

EGE UNIVERSITY
GRADUATE SCHOOL OF APPLIED AND NATURAL SCIENCES

Ph. D. THESIS

INVESTIGATION OF MINERAL MATTER EFFECT ON
PRODUCT YIELD AND COMPOSITION IN
LIQUEFACTION OF SOLID FUELS

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Murat SERT tarafından doktora tezi olarak sunulan “Investigation of Mineral Matter Effect on Product Yield and Composition in Liquefaction of Solid Fuels” başlıklı bu çalışma Ege Ünivesitesi Lisansüstü Eğitim ve Öğretim Yönetmeliği ile Ege Ünivesitesi Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 10 Nisan 2009 tarihinde yapılan tez savunma sınavında **aday oybirliği / oyçokluğu** ile başarılı bulunmuştur.

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ÖZET**KATI YAKITLARIN SIVILAŞTIRILMASINDA MİNERAL YAPININ ÜRÜN
VERİMİ VE BİLEŞİMİ ÜZERİNE ETKİLERİNİN ARAŞTIRILMASI**

Ülkemizde ve dünyada enerji ve kimyasal hammadde taleplerini önemli ölçüde karşılayabilecek olan katı yakıtlar arasında asfaltit, linyit ve bitümlü şistler yer almaktadırlar. Bu kaynakların ekonomik biçimde değerlendirilmesi büyük önem taşımaktadır. Bu tez kapsamında, asfaltit, linyit ve bitümlü şistlerin sıvı ve gaz ürünlere dönüştürülmesine yönelik olarak çalışmalar yapılmıştır. Gerçekleştirilmiş olan deneysel çalışmalarda numuneler öncelikle HCl, HNO₃ ve HF ile muamele edilmiş ve yapıdan sırasıyla karbonat, pirit ve silikatlı yapılar uzaklaştırılmıştır. Ham numuneler ile her bir adımda elde edilmiş demineralize örnekler sıcaklık programlı piroliz ve izotermal piroliz reaktörlerinde piroliz yapılmıştır. Bu numuneler aynı zamanda kritik üstü koşullarda su ile ekstraksiyon işlemine tabi tutulmuştur. Bunlara ek olarak demineralize edilmiş olan numunelerin hacim artışına bağlı şişme davranışları incelenmiş ve bu numuneler piroliz işlemlerine tabi tutulmuştur.

Piroliz ürünlerinden toplam akım örnekleme tekniği kullanılarak numuneler alınmış ve kapiler gaz kromatografi cihazında analizlenmiştir. Oluşan piroliz ürünleri karakterize edilmiş, lineer

parafin ve olefinler gruplandırılmıştır. Toplam hidrokarbon dönüşümleri hesaplanmıştır. Ayrıca kritik üstü koşullarda ekstraksiyon işlemleri sonrası reaktörde karbon dengesi yapılmıştır. Çözücü içinde şişme ölçümleri, bitümlü şist numunelerinin tam çözünme teorisi (Regular Solution Theory) ile yaklaşık bir uyum göstermiştir. Bu numuneler daha sonra piroliz işlemine tabi tutulmuşlardır. Tüm numunelerin mineral yapısının, piroliz verimi üzerine etkisi incelenmiştir. Organik karbonun organik ürünler olarak kazanım oranı izotermal piroliz işleminde karbon dengesi kurularak saptanmıştır.

Anathar kelimeler: Asfaltit, Bitümlü Şist, Linyit, Demineralizasyon, Piroliz, Süperkritik Ekstraksiyon, Solvent ile Şişirme

ABSTRACT**INVESTIGATION OF MINERAL MATTER EFFECT ON PRODUCT YIELD
AND COMPOSITION IN LIQUEFACTION OF SOLID FUELS**

Lignites, oils shales and asphaltites are alternative energy sources to meet the world and Turkey energy requirement. The effective usage of these fossil fuels is very important for depletion of energy sources. In this project, conversion conversion of asphaltite, lignite and oil shale to gas and liquid products were studied. In the experiment, these solid fuels were demineralized then original and demineralized samples were pyrolysed to investigate the mineral matter effect. For demineralization, HCl, HNO₃ and HF were used to remove carbonate, pyrite and silicates from organic structure, respectively. Raw and demineralized samples were pyrolysed in temperature programmed and isothermal pyrolysis reactor. These samples were also extracted with water under supercritical conditions. In addition to this, solvent swelling experiments were performed according to volume change of swollen difference and pyrolyzed in pyrolysis reactor.

Samples from pyrolysis products were taken into evacuated glass ampoules by using instantaneous total stream sampling

technique. Pyrolysis products were characterized and linear paraffins and 1-olefins were grouped by carbon number. Total hydrocarbon recoveries were determined. Also, supercritical water extraction experiments were performed raw and treated samples. Besides this, raw and demineralized oil shales were swollen by solvents and pyrolyzed in temperature programmed pyrolysis reactor. Results from solvent swelling measurements show that the volumetric solvent swelling of oil shales samples roughly follows the regular solution theory. These samples then were analyzed in capillary gas chromatography. According to the gas chromatographic analysis, the effect of demineralization on carbon conversion was estimated by carbon balance.

Keywords: Asphaltite, Oil Shale, Lignite, Demineralization, Pyrolysis, Supercritical Water Extraction, Solvent Swelling.

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x



TABLE OF CONTENTS

<u>Content</u>	<u>Page no</u>
ÖZET	V
ABSTRACT	VII
ACKNOWLEDGEMENT	IX
LIST OF FIGURES	
LIST OF TABLES	
NOMENCLATURE & ABBREVIATIONS	
1. INTRODUCTION	1
2. THEORETICAL BACKGROUND	5
2.1 Samples	5
2.1.1 Oil Shale	5
2.1.1.1 Definition and Classification of Oil Shales	5

TABLE OF CONTENTS (Continued)

<u>Content</u>	<u>Page no</u>
2.1.1.2 Geology of Oil Shale	9
2.1.1.3 Origin of oil shale	10
2.1.1.4 Historical Development of Oil in Turkey	11
2.1.1.5 Turkey's Oil Shale Deposits	12
2.1.1.6 Economic Evaluation of Oil Shale Reserves	14
2.1.2 Coal	19
2.1.2.1 Definition of coal	19
2.1.2.2 Uses of Coal	24
2.1.2.3 Lignite	29
2.1.3 Asphaltite	38
2.1.3.1 Definitions and Properties of Asphaltite	38

TABLE OF CONTENTS (Continued)

<u>Content</u>	<u>Page no</u>
2.1.3.2 Origin of Asphaltite	40
2.1.3.3 Asphaltite Reserves in the World	41
2.1.3.4 Asphaltite Reserves in Turkey	41
2.1.3.5 Usage Areas of Asphaltites	44
2.2 Methods	46
2.2.1 Demineralization	46
2.2.1.1 Chemical methods	49
2.2.2 Pyrolysis	57
2.2.3 Solvent Swelling	67
2.2.4 Supercritical Water Extraction	73
3. LITERATURE REVIEW	81

TABLE OF CONTENTS (Continued)

<u>Content</u>	<u>Page no</u>
3.1 Demineralization of Asphaltite, Lignite and Oil Shale	81
3.2 Pyrolysis of Asphaltite, Lignite and Oil Shale	91
3.3 Solvent Swelling of Asphaltite, Lignite and Oil Shale	102
3.4 Kinetics of Asphaltite, Oil Shale and Lignite	108
3.5 Supercritical Water Extraction of ASP, LIG and GOS	115
4. EXPERIMENTAL STUDY	122
4.1 Samples	122
4.2 Experimental Set-up and Procedure	123
4.2.1 Demineralization	123
4.2.2 Isothermal Fast Pyrolysis (IP)	126
4.2.3 Temperature Programmed Pyrolysis (TPP)	130

TABLE OF CONTENTS (Continued)

<u>Content</u>	<u>Page no</u>
4.2.4 Supercritical Water Extraction (SCWE)	134
4.2.5 Solvent Swelling	136
4.3 Analysis Methods	139
4.3.1 Ash Analysis of Demineralized Samples	140
4.3.2 IR Spectra of Demineralized Samples	140
4.3.3 Thermogravimetric Analysis of Samples	140
4.3.4 Gas Chromatographic Analysis (GC)	141
4.3.5 Total Organic Carbon Analysis (TOC)	146
5. RESULTS AND DISCUSSION	147
5.1 Demineralization	147
5.1.1 Demineralization of GOS	148

TABLE OF CONTENTS (Continued)

<u>Content</u>	<u>Page no</u>
5.1.2 Demineralization of Lignite	158
5.1.3 Demineralization of Asphaltite	168
5.2 Isothermal Pyrolysis (IP)	179
5.2.1 Isothermal Pyrolysis of GOS-R	179
5.2.2 Isothermal Pyrolysis of GOS-C	192
5.2.3 Isothermal Pyrolysis of GOS-N	201
5.2.4 Isothermal Pyrolysis of GOS-F	209
5.2.5 Isothermal Pyrolysis of ELIG-R	219
5.2.6 Isothermal Pyrolysis of ELIG-C	228
5.2.7 Isothermal Pyrolysis of ELIG-N	236
5.2.8 Isothermal Pyrolysis of ELIG-F	244

TABLE OF CONTENTS (Continued)

<u>Content</u>	<u>Page no</u>
5.2.9 Isothermal Pyrolysis of SASP-R	253
5.2.10 Isothermal Pyrolysis of SASP-C	262
5.2.11 Isothermal Pyrolysis of SASP-N	271
5.2.12 Isothermal Pyrolysis of SASP-F	280
5.3 Temperature-Programmed Pyrolysis	289
5.3.1 Temperature-Programmed Pyrolysis of Oil Shale	289
5.3.2 Temperature-Programmed Pyrolysis of Lignite	302
5.3.3 Temperature-Programmed Pyrolysis of Asphaltite	313
5.4 Solvent Swelling Studies	323
5.4.1 Solvent Swelling of Oil Shales	323
5.4.2 Thermal Properties of Swollen Oil Shale Samples	337

TABLE OF CONTENTS (Continued)

<u>Content</u>	<u>Page no</u>
5.4.3 TPP of Swollen Oil Shale Samples	341
5.4.4 Solvent Swelling Studies of Raw and Demineralized Lignite Samples	351
5.5 Supercritical Water Extraction	362
5.6 Thermogravimetrically Derived Kinetics of Pyrolysis	370
5.6.1 TGA (Thermogravimetric Analysis)	370
5.6.2 Kinetic Study of Samples	382
5.6.2.1 Kinetic Study of SASP	384
5.6.2.2 Kinetic Study of SLIG	387
5.6.2.3 Kinetic Study of GOS	392
5.6.2.4 Kinetic Study of Swollen GOS	398
6.0 CONCLUSION	404

TABLE OF CONTENTS (Continued)

<u>Content</u>	<u>Page no</u>
6.1 Demineralization of Oil Shale, Lignite and Asphaltite	404
6.2 Isothermal Pyrolysis of Oil Shale, Lignite and Asphaltite	407
6.3 TPP of Oil Shale, Lignite and Asphaltite	416
6.4 Solvent Swelling of Oil Shale, Lignite and Asphaltite	420
6.5 Kinetic Study of Oil Shale, Lignite and Asphaltite	423
6.6 Supercritical Water Extraction	424
REFERENCES	426
APPENDIX	439
RESUME	441



LIST OF FIGURES

Figure	Page
2.1.1.1.1 Schematic presentation organic-rich sedimentary rocks	8
2.1.1.3.1 Basic constituents of oil shale	10
2.1.1.5.1 Location of major oil shale deposits in Turkey	14
2.1.2.1.1 World coal reserves	20
2.1.2.1.2 The rank of coal	23
2.1.2.2.1 Generation of electricity worldwide	24
2.1.2.2.2 World electricity production and demands for 2030	27
2.1.2.2.3 Consumption of fossil fuels in the world from 1800's	28
2.1.2.3.1 Lignite production between 1991-2000 in Turkey	33
2.1.2.3.2 Uses of lignite in Turkey	36
2.1.3.1.1 Asphaltite with rock crystal	39
2.2.4.1 Phase diagram of water	78

LIST OF FIGURES (Continued)

Figure	Page
2.2.4.2 Properties of pure water as a function of temp. at 250 bar	79
4.2.1.1 The experimental setup of demineralization process	125
4.2.2.1 The schematic diagram of the IP reactor	127
4.2.3.1 A schematic diagram of the TPP equipment	131
4.2.3.2 Equipment details for the reactor	132
4.2.4.1 Schematic presentation of autoclave	135
4.2.5.1 Solvent swelling procedures	137
4.3.1 Schematic presentation of experiments and analysis	139
4.3.4.1 The special sampling system	142
4.3.4.2 Melting of capillary part of glass ampoule	142
4.3.4.3 The sample introducing system of GC	143
4.3.4.4 Flow sheet of capillary gas chromatography connected to sample introducing system	144

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
5.1.1.1 IR Spectra of GOS-R	155
5.1.1.2 IR Spectra of GOS-C	156
5.1.1.3 IR Spectra of GOS-N	156
5.1.1.4 IR Spectra of GOS-F	157
5.1.2.1 IR Spectra of ELIG-R	164
5.1.2.2 IR Spectra of ELIG-C	165
5.1.2.3 IR Spectra of ELIG-N	165
5.1.2.4 IR Spectra of ELIG-F	166
5.1.3.1 IR Spectra of SASP-R	176
5.1.3.2 IR Spectra of SASP-C	176
5.1.3.3 IR Spectra of SASP-N	177
5.1.3.4 IR Spectra of SASP-F	177

LIST OF FIGURES (Continued)

Figure	Page
5.2.1.1 Sample chromatogram of organic products of GOS-R	180
5.2.1.2 Volatile product evolution rate for IP of GOS-R	182
5.2.1.3 Volatile fraction of recovered hydrocarbons for IP of GOS-R (in C basis)	183
5.2.1.4 Conversion to solid residue of GOS-R for IP	184
5.2.1.5 Total hydrocarbon recovery for IP of GOS-R	186
5.2.1.6 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltene for IP of GOS-R	188
5.2.1.7 Cumulative n-Paraffin selectivity for IP of GOS-R	189
5.2.1.8 Cumulative 1-olefin selectivity for IP of GOS-R	190
5.2.2.1 Volatile product evolution rate for IP of GOS-C	192
5.2.2.2 Volatile fraction of recovered hydrocarbons for IP of GOS-C (in C basis)	194
5.2.2.3 Conversion to solid residue of GOS-C	195

LIST OF FIGURES (Continued)

Figure	Page
5.2.2.4 Total hydrocarbon recovery of IP of GOS-C	196
5.2.2.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltene for IP of GOS-C	198
5.2.2.6 Cumulative n-Paraffin selectivity for IP of GOS-C	199
5.2.2.7 Cumulative 1-olefin selectivity for IP of GOS-C	199
5.2.3.1 Volatile product evolution rate for IP of GOS-N	201
5.2.3.2 Volatile fraction of recovered hydrocarbon for IP of GOS-N (in C basis)	203
5.2.3.3 Conversion to solid residue of GOS-N for IP	204
5.2.3.4 Total hydrocarbon recovery of IP of GOS-N	204
5.2.3.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of GOS-N	206
5.2.3.6 Cumulative n-Paraffin selectivity for IP of GOS-N	207
5.2.3.7 Cumulative 1-olefin selectivity for IP of GOS-N	207

LIST OF FIGURES (Continued)

Figure	Page
5.2.4.1 Volatile product evolution rate for IP of GOS-F	209
5.2.4.2 Volatile fraction of recovered hydrocarbons for IP of GOS-F (in C basis)	211
5.2.4.3 Conversion to solid residue of GOS-F for IP	212
5.2.4.4 Total hydrocarbon recovery of IP of GOS-F	212
5.2.4.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of GOS-F	214
5.2.4.6 Cumulative n-Paraffin selectivity for IP of GOS-F	215
5.2.4.7 Cumulative 1-olefin selectivity for IP of GOS-F	216
5.2.4.8 Volatile hydrocarbon recoveries for raw and demineralized oil shale samples	217
5.2.5.1 Volatile product evolution rate for IP of ELIG-R	219
5.2.5.2 Volatile fraction recovered hydrocarbons for IP of ELIG-R (in Carbon basis)	220
5.2.5.3 Conversion to solid residue of ELIG-R for IP	222

LIST OF FIGURES (Continued)

Figure	Page
5.2.5.4 Total hydrocarbon recovery of IP of ELIG-R	223
5.2.5.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of ELIG-R	225
5.2.5.6 Cumulative n-Paraffin selectivity for IP of ELIG-R	226
5.2.5.7 Cumulative 1-Olefin selectivity for IP of ELIG-R	227
5.2.6.1 Volatile product evolution rate for IP of ELIG-C	229
5.2.6.2 Volatile fraction of recovered hydrocarbons for IP of ELIG-C (in Carbon basis)	231
5.2.6.3 Conversion to solid residue for IP of ELIG-C	231
5.2.6.4 Total hydrocarbon recovery of IP of ELIG-C	232
5.2.6.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of ELIG-C	234
5.2.6.6 Cumulative n-paraffin selectivity for IP of LIG-C	235
5.2.6.7 Cumulative 1-olefin selectivity for IP of LIG-C	235

LIST OF FIGURES (Continued)

Figure	Page
5.2.7.1 Volatile product evolution rate for IP of ELIG-N	236
5.2.7.2 Volatile fraction of recovered hydrocarbon for IP of ELIG-N (in carbon basis)	238
5.2.7.3 Conversion to solid residue of ELIG-N for IP	239
5.2.7.4 Total hydrocarbon recovery of IP of ELIG-N	239
5.2.7.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of ELIG-N	241
5.2.7.6 Cumulative n-Paraffin selectivity for IP of ELIG-N	242
5.2.7.7 Cumulative 1-olefin selectivity for IP of ELIG-N	243
5.2.8.1 Volatile product evolution rate for IP of ELIG-F	244
5.2.8.2 Volatile fraction of recovered hydrocarbon for IP of ELIG-F (in Carbon basis)	246
5.2.8.3 Conversion to solid residue of ELIG-F for IP	247
5.2.8.4 Total hydrocarbon recovery of IP of ELIG-F	247

LIST OF FIGURES (Continued)

Figure	Page
5.2.8.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of ELIG-F	249
5.2.8.6 Cumulative n-Paraffin selectivity for IP of ELIG-F	250
5.2.8.7 Cumulative 1-olefin selectivity for IP of ELIG-F	251
5.2.8.8 Volatile hydrocarbon recoveries for raw and demineralized lignite samples	252
5.2.9.1 Volatile product evolution rate for IP of SASP-R	253
5.2.9.2 Volatile fraction of recovered hydrocarbons for IP of SASP-R (in Carbon basis)	255
5.2.9.3 Conversion to solid residue of SASP-R for IP	256
5.2.9.4 Total hydrocarbon recovery for IP of SASP-R	257
5.2.9.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of SASP-R	259
5.2.9.6 Cumulative n-Paraffin selectivity for IP of SASP-R	260
5.2.9.7 Cumulative 1-olefin selectivity for IP of SASP-R	261

LIST OF FIGURES (Continued)

Figure	Page
5.2.10.1 Volatile product evolution rate for IP of SASP-C	263
5.2.10.2 Volatile fraction of recovered hydrocarbons for IP of SASP-C (in Carbon basis)	264
5.2.10.3 Conversion to solid residue of SASP-C for IP	265
5.2.10.4 Total hydrocarbon recovery for IP of SASP-C	266
5.2.10.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of SASP-C	268
5.2.10.6 Cumulative n-Paraffin selectivity for IP of SASP-C	269
5.2.10.7 Cumulative 1-olefin selectivity for IP of SASP-C	270
5.2.11.1 Volatile product evolution rate for IP of SASP-N	271
5.2.11.2 Volatile fraction of recovered hydrocarbons for IP of SASP-N (in Carbon basis)	273
5.2.11.3 Conversion to solid residue of SASP-N for IP	274
5.2.11.4 Total hydrocarbon recovery for IP of SASP-N	275

LIST OF FIGURES (Continued)

Figure	Page
5.2.11.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of SASP-N	277
5.2.11.6 Cumulative n-Paraffin selectivity for IP of SASP-N	278
5.2.11.7 Cumulative 1-olefin selectivity for IP of SASP-N	278
5.2.12.1 Volatile product evolution rate for IP of SASP-F	280
5.2.12.2 Volatile fraction of recovered hydrocarbons for IP of SASP-F (in Carbon basis)	282
5.2.12.3 Conversion to solid residue of SASP-F for IP	283
5.2.12.4 Total hydrocarbon recovery for IP of SASP-F	284
5.2.12.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of SASP-F	286
5.2.12.6 Cumulative n-Paraffin selectivity for IP of SASP-F	287
5.2.12.7 Cumulative 1-olefin selectivity for IP of SASP-F	287

LIST OF FIGURES (Continued)

Figure	Page
5.2.12.8 Volatile hydrocarbon recoveries for raw and demineralized asphaltite samples	288
5.3.1.1 Total product evolution rate of GOS-R	290
5.3.1.2 Total product evolution rate of GOS-C	290
5.3.1.3 Total product evolution rate of GOS-N	291
5.3.1.4 Total product evolution rate of GOS-F	291
5.3.1.5 Distribution of n-parafins in pyrolysis products by carbon number for GOS-R	293
5.3.1.6 Distribution of 1-olefins in pyrolysis products by carbon number for GOS-R	293
5.3.1.7 Distribution of n-paraffins in pyrolysis products by carbon number for GOS-C	294
5.3.1.8 Distribution of 1-olefins in pyrolysis products by carbon number for GOS-C	294
5.3.1.9 Distribution of n-parafins in pyrolysis products by carbon number for GOS-N	295

LIST OF FIGURES (Continued)

Figure	Page
5.3.1.10 Distribution of 1-olefins in pyrolysis products by carbon number for GOS-N	295
5.3.1.11 Distribution of n-parafins in pyrolysis products by carbon number for GOS-F	296
5.3.1.12 Distribution of 1-olefins in pyrolysis products by carbon number for GOS-F	296
5.3.1.13 n-Paraffins distribution in pyrolysis of GOS-R, GOS-C, GOS-N and GOS-F at the maximum product evolution temperature	298
5.3.1.14 1-olefins distribution in pyrolysis of GOS-R, GOS-C, GOS-N and GOS-F at the maximum product evolution temperature	299
5.3.1.15 Conversion levels of organic carbon to VHC, polyaromatics (asphaltenes -preasphaltenes)	300
5.3.2.1 Total product evolution rate of SLIG-R	302
5.3.2.2 Total product evolution rate of SLIG-C	303
5.3.2.3 Total product evolution rate of SLIG-N	303
5.3.2.4 Total product evolution rate of SLIG-F	304

LIST OF FIGURES (Continued)

Figure	Page
5.3.2.5 Distribution of n-paraffins in pyrolysis products by carbon number for SLIG-R	305
5.3.2.6 Distribution of 1-olefins in pyrolysis products by carbon number for SLIG-R	305
5.3.2.7 Distribution of n-paraffins in pyrolysis products by carbon number for SLIG-C	306
5.3.2.8 Distribution of 1-olefins in pyrolysis products by carbon number for SLIG-C	306
5.3.2.9 Distribution of n-paraffins in pyrolysis products by carbon number for SLIG-N	307
5.3.2.10 Distribution of 1-olefins in pyrolysis products by carbon number for SLIG-N	307
5.3.2.11 Distribution of n-paraffins in pyrolysis products by carbon number for SLIG-F	308
5.3.2.12 Distribution of 1-olefins in pyrolysis products by carbon number for SLIG-F	308
5.3.2.13 n-Paraffins distribution in pyrolysis of SLIG-R, SLIG-C, SLIG-N and SLIG-F at the maximum product evolution temperature	311

LIST OF FIGURES (Continued)

Figure	Page
5.3.2.14 1-olefins distribution in pyrolysis of SLIG-R, SLIG-C, SLIG-N and SLIG-F at the maximum product evolution temperature	311
5.3.3.1 Total product evolution rates of SASP-R	313
5.3.3.2 Total product evolution rates of SASP-C	314
5.3.3.3 Total product evolution rates of SASP-N	314
5.3.3.4 Total product evolution rates of SASP-F	315
5.3.3.5 Distribution of n-paraffins in pyrolysis products by carbon number for SASP-R	316
5.3.3.6 Distribution of 1-olefins in pyrolysis products by carbon number for SASP-R	316
5.3.3.7 Distribution of n-paraffins in pyrolysis products by carbon number for SASP-C	318
5.3.3.8 Distribution of 1-olefins in pyrolysis products by carbon number for SASP-C	318
5.3.3.9 Distribution of n-paraffins in pyrolysis products by carbon number for SASP-N	319

LIST OF FIGURES (Continued)

Figure	Page
5.3.3.10 Distribution of 1-olefins in pyrolysis products by carbon number for SASP-N	319
5.3.3.11 Distribution of n-paraffins in pyrolysis products by carbon number for SASP-F	320
5.3.3.12 Distribution of 1-olefins in pyrolysis products by carbon number for SASP-F	320
5.3.3.13 n-Paraffins distribution in pyrolysis of SASP-R, SASP-C, SASP -N and SASP-F at the maximum product evolution temperature	321
5.3.3.14 1-olefins distribution in pyrolysis of SASP-R, SASP-C, SASP-N and SASP-F at the maximum product evolution temperature	322
5.4.1.1 Swelling ratio of raw Göynük oil shale as a function of swelling solvent solubility parameters	326
5.4.1.2 Swelling ratio of demineralized Göynük oil shale as a function of swelling solvent solubility parameters	326
5.4.1.3 Changes of number average weight ($\bar{M}_c$) as a function of different density for raw GOS sample	334
5.4.1.4 Changes of number average weight ($\bar{M}_c$) as a function of different density for demineralized GOS sample	335

LIST OF FIGURES (Continued)

Figure	Page
5.4.2.1 Total weight loss curves derived from TGA data	338
5.4.2.2 Rate of decomposition curves derived from TGA data	339
5.4.2.3 Differential weight loss curves derived from TGA data	340
5.4.3.1 Volatile product evolution rate in the pyrolysis of GOS-K	342
5.4.3.2 Volatile product evolution rate in the pyrolysis of GOS-K-D	342
5.4.3.3 Volatile product evolution rate in the pyrolysis of GOS-K-P	343
5.4.3.4 Volatile product evolution rate in the pyrolysis of GOS-K-T	343
5.4.3.5 Cumulative n-paraffin selectivity of GOS-K	344
5.4.3.6 Cumulative n-paraffin selectivity of GOS-K-D	345
5.4.3.7 Cumulative n-paraffin selectivity of GOS-K-P	345
5.4.3.8 Cumulative n-paraffin selectivity of GOS-K-T	346
5.4.3.9 Cumulative 1-olefin selectivity of GOS-K	346

LIST OF FIGURES (Continued)

Figure	Page
5.4.3.10 Cumulative 1-olefin selectivity of GOS-K-D	347
5.4.3.11 Cumulative 1-olefin selectivity of GOS-K-P	347
5.4.3.12 Cumulative 1-olefin selectivity of GOS-K-T	348
5.4.3.13 Total carbon balance for raw and swollen GOS samples	350
5.4.4.1 Swelling ratio of raw ZLIG as a function of swelling solvent solubility parameter	353
5.4.4.2 Swelling ratio of demineralized ZLIG as a function of swelling solvent solubility parameter. $\delta = 10.4$	353
5.4.4.3 Swelling ratio of raw KLIG as a function of swelling solvent solubility parameter.	355
5.4.4.4 Swelling ratio of demineralized KLIG as a function of swelling solvent solubility parameter	355
5.4.4.5 Swelling ratio of raw CLIG as a function of swelling solvent solubility parameter	357
5.4.4.6 Swelling ratio of demineralized CLIG as a function of Swelling solvent solubility parameter	357

LIST OF FIGURES (Continued)

Figure	Page
5.5.1 Conversion of gas and liquid products of lignite samples after SCWE	364
5.5.2 Yield of the gas, liquid and solid residue of ELIG-R	365
5.5.3 Yield of the gas, liquid and solid residue of ELIG-C	365
5.5.4 Yield of the gas, liquid and solid residue of ELIG-N	366
5.5.5 Yield of the gas, liquid and solid residue of ELIG-F	366
5.5.6 Classification of gas products evolved from SCWE of ELIG-R	367
5.5.7 Classification of gas products evolved from SCWE of ELIG-C	368
5.5.8 Classification of gas products evolved from SCWE of ELIG-N	368
5.5.9 Classification of gas products evolved from SCWE of ELIG-F	369
5.6.1.1 Weight loss and rate of the decomposition curves for SASP-R	371

LIST OF FIGURES (Continued)

Figure	Page
5.6.1.2 Weight loss and rate of the decomposition curves for SASP-C	371
5.6.1.3 Weight loss and rate of the decomposition curves for SASP-N	372
5.6.1.4 Weight loss and rate of the decomposition curves for SASP-F	372
5.6.1.5 Weight loss and rate of the decomposition curves for SLIG-R	375
5.6.1.6 Weight loss and rate of the decomposition curves for SLIG-C	375
5.6.1.7 Weight loss and rate of the decomposition curves for SLIG-N	376
5.6.1.8 Weight loss and rate of the decomposition curves for SLIG-F	376
5.6.1.9 Weight loss and rate of the decomposition curves For GOS-R	378

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
5.6.1.10 Weight loss and rate of the decomposition curves For GOS-C	378
5.6.1.11 Weight loss and rate of the decomposition curves for GOS-N	379
5.6.1.12 Weight loss and rate of the decomposition curves for GOS-F	379



LIST OF TABLES

Table	Page
2.1.1.6.1 Average characteristic values of Turkey's oil shale deposits	16
2.1.1.6.2 Turkey's bituminous shale reserves in million tone	17
2.1.2.3.1 Worldwide reserves of lignite	32
2.1.2.3.2 Lignite production for different countries for selected years in million metric tone	34
2.1.3.4.1 Asphaltite reserves in Turkey	43
2.1.3.4.2 Chemical properties of Turkish asphaltites	44
2.1.3.4.3 Consumption of Asphaltite in Turkey according to years	44
2.2.4.1 Physicochemical properties of water as a function of temperature and pressure	75
4.1.1. The elemental analysis of GOS-R, ELIG-R, SLIG-R and ASP-R	122
4.2.1.1 The operating conditions of demineralization	124
4.2.2.1 Experimental schedule of isothermal pyrolysis	129
4.2.3.1 Experimental schedule of TPP	133
4.2.5.1 Experimental schedule for solvent swelling	138
4.3.4.1 Operating condition for capillary gas chromatography	145

LIST OF TABLES (Continued)

Table	Page
4.3.5.1 Operating conditions of TOC analyzer	146
5.1.1.1 Weight losses after demineralization of GOS-R with HCl	149
5.1.1.2 Ash analysis of GOS-C	150
5.1.1.3 Weight losses after demineralization of GOS-C with HNO ₃	152
5.1.1.4 Ash Analysis of GOS-N	153
5.1.1.5 Weight losses after demineralization of GOS-N with HF	154
5.1.1.6 Ash Analysis of GOS-F	155
5.1.2.1 Weight losses after demineralization of ELIG-R with HCl	159
5.1.2.2 Ash analysis of ELIG-C	160
5.1.2.3 Weight losses after demineralization of LIG-C with HNO ₃	161
5.1.2.4 Ash analysis of ELIG-N	162
5.1.2.5 Weight losses after demineralization of ELIG-N with HF	163
5.1.2.6 Ash analysis of ELIG-F	163
5.1.3.1 Weight losses after demineralization of SASP-R with HCl	169
5.1.3.2 Ash analysis of SASP-C	170
5.1.3.3 Weight losses after demineralization of SASP-C with HNO ₃	172
5.1.3.4 Ash analysis of SASP-N	175

LIST OF TABLES (Continued)

<u>Table</u>	<u>Page</u>
5.1.3.5 Weight losses after demineralization of SASP-N with HF	174
5.1.3.6 Ash analysis of SASP-F	175
5.2.1.1 The major constituents of organic compounds at pyrolysis of GOS-R	181
5.2.1.2 Amount of C in feed and C recovered as product in IP of GOS-R	183
5.2.1.3 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of GOS-R	187
5.2.1.4 Carbon content in solid residue of GOS-R	187
5.2.2.1 Amount of C in feed and C recovered as product in IP of GOS-C	193
5.2.2.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of GOS-C	196
5.2.2.3 Carbon content in solid residue of GOS-C	197
5.2.3.1 Amount of C in feed and C recovered as product in IP of GOS-N	202

LIST OF TABLES (Continued)

Table	Page
5.2.3.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of GOS-N	205
5.2.3.3 Carbon content in solid residue of GOS-N	205
5.2.4.1 Amount of C in feed and C recovered as product in IP of GOS-F	210
5.2.4.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of GOS-N	213
5.2.4.3 Carbon content in solid residue of GOS-F	214
5.2.5.1 Amount of C in feed and C recovered as product in IP of ELIG-R	220
5.2.5.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of ELIG-R	224
5.2.5.3 Carbon content in solid residue of ELIG-R	224
5.2.6.1 Volatile hydrocarbon products after IP of ELIG-C	230
5.2.6.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of ELIG-C	233
5.2.6.3 Carbon content in solid residue of ELIG-C	233

LIST OF TABLES (Continued)

<u>Table</u>	<u>Page</u>
5.2.7.1 Amount of C in feed and C recovered as product in IP of ELIG-N	237
5.2.7.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of ELIG-N	240
5.2.7.3 Carbon content in solid residue of ELIG-N	241
5.2.8.1 Amount of C in feed and C recovered as product in IP of ELIG-F	245
5.2.8.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of ELIG-F	248
5.2.8.3 Carbon content in solid residue of ELIG-F	249
5.2.9.1 Amount of C in feed and C recovered as product in IP of SASP-R	254
5.2.9.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of SASP-R	257
5.2.9.3 Carbon content in solid residue of SASP-R	258
5.2.10.1 Amount of C in feed and C recovered as product in IP of SASP-C	264

LIST OF TABLES (Continued)

Table	Page
5.2.10.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of SASP-C	267
5.2.10.3 Carbon content in solid residue of SASP-C	267
5.2.11.1 Amount of C in feed and C recovered as product in IP of SASP-N	272
5.2.11.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of SASP-N	275
5.2.11.3 Carbon content in solid residue of SASP-N	276
5.2.12.1 Amount of C in feed and C recovered as product in IP of SASP-F	281
5.2.12.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of SASP-F	284
5.2.12.3 Carbon content in solid residue of SASP-F	285
5.4.1.1 Solvent used for swelling of raw and demineralized oil shale and their solubility parameters. δ (cal/cm ³) ^{1/2}	324
5.4.1.2 Reversible Swelling of raw and demineralized GOS in Ethanol, Nitromethane	327

LIST OF TABLES (Continued)

Table	Page
5.4.1.3 Number average molecular weight per crosslink ($\bar{M}_c$) for raw GOS	331
5.4.1.4 Number average molecular weight per crosslink ($\bar{M}_c$) for demineralized GOS	333
5.4.1.5 Average molecular weight of raw and demineralized oil shale samples in different solvent	336
5.4.3.1 Total carbon balance for raw and swollen GOS samples	349
5.4.4.1 Solvents used for swelling of lignites	352
5.4.4.2 Swelling ratios of raw and demineralized KLIG	356
5.4.4.3 Reversible Swelling of raw KLIG, raw ZLIG and raw CLIG	358
5.5.1 The gas products volume of for lignite after SCWE	363
5.6.2.1 Set of reaction models applied to describe thermal decomposition in solid	383
5.6.2.2 Regresion coefficient for asphaltite samples	385
5.6.2.3 Activation energies of asphaltite samples	386
5.6.2.4 Temperature ranges of two pyrolysis regions of lignite	387

LIST OF TABLES (Continued)

Table	Page
5.6.2.5 Regresion coefficient for lignite samples at Region I	388
5.6.2.6 Activation energies of lignite samples for Region I	389
5.6.2.7 Regresion coefficient for lignite samples at Region II	390
5.6.2.8 Activation energy of lignite samples for Region II	391
5.6.2.9. Temperature ranges of two pyrolysis regions of oil shale	393
5.6.2.10 Regresion coefficient for oil shale samples at Region I	394
5.6.2.11 Activation energies of oil shale samples for Region I	395
5.6.2.12 Regresion coefficient for oil shale samples at Region II	396
5.6.2.13 Activation energy of oil shale samples for Region II	397
5.6.2.14. Temperature ranges of two pyrolysis regions of oil shale samples	399
5.6.2.15 Regresion coefficient for swollen GOS at Region I	400
5.6.2.16 Activation energies of swollen GOS for Region I	401
5.6.2.17 Regresion coefficient for swollen oil shale samples for Region II	402
5.6.2.18 Activation energies of swollen GOS for Region II	403

NOMENCLATURE AND ABBREVIATIONS**Symbols**

C_p	: Specific heat of water (kJ/kgK)
E	: Activation Energy (kJ/kmol)
m_c	: Mass flow rate of carbon in reference gas (mg C/min)
MW_c	: Atomic mass of carbon (g/mol)
n	: Molar flow rate of reference gas (mol/min)
N_c	: Product stream (mg C/min)
P	: Pressure (MPa)
p_{Kw}	: Ionic product of water
R	: Ideal gas constant (L.atm/mol.K)
T	: Temperature (K)
V	: Volumetric flow rate of reference gas (L/min)

NOMENCLATURE AND ABBREVIATIONS (Continued)

ε	: Static dielectric constant
η	: Viscosity of water (mPas)
λ	: Thermal conductivity of water (mW/mK)
ρ	: Density (g/cm ³)

Abbreviations

CLIG	: Çorum Lignite
DTA	: Differential Thermal Analysis
ELIG	: Soma Eynez Lignite
GC	: Gas Chromatography
GOS	: Göynük Oil Shale
IP	: Isothermal Pyrolysis
KLIG	: Soma Kırakdere Lignite

NOMENCLATURE & ABBREVIATIONS (Continued)

RPA	: Reference Gas Peak Area
SASP	: Şırnak Asphaltite
SCWE	: Supercritical Water Extraction
SLIG	: Soma Lignite
TC	: Total Carbon
TGA	: Thermogravimetric Analysis
THR	: Total Hydrocarbon Recovery
TOC	: Total Organic Carbon
TPA	: Total Peak Area
TPP	: Temperature Programmed Pyrolysis
VFHR	: Volatile Fraction of Recovered Hydrocarbons
ZLIG	: Soma Zeybek Lignite

NOMENCLATURE & ABBREVIATIONS (Continued)

x – R	: Raw sample
x – C	: Demineralized raw sample with HCl
x – N	: Demineralized x-C sample with HNO ₃
x – F	: Demineralized x-N sample with HF
x – D	: Swolled samples with DMSO
x – P	: Swolled samples with Pyridine
x – T	: Swolled samples with THF

1. INTRODUCTION

Fossil fuels supply over 80% of the world's energy needs. All fossil fuels, whether solid, liquid or gas is the result of organic material being covered by successive layers of sediment over the course of millions of years. Oil and natural gas were formed from the slow decomposition and burying of planktonic marine plants and animals that sank to the muds of the sea floor. Coal is derived from the accumulation of partially decayed land plants. As the sediment solidifies into rock, the organic material decomposes under the influence of great pressure and high temperature.

Coal is used in many different ways. It provides over 23% of global primary energy needs and 66% of total steel production. One of the most important ways we use coal is to make electricity. Currently, some 38% of the electricity generated worldwide is produced from coal. Electricity is used every day in many ways. Some examples of ways that we use electricity are heating, cooling and lighting our homes and cooking and refrigerating our food. By-products of coal are also used by companies to make items such as steel, cosmetics and tar.

Petroleum reserves are not wide spread in the world and limited compared to coal reserves, this caused an economical and political crisis. So, nations focused on to find alternative or safer energy

sources. New technologies for efficient coal utilization are now being developed for the largest coal consumer industries, such as environmentally acceptable fuels, steelmaking and electric power generation.

Oil shale deposits occur widely throughout the world, but the most extensive are in Colorado in the USA and at Sao Paulo in Brazil. In Turkey, the Mineral Research and Exploration Institute has characterized 5 billion tones of oil shale reserves in seven areas of western and central Anatolia. Because oil shales were formed by the inclusion of organic materials in inorganic sediments, they consist of organic and inorganic components. Liquid and gaseous fuels may be produced from oil shales.

The use of synthetic fuels is not widespread because producing it is more costly than refining petroleum. However, as world energy demands escalate the development of alternate energy sources escalate as well. The gradual reduction of the world's high value coal reserves have focused studies on the upgrading of lower rank coals to produce clean fuels. In developed countries, coal is not directly used after production. Reducing the mineral matter of fuel before usage is important not only economically but also technologically. Mineral matter and sulphur exhibit harmful effects on utilization of coal for combustion, carbonization, gasification, liquefaction, etc. purposes. These impurities poison the catalyst employed in coal conversion

processes. SO_2 produced during combustion leads to atmospheric pollution, acid rain and corrosion of boilers, pipelines and other machineries.

Demineralization of high sulphur/mineral coals to produce clean fuels can be achieved by both physical and chemical methods. The effectiveness of different methods for the purposes depends on the structure and composition of the minerals and their association in the coal. The physical methods is based on the differences in the physical properties of the minerals and the carbonaceous part of the coal. The chemical methods which involve treatment with different chemicals are effective for removing mineral matter. In chemical demineralization, acidic solutions such as HF, HCl, H_2SO_4 , HNO_3 , and basic solutions NaOH, KOH, $\text{Ca}(\text{OH})_2$ and combinations of these reagents can be used.

Solid fuels are important as energy sources and chemical feedstock worldwide. A growing interest has been especially shown in research in this field in countries such as Turkey which have large solid fuels deposits such as lignites, asphaltites and oil shales. Most coals consist primarily of a three dimensionally cross-linked macromolecular structure. There are different physical forces such as hydrogen-bonds or/and van der Waals forces as intermolecular forces between the molecules in this structure. The solvent molecules break apart these molecules and penetrate into the coal structure. As the solvent

molecules make their way into coal, it makes the coal swells. The use of a suitable solvent as a swelling agent aids both the solvent penetrating the pores and dissolved coal compounds migrating outward. The macromolecular network and swelling behavior of Göynük Oil Shales and demineralized Göynük Oil Shales and the effect of cross-link density on pyrolysis of these oil shales were investigated.

In this thesis, the effect of mineral matter in solid fuels on conversion to gas and liquid products was investigated by thermal methods and extraction under supercritical conditions. Beside this, the effects of mineral matter on swelling behavior of samples have been examined. Demineralization of asphaltite, lignite and oil shale were performed with HCl, HNO₃ and HF. In addition to this, DMSO, THF and pyridine were used for solvent swelling experiments. After these steps, these treated samples pyrolyzed in temperature programmed and isothermal pyrolysis reactor.

2. THEORETICAL BACKGROUND

2.1 Samples

2.1.1 Oil Shale

2.1.1.1 Definition and Classification of Oil Shales

Oil Shale is a general term applied to a group of fine light colors to dark brown shales rich enough in bituminous material (called kerogen). Kerogens are chemical compounds formed by the low grade metamorphism of organic molecules derived from decaying plant and animal matter. Kerogen is a complex mixture of compounds with large molecules containing mainly hydrogen and carbon but also oxygen, nitrogen, sulfur.

The term “Oil Shale” is a misnomer. It does not contain oil nor is it commonly shale. The organic material is chiefly kerogen, and the “shale” is usually a relatively hard rock called marl (WEC, 2002). Some terms used to describe oil shales are the following:

a) Most oil shales are fine-grained sedimentary rocks containing relatively large amounts of organic matter from which significant amounts of shale oil and combustible gas can be extracted by destructive distillation. Included in most definitions of “Oil Shale”,

either stated or implied, is the potential for the profitable extraction of shale oil and combustible gas or for burning as a fuel (Dyni, 2000).

b) An Oil Shale can also be defined as a compact rock of sedimentary origin with ash content of more than 33% and containing organic matter that yields oil when destructively distilled, but not appreciably when extracted with ordinary solvents (Kök, 2001).

c) Oil Shale is a general term applied to all fine-grained sedimentary rocks that yield liquid hydrocarbons in excess of 25 L per ton of rock when heated to about 500°C. Lithologically, these rocks may be shale, marl or carbonates, or transitional to coal and carbonaceous shale (Smith and Naylor, 2002).

Oil Shales, until recent years, have been an enigmatic group of rocks. Many oil shales were named after a locality, mineral or algal content, or type of product the shale yielded. Hutton (1987) developed a workable scheme of classifying oil shales on the basis of their depositional environments and by differentiating components of the organic matter with the aid of ultraviolet/blue fluorescent microscopy. This classification has proved useful in correlating components of the organic matter with the yields and chemistry of the oil obtained by retorting. The organic-rich sedimentary rocks were given in Figure 2.1.1.1.1 and divided into 3 groups, namely,

- a) humic coals and carbonaceous shales,
- b) bitumen-impregnated rock (tar sands and petroleum reservoir rocks), and
- c) oil shales.

On the basis of the depositional environment, 3 basic groups of oil Shales were recognized: terrestrial, lacustrine, and marine. Terrestrial Oil Shales include those composed of lipid-rich organic matter such as resins, spores, waxy cuticles, and corky tissue of roots and stems of vascular terrestrial plants commonly found in coal-forming swamps and bogs. Lacustrine Oil Shales are those containing lipid-rich organic matter derived from algae that lived in freshwater, brackish, or saline lakes. Marine Oil Shales are composed of lipid-rich organic matter derived from marine algae, acritarchs (unicellular microorganisms of questionable origin), and marine dinoflagellates (one-celled organisms with a flagellum) (Dyni, 2000).

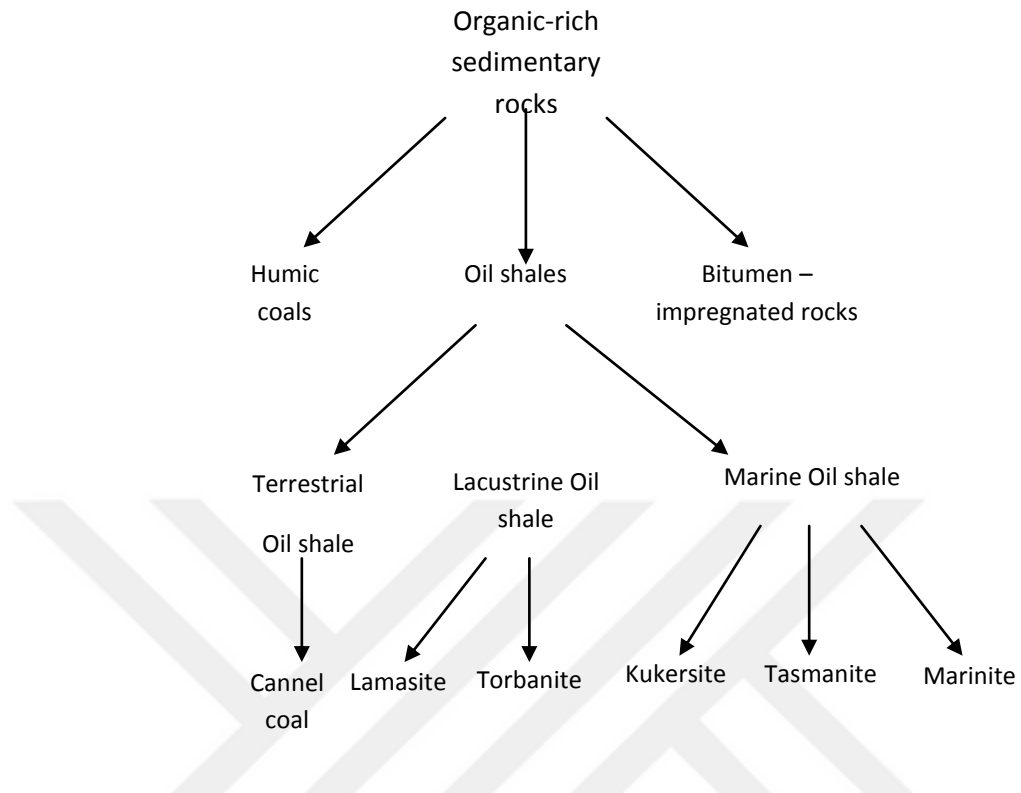


Figure 2.1.1.1.1 Schematic presentation organic-rich sedimentary rocks (Hutton, 1987)

2.1.1.2 Geology of Oil Shale

Oil shale consists of organic-rich sedimentary rock: it belongs to the group of sapropel fuels. It differs from bitumen-impregnated rocks (tar sands and petroleum reservoir rocks), humic coals and carbonaceous shale. While tar sands originate from the biodegradation of oil, heat and pressure have not transformed the kerogen in oil shales into petroleum. Coal contains a higher percentage of organic matter than oil shale. In commercial grades of oil shale the ratio of organic matter to mineral matter lies approximately between 0.75:5 and 1.5:5. At the same time, the organic matter in oil shale has an atomic ratio of hydrogen to carbon approximately the same as for crude oil and about two to three times higher than for coals.

Oil shale does not have a definite geological definition nor a specific chemical formula. Oil shales vary considerably in their mineral content, chemical composition, age, type of kerogen, and depositional history. Oil shale seams do not always have discrete boundaries and the carbonaceous content varies. Scottish oil shales frequently exhibit a change from no carbonaceous content through a range of carbonaceous content and back to non-carbonaceous shales. As a rule of thumb, the better the oil shale, the more chocolaty-brown the streak and the more woody the sound when struck by a hammer.

The organic components of oil shale derive from a variety of organisms, such as the remains of algae, spores, pollen, plant cuticles and corky fragments of herbaceous and woody plants, and cellular debris from other aquatic and land plants. Some deposits contain significant fossils; Germany's Messel Pit has the status of a Unesco World Heritage Site. The mineral matter in oil shale includes various fine-grained silicates and carbonates.

Geologists can classify oil shales on the basis of their composition as carbonate-rich shales, siliceous shales, or cannel shales. Another classification, known as the van Krevelen diagram, assigns kerogen types, depending on the hydrogen, carbon, and oxygen content of oil shales' original organic matter.

2.1.1.3 Origin of oil shale

Oil shale consists of sedimentary inorganic material containing a cross-linked macromolecular organic material called kerogen. Kerogen, from the Greek word meaning "oil generator", is a complex hydrocarbon molecule, petroleum's alkanes ancestor.

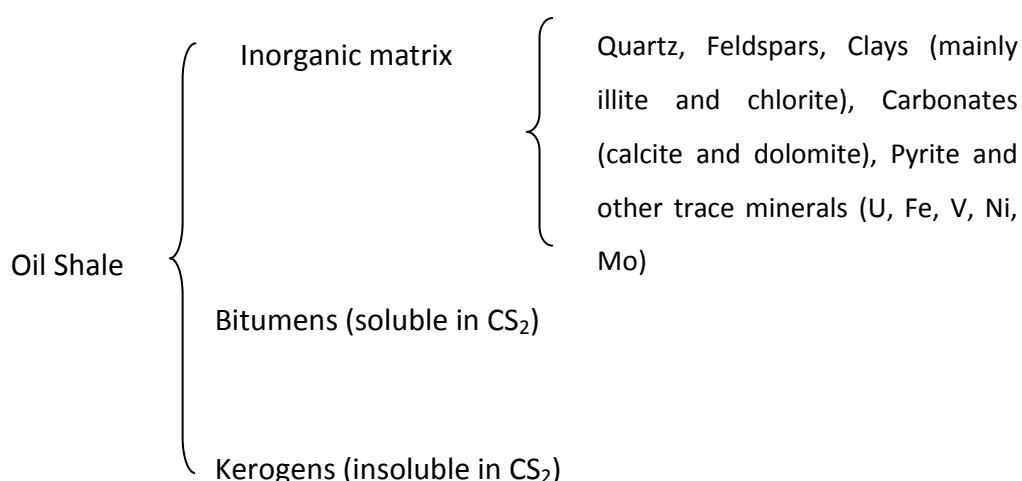


Figure 2.1.1.3.1 Basic constituents of oil shale

2.1.1.4 Historical Development of Oil in Turkey

The historical development of oil is briefly described below (TPAO, 1997). The Turkish historian Evliya Çelebi first mentioned the existence of oil in Turkey in the 18th century. Exploration began in the second half of the 19th century, when both domestic and foreign companies carried out exploration in Thrace. The first productive well, operated by the European Petroleum Company, was located in the Hora Deresi region (Thrace). After the Republic of Turkey was proclaimed in 1923, oil exploration resumed under the authority of the new government body empowered to explore for minerals and petroleum in Turkey. General Directorate of Mineral Research and Exploration (MTA) drilled several wells in the Southeast, primarily in the Raman region. In 1940, the first productive well, Raman 8, was drilled in the Raman oil field, setting the stage for later exploration of this large oil field. In 1951, the Garzan field was discovered in the same region, also as result of the MTA-sponsored explorations. In 1954, liberalized petroleum legislation opened up oil exploration to private companies both domestic and foreign. These changes in the government's petroleum policy were embodied in the petroleum law numbered 6326, which today governs all oil exploration activities. In the same year, law numbered 6327 established the Turkish Petroleum Corporation (TPAO), a national petroleum company. The TPAO took over from the MTA the exploration and exploitation of the petroleum

resources of the country. The Ministry of Energy and Natural Resources of Turkey was established in 1963 in order to assist in determining the objectives and policies for the energy sector and to enable exploration, development, production, and consumption of the energy resources in compliance with these objectives and policies. In line with these objectives, the Ministry of Energy and Natural Resources of Turkey (MENR) carries out its duties through the state enterprises under her control (Hepbaşlı, 2004).

Research into the utilization of Turkish oil shales has been going on since the 1970s. Oil shales comprise the second largest solid fuel deposit in Turkey, after lignites. Two of the largest deposits are at Göynük (109 tons) and Seyitömer, which are responsible for about 25% of the total reserves (Demirbaş, 2000).

2.1.1.5 Turkey's Oil Shale Deposits

Total world resources of Oil Shale are conservatively estimated at equivalent amount of 2.6 trillion barrels. However, petroleum-based crude oil is cheaper to produce today than shale oil because of the additional costs of mining and extracting the energy from Oil Shale. Because of these higher costs, only a few deposits of Oil Shale are currently being exploited in China, Brazil, and Estonia. However, with the continuing decline of petroleum supplies, accompanied by the

increasing costs of petroleum-based products, oil shale presents opportunities for supplying some of the fossil energy needs of the world in the years ahead (Dyni, 2000).

Turkey's Oil Shale reserves were determined on the basis of borehole data, while the oil shales are of the Palaeocene-Eocene and the middle-upper Miocene age. The host rocks are marl and clays, in which the OM is heterogeneously and finely dispersed. Turkey's current oil shale reserves are estimated at 1,865 million tons (Mt). The oil shale deposits are mainly located in Seyitömer-Kütahya, Himmetoğlu-(Göynük)-Bolu, Hatıldağ-Bolu, and Beypazari-Ankara fields. By far the largest known deposit is the Beypazari Oil Shale, which contains a total estimated resource of 1,058 Mt (Şener et. al., 1995; Şener and Gündoğdu, 1996; Ballice et. al., 1997; Kök, 2001). Generally, most Turkish studies have focused on Göynük and Seyitömer Oil Shale reserves for which the Fisher assay yields are high for Göynük and reasonable for Seyitömer (Olukçu et. al., 2002) . Location of major oil shale deposits in Turkey was given in Figure 2.1.1.5.1.

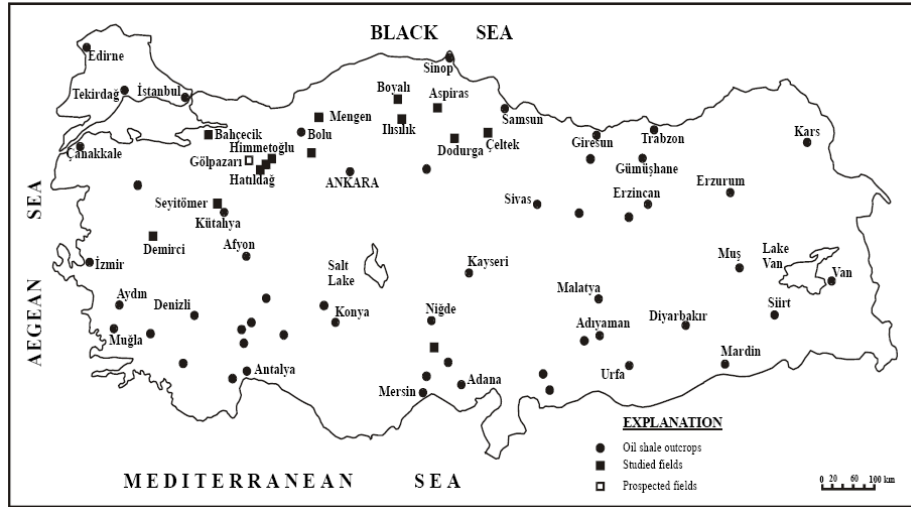


Figure 2.1.1.5.1 Location of major oil shale deposits in Turkey (Şener et. al., 1995)

2.1.1.6 Economic Evaluation of Oil Shale Reserves

Şener et al. (1995) undertook a comprehensive study on the economic evaluation of Oil Shale deposits in Turkey, as listed in Table 2.1.1.6.1, where average values are given. Turkey's bituminous shale reserves are also illustrated in Table 2.1.1.6.2. The main oil shale fields of the country, namely, Seyitömer, Himmetoğlu, Hatıldağ, and Beypazari, are summarized below.

(a) Seyitömer Oil Shale Field. In this field, unstable conditions prevailed during the formation and filling of the basin in the older Neogene. The main mineral components of Seyitömer Oil Shale are

quartz, dolomite, muscovite, illite, and smectite. A bituminous marl unit crops out around the Oil Shale field and has been penetrated by many drill holes for lignite prospecting. The characterization of the so-called economic-grade oil shale (EGOS), which theoretically can be utilized as fuel or for retorting, must be based on the quality of the Oil Shale as well as on the mining properties, mainly the thickness of the layers in question. In this field, EGOS varies considerably in thickness and quality in the lateral and vertical directions; the thickness ranges from 3 to 29.5 m, while the upper calorific and oil content values are in the range of 3.14 to 4.25 MJ/kg and 4 to 5.9wt%, respectively (Şener et.al., 1995; Kök, 2001).

(b) Himmetoğlu OS Field. Himmetoğlu Oil Shales are composed of, on a volumetric basis, liptinite (> 50%), huminite (20–50%), and inertinite (0–20%) maceral groups. An overlying zone of lignite contains brown coal (in DIN terminology) and subbituminous C coal (in ASTM terminology). The lowermost bituminous-banded marl (BBM) is generally a massive Oil Shale layer in the lower part, but becomes banded in the upper levels. The bituminous laminated marl (BLM) exhibits shallow-water penecontemporaneous sedimentary. The EGOS of Himmetoğlu is of average to poor quality, although it contains the Himmetoğlu Oil Shale, extremely rich shale with an oil content of 43% and an upper calorific value of > 20 MJ/kg. The reserves of the EGOS amount to 150 Mt, of which 99% is mineable by open casting if the

underlying lignite is also a mined structure (Şener et.al., 1995, Şener and Gündoğdu, 1996).

Table 2.1.1.6.1 Average characteristic values of Turkey's oil shale deposits (Şener et.al., 1995)

Deposits		Calorific Value (MJ/kg)	Total Organic Carbon (wt.%)	Oil content (wt.%)	Reserves (million tones)
Name of oil shale field	Location				
Seyitömer	Kütahya	3.55	6.9	5	110
Himmetoğlu	Göynük-Bolu	3.25	3.2	4.6	150
Hatıldağ	Bolu	3.24	5.6	5.3	547
Beypazarı	Ankara	3.40	4.8	5.4	1058
Total					1865

Table 2.1.1.6.2 Turkey's bituminous shale reserves in million tone
(SPO, 2001)

Name of Field	Proven	Probable	Possible	Total
Beypazarı-Ankara	327.684		205.970	327.684
Burhaniye-Balıkesir		15.600		15.600
Himmetoğlu-Bolu	65.698			65.698
Mengen-Bolu		50.000		50.000
Hatıldağ-Bolu	78.372	281.587		359.059
Bahçecik-Kocaeli		42.000		42.000
Seyitömer-Kütahya	83.320	38.850	63.292	122.170
Ulukışla-Niğde		130.000		130.000
Sarıcakaya-Eskişehir		300.000		300.000
Dodurga-Çorum		138.000		138.000
Çeltik-Amasya		90.000		90.000
Total	555.344	1.086.037	269.262	1.641.381

(c) Hatıldağ Oil Shale Field. This area is situated in the province of Bolu, southeast of Göynük. The Oil Shale occurs in the west part of an E-W oriented syncline of steeply dipping Paleocene- Eocene sediments. The Hatıldağ Oil Shales are composed of liptinite (> 80%), bituminite (5–10%), and huminite (5–10%). The EGOS reserves are totally 547 Mt, of which 150 Mt are mineable by open casting with an overburden-to-

Oil Shale ratio of up to 4:1 (Şener et.al., 1995; Şener and Şengüler, 1998).

(d) Beypazari Oil Shale Field. The microscopically recognizable organic material consists mainly of liptinite, huminite, and prebitumen. The EGOS reserves of the field are 1,058 Mt, of which 60 Mt is mineable by open casting. Besides this, the Beypazari-Cayirhan area ranks as the biggest oil shale deposit in Turkey (Şener et.al., 1995).



2.1.2 Coal

2.1.2.1 Definition of coal

Coal is a combustible, sedimentary, organic rock (composed primarily of carbon, hydrogen and oxygen) formed from vegetation, which has been consolidated between other rock strata to form coal seams and altered by the combined effects of microbial action, pressure and heat over a considerable time period. Coal is generally classified by what is known as "rank" which is based on the degree of transformation of the original plant material to carbon. Coal is the world's most abundant, safe and secure fossil fuel – it is also clean and cost-effective.

- **Abundant** – extensive reserves of coal are present in many countries; coal is mined in more than 50 countries. World coal reserves were given in Figure 2.1.2.1.1.
- **Safe** – coal is stable and hence the safest fossil fuel to transport, store and use.
- **Secure** – abundant reserves mean that coal users are guaranteed security of supply at competitive prices; hence electricity supplies for industrial and domestic use are assured.
- **Clean** – using current technologies, coal can now be burnt cleanly throughout the world.

- **Cost-effective** – globally, coal is a competitive fuel for the generation of electricity, without which modern life would be virtually impossible. It is the major energy source for power generation worldwide (emd.aapg.org).

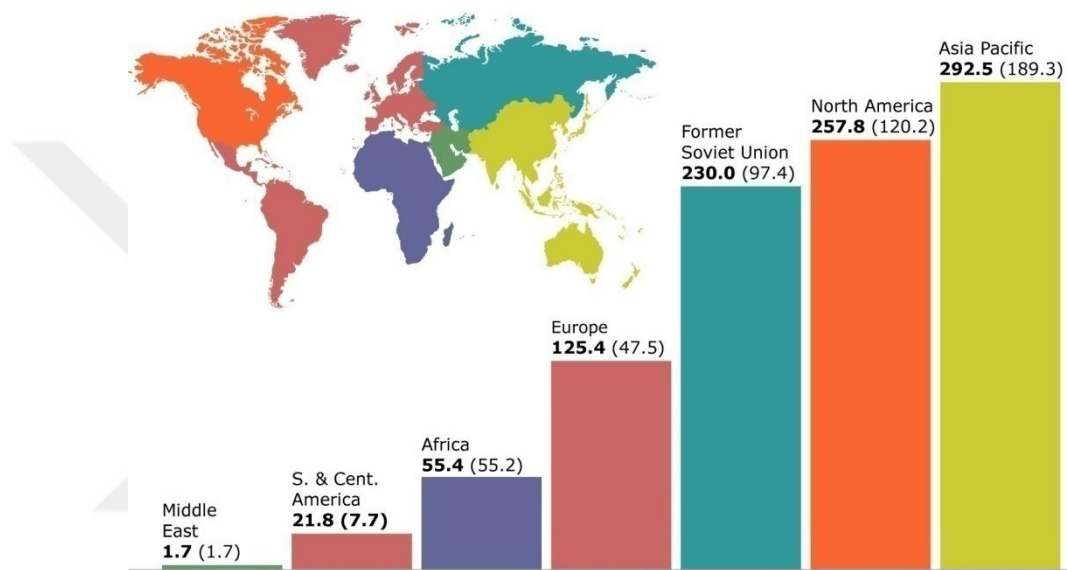


Figure 2.1.2.1.1 World coal reserves (x10⁹ tons; emd.aapg.org)

Coal is the altered remains of prehistoric vegetation that originally accumulated as plant material in swamps and peat bogs. The accumulation of silt and other sediments, together with movements in the earth's crust (tectonic movements) buried these swamps and peat bogs, often to great depth. With burial, the plant material was subjected to elevated temperatures and pressures, which caused

physical and chemical changes in the vegetation, transforming it into coal. Initially the peat, the precursor of coal, was converted into **lignite** or **brown coal** – coal-types with low organic ‘maturity’. Over many more millions of years, the continuing effects of temperature and pressure produced additional changes in the lignite, progressively increasing its maturity and transforming it into the range known as **sub-bituminous** coals. As this process continued, further chemical and physical changes occurred until these coals became harder and more mature, at which point they are classified as **bituminous** or hard coals. Under the right conditions, the progressive increase in the organic maturity continued, ultimately to form **anthracite**. The related diagram was given in Figure 2.1.2.1.2.

The degree of ‘metamorphism’ or coalification undergone by a coal, as it matures from peat to anthracite, has an important bearing on its physical and chemical properties, and is referred to as the ‘rank’ of the coal. Low rank coals, such as lignite and sub-bituminous coals, are typically softer, friable materials with a dull, earthy appearance; they are characterized by high moisture levels and a low carbon content, and hence a low energy content. Higher rank coals are typically harder and stronger and often have a black vitreous lustre. Increasing rank is accompanied by a rise in the carbon and energy contents and a decrease in the moisture content of the coal. Anthracite is at the top of the rank scale and has a correspondingly higher carbon and energy content and a lower level of moisture.

Rank classifications are based on a coal's content of fixed carbon, volatile carbon compounds, water, and ash, its heating value, and its coking properties. In the coalification process, coal first takes the form of peat, then progresses through lignite (brown coal), bituminous (soft coal), and finally to anthracite (hard coal) and graphite. Lignite has a low heating value and a high moisture content of 30 to 40 %. Since it weathers easily, lignite is not transported far but used to generate electricity in power plants (emd.aapg.org).

Large coal deposits only started to be formed after the evolution of land plants in the Devonian period, some 400 million years ago. Significant accumulations of coal occurred during the Carboniferous period (350-280 million years ago) in the Northern Hemisphere, the Carboniferous/Permian period (350-225 million years ago) in the Southern Hemisphere and, more recently, the late Cretaceous period to early Tertiary era (approximately 100-15 million years ago) in areas as diverse as the USA, South America, Indonesia and New Zealand.

In addition to carbon, coals contain hydrogen, oxygen, nitrogen and varying amounts of sulphur. High-rank coals are high in carbon and therefore heat value, but low in hydrogen and oxygen. Low-rank coals are low in carbon but high in hydrogen and oxygen content.

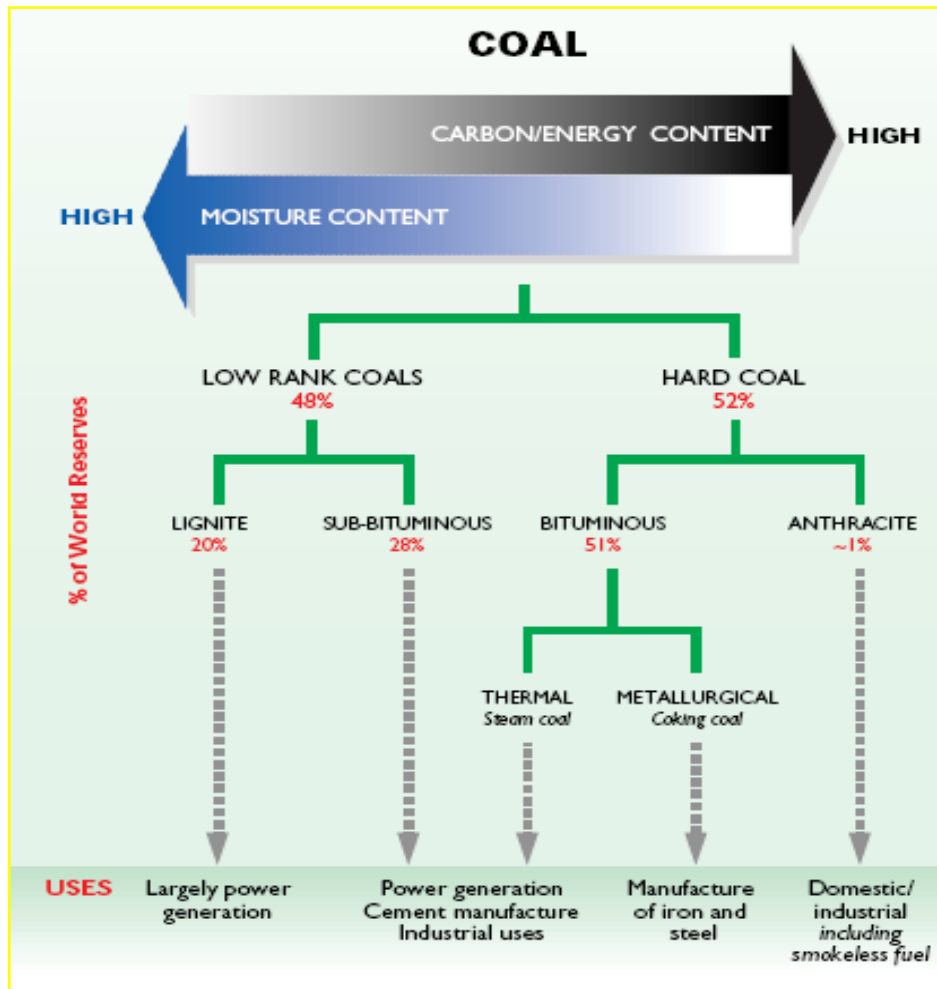


Figure 2.1.2.1.2 The rank of coal (ww.wci-coal.com)

2.1.2.2 Uses of Coal

Coal has many important uses, but most significantly in electricity generation, steel and cement manufacture and industrial process heating. In the developing world, the use of coal in the household, for heating and cooking, is important.

Coal is the major fuel source for electric power generation. Worldwide coal provides over 23% of global primary energy needs. More than half of total world coal production provides around 38% of the world's electricity and given in Figure 2.1.2.2.1 and almost 66 % of total global steel production is dependent on coal (www.wci-coal.com).

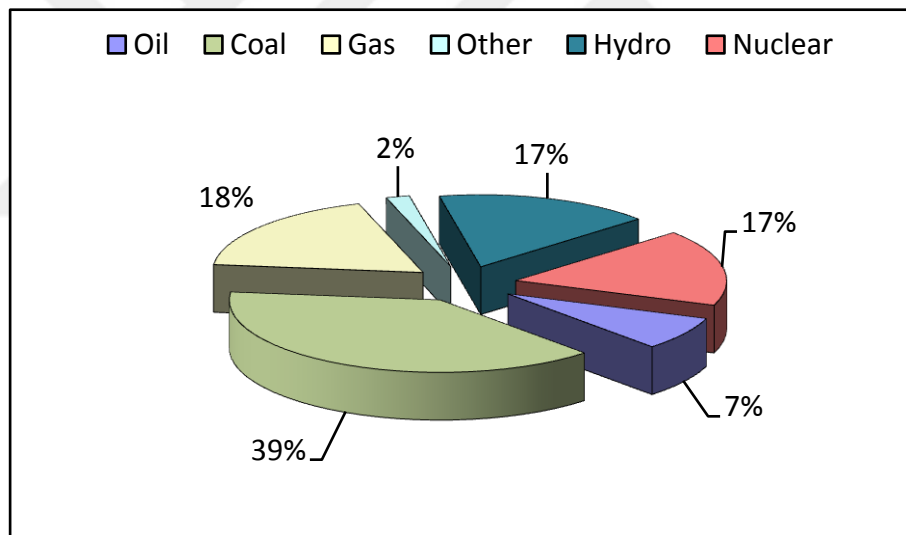


Figure 2.1.2.2.1 Generation of electricity worldwide

A number of countries are heavily dependent on coal for electricity, including in 2002:

- Poland 94.8%
- South Africa 93.0%
- India 78.3% (2001)
- Australia 76.9%
- PR China 76.2% (2001)
- Czech Republic 66.7%
- Greece 62.3%
- Germany 52.0%
- USA 49.9%
- Denmark 47.3%
- United Kingdom 32.9%
- European Union 27.2%

Modern life is unimaginable without electricity, which lights houses, buildings and streets, provides domestic and industrial heat, and powers most machinery used in homes, offices and factories. Without electricity, telecommunications, radio and television, most medical facilities and many of the most advanced industries would simply not exist. World electricity production and demands were given in Figure 2.1.2.2.2. Coal is also indispensable for iron and steel

production; some 70 % of steel production comes from iron made in blast furnaces using coal and coke.

Coal is found on every continent, and world coal reserves exceed 1 trillion tons. However, the largest reserves are found in the U.S., former Soviet Union, and China. The U.S. and former Soviet Union each have about 23 % of the world's reserves, and China has about 11 %. China, however, is the world's lead producer followed by the U.S.

Over 2000 active surface and underground mines are producing approximately 1 billion tons of coal a year in the U.S. At current consumption rates, the U.S. has a 240 year supply of coal reserves. Coals are generally termed steam (for use by power plants for electric generation) or coking (for conversion to coke for iron and steel making) (emd.aapg.org).

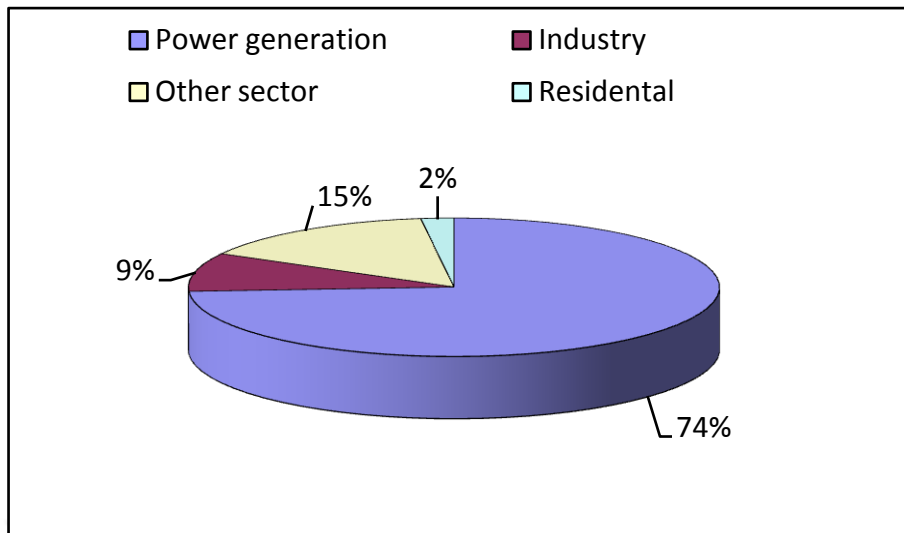


Figure 2.1.2.2.2 World electricity production and demands for 2030

Coal will continue to be an important primary energy resource (Figure 2.1.2.2.3), relative to both oil and gas, and to non-fossil fuels, with the application of emerging technologies and innovations ensuring that its global importance will continue into the current century.

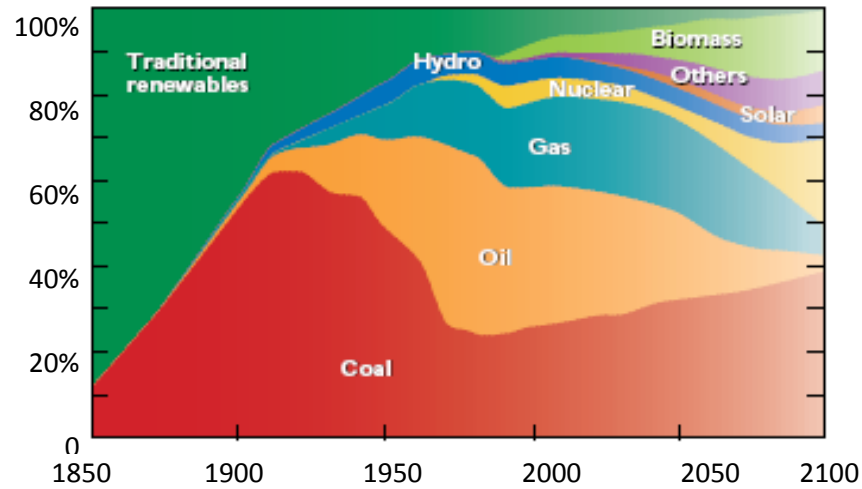


Figure 2.1.2.2.3 Consumption of fossil fuels in the world from 1800's

Turkey's natural energy resources are quite diversified; hard coal, lignite, asphaltite, oil, natural gas, hydro, geothermal, wood, animal and plant wastes, solar and secondary energy resources such as coke and briquettes are produced and consumed. Although Turkey's oil and natural gas reserves seem limited, coal reserves are quite abundant.

Turkey is located at a strategic place between the Middle and Near East where rich oil and natural gas reserves prevail and the Western world where the main energy consumption takes place. Turkey has made remarkable contribution to the establishment of co-operation for the stability of the region and still keeps on maintaining

her said policy. It is accepted that creating a balanced international co-operation setting is an important factor at acquiring more reliable energy supply policies.

Oil has the biggest share (44%) in total primary energy consumption, while natural gas has a share of 12%. Due to the diversification efforts of energy sources, use of natural gas that was newly introduced into Turkish economy has been growing rapidly. Natural gas consumption (6.8 billion m³) is assumed to increase by 11% and will reach to 31 billion m³ with a share of 18 percent in total consumption in 2010.

The annual oil consumption of Turkey is around 28.3 million tons. While 82 % of total consumption corresponding to 23.3 million tons is supplied from imports only 18 % is supplied from indigenous production.

2.1.2.3 Lignite

Definition of Lignite

Lignite is a dark brown to black combustible mineral formed over millions of years by the partial decomposition of plant material subject to increased pressure and temperature in an airless atmosphere. In simple terms, lignite is coal. Lignite has a high content of volatile

matter, which makes it more convertible into gas and liquid petroleum products than the higher-ranking coals.

Properties of Lignite

Coal is a complex mixture of organic and inorganic compounds that affect its reactivity. The organic matter of the lignite generally includes C, H and S. The macromolecular structure of coal varies with rank, and this variation influences its physical and chemical properties. The macromolecular structure of lignite consists of small aromatic units. As the rank of coal increases, the aromaticity and the ring condensation number also increase. Compared to lignites, bituminous coals have a higher carbon content, lower oxygen content and greater aromaticity and ring condensation number. Because of the open structure, lignites have a highly porous nature. About 90% of the total surface area of lignites is in the internal surface of pores because of the high surface area and high porosity, lignites are generally very reactive coals.

Bituminous coals have lower porosities and lower total surface areas than lignites, which results in a lower reactivity. It is apparent that the lignites with high volatile matter content have greater porosity. The chemical and physical structure of coal changes with increasing carbonization degree. The volatile matter, hydrogen, oxygen, moisture content and porosity continuously decrease. The

surface area of coal plays an important role in combustion. Oxygen must enter the pore mouths and penetrate into the particle. The oxidation occurs mainly at the surface of the pores. Thus, the combustion rate of a coal particle is proportional to the surface area and pore size distribution. The transfer of oxygen molecules into the pore surface and the transfer of the products back to the gas phase are easier for larger pores. An increase in the volatile matter content causes a decrease in the activation energy. The activation energy increases as the carbon content of the lignite increases (Haykırı et. Al, 2000).

Using Areas of Lignite

In 2000, lignite production was 30.9 million tons. Lignite reserves in the world were given in Table 2.1.2.3.1. Lignite production has averaged about 30 million tons in the past 10 years. Lignite production in Turkey was given Figure 2.1.2.3.1 and in world given in Table 2.1.2.3.2. (www.lignite.com)

Table 2.1.2.3.1 Worldwide reserves of lignite (billion tone)
(www.lignite.com)

Resources, 29,3 GJ*10 ⁶		
Country	Proved in Place	Proved Recoverable Reserves
Russia	110.000	100.000
Germany	102.000	56.150
Australia	46.000	41.900
USA	40.828	31.963
China	37.200	18.600
Yugoslavia	16.000	15.000
Poland	12.900	11.600
Turkey	7.705	6.986
Greece	5.312	3.000
Bulgaria	4.418	3.700
Canada	1.615	2.827
UK	1.000	500

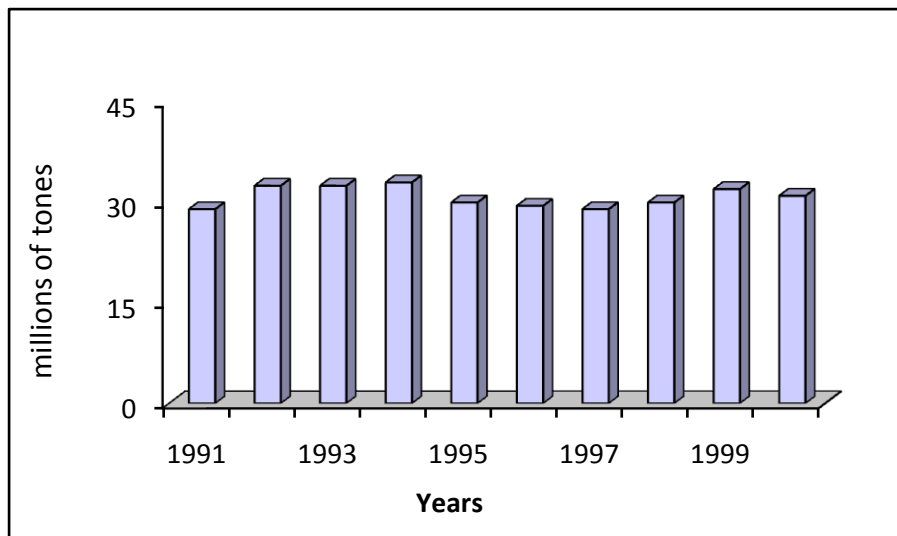


Figure 2.1.2.3.1 Lignite production between 1991-2000 in Turkey

Turkey is a rapidly growing energy consumer in its own right. Turkey has experienced extremely sharp economic growth in recent years, which was largely achieved through a rapidly increasing population. Because of its social and economic development of the country, the demand for energy and particularly for electricity is growing rapidly. The main indigenous energy resource is poor quality lignite (Demirbaş, 2000) .

Table 2.1.2.3.2 Lignite production for different countries for selected years in million metric tons (www.cia.com)

	1970	1980	1990	1991	1992	1993	1994	1995	1996
USA	5	43	80	78	82	81	80	78	80
Australia	24	33	46	49	51	48	50	51	50
Canada	7	17	31	31	33	34	36	36	36
Poland	33	37	68	69	67	68	67	65	62
Turkey	4	15	45	43	49	46	52	53	50
Germany	371	390	357	280	242	222	207	193	190
Greece	8	23	52	53	55	55	57	58	58
Romania	14	27	34	29	31	39	39	40	38

Turkey has hard coal (anthracite and bituminous) reserves of around 1.1 billion short tons, plus lignite reserves as high as 8 billion short tons. Around 40% of Turkey's lignite is located in the Afşin-Elbistan basin of southeastern Anatolia, while hard coal is mined only in one location of the Zonguldak basin of northwestern Turkey. Turkey

produced 74 million short tons (Mmst) of coal (mainly lignite) in 2000, and consumed 91 Mmst. Between 1990 and 2000, the number of workers in Turkey's coal sector fell from 63,993 to 35,665. Turkish coal is generally of poor quality and highly polluting. It is used mainly for power generation.

In Turkey, electricity is produced by thermal power plants, consuming coal, lignite, NG, fuel oil and geothermal energy, and hydro power plants. Domestic coal, geothermal and hydropower reserves of Turkey are approximately 1% of the world's total. Although it has some of almost all the conventional and renewable sources, Turkey is rich in only lignite and hydro resources. Lignite has the biggest share in total primary energy production by 43%. The complex geology consisting high risks inhibited exploration in our country. For this reason in primary energy production oil has a share of 13% and natural gas has a share of 1 %. Using areas of lignites in Turkey were given in Figure 2.1.2.3.2.

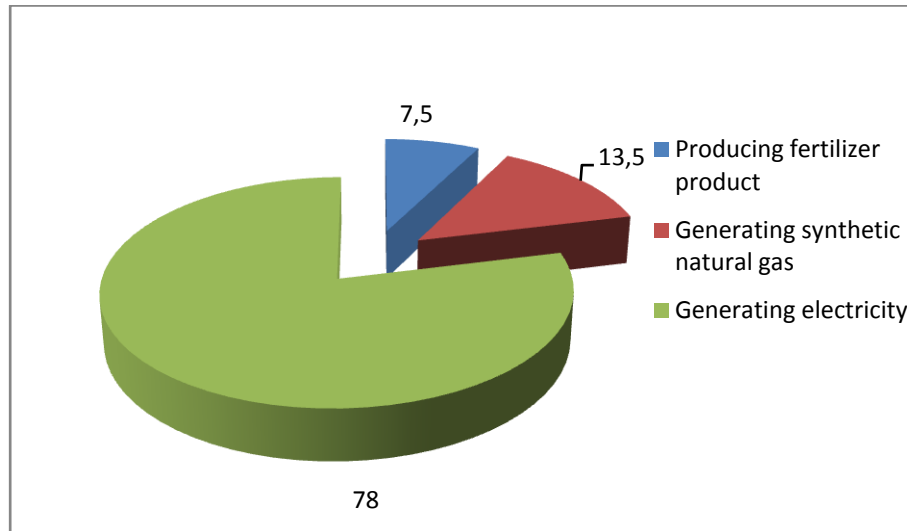


Figure 2.1.2.3.2 Uses of Lignite in Turkey (www.lignite.com)

The most abundant naturally occurring fossil fuels in Turkey are bituminous coal and lignite. Rich lignite deposits are spread all over the country. 34% of the lignite capacity is being worked, while 3% is being developed. Total coal reserves of Turkey are estimated to be 8.4×10^9 lignite and 1.1×10^9 t bituminous coal and total annual lignite production is about 65.2 Mt, of which 80% is consumed for electrical generation in the coal-fired power plants. The coal-fired power plants are widely distributed in Turkey, with the majority in the west.

Some of the largest lignite deposits are Afsin-Elbistan (3.2 billion tones), Beypazari-Ankara (400 million tones), Mengen-Bolu (100 million tones), Tunçbilek-Kütahya (328 million tones), Seyitömer-Kütahya (200

million tons), and Soma-Manisa (130 million tons. Lower heat values vary from 1100 to 4500 kcal/kg, some are even higher. However, their sulfur content is generally high. Soma (Manisa) and Tunçbilek (Kütahya) lignites are higher in heat content and lower in sulfur content (Şener and Gündoğdu, 1996). The biggest lignite deposits, 40% of the total, are in Elbistan. However, about 57% of the lignite reserves are of low calorific value, below 1500 kcal/kg. Better quality lignite of over 3000 kcal/kg only account for some 7%. Soma-Lignite is one of the largest deposits in Turkey and taken to be a representative for the other lignite deposits (Ballice and Reimert, 2002).

Especially in countries having planned economies, higher quality fuels are reserved for domestic heating, industrial fuels, and chemical feed stocks and the lower quality lignitic coals for electric power generation. The high reactivity of lignite, couple with relatively low cost at the mine, and relatively low cost of transportation product electricity or synthetic fuels, favor the construction of facilities for lignite use that are adjacent to the mine site.

2.1.3 Asphaltite

2.1.3.1 Definitions and Properties of Asphaltite

Generally asphaltic materials are formed by the migration of petroleum and solidification in cracks during tectonic movements. During and after the migration, petroleum loses its light components cracks into gas and undergoes series of complex chemical and physical changes (Ballice and Reimert, 2002). Asphaltite with rock crystal is shown in Figure 2.1.3.1.1.

In the past, there is no clear difference between the terms, tar sand and heavy oil. Heavy oil is originated from petroleum and it can be found in the rocks, which are close to petroleum reserves. Tar sand is sandy and sedimentary rock that contains bitumen like, heavy oil. Heavy oil and tar sand is the residual product of petroleum, which has been migrated and degraded in the porous rocks.

Oil sand and asphalted sand are called as asphaltite by considering chemical composition of hydrocarbon material of the rocks. The oil sands are very different from conventional oil and natural gas deposits. In conventional deposits, oil and gas are trapped in porous rocks. Drilling into the porous rock, releases the oil and gas, which then can be pumped to the surface. Or, in some cases, no pumping is necessary, where conventional fields are under pressure; oil and gas can be collected at the surface (oilsandsdiscovery.com).

Unlike conventional oil, the oil sands are a mixture of bitumen, sand, water and clay. Water makes up about four percent of the oil sand by weight. It surrounds each grain of sand, keeping it separate from the oil. Without this water envelope, the oil and the sand could not be separated by the water-based extraction. The bitumen, a particularly thick and tar-like hydrocarbon, surrounds the sand and water. The major challenge in developing oil sands is separating the bitumen from the sand, water and clay. Once separated, bitumen can be upgraded into high-quality oil called "synthetic crude", but it cannot be said "synthetic crude" until all the sand, water, clay and carbon has been removed.



Figure 2.1.3.1.1 Asphaltite with rock crystal

Solid form of hydrocarbon, which occurs as pure, natural bitumen; has a specific gravity of 1.05-1.10; hardness 2; color black; occurs in veins, lodes, and sedimentary rocks. On heating, it softens rapidly and flows like a liquid. It is used in waterproof coatings, wire insulation, and lacquer (Bolat et.al.,1998).

2.1.3.2 Origin of Asphaltite

Asphaltite is a petroleum-origin rock. It is formed from liquid or semi-liquid asphalt material present in deep, which is placed in split, crack and empty-space by transporting with the effects such as pressure, gravitation and temperature. Generally, asphaltic materials are formed by the migration of petroleum and solidification in cracks during tectonic movements.

Asphaltite which has a valuable energy resource with its high calorific value (2876–5536 kcal/kg), is a complex mixture consisting of compounds ranging from nonpolar aliphatic and naphthenic hydrocarbons to highly polar aromatic molecules containing heteroatoms such as oxygen, nitrogen and sulfur. These substances, originating from petroleum, are associated with mineral matter containing some valuable raw metals such as molybdenum, nickel, vanadium, and some radioactive metals such as uranium and thorium, and are also a potential source of hydrocarbons. It is a hard, blackish material, with a relatively high softening point of about 120–315°C. Asphaltite is a valuable source, includes rare minerals in its ash, and different percentages of gas are obtained when operated.

2.1.3.3 Asphaltite Reserves in the World

The two largest asphaltite reserves are the Athabasca Oil Sands in northern Alberta and the Orinoco River deposit in Venezuela. The Athabasca Oil Sand is just one of several deposits found in Canada. There is major oil sands deposit on Melville Island in the Canadian Arctic and three other smaller deposits in northern Alberta, the Peace River, Wabasca and Cold Lake deposits. In total, the Athabasca Oil Sands alone cover an area of more than 42000 km².

Some of the significant worldwide Oil Sand reserves are located in the following countries; Venezuela, Russia, Canada, United States, China, Madagascar, Brazil, Albania, Trinidad, Jordan.

2.1.3.4 Asphaltite Reserves in Turkey

In Turkey, the most important asphaltite deposits that are known are in Silopi and Şırnak areas, southeast of Turkey. In these regions, asphaltite reserves have different physical and chemical characteristics depending on the location of asphaltic material, geological formation and degree of metamorphosis.

The Mineral Research and Exploration Institute has determined over 79.969 million tons of asphaltite reserves in different areas in Turkey. Especially, deposits of it in our country are present in Şırnak

and Silopi river-basin and economical-thick vein-type beds are present in these regions. In addition to this, and a consequence of the researches and tests, it was confirmed that 44.5 million tons of this reserve is in visible quality.

Asphaltite deposits are around Şırnak and Silopi in Southeast Anatolian Region in Turkey. These deposits owned by TKİ (Turkey Coal Administration). The total reserves are about 82 million tons (This value includes the produced amount before). Yearly production in 1982 reaches the highest value (860000 tons), after this year production decreases with a wide range. The production at 1977 was 290000 tons.

Asphaltite has a high value (which is 4300 kcal/kg). Asphaltite includes rare minerals and can be used as solid fuels, as a suitable raw material for the production of synthetic petroleum. But, asphaltite is consumed as house fuel in many cities in East Anatolian Region. Synthetic petroleum production loses its fame, because the total amount of reserve is regarded as insignificant and the most of the suitable part of the reserve was consumed. Nowadays it is planned that asphaltite can be used as a fuel for thermic power stations.

Asphaltite reserves of Turkey were given in Table 2.1.3.4.1. As shown in table, all reserves are in Southeast Anatolian Regions. The total reserves include 82 million tons of asphaltite. But the reserve,

which can be operated, contains only 14 million tons of asphaltite. The chemical properties of Turkish Asphaltites are given in Table 2.1.3.4.2. The consumption of asphaltite according to years is given in Table 2.1.3.4.3. The values in the table are evaluated under constant stock assumption.

Table 2.1.3.4.1 Asphaltite reserves in Turkey (1000 ton)

Reserves	Visible	Probable	Possible	Total	Operable	Heat V. (kcal/kg)
Silopi-Harbul	17914	7851	-	25765	7000	5536
Silopi-Silip	3071	1335	-	4408	-	5485
Silopi-Üçkardeşler	9472	10861	-	-	-	-
Şırnak-Avgamasya	7481	673	-	8154	7000	4191
Şırnak-Milli	2000	2900	1600	6500	-	3400
Şırnak-Karatepe	500	2000	2500	5000	-	3695
Şırnak-Seridahlı	3534	1254	1279	6067	-	3174
Şırnak-Nivekara	300	1000	700	2000	-	3400
Şırnak-İspindoru	100	500	500	1100	-	3300
Şırnak-Segürük	550	450	-	1000	-	4500
Şırnak-Rutkekubat	551	53	-	604	-	2876
TOTAL	45473	28897	7579	81948	14000	

Table 2.1.3.4.2 Chemical properties of Turkish asphaltites

Reserves	Moisture (wt.%)	Ash (wt.%)	Sulphur (wt.%)	Volatile Matter (wt.%)	Heat Value (Kcal/kg)
Şırnak	0.1-5.4	38.52	4.0-6.7	19.4-44.9	3100-4500
Silopi	1.0-8.3	33-47	4.3-7.9	24.0-48.0	5000

Table 2.1.3.4.3 Consumption of Asphaltite in Turkey according to years

(1000 tons)	1989	1990	1991	1992	1993
Heating& Industry	405	512	400	456	323
TKI	405	249	139	193	99
Private sector	-	263	261	263	224
TOTAL	405	512	400	456	323

As it can be seen from Table 2.1.3.4.3, the consumption of asphaltite has an irregular development in last years. The reason of this situation is only the disorder of production conditions of asphaltite.

2.1.3.5 Usage Areas of Asphaltites

Since asphaltite deposits are limited all over the world and used as fuel, it hasn't had a special place in world economy until recently.

Together with the investigation of coal or petroleum-origin bitumen and pyrobitumen containing formations in the world as an alternative for the production of liquid/gas fuel and chemical raw material, this subject is updated in Turkey and the studies about the reorganization and evaluation of asphaltite are speed up. Most of the studies are carried out with Avgamasya-Şırnak asphaltite because of its large reserve, being an example for formations in Southeastern Anatolia. The asphaltite in Turkey has a higher-thermal value (2876–5536 kcal/kg) than lignites used previously by vicinity people in order to meet the house fuel. In 1965, it started to be produced by The New Celtek Coal and Mining Corporation Company. The production was continued in the suitable parts of open-plant in Avgamasya and partly Seguruk veins in Şırnak. They produced asphaltite, for example, in 1976, and was known to be sold to at least 21 cities including Ankara, Kayseri, Sivas, Kahramanmaraş, and Rize as well as east cities of Turkey (Kural, 1994). In the same year, the amount of produced tuvenan asphaltite was approximately 450,000 tons. The production has continued in the plants that are taken over by Turkey Coal Institute (TCI). The importance of asphaltite is due to the limited natural gas and petroleum resources of Turkey and being a rich-chemical raw material or synthetic liquid and gas fuel source.

2.2 METHODS

2.2.1 Demineralization

High ash and/or high sulfur coals are unsuitable for efficient use in carbonization, combustion, gasification or liquefaction. Due to the energy situation and the gradual depletion of high quality coal reserves of the world, more attention is being given to demineralization and/or desulfurization of low grade high ash and/or high sulfur coals to obtain environmentally acceptable clean fuels. The possibility for and the methods of upgrading by demineralization depends on the structure and composition of the minerals in coal, which again depends on the place and time of their deposition and formation. Mineral matter in coal exists essentially in three forms: true minerals, dissolved salts in pore water, and the elements associated with the hydrocarbonaceous matrix (Bolat et.al., 1998).

The main purpose in the demineralization is to remove mineral matter without influencing the organic structure of the coal.

Mineral matter is a complex mixture of inorganic minerals and elements except carbon, hydrogen, oxygen, nitrogen and sulphur. Clay minerals are the most abundant mineral species. Quartz is the second most abundant mineral phase. Other mineral matter forms are minor minerals and trace elements. These minor minerals include silicates or

shales (kaolinite type), calcite, gypsum, siderite, muscovite, carbonates, pyrites, disulphides, sulphides, sulphates and feldspars. There are some macro components whose concentrations generally exceed 1 wt. % in ash. These are firstly Al, Ca, Fe, S and Si and secondly, K, Mg, Na, P and Ti. It seems that excluding Si, which is almost entirely of mineral origin, the other inorganic elements have a mixed abundance in mineral and organic matter in a proportion.

Chemical processes, in general, are likely to be more expensive than physical processes in terms of both capital and operating costs. The methods used for chemical cleaning of coals include acid and alkali leaching under high pressure and at elevated temperatures and leaching by molten caustic baths. Demineralization can be attributed to the dissolution of water- and acid-soluble parts (generated during reaction) of the mineral matter present in coal and to the conversion of the non-water soluble portion into soluble parts due to oxidation of mineral matter such as pyrite. It has been found that using dilute to moderately concentrated NaOH solution, kaolin is converted into crystalline sodium derivatives. A great deal of effort has also been directed towards coal demineralization to a high level by various chemical methods. Among these, alkali/acid solution leaching has received much attention due to its demineralization efficiency. The basic solutions such as NaOH, KOH, $\text{Ca}(\text{OH})_2$, or acidic solutions such as HCl, H_2SO_4 , HNO_3 , and HF, as well as H_2O_2 , and combinations of these

reagents have been used (Karaca and Önal, 2003). This effectiveness of the chemicals on demineralization depends on the structure and composition of samples (Doymaz et.al., 2007).

The inorganic constituent of the oil shales, asphaltite and lignite affect the reactions of the organic matter both physically and chemically. The interaction between kerogen and the inorganic matrix during reactions is not well understood (Ballice and Sağlam, 2003).

A variety of chemical and physical procedures has been used in the past to isolate or concentrate the “insoluble” organic matter present in a sedimentary rock. Chemical methods of removing inorganic mineral matter are reviewed with particular reference to the action of hydrochloric acid, hydrofluoric acid, nitric acid (Saxby, 1969).

Physical and chemical methods developed up to 1958 for isolating organic matter from mineral matter have been discussed. Physical separation depends mainly upon flotation and centrifugation techniques in organic or inorganic solvents or mixtures, or on the different “wettability” properties of organic and inorganic matter in water and hydrocarbon solvents. However, such methods rarely give a complete separation and usually cannot be applied to sediments containing low concentrations of kerogen. Although extensive chemical alteration during physical treatment is unlikely, fractionation of

different types of kerogen is possible and quantitative recovery of organic matter is difficult. Hence chemical methods are desirable, particularly for samples containing small amounts of kerogen (~1%), although on occasions it is possible to use a combination of physical and chemical procedures.

2.2.1.1 Chemical methods

A number of reagents have been used to remove inorganic compounds selectively from carbonaceous sediments which had previously been finely ground and extracted with organic solvents. In the case of fine-grained sediments the amount of organic matter released during treatment with a particular reagent can often be useful in establishing the extent to which certain minerals are associated with kerogen. These reagents will now be considered individually with particular reference to their possible effect on kerogen molecules.

Hydrochloric acid

In varying concentrations (0.5N-10N) and at a range of temperatures (20°C-100°C) hydrochloric acid dissolves

most carbonates ($\text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$),

sulphides ($\text{ZnS} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\text{S}$), and

oxides and hydroxides; $(\text{Fe}(\text{OH})_3 + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 3\text{H}_2\text{O})$.

Pyrite (FeS_2) is the main sulphide mineral which cannot be completely removed in this way, although data of Ichikuni and Kamiya (1959) and Ichikuni (1960) indicate that it is slightly soluble in dilute HCl solutions.

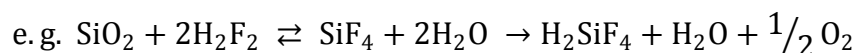
Hydrochloric acid will of course react with certain molecules and groups which may or may not be present in the kerogen. It has been shown that for a typical oil shale kerogen, 0.45% of the total kerogen and 8.2% of the total nitrogen were removed by treatment with 5N HCl, and solubilization of pyridine and aniline derivatives was suspected (Dancy and Giedroyc, 1950). In other work a loss of ~2.5% of the kerogen was attributed mainly to "mechanical losses", although in one HCl extract porphyrinic substances were identified and the nitrogen content of the shale dropped from 0.38% to 0.29%. Treatment of some Russian carbonaceous shale with 5% HCl has been shown to liberate up to 30% of the nitrogen-containing compounds in kerogen and, as expected, amino acids and sugars were identified in the extract. Similarly, from 30% to 50% of the nitrogen in most humic acids can be hydrolyzed by HCl, while for coals the proportion of hydrolyzable nitrogen decreases with increase in coalification.

An increase in the chlorine content of carbonaceous material due to hydrochloric acid treatment indicates that unsaturated groups may undergo addition reactions. Research on coals indicates that treatment with HCl leads, on average, to an increase of ~0.8% in the chlorine content of the coal.

In order to minimize possible alteration of kerogen, acetic and carbonic acids have been used as alternatives to hydrochloric acid for the removal of carbonates such as dolomite and calcite. A comparison of HCl and H₂CO₃ indicates that the resulting kerogen samples are analytically almost identical. For a “lean” Colorado oil shale, carbon percentages (based on original shale) were 6.40% (untreated), 6.12% (after HCl), and 6.26% (after H₂CO₃); corresponding values for a “rich” shale were 17.8%, 17.5% and 17.4% respectively. HCl dissolved ~4% more of the shale than did H₂CO₃, but chemical analyses showed that it consisted mainly of aluminum and iron compounds.

Hydrofluoric- acid

After hydrochloric acid treatment, 50% HF or a HF/HCl mixture is commonly used to remove quartz, silicates and clay minerals

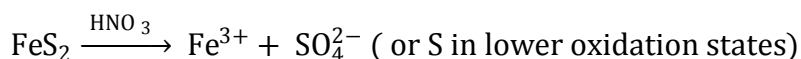


More basic rocks may form insoluble fluoride (CaF_2 ; $\text{MgAlF}_3 \cdot x\text{H}_2\text{O}$; $\text{NaAlF}_4 \cdot x\text{H}_2\text{O}$; $\text{Fe(II) [Al, Fe(III)]F}_3 \cdot x\text{H}_2\text{O}$) but not usually in the presence of HCl. Methods for dissolving complex fluorides when necessary have been described by Forsman and Hunt (1958) and by Long et al. (1968), who prefer ammonium carbonate to sodium carbonate as recommended by Dancy and Giedroyc (1950). Hydrofluoric acid, like HCl, reacts with certain organic groups and hence tends to alter some kerogen molecules which may not have reacted completely or at all with HCl. As evidence of this, the fluorine content of the organic matter may rise slightly due to addition reactions e.g., 0-0.38% F. In the case of coals there is usually no increase in fluorine content after HF treatment. Oxidation of kerogen, which may occur during HCl/HF treatment with the progressive decrease in the mineral content, is largely prevented by keeping the temperature below 60°C and not allowing the insoluble residue to evaporate to dryness.

Because of organic matter may be altered during HCl/HF treatment. Degens and Reuter (1964) have chosen to define kerogen as an organic substance which cannot be further extracted by organic solvents or become hydrolyzed by acids such as HCl, HF, and HClO_4 . However, regardless of definition, an understanding of organic matter in sediments requires a detailed study of both acid-soluble and acid-insoluble compounds, due regard being paid to the chemical properties of the acid involved.

Nitric acid

Dilute HNO₃ has been extensively used to dissolve pyrite but, as indicated by Forsman (1963), the accompanying kerogen may be oxidized or nitrated.



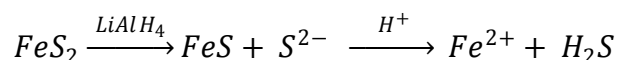
Mott (1950) showed that cold dilute HNO₃ does not readily dissolve pyrite in coal, but that boiling with 2N or 4N HNO₃ removes it completely. Normal acid under such conditions is not quite so effective. The magnitude of the change in the organic matter depends on the chemical nature of the kerogen as well as on the reaction conditions, but in many cases an apparent increase in oxygen and nitrogen content was observed (Down, 1939; Lawlor et al., 1963). Pyrite, for example, may be removed from St. Hilaire oil shale by HNO₃ (1.13 s.g.) but the nitrogen content is increased from 1.33% to 2.31%. The extent of oxidation of coals by nitric acid varies but the introduction of carboxyl groups is a major cause of the increase in oxygen content. Bands at ~1,330 and ~1,540 cm⁻¹ in the infrared spectrum of kerogen which had been treated with HNO₃ to remove FeS₂, have been attributed to R-NO₂ groups. Stanfield et al. (1951) and Neglia (1961) did not observe nitration of organic matter during dilute HNO₃ treatment but, in general, oxidation and nitration is to be expected, although the effect can be minimized by using dilute acid at

moderate temperatures (e.g., 2N HNO₃ at 50°C) for as short a time as possible.

Nitric acid has been used in studies on the oxidative degradation of kerogen. Typical reaction conditions are: 20-30% HNO₃; 110°C, air at 8 atm. pressure, 2 h (Veski et al., 1964); 58% HNO₃; 90°C-95°C, 8 atm. pressure, 4 h (Fomina et al., 1961); 60% HNO₃, 60°C-70°C, 40 h (Robinson et al., 1963). Oxidation and nitration of Colorado oil shale kerogen with HNO₃/H₂SO₄ (resp. 50%, 50%) at 50°C-54°C and 90°C-95°C result in 3.45 and 3.25% nitrogen in the respective products (Brower and Graham, 1958). The major part of the product from vigorous kerogen oxidation is usually carboxylic acids (solid, oily or HNO₃-soluble) with perhaps smaller amounts of hydrocarbons, terpenes, pyrrole resins, tannin, pigments, etc.

Lithium aluminum hydride

Lawlor et al. (1963) first proposed using LiAlH₄ in refluxing Tetrahydrofuran to remove pyrite from oil shale concentrates.



Under such powerful reducing conditions pyrite is readily attacked, but the kerogen also will be changed in specific ways. The oxygen content of the organic matter will in most cases be reduced, owing principally to the reduction of carbonyl, carboxyl and ester

groups to alcohols; these and other functional groups which will react with LiAlH_4 .

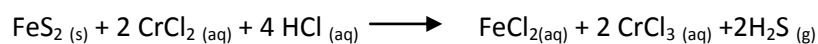
Infrared spectra before and after reduction highlight changes in the kerogen; the carbonyl absorption in the $5.9\ \mu$ region is eliminated, while the alcohol absorption at $9\text{--}10\ \mu$ appears to increase in intensity (Lawlor et al., 1963). However, if the initial pyrite concentration is high, satisfactory spectra cannot be obtained and it is difficult to estimate quantitatively, possible changes in the kerogen.

The ability of boiling tetrahydrofuran to dissolve organic molecules which are present in kerogen itself or are the products of reduction reaction may also be significant in certain cases. The failure of LiAlH_4 to increase the solubility of kerogen from the Green River Formation has been taken as evidence for the absence of ester and sulphide cross-linking groups (Jones and Dickert. 1965).

Chromous Chloride

It is described as a method for depyritization of kerogen preparations from typical petroleum source rock. The method uses acidic chromous chloride in aqueous solution and is an adaptation of the method as reported by Reaves in 1984, and Canfield et al. and Tuttle et al. in 1986. During recent years, this method has become a favored analytical method for determination of pyrite content in sediments and sedimentary rocks but it has not been examined previously as a kerogen purification technique.

The reduction of pyrite by acidic chromous chloride may be represented by the following reaction;



The formation of Cr^{3+} species which are more molecular orbital stabilized than Cr^{2+} is the most likely driving force for the above reaction. The reaction is conducted under nitrogen with gas flow carrying the H_2S to a trap where it is recovered as Ag_2S . Excess acid and acid soluble salts are removed from the residual kerogen by water washing (Acholla and Orr, 1993).

Sodium borohydride

Mclver (1967) reported the removal of pyrite from oil shale kerogen by treatment with NaBH_4 in aqueous solution. Being a milder reagent than LiAlH_4 , sodium borohydride should have less effect on organic matter. Groups reduced by LiAlH_4 but not normally attacked by NaBH_4 include:

R-COOH (acid), $(\text{R-CO})_2\text{O}$ (acid anhydride),

R-COOR (ester), R-CONR_2 , (amide), R-CN (nitrile),

R(arom.)-NO_2 (aromatic nitro), $\text{R-CH}_2\text{X}$ (alkyl halide),

$\text{R}_2\text{-C=C-R}_2$, (olefin) (Gaylord, 1956).

However, Mclver (1967) found that, despite repeated treatments with

NaBH_4 and separation of unreactive “shiny pyrite” by flotation in zinc bromide solution, the final carbonaceous product often still had a large inorganic content. Thus, this method does not appear to be very promising for samples containing a large proportion of pyrite.

Zinc and hydrochloric acid

Pure pyrite is readily dissolved by the reducing action of powdered zinc in concentrated HCl but if organic matter is present. FeS_2 is seldom completely removed even after several treatments (Dancy and Giedroyc, 1950; Forsman and Hunt, 1958; Forsman, 1963; Lawlor et al., 1963; Burlingame and Simoneit, 1968). The kerogen obtained after Zn/HCl treatment was found by McIver (1967) to resemble that resulting from reaction with NaBH_4 , an indication perhaps that organic matter is reduced to a similar extent by these two reagents.

2.2.2 Pyrolysis

Pyrolysis refers to the decomposition of organic matter by heat in the absence of air. Thermal decomposition is frequently used to mean the same, although it generally connotes the breakdown of inorganic compounds.

When coal, oil shale or tar sands are pyrolyzed, hydrogen-rich volatile matter is distilled and a carbon-rich solid residue is left behind.

A common synonym for pyrolysis is “devolatilization”. The carbon and mineral matter remaining behind is the residual char. In this regard, the term “carbonization” is sometimes used as a synonym for coal pyrolysis. However, carbonization has as its aim the production of a solid char, whereas in synthetic fuel production greatest interest centers on liquid and gaseous hydrocarbons.

Pyrolysis is one method to produce liquid fuels from coal, and it is the principal method used to convert oil shale and tar sands to liquid fuels. Moreover, as gasification and liquefaction are carried out at elevated temperatures pyrolysis may be considered a first stage in any conversion process.

By rigid definition, pyrolysis is thermal degradation in the complete absence of any external reactant (Hawkins, 1984). In pyrolysis, the product mixture and product quality can be influenced by many factors such as: catalyst, contact time, feed pre-treatment, feed material, heating rate, particle size of feed, moisture content of feed, pressure, reactor geometry, temperature, residence time, and reagents.

When organic materials are heated in the absence of air, they degrade to a gas, a liquid, and a solid. As it is mentioned above, it is possible to influence the proportions of the main products by

controlling the main reaction parameters of temperature, rate of heating, and vapor residence time. For example fast or flash pyrolysis is used to maximize either the gas or liquid products depending on temperature as summarized below:

Slow pyrolysis at low temperatures around 400 °C and long reaction times (which can range from 15 minutes to days in traditional beehive kilns) maximizes charcoal yields at about 30 % by weight.

Flash pyrolysis at temperatures of typically 500 °C; at very high rates and short vapor residence times of typically less than 1 s or 500 ms; maximizes liquid yields at up to 70 % dry basis.

Similar flash pyrolysis at relatively high temperatures of above 700 °C; at very high heating rates and similarly short residence times maximizes gas yields at up to 80 % by weight with minimum liquid and char production.

Conventional pyrolysis at moderate temperatures less than about 500 °C and low heating rates (with vapor residence times of 0.5 to 5 minutes) gives approximately equal proportions of gas, liquid and solid products (Bridgewater, 1994).

Cracking is to obtain volatile hydrocarbons from heavy hydrocarbons by changing chemical structure in the presence of heat. There are three types of cracking;

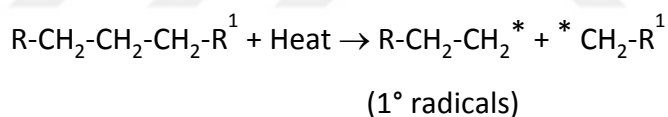
- Thermal cracking (pyrolysis)
- Catalytic cracking
- Hydro cracking

Thermal Cracking (Pyrolysis)

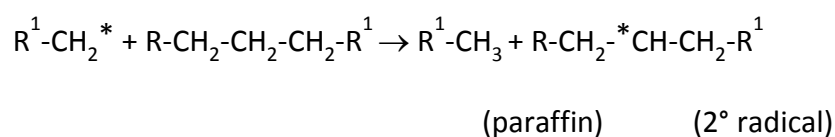
- Operations of the cracking of C-C or C-H bonds in large hydrocarbon molecules proceed at 450-600 °C, 750-950°C and over 1200 °C.

- Thermal cracking reactions are typical chain reaction, reaction steps follow as;

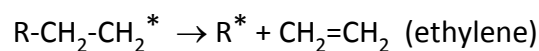
1. Existence of free radicals by cracking of C-C or C-H bonds,

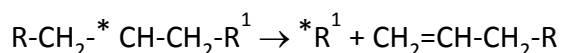


2. The transfer of radicals,



3. β -Cleavage





(α -olefin)

4. Conjunction of radicals

$R^\bullet + \dot{C}H_2-R^1 \rightarrow R-CH_2-R^1$ Although pyrolysis method has been used in obtaining tar, as adding to metallurgic coke and gas production from coal. It has been turned small amount of 10 % of the coal into liquid that is side product. In pyrolysis processes, due to thermal changes, unstable particles or large amount of radicals, which comes out, tend to combine again form polymerizes non-dissolving solid substance.

The study of pyrolysis is particularly that of coal can be dated from the end of the eighteenth century. Despite the many advances in understanding achieved since that time, there is still not a unified fundamental picture of the complex chemical and physical phenomena that take place, which given the raw material and the physical conditions of heating would enable a unique determination of the products.

Of most interest in the production of synthetic fuels is the prediction of the rate and amount of volatile yield and product distribution for a given raw material and set of pyrolysis conditions. Among the important chemical variables are the elemental and

functional compositions of the organic and inorganic matter, as well as the composition of the ambient gas in which the pyrolysis takes place. Among the more important basic physical variables are the final temperature, the time and rate of heating, the particle size distribution, the type and duration of any quenching, and the pressure.

Perhaps the best understood pyrolysis processes are the cracking and coking of petroleum. We recall that cracking means the breaking down of the hydrocarbons in the vapor phase to smaller molecular units, plus possibly some carbonaceous residue from the oil vapors. The most certainty in predicting product yield and distribution might be expected for tar sands, at least to the extent that the bitumen in the tar sands is related to conventional petroleum. The least certainty regarding product yield can be expected with coal pyrolysis. This is attributable to the fact that coal is not a unique chemical substance, but rather a complicated inhomogeneous mixture of different organic and inorganic materials of different petrographic compositions. The predictive capability for oil shale may fall somewhere between that of coal and tar sands. However, much less attention has been devoted to fundamental studies of oil shale pyrolysis than has been given to coal pyrolysis, a fact related to the relative importance of these materials in the past.

There are a number of features of pyrolysis common to coal, oil

shale, and tar sands. The composition of the raw material is important in determining the yield of volatile matter. The principal material property defining the yield is the hydrogen-to-carbon ratio. For lignite, sub bituminous, and bituminous coals, the proximate volatile matter will generally range between 30 and 50 mass %. It is to be emphasized that this yield is one obtained under controlled, slow heating assay conditions and is not necessarily optimum. The volatile matter value is a convenient and standardized measure. When the kerogen from Green River shale is pyrolyzed by the Fischer assay at 500°C, the volatile matter yield is about 80 to 85%. The volatile matter yield from the slow pyrolysis of Canadian and U.S. tar sand bitumens at 600°C is in the range of 83 to 88%.

The composition of the volatile products evolved in pyrolysis is largely determined by the raw organic material. For coals that are pyrolyzed at 500°C in an inert atmosphere under assay conditions of slow heating, the volatiles are composed of about 65 mass% gas and water, and about 35% tar and light oils. Oil shale kerogen volatiles are about 80% oil and 20% gas and water, while tar sand bitumen volatiles at 600°C are 90 to 95% liquids. In all cases, at 500°C the major constituents of the gas include carbon oxides, methane, hydrogen, and light hydrocarbons along with hydrogen sulfide and ammonia.

The pyrolysis temperature affects both the amount and

composition of the volatile yields. When coal, oil shale, and tar sand bitumen are heated slowly, rapid evolution of volatile products begins about 350 to 400°C, peaks sharply at about 450°C, and drops off very rapidly above 500°C. This is termed the stage of “active” thermal decomposition. There are three principal stages of pyrolysis. In the first stage, above 100°C and below, 300°C the evolution of volatile matter is not large and what is released is principally gas composed mainly of oxides of carbon and water. In the active or second stage of decomposition, about three-quarters of all the volatile matter ultimately released are evolved. The third stage is one most appropriately defined for coal, in which there is a secondary degasification associated with the transformation of the char, accompanied by the release of noncondensable gases, mainly hydrogen.

In all stages of pyrolysis, but particularly the higher temperature ones, it is important to distinguish between the “primary” volatile products of decomposition and those products which result from secondary cracking and coking reactions and from gasification reactions such as between the char and evolved water.

The effect of heating rate on the amount and composition of pyrolysis volatile yields has been an important question, particularly for coal, since it was demonstrated that when finely ground coal particles

are heated rapidly, larger yields than the proximate volatile matter yields could be obtained. Moreover, rapid heating to the peak decomposition temperatures around 500°C produced significantly larger tar fractions, suggesting the possibility of a means of converting coal to liquid hydrocarbons simply and with relatively large liquid yields. Traditional laboratory and assay heating conditions have been characterized by rates of temperature increase around 20°C/s during the period of rapid evolution of the volatile matter, so slow heating is defined to correspond to gradients about equal to or smaller than this value. Rapid heating is loosely defined in the literature as being larger than 10^3 to 10^5 °C/s.

Let us define the pyrolysis of any organic material as “slow” or “fast,” depending on whether the characteristic time required for heating the material to a specified final pyrolysis temperature is very much greater than, or very much less than, the characteristic pyrolysis reaction time. Such a definition presumes that a single characteristic pyrolysis time can be defined.

Particle size is known to influence pyrolysis yield. This effect may be related to heating rate, in that larger particles will heat up more slowly, so the average temperature particle will be lower, and hence volatile yields may be expected to be less. If the particle size is sufficiently small, it will be heated uniformly. No longer effect yield

below about 50 μm on coal particles. Similar results should apply to oil shale and the direct pyrolysis of tar sands.

Pressure may be expected to affect volatile yields, with higher pressures reducing the yields and lower ones increasing them. However, higher pressures favor cracking reactions, so high pressure will produce a larger volume of light hydrocarbon gases, whereas lower pressure will lead to larger tar and oil fractions.

Pyrolysis in a hydrogen atmosphere, termed hydrolysis, can increase the volatile yield and proportion of lower-molar-mass hydrocarbons. Hydrolysis is defined to include thermal decomposition and the attendant hydrogenation but not the hydrogasification of the char. Hydrogen reacts much faster with decomposing organic material and with the primary volatiles than with residual char.

2.2.3 Solvent Swelling

Oil shales consist of sedimentary inorganic material containing a crosslinked macromolecular organic structure called kerogen. Kerogens are three dimensionally crosslinked macromolecules and their chemical structures and geochemical alteration have been studied. Solvent method is the one of the simplest methods for characterizing the macromolecular structure of kerogens to gain insight into the geochemical process of maturation (Ballice and Larsen, 2003).

When a solid is typically dissolved into a liquid, the solid breaks up into individual molecules or ions which disperse throughout the liquid as much as possible, forming a solution. But what if the molecules in the solid are enough to be all tangled up with each other? The liquid disperses into the solid as much as it can, but the solid still remains largely intact. The solid does swell, however, as it absorbs liquid. This process is called solvent swelling. Perhaps most common example of this phenomenon is pasta swelling in hot water as the water molecules slip in between the starch molecules of the pasta.

Solvent swelling is the one of the simplest methods for characterizing the macromolecular structure of kerogen to gain insight into the geochemical process of maturation. The theory of solvent

swelling of crosslinked polymers was originally developed by Flory and Rehner.

At equilibrium, the free energy for dissolution of the swelling liquid in the polymer is exactly matched by an opposing elastic restoring force that depends on the number average length of the macromolecular chains between crosslinks.

The degree of solvent swelling can be used to calculate the chain length between crosslinks. The Flory-Rehner treatment assumes that there are present no specific interactions such as hydrogen bonding. It is assumed that Regular Solution Theory is followed (Ballice and Larsen, 2003).

The Regular Solution Theory

The kerogens are cross-linked macromolecular systems; regular solution theory provides a useful and convenient framework for describing the interactions between organic molecules and the kerogens.

The extent to which a kerogen is swollen when immersed in a solvent is taken as the measure of the solvent–kerogen interactions. The covalent cross-link density of the kerogen is fixed, thus the solvent influence on the amount of swelling depends on the magnitude of the

solvent- kerogen interactions. More favorable interaction leads to more swelling. If specific interactions occur between different parts of the kerogen molecule, they can serve as non - covalent cross-link.

Regular solution theory provides a good model of polymer–solvent interactions the central assumption of regular solution theory is that no specific interactions are occurring. Specific interaction include hydrogen bonding, strong dipole-dipole interactions, or any interaction which would yield a dimer or higher “mer” the entropy of mixing is therefore random. The enthalpy of mixing is calculated using the solubility parameter (δ).

$$\delta = \sqrt{\frac{\Delta E_{\text{vap}}}{V_{\text{mol}}}} \quad (2.2.3.1)$$

where ΔE_{vap} is the energy of vaporization and V_{mol} is the molar volume of the molecule in question. The theory is quantification of “like dissolves like”. The quantity and $\Delta E_{\text{vap}} / V_{\text{mol}}$ can be thought of the energy required to create a mole of holes in the liquid. In the absence of all specific interactions, the best solvent for a liquid is the liquid itself. All others will be poorer solvents, their interactions will be less. A direct extension of this is that for pairs of different liquids, those having the same solubility parameter will interact most strongly. The more their solubility parameters diverge, the less favorable their interactions. Again referring to “like dissolves like” and remembering

that specific interactions (all exothermic) are not allowed, the enthalpy of interaction of A and B will be 0 if $\delta_A = \delta_B$ and increasingly endothermic as δ_A and δ_B diverge.

These ideas can be directly extended to solid polymer- liquid systems. There is a driving force for dissolving the fluid in the polymer. Part of it is the concentration gradient and the other one is the interactions between the liquid and the polymer. The driving force for dissolution is opposed by the elastic restoring force of the network. It depends on the length of chains between branch points that is number average molecular weight between crosslink ($\bar{M}_c$). At equilibrium, the free energy of the solute-polymer interactions (ΔG_s) is exactly balanced by the elastic free energy (ΔG_e) which is opposing expansion of the polymer, that is $(\Delta G_s) = (\Delta G_e)$.

If the polymer-solvent combinations follow regular solution theory, there will be a maximum in solute uptake and thus a maximum in polymer swelling when the solute solubility parameter (δ_s) matches the polymer solubility parameter (δ_p). As the solubility parameters of the polymer and various solutes diverge, solute uptake and polymer swelling will be less. The theory predicts a bell shaped curve with no swelling for solvent quite unlike the polymer and a maximum near $\delta_s = \delta_p$.

Flory Rehner equation is

$$\bar{M}_c = - \frac{V_1 v_2^{1/3} \rho - (1/2) V_1 v_2 \rho}{\ln(1 - v_2) + v_2 + \chi v_2^2} \quad (2.2.3.2)$$

where ($\bar{M}_c$) is the number average molecular weight between cross-link, v_2 is volumetric fraction of polymer at equilibrium, V_1 is the solvent molar volume, and ρ is the polymer density, and χ is Flory Huggins Parameter.

$$\chi = \beta_1 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (2.2.3.3)$$

Where, β_1 is lattice constant (~ 0.35) and R is gas constant and T is temperature.

This equation doesn't hold unless the chain lengths between cross-links are large and so no longer follows a Gaussian distribution. In this point another theory must be used to remove the assumption of a Gaussian distribution of chain length and to introduce an additional parameter N, the number of rotatable segments between branch points named Kovac's equation which is given below

$$M_c^- = - \frac{V_1 v_2^{1/3} \rho + N^{-1} V_1 v_2^{-1/3} \rho}{\ln(1-v_2) + v_2 + \chi v_2^2} \quad (2.2.4.4)$$

Most coals consist primarily of a three dimensionally cross-linked macromolecular gel. There are different physical forces such as hydrogen-bonds, London, and van der Waals forces as intermolecular forces between the molecules in this gel. The solvent molecules break apart these molecules and penetrate into the coal structure. As the solvent molecules make their way into coal, the coal swells. The use of a suitable solvent as a swelling agent aids both the solvent penetrating the pores and dissolved coal compounds migrating outward (Tekeş et.al., 2002).

2.2.4 Supercritical Water Extraction

Water near or above its critical point (374 °C, 218 atm) is attracting increased attention as a medium for organic chemistry. Most of this new attention is driven by the search for more “green” or environmentally benign chemical processes. Using near critical or supercritical water (SCW) instead of organic solvents in chemical processes offers environmental advantages and may lead to pollution prevention. Interest in doing chemistry in SCW is not entirely new, however. There has been much previous research in this area with applications in synthetic fuels production, biomass processing, waste treatment, materials synthesis, and geochemistry (Savage, 1999).

Water near its critical point possesses properties very different from those of ambient liquid water. The dielectric constant is much lower, and the number and persistence of hydrogen bonds are both diminished. As a result, high-temperature water behaves like many organic solvents in that organic compounds enjoy high solubilities in near-critical water and complete miscibility with SCW. Moreover, gases are also miscible in SCW so employing a SCW reaction environment provides an opportunity to conduct chemistry in a single fluid phase that would otherwise occur in a multiphase system under more conventional conditions. The advantages of a single supercritical phase reaction medium are that higher concentrations of reactants can often

be attained and that there are no interphases mass transport processes to hinder reaction rates. The ion product, or dissociation constant (K_w) for water as it approaches the critical point, is about 3 orders of magnitude higher than it is for ambient liquid water. Accordingly, in addition to near-critical and supercritical water being an excellent solvent for organic compounds; it can also boast a higher H^+ and OH^- ion concentration than liquid water under certain conditions. As such, dense high-temperature water is an effective medium for acid- and base catalyzed reactions of organic compounds. In fact, the dissociation of water itself near the critical point generates a sufficiently high H^+ concentration that some acid-catalyzed organic reactions proceed without any added acid. As one exceeds the critical point, however, K_w decreases dramatically. For example, K_w is about 9 orders of magnitude lower at 600 °C and about 250 atm than it is at ambient conditions. SCW in this high-temperature, low-density region is a poor medium for ionic chemistry. Another difference between the properties (e.g., viscosity, dielectric constant, K_w) of SCW and ambient liquid water is that they vary continuously over much larger ranges in the supercritical state. This variation offers the possibility of using pressure and temperature to tune the properties of the reaction medium to optimal values for a given chemical transformation (Savage, 1999).

Important physicochemical properties of water are presented in Table 2.2.4.1 as a function of pressure and temperature. The density of SCW can be changed continuously from high (liquid-like) to low (gas-like) values without phase transition by varying the pressure and temperature (Bröll et.al., 1999).

Table 2.2.4.1 Physicochemical properties of water as a function of temperature and pressure (Bröll et.al., 1999)

	Normal water	Subcritical water	Supercritical water		Superheated steam
T(°C)	25	250	400	400	400
P (MPa)	0.1	5	25	50	0.1
ρ	0.997	0.8	0.17	0.58	0.0003
ϵ	78.5	27.1	5.9	10.5	1
PK_w	14	11.2	19.4	11.9	-
C_p	4.22	4.86	13	6.8	2.1
μ (mPas)	0.89	0.11	0.03	0.07	0.02
λ	608	620	160	438	55

The high relative static dielectric constant is 78.5 at 25 °C and drops to a value of about 6 at the critical point, thus clarifying the difference in the solution properties of SCW by comparison with normal water. The reasons for the relatively low value of the dielectric constant are found in the reduced number of hydrogen bonds brought

about by the density and temperature. At high pressure (i.e. high density) substances with ionic bonds (e.g. KCl, Na₂SO₄, NaOH) can be dissolved, and at low density nonpolar organic substances (e.g. cyclohexane) and gases (e.g. oxygen) can be dissolved. In the latter case SCW behaves almost like a nonaqueous solvent. According to quantum-mechanical calculations the molecules of supercritical water take part in the breakage and formation of chemical bonds by significantly lowering the activation energy (Bröll et.al., 1999).

In the supercritical region supercritical water exhibits very high specific heat capacities C_p (e.g. 29.2 kJ/kg at 400 °C and 29 MPa), [10] so that C_p can vary continuously over a wide range depending on the pressure and temperature. In highly exothermic reactions, such as partial oxidations in SCW, this could diminish the problem of hot spots (Bröll et.al., 1999).

The ionic product of water K_w is heavily dependent on density and temperature, so that this property can be used for optimizing acid/base-catalyzed reactions. At $pK_w < 14$ water is more suitable as a medium for heterolytic reactions, and at $pK_w > 14$ it is more suitable for homolytic reactions. However, the transition from heterolytic to homolytic is fluid and not sharply demarcated. The dynamic viscosity decreases with temperature at high density (collisional transfer of momentum) and increases with temperature at low density

(translational transfer of momentum). At moderate supercritical temperatures and high densities are only a tenth to a twentieth of its value under normal conditions. This leads to the expectation of advantages with regard to selectivity and space-time yield, especially in the case of heterogeneously catalyzed reactions, in which the overall reaction rate is often limited by mass transfer to and from the active centers. The attribution of a physical effect as the cause for the course of a particular chemical reaction in SCW is complicated since all the physical properties are highly dependent on temperature and pressure. Moreover, water can appear as a reactive component as well as a catalyst. Thermodynamic data for pure water are available over a wide range of pressures and temperatures. However, apart from a few binary systems which have been investigated corresponding data for aqueous multicomponent systems are often lacking. In these cases the lack of data on pressure and temperature-dependent specific volumes especially needs to be emphasized. These allow the exact determination of residence times in continuously operated reactors. Such data can be determined only by means of many experiments (Bröll et.al., 1999). Phase diagram of water and properties of water at 250 bars were given in Figure 2.2.4.1 and Figure 2.2.4.2, respectively.

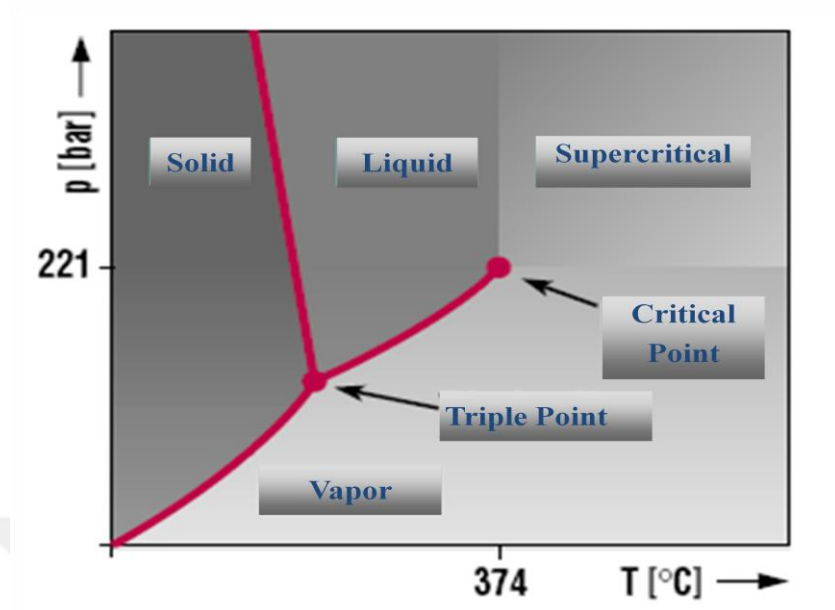


Figure 2.2.4.1 Phase diagram of water

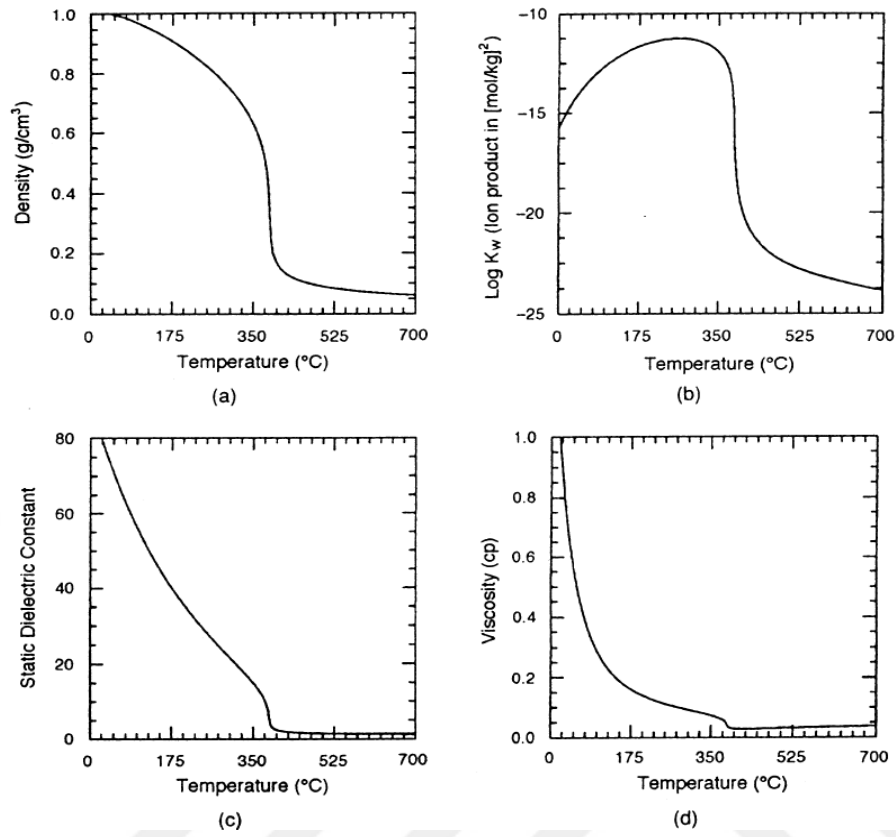


Figure 2.2.4.2 Properties of pure water as a function of temperature at 250 bar (Akiya and Savage, 2002)

The extraction of coals with supercritical fluids has been studied by a number of researchers over the last 20 years. One of the most important and interesting aspects of supercritical fluid extraction (SCFE) of coals is to ascertain the role or roles that the supercritical fluid plays in the extraction. The following appear to be the most likely major roles that the supercritical fluid may have:

- the supercritical fluid extracts the products from pyrolysis of coal;
- the supercritical fluid extracts smaller molecules which are present in coal but not bound to the coal matrix and
- the supercritical solvent attacks the coal structure.

In the first two cases, 'classical' supercritical extraction is occurring, and it would be expected that the conversion (extraction yield) would depend predominantly on the solvent density at the extraction conditions. There would be little, if any, effect of the chemical structure of the extracting fluid on the conversion. In these two cases, the extraction would be similar to extraction of coal-tar pitch at elevated temperatures. However, in case 3 the solvent structure would be of considerable importance.

3. LITERATURE REVIEW

3.1 Demineralization of Asphaltite, Lignite and Oil Shale

High ash and/or high sulfur coals are unsuitable for efficient use in carbonization, combustion, gasification or liquefaction. Due to the energy situation and the gradual depletion of high quality coal reserves of the world, more attention is being given to demineralization and/or desulfurization of low grade high ash and/or high sulfur coals to obtain environmentally acceptable clean fuels. The composition of the raw material, pyrolysis temperature, heating rate, particle size, pressure, and pyrolysis atmosphere are the major factors affecting the yield and composition of volatile matter. The fate of inorganic elements in pyrolysis and catalytic effects of mineral matter are in need of investigation. It is known that certain minerals exhibit definite catalytic effects in gasification and others exhibit catalytic effect in liquefaction. The effect of mineral matter on the pyrolysis yield and on the product distribution is, however, a fairly open question.

Bolat, Sağlam and Pişkin (1998) studied on the demineralization of a high ash bituminous coal. Demineralization of coal prior to usage offers some technical and cost-effective advantages since one of the most common limitations on coal processes results from high mineral matter content. In this work aimed at reducing the mineral matter content of high ash, low sulfur Amasra bituminous coal from Turkey,

since physical methods were of limited use for reducing the ash content of bituminous coals, demineralization was studied using different acids HF, HCl, HNO₃ and H₂SO₄. alone and 0.5 N aqueous NaOH in combination with either one or two of the acids. The use of extraction with 0.5 N NaOH followed by leaching with 10% HCl was the optimum approach for the chemical cleaning of the coal under study, the maximum degree of demineralization obtained being 46.78%. The alkali-treated coals were washed with 10, 20 and 30% HCl, HNO₃ and H₂SO₄. When the alkali-pretreated coals were washed with 10% HCl, HNO₃ or H₂SO₄ the reduction in ash content increased with 0.45, 1.30 and 2.17%, respectively. The increase in the degree of demineralization was 11.43% of the maximum when using 30% HCl for washing the alkali-treated coals. Using 10% aqueous HCl solution, the ash reduction was slightly increased, the maximum total degree of demineralization being 46.78%. 38.61% of mineral matter content of coal sample was removed by extraction with alkali and 10% HCl and 10% HNO₃ acid in succession. The observed weight loss in the HCl treatment of coal must be due to the removal of soluble components of mineral matter such as carbonates and sulphides (other than pyrites) and to the extraction by ion-exchange of some cations present in sheet silicates.

Karaca and Önal (2003) studied that, demineralization of lignites by single and successive pretreatment. Two Turkish lignites (Bolu-Mengen, Kütahya-Tunçbilek) were treated under atmospheric

and reflux conditions with 10–30% NaOH, 10% HCl and 10% H₂SO₄ solutions, singly and/or successive treatments to determine the effects of this treatment on the mineral matter and acidic functional groups. Characterization of the treated and untreated samples was by Fourier transform infrared spectroscopy. The process of successive pretreatment was found to be more effective than single steps in terms of demineralization and removal of carboxylate structures. During NaOH treatment, the first of successive steps, salts soluble in acid but not in water were determined. In successive demineralization steps with 30% NaOH and 10% HCl, a low level of 3.3 % ash was obtained for the Tunçbilek lignite. In addition, during the pretreatment, most of the Ca and K were exchanged with Na. 4 g coal was used in 80 ml of solution. The mixtures were treated for 1 h under reflux conditions while stirring. Then, the mixtures were left to cool to room temperature, followed by filtering and washing repeatedly with distilled water. The filter residues were dried at 100°C for 24 h under vacuum. The demineralization degree of the dried residues was calculated. The residues were also analyzed for ash level and functional groups. FT-IR spectra of the demineralized samples were obtained and the filtrate solutions were analyzed for Na, K, and Ca contents by AAS.

Açma et.al. (2000) studied on the effect of demineralization on the reactivity of lignites. In this study, effect of demineralization on the

combustion reactivity of 25 lignite samples, originating from different areas of Turkey, was investigated. Non-isothermal thermogravimetry, where the sample was heated in air where temperature increased at a linear rate of 40 K/min to 1273 K, has been used to investigate the combustion reactivity of the original and demineralized lignite samples. The activation energies calculated by two different methods and the burning profiles of the original and demineralized samples were compared and discussed. It was observed that the combustion reactivity of the samples was considerably influenced by the demineralization process applied.

Mukherjee et.al. (2001) studied the effect of hydrogen peroxide solution alone and in the presence of dilute sulfuric acid on desulfurization and demineralization of coal collected from the Makum coalfield situated at North-Eastern region, India, was investigated and the process conditions (temperature, time, and hydrogen peroxide and sulfuric acid concentrations) were optimized. Hydrogen peroxide (15%) alone leads to removal of over 76% pyritic sulfur and 70% sulfate sulfur and around 5% organic sulfur and 14% ash at 25 °C, which increases to almost complete removal of pyritic and sulfate sulfur and over 26% organic sulfur and 43% ash in the presence of 0.1 N H₂SO₄. The oxidation rate was found to increase significantly with increasing temperature (15 to 40°C) and hydrogen peroxide concentration (2.5 to 15%). The rate of reaction was found to be well represented by a

continuous reaction model that was second order with respect to pyritic sulfur. The activation energy for pyritic conversion in Boragolai and Ledo coal are 19.33×10^6 J/kmol and 39.72×10^6 J/kmol, respectively.

Ballice (2006) studied on the effect of the mineral matter of Göynük oil shale on the conversion of organic carbon in kerogen into volatile hydrocarbons, polycyclic aromatic hydrocarbons (asphaltenes, preasphaltenes), and carbon in the solid residue was investigated. Kerogen was isolated by successive HCl, HNO₃, and HF treatments. A series of temperature-programmed pyrolysis operations was performed with raw Göynük oil shale and each product of every demineralization process. The results show that removal of the material soluble in HCl and HNO₃ slightly affected the conversion of organic materials in the pyrolysis reactions. In contrast, removal of the material soluble in HF increased the conversion in pyrolysis reactions. This behavior is explained by the inhibitive effect of the silicate minerals. The leaching of mineral matter with HCl, HNO₃, and HF caused no remarkable change in the composition of volatile hydrocarbons.

Ballice (2005) studied on the effect of the mineral matter of Beypazari Oil Shale on the conversion of organic carbon of oil shale into volatile hydrocarbon, polycyclic aromatic hydrocarbons (asphaltenes, preasphaltenes) and carbon in solid residue was

investigated. Kerogen was isolated by successive HCl, HNO₃ and HF treatments. A series of temperature-programmed pyrolysis operation was performed with raw Beypazari Oil Shale, and each product of every demineralization process. A carbon balance of the pyrolysis process was established by determination of the recovery of total organic carbon as organic products, and carbon remaining in the reactor because of the coking reactions. The removal of the material soluble in HCl washing affected the conversion of organic materials in the pyrolysis reactions. Alkali and alkaline earth metal cations affect the reactivity of oil shales and the leaching of these mineral matters with HCl caused a slightly decreases in the conversion to volatile hydrocarbons. The removal of pyrites with HNO₃ did not affect the reactivity of the organic material in pyrolysis. But, removal of the material soluble in HF increased the conversion in pyrolysis reactions. It can be explained by the inhibitive effect of the silicate minerals. Complete removal of mineral matrix and isolation of kerogen increased the driving force for heat transfer since more heat was transferred from outside towards the inside of the oil shale particles.

Öztaş and Yürüm (2000) studied on the effects of mineral matter on the conversion of organic material in low temperature pyrolysis (300–500°C) of the vitrinite-rich Zonguldak bituminous coal and acid-washed coals were investigated. Calcium, iron and magnesium cations were removed from coal with HCl washing. The

results indicated that these cations had catalytic effects during pyrolysis. It was also observed that the conversion in the pyrolysis processes was increased with the removal of the illite, kaolinite, chlorite and quartz minerals. The volumetric swelling ratios of the chars obtained in different experimental conditions were measured using the pyridine swelling technique and the extent of crosslinking in the macromolecular network of chars was examined. It was found that the cross-linking increased as the pyrolysis temperature was increased from 300 to 500°C.

Elsamak et.al. (2003) studied on the chemical desulfurization of Turkish Çayırhan lignite with HI using microwave and thermal energy. The purpose of the present work was to investigate the effect of the concentration of HI and reaction time in the chemical desulfurization of Çayırhan lignite in a microwave energy set up and to compare the results with those obtained in a thermal heating system. As the concentration of the HI was increased, the extent of desulfurization was also increased in all the experiments done for all of the samples of lignite. The main difference between the thermal and microwave heating was the extremely short times for desulfurization in the case of microwave experiments. After desulfurization experiments S_{total}/C ratio of all of the samples decreased to a lower value than that of the raw lignite which was 0.034. The loss of the sulfur containing bands in the FTIR spectra of the desulfurized lignite showed that the HI treatment

was effective in the cleavage of dithioethers and thioetheric groups. Sulfur containing functionalities like thioethers and thiols although usually requiring strong reducing agents could be removed in significant amounts with concentrated hydroiodic acid from the coal matrix. The rapidity of the desulfurization reactions with microwave heating in concentrated HI was probably due to localized superheating which made HI more effective in the reactions such as with thioethers and thiols that normally resisted to cleavage by HI under thermal heating conditions.

Mukherjee and Borthakur (2003) studied on the effects of alkali treatment on ash and sulphur removal from Assam coal. The effects of leaching subbituminous coal samples from Boragolai and Ledo collieries of Makum coal field, Assam, India, with aqueous sodium hydroxide solution on removal of ash and sulphur, were investigated. Mild alkali treatment for relatively short period leads to removal of ash from the coal samples. Increase of alkali concentration and treatment time has negative effect on ash reduction due to formation and accumulation of insoluble sodium aluminosilicate. Boragolai coal is less demineralized than Ledo coal and is attributed to presence of higher amount of alkali-soluble silica and alumina. Alkali treatment leads to over 70% removal of the inorganic sulphur in the coal samples. Desulphurization increases with increase in alkali concentration and treatment time.

Wang and Tomita (1998) studied on the removal of mineral matter from some Australian coals by $\text{Ca(OH)}_2/\text{HCl}$ leaching was investigated. Four Australian coals, Blair Athol, Ebenezer, Newlands and Warkworth coals, were demineralized by Ca(OH)_2 digestion at 300°C, followed by washing with dilute HCl. Ash contents decreased from 8.8–15.4% to 1% for Blair Athol, Newlands and Warkworth coals, and from 14.9% to 2.8% for Ebenezer coal. The CaO/ash ratio is an important factor affecting coal demineralization; the maximum ash removals were achieved at CaO/ash ratios in the range 0.6–1 g/g for all the coals. The major minerals in the original coals were kaolinite and quartz, with some montmorillonite and carbonates. Kaolinite and quartz hydrothermally reacted with Ca(OH)_2 to form calcium-bearing hydrated silicates and aluminosilicates, such as tobermorite and hirscherite, that could be dissolved in acid. With increasing CaO/ash ratio in excess of the optimum value, the removal of quartz significantly decreased; there also remains some calcium in treated coal, depending on digestion conditions and coal type. A lower ash removal from Ebenezer is due to a lower quartz removal and more remaining calcium.

Doymaz et.al. (2007) studied on the removal of mineral from asphaltite by acid treatment. In this study, demineralization was studied using different acids (HCl, H_2SO_4 and HNO_3) at various concentrations. Maximum demineralization degree (approximately

40%) was found of asphaltite sample leaching with 5 and 10% HCl acids. FTIR and XRD were used to determine the functional groups of treated sample and the contents of ash, respectively.

Wu and Steel (2007) studied on the demineralization of a UK coal using HF and ferric ions. A UK bituminous coal has been used to study demineralization by two-stage chemical leaching. The first-stage uses hydrofluoric acid (HF) at 65 °C and reduces the ash content from 5.30 wt% to 1.37 wt% by mainly removing Al and Si containing minerals. Subsequent leaching by ferric ions decreases the ash content further to 990 ppm by removing most of the pyrite and fluorides formed during the HF leaching. Calorific value of the coal shows no change following leaching, which suggests no oxidation is occurring to the coal carbonaceous matrix. The mercury and sulfur contents, after the two-stage leaching sequence decreases by 40% and 26%, respectively.

3.2 Pyrolysis of Asphaltite, Lignite and Oil Shale

The availability of energy at a reasonable cost has always been a pre-condition for industrial growth, economic and social progress. Owing to the present worldwide energy crisis, low-grade fuels (oil shale, coal, tar sand, bitumen, etc.) have become an alternative resource in many countries in the world. Coal pyrolysis is the most important aspect of coal behavior because it occurs in all major coal conversion processes, like combustion, gasification, carbonization and liquefaction. Pyrolysis refers to the decomposition of organic matter by heat in the absence of air. When coal is pyrolyzed, hydrogen-rich volatile matter is distilled, and carbon-rich solid residue is left behind. Pyrolysis is one of the commonly used methods to produce liquid fuels from coal, and it is the principal method used to convert oil shale to liquid fuels. Moreover, as gasification and liquefaction are carried out at elevated temperatures, pyrolysis can be considered a first stage in any conversion process.

Khraisha et.al. (2003) studied on the spectroscopic and chromatographic analysis of oil shale. In this investigation, spectroscopic (FT-IR, UV-Vis, ¹H NMR) and chromatographic (GC) techniques were used to analyze two Jordanian shale oils, Sultani and El-Lajjun. The oils were extracted at different pyrolysis temperatures (400–500°C) using a fluidized bed reactor. The spectroscopic and

chromatographic analyses show that the variation of pyrolysis temperature has no significant effect on the composition of the produced oil. The HNMR results indicate that the protons of methyl and methylene represent the bulk of the hydrogen (90%) in most shale oil samples. GC analysis reveals that the oil samples contain n-alkanes with a predominant proportion of n-C₂₅. The spectroscopic and chromatographic analyses indicate that the variation in pyrolysis temperature has no significant effect on the composition of the oil produced. Both the Sultani and El-Lajjun shale oils have similar spectra. Shale oil is mainly aliphatic with a small amount of aromatic and olefinic compounds. HNMR ensures this finding, since the shale oil contains about 90% of methyl and methylene protons. FT-IR results also support this finding. The GC analysis of n-alkanes reveals that n-C₂₅ is the predominant and the greatest normal paraffin in the shale oil samples.

Nazzal (2002) investigated the effect of heating rate on the pyrolysis of oil shale. Oil shale samples from Jordan were pyrolysed in a fixed bed reactor at a heating rate varied from 2 to 30°C min⁻¹ up to a final temperature of 520°C under nitrogen and nitrogen/steam atmosphere. The influence of heating rate on the yield and composition of the oil, gases, water, and spent shale was determined. It was observed that the oil yield was increased as the heating rate was increased from 2 to 10 °C/min. Increasing the heating rate up to 30°C

min^{-1} caused a slight reduction in the oil yield. The main gases produced were H_2 , CO , CO_2 and CH_4 and also minor concentrations of alkane and alkenes gases. By increasing the heating rate from 2 to $30\text{ }^\circ\text{Cmin}^{-1}$, the evolution of the hydrocarbon gases was increased. The oil was analyzed for the elemental analysis and the atomic H/C ratio was obtained. The oils were fractionated into chemical classes (aliphatics, aromatics, esters, and polars compounds) using a mini-column liquid chromatography. The alkanes and alkenes hydrocarbon gases were increased with increasing heating rate. Alkene/alkane hydrocarbon gas ratios were determined and were linked to secondary reactions.

In the study of Olukçu et.al. (2002), Beypazari oil shale was subjected to conventional and free falling pyrolysis at different temperatures to investigate optimum liquefaction temperatures. The oils obtained were characterized by GC, ^1H NMR, IR and size exclusion chromatography to follow the molecular changes induced by the pyrolysis. Free falling pyrolysis gave the maximum degree of conversion of 61.9% at 873 K, whereas conventional pyrolysis gave a degree of conversion of 50.5% at 773 K. Conventional pyrolysis gave less *n*-alkenes-1 than that obtained from free falling pyrolysis at similar temperature. Polymerization reactions are predominant during conventional pyrolysis due to the longer reaction time. In contrast to

conventional pyrolysis, more cracking reactions occurred during the free falling pyrolysis.

Ballice and Yüksel (2002) studied on the thermal degradation of both Göynük oil shales (GOS) and Beypazari oil shales (BOS). The recovery of organic carbon as 1-olefins and *n*-paraffins was determined by temperature-programmed pyrolysis of oil shales. A fixed bed reactor under argon flow was used to pyrolyze small samples of oil shales. A special gas-phase sampling technique was used to determine the composition of products eluted from the reactor as a function of temperature and time. Hydrocarbon evolution data have been analyzed by Coats-Redfern and Chen-Nuttall combinations. It must be emphasized that the evaluation of temperature-programmed pyrolysis data by combined use of Coats-Redfern and Chen-Nuttall methods provide satisfactory mathematical approaches to obtain kinetic parameters for 1-olefins and *n*-paraffins formation from thermal degradation of Turkish oil shales. Using this method, it is possible to identify every stage of pyrolysis and derive values for kinetic parameters.

Çakal et.al.(2007) investigated the physical and chemical properties of Turkish lignites and their pyrolysis and gasification rates determined by thermogravimetric analysis. Pyrolysis and CO₂-gasification behavior of lignites representing four different deposits in

Turkey were investigated by Thermogravimetric Analysis (TGA) in the temperature range from 750°C to 1000°C. The rates of pyrolysis and CO₂-gasification were evaluated from the corresponding TGA profiles. As expected, maximum pyrolysis rates for each coal were shown to be constant with respect to the final carbonization temperature. Lignites used in this study are from the tertiary period, chosen from major coal deposits in Turkey and their carbon contents are in the range of 60–70% based on ultimate analysis. They have shown different gasification reactivities under similar conditions and the reactivity sequence was found to be temperature dependent.

In the study of Saydut et.al. (2008), separation of liquid fractions obtained from flash pyrolysis of asphaltite was investigated. The experiments on the flash pyrolysis of asphaltite (Avgamasya, Sirnak, SE Anatolia, Turkey) were carried out in a fixed bed reactor as a basic study. The investigation focused on the effects of pyrolysis temperature and asphaltite particle size on the product distribution and composition. Sample particle size sieve analysis of asphaltite was performed. Liquefaction of asphaltite, different particle size, and using flash pyrolysis was performed in a fixed bed reactor with a heating rate 40°C min⁻¹ at a temperature ranging from 400 to 800°C under nitrogen atmosphere. The effect of particle size and temperature on conversion and liquid yield was examined. The yield of asphaltite liquid at the condition of -0.60 + 0.25 mm and 550°C at reached a maximum 11.13

wt%. An optimum temperature for the liquid yield was found to be 550°C. The oil product was distilled by fractionally distillation to separate component. The pyrolysis studies provide important quantitative information on the identity, composition and structure of asphaltites. Oil was treated silica gel column chromatography. Using *n*-hexane, toluene and methanol, the oil was separated into aliphatic, aromatic and polar components, respectively. For further structural analysis, the pyrolysis oils aliphatic, aromatic and polar subfractions were conducted using FTIR. The results of this study provide fundamental data and optimal conditions to maximize light oils yields.

Ballice (2002) studied on the temperature programmed pyrolysis of lignite and asphaltite from Turkey. The aim of this research was to determine the volatile product distribution and product evolution rate during pyrolysis of lignite and asphaltite as a function of temperature and time. A fixed-bed reactor was used to pyrolyze small sample of lignite and asphaltite under an inert gas flow (argon). A special sampling technique was used for collecting organic products released from the reactor at different temperature and time intervals. The temperature at which product evolution rate is the highest proved to be 430°C both for lignite and asphaltite in pyrolysis operation. *n*-Paraffins and 1-olefins in aliphatic fraction of pyrolysis products were classified by carbon number. The hydrocarbons produced by pyrolysis of lignite and asphaltite contained 32.4 and 30.1 wt. % of *n*-paraffins,

respectively, at the maximum product release temperature. 1-Olefins produced by pyrolysis of lignite and asphaltite were determined and found as 10.2 and 16.6 wt. % of the pyrolytic oil, respectively. In addition, the performance of the experimental apparatus was investigated by establishing a carbon balance and the degree of recovery of total organic carbon of the samples as aliphatic hydrocarbons and in solid residue was determined. Conversion into volatile hydrocarbons was found to be lower but the amount of carbon in solid residue was higher for lignite than for asphaltite pyrolysis.

Ballice and Sağlam (2002) studied on temperature-programmed co-pyrolysis of Göynük-oil shale (GOS) with Şırnak-asphaltite (ASP) from Turkey was investigated. The aim of this research was to determine the volatile product distribution and product evolution rate of co-processing of GOS with ASP. A series copyrolysis operation was performed with GOS and ASP using a 1/2, 1/1, 2/1 total carbon ratio of GOS to ASP. A fixed-bed reactor was used to pyrolyse small sample of GOS and ASP mixture under an inert gas flow (Argon). A special sampling technique was used for collecting organic products eluted from the reactor at different temperature and time intervals. The co-pyrolysis products were analyzed by capillary gas chromatography and the total product evolution rate was investigated as a function of temperature and time. n-Paraffins and 1-olefins in aliphatic fraction of pyrolysis products were classified as a carbon number. In addition, the

recovery of total organic carbon as an organic volatile product was determined. The assessments were based on incorporating the results on temperature-programmed pyrolysis of GOS and ASP. The effect of co-processing of GOS with ASP was determined by calculating the difference between the experimental and the hypothetical mean value of conversion of total organic carbon into volatile products.

Nazzal (2008) studied on the effect of the grain size on the products yield and shale oil composition from the pyrolysis of Sultani oil shale. the influence of shale grain size of 0.20–0.60, 0.60–1.20, 1.20–3.33, and 3.33–5.60 mm were carried out on the oil shale pyrolysis in a semi-continuous fluidized bed and 50 gm fixed bed reactor under nitrogen and nitrogen/steam pyrolysis atmosphere. The final pyrolysis temperature was 520 °C, heating rate 12 °C min⁻¹, vapor residence time of 25 and 28 s for the fluidized bed and fixed bed pyrolysis, respectively, and shale residence time of 45 min. The oil yield was increased as the particle grain size was increased from 0.2–0.6 to 3.33–5.6 mm under both nitrogen and nitrogen/steam pyrolysis atmospheres. Increasing the particle grain size caused a decrease in the derived hydrocarbon gases and an increase in the carbon and hydrogen content in the derived oil. Decreasing the particle grain size (in the studied range) caused an increase in the PAH concentration in the derived oil. This increase has been suggested as a result of the

aromatization of the derived oils by the secondary decomposition reactions.

Yang and Chai (2006) studied on TG-FTIR study on catalytic pyrolysis of coal. The catalytic effects of alkali, alkaline earth and transition metals on pyrolysis of lignite and bituminous coals were investigated using TG-FTIR. The results indicate that the orders of catalytic effects on the pyrolysis of lignite and bituminous coals are $\text{Ni} > \text{Fe} \sim \text{Ca} > \text{K}$ and $\text{Ca} \sim \text{Fe} > \text{Ni} > \text{K}$, respectively. The maximal increments of conversion for the lignite and the bituminous coal are 10.1% and 6.4% with catalysts loaded. The CH_4 yield of the bituminous coal is larger than that of the lignite. The increase in yield of CO_2 , H_2O , CH_4 , and CO is dependent on the catalysts, which are closely related to the temperature region and coal ranks.

Ariunaa et.al. (2007) studied on the coal pyrolysis under synthesis gas hydrogen and nitrogen. Chinese Xundian and Mongolian Shiveevoo lignites, and Khoot oil shale were pyrolyzed under synthesis gas (SG) at temperature ranging from 400 to 800 °C for the lignites and from 300 to 600 °C for the oil shale with a heating rate of 10 °C/min in a fixed bed reactor. The results were compared with those obtained in pyrolysis under hydrogen and nitrogen. The results show that higher liquid yields with lower yields of char and gas are obtained in pyrolysis of oil shale under SG and H_2 than under N_2 , but

the differences are slight. It is found that the pyrite S can be easily removed and partially converted to organic S under various gaseous atmospheres. The total sulfur removal for oil shale is considerably less than lignite, which may be related to its high ash content. The higher total sulfur removal and the less organic S content in the presence of SG in comparison with that under N₂ and also under H₂ in pyrolysis of Xundian lignite may result from the action of CO in SG. However, CO does not show its function in pyrolysis of Khoot oil shale, which may also be related to the high ash content. The results show the possibility of using synthesis gas instead of pure hydrogen as the reactive gas for coal hydrolysis.

Sezer et.al. (2008) studied on the flash pyrolysis of Silopi asphaltite in a free fall reactor under vacuum. Flash pyrolysis experiments on asphaltite samples were performed in a free-fall reactor under vacuum to determine the effects of pyrolysis temperature, feed rate and particle size. Maximum liquid yield of 13 wt.% was obtained in free-fall reactor under vacuum when the pyrolysis temperature was 700 °C, feed rate was 0.4 g min⁻¹ and particle sizes were between 0.075 and 0.250 mm. The liquid products obtained at various pyrolysis conditions were analyzed by gas chromatography/mass spectrometer (GC/MS) and liquid products were classified as following: C₅–C₁₀, C₁₁–C₁₅, C₁₆–C₂₀ and C₂₀₊. The amount of saturated hydrocarbons decreased while the amount of unsaturated

hydrocarbons increased with increase of temperature. While percent of C_5 – C_{10} unsaturated hydrocarbons continuously increased with increase of temperature, the percent of C_{11} – C_{15} unsaturated hydrocarbons increased up to 750 °C and then started to diminish. Functional group analysis of solid residue was carried out using Fourier transform infrared spectrometry (FT-IR). The proximate analysis of solid residue indicated that percent of fixed carbon and ash increased with temperature.

Çit et.al. (2007) investigated on the effect of polymers on lignite pyrolysis. Effect of polypropylene (PP) and polyethylene terephthalate (PET) on lignite pyrolysis is studied in this work. Experiments are conducted in the temperature range of 400–700 °C in a tubular reactor. PP and PET are blended with lignite (M.K.P. lignite, Bursa, Turkey) in the polymer ratio of 33%, 50% and 67% (w/w), respectively. Tar, gas and char yields are calculated and plotted against to the temperatures they obtained for each experimental run. A remarkable synergetic effect between lignite and polymers is also found. The possible reasons of this variation are discussed. Analysis of the tars obtained by different experimental conditions is conducted by GC–MS technique. High yields of benzoic acid and biphenyl are obtained during the pyrolysis of PET and PET: lignite.

3.3 Solvent Swelling of Asphaltite, Lignite and Oil Shale

Tekeş et.al. (2002) studied on the volumetric swelling of Soma-Işıklar lignite (Turkey) has been studied. Methanol, toluene, benzene, dichloromethane, tetrahydrofuran (THF), pyridine, dioxane, ethylenediamine (ETDA), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were used as swelling agents. The effects of pre-swelling and acid washing (1 N HCl) on swelling ratio and on the extraction yields of the raw or pretreated lignites have been examined. Furthermore, the relationship between the degree of swelling and the solvent properties (solubility parameter (δ), donor number (DN), and cross-sectional area of the solvent molecules) was investigated. It was found that a strong relation between the degree of swelling and the donor numbers of the solvents exists. According to the results, it can be said that the cross-linked structure of the lignite is responsible for the swelling. Moreover, it was observed that pre-swelling and acid washing increased the extraction yields.

Ballice and Larsen (2003) studied on the effect of temperature and heating rate on the cross-link density of char samples. These char samples were obtained by pyrolysing Göynük oil shale by solvent swelling technique. The cross-link density decreases slightly with increasing pyrolysis temperature. The heating rate and thus the pyrolysis time had at most a small effect on the cross-link density.

Char–solvent interactions do not follow regular solution theory. The demineralized kerogen swells more than does the native kerogen (16% ash).

Larsen and Li (1994) studied on solvent swelling of Green River Kerogen. Kerogen has been isolated from Green River oil shale by dissolving the minerals in HF and HCl and also by using aqueous ammonium sulfate. The resulting kerogen samples were swollen in 28 different solvents. The volumetric solvent swelling of the kerogen roughly follows the predictions of regular solution theory for almost all of the solvents including good hydrogen bond acceptors. The solubility parameter from the swelling studies is close to that calculated from Siskin's structure. Hydrogen bonding does not seem to be an important factor because good hydrogen bonders show swellings similar to non-hydrogen bonders of similar solubility parameter. The inorganic content of the isolated kerogen does not have a large effect on solvent swelling. Samples containing 42% inorganics generally swell somewhat more than samples containing 5 % inorganics. The cross-link density of kerogen is high.

Önal and Akol (2003) studied on the influence of pretreatment on solvent swelling of Turkish lignites. In this study, three Turkish lignites (Beypazarı (LGN-1), Gölbaşı (LGN-2) and Kangal (LGN-3)) have been pretreated with the solutions of 0.1N HCl, 10% HCl, HCl–HF or

with air oxidation at 200°C. Swelling ratios of original and pretreated lignites have been determined by using 11 different solvents. Original and pretreated samples have been subjected to preswollen by using THF at room temperature. Toluene Soxhlet extraction experiments of these and unswollen samples have been also carried out. The effect of solvent swelling ratio on the extraction yields of the original and pretreated lignites have been examined. The results showed that the swelling ratios were high in hydrogen bonding solvents but low in non-hydrogen bonding solvents. It is found that the best solvent is 2-ethanolamine and second is pyridine for these lignites. The pretreatment increased the swelling values of the lignites by all solvents. Comparing with original lignites in all solvents except pyridine and 2-ethanolamine, the swelling values were not changed by oxidation. The results have indicated that both swelling and extraction yields generally increased after the pretreatments and the increments are higher with hydrogen bonding solvents.

Larsen and Shawver (1990) studied on solvent swelling studies on two rank coals. A Wyodak subbituminous coal, a Texas lignite, and their O-methylated and O-acetylated derivatives were swollen in both polar and nonpolar solvents (16 total). The lignite swollen with nonpolar solvents does not follow regular solution theory while the subbituminous coal does in spite of similar oxygen contents. The cross-link density of the subbituminous coal was calculated and is slightly

greater than that of Illinois No. 6 coal, consistent with the coalification process being a net depolymerization. Both of these coals contain similar amounts of organic oxygen, similarly distributed among the functional groups, yet one follows regular solution theory when swollen with organic solvents and the other does not.

Mesci et.al. (2001) studied on the effect of acid treatment on volumetric swelling ratios of coal. To remove Ca^{2+} ions, six low rank coals and one coking coal were treated with 0.1 and 1.0 N HCl for 24 h. IR spectra and proximate analysis of the lignites indicated that only slight structural changes had occurred during acid treatment. The swelling ratios of parent and acid-treated coal samples showed that removal of Ca^{2+} resulted in an increase in the swelling ratios. Higher swelling ratios were obtained with acid-washed coal samples. While the highest swelling ratios of the parent lignites were obtained in ethylenediamine, those of acid-treated samples were obtained in pyridine and dimethylformamide.

Hu et.al. (2000) studied on the effect of solvent swelling on liquefaction of Xinglong coal at less severe conditions. Xinglong coal, a sub-bituminous coal, was swollen with pyridine or tetrahydrofuran followed by liquefaction in a 70-ml autoclave apparatus. The experiments were carried out to investigate the effects of temperature, solvent, atmosphere and catalyst on the liquefaction of

solvent-swollen coal and untreated coal. The results indicate that the conversion of coal could be effectively improved in the temperature range of 320–420°C by swelling pretreatment. Molecular hydrogen shows no contribution to coal conversion during the liquefaction of pyridine-swollen coal in the absence of a catalyst and in the presence of hydrogen donor solvent such as tetralin. With the addition of a catalyst, the liquefaction conversion of pyridine-swollen coal is higher in H₂ than that in N₂. The swelling pretreatment of coal can improve the liquefaction yields, weaken the dependence of the process on the presence of molecular hydrogen and the hydrogen donation ability of the solvent, and increase the conversion of coal liquefaction.

Ballice (2003) studied on the volumetric swelling procedure was applied to Göynük and Beypazarı oil shales from Turkey by using 10 solvents and the crosslinking in the macromolecular network of oil shales were investigated using this technique. Results from solvent swelling measurements show that the volumetric solvent swelling of oil shales samples roughly follows the regular solution theory. The theory of solvent swelling of cross-linked polymers developed Flory–Rehner and extension of this theory by Kovac–Peppas was used to calculate number average molecular weight per cross-link of kerogen structure (M_c) in oil shale samples. Results indicate no remarkable difference between M_c values for Göynük oil shale (Kerogen Type I) and Beypazarı oil shale (Kerogen Type II).

Murata et.al. (2008) studied on the kinetic study on solvent swelling of coal particles. In this study, Solvent swelling experiments of coal particles of Taiheiyō and Witbank coals in pyridine at 15–50°C were conducted by using an orthogonal microscope coupled with an image analysis system and the newly prepared temperature-controlled cell. Two kinetic parameters, n (a number that crudely indicates the nature of the solvent diffusion) and k (a rate constant), were calculated based on time profile of volumetric swelling ratio. The authors examined the correlation between these parameters and volumetric swelling ratios, to find that there was linear correlation between n and $\ln(1/k)$. By using the proportional constant, the authors calculated activation energy of the swelling of both coals. The energy changed with respect to each particle. Average values were 71 kJ/mol for Taiheiyō coal and 55 kJ/mol for Witbank coal, respectively. These values agree well with the values reported in the literature. The authors also examined the effects of pretreatments of both coals. O-Acetylation and pyridine preextraction lead to decrease the energies drastically.

3.4 Kinetics of Asphaltite, Oil Shale and Lignite

Aboulkas et.al. (2008) was established different kinetic models for oil shale and LDPE mixture pyrolysis. A kinetic study of the pyrolysis of Oil Shale mixed with LDPE was carried out by thermogravimetric analysis (TGA). Different runs were performed at heating rates between 2 and 50 K/min. The results obtained from this comprehensive investigation indicated that they are three main degradation steps and the increase in the heating rate caused a lateral shift in the thermograms. The difference of weight loss between experimental and theoretical, calculated as algebraic sums of the mixture for different heating rates of 2, 10, 20 and 50 K/min, is about 8-11% at 670-840 K. These experimental results indicate a significant synergistic effect during pyrolysis of oil shale mixed with LDPE. Kissinger-Akahira-Sunose method, Friedman's method, Flynn-Wall-Ozawa method and Coats-Redfern have been used to determine the activation energies of materials degradation. The difference of weight loss between experimental and theoretical, calculated as algebraic sums of the mixture for different heating rates of 2, 10, 20 and 50 K min⁻¹, is about 8-11% at 670-840 K. These experimental results indicate a significant synergistic effect during pyrolysis of oil shale mixed with LDPE.

Khraisha et.al. (2002) studied on the thermal analysis of oil shale using thermogravimetry and differential scanning calorimetry. A non-isothermal experimental study using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was conducted for investigation of Jordanian shale oils. The analyses were performed in an inert atmosphere. The weight loss data show that the pyrolysis of shale oils takes place in one regime, and the major weight loss occurs in the range of 175-450°C. The DSC data reveals the endothermic behavior of the decomposed samples. The kinetics of the non-isothermal pyrolysis of shale oils has been derived using the TGA data. The first order of reaction shows a good fit with the weight loss data, and the activation energies vary from 20.61 to 29.55 kJ mol⁻¹.

Tonbul et.al. (2006) studied on thermal behavior of Harbul asphaltites (SE Anatolia, Turkey) using thermogravimetric analysis at atmospheric pressure and with nitrogen as the ambient gas. Asphaltite samples were ground and separated according to their size by sieving. Particle size distribution and chemical composition of asphaltite fractions are given. TG/DTG data of samples demonstrated two stages of mass loss. The first stage, called primary volatilization, occurs in the range of 200–600 °C, and the second stage, called secondary gasification, in the range of 600–800 °C. Kinetic parameters of pyrolysis of asphaltite samples (activation energy, Arrhenius constant and

reaction rate constant) were determined separately for both two stages using Coats-Redfern kinetic model.

Aboulkas et.al. (2008) studied on the pyrolysis of Moroccan oil shale-plastic mixtures by thermogravimetric analysis. Thermal degradation processes for a series of mixtures of oil shale/plastic were investigated using thermogravimetric analysis (TGA) at four heating rates of 2, 10, 20 and 50 K min⁻¹ from ambient temperature to 1273 K. High density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP) were selected as plastic samples. Based on the results obtained, three thermal stages were identified during the thermal degradation. The first is attributed to the drying of absorbed water; the second was dominated by the overlapping of organic matter and plastic pyrolysis, while the third was linked to the mineral matter pyrolysis, which occurred at much higher temperatures. Discrepancies between the experimental and calculated TG/DTG profiles were considered as a measurement of the extent of interactions occurring on co-pyrolysis. The maximum degradation temperatures of each component in the mixture were higher than those of the individual components; thus an increase in thermal stability was expected. In addition, a kinetic analysis was performed to fit thermogravimetric data.

The extent of conversion or the fraction of pyrolysed material, x , is defined by the expression

$$x = \frac{w_0 - w}{w_0 - w_f}$$

where w is the weight of the sample at a given time t ; w_0 and w_f refer to values at the beginning and the end of the weight loss event of interest. The rate of the kinetic process can be described by the following equation;

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x)$$

where $K(T)$ is a temperature-dependent reaction rate constant and $f(x)$ is a dependent kinetic model function. After integrating this eqn; the isoconversional integral method suggested independently by Flynn and Wall and Ozawa uses Doyle's approximation. This method is based on the equation:

$$\ln \beta = \ln \frac{AE}{Rg(x)} - 5.331 - 1.052 \frac{E}{RT}$$

Thus, for $x=\text{const.}$, the plot $\ln \beta$ vs $(1/T)$, obtained from thermograms recorded at several heating rates, should be a straight line whose slope can be used to evaluate the apparent activation

energy. The activation energies determined from the slope of $\ln \beta$ vs $1/T$ plots from the 6 to 18% conversion for degradation of organic matter of oil shale. It was found that the activation energies remain relatively constant between 6 and 16% conversion, which reveal that there is one dominant kinetic process. The mean value of the activation energies was 87 kJ/mol.

Li and Yue (2003) studied on the kinetics of pyrolysis. The pyrolysis experiments on oil shale samples from Fushun, Maoming, Huangxian, China, and Colorado, USA, were carried out with the aid of thermogravimetric analyzer (TGA) at a constant heating rate of 5 and 8°C/min. A kinetic model was developed which assumes several parallel first-order reactions with changed activation energies and frequency factors to describe the oil shale pyrolysis. The kinetic parameters of oil shale pyrolysis were determined on the basis of TGA data. The relationship between the kinetic parameters was further investigated and the correlation equations of x_1 – E and $\ln A$ – E were obtained. These equations show that the final fractional conversion of each parallel reaction, $x_1(j)$, can be expressed as an exponential function of the corresponding activation energy. The plot of $\ln A$ – E for different reactions becomes a straight line. These relationship equations can provide important information to understand the pyrolysis mechanism and to investigate the chemical structure of oil shale kerogen.

Elbeyli (2006) studied on the pyrolysis kinetics of asphaltite by thermal analysis. Pyrolysis properties and kinetic analysis of asphaltite were investigated by means of thermogravimetry (TG) and derivative thermogravimetry (DTG). Thermal experiments were carried out from ambient temperatures to 1000°C in nitrogen atmosphere at different heating rates. TG/DTG curves showed that the decomposition proceeds through two steps with DTG peaks corresponding to the weight loss obtained. Kinetic analysis of the asphaltite decomposition steps was carried out under non-isothermal conditions. Coats-Redfern method was used to analyze the TG data for determination of kinetic parameters. Activation energies (E_a) and pre-exponential factors (k_0) were calculated for different heating rates and compared. In this study, to determine the kinetic parameters for the pyrolysis of Şırnak asphaltite, the first order ($n = 1$) thermal decomposition model which was proposed in earlier solid-state decomposition works was assumed. The kinetic parameters, activation energy (E), and pre-exponential factor (k_0) were calculated from the fraction of sample decomposed (α) values by utilizing the mathematical equations of Coats-Redfern.

$$\text{for } n = 1; \ln \left[\frac{-\ln(1-x)}{T^2} \right] = \ln \frac{k_0 R}{\beta E} - \frac{E}{RT}$$

$$\text{for } n \neq 1; \ln \left[\frac{1 - (1-x)^{1-n}}{T^2(1-n)} \right] = \ln \frac{k_0 R}{\beta E} - \frac{E}{RT}$$

Activation energy (E_a) and preexponential factor (k_o) for primary pyrolysis reaction are calculated as 45.11 – 61.40 kJ/mol and 0.324–6.40 sn^{-1} , respectively. Also, activation energy and pre-exponential factor for second pyrolysis reaction are calculated as 23.49–27.74 kJ/mol and $1.58\text{--}6.89 \times 10^{-3} \text{ s}^{-1}$.

Tonbul and Saydut (2007) studied on thermal behavior and pyrolysis of Avgamasya Asphaltite. The pyrolysis and thermal behavior of Avgamasya (SE Anatolia, Turkey) asphaltite was performed using thermogravimetric analysis at atmospheric pressure in dynamic nitrogen atmosphere (30mL min^{-1}). Four heating rate profiles (2.5, 5, 10 and 20 K min^{-1}) were applied, with a final temperature 1123 K. Two-stage decomposition was observed in the experiments. During the stage 1, when the temperature is lower, only weaker chemical bonds are destroyed and some small gaseous molecules are produced. During the stage 2, when temperature is higher, the cracking is faster and stronger chemical bonds are broken, so that larger molecules decompose into small molecules in the gaseous phase. Kissinger (differential) and Coats-Redfern (integral) methods were applied to thermogravimetric data to obtain kinetic parameters (activation energy and Arrhenius constant). Activation energy values vary from 180.64 to $197.40 \text{ kJmol}^{-1}$ for stage 1 and from 127.76 to $198.78 \text{ kJmol}^{-1}$ for stage 2.

3.5 Supercritical Water Extraction of Asphaltite, Lignite and Oil Shale

Water, in many respects, shows unique properties that are well characterized at ordinary conditions. Water can also exist, and has been investigated, at states far above its critical temperature of 647 K, where it can be gradually compressed from gas-like to liquid-like densities. The resulting dense supercritical states possess remarkable properties which differ largely from those at normal conditions. Adopting a term from geochemistry, such supercritical, aqueous systems are often denoted as hydrothermal fluids. Investigations of density variations are the key to understanding fluid behavior because such experiments allow the temperature dependence of the fluid properties to be separated from their volume dependence. In many chemical and engineering applications supercritical water acts as a solvent or working fluid. For example, in steam power plants, the liquid phase may extend up to more than 600 K, and superheated vapor can reach temperatures up to more than 900 K. Other applications include, gas and oil recovery, hydrothermal crystal growth, and high temperature electrochemistry. The exceptional properties of supercritical water also form major motives for searching for industrial utilization of it as an ecologically benign solvent in chemical reactions. By tuning temperature and pressure, states can be achieved in which water becomes completely miscible with nonpolar compounds, while polar and ionic compounds remain highly soluble as well. In addition,

the viscosity remains low, even at liquid-like densities, which enhances mass transfer and diffusion-controlled chemical reactions. There are many interesting reactions, such as the oxidation, pyrolysis, and hydrolysis of organic compounds, where supercritical water acts as a solvent or reactant or catalyst.

Zang et.al. () studied on the pyrolysis of a high-ash peat in supercritical water. The effects of the addition of CaO, temperature, and residence time on the conversion and product yields of a high-ash peat in supercritical water was investigated. The experiments were carried out in an autoclave in the temperature range of 623–773 K at pressure up to 30 MPa. At a Ca/C molar ratio of 0.46, almost no CO₂ remained in gas phase. It was found that CaO facilitates the extraction of volatile matter from peat and the decomposition of volatile matter to small molecular compounds. Moreover, CaO catalyses the steam reforming reaction of hydrocarbons and the water-shift reaction. The addition of KOH might favor the reforming reaction of oil product to hydrogen and carbon dioxide. Furthermore, the yield of oil reaches a maximum at the temperature approximately 723 K. A threefold increase in the yield of oil product was observed under 36.5 MPa compared with pyrolysis. However, the polar compounds decomposed with the prolongation of reaction time.

In the study of Cheng et.al. (2004), conversion of Xiaolongtan lignite in sub- and supercritical water (SCW) was studied in an autoclave in the temperature range of 350–550 °C and water density 0–0.21 g/cm³ for 0–60 min under N₂ atmosphere. The experiments were carried out to investigate the effect of temperature, water density and reaction time on gas yields, liquid yields and product components. The results clearly indicate that the key factor that affects the product distribution is reaction temperature. Compared with temperature, the influence of water density and reaction time is less significant. To clarify the role of water in conversion of coal, experiments under nitrogen were also carried out. Comparing with the pyrolysis process without water under N₂ atmosphere, conversion of coal is enhanced in the presence of water.

Hu et.al. (1998) studied on the extraction of lignite with water sub- and supercritical states. The experiments were carried out to investigate the effect of temperature on extract formation rate, extract yields and product components at different pressures and end temperatures. The results indicated that the extract formation rate has a maximum with the variation of temperature. The temperature corresponding to the maximum extract formation rate, changing with the pressure, is between 400 and 450°C. The extraction yields vary with the conditions. With the increase of end temperature, the conversion also increases, but the increment is mainly gas and light oil.

The main fraction in extract is preasphaltene and the main gas component is CO₂.

Meng et.al. (2006) studied on the extraction of oil sand with sub- and supercritical water. Tumuji oil sand from Inner Mongolia was subjected to sub- and supercritical water extraction on a semicontinuous apparatus. The experiments were carried out to investigate the effect of temperature on extract yield, formation rate, and product components at different pressures. The results indicated that extract yield increases with the increase of pressure and a maximum extract yield of 81.1 wt % could be obtained at 30 MPa. The formation rate of extract has a maximum with the variation of temperature. With increase of pressure from 20 to 30 MPa, the maximum extract formation rate increases from 32.99×10^{-5} to $58.37 \times 10^{-5} \text{ s}^{-1}$ and the temperature corresponding to the maximum extract formation rate moves from 412 to 390 °C. The extract was fractionated into oil, asphaltene, and preasphaltene, and the oil was further fractionated into saturates, aromatics, and resin. The results show that formation rates of saturates, aromatics, and resin all have a maximum with the variation of temperature. The temperature corresponding to the maximum formation rates of saturates and aromatics decreases, while that of resin increases with increase of pressure. The gas yield is quite low, and the main gas components are CO₂, CH₄, and H₂.

Adschiri et.al. (2000) studied on the extraction of Taiheiyo coal with supercritical water-HCOOH mixture. Taiheiyo coals were extracted with supercritical toluene (SC-toluene) (653 K, 20 MPa), supercritical water (SCW) (653 K, 35 MPa) and formic acid (HCOOH)-SCW mixed solvents (653 K, 35 MPa) using a semi-batch type system. The results clearly indicate that the coal conversion ($=1 - \text{weight of residual coal (daf)} / \text{weight of loaded coal (daf)}$) and the liquid yield ($= \text{weight of liquid extracts} / \text{weight of loaded coal}$) in HCOOH-SCW were higher than those in SCW and SC-toluene. A considerable portion of coal is thus converted into light oils probably through hydrolysis and hydrogenation in HCOOH-SCW.

In the study of Aida et.al. (2002), extraction of Taiheiyo coal with supercritical water-phenol mixtures was investigated. Taiheiyo Japanese sub-bituminous coal was extracted with supercritical water (SCW) and phenol mixtures at 673 K and at over fluid densities ranging from 0 to 0.5 g/cm³. The extraction yield with SCW was 0.55-0.6, but increased with increasing the ratio of phenol to water, showing a maximum of 0.7 at water-phenol ratio of 4.5:0.5 and then decreased to 0.5-0.55 for pure phenol.

Kershaw (1986) studied on the extraction of Victorian Brown coals with supercritical water. At 380°C and 22 MPa conversions of 42-54 % and extract yields of 20-26% were obtained, significantly higher

than with toluene under the same conditions. The extracts were separated into oils, asphaltenes and pre-asphaltenes and these were studied by NMR spectroscopy combined with elemental, OH and molecular weight analyses. The extracts have a high asphaltene and pre-asphaltene content, together with a high oxygen content, especially in the asphaltene and pre-asphaltene fractions. Long alkyl chains were present in the oils and asphaltenes. Temperature had little effect on the extraction, whereas pressure has a marked effect on both the conversion and the composition of the extract. The major difference between the toluene and water extracts is the higher oxygen content of the latter. There was a considerable improvement in the conversion using 0.5 M NaOH rather than water. Analyses of some of the chars were also carried out.

In the study of Deshpande et.al. (1983), extraction of coal using supercritical water was investigated. An experimental apparatus was developed to inject coal into an autoclave containing preheated supercritical water. The supercritical water appears to act as both solvent and reactant in the conversion of coal to gases and liquids. Experiments were carried out with German Brown coal, lignite and bituminous coal and with glucose at subcritical and supercritical water densities. A significantly larger quantity of char was obtained when operating at subcritical densities and when the coal was mixed with water before heating to supercritical conditions. Smaller amounts of

char were obtained as density increased and as reaction time increased.

According to literature study listed above, there are few studies on the pyrolysis of demineralized lignite, asphaltite and oil shale. And also there is no study on the supercritical water extraction of demineralized lignite, asphaltite and oil shales in the literature. With the help of these experimental studies, new results may be added to the literature.



4. EXPERIMENTAL STUDY

4.1 Samples

In this project, the investigations were performed with Göynük Oil Shale (GOS-R) obtained from Göynük, Bolu; Eynez Lignite (ELIG-R) obtained from Eynez, Soma Lignite (SLIG-R) obtained from Soma, and Şırnak Asphaltite (SASP-R) obtained from Şırnak. For the experiments, these samples were crushed and ground in a jaw mill until the desired particle size was obtained. The sample was sieved to obtain a < 0.1 mm fraction and dried at 105 °C under N₂ atmosphere. The elemental analysis of GOS-R, ELIG-R, SLIG-R and ASP-R are given in Table 4.1.1. Elemental analysis of these samples was performed in Engler Bunte Institute, Karlsruhe University-Germany.

Table 4.1.1 The elemental analysis of GOS-R, ELIG-R, SLIG-R and SASP-R

Analysis (wt. %)	GOS-R	ELIG-R	SLIG-R	ASP-R
C (total)	56.34	65.60	60.40	42.42
H	7.20	5.10	5.60	3.13
N	0.97	1.00	0.90	0.62
S (total)	4.12	< 1.00	1.20	6.12

4.2 Experimental Set-up and Procedure

4.2.1 Demineralization

The main purpose in the demineralization is to remove mineral matter without influencing the organic structure. Demineralization can be carried out with physical and chemical methods. The methods of upgrading by demineralization depend on the structure and composition of the minerals in fossil fuel. In this study, oil shale, asphaltite and lignite samples were demineralized with chemicals which are HCl, HNO₃ and HF, successively.

At the beginning of the experiments, optimum demineralization conditions must be investigated. So, solid samples were treated with these acids at varying concentrations and reaction time. For each experiment, 1 g of sample was used in 20 ml of acid solution at room temperature. The mixtures were treated for varying time while stirring followed by filtering and washing repeatedly with distilled water at 60 °C. The filter residues were dried at 60 °C for 24 h under vacuum. The operating conditions of demineralization were given in Table 4.2.1.1.

Table 4.2.1.1 The operating conditions of demineralization

Acid	Acid concentration (vol. %)	Demineralization time (h)
HCl	5, 10, 20, 31	8, 16, 24, 32, 40, 48
HNO ₃	5, 10, 20	1, 2, 3, 4, 5, 6
HF	55	8, 16, 24, 32, 40, 48

After treating the samples with acids, the dried samples were combusted in high temperature furnace to investigate ash content. Firstly, 0.5 g of sample was weighed. After putting the sample into high temperature furnace, it was heated from room temperature to 450°C for 1 hour. Then it was heated from 450°C to 750°C for 1 hour. Finally, sample was cooled to room temperature and weighed to calculate mass of mineral matter.

Optimum operating conditions were achieved by three methods;

1. Total weight Loss: After drying, demineralized samples were weighed and weight loss was calculated.
2. Ash analysis
3. IR Spectras: IR spectrum analysis was performed with KBr.

Percent weight losses were compared after demineralization process for all samples. More weight loss means removal of more

mineral matter from organic body. Another important point is to compare the weight losses after ash analysis. How much mineral matter was removed from sample by demineralization, It was obtained less mineral matter after ash analysis. By comparing these results, optimum demineralization conditions were determined with the help of IR spectras. The experimental setup of demineralization process was given in Figure 4.2.1.1.

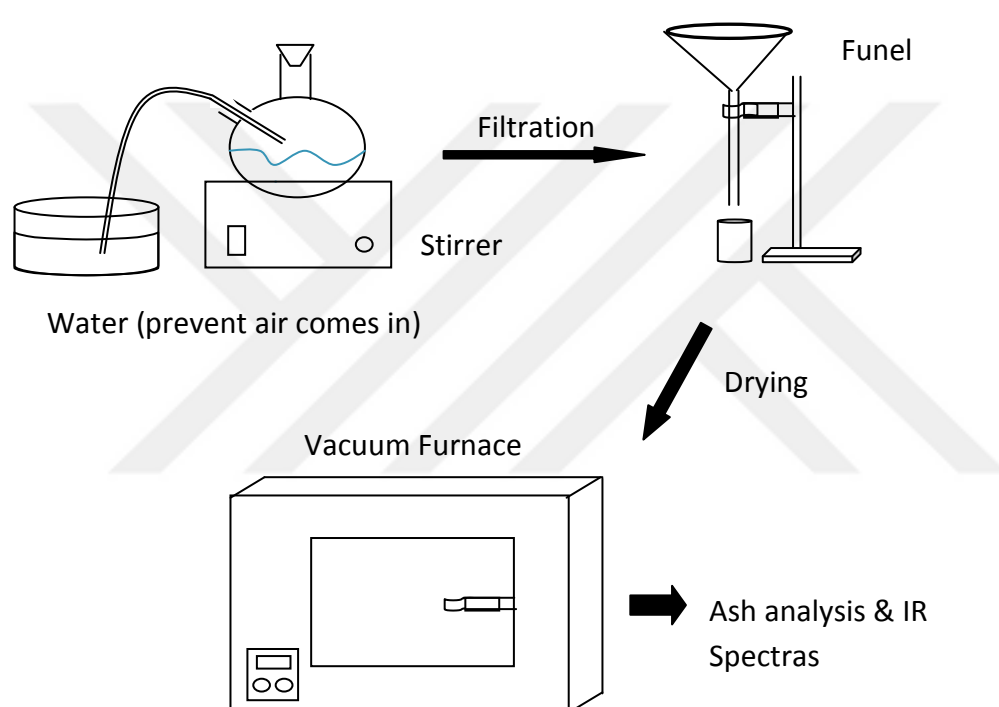


Figure 4.2.1.1 The experimental setup of demineralization process

4.2.2 Isothermal Pyrolysis (IP) of Samples

Isothermal pyrolysis experiments were carried out in the stainless steel reactor given in Figure 4.2.2.1. The vertical reactor which is made up from S316 stainless steel was 120 cm in height and 5.5 cm in internal diameter. A stream of N_2 (80 mL/min) was introduced at the reactor. There were two heating zones in the reactor. These zones were the bottom of the reactor, and the special sampling system. The bottom of the reactor, which is the pyrolysis region, was heated to desired pyrolysis temperature (450, 500, 550, 600 and 650 °C). The bottom zone heater is connected to a programmer and controller (PID controller; ± 0.5 °C) whereas the other is controlled manually via variac. The sampling zone was heated up to 250 °C. There was a moving piston at the top of the reactor.

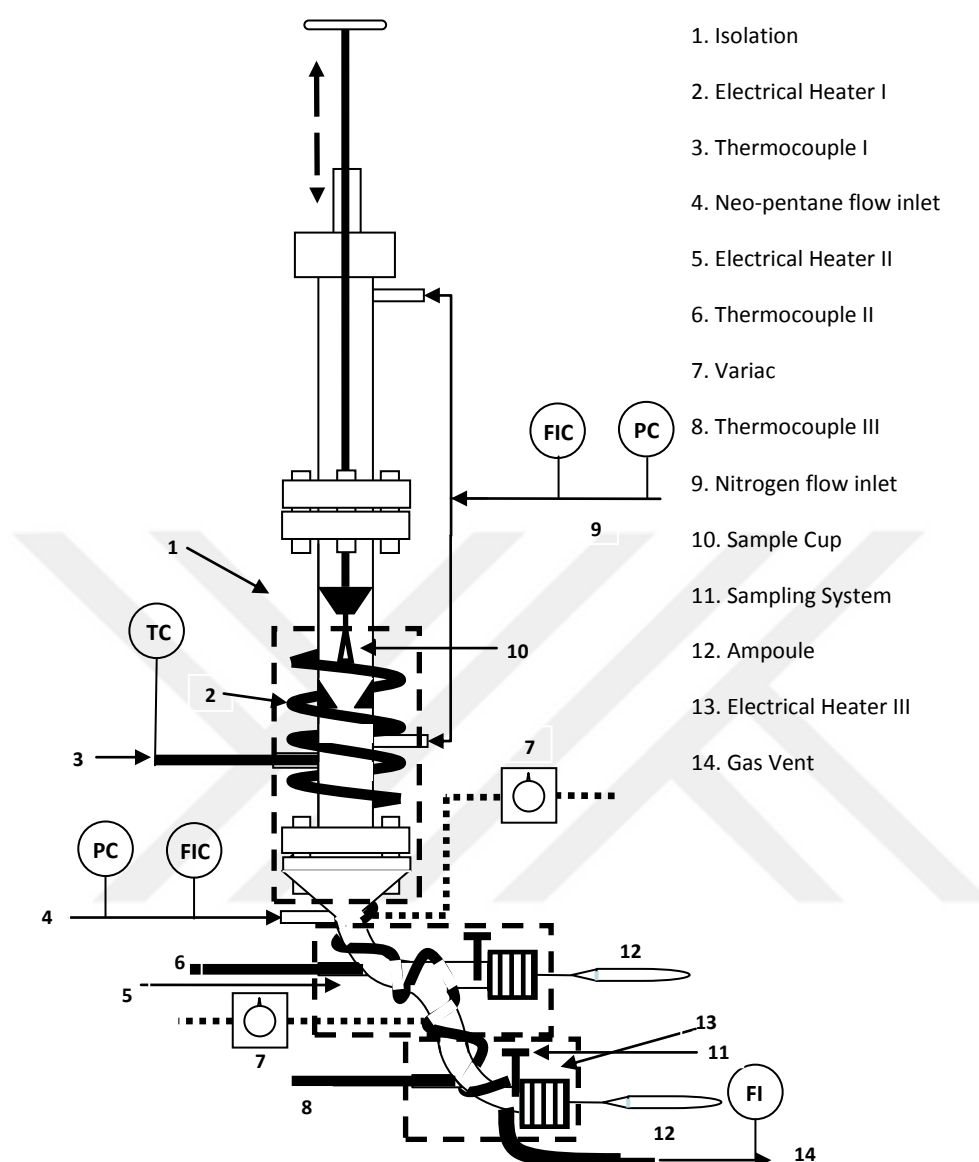


Figure 4.2.2.1 The schematic diagram of the isothermal pyrolysis reactor

For the pyrolysis experiment, 0.5 g of samples was poured into the sampling unit which is connected to moving piston. After that, reactor was tightly closed to prevent gas in/out. Another important step is adjusting gas flow rates accurately. Gas flow rates, nitrogen as a carrier gas and neo-pentane as a reference gas, were adjusted 80 mL/min and 40 mL/min, respectively by using electronic flow meter. Then the reactor was started to heat from room to pyrolysis temperature. When the desired pyrolysis temperatures have been reached, the piston was pushed down until sample enters the pyrolysis region and pyrolysis has been started. Pyrolysis products were swept out of the reactor by N₂ and mixed with reference gas (40 mL/min 0.507 vol. % neopentane in N₂) before passing to a special sampling. The time required to complete pyrolysis was selected to be 20 minutes so as to compare the degree of conversion of fossil fuels as a function of temperature. The residual solid remaining in the reactor was weighed as spent shale at the end of each pyrolysis runs. Experimental schedule of isothermal pyrolysis is given in Table 4.2.2.1.

Table 4.2.2.1 Experimental schedule of isothermal pyrolysis

Sample	Temperature (°C)				
	450	500	550	600	650
GOS-R	450	500	550	600	650
GOS-C	450	500	550	600	650
GOS-N	450	500	550	600	650
GOS-F	450	500	550	600	650
SASP-R	450	500	550	600	650
SASP-C	450	500	550	600	650
SASP-N	450	500	550	600	650
SASP-F	450	500	550	600	650
ELIG-R	450	500	550	600	650
ELIG-C	450	500	550	600	650
ELIG-N	450	500	550	600	650
ELIG-F	450	500	550	600	650

4.2.3 Temperature Programmed Pyrolysis (TPP) of Samples

A schematic diagram of experimental set-up was given in Figure 4.2.3.1. The experimental arrangement for pyrolysis comprised a gas delivery system, vaporizer, electrically heated fixed bed reactor, product recovery system and continuous gas analyzer. The gas delivery system consists of cylinders of nitrogen, synthetic air and reference gas (volume 0.507 % neopentane in nitrogen). In order to carry out the pyrolysis with a steam as optional, a vaporizer was fixed to the experimental set-up. Water can be fed from metering pumps into vaporizer where they are mixed with inert gas, nitrogen, before passing into reactor. The reactor shield shown in Figure 4.2.3.2 consisted of a stainless steel tube (400 mm long, 15 mm ID) was enclosed in a temperature programmable furnace heated by a three zone heater made from cylindrical ceramic block on to which heating wires are wrapped. A Duran-glass reactor tube (10 mm ID), which filled with the pyrolysis samples and quartz sand as a support at the lower and upper part of the sample bed, was located into the reactor shield.

Nitrogen and neo-pentane flow rates were adjusted as 80 mL/min and 10 mL/min, respectively. Then the reactor was heated to 550 °C at a rate of 2°C/min. The pyrolysis products were swept out of the reactor with inert gas (nitrogen) in to the heated line connected to the sampling system. The special sampling apparatus was used for

collecting the pyrolysis products at different reactor temperatures and time intervals during the reaction by means of evacuated glass ampoule.

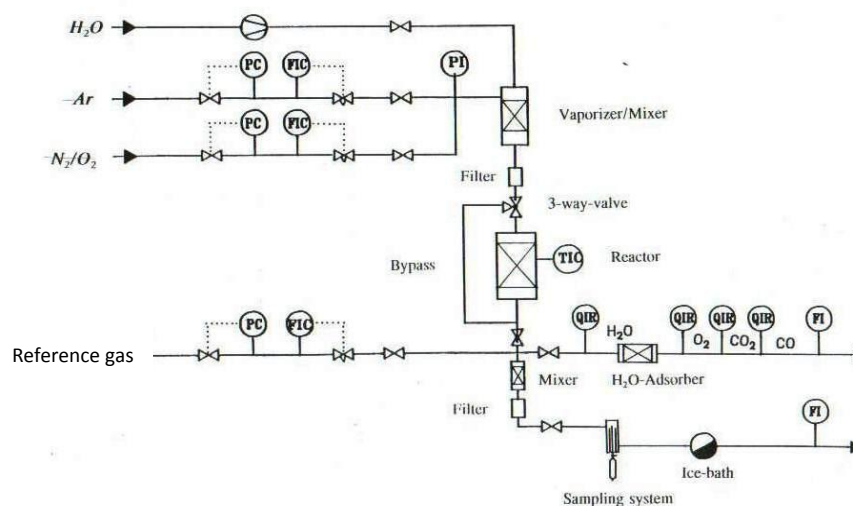


Figure 4.2.3.1 A schematic diagram of the temperature programmed pyrolysis equipment

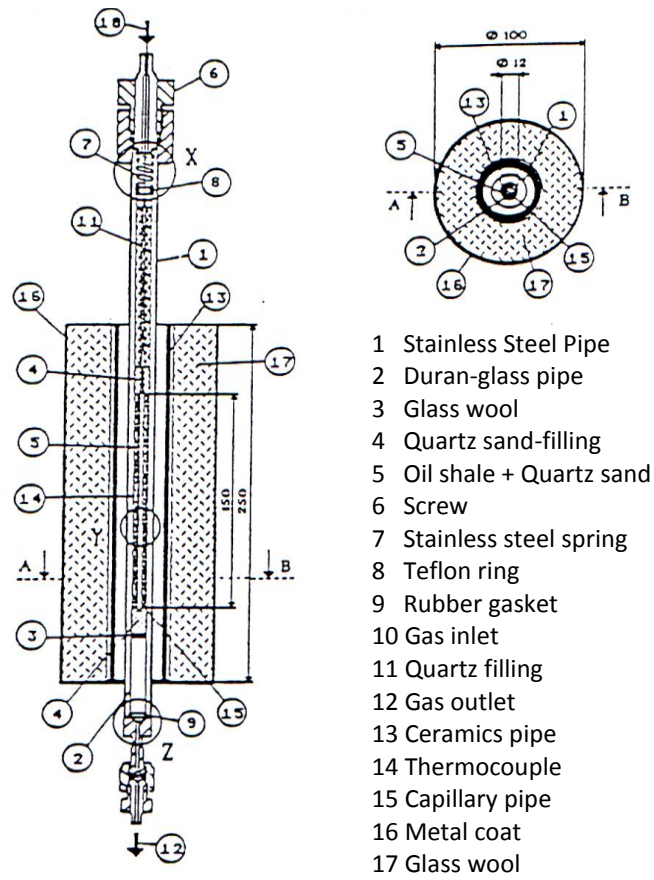


Figure 4.2.3.2 Equipment details for the reactor

The experimental schedule of temperature programmed pyrolysis is given in Table 4.2.3.1.

Table 4.2.3.1 Experimental Schedule of Temperature Programmed Pyrolysis

Sample	Heating Rate (°C/min)	Initial Temperature (°C)	Final Temperature (°C)
GOS-R	2	25	550
GOS-C	2	25	550
GOS-N	2	25	550
GOS-F	2	25	550
SASP-R	2	25	550
SASP-C	2	25	550
SASP-N	2	25	550
SASP-F	2	25	550
ELIG-R	2	25	550
ELIG-C	2	25	550
ELIG-N	2	25	550
ELIG-F	2	25	550

4.2.4 Supercritical water extraction (SCWE) of Samples

The investigations were performed with raw and demineralized samples of lignite. The samples were sieved to obtain a < 0.1 mm fraction and dried under vacuum. Samples were weighed as 2 g in carbon basis and 25 g water was used for each experiment. Supercritical water extraction experiments were carried out stainless steel (S316) autoclave which has 106 ml volume. The autoclave was given in Figure 4.2.4.1. After addition of solid sample and water to the reactor, the air was displaced from the apparatus with an inert gas stream (nitrogen). The reactor was heated to the desired temperature at 7 K min^{-1} and held at this temperature for 1 h. The reaction temperatures were 400, 450 and 500 °C for supercritical water extraction experiments. At the end of the experiments, gas products were analyzed in gas chromatography, liquid and solid products were analyzed in TOC analyzer.

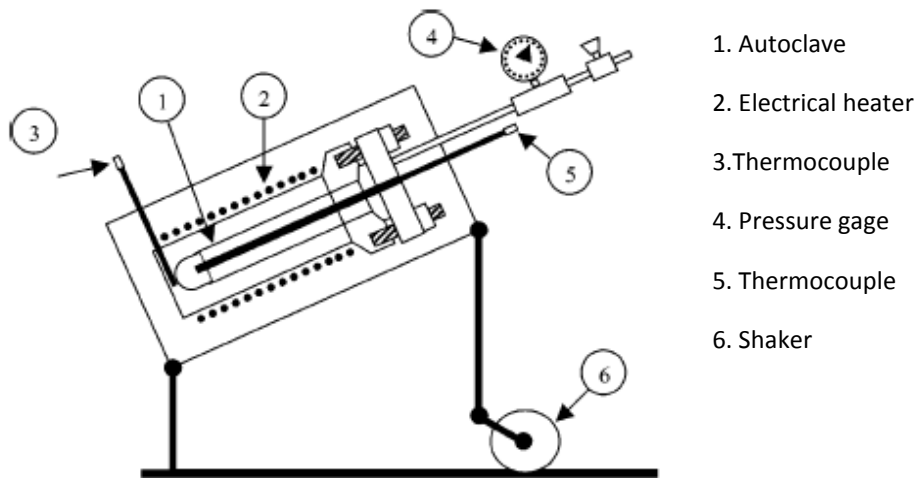


Figure 4.2.4.1 Schematic presentation of autoclave

4.2.5 Solvent Swelling Studies

To apply solvent swelling to kerogen, one first needs to isolate the kerogen. An ideal isolation method will recover all organic components without altering their structures. Kerogen can be isolated by both physical and chemical methods. Among chemical methods, HCl/HF demineralization is the most effective one.

The investigations were performed with oil shale sample obtained from Göynük, Bolu oil shale deposits in Turkey. Firstly, 1 g of oil shale sample was demineralized with HCl and HF successively. HCl-HF treated oil shale samples (GOS-K) were used in solvent swelling experiments. About 0.5 g of oil shale sample was put into a flask, mixed with DMSO, Pyridine and THF, separately. After waiting 48 h, solvents were removed in a rotary evaporator.

The samples were placed in 6 mm o.d tube and centrifuged for 3 min. The height of the samples was measured (h_1). Excess organic solvent was added to the tube, the contents of the tube were mixed, after some time was again centrifuged for 3 min and the height of the sample (h_2) was measured. Swelling measurements for each sample were repeated until there was no further volume change over several days, indicating that equilibrium had been reached. It was sometimes necessary to add fresh solvent to the tubes if the amount of

extractable material was significant as judged by color of the solvent contaminated. This was done by removing the contaminated solvent after centrifugation, using a syringe and adding the fresh solvent. Solvent swelling procedure was shown in Figure 4.2.5.1.

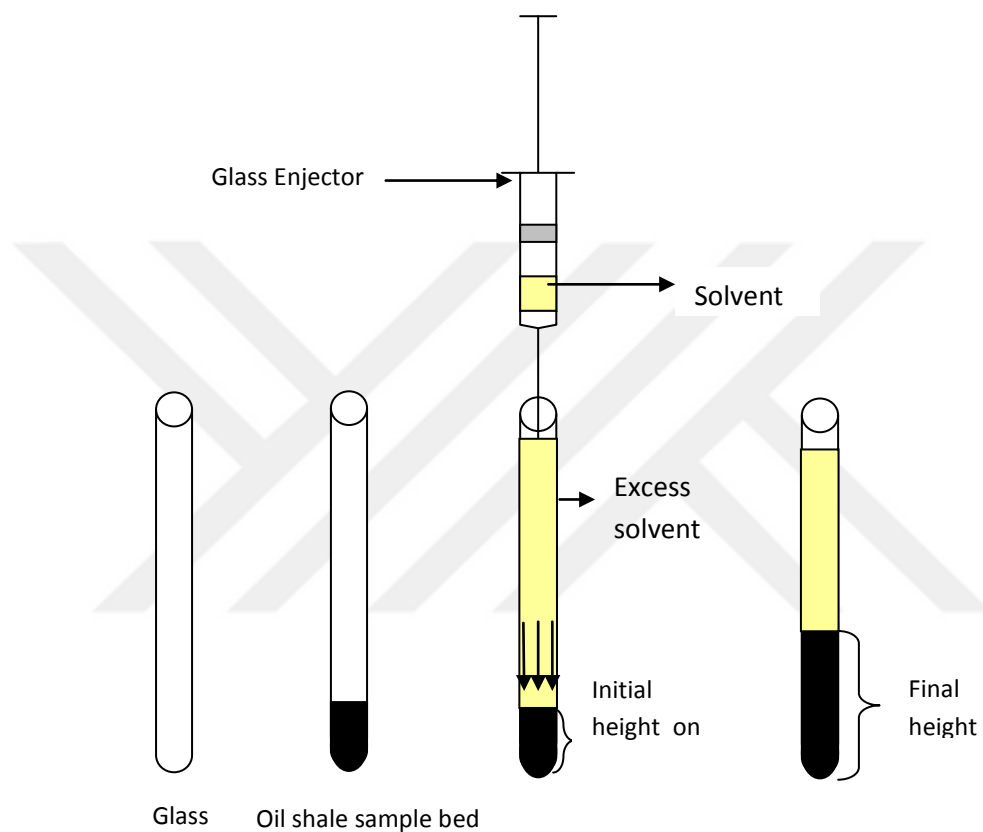


Figure 4.2.5.1 Solvent swelling procedures

To observe the effect of solvent swelling on the decomposition of kerogen, HCl-HF treated (GOS-K) and swollen with DMSO (GOS-K-D), Pyridin (GOS-K-P) and THF (GOS-K-T) samples were pyrolyzed. After

temperature-programmed pyrolysis experiments, products were identified by gas chromatography. Experimental schedule for solvent swelling and temperature-programmed pyrolysis of swollen samples was given in Table 4.2.5.1.

Table 4.2.5.1 Experimental schedule for solvent swelling

Solvent Swelling			
GOS-K	DMSO		
	Pyridine		
	THF		
Temperature Programmed Pyrolysis of Swollen Samples			
Sample	T _{initial} (°C)	T _{final} (°C)	Heating Rate (°C/min)
GOS-K	25	550	2
GOS-K-D	25	550	2
GOS-K-P	25	550	2
GOS-K-T	25	550	2

4.3 Analysis Methods

Experimental study comprises of demineralization, pyrolysis, solvent swelling and supercritical water extraction. After these processes, products were characterized by different methods and instruments. Figure 4.3.1 shows the schedule of analysis methods after experiments.

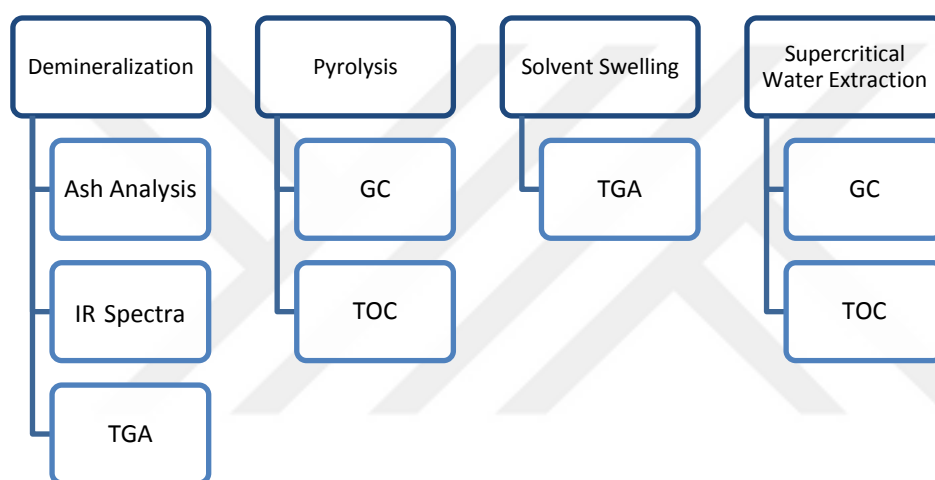


Figure 4.3.1 Schematic presentation of experiments and analysis

4.3.1 Ash Analysis of Demineralized Samples

Ash analysis was performed for demineralized samples. In order to determine the mineral matter of demineralized solid fuels, they were combusted in high temperature furnace as explained Section 4.2.1

4.3.2 IR Spectra of Demineralized Samples

Infrared Spectra of the samples were taken by preparing of KBr discs of samples. Oil shale, asphaltite and lignite samples of known weight of 3 mg were hand ground to a fine powder. Each sample was mixed with 97 mg of dry KBr powder, uniformly mixed and reground. The entire samples was transferred a disc and pressed under vacuum in the standard way.

Spectras were recorded between 4000 and 400 cm^{-1} using a Shimadzu Model spectrometer, Spectra of the raw and demineralized oil shale, asphaltite and lignite samples are given in Section 5.1.

4.3.3 Thermogravimetric Analysis of Samples

Thermogravimetric analysis of samples was performed with nitrogen flow rate of 15 mL/min. The heating rate for the analysis is 5 °C/min.

4.3.4 Gas Chromatographic Analysis

Product stream of pyrolysis of oil shale, asphaltite and lignite contains multi component mixtures of gases and vapors. The analysis of total stream mixtures was performed by using of special sampling system. For this purpose, hot product stream containing gases and vapors was led in to pre-evacuated glass ampoules as shown in Figure 4.3.4.1. The samples were sealed within the ampoules by means of a gas burner as seen in Figure 4.3.4.2 and were analyzed with a specially developed system, given in Figure 4.3.4.3, fitted to capillary gas chromatography. The schematic diagram of this system and gas chromatography are shown in Figure 4.3.4.4. The sealed ampoules can be stored for a long period of time, depending on the stability of the sample.

This technique offers a number of advantages: simplification of sampling compared to conventional procedures of fractionation for product recovery, safe handling and storage of the total sample, uncoupling sampling from analysis, and sampling at small intervals which allows studying in stationary system. Prof. Dr. Hans Schulz et. al. developed this sampling technique for gas/vapor multicomponent mixtures.

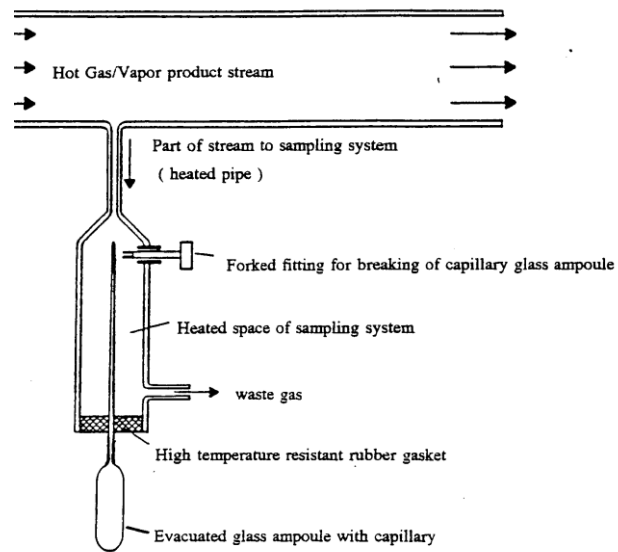


Figure 4.3.4.1 The special sampling system

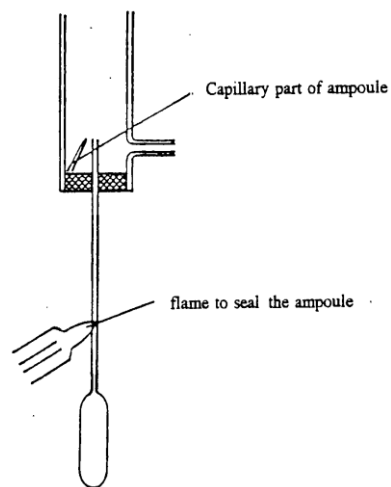


Figure 4.3.4.2 Melting of capillary part of glass ampoule

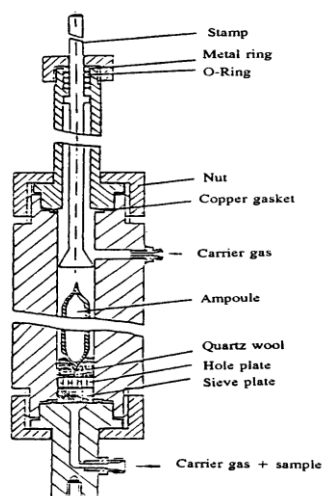


Figure 4.3.4.3 The sample introducing system of gas chromatography

Pyrolysis products were analyzed by using of a Hewlett Packard (HP 6890) capillary gas chromatography. The ampoules containing pyrolysis products were heated up to about 250 °C in the specially designed sample introducing system connected to the gas chromatography in Figure 4.3.4.3. Hydrogen gas was used as a carrier gas and Flame Ionization Detector (FID) was employed for analysis. The operating conditions of gas chromatography were given in Table 4.3.4.1.

Characteristic chromatogram of pyrolysis products of oil shale were shown in Figure 5.2.1.1.

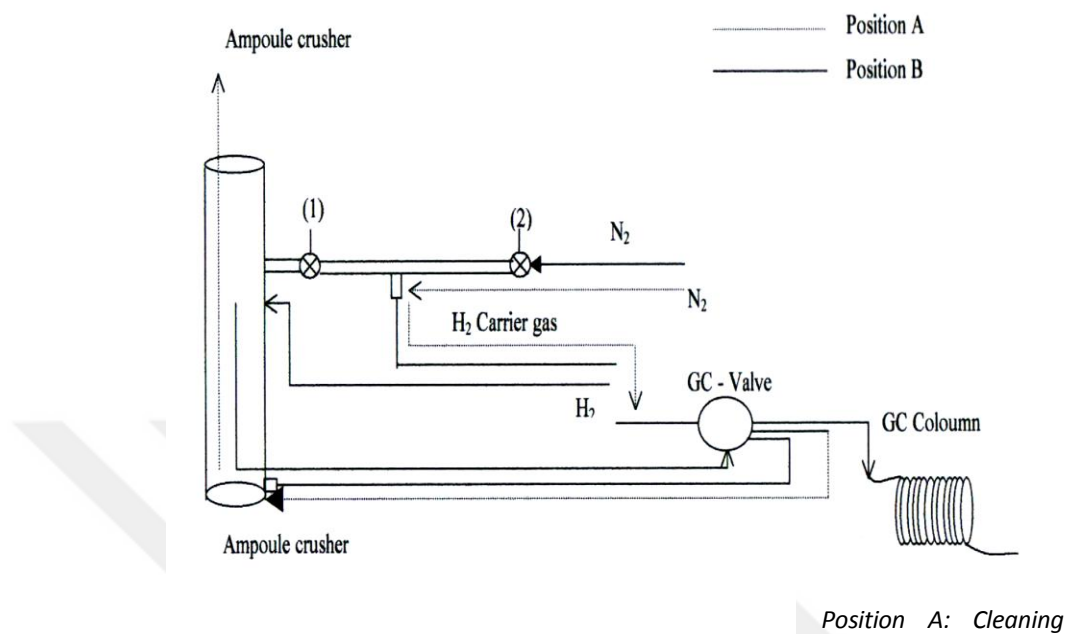


Figure 4.3.4.4 Flow sheet of capillary gas chromatography connected to sample introducing system

position: Valve 1 (Close), Valve 2 (Open) GC-Valve (Off).

Position B: Analysis position: Valve 1 (Open), Valve (Close) GC-Valve (On).

Table 4.3.4.1 Operating condition for capillary gas chromatography

Gas Chromatography	HP 6890
Column	HP-1, 100 m x 0.25 mm fused silica
Stationary phase	Cross linked methyl siloxane
Film thickness	0.5 μm
Carrier gas	Hydrogen
Detector	Flame Ionization (FID)
Detector temperature	350°C
Temp. Program	Starting temperature -80°C isothermal 3 min 30°C/min to -30°C, isothermal 1.5 min 25°C/min to 0°C isothermal 2.0 min 10°C/min to 25°C isothermal 1 min 10°C/min to 275°C isothermal 3 min
Injector temperature	290°C

4.3.5 Total Organic Carbon Analysis

Total organic carbon (TOC) of liquid products or solid residue was analyzed by Shimadzu TOC-VCPH Analyzer and Solid Sample Module (SSM-5000A). Three trials were made for each experimental condition and resulted in errors of less than 5%. Actually, all experiments gave a high reproducibility during the experimental process. Operating conditions of TOC analyzer are given in Table 4.3.5.1.

Table 4.3.5.1 Operating conditions of TOC analyzer

Model	TOC-Vcph PC controlled TOC analyzer
Analysis Method	680°C Combustion; Nondispersive Infrared (NDIR)
Analytes Measured	Total Organic Carbon; Total Carbon; Total Inorganic Carbon; Non-Purgeable Organic Carbon; Purgeable Organic Carbon; TN (Total Nitrogen)
Measurement Range (ppm)	TC : 0 to 25000 IC : 0 to 30000
Measurement accuracy (Responsibility)	CV 1.5% max.

5. RESULTS AND DISCUSSION

5.1 Demineralization

Because of the difficulty of removing all inorganic matter from oil shale or coal samples without losing or altering part of the organic structure, a number of studies of the effects of demineralization on coal structure, properties, and reactivity have been carried out with conflicting results. Despite attempts with a number of chemical reagents, no general method has been developed that can completely separate the unchanged organic structure from the complex sedimentary mixture. The conventional hydrochloric/hydrofluoric acid treatment is effective for removing most carbonate, oxide, and monosulfide minerals from sedimentary rocks and leaving the kerogen and pyrite largely unaffected.

Effective removal of pyrite is usually the main problem. Petroleum geochemists have long been interested in obtaining pyrite-free and chemically unaltered organic structure concentrates. Quantitative removal of pyrite is not possible without alteration of the organic composition. The magnitude of the change in the organic matter depends on the chemical nature of the sample as well as on the reaction conditions. In this study, pyrite was removed by applying HNO_3 acid treatments at moderate temperatures.

5.1.1 Demineralization of Oil Shale

Oil shale samples were obtained from the Göynük oil shale deposit located near the town of Bolu in northwestern Turkey. This deposit is the largest oil shale deposits in Turkey.

Oil shale samples were demineralized with HCl, HNO₃ and HF by method described in Section 2.1. Oil shale samples demineralized by HCl with different concentrations and treating times to remove carbonate structure of sample. Weight losses of GOS-R after demineralization with HCl were calculated and tabulated in Table 5.1.1.1.

Table 5.1.1.1 Weight losses after demineralization of GOS-R with HCl

Time (h)	Concentration (%)	Sample (g)	Weight Loss (g)	Weight Loss (%)
8	5	1	0.1602	16.02
	10		0.1612	16.12
	20		0.1770	17.70
	31.5		0.1618	16.18
16	5	1	0.1321	13.21
	10		0.1426	14.26
	20		0.1365	13.65
	31.5		0.1479	14.79
24	5	1	0.1528	15.28
	10		0.1568	15.68
	20		0.1561	15.61
	31.5		0.1575	15.75
32	5	1	0.1378	13.78
	10		0.1501	15.01
	20		0.1412	14.12
	31.5		0.1556	15.56
40	5	1	0.1568	15.68
	10		0.1611	16.11
	20		0.1898	18.98
	31.5		0.1847	18.47
48*	5	1	0.1883	18.83
	10*		0.1936	19.36
	20		0.1855	18.55
	31.5		0.1820	18.20

To obtain ash level of samples, combustion of GOS-C was investigated and results were tabulated in Table 5.1.1.2.

Table 5.1.1.2 Ash analysis of GOS-C

Time (h)	Concentration (%)	Sample (g)	Ash level (g)	Ash level (%)
8	5	0.5	0.0679	13.58
	10		0.0678	13.56
	20		0.0681	13.62
	31.5		0.0648	12.96
16	5	0.5	0.0664	13.28
	10		0.0646	12.92
	20		0.065	13.30
	31.5		0.0669	13.38
24	5	0.5	0.0643	12.86
	10		0.0631	12.62
	20		0.0602	12.04
	31.5		0.0647	12.94
32	5	0.5	0.0644	12.88
	10		0.0639	12.78
	20		0.0626	12.52
	31.5		0.0613	12.26
40	5	0.5	0.0619	12.38
	10		0.0627	12.54
	20		0.0641	12.82
	31.5		0.0589	11.78
48*	5	0.5	0.0583	11.66
	10*		0.0584	11.68
	20		0.0588	11.76
	31.5		0.0586	11.72

According to Table 5.1.1.1 and Table 5.1.1.2, in demineralization of GOS with HCl optimum acid concentration and time was selected as 10% and 48 h, respectively. Attempts were also made to demineralize oil shale by leaching with 5, 10, 20 and 31.5% HCl. In a comparison, the degree of demineralization decreased as the concentration of acids used for leaching increased from 10% to 20% and to 31.5%. This may be due to a lower removal of clay, quartz and pyrite and a higher dissolution of oil shale and the consequent formation of some stable components that could not be removed.

After treating by HCl, oil shale samples (GOS-C) were demineralized with HNO_3 to remove pyrite structure of samples. Weight losses of GOS-C and results of ash analysis were tabulated in Table 5.1.1.3 and Table 5.1.1.4.

Table 5.1.1.3 Weight losses after demineralization of GOS-C with HNO_3

Time (h)	Concentration (%)	Sample (g)	Weight Loss (g)	Weight Loss (%)
1*	5*	1	0.1396	13.96
	10		0.1119	11.19
	20		0.8800	8.80
2	5	1	0.1319	12.19
	10		0.1104	11.04
	20		0.1006	10.06
3	5	1	0.1340	13.40
	10		0.1104	11.04
	20		0.1006	10.06
4	5	1	0.1443	14.43
	10		0.1338	13.38
	20		0.1009	10.09
5	5	1	0.1419	14.19
	10		0.1130	11.30
	20		0.1206	12.06
6	5	1	0.1224	12.24
	10		0.9700	9.70
	20		0.9100	9.10

Table 5.1.1.4 Ash Analysis of GOS-N

Time (h)	Concentration (%)	Sample (g)	Ash level (g)	Ash level (%)
1*	5*	0.5	0.0582	11.64
	10		0.0583	11.66
	20		0.0555	11.10
2	5	0.5	0.0584	11.68
	10		0.0578	11.56
	20		0.0524	10.48
3	5	0.5	0.0654	12.48
	10		0.0555	11.10
	20		0.0524	10.58
4	5	0.5	0.0581	11.62
	10		0.0564	11.30
	20		0.0513	10.27
5	5	0.5	0.0577	11.53
	10		0.0533	10.65
	20		0.0511	10.22
6	5	0.5	0.0598	11.96
	20		0.0532	10.64
	20		0.0511	10.23

In demineralization of GOS-C with HNO_3 , as concentration of acid solution increases and demineralization time increases, weight loss decreases. This may be explained as the obtaining the new carbonyl groups and/or connecting of the nitro groups to organic

structure. So, in the demineralization of GOS-C with HNO_3 , optimum acid concentration and time was selected as 5 % and 1 h, respectively.

HCl- HNO_3 treated samples (GOS-N), was demineralized with 40 % HF to remove silicate structure from organic structure. Demineralization times as selected as 8, 16, 24, 32, 40 and 48 h, and results were tabulated in Table 5.1.1.5 and Table 5.1.1.6.

Table 5.1.1.5 Weight losses after demineralization of GOS-N with HF

Time (h)	Concentration (%)	Sample (g)	Weight Loss (g)	Weight Loss (%)
8*	~ 40	1	0.2340	23.40
16			0.2265	22.65
24			0.2279	22.79
32			0.2094	20.94
40			0.3138	31.38
48			0.2283	22.83

In demineralization of GOS-N with HF, demineralization time was selected as 8 h.

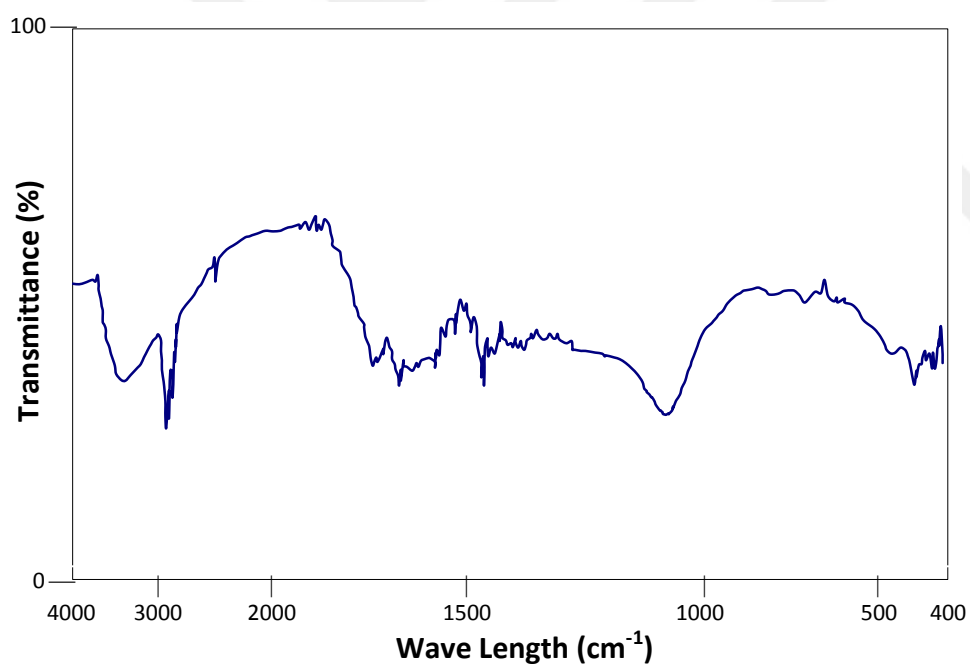
IR analysis of GOS-R, GOS-C, GOS-N and GOS-F are given in

Figure 5.1.1.1 -

Figure **5.1.1.4.**

Table 5.1.1.6 Ash Analysis of GOS-F

Time (h)	Concentration (%)	Sample (g)	Ash level (g)	Ash level (%)
8*	~ 40	0.5	0.075	1.50
16			0.092	1.84
24			0.094	1.88
32			0.075	1.67
40			0.082	1.64
48			0.098	1.98

**Figure 5.1.1.1** IR Spectra of GOS-R

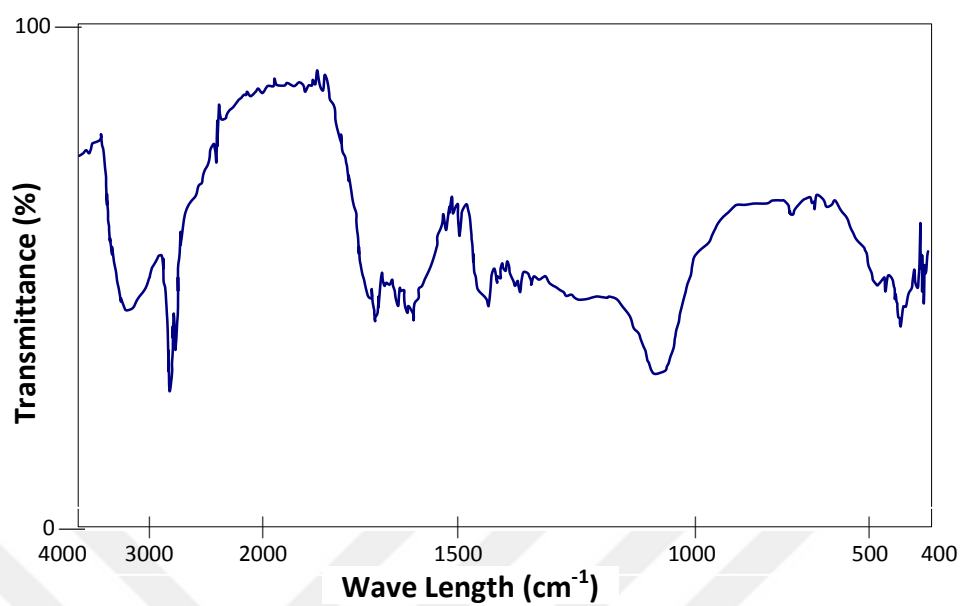


Figure 5.1.1.2 IR Spectra of GOS-C

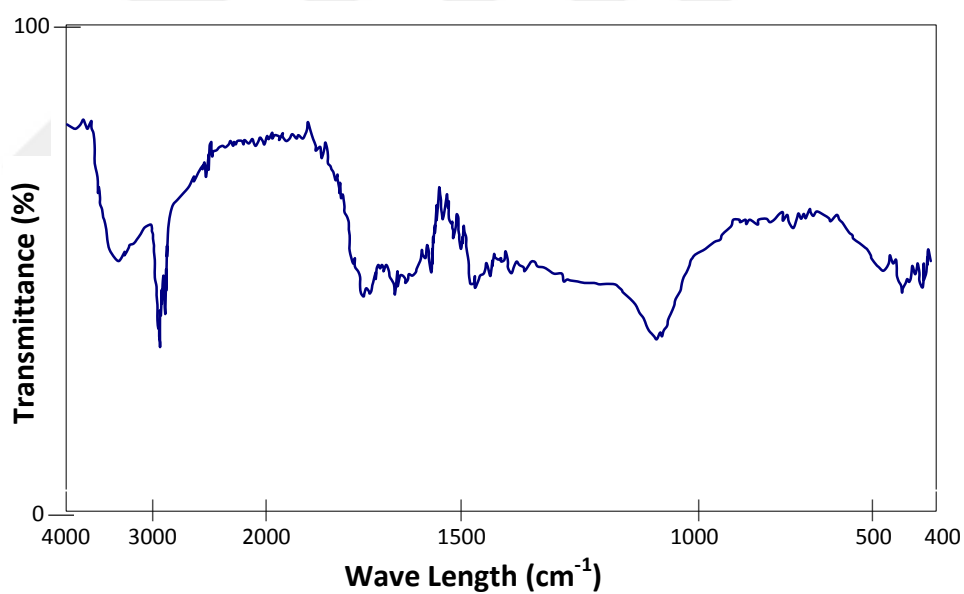


Figure 5.1.1.3 IR Spectra of GOS-N

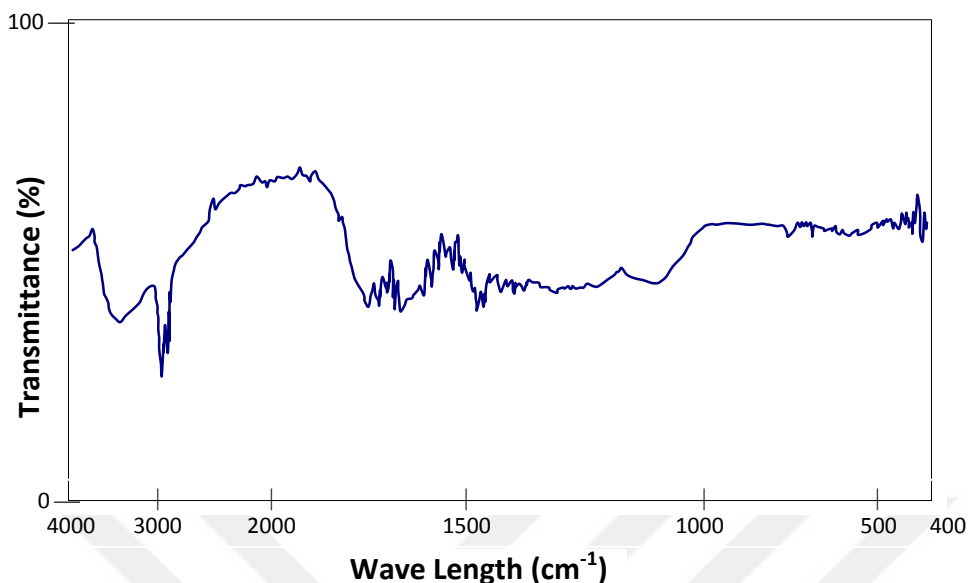


Figure 5.1.1.4 IR Spectra of GOS-F

IR study of oil shale before and after demineralization has been carried out to follow a new bond making in demineralization. An alteration might be due to the oxidation of organic structure during pyrite removal with nitric acid. IR spectra of the samples were recorded between 4000 and 400 cm^{-1} . IR study of oil shale after demineralization showed no change in the aliphatic CH stretching frequency and bands range at 1330 and 1540 cm^{-1} corresponding to R- NO_2 groups. It can be stated that the oxidation of aliphatic CH bonds groups would not be expected and so any oxidation that might occur would have a little impact on the substantial CH groups present. More importantly ones if there is an evidence of newly formed carbonyl

groups in $1700\text{--}1750\text{ cm}^{-1}$ where kerogen oxidation is often apparent and which represent absorption bands with high extinction coefficient.

The bands at 2924 and 2855 cm^{-1} are the asymmetric and symmetric stretching modes of methylene groups,; the bands at 2956 and 2872 cm^{-1} are the asymmetric and symmetric modes of methyl groups and the 2895 cm^{-1} band has a contribute from lone CH group.

5.1.2 Demineralization of Lignite

Lignite samples were demineralized with HCl, HNO_3 and HF, successively. Demineralization of ELIG-R with 5%, 10%, 20% and 31.5% HCl were carried out firstly. Weight losses after demineralization with HCl were calculated and tabulated in Table 5.1.2.1.

Table 5.1.2.1 Weight losses after demineralization of ELIG-R with HCl

Time (h)	Concentration (%)	Sample (g)	Weight Loss (g)	Weight Loss (%)
8	5	1	0.1949	19.49
	10		0.1952	19.52
	20		0.2157	21.57
	31.5		0.2243	22.43
16	5	1	0.1635	16.35
	10		0.1670	16.70
	20		0.2018	20.18
	31.5		0.2072	20.72
24*	5	1	0.1879	18.79
	10		0.1961	19.61
	20*		0.2256	22.56
	31.5		0.2062	20.62
32	5	1	0.1967	19.67
	10		0.2016	20.16
	20		0.2057	20.57
	31.5		0.2491	24.91
40	5	1	0.1753	17.53
	10		0.1761	17.61
	20		0.1605	16.05
	31.5		0.1670	16.70
48	5	1	0.1744	17.44
	10		0.1401	14.01
	20		0.1388	13.88
	31.5		0.1384	13.84

Ash level of ELIG-C samples was obtained after combustion of sample and results were calculated and tabulated in Table 5.1.2.2.

Table 5.1.2.2 Ash analysis of ELIG-C

Time (h)	Concentration (Vol. %)	Sample (g)	Ash level (g)	Ash level (%)
8	5	0.5	0.0184	3.68
	10		0.0078	1.56
	20		0.0077	1.54
	31.5		0.0076	1.51
16	5	0.5	0.0072	1.44
	10		0.0065	1.30
	20		0.0074	1.48
	31.5		0.009	1.80
24*	5	0.5	0.0074	1.47
	10		0.0077	1.53
	20*		0.0062	1.23
	31.5		0.0076	1.51
32	5	0.5	0.0067	1.34
	10		0.0073	1.46
	20		0.0061	1.22
	31.5		0.0077	1.54
40	5	0.5	0.0061	1.22
	10		0.0069	1.38
	20		0.0069	1.38
	31.5		0.0062	1.24
48	5	0.5	0.0067	1.34
	10		0.0066	1.32
	20		0.0068	1.36
	31.5		0.0064	1.28

According to results of weight loss and ash level, concentration of HCl solution and demineralization time was selected as 20 % and 24 h, respectively. A higher degree of demineralization was obtained with

20 % HCl (22.56%). HCl was also reported as the most effective acid for demineralization of lignite (Bolat et.al., 1998)

After demineralization of ELIG-R with HCl, ELIG-C was demineralized with HNO_3 solution to remove pyrite minerals from organic structure. Results of demineralization with HNO_3 were calculated and tabulated in Table 5.1.2.3.

Table 5.1.2.3 Weight losses after demineralization of ELIG-C with HNO_3

Time (h)	Concentration (vol. %)	Sample (g)	Weight Loss (g)	Weight Loss (%)
1	5*	1	0.1152	11.52
	10		0.1094	10.94
	20		0.1020	10.20
2	5	1	0.1099	10.99
	10		0.1135	11.35
	20		0.1105	11.05
3	5	1	0.1242	12.42
	10		0.1166	11.66
	20		0.1083	10.83
4	5	1	0.1080	10.80
	10		0.1150	11.50
	20		0.1050	10.50
5	5	1	0.1176	11.76
	10		0.1105	11.05
	20		0.1113	11.13
6	5	1	0.1158	11.58
	10		0.1142	11.42
	20		0.1313	13.13

Ash analysis of ELIG-N was calculated by combustion of ELIG-N samples and results were tabulated in Table 5.1.2.4.

Table 5.1.2.4 Ash analysis of ELIG-N

Time (h)	Concentration (vol. %)	Sample (g)	Mineral (g)	Mineral (%)
1	5*	0.5	0.0055	1.10
	10		0.0068	1.36
	20		0.0061	1.22
2	5	0.5	0.0072	1.44
	10		0.0081	1.62
	20		0.0087	1.74
3	5	0.5	0.0064	1.28
	10		0.0071	1.42
	20		0.0096	1.92
4	5	0.5	0.0059	1.18
	10		0.0067	1.34
	20		0.0059	1.18
5	5	0.5	0.0095	1.90
	10		0.0101	2.02
	20		0.0097	1.94
6	5	0.5	0.0099	1.98
	10		0.0066	1.32
	20		0.0108	2.16

According to results of weight loss and ash level, concentration of HNO_3 solution and demineralization time was selected as 5 % and 1 h, respectively. The effects of nitric acid treatment on the ash removal of lignite samples are shown in Table 5.1.2.4.

After demineralization of LIG-C with HNO_3 , LIG-N samples were demineralized with 40 % HF solution with different demineralization times. Weight losses after HF treatment were calculated and tabulated in Table 5.1.2.5 and results of ash analysis of LIG-N samples were shown in Table 5.1.2.6.

Table 5.1.2.5 Weight losses after demineralization of LIG-N with HF

Time (h)	Concentration (%)	Sample (g)	Weight Loss (g)	Weight Loss (%)
8*	~ 40	1	0.0661	6.61
16			0.0655	6.55
24			0.0676	6.76
32			0.0681	6.81
40			0.0688	6.88
48			0.0691	6.91

Table 5.1.2.6 Ash analysis of LIG-F

Time (h)	Concentration (%)	Sample (g)	Ash level (g)	Ash level (%)
8*	~ 40	0.5	0.0053	1.06
16			0.0062	1.24
24			0.0064	1.28
32			0.0075	1.50
40			0.0082	1.74
48			0.0088	1.76

According to results of weight loss and ash level, demineralization time was selected as 8 h, respectively. HF removes silicate minerals from organic structure.

IR analysis of ELIG-R, ELIG-C, ELIG-N and ELIG-F were shown in

Figure 5.1.2.1 - Figure 5.1.2.4.

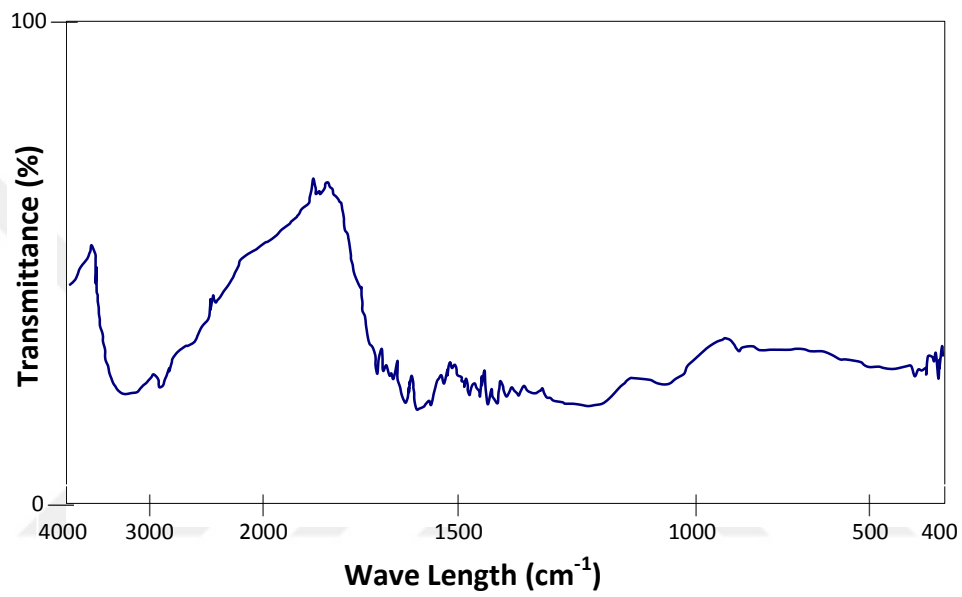


Figure 5.1.2.1 IR Spectra of ELIG-R

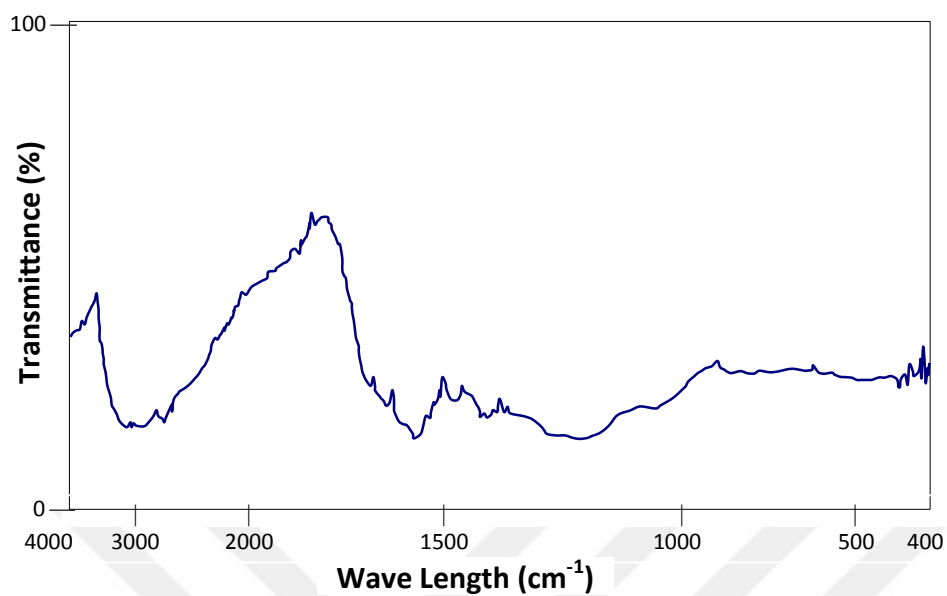


Figure 5.1.2.2 IR Spectra of ELIG-C

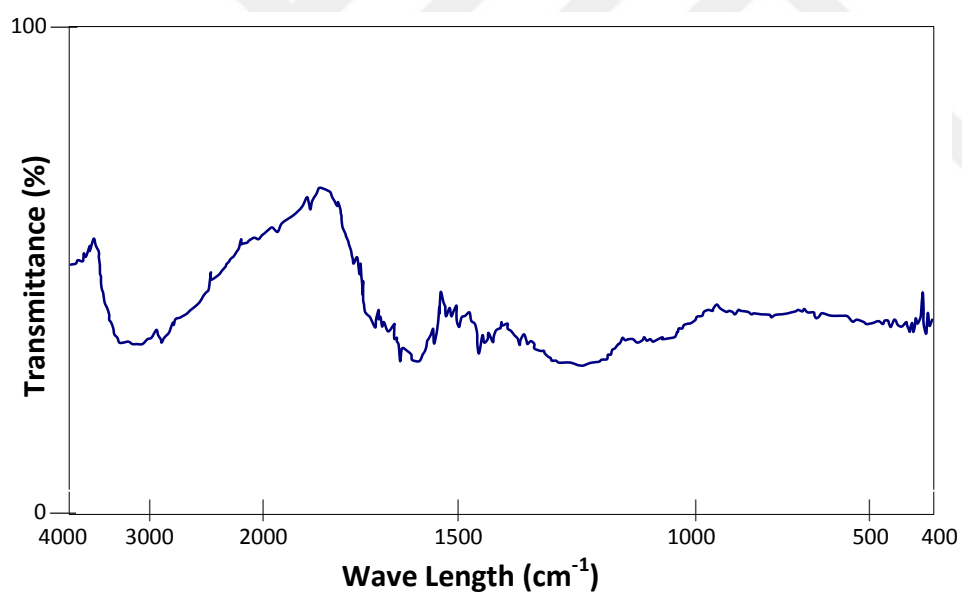


Figure 5.1.2.3 IR Spectra of ELIG-N

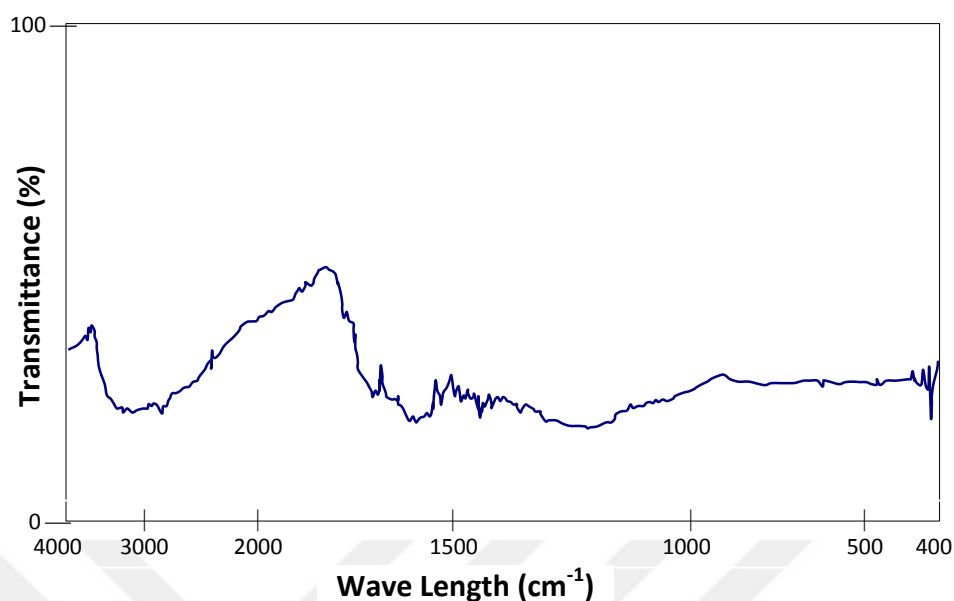


Figure 5.1.2.4 IR Spectra of ELIG-F

Raw lignite samples show that O-H stretching vibrations are situated at 3752 cm^{-1} . The peaks for O-H groups at $3600\text{--}3800\text{ cm}^{-1}$ appear to be for those associated with clay minerals. The aromatic hydrogen band at 3040 cm^{-1} is absent in the raw lignite sample indicating its highly substituted and condensed nature. The peak at 2920 cm^{-1} appearing as sharp peaks of medium intensity, may be assigned to aliphatic and alicyclic CH_3 , CH_2 and CH groups although the major contribution is expected to be due to CH_2 groups. The peak at 1699 cm^{-1} appears to indicate the presence of carbonyl (C=O) content. The peak around 1600 cm^{-1} in the coal is observed due to aromatic C=C , vinylic C=C and possibly due to other O-containing functional groups. The oxygen containing functional groups found in coal

specifically include phenols and alcohols, ethers, carboxylic acid and carbonyls. The band at 1710 cm^{-1} , assigned to carbonyl/carboxyl groups as in lactone, carboxylic acid. Raw samples contained $1600\text{--}1550$ and $1420\text{--}1300\text{ cm}^{-1}$ asymmetric and symmetric carboxylate structures. A band at 1436 cm^{-1} in the coal was observed. This is mainly due to CH_3 asymmetric deformation and CH_2 group in bridges but may also be partly due to aromatic $\text{C}=\text{C}$ and strongly hydrogen bonded $\text{O}\text{--}\text{H}$ groups. The band at 1372 cm^{-1} is mainly due to CH_3 symmetric deformation while --CH_3 and --CH_2 in cyclic structures may also partly contribute to this band.

IR spectra of LIG-C shows similar spectrum except $1400\text{--}1550\text{ cm}^{-1}$ band of carboxylate reduced.

Spectrum of HCl-HNO_3 treated sample shows a band at 420 cm^{-1} assigned to pyrite (FeS_2), demineralization of HNO_3 causes bonding of nitro groups and produces pyrite molecules, this is an unwanted situation and effect of demineralization with HNO_3 on lignite samples is negligible.

Most of the peaks in FT-IR spectra of raw lignite between 1100 and 400 cm^{-1} can be assigned to clay minerals such as quartz, kaolinite, illite and the montmorillonite group. The $\text{Si}\text{--}\text{O}\text{--}\text{Si}$ stretching vibration causes absorption at 1031 cm^{-1} and 1008 cm^{-1} . Demineralization of LIG-N with HF causes the removing of these minerals.

5.1.3 Demineralization of Asphaltite

Asphaltite samples were obtained from the Şırnak asphaltite (SASP) deposit located in southeastern Turkey. This deposit is the largest in Turkey.

Asphaltite samples were demineralized with HCl, HNO₃ and HF by method described in Section 2.1. Asphaltite samples firstly demineralized by HCl with different concentrations and treating times to remove carbonate structure of sample. Weight losses and ash analysis data of SASP-R after demineralization with HCl were calculated and tabulated in Table 5.1.3.1 and Table 5.1.3.2, respectively.

Table 5.1.3.1 Weight losses after demineralization of SASP-R with HCl

Time (h)	Concentration (%)	Sample (g)	Weight Loss (g)	Weight Loss (%)
8	5	1	0.4211	42.11
	10		0.4259	42.59
	20		0.4377	43.77
	31.5		0.4393	43.93
16	5	1	0.3878	43.21
	10		0.3805	38.05
	20		0.3861	38.61
	31.5		0.4114	41.14
24*	5	1	0.4029	40.29
	10*		0.3922	39.22
	20		0.4188	41.88
	31.5		0.4089	40.89
32	5	1	0.4338	43.38
	10		0.4295	42.95
	20		0.4308	43.08
	31.5		0.4214	42.14
40	5	1	0.4320	43.20
	10		0.4276	42.76
	20		0.4301	43.01
	31.5		0.4222	42.22
48	5	1	0.4162	41.62
	10		0.4614	46.14
	20		0.1383	13.83
	31.5		0.4118	41.18

Table 5.1.3.2 Ash analysis of SASP-C

Time (h)	Concentration (%)	Sample (g)	Ash level (g)	Ash level (%)
8	5	0.5	0.0679	13.58
	10		0.0678	13.56
	20		0.0681	13.62
	31.5		0.0648	12.96
16	5	0.5	0.0664	13.28
	10		0.0646	12.92
	20		0.0650	13.30
	31.5		0.0669	13.38
24*	5	0.5	0.0643	12.86
	10*		0.0631	12.62
	20		0.0602	12.04
	31.5		0.0647	12.94
32	5	0.5	0.0644	12.88
	10		0.0639	12.78
	20		0.0626	12.52
	31.5		0.0613	12.26
40	5	0.5	0.0619	12.38
	10		0.0627	12.54
	20		0.0641	12.82
	31.5		0.0589	11.78
48	5	0.5	0.0578	11.56
	10		0.0581	11.62
	20		0.0588	11.76
	31.5		0.0586	11.72

In demineralization of SASP-R with HCl, concentration of HCl solution and demineralization time was selected as 10 % and 24 h, respectively. A higher degree of demineralization was obtained with 10 % HCl (39%). This result is in good accordance with literature (Gülen et.al., 2005). It is suggested that smaller molecules can more easily diffuse into the sample particles and solid mass. It is known that a significant amount of calcium passes into solution upon HCl treatment. As expected, HCl treatment was more effective in ash reduction (Önal and Ceylan, 1995).

After demineralization of SASP-R with HCl, SASP-C samples were demineralized with HNO_3 . Results of weight losses and ash analysis were calculated and tabulated in Table 5.1.3.3 and Table 5.1.3.4, respectively

Table 5.1.3.3 Weight losses after demineralization of SASP-C with HNO_3

Time (h)	Concentration (vol. %)	Sample (g)	Weight Loss (g)	Weight Loss (%)
1	5*	1	0.0810	8.10
	10		0.0972	9.72
	20		0.1270	12.70
2	5	1	0.1327	13.27
	10		0.1313	13.13
	20		0.1265	12.65
3	5	1	0.1417	14.17
	10		0.1391	13.91
	20		0.1333	13.33
4	5	1	0.1208	12.08
	10		0.1269	12.69
	20		0.1173	11.73
5	5	1	0.1615	16.15
	10		0.2221	22.21
	20		0.1525	15.25
6	5	1	0.1377	13.77
	10		0.2106	21.06
	20		0.1724	17.24

Table 5.1.3.4 Ash analysis of SASP-N

Time (h)	Concentration (vol. %)	Sample (g)	Ash level (g)	Ash level (%)
1*	5*	0.5	0.0510	10.20
	10		0.0554	11.08
	20		0.0644	12.88
2	5	0.5	0.0575	11.50
	10		0.0602	12.04
	20		0.0651	13.02
3	5	0.5	0.0603	12.06
	10		0.0664	13.28
	20		0.0617	12.34
4	5	0.5	0.0642	12.84
	10		0.0718	14.36
	20		0.0756	15.12
5	5	0.5	0.0692	13.84
	10		0.0767	15.34
	20		0.0759	15.18
6	5	0.5	0.0701	14.02
	10		0.0777	15.54
	20		0.0792	15.86

In demineralization of SASP-C with HNO_3 , concentration of HNO_3 solution and demineralization time was selected as 5 % and 1 h, respectively.

In demineralization of SASP-C with HNO_3 , as concentration of acid increases, there is a slightly increase in the demineralization

degree because of the dissolution of asphaltite. In the high concentrations of acid, the degree of demineralization decreased, because of the formation of some stable components that could not be removed.

Nitric acid treatment of HCl treated asphaltite would remove those components of mineral matter, such as pyrites, which need to be oxidized prior to their solubilization (Bolat et.al.1998).

And finally, SASP-N samples were demineralized with 40% HF solutions with specified demineralization times. Results of demineralization with HF solution were shown in Table 5.1.3.5 and Table 5.1.3.6.

Table 5.1.3.5 Weight losses after demineralization of SASP-N with HF

Time (h)	Concentration (%)	Sample (g)	Weight Loss (g)	Weight Loss (%)
8*	~ 40	1	0.3980	39.80
16			0.3379	33.79
24			0.3550	35.50
32			0.2233	22.33
40			0.3431	34.31
48			0.4805	48.05

Table 5.1.3.6 Ash analysis of SASP-F

Time (h)	Concentration (%)	Sample (g)	Ash (g)	Ash (%)
8*	~ 40	0.5	0.0267	5.34
16			0.0266	5.32
24			0.0276	5.52
32			0.0287	5.74
40			0.0286	5.72
48			0.0317	6.34

In demineralization of SASP-N with HF, concentration of HF solution and demineralization time was selected as ~ 40 % and 8 h, respectively. A higher degree of demineralization was obtained with 40% HF (39.8 %). As the treating times increases, the degree of demineralization decreased because of the formation of some fluorides such as calcium fluorides (Wu and Steel, 2007).

IR analysis of asphaltite samples were shown in Figure 5.1.3.1 - Figure 5.1.3.4.

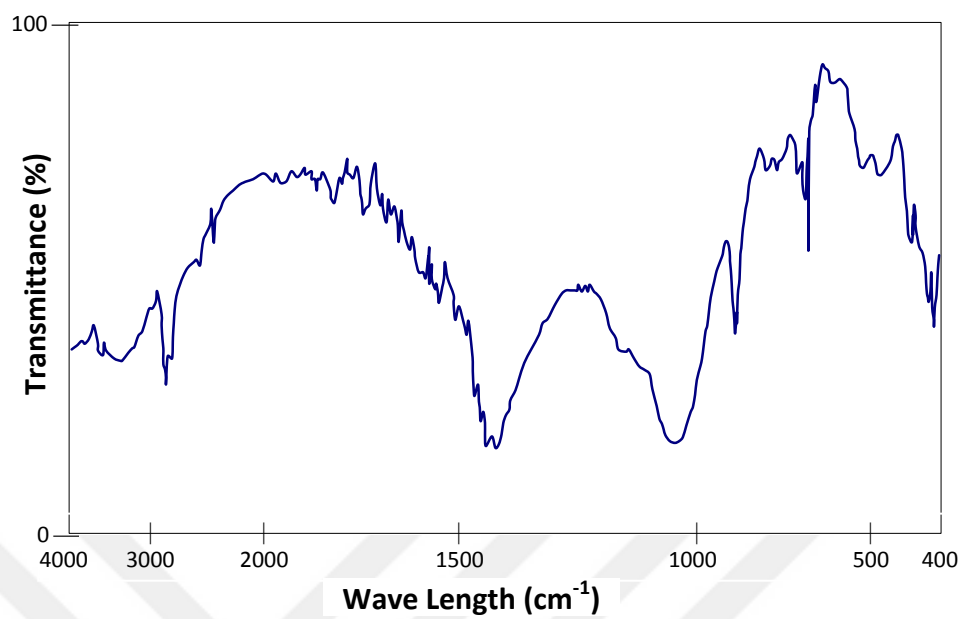


Figure 5.1.3.1 IR Spectra of SASP-R

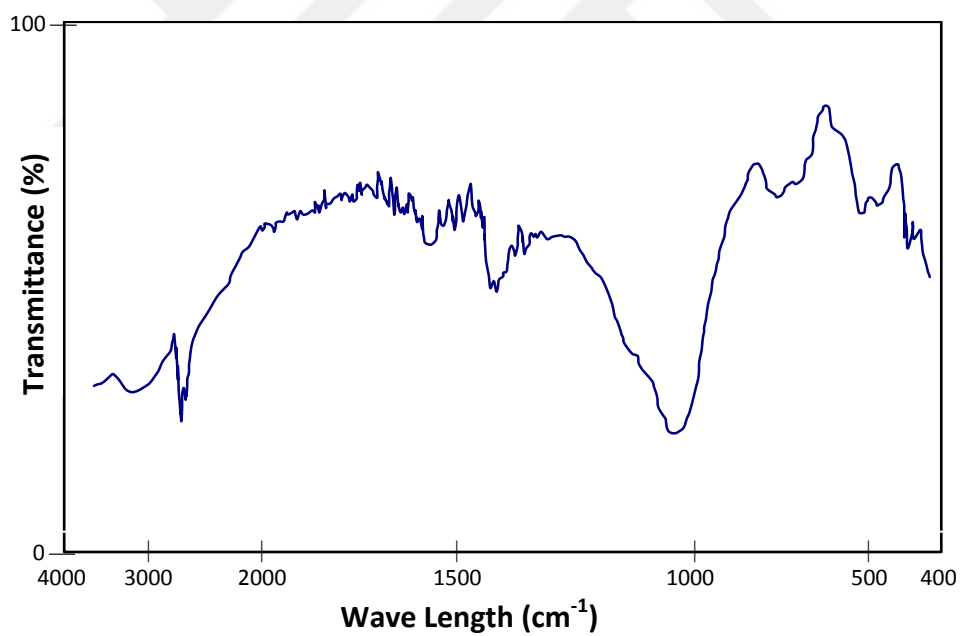


Figure 5.1.3.2 IR Spectra of SASP-C

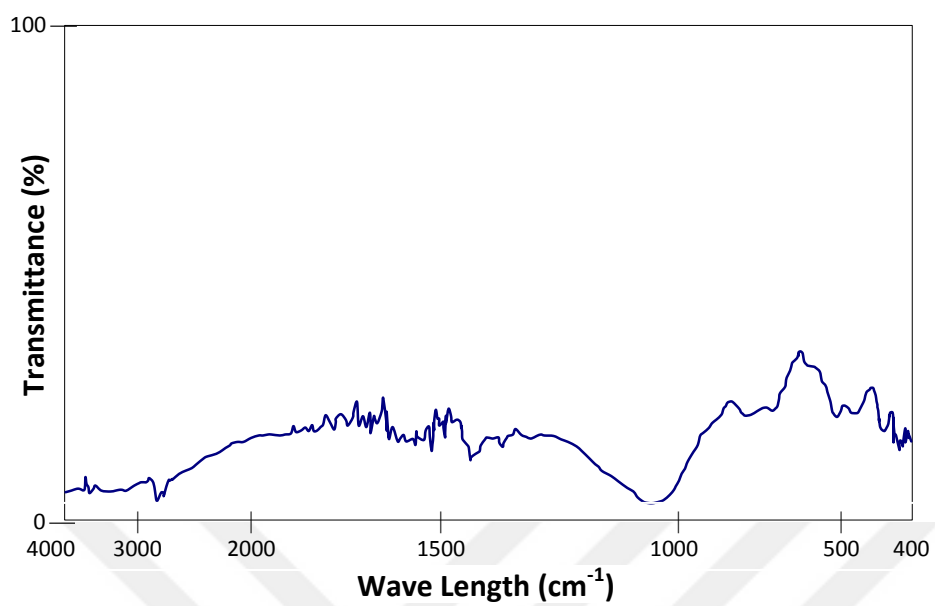


Figure 5.1.3.3 IR Spectra of SASP-N

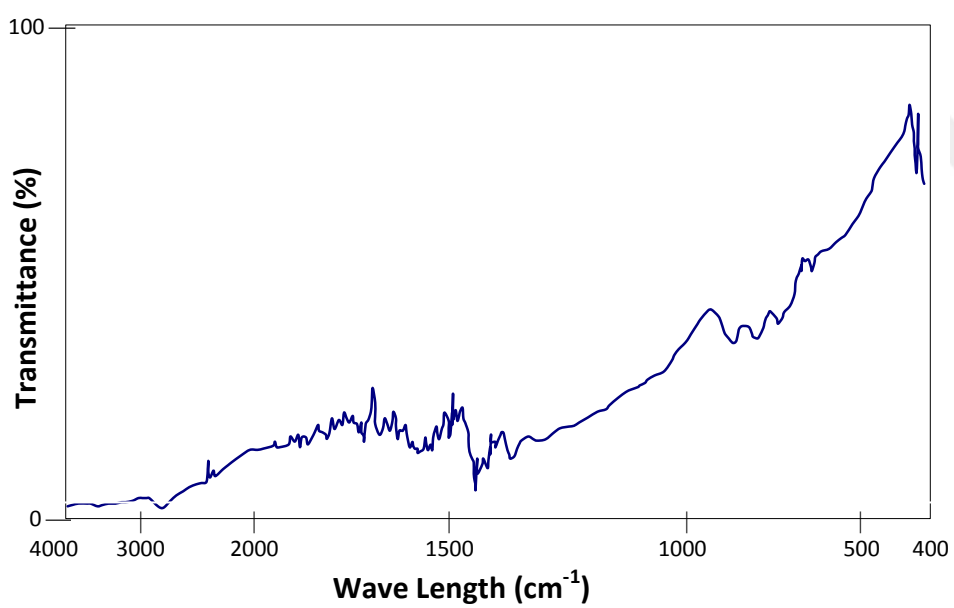


Figure 5.1.3.4 IR Spectra of SASP-F

The original asphaltite sample gives peaks between 450-600 cm^{-1} because of the mineral matter content of sample. These bands are difficult to assign precisely since they may belong to both minerals and to the (out of plane C-H bending of) aromatic structures in asphaltite.

1452 and 1626 cm^{-1} bands are aromatic C=C stretching and C=O stretching bands, respectively. Aliphatic C-H groups give absorbance at 2851 cm^{-1} . Absorbance at 2918 cm^{-1} shows the presence of CH_3 and CH_2 groups. Bands at about 3467 cm^{-1} belong to O-H stretching. Beyond 3500 cm^{-1} , it is possible to expect the existence of the clay minerals.

In demineralization of asphaltite with HF, there are structure differences between 450-600 cm^{-1} and 900-1100 cm^{-1} , because of the removal of silicates.

5.2 Isothermal Pyrolysis (IP) Studies

Isothermal Pyrolysis experiments carried out in a vertical reactor by a method as described in Section 2.2.

5.2.1 Isothermal Pyrolysis of GOS-R

Isothermal pyrolysis of GOS-R, GOS-C, GOS-N and GOS-F samples were carried out at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C.

During the pyrolysis, samples which are taken at different times were analyzed for every temperature. At the end of the experiment, area values according to C number were calculated from chromatograms.

A sample chromatogram and compounds for the isothermal pyrolysis of GOS sample was shown in Figure 5.2.1.1 and Table 5.2.1.1.

In isothermal pyrolysis experiments, nitrogen was used as swept gas at a flow rate of 80 mL/min and neopentan was used as reference gas with a flow rate of 40 mL/min and volume percentage of neopentan in nitrogen was 0.49%. The estimation of chromatograms can be done by calculation of reference gas carbon content in terms of mg-C as explained in Appendix I.

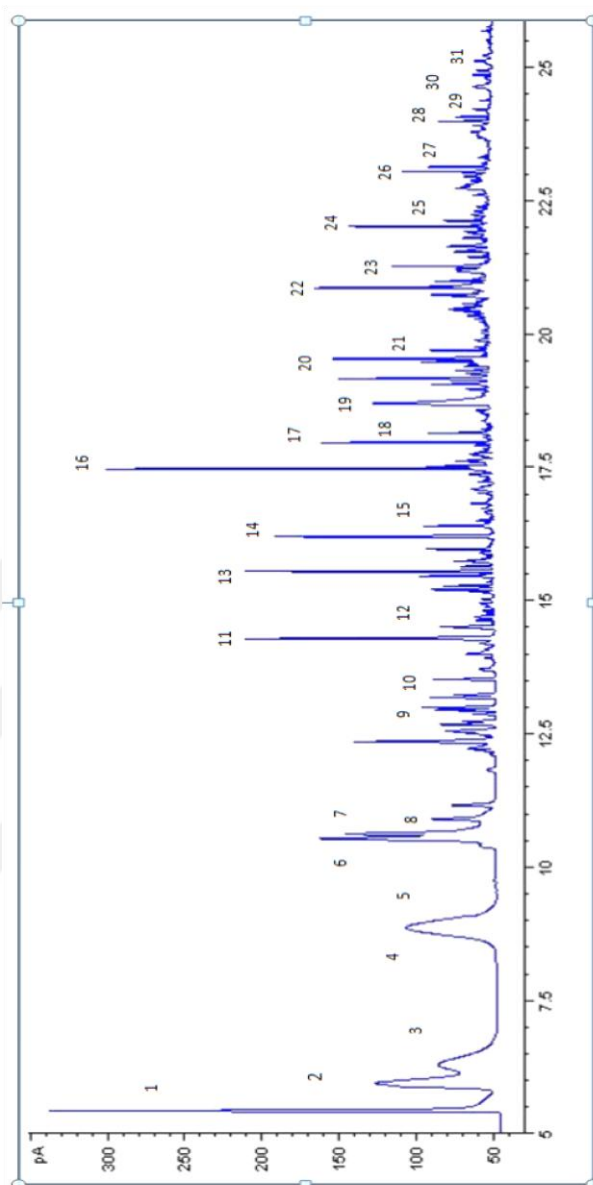


Figure 5.2.1.1 Sample chromatogram of organic products of GOS-R at 550 °C

Table 5.2.1.1 The major constituents of organic compounds at pyrolysis of GOS-R

#	Organic compounds	#	Organic compounds
1	Methane	17	1-Octene
2	Ethene	18	Octane
3	Ethane	19	Xylene
4	1-Propene	20	1-Nonene
5	Propane	21	Nonane
6	1-Butene	22	1-Decene
7	Butane	23	Decane
8	Neo-pentane (ref. gas)	24	1-Dodecene
9	1-Pentene	25	Dodecane
10	Pentane	26	1-Tridecene
11	1-Hexene	27	Tridecane
12	Hexane	28	1-Tetradecene
13	Benzene	29	Tetradecane
14	1-Heptene	30	1-Pentadecene
15	Heptane	31	Pentadecane
16	Toluene		

At the end of the isothermal pyrolysis of GOS-R, volatile product evolution rate of GOS-R was shown in Figure 5.2.1.2.

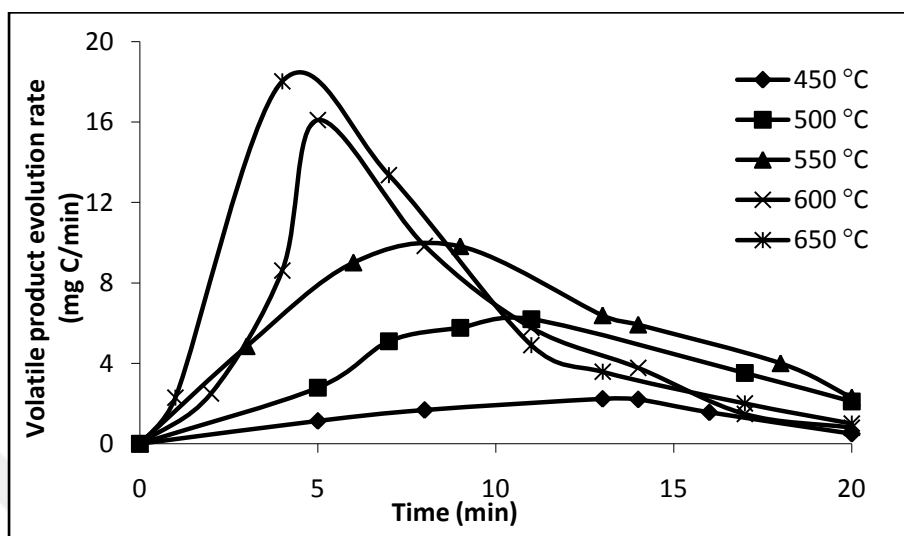


Figure 5.2.1.2 Volatile product evolution rate for IP of GOS-R

As given in Figure 5.2.1.2, as pyrolysis temperature increases, maximum rate of decomposition occurs at shorter time, then maximum points of plots shifts right to left.

For each temperature, area which is under the volatile evolution rate graph was calculated by Simpson's rule. Calculation procedure was given in Appendix II. Total amount of volatile product evolution was tabulated in Table 5.2.1.2.

Table 5.2.1.2 Amount of C in feed and C recovered as product in IP of GOS-R

T (°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	281.7	51.5	18.28
500	281.7	76.5	27.16
550	281.7	101.7	35.92
600	281.7	128.1	45.47
650	281.7	141.4	50.20

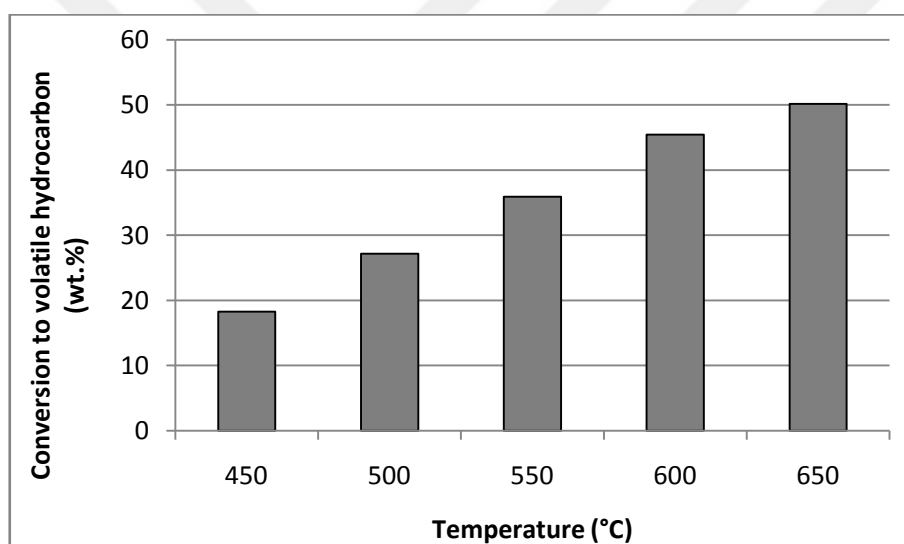


Figure 5.2.1.3 Volatile fraction of recovered hydrocarbons for IP of GOS-R (in carbon basis)

Figure 5.2.1.3 represents volatile hydrocarbon recovery at each temperature. In the isothermal pyrolysis of GOS-R, volatile

hydrocarbon recovery increased with increasing temperature. Volatile hydrocarbon recovery was calculated and found as 18.28 %, 27.16 %, 35.92 %, 45.47 % and 50.20 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.1.4. In isothermal pyrolysis, solid residue of GOS-R was found as 46.02 %, 42.33 %, 40.64 %, 39.37 % and 37.33 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

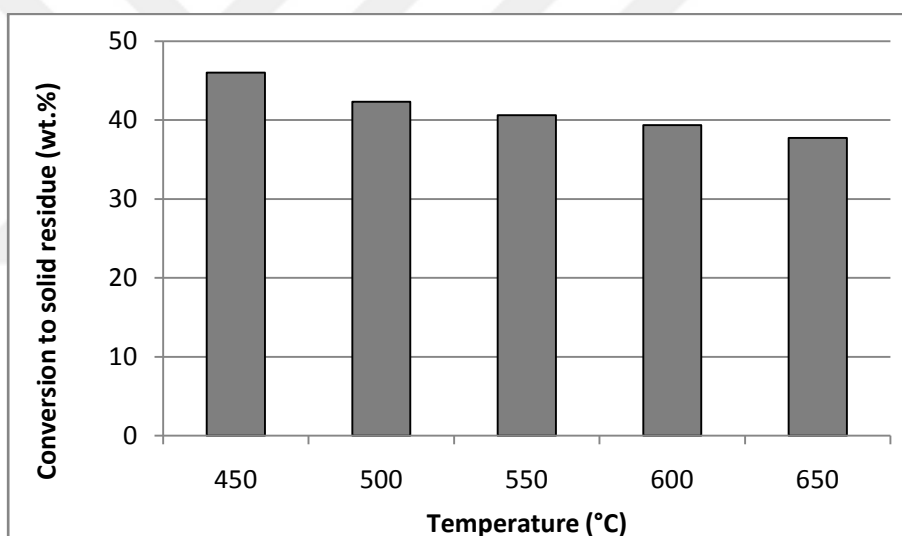


Figure 5.2.1.4 Conversion to solid residue of GOS-R for IP (in weight basis)

As shown from Figure 5.2.1.4, conversion to solid residue decreased with increasing temperature. This can be explained by the increasing trend of low molecular weight volatile hydrocarbon products. At high pyrolysis temperatures and at the same reaction times, products did not condense to higher molecular weight hydrocarbons, adversely, they decomposed to low molecular weight volatile hydrocarbons, so, volatile fraction of the recovered hydrocarbons increased.

In isothermal pyrolysis of GOS-R, total hydrocarbon recoveries were calculated as 53.98 %, 57.67 %, 59.36 %, 60.63 % and 62.67 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries at each pyrolysis temperature were calculated by subtracting coke conversion values from 100 %. Total hydrocarbon recoveries in isothermal pyrolysis of GOS-R were shown in Figure 5.2.1.5.

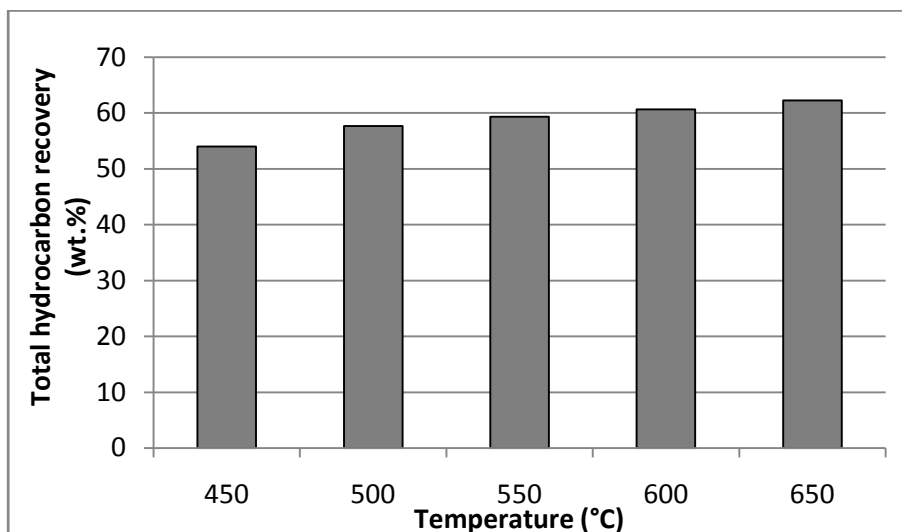


Figure 5.2.1.5 Total hydrocarbon recovery of IP of GOS-R (in weight basis)

It can easily be seen that volatile fraction of recovered hydrocarbons was lower than total hydrocarbon recovery at all pyrolysis temperatures. This denotes that the products of isothermal pyrolysis of GOS-R at all pyrolysis temperatures mainly consist of polyaromatics and high molecular weight hydrocarbons. The increase in conversion of volatile fraction of recovered hydrocarbons with increasing temperature indicates that molecular weight of hydrocarbons shows a decreasing trend with increasing temperature. The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery were found as 0.34, 0.47, 0.61, 0.75 and

0.81 at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. These values were tabulated at Table 5.2.1.3.

Table 5.2.1.3 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in isothermal pyrolysis of GOS-R

Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.34	0.47	0.61	0.75	0.81

After isothermal pyrolysis of GOS-R, amount of C in solid residue was identified by TOC analyzer and results were shown in Table 5.2.1.4.

Table 5.2.1.4 Carbon content in solid residue of GOS-R (in carbon basis)

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	281.7	230.1	48.51	111.62	39.62	42.09
500	281.7	211.6	47.04	99.56	35.34	37.50
550	281.7	203.2	46.71	94.91	33.69	30.38
600	281.7	196.8	45.08	88.74	31.50	23.02
650	281.7	188.7	42.54	80.23	28.48	21.32

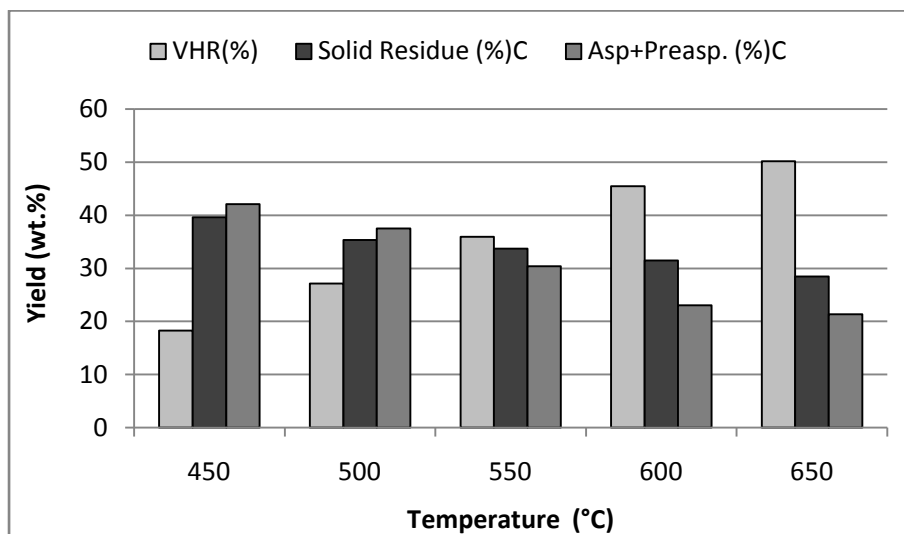


Figure 5.2.1.6 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of GOS-R (in carbon basis)

Figure 5.2.1.6 shows, in contrast to solid residue, gas yield increases, as temperature increases. The yield of C in solid residue decreased because of volatilization.

Volatile fraction of recovered hydrocarbons analyzed by gas chromatographic technique, were classified according to carbon number. For this purpose the products were classified as; gases, C_1 - C_4 or C_2 - C_4 and liquids, C_5 - C_9 , C_{10} - C_{15} and C_{16+} .

To calculate the cumulative values of n-paraffins and 1-olefins, peak areas of linear paraffins and olefins were calculated from chromatograms. Then, product evolution rates of n-paraffins and

1-olefins were calculated by using Eq. (5.2.1.1). Product evolution rates along time were obtained at each temperature for n-paraffins and 1-olefins. The area under the curves were calculated, and divided to total amount of product, cumulative graphs of n-paraffins and 1-olefins were shown in Figure 5.2.1.7 and Figure 5.2.1.8.

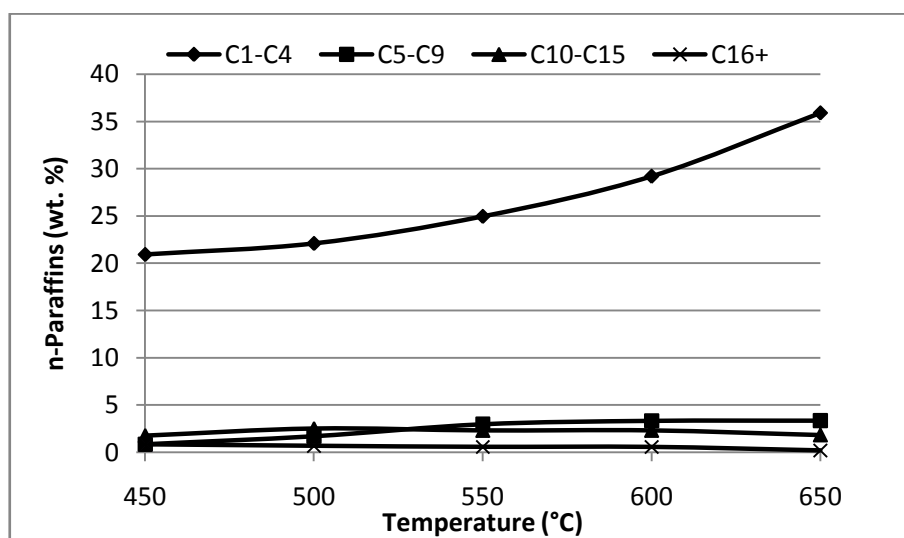


Figure 5.2.1.7 Cumulative n-paraffin selectivity for IP of GOS-R

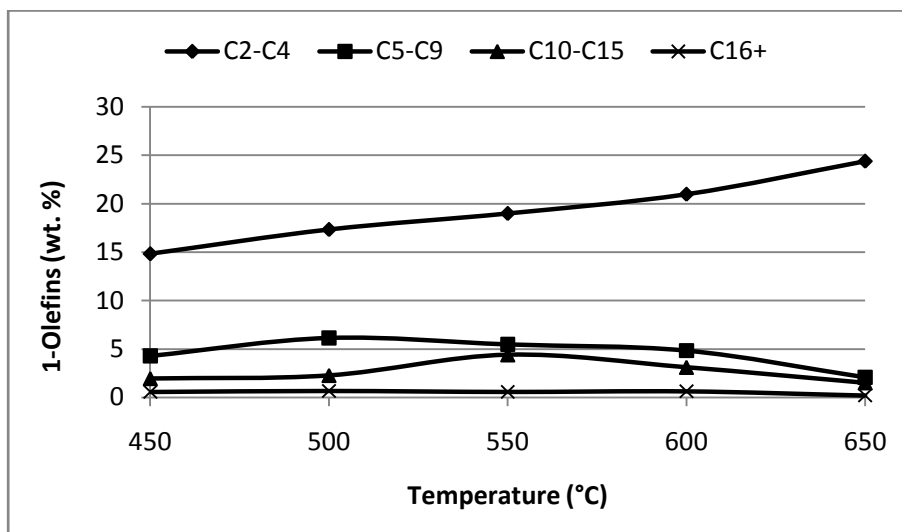


Figure 5.2.1.8 Cumulative 1-olefin selectivity for IP of GOS-R

These values help to determine the exact product characteristics obtained at the end of each pyrolysis run. To be able to comment on the product characteristics, cumulative fractions of the groups formed at the end of each run should be considered because just by looking to the selectivities of these groups at each time; it is almost impossible to determine a trend. These values are not in agreement with each other due to uncontrolled thermal cracking mechanisms.

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Also, it can be seen that *n*-paraffin and 1-olefin gaseous products constitute the highest portion of the pyrolysis products. Cumulative C₁-C₄ and C₂-C₄ selectivities increased as temperature increased, particularly above 550 °C, there are

considerable increase in these groups because of the cracking of C_{5+} hydrocarbons at high temperatures. At the same graphs, there is a sharp decrease in C_5-C_9 groups because of the decomposition of liquid products at high temperatures.



5.2.2 Isothermal Pyrolysis of GOS-C

Up to this point, thermal decomposition of raw oil shale was investigated, to investigate the effect of mineral matter on the thermal decomposition, isothermal pyrolysis of HCl-treated oil shale samples were carried out at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650°C.

Volatile product evolution rates were obtained as described above and Figure 5.2.2.1 represents the product evolution rates of isothermal pyrolysis of GOS-C at different temperatures.

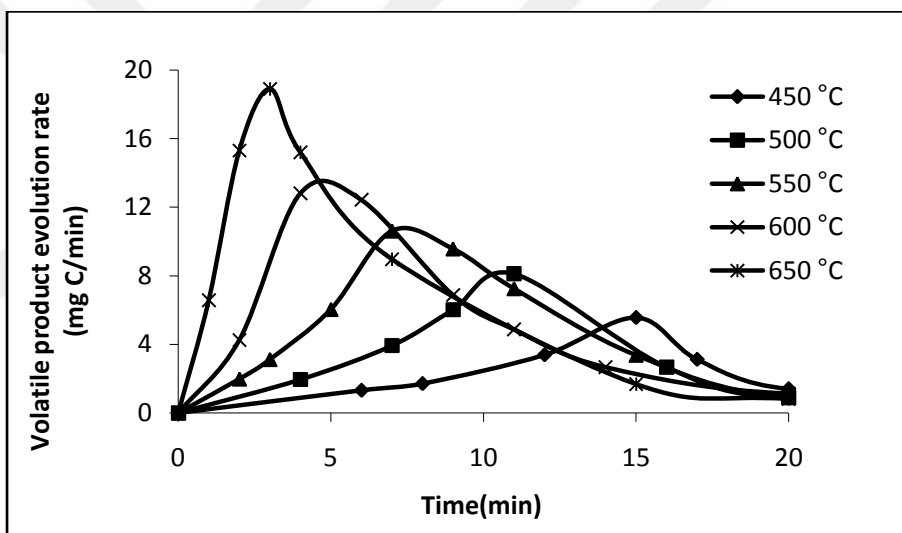


Figure 5.2.2.1 Volatile product evolution rate for isothermal pyrolysis of GOS-C

As shown from Figure 5.2.2.1, as pyrolysis temperature increases, maximum rate of decomposition occurs at shorter time, then maximum points of plots shifts right to left.

The total amount of volatile product evolution for isothermal pyrolysis of GOS-C was tabulated in Table 5.2.2.1.

Table 5.2.2.1 Amount of C in feed and C recovered as product in IP of GOS-C

T (°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	300	44.9	14.97
500	300	67.2	22.40
550	300	98.1	32.70
600	300	111.2	37.07
650	300	125.6	41.87

Volatile hydrocarbon recovery was found as 14.97 %, 22.40 %, 32.70 %, 37.07 % and 41.87 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Figure 5.2.2.2 represents volatile hydrocarbon recovery at each temperature.

In isothermal pyrolysis, solid residue of GOS-C was found as 43.94 %, 41.40 %, 39.88 %, 37.94 % and 33.98 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.2.3.

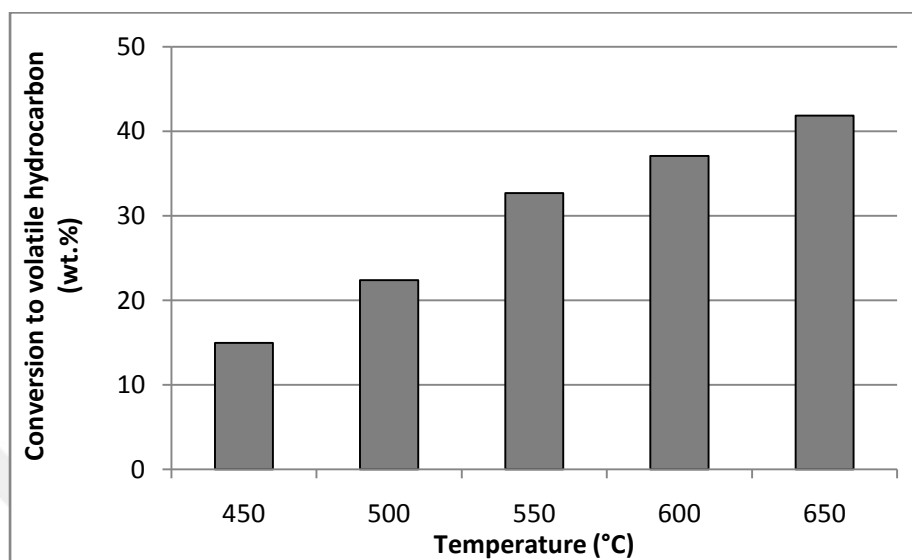


Figure 5.2.2.2 Volatile fraction of recovered hydrocarbons for IP of GOS-C (in carbon basis)

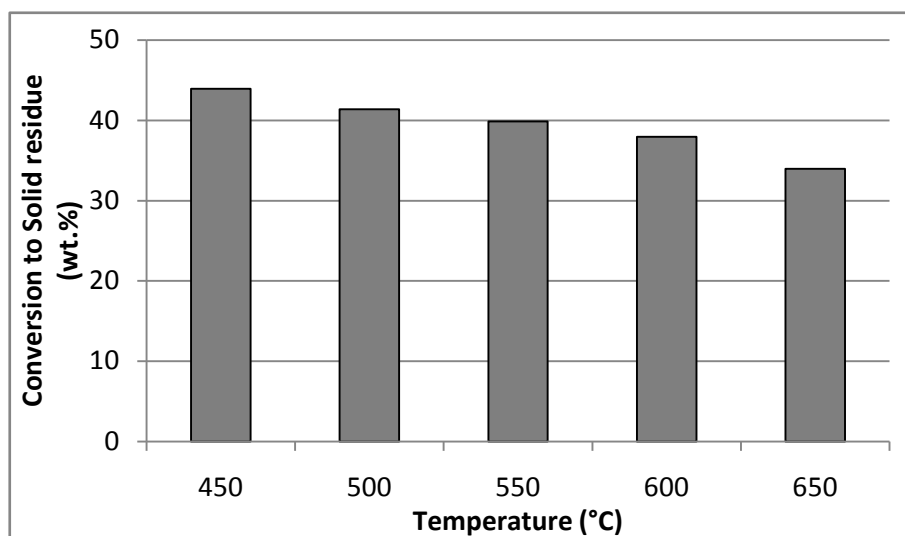


Figure 5.2.2.3 Conversion to solid residue of GOS-C for isothermal pyrolysis (in weight basis)

In isothermal pyrolysis of GOS-C, conversion to solid residue decreased from 43.94 wt% to 33.98 wt %, as temperature increases from 450 °C to 650 °C.

In isothermal pyrolysis of GOS-C, total hydrocarbon recoveries were calculated as 56.06 %, 58.60 %, 60.12 %, 62.06 % and 66.02 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries at each pyrolysis temperature were calculated by subtracting coke conversion values from 100 %. Total hydrocarbon recoveries in isothermal pyrolysis of GOS-C were shown in Figure 5.2.2.4.

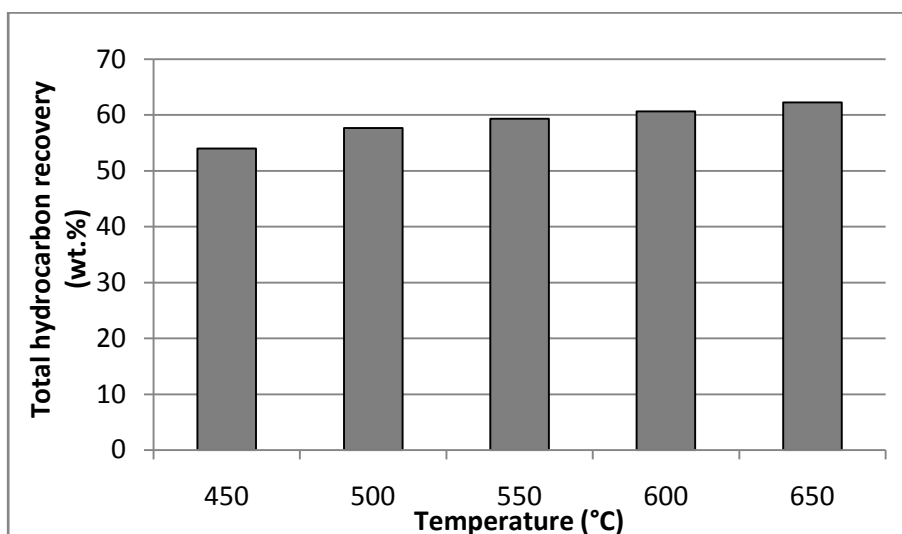


Figure 5.2.2.4 Total hydrocarbon recovery of isothermal pyrolysis of GOS-C (in weight basis)

The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery were found as 0.27, 0.38, 0.54, 0.60 and 0.63 of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. These values were tabulated at Table 5.2.2.2.

Table 5.2.2.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in isothermal pyrolysis of GOS-C

Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.27	0.38	0.54	0.60	0.63

After isothermal pyrolysis of GOS-C, amount of C in solid residue was identified by TOC analyzer and results were shown in Table 5.2.2.3.

Table 5.2.2.3 Carbon content in solid residue of GOS-C

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	300.0	219.7	50.02	109.89	36.63	48.40
500	300.0	207.0	48.60	100.60	33.53	44.07
550	300.0	199.4	47.37	94.46	31.49	35.81
600	300.0	189.7	46.19	87.62	29.21	33.73
650	300.0	169.9	45.52	77.34	25.78	32.35

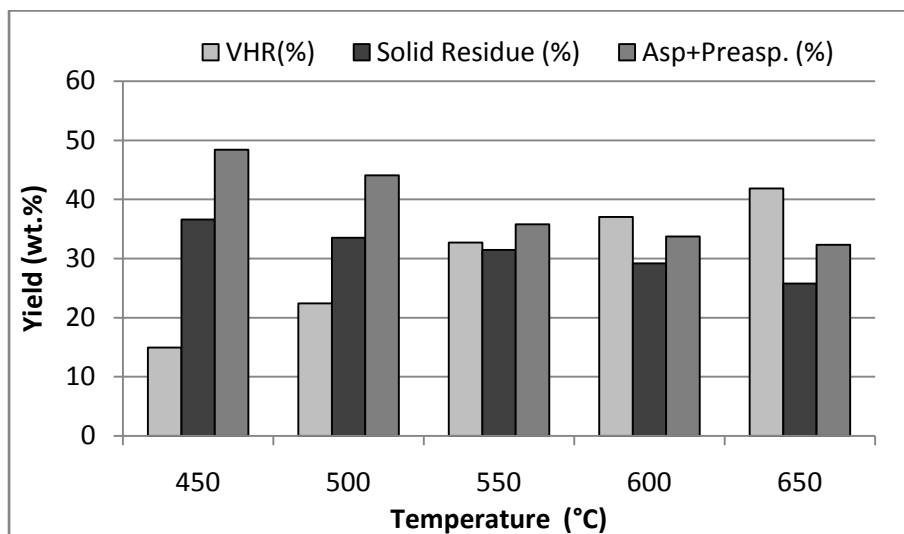


Figure 5.2.2.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of GOS-C (in carbon basis)

Figure 5.2.2.5 shows gas yield is directly proportional to temperature. Solid residue and Asphaltene & Preasphaltane yield decreased with increasing temperature.

At the end of the isothermal pyrolysis of GOS-C, cumulative graphs of n-paraffins and 1-olefins were obtained and shown in Figure 5.2.2.6 and Figure 5.2.2.7.

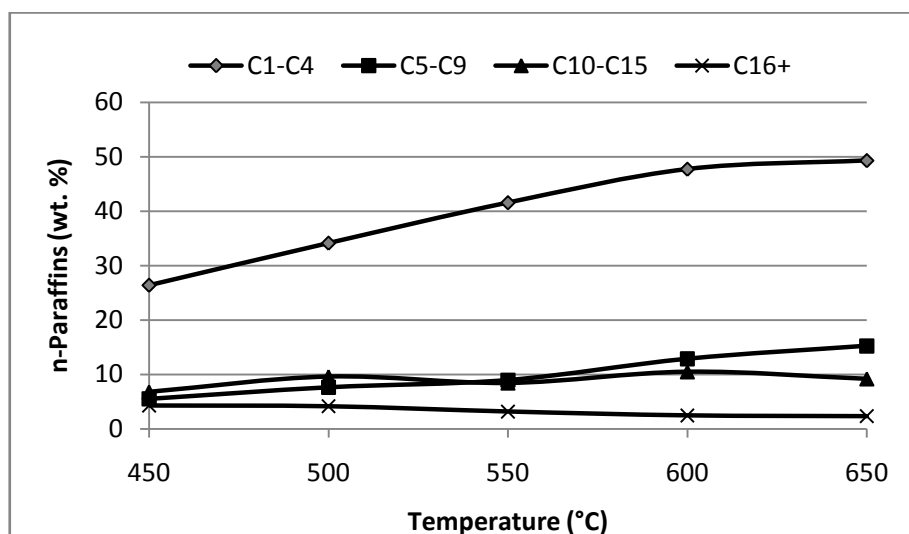


Figure 5.2.2.6 Cumulative n-paraffin selectivity for IP of GOS-C

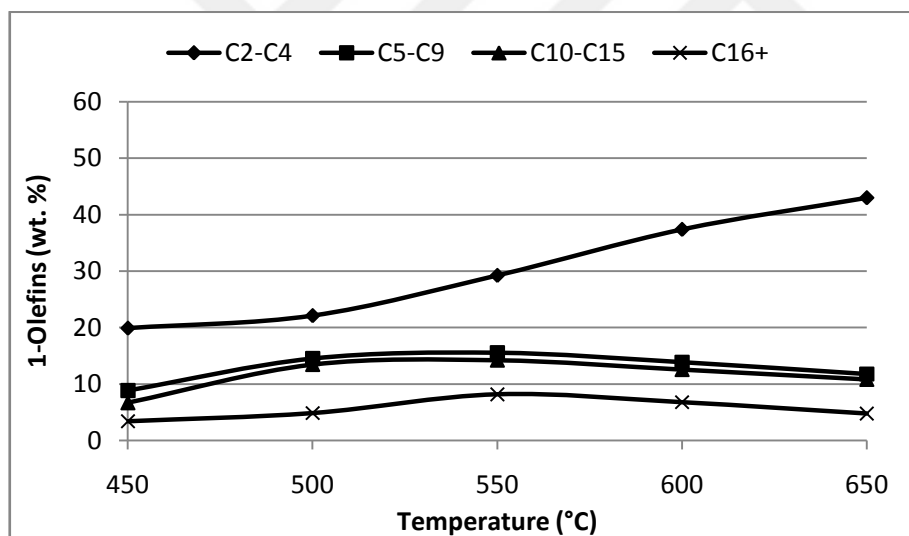


Figure 5.2.2.7 Cumulative 1-olefin selectivity for IP of GOS-C

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Also, it can be seen that *n*-paraffin and 1-olefin gaseous products constitute the highest portion of the pyrolysis products. Cumulative C₁-C₄ and C₂-C₄ selectivities increased as temperature increased, particularly above 550 °C; there are considerable increases in these groups because of the cracking of C₅+ hydrocarbons at high temperatures.



5.2.3 Isothermal Pyrolysis of GOS-N

Isothermal pyrolysis of GOS-N were carried out at temperatures of 450, 500, 550, 600 and 650 °C, by using HCl-HNO₃ treated oil shale samples.

Volatile product evolution rates depending on time at different temperatures were shown in Figure 5.2.3.1.

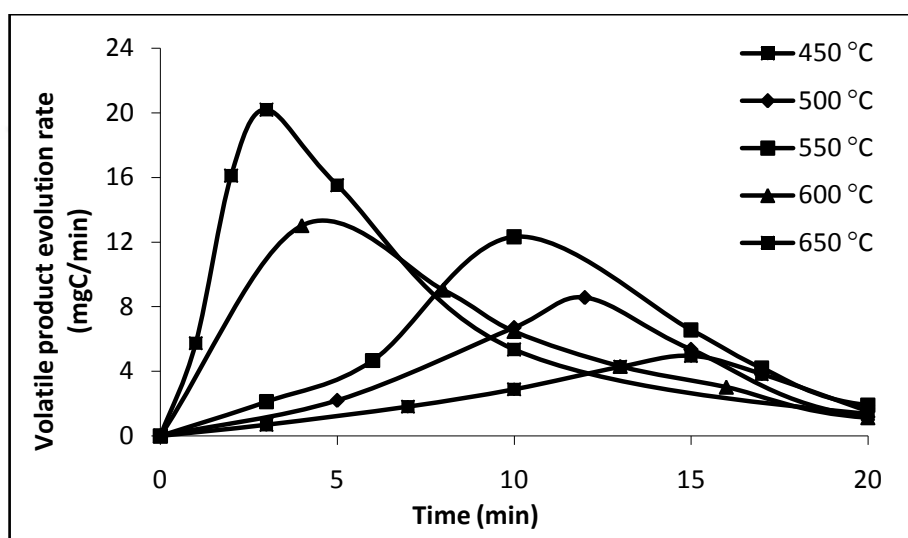


Figure 5.2.3.1 Volatile product evolution rate for isothermal pyrolysis of GOS-N

As stated earlier, when pyrolysis temperature increases, maximum rate of decomposition occurs at shorter time, then maximum points of plots shifts right to left.

The total amount of volatile product evolution for isothermal pyrolysis of GOS-N was tabulated in Table 5.2.3.1.

Table 5.2.3.1 Amount of C in feed and C recovered as product in IP of GOS-N

T (°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	299.3	47.1	15.73
500	299.3	77.3	25.82
550	299.3	114.7	38.32
600	299.3	128.5	43.93
650	299.3	143.1	47.80

Volatile hydrocarbon recovery was found as 15.73 %, 25.82 %, 38.32 %, 43.93 % and 47.80 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Figure 5.2.3.2 represents volatile hydrocarbon recovery at each temperature.

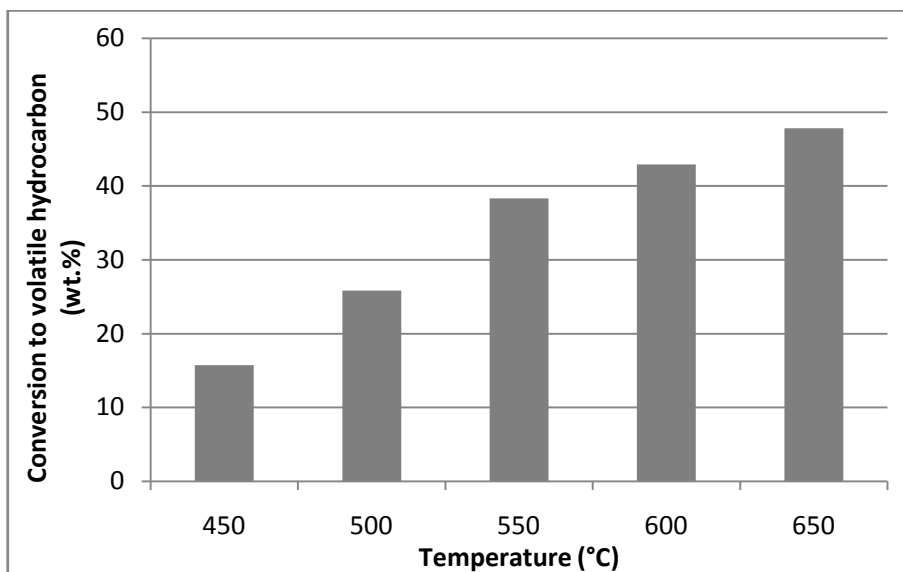


Figure 5.2.3.2 Volatile fraction of recovered hydrocarbon for IP of GOS-N (in carbon basis)

In isothermal pyrolysis, solid residue of GOS-N was found as 38.95 %, 37.40 %, 35.84 %, 34.13 % and 31.47 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.3.3. Total hydrocarbon recoveries were also calculated as 61.05 %, 62.60 %, 64.16 %, 65.87 % and 68.53 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. THR values were given in Figure 5.2.3.4.

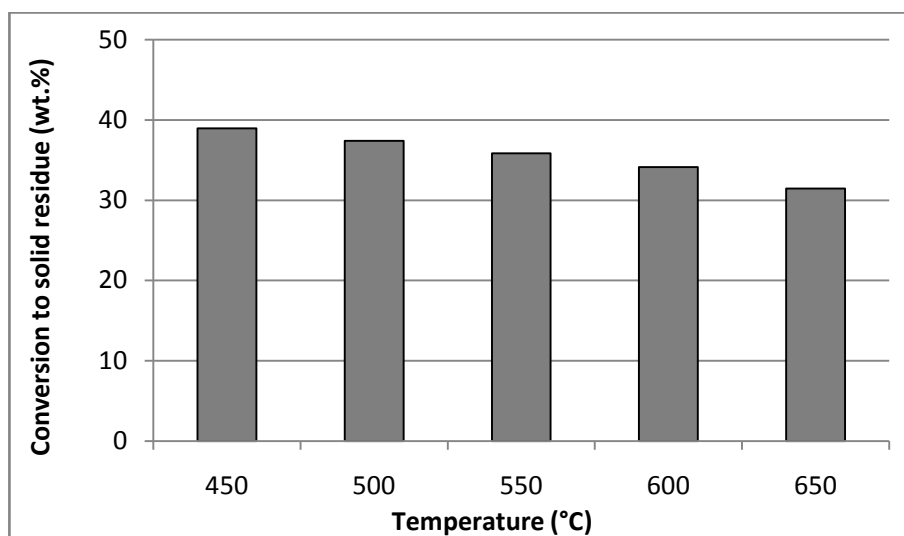


Figure 5.2.3.3 Conversion to solid residue of GOS-N for isothermal pyrolysis (in weight basis)

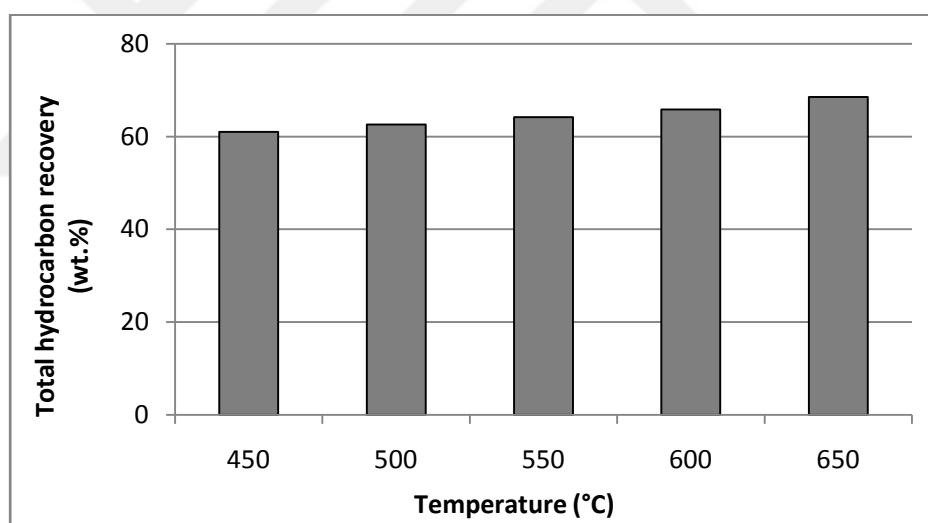


Figure 5.2.3.4 Total hydrocarbon recovery of isothermal pyrolysis of GOS-N (in weight basis)

The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery were found as 0.26, 0.41, 0.60, 0.65 and 0.70 of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. These values were tabulated at Table 5.2.3.2.

Table 5.2.3.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in isothermal pyrolysis of GOS-N

Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.26	0.41	0.60	0.65	0.70

After isothermal pyrolysis of GOS-N, amount of C in solid residue was identified by TOC analyzer and results were shown in Figure 5.2.3.5. The carbon content of GOS-N was given in Table 5.2.3.3.

Table 5.2.3.3 Carbon content in solid residue of GOS-N

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	299.3	194.7	57.20	111.40	37.21	47.05
500	299.3	187.0	52.99	99.09	33.10	41.08
550	299.3	179.2	48.12	86.23	28.81	32.88
600	299.3	170.7	46.11	78.69	26.29	30.79
650	299.3	157.4	45.52	71.63	23.93	28.27

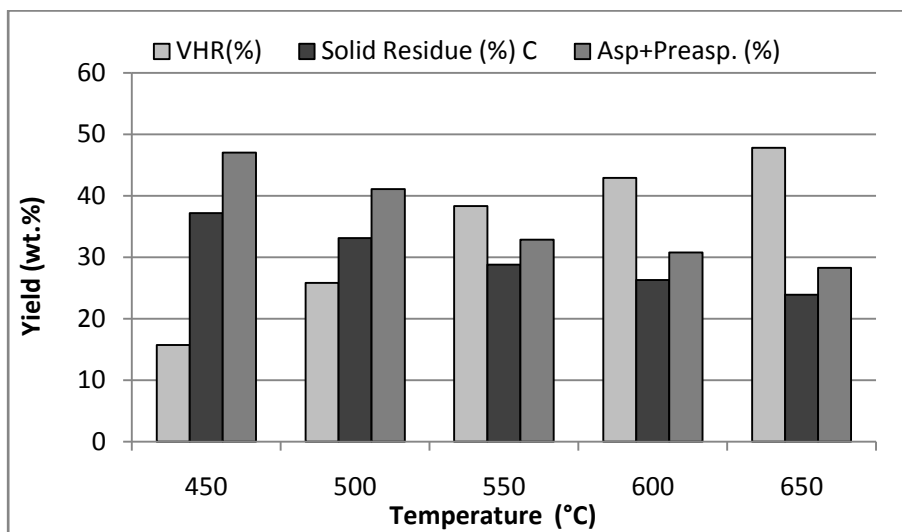


Figure 5.2.3.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of GOS-N (in carbon basis)

Figure 5.2.3.5 shows gas and solid residue yield, as temperature increases, Asphaltene & preasphaltene yield decreases and yield of C in solid residue decreased because of volatilization.

At the end of the isothermal pyrolysis of GOS-N, cumulative graphs of n-paraffins and 1-olefins were obtained and shown in Figure 5.2.3.6 and Figure 5.2.3.7, respectively

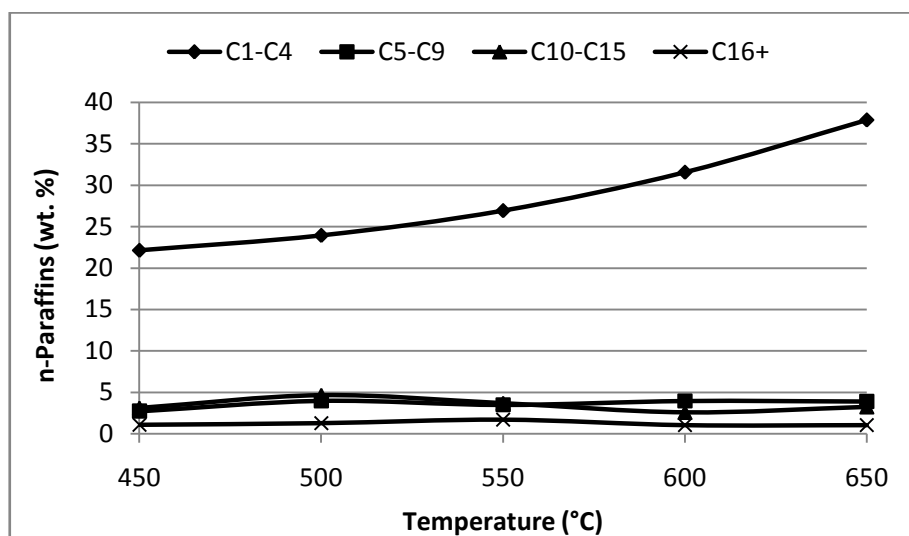


Figure 5.2.3.6 Cumulative n-paraffin selectivity for IP of GOS-N

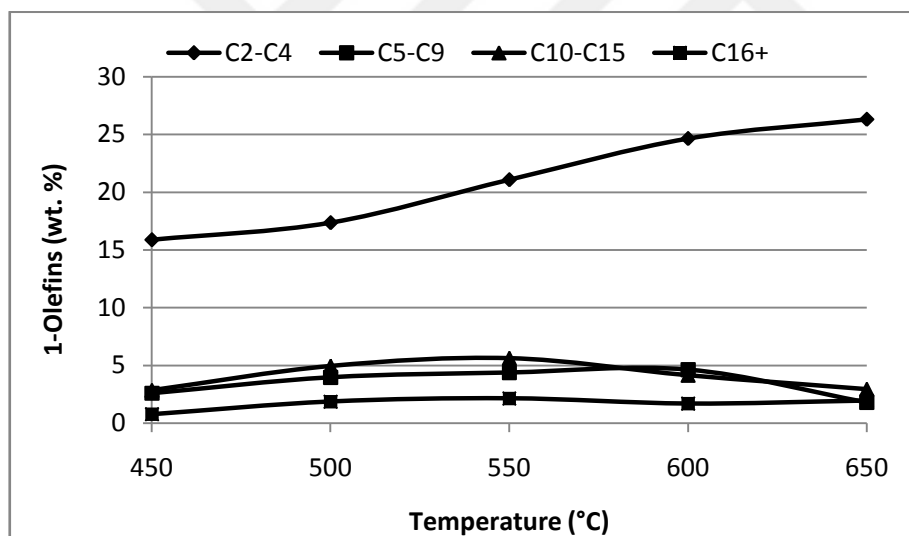


Figure 5.2.3.7 Cumulative 1-olefin selectivity for IP of GOS-N

Cumulative n-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Cumulative C_1-C_4 and C_2-C_4 selectivities increased as temperature increased, particularly above 550 °C, there are considerable increase in these groups because of the cracking of C_{5+} hydrocarbons at high temperatures.



5.2.4 Isothermal Pyrolysis of GOS-F

Isothermal pyrolysis of GOS-F were carried out at temperatures of 450, 500, 550, 600 and 650°C, by using HCl-HNO₃-HF treated oil shale samples.

Volatile product evolution rates depending on time at different temperatures were shown in Figure 5.2.4.1.

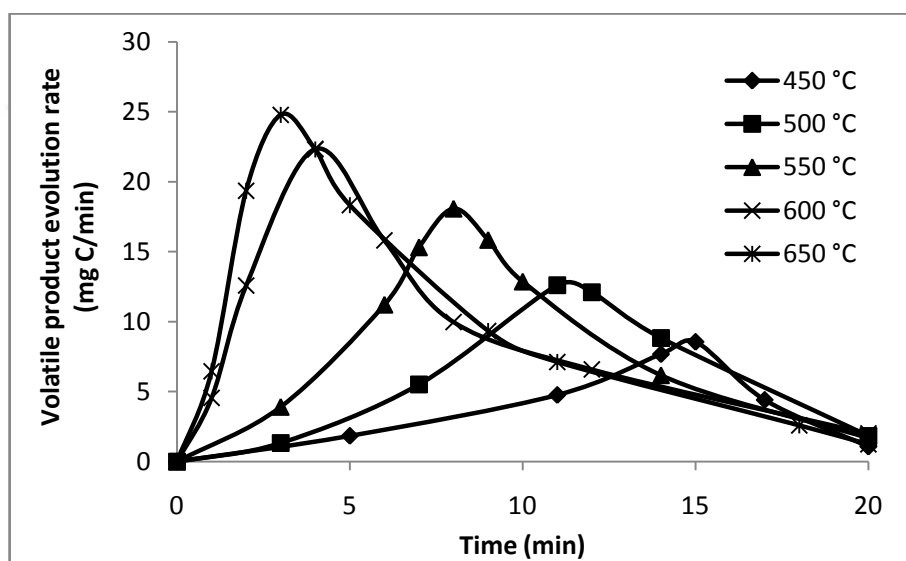


Figure 5.2.4.1 Volatile product evolution rate for isothermal pyrolysis of GOS-F

The total amount of volatile product evolution for isothermal pyrolysis of GOS-F was tabulated in Table 5.2.4.1.

Table 5.2.4.1 Amount of C in feed and C recovered as product in IP of GOS-F

T (°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	337.9	68.2	20.18
500	337.9	113.9	33.70
550	337.9	145.6	43.08
600	337.9	176.2	52.14
650	337.9	186.1	55.07

Volatile hydrocarbon recovery was found as 20.18 %, 33.70 %, 43.08 %, 52.14 % and 55.07 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Figure 5.2.4.2 represents volatile hydrocarbon recovery at each temperature.

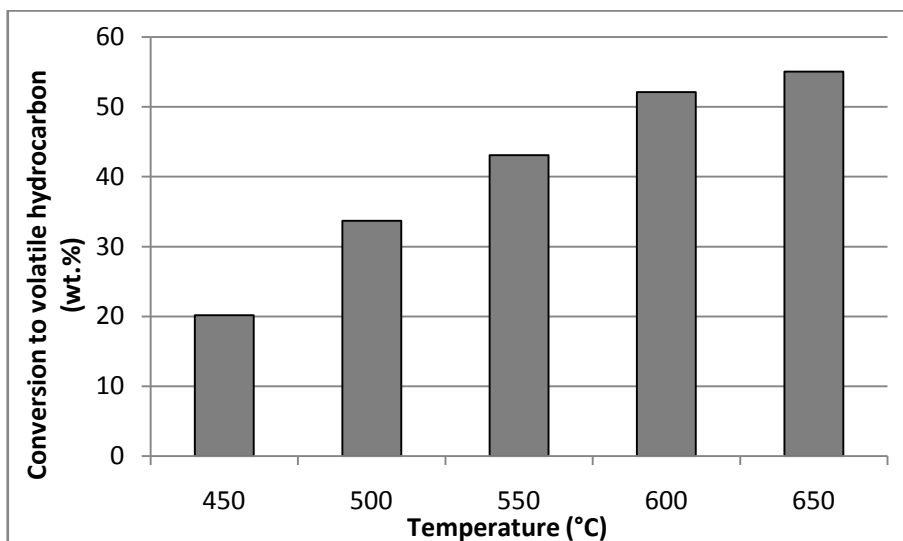


Figure 5.2.4.2 Volatile fraction of recovered hydrocarbons for IP of GOS-F (in carbon basis)

In isothermal pyrolysis, solid residue of GOS-F was found as 36.08 %, 34.12 %, 31.26 %, 30.40 % and 27.96 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.4.3.

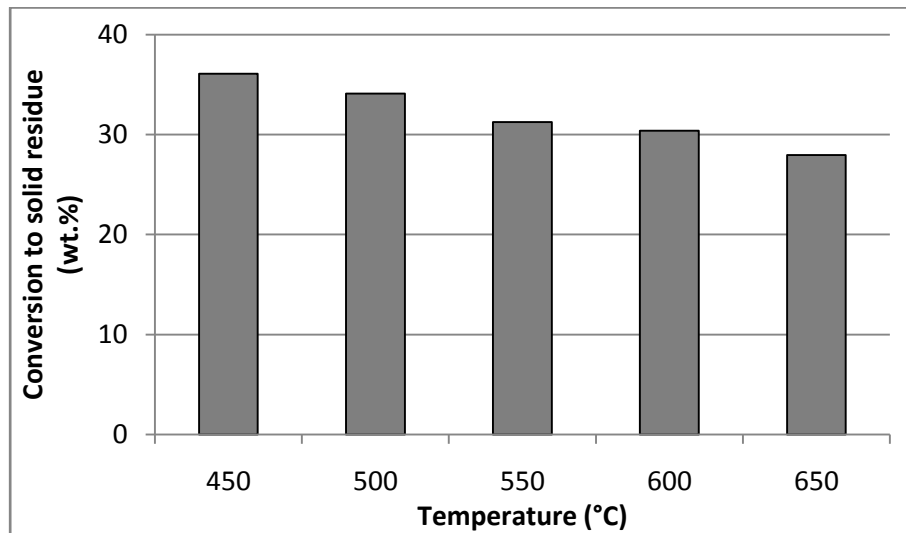


Figure 5.2.4.3 Conversion to solid residue of GOS-F for isothermal pyrolysis (in weight basis)

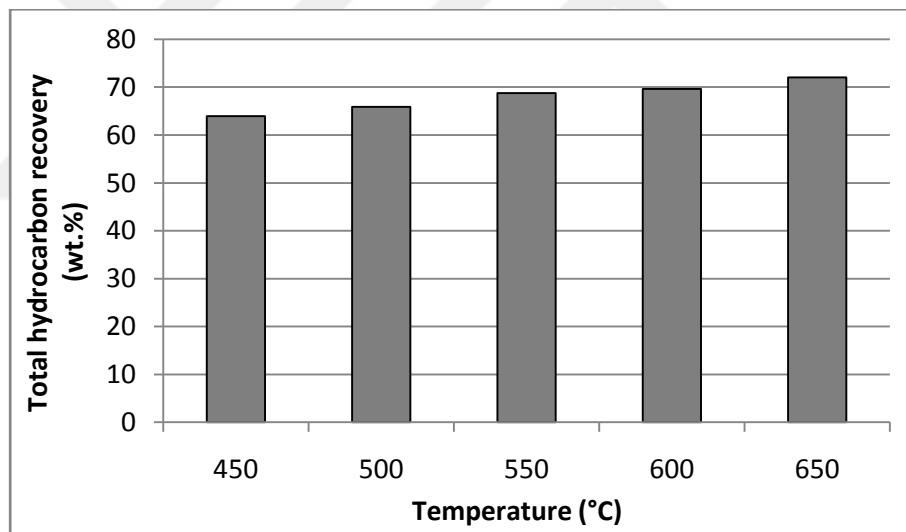


Figure 5.2.4.4 Total hydrocarbon recovery of isothermal pyrolysis of GOS-F (in weight basis)

In isothermal pyrolysis of GOS-F, total hydrocarbon recoveries were calculated as 63.92, 65.88, 68.74, 69.60 and 72.04 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries in isothermal pyrolysis of GOS-F were shown in Figure 5.2.4.4.

The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery were found as 0.32, 0.51, 0.63, 0.75 and 0.76 of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. These values were tabulated at Table 5.2.4.2.

Table 5.2.4.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in isothermal pyrolysis of GOS-F

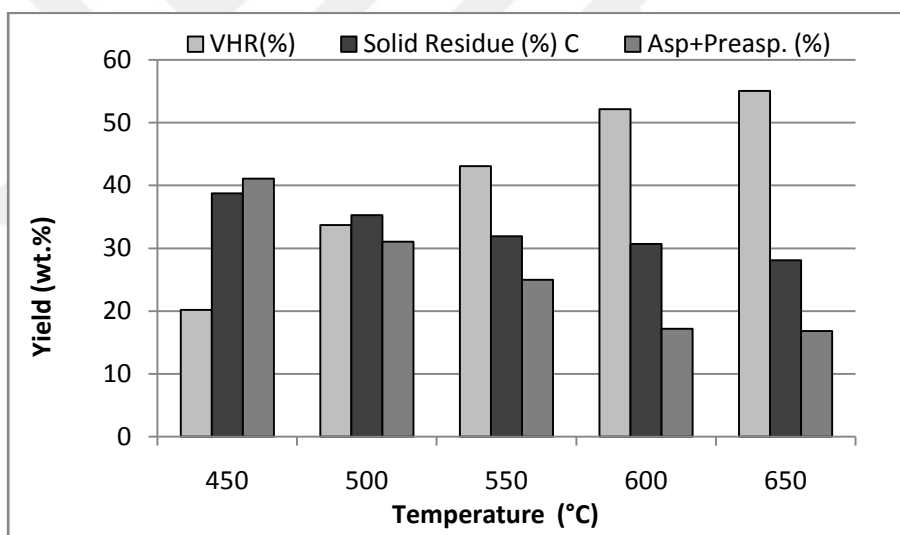
Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.32	0.51	0.63	0.75	0.76

After isothermal pyrolysis of GOS-C, amount of C in solid residue was identified by TOC analyzer and results were shown in Table 5.2.4.3.

Figure 5.2.4.5 shows gas and solid residue yield, as temperature increases, Asphaltene & preasphaltene yield increases and yield of C in solid residue decreased because of volatilization

Table 5.2.4.3 Carbon content in solid residue of GOS-F

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	337.9	180.4	72.60	130.98	38.76	41.06
500	337.9	170.6	69.86	119.18	35.27	31.03
550	337.9	156.3	69.02	107.88	31.92	25.00
600	337.9	152.0	68.27	103.77	30.71	17.16
650	337.9	139.8	67.94	94.98	28.10	16.83

**Figure 5.2.4.5** Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of GOS-F

At the end of the isothermal pyrolysis of GOS-F, cumulative graphs of n-paraffins and 1-olefins were obtained and shown in Figure 5.2.4.6 and Figure 5.2.4.7.

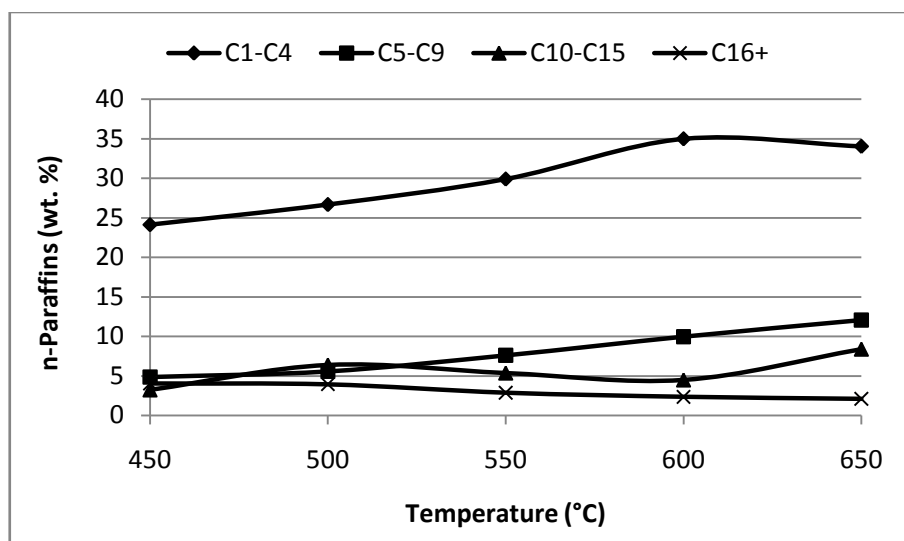


Figure 5.2.4.6 Cumulative n-paraffin selectivity for IP of GOS-F

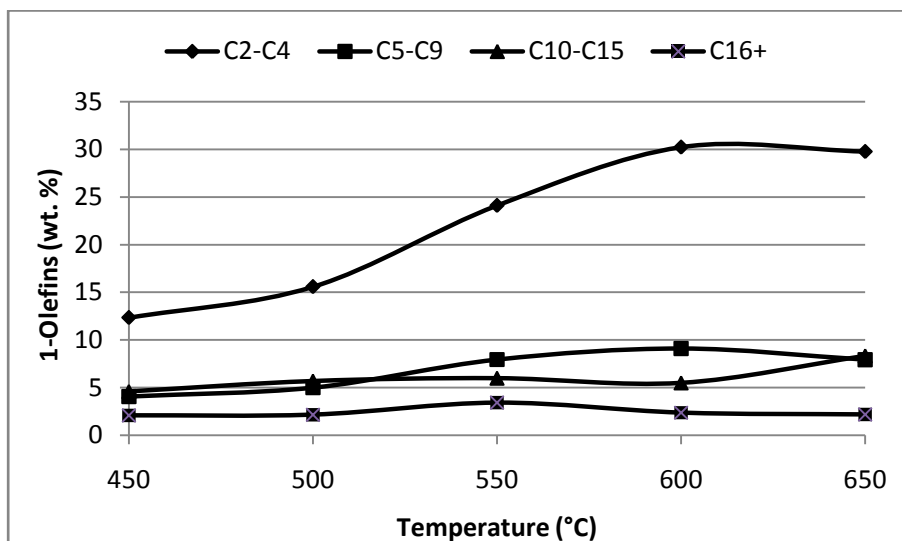


Figure 5.2.4.7 Cumulative 1-olefin selectivity for IP of GOS-F

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Also, it can be seen that *n*-paraffin and 1-olefin gaseous products constitute the highest portion of the pyrolysis products. Cumulative C₁-C₄ and C₂-C₄ selectivities increased as temperature increased, particularly above 550 °C, there are considerable increase in these groups because of the cracking of C₅₊ hydrocarbons at high temperatures. Due to the polymerization reactions between gas products, *n*-paraffin and 1-olefin selectivity decreased after 600 °C. As seen in Figures above, the yield of liquid and heavy fractions increased

In order to compare isothermal pyrolysis of raw and demineralized oil shale samples, the total amount of volatile product of these samples depending on temperature were shown in Figure 5.2.4.8.

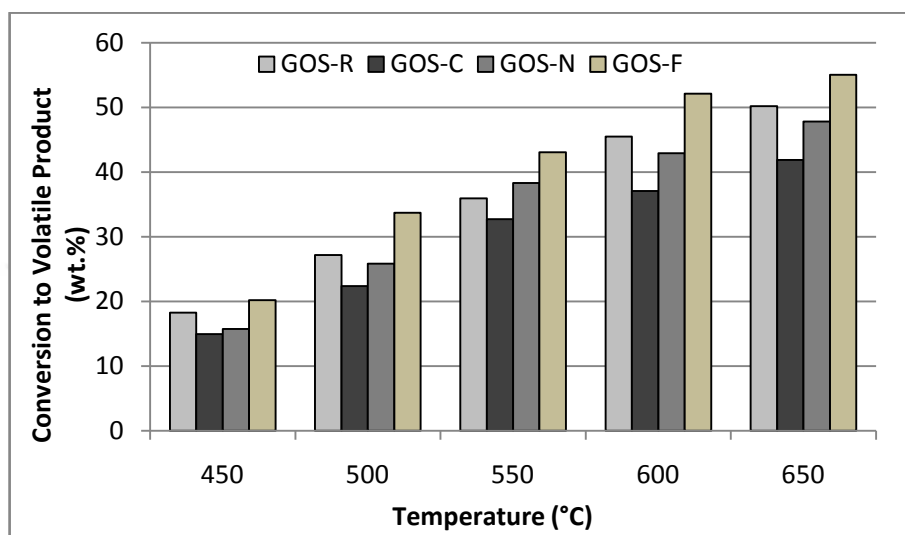


Figure 5.2.4.8 Volatile hydrocarbon recoveries for raw and demineralized oil shale samples

Yield of volatile hydrocarbons increased after leaching of kerogen with HCl, HNO₃ and HF. At high temperatures, yield of volatile hydrocarbons decreased because of oxidation of nitric acid in the leaching with HNO₃.

The yield of total volatile hydrocarbons increased for the kerogen sample after silicate removal (GOS-F). This tendency was explained due mainly to both the driving force for heat transfer since

more heat was transferred from outside towards the inside of the oil shale particles, thus pyrolysis reaction might have occurred with ease and diffusion limitation might have decreased due to the lack of mineral matrix (Ballice, 2005). Removal of pyrites with HNO_3 did not affect the reactivity of the organic material in pyrolysis.

The inhibition effect of the silicates seemed to be greater than the catalytic effect of the calcite minerals in the pyrolysis reactions. The removal of the silicates by HF washing of GOS caused a change in the production of the volatiles. The recovery of hydrocarbon yield increased in pyrolysis of GOS-F whereas the deposition of carbon in solid residue decreased.

Pyrolysis reactions of silicate-free oil shale (GOS-F) did not show the catalytic effect of the silicate minerals aiding the coking reactions and deposition of carbon in solid residue. For that reasons, the discrepancy assigned to asphaltenic, preasphaltenic hydrocarbons for GOS-N was found to be higher than those for GOS-R, GOS-C and GOS-F.

5.2.5 Isothermal Pyrolysis of ELIG-R

Isothermal pyrolysis of ELIG-R was carried out at temperatures of 450, 500, 550, 600 and 650°C.

At the end of the isothermal pyrolysis of ELIG-R, volatile product evolution rate of ELIG-R was shown in Figure 5.2.5.1.

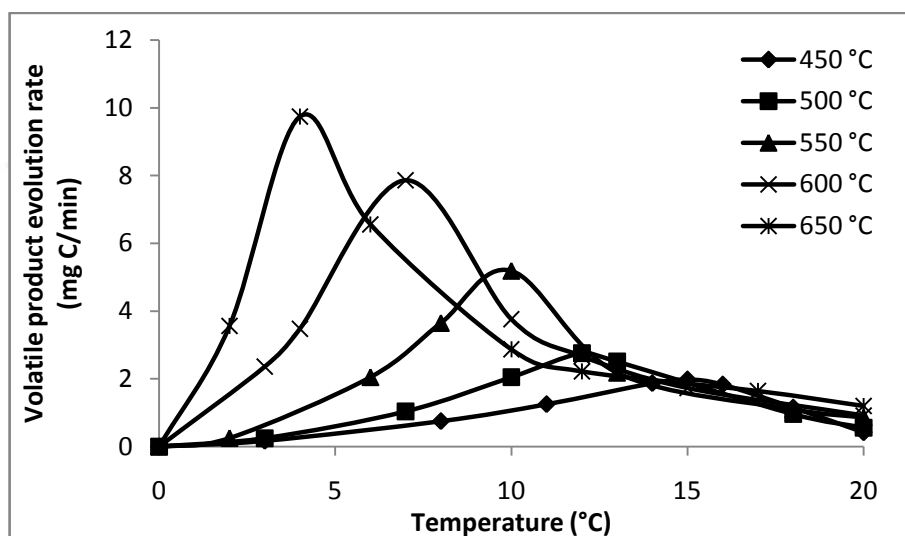


Figure 5.2.5.1 Volatile product evolution rate for isothermal pyrolysis of ELIG-R

As shown from Figure 5.2.5.1, as pyrolysis temperature increases, maximum rate of decomposition occurs at shorter time, then maximum points of plots shifts right to left.

For each temperature, area which is under the volatile evolution rate graph, was calculated and total amount of volatile product evolution was tabulated in Table 5.2.5.1.

Table 5.2.5.1 Amount of C in feed and C recovered as product in IP of ELIG-R

T(°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	328.0	18.39	5.61
500	328.0	24.88	7.59
550	328.0	40.07	12.22
600	328.0	60.49	18.44
650	328.0	69.44	21.17

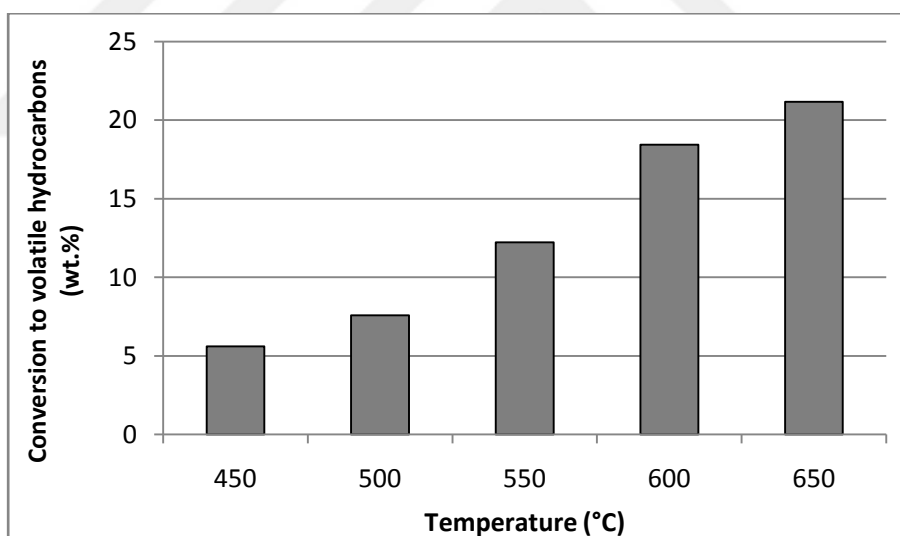


Figure 5.2.5.2 Volatile fraction recovered hydrocarbons for IP of ELIG-R (in carbon basis)

In the isothermal pyrolysis of ELIG-R, volatile hydrocarbon recovery increased with increasing temperature. Volatile hydrocarbon recovery was analyzed by our analytical technique and found as 5.61 %, 7.59 %, 12.22 %, 18.44 % and 21.17 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Figure 5.2.5.2 represents volatile hydrocarbon recovery at each temperature.

In isothermal pyrolysis, solid residue of ELIG-R was found as 67.28 %, 65.36 %, 64.14 %, 62.26 % and 58.00 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.5.3.

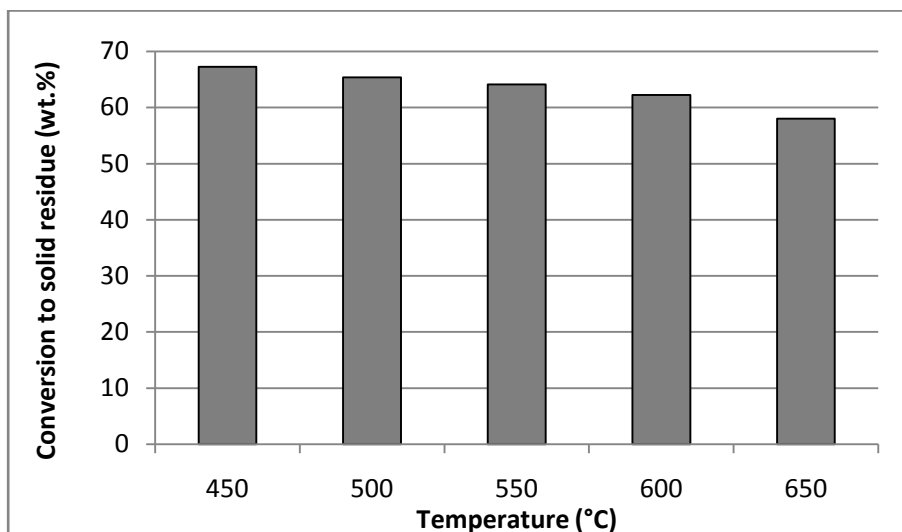


Figure 5.2.5.3 Conversion to solid residue of ELIG-R for IP (in weight basis)

As shown from Figure 5.2.5.3, conversion to solid residue decreased with increasing temperature because of increasing of low molecular weight volatile hydrocarbons. In isothermal pyrolysis of ELIG-R, total hydrocarbon recoveries were calculated as 32.72 %, 34.64 %, 35.86 %, 37.74 % and 42.00 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries at each pyrolysis temperature were calculated by subtracting coke conversion values from 100 %. Total hydrocarbon recoveries in isothermal pyrolysis of ELIG-R were shown in Figure 5.2.5.4.

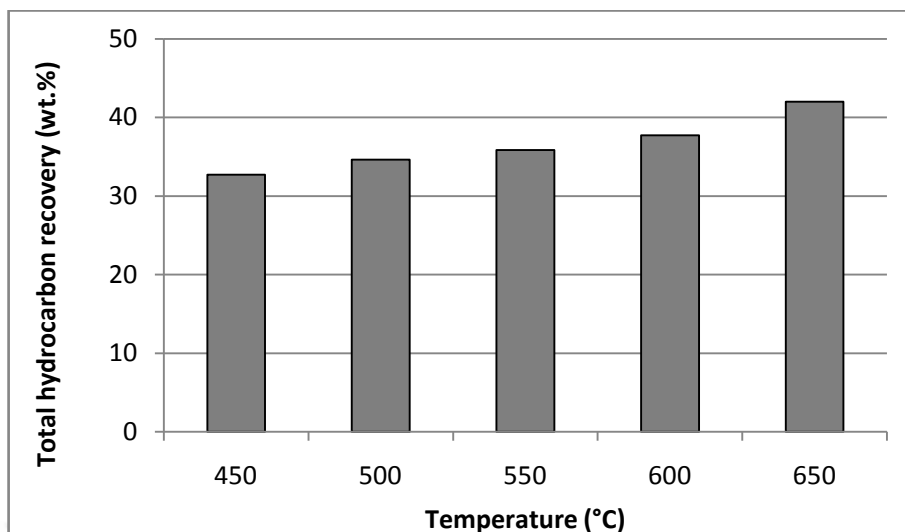


Figure 5.2.5.4 Total hydrocarbon recovery of isothermal pyrolysis of ELIG-R (in weight basis)

The increase in conversion of volatile fraction of recovered hydrocarbons with increasing temperature indicates that molecular weight of hydrocarbons shows a decreasing trend with increasing temperature. The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery were found as 0.17, 0.22, 0.34, 0.49 and 0.50 at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. These values were tabulated at Table 5.2.5.2.

Table 5.2.5.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in isothermal pyrolysis of LIG-R

Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.17	0.22	0.34	0.49	0.50

After isothermal pyrolysis of ELIG-R, amount of C in solid residue was identified by TOC analyzer and results were shown in Table 5.2.5.3.

Table 5.2.5.3 Carbon content in solid residue of ELIG-R

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	328.0	336.4	57.19	192.39	58.65	35.74
500	328.0	326.8	58.67	191.73	58.46	33.96
550	328.0	320.7	59.68	191.39	58.35	29.43
600	328.0	311.3	61.12	190.27	58.01	23.55
650	328.0	290.0	65.03	188.59	57.50	21.33

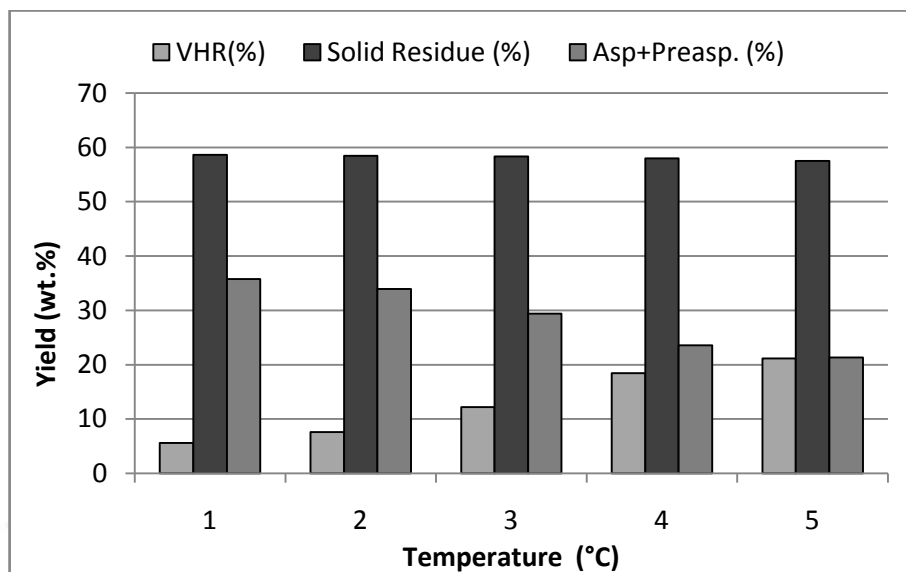


Figure 5.2.5.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of ELIG-R

Figure 5.2.5.5 shows gas, solid residue and Asp+Preasphaletene yield. As temperature increases, in contrast to the yield of gas product, the yield of C in solid residue decreased because of volatilization. Since thermal bond scissions increase with the pyrolysis temperature, the increase in yield of gas product at higher temperatures is expected. Acidic groups liberate from the lignite structure around 300 °C. Cleavage of long chain aliphatic and etheric bridges occurring at 300–350 °C might increase pyrolysis conversion. The cleavage of aryl–alkyl ether and Ethylene Bridge begins at 400 °C. Breaking of anhydrite groups and aryl–aryl etheric and methylene bridges increases at

temperatures around 500 °C and therefore conversion to volatile organic matter was the highest at 650 °C.

Volatile fraction of recovered hydrocarbons analyzed by gas chromatographic technique, were classified according to carbon number. For this purpose the products were classified as; gases, C₁-C₄ or C₂-C₄ and liquids, C₅-C₉, C₁₀-C₁₅ and C₁₆+

Cumulative n-paraffin and 1-olefin selectivity for ELIG-R samples were calculated and shown in Figure 5.2.5.6 and Figure 5.2.5.7.

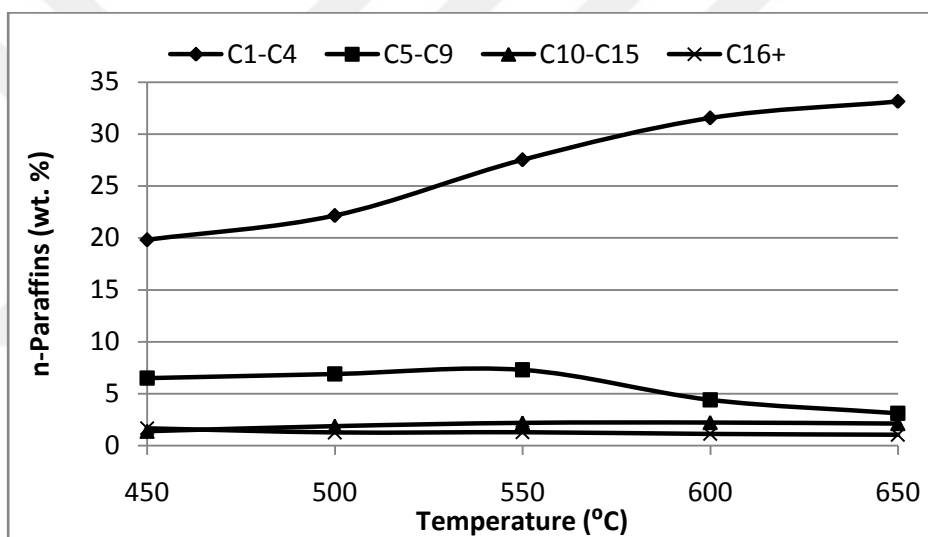


Figure 5.2.5.6 Cumulative n-paraffin selectivity for IP of ELIG-R

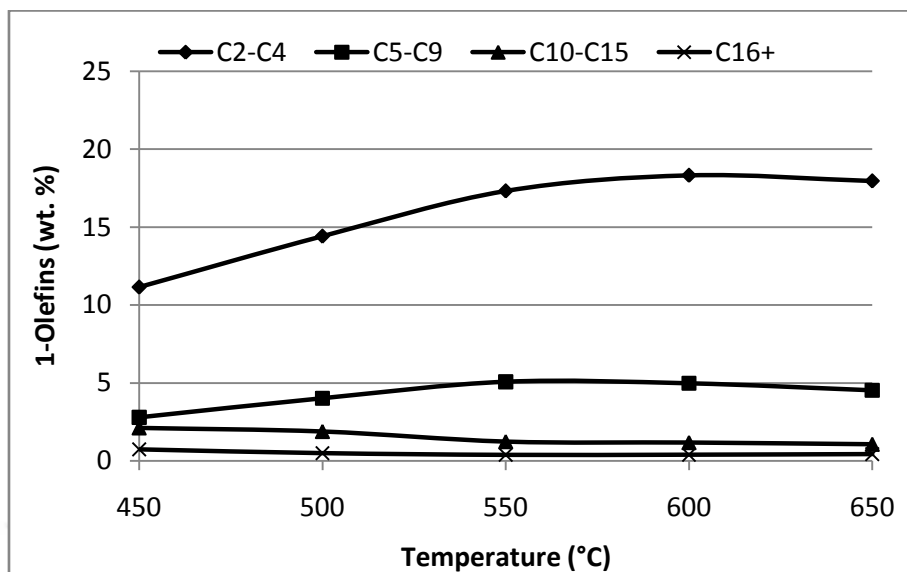


Figure 5.2.5.7 Cumulative 1-olefin selectivity for IP of ELIG-R

Cumulative n-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Also, it can be seen that n-paraffin and 1-olefin gaseous products constitute the highest portion of the pyrolysis products. Cumulative C_1 - C_4 and C_2 - C_4 selectivity increased as temperature increased, because of the cracking of C_{5+} hydrocarbons at high temperatures.

5.2.6 Isothermal Pyrolysis of ELIG-C

The mineral matter present in the lignite structure and inorganic compounds changes the behavior of lignite in gasification and pyrolysis processes. Particularly it has been shown that clays, which exist in lignite, affect the lignite gasification and catalyze hydrogen transfer to lignite. Pyrite is a strong catalyst in lignite liquefaction. Although quartz is inert chemically, it behaves as a diluting reactant in hydrol liquefaction. The mineral matter, which exists in the coal structure, has an active effect in pyrolysis reactions. CaO and CaCO₃ are active in cracking oxygen functional groups in coal. A large portion of oxygen in coal exists in acidic functional groups such as phenol or carboxylic acids. The strongly basic CaO might react with these groups. CaCO₃, which decomposed to CaO during pyrolysis might strongly influence the pyrolytic behavior of coal.

Up to this point, thermal decomposition of raw lignite was investigated, to investigate the effect of mineral matter on the thermal decomposition, isothermal pyrolysis of HCl-treated lignite samples were carried out at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C.

Volatile product evolution rates were obtained as described above and Figure 5.2.6.1 represents the product evolution rates of isothermal pyrolysis of ELIG-C at different temperatures.

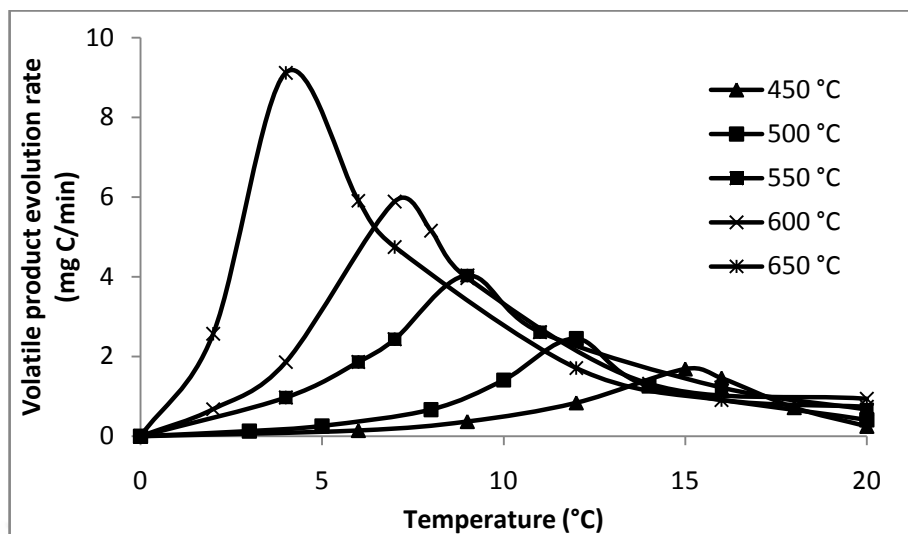


Figure 5.2.6.1 Volatile product evolution rate for isothermal pyrolysis of ELIG-C

As given from Figure 5.2.6.1, as pyrolysis temperature increases, maximum rate of decomposition occurs at shorter time, then maximum points of plots shifts right to left.

The total amount of volatile product evolution for isothermal pyrolysis of ELIG-C was tabulated in Table 5.2.6.1.

Table 5.2.6.1 Amount of C in feed and C recovered as product in IP of LIG-C

T (°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	340.5	11.78	3.46
500	340.5	15.68	4.60
550	340.5	31.59	9.28
600	340.5	42.15	12.38
650	340.5	58.59	17.21

Volatile hydrocarbon recovery was found as 3.46 %, 4.60 %, 9.28 %, 12.38 % and 17.21 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Figure 5.2.6.2 represents volatile hydrocarbon recovery at each temperature.

In isothermal pyrolysis, solid residue of ELIG-C was found as 66.22 %, 64.88 %, 62.14 %, 61.22 and 55.40 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.6.3.

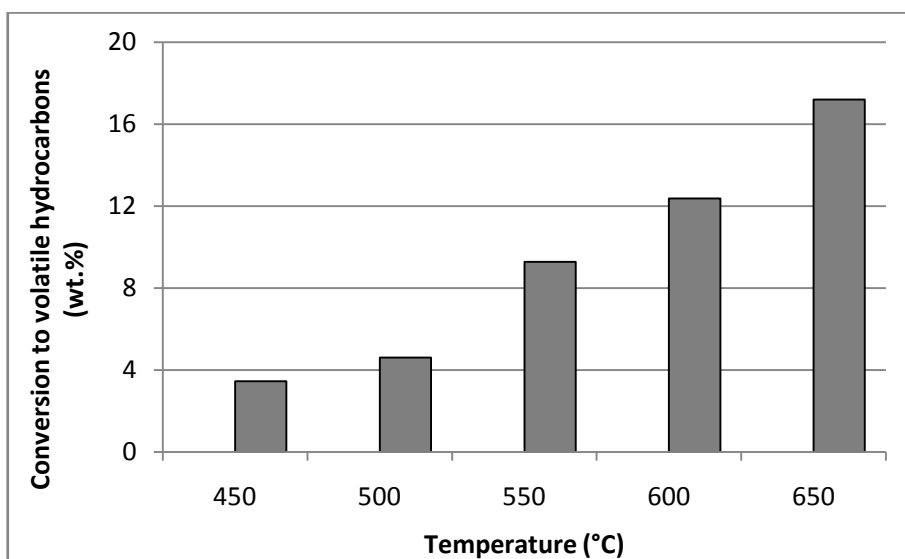


Figure 5.2.6.2 Volatile fraction of recovered hydrocarbons for IP of ELIG-C (in carbon basis)

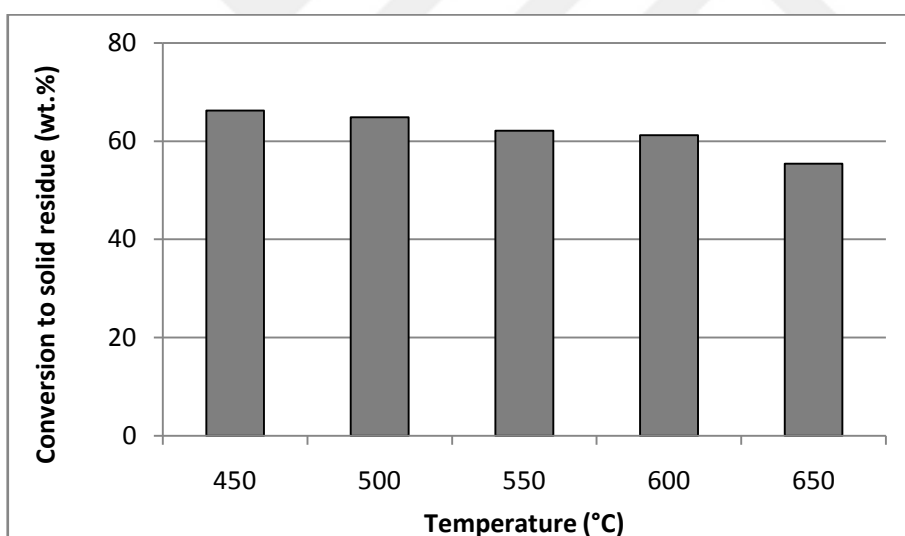


Figure 5.2.6.3 Conversion to solid residue for IP of ELIG-C (in weight basis)

In isothermal pyrolysis of ELIG-C, total hydrocarbon recoveries were calculated as 33.78, 35.12, 37.86, 38.78 and 44.60 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries at each pyrolysis temperature were calculated by subtracting coke conversion values from 100 %. Total hydrocarbon recoveries in isothermal pyrolysis of ELIG-C were shown in Figure 5.2.6.4.

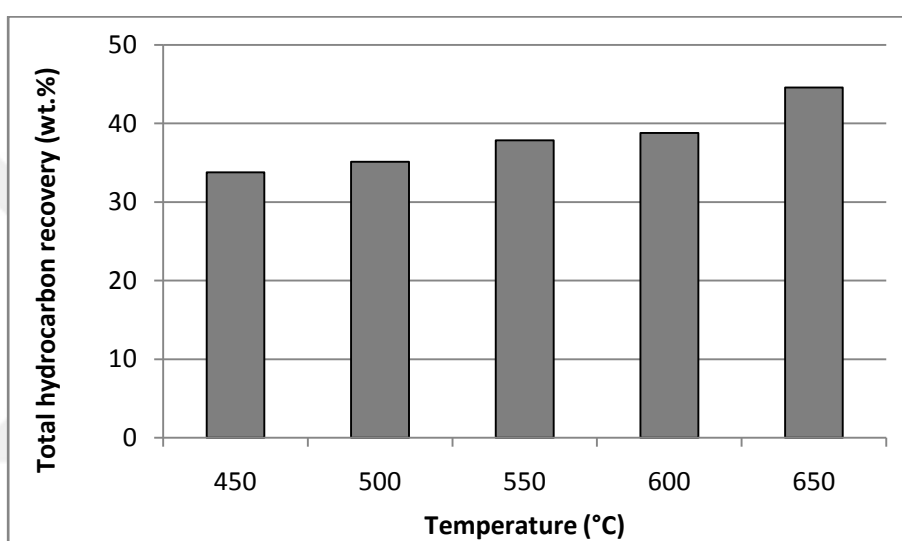


Figure 5.2.6.4 Total hydrocarbon recovery of isothermal pyrolysis of ELIG-C (in carbon basis)

The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery were found as 0.10, 0.13, 0.25, 0.32 and 0.39 of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. These values were tabulated at Table 5.2.6.2.

Table 5.2.6.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in isothermal pyrolysis of ELIG-C

Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.10	0.13	0.25	0.32	0.39

After isothermal pyrolysis of ELIG-C, amount of C in solid residue was identified by TOC analyzer and results were shown in Table 5.2.6.3 and it was shown in Figure 5.2.6.5.

Table 5.2.6.3 Carbon content in solid residue of ELIG-C

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	340.5	331.1	61.74	204.42	60.04	36.50
500	340.5	324.4	63.00	204.37	60.02	35.37
550	340.5	310.7	65.61	203.85	59.87	30.85
600	340.5	306.1	66.33	203.04	59.63	27.99
650	340.5	277.0	70.12	194.23	57.04	25.75

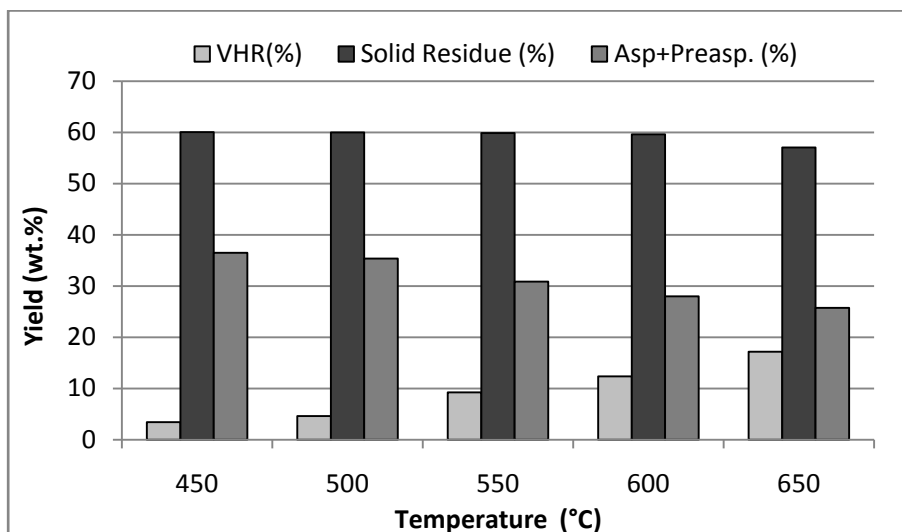


Figure 5.2.6.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of ELIG-C

At the end of the isothermal pyrolysis of ELIG-C, cumulative graphs of *n*-paraffins and 1-olefins were obtained and shown in Figures Figure 5.2.6.6 and Figure 5.2.6.7.

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Also, it can be seen that *n*-paraffin and 1-olefin gaseous products constitute the highest portion of the pyrolysis products. Cumulative C₁-C₄ and C₂-C₄ selectivities increased as temperature increased.

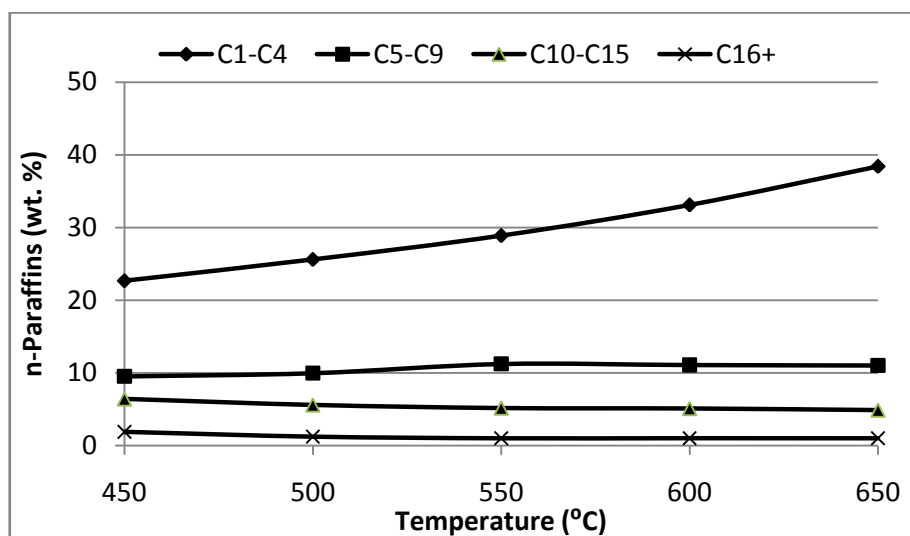


Figure 5.2.6.6 Cumulative n-paraffin selectivity for IP of ELIG-C

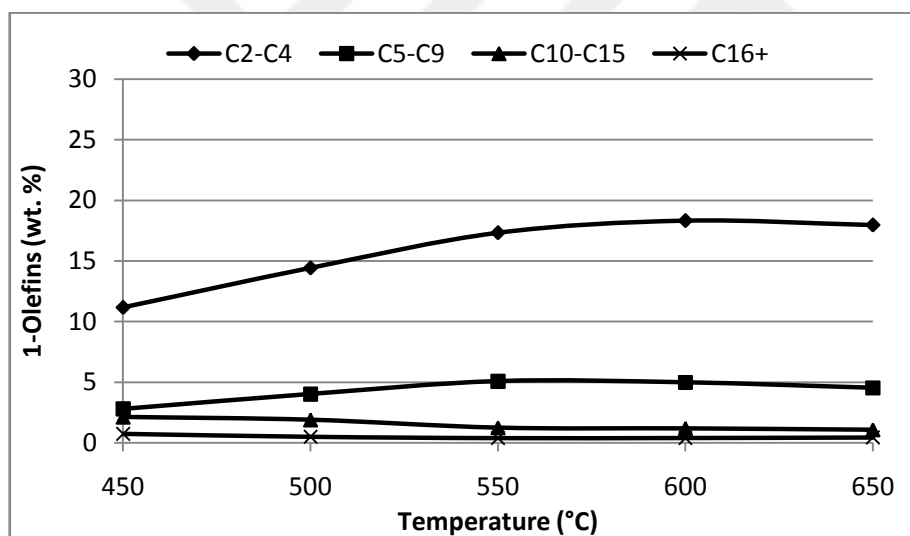


Figure 5.2.6.7 Cumulative 1-olefin selectivity for IP of ELIG-C

5.2.7 Isothermal Pyrolysis of ELIG-N

Isothermal pyrolysis of ELIG-N were carried out at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650°C, by using HCl-HNO₃ treated lignite samples.

Volatile product evolution rates depending on time at different temperatures were shown in Figure 5.2.7.1.

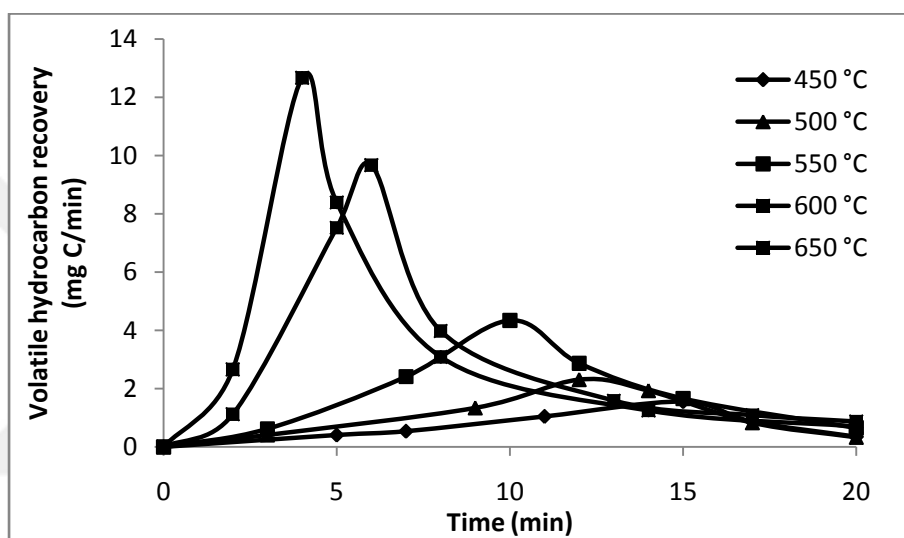


Figure 5.2.7.1 Volatile product evolution rate for isothermal pyrolysis of ELIG-N

As stated earlier, as pyrolysis temperature increases, maximum rate of decomposition occurs at shorter time, then maximum points of plots shifts right to left.

The total amount of volatile product evolution for isothermal pyrolysis of ELIG-N was tabulated in Table 5.2.7.1.

Table 5.2.7.1 Amount of C in feed and C recovered as product in IP of ELIG-N

T (°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	337.5	14.41	4.27
500	337.5	21.12	6.26
550	337.5	35.46	10.51
600	337.5	53.73	15.92
650	337.5	59.37	17.59

Volatile hydrocarbon recovery was found as 4.27 %, 6.26 %, 10.51 %, 15.92 % and 17.59 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Figure 5.2.7.2 represents volatile hydrocarbon recovery at each temperature.

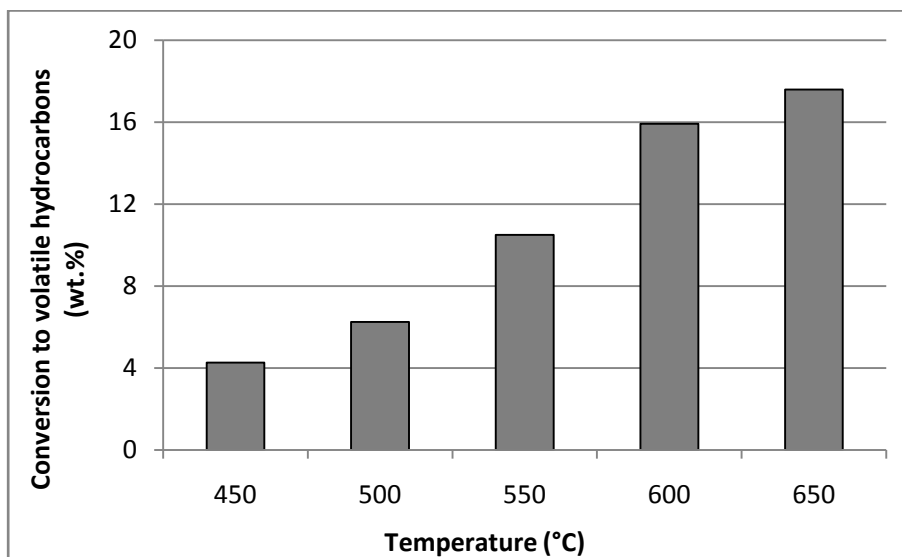


Figure 5.2.7.2 Volatile fraction of recovered hydrocarbon for IP of ELIG-N (in carbon basis)

In isothermal pyrolysis, solid residue of ELIG-N was found as 63.60 %, 62.66 %, 60.62 %, 58.62 % and 53.62% by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.7.3.

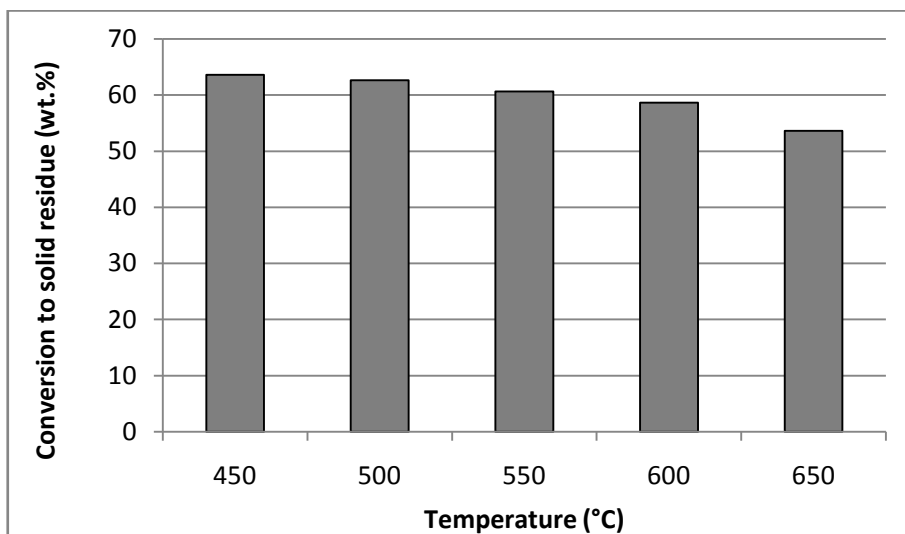


Figure 5.2.7.3 Conversion to solid residue of ELIG-N for isothermal pyrolysis (in weight basis)

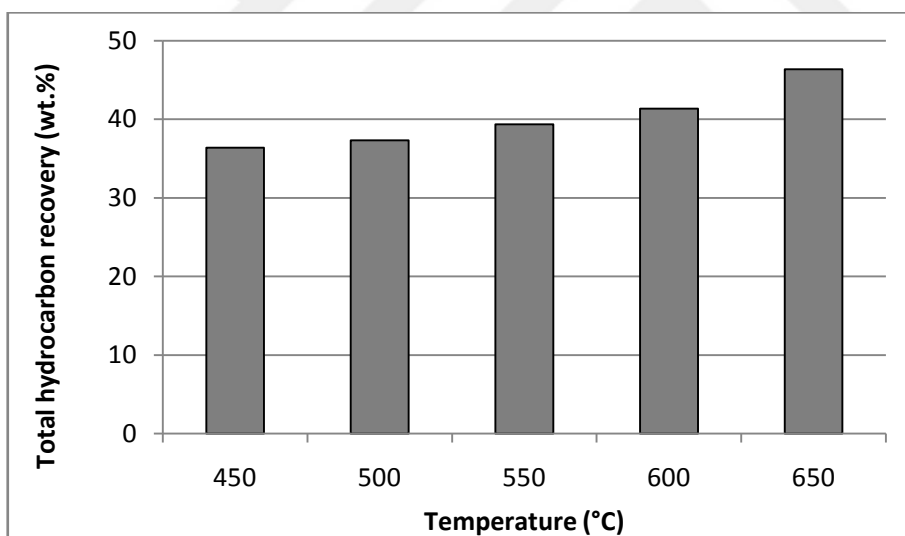


Figure 5.2.7.4 Total hydrocarbon recovery of isothermal pyrolysis of ELIG-N (in weight basis)

In isothermal pyrolysis of ELIG-N, total hydrocarbon recoveries were calculated as 36.40 %, 37.34 %, 39.38 %, 41.38 % and 46.38 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries in isothermal pyrolysis of ELIG-N were shown in Figure 5.2.7.4.

The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery were found as 0.12, 0.17, 0.27, 0.37 and 0.38 of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. These values were tabulated at Table 5.2.7.2.

Table 5.2.7.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in isothermal pyrolysis of ELIG-N

Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.12	0.17	0.27	0.37	0.38

After isothermal pyrolysis of ELIG-N, amount of C in solid residue was identified by TOC analyzer and results were shown in Table 5.2.7.3.

Table 5.2.7.3 Carbon content in solid residue of ELIG-N

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	337.5	318.0	62.11	197.51	58.52	37.21
500	337.5	313.3	62.87	196.97	58.36	35.38
550	337.5	303.1	63.95	193.83	57.43	32.06
600	337.5	293.1	64.66	189.52	56.15	27.93
650	337.5	268.1	74.50	189.01	56.00	26.41

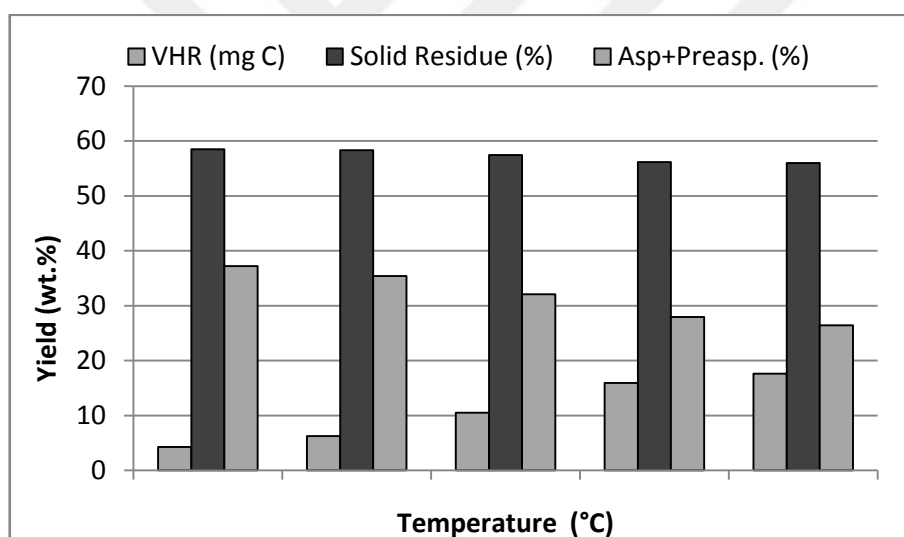
**Figure 5.2.7.5** Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of ELIG-N

Figure 5.2.7.5 shows gas and solid residue yield, as temperature increases, yield of gas product and yield of C in solid residue increased because of volatilization.

At the end of the isothermal pyrolysis of ELIG-N, cumulative graphs of n-paraffins and 1-olefins were obtained and shown in Figures Figure 5.2.7.6 and Figure 5.2.7.7.

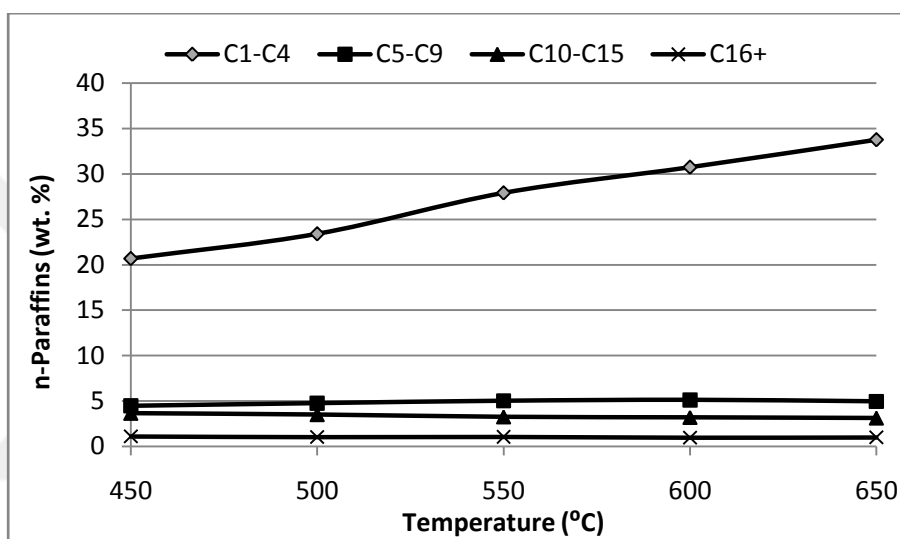


Figure 5.2.7.6 Cumulative n-paraffin selectivity for IP of ELIG-N

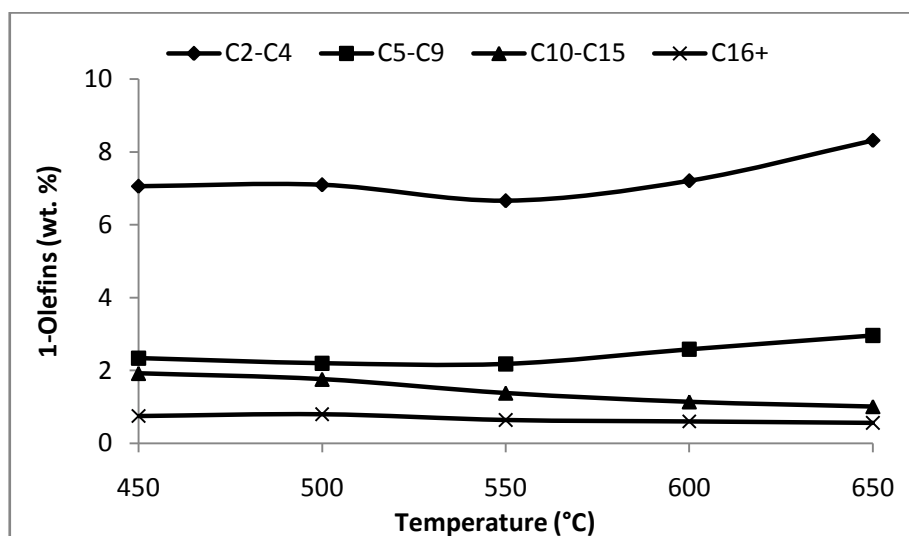


Figure 5.2.7.7 Cumulative 1-olefin selectivity for IP of ELIG-N

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions especially C₁-C₄ group, increased with increasing pyrolysis temperature.

5.2.8 Isothermal Pyrolysis of ELIG-F

Isothermal pyrolysis of LIG-F were carried out at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650°C, by using HCl-HNO₃-HF treated oil shale samples.

Volatile product evolution rates depending on time at different temperatures were shown in Figure 5.2.8.1.

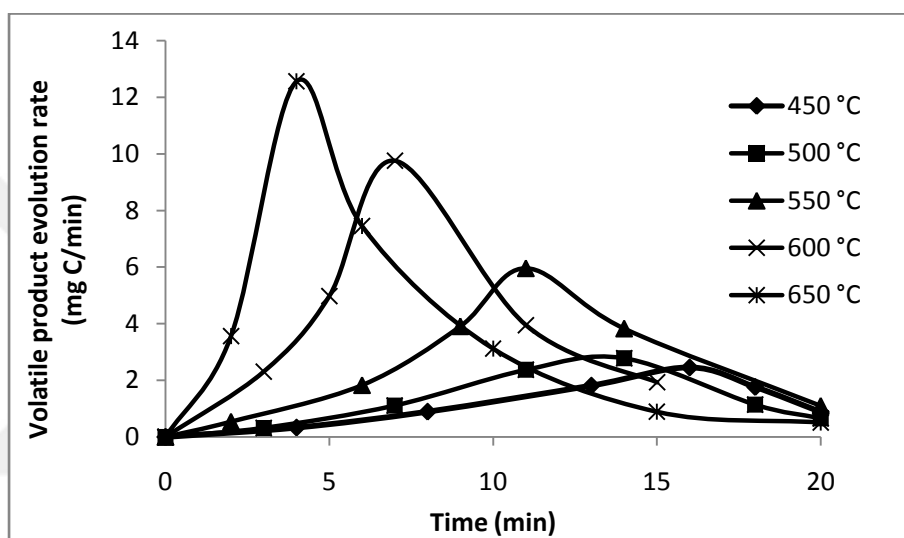


Figure 5.2.8.1 Volatile product evolution rate for isothermal pyrolysis of ELIG-F

The total amount of volatile product evolution for isothermal pyrolysis of ELIG-F was tabulated in Table 5.2.8.1.

Table 5.2.8.1 Amount of C in feed and C recovered as product in IP of ELIG-F

T (°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	338.50	23.12	6.83
500	338.50	27.88	8.24
550	338.50	51.84	15.31
600	338.50	69.32	20.48
650	338.50	71.45	21.11

Volatile hydrocarbon recovery was found as 6.83 %, 8.24 %, 15.31 %, 20.48 % and 21.11 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Figure 5.2.8.2 represents volatile hydrocarbon recovery at each temperature.

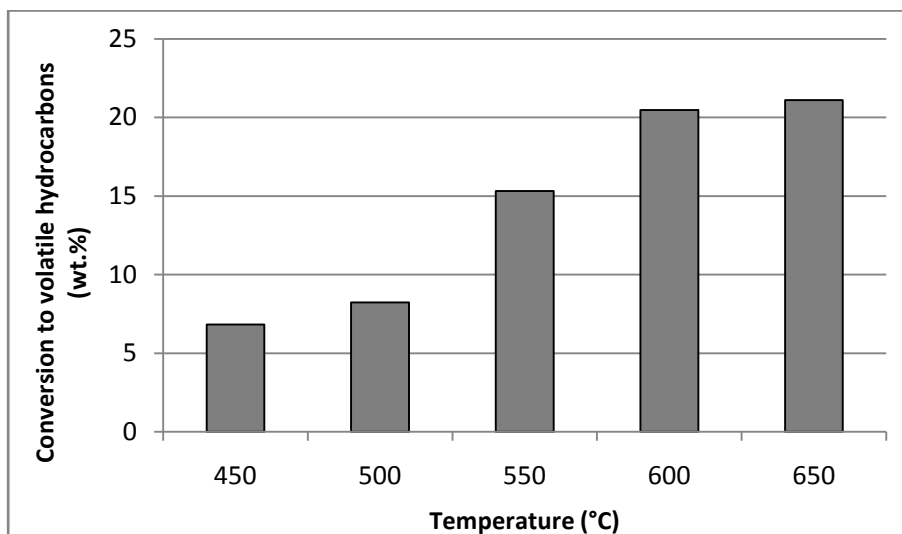


Figure 5.2.8.2 Volatile fraction of recovered hydrocarbon for IP of ELIG-F (in carbon basis)

In isothermal pyrolysis, solid residue of ELIG-F was found as 63.10 %, 62.04 %, 60.10 %, 58.42 % and 52.56 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.8.3.

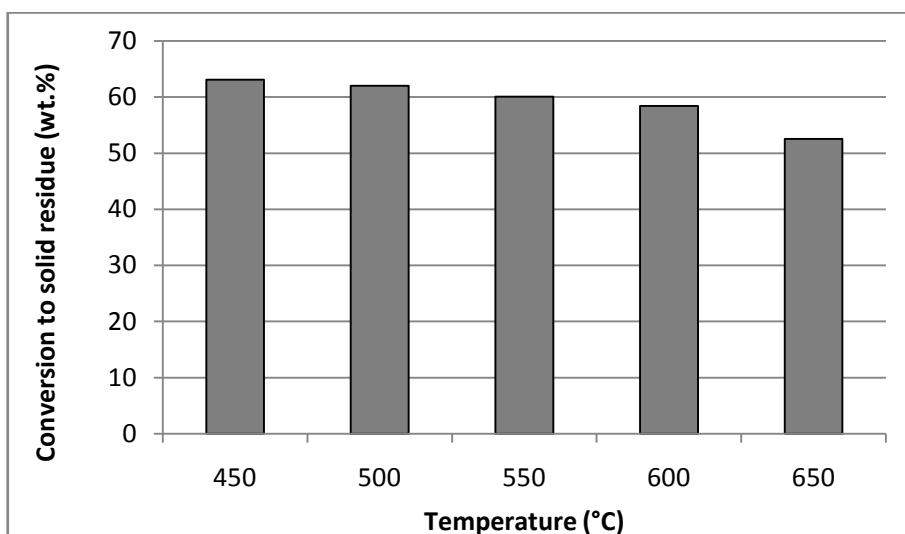


Figure 5.2.8.3 Conversion to solid residue of ELIG-F for isothermal pyrolysis (in weight basis)

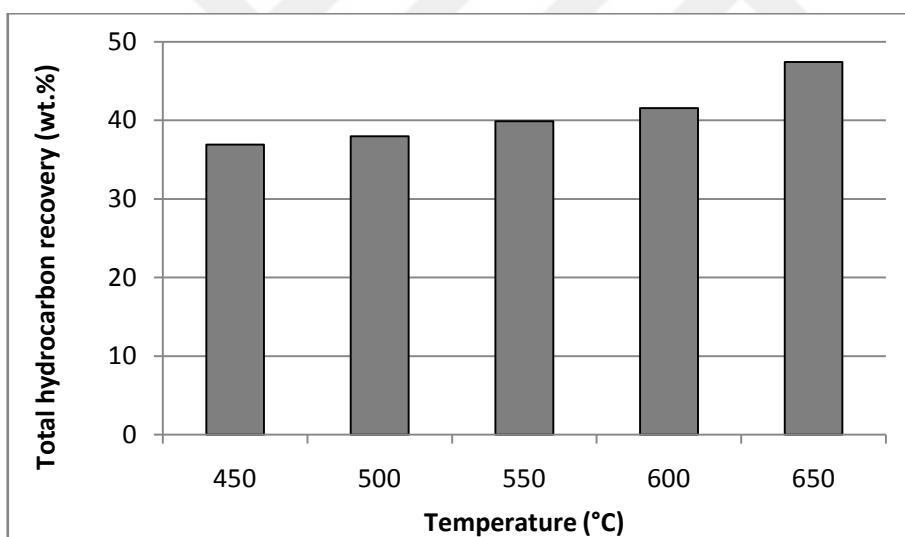


Figure 5.2.8.4 Total hydrocarbon recovery of isothermal pyrolysis of ELIG-F (in weight basis)

In isothermal pyrolysis of ELIG-F, total hydrocarbon recoveries were calculated as 36.90 %, 37.96 %, 39.90 %, 41.58 %, and 47.44 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries in isothermal pyrolysis of LIG-F were given in Figure 5.2.8.4.

The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery were found as 0.19, 0.22, 0.38, 0.39 and 0.44 of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. These values were tabulated at Table 5.2.8.2.

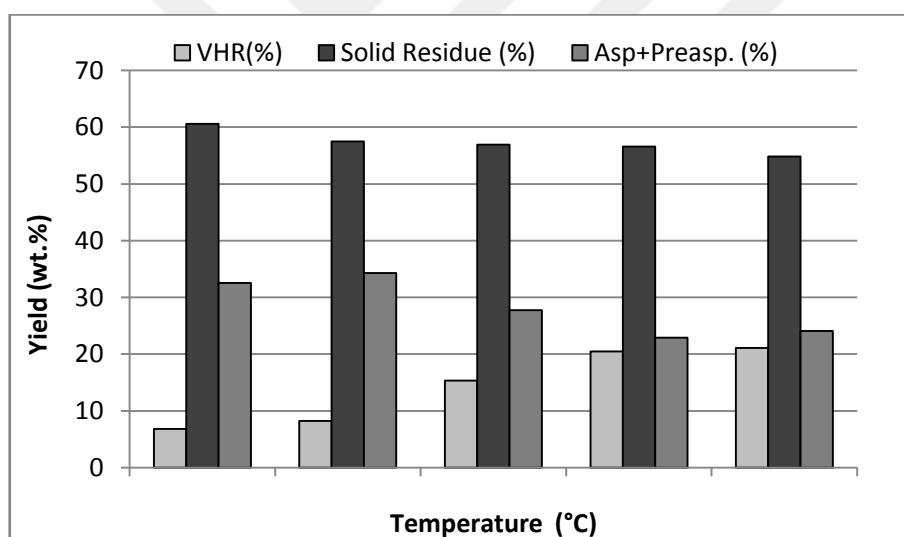
Table 5.2.8.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in isothermal pyrolysis of ELIG-F

Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.19	0.22	0.38	0.39	0.44

After isothermal pyrolysis of ELIG-F, amount of C in solid residue was identified by TOC analyzer and results were shown in Table 5.2.8.3 and Figure 5.2.8.5, respectively.

Table 5.2.8.3 Carbon content in solid residue of ELIG-F

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	338.5	345.5	59.38	205.16	60.61	32.56
500	338.5	310.2	62.74	194.62	57.49	34.27
550	338.5	300.5	64.11	192.65	56.91	27.77
600	338.5	292.1	65.59	191.59	56.60	22.92
650	338.5	262.8	70.59	185.51	54.84	24.09

**Figure 5.2.8.5** Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of ELIG-F

At the end of the isothermal pyrolysis of ELIG-F, cumulative graphs of n-paraffins and 1-olefins were obtained and shown in Figure 5.2.8.6 and Figure 5.2.8.7.

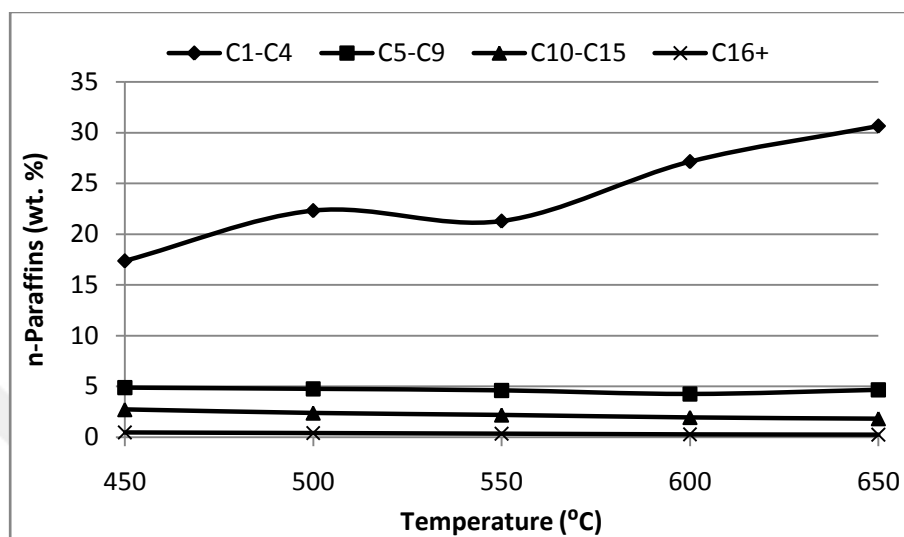


Figure 5.2.8.6 Cumulative n-paraffin selectivity for IP of ELIG-F

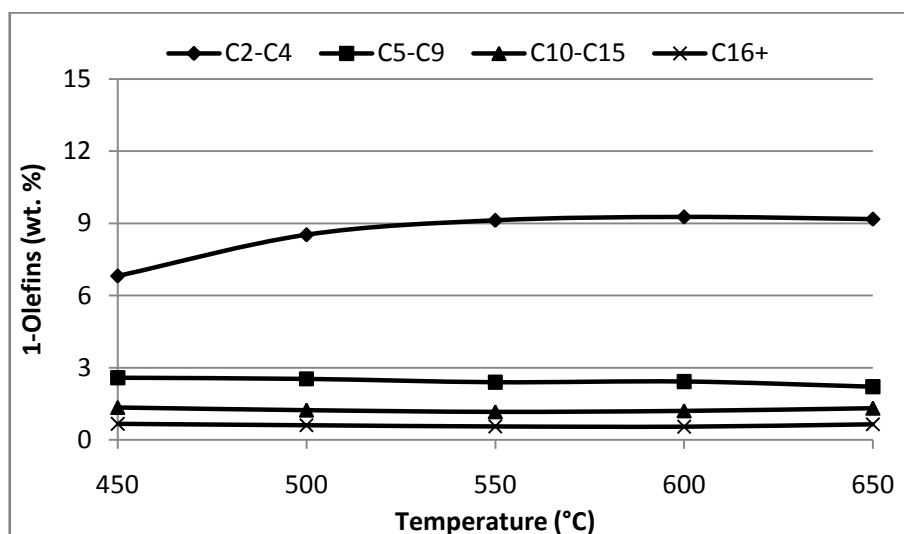


Figure 5.2.8.7 Cumulative 1-olefin selectivity for IP of ELIG-F

Cumulative n-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature.

In order to compare isothermal pyrolysis of raw and demineralized lignite samples, the total amount of volatile product of these samples depending on temperature were given in Figure 5.2.8.8.

Yield of volatile hydrocarbons decreased after leaching of lignite with HCl. Washing with HCl removes CaCO_3 , FeCO_3 and MgCO_3 and partially chlorite minerals from lignite structure.

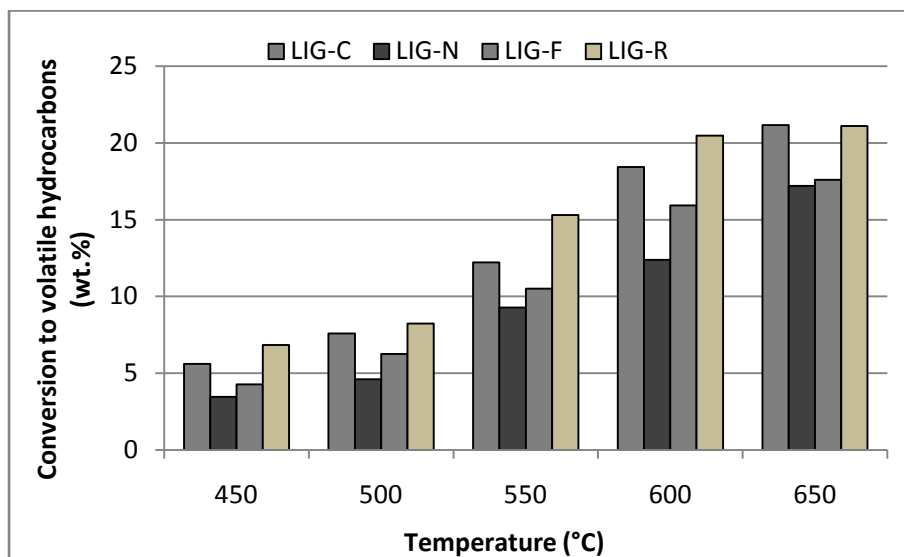


Figure 5.2.8.8 Volatile hydrocarbon recoveries for raw and demineralized lignite samples

Removal of pyrites with HNO_3 did not affect the reactivity of the organic material in pyrolysis.

Silicates inhibited the rate of conversion of pyrolysis processes, so leaching of lignite with HF did not affect the reactivity of the organic material in pyrolysis.

Cumulative $\text{C}_1\text{-C}_4$ gas fraction increased after leaching of lignite with HCl and there is no effect of leaching with HNO_3 and HF on the formation of gas products.

5.2.9 Isothermal Pyrolysis of SASP-R

Isothermal pyrolysis of SASP-R was carried out at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C.

At the end of the isothermal pyrolysis of SASP-R, volatile product evolution rate of SASP-R was shown in Figure 5.2.9.1.

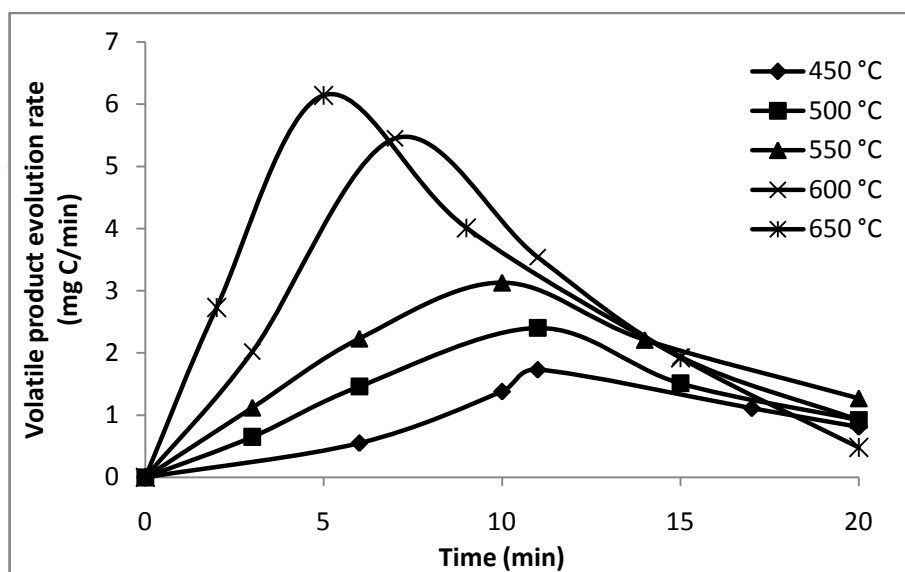


Figure 5.2.9.1 Volatile product evolution rate for isothermal pyrolysis of SASP-R

As seen from Figure 5.2.9.1, when pyrolysis temperature increases, maximum rate of decomposition occurs at shorter time. So, maximum points of plots shifts right to left.

The total amount of volatile product evolution for isothermal pyrolysis of SASP-R was tabulated in Table 5.2.9.1.

Table 5.2.9.1 Amount of C in feed and C recovered as product in IP of SASP-R

T (°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	212.1	18.2	8.58
500	212.1	27.8	13.11
550	212.1	39.1	18.43
600	212.1	54.6	25.74
650	212.1	60.8	28.67

Volatile hydrocarbon recovery was found as 8.58 %, 13.11 %, 18.43 %, 25.74 % and 28.67 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Figure 5.2.9.2 represents volatile hydrocarbon recovery at each temperature.

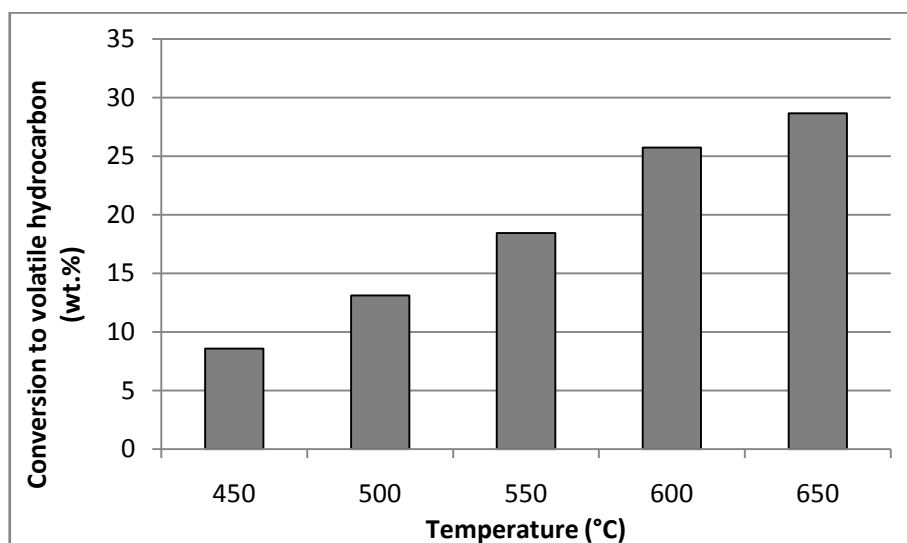


Figure 5.2.9.2 Volatile fraction of recovered hydrocarbons for IP of SASP-R (in carbon basis)

In isothermal pyrolysis, solid residue of SASP-R was found as 80.10 %, 75.90 %, 74.85 %, 71.09 % and 67.90 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.9.3.

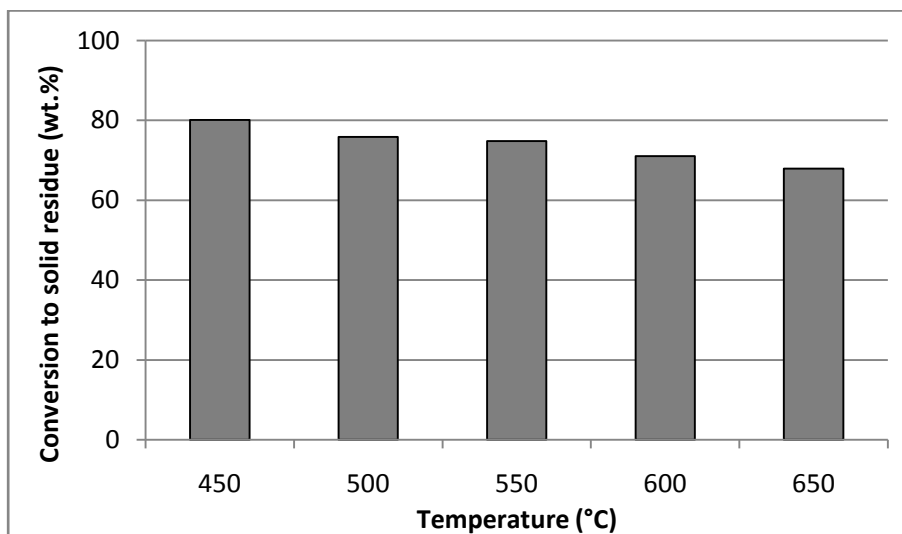


Figure 5.2.9.3 Conversion to solid residue of SASP-R for isothermal pyrolysis (in weight basis)

In isothermal pyrolysis of SASP-R, total hydrocarbon recoveries were calculated as 19.90 %, 24.10 %, 25.15 %, 28.91 % and 32.10 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries at each pyrolysis temperature were calculated by subtracting coke conversion values from 100 %. Total hydrocarbon recoveries in isothermal pyrolysis of SASP-R were shown in Figure 5.2.9.4.

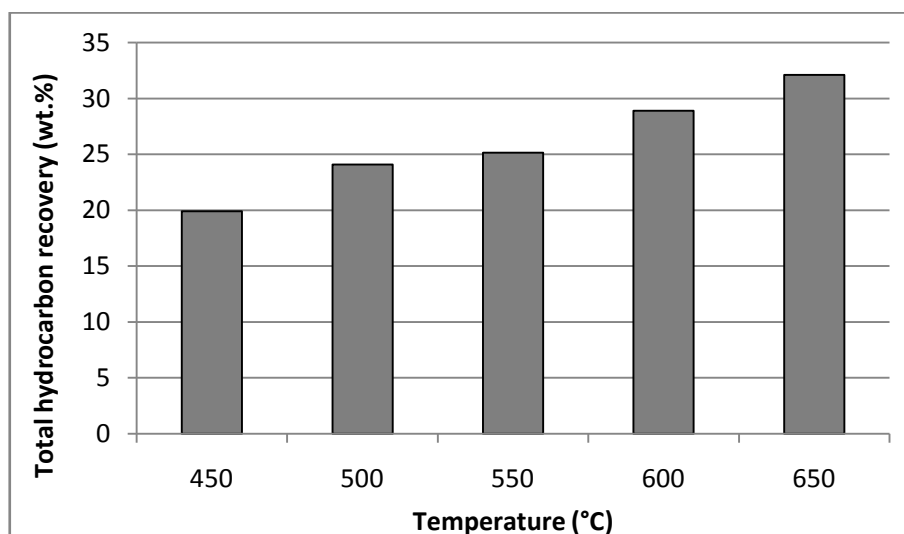


Figure 5.2.9.4 Total hydrocarbon recovery for isothermal pyrolysis of SASP-R (in weight basis)

The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery were found as of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. These values were tabulated at Table 5.2.9.2.

Table 5.2.9.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in isothermal pyrolysis of ASP-R

Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.43	0.54	0.73	0.79	0.89

After isothermal pyrolysis of GOS-R, amount of C in solid residue was identified by TOC analyzer and results were shown in Table 5.2.9.3.

Table 5.2.9.3 Carbon content in solid residue of SASP-R

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	212.1	400.5	36.31	145.42	68.56	22.86
500	212.1	379.5	33.97	128.92	60.78	26.11
550	212.1	374.3	32.98	123.44	58.20	23.36
600	212.1	355.5	28.37	100.86	47.55	26.71
650	212.1	339.4	27.57	93.60	44.13	27.20

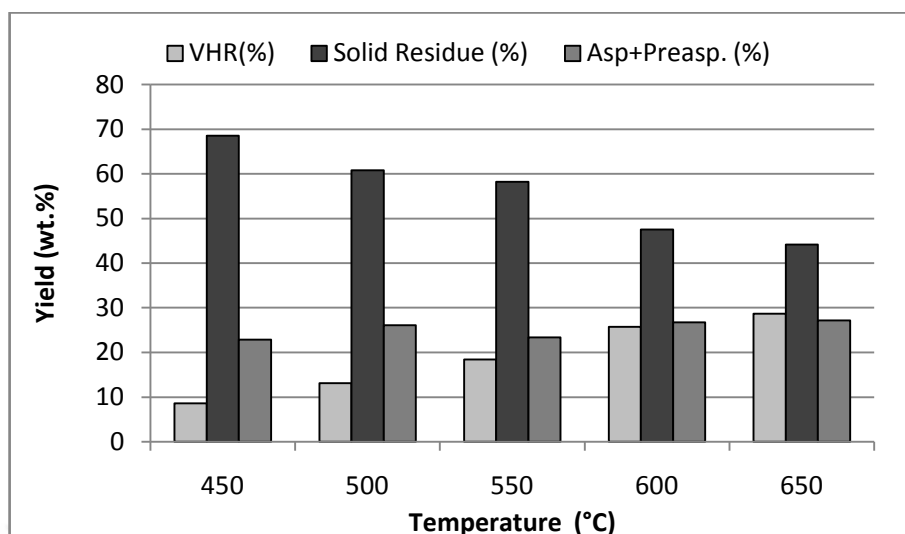


Figure 5.2.9.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of SASP-R

Figure 5.2.9.5 shows gas and solid residue yield, as temperature increases, yield of gas product and yield of C in solid residue decreased because of volatilization.

Volatile fraction of recovered hydrocarbons analyzed by gas chromatographic technique, were classified according to carbon number. For this purpose the products were classified as; gases, C₁-C₄ or C₂-C₄ and liquids, C₅-C₉, C₁₀-C₁₅ and C₁₆+

Thermal cracking of the preasphaltenes and asphaltene become important above 400 °C and the yield of hexane soluble hydrocarbons increases with temperature over this range during the pyrolysis of asphaltite. Above 450 °C temperature range, n-paraffins and 1-olefins

are formed mainly by the decomposition of asphaltenes and preasphaltenes (Ballice, 2002).

At the end of the isothermal pyrolysis of SASP-R, cumulative graphs of n-paraffins and 1-olefins were obtained and shown in Figures Figure 5.2.9.6 and Figure 5.2.9.7.

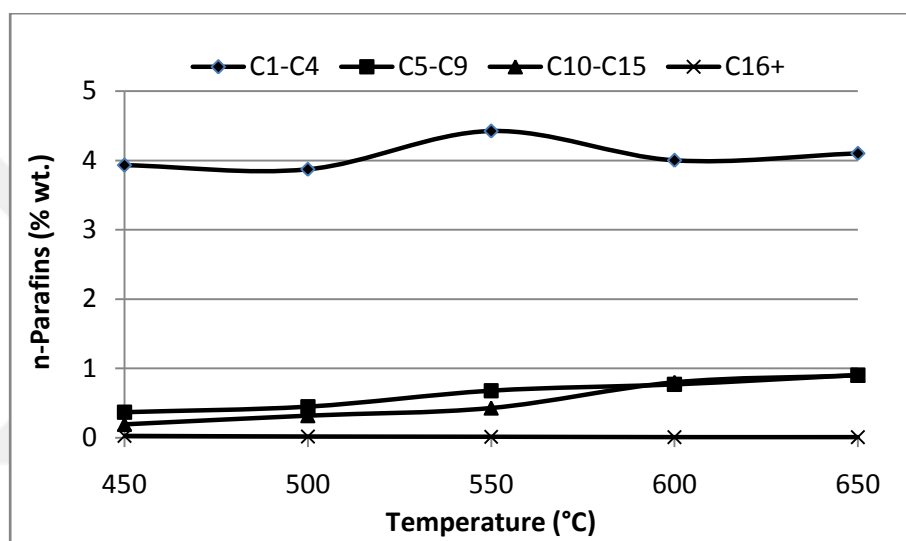


Figure 5.2.9.6 Cumulative n-paraffin selectivity for IP of SASP-R

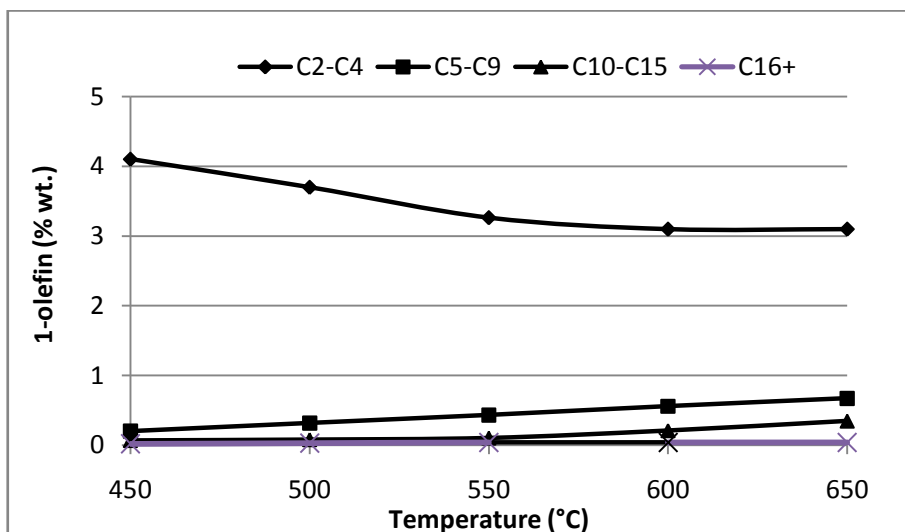


Figure 5.2.9.7 Cumulative 1-olefin selectivity for IP of SASP-R

Cumulative *n*-paraffin selectivity graphs at each pyrolysis temperature show that gas fractions nearly remain constant with increasing pyrolysis temperature. But gas fraction of olefins slightly decreased with increasing temperature. Increase in liquid and heavy molecular weight fraction could be explained by polymerization reaction of gas product.

5.2.10 Isothermal Pyrolysis of SASP-C

The inorganic fraction of asphaltites is dramatically different from that of other fossil fuels such as oil shale and coal. Asphaltites are non-homogenous mixture of bitumen, quartz and water. The overwhelming preponderance of the inorganic material is quartz sand and clays, less than 1% are calciferous and iron based minerals. To investigate the effect of mineral matter on the thermal decomposition, isothermal pyrolysis of HCl-treated asphaltite samples were carried out at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650°C.

At the end of the isothermal pyrolysis of HCl-treated asphaltite samples (SASP-C), volatile product evolution rate depending on temperature was obtained and shown in Figure 5.2.10.1.

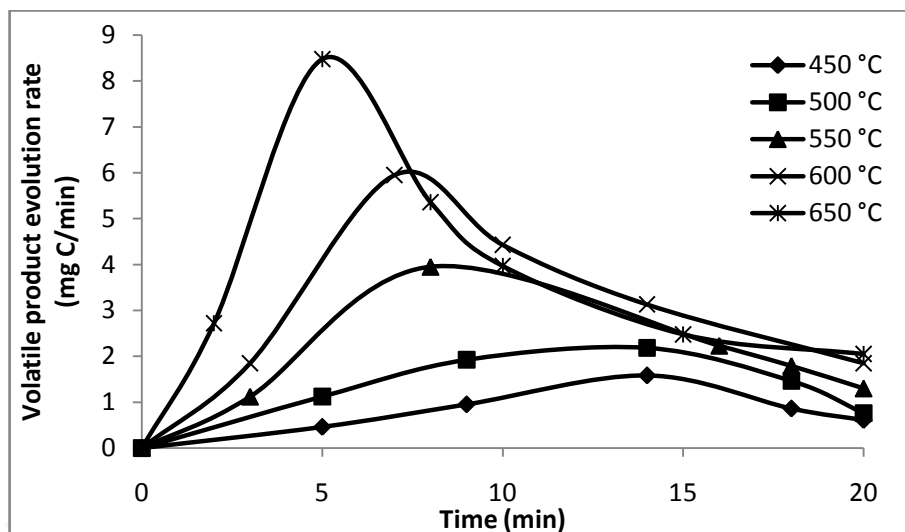


Figure 5.2.10.1 Volatile product evolution rate for isothermal pyrolysis of SASP-C

As shown from Figure 5.2.10.1, as pyrolysis temperature increases, maximum rate of decomposition occurs at shorter time, then maximum points of plots shifts right to left.

The total amount of volatile product evolution for isothermal pyrolysis of SASP-R was tabulated in Table 5.2.10.1.

Volatile hydrocarbon recovery was found as 5.92 %, 10.49 %, 16.93 %, 22.53 %, and 27.49 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Figure 5.2.10.2 represents volatile hydrocarbon recovery at each temperature.

Table 5.2.10.1 Amount of C in feed and C recovered as product in IP of SASP-C

T (°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	282.3	16.7	5.92
500	282.3	29.6	10.49
550	282.3	47.8	16.93
600	282.3	63.6	22.53
650	282.3	77.6	27.49

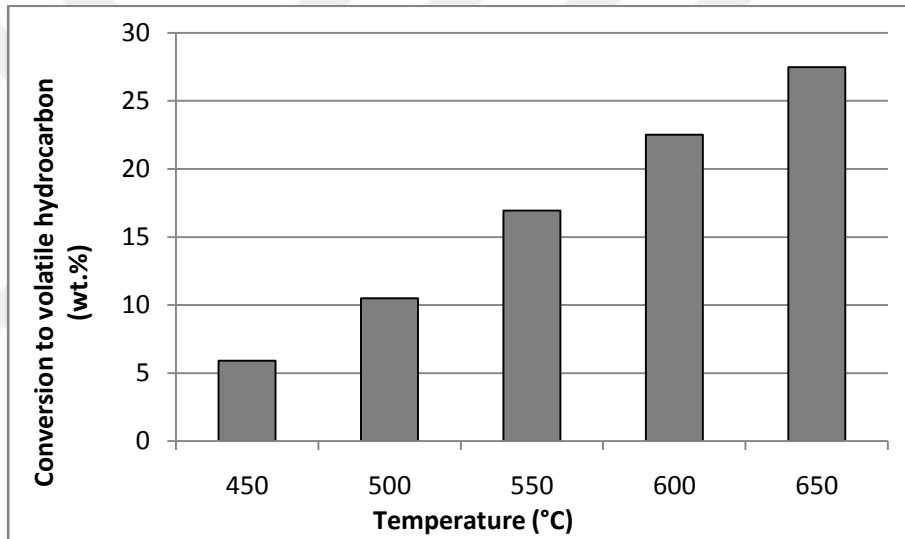


Figure 5.2.10.2 Volatile fraction of recovered hydrocarbons for IP of SASP-C (in carbon basis)

In isothermal pyrolysis, solid residue of SASP-C was found as 78.82 %, 74.38 %, 72.25 %, 67.50 % and 64.79% by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.10.3.

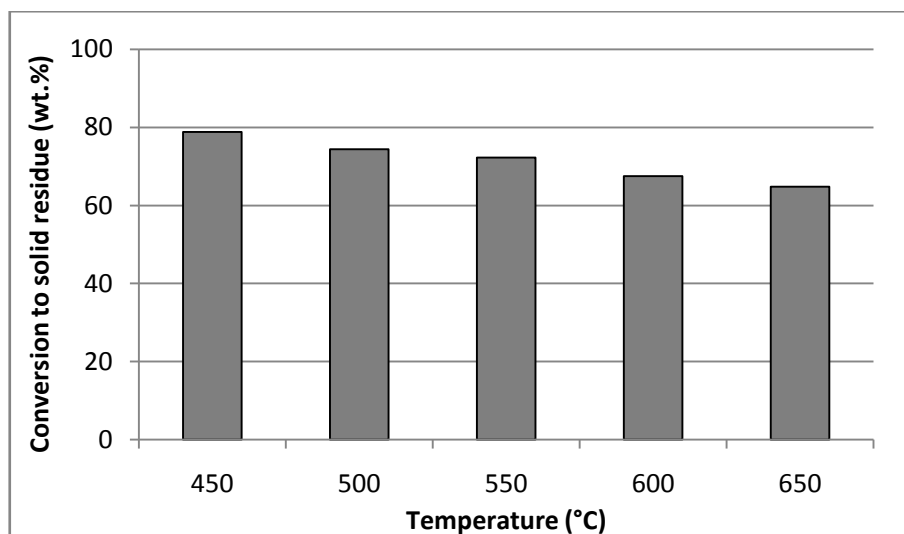


Figure 5.2.10.3 Conversion to solid residue of SASP-C for isothermal pyrolysis (in weight basis)

In isothermal pyrolysis of SASP-C, conversion to solid residue decreased from 78.82 wt % to 64.79 wt %, as temperature increases from 450°C to 650°C.

In isothermal pyrolysis of SASP-C, total hydrocarbon recoveries were calculated as 21.18 %, 25.62 %, 27.75 %, 32.50 % and 35.21 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C

and 650 °C, respectively. Total hydrocarbon recoveries in isothermal pyrolysis of SASP-C were shown in Figure 5.2.10.4.

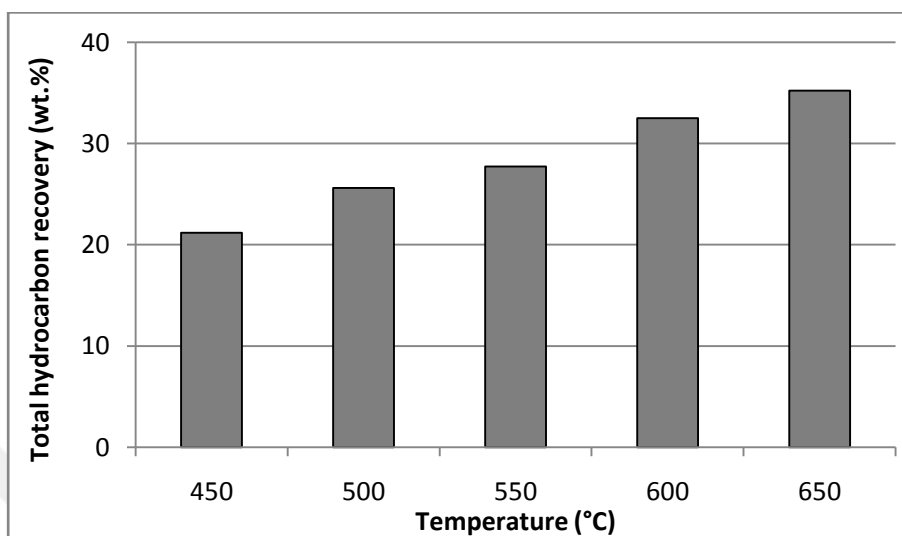


Figure 5.2.10.4 Total hydrocarbon recovery for isothermal pyrolysis of SASP-C (in weight basis)

The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery were found as 0.28, 0.41, 0.61, 0.69 and 0.78 of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. These values were tabulated at Table 5.2.10.2.

Table 5.2.10.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in isothermal pyrolysis of SASP-C

Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.28	0.41	0.61	0.69	0.78

After isothermal pyrolysis of SASP-C, amount of C in solid residue was identified by TOC analyzer and results given in Table 5.2.10.3 and shown in Figure 5.2.10.5.

Table 5.2.10.3 Carbon content in solid residue of SASP-C

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	282.3	394.1	56.95	224.44	79.49	14.60
500	282.3	371.9	51.26	190.64	67.52	22.00
550	282.3	361.3	47.33	171.00	60.56	22.51
600	282.3	327.5	46.80	157.95	55.94	21.53
650	282.3	323.9	46.20	149.64	53.00	19.52

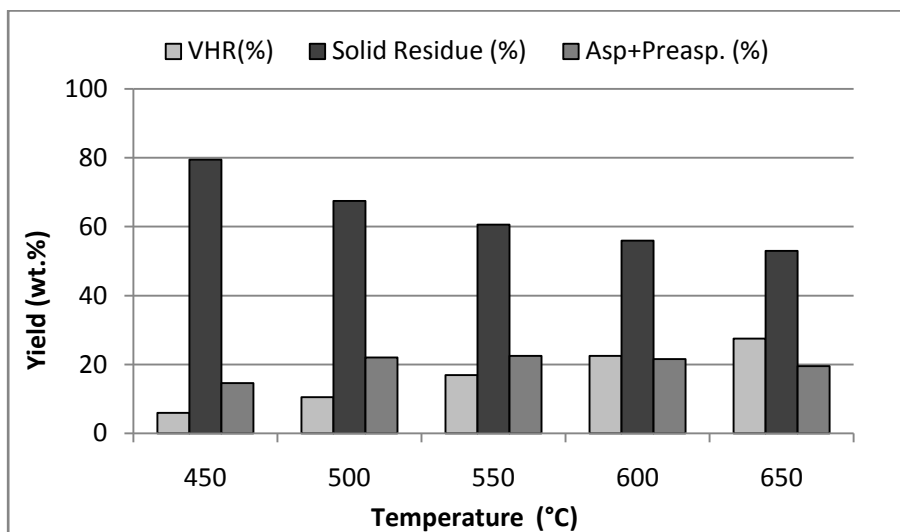


Figure 5.2.10.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of SASP-C

In contrast to the gas yield, solid residue yield decreased as temperature increased. The yield of gas product increased because of volatilization. But C yield in solid residue decreased in Figure 5.2.10.5.

Asphaltites, originating from petroleum, are associated with mineral matter containing some valuable raw metals such as Mo, Ni, V, and some radioactive metals (e.g., U and Th) and are also a potential source of hydrocarbons. The quality of these asphaltites, however, is poor in terms of their ash yield and sulfur content (Karayığit and Querol, 2002). As temperature increases, C yield in solid residue decreased. The reason for behavior of asphaltites seems to be caused by the presence of elemental sulfur. The ability of sulfur to interact at

high temperatures with hydrocarbons, is leading to sewing of molecules and formation of high-molecular products (Savel'ev et.al., 2008).

At the end of the isothermal pyrolysis of SASP-C, cumulative graphs of n-paraffins and 1-olefins were obtained and shown in Figures Figure 5.2.10.6 and Figure 5.2.10.7.

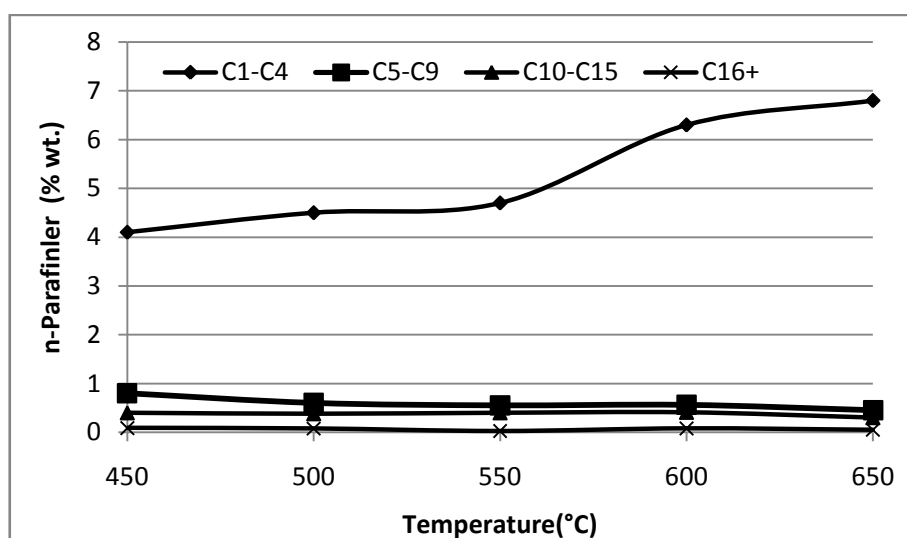


Figure 5.2.10.6 Cumulative n-paraffin selectivity for IP of SASP-C

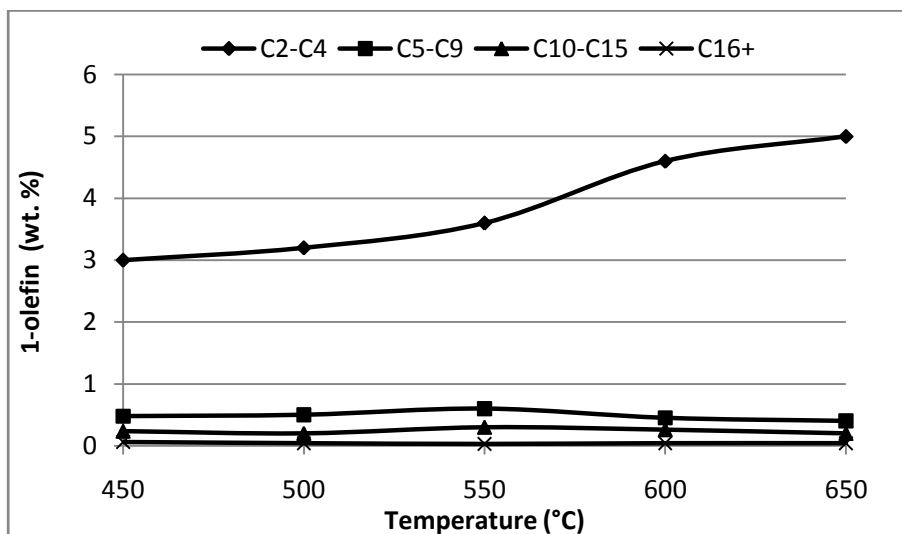


Figure 5.2.10.7 Cumulative 1-olefin selectivity for IP of SASP-C

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Also, it can be seen that *n*-paraffin and 1-olefin gaseous products constitute the highest portion of the pyrolysis products. Cumulative C₁-C₄ and C₂-C₄ selectivities increased as temperature increased, particularly above 550 °C, there are considerable increase in these groups because of the cracking of C₅+ hydrocarbons at high temperatures. At the same graphs, there is a sharp decrease in C₅-C₉ groups because of the decomposition of liquid products at high temperatures.

5.2.11 Isothermal Pyrolysis of SASP-N

Isothermal pyrolysis of SASP-N was carried out at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, by using HCl-HNO₃ treated samples.

At the end of the isothermal pyrolysis of HCl-HNO₃ treated asphaltite samples (SASP-N). Volatile product evolution rate depending on temperature was obtained and shown in Figure 5.2.11.1.

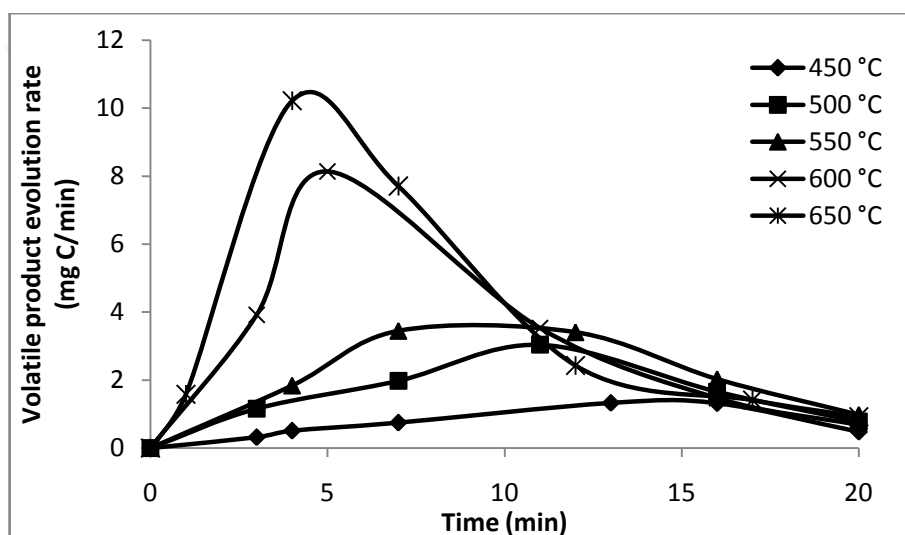


Figure 5.2.11.1 Volatile product evolution rate for isothermal pyrolysis of SASP-N

As pyrolysis temperature increases, maximum rate of decomposition occurs at shorter time, then maximum points of plots shifts from right to left.

The total amount of volatile product evolution for isothermal pyrolysis of SASP-N was tabulated in Table 5.2.11.1.

Table 5.2.11.1 Amount of C in feed and C recovered as product in IP of SASP-N

T (°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	279.2	16.8	6.02
500	279.2	34.9	12.50
550	279.2	49.2	17.62
600	279.2	68.3	24.46
650	279.2	76.2	27.29

Volatile hydrocarbon recovery was found as 6.02 %, 12.50 %, 17.62 %, 24.46 % and 27.29 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Figure 5.2.11.2 represents volatile hydrocarbon recovery at each temperature.

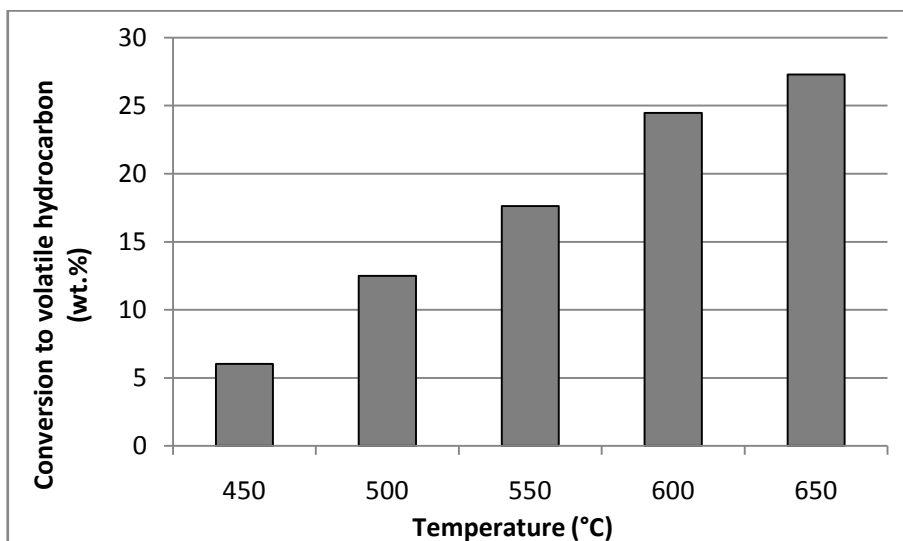


Figure 5.2.11.2 Volatile fraction of recovered hydrocarbons for IP of SASP-N (in carbon basis)

In isothermal pyrolysis, solid residue of SASP-N was found as 76.71 %, 73.21 %, 71.43 %, 64.20 % and 62.52 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.11.3.

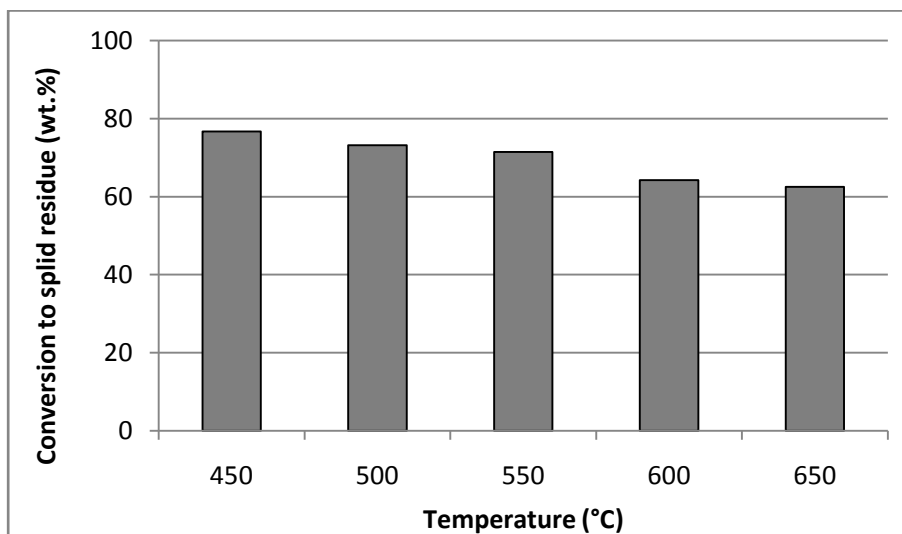


Figure 5.2.11.3 Conversion to solid residue of SASP-N for isothermal pyrolysis (in weight basis)

In isothermal pyrolysis of SASP-N, total hydrocarbon recoveries were calculated as 23.29 %, 26.79 %, 28.57 %, 35.80 % and 37.48 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries in isothermal pyrolysis of SASP-N were shown in Figure 5.2.11.4.

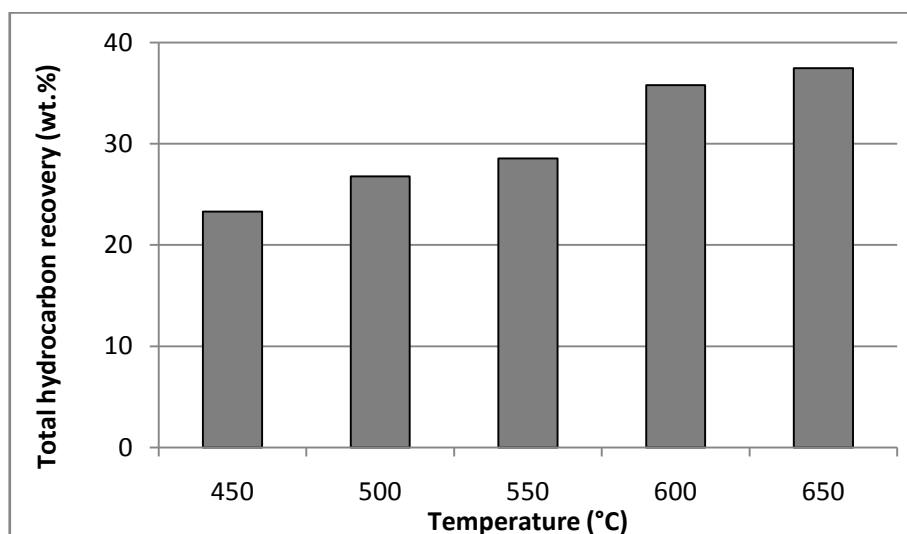


Figure 5.2.11.4 Total hydrocarbon recovery for isothermal pyrolysis of SASP-N (in weight basis)

The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery were found and these values were tabulated at Table 5.2.11.2.

Table 5.2.11.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in isothermal pyrolysis of SASP-N

Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.26	0.47	0.62	0.68	0.73

After isothermal pyrolysis of SASP-N, amount of C in solid residue was identified by TOC analyzer and results were given in Table 5.2.11.3 and presented in Figure 5.2.11.5.

Table 5.2.11.3 Carbon content in solid residue of SASP-N

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	279.2	383.5	53.15	203.83	73.01	20.98
500	279.2	366.1	51.25	187.63	67.20	20.30
550	279.2	357.2	48.51	173.28	62.06	20.32
600	279.2	321.0	48.34	155.20	55.59	19.95
650	279.2	312.6	47.01	146.92	52.62	13.68

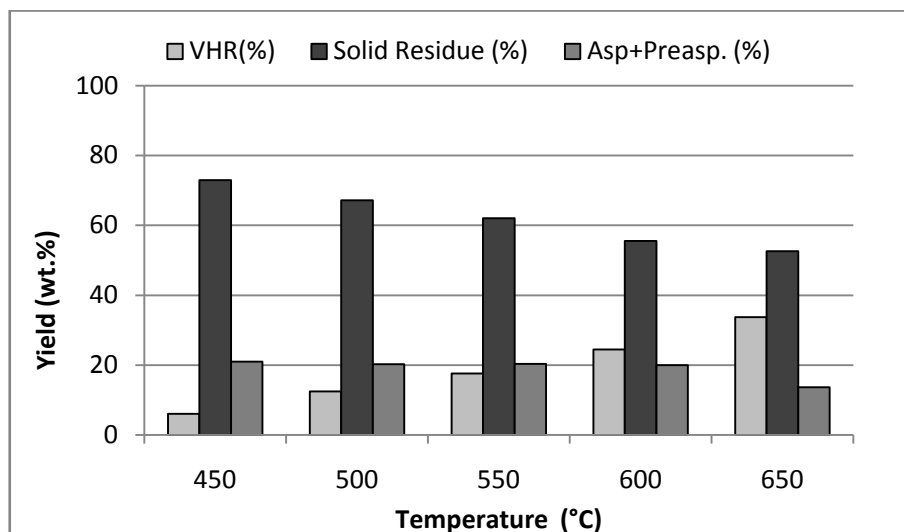


Figure 5.2.11.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP of SASP-N

Figure 5.2.11.5 shows solid residue yield decreases, as temperature increases. The yield of gas product increased because of volatilization. But C yield in solid residue decreased as explained before.

At the end of the isothermal pyrolysis of SASP-N, cumulative graphs of n-paraffins and 1-olefins were obtained and shown in Figures Figure 5.2.11.6 and Figure 5.2.11.7.

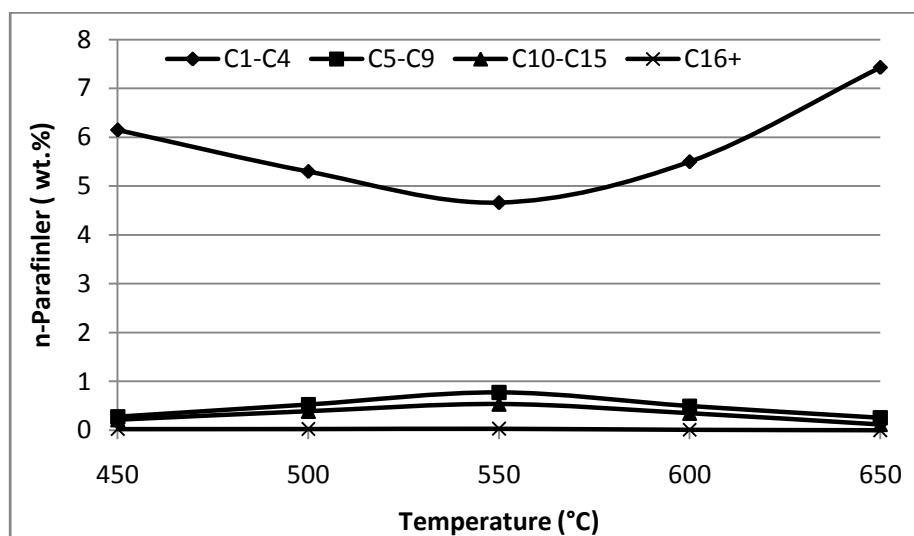


Figure 5.2.11.6 Cumulative n-paraffin selectivity for IP of SASP-N

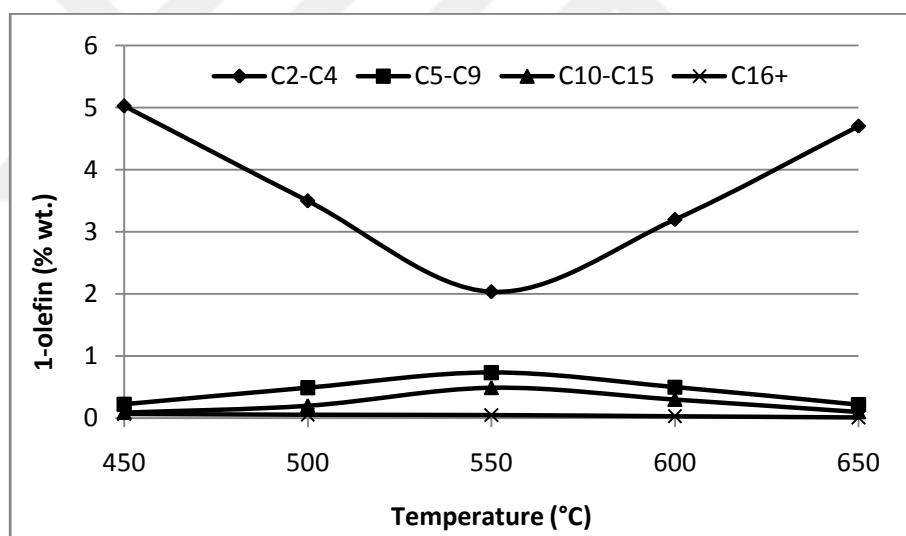


Figure 5.2.11.7 Cumulative 1-olefin selectivity for IP of SASP-N

Light fractions of both cumulative n-paraffin and 1-olefins decreased as temperature increases. Fewer than 550°C, amount of gas products decreased because of the formation of polymerization reactions. Amount of liquid products increased then above 550°C, amount of gas products increased because of the volatilization.



5.2.12 Isothermal Pyrolysis of SASP-F

Isothermal pyrolysis of SASP-F was performed at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650°C.

At the end of the isothermal pyrolysis of HCl-HNO₃-HF treated asphaltite samples (SASP-F). Volatile product evolution rate depending on temperature was obtained and shown in Figure 5.2.12.1.

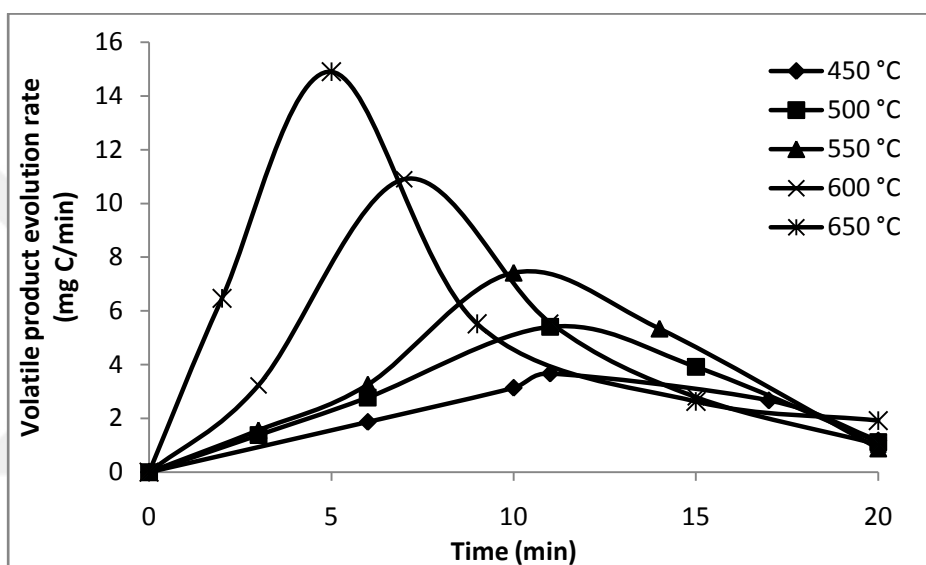


Figure 5.2.12.1 Volatile product evolution rate for isothermal pyrolysis of SASP-F

The total amount of volatile product evolution for isothermal pyrolysis of SASP-F was tabulated in Table 5.2.12.1.

Table 5.2.12.1 Amount of C in feed and C recovered as product in IP of SASP-F

T (°C)	Feed (mg C)	Product (mg C)	VHR (%)
450	385.3	46.7	12.12
500	385.3	62.4	16.20
550	385.3	75.4	19.57
600	385.3	91.7	23.80
650	385.3	117.5	30.50

Volatile hydrocarbon recovery was found as 12.12 %, 16.20 %, 19.57 %, 23.80 % and 30.50 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Figure 5.2.12.2 represents volatile hydrocarbon recovery at each temperature.

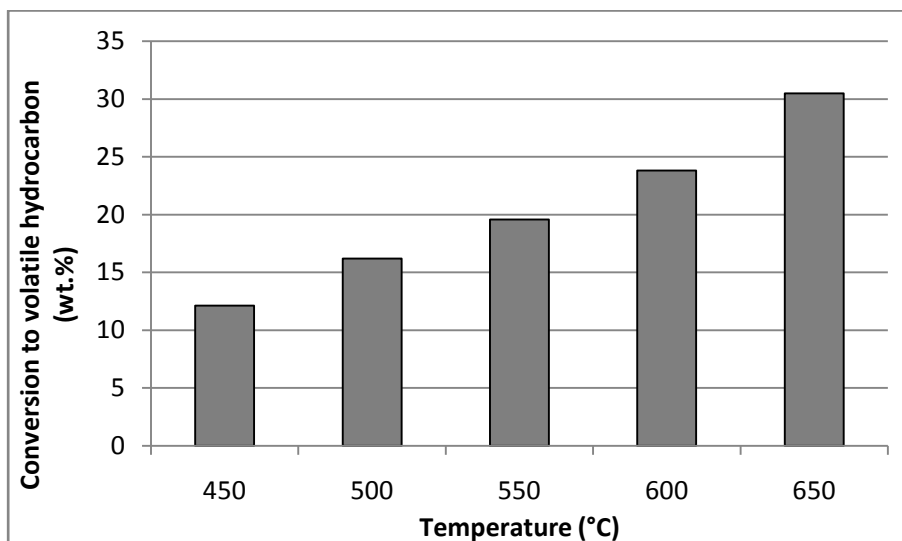


Figure 5.2.12.2 Volatile fraction of recovered hydrocarbons for IP of SASP-F (in carbon basis)

In isothermal pyrolysis, solid residue of SASP-F was found as 57.39 %, 54.51 %, 52.47 %, 50.04 % and 48.89 % weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Conversion values of solid residue at each pyrolysis temperature were given in Figure 5.2.12.3.

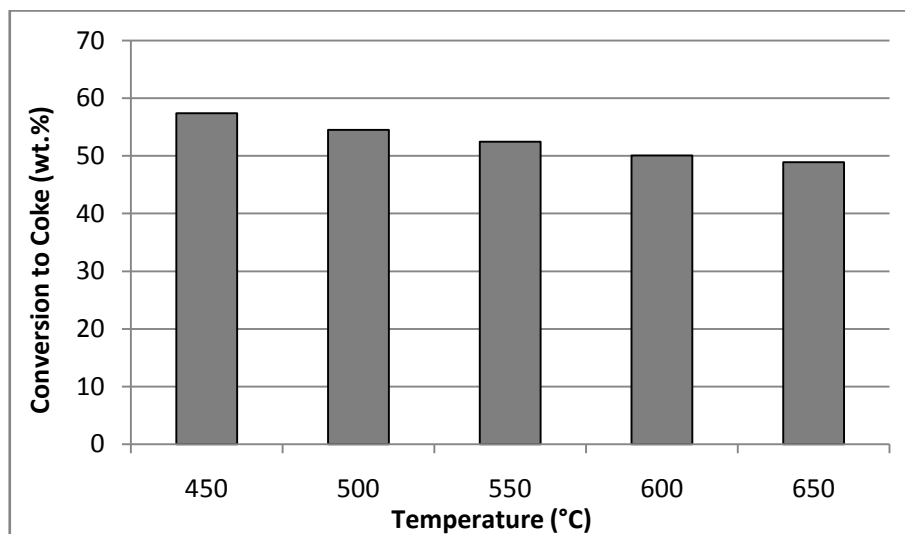


Figure 5.2.12.3 Conversion to solid residue of SASP-F for isothermal pyrolysis (in weight basis)

In isothermal pyrolysis of SASP-F, total hydrocarbon recoveries were calculated as 42.61 %, 45.49 %, 47.53 %, 49.96 % and 51.11 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries in isothermal pyrolysis of SASP-F were shown in Figure 5.2.12.4.

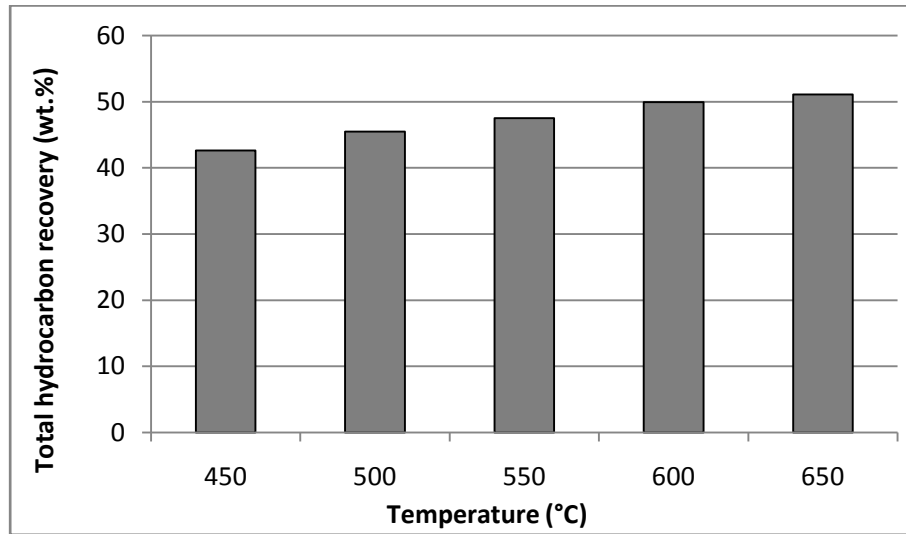


Figure 5.2.12.4 Total hydrocarbon recovery for IP of SASP-F (in weight basis)

The ratios of volatile fraction of the recovered hydrocarbons to the total hydrocarbon recovery was calculated as 0.28, 0.36, 0.41, 0.48, and 0.60 and tabulated at Table 5.2.12.2.

Table 5.2.12.2 The ratio of volatile fraction recovered hydrocarbons to total hydrocarbon recovery in IP of SASP-F

Temperature (°C)	450	500	550	600	650
VFRH/THCR	0.28	0.36	0.41	0.48	0.60

After isothermal pyrolysis of SASP-F, amount of C in solid residue was identified and shown in Figure 5.2.12.5 and given in Table 5.2.12.3.

Table 5.2.12.3 Carbon content in solid residue of SASP-F

Temp. (°C)	Feed (mg C)	Solid residue (mg)	C content of solid residue (% C)	Solid residue (mg C)	C recovered in solid residue (% C)	Asp. + Preasp. (% C)
450	385.3	286.9	77.67	222.84	57.83	30.05
500	385.3	272.3	76.28	207.70	53.90	29.91
550	385.3	262.4	75.12	197.11	51.15	29.28
600	385.3	250.2	74.97	187.57	48.68	27.53
650	385.3	244.4	73.87	180.54	46.85	22.66

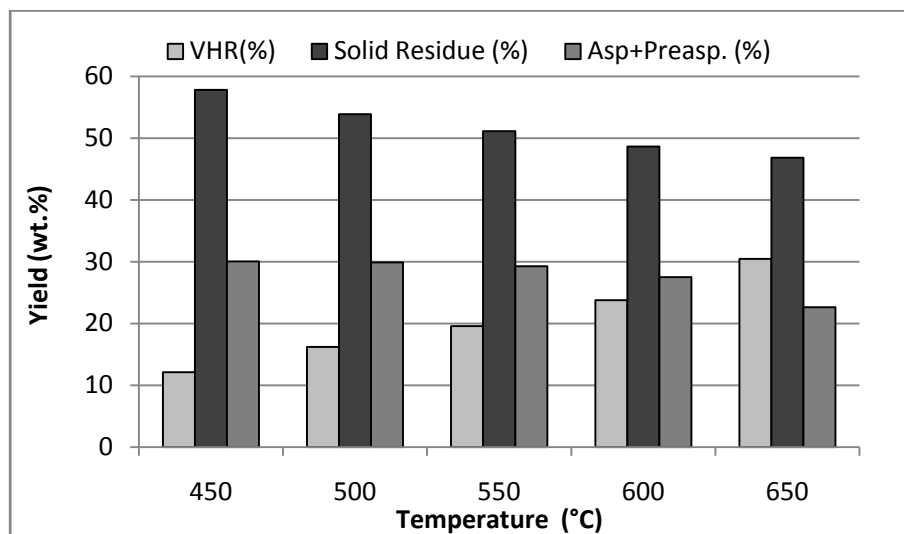


Figure 5.2.12.5 Yield of volatile hydrocarbons, solid residue and Asp+Preasphaltenes for IP SASP-F

At the end of the isothermal pyrolysis of SASP-F, cumulative graphs of n-paraffins and 1-olefins were obtained and shown in Figure 5.2.12.6 and Figure 5.2.12.7.

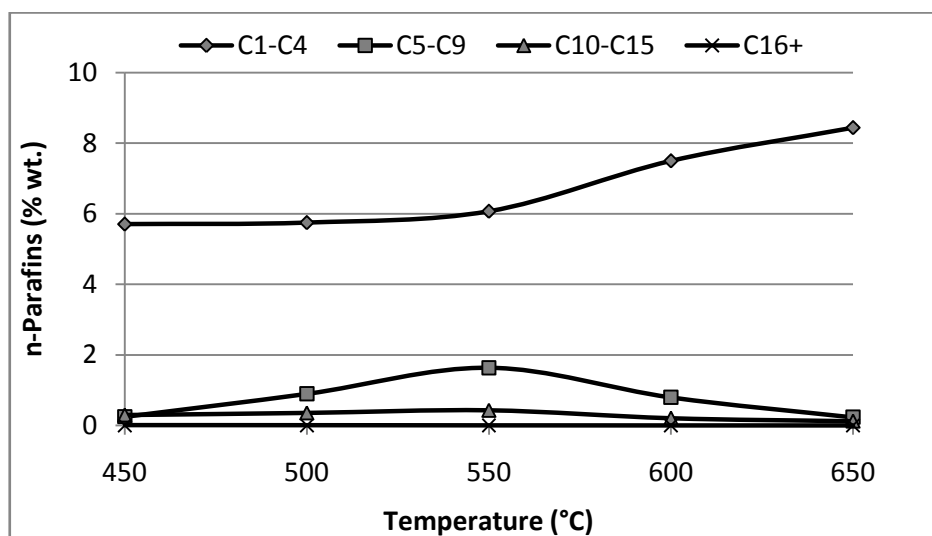


Figure 5.2.12.6 Cumulative n-paraffin selectivity for IP of SASP-F

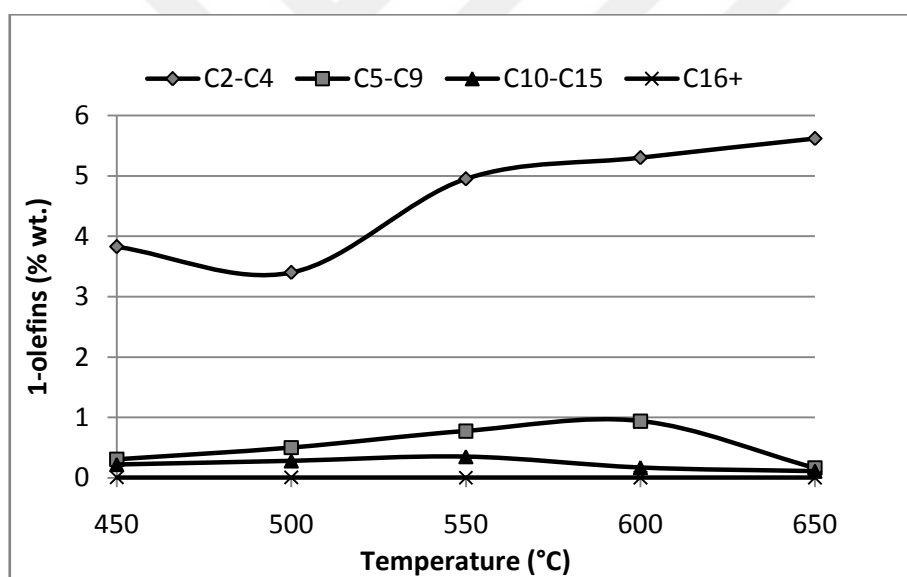


Figure 5.2.12.7 Cumulative 1-olefin selectivity for IP of SASP-F

Cumulative n-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature.

Yield of volatile hydrocarbons decreased after leaching of asphaltite with HCl. Washing with HCl removes CaCO_3 , FeCO_3 and MgCO_3 and partially chlorite minerals from asphaltite structure. Volatile hydrocarbon recoveries for asphaltite were given in Figure 5.2.12.9

The mineral matter of the asphaltites is mainly made up of calcite, dolomite, pyrite, quartz, and minor quantities of feldspar, clay mineral (illite), and gypsum.

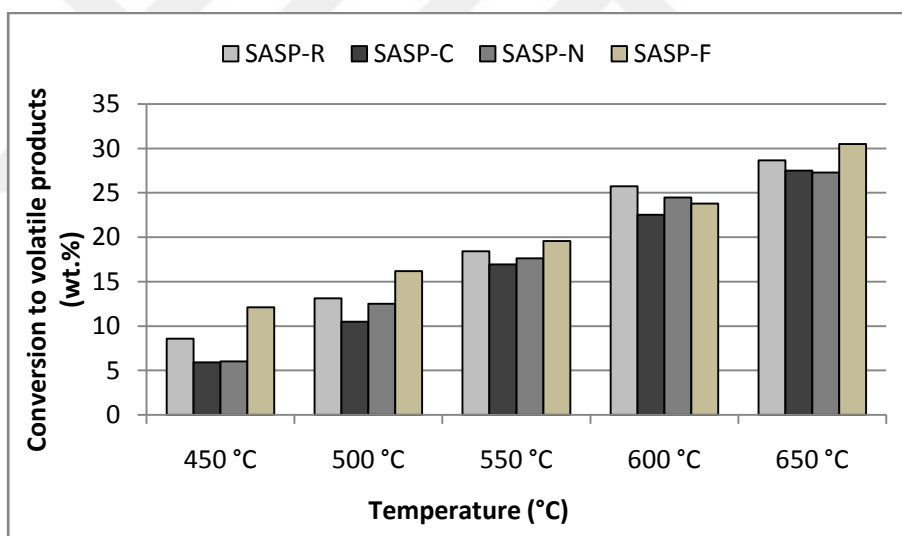


Figure 5.2.12.10 Volatile hydrocarbon recoveries for raw and demineralized asphaltite samples

5.3 Temperature-Programmed Pyrolysis

The effect of the mineral matter of oil shale, asphaltite and lignite on the conversion of organic carbon of these samples into volatile hydrocarbon and carbon in solid residue was investigated by the temperature-programmed pyrolysis of raw and demineralized samples.

5.3.1 Temperature-Programmed Pyrolysis of Oil Shale

Temperature-programmed pyrolysis of raw and demineralized oil shale samples were performed in an electrically heated reactor as described in Section 2.3.

After the completion of each pyrolysis run, products were identified with gas chromatography. After evaluating the chromatograms as described previous section, volatile product evolution rates were determined. The effect of temperature and time on the rate of total product evolution in the pyrolysis of raw Göynük Oil Shale (GOS-R), HCl-treated Göynük Oil Shale (GOS-C), HCl-HNO₃ treated Göynük Oil Shale (GOS-N) and HCl-HNO₃-HF treated Göynük Oil Shale (GOS-F) were shown in Figure 5.3.1.1 - Figure 5.3.1.4.

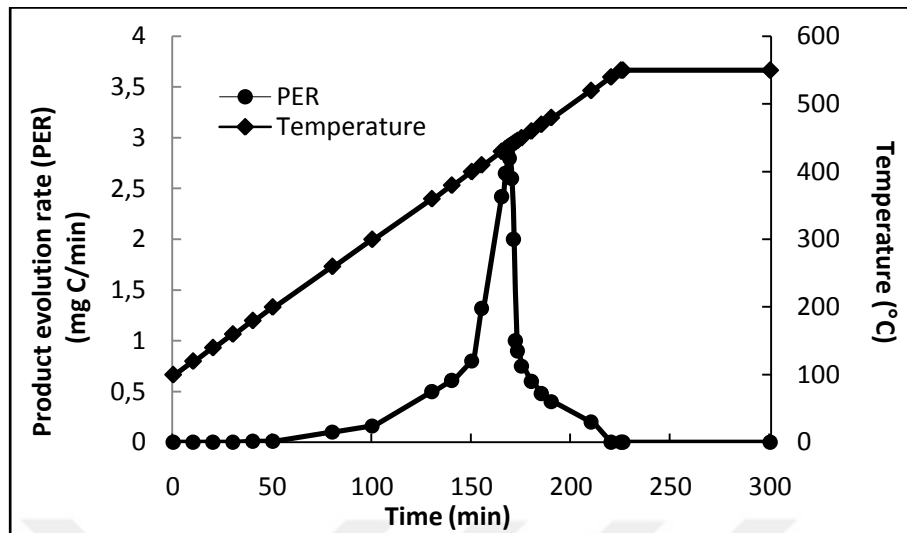


Figure 5.3.1.1 Total product evolution rate of GOS-R

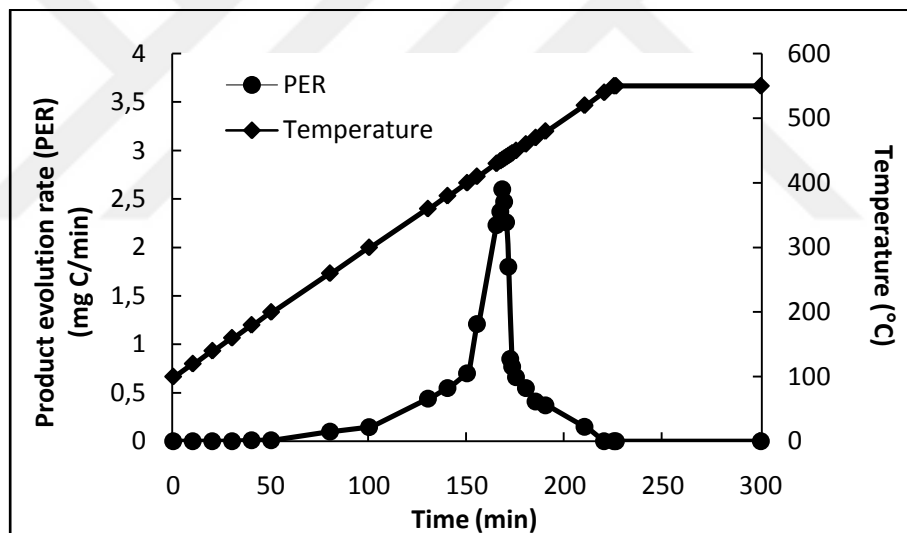


Figure 5.3.1.2 Total product evolution rate of GOS-C

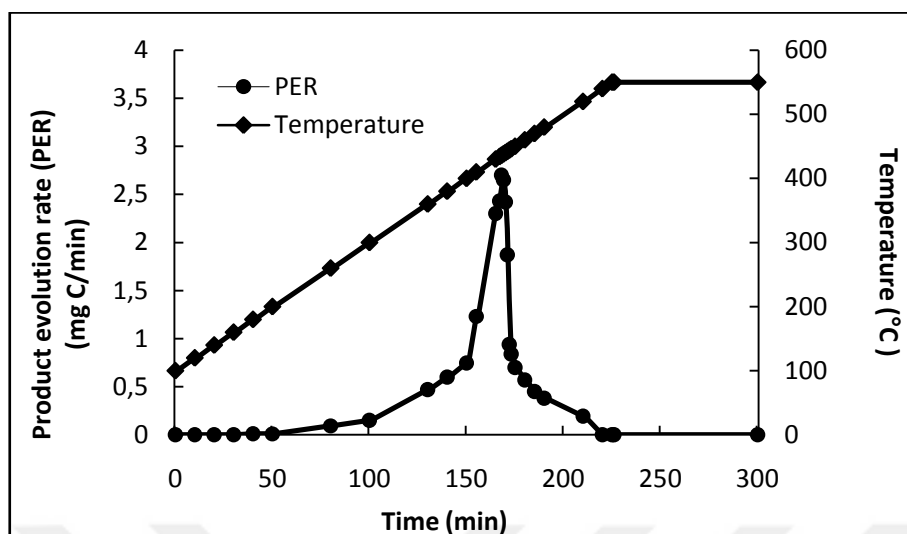


Figure 5.3.1.3 Total product evolution rate of GOS-N

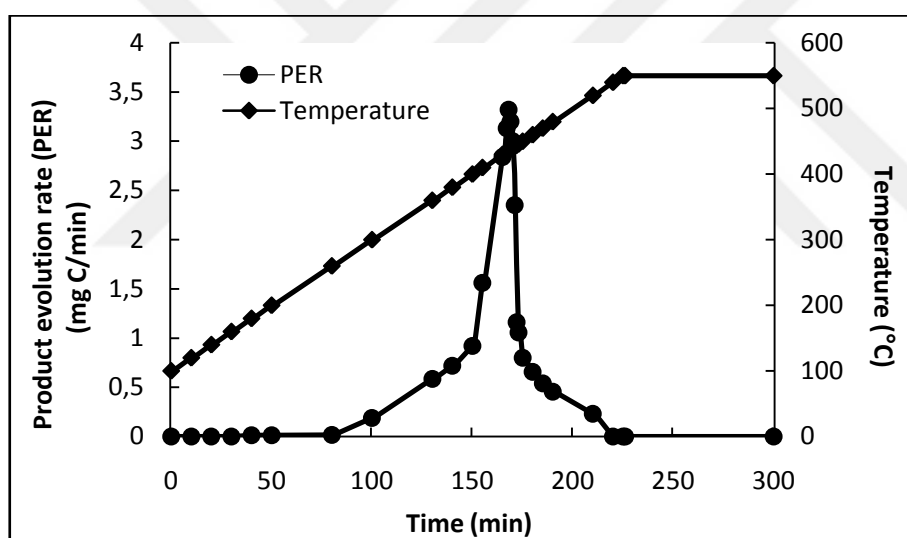


Figure 5.3.1.4 Total product evolution rate of GOS-F

The temperature at which the products evolution is the greatest are seen to be approximately 440°C for each pyrolysis runs.

The n-paraffins produced by GOS-R were classified by C-number, with the results given in Figure 5.3.1.5. In this classification, low molecular weight hydrocarbons (methane, ethane, propane and butane) were combined into one group, C₁–C₄, as shown in Figure 5.3.1.5. The C₅–C₉, C₁₀–C₁₅, and C₁₆+, fractions were also similarly grouped, respectively, at the maximum product evolution temperature.

1-olefins produced by GOS-R, and its demineralization products were classified by C-number, with the results given in Figure 5.3.1.6. In this classification, low-molecular weight hydrocarbons (ethene, propene and butene) were combined into one group, C₂–C₄, as shown in Figure 5.3.1.6. The C₅–C₉, C₁₀–C₁₅, and C₁₆+, fractions were also similarly grouped.

In the same way, distribution of n-paraffins and 1-olefins produced by temperature-programmed pyrolysis of demineralized GOS samples were shown in Figure 5.3.1.7 - Figure 5.3.1.12.

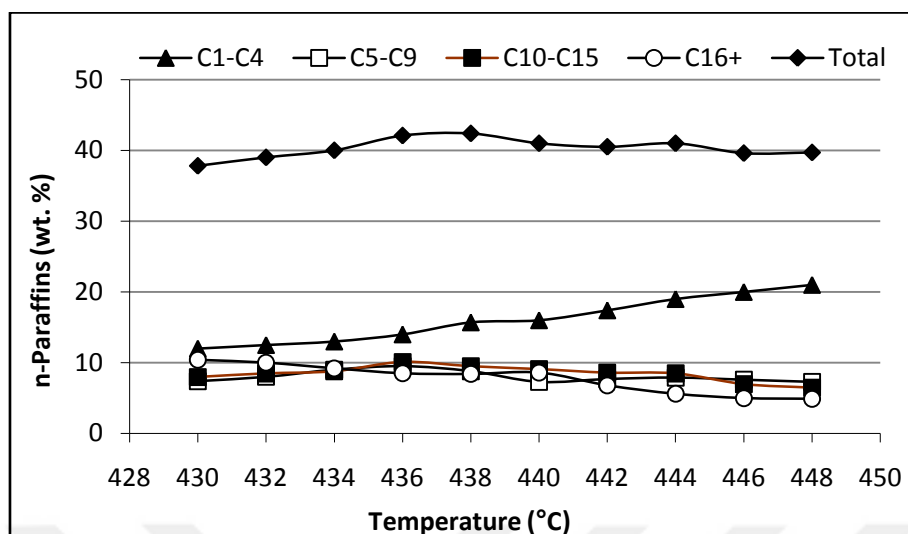


Figure 5.3.1.5 Distribution of n-paraffins in pyrolysis products by carbon number for GOS-R

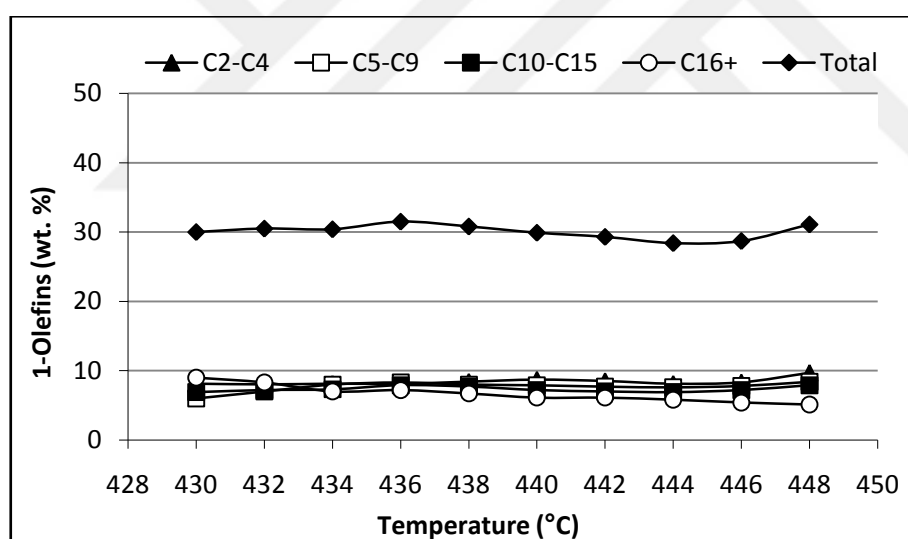


Figure 5.3.1.6 Distribution of 1-olefins in pyrolysis products by carbon number for GOS-R

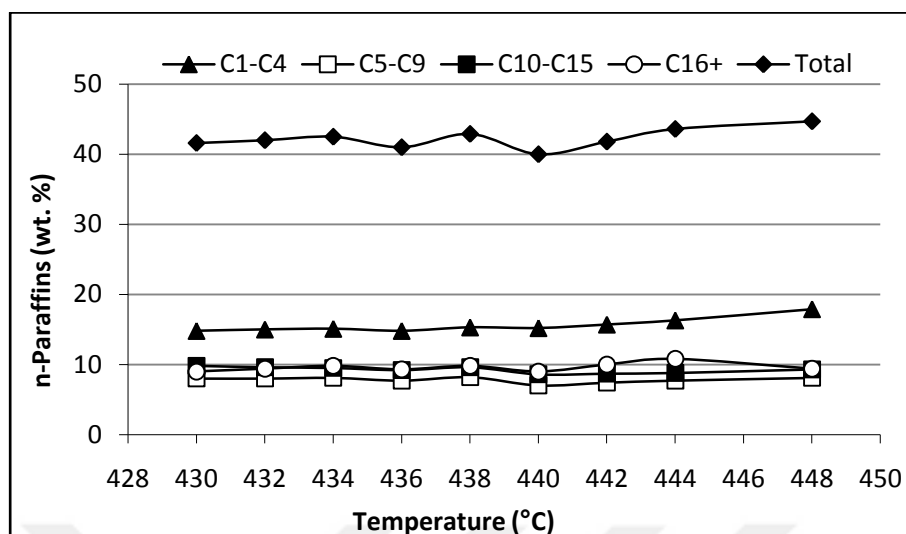


Figure 5.3.1.7 Distribution of n-paraffins in pyrolysis products by carbon number for GOS-C

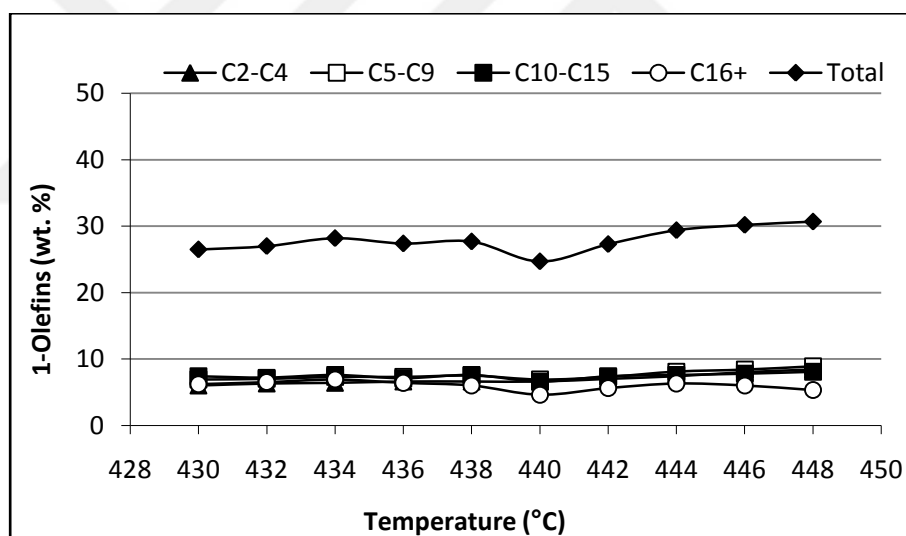


Figure 5.3.1.8 Distribution of 1-olefins in pyrolysis products by carbon number for GOS-C

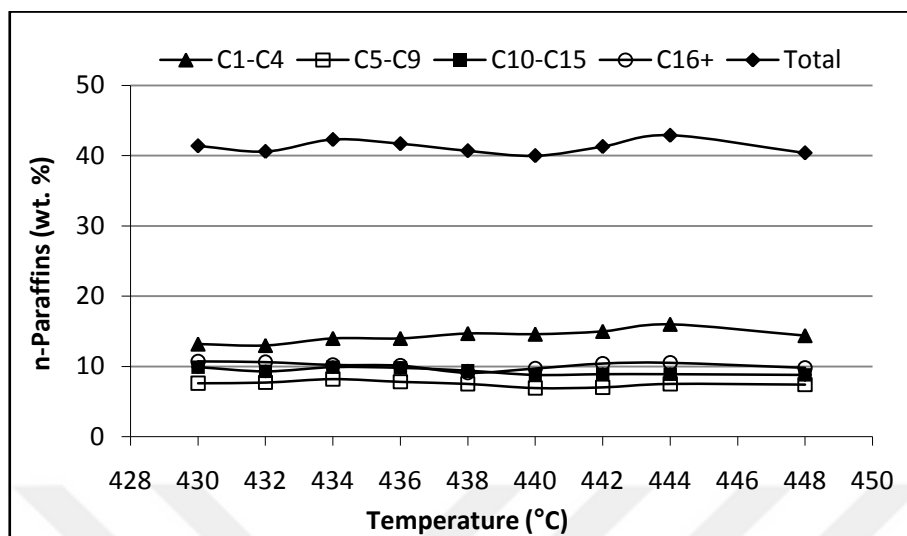


Figure 5.3.1.9 Distribution of n-paraffins in pyrolysis products by carbon number for GOS-N

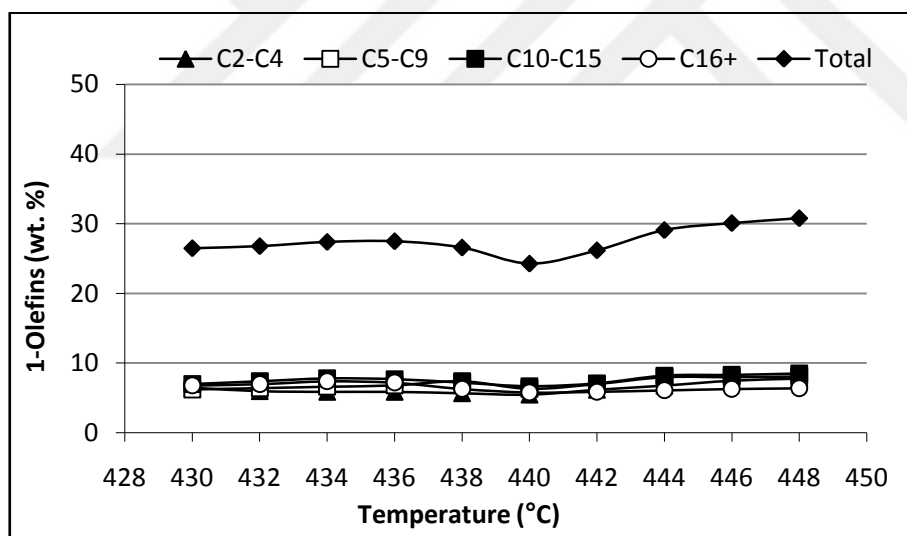


Figure 5.3.1.10 Distribution of 1-olefins in pyrolysis products by carbon number for GOS-N

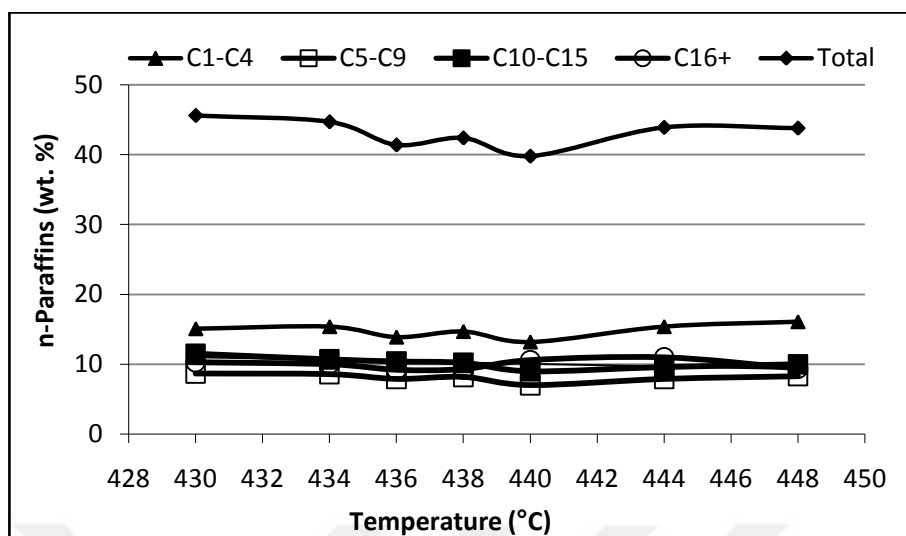


Figure 5.3.1.11 Distribution of n-paraffins in pyrolysis products by carbon number for GOS-F

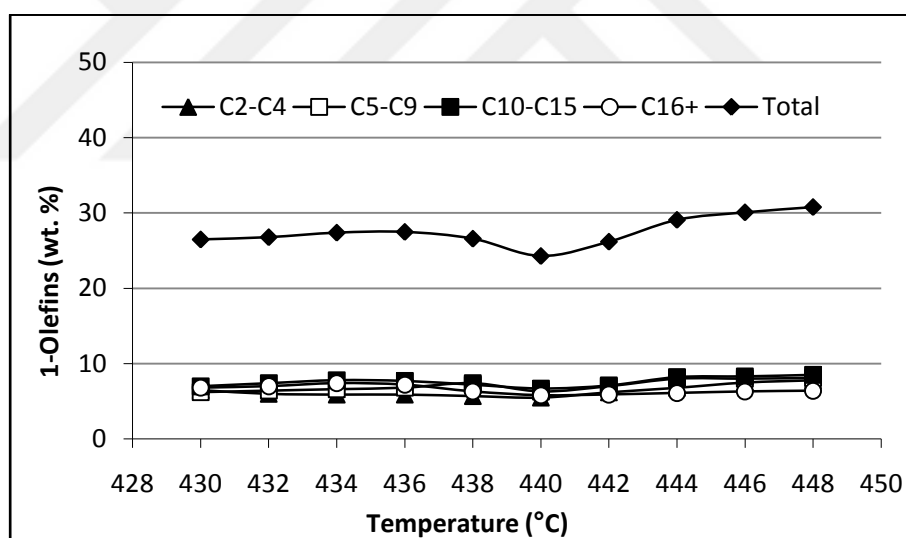


Figure 5.3.1.12 Distribution of 1-olefins in pyrolysis products by carbon number for GOS-F

The *n*-paraffin formation rate is higher than that of 1-olefins. The *n*-paraffins produced at high and low temperature consist mainly of methane. This is because the thermal decomposition of kerogen in oil shale takes place in two broad reaction steps. The first, breakdown of kerogen to bitumen and low-molecular-weight hydrocarbons consisting mainly of methane, occurs at lower temperature. Decomposition of bitumen to gas and oil and formation of heavy fractions by secondary reactions takes place in the second step. The hydrocarbons produced by pyrolysis of GOS-R, GOS-C, GOS-N, and GOS-F contained 41.0 %, 40.0 %, 40.0 %, and 39.8 wt.% of *n*-paraffin, respectively, at the maximum product evolution temperature. The values of 1-olefins produced by pyrolysis of GOS-R, GOS-C, GOS-N, and GOS-F were 29.9 %, 24.7 %, 24.3 %, and 24.8 wt %, respectively, at the maximum product evolution temperature. The *n*-paraffin and 1-olefins produced by GOS-R products were classified by carbon number at the temperature range between 428 and 450 °C. This is the temperature range at which the decomposition rate in pyrolysis is higher than that of the rate for pyrolysis temperatures before and after this range.

The results of *n*-paraffins distribution in the pyrolysis products of GOS-R, GOS-C, GOS-N and GOS-F were summarized in Figure 5.3.1.13.

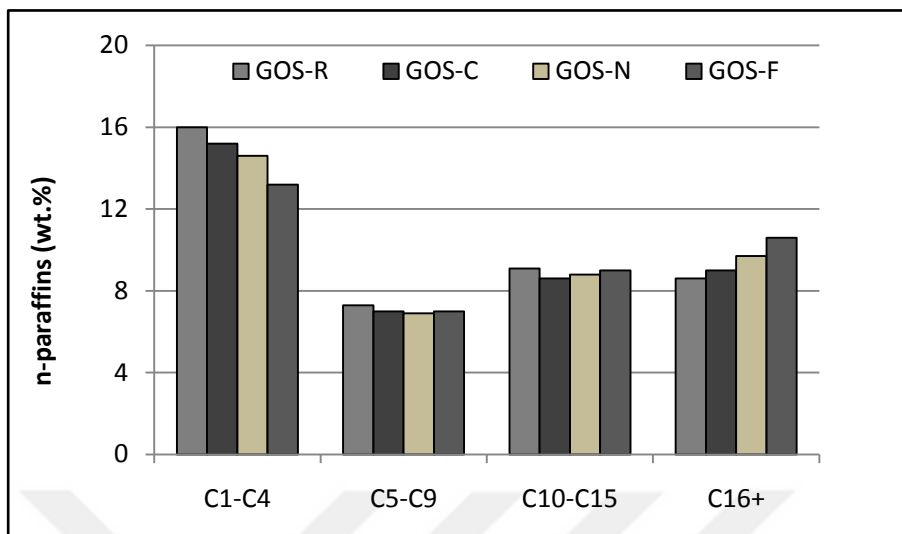


Figure 5.3.1.13 n-Paraffins distribution in pyrolysis of GOS-R, GOS-C, GOS-N and GOS-F at the maximum product evolution temperature

As given in Figure 5.3.1.13, the n-paraffin gas yield (C_1 - C_4) showed a slightly decrease in the pyrolysis of GOS-C, GOS-N, and GOS-F compared to the gas yield in the pyrolysis of GOS-R. The n-paraffin formation rate was higher than that of 1-olefins during pyrolysis. n-Paraffin consists mainly of low-molecular-weight volatile hydrocarbons. The yield of the C_{16+} n-paraffins in the pyrolysis products of GOS-F was found to be slightly higher than that of the C_{16+} n-paraffins in the pyrolysis products of GOS-R, GOS-C, and GOS-N.

The 1-olefin gas yield (C_2 - C_4) showed a slightly decrease in the pyrolysis of GOS-C, GOS-N, and GOS-F compared to the gas yield in the pyrolysis of GOS-R. It was given in Figure 5.3.1.14. The leaching of

mineral matter with HCl, HNO₃, and HF did not cause a marked change in the distribution of 1-olefins by carbon number of C₅-C₉, C₁₀-C₁₅ and C₁₆+

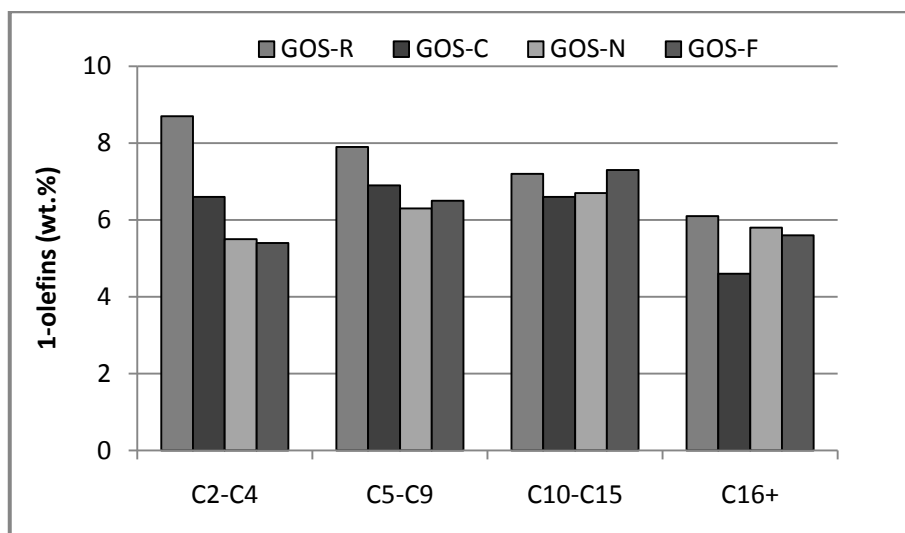


Figure 5.3.1.14 1-olefins distribution in pyrolysis of GOS-R, GOS-C, GOS-N and GOS-F at the maximum product evolution temperature

A carbon balance of the pyrolysis process was established by determining the recovery of total organic carbon as organic products and the carbon remaining in the reactor because of the coking reactions. Changes in the degree of organic conversion in the pyrolysis of GOS-R, GOS-C, GOS-N, and GOS-F are shown in Figure 5.3.1.15.

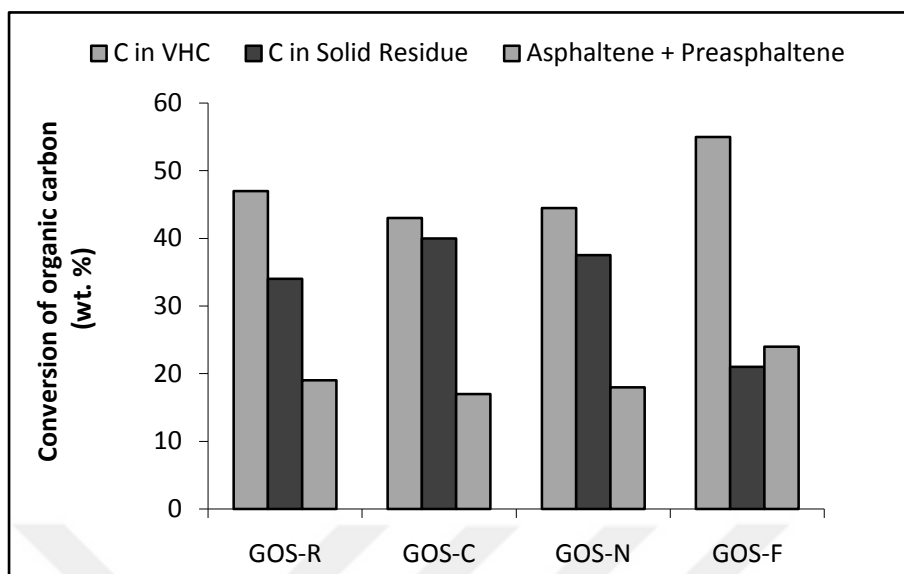


Figure 5.3.1.15 Conversion levels of organic carbon to VHC, polyaromatics (asphaltenes -preasphaltenes)

Carbon balance a calculation showed that 47 wt. % of the organic carbon in GOS-R was converted to volatile organic compounds and 34.0 wt. % was converted to carbon-rich solid residue. Conversion values to volatile hydrocarbons for the GOS-C and GOS-N samples within the same temperature limits were 43.0 % and 44.5 % wt., respectively.

The leaching of the mineral matter with HCl caused a slight decrease in the conversion to volatile hydrocarbons, but the removal of pyrites with HNO_3 did not affect the reactivity of the organic material in the pyrolysis of GOS-N. This behavior can be explained by the presence of mineral matter in the GOS-R samples. Alkali and

alkaline earth metal cations affect the reactivity of oil shales. Removal of these minerals might have changed the behavior of GOS-C in pyrolysis, and thus, GOS-C samples gave rise to lower conversions than GOS-R samples.

Pyrolysis of GOS-F samples gave rise to higher conversions than pyrolysis of GOS-R, GOS-C, and GOS-N samples. Conversion of organic carbon to volatile hydrocarbons for the GOS-F sample within the same temperature limits was 55 wt. %. This result shows that removal of the material soluble in HCl (and also HCl/HNO₃) slightly affected the conversion of organic materials in the pyrolysis reactions. In contrast, removal of the material soluble in HF increased the conversion in the pyrolysis reactions of GOS-F. This behavior can be explained by the inhibitive effect of the silicate minerals. The inhibition effect of the silicates seemed to be greater than the catalytic effect of the calcite minerals in the pyrolysis reactions of GOS-R, GOS-C, and GOS-N. Thus, removal of the silicates by HF washing caused a moderate increase in the production of the volatiles. Our results are in accord with the findings of the Yurum et al. concerning the effect of the mineral matrix on the pyrolysis kinetics of oil shale.

5.3.2 Temperature-Programmed Pyrolysis of Lignite

Temperature-programmed pyrolysis of raw and demineralized lignite samples was performed. After the completion of each pyrolysis run, products were identified with gas chromatography and then volatile product evolution rates were determined. The effect of temperature and time on the rate of total product evolution in the pyrolysis of raw lignite (SLIG-R), HCl-treated lignite (SLIG-C), HCl-HNO₃ treated lignite (SLIG-N) and HCl-HNO₃-HF treated lignite (SLIG-F) were shown in Figure 5.3.2.1 - Figure 5.3.2.4.

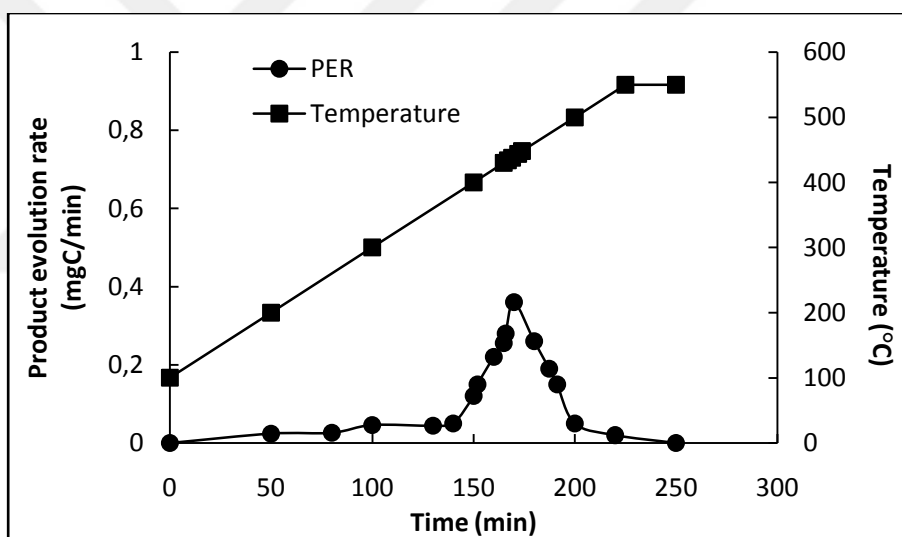


Figure 5.3.2.1 Total product evolution rate of SLIG-R

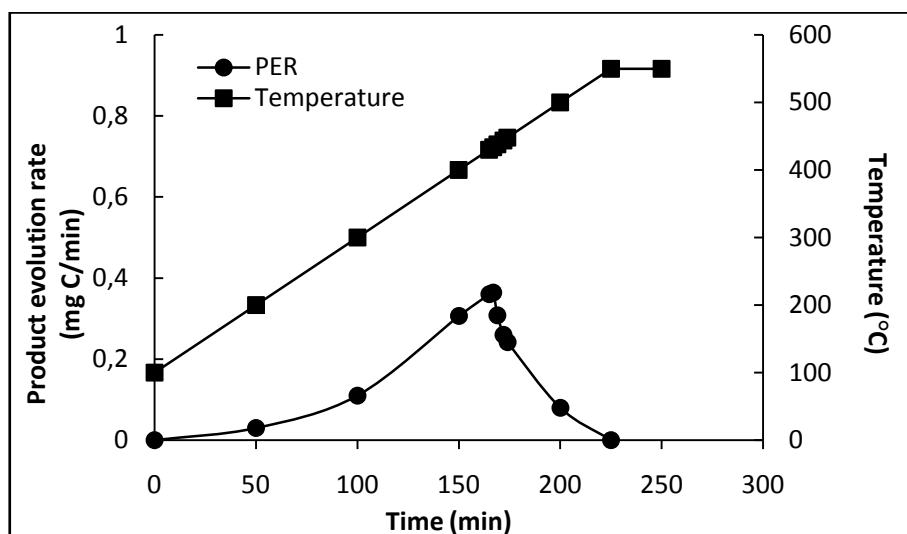


Figure 5.3.2.2 Total product evolution rate of SLIG-C

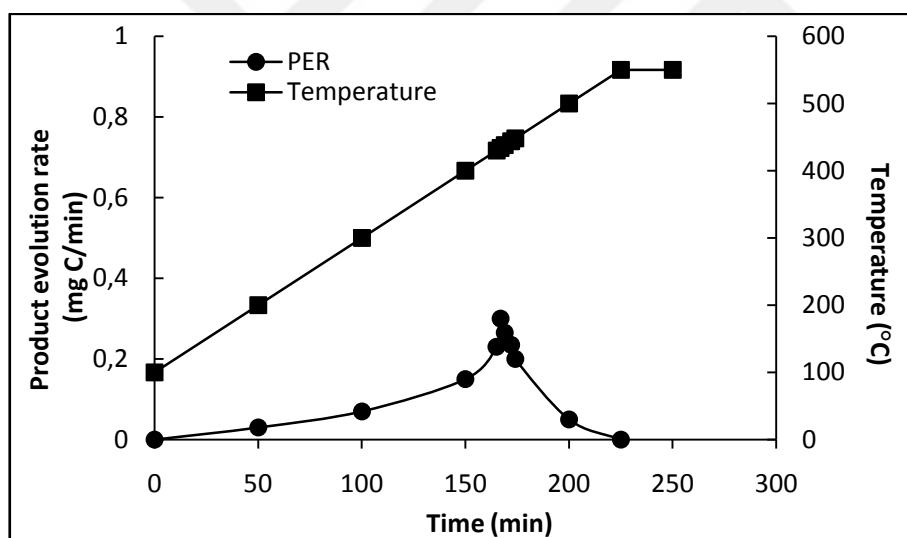


Figure 5.3.2.3 Total product evolution rate of SLIG-N

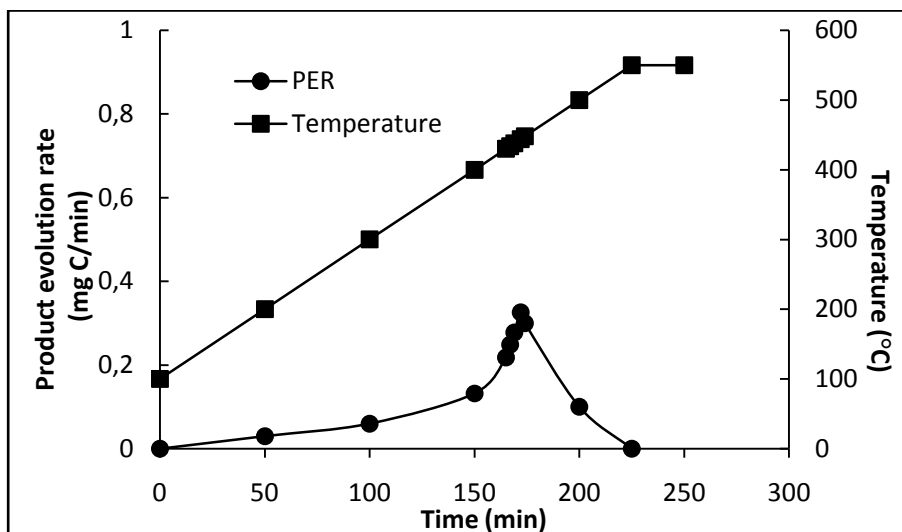


Figure 5.3.2.4 Total product evolution rate of SLIG-F

The temperature at which the products evolution is the greatest are seen to be 440°C for each pyrolysis runs.

The n-paraffins and 1-olefins produced by SLIG-R were classified by C-number, with the results given in Figure 5.3.2.5 and Figure 5.3.2.6, respectively.

In the same way, distribution of n-paraffins and 1-olefins produced by temperature-programmed pyrolysis of demineralized lignite samples were shown in Figure 5.3.2.7 - Figure 5.3.2.8.

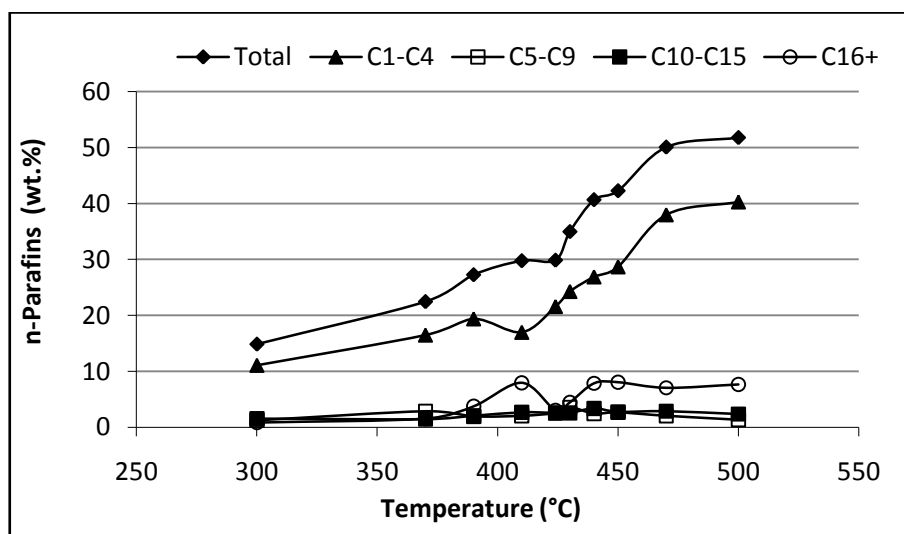


Figure 5.3.2.5 Distribution of n-paraffin in pyrolysis products by carbon number for SLIG-R

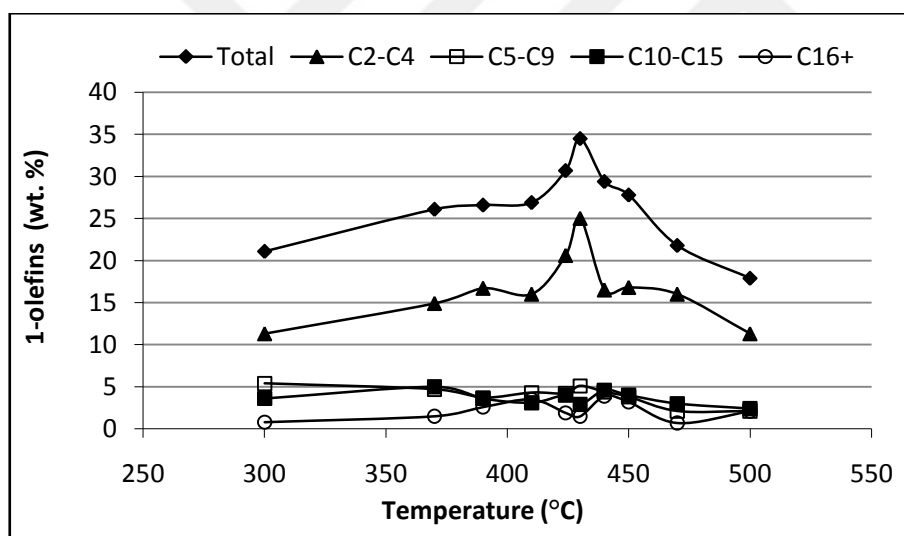


Figure 5.3.2.6 Distribution of 1-olefins in pyrolysis products by carbon number for SLIG-R

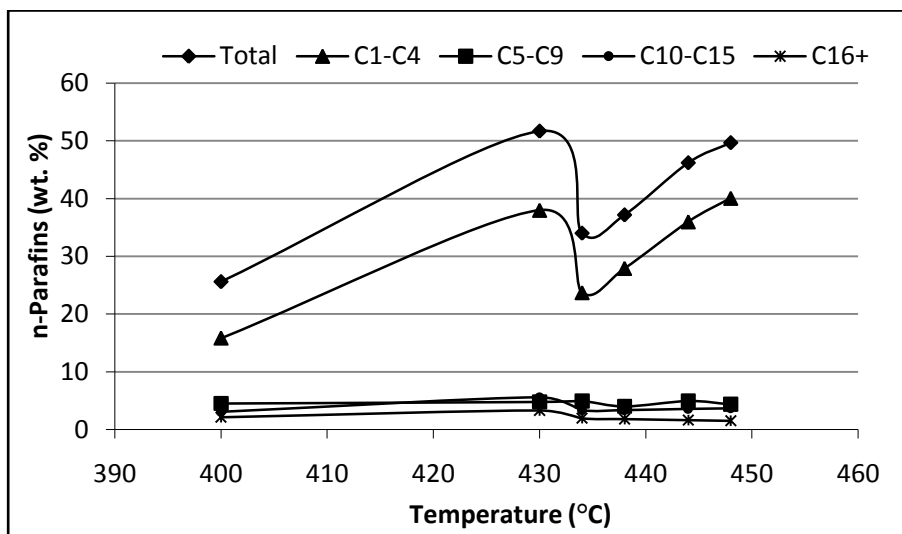


Figure 5.3.2.7 Distribution of n-paraffins in pyrolysis products by carbon number for SLIG-C

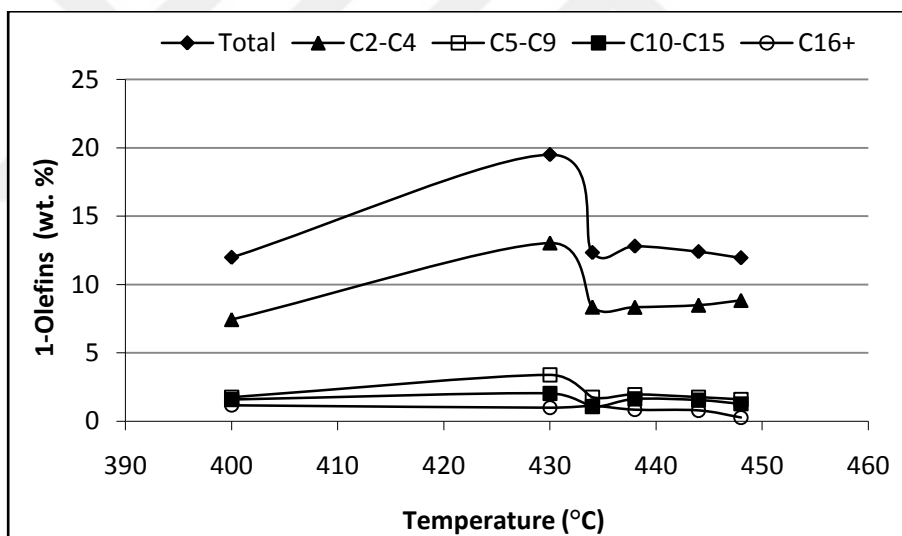


Figure 5.3.2.8 Distribution of 1-olefins in pyrolysis products by carbon number for SLIG-C

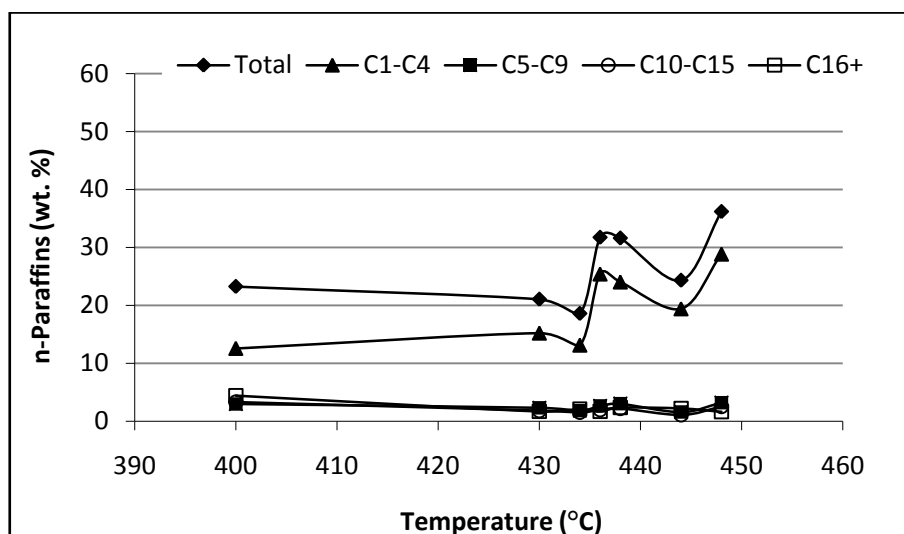


Figure 5.3.2.9 Distribution of n-paraffins in pyrolysis products by carbon number for SLIG-N

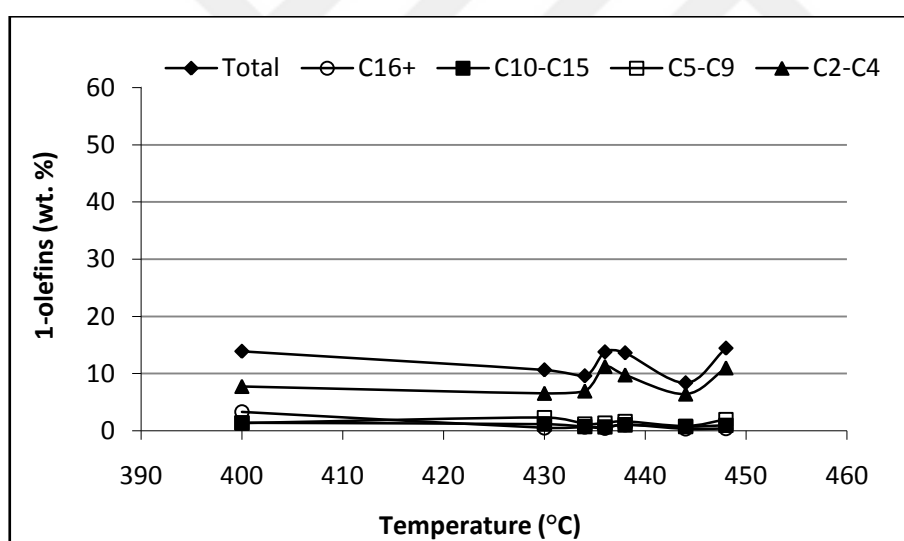


Figure 5.3.2.10 Distribution of 1-olefins in pyrolysis products by carbon number for SLIG-N

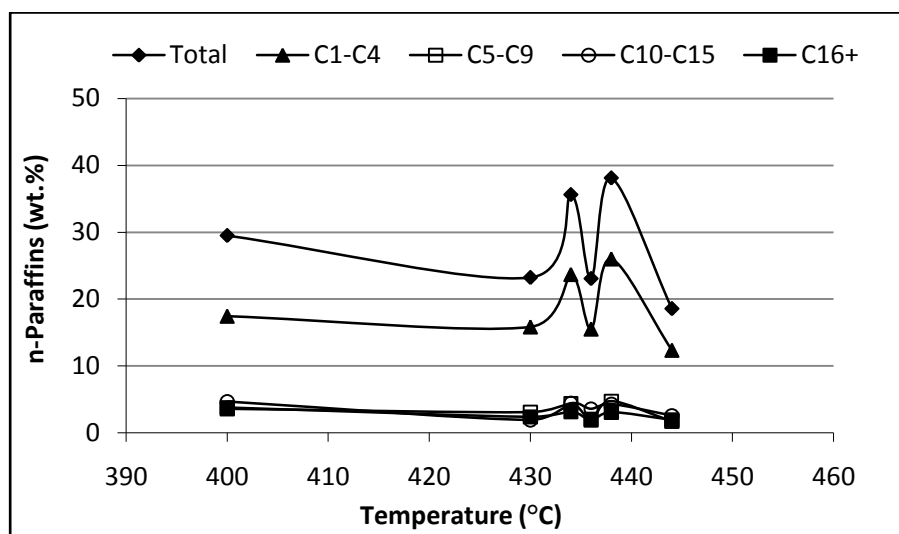


Figure 5.3.2.11 Distribution of n-paraffins in pyrolysis products by carbon number for SLIG-F

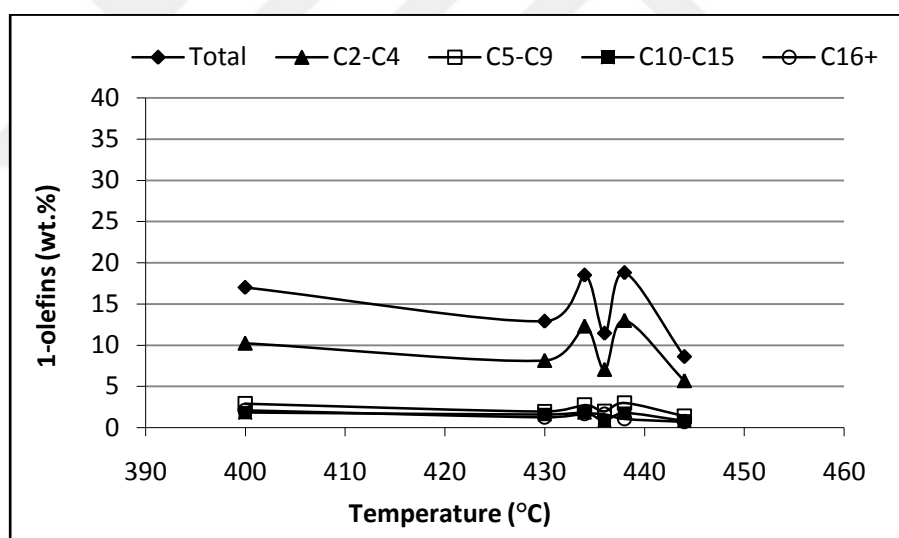


Figure 5.3.2.12 Distribution of 1-olefins in pyrolysis products by carbon number for SLIG-F

Once the primary volatiles are formed in the coal matrix during pyrolysis, their fate is governed by competing recombination, cracking and de-volatilization processes. The transport of the primary volatile occurs in three stages:

- transport of the volatile to the external surface of coal particles,
- removal of the volatile from the external surface of the coal into the bulk gas phase,
- transport of the volatile in the gas phase from the hot zone to cool parts of the system.

In pyrolysis, coal is converted thermally into gas, liquid and solid products through primary de-volatilization reactions. Thermally unstable primary volatile products can undergo secondary reactions during any of the above mentioned stages. Such reactions lead either to cracking into smaller molecular mass products or re-polymerization towards char production. The analysis of samples taken at the different time intervals during the pyrolysis of lignite indicated a change in the C-number distribution of n-paraffins and 1-olefins. The n-paraffins formation rate is higher than that of 1-olefins at each temperature as shown in Figure 5.3.2.9 and Figure 5.3.2.10, respectively. n-Paraffins consist mainly of low-molecular weight hydrocarbons such as C_1 – C_4 and high-molecular weight volatile hydrocarbons such as C_{16+} fractions. This is interpreted that lignite in pyrolysis processing breakdown thermally to form low-molecular weight fragments, which are

extremely labile, and immediately start to undergo secondary condensation reactions to form char/coke with the co-production of condensable and non-condensable volatiles. The reactions involved in coal pyrolysis include cleavage and ring opening of large molecules with addition of hydrogen to stabilize the products.

The *n*-paraffin formation rate is higher than that of 1-olefins. The hydrocarbons produced by pyrolysis of SLIG-R, SLIG-C, SLIG-N, and SLIG-F contained 35.0 %, 35.9 %, 41.7 %, and 34.6 wt % of *n*-paraffin, respectively, at the maximum product evolution temperature.

The values of 1-olefins produced by pyrolysis of SLIG-R, SLIG-C, SLIG-N, and SLIG-F were 34.5 %, 6.7 %, 10.6 %, and 10.2 wt %, respectively, at the maximum product evolution temperature.

The results of *n*-paraffin and 1-olefin distribution in the pyrolysis products of SLIG-R, SLIG-C, SLIG-N and SLIG-F were summarized in Figure 5.3.2.13 and Figure 5.3.2.14

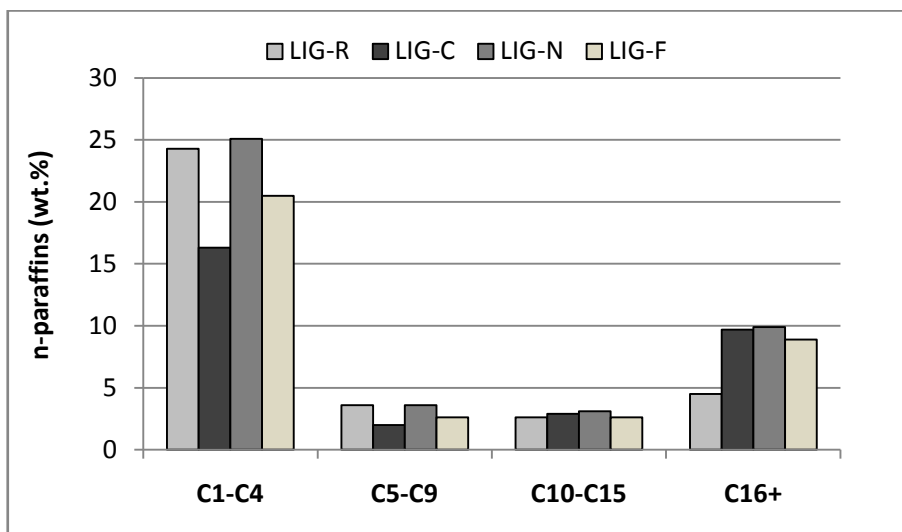


Figure 5.3.2.13 n-Paraffins distribution in pyrolysis of SLIG-R, SLIG-C, SLIG-N and SLIG-F at the maximum product evolution temperature

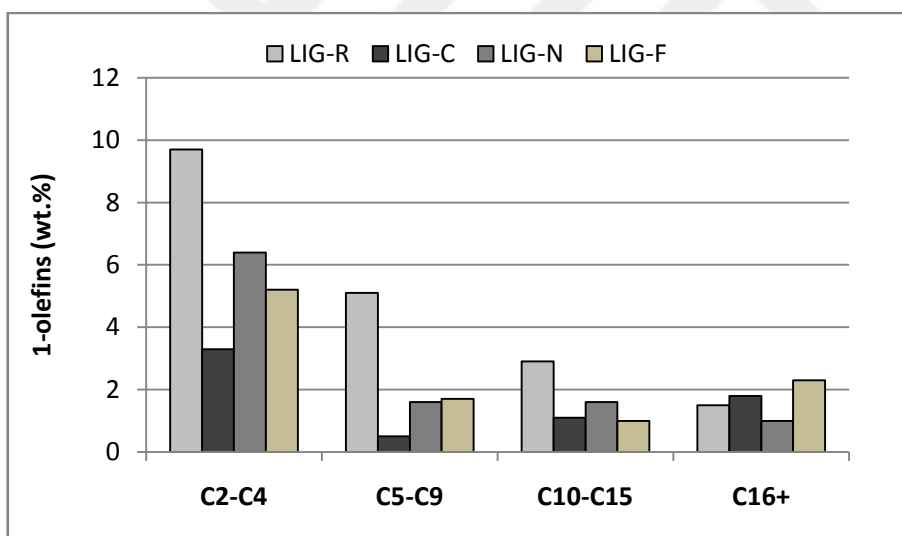


Figure 5.3.2.14 1-olefins distribution in pyrolysis of SLIG-R, SLIG-C, SLIG-N and SLIG-F at the maximum product evolution temperature

As shown from Figure 5.3.2.13, the n-paraffin gas yield (C_1 - C_4) showed a sharply increase in the pyrolysis of SLIG-C compared to the gas yield in the pyrolysis of SLIG-R, SLIG-N and SLIG-F.

The yield of the C_{16+} n-paraffins in the pyrolysis products of SLIG-N was found to be higher than that of the C_{16+} n-paraffins in the pyrolysis products of SLIG-R, SLIG-C, and SLIG-F. Leaching of mineral matter with HCl causes the polymerization reactions, and yield of C_1 - C_4 decreases, yield of C_{16+} increases.

The 1-olefin gas yield (C_2 - C_4) showed a sharply decrease in the pyrolysis of SLIG-C, SLIG-N, and SLIG-F compared to the gas yield in the pyrolysis of SLIG-R. Demineralization process increases n-paraffin formation, and decreases the 1-olefin. The leaching of mineral matter with HCl, HNO_3 , and HF did not cause a marked change in the distribution of 1-olefins by carbon number of C_5 - C_9 , C_{10} - C_{15} and C_{16+} .

5.3.3 Temperature-Programmed Pyrolysis of Asphaltite

Temperature-programmed pyrolysis of raw and demineralized asphaltite samples was performed. After the completion of each pyrolysis run, products were identified with gas chromatography and then volatile product evolution rates were determined. The effect of temperature and time on the rate of total product evolution in the pyrolysis of raw asphaltite (SASP-R), HCl-treated asphaltite (SASP-C), HCl-HNO₃ treated asphaltite (SASP-N) and HCl-HNO₃-HF treated asphaltite (SASP-F) were shown in Figure 5.3.3.1 - Figure 5.3.3.4.

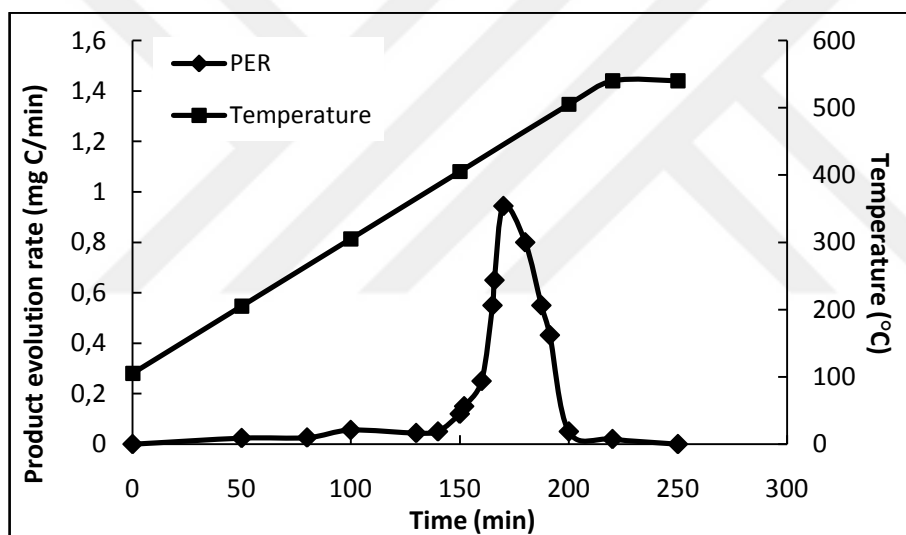


Figure 5.3.3.1 Total product evolution rates of SASP-R

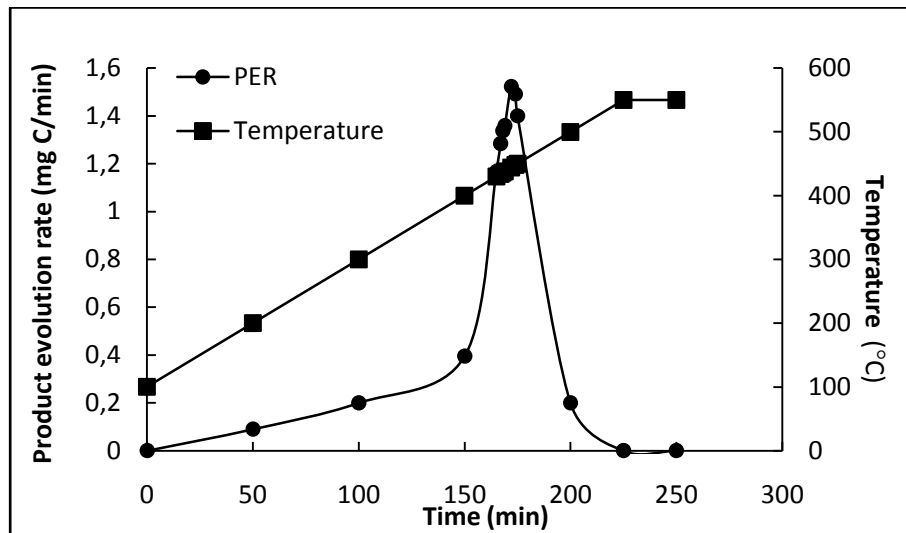


Figure 5.3.3.2 Total product evolution rates of SASP-C

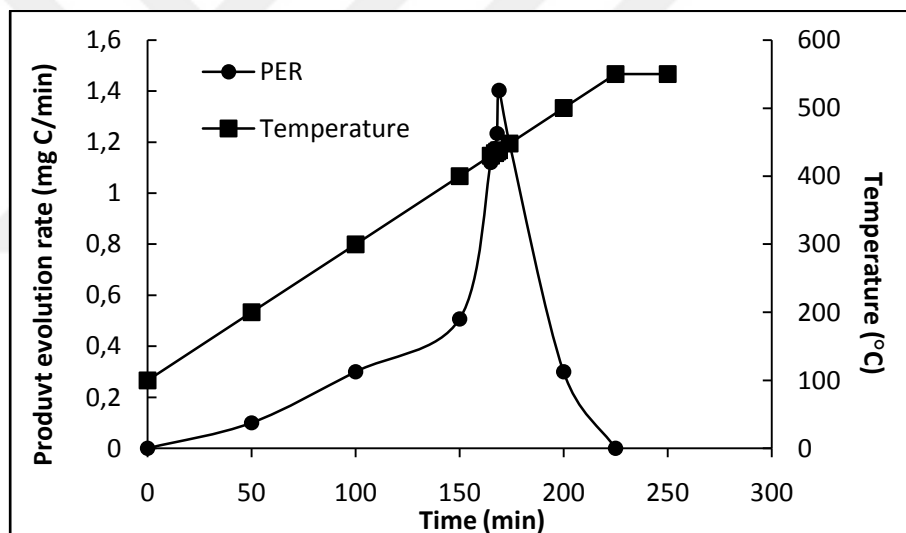


Figure 5.3.3.3 Total product evolution rates of SASP-N

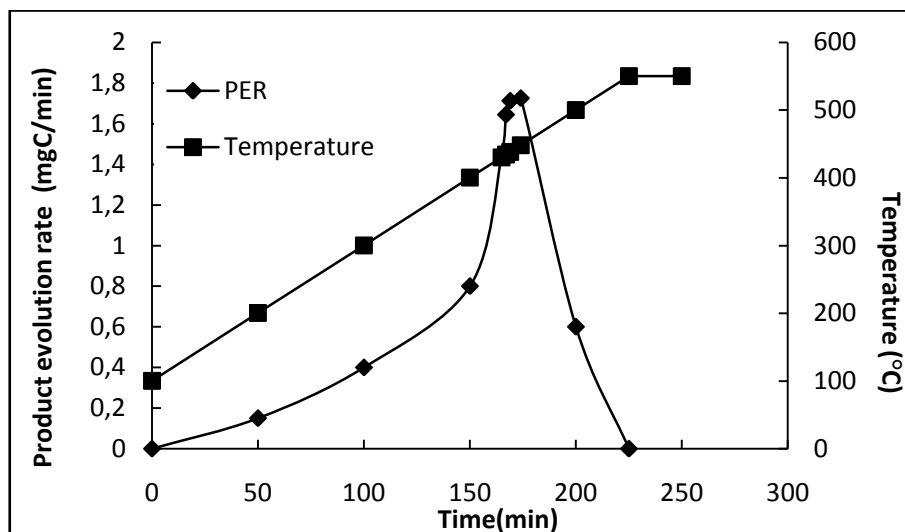


Figure 5.3.3.4 Total product evolution rates of SASP-F

The temperature at which the products evolution is the greatest are seen to be 440°C for each pyrolysis runs.

The n-paraffins and 1-olefins produced by SASP-R were classified by C-number, with the results given in Figure 5.3.3.5 and Figure 5.3.3.6, respectively.

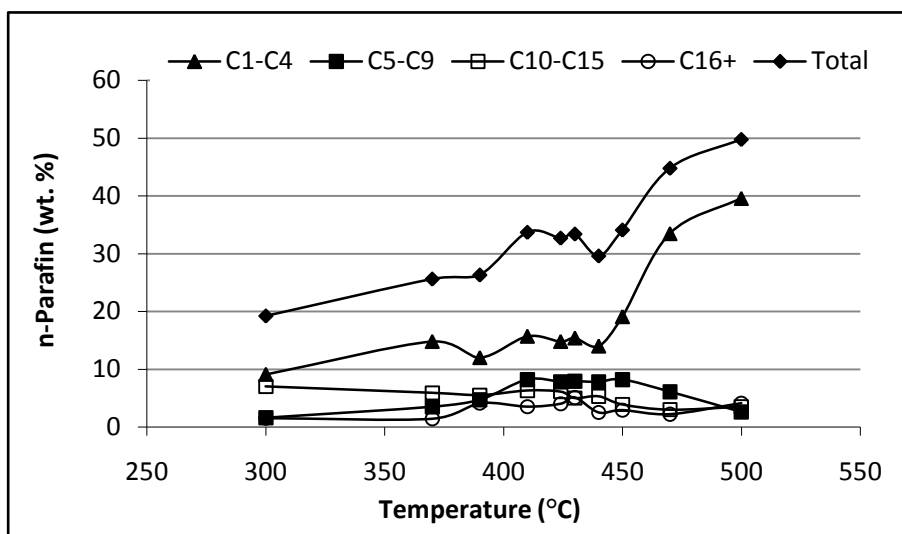


Figure 5.3.3.5 Distribution of n-paraffins in pyrolysis products by carbon number for SASP-R

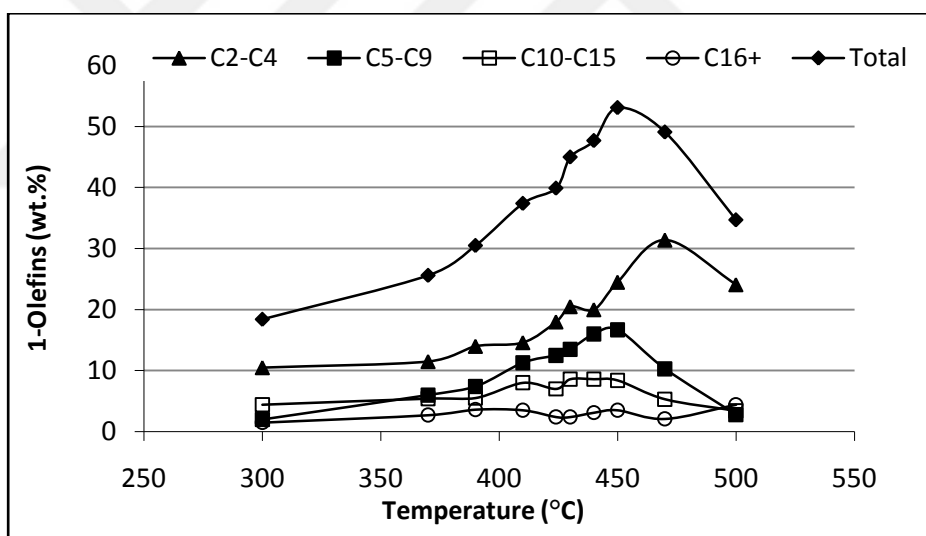


Figure 5.3.3.6 Distribution of 1-olefins in pyrolysis products by carbon number for SASP-R

Asphaltites are generally believed to be formed by migration of petroleum followed by alteration burial. Light fractions are lost, and a variety of biodegradation, oxidation and other chemical reactions are thought to occur with a concomitant increase in molecular weight and decrease in H/C ratio.

Coal and asphaltite are different in origin and the effects originating in the alteration of the original oil during asphaltite formation are shown by the content and analysis of the n-paraffins and 1-olefins. The smooth n-alkane and 1-olefins distribution and the predominance of C₅–C₉, C₁₀–C₁₅ series in the pyrolysis product distribution are both indicative for the effect of the different origin. The analysis of products collected at different time intervals during the pyrolysis of asphaltite indicated also a change in the C-number distribution of n-paraffins and 1-olefins. The n-paraffins formation rate is higher than that of 1-olefins at each temperature.

In the same way, distribution of n-paraffins and 1-olefins produced by temperature-programmed pyrolysis of demineralized SASP samples were shown in Figure 5.3.3.7 - Figure 5.3.3.12.

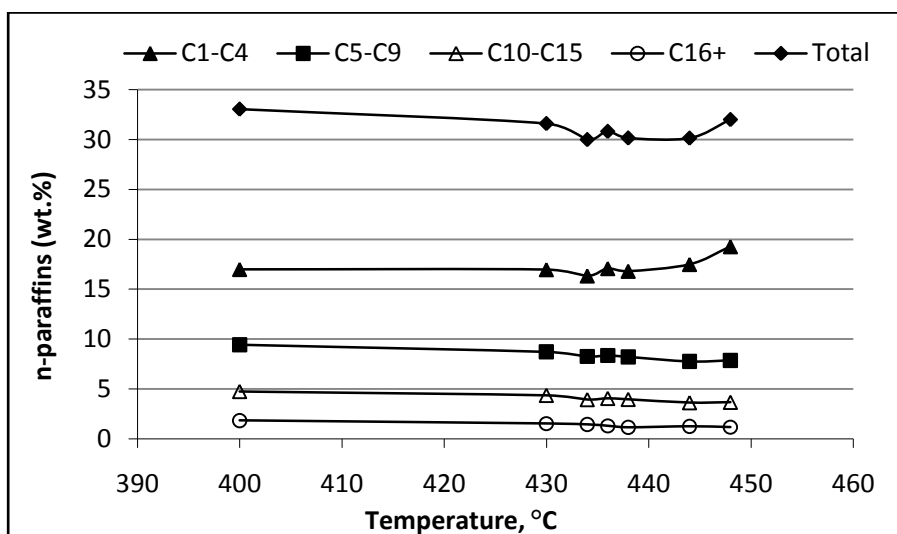


Figure 5.3.3.7 Distribution of n-paraffins in pyrolysis products by carbon number for SASP-C

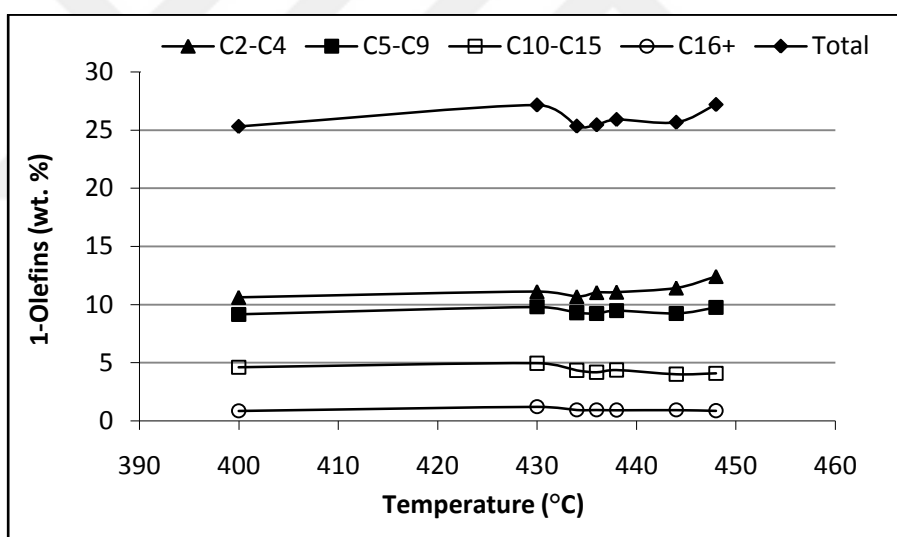


Figure 5.3.3.8 Distribution of 1-olefins in pyrolysis products by carbon number for SASP-C

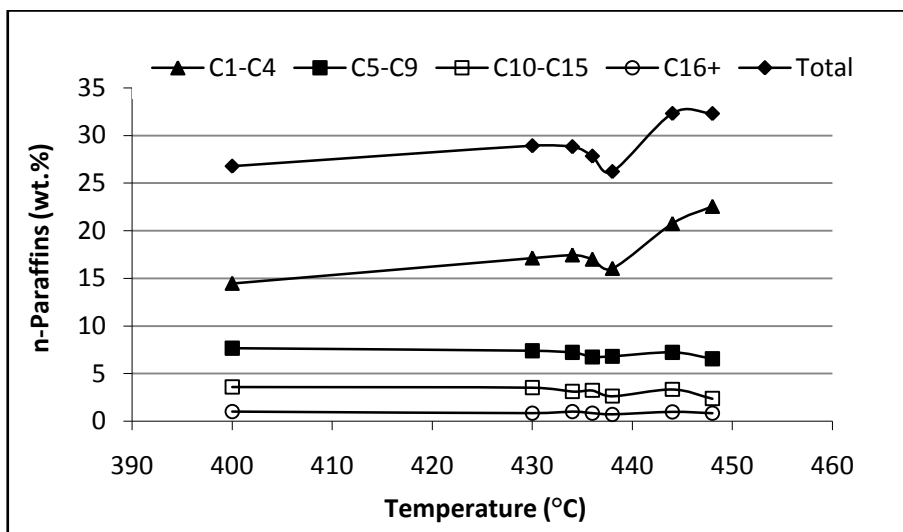


Figure 5.3.3.9 Distribution of n-paraffins in pyrolysis products by carbon number for SASP-N

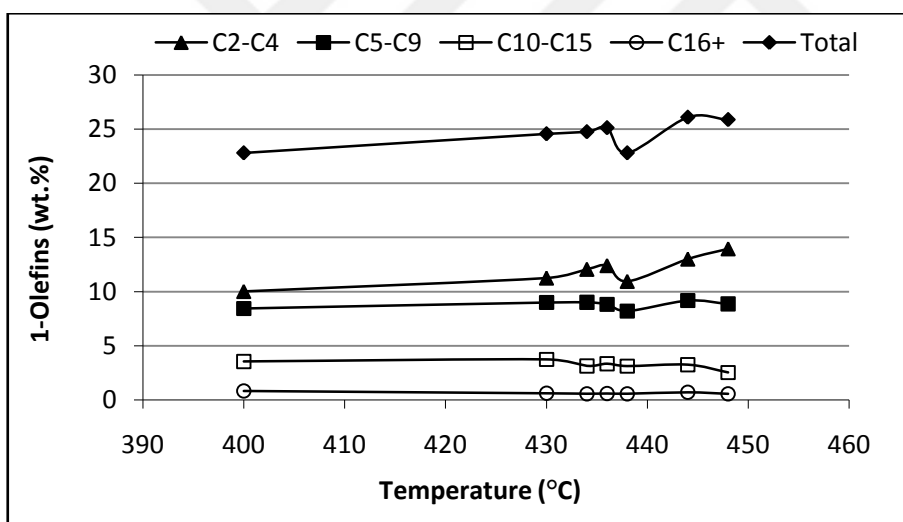


Figure 5.3.3.10 Distribution of 1-olefins in pyrolysis products by carbon number for SASP-N

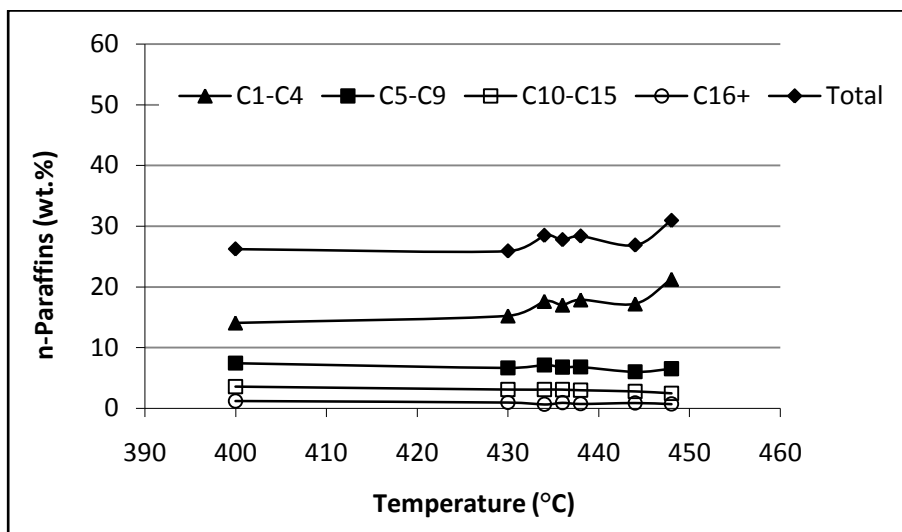


Figure 5.3.3.11 Distribution of n-paraffins in pyrolysis products by carbon number for SASP-F

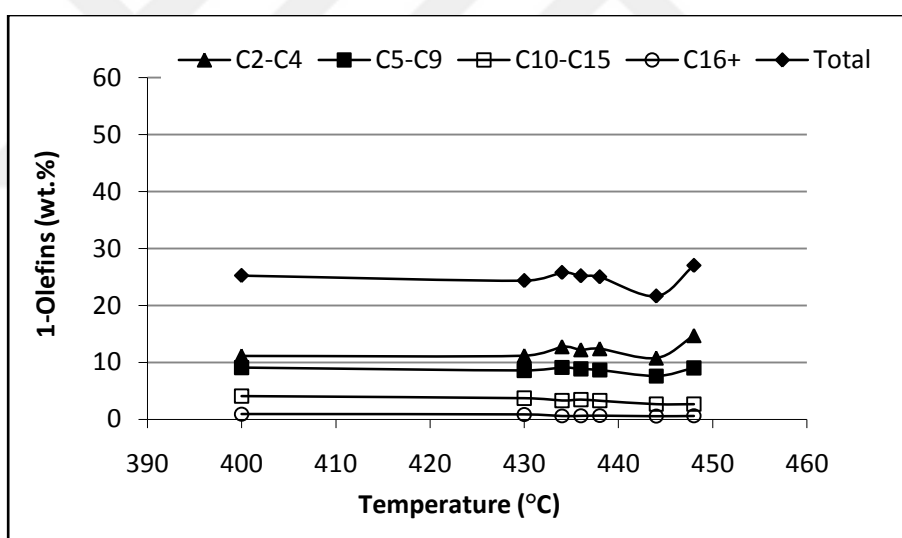


Figure 5.3.3.12 Distribution of 1-olefins in pyrolysis products by carbon number for SASP-F

The hydrocarbons produced by pyrolysis of SASP-R, SASP-C, SASP-N, and SASP-F contained 33.4 %, 31.6 %, 28.9 %, and 25.9 wt % of *n*-paraffin, respectively, at the maximum product evolution temperature.

The values of 1-olefins produced by pyrolysis of SASP-R, SASP-C, SASP-N, and SASP-F were 45.0 %, 27.2 %, 24.6 %, and 24.4 % wt %, respectively, at the maximum product evolution temperature.

The results of *n*-paraffins distribution in the pyrolysis products of SASP-R, SASP-C, SASP-N and SASP-F were summarized in Figure 5.3.3.13.

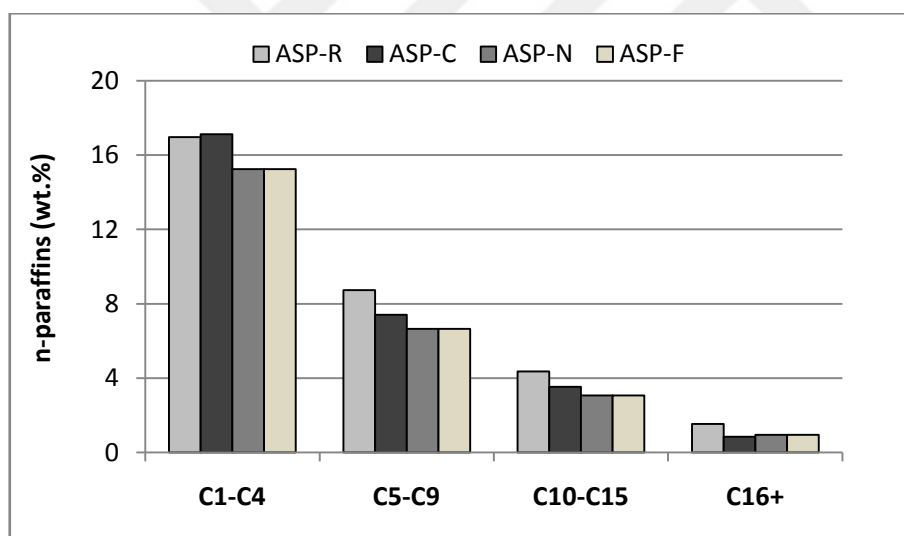


Figure 5.3.3.13 n-Paraffins distribution in pyrolysis of SASP-R, SASP-C, SASP-N and SASP-F at the maximum product evolution temperature

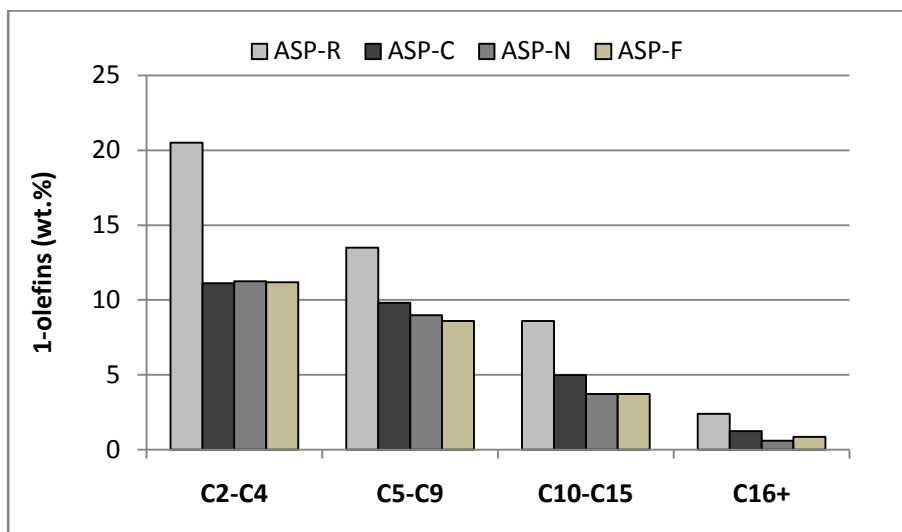


Figure 5.3.3.14 1-olefins distribution in pyrolysis of SASP-R, SASP-C, SASP-N and SASP-F at the maximum product evolution temperature

As shown from Figure 5.3.3.13 and Figure 5.3.3.14, heavier fractions and liquid products decomposed to gas products of SASP-R. So, heavy fractions become very small when compared to C₁-C₄ and C₂-C₄ groups.

The analysis of samples taken at the different time intervals during the pyrolysis of asphaltite indicated also a change in the C-number distribution of n-paraffins and 1-olefins. n-Paraffins consist mainly of low-molecular weight hydrocarbons such as C₁-C₄ in aliphatic hydrocarbon fraction of the pyrolysis products of asphaltite.

5.4 Solvent Swelling Studies

5.4.1 Solvent Swelling of Göynük Oil Shale

The investigations were performed with oil shale sample obtained from Göynük-Bolu shale deposits in Turkey. Swelling behaviour of raw and HCl-HF treated GOS samples were studied by using the volumetric swelling technique.

All solvents used in swelling experiments were listed in Table 5.4.1.1. Solvent swelling procedure was given in Section 4.2.4. The volumetric swelling ratios were calculated as

$$Q_v = \frac{h_2}{h_1} \quad (5.4.1.1)$$

where h_1 , is the height of sample bed before swelling and h_2 is the height of sample bed after swelling (at equilibrium)

$$Q_v = \frac{(v_c + v_s)}{v_c} \quad (5.4.1.2)$$

where v_s , is the volume of solvent absorbed by a unit volume of oil shale, v_c .

Table 5.4.1.1 Solvent used for swelling of raw and demineralized oil shale and their solubility parameters. δ (cal/cm³)^{1/2}

Solvent	Type	δ (cal/cm ³) ^{1/2}
Acetonitrile	Polar	11.9
Nitromethane	Polar	12.7
Nitrobenzene	Polar	10.0
Isopropil Alcohol	H-bonding	11.5
Ethanol	H-bonding	12.8
Dimethyl Sulfoxide	H-bonding	13.0
Tetrahydrofuran	H-bonding	9.10
Pyridine	H-bonding	10.7
Tetralin	Nonpolar	9.50
Cyclohexane	Nonpolar	8.20
n-Heptane	Nonpolar	7.40
Benzene	Nonpolar	8.20
Carbon tetrachloride	Nonpolar	9.60
n- Hexane	Nonpolar	7.30
Toluene	Nonpolar	8.90
Xylene	Nonpolar	8.80

The volumetric swelling ratios of the oil shale samples were measured using 16 different solvents, the extent of the cross-linking in the macromolecular network of oil shales were examined. The change

in the volumetric swelling ratios of raw and demineralized oil shale samples were presented in Figure 5.4.1.1 and Figure 5.4.1.2.

Kerogen has been isolated completely and the effects of mineral matter on swelling behavior of samples have been examined. The effect of mineral matter has indicated that the inorganic content of isolated kerogen did not have a large effect on swelling and the presence of the mineral matter did not seem to hinder swelling behavior for Göynük oil shale.



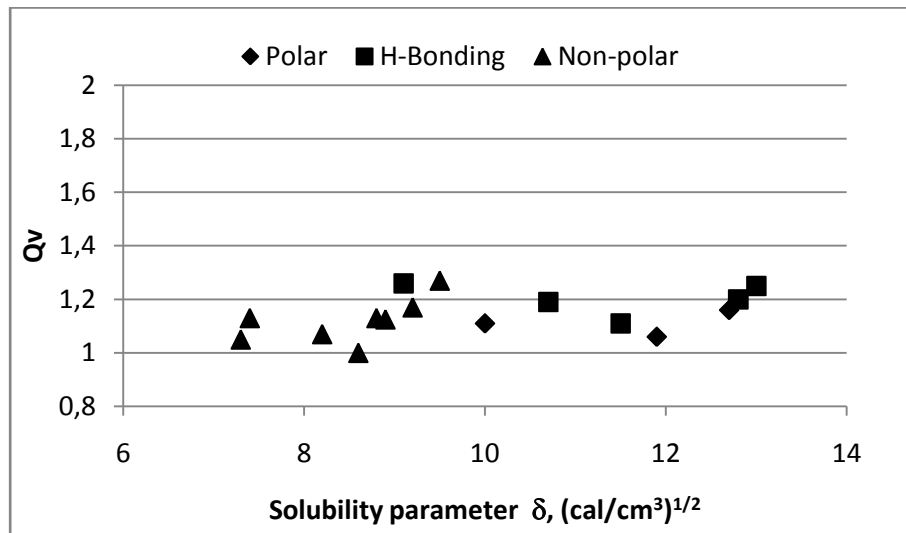


Figure 5.4.1.1 Swelling ratio of raw GOS as a function of swelling solvent solubility parameters

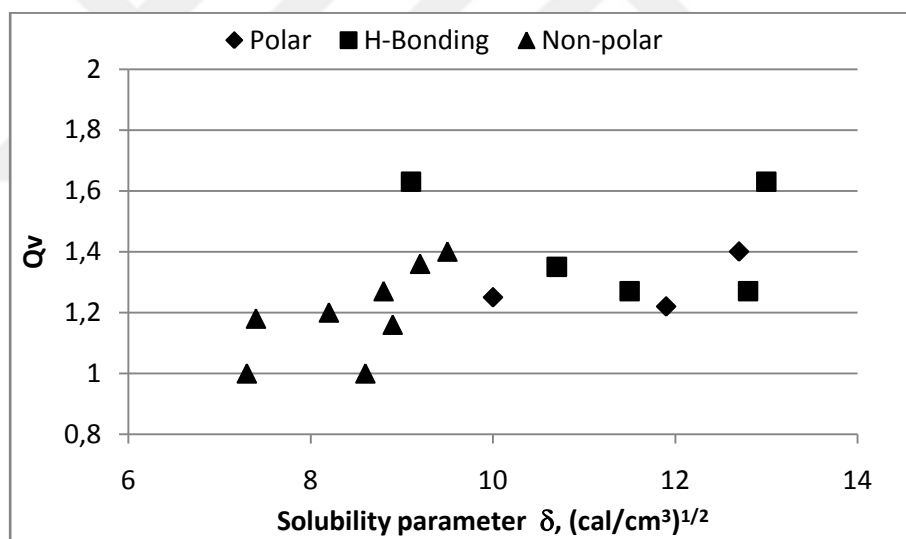


Figure 5.4.1.2 Swelling ratio of demineralized GOS as a function of swelling solvent solubility parameters

Reversibility of swelling process has been also investigated by carrying out re-swelling experiments and results were given in Table 5.4.1.2. The tubes from first swelling were subjected to solvent removal and dried under vacuum. Before re-swelling measurement was made, the samples were again centrifuged for 5 min and the height of oil shale samples in tubes was recorded. According to the results, the oil shale samples after three swelling measurement swelled reversible and the height of dry bed for oil shale samples did not change due to re-swelling. It is necessary to establish the reversibility of the swelling measurements. If the swelling do not give the same results when a same dried and reswollen, then either the initial or final state is not at equilibrium. In literature, some studies on kerogen swelling have been reported whose swelling is not reversible (Larsen and Parikh, 2002).

Table 5.4.1.2 Reversible Swelling of Raw and demineralized Göynük oil shale in Ethanol, Nitromethane

Solvent	Sample	1stSwelling (Q_v)	2nd Swelling (Q_v)	3rd Swelling (Q_v)
Ethanol	Raw GOS	1.13	1.25	1.32
Nitromethane	Demineralized GOS	1.25	1.40	1.45

Regular solution theory predicts that there should be a maximum in the plot of swelling vs. solubility parameter of the polymer, in our case, polymer is the kerogen of oil shale, if the polymer sample and solvent combination follow regular solution theory there will be a maximum in polymer swelling when the solubility parameter of solvent matches the polymer solubility parameter. As the solubility parameter of the polymer and different solvent diverge, swelling will be less. The regular solution theory predicts a bell shaped curve with no swelling for solvents quite unlike the polymer and maximum when solubility parameter of solvent and polymer nearly equal. It can be clearly seen from Figure 5.4.1.1 and Figure 5.4.1.2 for swelling ratio of Göynük oil shales, solvent system seems to roughly follow regular solution theory. Drawing the curves by eye, the maxima fell $9.8 \text{ (cal/cm}^3)^{1/2}$, $9.7 \text{ (cal/cm}^3)^{1/2}$, raw Göynük and demineralized Göynük, respectively. This is in quite good agreement with literature values (Ballice and Larsen, 2003).

It can be clearly seen from figures for swelling ratio vs. solubility parameter that Göynük oil shale or isolated samples of both oil shale (kerogen)/solvent system seems to follow regular solution theory for all solvents used in the experiments. Polar solvents behave similar to non-polar solvents whereas only hydrogen bonding solvents showed enhanced swelling for Göynük oil shales. The solvent having the solubility parameter near that of hydrogen bonding solvent give less

than expected swelling. This behavior is due to the interaction between hydroxyl groups in oil shale structure or in the case of need kerogen due to the partially oxidation of organic structure aiding oxygenated functional groups and hydrogen bonding solvents. There are many data on the interaction of kerogen with organic liquids (Ballice et al., 2003). The swelling of Type I (Green River and Rundle) and Type III (Pittsburg No.8 coal) kerogen have been investigated by Larsen et al. It has been observed that more polar high O/C Type I kerogen came close to regular solution behavior but the data for polar and non-polar liquids were scattered. It has been interpreted as a specific interaction with hydrogen bonding solvents.

Swelling ratios are similar for raw and demineralized Göynük oil shale. To improve solvent solid contact as well as to get a homogenous sample bed in glass tube with 6 o.d, the fraction < 0.1 mm size was taken for the experiments. This fraction is more convenient and results are reproducible.

Solvent swelling technique is as effective as with oil shale as it was coal. Tekes (2002) studied on the solvent swelling of lignite which is provided from Soma – Işıklar. In this study, strongest swelling of lignite occurs in pyridine, H-bonding solvent. And the solubility parameter was found as $21.3 \text{ (MPa)}^{1/2}$ for Soma lignite. According to the study of Otake (1997), it was noted that particle size had an effect on observed swelling behavior of oil shales, due to artifacts associated

with particle packing. This effect is attributable to particle size distribution, rather than the actual size of the particles (small particles tend to pack into interstitial spaces between larger). This was observed to lead to irreproducible results when samples of broad range of particle size were examined. Consequently, all the swelling experiments presented here have been performed with narrow size distribution samples.

Both the Flory–Rehner and Kovac treatments were used to calculate the number average molecular weights between crosslinks

$\left(\bar{M}_c\right)$ The resulting Flory–Rehner equation is

$$\bar{M}_c = - \frac{V_1 v_2^{1/3} \rho - (1/2) V_1 v_2 \rho}{\ln(1 - v_2) + v_2 + \chi v_2^2} \quad (5.4.1.3)$$

Kovac's equation is given below. The principal change of this equation is removing the assumption of Gaussian distribution of chain length and to introduce an additional parameter N , the number of rotatable segments between branch points.

$$\bar{M}_c = - \frac{V_1 v_2^{1/3} \rho + N^{-1} V_1 v_2^{-1/3} \rho}{\ln(1 - v_2) + v_2 + \chi v_2^2} \quad (5.4.1.4)$$

The solubility parameter of raw Göynük, demineralized Göynük oil shales were assumed to be $9.8 \text{ (cal/cm}^3)^{1/2}$, $9.7 \text{ (cal/cm}^3)^{1/2}$ using

Figure 5.4.1.1 and Figure 5.4.1.2. The calculation results are reported in Table 5.4.1.2, Table 5.4.1.3, Table 5.4.1.4 and Table 5.4.1.5, for density 1.4 g/cm^3 and for raw Göynük and demineralized Göynük oil shales. (Shale density: 1.4 g/cm^3)

Table 5.4.1.3 Number average molecular weight per crosslink ($\bar{M}_c$) for raw Göynük oil shale (Density: 1.4 g/cm^3)

Solvents	δ (cal/cm^3) ^{1/2}	Flory Rehner	Flory Kovac		
			N=1	N=2	N=3
Acetonitrile	11.9	103.52	394.37	289.19	254.13
Isopropyl	11.5	200.28	758.16	533.41	485.17
Tetraline	9.5	284.52	1066.86	770.36	671.52
Nitrobenzene	10.0	130.40	495.01	362.07	317.76
Cyclohexane	8.2	183.41	700.66	514.86	452.93
THF	9.1	328.36	1225.57	869.33	750.58
Benzene	9.2	173.63	652.32	472.43	412.48
Toluene	8.9	102.91	395.32	291.41	256.78
Xylene	8.8	198.78	752.67	549.41	481.65
Pyridine	10.7	178.42	670.71	486.02	424.46
Average		197.85	746.36	541.03	472.59

The number average molecular weight between crosslinks ($\bar{M}_c$) was unrealistically low for solvent–oil shale systems being the solubility parameter difference greater than two [$(\delta_{\text{oil shale}} - \delta_{\text{solvent}}) > 2$]. For that

reason, the systems being the oil shale – solvent solubility parameters difference less than two [$(\delta_{\text{oil shale}} - \delta_{\text{solvent}}) < 2$] were used to obtained more realistic values. The Flory–Rehner equation gave ($\bar{M}_c$) as 180 for Göynük oil shale and 160 for Beypazarı oil shale.

The density of oil shale samples was varied for different values and the effect of density of samples on ($\bar{M}_c$) values were also investigated. Changing of ($\bar{M}_c$) with density were shown in Figure 5.4.1.3 and Figure 5.4.1.4, respectively.

Table 5.4.1.4 Number average molecular weight per crosslink ($\bar{M}_c$) for demineralized Göynük oil shale (Density: 1.4 g/cm³)

Solvents	δ (cal/cm ³) ^{1/2}	Flory Rehner	Flory Kovac		
			N=1	N=2	N=3
Acetonitrile	11.9	29.98	120.98	90.13	79.84
Isopropyl	11.5	67.44	274.09	203.16	179.52
Ethanol	12.8	408.59	2590.33	1903.44	1674.48
Nitromethane	12.7	141.15	631.65	465.63	410.29
Tetraline	9.50	190.23	710.81	518.85	454.87
Nitrobenzene	10.0	68.72	268.15	198.63	175.46
Cyclohexane	8.20	72.75	272.37	202.71	179.49
THF	9.10	116.86	433.41	316.54	277.58
Benzene	9.20	85.65	323.37	238.15	209.75
n-Hexane	7.30	242.12	735.53	548.14	485.68
Toluene	8.90	83.28	314.17	232.55	205.34
Xylene	8.80	103.20	385.15	284.84	251.41
Pyridine	10.7	89.65	348.69	256.41	225.65
Average		97,53	370,02	272,42	239,89

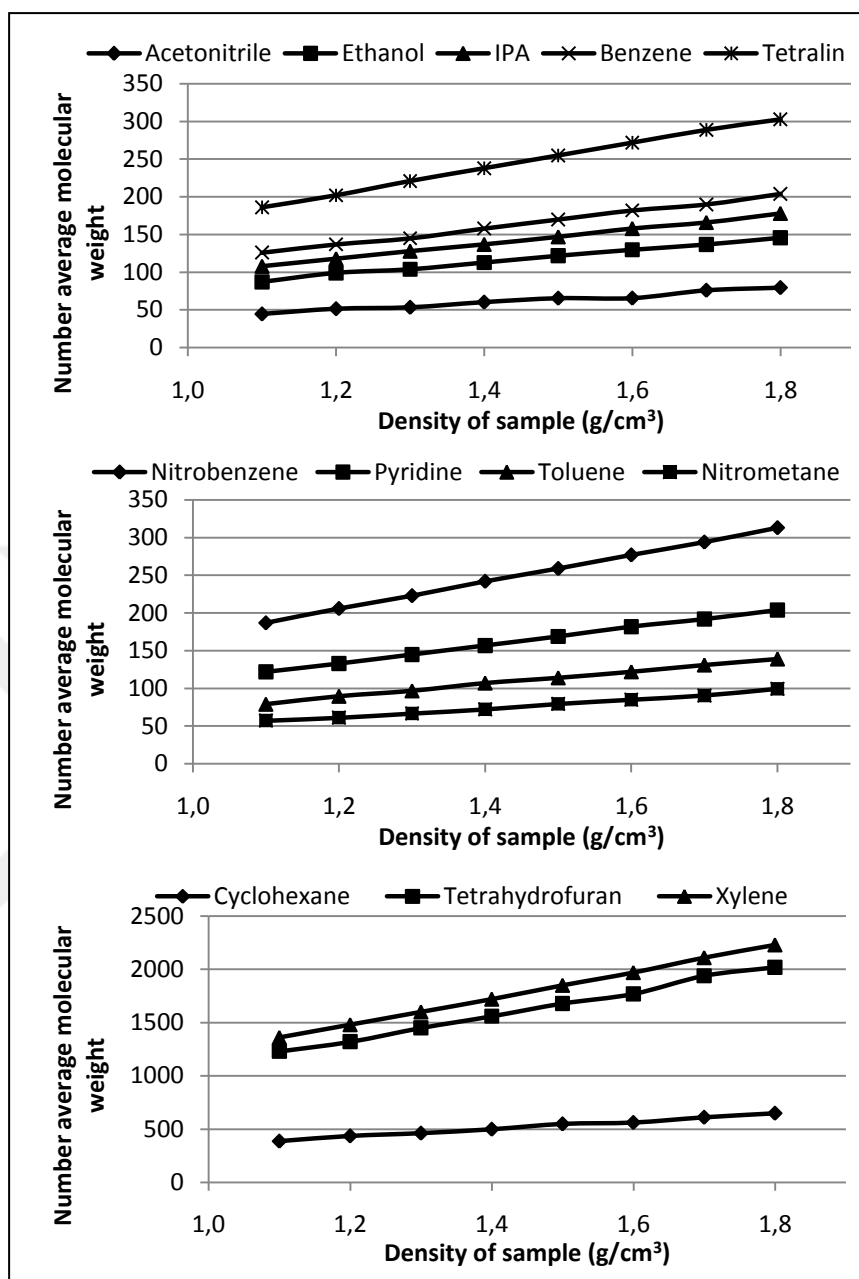


Figure 5.4.1.3 Changes of number average weight ($\bar{M}_n$) as a function of different density for raw GOS sample

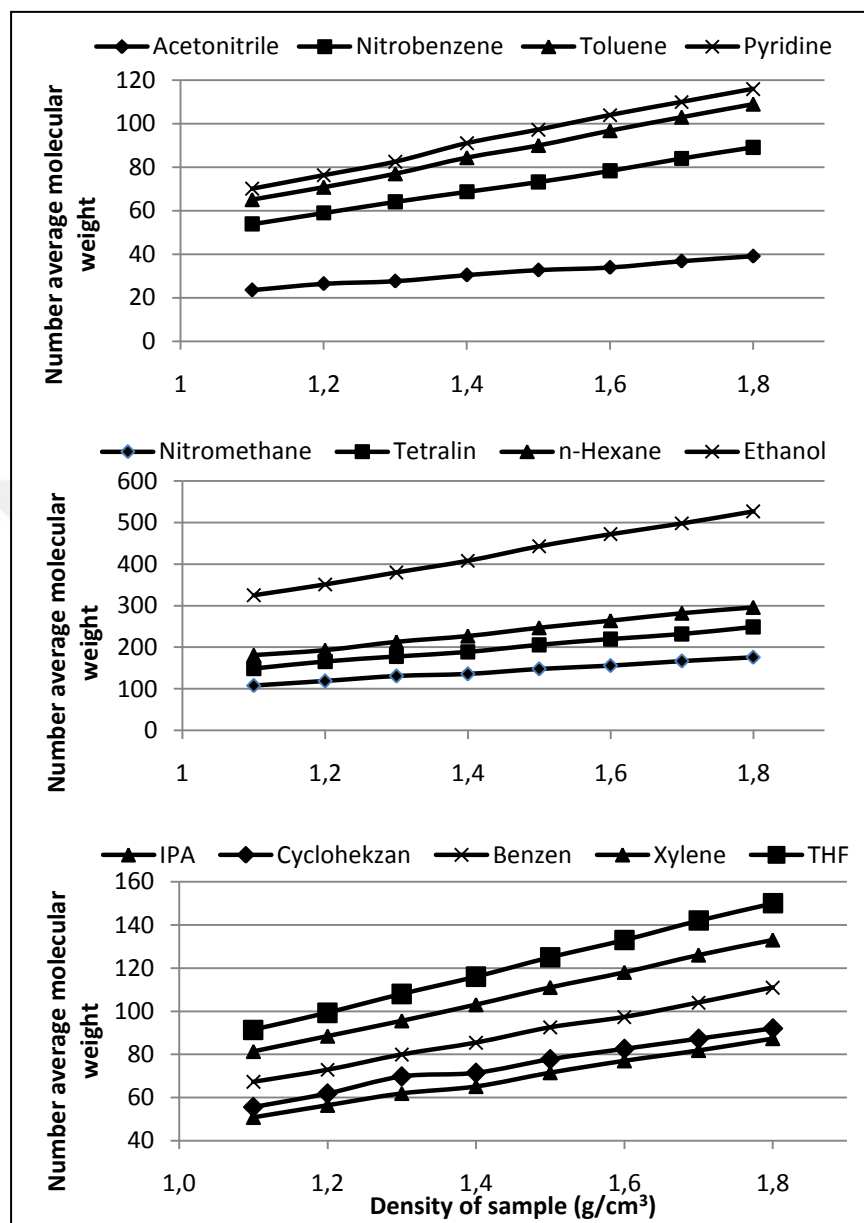


Figure 5.4.1.4 Changes of number average weight (M_n) as a function of different density for demineralized GOS sample

Table 5.4.1.5 Average molecular weight of raw and demineralized oil shale samples in different solvent

Sovents	Raw GOS	Demineralized GOS
Acetonitrile	31.04	107.23
Isopropyl	69.85	207.38
Ethanol	423.17	-
Nitromethane	146.19	-
Tetraline	197.02	294.68
DMSO	-	-
Nitrobenzene	71.17	135.03
Cyclohexane	75.34	189.96
THF	121.03	337.83
n-Heptene	-	-
Benzene	88.70	179.83
Carbontetrachloride	-	-
n-Hexane	240.38	-
Toluene	86.22	106.58
Xylene	106.89	205.89
Pyridine	92.53	184.79

5.4.2 Thermal Properties of Swollen Oil Shale Samples

Information on thermal properties as well as physical change during solvent swelling of oil shales will surely be useful for kerogen structure understanding. TGA appears to be a powerful tool for evaluating the extent of heating effects caused by kerogen structure changes because of solvent swelling. The kerogen samples were analyzed with TGA before and after swelling experiments. Figure 5.4.2.1, Figure 5.4.2.2 and Figure 5.4.2.3 shows the weight loss values derived from TGA data.

The TGA data was evaluated at 120-200°C corresponding to weight loss due to the water content and/or any residual solvent. The evaluations showed that swelling have no additional effect on weight loss of kerogen at given range.

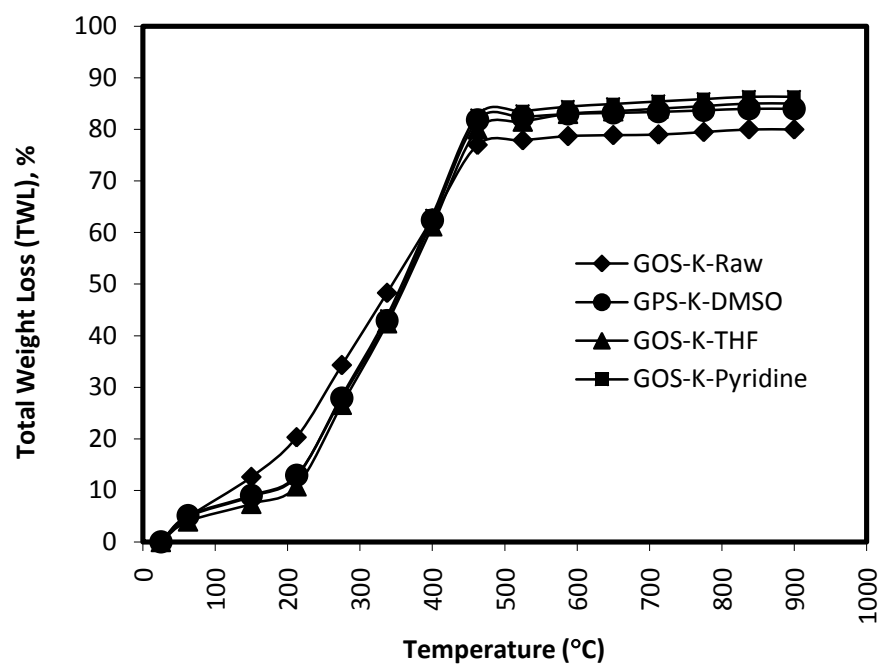


Figure 5.4.2.1 Total weight loss curves derived from TGA data

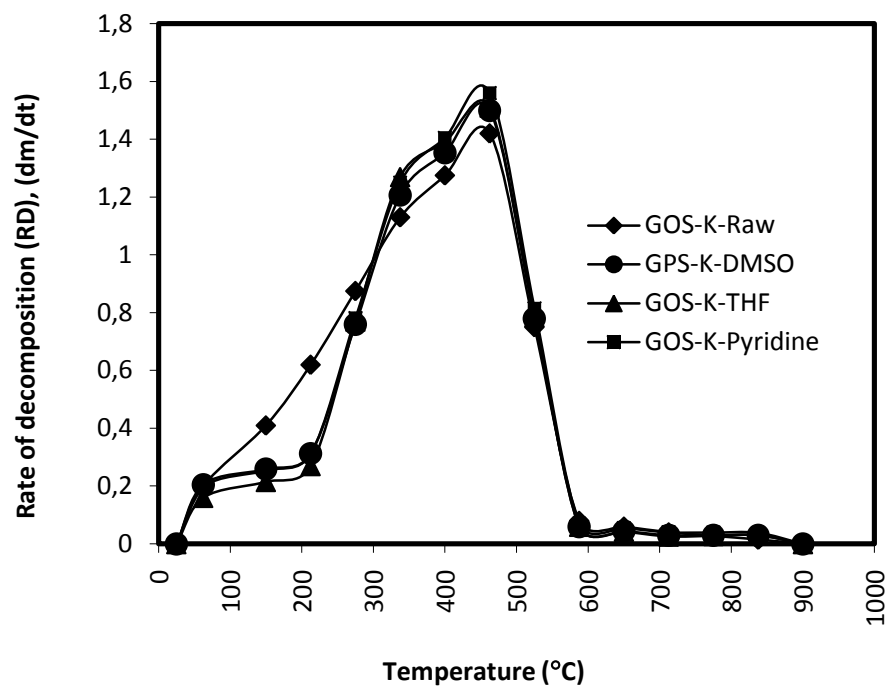


Figure 5.4.2.2 Rate of decomposition curves derived from TGA data

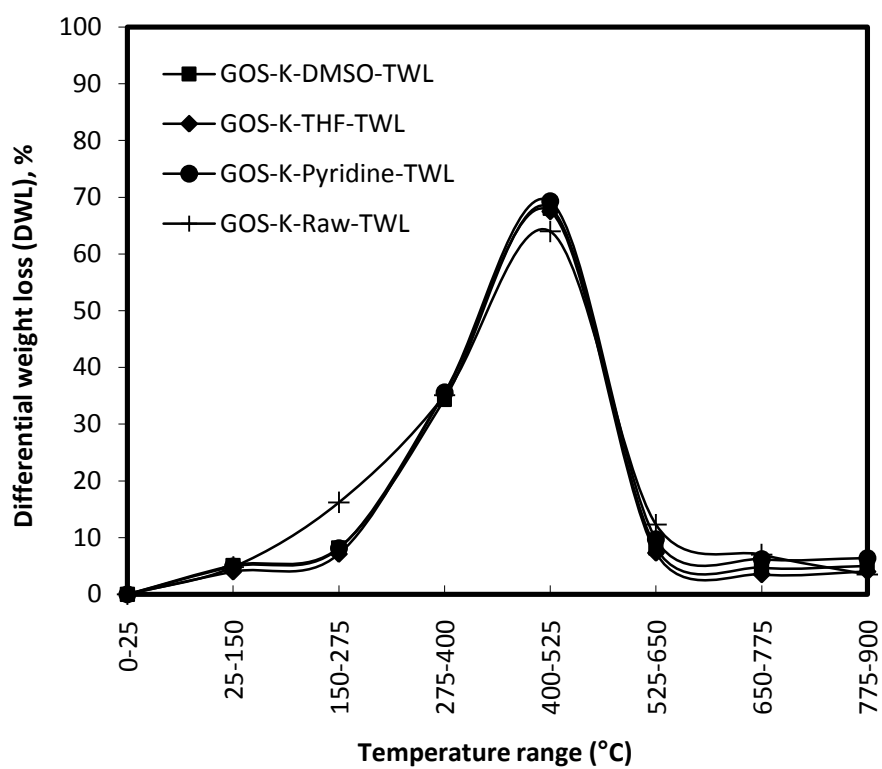


Figure 5.4.2.3 Differential weight loss curves derived from TGA data

5.4.3 Temperature-Programmed Pyrolysis of Swollen Oil Shale

Samples

Information on product distribution during pyrolysis of swollen kerogen will be useful for understanding thermal decomposition of kerogen structure. It is well known that kerogen is a cross-linked structure and after being soaked in a solvent kerogen molecules are diassociated, reassociated and rearranged in lower energy conformation. After swelling of the demineralised Oil Shale Samples (kerogen) in Pyridine, DMSO and THF, temperature-programmed pyrolysis was investigated. These solvents are hydrogen bonding solvents and swell the kerogen more than do the polar and non-polar solvents that show similar results (Larsen et.al., 1994). A series pyrolysis operation performed with kerogen and swollen kerogen. The effect of temperature and time on the rate of total product evolution in the pyrolysis of Göynük oil shale (GOS-K), DMSO-swollen oil shale (GOS-K-D), pyridine-swollen oil shale (GOS-K-P) and THF-swollen oil shale (GOS-K-T) were shown in Figure 5.4.3.1 and Figure 5.4.3.4.

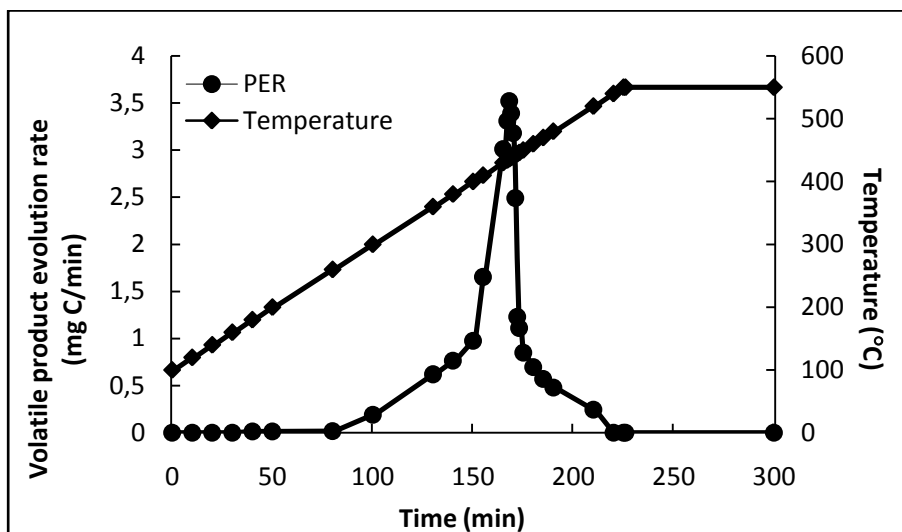


Figure 5.4.3.1 Volatile product evolution rate in the pyrolysis of GOS-K

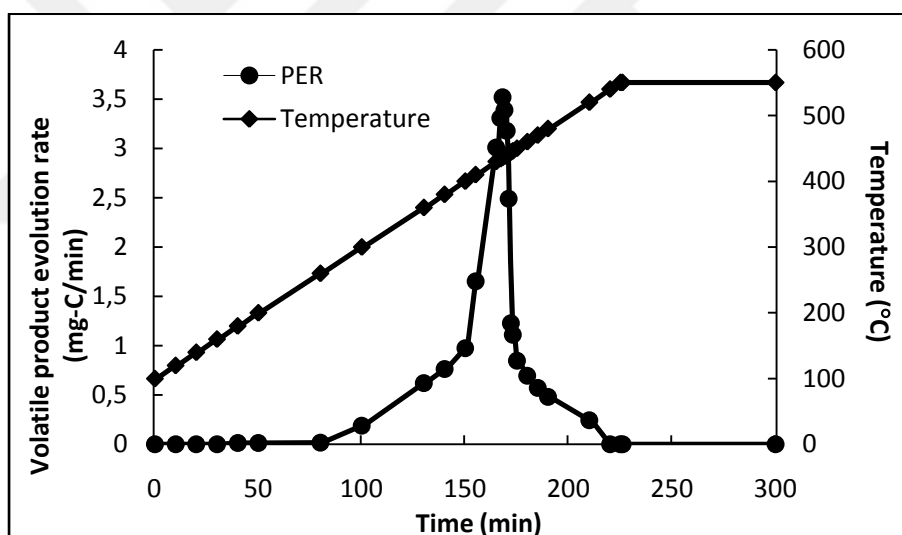


Figure 5.4.3.2 Volatile product evolution rate in the pyrolysis of GOS-K-D

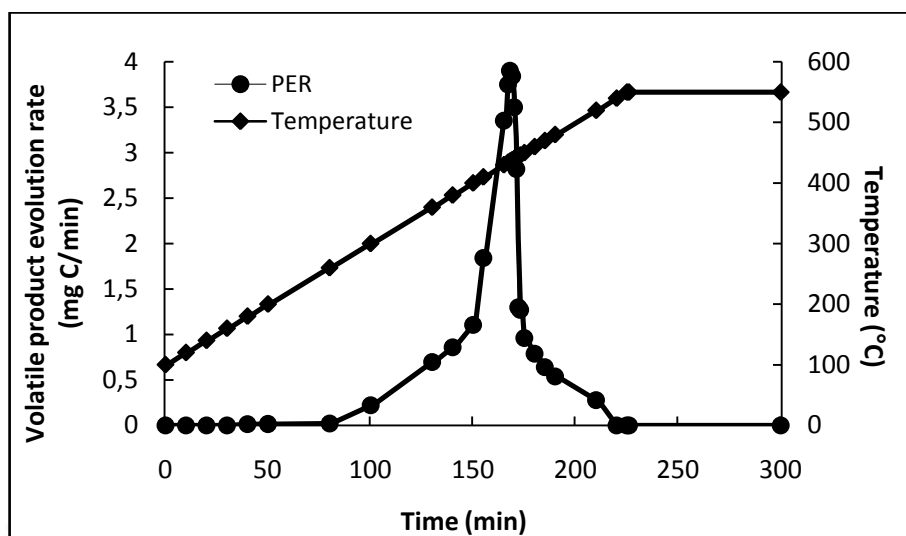


Figure 5.4.3.3 Volatile product evolution rate in the pyrolysis of GOS-K-P

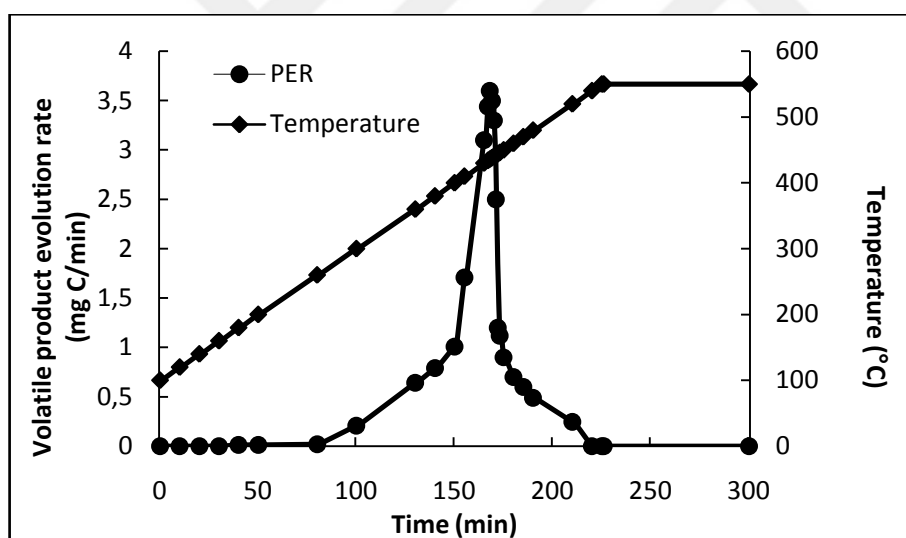


Figure 5.4.3.4 Volatile product evolution rate in the pyrolysis of GOS-K-T

In all cases, the temperature is seen to be product evolution is highest about 440 °C. The pyrolysis profile of GOS is in good agreement with literature (Ballice et.al., 1997). For kerogen swollen by DMSO, Pyridine and THF, the volatile hydrocarbon recovery increased from 55 wt.% to 59, 60.5 and 66 wt.%, respectively. Kerogen reactivity may be enhanced because the solvent swelling expended the macromolecular network and reduced the mass transfer limitations. During pyrolysis of swollen kerogen, small molecules are liable to escape from macromolecular network of kerogen structure and restrain the polymerization of small molecules within the expended network.

Cumulative n-paraffin and 1-olefin values of samples are given in Figure 5.4.3.5 - Figure 5.4.3.12.

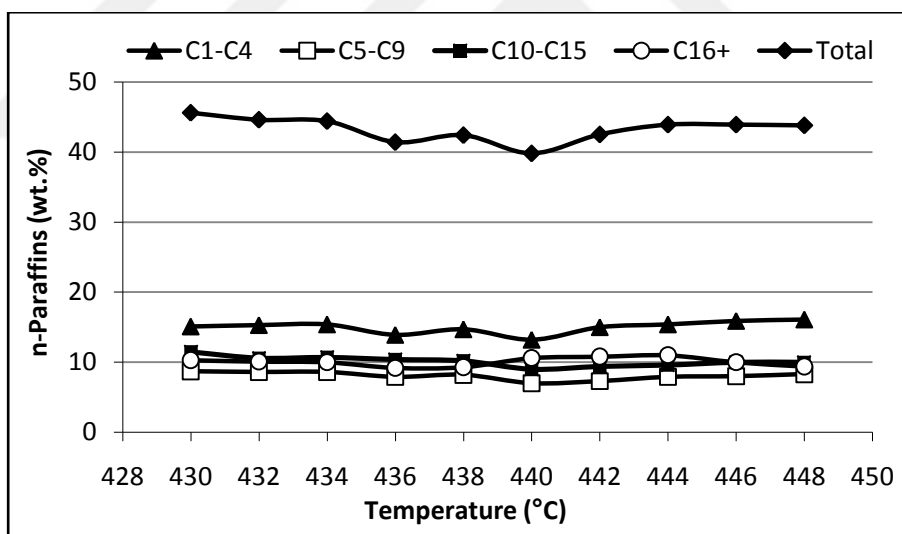


Figure 5.4.3.5 Cumulative n-paraffin selectivity of GOS-K.

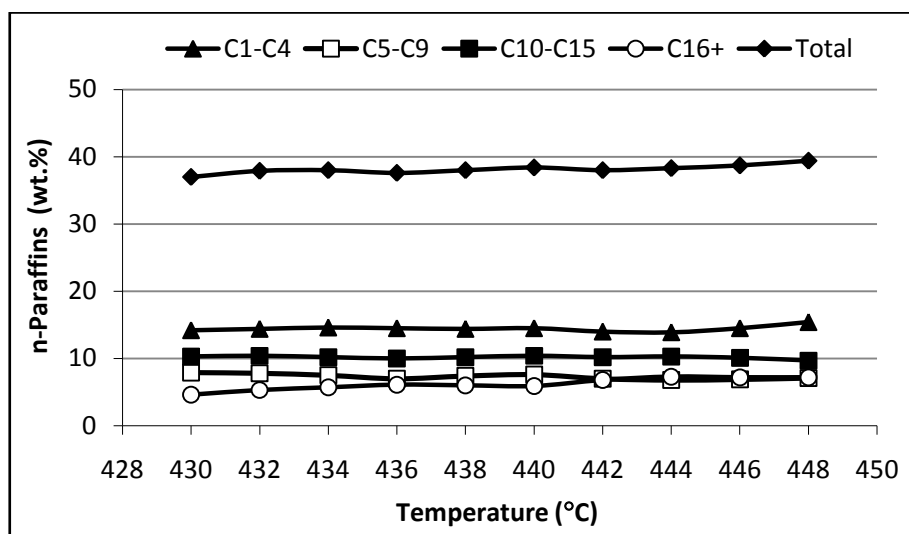


Figure 5.4.3.6 Cumulative n-paraffin selectivity of GOS-K-D

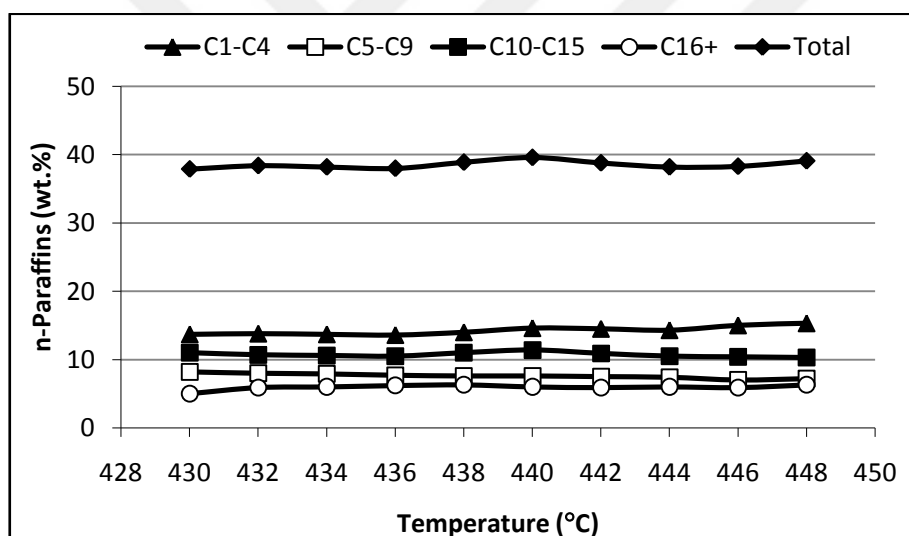


Figure 5.4.3.7 Cumulative n-paraffin selectivity of GOS-K-P

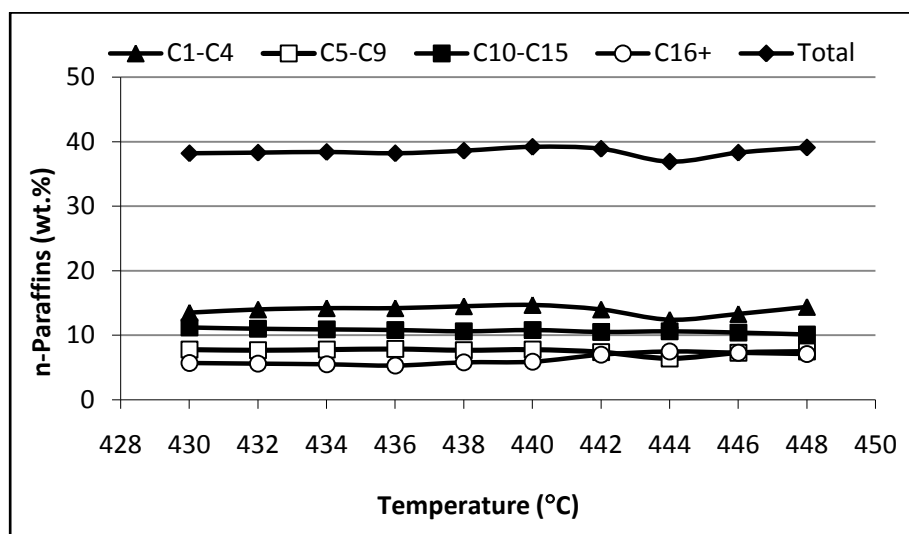


Figure 5.4.3.8 Cumulative n-paraffin selectivity of GOS-K-T

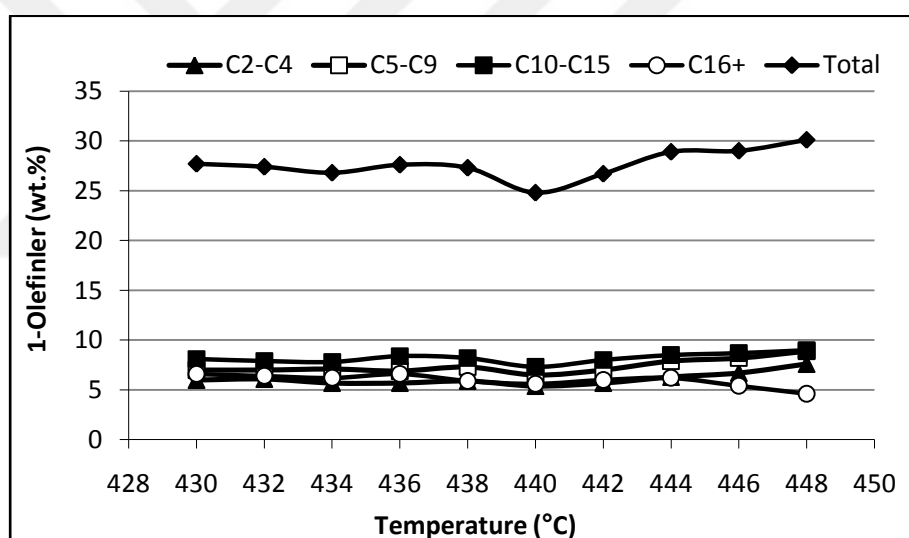


Figure 5.4.3.9 Cumulative 1-olefin selectivity of GOS-K.

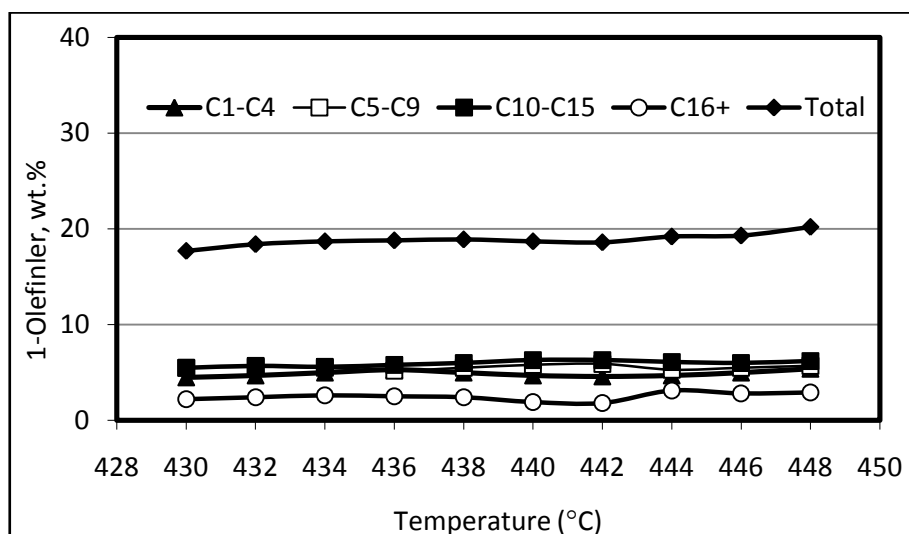


Figure 5.4.3.10 Cumulative 1-olefin selectivity of GOS-K-D

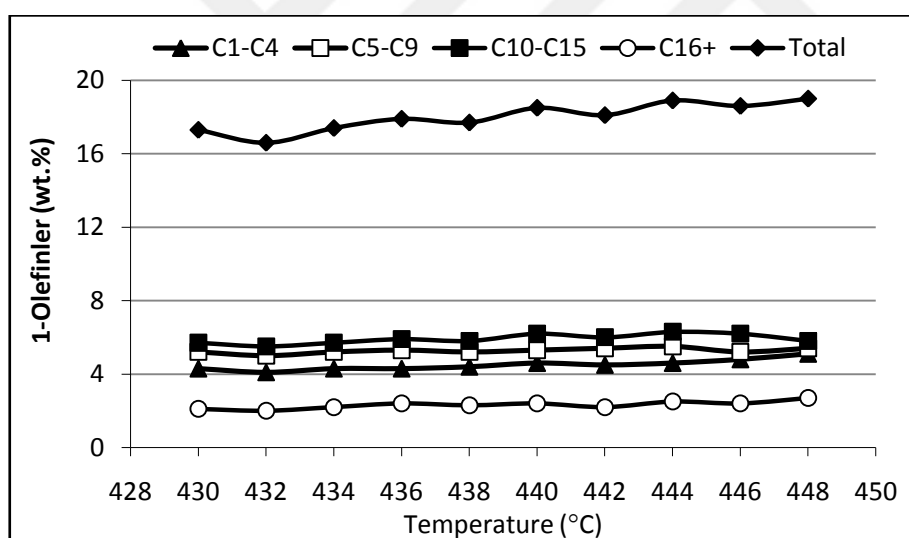


Figure 5.4.3.11 Cumulative 1-olefin selectivity of GOS-K-P

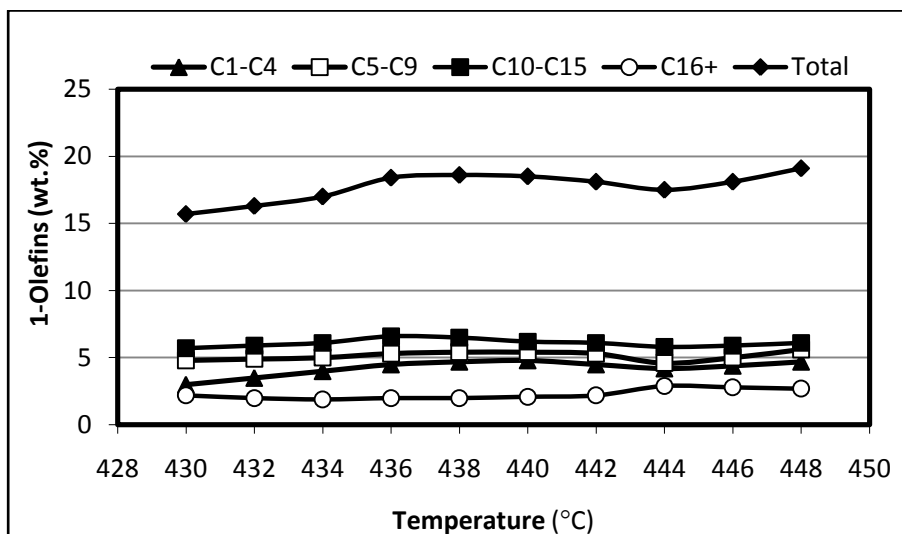


Figure 5.4.3.12 Cumulative 1-olefin selectivity of GOS-K-T

The hydrocarbons produced by pyrolysis of GOS-K, GOS-K-DMSO, GOS-K-Pyridine and GOS-K-THF contained 39.8, 38.4, 38.4, and 39.2 wt.% of n-paraffins, respectively, at the maximum product evolution temperature. The values of 1-olefins produced by pyrolysis of GOS-K, GOS-K-DMSO, GOS-K-Pyridine and GOS-K-THF were 24.8, 18.7, 18.5, and 18.5 wt.%, respectively, at the maximum product evolution temperature. The 1-olefins yield showed a slightly decreased in pyrolysis of swollen samples compared to the Pyrolysis of GOS-K. Formation of 1-olefins is mainly due to thermal decomposition of n-paraffins and diffusion of volatile hydrocarbons such as n-paraffins from the reaction sites to the surface of the solid particles are needed a driving force. The driving forces for the removal of volatile hydrocarbons are its vapor pressure and flow rate of the sweep gas. In

slow pyrolysis, these forces are smaller, residence times of released pyrolysis products longer, and degradation greater. The sweep gas reduces residence time and degradation of released products, but can have no significant effect on intra-particle reactions. Crosslink density of kerogen structure may also effect diffusion of pyrolysis products such as n-paraffins through network structure and solvent swelling expand network and can reduce the diffusion limitations of pyrolysis products through mineral matrix.

At the end of the each pyrolysis run, total organic carbon in solid residue was calculated by TOC analyzer. Total carbon balance for temperature-programmed pyrolysis of swollen samples was shown in Table 5.4.3.1 and Figure Figure 5.4.3.13.

Table 5.4.3.1 Total carbon balance for raw and swollen oil shale samples

Sample	VHC (wt. %)	Solid (wt. %)	Preasp.+ Asp. (wt. %)
GOS-K	55	21	24
GOS-K-DMSO	59	19.6	21.4
GOS-K-Pyridine	66	18	16
GOS-K-THF	60.5	21.6	17.9

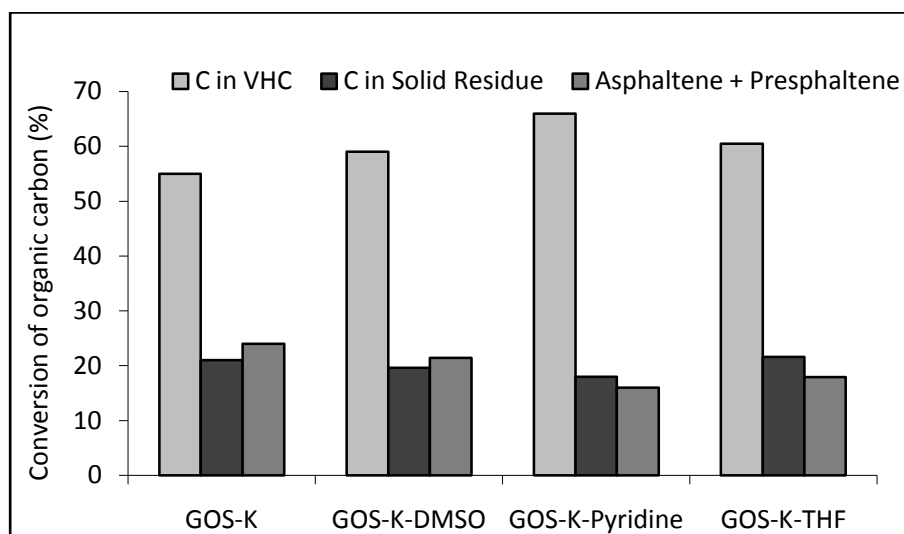


Figure 5.4.3.13 Total carbon balance for raw and swollen GOS samples

5.4.4 Solvent Swelling Studies of Lignite Samples

The swelling behavior of demineralized and raw Soma Kırakdere (KLIG), Soma Zeybek (ZLIG) and Çorum lignites (CLIG) in 16 organic solvents was studied by using the volumetric swelling technique. These solvents were listed in Table 5.4.4.1. Five of the solvents were hydrogen-bonding, three of them polar and the remaining were non-polar with varying solubility parameters. The swelling ratios of lignite samples and the extent of the cross-linking in the macromolecular structure were tried to examine.

To improve solvent solid contact as well as to get a homogenous sample bed in glass tube with 6.0 o.d, the fraction < 0.1 mm size was taken for the experiments. This fraction is more convenient and results are reproducible. According to the study of Otake et al. (1997), it was noted that particle size had an effect on observed swelling behavior of coals, due to artifacts associated with particle packing. This effect is attributable to particle size distribution, rather than the actual size of the particles (small particles tend to pack into interstitial spaces between larger). This was observed to lead to irreproducible results when samples of broad range of particle size were examined. Consequently, all the swelling experiments presented here have been performed with narrow size distribution samples.

The change in the volumetric swelling ratios of lignite samples were presented in Figures 5.4.4.1, 5.4.4.2, 5.4.4.3 and 5.4.4.4. If the

polymer sample and solvent couple follow regular solution theory, there will be a maximum in polymer swelling when the solubility parameter of solvent matches the polymer solubility parameter. Theory predicts a bell shaped curve with no swelling for solvents quite unlike the polymer and maximum when solubility parameter of solvent and polymer nearly equal.

Table 5.4.4.1 Solvents used for swelling of lignites

Solvent	Type	δ (cal/cm ³) ^{1/2}
Acetonitrile	Polar	11.9
Nitromethane	Polar	12.7
Nitrobenzene	Polar	10.0
Isopropil Alcohol	H-bonding	11.5
Ethanol	H-bonding	12.8
Dimethyl Sulfoxide	H-bonding	13.0
Tetrahydrofuran	H-bonding	9.10
Pyridine	H-bonding	10.7
Tetralin	Nonpolar	9.50
Cyclohexane	Nonpolar	8.20
n-Heptane	Nonpolar	7.40
Benzene	Nonpolar	8.20
Carbon tetrachloride	Nonpolar	9.60
n- Hexane	Nonpolar	7.30
Toluene	Nonpolar	8.90
Xylene	Nonpolar	8.80

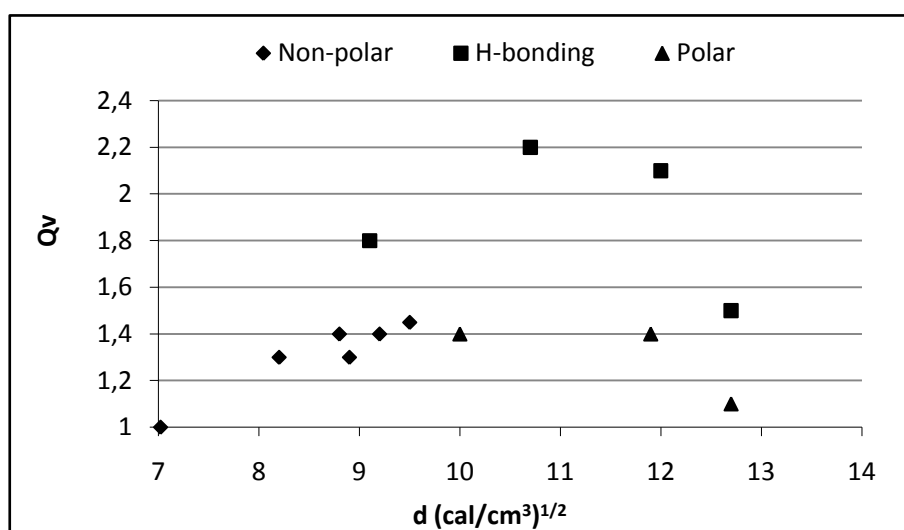


Figure 5.4.4.1 Swelling ratio of raw ZLIG as a function of swelling solvent solubility parameter. $\delta = 10.4$

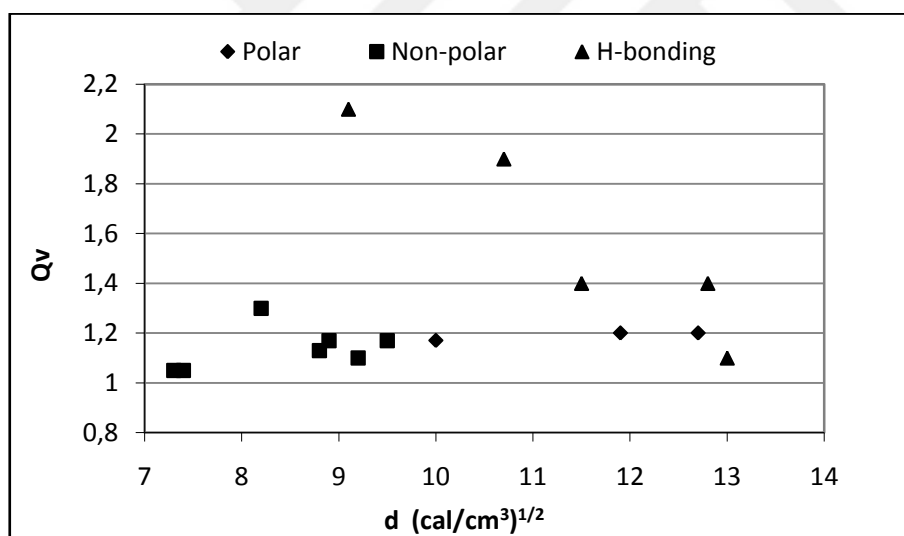


Figure 5.4.4.2 Swelling ratio of demineralized ZLIG as a function of swelling solvent solubility parameter.

The organic structure has been isolated from mineral matter to understand the effect of minerals on the swelling process.

When the swelling degree of isolated and non-isolated lignite samples is compared it is obvious that demineralization enhanced the swelling degree of samples.

If we compare the lignite samples, it is obvious from the Figures 5.4.4.1, 5.4.4.2, 5.4.4.3 and 5.4.4.4 that enhanced swelling has been observed in isolated samples of lignites with respect to raw samples both in Zeybek and Kırakdere. Swelling ratios of raw and demineralized KLIG were compared in the Table 5.4.4.2.

It can be clearly seen from Figure 5.4.4.1 that lignite-solvent system seems to follow regular solution theory roughly especially for polar and non-polar solvents.

By drawing the curve by eye in Figure 5.4.4.1, the maxima fell between $10.4 \text{ (cal/cm}^3)^{1/2}$, which is the solubility parameter of the lignite sample and this is also agreeing with the literature data.

Polar solvents behave similar to non-polar solvents whereas only hydrogen bonding solvents except ethanol and isopropyl alcohol showed enhanced swelling both in raw and isolated samples of Zeybek and Kırakdere lignites.

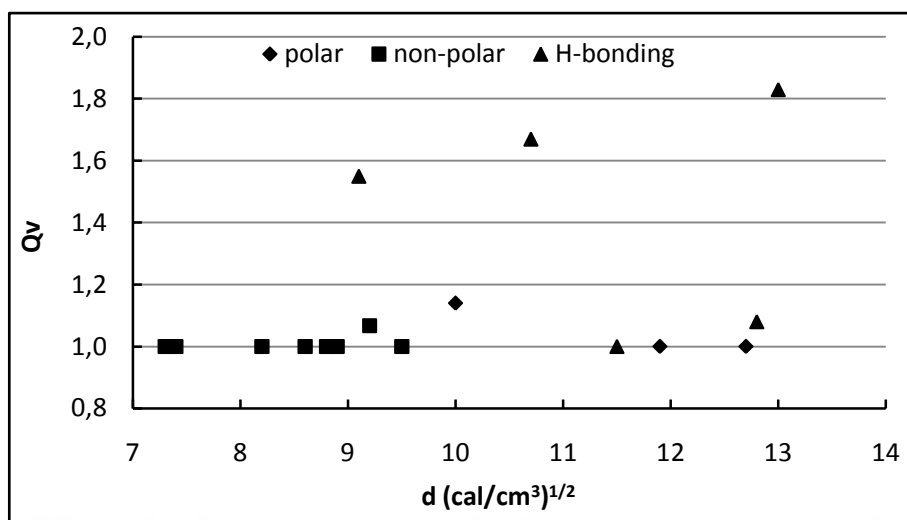


Figure 5.4.4.3 Swelling ratio of raw KLIG as a function of swelling solvent solubility parameter

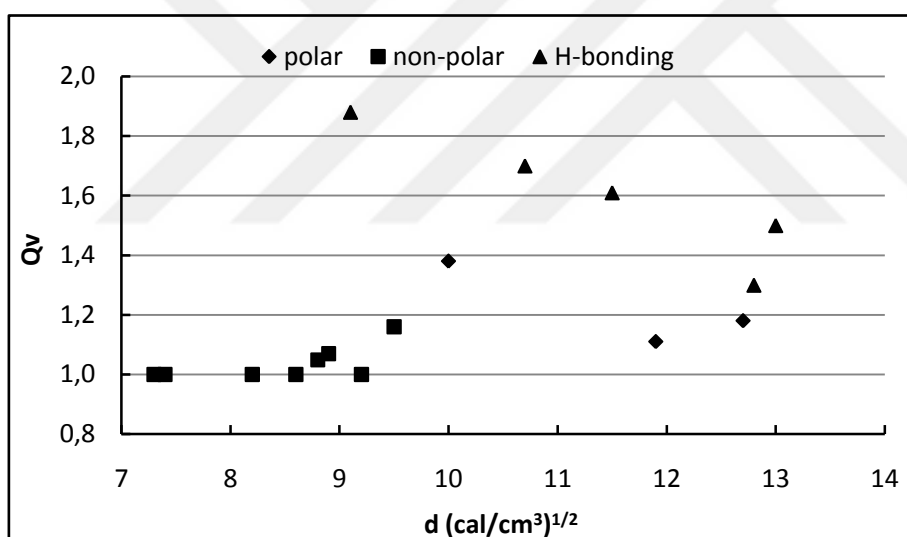


Figure 5.4.4.4 Swelling ratio of demineralized KLIG as a function of swelling solvent solubility parameter

Table 5.4.4.2 Swelling ratios of raw and demineralized KLIG. Where n is non polar, p is polar, H is hydrogen bonding solvents. $Q_v = h_2/h_1$

Swelling ratio for lignite samples		
Solvents	Q_v (raw.)	Q_v (iso.)
Acetonitrile	1.0	1.11
Isopropyl Alcohol	1.0	1.61
Ethanol	1.08	1.30
Nitromethane	1.0	1.18
Tetralin	1.0	1.16
Dimethyl Sulfoxide	1.83	1.50
Nitrobenzene	1.14	1.38
Cyclohexane	1.0	1.0
Tetrahydrofuran	1.55	1.88
n- Heptane	1.0	1.0
Benzene	1.1	1.0
Carbon tetrachloride	1.0	1.07
n- Hexane	1.0	1.0
Toluene	1.0	1.07
Xylene	1.0	1.05
Pyridine	1.67	1.7

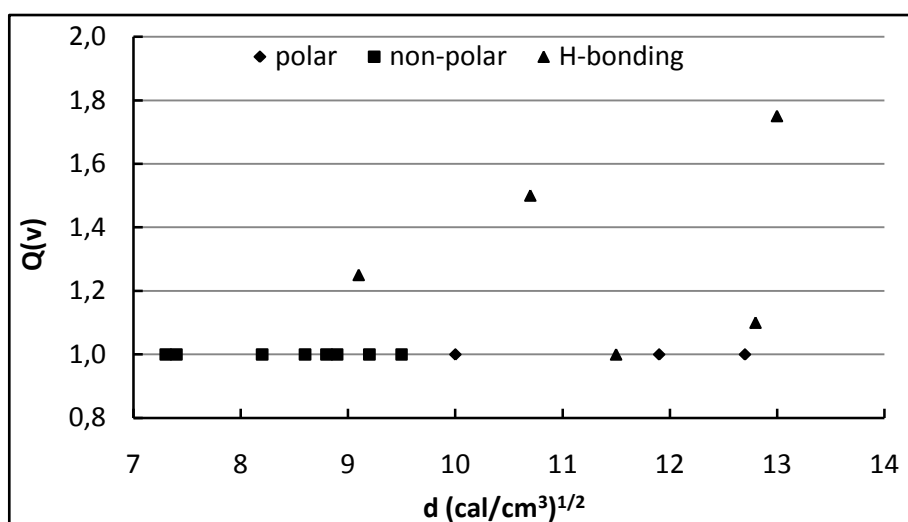


Figure 5.4.4.5 Swelling ratio of raw CLIG as a function of swelling solvent solubility parameter

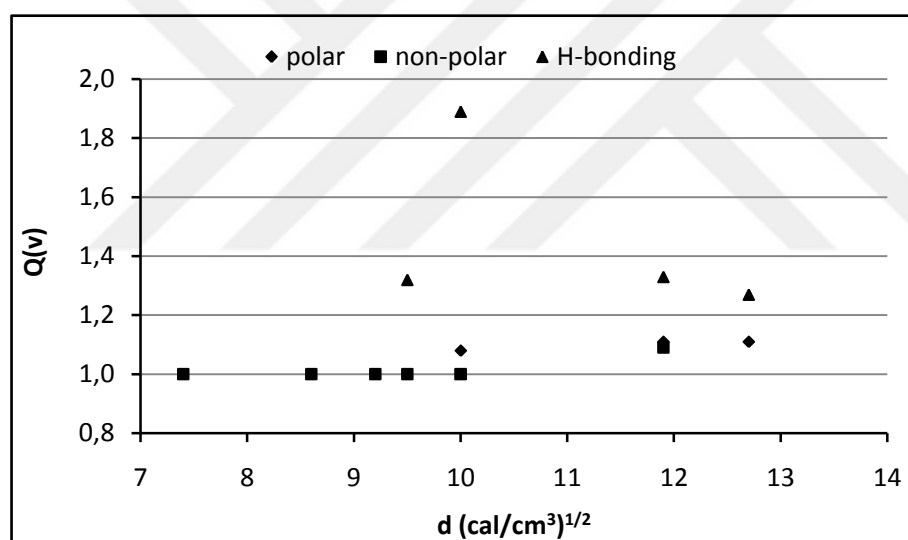


Figure 5.4.4.6 Swelling ratio of demineralized CLIG as a function of swelling solvent solubility parameter

Although there are some examples in the studies which states that inorganic content does not have a large effect on swelling, enhanced swelling has been observed in isolated samples of lignites possibly due to the fact that weak linkages are disrupted and the guest components are freed by the action of solvents on the bonds. As a result, this made easier the diffusion of solvent through coal particles.

The results of the reversibility of swelling are given in Table 5.4.4.3. It is necessary to establish the reversibility of the swelling measurements. If the swelling do not give the same results when a same dried and reswollen, then either the initial or final state is not at equilibrium. In literature, some studies on kerogen swelling have been reported whose swelling is not reversible (Larsen and Parikh, 2002).

Table 5.4.4.3 Reversible Swelling of raw KLIG, raw ZLIG and raw CLIG in DMSO, THF, Pyridine, Ethanol, Nitrobenzene and 2-Propanol.

Solvent	Sample	1 st Swelling	2 nd Swelling	3 Rd Swelling
THF	R-,KLIG	1.4	1.4	1.5
DMSO	R-KLIG	2.2	2.2	2.1
Pyridine	R-ZLIG	1.9	1.8	1.9
Ethanol	R-ZLIG	1.3	1.3	1.4
2-Propanol	R-CLIG	1.1	1.1	1.1
Nitrobenzene	R-CLIG	1.2	1.3	1.2

When we look at pyridine's solubility parameter, which is $10.7 \text{ (cal/cm}^3)^{1/2}$, it can be seen that it is near that of nitrobenzene [$10 \text{ (cal/cm}^3)^{1/2}$] but shows enhanced swelling when they are compared. This behavior is likewise for the other non-polar and polar solvents, which have solubility parameters near that of pyridine.

Except raw ZLIG, other lignite-solvent systems do not follow the regular solution theory, as they don't form a bell shaped curve when the solubility parameters of the solvents and swelling ratios are plotted on the coordinate system.

There are some troubling deviations from the regular solution theory in our results. According to the literature data, the deviation from the Flory-Rehner Theory is most probably related to the acid functionality groups that increase interactions with basic solvents enhancing their swelling ratios. For the plots of swelling ratios vs. Solubility parameters, there is a clear distinction between the hydrogen bonding solvents and the others. The hydrogen bonding solvents swell all lignite samples more than do the polar and non-polar solvents that similar results. This is interesting because some studies on oil shale kerogen follow regular solution theory (Larsen and Parikh, 2002). Regular solution theory predicts that there should be a maximum in the plot of swelling versus solubility parameter of the organic structure. Figure 5.4.4.2 show rough agreement with this prediction and scattering of the swelling data for H-bonding solvent

and anomalously high swelling will not change the maxima of the curve. It will show only excess swelling rather than the other solvent. According to the literature data, great deviation for H-Bonding solvents (such as Pyridine, Tetrahydrofuran and Dimethyl Sulfoxide) was due to the special interaction with organic structure rather than mineral effect. Illinois coal was investigated for its swelling behavior by Larsen et al., 1997. There are abundant data on coal swelling and on coal-solvent interactions. There are too many studies to list here so a few leading references must suffice (Suuberg et al., 1994, Quinta and Larsen, 1998, Turpin et al., 1996). The swelling of coal in non-polar solvents follows regular solution theory and leads to find the solubility parameter more accurately. The great swelling ratios for H-bonding solvent (Pyridine, Tetrahydrofuran and Dimethyl Sulfoxide) can be explained as follows: The swelling systems (Solid-Solvent) which interact specifically with the organic structure, by forming hydrogen bond to a specific site in the polymer, diverge from regular solution theory. The stronger specific interactions lead to greater solvent uptake resulting enhanced swelling. If we extent the regular solution theory to solid-polymer-liquid system, the solid (cross-linked and insoluble polymer) is solvent and the organic liquid dissolved in it is the solute. For example, hydrogen bond between different polymer chains in organic coal structure may persist in non-polar solvents and serve as a cross-link. A good hydrogen bonding solute may disrupt the polymer-polymer hydrogen bond replacing it by polymer-solute bond(s). In this

case, a crosslink based on hydrogen bonds have been destroyed. The more lightly cross-linked a polymer is, the more it will swell. In literature it has also been stated that the hydrogen-bond-accepting solvents showed strongly enhanced swelling and this enhancement is a linear function of their heats of hydrogen bonding with phenol (Larsen et al., 1985).



5.5 Supercritical Water Extraction (SCWE)

The supercritical water extraction experiments were performed with raw and demineralized samples of lignite at the reaction temperatures of 400, 450 and 500 °C. Experiments were carried out as described in Section 2.2.4.

At the end of each experiment, gas products were identified by gas chromatography. Liquid and solid products were filtered and liquid products were analyzed by TOC to calculate carbon content. Solid products were washed with THF to remove organic compounds coming from liquid products, and then dried under vacuum. Finally, these products were analyzed in TOC analyzer, SSM module.

At the end of the each SCWE experiment, the volume of gas product was measured and tabulated in Table 5.5.1.

Table 5.5.1 The gas products volume of for Lignite after SCWE (mL)

Sample	400 °C	450 °C	500°C
ELIG-R	280	390	540
ELIG-C	260	380	560
ELIG-N	260	360	550
ELIG-F	345	510	660

In the gaseous product, CO, CO₂, H₂, CH₄, C₂H₄, C₃H₆ and C₄₊ were analyzed by gas chromatography. From the weight of residue, liquid and the volume of gas and the gas composition, residue yield, liquid yield and gas yield at different temperatures were determined. The weight of gas product was calculated from average molecular weight and the volume of gas at standard temperature and pressure.

The conversion and the yield of gas, liquid and residue are, respectively, given by;

$$\text{Conversion (\%)} = 100 - \left[\frac{\text{wt of C in residue}}{\text{wt of C in sample}} \right]$$

$$\text{Yield of gas (\%)} = \left(\frac{\text{weight of C in gas product}}{\text{weight of C in sample}} \times 100 \right)$$

$$\text{Yield of liquid (\%)} = \left(\frac{\text{weight of C in liquid product}}{\text{weight of C in sample}} \times 100 \right)$$

$$\text{Yield of residue (\%)} = \left(\frac{\text{weight of carbon in residue}}{\text{weight of carbon in sample}} \right) \times 100$$

Figure 5.5.1 shows the conversion of ELIG-R, ELIG-C, ELIG-N and ELIG-F in SCWE.

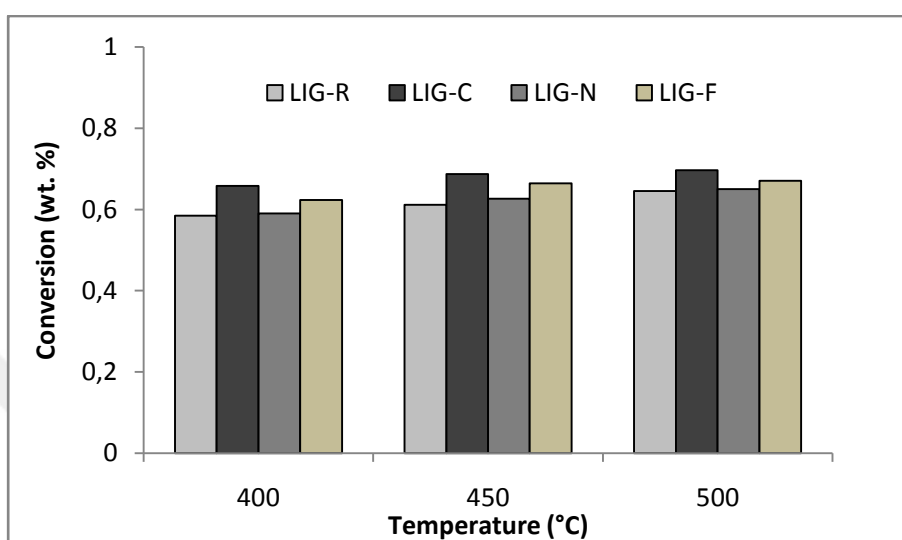


Figure 5.5.1 Conversion of gas and liquid products of lignite samples after SCWE.

According to the figure above, conversion slightly increases as the temperature increase. At low temperature, few organic substances can be extracted because of the low solubility of water to relatively heavy organic substance from waters high dielectric constant at low temperature. The change of product yields with increasing temperature was shown in Figures 5.5.2-5.5.5.

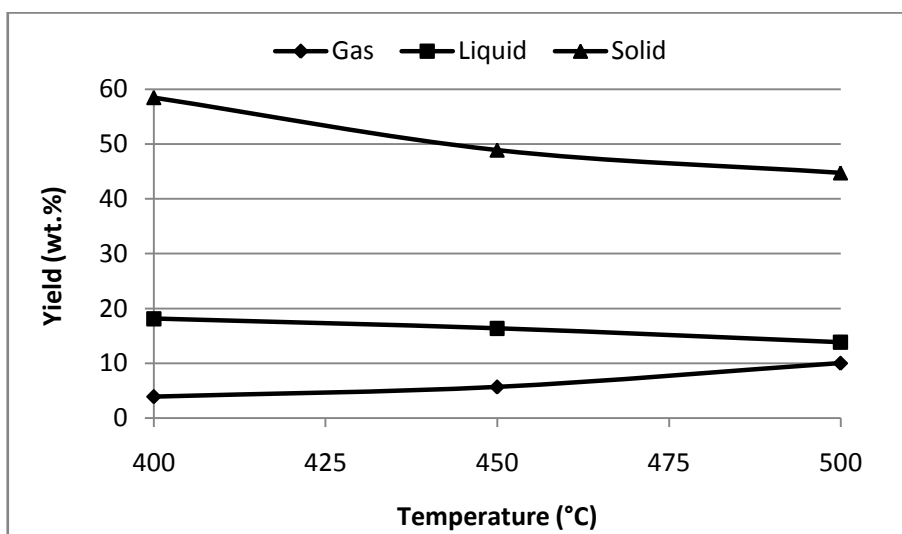


Figure 5.5.2 Yield of the gas, liquid and solid residue of ELIG-R

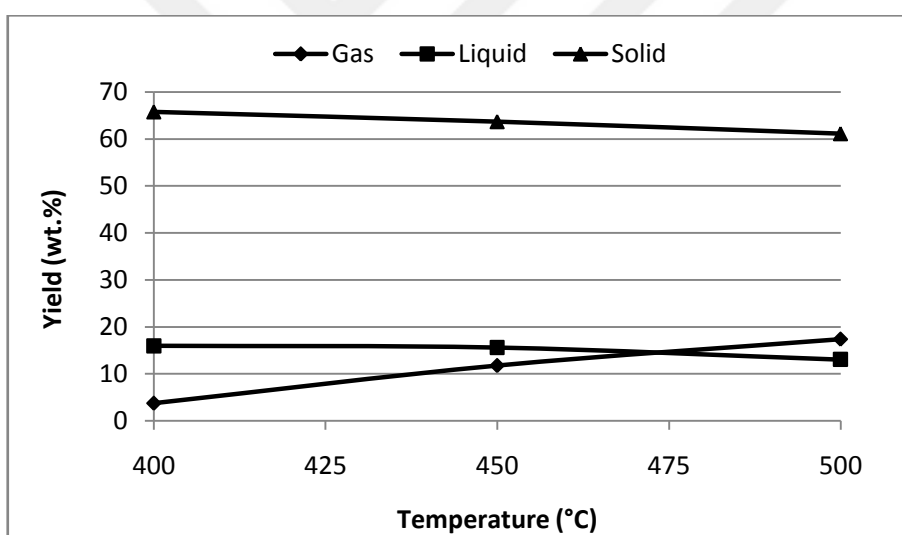


Figure 5.5.3 Yield of the gas, liquid and solid residue of ELIG-C

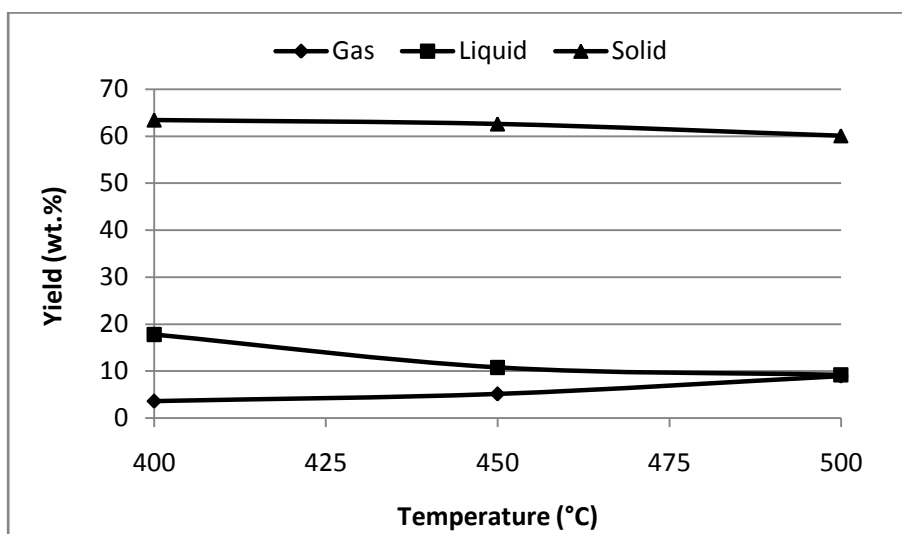


Figure 5.5.4 Yield of the gas, liquid and solid residue of ELIG-N

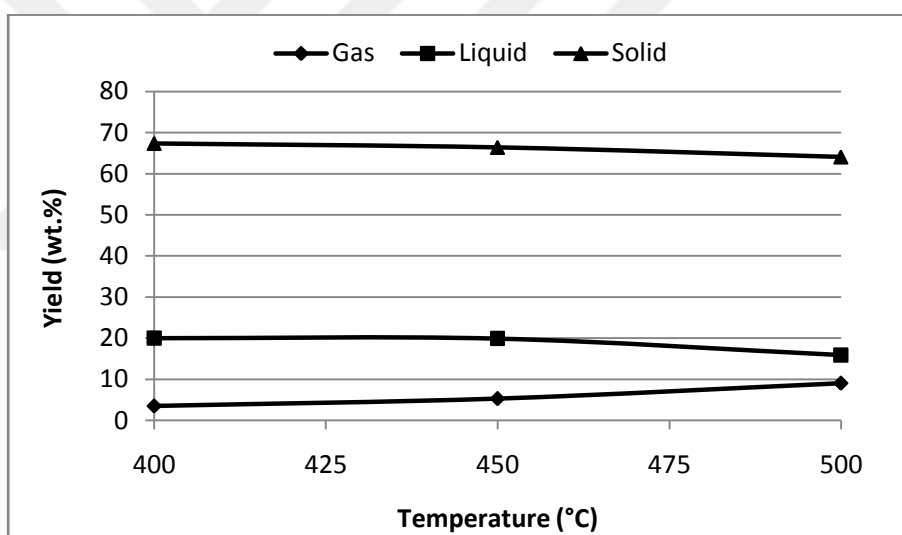


Figure 5.5.5 Yield of the gas, liquid and solid residue of ELIG-F

As temperature increases yield of gas increased, yields of liquid and solid decreased for all lignite samples. At high temperature, the secondary reaction take place, and extractable substance will be converted into gas, low molecular weight products and unextractable big molecules.

The effects of temperature on the gas composition are shown in Figure 5.5.6 – Figure 5.5.9.

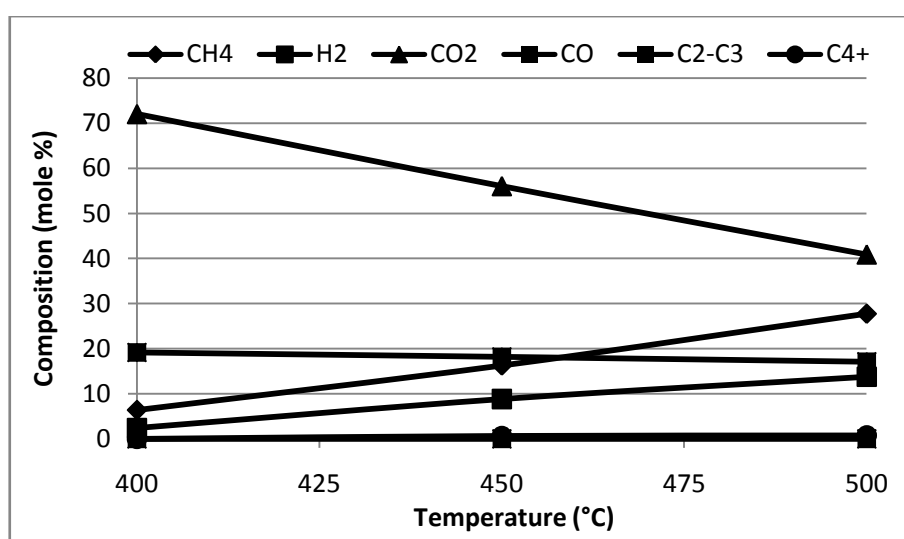


Figure 5.5.6 Classification of gas products evolved from SCWE of ELIG-R

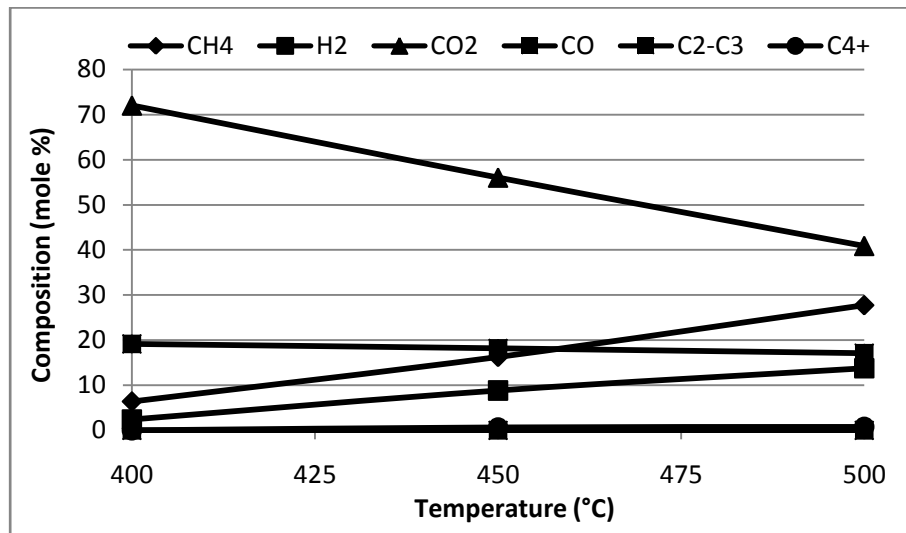


Figure 5.5.7 Classification of gas products evolved from SCWE of ELIG-C

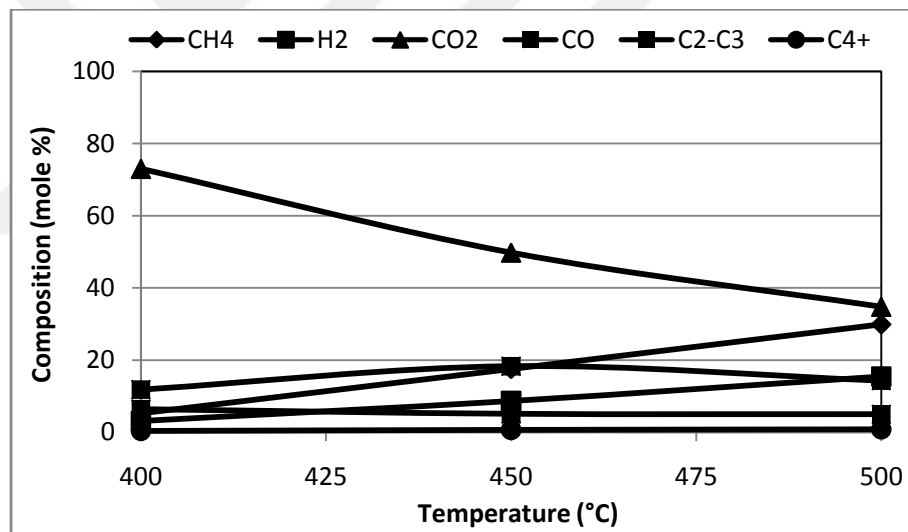


Figure 5.5.8 Classification of gas products evolved from SCWE of ELIG-N

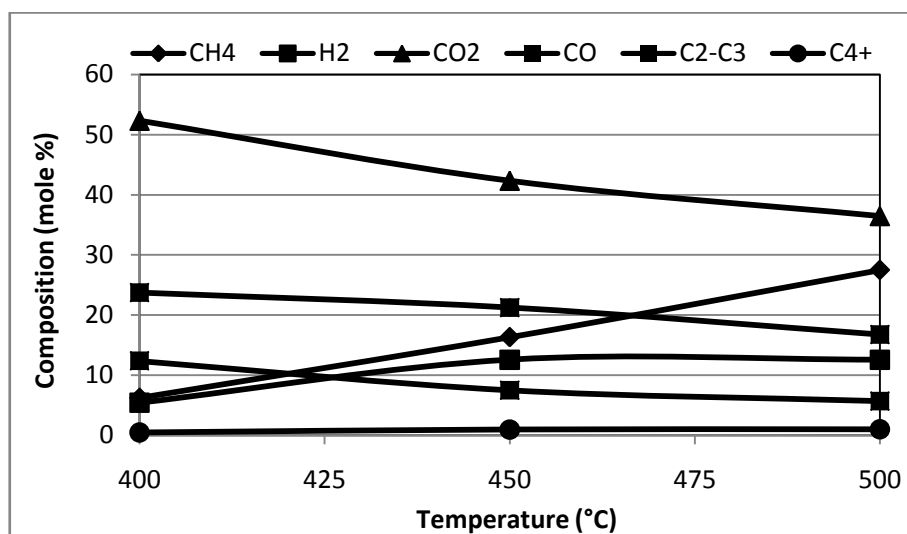


Figure 5.5.9 Classification of gas products evolved from SCWE of ELIG-F

The analysis of gas product show that the main product in gas is CO₂, its composition is more than 50 % at 400°C for all samples. With increases of temperature, CO₂ mole percent decreases. From the effect of temperature on gas formation rate of CH₄, H₂, C₂-C₃ increases with increasing temperature.

5.6 Thermogravimetrically Derived Kinetics of Pyrolysis

5.6.1 TGA (Thermogravimetric Analysis)

Pyrolysis experiments were carried out by non-isothermal thermogravimetry using TGA analyzer. The experimental procedure involved placing the sample (app. 100 mg) into a platinum crucible and heating to 880 °C at a linear heating rate of 5 °Cmin⁻¹ in the nitrogen flow of 15 mL min⁻¹.

The weight losses occurring in correspondence to the temperature rise were continuously recorded with a computer working in coordination with the furnace and the control unit of the analyzer, in order to collect the data required to determine the pyrolysis characteristics and kinetics of the samples.

Thermogravimetric Analysis of SASP

Figures 5.6.1.1 - 5.6.1.4 shows the weight losses and differential weight losses of raw and demineralized asphaltite samples, respectively.

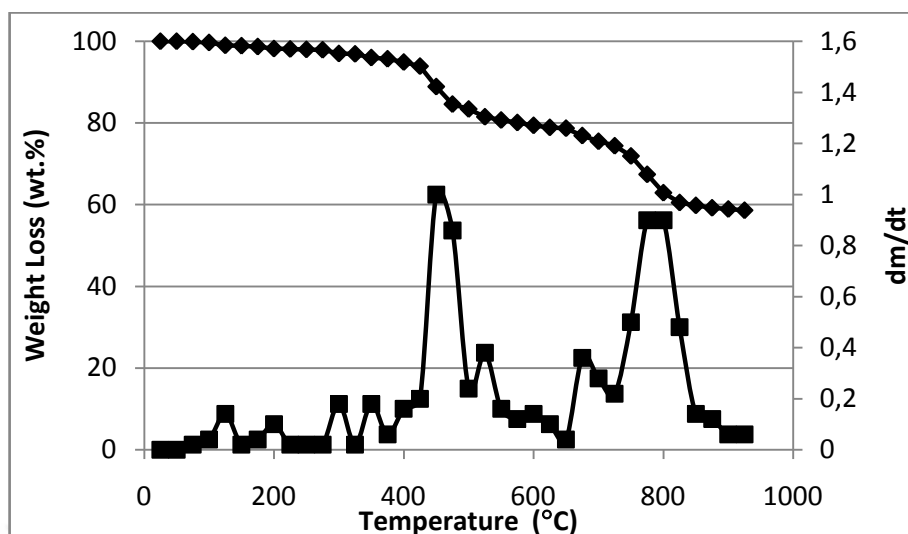


Figure 5.6.1.1 Weight loss and rate of the decomposition curves for SASP-R

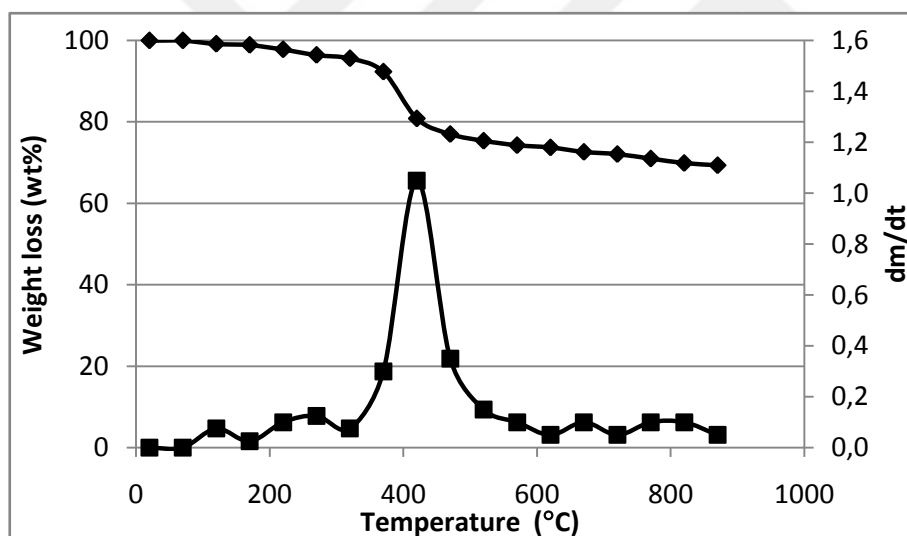


Figure 5.6.1.2 Weight loss and rate of the decomposition curves for SASP-C

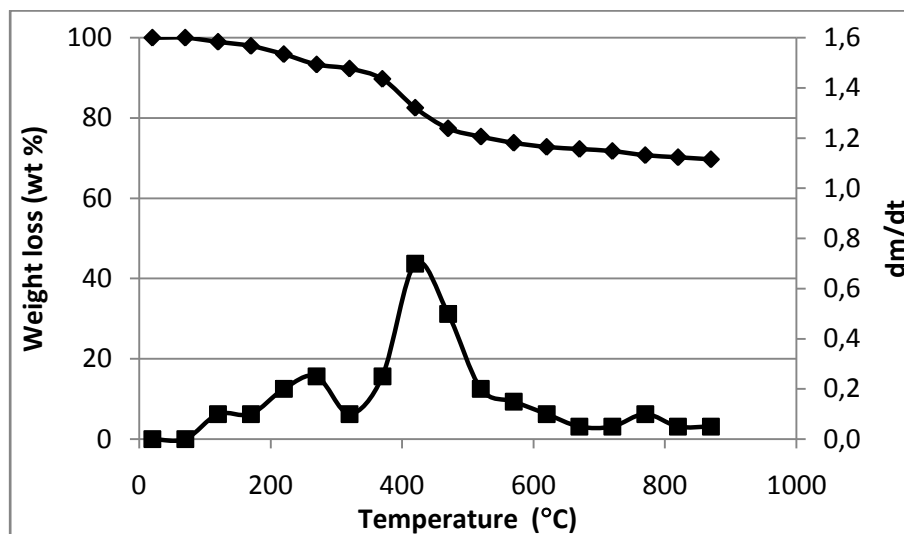


Figure 5.6.1.3 Weight loss and rate of the decomposition curves for SASP-N

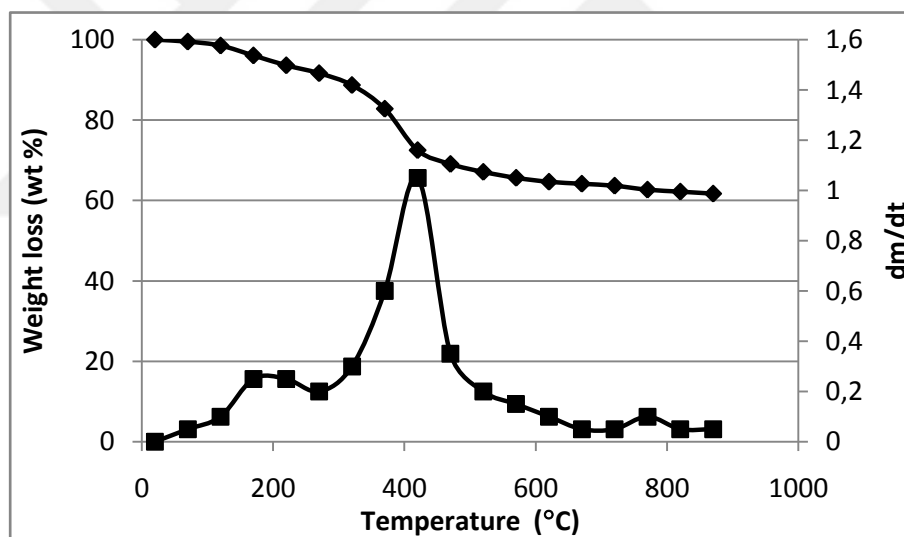


Figure 5.6.1.4 Weight loss and rate of the decomposition curves for SASP-F

As given from Figure 5.6.1.1, TG data of asphaltite samples demonstrated two weight losses. Below 200 °C, there was no mass loss. Since SASP has not got large groups that can bond water molecules. Then there is just little decrease in asphaltite mass from 25 to 130 °C. The results obtained by TG analysis indicated that the first endothermic effect is due to loss of free and chemically bounded water for SASP. Weight loss increases above the temperature of 150 °C. Absorbed, adsorbed and decomposed light fractions appear between 150 – 375 °C.

Primary volatilization of the sample occurred in the range of 400 - 600 °C. The decomposition products of asphaltite are obtained between these temperatures. At the initial stage of volatilization of low molecular mass species takes place. Owing to the temperature rise, large molecules are cracked into small fragments. During this phase of pyrolysis, volatiles are transported to the external surfaces of the asphaltite particles. Then, the volatile fragments are removed from the surface of the asphaltite into the bulk gas phase.

In the range of 600 - 800 °C the second mass loss region was observed. During this stage, called secondary gasification region, mainly decomposition of primary volatile fragments takes place, and very low amounts of CO and CO₂ are also formed as a result of carbonization of the residual solid under the effect of excess heat. Nitrogen and sulfur bonds are broken in addition to this, organic

decomposition goes on. As the temperature increases, CaCO_3 decomposes up to 750 °C. Because of the sulfur components are great amount, existence of metal sulphates are accepted above the temperature of 750 °C.

The temperatures of maximum rate of weight loss may be used as an indicator for the coal reactivity in pyrolysis or devolatilization. As the reactivity increases, the maximum devolatilization temperature is expected to decrease. In this manner, in all asphaltite samples, temperature of the maximum rate of weight loss is the same (420 °C). But in demineralized asphaltite samples, secondary pyrolysis is not significant when compared with raw asphaltite sample.

Thermogravimetric Analysis of SLIG

Figures 5.6.1.5 - 5.6.1.8 shows the weight losses and differential weight losses of raw and demineralized lignite samples, respectively.

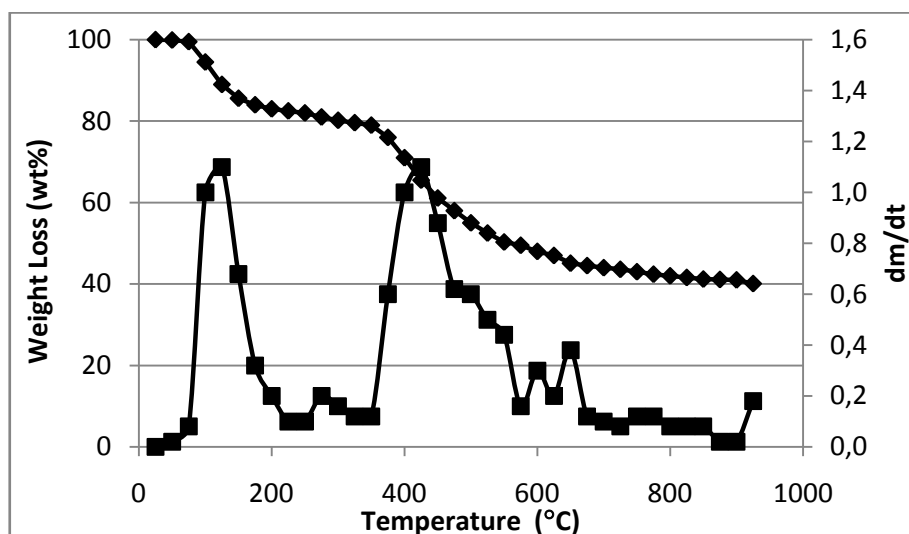


Figure 5.6.1.5 Weight loss and rate of the decomposition curves for SLIG-R

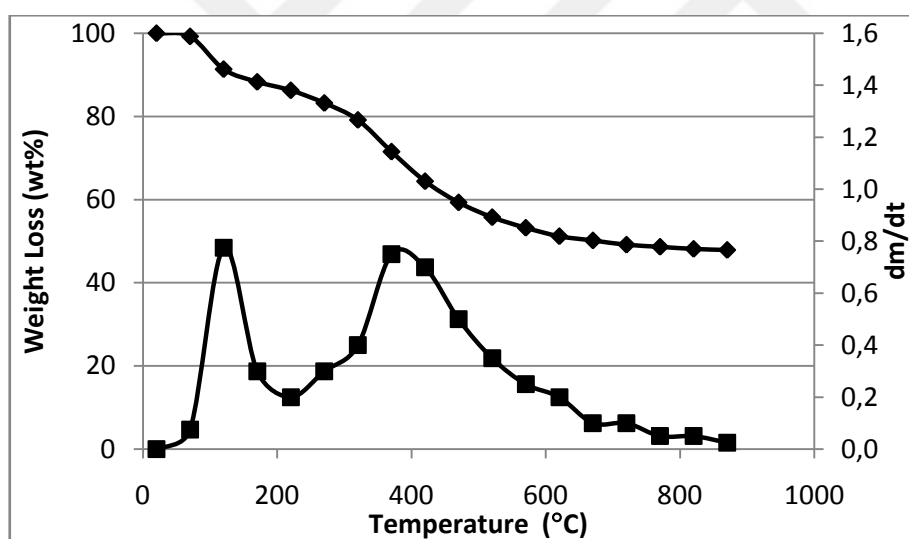


Figure 5.6.1.6 Weight loss and rate of the decomposition curves for SLIG-C

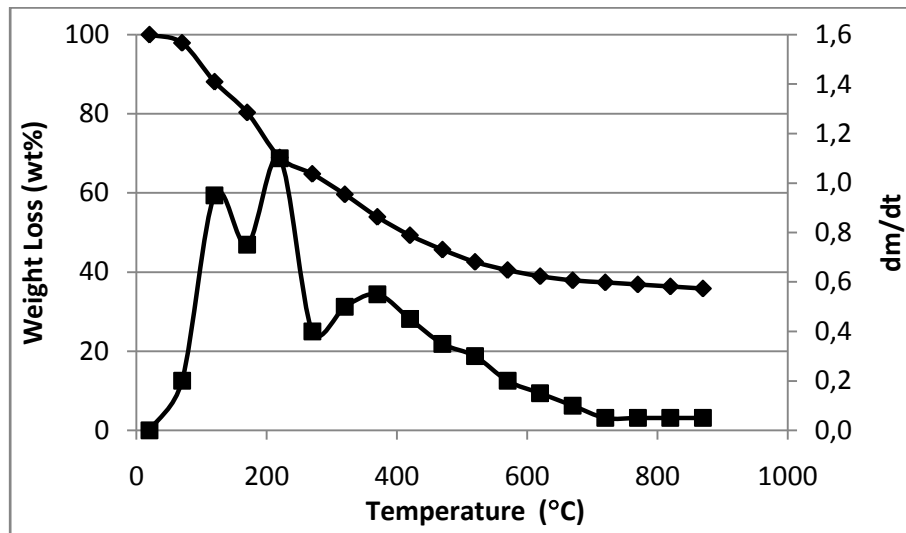


Figure 5.6.1.7 Weight loss and rate of decomposition curves for SLIG-N

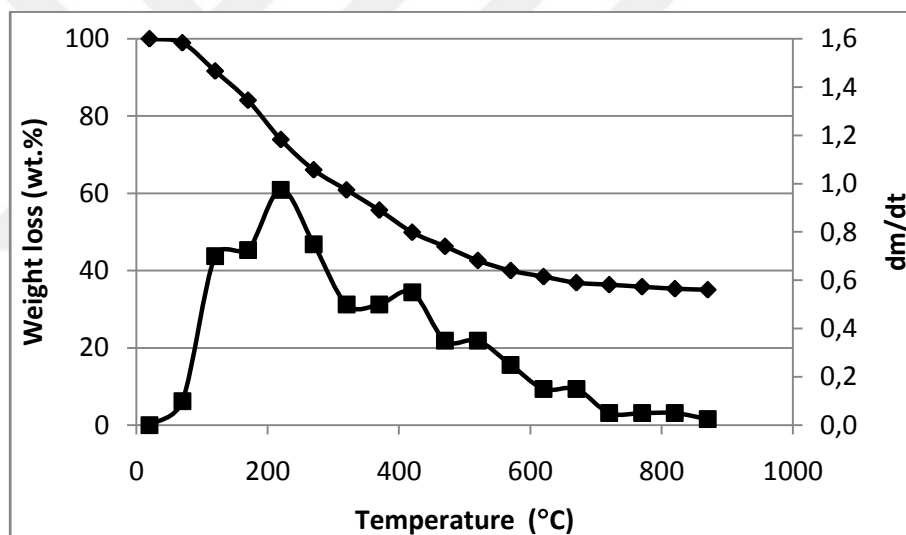


Figure 5.6.1.8 Weight loss and rate of decomposition curves for SLIG-F

The weight loss of raw lignite sample for a heating rate of 5°C/min is represented in Figures 5.6.1.5. The figures indicate that sample lose almost completely its moisture below 150 °C. The required energy to breakdown the hydrogen bonds between polar groups may be obtained above 150 °C. The essential weight loss occurs mainly in the 400 °C – 600 °C region. Slow weight loss was observed for lignite sample in the temperature range of 250 - 300 °C. This loss may be attributed to the loss of a small amount of pyrolysis water as a result of the decomposition of the phenolic structures, the carbonyl groups or the peroxy radicals. The rapid devolatilization after 300°C is associated with the primary carbonization. After the 300 °C, big organic molecules breakdown between the temperatures of 330 - 550 °C. Inorganic decomposition starts above 550 °C, such as MgCO_3 and CaCO_3 .

As the mineral matter is removed from lignite structure, the weight losses decrease. All samples indicate that weight loss up to 200 °C due to their moisture.

Thermogravimetric Analysis of GOS

Figures 5.6.1.9 - 5.6.1.12 shows the weight losses and differential weight losses of raw and demineralized oil shale samples, respectively.

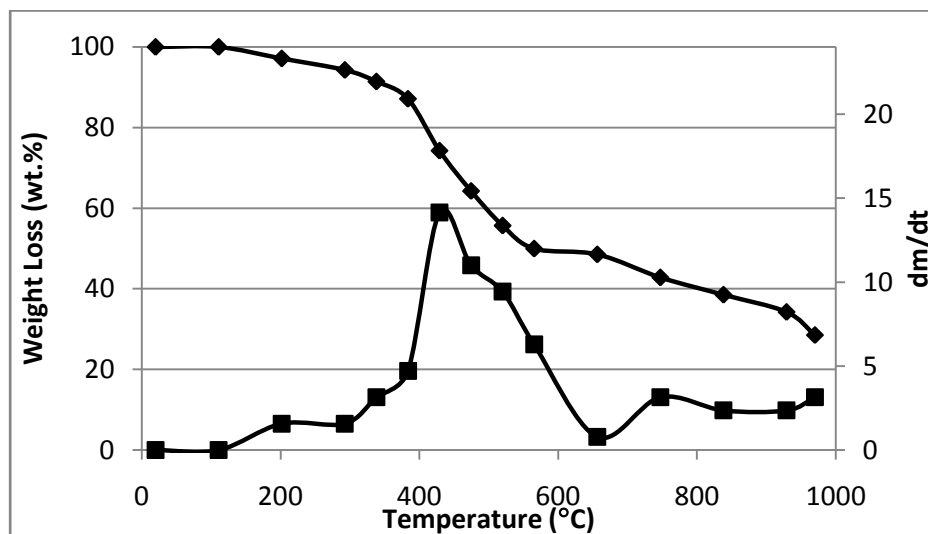


Figure 5.6.1.9 Weight loss and rate of decomposition curves for GOS-R

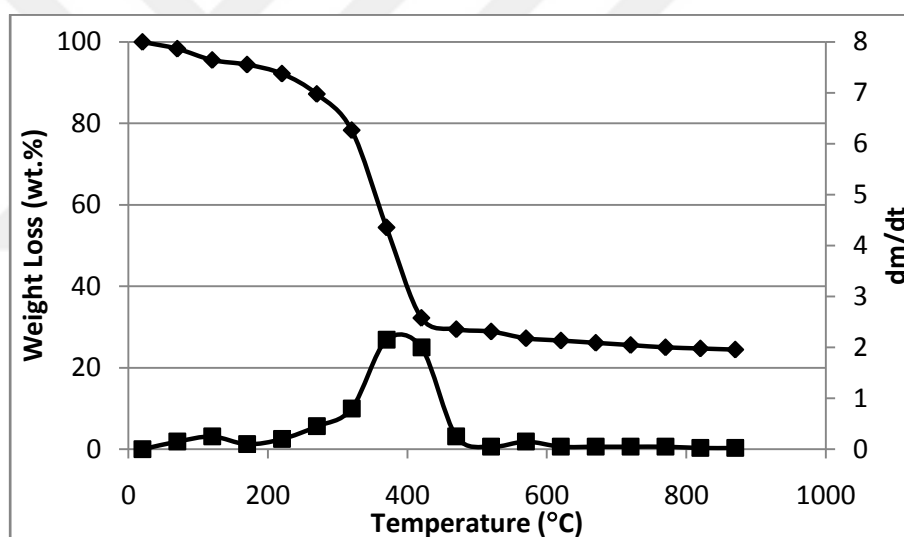


Figure 5.6.1.10 Weight loss and rate of decomposition curves for GOS-C

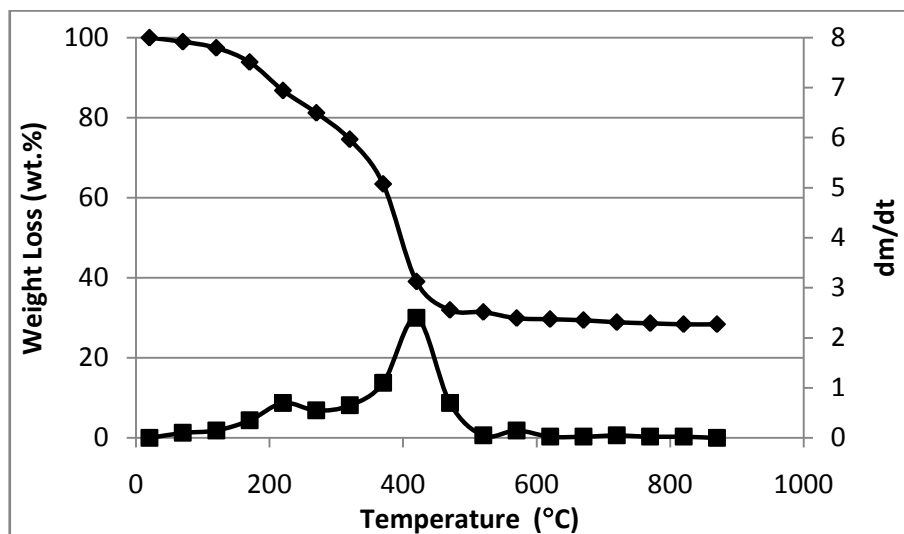


Figure 5.6.1.11 Weight loss and rate of decomposition curves for GOS-N

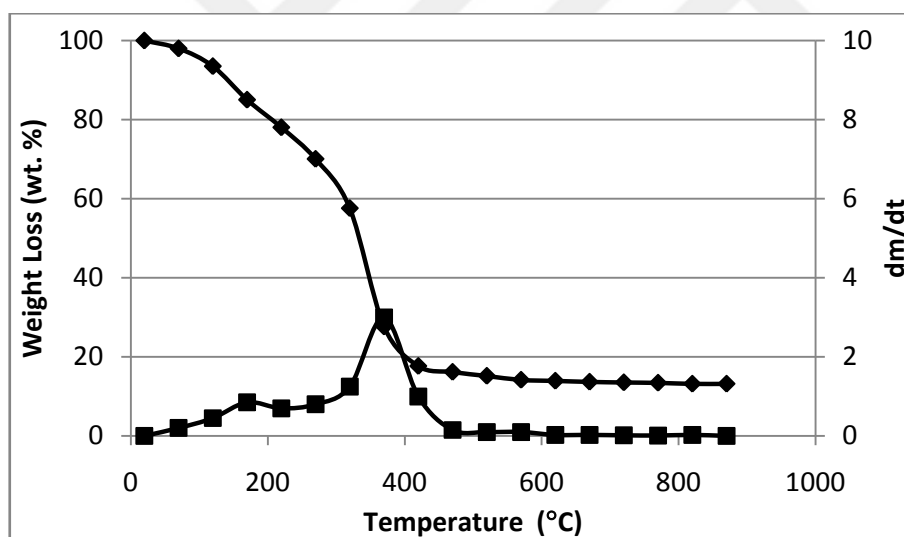


Figure 5.6.1.12 Weight loss and rate of decomposition curves for GOS-F

Weight loss of GOS-R in the low-temperature region, from ambient up to approximately 200 °C, has been attributed to the loss of moisture, interlayer water from clay minerals and also to decomposition of mineral nahcolite (NaHCO_3) which is one of the minerals present in the raw shale. Clay minerals present in oil shale may release structure water over a wide range of temperature up to about 550 °C, physical changes, such as softening and molecular rearrangement associated with the release of gases in kerogen prior to its decomposition to bitumen may occur as well. Above all, in this stage the predominant cause of mass loss is simply moisture.

Usually, the weight loss in this stage is considered the measure of water present in oil shale. The weight loss in the region from about 200 to 600 °C occurs on account of the hydrocarbonaceous material. Below 350 °C the weight loss is small. The main weight loss begins about 350 °C, from then on, the rate of weight loss increases rapidly attributed to formation of volatile hydrocarbons. Between 600 °C and 900 °C, the weight loss is attributed to decomposition of carbonate minerals such as calcite, dolomite, ankerite, and others. At the same time, CO_2 (the product of carbonate decomposition) which at high temperature reacts with residual char to form CO also causes some weight loss.

The weight loss due to decomposition of inorganic matter for SLIG is greater than that of SASP. The reason is that, high organic carbon content of lignite. Produced aliphatic hydrocarbons are not

great amount in SLIG but formed polyaromatics, which cannot be, analyzed our technique makes this difference. And by cracking of the asphaltene to aliphatic hydrocarbons as the temperature rises. Similar results have been reported by the other researchers. (Ceylan, 1999)



5.6.2 Kinetic Study of Samples

The rate of conversion, dx/dt for TG experiment at constant rate of temperature change, $\beta=dT/dt$ may be expressed by

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x) \quad (5.6.2.1)$$

where $f(x)$ is the function of conversion, such as $(1-x)$ for first order reaction, E is the activation energy, A is the Arrhenius factor, R is the gas constant and x is the degree of advance defined by

$$x = \frac{w_o - w}{w_o - w_f} \quad (5.6.2.2)$$

where w is the weight of the sample at a given time t , w_o and w_f , refer to values at the beginning and the end of the weight loss.

Equation (1) can be written as;

$$\frac{dx}{dT} \frac{dT}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x) \quad (5.6.2.3)$$

or

$$\frac{dx}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(x) \quad (5.6.2.4)$$

where β is dT/dt .

Integration of Equation (5.6.2.4) gives the Coats-Redfern Equation;

$$\ln\left[\frac{g(x)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (5.6.2.5)$$

where $g(x)$ is the integrated form of $f(x)$. According to Eqn.(5.6.2.5), a plot of $\ln(g(x)/T^2)$ versus $1/T$ gives a straight line of slope $-E/R$.

In calculations, 15 different types of kinetic models which are dependent on the mechanism of the degradation reaction were employed to define the kinetic expression. TGA data were employed to these models tabulated in Table 5.6.2.1.

Table 5.6.2.1 Set of reaction models applied to describe thermal decomposition in solid

Model		$f(x)$	$g(x)$
1	First order	$(1-x)$	$-\ln(1-x)$
2	Second order	$(1-x)^2$	$(1-x)^{-1}-1$
3	Third order	$(1-x)^3$	$[(1-x)^{-2}-1]/2$
4	Power Law (P2)	$2x^{1/2}$	$x^{1/2}$
5	Power Law (P3)	$3x^{2/3}$	$x^{1/3}$
6	Power Law (P4)	$4x^{3/4}$	$x^{1/4}$
7	One Dimensional Diff.	$1/2x$	x^2
8	Contracting Area	$2(1-x)^{1/2}$	$[1-(1-x)^{1/2}]$
9	Contracting Volume	$3(1-x)^{2/3}$	$[1-(1-x)^{1/3}]$
10	Two Dimensional Diff.	$[-\ln(1-x)]^{-1}$	$[(1-x)\ln(1-x)]+x$
11	Three Dim. Diff.	$3(1-x)^{2/3}/[2(1-(1-x)^{1/3})]$	$[1-(1-x)^{1/3}]^2$
12	Ginstling Brounshtein	$3/2((1-x)^{-1/3}-1)$	$(1-(2x/3)-(1-x)^{2/3})$
13	Avrami-Efore'ev	$2(1-x)[- \ln(1-x)]^{1/2}$	$[- \ln(1-x)]^{1/2}$
14	Avrami-Efore'ev	$3(1-x)[- \ln(1-x)]^{2/3}$	$[- \ln(1-x)]^{1/3}$
15	Avrami-Efore'ev	$4(1-x)[- \ln(1-x)]^{3/4}$	$[- \ln(1-x)]^{1/4}$

5.6.2.1 Kinetic Study of SASP

Under the effect of extreme heat, most of the hydrocarbon compounds endure permanent chemical and physical change. Pyrolysis, which is an endothermic reaction, involves the cracking and conversion of hydrocarbon molecules in an inert atmosphere. It is stated in the literature that the solid fuels are converted into gaseous, liquid and solid products through successive devolatilization reactions developing in accordance with temperature increases during pyrolysis. The chemical reactions comprising the pyrolysis of solid fuels occur generally according to the following sequence. At first, free radicals form via thermal cracking of the bonds among the atomic clusters. Subsequently, these free radicals become stabilized by means of internal rearrangement of the atoms or by collision with other species. In addition, tar products contain unstable free radicals among which recombination activities take place. Consequently, the lighter fractions of the stabilized species are lost as volatiles whereas the heavier molecules form and remain as the part of the char production (Altun, 2003).

As shown from TGA curves asphaltite samples decomposed in a single stage, between 375-525°C. Kinetic calculations according to Coats-Redfern equation were performed in this temperature range.

R^2 values for each model for asphaltite samples determined using the Coats Redfern method and shown in Table 5.6.2.2.

Table 5.6.2.2 Regression coefficient for SASP samples

	R^2			
Model	SASP-R	SASP-C	SASP-N	SASP-F
1	0.9239	0.9086	0.9527	0.9243
2	0.9310	0.9544	0.9629	0.9769
3	0.9395	0.9412	0.9591	0.9680
4	0.8202	0.6004	0.1278	0.0170
5	0.5197	0.0400	0.7577	0.7512
6	0.0017	0.3636	0.9309	0.9083
7	0.9353	0.8933	0.9437	0.8821
8	0.9191	0.8808	0.9318	0.8648
9	0.9208	0.8911	0.9407	0.8894
10	0.9352	0.9064	0.9544	0.9098
11	0.9309	0.9200	0.9612	0.9352
12	0.9378	0.9114	0.9580	0.9198
13	0.8624	0.8251	0.8583	0.7548
14	0.6992	0.6044	0.1806	0.0328
15	0.2327	0.1064	0.6771	0.6036

According to Table 5.6.2.2, TGA data of raw and demineralized asphaltite samples were represented by Model 2 which is second order reaction mechanism and activation energies according to Model 2 were calculated and tabulated in Table 5.6.2.3.

Table 5.6.2.3 Activation energies of asphaltite samples

Activation energy (kJ/mol)			
SASP-R	SASP-C	SASP-N	SASP-F
62.4	56.5	42.0	43.8

As the mineral matter was removed from organic structure, activation energy decreased. Treatment by HNO_3 caused the large effect because of the decomposition of nitro-groups.

For instance, Altun et al. carried out a similar study and calculated the activation energies of pyrolysis of Silopi asphaltite. In their study, calculated activation energies varied from 50.7 to 61.9 kJ mol^{-1} for stage 1 and from 26.1 to 37.4 kJ mol^{-1} for stage 2. Jaber and Probert applied TG and DTG to two different Jordanian oil shales and calculated the activation energies which varied from 54.7 to 86.2 kJ mol^{-1} for stage 1 and from 149 to 203 kJ mol^{-1} for stage 2.

Although there are many studies on the pyrolysis kinetics of oil shale, there is just a few studies on the pyrolysis kinetics of demineralized oil shales.

Karayıldırım et.al. studied on the pyrolysis kinetics of demineralized asphaltite samples. They have found the activation energies as 137.7, 110.5, 68.8 and 67.9 for SASP-R, SASP-C, SASP-N and SASP-F, respectively. TGA data were recorded with the same sample,

Şirnak asphaltite. The difference with our study may come from employed kinetic models. They have found the reaction order between 2.03-0.79.

5.6.2.2 Kinetic Study of SLIG

Lignite samples were pyrolyzed in two stages, namely primary region and secondary region. Coats-Redfern method was used to determine activation energies for each region. Table 5.6.2.4 shows the temperature ranges of these pyrolysis regions.

Table 5.6.2.4 Temperature ranges of two pyrolysis regions of SLIG samples

	Temperature Range	
	Primary Region (°C)	Secondary Region (°C)
SLIG-R	345-445	445-545
SLIG-C	345-445	445-545
SLIG-N	345-445	445-545
SLIG-F	345-445	445-545

R^2 values for each model for lignite samples determined using the Coats Redfern method for region I and shown in Table 5.6.2.5.

Table 5.6.2.5 Regresion coefficient for lignite samples at Region I

	R^2			
Model	SLIG-R	SLIG-C	SLIG-N	SLIG-F
1	0.97	0.98	0.98	0.98
2	0.98	0.99	0.99	0.99
3	0.96	0.98	0.98	0.97
4	0.36	0.88	0.97	0.97
5	0.96	0.97	0.99	0.95
6	0.89	0.98	0.97	0.96
7	0.96	0.97	0.95	0.96
8	0.97	0.95	0.48	0.87
9	0.95	0.96	0.54	0.86
10	0.96	0.96	0.95	0.94
11	0.92	0.97	0.96	0.96
12	0.91	0.98	0.96	0.96
13	0.86	0.98	0.98	0.97
14	0.90	0.91	0.98	0.98
14	0.92	0.93	0.94	0.95

According to Table 5.6.2.5, TGA data of lignite samples were represented by Model 2 which is second order reaction mechanism and activation energies according to Model 2 were calculated and tabulated in Table 5.6.2.6.

Table 5.6.2.6 Activation energies of SLIG samples for Region I

Activation energy (kJ/mol)			
SLIG-R	SLIG-C	SLIG-N	SLIG-F
34.25	31.61	17.44	19.53

After demineralization of SLIG-R with HCl and HNO₃, activation energy decreased because of removal of carbonates and pyrite. In HNO₃ treated sample, activation energy decreased, since nitro-compounds decomposed at lower temperature and consequently mass loss increased and remainder required lower activation energy.

R² values of each model for lignite samples determined using the Coats-Redfern method for region II were shown in Table 5.6.2.7.

Table 5.6.2.7 Regression coefficient for lignite samples at Region II

	R²			
Model	LIG-R	LIG-C	LIG-N	LIG-F
1	0.97	0.96	0.97	0.97
2	0.99	0.99	0.99	0.99
3	0.96	0.97	0.98	0.98
4	0.95	0.95	0.95	0.95
5	0.96	0.98	0.94	0.96
6	0.95	0.97	0.97	0.96
7	0.96	0.98	0.67	0.68
8	0.98	0.96	0.93	0.90
9	0.94	0.66	0.68	0.92
10	0.96	0.96	0.95	0.95
11	0.92	0.97	0.97	0.93
12	0.94	0.98	0.97	0.97
13	0.89	0.98	0.96	0.98
14	0.92	0.93	0.98	0.98
15	0.91	0.90	0.92	0.94

According to Table 5.6.2.7, TGA data of lignite samples were represented by Model 2 which is second order reaction mechanism and activation energies according to Model 2 were calculated and tabulated in Table 5.6.2.8.

Table 5.6.2.8 Activation energy of SLIG samples for Region II

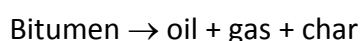
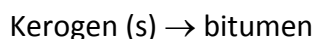
Activation energy (kJ/mol)			
SLIG-R	SLIG-C	SLIG-N	SLIG-F
34.46	32.41	26.50	30.47

In region II, activation energies decreased for demineralized lignite samples. As expected, removal of mineral matter from organic structure causes the reduction of required energy to decomposition. Demineralized lignite samples exhibit lower activation energies in comparison those of parent lignites. The acid treatments during the demineralization process cause the cleavage several types of bonding. These type effects may result in lower activation energies for the devolatilization process.

Durusoy et.al. calculated the activation energy for the untreated lignite sample and was found as 23.8 kJ/mol. Also Gldoğan et.al. studied on the pyrolysis kinetics of Tunçbilek lignite and they have found the activation energies between 15-59 kJ/mol. In the study of Elbeyli and Pişkin, thermogravimetric analysis was used to study the pyrolysis kinetics of Turkish bituminous coals. The data indicate that the pyrolysis of coals is a 1-stage process. The decomposition stage 350-700 °C has a best fit with first-order kinetics with activation energy between 65-97 kJ/mol.

5.6.2.3 Kinetic Study of GOS

Numerous attempts addressing the mechanistic and kinetic points of view have been made to understand the processes occurring during oil shale pyrolysis. Hubbard and Robinson obtained rate data could be interpreted in terms of two successive reactions;



where the bitumen product refers to lower molecular weight components which are vaporizable.

The thermal behavior of oil shale may exhibit characteristics of both the inorganic (mineral) and organic (kerogen+bitumen) components. Kerogen is defined as the fraction of the organic matter in a sedimentary rock that is insoluble in common petroleum solvents. Bitumen is soluble in organic solvents but represents only a small amount of organic matter in an oil shale (Kok, 2001). To investigate the effect of mineral in oil shale, isothermal thermogravimetric analysis of raw and demineralized oil shale samples were carried out at a heating rate of 5 K/min.

Oil shale samples were pyrolyzed in two stages, namely primary region and secondary region. Coats-Redfern method was used to

determine activation energies for each region. Table 5.6.2.9 shows the temperature ranges of these pyrolysis regions.

Table 5.6.2.9 Temperature ranges of two pyrolysis regions of GOS samples

	Temperature Range	
	Primary Region (°C)	Secondary Region (°C)
GOS-R	300-420	420-550
GOS-C	300-420	420-550
GOS-N	300-420	420-550
GOS-F	300-420	420-550

R^2 values of each model for GOS samples determined using the Coats-Redfern method for Region I and shown in Table 5.6.2.10.

Table 5.6.2.10 Regression coefficient for oil shale samples at Region I

	R^2			
Model	GOS-R	GOS-C	GOS-N	GOS-F
1	0.97	0.96	0.98	0.92
2	0.98	0.99	0.99	0.95
3	0.99	0.98	0.97	0.94
4	0.97	0.96	0.97	0.93
5	0.97	0.97	0.98	0.92
6	0.96	0.98	0.97	0.92
7	0.96	0.97	0.97	0.86
8	0.95	0.97	0.94	0.90
9	0.97	0.97	0.96	0.90
10	0.97	0.97	0.96	0.88
11	0.96	0.96	0.95	0.91
12	0.96	0.96	0.95	0.86
13	0.98	0.95	0.98	0.87
14	0.97	0.95	0.98	0.63
15	0.97	0.96	0.96	0.67

According to Table 5.6.2.10, TGA data of all GOS samples were represented by Model 2 which is second order reaction mechanism and activation energies according to Model 2 were calculated and tabulated in Table 5.6.2.11.

Table 5.6.2.11 Activation energies of oil shale samples for Region I

Activation energy (kJ/mol)			
GOS-R	GOS-C	GOS-N	GOS-F
48.76	45.59	12.59	34.19

After demineralization of GOS-R with HCl and HNO₃, activation energy decreased because of removal of carbonates and pyrite. In HNO₃ treated sample, activation energy decreased, since nitro-compounds decomposed at lower temperature and consequently mass loss increased and remainder required lower activation energy.

In the same manner, all calculations were repeated for Region II. R² values of employed models and activation energies of oil shale samples were tabulated in Tables 5.6.2.12 and 5.6.2.13, respectively.

Table 5.6.2.12 Regression coefficient for oil shale samples at Region II

	R^2			
Model	GOS-R	GOS-C	GOS-N	GOS-F
1	0.97	0.96	0.97	0.94
2	0.98	0.99	0.99	0.96
3	0.99	0.98	0.98	0.95
4	0.96	0.96	0.97	0.94
5	0.97	0.97	0.98	0.93
6	0.98	0.97	0.96	0.93
7	0.98	0.96	0.96	0.90
8	0.95	0.96	0.94	0.90
9	0.94	0.95	0.97	0.92
10	0.95	0.95	0.97	0.92
11	0.98	0.97	0.96	0.94
12	0.96	0.94	0.96	0.90
13	0.97	0.93	0.97	0.91
14	0.96	0.93	0.97	0.91
15	0.97	0.96	0.98	0.90

According to Table 5.6.2.12, TGA data of all GOS samples were represented by Model 2 which is second order reaction mechanism and activation energies according to Model 2 were calculated and tabulated in Table 5.6.2.13.

Table 5.6.2.13 Activation energy of oil shale samples for Region II

Activation energy (kJ/mol)			
GOS-R	GOS-C	GOS-N	GOS-F
102.62	97.84	66.33	61.47

As shown from Table 5.6.2.13, activation energy decreased after demineralization of raw oil shale. Since removing of mineral matter caused the reduction in required energy for decomposition.

The pyrolysis kinetics of oil shales by evaluating TGA data were investigated by many researchers. Kok studied on the pyrolysis kinetics of Seyitömer oil shale, and the data indicate that the pyrolysis of oil shale is a 2-stage process. He found that the first zone activation energies are higher than the second region. This situation can be explained such that organic compounds mostly decompose at lower temperatures than other mineral type compounds. Torrente et.al. studied on the pyrolysis kinetics of Spain oil shale by non-isothermal thermogravimetric analysis data and they found activation energy as 167 kJ/mol. Aboulkas et.al (2008) calculated the activation energy for oil shale with the heating rate of 5 °C/min, and found as 80 kJ/mol. In the study of Kök and İşcan (2007), the activation energies were in the range of 41.8–215.4 kJ/mol for Himmetoğlu oil shale and 22.9–141.3 kJ/mol for Mengen oil shale. On the other hand, the activation energies of Çan oil shale were found in the range of 13.1–169.7 kJ/mol.

Pyrolysis behavior of demineralization products provides useful information for the interaction between kerogen and inorganic matrix of the oil shale. Mineral matter present in oil shales is believed to play an important role in the thermally induced catalytic alteration of kerogen during petroleum formation (Evans 1983). Minerals decrease the oil yield in favour of gaseous products during pyrolysis reactions of oil shales.

Karayıldırım et.al. (2004) studied on the pyrolysis kinetics of demineralized Göynük oil shales and surprisingly they have found that activation energies increased after demineralization. They explained this situation by nitration and changing the oil shale composition after demineralization.

5.6.2.4 Kinetic Study of Swollen GOS

The swelling of the demineralized oil shale samples (kerogen) in DMSO, pyridine and THF was accomplished by using the volumetric swelling technique. Göynük oil shale samples were demineralized with HCl, HNO₃ and HF by standard methods, called as GOS-K. TGA data of GOS-K and swollen oil shale samples, namely GOS-K-DMSO, GOS-K-THF, and GOS-K-Pyridine, were recorded and kinetic study was employed as explained above. Swollen oil shale samples were pyrolyzed in two stages, namely primary region and secondary region. Coats-Redfern method was used to determine activation energies for

each region. Table 5.6.2.14 shows the temperature ranges of these pyrolysis regions.

Table 5.6.2.14 Temperature ranges of two pyrolysis regions of oil shale samples

	Temperature Range	
	Primary Region (°C)	Secondary Region (°C)
GOS-K-DMSO	275-385	385-500
GOS-K-THF	275-385	385-500
GOS-K-P	275-385	385-500

R^2 values of each model for swollen oil shale samples determined using the Coats-Redfern method for region I and shown in Table 5.6.2.15.

Table 5.6.2.15 Regresion coefficient values for swollen oil shale samples at Region I

Model	GOS-K-DMSO	GOS-K-THF	GOS-K-Pyridine
1	0.97	0.97	0.97
2	0.96	0.96	0.97
3	0.95	0.96	0.96
4	0.96	0.95	0.93
5	0.96	0.94	0.93
6	0.95	0.94	0.91
7	0.95	0.94	0.92
8	0.94	0.89	0.93
9	0.86	0.88	0.93
10	0.87	0.88	0.88
11	0.90	0.90	0.90
12	0.94	0.93	0.91
13	0.94	0.94	0.92
14	0.92	0.94	0.91
15	0.92	0.93	0.91

According to Table 5.6.2.15, TGA data of swollen oil shale samples were represented by Model 2 to compare raw GOS sample. Activation energies according to Model 2 were calculated and tabulated in Table 5.6.2.16.

Table 5.6.2.16 Activation energies of swollen oil shale samples for Region I

Activation energy (kJ/mol)			
GOS-K	GOS-K-DMSO	GOS-K-THF	GOS-K-Pyridine
34.19	33.2	32.6	29.7

Activation energy of GOS-K was found to be 29.19 kJ/mol, as shown from Table 5.6.2.16, activation energies of swollen oil shale samples were decreased. Since solvent swelling caused changes in the physical structure of macromolecular network. Kerogen reactivity was enhanced because the molecular network was expanded by solvent swelling and expansion of network structure upon swelling increased the decomposition rate in pyrolysis. Solvent swelling breaks the non-covalent bonds and expands the molecular network structure and large molecules become liable to escape through the network structure with the less severity char formation.

Pyridine has lowest activation energy, this may due to the nitrogen retained in the kerogen matrix. According to literature, nitrogen containing compounds have been reported to enhance coal conversion (Tagaya, 1987).

R^2 values of each model for swollen oil shale samples determined using the Coats-Redfern method for region II and shown in Table 5.6.2.17.

Table 5.6.2.17 Regression coefficient for swollen oil shale samples at Region II

Model	GOS-K-DMSO	GOS-K-THF	GOS-K-Pyridine
1	0.97	0.97	0.97
2	0.96	0.97	0.97
3	0.95	0.96	0.96
4	0.96	0.95	0.93
5	0.96	0.94	0.93
6	0.95	0.94	0.91
7	0.95	0.94	0.92
8	0.94	0.89	0.93
9	0.86	0.88	0.93
10	0.87	0.88	0.88
11	0.90	0.90	0.90
12	0.94	0.93	0.91
13	0.94	0.94	0.92
14	0.92	0.94	0.91
15	0.92	0.93	0.91

According to Table 5.6.2.17, TGA data of swollen oil shale samples were represented by Model 2 which is second order reaction. Activation energies according to Model 2 were calculated and tabulated in Table 5.6.2.18.

Table 5.6.2.18 Activation energies of swollen oil shale samples for Region II

Activation energy (kJ/mol)			
GOS-K	GOS-K-DMSO	GOS-K-THF	GOS-K-Pyridine
61.47	60.4	58.6	54.4

6. CONCLUSION

6.1 Demineralization of Oil Shale, Lignite and Asphaltite

A simple classification of lignite, asphaltite and oil shale can be made as moisture, mineral matter and fixed carbon. Mineral matter in these samples exists essentially in three forms: true minerals, dissolved salts in pore water and the elements associated with the hydrocarbonaceous matrix. Mineral matter is a complex mixture of inorganic minerals and elements except carbon, hydrogen, oxygen, nitrogen and sulphur. Clay minerals are the most abundant mineral species. Quartz is the second most abundant mineral phase. Other mineral matter forms are minor minerals and trace elements. These minor minerals include silicates or shales (kaolinite type), calcite, gypsum, siderite, muscovite, carbonates, pyrites, disulphides, sulphides, sulphates and feldspars.

The main purpose in the demineralization was to remove mineral matter without influencing the organic structure. So, in this study, it was aimed to reduce mineral content of asphaltite, oil shale and lignite samples by chemical methods. After leaching with HCl, HCl+HNO₃, and HCl+HNO₃+HF, removed mineral matter was calculated and optimum acid concentration and treating times were found.

Demineralization of Göynük Oil Shale (GOS)

Leaching with different HCl concentrations such as 5 %, 10 %, 20 % and 31.5 % were attempted. In demineralization of oil shale with HCl, optimum acid concentration and time was selected as 10 % and 48 h, respectively. 19.36 % of mineral matter of oil shale sample was removed by treating 10 % HCl.

HCl-treated oil shale samples were treated by HNO₃ solutions with concentrations of 5 %, 10 % and 20 %. In the demineralization of GOS-C with HNO₃, optimum acid concentration and mixing time were selected as 5 % and 1 h, respectively. As concentration of acid solution increases, weight loss decreases. This may be explained as the obtaining the new carbonyl groups and/or connecting of the nitro groups to organic structure. 13.96 % of mineral matter of oil shale sample was removed by treating HNO₃.

HCl-HNO₃ treated oil shale samples, was demineralized for 8 hours with 40% HF to remove silicate structure from organic structure. Treating with HF with a concentration of 40 % removes 23.40 % of mineral matter of oil shale sample.

Demineralization of Eynez Lignite (ELIG)

Lignite samples were also demineralized with HCl, HNO₃ and HF solutions successively. According to results of weight loss and ash level, concentration of HCl solution and demineralization time was selected

as 20 % and 24 h, respectively. A higher degree of demineralization was obtained with 20 % HCl as 22.56 %.

After demineralization of LIG-R with HCl, LIG-C was demineralized with HNO_3 solution to remove pyrite minerals from organic structure. Optimum concentration of HNO_3 solution and demineralization time was selected as 5% and 1 h, respectively. In these conditions, 11.52 % of mineral matter was removed from organic structure.

LIG-N samples were demineralized with 40 % HF solution with different demineralization times. According to results of weight loss and ash level, demineralization time was selected as 8 h and 6.61 % of mineral matter was removed from organic structure. HF removes silicate minerals from organic structure.

Demineralization of Şirnak Asphaltite (SASP)

Asphaltite samples firstly demineralized by HCl with different concentrations and treating times to remove carbonate structure of sample. In demineralization of ASP-R with HCl, concentration of HCl solution and demineralization time was selected as 10% and 24 h, respectively. A higher degree of demineralization was obtained with 10 % HCl as 39.22 %.

In demineralization of ASP-C with HNO_3 , concentration of HNO_3 solution and demineralization time was selected as 5 % and 1 h, respectively. In the high concentrations of acid, the degree of

demineralization decreased, because of the formation of some stable components that could not be removed. 8.10 % of weight loss was obtained in demineralization of asphaltite with HNO_3 .

ASP-N samples were demineralized with 40 % HF solutions with specified demineralization times. In demineralization of ASP-N with HF, concentration of HF solution and demineralization time was selected as 40 % and 8 h, respectively. A higher degree of demineralization was obtained with 40 % HF (39.8%). As the treating times increases, the degree of demineralization decreased because of the formation of some fluorides such as calcium fluorides.

6.2 Isothermal Pyrolysis of Oil Shale, Lignite and Asphaltite

Isothermal Pyrolysis of Göynük Oil Shale (GOS)

Isothermal pyrolysis of GOS-R, GOS-C, GOS-N and GOS-F samples were carried out at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C.

As pyrolysis temperature increases, maximum rate of decomposition occurs at shorter time, then maximum points of plots shifts right to left for all solid samples. Volatile hydrocarbon recovery increased with increasing temperature.

Volatile hydrocarbon recovery of GOS-R was calculated and found as 18.28 %, 27.16 %, 36.10 %, 45.47 % and 50.20 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C,

550 °C, 600 °C and 650 °C, respectively. In isothermal pyrolysis, solid residue of GOS-R was found as 46.02 %, 42.33 %, 40.64 %, 39.37 % and 37.33 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries were calculated as 53.98 %, 57.67 %, 59.36 %, 60.63 % and 62.67 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

In IP of GOS-R, as temperature increases, yield of gas product and yield of C in solid residue increased because of volatilization.

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Cumulative C₁-C₄ and C₂-C₄ selectivities increased as temperature increased, particularly above 550 °C; there is considerable increase in these groups because of the cracking of C₅₊ hydrocarbons at high temperatures. At the same graphs, there is a sharp decrease in C₅-C₉ groups because of the decomposition of liquid products at high temperatures.

In the pyrolysis of GOS-C, volatile hydrocarbon recovery was found as 14.97 %, 22.40 %, 32.70 %, 37.07 % and 41.87 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

In isothermal pyrolysis, solid residue of GOS-C was found as 43.94, 41.40, 39.88, 37.94 and 33.98 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries were calculated as 56.06, 58.60, 60.12, 62.06 and 66.02 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Also, it can be seen that *n*-paraffin and 1-olefin gaseous products constitute the highest portion of the pyrolysis products. Cumulative C₁-C₄ and C₂-C₄ selectivities increased as temperature increased, particularly above 550 °C; there are considerable increases in these groups because of the cracking of C₅₊ hydrocarbons at high temperatures.

In isothermal pyrolysis of GOS-N, volatile hydrocarbon recovery was found as 15.73 %, 25.82 %, 38.32 %, 43.93 % and 47.80 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Solid residue of GOS-N was found as 38.95, 37.40, 35.84, 34.13 and 31.47 % by weight. Total hydrocarbon recoveries were calculated as 61.05, 62.60, 64.16, 65.87 and 68.53 % by weight.

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with

increasing pyrolysis temperature. Cumulative C_1 - C_4 and C_2 - C_4 selectivities increased as temperature increased, particularly above 550°C, there are considerable increase in these groups because of the cracking of C_{5+} hydrocarbons at high temperatures.

For the isothermal pyrolysis of GOS-F, volatile hydrocarbon recovery was found as 20.18 %, 33.70 %, 43.08 %, 52.14 % and 55.07 % by weight (in carbon basis) at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Solid residue of GOS-F was found as 36.08, 34.12, 31.26, 30.40 and 27.96 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries were calculated as 63.92, 65.88, 68.74, 69.60 and 72.04 % by weight at the same pyrolysis temperatures.

Although cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Paraffin and olefin selectivity decreased after 600 °C.

It can be seen that *n*-paraffin and 1-olefin gaseous products constitute the highest portion of the pyrolysis products. The yield of total volatile hydrocarbons increased for the kerogen sample after silicate removal (GOS-F). This tendency was explained due mainly to both the driving force for heat transfer since more heat was transferred from outside towards the inside of the oil shale particles,

thus pyrolysis reaction might have occurred with ease and diffusion limitation might have decreased due to the lack of mineral matrix.

Isothermal Pyrolysis of Eynez Lignite (ELIG)

In the isothermal pyrolysis of ELIG-R, volatile hydrocarbon recovery increased with increasing temperature. Volatile hydrocarbon recovery was analyzed by our analytical technique and found as 5.61 %, 7.59 %, 12.22 %, 18.44 % and 21.17 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Solid residue of ELIG-R was found as 67.28 %, 65.36 %, 64.14 %, 62.26 % and 58.00 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries were also calculated as 32.72 %, 34.64 %, 35.86 %, 37.74 % and 42.00 % by weight at given pyrolysis temperatures. Cumulative n-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Also, it can be seen that n-paraffin and 1-olefin gaseous products constitute the highest portion of the pyrolysis products.

The total amount of volatile product evolution for isothermal pyrolysis of ELIG-C was calculated. Volatile hydrocarbon recovery was found as 3.46 %, 4.60 %, 9.28 %, 12.38 % and 17.21 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

In isothermal pyrolysis, solid residue of ELIG-C was found as 73.20 %, 69.32 %, 64.28 %, 62.14 % and 57.94 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries were calculated as 33.78 %, 35.12 %, 37.86 %, 38.78 % and 44.60 % by weight at the same pyrolysis temperatures.

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature for ELIG-C.

In isothermal pyrolysis of ELIG-N, volatile hydrocarbon recovery was found as 4.27 %, 6.26 %, 10.51 %, 15.92 % and 17.59 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Solid residue of ELIG-N was found as 63.60, 62.66, 60.62, 58.62 and 53.62% by weight. Total hydrocarbon recoveries were calculated as 36.40, 37.34, 39.38, 41.38 and 46.38 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions especially C₁-C₄ group, increased with increasing pyrolysis temperature.

Volatile hydrocarbon recovery of ELIG-F was found as 6.83 %, 8.24 %, 15.31 %, 20.48 % and 21.11 % by weight (in carbon basis) at the

isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Solid residue of ELIG-F was found as 63.10 %, 62.04 %, 60.10 %, 58.42 % and 52.56 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries were calculated as 36.90 %, 37.96 %, 39.90 %, 41.58 %, and 47.44 % by weight at pyrolysis temperatures.

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature.

Isothermal Pyrolysis of Şirnak Asphaltite (SASP)

In isothermal pyrolysis of SASP-R, volatile hydrocarbon recovery was found as 8.58 %, 13.11 %, 18.43 %, 25.74 % and 28.67 % by weight (in carbon basis) at the temperature of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Solid residue of SASP-R was found as 80.10 %, 75.90 %, 74.85 %, 71.09 % and 67.90 % by weight at given temperature above. In isothermal pyrolysis of ASP-R, total hydrocarbon recoveries were calculated as 19.90 %, 24.10 %, 25.15 %, 28.91 % and 32.10 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Thermal cracking of the preasphaltenes and asphaltene become important above 400 °C and the yield of hexane soluble hydrocarbons increases with temperature over this range during the pyrolysis of asphaltite. Above 450 °C temperature range, *n*-paraffins and 1-olefins are formed mainly by the decomposition of asphaltenes and preasphaltenes. Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions nearly remain constant with increasing pyrolysis temperature.

At the end of the isothermal pyrolysis of HCl-treated asphaltite samples (SASP-C), volatile product evolution rate depending on temperature was obtained and volatile hydrocarbon recovery was found as 5.92 %, 10.49 %, 16.93 %, 22.53 %, and 27.49 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

In isothermal pyrolysis, solid residue of SASP-C was found as 78.82 %, 74.38 %, 72.25 %, 67.50 % and 64.79 % by weight at the pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Total hydrocarbon recoveries were calculated as 21.18 %, 25.62 %, 27.75 %, 32.50 % and 35.21 % by weight at given pyrolysis temperatures.

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with

increasing pyrolysis temperature. Cumulative C₁-C₄ and C₂-C₄ selectivity increased as temperature increased, particularly above 550°C.

Volatile hydrocarbon recovery of SASP-N was found as 6.02 %, 12.50 %, 17.62 %, 24.46 % and 27.29 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

In isothermal pyrolysis, solid residue of SASP-N was found as 76.71 %, 73.21 %, 71.43 %, 64.20 % and 62.52 % by weight. Total hydrocarbon recoveries were also calculated as 8.5, 12.98, 22.56, 24.36 and 27.47% by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Cumulative n-paraffin and 1-olefin groups decreased as temperature increases. Fewer than 550 °C, amount of gas products decreased because of the formation of polymerization reactions. Amount of liquid products increased then above 550 °C, amount of gas products increased because of the volatilization.

Volatile hydrocarbon recovery of SASP-F was found as 12.12 %, 16.20 %, 19.57 %, 23.80 % and 30.50 % by weight (in carbon basis) at the isothermal pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Solid residue of SASP-F was found as 57.39 %, 54.51 %, 52.47 %, 50.04 % and 48.89 % weight at the pyrolysis temperatures. Total

hydrocarbon recoveries were calculated as 42.61 %, 45.49 %, 47.53 %, 49.96 % and 51.11 % by weight at pyrolysis temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively.

Cumulative *n*-paraffin and 1-olefin selectivity graphs at each pyrolysis temperature show that gas fractions increased with increasing pyrolysis temperature. Yield of volatile hydrocarbons increased after leaching of lignite with HCl. Washing with HCl removes CaCO₃, FeCO₃ and MgCO₃ and partially chlorite minerals from asphaltite structure.

6.3 Temperature-Programmed Pyrolysis of Oil Shale, Lignite and Asphaltite

Temperature-Programmed Pyrolysis of Oil Shale

Temperature-programmed pyrolysis of raw and demineralized oil shale samples were performed in an electrically heated reactor. After the completion of each pyrolysis run, products were identified with gas chromatography. After analyzing the chromatograms, volatile product evolution rates were determined. The effect of temperature and time on the rate of total product evolution in the pyrolysis of raw Göynük Oil Shale (GOS-R), HCl-treated Göynük Oil Shale (GOS-C), HCl-HNO₃ treated Göynük Oil Shale (GOS-N) and HCl-HNO₃-HF treated Göynük Oil Shale (GOS-F) were investigated.

The temperature at which the products evolution is the greatest are seen to be approximately 440 °C for each pyrolysis runs.

The *n*-paraffins and 1-olefins were also grouped by carbon number as C_1 – C_4 (C_2 – C_4), C_5 – C_9 , C_{10} – C_{15} , and C_{16+} .

The *n*-paraffin formation rate is higher than that of 1-olefins. The *n*-paraffins produced at high and low temperature consist mainly of methane. This is because the thermal decomposition of kerogen in oil shale takes place in two broad reaction steps. The first, breakdown of kerogen to bitumen and low-molecular-weight hydrocarbons consisting mainly of methane, occurs at lower temperature. Decomposition of bitumen to gas and oil and formation of heavy fractions by secondary reactions takes place in the second step. The hydrocarbons produced by pyrolysis of GOS-R, GOS-C, GOS-N, and GOS-F contained 41.0 %, 40.0 %, 40.0 %, and 39.8 wt % of *n*-paraffin, respectively, at the maximum product evolution temperature. The values of 1-olefins produced by pyrolysis of GOS-R, GOS-C, GOS-N, and GOS-F were 29.9 %, 24.7 %, 24.3 %, and 24.8 wt %, respectively, at the maximum product evolution temperature. The *n*-paraffin and 1-olefins produced by GOS-R products were classified by carbon number at the temperature range between 428 °C and 450 °C. This is the temperature range at which the decomposition rate in pyrolysis is higher than that of the rate for pyrolysis temperatures before and after this range.

n-Paraffin gas yield (C_1 – C_4) showed a slightly decrease in the pyrolysis of GOS-C, GOS-N, and GOS-F compared to the gas yield in the pyrolysis of GOS-R. The *n*-paraffin formation rate was higher than that

of 1-olefins during pyrolysis. n-Paraffin consists mainly of low-molecular-weight volatile hydrocarbons. The yield of the C₁₆₊ n-paraffins in the pyrolysis products of GOS-F was found to be slightly higher than that of the C₁₆₊ n-paraffins in the pyrolysis products of GOS-R, GOS-C, and GOS-N.

The 1-olefin gas yield (C₂-C₄) showed a slightly decrease in the pyrolysis of GOS-C, GOS-N, and GOS-F compared to the gas yield in the pyrolysis of GOS-R. The leaching of mineral matter with HCl, HNO₃, and HF did not cause a marked change in the distribution of 1-olefins by carbon number of C₅-C₉, C₁₀-C₁₅ and C₁₆₊.

A carbon balance of the pyrolysis process was established by determining the recovery of total organic carbon as organic products and the carbon remaining in the reactor because of the coking reactions. Carbon balance a calculation showed that 47 wt. % of the organic carbon in GOS-R was converted to volatile organic compounds and 34.0 wt. % was converted to carbon-rich solid residue. Conversion values to volatile hydrocarbons for the GOS-C and GOS-N samples within the same temperature limits were 43.0 % and 44.5 wt. %, respectively.

Temperature-Programmed Pyrolysis of Lignite

The temperature at which the products evolution is the greatest are seen to be 440 °C for each pyrolysis runs of lignite.

The *n*-paraffin formation rate is higher than that of 1-olefins. The hydrocarbons produced by pyrolysis of ELIG-R, ELIG-C, ELIG-N, and ELIG-F contained 35.0 %, 35.9 %, 41.7 %, and 34.6 wt % of *n*-paraffin, respectively, at the maximum product evolution temperature. The values of 1-olefins produced by pyrolysis of ELIG-R, ELIG-C, ELIG-N, and ELIG-F were 34.5 %, 6.7 %, 10.6 %, and 10.2 wt %, respectively, at the maximum product evolution temperature.

n-Paraffin gas yield (C_1 - C_4) showed a sharply decrease in the pyrolysis of ELIG-C compared to the gas yield in the pyrolysis of ELIG-R, ELIG-N and ELIG-F. The yield of the C_{16+} *n*-paraffins in the pyrolysis products of ELIG-N was found to be higher than that of the C_{16+} *n*-paraffins in the pyrolysis products of ELIG-R, ELIG-C, and ELIG-F.

The 1-olefin gas yield (C_2 - C_4) showed a sharply decrease in the pyrolysis of ELIG-C, ELIG-N, and ELIG-F compared to the gas yield in the pyrolysis of ELIG-R. Demineralization process increases *n*-paraffin formation, and decreases the 1-olefin.

Temperature-Programmed Pyrolysis of Asphaltite

The temperature at which the products evolution is the greatest are seen to be 440 °C for each asphaltite pyrolysis runs.

The hydrocarbons produced by pyrolysis of ASP-R, ASP-C, ASP-N, and ASP-F contained 33.4 %, 31.6 %, 28.9 %, and 24.4 wt % of *n*-paraffin, respectively, at the maximum product evolution temperature.

The values of 1-olefins produced by pyrolysis of ASP-R, ASP-C, ASP-N, and ASP-F were 45.0 %, 27.2 %, 24.6 %, and 24.4 wt %, respectively, at the maximum product evolution temperature. The analysis of samples taken at the different time intervals during the pyrolysis of asphaltite indicated also a change in the C-number distribution of n-paraffins and 1-olefins. n-Paraffins consist mainly of low-molecular weight hydrocarbons such as C₁–C₄ in aliphatic hydrocarbon fraction of the pyrolysis products of asphaltite.

6.4 Solvent Swelling of Oil Shale, Lignite and Asphaltite

Solvent Swelling of Göynük Oil Shale

In swelling studies, the swelling behaviour of GOS samples was investigated by measuring the swelling ratio in 16 different solvents. The number of polar, H-bonding and nonpolar solvents was 3, 5 and 8, respectively. Before solvent swelling process, kerogen has been isolated completely and the effects of mineral matter on swelling behavior of samples have been examined. Among these solvents, pyridine, DMSO and THF give better results. It was found that hydrogen bonding solvents swell the kerogen than do the polar and nonpolar solvents. These solvents have greater affinities to kerogen molecules and give a better permeability, resulting in a larger swelling ratio.

To investigate the thermal behavior of swollen GOS samples, thermogravimetric analysis was employed. The weight loss due to the

water content of the samples, takes place mainly at temperatures of 25–150 °C. The thermal decomposition of the GOS-K-DMSO, GOS-K-THF, GOS-K-Pyridine and GOS-K-Raw take place above 275 °C, with the maximum rate at 440 °C. At temperatures above 525 °C another endothermic effect was observed as results of coking of heavy fractions produced during kerogen decomposition of the samples.

It is well known that kerogen is a cross-linked structure and after being soaked in a solvent kerogen molecules are diassociated, reassociated and rearranged in lower energy conformation. After swelling of the demineralized GOS (kerogen) in Pyridine, DMSO and THF, temperature-programmed pyrolysis was investigated.

The effect of temperature and time on the rate of volatile product evolution in pyrolysis of GOS-K, GOS-K-DMSO, GOSK-Pyridine and GOS-K-THF are shown in Figures 5.4.3.1-5.4.3.4. The pyrolysis behavior of swollen kerogen is different from that of untreated kerogen. Kerogen reactivity may be enhanced because the solvent swelling expanded the macromolecular network and reduced the mass transfer limitations.

For kerogen swollen by DMSO, Pyridine and THF, the volatile hydrocarbon recovery increased from 55.0 wt. % to 59.0 %, 60.5 % and 66.0 wt. %, respectively. The hydrocarbons produced by pyrolysis of GOS-K, GOS-K-DMSO, GOS-K-Pyridine and GOS-K-THF contained 39.8 %, 38.4 %, 38.4 %, and 39.2 wt. % of n-paraffins, respectively, at the

maximum product evolution temperature. The values of 1-olefins produced by pyrolysis of GOS-K, GOS-K-DMSO, GOS-K-Pyridine and GOS-K-THF were 24.8 %, 18.7 %, 18.5 %, and 18.5 wt. %, respectively, at the maximum product evolution temperature.

A carbon balance of the pyrolysis process was established by determining the recovery of total organic carbon as organic products and carbon remaining in the reactor because of coking reactions. Changes in the degree of organic conversion in the pyrolysis of GOS-K, GOS-K-DMSO, GOS-K-Pyridine and GOS-K-THF were shown in Figure 5.4.3.13. Carbon balance calculations showed that 55 wt% of the organic carbon in GOS-K was converted to volatile organic compounds and 21 wt% was converted to carbon rich solid residue.

In the swelling behavior of lignite samples, the swelling behavior of demineralized and raw Soma Kırakdere, Soma Zeybek and Çorum lignites in 16 organic solvents was studied by using the volumetric swelling technique. Five of the solvents were hydrogen-bonding, three of them polar and the remaining were non-polar with varying solubility parameters.

When the swelling degree of isolated and non-isolated lignite samples is compared it is obvious that demineralization enhanced the swelling degree of samples.

Polar solvents behave similar to non-polar solvents whereas only hydrogen bonding solvents except ethanol and isopropyl alcohol

showed enhanced swelling both in raw and isolated samples of Zeybek and Kırakdere lignites.

6.5 Kinetic Study of Oil Shale, Lignite and Asphaltite

Kinetic Study of Asphaltite Samples

In the kinetic study of asphaltite samples, 15 different kinetic models were employed to TGA data at a heating rate of 5K/min. Kinetic study was carried out in a single temperature interval of 375 - 525 °C and by Coats-Redfern method.

TGA data of raw and demineralized asphaltite samples were represented by Model 2 which is second order reaction mechanism.

Activation energies of SASP-R, SASP-C, SASP-N and SASP-F were found as 62.4, 56.5, 42.0 and 43.8 kJ/mol, respectively. As the mineral matter was removed from organic structure, activation energy decreased. Treatment by HNO₃ caused the large effect because of the decomposition of nitro-groups.

Kinetic Study of Lignite Samples

Similarly, in the kinetic study of lignite samples, 15 kinetic models were employed to TGA data in two stage process which are 345 – 445 °C and 445 - 545°C.

TGA data of lignite samples were represented by Model 2 which is second order reaction mechanism. Activation energies of SLIG-R,

SLIG-C, SLIG-N and SLIG-F for Region I, were found as 34.25, 31.61, 17.44 and 19.53 kJ/mol, respectively.

In Region II, activation energies of SLIG-R, SLIG-C, SLIG-N and SLIG-F were found as 34.36, 32.41, 26.50 and 30.47 kJ/mol, respectively.

Kinetic Study of Oil shale Samples

Similarly, in the kinetic study of oil shale samples, 15 kinetic models were employed to TGA data in two stage process which are 300 – 420 °C and 420 – 550 °C.

TGA data were represented by Model 2 which is second order reaction mechanism, for each temperature interval.

In Region I, activation energies of SASP-R, SASP-C, SASP-N and SASP-F were found as 48.76, 45.59, 12.59 and 34.19, respectively.

In Region II, activation energies of SASP-R, SASP-C, SASP-N and SASP-F were found as 102.62, 97.84, 66.33 and 61.47, respectively.

6.6 Supercritical Water Extraction

The supercritical water extraction experiments were performed with raw and demineralized samples of lignite at the reaction temperatures of 400, 450 and 500 °C.

In the gaseous product, CO, CO₂, H₂, CH₄, C₂H₄, C₃H₆ and C₄₊ were analyzed by gas chromatography. Gas product yield was increased with increasing temperature for raw and demineralized

lignite samples. At low temperature, few organic substances can be extracted because of the low solubility of water to relatively heavy organic substance from waters high dielectric constant at low temperature. The change of product yields with increasing temperature was shown in Figures 5.5.2-5.5.5.

As temperature increases yield of gas increased, yields of liquid and solid decreased for all lignite samples. At high temperature, the secondary reaction take place, and extractable substance will be converted into gas, low molecular weight products and unextractable big molecules.

The analysis of gas product show that the main product in gas phase is CO₂, its composition is more than 50 % at 400 °C for raw and demineralized lignite samples. With increases of temperature, CO₂ yield decreases.

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APPENDIX I

Calculation of Volatile Product Evolution Rate

Flow rate of neopentan;

$$V = (20 \text{ mL/min})(0.0049) = 9.8 \times 10^{-5} \text{ mL/min}$$

By using ideal gas law ($PV=nRT$) , moles of neopentan was calculated as

$$\eta_{NP} = 4.01 \times 10^{-6} \text{ mol/min}$$

Neopentan consists of 5 C atoms, so moles of C was calculated as;

$$n = (5)(4.01 \times 10^{-6} \text{ mol/min}) = 2 \times 10^{-5} \text{ mol/min}$$

$$\text{Mass of C ; } m_c = nMW = (2 \times 10^{-5} \text{ mol/min})(12 \text{ g/mol}) = 0.241 \text{ mg C/min}$$

At each time interval, volatile product evolution rate was calculated by the following formula;

$$N_c = m_c \frac{\text{TPA} - \text{RPA}}{\text{RPA}} \quad (\text{mg C/min})$$

APPENDIX II**Numerical Integration**

The area of volatile product evolution rate versus time curves were calculated by Simpson's Rule. The formula is given below:

$$I = \int_{x_0}^{x_n} f(x)dx = \frac{h}{3} \left[(f_0 + f_n + 4(\sum_{i=odd} f_i) + 2(\sum_{i=even} f_i)) \right]$$

RESUME

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