be accomplished [7].

1. The complex, high molecular mass structure of coal must be broken down into relatively small molecules.
2. The hydrogen content must be increased.
3. The heteroatom content (oxygen, nitrogen and sulphur) must be reduced.
4. The mineral matter must be removed.

There are three main conversion routes, namely pyrolysis, direct and indirect liquefaction. As a means of producing coal and oil shale liquids, pyrolysis is of minimal value because most of the coal and oil shale is converted to char rather than to gases or liquids [2,3]. Indirect liquefaction involves gasifying coal at high temperatures in the presence of oxygen to form a mixture of carbon monoxide and hydrogen, commonly known as synthesis gas, which is then catalytically converted into a mixture of liquid hydrocarbon products [2,9,113].

The overall aim in coal liquefaction processes is to increase the hydrogen to carbon ratio of the reactor feedstock [12]. Direct liquefaction occurs in three main stages which are (i) dissolving the coal in a suitable solvent, through reaction with hydrogen, (ii) separation of the mineral matter and undissolved coal, and (iii) recovery of the products and recycle of the solvent. The various approaches to direct liquefaction can be classified according to the order in which the stages take place and the extent to which they are combined [7].

During all liquefaction processes, coal/oil shale is heated in a solvent stream, with/without catalyst and/or under hydrogen pressure, which causes the coal to

break down into smaller fragments [12]. One of the most important aspects of liquefaction is control of dissolution step, which involves the transition from solid coal to initial dissolved products [114]. Relative to subsequent steps, dissolution is a fast process that involves both physical and chemical changes in the coal. Penetration and swelling by the hydrogen-donor solvent occurs, resulting in extraction of organics dissolved in the macromolecular network and changes in the morphology of coal particles [114].

The hydrogen-donor solvents are usually a recycled fractions from the hydrogenation reactors, so called because they thermally react, donating hydrogen radicals to coal. This enables the formation of lighter fragments with hydrogen to carbon ratios greater than the parent coal; for example, tetralin donates hydrogen to form naphthalene with the transfer of hydrogen to the coal [12].

The distillate products recovered from the initial liquefaction stage require further upgrading/hydrotreating to form usable hydrocarbons. This is usually accomplished in a second stage hydrogenation reactor in which the solvent stream containing the coal extracts is passed through a catalyst bed under hydrogen pressure. A fraction of the second stage products is then recycled to the primary hydrogenation stage to solubilise more coal [12].

2.5.2 Hydrogen donor solvent extraction of coal

The type of solvent utilised in coal liquefaction plays a key role in coal conversion [115]. Liquefaction efficiency is affected by the quality of the feed solvent because the solvent participates not only in physical dispersion of coal molecules but also in chemical stabilisation of thermally produced coal free radicals [116,117]. The solvent acts as a medium to aid in the transport of hydrogen, and in heat transfer. It also transports the liquefaction products out of the coal matrix [115]. Several studies have been carried out to correlate the behaviour of model or practical recycle solvents with their structural characteristics [118]. As mentioned earlier, hydrogen donor species in the solvent play an important role in hydrogen transfer to the coal in all direct liquefaction processes. In particular, reaction with molecular

hydrogen and rearrangement of internal hydrogen also appear to be promoted if the solvent possesses hydrogen donor properties [7].

Effective conversion can be achieved only with external hydrogen [119]. Although the donation of hydrogen to coal may be achieved by transfer from a donor solvent and by reaction with molecular hydrogen, clearly transfer from a donor solvent is the only mechanism operating when a hydrogen overpressure is not used [7].

The chemical action of donor solvents may be illustrated using the example of tetralin (Figure 2.11) [7]. Tetralin can decompose, releasing four atoms of donor hydrogen, as it is converted to naphthalene. The reaction is, however, reversible and naphthalene may be rehydrogenated to tetralin. The rehydrogenation may also proceed further and produce decalin [7]. Although decalin contains more hydrogen than tetralin, it is a much less effective donor solvent for coal [7,120].

Shibaoka [121] observed differing behaviour of coal during heating with various solvents in the 340-390 °C range, and found that tetralin caused coal particles to swell and become plastic, but in naphthalene the coal only swelled and in decalin neither greatly swelling nor plasticity has occurred. These observations indicate the significance of the hydrogen donor ability of tetralin towards coal [122].

For coal liquefaction, highly effective solvents can be prepared by selecting a suitable combination of solvent components including apparent poor hydrogen-donors. In order to understand the role of solvent-solvent interactions during coal liquefaction, Chiba et al. [118] used binary solvent systems comprising indene and tetralin or decalin. Tetralin and decalin are well known as donor and non-donor solvents, respectively. However, it was found that the addition of indene was extremely effective for decalin. Thus, bimolecular reactions of indene with tetralin or decalin may provide active intermediates, which promote the liquefaction of coal as the active hydrogen donors, hydrogen acceptors or scavengers for stabilising coal radicals [118].

Tagaya et al.[123] used mixtures of tetralin and compounds having reducible structures, indene and benzophenone in order to liquefy three types of coal. When indene was mixed with tetralin, indene contributes directly to an increase in coal

conversion. However, it was found that benzophenone mixing caused a reduction in coal conversion, which indicated the presence of hydrogen abstraction by benzophenone from coal and caused regressive reactions of coal.

The solubility of a given coal depends not only on the type of solvent employed but also on extraction temperature, coal rank and maceral composition [24].

It has been found that high extraction yields of around 90 % coal can only be obtained by carrying out extractions within the temperature range of 375 - 475 °C. At lower temperatures, solvents alone can not promote covalent bond cleavage. Above 475 °C, thermal cracking of the extract to gas and insoluble char occurs. All the direct liquefaction processes under development generally operate within this comparatively narrow range of temperatures [7]. The maximum extraction yields are obtained with bituminous coals, lower yields are obtained with sub-bituminous coals and lignites [7].

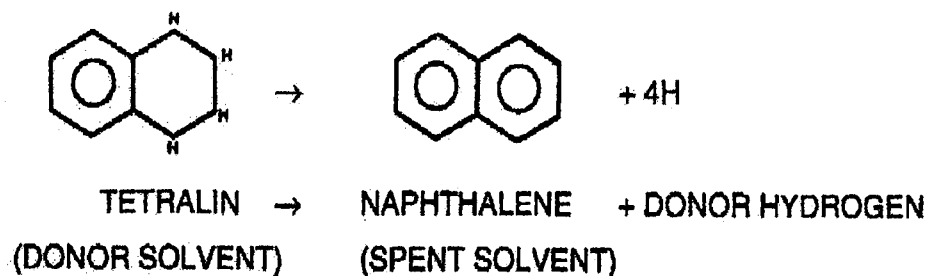
It has been shown that coal reactivity depends on rank: the higher the rank, the lower the hydrogen transfer reactivity [122]. Lower-rank coals are richer in oxygen, have a greater variety of functional groups, and respond more rapidly to heating. However, the rapid thermal decomposition will be followed by retrogressive cross-linking reactions of the primary products unless the availability and transferability of reactive hydrogen are sufficiently high. Thus, the effective control of dissolution requires the attainment of a balance between the process of bond cleavage and hydrogenative stabilisation of the cleaved coal fragments [116].

2.5.3 Reaction mechanisms in liquefaction

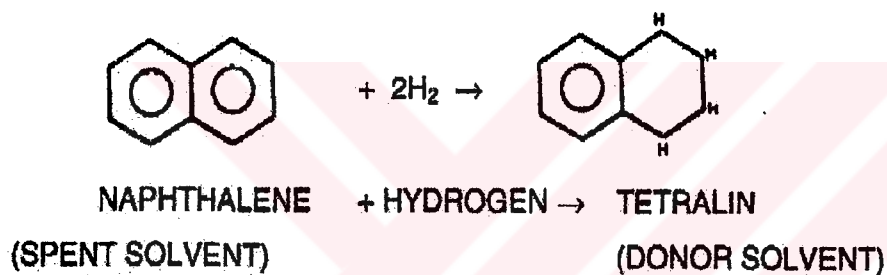
As mentioned before, coal structure has been thought to come apart during pyrolysis upon application of heat [124, Section 2.4]. Free radicals, which occur as a result of bond cleavage during pyrolysis of coal, are very reactive and can undergo secondary reactions [1,125]. Although the details of retrogressive reactions are still obscure, hydrogen donation to coal fragments is known to be a key reaction for the suppression of the retrogressive reactions [126]. Coals are themselves hydrogen atom donors and the need for hydrogen may be satisfied internally. But it may also require diffusion of an external hydrogen donor to the

radical site [127]. In the conventional liquefaction mechanism of weak-bond-scission-radical-capping mode, the hydrogen-donor solvent merely serves to stabilise or scavenge radicals generated in the spontaneous scission of inherently weak linkages in the coal structure by donating hydrogen atoms [15,128,129].

HYDROGEN DONATION



SOLVENT HYDROGENATION



OVER-HYDROGENATION

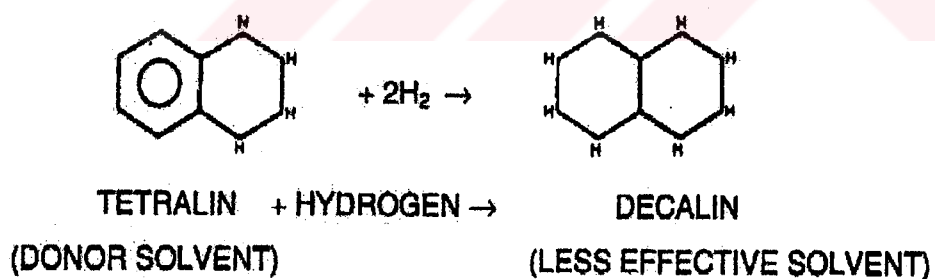


Figure 2.11. Donor solvent reactions [7].

2.5.4 Characterisation of hydrogenation products

The species formed as coal is hydrogenated to produce distillate fuels can be classified by using their solubility in various solvents [7]. The most usual classification is in terms of solubility in benzene or toluene and an aliphatic hydrocarbon (n-pentane, n-hexane, n-heptane or cyclohexane). A decreasing sequence of solvent power is observed in the order pyridine > THF > toluene > cyclohexane > n-pentane [2]. The classification of components is illustrated in Figure 2.12 [7]. Preasphaltenes and asphaltenes are operationally defined as materials derived from coal, which is, respectively, (i) insoluble in toluene and (ii) soluble in benzene or toluene, but insoluble in a low-boiling alkane solvents [2]. Materials soluble in n-hexane are generally referred to as oils and materials insoluble in n-hexane that are soluble in toluene are generally referred to as asphaltenes [7].

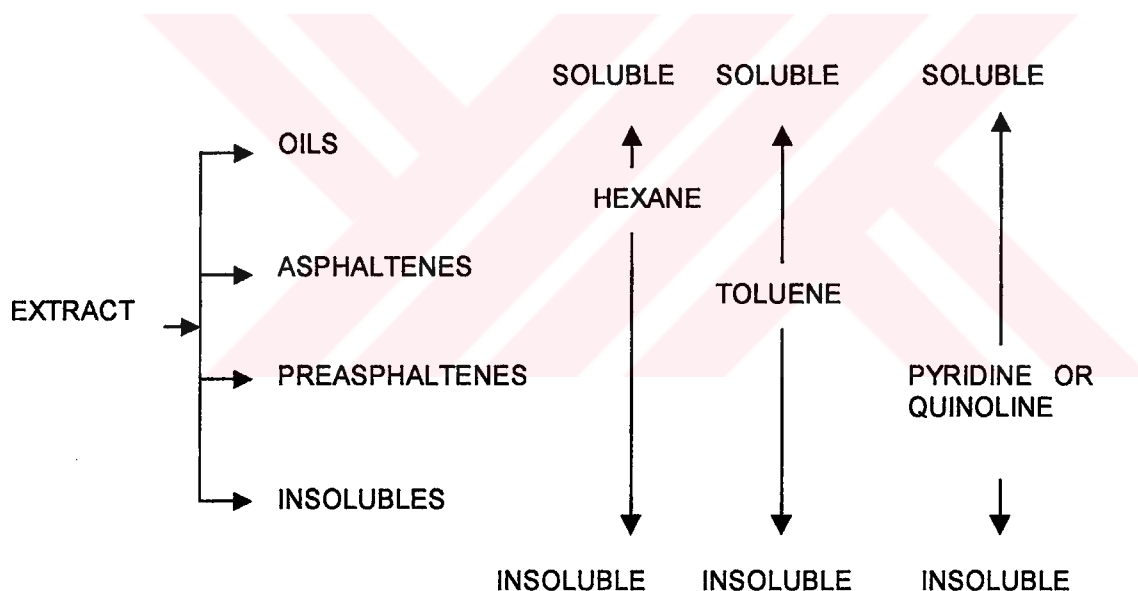


Figure 2.12. Classification of liquefaction products by solubility [7].

The kinetics of extraction and hydrogenation is depicted in Figure 2.13 [7]. The rate of coal conversion and hydrogen transfer is controlled by the rate of thermal decomposition of the coal [9]. The coal breaks down first into preasphaltenes, which in turn break down into asphaltenes and oils. The decomposition of the coal

to form preasphaltenes is a comparatively rapid process and is responsible for the high initial rate at which coal is taken into solution. The decomposition of the high molecular mass preasphaltenes and asphaltenes to form the lower oils is comparatively slow and requires extensive hydrogenation [7,114].

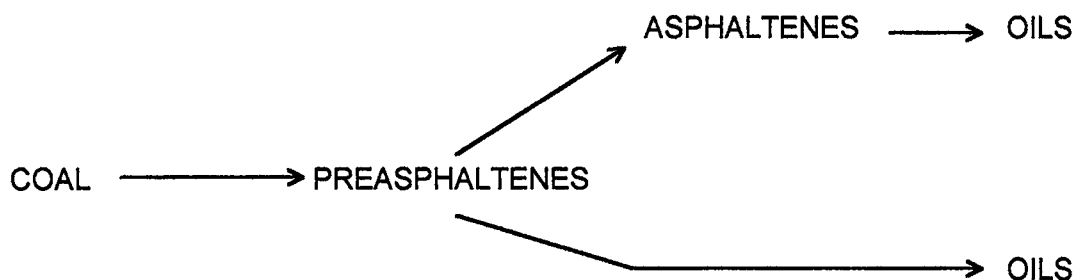


Figure 2.13. Model reaction scheme for coal liquefaction [7].

2.6 Pretreatments for Coal Liquefaction

2.6.1 Physical (type I) pretreatments

The use of physical pretreatments, particularly pre-swelling and pre-extracting coals in both polar and non-polar solvents, to enhance the liquefaction of coal has recently attracted considerable interest. Such pretreatments are proposed to open up the microporous structure in coals, allowing the solvent and hydrogen to penetrate the particles more easily [19,130]. Such pretreatments will be classified into two types. Type I are physical pretreatments, primarily aimed at reducing mass-transfer limitations between the coal and liquefaction media. Type II are chemical pretreatments, designed to affect the liquefaction chemistry [19].

Type I pretreatments include solvent swelling or pre-soaking in the liquefaction solvent, to enhance liquefaction yields. However, the most straightforward type I pretreatment is a reduction in particle size. This subject has been reviewed by Whitehurst et al. [131] who concluded that, while some variations in conversion were observed for different particle sizes, there were no significant mass-transfer limitations in coal liquefaction, especially when good hydrogen-donor solvents were used in well-agitated systems [19].

Type I pretreatments that have been found to result in increased conversions involve soaking coals at 300 °C in suitable solvents prior to liquefaction. In a study made by Pollack et al. [19], it was reported that pre-soaking in the liquefaction solvent resulted in small but consistent increases in conversions in a donor-solvent liquefaction system at temperatures below 425 °C [19]. Also pre-soaking coal/hydrogen-donor solvent slurries at 250 °C has increased conversions and the level of hydrogen transfer at short contact times (SCT<10 min) demonstrating the importance of solvent accessibility [21].

In addition, heat soaking of coal in coal-derived liquids at high temperatures, but below the point where liquefaction is to be carried out, is a method to pretreat coal [37]. Bendale [132] used two high volatile bituminous coals for soaking in three different coal-derived liquids at 350 °C and found that soaking in a coal-derived liquid at 300 to 400 °C provides very effective disintegration of coal molecules.

Miura et. al.[133] made flash pyrolysis of the coal preheated at 150-200 °C in order to examine if the thermal breakage of the hydrogen bond prior to the pyrolysis contributes to increase the total volatile matter. It was found that this method was effective for lower rank coals, which had many non-covalent bonds.

Pretreatments of coal by solvent-swelling and/or extraction may increase conversion and quality of the yield obtained from liquefaction. The magnitudes of the improvements in conversion generally parallel the extent to which the solvent swells the coal [130,134].

Rincon and Cruz [16] found that the conversion of a Colombian coal increased when swollen with tetrahydrofuran. Baldwin and co-workers [135] confirmed the beneficial effect of solvent swelling on coal liquefaction by obtaining better yield quality for the tetrahydrofuran-swollen Illinois No.6 coal [134]. Joseph [15] determined a direct correlation between the extent of preswelling and the conversion of coal under liquefaction conditions [17].

Artok et al. [17] reported that pre-swelling with methanol or pyridine has little effect on liquefaction of the Blind Canyon high volatile bituminous coal, but both tetrahydrofuran and tetrabutylammoniumhydroxide (TBAH) provide increased

conversion, as a result of improved preasphalthene yields [17,134]. In addition, for the Texas lignite, it is reported that conversion of solvent-pretreated samples increased in the order: THF < methanol < pyridine << TBAH. TBAH and pyridine provide the highest oil plus gas yields [134].

It was reported that the preswollen coals with THF improve the THF-soluble materials after liquefaction with tetralin and hydrogen-donor solvents. It has been recognised that tetralin plays an important role in stabilising the coal-derived fragments through hydrogen transfer [16]. In addition, Joseph [15] reported that preswelling of demineralized coal improves product quality during subsequent liquefaction.

Kuznetsov et.al.[136] used Kansk-Achinsk brown coal and studied the liquefaction and swelling in tetralin, methanol and ethanol, and in binary mixtures. Tetralin is found to be the most effective liquefaction solvent, whereas methanol and ethanol are the active ones in coal swelling. Synergistic effects are observed when the mixtures of tetralin and methanol or ethanol are used for liquefaction and swelling. The effect of binary solvents is shown to be due to the ability of alcohol components to cause brown coal to swell, improving the availability of the fragments of coal matter for the reactive hydrogen donor tetralin molecules.

Pyrolysis of coal swollen by tetralin is also an effective method to increase significantly the total volatiles as well as the tar yield [72]. However, this does not affect the pyrolysis yields at temperatures lower than 500 °C [76].

When coal is exposed to a sufficient amount of pyridine, many of the non-covalent bondings in coal are broken even at room temperature [72,89, as described in Section 2.3]. Mae et al. [72] reported that the pyridine in the swollen coal breaks strong non-covalent bonds effectively and then associates strongly with the functional groups such as -COOH and -OH. On pyrolyzing the coal, the pyridine suppresses the decomposition, namely the cross-linking, of the functional groups, which will contribute to suppress the char-forming reactions. This effect is reflected in the decrease in the yield of CO, CO₂ and H₂O and in the increase in the tar yield [72].

As mentioned above, tetralin increased volatile yields when pyrolysis was performed below 485 °C. On the other hand, pyridine swelling suppressed cross-linking reactions by 400 °C, leading to an increase in both the total volatiles and the tar yield. Because of this, Mae et al. [72] tried flash pyrolysis combining the two treatments in both solvents and it was found that the total volatiles and the tar yield were improved. These increases were brought about by more effective hydrogen transfer from tetralin to the coal fragments.

Pre-swelling of bituminous and lower rank coals with a suitable solvent, followed by removal of the swelling agent, can significantly enhance conversion and product quality during subsequent liquefaction. In addition, thermal pretreatment at a range of temperatures lower than those needed for pyrolytic reactions can significantly affect the penetrability and swellability of coals. This suggests that judicious use of effective swelling solvents for coal at appropriate temperatures, can affect mass transport of reagents or catalysts into or out of the coal matrix [137].

The enhancement depends up on both coal rank and the swelling agent [18]. One explanation for the improved conversions is that solvent swelling or extraction imparts increased flexibility or molecular mobility, to the insoluble coal matrix and facilitates favourable chemistry occurring during liquefaction [130,136].

The beneficial effect of swelling may be due to the expansion of the coal macromolecular structure, making it more accessible to hydrogen donor solvent [18,130]. This contact is important during the initial stages of liquefaction, when intramolecular bond cleavage and the formation of coal-derived free radicals are prevalent. Effective capping of these free radicals by hydrogen is necessary to reduce the possibility of retrogressive reactions that may lead to undesirable products. Coal swelling can enhance catalyst distribution and so improve hydrogen transfer from the donor solvent or hydrogen gas to the reaction sites [15,18,57,138].

2.6.2 Chemical (type II) pretreatments

Beneficial type II pretreatments used for coal liquefaction include alkylation and hydrothermal processing. Mild alkylation in which only relatively small proportions of OH groups are derivatised was shown to be a beneficial pretreatment for a sub-

bituminous coal. A recent example of an alkylation pretreatment is the work by Baldwin et.al. [135]. Baldwin and co-workers [135] improved conversion of low-rank coals by minimising organic oxygen coupling sites which initiate retrogressive reactions [139].

In hydrothermal pretreatments, coal and water are heated together and then separated. It was reported [19] that improvements in pyrolysis conversions were obtained after steam and hot water pretreatments. Minkova et. al. [140], and Rubel and Coburn [141] have found that the use of steam as a sweep gas gives rise to marked increases in oil yield for coals and oil shales, respectively [107]. For instance, steam enhanced conversion in fixed-bed pyrolysis of Goynuk oil shale [107]. The increase in yields due to these pretreatments is probably due to chemical changes in the coal structure. It was reported [19] that the pretreatment disrupts chemical associates between the organic and mineral phases of the coal causing the release of organic matter.

2.6.3 Adverse factors affecting coal liquefaction

Both water and exchangeable cations in coal, can have an adverse effect on liquefaction [142,143].

Sub-bituminous coals and lignites, commonly known as low-rank coals contain substantially more organic oxygen than bituminous coals [143,144]. Further, a significant part of the organic oxygen is present as carboxylic acid groups to which cations of alkali and alkaline earth metals can be associated [143,145]. The concentration of these groups decreases sharply with increasing coal rank [143,145].

The alkali and alkaline earth metal cations profoundly influence the properties and utilisation of chars and low-rank coals. For example, these cations increase the coal moisture sorption capacity [143,146,147]. In addition, exchangeable alkali and alkaline earth metal cations, such as Na^+ , K^+ , and Ca^{2+} , have been found to reduce conversion and product quality during liquefaction. The adverse effect, which increases in the order $\text{Na}^+ < \text{K}^+ \ll \text{Ca}^{2+}$, is probably due to these cations inhibiting hydrogen transfer from the donor solvent or H_2 gas to the free radical sites

[143,146]. For example, in brown coal, Ca forms ionic cross-links between -COOH groups. Removing the Ca prior to liquefaction has brought about increases in liquefaction yields [133]. In order to reduce the deleterious effect of metal cations on the liquefaction of low rank coals, it is beneficial to swell the coals in organic solvents prior to liquefaction [143].

Tyler et.al.[148] investigated the influence of cations on the pyrolysis behaviour of low-rank coals. It is reported [148] that removal of cations present in the coals by acid washing markedly increased the yields of both tar and volatile matter. The converse was also observed in that the addition of Ca^{+2} ions to an acid-form coal reduced the yields. The reversibility of the phenomena shows that the increase in yields on cation removal is not the result of any permanent chemical modification or degradation of the organic structure of the coal during the acid treatment [103,148]. Three explanations for the influence of cations are suggested [148]. Firstly, the presence of cations in the coal micropore system may impede the diffusion of large tar molecules to the surface of the coal particle, thus reducing the quantity of tar volatilised. Secondly, the cations may catalyse the polymerisation or condensation of tar molecules before volatilisation can occur. Thirdly, the formation of carboxylates possibly increases the stability of the surface groups which in turn slows the release of organic fragments from the coal structure.

The demineralisation of coal has been reported to have a favourable effect towards tar production during the pyrolysis. Solomon [103] explains this tendency as a consequence of the reduction of the degree of cross-linking of the coal structure [149]. The role of exchangeable cations in cross-linking reactions was demonstrated by removing these ions from Zap lignite by demineralisation. Demineralized lignite shows a lower rate and extent of cross-linking and higher tar yield due to the reduced mineral content [103].

Mochida [150] reported that hydrochloric acid can be used to remove bivalent cations from low rank coals, thereby reducing co-ordination between oxygen-containing functional groups and allowing better contact between coal and solvent during the initial stages of dissolution. Joseph [143] used ion exchange techniques to remove the various cations (calcium, magnesium, sodium, and potassium) from Wyodak subbituminous coal and North Dakota lignite and reported that their

removal from each low-rank coal improved conversion and product quality under relatively severe conditions. This result was attributed to hydrogen transfer being inhibited by the presence of alkali and alkaline earth cations [151]. The benefit of removing cations with acidic pretreatment to increase coal conversion at low-severity conditions using hydrogen donors was demonstrated by Beasley et.al. [139]. Acidic pretreatment removed Ca and Mg, and improved coal conversion of all three coals, Wyodak and Black Thunder mine sub-bituminous, and North Dakota Belulah-Zap lignite [139].

Serio [142] also found that ion-exchanged and demineralized low-rank coals were more reactive at high reaction severity because of reduced cross-linking occurring the treated coals during the initial stages of dissolution [152]. Franklin et. al. [153] reported that demineralizing a Wyodak lignite prior to pyrolysis brought about an increase in the total volatiles [137,153].

2.6.4 Effect of water content and drying on liquefaction yields

As described earlier, the physical structure of coal consists of an organic matrix and inorganic matter containing an extensive network of pores, which usually contain water in appreciable quantities [147]. Vorres et. al. [147] reported that there are two types of water. A more readily released form, such as that found in the central part of larger water-filled pores, would be lost initially. Another type held at functional groups or active sites on the surface would be released more slowly [147].

In order to improve the economics of coal liquefaction, drying especially for the lower rank coals is necessary [147,154,155].

There are a number of theoretical advantages to drying coal prior to liquefaction. Because conversion and kinetics are heavily dependent upon the partial pressure of hydrogen in the liquefaction reactor, the removal of moisture in the coal allows the partial pressure of hydrogen to be increased without increasing the operating pressure. In addition, removal of most of the water from the coal prior to liquefaction reduces the cost of both separating water from the coal liquids after liquefaction and

subsequent waste water treatment. Finally, moisture in the coal reduces the throughput of coal on a dry basis for reactors with fixed capacities [155].

However, there is considerable evidence to show that some methods of drying have a detrimental effect on the liquefaction behaviour of coals [155,156]. It was reported that drying a subbituminous coal did not affect the total conversion, except in air. This gave a somewhat lower conversion, which may be a result of preoxidation. Indeed, the highest conversion was obtained by vacuum drying [157].

The most common method of coal drying is to heat the coal in air to some elevated temperature to drive off the moisture. Even a simple process such as this can cause changes in coals, particularly low-rank coals. For example, subbituminous coals contract and crack on drying. Furthermore, only about 60 % of the moisture removed can be reversibly replaced. This is attributed to the collapse in the gel structure of the low-rank coals [147,155]. This behaviour might also be observed if the open pores which provide the escape path of the water molecules become partly blocked due to collapse of the gel structure containing moisture or some of the pores themselves. The gel structure debris may partly block the pores, restricting outward diffusion and reducing the rates [147]. On the other hand, it has been found that dried Illinois bituminous coal can re-absorb about the same amount of water as it loses in drying. However, some coals dried at room temperature reabsorb more water than when they are dried at a higher temperature [155]. This suggests that low temperature drying does not significantly alter the physical structure of bituminous coals. However, because water is an integral part of the gel structure of low-rank coals, drying might alter the physical structure of these coals [155,158].

Thermal drying can cause changes in the chemical structure of the coal, which in turn can affect the liquefaction properties. Low-rank coals show a strong tendency to form cross-links even at relatively low temperatures because of the high concentrations of labile oxygen functionalities such as carboxyl, hydroxyl, and methoxyl [155].

3. EXPERIMENTAL

3.1 Coal Samples

Coal samples used for this study were Can and Tuncbilek lignites, and Zonguldak bituminous coal. Also Goynuk (B) oil shale samples were used. Can and Tuncbilek lignites and oil shale samples were collected from the mines, and Zonguldak coal samples were provided by Turkish Coal Establishment (TKI). The coals and oil shale samples were all crushed and sieved to $-150\ \mu$ - $+90\ \mu$ particle size.

In addition, two bituminous coals Pittsburgh No.8 and Point of Ayr were used. These samples were obtained from Argonne and Coal Research Establishment (CRE) Coal Sample Banks, and were sieved to $-100\ \mu$ and $-212\ \mu$, respectively.

The proximate and ultimate analysis of the coals and oil shale investigated are listed in Table 3.1.

3.2 Solvent Treatments

The coals were treated using three non-polar and two polar solvents, namely chlorobenzene, toluene, chloroform, and tetrahydrofuran and methanol, which have boiling points of 132, 111, 62 and 65 and 66 °C, respectively.

For each coal, 10 g. of sample, dried in vacuo at 50 °C, was treated in a Soxhlet apparatus with either chlorobenzene, tetrahydrofuran or methanol and for some cases also with either toluene or chloroform until the solvent draining from the coal was clear (minimum 72 hours). It had been established that replacing nitrogen with air during the pre-treatment again had no discernible effect on the tetralin extraction conversions [22]. The extracted coals were then dried in vacuo at 50 °C for up to

one week to ensure that the residual solvent content was below 1 % w/w. The untreated coals were dried in the same way prior to the thermolysis and liquefaction experiments.

Table 3.1. Proximate and ultimate analysis of the coals and oil shale used.

	Can	Tuncbilek	Karadon	Kurtserif	Pittsburgh No.8	Point of Ayr	Goynuk (B) Oil Shale
Proximate analysis							
Moisture(%a.d.)	12.74	9.39	1.18	1.02	1.7	2.4	9.45
Ash (% d.b.)	9.95	18.77	10.22	9.60	9.3	10.0	24.58
V.M. (% daf)	40.47	37.49	26.83	28.94	37.8	31.1	74.45
F.C. (% daf)	59.53	62.51	73.17	71.06	62.2	68.9	25.55
Ultimate analysis (% daf)							
C	68.77	75.70	88.46	88.59	84.90	74.24	75.97
H	6.20	5.97	4.76	4.90	5.98	4.90	9.40
N	1.86	2.80	1.19	0.93	1.64	1.57	1.10
O ^(a)	16.86	13.72	5.59	5.58	5.01	17.35	7.38
Total S	6.31	1.81	Trace or nil	Trace or nil	2.47	1.94	6.15

a.d. - as analysed

d.b. - dry basis

daf - dry ash free basis

(a) – by difference

3.3 Experimental Procedures

The following experiments were conducted, mainly at 400 °C on the untreated, chlorobenzene, tetrahydrofuran, and methanol-treated samples. In addition, for some coals, toluene and chloroform-treated samples were used as well.

1. Thermolysis (solvent-free) under autogeneous pressure, the residence time being 60 minutes.
2. Hydrogen-donor solvent extraction experiments with tetralin, were carried out using two different residence time. These were:
 - Short contact time (SCT) tetralin extraction, applied to the untreated and treated coals using 2 g. tetralin (at 400°C) with a contact time of 15 minutes;

- Tetralin extraction, applied to the untreated and chlorobenzene-treated coals using 2 g. tetralin (at 400°C) with a contact time of 60 minutes.

For the thermolysis experiments and tetralin extractions, 1 g. of coal and, for the latter, 2 g. of tetralin were loaded into a microreactor which was submerged in a fluidised sandbath at 400 °C for the desired residence time and was agitated using a flask shaker.

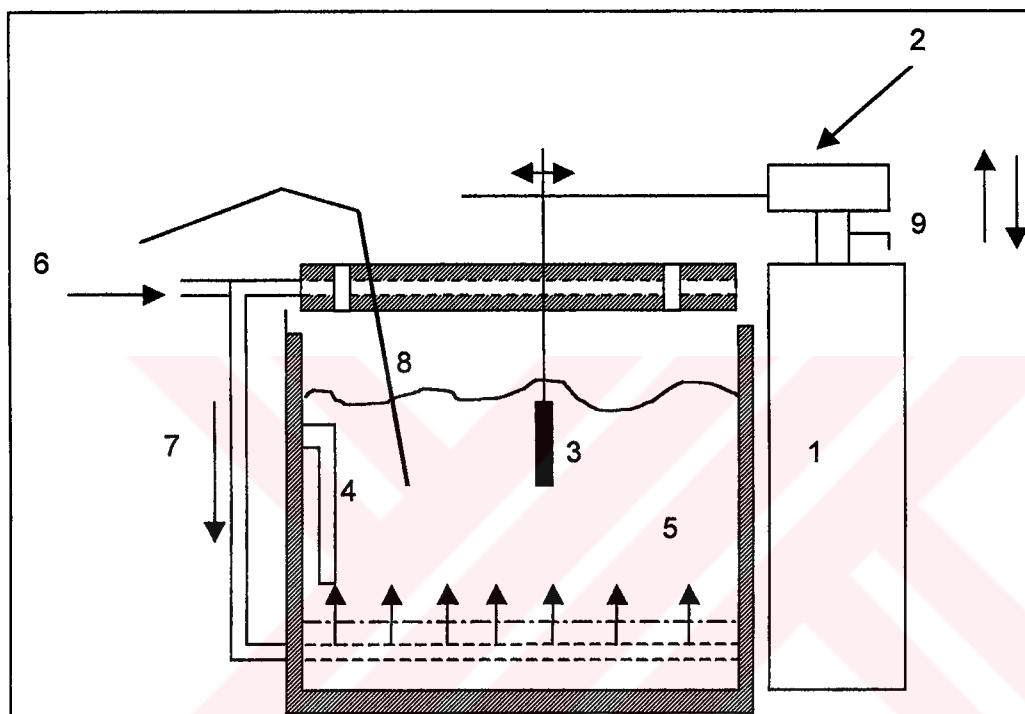
The heat-up period for the thin-walled 12.7 mm o.d. microreactors had previously been shown to be less than 2 minutes [22]. After extraction, the reactor contents were recovered by filling the microreactor with dichloromethane (DCM) and placing it in an ultrasonic bath. The DCM washings were refluxed for 5 hours, filtered through phase separating paper and then the DCM-solubles were recovered by evaporating the filtrate to dryness. The DCM-insolubles were weighed after drying in vacuo at 50 °C and were then refluxed in pyridine for 5 hours and filtered to determine the yield of pyridine-insolubles. However, before drying, the pyridine-insolubles were washed with DCM in order to reduce the residual pyridine to a level at which it could be removed by vacuum drying at 100 °C. The amounts of hydrogen donated to the coals during the tetralin extractions were calculated from the mass ratios of tetralin to naphthalene in the recovered DCM solutions determined by capillary gas chromatography.

For this study, two different fluidised sandbaths were used. Figures 3.1 and 3.2 give schematic representations of the sandbaths used at Istanbul Technical and Strathclyde Universities, respectively. The microreactor used for each sandbath was same. The stainless steel microreactor's length was 175 mm with an internal diameter of 10 mm. The length of the rod , which is connected to the top part of the reactor and used to plunge the reactor into the sandbath was 380 mm long. Top and bottom part of the reactor were screw fitted.

As can be seen from Figure 3.1, firstly compressed air enters the cover of the system, and leaves the cover making a U circulation. Secondly, the heated air goes down to the sandbath, and leaves the system making sand fluidised. When the fluidised bed temperature reaches the required value, the microreactor is

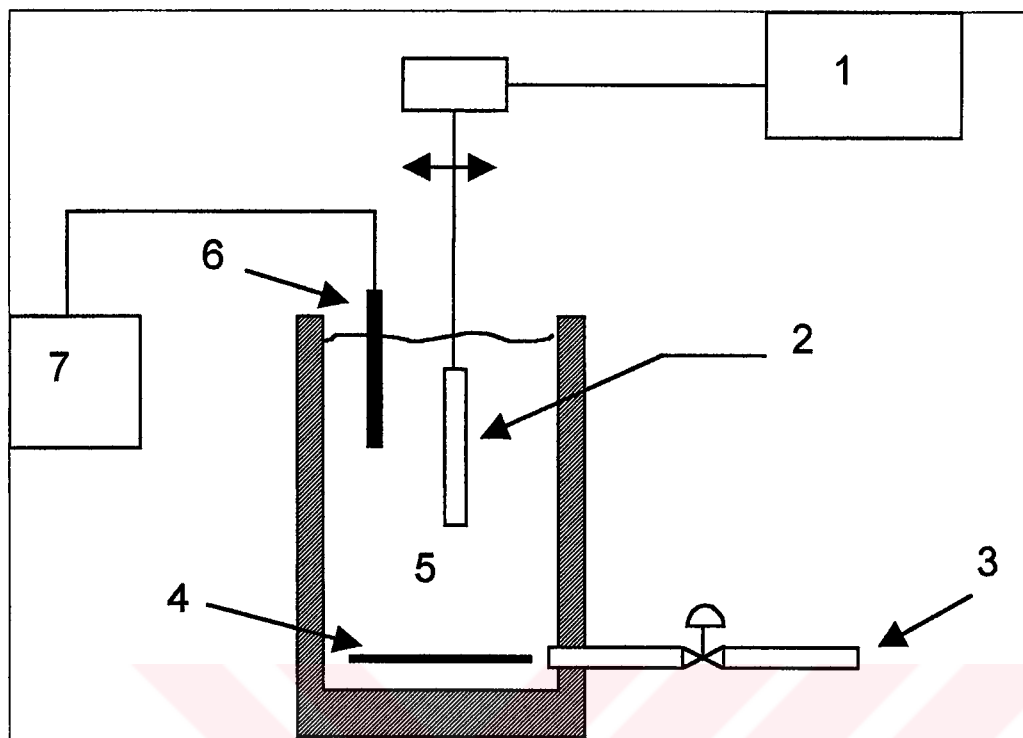
submerged into the sand. The microreactor is vibrated slowly with the help of a shaking mechanism. During the reaction time, temperature is kept at a constant value by the controller.

In Figure 3.2, the compressed air passes through the heating elements, and then makes the sand fluidised. For both of the systems compressed air mixes the sand so that the temperature will be uniform inside the sandbath.



1. Control Panel
2. Shaking mechanism
3. Microreactor
4. Heating coil
5. Sand bed
6. Compressed air entrance
7. Circulation of warm air
8. Thermocouple
9. Handle (to pull up and down the reactor)

Figure 3.1. Schematic diagram of fluidised sandbath system at ITU.



1. Flask shaker
2. Microreactor
3. Compressed air
4. Heating elements
5. Sand
6. Thermocouple
7. Temperature controller

Figure 3.2. Schematic diagram of fluidised sandbath at Strathclyde University.

3.4 Characterisation

As mentioned earlier, capillary gas chromatography was used to determine the ratio of tetralin to naphthalene in the DCM-solubles recovered from the tetralin extractions. In order to find out the effects of pretreatments on coal structure Thermal Gravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and swelling experiments were carried out.

3.4.1 Chromatographic separation

The International Union of Pure and Applied Chemistry (IUPAC) defines chromatography as a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary while the other moves in a definite direction [159]. Chromatography is based upon the general principles of phase distribution. The method involves the selective removal of the components of one phase from that phase as it is flowing past (or through) a second stationary phase. The removal of a component by the stationary phase is an equilibrium process, and the molecules of that component re-enter the mobile phase. Separation of two or more components in the mobile phase will result when the equilibrium constants for the distribution of these components between the two phases differ [159,160].

Chromatographic analysis for volatile compounds is usually carried out by capillary column gas chromatography [2].

3.4.1.1 Gas chromatography

In gas chromatography (GC), the mixture to be separated is vaporised and carried along a column by a flowing inert gas, such as nitrogen or helium (the carrier gas). The gaseous mixture is the mobile phase [160]. The stationary phase is held as a thin coating on the surface of an adsorbent solid, called the support, and is contained inside a column [12].

The differences in physical and chemical properties of the individual components determine their relative affinity for the stationary and mobile phase. Therefore, components will migrate through the system at differing rates depending on their retardation resulting from attraction onto the stationary phase. The least retarded component, having an equilibrium ratio which least favours the stationary phase, will be eluted first, i.e. moves fastest through the system. The most retarded component moves the slowest and is eluted last [159]. Due to selective phase distribution of the

components of the mixture between the mobile and stationary phases, these components may move through the column at different rates and thus be separated [160].

The sample to be separated is introduced by means of a syringe into the flow system at the injection port, which is individually heated to facilitate vaporisation of the sample. The vaporised sample is then swept into the column by the carrier gas. As the sample passes through the column, its components separate into individual bands in the carrier gas which then pass through the detector. The detector produces an electronic signal whose voltage is proportional to the amount of material different from the carrier gas itself present in the gas stream. The recorder plots this voltage as a function of time to give the gas chromatogram [160].

The elapsed time necessary for a given component to pass from the injection port to the detector is known as its retention time. Four important experimental factors affect the retention time of a compound: (i) the nature of the stationary liquid phase; (ii) length of the column; (iii) the temperature at which the column is maintained; and (iv) the rate of flow of inert gas. The retention time is independent of the presence (or absence) of other components in the mixture. For any given column and set of conditions (temperature and flow rate), the retention time is a property of the compound [160].

3.4.1.2 Gas chromatographic analysis

In order to calculate the amounts of hydrogen transferred from tetralin to the coals during extraction, the tetralin to naphthalene ratio of the recovered product was used. For this purpose, the oils obtained by precipitating asphaltenes from the DCM-solubles using n-hexane were analysed by GC.

The oils were subjected to capillary GC analysis with FID detection using a 25m x 0.25mm i.d. capillary column coated with BPSILI-POLY (DIMETHYLSILOXANE). 0.5 µl sample was injected on-column into a Carlo Erba Strumentazione 4130 GC

operating under a temperature program of 50 °C (1 min) to 120 °C (2 min) at a ramp rate of 5 °C/min. The carrier gas was helium. Detector and injector temperatures were 300 °C.

3.4.2 Solvent swelling

As described in Section 2.3, the swelling of coal in solvents is an often-used technique in order to investigate its structure, and the changes in its structure [51]. These measurements can be carried out using volumetric and gravimetric measurements. Volumetric swelling is based on packed particle beds whereas the other one using solvent sorption from the vapour phase [51,60,161].

In volumetric swelling, ground coal is placed in a glass tube, centrifuged to pack the particles, and the height of the resulting coal column is measured. Excess solvent is added and shaken, and the coal is allowed to swell. The tube is centrifuged again and the height of the coal column is remeasured. Once constant height has been reached, the system has reached equilibrium swelling. The swelling ratio is taken as the ratio of the swollen height to the dry height [48,60,161,162]. The extent of volumetric swelling is proportional to the increase in height of the column of coal [58].

In a gravimetric swelling experiment, the coal is exposed to solvent vapours and its increase in mass is recorded. The mass increase is due to sorption of solvent by the coal. Part of this sorption is due to the solvent dissolving in the solid coal and swelling it, but part is due to the condensation of the solvent in the coal pores. Thus, the weight increase is larger than that due to solvent swelling. Because of that correction is needed for pore filling. The other factor, the presence of extractable material must be removed from the coal. If it is not removed, it will dissolve in the swelling solvent, which condenses in the pores. This will lower the vapour pressure of that solvent, and more fresh solvent will condense to dilute the solution. As a result, very long times are required to reach apparent equilibrium swelling (constant weight) and the observed weight increase is greater than that

actually due to solvent swelling of the coal [60,161]. Because of that, the vapour sorption techniques require pre-extraction of the coal and corrections for pore filling [58].

Although it has been shown [51,60] that the two techniques are equivalent, volumetric method is being preferred. Because it has two distinct advantages over the gravimetric technique: first, the volumetric technique is much more rapid; second, it is insensitive to solvent that fills pores and, hence, no correction is required to obtain the 'true' swelling ratio [51,58,60].

3.4.2.1 Solvent swelling measurements

Solvent swelling measurements [48,60,67,162] were conducted on the untreated, chlorobenzene, methanol, tetrahydrofuran, toluene and chloroform treated samples using pyridine, methanol, tetrahydrofuran and tetralin as swelling solvents.

The coal samples were placed in test tubes, which are 6 mm in diameter and 75 mm in height. The tubes were shaken to ensure good packing and the height of the coal column which was about 10 mm, was measured using a micrometer. Excess solvent was then added, the tubes were stoppered and shaken each day until equilibrium was established, that is the height of the coal in solvent did not rise any further. The equilibrium times were 10 to 15 days at room temperature.

The swelling ratio was measured as the height of the swollen coal (H_F) divided by the height of the untreated coal (H_I), i.e. H_F / H_I .

3.4.3 Thermal analysis

Specific physical properties of a material is measured as a function of temperature in thermal analysis. Thermal analysis is useful in both quantitative and qualitative analysis. Samples may be identified and characterised by qualitative investigations of their thermal behaviour. Quantitative results are obtained from changes in weight and enthalpy as the sample is heated [163].

In a thermal analysis system, the sample is heated at a programmed rate in the controlled environment of the furnace. Changes in selected properties of a sample

are monitored by specific transducers, which generate voltage signals. The signal is then amplified, digitised, and stored on a magnetic disc along with the corresponding direct temperature responses from the sample. The data may also be displayed or plotted in real time [163].

3.4.3.1 Thermogravimetric analysis

Thermogravimetry (TG) or thermogravimetric analysis (TGA) provides a quantitative measurement of any weight changes associated with thermally induced transitions [2,163]. For example, TG can record directly the loss in weight as a function of temperature or time (when operating under isothermal conditions) for transitions that involve dehydration or decomposition. Thermogravimetric curves are characteristic of a given compound or material due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges. The rates of these thermally induced processes are often a function of the molecular structure. Changes in weight result from physical and chemical bonds forming and breaking at elevated temperatures. These processes may evolve volatile products or form reaction products that result in a change in weight of the sample [163].

TG data are useful in characterising materials as well as in investigating the thermodynamics and kinetics of the reactions and transitions that result from the application of heat to these materials. The usual temperature range for TG is from ambient to 1200 °C in either inert or reactive atmospheres [163].

In TG, the weight of the sample is continuously recorded as the temperature is increased. Samples are placed in a crucible or shallow dish that is positioned in a furnace on a quartz beam attached to an automatic recording balance. The quartz beam is maintained in the null position by the current flowing through the transducer coil of an electromagnetic balance. A pair of photosensitive diodes acts as a position sensor to determine the movement of the beam. Any change in the weight of the sample causes a deflection of the beam, which is sensed by one of the photodiodes. The beam is then restored to the original null position by a feedback

current sent from the photodiodes to the coil of the balance. The current is proportional to the change in weight of the sample. Sample size range from 1 to 300 mg [163].

Thermal analysis is affected by the experimental conditions. Deviations caused by instrumental factors include furnace atmosphere, size and shape of the furnace and sample holder, sample holder material and its resistance to corrosive attack, wire and bead size of the thermocouple junction, heating rate, speed and response of the recording equipment, and location of the thermocouples in the sample and reference chambers. Another set of factors that influence the results depends on the sample characteristics; these include layer thickness, particle size, packing density, amount of sample, thermal conductivity of the sample material, heat capacity, the ease with which gaseous effluents can escape, and the atmosphere surrounding the sample [163].

3.4.3.2 TGA measurements

In order to obtain information on the decomposition of the untreated and treated coal and oil shale samples as a function of temperature, thermogravimetric analyses was performed on 10-30 mg of samples. A four step heating procedure is used, which is, i) heating from 25 °C to 110 °C at a rate of 50 °C/min, ii) hold for 30 minutes at 110 °C, iii) heating from 110 °C to 850 °C at a rate of 50 °C/min, iv) hold for 40 minutes at 850 °C.

For this analysis, a Shimadzu-TGA 50 Analysis equipment is used.

3.4.4 Scanning electron microscopy

Electron microscopical examination of carbons present excellent opportunities for structural study and problems in specimen preparation and interpretation of the images produced [164].

Scanning Electron Microscopy (SEM) is established as a means of characterisation of surface topography, mainly because of the large depth of focus available and the high magnifications currently possible (up to X 200 000) [164,165].

SEM uses the scattering of electrons from the surface of the sample to reveal the topography of material. It also utilises the scattering power of different materials to distinguish them [164].

SEM is an excellent method for monitoring the changes in topography following various treatments, such as heat treatment, solvent treatment etc [164].

Specimens of carbons are mounted on suitable stubs. The surfaces of the carbon are usually coated with gold. Gold coating the specimens gives a much better resolution of the topographical features [164].

3.4.4.1 Scanning electron microscopy analysis

Specimens were coated with gold for SEM photographs. They were then polished according to standard procedures using silver. Micrographs were acquired using a Jeal-JSM-T330 scanning electron microscope.



4. CONVERSION TRENDS

4.1 Liquefaction and Thermolysis Experiments: General Aspects

As mentioned in Section 3.3, the hydrogen-donor solvent liquefaction experiments without a hydrogen over-pressure were conducted using tetralin as solvent with solvent to coal mass ratios of 2:1 for periods of 15-60 minutes at 400 °C. Thermolysis experiments have been carried out at 400 °C for 60 minutes.

4.1.1 Conversion calculations and precision

For these experiments, mass balances were calculated on % dry ash free coal basis as follows.

$$\text{weight of coal sample} = A \text{ grams} \quad (4.1a)$$

$$\text{weight of ash} = B \text{ grams (from \% ash} \cdot A) \quad (4.1b)$$

$$\text{weight of dry ash free (daf) coal} = C \text{ grams (A - B)} \quad (4.1c)$$

4.1.1.1 Dichloromethane conversion

$$\text{weight of DCM-solubles} = D \text{ grams} \quad (4.2a)$$

$$\text{weight of DCM-insolubles} = E \text{ grams} \quad (4.2b)$$

$$\% \text{ DCM-insolubles} = [(E-B) / C] \cdot 100 \quad (4.3)$$

$$\text{Total DCM conversion} = 100 - \text{DCM-insolubles}^* \quad (4.4)$$

*DCM-insolubles include DCM-soluble liquid product, water and gas.

4.1.1.2 Pyridine conversion

$$\text{weight of DCM-insolubles used for pyridine reflux} = F \text{ grams} \quad (4.5a)$$

$$\text{weight of pyridine-insoluble} = G \text{ grams} \quad (4.5b)$$

$$\text{The \% DCM-insolubles used} = (F / E) * 100 = \% H \quad (4.5c)$$

$$\text{work up} = (100 * G) / (\% H) = J \text{ grams} \quad (4.6)$$

$$\% \text{ pyridine-insolubles} = [(J - B) / C] * 100 \quad (4.7)$$

$$\% \text{ pyridine-solubles/DCM-insolubles} = 100 - \% \text{ DCM-solubles} - \% \text{ pyridine-insolubles} \quad (4.8)$$

4.1.2 Repeatability of liquefaction and thermolysis experiments

Liquefaction and thermolysis experiments were carried out in single, duplicate and, in some cases triplicate runs. Tables 4.1 and 4.2 present the results obtained from triplicate thermolysis and tetralin extraction of Goynuk (B) oil shale and Karadon, respectively.

Table 4.1. Yields from triplicate thermolysis experiments on Goynuk (B) oil shale (at 400 °C).

% daf oil shale		
DCM-conv.*	Pyr-sols./ DCM-insols.	Pyr-insols.
60	15	25
65	15	20
59	8	33

* - includes DCM-soluble liquid product + water + gas

Table 4.2. Yields from triplicate tetralin extraction experiments on untreated Karadon (at 400 °C).

% daf coal		
DCM-conv.*	Pyr-sols./ DCM-insols.	Pyr-insols.
16	29	55
13	30	57
14	25	61

* - includes DCM-soluble liquid product + water + gas

As Tables 4.1 and 4.2 indicate, DCM-conversion differ by 1-6 % whereas DCM-insolubles and pyridine-insolubles differ by 1-7 % and 2-13 % in these triplicate experiments. Although pyridine-insolubles were dried at 100 °C in vacuo to take away the pyridine totally, the repeatability is not as good as other solvents.

These two examples indicate that the repeatability of the product work-up procedure (DCM-conversion) is in the range $\pm 2-3$ % daf coal for tetralin extractions whereas ± 5 % daf coal for thermolysis experiments.

4.1.3 Calculation of % hydrogen donated in tetralin extractions

This was calculated on dry ash free coal since the molecular masses of tetralin and naphthalene are 132 and 128, respectively, for every mole of tetralin dehydrogenated, 4 g hydrogen is transferred to coal.

When X gram of tetralin is used, this is equivalent to:

$$Y = (X / 132) \text{ moles} \quad (4.9)$$

Therefore, the weight of hydrogen available for transfer is:

$$Z = Y * 4 \quad (4.10)$$

From the traces obtained from GC analysis, using the % area of tetralin and naphthalene gives:

$$A = [(\% \text{ area naphthalene}) / (\% \text{ area tetralin} + \% \text{ area naphthalene})] * 100 \quad (4.11)$$

Therefore, weight of hydrogen transferred,

$$B = A * Z \quad (4.12)$$

On a % daf coal basis, % hydrogen transferred,

$$\% C = (B / \text{weight of daf coal}) * 100 \quad (4.13)$$

For instance, from triplicate experiments of chlorobenzene-treated Goynuk (B) oil shale, hydrogen transfer amounts were found as 1.82, 1.83 and 1.85, and the mean was 1.83. The repeatability of % hydrogen transfer amount in tetralin extraction experiments is found to be around ± 0.01 - 0.02 %.

4.2 Conversions for Thermolysis and Short Contact Time Tetralin Liquefaction Experiments

4.2.1 General trends

The results for the short contact time tetralin liquefaction and thermolysis tests on the untreated and chlorobenzene-treated Pittsburgh No.8, Point of Ayr, Karadon, Kurtserif, Tuncbilek and Can, and for Goynuk oil shale are listed in Tables 4.3 to 4.8. In addition, the results of toluene and chloroform treated Pittsburgh No.8, Point of Ayr and Can samples are also given in Tables 4.3, 4.4 and 4.7.

The thermolysis and short contact time tetralin liquefaction results of untreated, chlorobenzene, toluene and chloroform treated Pittsburgh No.8 and Point of Ayr samples are also given in Tables 4.3 and 4.4 in order to make a comparison with an earlier study [23]. The Tables also include the thermolysis results for untreated and chlorobenzene-treated Pittsburgh No.8 and Point of Ayr samples obtained by McArthur [22].

Further, for this study some of the experiments have been repeated with Pittsburgh No.8, Point of Ayr, Can and with Goynuk (B) oil shale both at Istanbul Technical and Strathclyde University laboratories in order to check if the experimental conditions are same with the earlier studies [22,23], and also to see if two different experimental set ups have any effect on the results.

In the earlier study [23], it was noted that for chlorobenzene-treated Pittsburgh No.8, the yields of both pyridine and DCM-soluble products (extract plus gas plus water) were lower than those obtained initially, McArthur [22]. However, when the reaction temperature in the sandbath was checked, it was found to be 385 °C as opposed to 400 °C previously. Because of that, tests with tetralin were conducted on the untreated and chlorobenzene-treated samples of Pittsburgh No.8 at 400 °C. Point of Ayr thermolysis and short contact time tetralin extractions also were conducted at 385 and 400 °C, respectively.

In this study, the thermolysis and short contact time tetralin extraction experiments were both conducted at 400 °C at Strathclyde University. However, during the experiment at Technical University, it was noted that the change in temperature during 15 and 60 minutes experiments was between 392-408 °C, which had an adverse effect on the results.



Table 4.3. Effect of non-polar solvent treatment on the conversion of Pittsburgh No.8.

Treatment	% daf coal		
	DCM-conv.*	Pyr-sols./ DCM-insols.	Pyr-insols.
<u>Thermolysis</u>			
<u>Set up(1).(at 385 °C)</u>			
Untreated ^(b)	9 (11) ^a	33	58
Chlorobenzene ^(a)	(22) ^a		
Toluene ^(b)	18	19	65
Chloroform ^(b)	17	15	68
<u>SCT Liquefaction (Tetralin)</u>			
<u>Set up(1).(at 385 °C)</u>			
Untreated ^(b)	16	52	32
Chlorobenzene ^(b)	24	57	19
Toluene ^(b)	33	50	18
Chloroform ^(b)	32	41	27
<u>Set up(1).(at 400 °C)</u>			
Untreated ^(b)	30	60	10
Chlorobenzene ^(b)	49	42	9
<u>Set up(1).(at 400 °C)</u>			
Untreated	32	47	21
Chlorobenzene	46	36	18
	47	30	23

* - includes DCM-soluble liquid product + water + gas

Set up(1): Experiments have been conducted using the system at Figure 3.2.

Set up(2): Experiments have been conducted using the system at Figure 3.1.

(a) : [22].

(b) : [23].

Table 4.4. Effect of non-polar solvent treatment on the conversion of Point of Ayr.

Treatment	% daf coal		
	DCM-conv.*	Pyr-sols./ DCM-insols.	Pyr-insols.
<u>Thermolysis</u>			
<u>Set up(1),(at 385 °C)</u>			
Untreated ^(b)	6 (8) ^a	31	63
Chlorobenzene ^(b)	8(13) ^a	18	74
Toluene ^(b)	11	18	71
Chloroform ^(b)	14	24	63
<u>Set up(1),(at 400 °C)</u>			
Untreated	13	6	81
<u>Set up(2)</u>			
Untreated	14	80	6
	12	82	6
<u>SCT Liquefaction (Tetralin)</u>			
<u>Set up(1),(at 400°C)</u>			
Untreated ^(b)	26	41	34
Chlorobenzene ^(b)	29	33	38
Toluene ^(b)	30	38	38
Chloroform ^(b)	28	38	34
<u>Set up(2)</u>			
Untreated	47	31	22

* - includes DCM-soluble liquid product + water + gas

Set up(1): Experiments have been conducted using the system at Figure 3.2.

Set up(2): Experiments have been conducted using the system at Figure 3.1.

(a): [22].

(b): [23].

4.2.2 General aspects

4.2.2.1 Repeatability of experiments

In this study, some of the Point of Ayr and Pittsburgh No.8 thermolysis and short contact time tetralin liquefaction experiments have been repeated using the experimental set up at Figure 3.2 as mentioned in Section 4.2.1.

In thermolysis experiment, in the earlier study [23], for the untreated Point of Ayr, the yield of DCM-soluble products was 6 % at 385 °C. In this study, it was found to be 13 % at 400 °C. Pyridine-solubles were 31 % and 6 %, and pyridine-insolubles were 63 % and 81 %, for the earlier study (at 385 °C) [23] and for this study (at 400 °C), respectively. The difference between pyridine-insolubles was probably because of not removing pyridine from the insolubles properly, which effects pyridine-soluble amount directly as conversion calculations were made by using insoluble-amount (Section 4.1.2.).

In tetralin extraction experiments, DCM-soluble amounts for untreated and chlorobenzene-treated Pittsburgh No.8 were 30 % and 49 % from an earlier study [23], respectively. In this study, DCM-soluble amounts for untreated and chlorobenzene-treated coal were 32 % and 47 %, respectively. Pyridine-soluble amounts were 60 % and 42 % for untreated and chlorobenzene-treated coals from earlier study [23], respectively. For this study, pyridine-soluble amounts were 47 % and 33 % for untreated and chlorobenzene-treated coals, respectively. For pyridine-insoluble amounts, there was a difference, probably because of the same reason mentioned above (Section 4.1.2.).

As seen from the results, although there was a difference for pyridine-solubles and insolubles, the repeatability of DCM-soluble products is found to be satisfactory. This was substantiated by the literature results [23] which are in reasonable agreement with present study.

Table 4.5. Effect of chlorobenzene treatment on the conversion of Karadon and Kurtserif.

Treatment	% daf coal		
	DCM-conv.*	Pyr-sols./ DCM-insols.	Pyr-insols.
<u>Thermolysis</u>			
<u>Set up(1).(at 400°C)</u>			
Karadon			
Untreated	12	22	66
Chlorobenzene	13	24	63
Kurtserif			
Untreated	13	11	76
	8	10	82
Chlorobenzene	8	16	76
<u>SCT Liquefaction</u>			
<u>(Tetralin)</u>			
<u>Set up(1).(at 400 °C)</u>			
Karadon			
Untreated	16	29	55
	13	30	57
	14	25	61
Chlorobenzene	26	21	53
	17	19	64
Kurtserif			
Untreated	27	24	49
	22	31	47
Chlorobenzene	27	21	52

* - includes DCM-soluble liquid product + water + gas

Set up(1): Experiments have been conducted using the system at Figure 3.2.

Set up(2): Experiments have been conducted using the system at Figure 3.1.

Table 4.6. Effect of chlorobenzene treatment on the conversion of Tuncbilek.

Treatment	% daf coal		
	DCM-conv.*	Pyr-sols./ DCM-insols.	Pyr-insols.
<u>Thermolysis</u>			
<u>Set up(1).(at 400 °C)</u>			
Untreated	23	30	47
Chlorobenzene	15	5	80
<u>Set up(2).(at 400 °C)</u>			
Untreated	19	26	55
<u>SCT Liquefaction</u>			
<u>(Tetralin)</u>			
<u>Set up(1).(at 400°C)</u>			
Untreated	23	56	21
Chlorobenzene	28	43	29
	30	39	31

* - includes DCM-soluble liquid product + water + gas

Set up(1): Experiments have been conducted using the system at Figure 3.2.

Set up(2): Experiments have been conducted using the system at Figure 3.1.

4.2.2.2 Effect of different experimental set ups on the conversions

In thermolysis experiments, for untreated Tuncbilek (Table 4.6), DCM-conversions were 19 % and 23 % for the systems at Figures 3.1 and 3.2, respectively. Pyridine-soluble and insolubles were 26 % - 55 %, and 30 % - 47 % for the systems at Figures 3.1 and 3.2 (Figure 4.1). DCM-conversions for untreated Goynuk oil shale (Table 4.8) were 69 % and 61 % for the systems used. Pyridine-soluble and insoluble amounts were similar (Figure 4.1). For tetralin extraction experiments (Figure 4.2), for untreated Point of Ayr (Table 4.4), DCM-conversion were 26 % and 47 % for each system used (Figure 3.1 and 3.2). Pyridine-solubles and insolubles were 41 % - 34 %, and 31 % - 22 % for the systems at Figure 3.2 and 3.1, respectively. DCM-conversions for untreated Goynuk oil shale were 74 % and 80 % for the systems used. Pyridine-soluble and insoluble amounts were similar (Figure 4.2). As mentioned in Section 4.2.1., both thermolysis and tetralin extraction experiments were conducted at 400 °C at the set up shown in Figure 3.2. However, at the set up shown in Figure 3.1, the temperature was checked continuously and

found that the change during 15 and 60 minutes experiments was in between 392-408 °C. As the temperature was not constant during reaction time, the products were lower or higher than the expected ones at 400 °C.

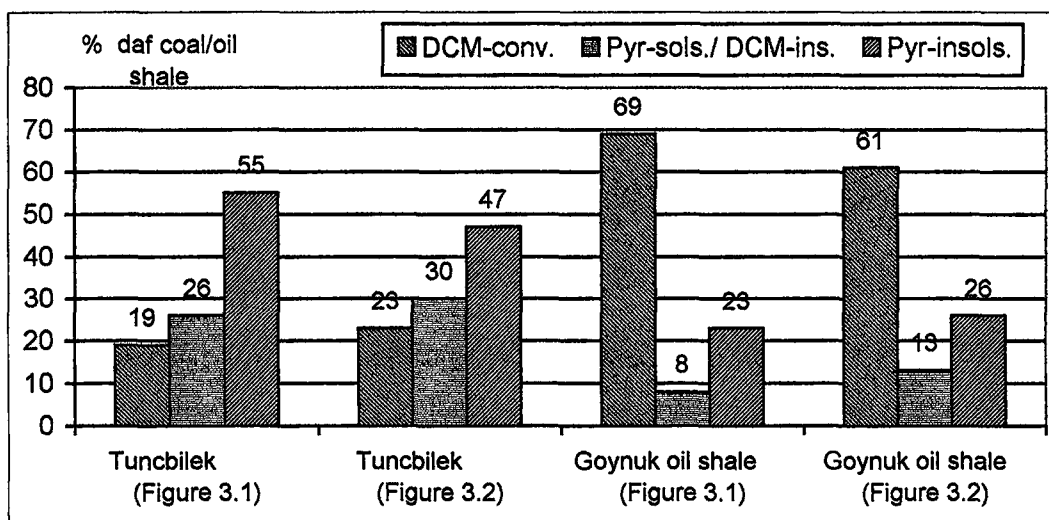


Figure 4.1. Conversion results of untreated Tuncbilek and Goynuk oil shale at thermolysis experiments.

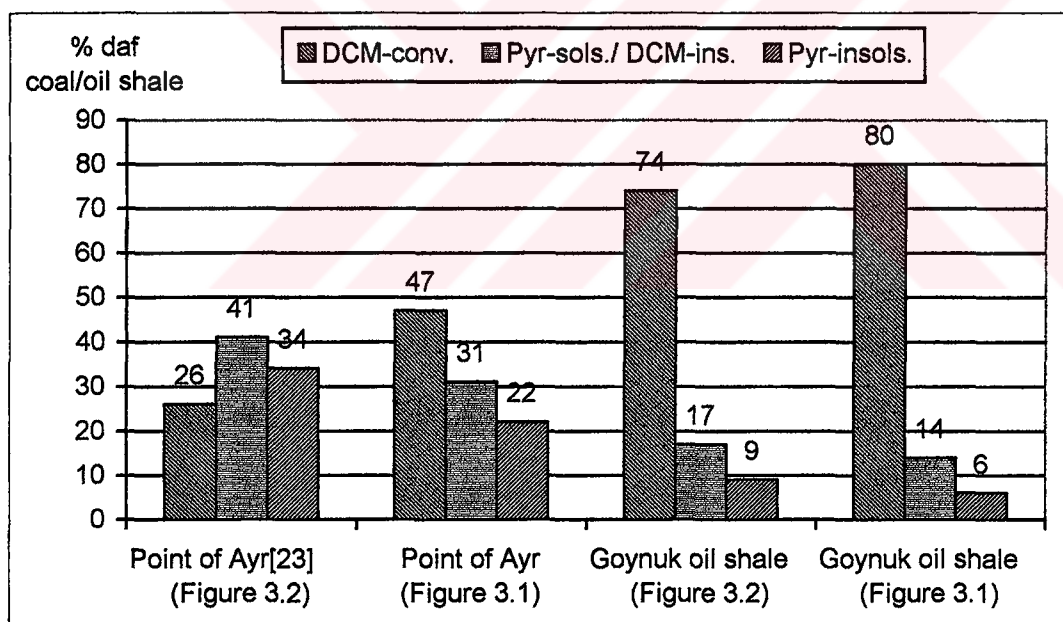


Figure 4.2. Conversion results of untreated Point of Ayr and Goynuk (B) oil shale at SCT tetralin extraction (400 °C).

Table 4.7. Effect of non-polar solvent treatment on the conversion of Can.

Treatment	% daf coal		
	DCM-conv.*	Pyr-sols./ DCM-insols.	Pyr-insols.
<u>Thermolysis</u>			
<u>Set up(2),(at 400°C)</u>			
Untreated	22	66	12
	21	66	13
	21	66	13
Chlorobenzene	26	62	12
	21	66	13
Toluene	22	65	13
	20	67	13
Chloroform	20	67	13
	22	65	13
<u>Set up(1),(at 400°C)</u>			
Untreated	27	9	64
Chlorobenzene	22	5	73
Toluene	20	9	71
Chloroform	21	9	70
<u>SCT Liquefaction</u> <u>(Tetralin)</u>			
<u>Set up(1),(at 400°C)</u>			
Untreated	45	22	33
	39	22	39
Chlorobenzene	38	29	33
Toluene	36	8	56
Chloroform	41	39	20

* - includes DCM-soluble liquid product + water + gas

Set up(1): Experiments have been conducted using the system at Figure 3.2.

Set up(2): Experiments have been conducted using the system at Figure 3.1.

Table 4.8. Effect of chlorobenzene treatment on the conversion of Goynuk (B) oil shale

Treatment	% daf oil shale		
	DCM-conv.*	Pyr-sols./ DCM-insols.	Pyr-insols.
<u>Thermolysis</u>			
<u>Set up(2)</u>			
Untreated	69	9	22
	68	7	25
<u>Set up(1).(at 400°C)</u>			
Untreated	60	15	25
	65	15	20
	59	8	33
Chlorobenzene	68	9	23
	69	9	22
	70	3	27
<u>SCT Liquefaction (Tetralin)</u>			
<u>Set up(2)</u>			
Untreated	80	14	6
<u>Set up(1).(at 400 °C)</u>			
Untreated	73	16	11
	75	20	5
	74	15	11
Chlorobenzene	77	13	10
	80	15	5
	78	13	9

* - includes DCM-soluble liquid product + water + gas

Set up(1): Experiments have been conducted using the system at Figure 3.2.

Set up(2): Experiments have been conducted using the system at Figure 3.1.

4.3 Effect Of Chlorobenzene Treatment on the Conversions of Different Rank Coals in Thermolysis and Tetralin Liquefaction Experiments

Generally, the coal liquefaction was carried out at temperature greater than 400 °C and at high pressures. Recently, a lot of the research work were concentrated to develop methods for dissolving coal at lower reaction severity. However, lowering the reaction severity reduces coal conversion reaction rates and liquid product yields unless the intrinsic coal reactivity can be sufficiently enhanced using some methods [Section 2.6, 166]. Experimental work on pre-swelling and pre-extracting of bituminous and lower-rank coals with a suitable solvent, enhances conversion during subsequent liquefaction. The enhancement depends on coal rank and solvent [18, Section 2.6].

In this study, coal and oil shale samples were treated with chlorobenzene in order to find out the effect of pretreatment on conversions in thermolysis (1 hr, 400 °C) and tetralin extraction (15 min., 400 °C) experiments. As mentioned in Section 4.1.2, some of the experiments were carried out in single, double, and in some cases triplicate runs. For double and triplicate runs, mean values of the experimental results were used in the following sections.

As mentioned in Section 1.3, chlorobenzene breaks no coal-coal hydrogen bonds [89,167], and does not form hydrogen bond to coals [82,168] but, has a reasonable affinity for them and is a good non-polar swelling solvent [82].

4.3.1 Effect of chlorobenzene treatment on bituminous coals

Tables 4.3, 4.4 and 4.5 show the thermolysis and short contact time tetralin extraction results of Pittsburgh No.8, Point of Ayr, Karadon and Kurtserif.

In thermolysis experiments, in the earlier studies [22,23], it was found that chlorobenzene treatment increases the yields of DCM-soluble products for bituminous coals. For instance, DCM-soluble products of Point of Ayr increased from 6 % to 8 % at 385 °C [23], and from 8 % to 13 % at 400 °C [22]. For Pittsburgh

No.8, the increase was from 11 % to 22 % at 400 °C [22]. At lower temperature (385 °C), an increase occurs, but not as much as at 400 °C.

In this study, chlorobenzene did not have any effect on the two bituminous coals investigated. For Karadon and Kurtserif, the DCM-solubles were 12 % and 10 % for untreated coals, and 13 % and 8 % for chlorobenzene-treated samples at 400°C, respectively.

In tetralin extraction experiments, the DCM-conversions for the untreated and chlorobenzene-treated Pittsburgh No.8 at 385 °C were 16 % and 24 %, respectively [23]. At 400 °C, the DCM-conversions increased from 32 % to 47 % for Pittsburgh No.8. As seen from Table 4.3, the increase in DCM-conversion was followed by a decrease in pyridine-soluble and insoluble amounts at 400 °C. The increase in DCM-conversions was higher at 400 °C than at 385 °C like in thermolysis results. At 415 °C, for Pittsburgh No.8 tetralin extraction, DCM-conversions obtained previously were [22] 43 % and 63 % for untreated and chlorobenzene-treated coal samples, respectively. The increase of 15 % (at 400 °C) and 20 % (at 415 °C) daf coal in the yield of DCM-soluble products indicated improved solvent transport has been achieved with more hydrogen being available to promote the thermal breakdown of pyridine-soluble/DCM-insoluble material to oil. For Point of Ayr, - conversions at 400 °C were 26 % and 29 % for untreated and chlorobenzene-treated coal samples, respectively in the earlier studies [22,23].

DCM-conversions for Karadon (Table 4.5) were 14 % and 22 % for untreated and chlorobenzene-treated samples, respectively. The pyridine-solubles was decreased from 28 % to 20 % whereas pyridine-insolubles was same. For Kurtserif (Table 4.5), DCM-conversions were 25 % and 27 % for untreated and chlorobenzene-treated samples. Pyridine-insolubles were increased from 48 % to 52 % while pyridine-solubles decreased from 27 % to 21 %.

Chlorobenzene has been established as a swelling solvent with reasonable affinity for bituminous coals, and also one, which undergoes no specific interactions with these coals [61]. It was found that [56,82] warming Pittsburgh No.8 in chlorobenzene causes the coal to rearrange into a more stable configuration, which

favours the solvent transport inside the coal [22]. The results obtained in this study indicated that chlorobenzene treatment, especially in tetralin extraction, had significantly improved total conversion to DCM-soluble products for Pittsburgh No.8, but there was somehow smaller increases in the conversions for Point of Ayr, Karadon and Kurtserif. For bituminous coals, improvements in DCM-conversions can often accompanied by reductions in overall conversion to pyridine-solubles, which meant that because of improved solvent transport, hydrogen donor molecules were able to reach to the active sites. This result in avoidance of retrogressive reactions of the small fragments which in turn resulted in higher yields of oil type molecules [57].

4.3.2 Effect of chlorobenzene treatment on low-rank coals

Tables 4.6 and 4.7 show the thermolysis and tetralin extraction results of Tuncbilek and Can at 400 °C. For both coals, in the thermolysis experiments, DCM-soluble products and pyridine solubles decreased while pyridine-insolubles increased. Chlorobenzene-treatment decreased the amount of DCM-soluble products from 23 % to 15 % and pyridine-solubles from 30 % to 5 % whereas pyridine-insolubles increased from 47 % to 80 % for Tuncbilek. For Can, DCM-solubles and pyridine-solubles decreased from 27 % to 22 % and 9 % to 5 %, respectively. Pyridine-insolubles increased from 64 % to 73 %.

In tetralin extraction of Tuncbilek DCM-conversions were increased from 23 % to 29 %. Pyridine-solubles decreased from 56 % to 41 % whereas pyridine-insolubles increased from 21 % to 30 %. For Can, DCM-conversions were decreased from 42 % to 38 %, and pyridine-solubles increased from 22 % to 29 % whereas pyridine-insolubles decreased to from 36 % to 33 %.

Both in thermolysis and short contact time tetralin liquefaction DCM-conversion results of Can was different from Pittsburgh No.8. Tuncbilek also gave similar results with Can in thermolysis experiments whereas for tetralin liquefaction results were similar with the bituminous coal.

Snape et al. [34] reported that the chlorobenzene pretreatment reduced the yield of DCM-solubles in tetralin extraction for Wyodak APCS sub-bituminous coal. The

difference in behaviour of low-rank coals investigated thus far is attributed to the vastly differing reaction chemistry with bituminous coals. Indeed, there is much recent evidence to suggest that factors other than solvent treatment, particularly moisture removal [147,154,Section 2.6.4] and ion-exchange at carboxylic sites (i.e. Ca^{+2} etc. for H^{+}) [142,143,146,151,152,Section 2.6.3] profoundly affect the liquefaction of low-rank coals. Whilst, effect of moisture removal has been found both to increase [147] and decrease [154] oil yields depending upon the liquefaction regime employed, removal of calcium inevitably gives rise to improved oil yields [142,143,146,149,152] through the removal of calcium dicarboxylate bridging structures [Section 2.6.3].

4.3.3 Effect of chlorobenzene treatment on an oil shale

Table 4.8 shows the yields of DCM-solubles, pyridine solubles and insolubles obtained from thermolysis and short contact time (15 minutes) tetralin liquefaction experiments carried out at 400 °C on Goynuk oil shale before and after chlorobenzene-treatment. In the thermolysis experiments, chlorobenzene-treatment increased the amount of DCM-soluble products from 61 % to 69 %, whereas pyridine-solubles decreased from 13 % to 7 %, and pyridine-insolubles was almost the same. In tetralin extraction experiments, the increases in DCM-soluble products was small, which was 74 % to 78 %. Pyridine-solubles decreased from 17 % to 14 % while pyridine-insolubles was the same.

When compared with Pittsburgh No.8 investigated in earlier studies [22,23], there was not a significant increase in the yield of DCM-solubles from thermolysis and tetralin extraction experiments of Goynuk oil shale.

4.3.4 Comparison of the effect of chlorobenzene-treatment for different rank coals and an oil shale

Figure 4.3 and 4.4 show the DCM-conversion results of untreated and chlorobenzene-treated samples from thermolysis and tetralin extraction experiments. Goynuk (B) oil shale gave the highest conversion compared to other coals both in thermolysis and tetralin extraction, but the increases in DCM-conversion were smaller compared to Pittsburgh No.8 after chlorobenzene-

treatment. For the three other bituminous coals investigated, there was not a significant change in DCM-conversion results as seen from Figures 4.3 and 4.4. For the two low-rank coals, chlorobenzene-treatment decreased the conversions in thermolysis experiments. In tetralin extraction experiments, there was an increase in the conversions of Tuncbilek whereas a decrease for Can.

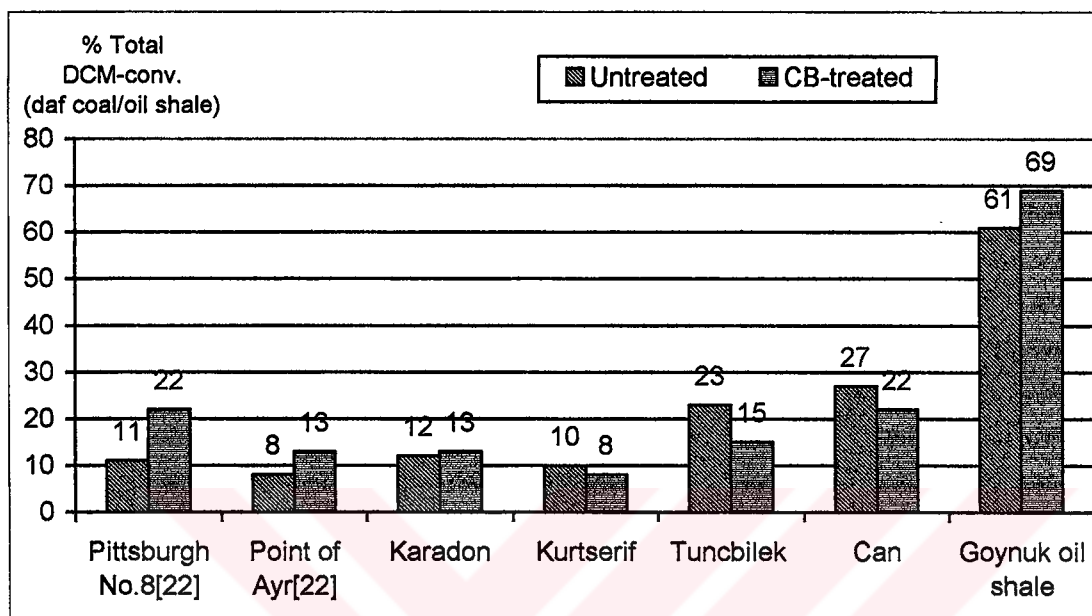


Figure 4.3. Thermolysis results of coals and oil shale at 400 °C.

It is noticed that the effect of chlorobenzene-treatment on the increase in the amount of DCM-conversions of samples were in the order of, low-rank coals < oil shale < bituminous coals in the thermolysis experiments, and for tetralin extraction experiments the order was: low-rank coals < oil shale < bituminous coals.

As seen, the effects of chlorobenzene-treatment were extremely varied and depended both upon the coal (or oil shale) and the liquefaction regime used. The increases in DCM-conversions were more in tetralin extractions compared to thermolysis experiments although reaction time was shorter. Also, the increase in the amount of DCM-conversion for chlorobenzene-treated sample was higher than untreated sample for bituminous coal and oil shale whereas a decrease was observed in the lignite experiments. The reason for the increase in DCM-conversion in tetralin extraction was probably because of effective hydrogen transfer from tetralin to coal at the initial stages of liquefaction which decreased the chance of

occurrence of retrogressive char forming reactions [Section 2.5.3]. For chlorobenzene-treated bituminous coals and oil shale, the reason for the DCM-conversion increase compared to untreated samples was attributed to the improved solvent transport after chlorobenzene-treatment. However, chlorobenzene-treatment seemed to have adverse effect on the structure of low-rank coals [Section 2.6.3].

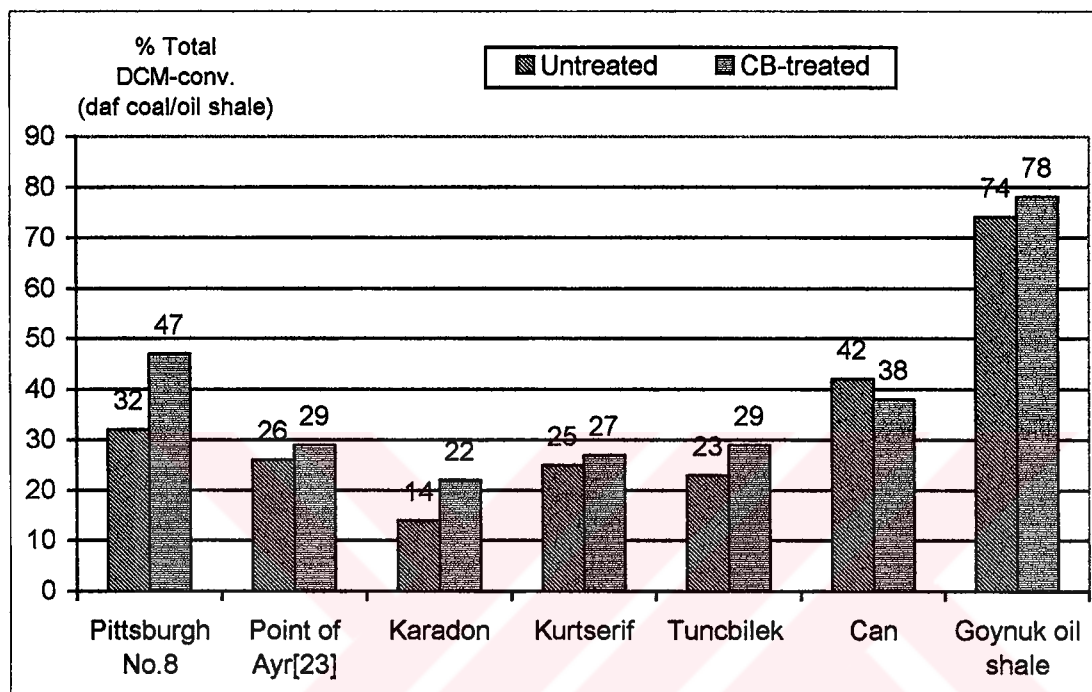


Figure 4.4. Short contact time tetralin extraction results of coals and oil shale at 400 °C.

4.4 Effect of Time on the Conversions in Tetralin Extraction

Figures 4.5 and 4.6 present the product yields from the series of experiments on Pittsburgh No.8 in which the extraction time was varied between 15 and 60 min. (at 400 °C) from an earlier study [23]. The results indicated that increased yields of DCM-solubles were obtained upon chlorobenzene treatment across a wide conversion range, but the increases were smaller at higher levels of conversion. The amounts of hydrogen transferred to the coal during extraction (ca 0.6 % daf coal) were similar for the untreated and chlorobenzene-treated coals at the short contact time of 15 minutes. This finding might suggest that the improved oil (DCM)

yields arise primarily from the changes in the conformational structure of the coals limiting char-forming reactions rather than cleaving more bonds *per se*. However, for times over 30 min, the amounts of hydrogen transferred were somewhat higher indicating that the conformational changes result in more bond cleavage [23,169].

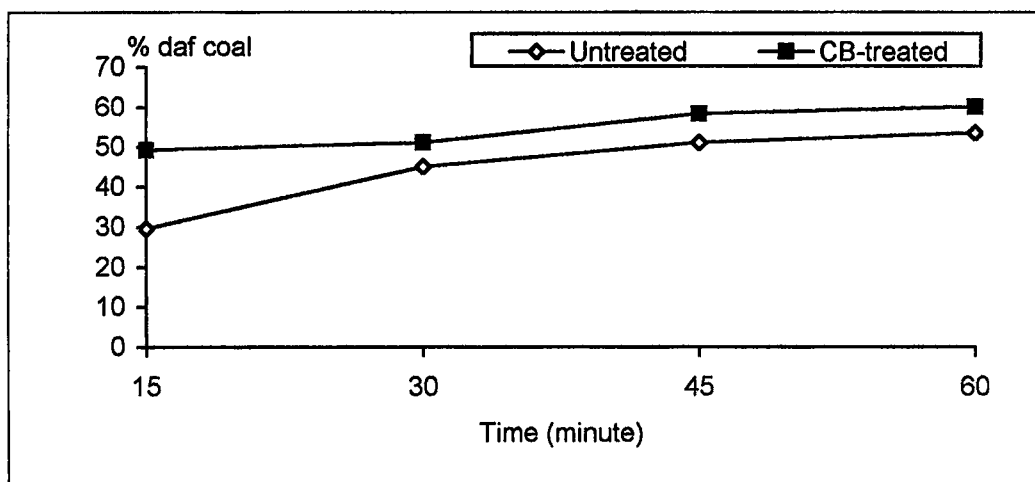


Figure 4.5. Effect of extraction time on yields of DCM-solubles for Pittsburgh No.8 in tetralin extraction [23].

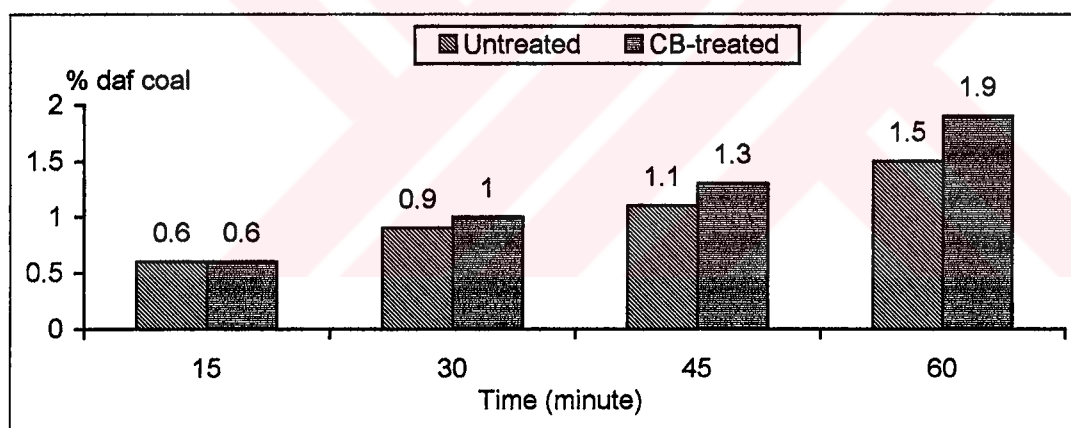


Figure 4.6. Effect of extraction time on amount of hydrogen transferred for Pittsburgh No.8 in tetralin extraction [23].

Figure 4.7 and 4.8 show the result of DCM-soluble products and % hydrogen-transfer for Goynuk (B) oil shale in which the extraction time varied between 15 and 60 minutes (at 400 °C). As seen from Figure 4.7, there was a small increase in DCM-conversion at 15 minutes, but with increasing time, the results were almost same for untreated and chlorobenzene-treated samples. The amounts of hydrogen transferred (Figure 4.8) to the oil shale during extraction at the short contact time of

15 minutes were somewhat different for untreated and chlorobenzene-treated oil shale. There was an increase from 0.9 % to 1.8 %. However, for time over 30 minutes, the amounts of hydrogen transferred were almost same. There was a small increase in quantity of DCM-soluble products at 15 minutes, but with increasing time, the results were almost same for untreated and chlorobenzene-treated samples (Figure 4.7).

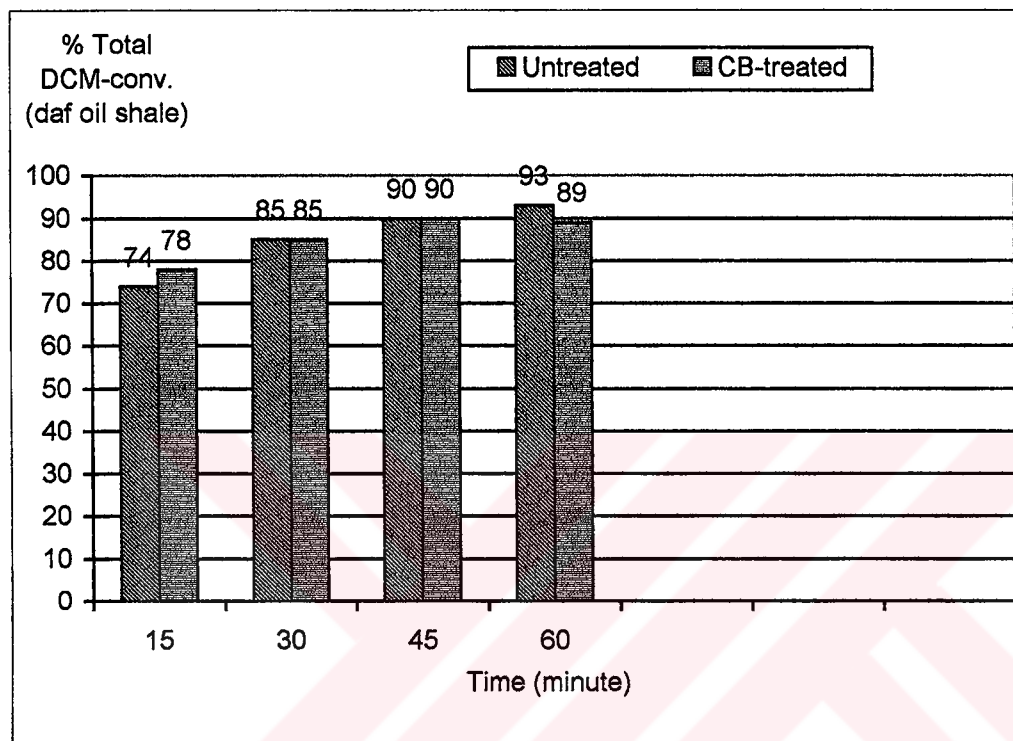


Figure 4.7. % DCM-conversion for Goynuk (B) oil shale in tetralin extraction at 400 °C.

Figures 4.4 and 4.9 present the DCM-soluble product yields, and Figures 4.10 and 4.11 present the amounts of hydrogen transferred on the coals and oil shale in which the extraction time was 15 and 60 minutes respectively, at 400 °C. The results of Figure 4.4 indicated that only for Pittsburgh No.8, there was a significant increase in DCM-conversion whereas for Can there was a decrease. For Point of Ayr, Karadon, Kurtserif and Tuncbilek, and oil shale, the increase in the DCM-conversions were low compared to Pittsburgh No.8. When the tetralin extraction time was 60 minutes, the increase in DCM-conversion for chlorobenzene-treated Pittsburgh No.8 and Point of Ayr were low. For chlorobenzene-treated Karadon, Kurtserif, Tuncbilek, and Goynuk oil shale DCM-conversions decreased with respect

to untreated coals and oil shale. For Can, DCM-conversions were same for untreated and chlorobenzene-treated coals (Figure 4.9).

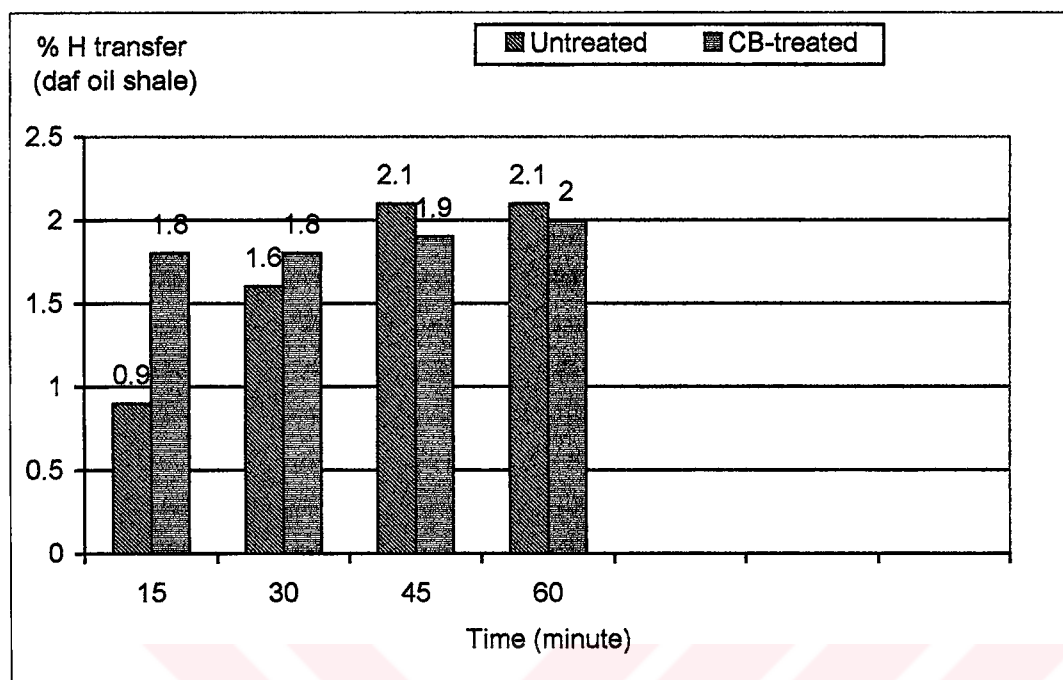


Figure 4.8. % hydrogen transfer amount for Goynuk oil shale in tetralin extraction at 400 °C.

Both for coal and oil shale, the results indicated that increased (or decreased) yields of DCM-solubles were obtained upon chlorobenzene treatment up to the structural differences of the samples used in short contact time liquefaction, but the increases (or decreases) were smaller at higher levels of conversion.

The amounts of hydrogen transferred to the coal during extraction were similar for the untreated and chlorobenzene-treated coals, except for oil shale as mentioned above, used at short contact time of 15 minutes (Figure 4.10). For only Can, there was a decrease in the % hydrogen transfer from 1.8 % to 1.6 % implying that chlorobenzene treatment had an adverse effect on coal structure. As the hydrogen transferred to the coal during extraction were similar for untreated and chlorobenzene-treated coals except for Can, this finding might suggest that the improved oil (DCM) yields arise primarily from the changes in the conformational structure of the coals limiting char-forming reactions rather than cleaving more bonds per se. The only difference between the coals used in % hydrogen transfer at

15 minutes was because of the rank of coals. For the only oil shale investigated, hydrogen transfer amount was different than coals, probably because of structural differences from coal. At 15 minutes, for Pittsburgh No.8, Point of Ayr, Karadon and Kurtserif, hydrogen transfer was between 0.5-0.8 %, whereas for low-rank coals, it was in between 1.0-1.8 %. This was probably due to low-rank coals being more reactive than higher rank coals [Section 2.5.2].

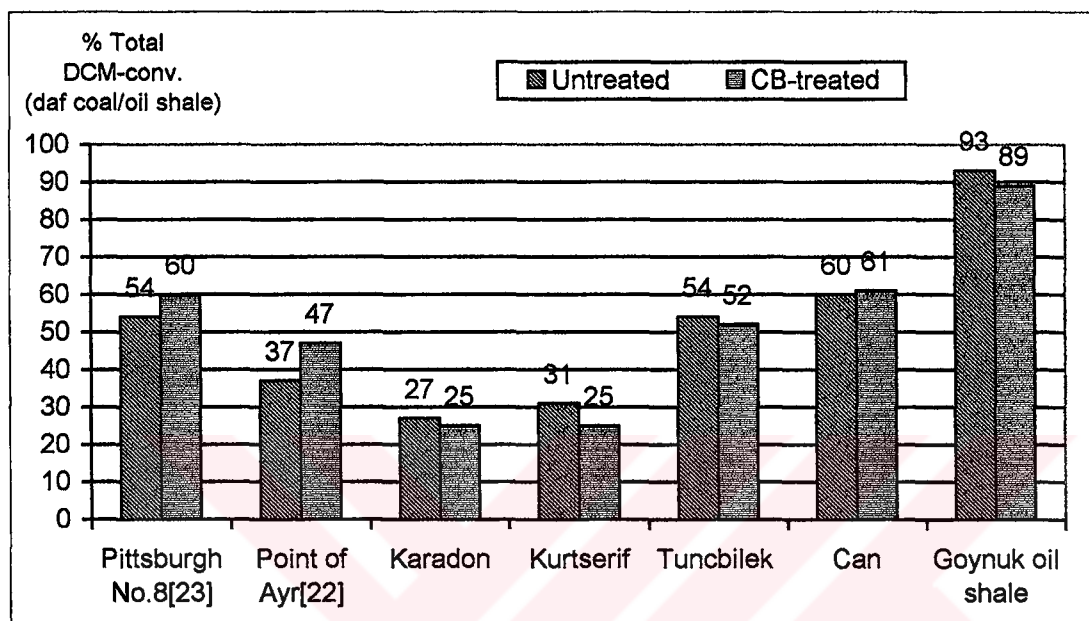


Figure 4.9. DCM-conversion of coals and oil shale in tetralin extraction for 60 minutes at 400 °C.

However, when the extraction time was 60 minutes, the amounts of hydrogen transferred were increased in different amounts for untreated and chlorobenzene-treated coals showing the effect of chlorobenzene-treatment on different rank of coals (Figure 4.11). For Pittsburgh No.8, the amounts of hydrogen transferred increased from 1.5 % to 1.9 % indicating that the conformational changes result in more bond cleavage as mentioned above [22,23]. For Point of Ayr, hydrogen transferred was 0.9 % and 1.1 % for untreated and chlorobenzene-treated coals, respectively. For Karadon and Kurtserif, the amounts of hydrogen transferred were 1.2 % and 1.3 % for untreated, and 1.3 % and 1.4 % for chlorobenzene-treated coals, respectively. There was not so much increase for Karadon and Kurtserif in hydrogen transfer amounts which was parallel with small increase in DCM-conversions. For the low-rank coals, there was a decrease in the hydrogen transfer

of chlorobenzene-treated coals, probably because of detrimental effect of chlorobenzene treatment on the structure of low-rank coals, which separated them from bituminous coals. The chlorobenzene-treatment probably caused changes, which prevented tetralin molecules to move inside the structure. For Tuncbilek and Can, the hydrogen transferred were 2.2 % and 2.6 % for untreated, and 1.4 % and 2.0 % for chlorobenzene-treated samples, respectively. The amount of hydrogen-transferred for untreated and chlorobenzene-treated Goynuk oil shale were same like Karadon, Kurtserif and Point of Ayr.

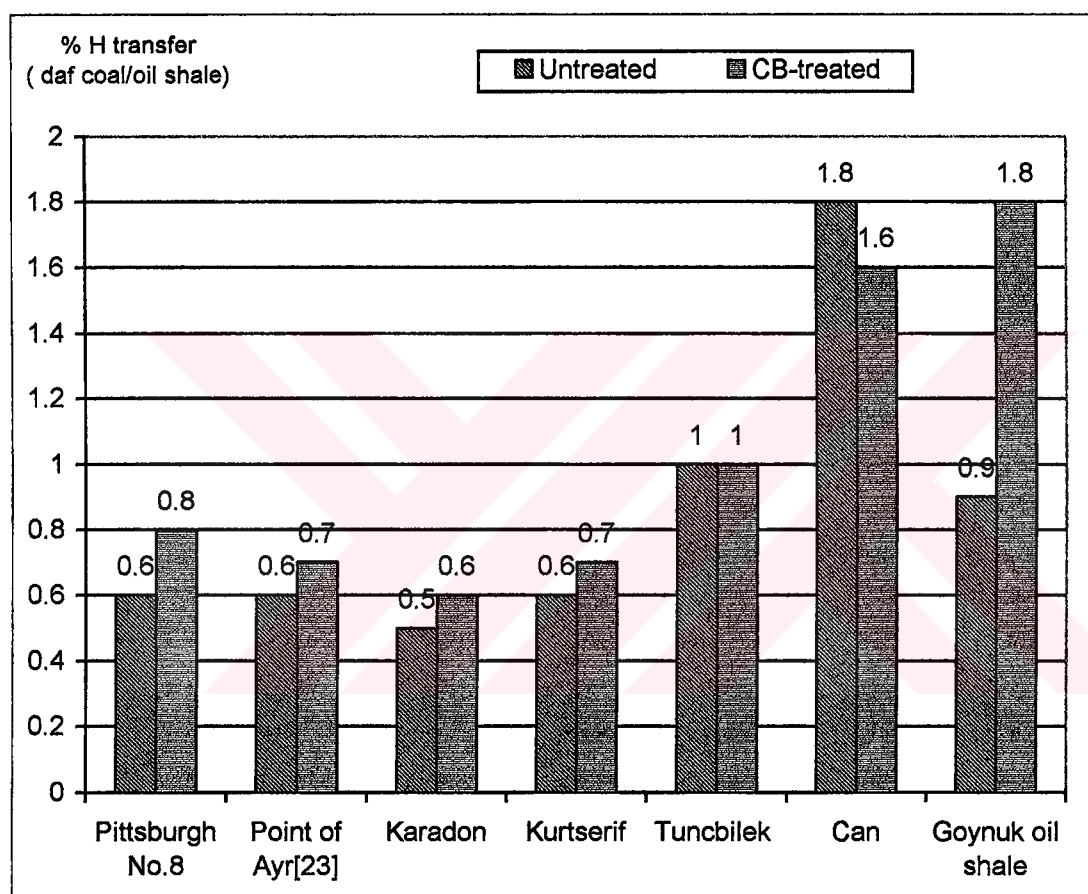


Figure 4.10. % hydrogen transfer amount at SCT tetralin liquefaction at 400 °C.

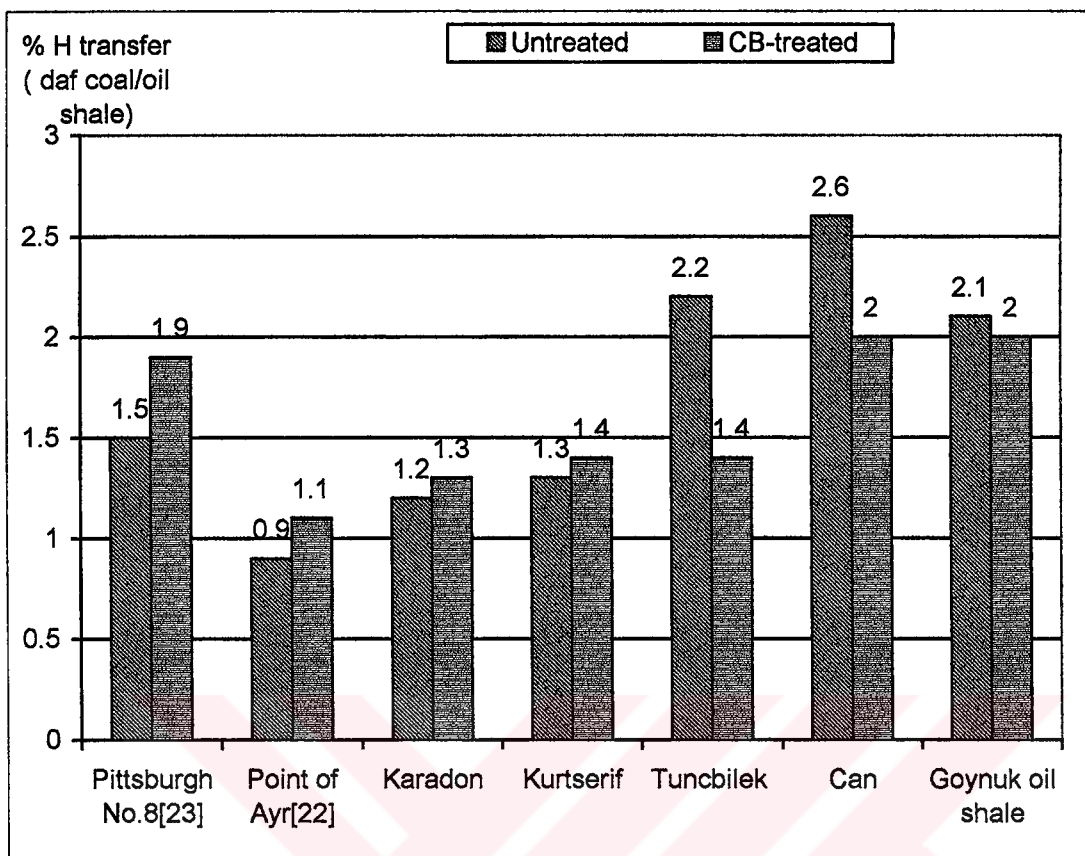


Figure 4.11. % hydrogen transfer amount in tetralin extraction for 60 minutes at 400 °C.

4.5 Effect of Toluene and Chloroform Treatment on the Conversions in Thermolysis and Tetralin Extractions

4.5.1 Effect of toluene and chloroform treatment on bituminous coals

In an earlier study [23], Pittsburgh No.8 and Point of Ayr were treated with toluene and chloroform in addition to chlorobenzene, both of which are non-polar solvents. The results are listed in Tables 4.3 and 4.4 for the thermolysis and tetralin extraction experiments conducted on the coals treated with three non-polar solvents. The yields of DCM-solubles, pyridine-solubles/DCM-insolubles and pyridine-insolubles were generally similar for chlorobenzene, toluene and chloroform-treated samples. Figures 4.12 and 4.14 present the tetralin extraction results and Figures 4.13 and

4.15 show the amounts of hydrogen transferred from tetralin to the coals. These results further demonstrated that chlorobenzene and the two other non-polar solvents had significantly improved total conversion to DCM-soluble products for Pittsburgh No.8, but there was a much smaller increase in the conversion for Point of Ayr. DCM-soluble yields for Pittsburgh No.8 increased from 16 % to 24-32 % (at 385 °C) and for Point of Ayr only from 26 % to 28-30 % (at 400 °C). For Pittsburgh No.8, the amount of hydrogen transferred was in the range of 0.3 % - 0.5 % and for Point of Ayr, 0.6 % - 0.7 %. However, the amounts of hydrogen transferred from tetralin were almost similar for the untreated, chlorobenzene, toluene, and chloroform-treated coals. In thermolysis experiments, increases in the yields of DCM-solubles occurred after the non-polar solvent treatments. For Pittsburgh No.8, DCM-soluble yields increased from 9 % to 17 % and for Point of Ayr from 6 % to 8 - 13 % (Tables 4.2 and 4.3) [23].

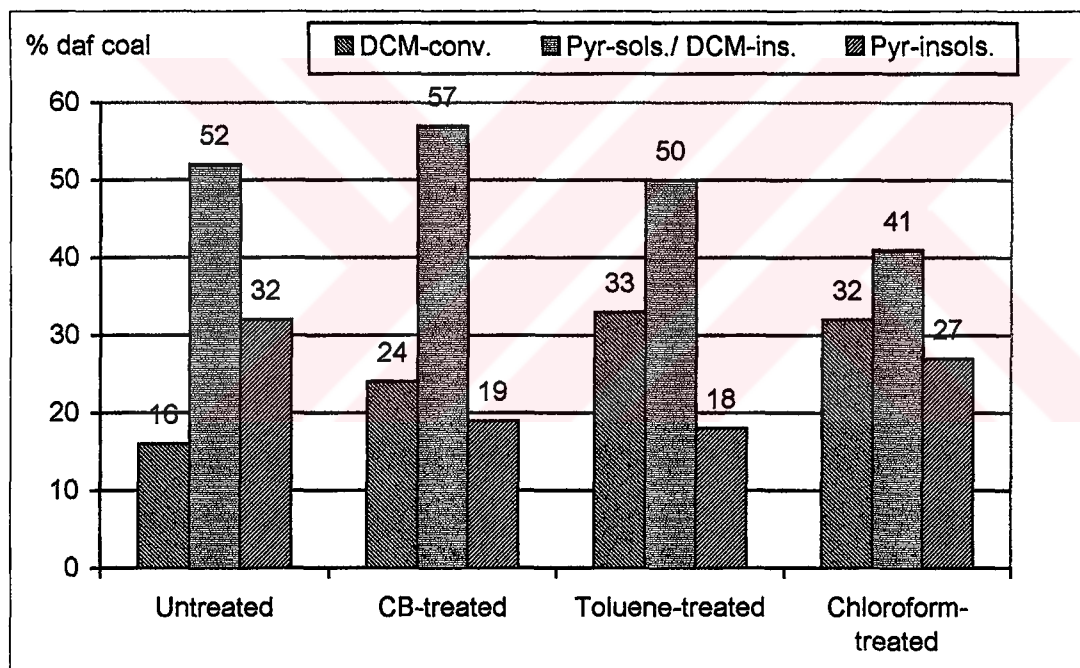


Figure 4.12. Conversions of non-polar solvent treated Pittsburgh No.8 in short contact time tetralin liquefaction at 385 °C [23].

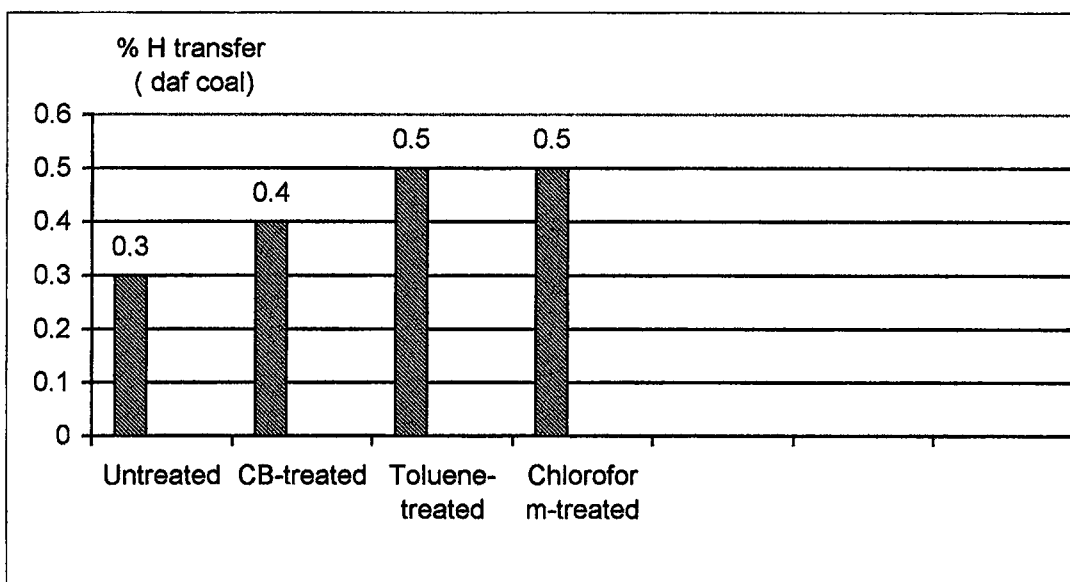


Figure 4.13. Effects of chlorobenzene and other non-polar solvent treatments on the amount of hydrogen transferred from tetralin to Pittsburgh No.8 at 385 °C [23].

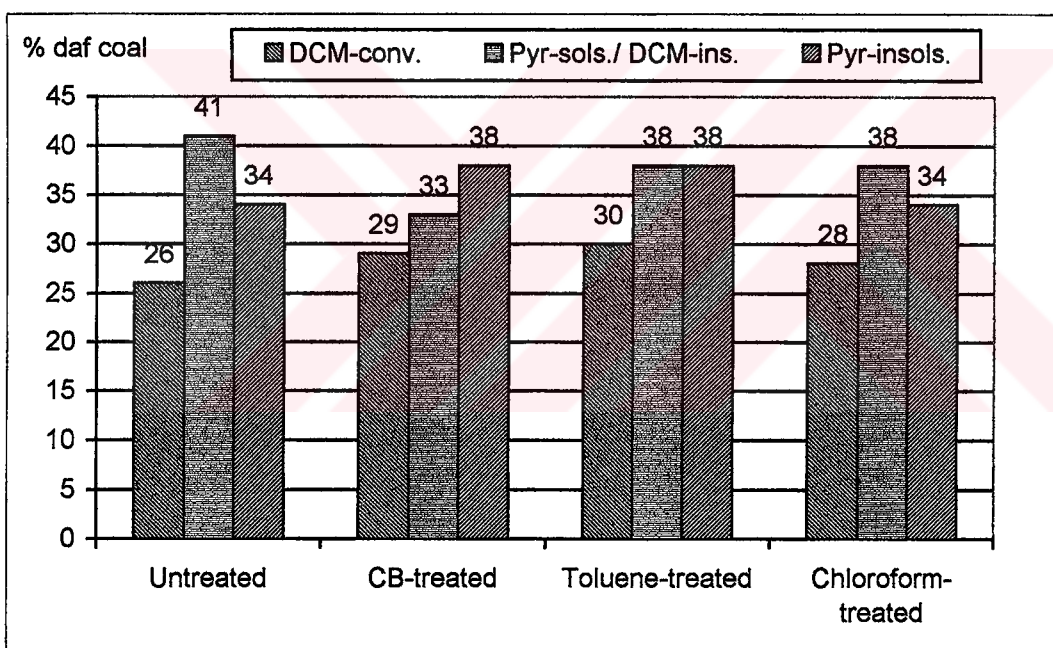


Figure 4.14. Conversions of non-polar solvent treated Point of Ayr in short contact time tetralin liquefaction at 400 °C [23].

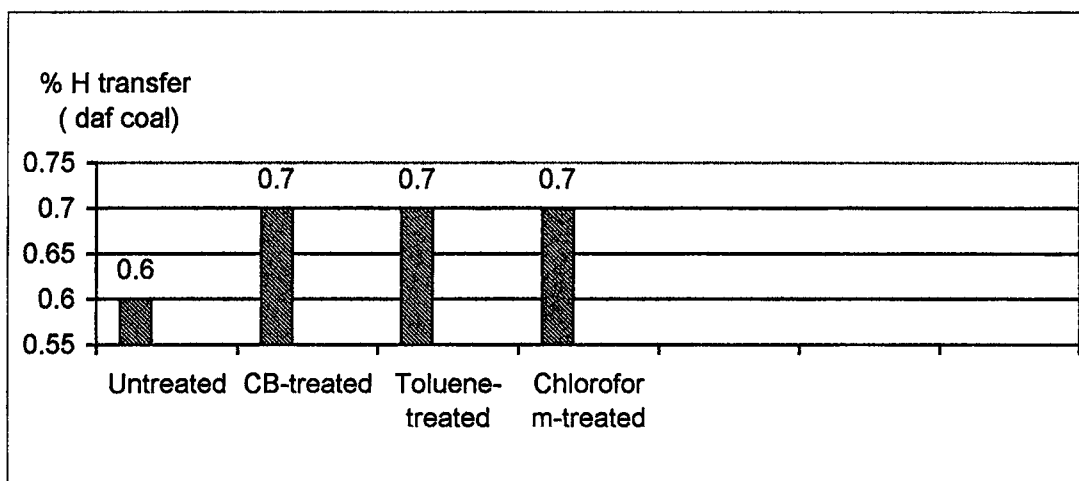


Figure 4.15. Effect of chlorobenzene and other non-polar solvent treatments on the amount of hydrogen transferred from tetralin to Point of Ayr at 400 °C [23].

4.5.2 Effect of toluene and chloroform treatment on low-rank coals

Can was treated with toluene and chloroform in addition to chlorobenzene, and further, thermolysis and tetralin extraction experiments were conducted on treated coals at 400 °C. The results are given at Table 4.7. As mentioned in Section 4.2.2.2, there were differences in the results obtained using the systems shown in Figures 3.1 and 3.2 when compared. However, the yields of DCM-solubles, pyridine-solubles/DCM-insolubles and pyridine-insolubles were generally similar for chlorobenzene, toluene and chloroform-treated samples for all of the experimental set up used in thermolysis experiments.

Figures 4.16 and 4.17 present the tetralin extraction results and the amounts of hydrogen transferred from tetralin to the coals. The results further demonstrated that chlorobenzene and the two other non-polar solvent treatments did not have significant effect on the experiments of lignite.

DCM-soluble yields for Can was 42 % for untreated and between 36 % - 41 % for treated coals at 400 °C. The amount of hydrogen transferred was in the range of 1.4 % – 1.9 %. The amounts of hydrogen transferred from tetralin were almost similar for untreated and treated coals, but similarity was not as good as seen for bituminous coals. In thermolysis experiments, decreases in the yields of DCM-

solubles occurred after the non-polar solvent treatments. DCM-soluble yields decreased from 27 % to 20 – 22 % (Table 4.7).

The yields of total DCM-soluble products for the toluene and chloroform-treated Can were generally similar to those for their chlorobenzene-treated counter parts, and were almost lower than those for the untreated coal.

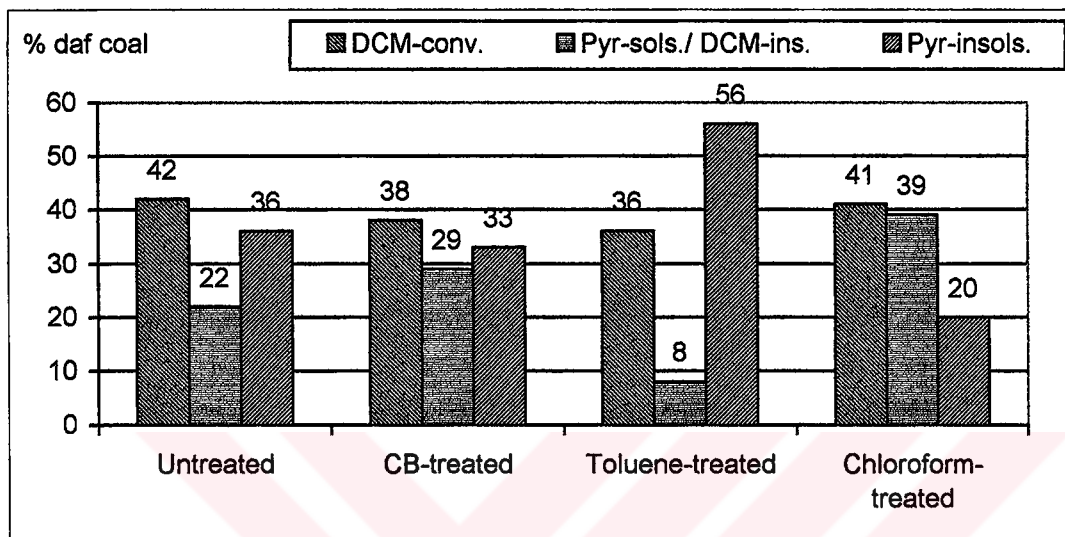


Figure 4.16. Conversions of non-polar solvent-treated Can in short contact tetralin liquefaction at 400 °C.

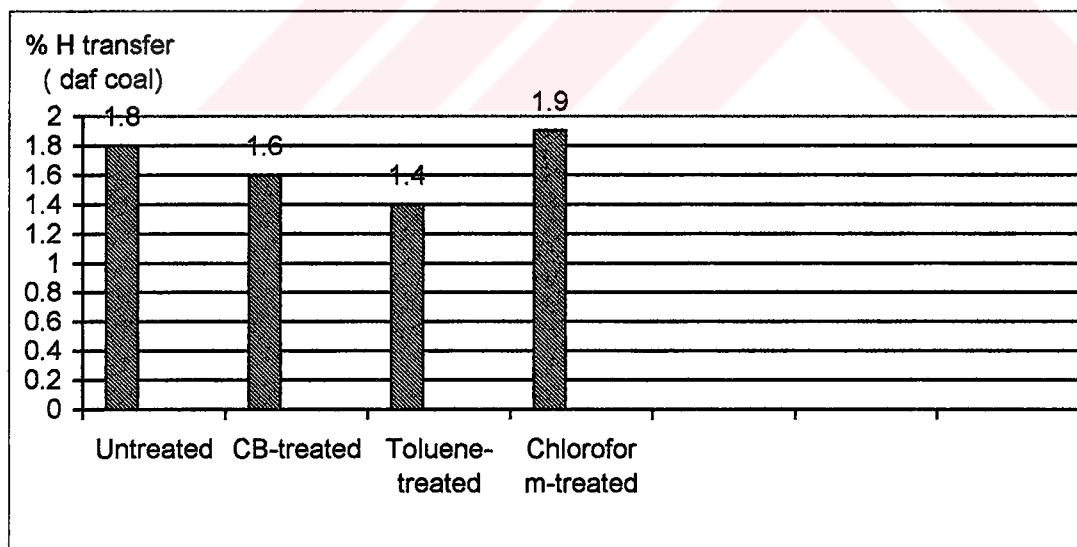


Figure 4.17. % hydrogen transfer amounts for Can in short contact time tetralin liquefaction at 400 °C.

4.5.3 Comparison of the effects of non-polar solvents for bituminous and low-rank coals

For Pittsburgh No.8 and Point of Ayr, the yields of total DCM-soluble products for the toluene and chloroform-treated coals were generally similar to those for their chlorobenzene-treated counterparts and were significantly higher than those for the untreated coal [23]. The yields of DCM-soluble products for chlorobenzene, toluene and chloroform-treated Can were generally similar and were lower than those for the untreated coal.

These results imply that the conformational changes induced by the three relatively non-polar solvents are similar and are not dependent on temperature for the solvent boiling range investigated (ca 60 to 130°C) [22,23,169]. In addition, non-polar solvent treatment increased the DCM-conversion for bituminous coals [23] whereas decreased for low-rank coals, because of the reasons mentioned in Section 2.6.3 and 2.6.4

4.6 Effect of Methanol and Tetrahydrofuran Treatment on the Conversions of Different Rank Coals and an Oil Shale in Thermolysis and Short Contact Time Tetralin Liquefaction

As mentioned in Section 1.3, polar solvents like tetrahydrofuran and methanol are expected to disrupt the coal-coal hydrogen bonds [61,75,89,167]. In this section, the effect of methanol and tetrahydrofuran on the conversions of different rank coals and an oil shale in thermolysis (60 min. at 400 °C) and in short contact time tetralin liquefaction (15 min, at 400 °C) were reported for three bituminous and two low-rank coals and an oil shale. Thermolysis and tetralin liquefaction experiments were both conducted using the system at Figure 3.2.

4.6.1 Effect of methanol and tetrahydrofuran treatment on the conversions of bituminous coals

Table 4.9 presents the results from thermolysis and tetralin extraction of Pittsburgh No.8, Karadon and Kurtserif. In thermolysis, the amount of DCM-soluble products for Pittsburgh No.8 was decreased from 11 % to 8 % after tetrahydrofuran-treatment, whereas increased to 23 % for methanol-treatment. For Kurtserif, DCM-soluble products increased from 11 % to 14 % for tetrahydrofuran treatment, but decreased to 9 % for methanol-treatment. Karadon showed a similar trend with tetrahydrofuran-treated Kurtserif, and DCM-soluble products increased from 12 % to 18 %. Thermolysis results showed that polar solvent treatment did not have any significant effect on conversions.

In tetralin extraction experiments, in general, there was an increase in DCM-soluble products and in the amount of pyridine-solubles followed by a decrease in the amount of pyridine-insolubles when compared to thermolysis experiments. For tetrahydrofuran and methanol-treated Pittsburgh No.8, the DCM-solubles increased to 24 % and 28 %, but the values were still less than the amount for untreated coal (32 %). Also, the increase in methanol-treated coal was small when compared with the thermolysis results. For untreated and tetrahydrofuran-treated Kurtserif, the DCM-soluble amount was 25 % for each, whereas there was no change for methanol-treated sample (9 - 10 %). There was a small increase for untreated and tetrahydrofuran-treated Karadon, 14 % and 22 %, respectively.

The effects of tetrahydrofuran and methanol-treatment on the DCM-conversion of Pittsburgh No.8 in thermolysis follows the following order: tetrahydrofuran-treated < untreated < methanol-treated, and in tetralin extraction the order is: tetrahydrofuran-treated < methanol-treated < untreated coal. For Kurtserif the trend is in the order of: methanol-treated < untreated < tetrahydrofuran-treated coal in thermolysis experiments, and in tetralin extraction the order is: methanol-treated < untreated = tetrahydrofuran-treated coal.

Table 4.9. Effect of methanol and tetrahydrofuran treatment on the conversion of Pittsburgh No.8, Karadon and Kurtserif.

% daf coal				
Coal	Treatment	DCM-conv.*	Pyr-sols./ DCM-insols.	Pyr-insols.
<u>Thermolysis</u> <u>(at 400°C)</u>				
Pittsburgh No.8	Untreated	11 ^(a)		
	Tetrahydrofuran	8	27	65
	Methanol	23	26	51
Kurtserif	Untreated	11	10	79
	Tetrahydrofuran	14	14	72
	Methanol	9	10	81
Karadon	Untreated	12	22	66
	Tetrahydrofuran	18	9	73
<u>SCT</u> <u>Liquefaction</u> <u>(Tetralin,</u> <u>at 400 °C)</u>				
Pittsburgh No.8	Untreated	32	47	21
	Tetrahydrofuran	24	39	37
	Methanol	28	41	31
Kurtserif	Untreated	25	27	48
	Tetrahydrofuran	25	39	36
	Methanol	10	30	60
Karadon	Untreated	14	28	58
	Tetrahydrofuran	22	27	51

* - includes DCM-soluble liquid product + water + gas

(a) : [22].

4.6.2 Effect of methanol and tetrahydrofuran treatment on low-rank coals

The results from thermolysis and tetralin extraction of methanol and tetrahydrofuran-treated Tuncbilek and Can are shown in Table 4.10. In thermolysis, the amount of DCM-soluble products for Tuncbilek was 23 % for untreated and methanol-treated coals whereas for tetrahydrofuran-treated coal it was 17 %. For both tetrahydrofuran and methanol-treated coals, the amount of pyridine-solubles decreased followed by an increase in pyridine-insolubles. For Can, DCM-soluble product amount decreased from 27 % to 20 % and 23 % for tetrahydrofuran and methanol-treated samples, respectively.

In tetralin extraction, in general, there was an increase in DCM-soluble products and pyridine-solubles followed by a decrease in the amount of pyridine-insolubles. For tetrahydrofuran and methanol-treated Tuncbilek, DCM-soluble products increased from 23 % to 32 % and 33 %, respectively. For Can, DCM-soluble products were 42 % and 43 % for untreated and methanol-treated coals, and for tetrahydrofuran-treated coal, it was 39 %. The increase in the conversion of Can was higher than for Tuncbilek.

The effects of tetrahydrofuran and methanol on DCM-conversion is in the following order for Tuncbilek in thermolysis: tetrahydrofuran-treated < untreated = methanol-treated coal, and in tetralin extraction the order is: untreated < tetrahydrofuran-treated $\leq$ methanol-treated coal. For Can in thermolysis the trend is in the order of: tetrahydrofuran-treated < methanol-treated < untreated coal, and in tetralin extraction: tetrahydrofuran-treated < untreated $\leq$ methanol-treated coal.

Table 4.10. Effect of methanol and tetrahydrofuran treatment on the conversion of Tuncbilek and Can.

% daf coal				
Coal	Treatment	DCM-conv.*	Pyr-sols./ DCM-insols.	Pyr-insols.
<u>Thermolysis</u> <u>(at 400°C)</u>				
Tuncbilek	Untreated	23	30	47
	Tetrahydrofuran	17	5	78
	Methanol	23	10	67
Can	Untreated	27	9	64
	Tetrahydrofuran	20	9	71
	Methanol	23	13	64
<u>SCT</u> <u>Liquefaction</u> <u>(Tetralin,</u> <u>at 400 °C)</u>				
Tuncbilek	Untreated	23	56	21
	Tetrahydrofuran	32	27	41
	Methanol	33	36	31
Can	Untreated	42	22	36
	Tetrahydrofuran	39	29	32
	Methanol	43	20	37

* - includes DCM-soluble liquid product + water + gas

4.6.3 Effect of methanol and tetrahydrofuran treatment on oil shale

The results from thermolysis and tetralin extraction of methanol and tetrahydrofuran-treated Goynuk (B) oil shale are shown in Table 4.11. In thermolysis, the amount of DCM-soluble products was 61 % for both untreated and tetrahydrofuran-treated oil shale, and 65 % for methanol-treated oil shale. Pyridine-solubles increased significantly for methanol-treated oil shale whereas pyridine-insolubles decreased.

In tetralin extraction, the amount of DCM-solubles increased whereas pyridine-solubles and insolubles decreased. For tetrahydrofuran and methanol-treated oil shale, the DCM-soluble products increased from 74 % to 81 %. The effects of methanol and tetrahydrofuran treatment were almost the same for Goynuk oil shale.

Table 4.11. Effect of methanol and tetrahydrofuran treatment on the conversion of Goynuk (B) oil shale.

% daf oil shale				
	Treatment	DCM-conv.*	Pyr-sols./ DCM-insols.	Pyr-insols.
<u>Thermolysis</u> (at 400°C)				
	Untreated	61	13	26
	Tetrahydrofuran	61	21	18
	Methanol	65	34	1
<u>SCT</u> <u>Liquefaction</u> (Tetralin, at 400 °C)				
	Untreated	74	17	9
	Tetrahydrofuran	81	11	8
	Methanol	81	16	3

* - includes DCM-soluble liquid product + water + gas

4.6.4 Comparison of the effect of tetrahydrofuran and methanol-treatment for different rank coals and an oil shale

4.6.4.1 Comparison of the effect of treatments on DCM conversion

The DCM-conversion results of untreated, tetrahydrofuran and methanol-treated samples from thermolysis and tetralin extraction experiments are presented in Figures 4.18 and 4.19. Goynuk (B) oil shale showed the highest yield, in both thermolysis and tetralin extraction experiments. The increases in DCM-conversion were low. In thermolysis, untreated and tetrahydrofuran-treated shale gave the

same amount of DCM-conversion, whereas for methanol-treated shale, there was a small increase in the yield. At tetralin extraction, after treatments the DCM-conversion was same and higher than untreated shale yield.

Tetrahydrofuran treatment decreased Pittsburgh No.8 DCM-conversion whereas ended up with small increase for Kurtserif and Karadon both in thermolysis and tetralin extraction experiments. For the low-rank coals, treatment decreased the conversion in thermolysis. In tetralin extraction experiments, there was an increase in the conversion for Tuncbilek whereas a decrease for Can. After methanol-treatment, there was an increase for Pittsburgh No.8 both in tetralin extraction and thermolysis experiments, but it was still lower than the untreated coal. For Kurtserif there was no change in the yield even tetralin was used. For low-rank coals, there was no change for Tuncbilek and a decrease for Can in thermolysis. In tetralin extraction, there was an increase for Tuncbilek whereas no change for Can.

It is noticed that the increase effect of tetrahydrofuran-treatment to the amount in DCM-conversion is in the order of: low rank coals < bituminous coals < oil shale and for methanol-treatment the order is: low-rank coals < oil shale < bituminous coals in thermolysis experiments. For tetralin extraction experiments after both treatments the order is: bituminous coals < low-rank coals < oil shale. If untreated samples DCM-conversions are considered, the order is: bituminous coals < low-rank coals < oil shale in thermolysis experiments, and in tetralin extraction experiments, the order is: bituminous coals $\leq$ low-rank coals < oil shale.

As seen from Figures 4.18 and 4.19, the effects of tetrahydrofuran and methanol-treatment were varied and depended both upon the sample and liquefaction regime used.

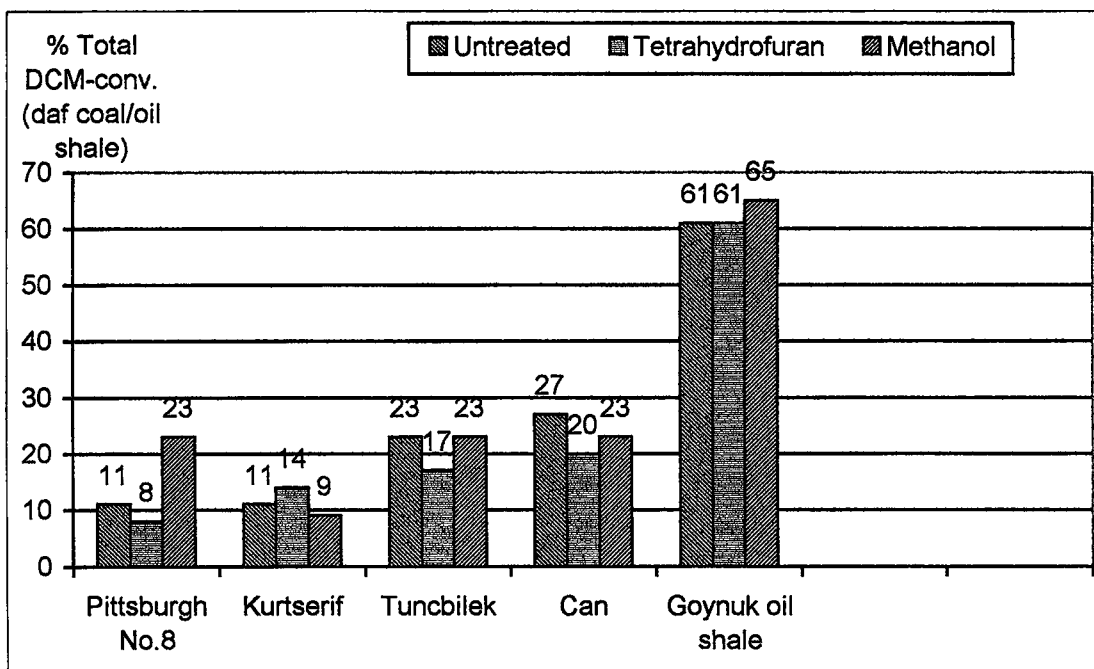


Figure 4.18. Effect of polar solvent treatment on the conversion in thermolysis experiments (400 °C).

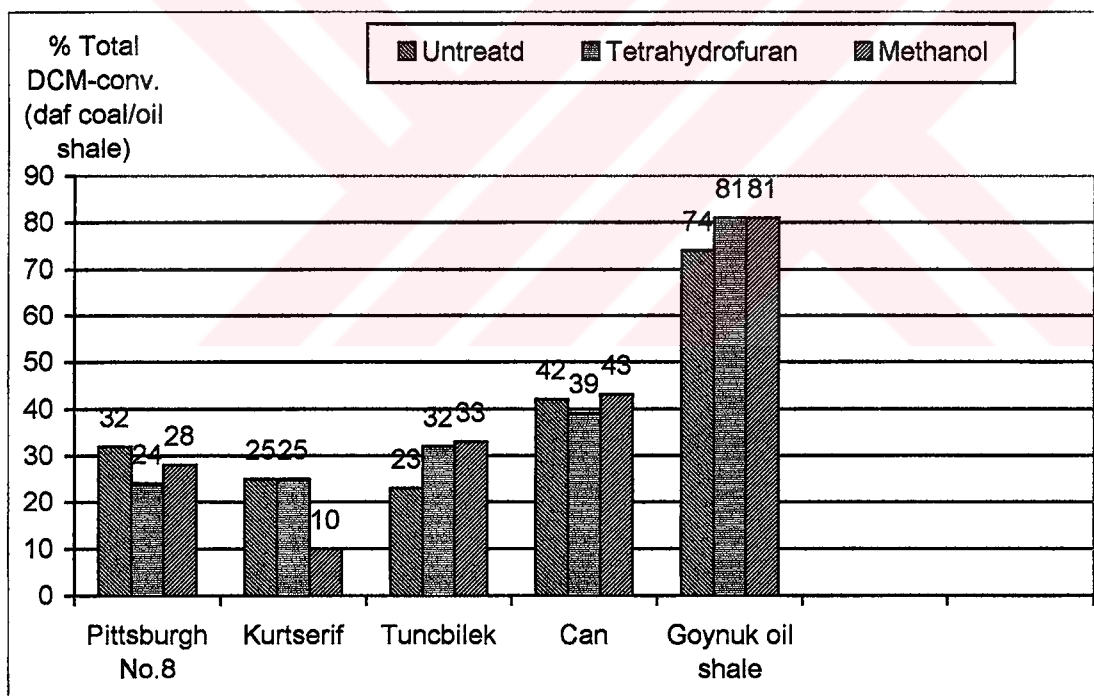


Figure 4.19. Effect of polar solvent treatment on the conversions in tetralin extraction (400 °C, 15 minutes).

4.6.4.2 Comparison of the effect of treatments on the amount of hydrogen transferred

The amount of hydrogen transferred at short contact time tetralin liquefaction at 400 °C is shown in Figure 4.20. The amounts of hydrogen transferred to the coals and oil shale after tetrahydrofuran and methanol-treatment varied depending on the solvent treatment and sample used. The hydrogen transfer for Pittsburgh No.8 was same (0.4 %) for methanol and tetrahydrofuran-treated coals and was almost similar to the untreated coal (0.6 %). As mentioned above, the DCM-conversions for both treatments decreased which was parallel with the decrease in hydrogen transfer amounts. For Kurtserif, the amount was 0.6 % and 0.5 % for untreated and tetrahydrofuran-treated samples, whereas for methanol-treated coal, it was 0.2 %. It seems that neither tetrahydrofuran nor methanol treatment are effective on Kurtserif which is supported by DCM-conversion results, as well.

For Tuncbilek, the hydrogen transfer increased from 1 % to 1.7 % and 1.5 % for tetrahydrofuran and methanol-treated samples, respectively. The DCM-conversion of Tuncbilek did not show any increase in thermolysis experiments, but in tetralin extraction there was an increase after both treatments. The reason for the increase was probably because of cleaving more bonds, as the transfer of hydrogen amount was different from the untreated coal. The hydrogen-transferred for Can were almost same for untreated and treated samples (1.8-2.0 %). In thermolysis, the DCM-conversion decreased after both treatments. In tetralin extraction, with the use of hydrogen-donor solvent, the disadvantage which occurred after polar solvent treatment disappeared as giving the same amount of DCM-conversion and hydrogen transfer amounts with untreated coal, but there was no further increase implying that there was a positive effect of treatment. For tetrahydrofuran and methanol-treated Goynuk oil shale, the hydrogen transferred was increased from 0.9 % to 1.4 % and 1.7 %, respectively. The DCM-conversions in thermolysis was almost same for untreated and treated shales. In tetralin extraction, there was an increase in yield, which was also parallel with the amount of hydrogen transferred. It seems that there is more bond cleavage after treatments.

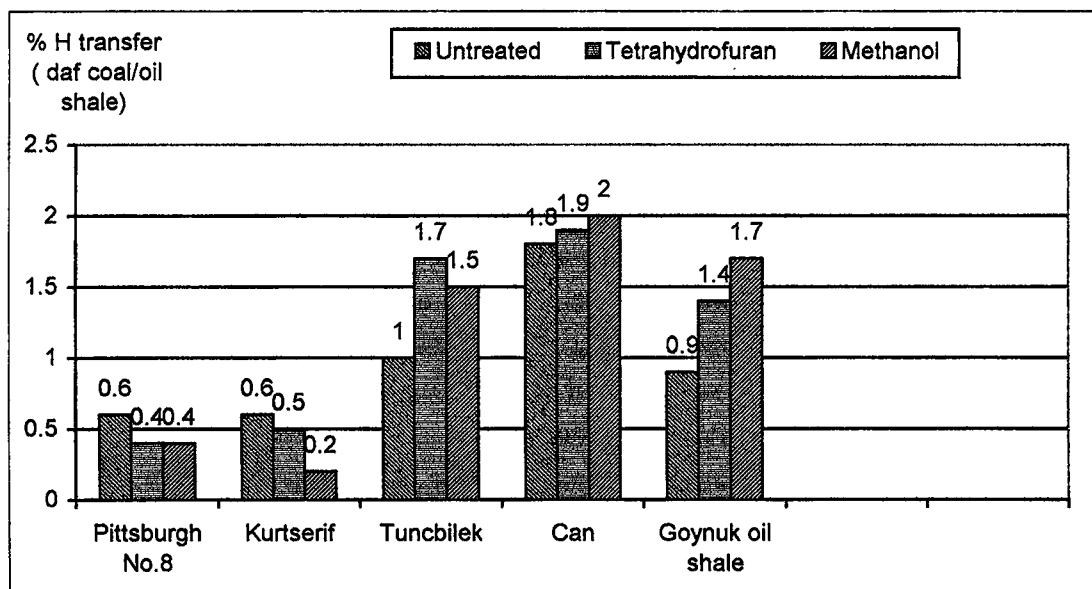


Figure 4.20. % hydrogen transferred at short contact time tetralin liquefaction at 400 °C.

4.7 Comparison of the Effects of Polar and Non-Polar Solvent Treatments on the Conversion of Coal and an Oil Shale

The results of the thermolysis and short contact time tetralin extraction experiments are given in Figures 4.21 and 4.22, and the hydrogen transfer amounts of coals and oil shale are given in Figure 4.23.

4.7.1 Effect of treatments on bituminous coals

For Pittsburgh No.8, chlorobenzene-treatment increased the DCM-conversions both in thermolysis (Figure 4.21) and tetralin extraction (Figure 4.22) experiments. However, tetrahydrofuran-treatment did not result with an increase in DCM-conversion whereas for methanol-treated sample somehow there was an increase like for chlorobenzene-treated coal. For polar solvent treated samples, the DCM-conversions were lower than untreated coal conversion in tetralin extraction. For Pittsburgh No.8, the amount of hydrogen transferred (Figure 4.23) for chlorobenzene-treated coal was almost similar with untreated coal. For tetrahydrofuran and methanol-treated samples, the amount of hydrogen transferred was lower than untreated and chlorobenzene-treated samples.

The DCM-conversions for Kurtserif was almost same for untreated and treated coals in thermolysis (Figure 4.21). In tetralin extraction, untreated, chlorobenzene and tetrahydrofuran-treated samples gave similar conversions (Figure 4.22). However, for the methanol-treated sample, DCM-conversions were same both in thermolysis and tetralin extraction experiments, implying that methanol was not an effective solvent for this coal. For Kurtserif, hydrogen transfer amounts for untreated, chlorobenzene and tetrahydrofuran-treated samples were same whereas for methanol it was lower (Figure 4.23).

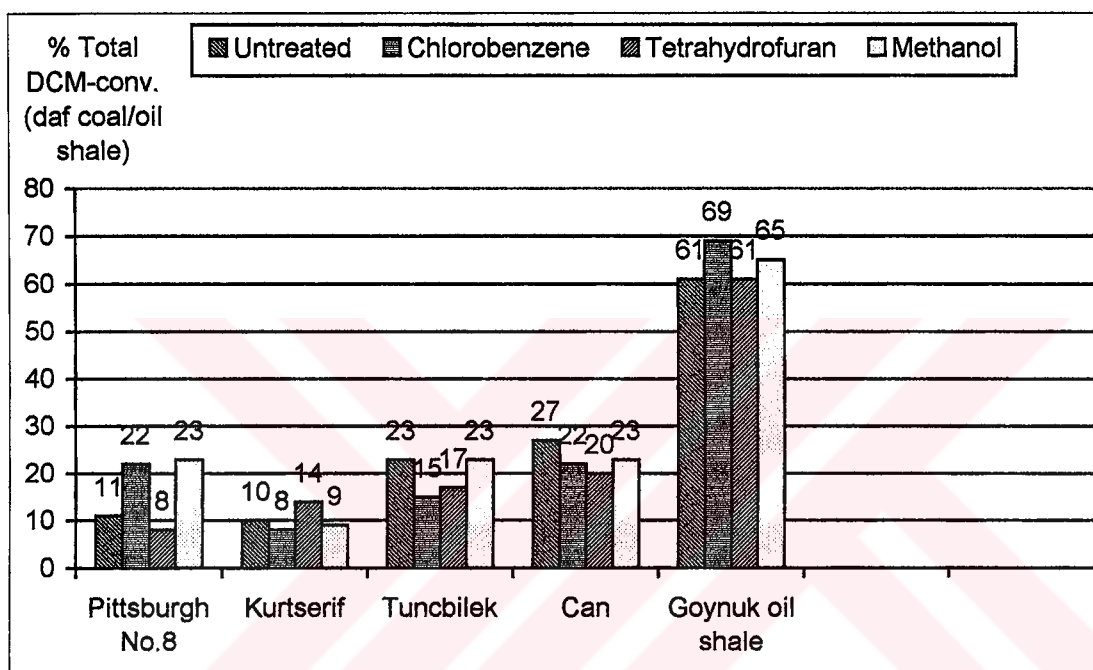


Figure 4.21. DCM-conversions of untreated and treated coals and oil shale in thermolysis experiments (400 °C).

It seems that chlorobenzene is an effective treatment solvent for Pittsburgh No.8 whereas not for Kurtserif. In order to find out the reason of the different behaviour of two bituminous coals, further tests were made and the results were given in Chapter 5. In addition, polar solvents like methanol and tetrahydrofuran were not good treatment solvents at least for these two coals and in these liquefaction conditions.

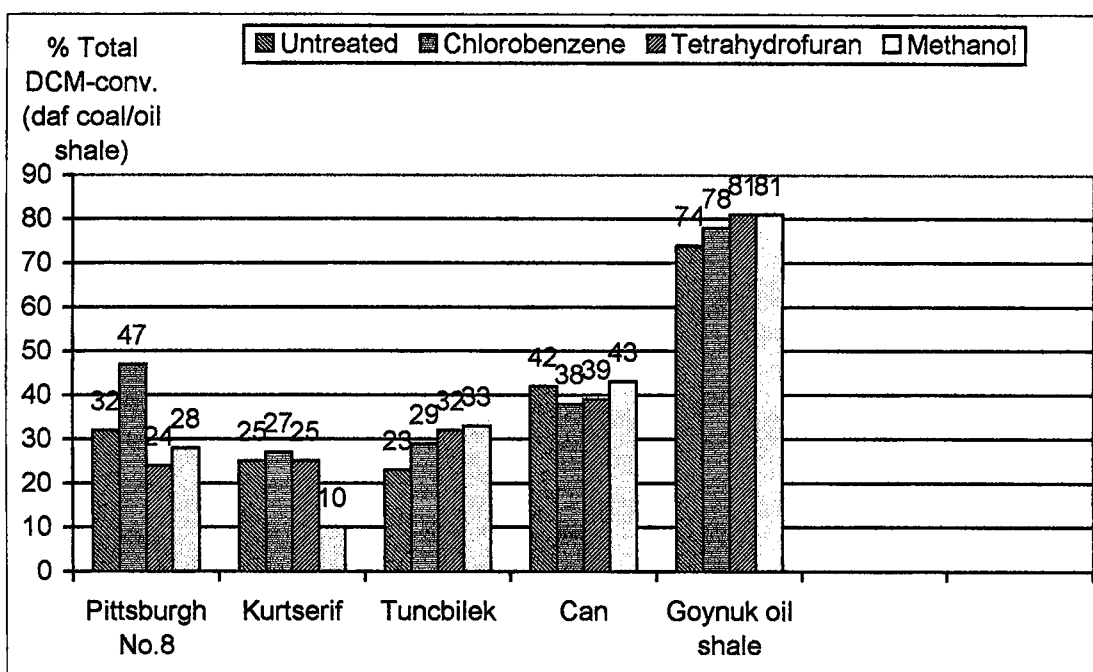


Figure 4.22. DCM-conversions of untreated and treated coals and oil shale in short contact time tetralin liquefaction (400 °C).

4.7.2 Effect of treatments on low-rank coals

As seen from Figure 4.21, chlorobenzene and tetrahydrofuran-treatment decreased the DCM-conversions for Tuncbilek and Can in thermolysis. Methanol-treated Tuncbilek gave similar conversion with untreated sample whereas for Can, there was a decrease.

In tetralin extraction (Figure 4.22), there was an increase in DCM-conversion of chlorobenzene, tetrahydrofuran and methanol-treated samples of Tuncbilek. For chlorobenzene-treated Tuncbilek, from hydrogen transfer amounts, it is noticed that the increase in DCM-conversion was probably because of conformational changes preventing char forming retrogressive reactions rather than cleaving more bonds. Because the hydrogen transfer amounts for untreated and treated coals were same. For tetrahydrofuran and methanol-treated samples, there was an increase in the amount of hydrogen transfer with small increase in DCM-conversions of treated coals with respect to untreated coal, probably because of more bond cleavage (Figure 4.23).

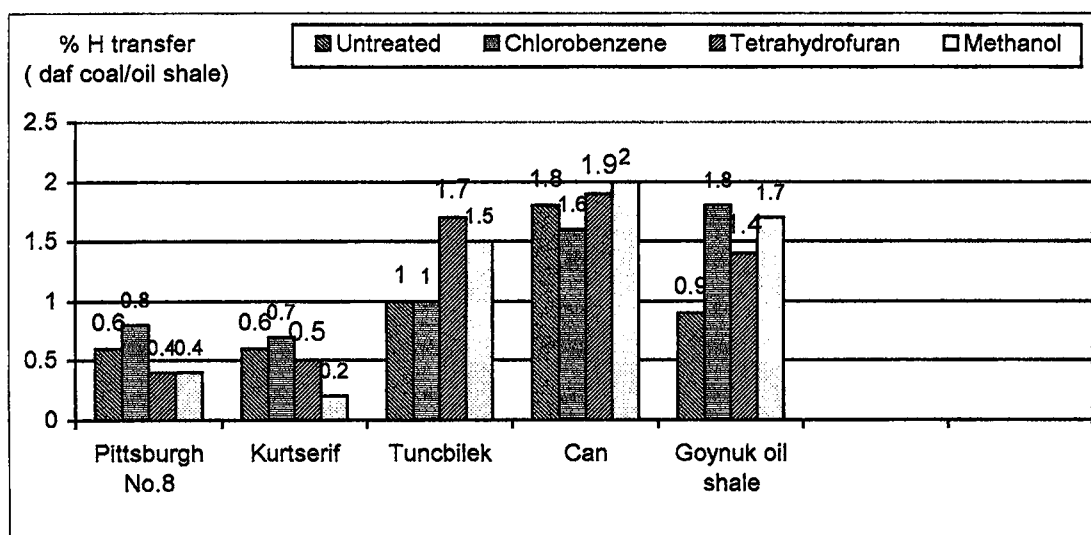


Figure 4.23. % hydrogen transfer amount in tetralin extraction for 15 minutes at 400 °C.

For Can, the DCM-conversions were almost same for untreated and treated coals in tetralin extraction (Figure 4.22). The hydrogen transfer was similar with untreated, tetrahydrofuran and methanol-treated samples whereas there was a decrease in chlorobenzene-treated coal (Figure 4.23).

These experimental results showed that chlorobenzene-treatment was slightly effective on Tuncbilek, which has seen from tetralin liquefaction experiments whereas in Can, conformational changes occurred which decreased the hydrogen transfer amount to the active sites. Polar solvents did not show significant change on Can, but for Tuncbilek there was a little increase in conversions.

4.7.3 Effect of treatments on an oil shale

As seen from Figures 4.21 and 4.22, the DCM-conversions were same for untreated and tetrahydrofuran-treated samples and there was an increase for chlorobenzene and methanol-treated samples in thermolysis. In tetralin extraction, there was an increase for both treated shales with respect to untreated shale. In tetralin extraction, the amount of hydrogen transferred was higher than the untreated oil shale for treated samples, probably because of more bond cleavage (Figure 4.23). The amount of hydrogen transferred for tetrahydrofuran-treated shale

was less than the other two treated shales. Polar and non-polar solvent treatments seemed to be not so effective for oil shale from liquefaction experiment results.

4.7.4 Discussion

Chlorobenzene treatment effected liquefaction behaviour under a number of regimes including extraction with both hydrogen-donor and non-donor solvents and dry (solvent-free) hydrogenation of bituminous coals as reported by Snape et al. [22,169-171].

The effect of chlorobenzene treatment can be different according to the coal rank and oil shale used [Section 4.3]. The results have indicated that the chlorobenzene treatment has improved total conversion to DCM-soluble products for Pittsburgh No.8 [22,23], but increases in the conversion for other bituminous coals and Goynuk (B) oil shale were smaller compared to Pittsburgh No.8. Point of Ayr, which is used in the earlier studies [22,23], showed a small increase in DCM-conversion, whereas for Karadon and Kurtserif, there were not significant change. The only oil shale used, Goynuk, did not have any significant increase in DCM-conversion. For the other two low-rank coals, Tuncbilek and Can, treatment reduced the DCM-conversions in thermolysis. However, for Tuncbilek DCM-conversion showed an increase in tetralin extraction, but Can did not. The decrease in DCM-conversions and hydrogen transfer amounts of low-rank coals reflect the differences in liquefaction with bituminous coals as mentioned in Section 4.3.2.

In the earlier studies [22,23,Section 4.5.1], toluene and chloroform treatments gave rise to similar changes like chlorobenzene-treatment in conversion during tetralin liquefaction and in thermolysis experiments, implying that the conformational changes are general for all non-polar solvents for bituminous coals. For Can, toluene and chloroform treatments ended up with similar decreases like chlorobenzene-treatment in conversion both in tetralin liquefaction and in thermolysis experiments, implying again that the effects of all non-polar solvents are general for lignite [Section 4.5.2].

Tetrahydrofuran and methanol treatments gave similar results for Goynuk (B) oil shale and lignites used [Section 4.6.2 and 4.6.3]. For Pittsburgh No.8, DCM-soluble

amount is decreased even being less than the untreated coal after polar-solvent treatments in tetralin liquefaction. The other bituminous coal, Kurtserif had similar trends after chlorobenzene and tetrahydrofuran-treatment, but methanol-treatment made no change in conversion in tetralin extraction at all [Section 4.6.1]. It seemed that tetrahydrofuran and methanol-treatment were not efficient agents for the coals and oil shale used under these liquefaction conditions used.

Although only a limited number of coals and oil shale have been investigated in this study and in earlier studies [22,23], the overall results have demonstrated that the effects of chlorobenzene, tetrahydrofuran and methanol treatment are extremely varied and depend both upon the coal and oil shale and liquefaction regime used.



5. CHARACTERISATION

5.1 Solvent Swelling

In this study, pyridine, tetrahydrofuran, methanol and tetralin swelling measurements have been conducted on the untreated, chlorobenzene, tetrahydrofuran and methanol-treated samples of the coals and oil shale (Table 5.1 to 5.7). For Can, toluene and chloroform-treated samples are subjected to swelling with pyridine, as well (Table 5.12).

Table 5.1. Swelling ratios for Can

	Swelling Solvents			
Treatment	Pyridine	Tetrahydrofuran	Methanol	Tetralin
Untreated	1.94	1.82	1.52	1.27
Chlorobenzene-treated	1.98	1.80	1.55	1.31
Tetrahydrofuran-treated	2.04	1.73	1.58	1.41
Methanol-treated	2.69	1.95	1.58	1.31

Table 5.2. Swelling ratios for Tuncbilek

	Swelling Solvents			
Treatment	Pyridine	Tetrahydrofuran	Methanol	Tetralin
Untreated	2.39	1.72	1.36	1.32
Chlorobenzene-treated	2.51	1.76	1.48	1.47
Tetrahydrofuran-treated	2.59	1.83	1.50	1.53
Methanol-treated	2.17	1.61	1.43	1.30

Table 5.3. Swelling ratios for Goynuk (B) oil shale

	Swelling Solvents			
Treatment	Pyridine	Tetrahydrofuran	Methanol	Tetralin
Untreated	1.54	1.53	1.34	1.30
Chlorobenzene-treated	1.72	1.65	1.31	1.44
Tetrahydrofuran-treated	1.92	1.50	1.31	1.37
Methanol-treated	1.63	1.55	1.21	1.32

Table 5.4. Swelling ratios for Karadon

	Swelling Solvents			
Treatment	Pyridine	Tetrahydrofuran	Methanol	Tetralin
Untreated	1.47	1.13	1.21	1.29
Chlorobenzene-treated	1.47	1.21	1.26	1.22
Tetrahydrofuran-treated	1.48	1.11	1.11	1.25

Table 5.5. Swelling ratios for Kurtserif

	Swelling Solvents			
Treatment	Pyridine	Tetrahydrofuran	Methanol	Tetralin
Untreated	1.57	1.21	1.23	1.20
Chlorobenzene-treated	1.58	1.42	1.11	1.20
Tetrahydrofuran-treated	1.58	1.23	1.27	1.21
Methanol-treated	1.31	1.22	1.13	1.36

Table 5.6. Swelling ratios for Pittsburgh No.8

	Swelling Solvents			
Treatment	Pyridine	Tetrahydrofuran	Methanol	Tetralin
Untreated	2.74 ^(a)	2.40	1.43	1.17
Chlorobenzene-treated	3.10 ^(a)	-	-	-
Tetrahydrofuran-treated	2.52	1.93	1.52	1.85
Methanol-treated	2.11	1.74	1.26	1.26

(a) [23].

Table 5.7. Swelling ratios for Point of Ayr

Treatment	Swelling Solvents			
	Pyridine	Tetrahydrofuran	Methanol	Tetralin
Untreated	2.75 ^(a)	1.63	1.29	1.06
Chlorobenzene-treated	2.88 ^(a)	-	-	-

(a) [23].

5.1.1 Effect of coal rank on solvent swelling

When contacted with a suitable solvent, coals will often absorb their own weight in solvent with a resulting volumetric expansion that can be as large as 100 %. The nature of this solvent/coal interaction is very solvent and coal specific, i.e. not all coals will swell and only certain solvents are effective [172,Section 2.3].

The level of the swelling for different solvents appears to be rank-dependent [17,55,Section 2.3], because of that it is necessary to carry out experiments on different rank of coals. In this study, as mentioned above, polar solvents, pyridine, tetrahydrofuran, methanol, and a non-polar solvent, tetralin have been used as swelling solvents.

5.1.1.1 Effect of coal rank on polar solvent swelling

The cross-links in coal occur as covalent linkages and hydrogen bonds. Polar basic swelling solvents like pyridine, tetrahydrofuran and methanol swell coal by disruption of these hydrogen bonds [77,173,Section 2.3]. For instance, during the swelling of low-rank coals with methanol, new hydrogen bondings are formed between methanol molecules and the oxygen functional groups involved in the hydrogen bondings in the original coal [75,174].

An increase in solvent basicity increases both the extent and rate of swelling of raw coal. Therefore, solvents of high basicity are recommended in order to achieve maximum swelling if extents of swelling are to be compared for coals of different rank. Pyridine has the appropriate balance of basicity and steric properties to swell the coal to its maximum extent [80,175,Section 2.3]. It is known to be a very strong hydrogen bond acceptor and is known to break coal-coal hydrogen bonds even at

room temperature [82,Section 2.3]. If pyridine selectivity breaks coal-coal interactions which serve as cross-links, the addition of small amounts of pyridine should enormously increase coal swelling because it will reduce the coals cross-linking [61]. Painter et. al. [176] used Illinois No.6 bituminous coal for pyridine swelling experiments. It was found that the fraction of coal-coal hydrogen bonds decreases upon the addition of just small amounts (10-20 %) of pyridine, while the fraction of coal segments hydrogen bonded to solvent increases.

Swelling is always greatest in pyridine, next in tetrahydrofuran. Pyridine breaks most, if not all, coal-coal hydrogen bonds, leaving a network hold together primarily by covalent bonds. Tetrahydrofuran is consistent with this since tetrahydrofuran is known to break only a portion of coal-coal hydrogen bonds [89]. Methanol is the least efficient swelling agent [18]. As seen from Tables 5.1 to 5.7, for untreated and treated coals and oil shales, pyridine swelling ratio is highest among the other polar solvents used.

Sanada and Honda [87] showed that in polar solvents, the swelling degree is almost constant over the range from 65 to 87 per cent (daf) carbon content and decreases suddenly with further increase of rank. The pyridine, tetrahydrofuran and methanol swelling results of this study (Table 5.8) also showed that there is a decrease after 87 per cent carbon content, but between 65 to 87 per cent carbon it was almost constant for tetrahydrofuran and methanol whereas not so much for pyridine.

The swelling ratio of all samples are highest in pyridine when compared to tetrahydrofuran and methanol swelling results, as it is a strong hydrogen bond acceptor as mentioned above. The swelling results of lignites, Can and Tuncbilek, 1.94 and 2.39, were lower than the results of bituminous coals, Point of Ayr and Pittsburgh No.8, which were 2.75 and 2.74. It is known that hydrogen bonds are major interactions in coals of lower rank [84].

Table 5.8. Swelling ratios and % C (daf basis) of untreated coals and oil shale

	%C (daf)	Pyridine	Tetrahydrofuran	Methanol	Tetralin
Can	68.77	1.94	1.82	1.52	1.27
Tuncbilek	75.70	2.39	1.72	1.36	1.32
Point of Ayr	74.24	2.75 ^(a)	1.63	1.29	1.06
Goynuik Oil Shale	75.97	1.54	1.53	1.34	1.30
Pittsburgh No.8	84.90	2.74 ^(a)	2.40	1.43	1.17
Karadon	88.46	1.47	1.13	1.21	1.29
Kurtserif	88.59	1.57	1.21	1.23	1.20

(a) [23].

In the lignite macromolecule may be covalent cross-links were dominate and because of that may be the swelling ratio for the lignite in pyridine is lower than for the bituminous coals [94]. Another reason may be because lignites contain more moisture in their structure, which decreases their swelling capacity, compared to bituminous coals [Section 2.6.4,17]. The swelling results for tetrahydrofuran were 1.82 and 1.72, and for methanol 1.52 and 1.36 for Can and Tuncbilek, respectively. For Pittsburgh No.8 and Point of Ayr, the swelling results for tetrahydrofuran were 2.40 and 1.63, and for methanol 1.29 and 1.43, respectively. For both lignite and bituminous coals, the swelling results were lower than the ones for pyridine, but showed a similar trend as in pyridine. Therefore, lignites give less swelling and extractability for methanol, tetrahydrofuran and pyridine than bituminous coals [15,17]. Lignites have more acidic functional groups than bituminous coals; therefore, swelling of lignite increases with increasing basicity of solvents (Table 5.8) [17].

When the hydrogen-bonding-accepting solvent, such as pyridine is used, the hydrogen bonding mainly occur between hydroxyl in coal and solvent. As the rise of coal rank, the oxygen and hydroxyl content decrease, which leads to less hydroxyl to form hydrogen bond with solvent [177]. Coal becomes steadily more close-packed up to the low volatile bituminous range suggesting that coal becomes more cross-linked. The cross-links are not hydrogen bonds at high ranks, so the bonds must be van der Waals type or covalent bonds [173]. The charge transfer

interaction is one of the important relatively strong interactions in bituminous coal, as well [19,84]. Some portions of charge-transfer complexes in the coal cannot be solvated with pyridine [84]. As a result of which the swelling ratio decreases with the increase of coal rank [177]. Honda and Sanada [87] also showed that there is a decrease after 87 per cent carbon content, and in this study, pyridine swelling ratios of Zonguldak region Karadon and Kurtserif bituminous coals, which have 88 per cent carbon content, decreased to 1.47 and 1.57, even less than lignite. The swelling results in tetrahydrofuran was 1.13 and 1.21, and in methanol 1.21 and 1.23, for Karadon and Kurtserif, respectively. The results show that pyridine is more effective than the two other polar solvents used, as well.

Yagmur et.al. [70] showed that the swelling ratio of lignite in a strong basic solvent like pyridine is higher than the swelling ratio of Zonguldak region bituminous coal. They indicated that lignites contain more carboxyl and hydroxyl groups than higher rank bituminous coals.

Goynuk (B) oil shale, which has 75.97 per cent carbon content, behaved different from coal having similar carbon content. Pyridine and tetrahydrofuran swelling results for oil shale were 1.54 and 1.53, showing that they had similar effects on oil shale whereas for methanol it was lower being 1.34. The behaviour is attributed to the differences in the organic structure of coal and oil shale, which is probably because of having not so much bond that can be disrupted with polar solvent swelling.

5.1.1.2 Effect of coal rank on non-polar solvent swelling

The interactive force between solvents and coal functional groups is very weak for the non-polar solvents. However, coals are not swollen measurably by non-polar solvents at room temperature. For instance, tetralin itself does not have the potential to swell the coal at room temperature, because the interactive force of tetralin with coal is much weaker than the strength of non-covalent bonding [75].

As seen from Tables 5.1 to 5.7 that for untreated and treated coals and oil shale, the swelling ratios were lower compared to the other polar swelling solvents. The

swelling ratios for untreated coals and oil shale (Table 5.8) changed between 1.06 to 1.32 showing that tetralin swelling at room temperature was rank independent.

5.1.2 Effect of solvent treatment to the solvent swelling ratio

The coals and oil shale are treated with chlorobenzene [Section 1.3 and 4.3, 61,82,89]. In addition to chlorobenzene treatment, polar solvents like tetrahydrofuran and methanol are used for treatment of coals and oil shale.

Tables 5.9, 5.10 and 5.11 show the swelling ratios of chlorobenzene, tetrahydrofuran and methanol-treated coals and oil shale, respectively. As seen, with an increase in swelling solvent polarity, the ability of a solvent to swell coal is also increased [Section 5.1.1.1,173].

Table 5.9. Swelling ratios and % C (daf basis) of chlorobenzene-treated coals and an oil shale

	%C (daf)	Pyridine	Tetrahydrofuran	Methanol	Tetralin
Can	68.77	1.98	1.80	1.55	1.31
Tuncbilek	75.70	2.51	1.76	1.48	1.47
Point of Ayr	74.24	2.88 ^(a)	-	-	-
Goynuk Oil Shale	75.97	1.72	1.65	1.31	1.44
Pittsburgh No.8	84.90	3.10 ^(a)	-	-	-
Karadon	88.46	1.47	1.21	1.26	1.22
Kurtserif	88.59	1.58	1.42	1.11	1.20

(a) [23].

Table 5.10. Swelling ratios and % C (daf basis) of tetrahydrofuran-treated coals and an oil shale

	%C (daf)	Pyridine	Tetrahydrofuran	Methanol	Tetralin
Can	68.77	2.04	1.73	1.58	1.41
Tuncbilek	75.70	2.59	1.83	1.50	1.53
Goynuk Oil Shale	75.97	1.92	1.50	1.31	1.37
Pittsburgh No.8	84.90	2.52	1.93	1.52	1.85
Karadon	88.46	1.48	1.11	1.11	1.25
Kurtserif	88.59	1.58	1.23	1.27	1.21

Table 5.11. Swelling ratios and % C (daf basis) of methanol-treated coals and oil shale

	%C (daf)	Pyridine	Tetrahydrofuran	Methanol	Tetralin
Can	68.77	2.69	1.95	1.58	1.31
Tuncbilek	75.70	2.17	1.61	1.43	1.30
Goyluk Oil Shale	75.97	1.63	1.55	1.21	1.32
Pittsburgh No.8	84.90	2.11	1.74	1.26	1.26
Kurtserif	88.59	1.31	1.22	1.13	1.36

As mentioned in Section 5.1.1.1, even after chlorobenzene, tetrahydrofuran and methanol treatments of coals, the swelling degree [Tables 5.9 to 5.11] in polar solvents is still constant over the range from 65 to 87 per cent (daf) carbon content and decreases suddenly with further increase of rank [87].

For Can (Table 5.1), chlorobenzene and tetrahydrofuran treatment seemed not to make any changes in the structure as the pyridine and tetrahydrofuran swelling ratios were almost same with untreated lignite. After methanol-treatment, the pyridine swelling ratio was increased from 1.94 to 2.69, respectively, probably meaning that more covalent or non-covalent bonds were broken. Tetrahydrofuran swelling results for untreated and chlorobenzene-treated lignites were same (1.82, 1.80) whereas there was decrease after tetrahydrofuran treatment (1.73) and an increase following methanol treatment (1.95). Methanol swelling ratios for untreated and chlorobenzene-treated lignites were 1.52 and 1.55, respectively. Methanol and tetrahydrofuran treated lignites had same results being 1.58. The only non-polar swelling solvent used, tetralin did not swell the untreated lignite much, the swelling ratio was 1.27, and for the other treated lignites, it was around 1.30-1.40. From these results, it is seen that the swelling ratios for chlorobenzene and tetrahydrofuran-treated Can was almost similar with untreated lignite except methanol-treatment. The pyridine and tetrahydrofuran swelling ratios of methanol-treated lignite were higher than untreated lignite meaning that there was a change in the structure of Can which ended up with an increase of swelling ratio.

The pyridine and tetrahydrofuran swelling ratio of untreated Tuncbilek (Table 5.2) were 2.39 and 1.72, respectively. Methanol and tetralin swelling ratios for untreated

lignite were almost same (1.36-1.32). Pyridine swelling ratio increased to 2.51 whereas there was no change for tetrahydrofuran ratio (1.76) for chlorobenzene-treated lignite when compared with untreated lignite. Methanol and tetralin swelling ratios of chlorobenzene-treated lignite showed same increase being 1.48, 1.47 and there was not so much change with respect to untreated lignite. For tetrahydrofuran-treated lignite, pyridine and tetrahydrofuran swelling ratios increased to 2.59 and 1.83, respectively; methanol and tetralin ratios increased to 1.50 and 1.53 but still almost same with chlorobenzene-treated lignite results. After methanol treatment, both pyridine, tetrahydrofuran, methanol and tetralin swelling ratios decreased to 2.17, 1.61, 1.43 and 1.30, respectively. For Tuncbilek, methanol-treated lignite swelling results were even lower than untreated lignite. Chlorobenzene and tetrahydrofuran-treated lignite swelling results were higher than untreated lignites showing that there were some structural changes in Tuncbilek.

The swelling results of untreated and treated Goynuk (B) oil shale are given at Table 5.3. For untreated shale, pyridine and tetrahydrofuran swellings gave similar results (1.54, 1.53), and methanol and tetralin swellings were similar as well (1.34, 1.30). Chlorobenzene-treated shale's swelling results were higher than untreated shale. For instance, pyridine and tetrahydrofuran swelling increased to 1.72 and 1.65, respectively. Tetralin swelling increased to 1.44, but methanol swelling was almost same with untreated shale. For tetrahydrofuran-treated shale, only pyridine swelling ratio increased to 1.92, the rest was almost similar with untreated shale. For methanol-treated shale, there was an increase in pyridine swelling ratio but less than the ones for chlorobenzene and tetrahydrofuran-treated shale swelling results. It seems that chlorobenzene and tetrahydrofuran treatments were little effective for Goynuk oil shale compared to the coals.

As mentioned in Section 5.1.1.1, after 87 per cent carbon content (daf) coal, the swelling ratio decreases suddenly for polar solvent and also for non-polar solvents [87]. For untreated Karadon (Table 5.4) and Kurtserif (Table 5.5), swelling results were very low, only the pyridine swelling ratio was high, being 1.47 and 1.57, respectively. When chlorobenzene and tetrahydrofuran treatment results were compared, it was seen that they were almost same with untreated coal. Kurtserif was also treated with methanol. After methanol treatment, even pyridine swelling

ratio was decreased to 1.31. These results also imply that for coals above 87 per cent carbon content, like Karadon and Kurtserif, chlorobenzene, tetrahydrofuran and methanol treatments do not make any changes in the structure of coal that ends up with an increase in swelling ratio.

Pittsburgh No.8 (Table 5.6) is used to compare the results of an earlier study [23]. Pyridine and tetrahydrofuran swelling results of untreated coal were 2.74 and 2.40. These results were highest swelling ratios among the other untreated coals used. With the other two swelling solvents, methanol and tetralin, Pittsburgh No.8 also gave very low swelling ratios. For chlorobenzene-treated coal, pyridine swelling result was 3.10, showing that chlorobenzene-treatment was very effective on Pittsburgh No.8. Tetrahydrofuran treatment did not give high swelling result like chlorobenzene treatment. After tetrahydrofuran-treatment, pyridine and tetrahydrofuran swelling ratios were decreased to 2.52 and 1.93, respectively. The swelling ratios decreased more after methanol treatment. For instance, pyridine and tetrahydrofuran swelling results decreased to 2.11 and 1.74, respectively. Methanol and tetralin swellings did not show any change either. These results indicated that except chlorobenzene-treatment, the other two treatments, tetrahydrofuran and methanol, probably altered the coal structure in return which decreased the swelling ratios. Point of Ayr (Table 5.7) is second coal used to make a comparison like with Pittsburgh No.8 [23]. Pyridine swelling result was high like Pittsburgh. Chlorobenzene treatment increased the pyridine swelling ratio from 2.75 to 2.88 showing that treatment effected the coal structure [23].

5.1.3 Effect of other non-polar solvent treatments to the swelling ratio

Can was treated with the other non-polar solvents and found that there was a similar behaviour with bituminous coals used in an earlier study [23]. Pyridine swelling ratios of untreated, chlorobenzene, toluene and chloroform-treated Pittsburgh No.8, Point of Ayr and Can are presented at Table 5.12.

Table 5.12. Pyridine swelling ratios of untreated, chlorobenzene, toluene and chloroform-treated Pittsburgh No.8, Point of Ayr and Can.

Treatment	Pittsburgh No.8 ^(a)	Point of Ayr ^(a)	Can
Untreated	2.74	2.75	1.94
Chlorobenzene-treated	3.10	2.88	1.98
Toluene-treated	3.29	2.95	2.16
Chloroform-treated	3.09	2.85	2.06

(a) [23].

Table 5.12 indicated that swelling ratios for Pittsburgh No.8 increased from 2.74 to 3.10, 3.29 and 3.09 upon chlorobenzene, toluene and chloroform treatment, respectively [23]. The pyridine swelling ratios for Point of Ayr, also increased upon solvent treatments, but to a lesser extent than for Pittsburgh No.8 [23]. There was not an increase in swelling of Can like the two other bituminous coals, but it was noticed that the effect of toluene and chloroform treatment to the swelling ratio were almost same as chlorobenzene treatment.

These results provide a further indicator that conformational changes induced by the non-polar solvents investigated are probably similar. In addition, the swelling results for each rank coal imply that non-polar solvent treatment of coal and conformational changes occurred are all rank-dependent.

5.1.4 Result of solvent swelling

While the exact nature of the chemical effect caused by swelling is not known, it is thought that weak linkages in the coal matrix, such as hydrogen bonds and polar complexes, are disrupted by the action of the solvent, creating more mobility for the coal matrix and freeing 'guest molecules' which are occluded in the coal structure [172, Section 2.3]. This necessarily implies the creation of void volumes within the coal [173].

It can be difficult for weak solvents such as methanol to break the associates and to penetrate the inside of coal, resulting in the low swelling ratio. A stronger solvent such as tetrahydrofuran or pyridine can disrupt some associates, extract much more

solubles, and decrease the cross-link density, resulting in an increase in the swelling ratio [178]. As seen from Tables 5.8 to 5.11, the swelling ratio increases in the order of tetralin < methanol < tetrahydrofuran < pyridine.

In addition, it is mentioned in Section 5.1.1.1 that, solvents of high basicity like pyridine, are recommended in order to achieve maximum swelling if extents of swelling are to be compared for coals of different rank [Tables 5.8 to 5.11]. The pyridine swelling ratios for untreated samples are in the order of: Karadon < Goynuk oil shale < Kurtserif < Can < Tuncbilek < Pittsburgh No.8. For chlorobenzene-treated samples the order is almost same with untreated samples being: Karadon < Kurtserif < Goynuk oil shale < Can < Tuncbilek < Pittsburgh No.8. For tetrahydrofuran-treated samples the order is: Karadon < Kurtserif < Goynuk oil shale < Can < Tuncbilek < Pittsburgh No.8. The order for methanol-treated samples is: Kurtserif < Goynuk oil shale < Pittsburgh No.8 < Tuncbilek < Can. The swelling ratios are in the same order for untreated, chlorobenzene and tetrahydrofuran-treated samples whereas for methanol-treated samples the order has changed. The swelling results showed that even after solvent treatments, Karadon and Kurtserif did not show an increase in swelling ratios. Goynuk oil shale showed a little change but not significant. Can and Tuncbilek showed an increase but not as much as Pittsburgh No.8.

The effect of treatment on the swelling ratio of Can is in the order: untreated < chlorobenzene < tetrahydrofuran < methanol. The order for Tuncbilek is: methanol < untreated < chlorobenzene < tetrahydrofuran. For Pittsburgh No.8, the order is: methanol < tetrahydrofuran < untreated < chlorobenzene. The order for Goynuk (B) oil shale is: untreated < methanol < chlorobenzene < tetrahydrofuran. For Karadon the order is: untreated = chlorobenzene = tetrahydrofuran, and for Kurtserif, the order is: methanol < untreated = chlorobenzene = tetrahydrofuran.

Swelling is a sensitive probe of the degree of cross-linking of the coal. Increased swelling indicates covalent bonds or non-covalent bonds have been broken, meaning low density of cross-links, and a swelling decrease indicates more bonds (covalent and/or non-covalent) have been formed, meaning high cross-link density [155,175,Section 2.3].

5.2 TGA Analysis of Untreated and Treated Coals and an Oil Shale

In order to have comparative information on thermal behaviour of untreated and treated coals and oil shale, most of the samples are subjected to thermogravimetric analysis under nitrogen atmosphere. Small quantities of the coal samples were heated in the pan of a microbalance and the weight loss was monitored continuously [179].

A representative TG/DTG scan on the untreated, chlorobenzene, tetrahydrofuran and methanol-treated Tuncbilek are shown in Figure A.1 a, b, c and d, respectively.

Table 5.13. TGA of untreated, chlorobenzene, tetrahydrofuran and methanol-treated Tuncbilek.

Treatment	1 st weight loss ends		2 nd weight loss beginning		Maximum weight loss		Total weight loss		
	Time (min.)	Temp (°C)	Time (min.)	Temp (°C)	Time (min.)	Temp (°C)	% weight	Time (min.)	Temp (°C)
Untreated	4	103	32	103	40	464	66.12	94	700
Chlorobenzene-treated	5	109	5 (ii) 33	109 115	40	488	79.07	94	700
Tetrahydrofuran-treated	5	103	5 (ii) 34	103 166	40	493	39.48	94	700
Methanol-treated	5	105	5 (ii) 34	105 177	40	511	45.13	94	700

As seen from Table 5.13, the first weight loss is around 103-110 °C, represents the moisture loss in the samples. After that except for untreated sample, the weight loss continues slowly upto around 115, 166, and 177 °C for chlorobenzene, tetrahydrofuran and methanol-treated samples, respectively. For untreated lignite, the weight loss begins around 103 °C and reaches a maximum at 464 °C and upto 700 °C a rather slow drop in loss rate follows. Chlorobenzene, tetrahydrofuran and methanol-treated lignites present maximum weight loss at 488, 493, 511 °C, respectively. At the end of the TGA run 66.12, 79.07, 39.48 and 45.13 % of the weight of untreated, chlorobenzene, tetrahydrofuran and methanol-treated lignites are observed to be lost. The weight losses after moisture loss, are in a slow rate for untreated and chlorobenzene-treated samples whereas for tetrahydrofuran and methanol-treated samples, it is more rapid. Total weight loss is almost similar for chlorobenzene-treated coal with untreated lignite. The weight losses for

tetrahydrofuran and methanol-treated lignites are similar with each other but less than the two others. The reason for chlorobenzene-treated lignite to be similar with untreated lignite, is may be chlorobenzene relaxes the coal structure without more specific change.

Figure A.2 a, b and c presents the TG/DTG scan on the untreated, tetrahydrofuran and methanol-treated Pittsburgh No.8. TG could not be taken for chlorobenzene-treated coal because of sample shortage.

Table 5.14. TGA of untreated, tetrahydrofuran and methanol-treated Pittsburgh No.8.

Treatment	1 st weight loss ends		2 nd weight loss beginning		Maximum weight loss		Total weight loss		
	Time (min.)	Temp (°C)	Time (min.)	Temp (°C)	Time (min.)	Temp (°C)	% weight	Time (min.)	Temp (°C)
Untreated	4	118	35	223	40	466	68.90	94	700
Tetrahydrofuran-treated	4	105	(i) 5	105	(i) 35	216	39.72	94	700
			(ii) 35	216	(ii) 40	525			
Methanol-treated	4	105	35	230	40	472	59.31	94	700

The first weight loss at around 105-110 °C represents the moisture in Pittsburgh No.8. The weight loss increases around 220 °C and reaches a maximum at around 466, 472 and 525 °C for untreated, methanol and tetrahydrofuran-treated coals, respectively. When the temperature reaches up to 700 °C, the weight losses for untreated, methanol and tetrahydrofuran-treated samples are 68.90 %, 59.31 % and 39.72 %, respectively. The weight loss rate for untreated sample after 220 °C is rather slow whereas for methanol and tetrahydrofuran-treated sample is more quick. The total weight loss percentage amounts for methanol and tetrahydrofuran-treated samples are lower than the untreated coal.

Figure A.3 a, b and c present the TG/DTG scan on the chlorobenzene, tetrahydrofuran and methanol-treated Kurtserif.

Table 5.15. TGA of chlorobenzene, tetrahydrofuran and methanol-treated Kurtserif.

Treatment	1 st weight loss ends		2 nd weight loss beginning		Maximum weight loss		Total weight loss		
	Time (min.)	Temp (°C)	Time (min.)	Temp (°C)	Time (min.)	Temp (°C)	% weight	Time (min.)	Temp (°C)
Chlorobenzene-treated	5	112	34	138	(i) 36 (ii) 40	269 492	55.67	94	700
Tetrahydrofuran-treated	4	109	33	161	40	585	29.99	94	700
Methanol-treated	4	103	34	178	40	499	34.56	94	700

As seen from Figure A.3 a, b and c, there is a weight loss around 100-110 °C, again which is moisture loss. The weight loss after moisture removal begins around 140-180 °C and reaches a maximum at around 500-600 °C for all the treated coals. The weight loss rate is rather slow for chlorobenzene-treated coal compared to polar solvent treated coals. The total weight loss percent are 55.67, 29.99 and 34.56 % for chlorobenzene, tetrahydrofuran and methanol-treated coals, respectively. Polar solvents, tetrahydrofuran and methanol-treated coals total weight loss percent are lower than chlorobenzene-treated coal.

The TG/DTA results for Goynuk(B) oil shale are given at Figure A.4 a, b, c and d for untreated, chlorobenzene, tetrahydrofuran and methanol-treated shale.

Table 5.16. TGA of untreated, chlorobenzene, tetrahydrofuran and methanol-treated Goynuk oil shale.

Treatment	1 st weight loss ends		2 nd weight loss beginning		Maximum weight loss		Total weight loss		
	Time (min.)	Temp (°C)	Time (min.)	Temp (°C)	Time (min.)	Temp (°C)	% weight	Time (min.)	Temp (°C)
Untreated	4	103	35	224	39	436	75.69	64	700
Chlorobenzene-treated	4	103	35	235	39	442	76.62	64	700
Tetrahydrofuran-treated	4	109	(i) 4 (ii) 33	109 155	40	488	62.68	64	700
Methanol-treated	4	109	34	201	39	580	79.02	64	700

The moisture loss ends up around 100 – 110 °C for all treated and untreated shale. At 220 – 235 °C weight loss began, reaching a maximum at 430 – 580 °C and ends at 700 °C. The total weight loss percent are 75.69, 76.62, 62.68 and 79.02 % for

untreated, chlorobenzene, tetrahydrofuran and methanol-treated shales, respectively. Total weight loss percent except tetrahydrofuran-treated sample are all the same. Chlorobenzene did not show any particular effect.

As mentioned above, Tables 5.13, 5.14, 5.15 and 5.16 show some of the values of certain points on the TG/DTG scans of Tuncbilek, Pittsburgh No.8 and Kurtserif coals, and Goynuk (B) oil shale. From these Tables, it is noticed that the effect of treatments in general have ended up with some similarities. There was not substantial change in the first weight loss temperature which was the loss of moisture whereas second weight loss beginning temperature has changed after treatments. For instance, for untreated Tuncbilek, volatile matter loss beginning temperature was 103 °C, but for the chlorobenzene, tetrahydrofuran and methanol-treated lignite, it was 115, 166 and 177 °C, respectively. It is also noticed that untreated and non-polar solvent treated samples' volatile matter loss beginning temperatures were almost similar whereas after polar solvent treatment there was an increase in the temperature. A similar trend has been seen in maximum weight loss temperature, as well. For example, Goynuk oil shale's maximum weight loss temperatures were 436, 442, 488 and 580 °C for untreated, chlorobenzene, tetrahydrofuran and methanol-treated shale, respectively. There was an increase in the maximum weight loss temperature, and the increase was more in the case of polar solvent treatments. In addition, there was also another similarity in the total weight loss percent of coals and oil shale. For Tuncbilek, the total weight loss percents were 66.12, 79.07, 39.48 and 45.13 % for untreated, chlorobenzene, tetrahydrofuran and methanol-treated lignites, respectively. The values for untreated and chlorobenzene-treated lignites were close to each other. However, the values for polar solvent-treated samples decreased with respect to untreated and chlorobenzene-treated samples. The similar behaviour was seen in Pittsburgh No.8 and Kurtserif. For Pittsburgh, the percent for untreated coal was 68.90 % whereas for tetrahydrofuran and methanol-treated coals the percents were 39.72 and 59.31 %, respectively. For Kurtserif, the amount for chlorobenzene-treated coal was 55.67 % whereas for tetrahydrofuran and methanol-treated coal, the percents

were 29.99 and 34.56 %, respectively. Total weight loss percents were 75.69, 76.62, 62.68 and 79.02 % for untreated, chlorobenzene, tetrahydrofuran and methanol-treated Goynuk oil shale, respectively.

It is thought that the reason for the increase in temperature of treated samples and the decrease in the total weight lost percent is because of different effect of solvents. As mentioned in Section 1.3, chlorobenzene has the advantage of extracting virtually no organic matter from coals and it does not disrupt hydrogen bonds significantly [22]. On the other hand, polar solvents remove some of the organic matter from coal and hydrogen bonds are being disrupted [22]. As chlorobenzene relaxes the coal/oil shale structure with less effect to the bonds with respect to polar solvents, it is thought that in the case of non-polar solvent treatment, there is not much change in the temperature and total weight loss percent. However, after polar solvent treatments, as they effect the hydrogen bonding, probably there is an increase in the cross-links which ends up with an increase in the temperature and a decrease in the total weight loss percent. The newly formed cross-links probably keeps the structure packed up closely to each other which decreases the total weight loss percent. It is thought that in order to break down these cross-links high temperatures are needed which ends up with an increase in the temperature.

Goynuk oil shale had different total weight loss percent when compared with the results of the coals. Although there was an increase in temperature as mentioned before, the total weight loss percents for untreated and polar solvent-treated Goynuk oil shale were similar. It is thought that polar solvent treatment ends up with a new arrangement of bonds in the structure, which needs high temperatures to break, but does not remove organic matter as in the case of coals.

5.3 Electron Microscopic Analysis of Untreated and Treated Coals and an Oil Shale

In order to obtain information about the effect of solvent treatment on coal and oil shale structure, untreated, chlorobenzene and tetrahydrofuran-treated samples are subjected to SEM analysis. Methanol-treated samples are not used because it is

thought that the treatment effect of methanol on coal is weaker than tetrahydrofuran as mentioned in Section 5.1.1.1. The electron micrograms of Tuncbilek, Kurtserif and Pittsburgh No.8, and Goynuk oil shale are given in Figures B.1, B.2, B.3, and B.4 respectively.

Figure B.1 presents the SEM analysis of untreated, chlorobenzene and tetrahydrofuran-treated Tuncbilek. Untreated coal's surface seems to be smooth and less porous than treated ones.

SEM result of Kurtserif is shown in Figure B.2. The untreated coal surface is rough and seems not so porous. After chlorobenzene and tetrahydrofuran treatment, the surface becomes more smooth. Figure B.3 presents the results of Pittsburgh No.8. Untreated coal surface seems to be smooth whereas after chlorobenzene-treatment it becomes more rough and porous. Tetrahydrofuran-treatment does not seem to effect the coal, as seen from the surface.

Untreated, chlorobenzene and tetrahydrofuran-treated Goynuk oil shale have almost similar surface structure (Figure B.4). Both of them are porous and rough.

5.4 Discussion

In order to find out the effect of polar and non-polar solvent treatment on the coal and oil shale, swelling tests, TGA and SEM analysis were made on the untreated and treated coals and oil shale.

In the swelling experiments, it was noticed that if tetralin, methanol, tetrahydrofuran and pyridine were used as a swelling solvent for untreated and treated coals and oil shale, the swelling ratio increased in the order of tetralin < methanol < tetrahydrofuran < pyridine. Tetralin, which was non-polar, did not swell the coal and oil shale at room temperature as mentioned in Section 5.1.1.2.

In addition, the pyridine, tetrahydrofuran and methanol swelling results of untreated Can, Tuncbilek and Pittsburgh No.8 were almost constant in the range from 65 to 87 per cent (daf) carbon content, and with further increases in the carbon content (over 87 percent (daf)), the swelling values of Karadon and Kurtserif decreased (Table

5.8). After chlorobenzene, tetrahydrofuran and methanol-treatments, the swelling behaviour was almost same with untreated coals in the range mentioned above when pyridine, tetrahydrofuran and methanol are used as a swelling solvents, and decreases suddenly with further increase of rank (Tables 5.9, 5.10 and 5.11). Sanada and Honda [87] also reported that in polar solvents, the swelling degree is almost constant over the range from 65 to 87 percent (daf) carbon content and decrease suddenly with further increase of rank.

As mentioned in Section 5.1.1.1, pyridine had the appropriate solvent to swell the coal to its maximum extent if a comparison has to be made between different rank coals. When pyridine swelling results are considered :

- The swelling ratios for chlorobenzene and tetrahydrofuran-treated Can (Table 5.1) were slightly higher with respect to untreated coal except methanol-treatment. The pyridine swelling ratio of methanol-treated lignite was higher than untreated lignite probably because more bonds were broken as mentioned in Section 5.1.4.
- For Tuncbilek (Table 5.2), chlorobenzene and tetrahydrofuran-treated lignite swelling results were a little higher than untreated lignite except methanol-treated one.
- The swelling ratios of chlorobenzene and tetrahydrofuran-treated Goynuk oil shale (Table 5.3) were higher than untreated shale whereas for methanol-treated shale, there was an increase but not so significant.
- For Karadon and Kurtserif (Tables 5.4 and 5.5), the swelling ratios of untreated, chlorobenzene and tetrahydrofuran-treated coal were almost same, meaning that treatments did not have an effect on coal structure. For methanol-treated Kurtserif, there was a slight decrease in the swelling ratio may be because more bonds were formed [Section 5.1.4]. These results also implied that for coals above 87 percent carbon content, solvent treatment did not make changes in the structure of coal that ended up with an increase in the swelling ratio.

Pittsburgh No.8 and Point of Ayr from an earlier study [23] and Can were treated with chlorobenzene, toluene and chloroform, and swollen by pyridine. Pittsburgh No.8 and Point of Ayr showed similar increases in swelling ratio with respect to untreated coals [23]. In this study, Can gave similar swelling ratios both for untreated and treated samples. These results together with the earlier results from earlier study [23] provided a further indicator that conformational changes induced by the non-polar solvents investigated were probably similar. In addition, the swelling results for each rank coal implied that non-polar solvent treatment of coal and conformational changes occurred were all rank-dependent [Section 5.1.3].

The TGA results of Tuncbilek, Pittsburgh No.8 and Kurtserif coals, and Goynuk (B) oil shale [Section 5.2, Appendix A] showed almost similar trends after chlorobenzene, tetrahydrofuran and methanol-treatments. There was not substantial change in the first weight loss temperature which was the loss of moisture whereas second weight loss beginning temperature has changed after treatments. In addition, untreated and non-polar solvent treated samples' volatile matter loss beginning and maximum weight loss temperatures were almost similar for untreated and non-polar solvent treated samples whereas after polar solvent treatment there was an increase in the temperature. There was also another similarity in the total weight loss percent of coals and oil shale. The total weight loss percent were almost similar for untreated and non-polar solvent treated samples, and for polar solvent-treated samples the values decreased. It is thought that the reason for the increase in temperature of treated samples and the decrease in the total weight lost percent was because of different effect of solvents. As mentioned in Section 1.3, chlorobenzene has the advantage of extracting virtually no organic matter from coals and it does not disrupt hydrogen bonds significantly [22]. On the other hand, polar solvents remove some of the organic matter from coals and hydrogen bonds are being disrupted [22]. As chlorobenzene relaxes the coal/oil shale structure with less effect to the bonds with respect to polar solvents, it is thought that in the case of non-polar solvent treatment, there was not much change in the temperature and total weight loss percent. However, after polar solvent treatments, as they effected the hydrogen bonding, probably there was an increase in the cross-links which ended up with an increase in the temperature and a decrease in the total weight loss percent. The newly formed cross-links probably kept the structure packed up

closely to each other which decreased the total weight loss percent. It is thought that in order to break down these cross-links high temperatures were needed which ended up with an increase in the temperature. Goynuk oil shale had different total weight loss percent when compared with the results of the coals. Although there was an increase in temperature as mentioned in Section 5.2, the total weight loss percent for untreated, non-polar and polar solvent-treated Goynuk oil shale were similar. It is thought that polar solvent treatment ended up with a new arrangement of bonds in the structure which needed high temperatures to break, but did not remove organic matter as in the case of coals.

The SEM analysis of coals and oil shale [Section 5.3, Appendix B] gave information only about their surface view. Goynuk oil shale had similar surface structure after solvent treatments with untreated shale. Untreated Tuncbilek's surface seemed to be smooth and less porous than treated ones. Chlorobenzene and tetrahydrofuran-treated Kurtserif surface became smoother with respect to untreated coal. The only coal, which seemed to have changes on the surface was Pittsburgh No.8. Tetrahydrofuran-treatment did not show any change as seen from outer surface with respect to chlorobenzene-treated coal. After chlorobenzene-treatment, it seemed that the surface became more rough and porous.

6. CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

From this investigation, the effects of non-polar and polar solvent treatments on liquefaction behaviour of Pittsburgh No.8, Karadon, Kurtserif, Can and Tuncbilek coals, and Goynuk (B) oil shale, the following conclusions can be made.

1. The effect of chlorobenzene treatment can be different according to the coal rank and oil shale used. Chlorobenzene-treatment ended up with an increase in oil (DCM) yield for Pittsburgh No.8 bituminous coal whereas for Kurtserif, no significant increase has occurred in the yield of liquefaction experiments. For Can and Tuncbilek lignites, treatment decreased or ended up with little increase in the oil (DCM) yield. Chlorobenzene-treatment did not show significant effect on the oil yield of Goynuk oil shale.
2. Tetrahydrofuran and methanol treatments gave similar oil (DCM) yields for Goynuk oil shale, Can and Tuncbilek with respect to chlorobenzene-treated counterparts. For Pittsburgh No.8 bituminous coal, oil yields decreased whereas for Kurtserif, polar solvents did not effect the oil yields.
3. The pyridine swelling ratios of chlorobenzene and tetrahydrofuran-treated Can and Tuncbilek did not show too much change with respect to untreated coals. But, after methanol-treatment lignites showed either a decrease or an increase showing the differences in their composition. For chlorobenzene and tetrahydrofuran-treated Goynuk oil shale, the swelling ratios increased with respect to untreated sample whereas for methanol-treated sample, there was only a slight increase. Pittsburgh No.8, which has 84.90 per cent (daf) carbon content, showed significant swelling when treated with chlorobenzene. Kurtserif, which has 88.59 per cent (daf) carbon content, there was no

swelling after chlorobenzene-treatment. After tetrahydrofuran and methanol-treatments there was a decrease in the swelling ratios of Pittsburgh No.8 and for Kurtserif there was no swelling either. The swelling results showed that for Pittsburgh No.8, which has less than 87 per cent (daf) carbon content, the treatments ended up with an increase or decrease in the swelling ratio whereas for Kurtserif, which has over this value, showed no significant change in the swelling ratio.

4. Pretreatments with toluene and chloroform ended up with similar decreases in conversion for lignite during thermolysis and short contact time tetralin liquefaction as for chlorobenzene. In addition, pyridine swelling measurements have confirmed that the changes brought about by solvent treatment are similar for chlorobenzene, toluene and chloroform for lignite. This implies that the conformational changes induced by the three relatively non-polar solvents are similar and are not dependent on the temperature for the solvent boiling range investigated.
5. The TGA results of Tuncbilek, Pittsburgh No.8 and Kurtserif coals, and Goynuk (B) oil shale showed almost similar trends after chlorobenzene, tetrahydrofuran and methanol-treatments. Untreated and non-polar solvent treated samples' weight loss beginning and maximum weight loss temperatures were almost similar whereas after polar solvent treatment there was an increase in the temperature. In addition, the total weight loss percent were almost similar for untreated and non-polar solvent treated samples, and for polar solvent-treated samples the values decreased. As chlorobenzene relaxes the coal/oil shale structure with less effect to the bonds with respect to polar solvents, it is thought that in the case of non-polar solvent treatment, there was not much change in the temperature and total weight loss percent. However, after polar solvent treatments, as they effected the hydrogen bonding, probably there was an increase in the cross-links, which ended up with an increase in the temperature and a decrease in the total weight loss percent.

6. The SEM analysis of Tuncbilek and Kurtserif coals, and Goynuk (B) oil shale, showed that there was not significant change after treatments. The only coal, which seemed to have changes on the surface was Pittsburgh No.8. After chlorobenzene-treatment, it seemed that the surface became more rough and porous.

6.2 Future Work

It is necessary to ascertain the effect of polar and non-polar solvent treatments on a wider range of coals and oil shale in order to provide a broader picture of the conformational changes induced. In addition, structural analysis to determine the effect of treatments on coal and oil shale still continues. Furthermore, to determine the effect of water and drying on low-rank coals, research is underway.



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APPENDIX A. TGA GRAPHS

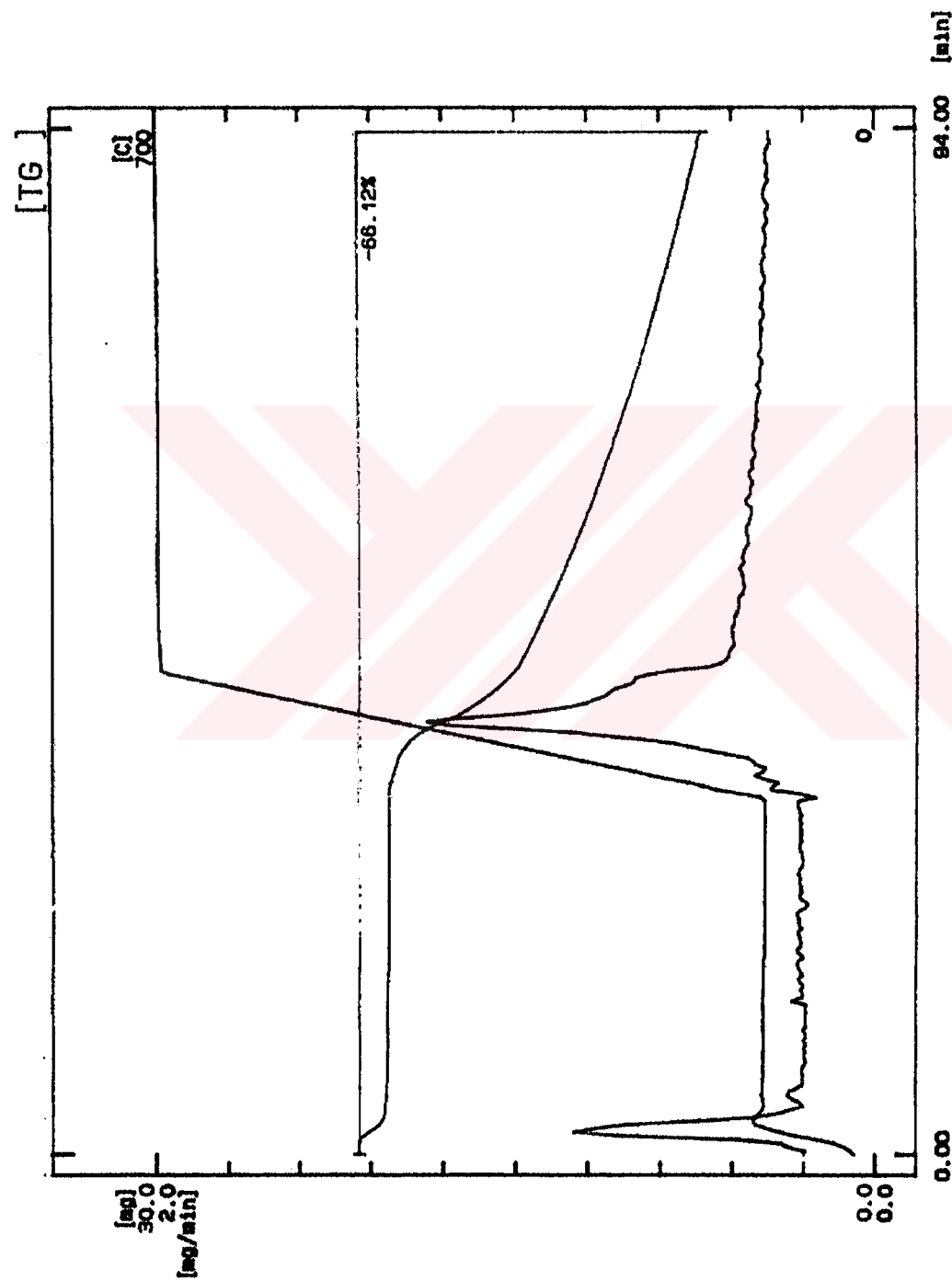


Figure A.1a. TG/DTG scan of untreated Tuncbilek.

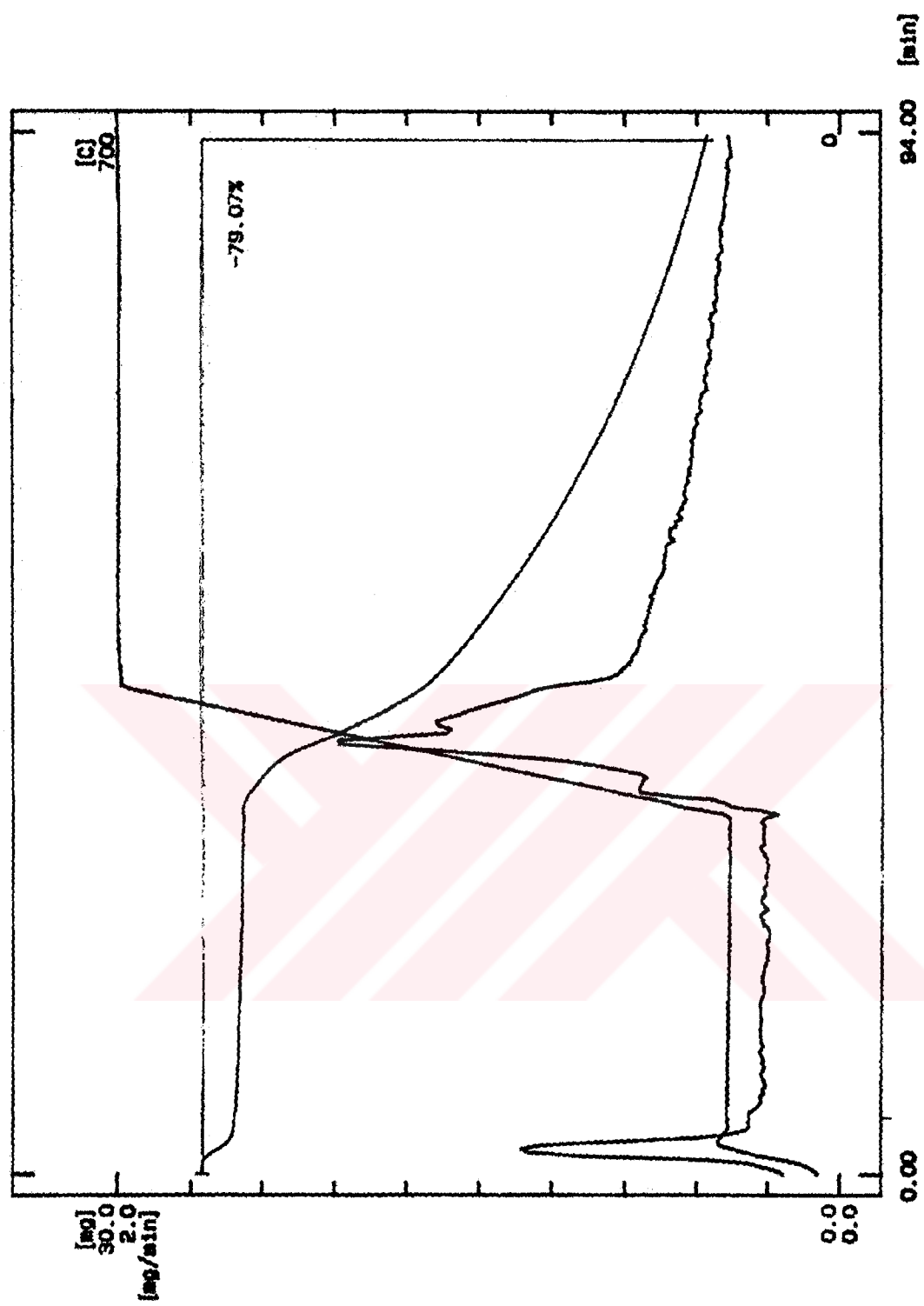


Figure A.1b. TG/DTG scan of chlorobenzene-treated Tuncbilek.

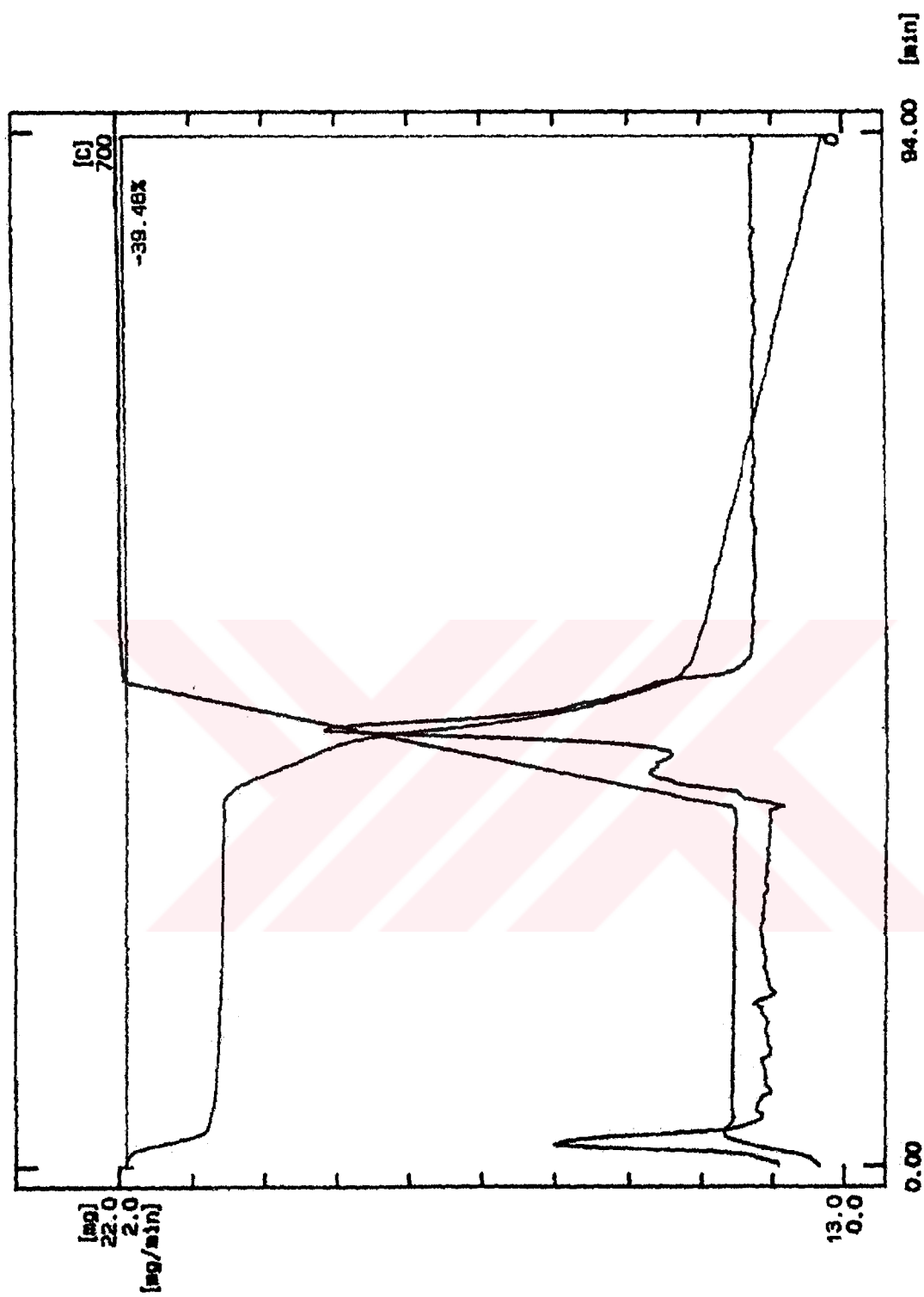


Figure A.1c. TG/DTG scan of tetrahydrofuran-treated Tuncbilek.

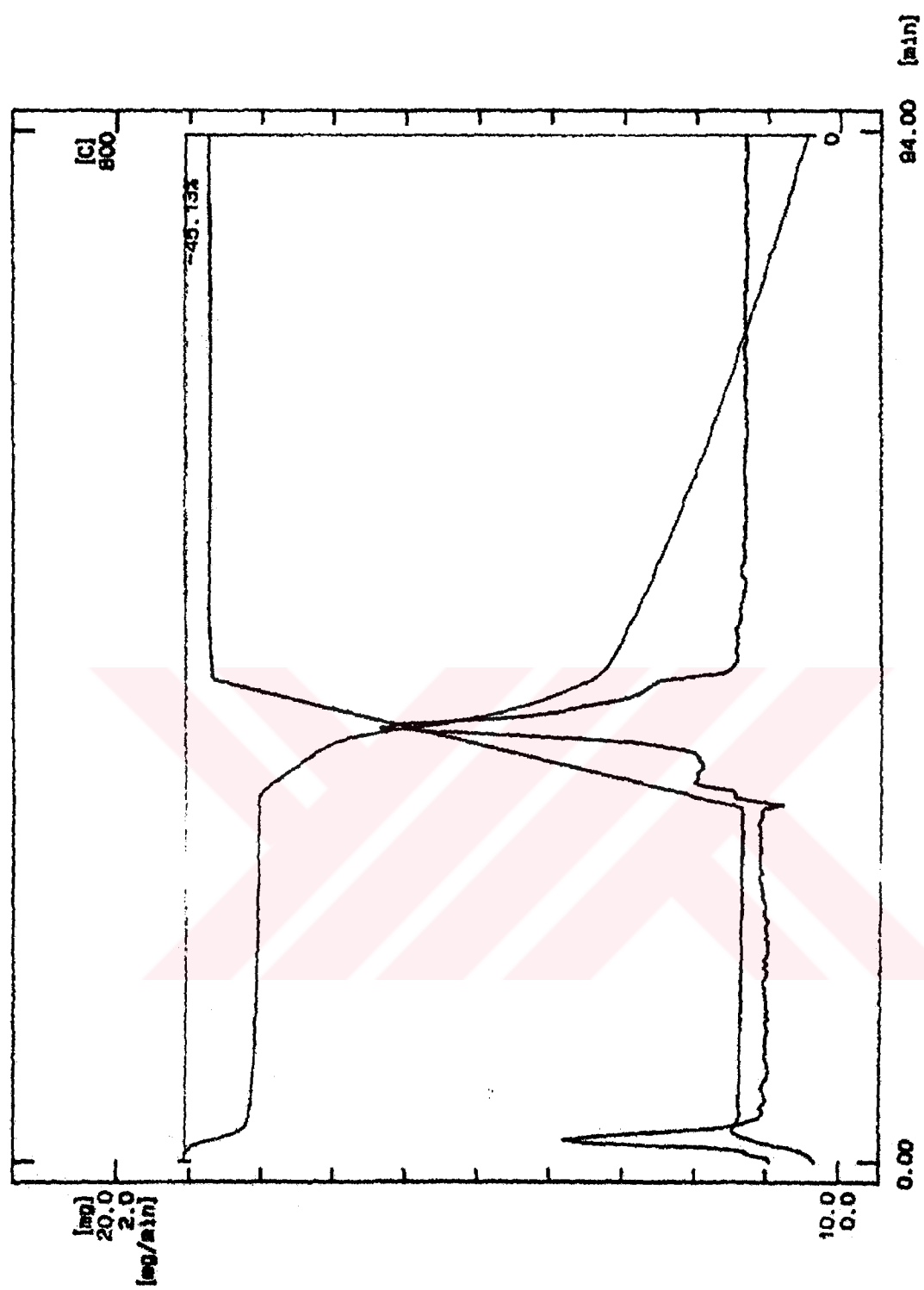


Figure A.1d. TG/DTG scan of methanol-treated Tuncbilek.

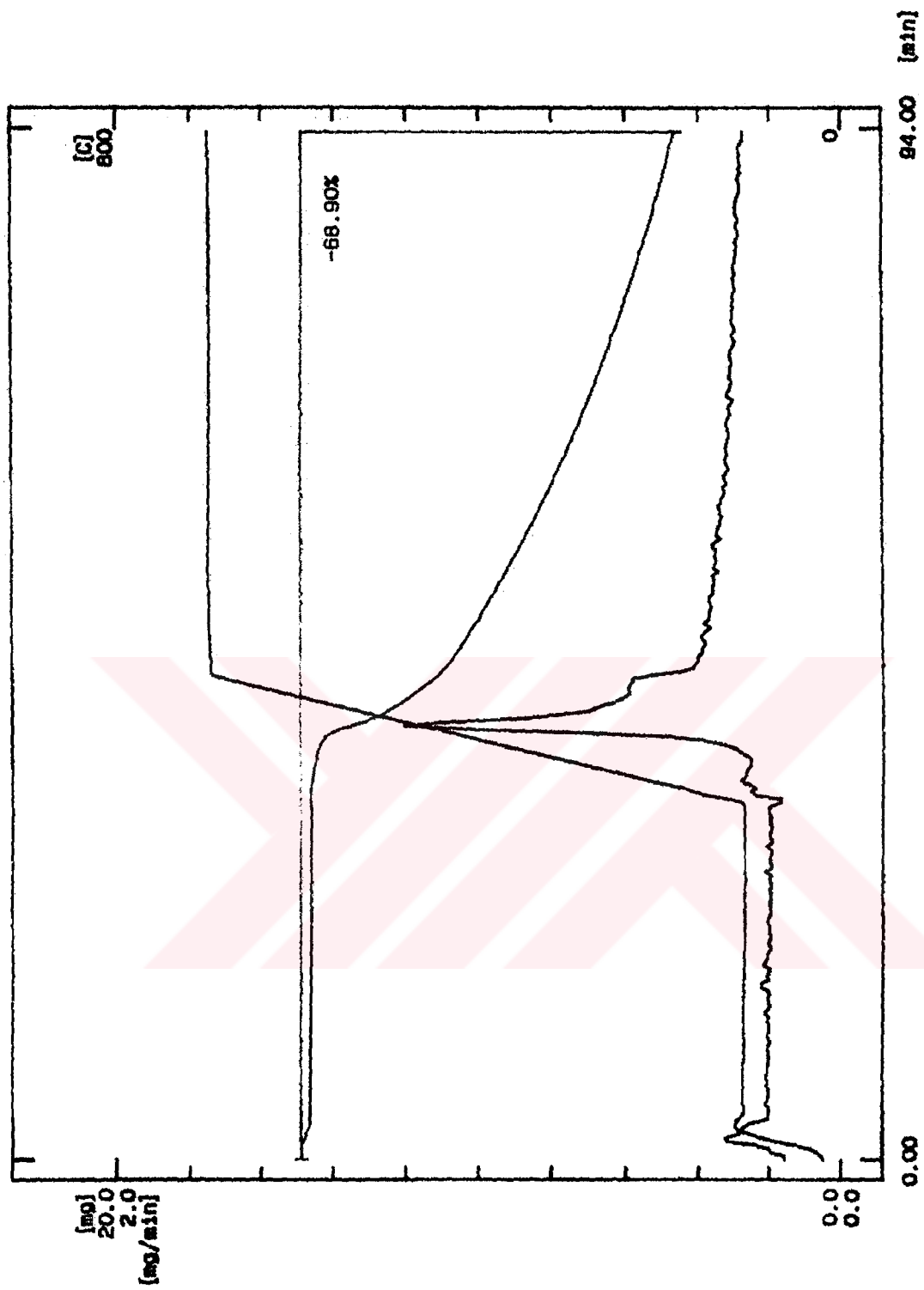


Figure A.2a. TG/DTG scan of untreated Pittsburgh No. 8.

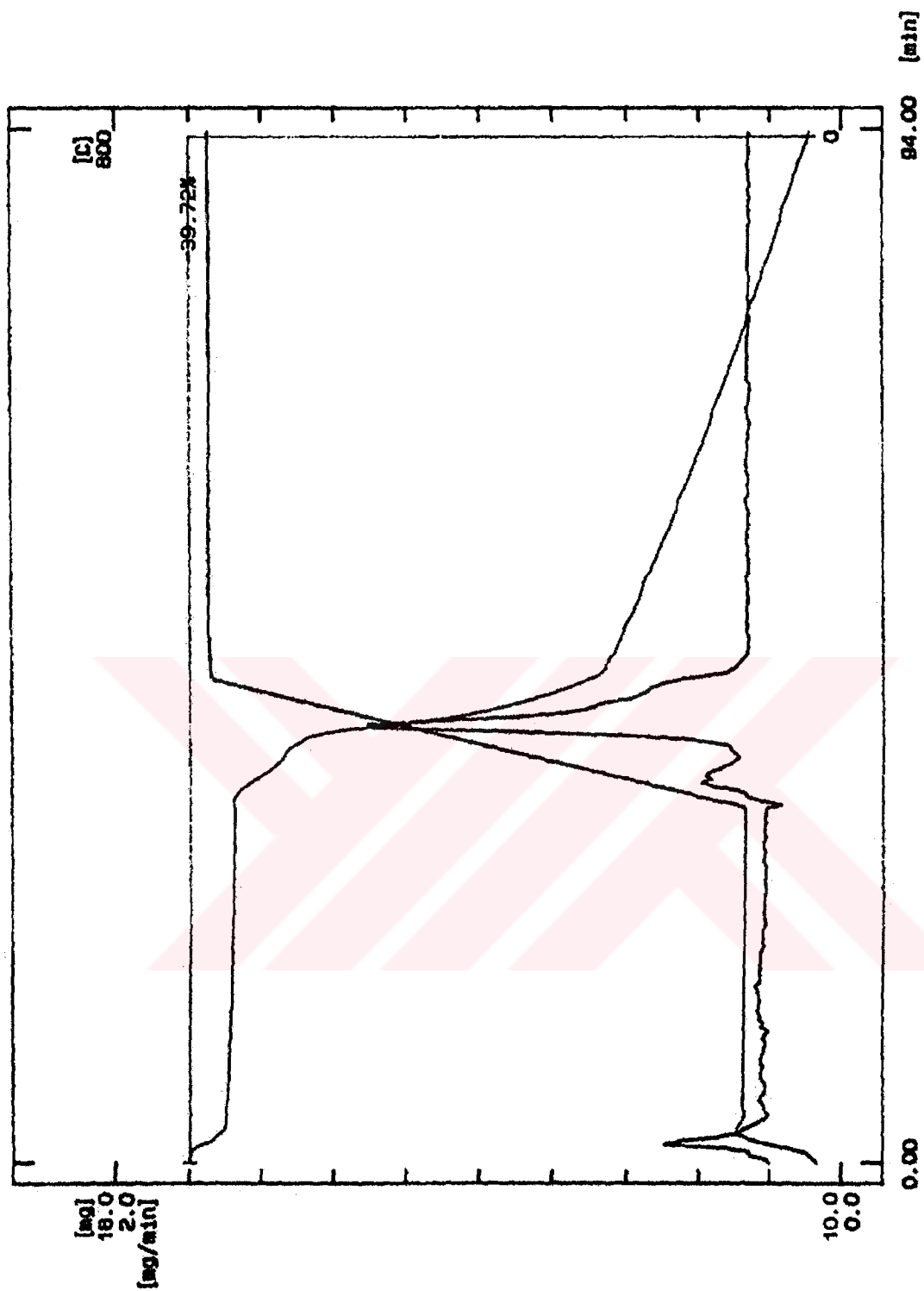


Figure A.2b. TG/DTG scan of tetrahydrofuran-treated Pittsburgh No.8.

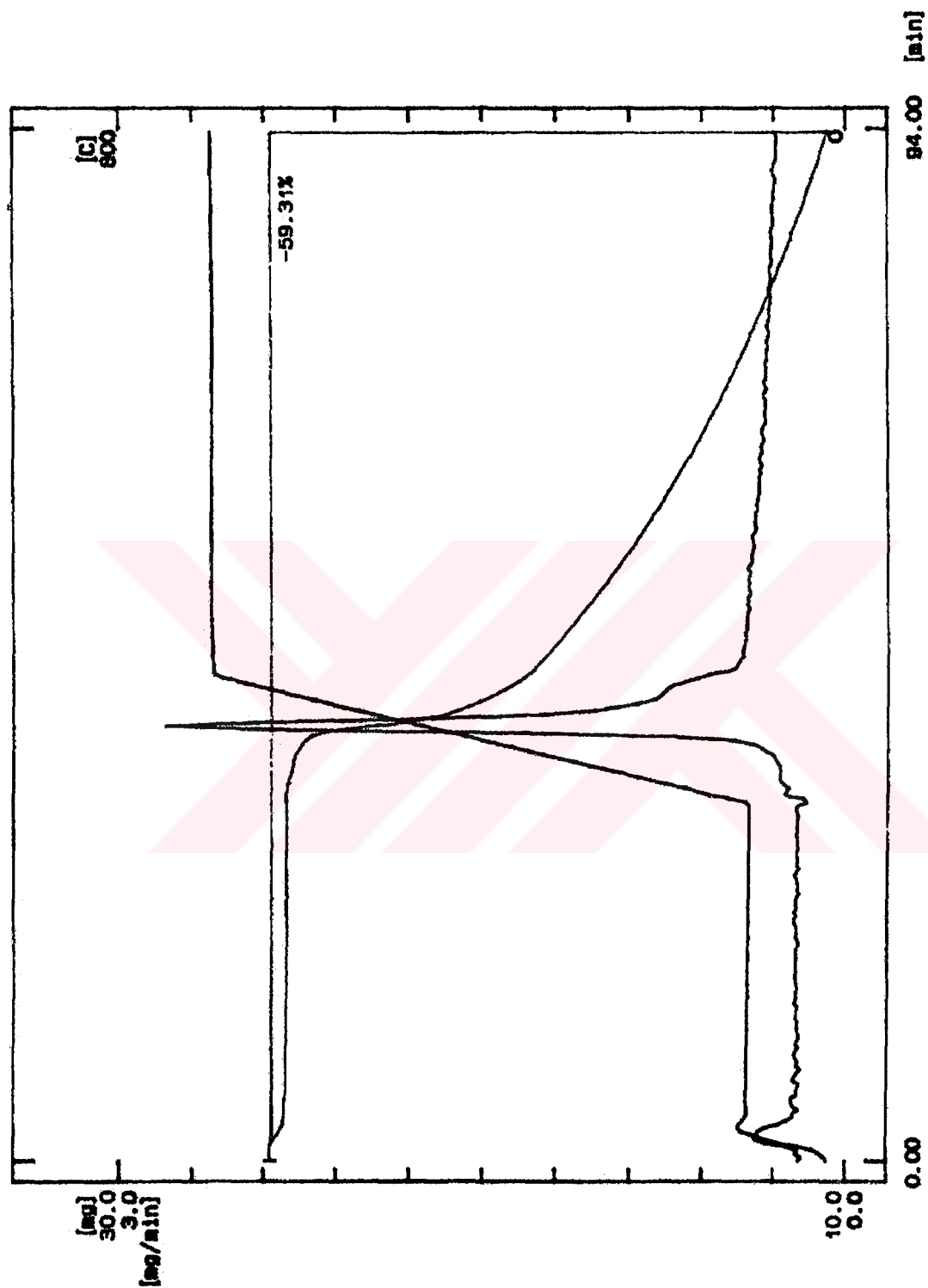


Figure A.2c. TG/DTG scan of methanol-treated Pittsburgh No. 8.

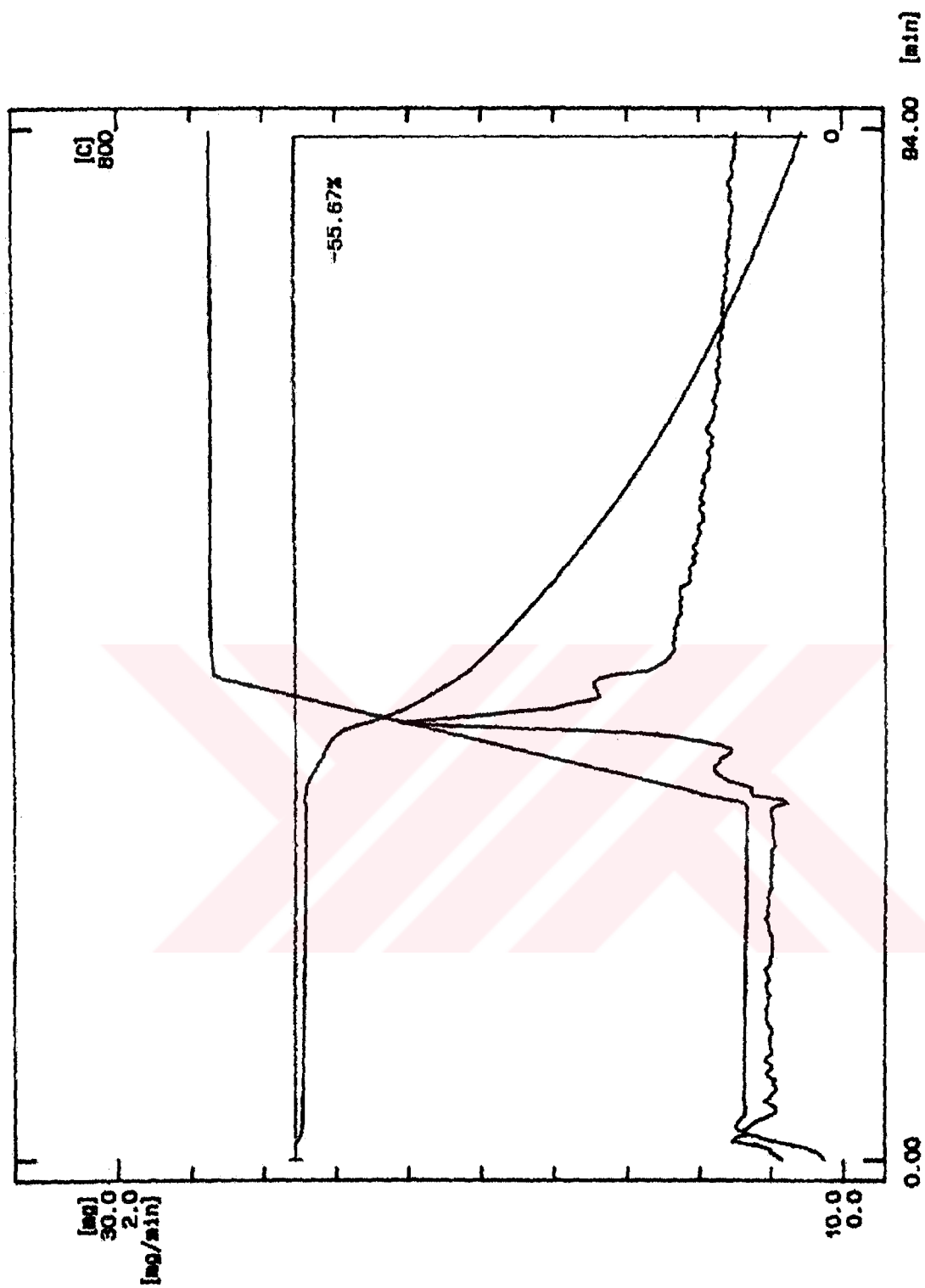


Figure A.3a. TG/DTA scan of chlorobenzene-treated Kurtserif.

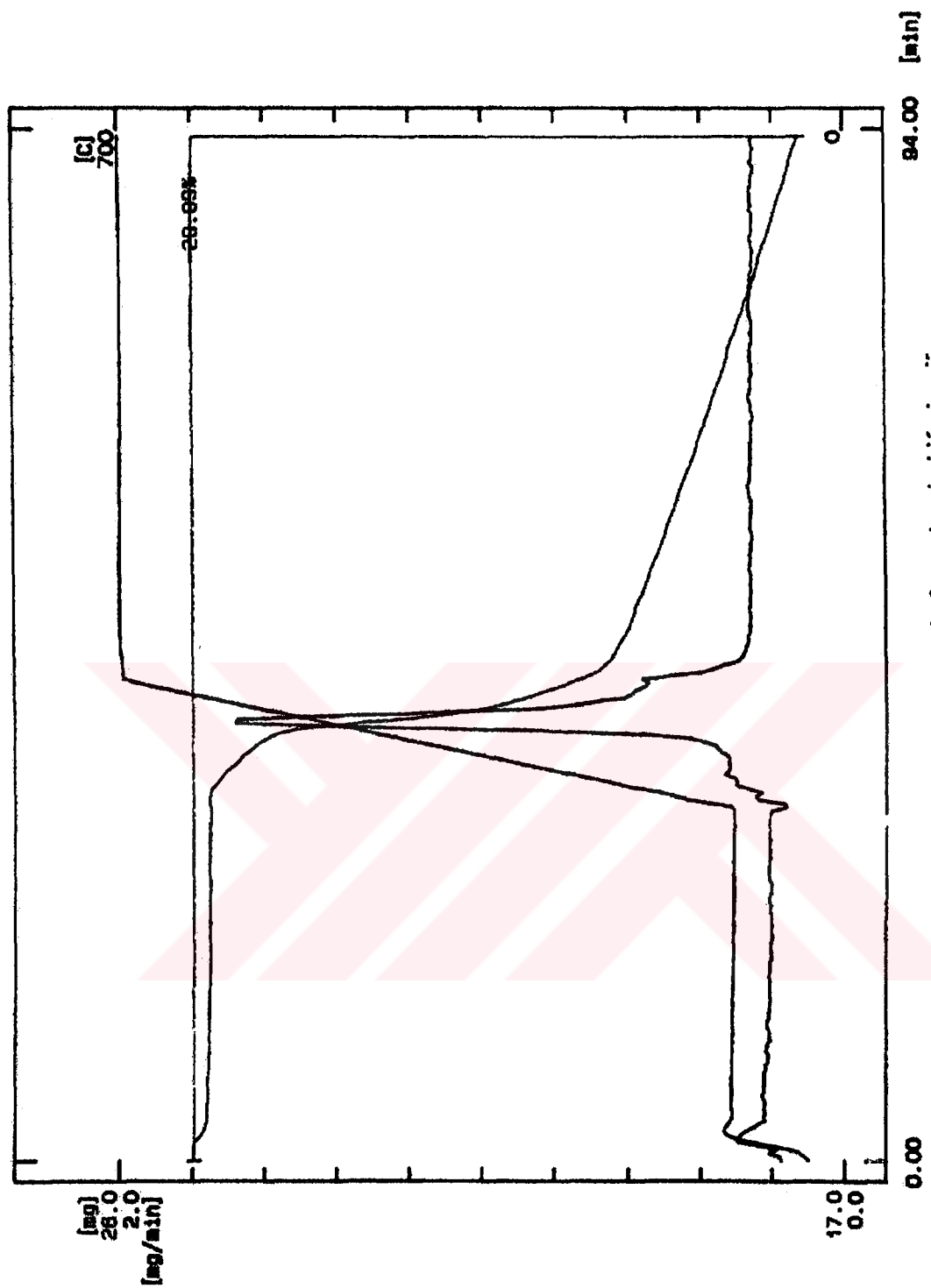


Figure A.3b. TG/DTG scan of tetrahydrofuran-treated Kurtserif.

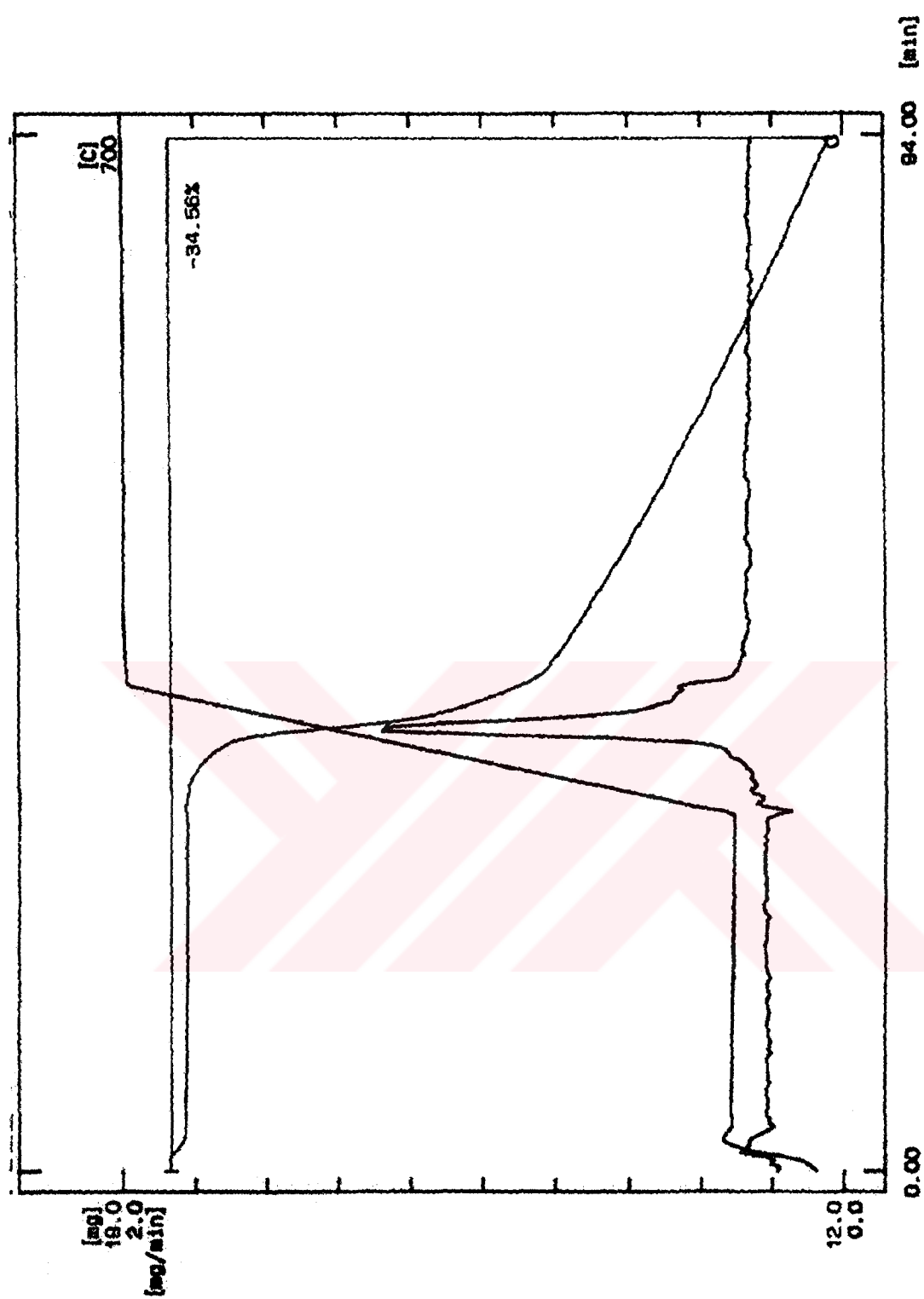


Figure A.3c. TG/DTG scan of methanol-treated Kurtserif.

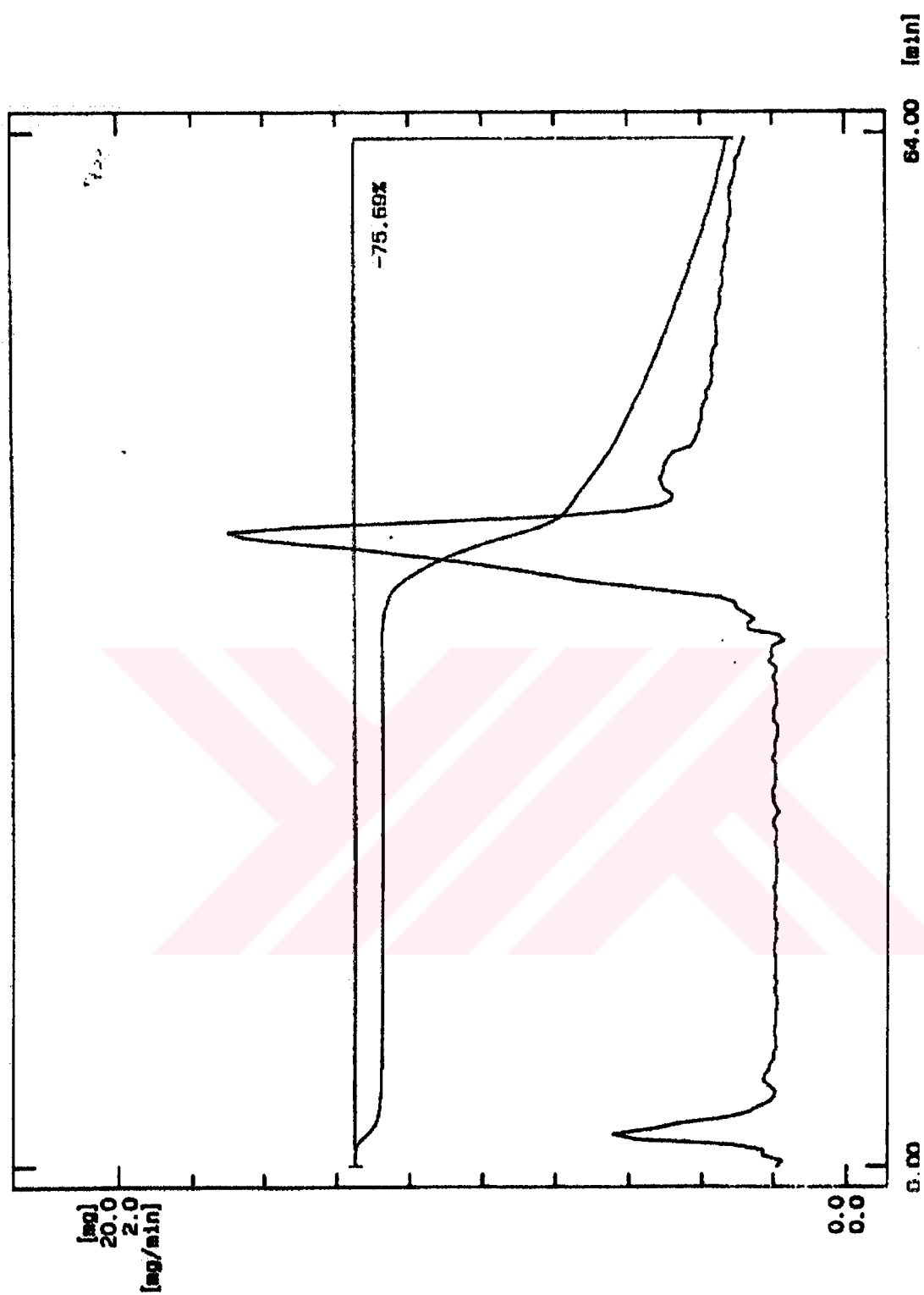


Figure A.4a. TG/DTG scan of untreated-treated Goynuk oil shale.

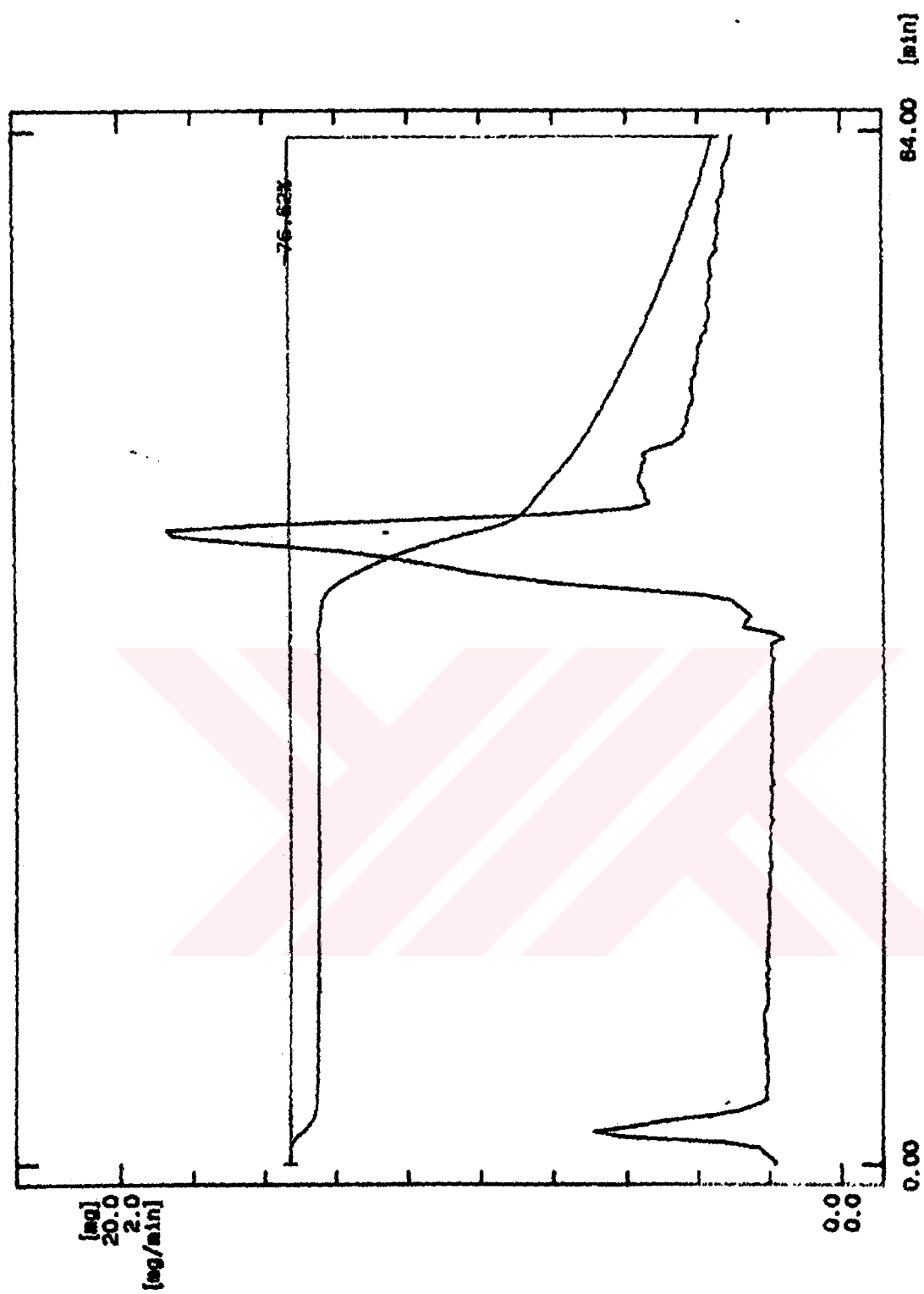


Figure A.4b. TG/DTG scan of chlorobenzene-treated Goynuk oil shale.

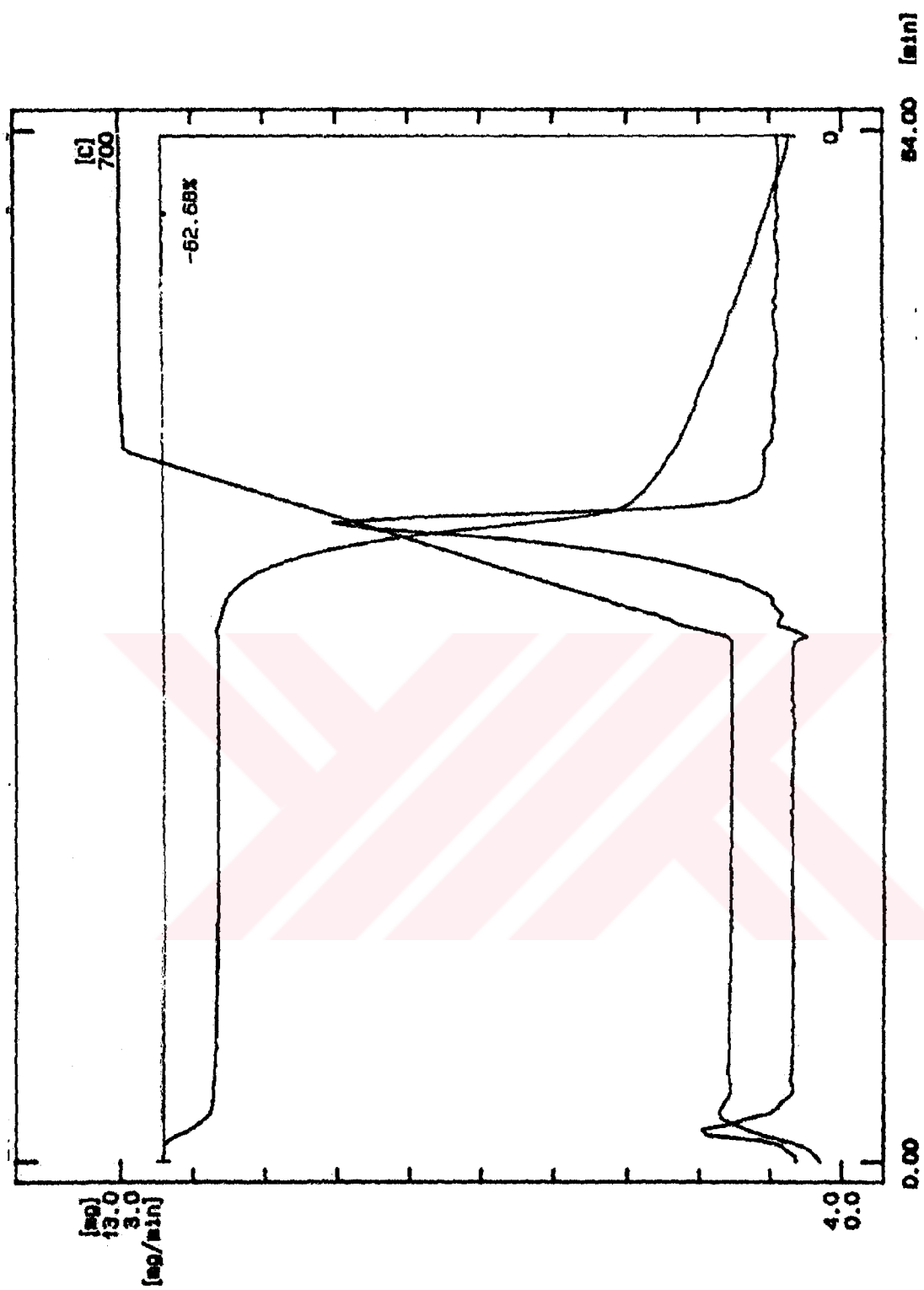


Figure A.4c. TG/DTG scan of tetrahydrofuran-treated Goynuk oil shale.

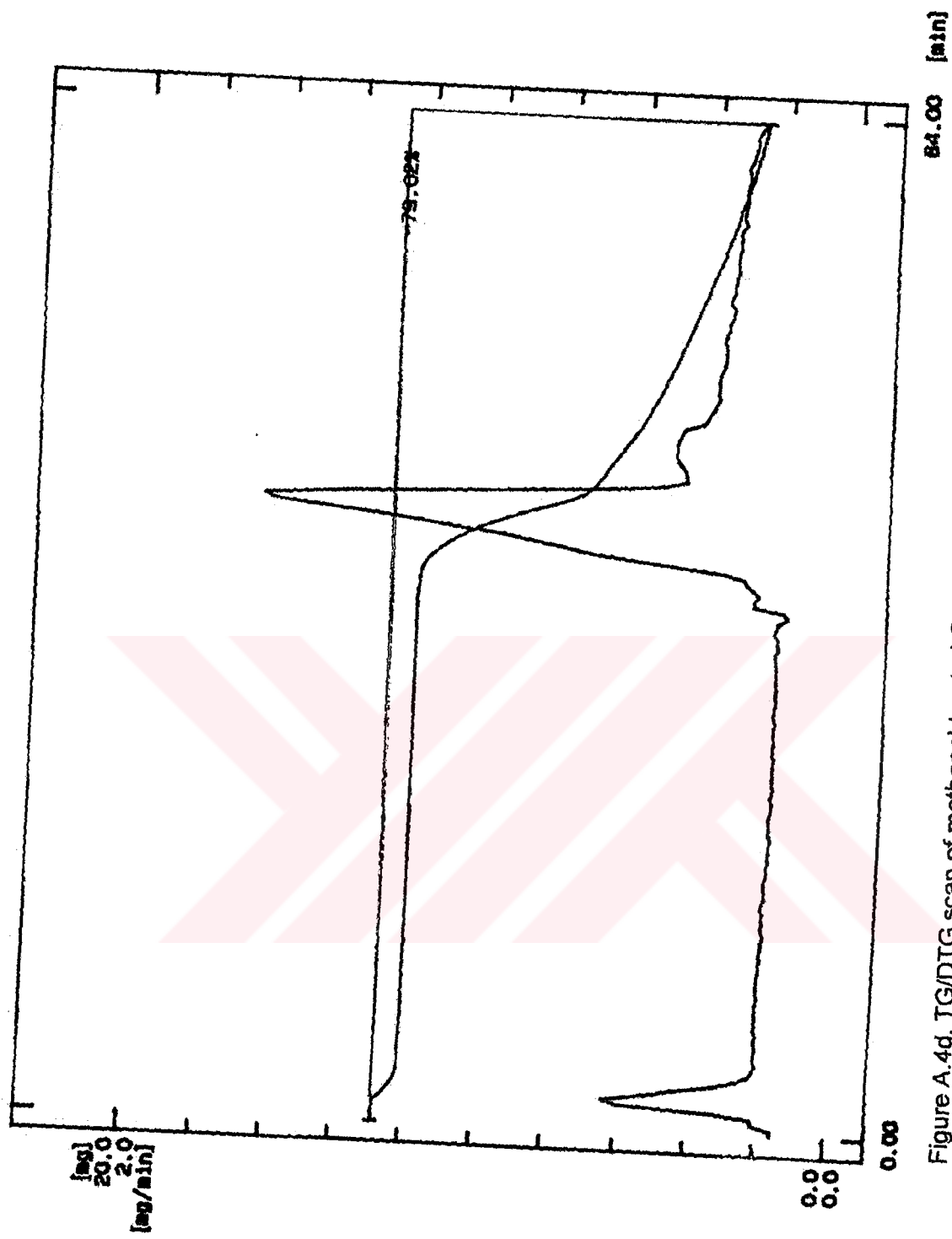


Figure A.4d. TG/DTG scan of methanol-treated Goynuk oil shale.

APPENDIX B. SEM PHOTOGRAPHS

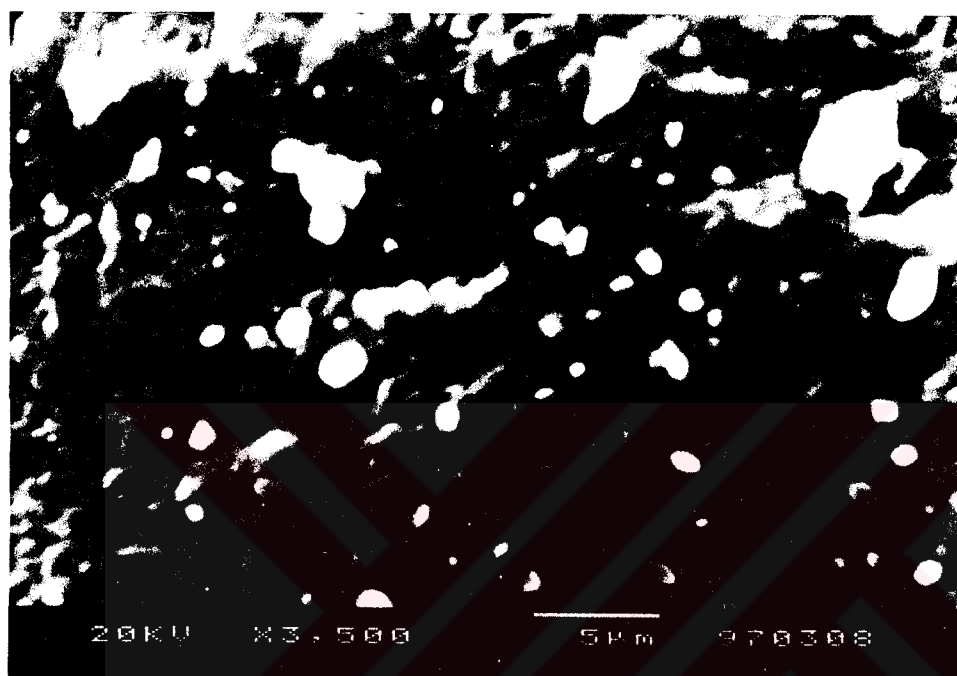


Figure B.1a. SEM photograph of untreated Tuncbilek.

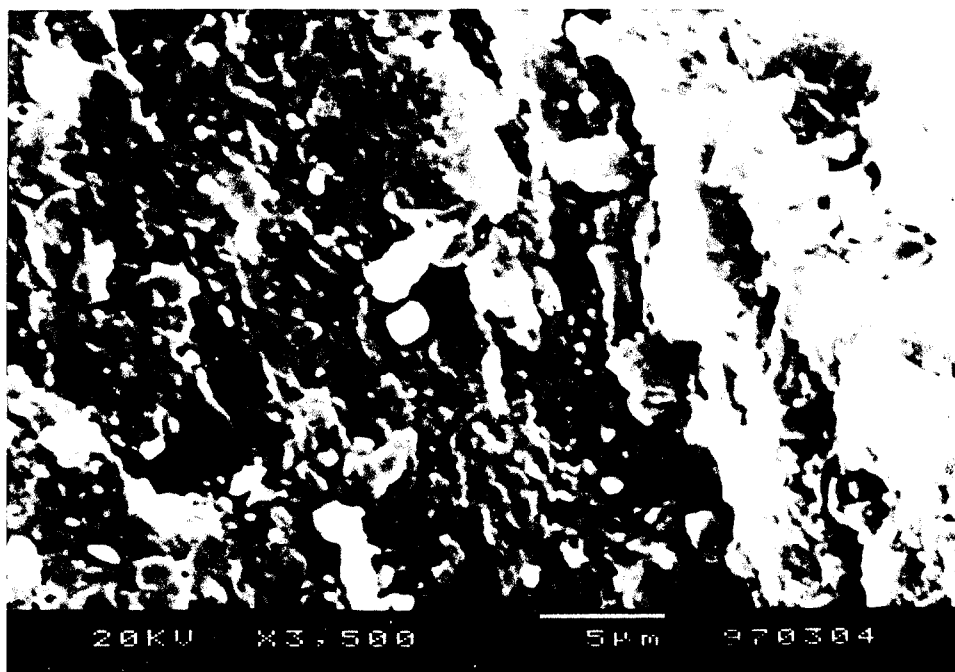


Figure B.1b. SEM photograph of chlorobenzene-treated Tuncbilek.



Figure B.1c. SEM photograph of tetrahydrofuran-treated Tuncbilek.

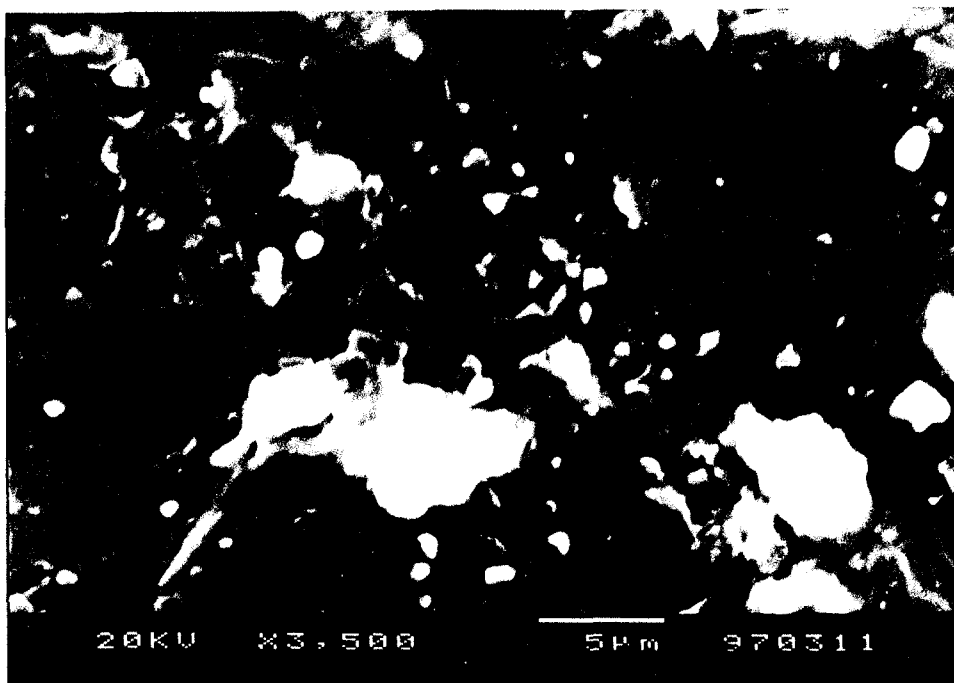


Figure B.2a. SEM photograph of untreated Kurtserif.

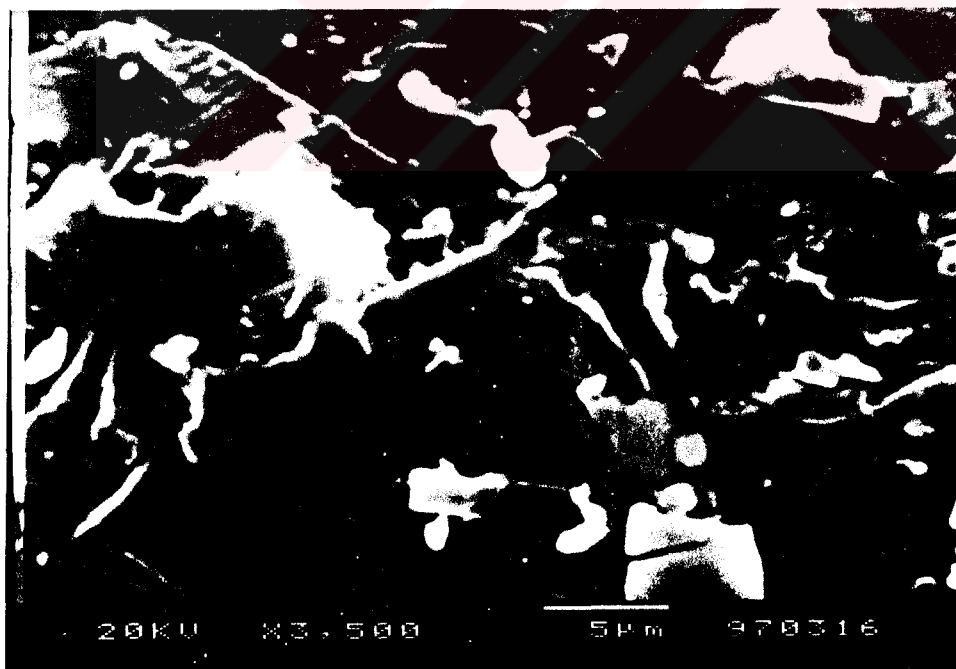


Figure B.2b. SEM photograph of chlorobenzene-treated Kurtserif.



Figure B.2c. SEM photograph of tetrahydrofuran-treated Kurtserif.

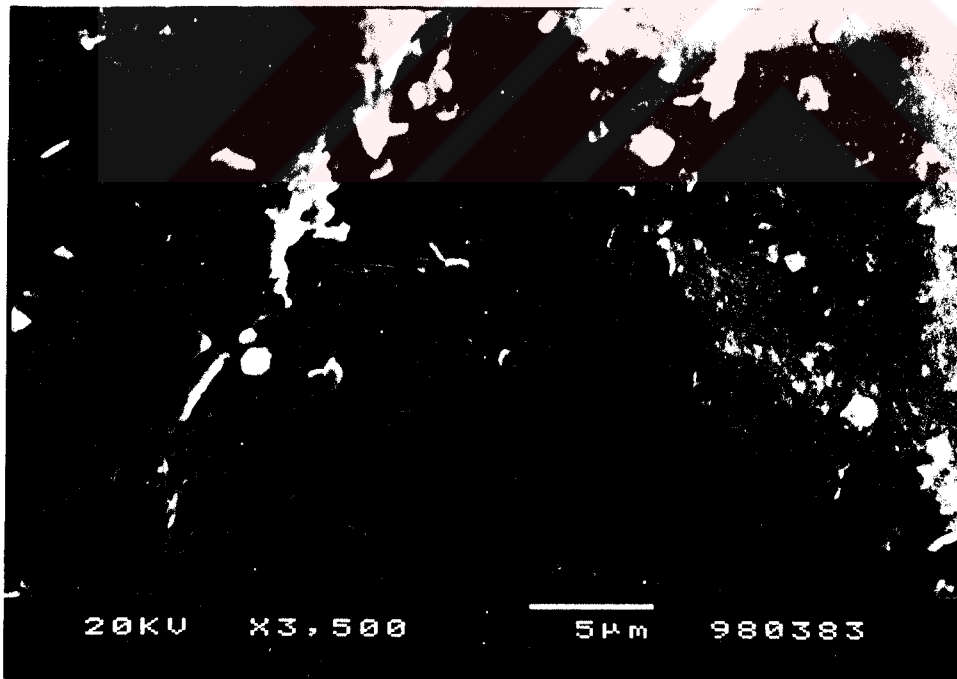


Figure B.3a. SEM photograph of untreated Pittsburgh No.8.

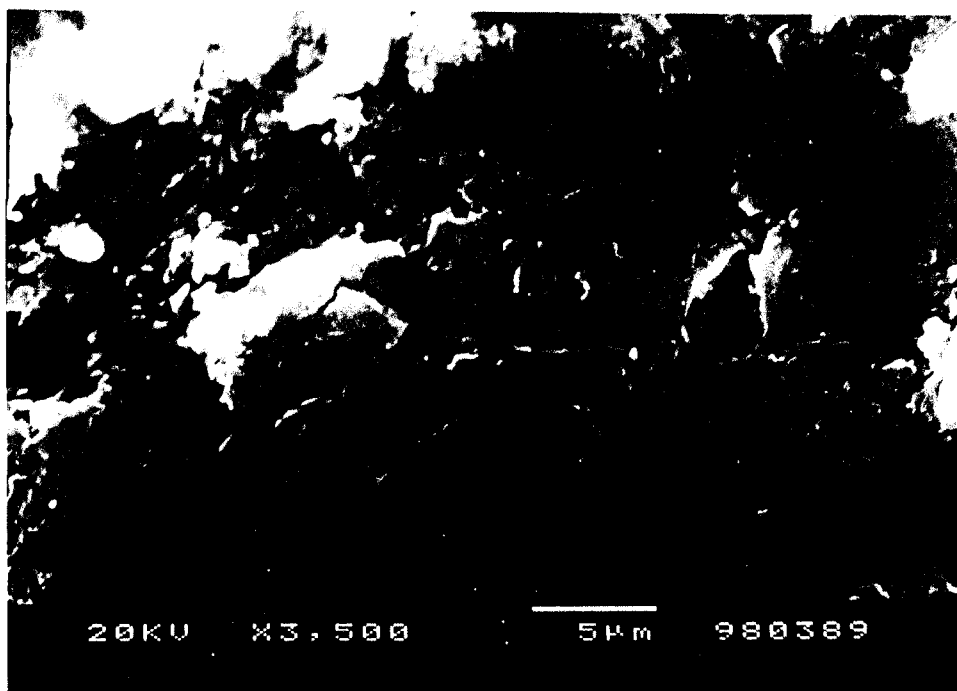


Figure B.3b. SEM photograph of chlorobenzene-treated Pittsburgh No.8.

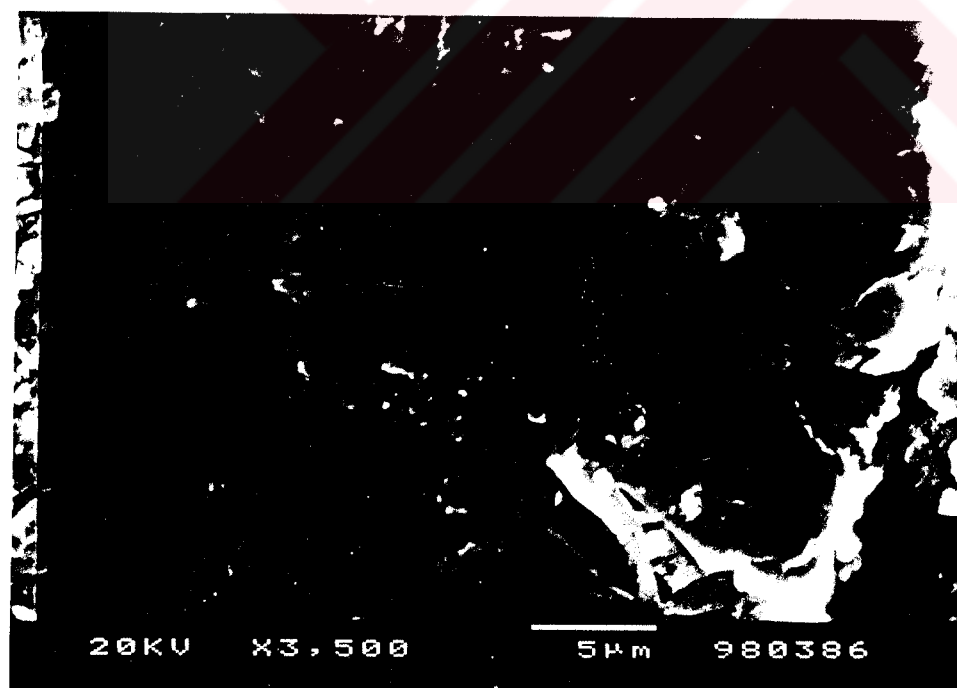


Figure B.3c. SEM photograph of tetrahydrofuran-treated Pittsburgh No.8.

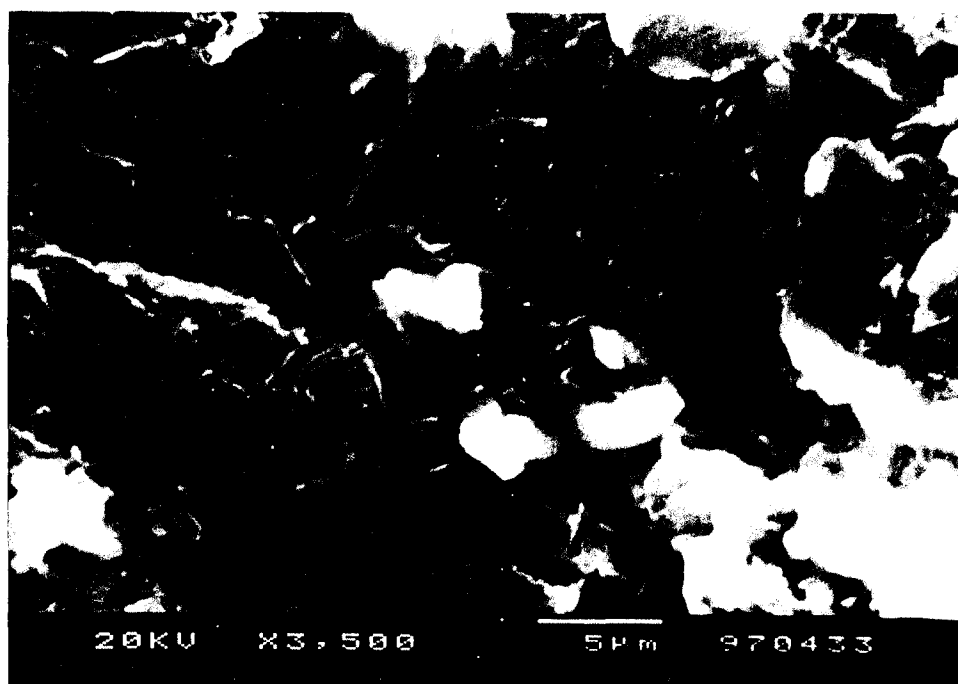


Figure B.4a. SEM photograph of untreated Goynuk (B) oil shale.

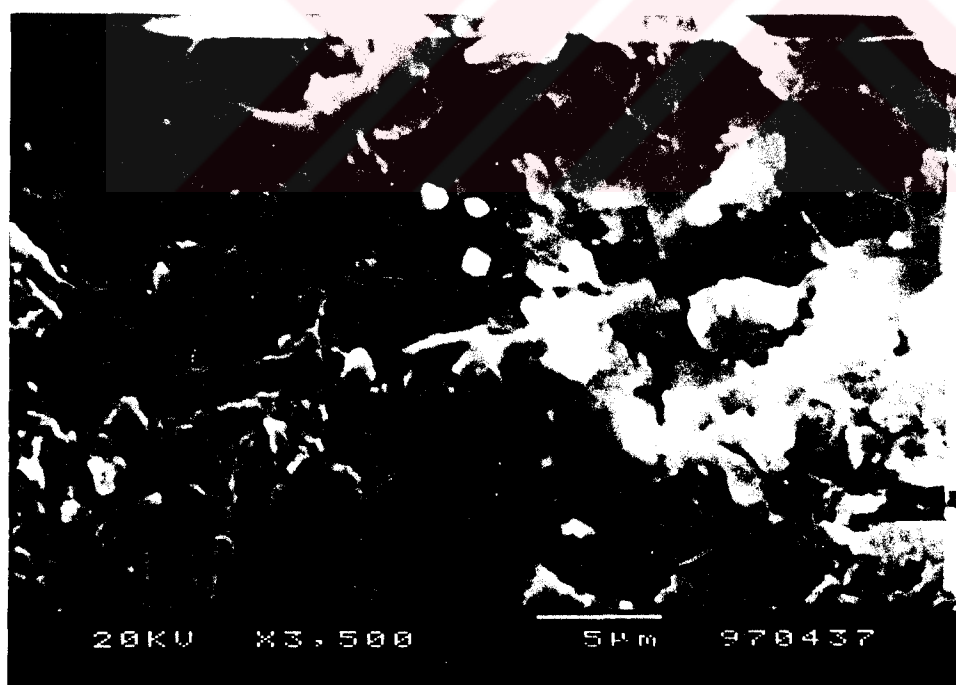


Figure B.4b. SEM photograph of chlorobenzene-treated Goynuk (B) oil shale.

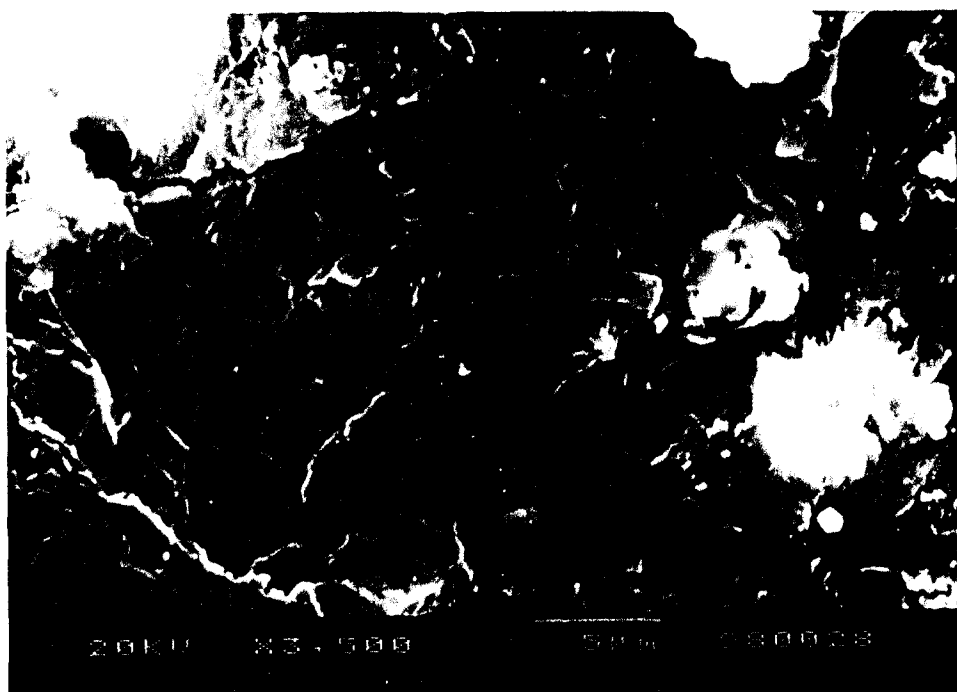


Figure B.4c. SEM photograph of tetrahydrofuran-treated Goynuk (B) oil shale.

CURRICULUM VITAE

Z. Işık Çepni-Çömlekçi was born in İstanbul in 1967. After her graduation from İstanbul Kadıköy Anadolu College in 1985, she entered to the İstanbul Technical University (İTÜ), Department of Chemical Engineering. She recieved her B.Sc. and M.Sc. degrees in Chemical Engineering in 1989 and 1991. She started Ph.D. in 1991 at Chemical Engineering Department of İTÜ. She won a 1993-1994 period British Gas/Strathclyde University Scholarship where she got M.Phil Degree at Pure and Applied Chemistry Department. In 1996-1997 period, she got scholarship from TUBITAK to continue Ph.D. research at Strathclyde University. She worked as a research assistant at the Chemical Engineering Department of İTÜ during the period October 1991-1998.

