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NOT TO BE TAKEN FROM THIS ROOM

EXTRACTION OF LIGNITES FROM
ÇAN, SOMA AND TUNÇBİLEK WITH
DONOR AND NON-DONOR SOLVENTS IN
SOXHLET EXTRACTOR AND AUTOCLAVE

by

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ABSTRACT

The extraction of Çan (Çanakkale), Soma (Manisa) and Tunçbilek (Tavşanlı) lignite samples were investigated in a) Soxhlet extractors, b) a 1 lt autoclave. Benzene, hexane, benzene-ethanol mixture, toluene, tetrahydrofuran (THF) and pyridine were used as solvents and the effects of particle size, siphon number, solvent to lignite ratio (S/L) on extraction yields were investigated in Soxhlet extractors. It was observed that as the boiling point of the extracting solvent (except for THF and benzene-ethanol mixture), the particle size of lignite samples, the siphon number, the rank (except for pyridine extraction) and the lignite to solvent ratio increased, the Soxhlet extraction yield increased also.

The extraction in the autoclave was done with tetralin and a) under N_2 pressure, b) under H_2 pressure. The temperature was fixed at $325^\circ C$, the maximum possible safe operating temperature of the autoclave. The effect of pressure, solvent to lignite ratio and reaction time on the extraction yields were determined using Tunçbilek (Tavşanlı) lignite samples under N_2 pressure. It was observed that the extraction yields increased as the extraction time, the solvent to lignite ratio and pressure increased and decreased as the % carbon (daf) increased in the

lignite sample.

The extractions under H_2 pressure (hydroliquefaction) were carried out at a fixed reaction time of 60 min, pressure of 60 atm and solvent to lignite ratio of 10. The yields of extraction under H_2 pressure showed a similar trend as under N_2 pressure but were slightly higher.

SOXHLET CİHAZINDA VE OTOKLAVDA
ÇAN, SOMA, TUNÇBİLEK LİNYİTLERİNİN
HİDROJEN VEREN VE VERMEYEN ÇÖZÜCÜLERLE
ÖZÜTLENMESİ

ÖZET

Çan (Çanakkale), Soma (Manisa), Tunçbilek (Tavşanlı) linyit nümunelerinin özütlenmesi a) Soxhlet cihazında, ve b) otoklavda incelenmiştir. Çözücü olarak benzen, heksan, benzen-etanol karışımı, toluen, tetrahidrofuran (THF) ve piridin kullanılmıştır. Tane büyüklüğünün, sifon sayısının ve çözücü/linyit oranının özütleme verimi üzerindeki etkisi incelenmiştir. Çözücü kaynama noktası (THF ve benzen-etanol karışımı hariç), linyit tane büyüklüğü, sifon sayısı ve linyit/çözücü oranı arttırıldıkça, özütleme veriminin arttığı tesbit edilmiştir. Piridinle özütlemenin haricinde, linyit yaşı arttıkça verimin de arttığı görülmüştür.

Otoklav içindeki özütleme tetralinle ve a) azot, b) hidrojen basıncı altında yapılmıştır. Sıcaklık 325 °C de sabit tutulmuştur. Tunçbilek (Tavşanlı) linyit nümuneleri azot basıncı altında özütlenerek, basıncın, çözücü/linyit oranının ve reaksiyon süresinin özütleme verimi üzerindeki etkisi incelenmiştir. Verimin reaksiyon süresi, çözücü/linyit oranı ve basınçla arttığı, fakat linyit nümunelerinin karbon yüzdeleri ile azaldığı tesbit edilmiştir.

Hidrojen basıncı altındaki özütleme çalışmaları boyunca, reaksiyon süresi 60 dakika, çözücü/linyit oranı 10 ve basınç 60 atmosfer'de sabit tutulmuştur. Hidrojen atmosferindeki özütleme verimlerinin, azot basıncı altındaki özütleme verimlerine oranla az da olsa daha yüksek olduğu görülmüştür.

TABLE OF CONTENTS

Acknowledgements	1
Abstract	111
Özet	v
Table of Contents	vii
List of Tables	ix
List of Figures	x
CHAPTER 1. INTRODUCTION	1
CHAPTER 2. LIQUEFACTION OF COAL	2
2.1 CHEMISTRY OF COAL	6
2.1.1 Rank of Coal	6
2.1.2 Chemical Composition of Coal	8
2.2 TYPES OF LIQUEFACTION PROCESSES	10
2.2.1 Pyrolysis	11
2.2.2 Indirect Liquefaction	12
2.2.3 Solvent Extraction	12
2.2.3.1 Solvent Classification	13
2.2.3.2 The Action of Solvents on Coal	15
2.2.3.3 Extraction Parameters	20
2.2.4 Direct Liquefaction by Hydrogenation	24

CHAPTER 3. EXPERIMENTAL	30
3.1 APPARATUS USED	30
3.1.1 Soxhlet Extraction	30
3.1.2 Autoclave Extraction and Hydroliquefaction	32
3.1.3 Solvent Removal and Gas Analysis	35
3.2 MATERIAL USED	35
3.2.1 Lignite Samples	35
3.2.2 Solvents	41
3.2.3 Chemicals of Orsat Analyzer	42
3.3 EXPERIMENTAL PROCEDURE	42
3.3.1 Soxhlet Extraction	42
3.3.2 Autoclave Extraction and Hydroliquefaction	43
3.3.3 Solvent Removal and Gas Analysis	45
CHAPTER 4. RESULTS AND DISCUSSION	46
4.1 SOXHLET EXTRACTION	46
4.2 AUTOCLAVE EXTRACTION AND HYDROLIQUEFACTION	59
CHAPTER 5. CONCLUSION AND RECOMMENDATIONS	69
5.1 CONCLUSION	69
5.2 RECOMMENDATIONS	70
LIST OF REFERENCES	72
APPENDIX	80
App.1 Construction of Drying Curves for Lignite Samples	81
App.2 Determination of Autoclave Controller Settings	83

LIST OF TABLES

TABLE

2.1	Chemical Composition of Coals with Different Ranks	9
3.1	Proximate and Ultimate Analysis of Çan (Çanakkale) lignite sample	38
3.2	Proximate and Ultimate Analysis of Soma (Manisa) lignite (+18Lave) sample ..	39
3.3	Proximate and Ultimate Analysis of Tunçbilek (Tavşanlı) lignite (+18Lave) sample	40
3.4	Heating Values of Lignite Samples used ..	41
3.5	Boiling Points of Solvents used	41
4.1	Quantitative Results of Soxhlet Extraction	47
4.2	Quantitative Results of Soxhlet Extraction (Rank and Solvent Effects) ...	52
4.3	Results of Tetralin Extraction of Lignite Samples under A) N ₂ , B) H ₂ pressure	60
4.4	Oil, Asphaltene, Asphaltol and Residue Yields of Soma (Manisa) Lignite Sample ..	67
4.5	Orsat Analysis of Gases from Run 16 of TABLE 4.3	68

LIST OF FIGURES

FIGURE

2.1	World Reserves and Consumption of Fossil Fuels	4
2.2	Anticipated World Production of Petroleum and Coal	5
2.3	Results of Extraction of Various Coals with Pyridine	15
2.4	Relation between Pyridine and Benzene-Ethanol Extraction Yields and Extraction Times	16
2.5	Yields of Pyridine and Benzene-Ethanol Extraction of Different Coals	17
2.6	Comparison of Solubility Parameters of Various Coals and Specific Solvents	17
2.7	Extraction Yields of Pyridine and Ethanolamine as a Function of the Rank of Coal	18
2.8	Hydrogenation of Coal by a Hydrogen-Donor Solvent, Tetralin	20
2.9	A Scheme for H-donor Liquefaction of Coal	26
3.1	Soxhlet Extraction Apparatus	31
3.2	High Pressure Autoclave	32
3.3	Evaporator and Vacuum System	36

3.4	Orsat Gas Analyzer	37
4.1	Effect of Particle Size on Extract Yield of Çan (Çanakkale) Lignite using Pyridine as Solvent	48
4.2	Effect of Siphon Number on Extract Yield of Çan (Çanakkale) Lignite using Pyridine as Solvent	50
4.3	Effect of Solvent to Lignite Ratio on Extract Yield of Çan (Çanakkale) Lignite using Pyridine as Solvent	51
4.4	Extraction Yields with Pyridine	55
4.5	Effect of Solvents on Extraction Yields as a Function of %C	56
4.6	Effect of Solvents on Extraction Yields as a Function of H/C Ratio	58
4.7	Effect of Rank on Extract Yield	61
4.8	Effect of Tetralin to Lignite Ratio on Extract Yield	62
4.9	Effect of Pressure on Extract Yield	64
4.10	Effect of Reaction Time on Extract Yield	65
4.11	Effect of Hydrogen Pressure on the Yield as a Function of %C	66
A.1.1	Drying Curve of Lignite Sample from Çan	81
A.1.2	Drying Curve of Lignite Sample from Soma	82
A.1.3	Drying Curve of Lignite Sample from Tunçbilek	82
A.2.1	Test Results of Controller Settings (I)	84
A.2.2	Test Results of Controller Settings (II)	85
A.2.3	Test Results of Controller Settings(III)	85

CHAPTER 1

INTRODUCTION

The change in the world energy situation influenced the revival of interest in coal conversion technology. Processes are being continuously developed to convert coal into clean gaseous and liquid fuels. The coal conversion is presently very expensive because it requires complex technology. Research is done to develop coal conversion technologies economically competitive with petroleum, because the coal reserves are much larger than those of oil and natural gas, and coal is considered to be the main fossil fuel of the future.

Turkey has large lignite reserves but they are used as fuel without any pretreatment. In order to develop an economical coal conversion technology suitable for Turkish lignites, a better understanding of the behaviour of lignites and the parameters affecting their conversion are required.

The purpose of this work is to study the parameters affecting the lignite extraction with non-donor solvents in Soxhlet extractor and a hydrogen donor solvent (tetralin) in a batch autoclave under N_2 or H_2 pressure.

CHAPTER 2

LIQUEFACTION OF COAL

The modern chemical industry before 1940's was based upon coal which was burned to produce steam and electric power. Also, carbon and hydrogen of coal were used for production of organic chemicals, and carbon of coal was used for production of inorganic chemicals (Dauphiné, 1978). In the late 1940's the size, growth rate and raw material base of the chemical industry changed completely. Coal as a fuel could not compete with natural gas and fuel oil which were produced at much lower prices. So, the coal-based chemical technology was replaced with petroleum-based chemical technology (Dauphiné, 1978).

Nowadays, the problem is to produce fuel and chemical feedstocks to the large and continuously increasing chemical industry. The change in the world energy conditions and the finite nature of the petroleum reserves are the major reasons for the revival of interest in coal conversion technology in recent years (Dauphiné, 1978).

The disadvantage of coal as a fuel is in its being a solid with transportation and burning problems. It gives off sulfur dioxide, soot and flyash on combustion (Dauphiné, 1978). In

converting the coal to clean gaseous and liquid fuels, nitrogen and sulfur in it can be recovered as valuable by-products (Wise, 1971). Also, the fuel obtained may be easily stored, handled and used. So, it can be deduced that the purpose of all the processes that convert coal into a liquid substitute for crude oil or a product derived from crude oil, is to produce easily transportable fuels, or chemical feedstocks low in sulfur content and free of ash, thus at the same time satisfying the pollution regulations (Yavorsky, 1973; Wise, 1971; Seapan, 1981). The production of liquid fuels from coal requires a complex and quite difficult technology. High temperature and pressures are required and the equipment necessary for operation under these conditions and in corrosive medium, are very expensive (Dauphiné, 1978). So, this is the reason for the coal liquefaction plants to be so expensive.

In the long run, coal is bound to substitute petroleum and natural gas because the coal reserves are much larger than the petroleum and natural gas reserves, as shown in Fig. 2.1. It is reported that petroleum will remain available to the chemical industry at fair costs until after 1990 and it will remain the preferred source of fuel and raw materials (Dauphiné, 1978) for some time. In Fig. 2.2 anticipated world production of petroleum and coal (Falbe, 1980) are shown.

The lignite reserves of Turkey are estimated as 8.0 billion tons and that of bituminous coals as 1.5 billion tons (MTA, 1982). Presently, in Turkey, lignites are utilized in thermoelectrical-centrals, light industries and domestic heating

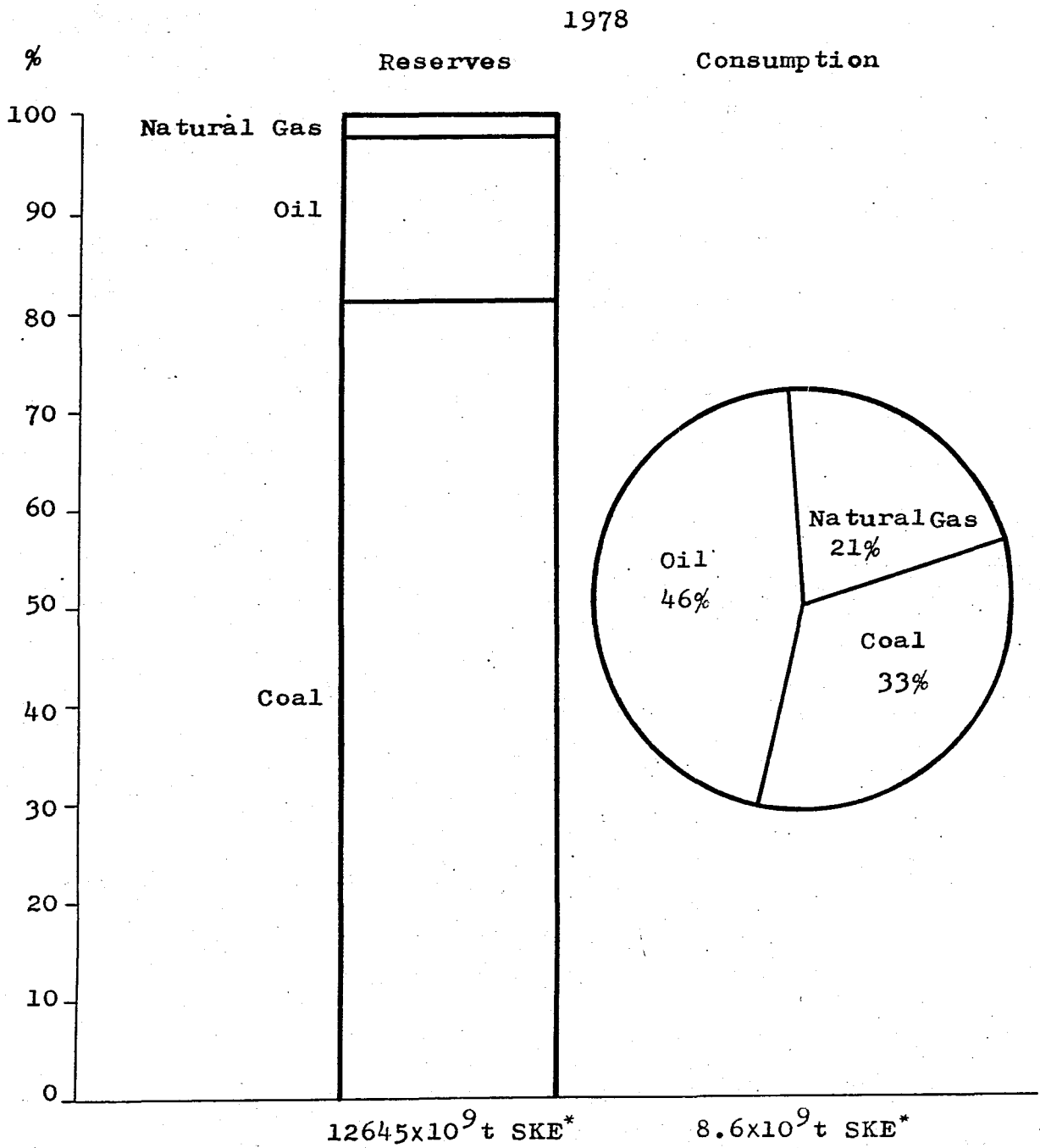
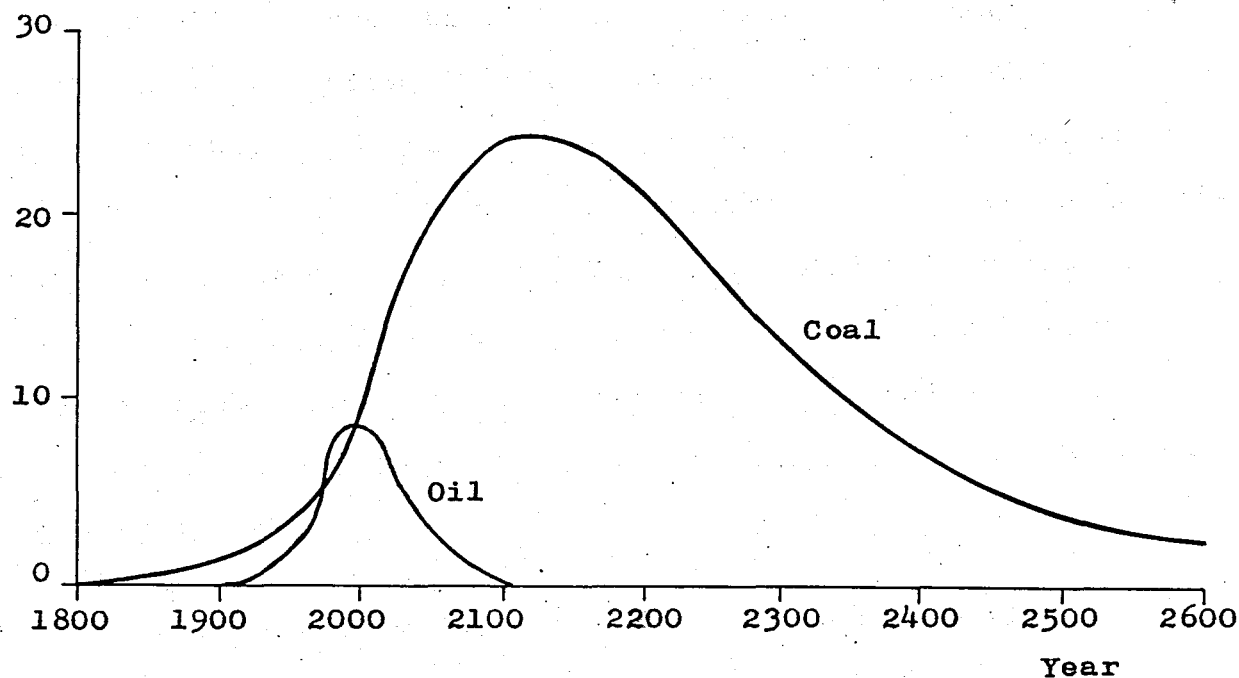


Figure 2.1 World reserves and consumption of fossil fuels (Falbe, 1980)

Production
in 10^9 tsKE*



*1tsKE(Hard Coal Unit) = 29.3×10^6 kJ

Figure 2.2 Anticipated world production of petroleum and coal (Falbe, 1980)

without any technological pretreatment. Turkish lignites have high contents of moisture, mineral matter and sulfur (Nakoman, 1971; TKİ, 1973) and because of this reason pretreatment is necessary to keep the environment clean. Valuable gas and liquid products may be obtained by liquefying lignites. They could replace the petroleum derived products. Turkey has a relatively low production of petroleum but a great demand for clean fuel oil and transportation oil. As a result, there is a heavy dependence

on foreign oil sources which is not desirable for many reasons. From this point of view, development of lignite conversion technology in Turkey, appears to be a necessity. The valuable bituminous coal reserves in Turkey are reported to be just-enough only for metallurgical industry (MTA, 1982). For this reason they can not be considered to be used for conversion to liquid and gaseous products. But lignites seem to be just suitable, and the research and development should be concentrated on the conversion of lignites.

However, it must be pointed out that coal liquefaction technologies do not produce fuels and chemical feedstocks as economical as technologies based on petroleum. Nevertheless this work is based on the better understanding of the behaviour of Turkish lignites under extraction and hydroliquefaction conditions.

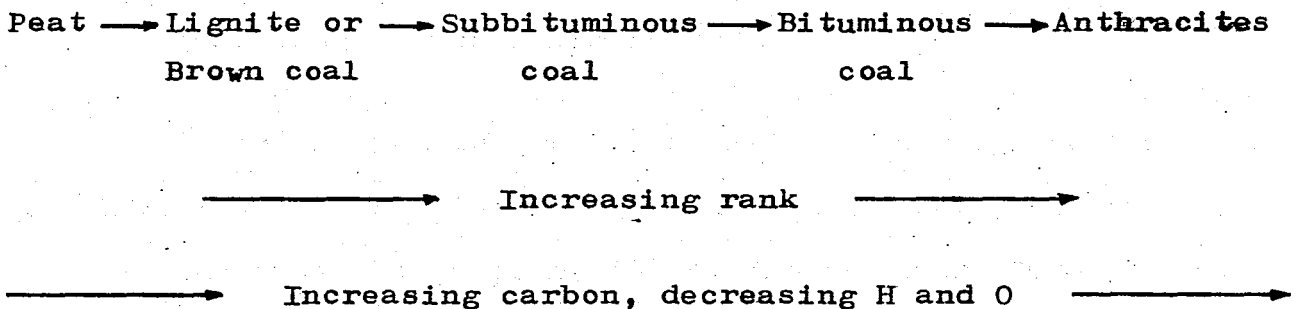
2.1 CHEMISTRY OF COAL

2.1.1 Rank of Coal

Coal is a mixture of macromolecules which are not repeating monomers as in polymers. It is a complex and variable material. Coal can be considered as a cross-linked high polymer composed of condensed aromatic aggregates and connecting links (Seapan, 1981).

A useful method of characterization is the rank system

of classification. This type of classification is based on the extent of coalification of the original plant, the remains of which have been metamorphosed to peat, lignite, low-rank and high-rank coals and antracites (Wise, 1971; Macrae, 1966). The metamorphic development corresponds to an enrichment process increasing the carbon content of the coal. Classification is as follows (Seapan, 1981):



The higher the rank, the higher the percentage of carbon is, and the lower the contents of hydrogen (H), oxygen (O), volatile matter (VM) (Taupitz, 1977) are. Heat content, which is nearly constant for the higher ranking coals is also useful as a rank parameter for lignites. The hydrogen content is normally fairly constant (~5%) through all ranks up to anthacite (Pettrakis, 1980). For coals lower than bituminous rank, moisture content decreases with increasing rank; a similar decrease in oxygen content is reported (Pettrakis, 1980). So, it can be observed that many components can serve as rank determiners but the common ones are carbon content and the C/H ratio of coal (Karr, 1978; Pettrakis, 1980).

The rank of coal doesn't define completely its properties. Different coals of the same rank may have variations in their chemical compositions (Ward, 1974). Variations in elemental analysis complicates the classification and also determination of chemical nature of coal. True rank can not always be determined because of different formations of this sedimentary organic rock called coal (Taupitz, 1977).

2.1.2 Chemical Composition of Coal

Coal is formed from plant matter and different amounts of mineral substance: the organic macerals and the inorganic crystalline minerals (Seapan, 1981). The macerals form the combustible part of the coal, while the minerals form the ash. Macerals are divided into three groups (Taupitz, 1977): vitrinite, exinite and inertinite (Seapan, 1981). Vitrinite is oxygen-rich, exinite is hydrogen-rich and inertinite is carbon-rich (Petra-kis, 1980). The major constituents of coal minerals are iron, silica and alumina. The presence of coal minerals can accelerate liquefaction reactions in coal processes (Guin, 1978). They catalyse the hydrogenation of the donor solvent in coal extractions (Guin, 1978).

A significant difference between crude oil and coal is that C/H ratio is higher in coal (Fox, 1974). Coal has a typical H/C ratio of about 0.8. To change to liquid form this ratio need be increased to 1.8 or to around 2.0 (Crynes, 1981). Another im-

portant difference is in the form of contaminants. Elements such as S, N, O are common to both of them but coal has a different type of contaminants, namely ash. The ash is the most important contaminant because it is the most difficult to remove and it is present in large amounts ranging from 5 to 30 per cent (Fox, 1974). Another very important contaminant which is present in large amounts is sulfur. During the processing of coal sulfur can be removed as hydrogen sulfide using hydrogen gas (Ruether, 1977).

Typical elemental analysis of coal of various ranks are shown in TABLE 2.1. The chemical composition of coal is usually represented in terms of its "proximate" and/or "ulti-

TABLE 2.1 CHEMICAL COMPOSITION OF COALS WITH DIFFERENT RANKS (Ward, 1974)

	Anthracite	Medium volatile Bituminous	High volatile A.Bituminous	High volatile B.Bituminous	Lignite
<u>C</u>	93.7	88.4	84.5	80.3	72.7
<u>H</u>	2.4	5.0	5.6	5.5	4.2
<u>O</u>	2.4	4.1	7.0	11.1	21.3
<u>N</u>	0.9	1.7	1.6	1.9	1.2
<u>S</u>	0.6	0.8	1.3	1.2	0.6
<u>H/C</u>	0.31	0.67	0.79	0.82	0.69

mate" analysis. Moisture and mineral matter are considered as foreign substances and the coal analysis is presented on the dry basis, dry and ash-free (daf) basis and dry and mineral matter-free (dmmf) basis (Seapan, 1981; Petrakis, 1980).

2.2 TYPES OF LIQUEFACTION PROCESSES

Coal is the largest potential source of substitute liquid fuels. Coal can be liquefied by exposing it to hydrogen gas or a hydrogen donor solvent under pressure and in many processes in the presence of a catalyst (Wise, 1971). Coal can also be distilled by heating at high temperatures such that its volatile components are separated and then, condensed and collected as liquids (Swabb, 1978). The net result is to i) add hydrogen, ii) take away carbon or iii) break the coal down to individual carbon atoms and rebuild.

The overall objectives of liquefaction processes include the increase of atomic H/C ratio of coal from 0.8 - 0.9 (Dauphine, 1971) to 1.1 for primary coal liquid, 1.6 for an aromatic gasoline and 2.0 for some other type of liquid product (Wise, 1971; O'Hara, 1980) by adding hydrogen. The oxygen, sulfur and nitrogen contents must be reduced to nearly zero level and the inorganic material including unconverted coal must be totally removed (Seapan, 1981).

The products derived from coal could compete with

petroleum derived products in two markets. One of them uses low ash and low sulfur boiler fuels used for clean electric power and industrial steam generation. The other market uses high grade fuels such as gasoline, methanol, diesel oil, heating oil and chemical feedstocks (Fossil Energy Research Program, 1976).

The most important methods of liquefaction are (O'Hara, 1976; O'Hara et al., 1977; Fossil Energy Research Program, 1976): 1) pyrolysis, 2) indirect liquefaction, 3) solvent extraction and 4) direct liquefaction by hydrogenation.

2.2.1 Pyrolysis

Coal is heated to high temperature in absence of air, and thus gas, tar and char are produced (Sinha et al., 1978). Gas is used as fuel. Tar can be hydrogenated to obtain low sulfur synthetic crude. Char can be gasified using steam or steam and air to produce syngas (H_2+CO). The syngas can be treated to remove contaminants such as hydrogen sulfide and used to produce electricity, methanol or ammonia and also liquids by Fischer-Tropsch technology (O'Hara, 1976; Simeons, 1978).

Overall conversion and product quality are dependent on rate of heating, temperature and hydrogen content of the atmosphere of pyrolysis (Taupitz, 1977). In normal pyrolysis, good recoveries are obtained at low or high temperatures by quick removal of vapors by a stripping gas. In pressure pyrolysis on the

other hand, less liquid products are obtained because high pressure is unfavorable for gas formation. The products have high content of carbon and low content of hydrogen (Taupitz, 1977).

2.2.2 Indirect Liquefaction

The conditions of process are so severe that almost all the existing chemical bonds are broken. In the presence of oxygen and steam, new chemical bonds are formed and simple gaseous molecules of hydrocarbons, hydrogen and carbon monoxide are produced (Lurgi, 1978). The mixture of (H_2+CO) is used to produce liquid hydrocarbons by Fischer-Tropsch synthesis. Liquid hydrocarbons can also be produced from (H_2O+CO) mixture by Kolbel Engelhardt process.

Fischer-Tropsch synthesis is being used today by the South African Coal, Oil and Gas Corp., Ltd. (SASOL) in Sasolburg, South Africa (Swabb, 1978). Coal is gasified with steam by the Lurgi technology to produce carbon monoxide and hydrogen which are then used to produce liquid hydrocarbons (Fox, 1974; Hammond, 1976; Gillmore, 1972).

2.2.3 Solvent Extraction

The separation techniques used in the early days of organic chemistry were distillation, crystallization and solvent

extraction (Wise, 1971). Among them, only the last one could be applied to coal, a nonvolatile and noncrystalline material. Solvent extraction is done with successive different solvents. These extractions are based on the property of some solvents to break weak bonds in coal and they are used for studying the composition of coal (Seapan, 1981)..

Oele and coworkers (1951) distinguished the following groups of operations in the study of coal extraction:

- 1) Nonspecific extraction: a few percent of coal is dissolved at temperatures lower than 100 °C. Extract consists of resins and waxes (Seapan, 1981; Oele, 1951). The extract obtained is not typical of the structure of coal.
- 2) Specific extraction: 20-40% of coal is extracted at temperatures lower than 200 °C. The nature of extract is nearly the same as the parent coal and the insoluble coal (Seapan, 1981; Oele, 1951).
- 3) Extractive disintegration: the temperatures are higher than 200 °C. This operation is also called solvolysis (Seapan, 1981).
- 4) Extractive chemical disintegration: hydrogen donor solvents are used at temperatures higher than 300 °C.

2.2.3.1 Solvent Classification

Solvent for the dissolution of coal can be divided into the following three categories (Ward, 1974):

- (1) those that dissolve small fractions of the coal by simple solvation processes,
- (2) those that break up coal structures by donating hydrogen,
- (3) those that cause a redistribution of hydrogen and are usually coal derived products.

Another classification of solvents with respect to their effects on coal is suggested as follows (Wise, 1971):

- (1) Nonspecific solvents: they extract only traces of materials at temperatures up to about 150 °C,
- (2) Specific solvents: they are defined by Dryden (1951) as solvents dissolving appreciable amounts of coal at temperatures below 250 °C, by a process of physical solution. These solvents are capable of dissolving the loosely cross-linked or uncross-linked macromolecular structure (Seapan, 1981),
- (3) Degrading solvents: these are good solvents at high temperatures (450 °C). The solvent may be recovered unchanged from solution. Their action depends on the thermal degradation of the coal to smaller and more soluble fragments,
- (4) Reactive solvents: these solvents dissolve coal by reacting chemically with it. The properties of the extracts are different from those of the extracts obtained with degrading solvents. The solvent-free extract and residues weigh more than the parent coal, indicating the severe chemical changes occurring during the extraction process,

(5) Highly reactive solvents: they cause high degradation of the coal to smaller molecules.

2.2.3.2 The Action of Solvents on Coal

Specific Solvents. They are not commonly investigated by coal technologists because of the low extract yields compared with those obtained with degrading solvents (Wise, 1971). Also, many of them, pyridine for example, are too expensive to be used commercially. Pyridine can dissolve 2 to 35% of the coal depending on the rank (Dormans, 1960). In Fig. 2.3 the extraction yields of various coals in pyridine are shown. Here, E/C represents the ratio of extract to coal and C the content of carbon in the coal.

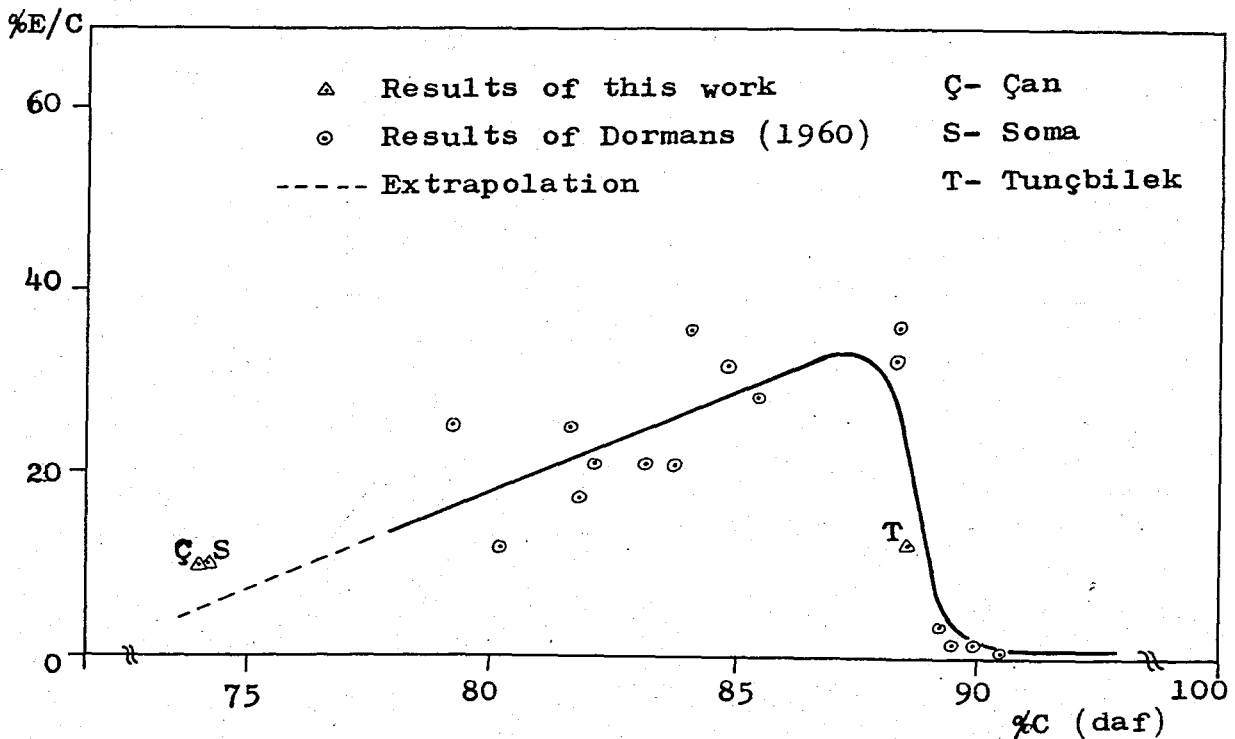


Figure 2.3 Results of extraction of various coals with pyridine

Two graphs comparing the extraction yields of pyridine and benzene-ethanol mixture are shown in Fig. 2.4 and Fig. 2.5.

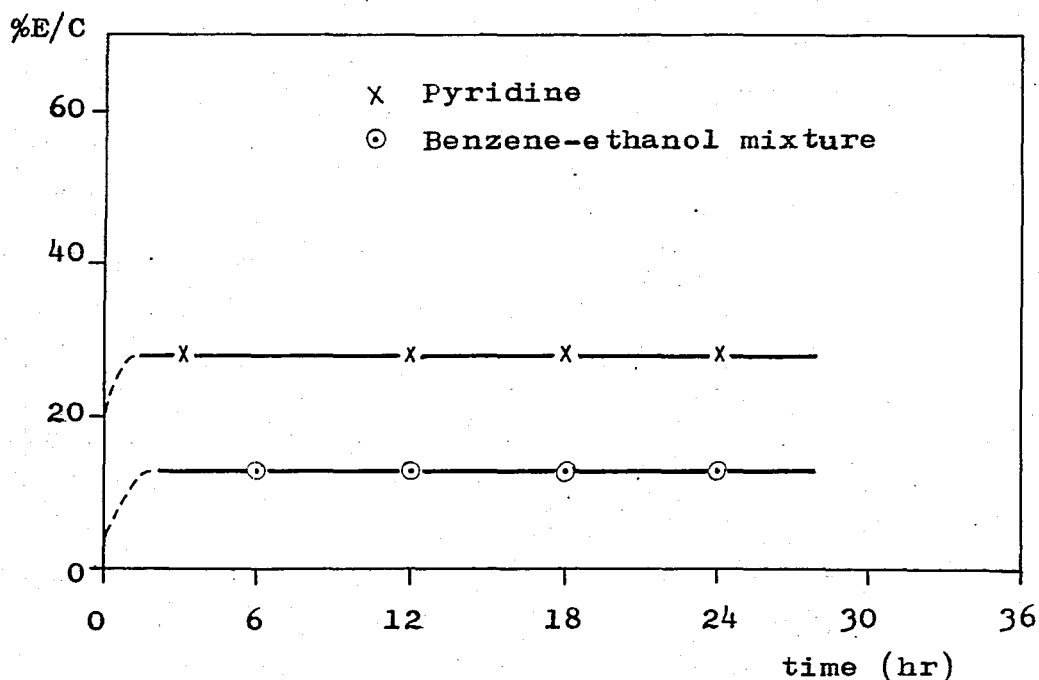


Figure 2.4 Relation between pyridine and benzene-ethanol extraction yields and extraction times (Ōuchi, 1965)

A decrease in extraction yield with very high rank coals, are given by Dormans (1960) and vanKrevelen (1961)(see Fig. 2.3). For good solubility a parameter characteristic of coal, δ_p , estimated from the chemical analysis of the coal and known atomic parameters of coal, should be equal or nearly equal to a parameter δ_s characteristic of the solvent (vanKrevelen, 1965). Fig. 2.6 shows that ethanolamine should be a good solvent for low rank coals but pyridine should be better for higher rank coals.

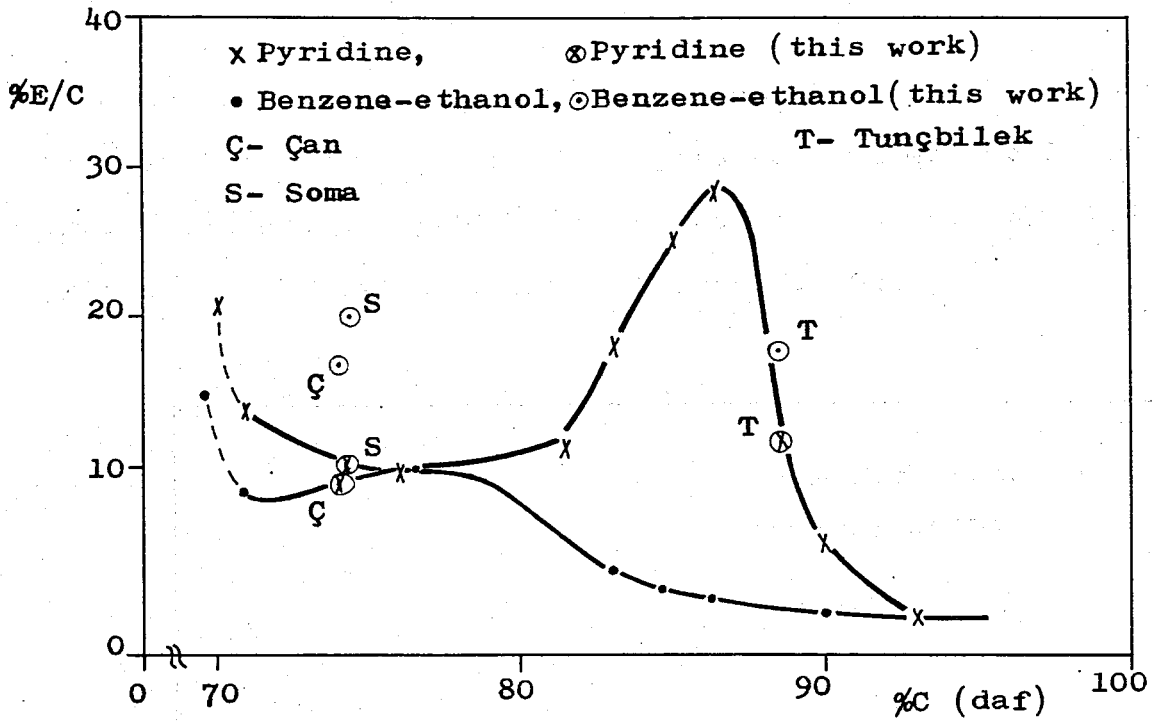


Figure 2.5 Yields of pyridine and benzene-ethanol extraction of different coals (Ouchi, 1965)

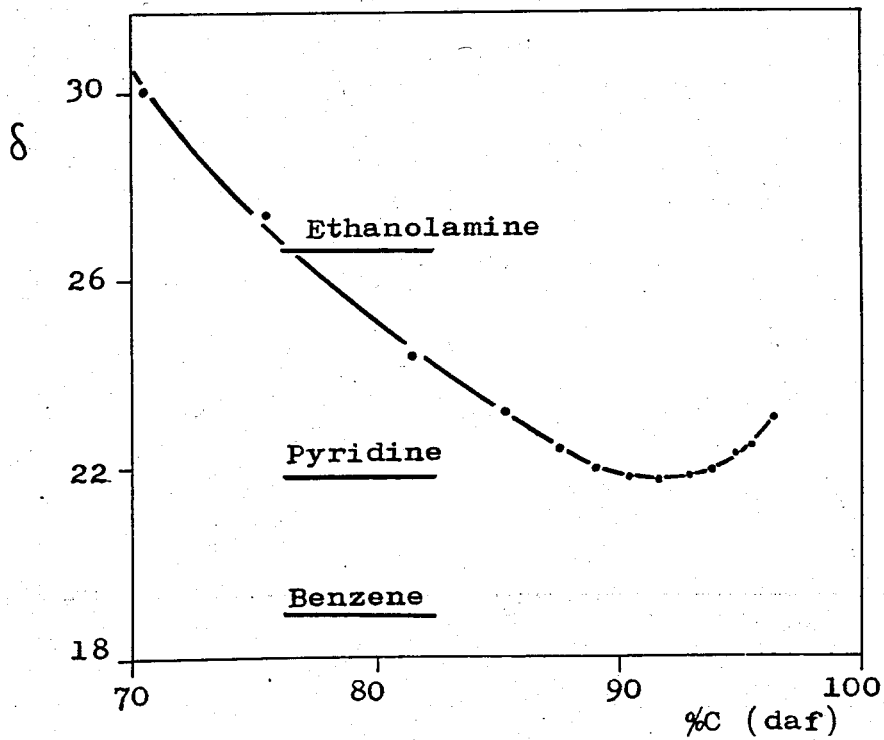


Figure 2.6 Comparison of solubility parameters of various coals and specific solvents (Wise, 1971)

The same behaviour can be deduced from Fig. 2.7 where it can be observed that ethanolamine is a good solvent for coals with carbon contents of 75-83% but for carbon contents of 87-90%, pyridine is the better solvent (Dormans, 1960).

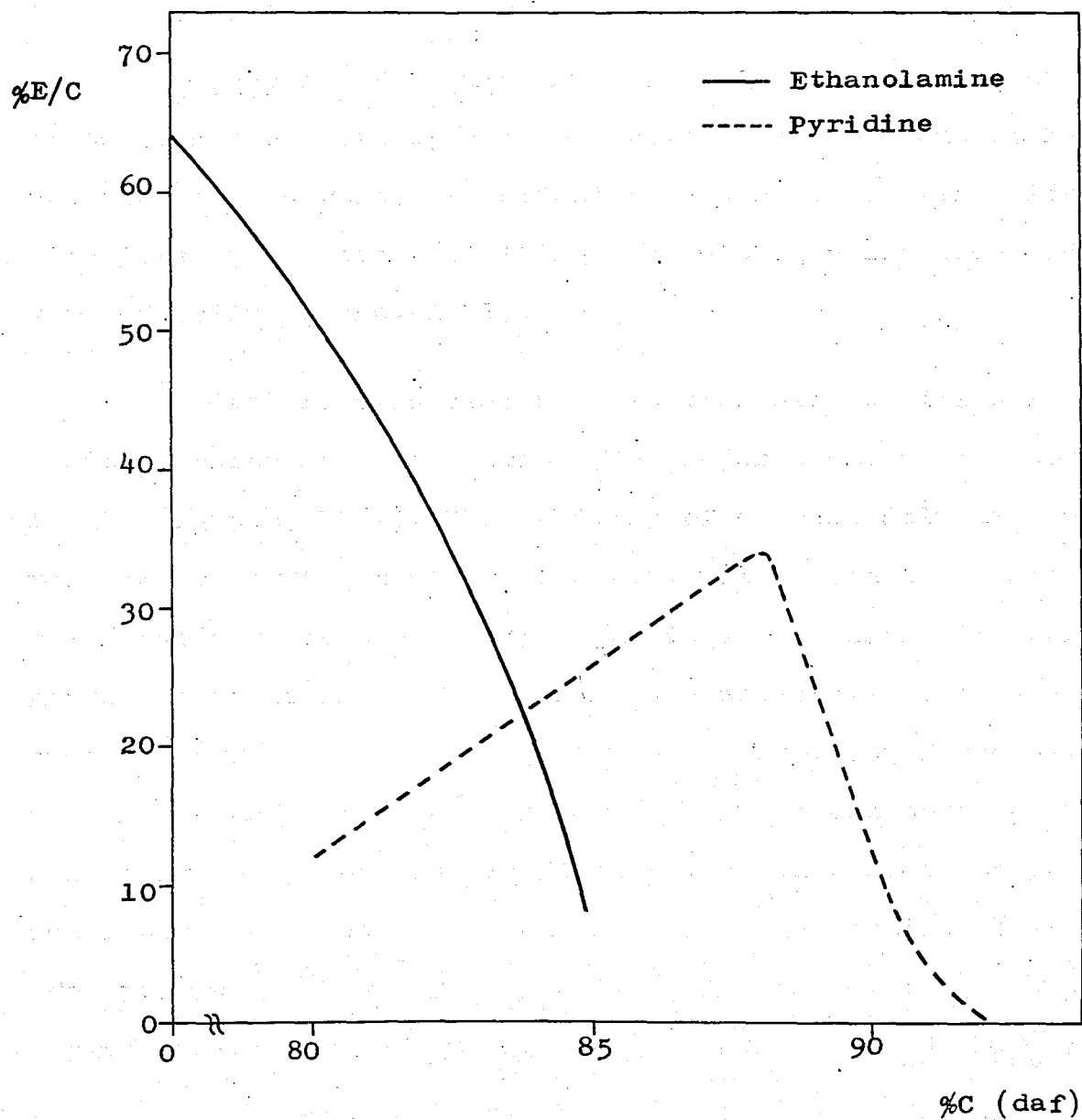


Figure 2.7 Extraction yields of pyridine and ethanolamine as a function of the rank of coal (Dormans, 1960)

Degrading Solvents. The mechanism of the action of degrading solvents on coal is complex and much of the work has been done with tar-oil fractions which contain many different chemical compounds. One example to this type of solvents is anthracene oil (Wise, 1971).

Reactive Solvents. Hydrogen transfer to coal can take place from these hydrogen donor solvents. The extent of hydrogen donation of a particular solvent is dependent on its molecular structure. Compounds containing ring nitrogen are observed to be very effective (Wise, 1971):

Coal is dissociated by thermal decomposition into free radicals which are stabilized by hydrogen atoms from a donor molecule (Seapan, 1981). The activity of a spent solvent can be restored by hydrogen under pressure. The presence of catalyst is not necessary because hydrogen gas is very soluble in such solvents and transfer to coal can take place easily from dissolved hydrogen (Wise, 1971). A general representation of the attack of coal by H-donors is shown in Fig. 2.8. Coal can both accept and donate hydrogen just as tetralin, which can convert to decalin and naphthalene (Kang, 1977). The H-donor attacking the coal may add hydrogen forming hydroaromatic rings and eliminating sulfur, oxygen and nitrogen from the coal structure as H_2S , H_2O and NH_3 (Wise, 1971; Ruether, 1977).

Hydrogen donor solvents are effective at high tempera-

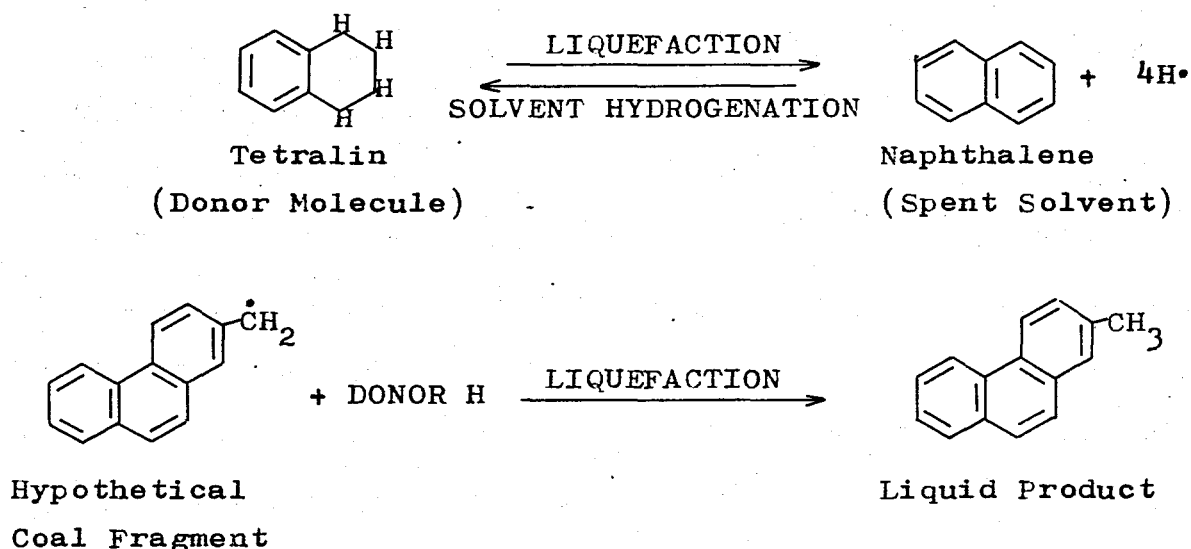


Figure 2.8 Hydrogenation of coal by a hydrogen donor solvent, tetralin (Furlong, 1976)

tures where degradation of coal can occur. The contact at high temperatures between coal and solvent must be just enough for the coal to absorb solvent and become a gel. Then, the gel structure breaks down to form the coal solution. But if the contact time is too long, polymerization will occur and loss of solvent will be observed (Wise, 1971).

2.2.3.3 Extraction Parameters

It has been shown in literature that both physical and chemical processes are involved in the dissolution of coal (Ward, 1974). The solubility of coal is not only a function of its ge-

neral structure and chemical functionality, but depends also on physical and chemical interaction of coal with the solvent (Ward, 1974). Therefore, coal liquefaction process is a complex interaction (Neavel, 1976) involving 1) physical breakdown of the particles, 2) thermally induced bond rupture rates, 3) competition between recombination and donor hydrogen stabilization. Golumbic et al. (1950) considered the physical nature of a compound to be more important than the chemical one in determining its effectiveness as a solvent.

Kreulen (vanKrevelen, 1961) believed that solid coal is made up of micelle nuclei encased in protective oleophylic layers and embedded in an oily medium. This was an explanation for the surface tension effects of solvents, the influence of temperature and rank on the extraction yield. So, coal was regarded as a colloid. Around 1930's, more and more workers on this subject believed that coal extracts are colloidal systems. Kreulen (vanKrevelen, 1961) defined the organosols as a dispersed phase of micelle nuclei (humic substances protected by a layer made up of bitumen), and of a dispersion medium (molecularly dissolved part of coal, the oily bitumen). Kreulen further explained that the micelle nuclei and the protective layer can not be quantitatively separated by solvents because of the strong coherence existing between them. He also reported that the mean size of the micelle nuclei increases with rank and the organosols are unstable because the protective layer merge gradually into the dispersion medium. The stability is go-

verned by the micelle-liquid interfacial tension. So, stability increases as the surface tension of the solvent increases.

Dryden (1951), reported that Kreulen's conception put undue stress on the physical character of the solvent. He concluded that the most important factors are the chemical properties of the solvent. Dryden stated that a good solvent always contains a nitrogen or oxygen atom possessing an unshared pair of electrons, and all the other things being equal, nitrogen compounds are better solvents than the oxygen compounds. The most favourable solvents are found to be those that contain at least one primary amino group attached to methylene and heterocyclic bases, such as pyridine. The results obtained by Kamiya et al. (1981) suggested that three-ring aromatic compounds are better solvents than two-ring aromatics because coal fragments are more soluble and reactive toward free radicals.

Effectiveness of a solvent depends on the properties of coal to be extracted, especially on the rank (Darlage, 1975; Golumbic, 1950). According to Golumbic (1950), as the oxygen and volatile matter in coal decreases, rank increases and the yield of pyridine extract increases. Oxidation of coal before and/or during the extraction may occur and it lowers the extraction yield (vanKrevelen, 1961). Mineral matter content is also important (Given, 1975) and it affects the yield in various ways.

Other important parameters in extraction are temperature, pressure, solvent to coal ratio, particle size, drying of

coal samples. The extraction treatment with specific solvents is done near the boiling point of the solvent because it has been determined that yields do not increase at higher temperatures (Dormans, 1960). So, extraction in solvents with higher boiling temperatures leads to increased yields. This is not the same with reactive solvents. The thermally induced bond rupture step in the extraction process in this case, is more important. In general, increasing the reaction temperature increases the extraction yield (vanKrevelen, 1961).

Increasing pressure of the extraction medium results in increased conversion (Blessing, 1977) and in rapidly increasing oil yield (Severson, 1977).

Dryden (1951) showed that solvent to coal ratio has no influence on the final extraction yield. Experiments done by Neavel (1976) indicated no effect on extraction rate or ultimate extraction yield in runs with a tetralin to coal ratio of more than 2/1. But, according to Severson et al. (1977) the yields increase with increasing solvent to coal ratio.

It is reported that particle size of the coal samples has no influence on the final extraction yield (vanKrevelen, 1961); but according to Oele et al. (1951), the particle size affects the percent extraction values which are directly related with the effectiveness of solvent. The yield of extract decreases with decrease in particle size for effective solvents. Just the opposite may be observed for less effective solvents. The rate

of extraction can be increased by grinding (vanKrevelen, 1961) and may be independent of particle size (Curran, 1967). Oele and coworkers (1951) showed that the yield of extract can be increased by grinding the coal sample to less than 1μ .

In the case of specific solvents, drying of coal and refining the solvent from water tends to increase the yield (vanKrevelen, 1961). This is not the case for reactive solvents. Small amounts of water in the system can play the role of a catalyst during the extraction (Oelert, 1976).

Wynne-Jones (Dryden, 1951) stated that coal extracts are for the greater part in molecularly dispersed state but large particles of colloidal dimensions are also present. Also, Pierron (1960) calls attention to the possibility that extract yields for certain coals may be high due to colloidal dispersion of coal in the solvent. It is Curran et al.'s (1967) opinion that coal extracts are true solutions and not colloidal mixtures. Brown (vanKrevelen, 1961; Harrison, 1975) concluded that the extracts and the undissolved residue contained similar chemical structures.

2.2.4 Direct Liquefaction by Hydrogenation

There are mainly two types of hydrogenation of coal (Lurgi, 1978): (1) Addition of hydrogen can be realized directly using hydrogen gas at high pressure (120-330 atm) and high

temperature (350-475 °C) (Lurgi, 1978), (2) Hydrogenation is done by slurring the coal in the coal-derived solvent; then, it is mixed with a hydrogen containing gas and reacted by high temperature and pressures. The reactions can be noncatalytic, pseudo-catalytic or catalytic (O'Hara, 1976).

When the coal is heated to 325-350 °C, the rupture of links becomes significant and it increases rapidly with increase in temperature. Most processes are conducted at temperatures around 475-500 °C (Wiser, 1978). A scheme is given by Ignasiak and Brown (1980) showing the major reactions taking place during H-donor liquefaction of coal (Fig. 2.9). It is believed that solubilization of coal with formation of oils, asphaltenes and pre-asphaltenes or asphaltols (Farcasiu, 1977) is a result of cleavage of a limited number of covalent bonds (Whitehurst, 1977). The coal dissolution is fast and requires very little hydrogen consumption (Whitehurst, 1977). The presence of hydrogen gas in the early stages of conversion is not critical but a good hydrogen-donor solvent must be present (Whitehurst, 1977). It appears that cleaved bonds are stabilized by internal hydrogen disproportionation (Ignasiak, 1980). Breakages are in general at heteroatoms such as sulfur, nitrogen and oxygen which may be split out as gases such as hydrogen sulfide, ammonia and water (Ruether, 1977). The fragments formed in the solubilization stage may resolidify when cooling occurs, because of recombination of them. To form products with smaller molecular weights, longer reaction times are to be used (Ruether, 1977). The fragments (called

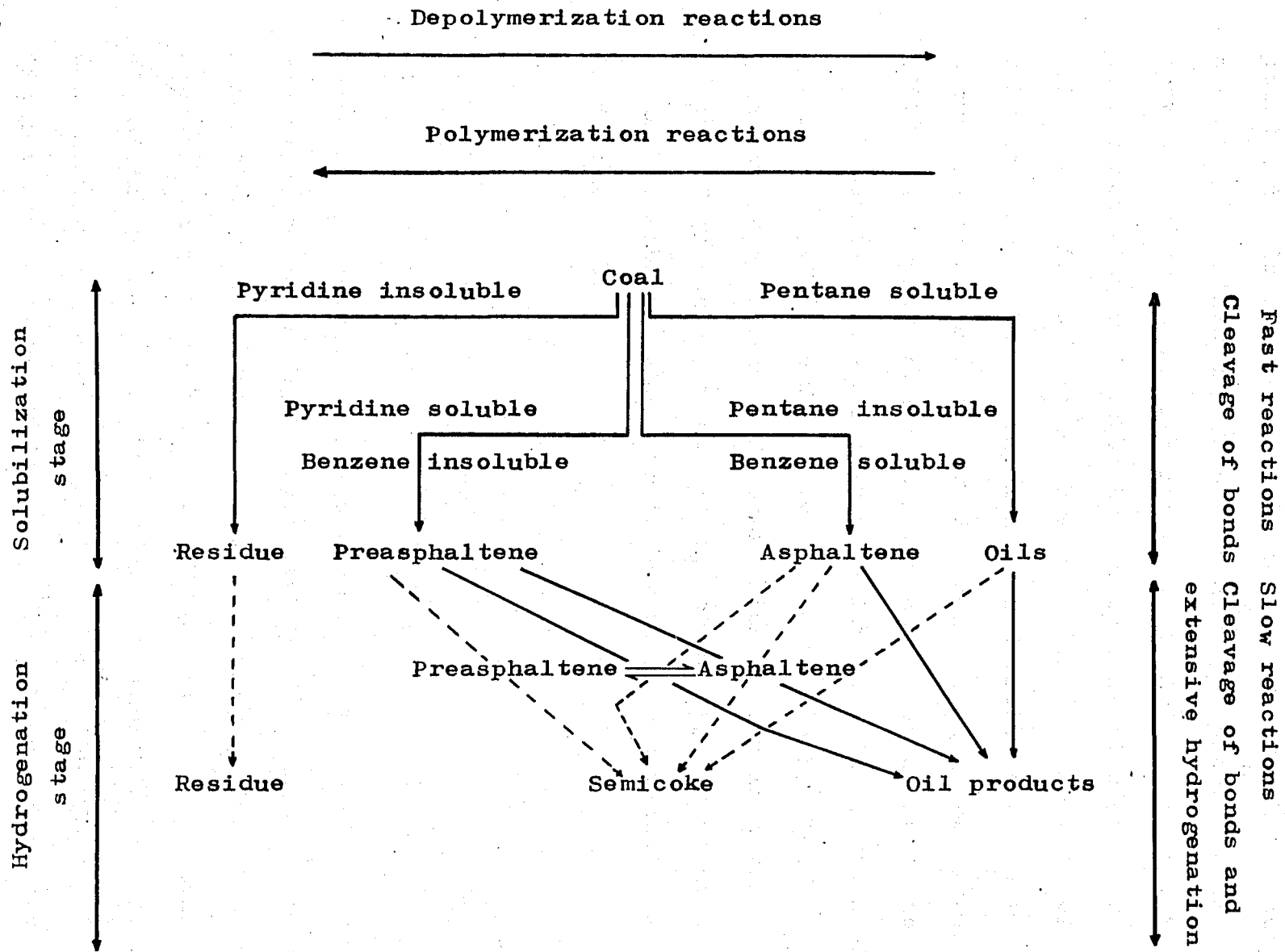
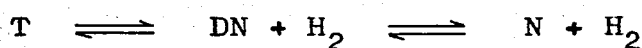


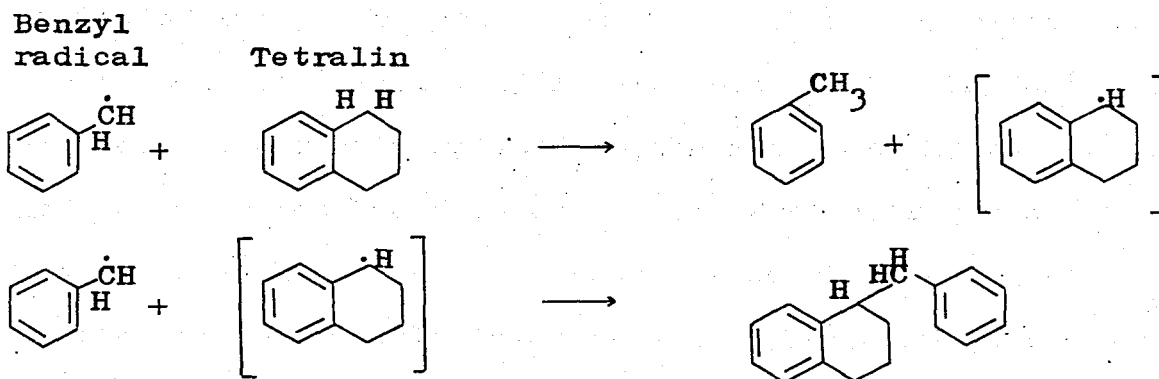
Figure 2.9 A scheme for H-donor liquefaction of coal
 (Ignasiak, 1980)

free radicals) are stabilized by reacting with a H-donor compound which is usually the solvent. Compounds within coal itself can also stabilize the free radicals by a process called as autogeneous hydrogen transfer (Neavel, 1976). Two fragments may also react with each other by repolymerisation and larger molecules resisting to further breakage result. The role of the solvent is said to be not explicitly understood because the reactions are numerous and they all occur simultaneously (Gangwer, 1981). The typical and most frequently used hydrogen donor solvent in coal liquefaction studies is tetralin (Wise, 1971; vanKrevelen, 1961; Guin, 1978; Cronauer, 1979). The net hydrogenation of coal during H-donor liquefaction involves the addition of hydrogen present as H₂ to the organic structure via the donor solvent. The overall heterogeneous reaction sequence is described by:

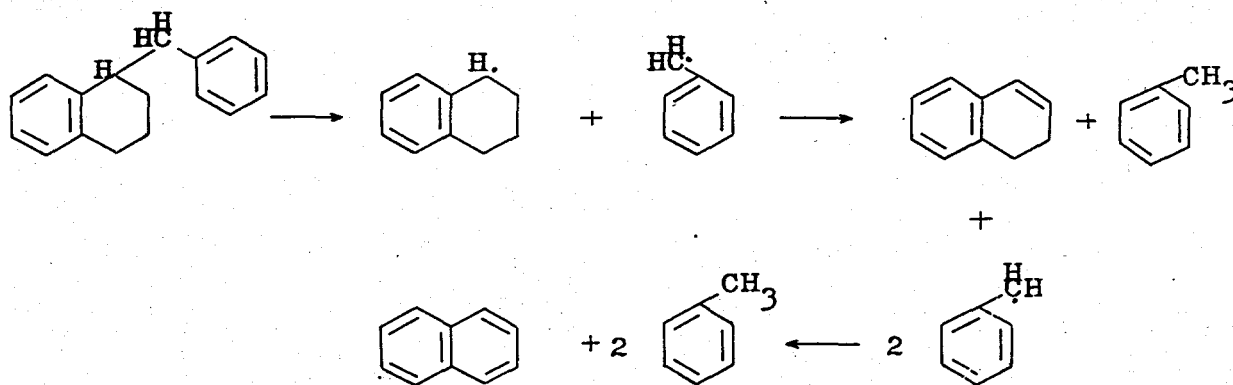


where DN behaves as a reactive intermediate. Here, T, DN and N represent tetralin, 1,2-dihydronaphthalene and naphthalene, respectively. Also, it has been shown that tetralin thermally dehydrogenates to naphthalene and rearranges to methylindan in either the presence or absence of free radicals. The free radicals usually accelerate these reactions which compete with olefin forming reactions (Cronauer, 1979). When reactions were performed in the 300-400 °C temperature range, adducts have been

shown to occur equally with tetralin and mesitylene. They both are reported to be stable up to 400 °C. This fact suggested that stabilization occurs by abstraction of hydrogen by free radicals. So, Cronauer et al. (1979) stated that during low temperature reactions, adducts form between good donor solvents (tetralin, for example) and acceptor free radicals. Equations below illustrate the competition between C· and H· (Cronauer, 1979):



Benzyl free radical can abstract hydrogen atom from tetralin, leaving a free radical which can combine with another benzyl radical. When reactions are performed around 450 °C, cleavage occurs as represented below (Cronauer, 1979):



Breaking of C-C and C-O bonds accounts for the following (Gates, 1979): a) evolution of some light products directly from coal matrix, b) production of highly reactive intermediates able to abstract hydrogen from molecules like tetralin or from coal itself, c) further reactions between highly reactive intermediates resulting in larger molecules.

The main objective of hydroliquefaction is the generation of liquid products. But large amounts of gaseous products are formed too (Seapan, 1981; Gillmore, 1972). The nature of products is directly related to the amount of hydrogen added. Most of hydrogen added to coal, come from hydrogen donor solvent. The hydrogen gas at high pressure is used to regenerate the effectiveness of spent solvent (Wiser, 1978). The gaseous products are mainly light hydrocarbons, hydrogen sulfides, carbon oxides and water vapor. The liquid products are mixtures of polynuclear hydrocarbons. They are sulfur, nitrogen and oxygen containing organic compounds. In addition, trace amounts of ash and mineral matter are present which act as nucleus upon which the precipitation of coal fragments can occur (Kang, 1977). The undissolved coal and the mineral matter form the solid residue (Seapan, 1981).

CHAPTER 3

EXPERIMENTAL

Coal extraction work performed here can be classified as: 1) Soxhlet extraction, 2) Autoclave extraction and hydroliquefaction. In the Soxhlet extraction part, Çan (Çanakkale), Soma (Manisa), Tunçbilek (Tavşanlı) lignites have been extracted with different types of solvents and the effects of particle size, siphon number, solvent to lignite ratio (S/L) on the extraction yields were observed. The autoclave extraction and hydroliquefaction of the same types of lignites used in Soxhlet extractions, were done using tetralin as solvent. Either N_2 or H_2 gas was used as the pressurizing medium. The effects of pressure, solvent to lignite ratio, reaction time on the yields were observed. The residue from one run was extracted with hexane, benzene and pyridine and the oil, asphaltene and preasphaltene percentages were determined. For the same run, gas analysis was done by an Orsat Analyzer.

3.1 APPARATUS USED

3.1.1 Soxhlet Extraction

The apparatus used in this part was Soxhlet extractor with bulbed condenser, manufactured by Teknik Cam. Heating mantle and pyrometer were used for heating and temperature control. The power was controlled with a powerstat. The apparatus is shown in Fig. 3.1.

- 1- Soxhlet Apparatus
- 2- Powerstat
- 3- Pyrometer
- 4- Heating mantle

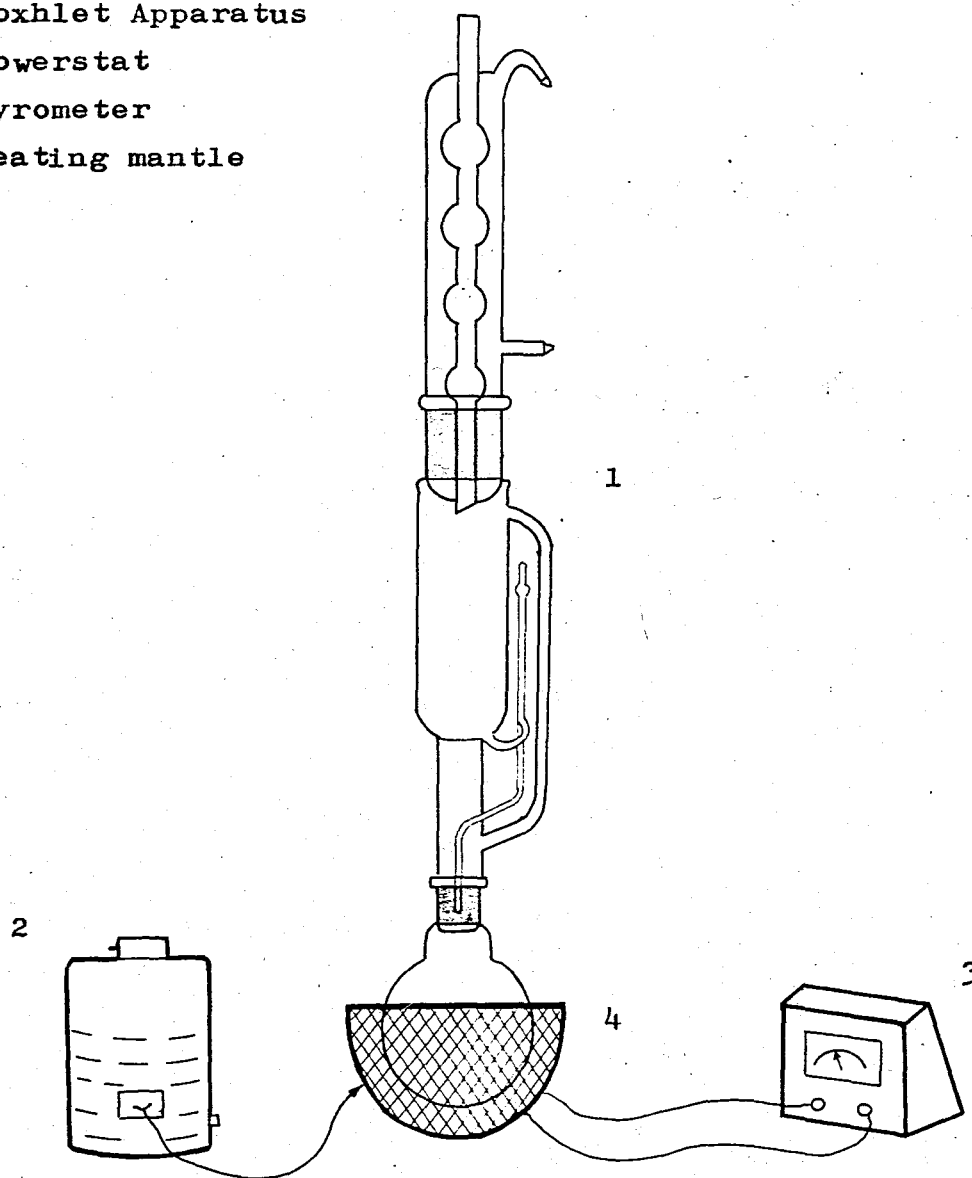


Figure 3.1 Soxhlet extraction apparatus

3.1.2 Autoclave Extraction and Hydroliquefaction

A schematic diagram of the high pressure autoclave used, is given in Fig. 3.2.

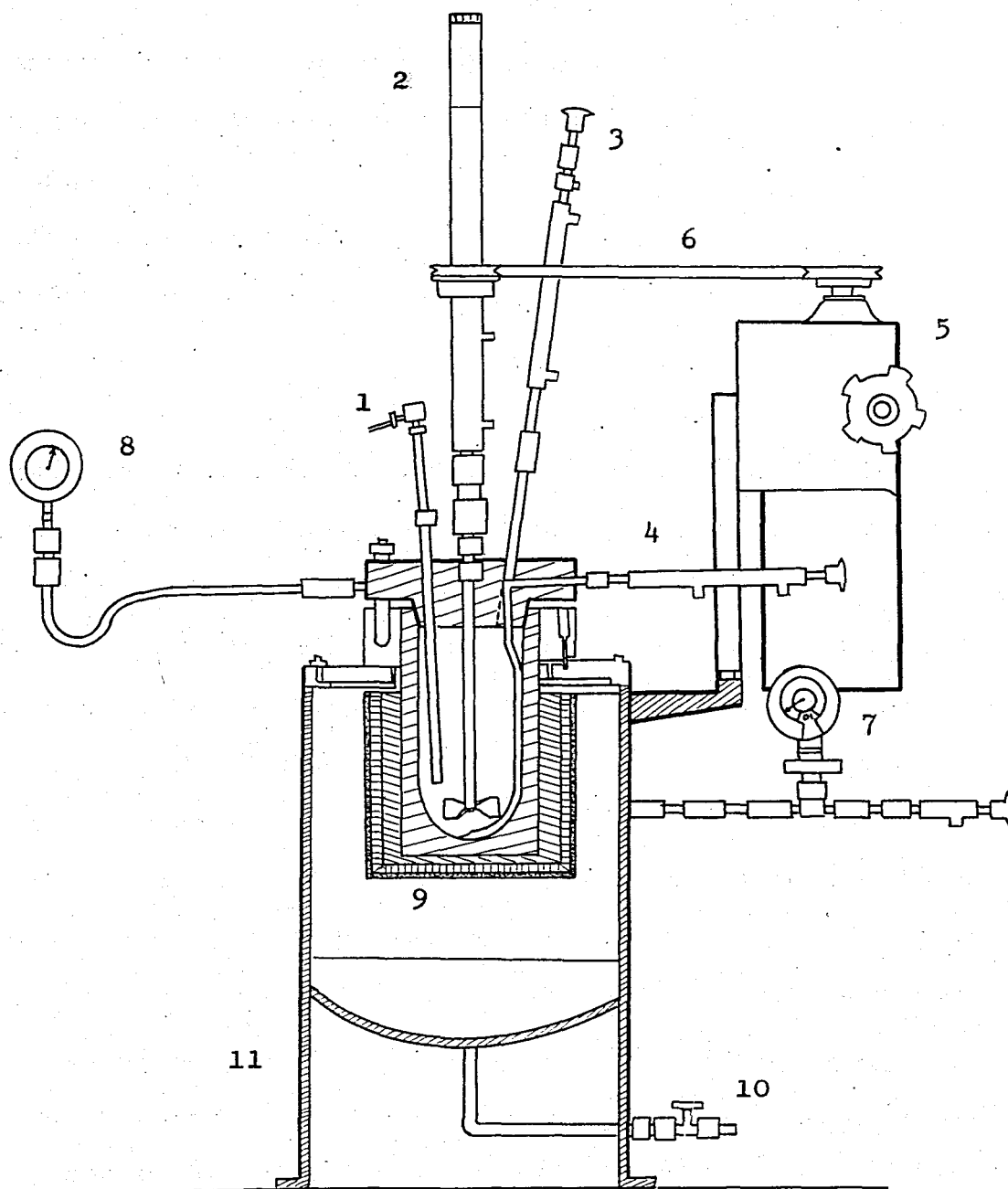


Figure 3.2 High pressure autoclave

- 1- Double thermocouple,
- 2- Magnetic stirrer with cooler,
- 3- Purge valve with condenser,
- 4- Angle valve with pressure condenser,
- 5- Stirrer speed regulating box,
- 6- Belt,
- 7- Minimum-contact manometer (0-1atm),
- 8- Maximum-contact manometer (0-400atm),
- 9- Heating jacket,
- 10- Cooling air purge valve,
- 11- Supporting frame.

The autoclave was a conventional 1 lt stainless Cr-Ni-Mo-steel batch autoclave manufactured by Andreas Hofer of West Germany. Its maximum working pressure and temperature are 325 atm and 350 °C, respectively. The vessel, 80 mm in diameter and 235 mm in depth is seamlessly forged, at one end with hemispherical bottom, at the other end with screwed-on flange, with eight necked-down bolts screwed on the flange and pre-screwed straight cover. On cover there is one double thermocouple tube (6 mm i.d.), one pressure gauge tube with pressure gauge 0-400 bar indicating range, one fine regulating valve with dip tube, 2 mm i.d., for the gas inlet or outlet, two lateral lifting bolts to be screwed off, one auxiliary equipment tube and two other fine regulating valves, one of them containing a high pressure cooler.

The autoclave is equipped with supporting frame and heat protection jacket. The electric heating is built-in in this jacket with a heating capacity of approximately 4.2 kW. In case if needed, an air cooling system can be used for cooling. The air inlet pressure is controlled by a minimum-contact manometer as shown in Fig. 3.2. A maximum-contact manometer controls the autoclave inner pressure.

The permanent magnet revolving agitator (Type DR 1) is driven by 0.5 kW motor. The maximum speed attainable by agitator is 2700 rpm but the speed of the driven motor is in the range of 155 to 1400 rpm. The speed is adjusted by a control knob on the speed regulating box. The motion is transferred from motor to the magnetic agitator by a V-belt pulley on a V-belt. The water cooling system on the stirrer was operated when operating temperatures exceeded 300 °C. The stirring speed is measured by a tachometer with a reading range of 0-5000 rpm.

An Fe-Ko DIN double thermo-couple was used for temperature readings which are analyzed by the electronic PD/PID (proportional-differential / proportional-integral-differential) type continuous regulator. The pressure, temperature and stirring speed controlling device has a visual fault indicator and a sound alarm (ring buzzer).

3.1.3 Solvent Removal and Gas Analysis

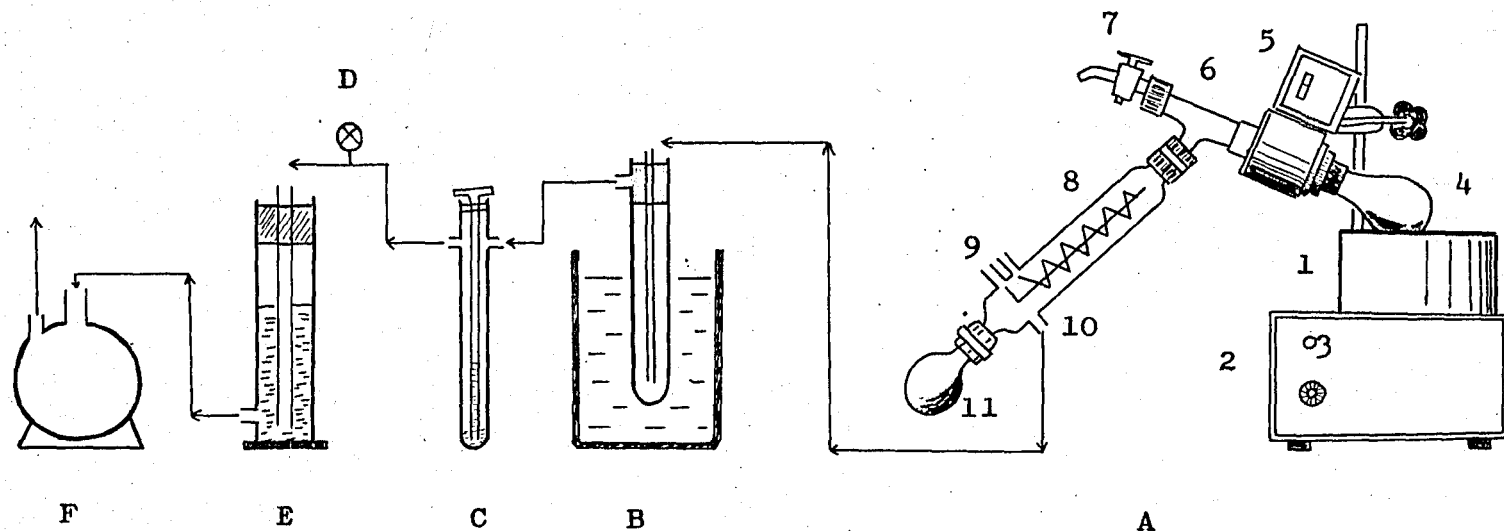
The solvents were removed from the lignite extract solution such that extract amount could be weighed and yield calculated. Tetrahydrofuran, pyridine and tetralin were removed from extract solutions using a vacuum rotary evaporator, Rotavapor-M, manufactured by Büchi Laboratory-Techniques Ltd. of Switzerland. The apparatus connected to the vacuum system is schematically shown in Fig. 3.3. The other solvents, hexane, benzene, benzene-ethanol mixture and toluene, were removed by one stage atmospheric distillation.

The residue of run done under H_2 pressure of 75 atm was extracted with hexane, benzene and pyridine in the Soxhlet apparatus, previously described. Analysis of gas products of the same run were performed with an Orsat analyzer. The gas product was analyzed for carbon dioxide, oxygen and carbon monoxide, only. The Orsat analyzer is shown in Fig. 3.4.

3.2. MATERIAL USED

3.2.1 Lignite Samples

The lignite samples of Çan (Çanakkale), Soma (Manisa) and Tunçbilek (Tavşanlı) were obtained from MTA. The proximate and ultimate analysis of samples are shown in TABLES 3.1, 3.2 and 3.3. Hydrogen, nitrogen and carbon analysis were done at



A-- Evaporator,

1- Heating bath,

2- Thermostat,

3- Signal lamp,

4- Evaporating flask,

5- Drive unit,

6- Distribution piece
with vapor duct,

7- Introduction stopcock,

8- Condenser,

9- Cooling water

connections,

10- Vacuum connections,

11- Receiving flask,

B-- Solvent trap with
icy water,

C-- Mercury manometer,

D-- Purge valve,

E-- Moisture trap with
dessicant,

F-- Vacuum pump.

Figure 3.3

Evaporator and vacuum system

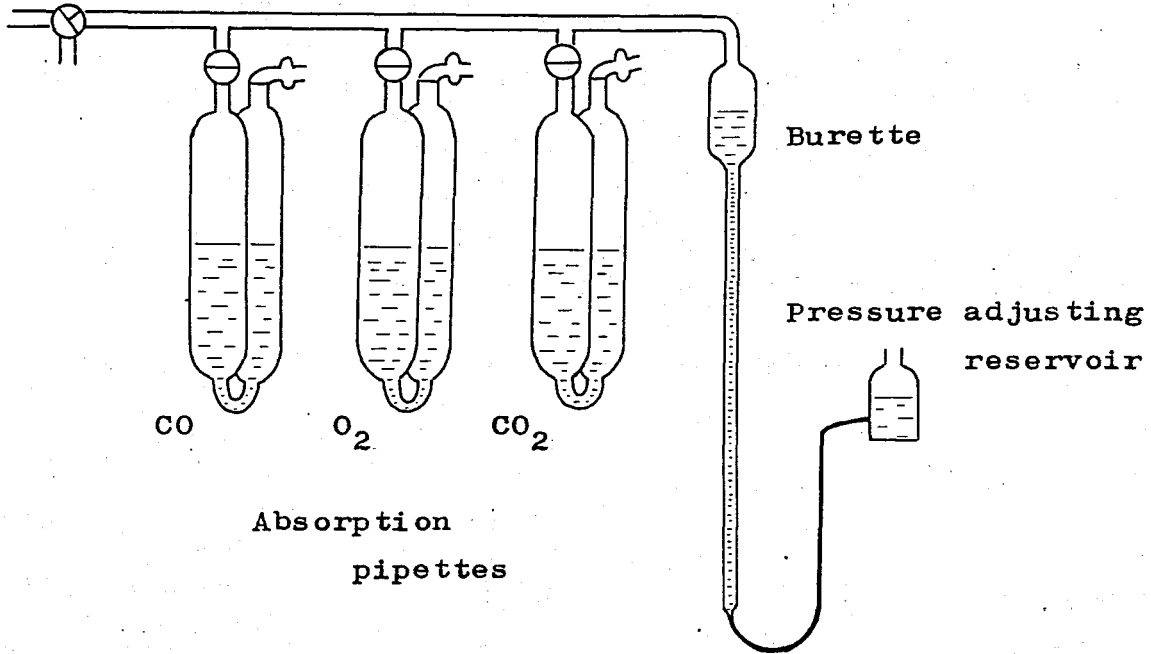


Figure 3.4 Orsat gas analyzer

İ.Ü. Eczacılık Fakültesi. Oxygen percentage was calculated by difference. The moisture, ash and heating values shown in TABLE 3.4 were given by MTA.

The lignite samples were first ground to the desired mesh (e.g. 60, 80, 100, 120) dried in air oven at 105 °C for time intervals previously determined for each coal and then stored in a dessicator. The drying time values were determined as explained in App. 1. The drying curves thus constructed are shown in Figs. A.1.1, A.1.2, A.1.3. The sulfur and volatile matter contents were determined by "TS363" and "TS711" methods of TSE.

TABLE 3.1 PROXIMATE AND ULTIMATE ANALYSIS OF
ÇAN (ÇANAKKALE) LIGNITE SAMPLE

	Coal, as received	Coal, moisture free	Coal, moisture and ash free
<u>Proximate analysis, %</u>			
Moisture	21.57	-	-
Volatile matter	47.86	61.02	78.43
Fixed carbon	13.16	16.78	21.57
Ash	17.41	22.20	-
Total	100.00	100.00	100.00
<u>Ultimate analysis, %</u>			
Hydrogen	5.48	3.93	5.05
Carbon	45.10	57.50	73.91
Nitrogen	-	-	-
Oxygen	29.52	13.19	16.95
Sulfur	2.49	3.18	4.09
Ash	17.41	22.20	-
Total	100.00	100.00	100.00

TABLE 3.2 PROXIMATE AND ULTIMATE ANALYSIS OF
SOMA (MANISA) LIGNITE (+18 LAV^{*}) SAMPLE

	Coal, as received	Coal, moisture free	Coal, moisture and ash free
<u>Proximate analysis, %</u>			
Moisture	19.37	-	-
Volatile matter	32.14	39.86	51.68
Fixed carbon	30.05	37.27	48.32
Ash	18.44	22.87	-
Total	100.00	100.00	100.00
<u>Ultimate analysis, %</u>			
Hydrogen	6.61	5.53	7.17
Carbon	46.00	57.05	73.97
Nitrogen	-	-	-
Oxygen	27.97	13.33	17.28
Sulfur	0.98	1.22	1.58
Ash	18.44	22.87	-
Total	100.00	100.00	100.00

* Washed lignite sample

TABLE 3.3 PROXIMATE AND ULTIMATE ANALYSIS OF
TUNÇBİLEK (TAVŞANLI) LIGNITE (+18 LAVÉ*) SAMPLE

	Coal, as received	Coal, moisture free	Coal, moisture and ash free
<u>Proximate analysis, %</u>			
Moisture	15.58	-	-
Volatile matter	32.12	38.05	52.67
Fixed carbon	28.86	34.18	47.33
Ash	23.44	27.77	-
Total	100.00	100.00	100.00
<u>Ultimate analysis, %</u>			
Hydrogen	6.01	5.08	7.03
Carbon	53.95	63.91	88.48
Nitrogen	-	-	-
Oxygen	15.27	1.71	2.37
Sulfur	1.29	1.53	2.12
Ash	23.44	27.77	-
Total	100.00	100.00	100.00

* Washed lignite sample

TABLE 3.4 HEATING VALUES OF LIGNITE SAMPLES USED

	<u>ÇAN</u>	<u>SOMA</u>	<u>TUNÇBİLEK</u>
Lower heating value (Kcal/Kg)	5011	4851	5551
Higher heating value (Kcal/Kg)	5242	5082	5766

3.2.2 Solvents

The solvents used in the Soxhlet extraction part were specific and nonspecific solvents with normal boiling points as given in TABLE 3.5. Boiling point of benzene-ethanol mixture

TABLE 3.5 BOILING POINTS OF SOLVENTS USED (Perry, 1973)

<u>Solvent</u>	<u>Boiling point (°C)</u>
Benzene-ethanol	55-6
Tetrahydrofuran	65-6
Hexane	68.7
Benzene	80.1
Toluene	110.8
Pyridine	115.4
Ethanolamine	172.8
Tetralin	207.2

(7/3 v/v), was determined experimentally. The H-donor solvent used in autoclave extraction and hydroliquefaction was tetralin. Its boiling point is also shown in the same table.

3.2.3 Chemicals of Orsat Analyzer

Carbon monoxide was absorbed in acidic cuprous chloride solution. Oxygen and carbon dioxide were determined by absorption in alkaline pyrogallol solution and strong caustic potash solution, respectively (Thorpe, 1945).

3.3 EXPERIMENTAL PROCEDURE

3.3.1 Soxhlet Extraction

All extractions were performed using two Soxhlet extraction apparatus at the same time. Each run was performed twice to reproduce the results. The lignite sample was weighed in a paper thimble and placed into the Soxhlet apparatus. The water cooler system was then operated after having checked all the connections. The powerstat was adjusted such that the heater temperature reached and slightly exceeded the boiling temperature of the extraction solvent in the flask and thus the boiling rate was sufficient for the required siphon number.

At the end of the extraction, the wet lignite resi-

dues were dried in an air oven at 105°C until constant weight. The dried thimbles containing unextracted lignite were weighed and the weight difference and the % (C-R)/C value was determined.

The residue of one autoclave hydroliquefaction run (run under H₂ pressure of 75 atm at room temperature) was extracted with hexane, benzene and pyridine, successively. The solids were extracted to exhaustion. The wet solids obtained after extraction with each solvent, were dried in air oven at 105°C to constant weight. The oil, asphaltene and preasphaltene yields were then calculated. The liquid products obtained were taken to rotary evaporator to separate the solvent from extract. The extract obtained was weighed and percentage yield was calculated.

3.3.2 Autoclave Extraction and Hydroliquefaction

For each run 500 ml of tetralin was used in the reactor. The previously weighed amount of lignite sample was added and the unit was sealed by tightening the bolts to the correct positions indicated by the arrows on the bolts and screws. The reactor was then flushed with nitrogen at low pressure (2 atm) all valves but the purge valve being closed. The air in reactor was blown out in this manner for 10-15 minutes. Then, N₂ or H₂ was sent to the reactor. As stated earlier, the extraction study was carried out separately, both under N₂ and H₂ pressure. Meanwhile, all the valves and joints were checked for leakage at the

intended reaction pressure.

After pressurizing the reactor, the temperature and stirrer speed were set to 325 °C and 750 rpm, respectively. Then heating and stirring of the reactor were started and the stirrer cooler was turned on. The temperature was set by using the temperature set knob on the controller. The stirrer speed was adjusted manually by the control wheel on the speed regulating box. The other controller setting values, X_p (proportional band), M_p (maximum power) and Limit (limit alarm) were determined previously by testing the temperature values versus time using tetralin under nitrogen pressure in the reactor. Results of the experiments performed to determine the optimum settings are given in Figs. A.2.1, A.2.2, A.2.3. With the chosen settings, the desired operating temperature (325 °C) was reached after 65 minutes. The autoclave was operated at this temperature for 60 minutes for all runs except for runs 10, 11, 12 in which reaction times were changed to see their effects on extraction yields.

When reaction period was achieved, the reactor vessel was cooled overnight to room temperature and opened. The contents were removed and passed through thimbles. The solids were washed out twice with fresh solvent (tetralin). The solids were dried in air oven at 105 °C until constant weight. The solvent in extract solution was separated from the extract by a rotary evaporator. The percentage of yield was calculated.

For the runs performed under H_2 pressure, the nitrogen present in reactor was purged out after the leakage tests were finished. The reactor was vented to atmospheric pressure. All the other valves closed, the hydrogen valve was opened and the reactor was flushed with hydrogen at low pressure for 15 minutes. Then, the reactor was pressurized with H_2 to the desired reaction pressure and the experiment was started.

3.3.3 Solvent Removal and Gas Analysis

The extract solution from each run was transferred to the evaporating flask of rotary evaporator and the vacuum pump was started. The vacuum pressure was adjusted by a purge valve. The evaporating flask, half of which is submerged in an electrically heated water bath, was continuously rotated by a driving unit. The temperature of water bath and the vacuum pressure were adjusted so that the solvent could evaporate as rapidly as possible. The extract thus obtained was weighed and the yield was calculated.

Gas analysis in Orsat analysis can be summarized as follows. Known amounts of gas samples were taken in burette and then passed successively through the absorbing solutions (see Section 3.2.3). The difference in volumes of gas in burette before and after the experiment, gave the volume of gas component absorbed. The amount of gas absorbed by each solution was recorded and results were given in volume percent (Thorpe, 1945).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 SOXHLET EXTRACTION

Experiments were designed to study the effects of particle size, siphon number, solvent to lignite ratio (S/L) and action of different solvents on the percent extraction yield using three different types of lignites. All the results are reported on two bases: % E/C (percent extract/dry lignite sample) and % (C-R)/C (percent dry lignite sample minus residue, all over dry lignite sample). % E/C may exceed its true value because the extract contains solvent in the free or polymerized form. On the other hand, although % (C-R)/C is independent of retained solvent in the extract, its value is dependent on gas losses and on retained solvent in the residue. Negative results will be obtained for % (C-R)/C when the weight of residue exceeds that of dry coal sample because of solvent retention in residue (Wise, 1971). As a result, this work is based on % E/C calculations.

The results of particle size effect are shown in

TABLE 4.1 and Fig. 4.1. The curve drawn in Fig. 4.1 was obtained by linear regression. Pairs of runs 3-4, 10-11, 12-13 and 14-15

TABLE 4.1 QUANTITATIVE RESULTS OF SOXHLET EXTRACTION

Run	Solvent	Lignite	Particle size, mesh	Siphon number	S/L	%E/C	%(C-R)/C
1	P	Ç	60	8	20	3.75	3.61
2	P	Ç	60	16	20	4.73	4.52
3	P	Ç	60	16	20	4.63	4.12
4	P	Ç	60	16	20	4.68	4.27
5	P	Ç	60	21	20	4.79	5.13
6	P	Ç	60	28	20	7.18	6.93
7	P	Ç	60	28	10	7.52	6.93
8	P	Ç	60	28	15	7.61	7.05
9	P	Ç	60	28	25	7.28	7.94
10	P	Ç	80	16	20	4.26	4.75
11	P	Ç	80	16	20	4.22	3.99
12	P	Ç	100	16	20	3.70	3.10
13	P	Ç	100	16	20	3.82	3.70
14	P	Ç	120	16	20	3.29	2.15
15	P	Ç	120	16	20	3.40	3.51

P- Pyridine, Ç- Çan

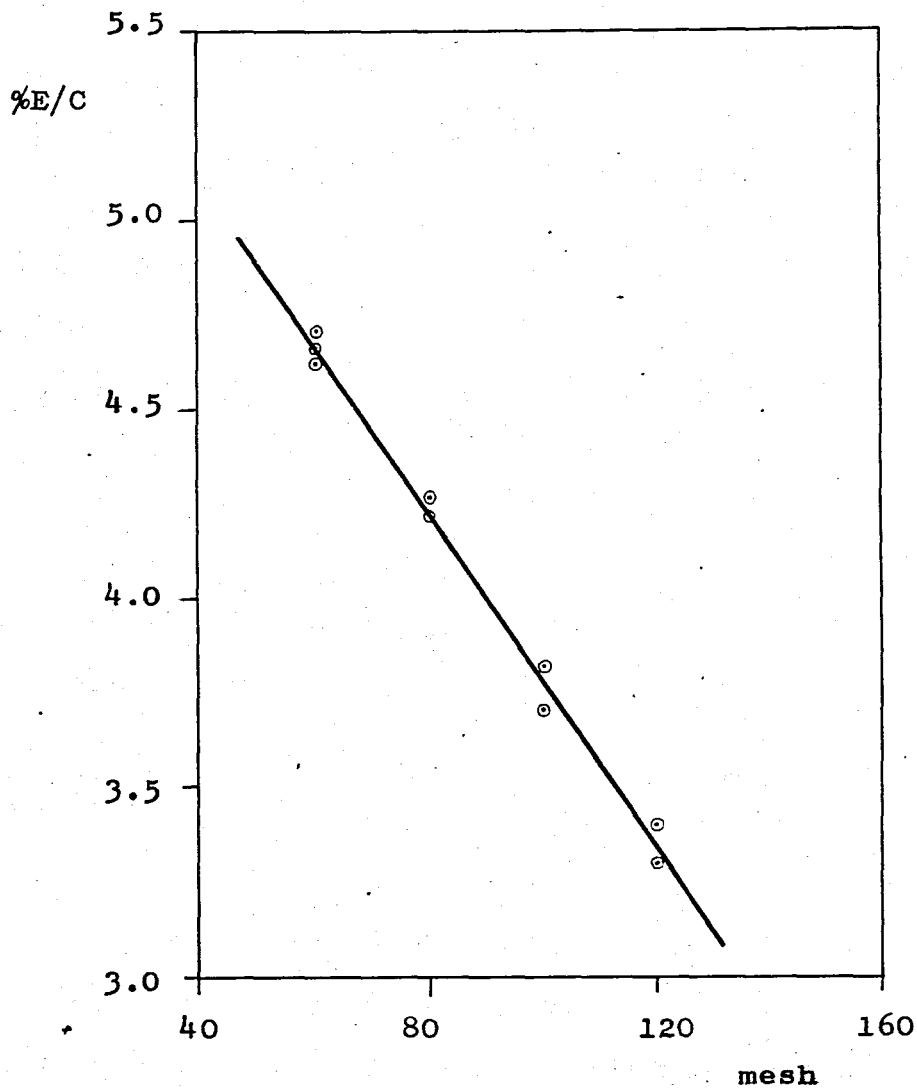


Figure 4.1 Effect of particle size on extract yield of Çan (Çanakkale) lignite using pyridine as solvent (siphon number = 16, S/L = 20)

were performed at the same conditions to measure the reproducibility of results. The reproducibility was observed to be within $\pm 3\%$ of $\%E/C$, but poor reproducibility was observed for $\%(C-R)/C$, due to the high solvent retention in residue. Decrease in yield

is observed as particle size decreased. Similar behavior is also reported in literature (Oele, 1951). Extractions were done for a time period of 7 hr, not to exhaustion. So, the results obtained are not the final extraction yields. Nevertheless, they give an indication about the effects of various parameters on the extraction yields.

The second parameter studied, was the siphon number. The power supplied to the heater could be varied and it was adjusted to obtain the required siphon rate. The values for siphon numbers obtained during 7 hr extraction runs and the results of extraction yields are reported in TABLE 4.1. A graph showing the relation between yield and siphon number is given in Fig. 4.2. It is seen that extraction yield increases with siphon number. The curve in this figure was obtained by least-squares method. It can be deduced that the yield increases with the contact time between lignite sample and fresh solvent.

There are contradictory results about solvent to coal ratio effect in the literature (Darlage, 1975; Neavel, 1976; Severson, 1977). Experiments done in this work showed that yield decreases with increase in solvent to lignite ratio, when Çan (Çanakkale) lignite samples were extracted with pyridine for 7 hrs (runs 6, 7, 8, 9 in TABLE 4.1). The effect of solvent to lignite ratio on extract yield is also shown in Fig. 4.3. The curve was drawn using linear regression method.

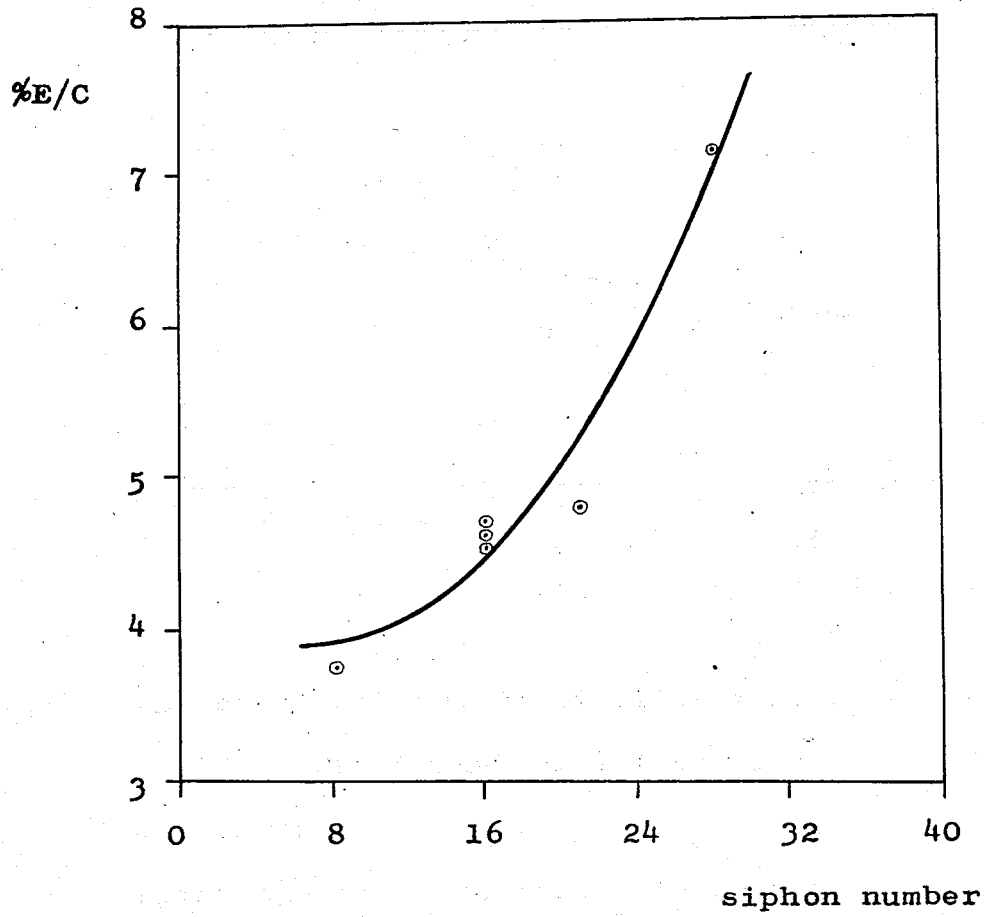


Figure 4.2 Effect of siphon number on extract yield of Çan (Çanakkale) lignite using pyridine as solvent (particle size = 60 mesh, S/L = 20)

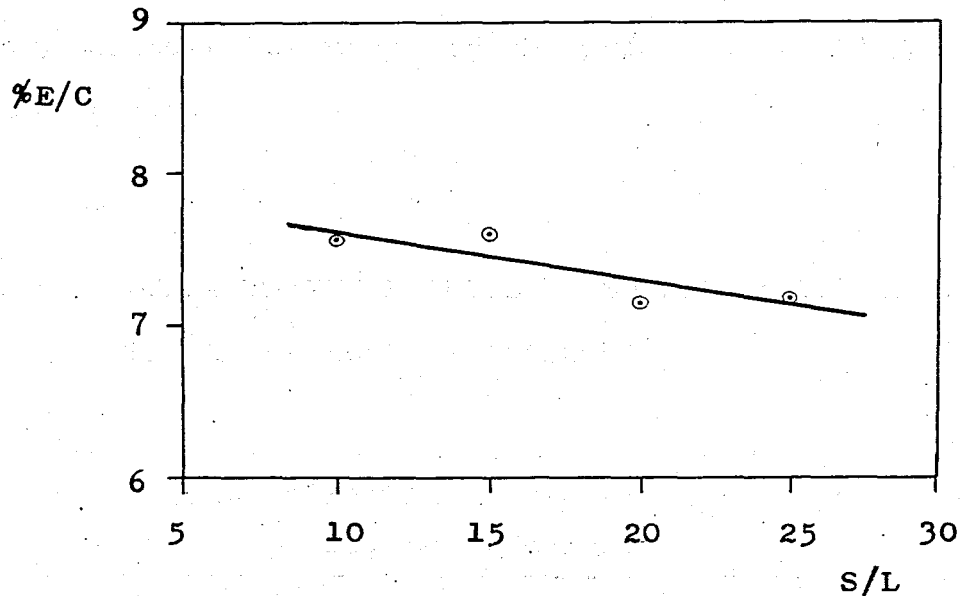


Figure 4.3 Effect of solvent to lignite ratio on extract yield of Çan (Çanakkale) lignite using pyridine as solvent (particle size = 60 mesh, siphon number = 28)

It is stated that the effectiveness of a solvent depends on the rank of the coal (Darlage, 1975). Carbon percentage on moisture and ash free basis (daf) is commonly used to define the rank of the coal. In this work also, ranks of lignites were determined according to the carbon contents of lignites. The rank increases as follows: Çan → Soma → Tunçbilek (see TABLES 3.1, 3.2, 3.3). In the literature it is reported that extraction yield increases with rank (vanKrevelen, 1961; Golumbic, 1950). The effect of rank on the extraction yield was studied by ex-

traction of Çan, Soma and Tunçbilek lignite samples with different solvents. The results showing the effects of rank and the boiling points of solvents on the %E/C and %(C-R)/C, are given in TABLE 4.2.

TABLE 4.2 QUANTITATIVE RESULTS OF SOXHLET EXTRACTION
(RANK AND SOLVENT EFFECTS)

Run	Solvent	Lignite	Particle size, mesh	Siphon number	S/L	%E/C	%(C-R)/C
16	B-E	Ç	60	E	25	17.05	17.87
17	B-E	S	60	E	25	19.78	19.93
18	B-E	T	60	E	25	17.95	18.05
19	THF	Ç	60	E	25	5.32	7.53
20	THF	S	60	E	25	6.52	10.00
21	THF	T	60	E	25	6.19	9.08
22	H	Ç	60	E	25	1.13	1.01
23	H	S	60	E	25	2.02	1.98
24	H	T	60	E	25	1.78	1.53
25	B	Ç	60	E	25	2.56	2.81
26	B	S	60	E	25	3.11	3.67
27	B	T	60	E	25	2.99	3.48
28	TO	Ç	60	E	25	5.71	3.08
29	TO	S	60	E	25	9.02	4.23
30	TO	T	60	E	25	6.00	3.46

TABLE 4.2 QUANTITATIVE RESULTS OF SOXHLET EXTRACTION
(RANK AND SOLVENT EFFECTS) (continued)

Run	Solvent	Lignite	Particle size, mesh	Siphon number	S/L	%E/C	%(C-R)/C
31	P	Ç	60	E	25	9.80	6.76
32	P	S	60	E	25	9.28	5.37
33	P	T	60	E	25	11.85	7.35
34	EA	Ç	60	E	25	204.62	-
35	EA	S	60	E	25	-	-
36	EA	T	60	E	25	161.00	-

B-E - Benzene-ethanol mixture,

THF - Tetrahydrofuran,

H - Hexane,

B - Benzene,

TO - Toluene,

P - Pyridine,

EA - Ethanolamine,

Ç - Çan,

S - Soma,

T - Tunçbilek,

E - Exhaustion.

Benzene-ethanol mixture (7/3 v/v), tetrahydrofuran, hexane, benzene, toluene, pyridine and ethanolamine were used to extract Çan, Soma and Tunçbilek lignite samples. The results given in TABLE 4.2 show higher yields in extraction with solvents having higher boiling points (see also TABLE 3.5), with the exception of benzene-ethanol mixture and tetrahydrofuran. Fig. 2.5 shows the relation between pyridine and benzene-ethanol extraction yields and rank of various lignites extracted. The results obtained in this work are also plotted on the same figure for comparison. Results of this work for pyridine fit the curve taken from literature, but the benzene-ethanol extraction yields obtained in this work are higher than the values reported by Ōuchi et al. (1965). The results of extraction by pyridine of this work are also compared against the results reported by vanKrevelen (1961) (see Fig. 4.4). As it is seen, the data of this work agree with vanKrevelen's data. The yields obtained with benzene-ethanol mixture and tetrahydrofuran (see Fig. 4.5), which are higher than those reported in literature (see Fig. 2.5), may be due to inefficient separation of solvent from the solvent-extract solution. The solvent removal from extract solutions obtained in runs 16, 17, 18, 19, 20 and 21 of TABLE 4.2 were accomplished by simple stage distillation. This type of solvent removal has poor efficiency because a considerable amount of solvent remains in the extract. Large yield values are obtained here because of unremovable solvent.

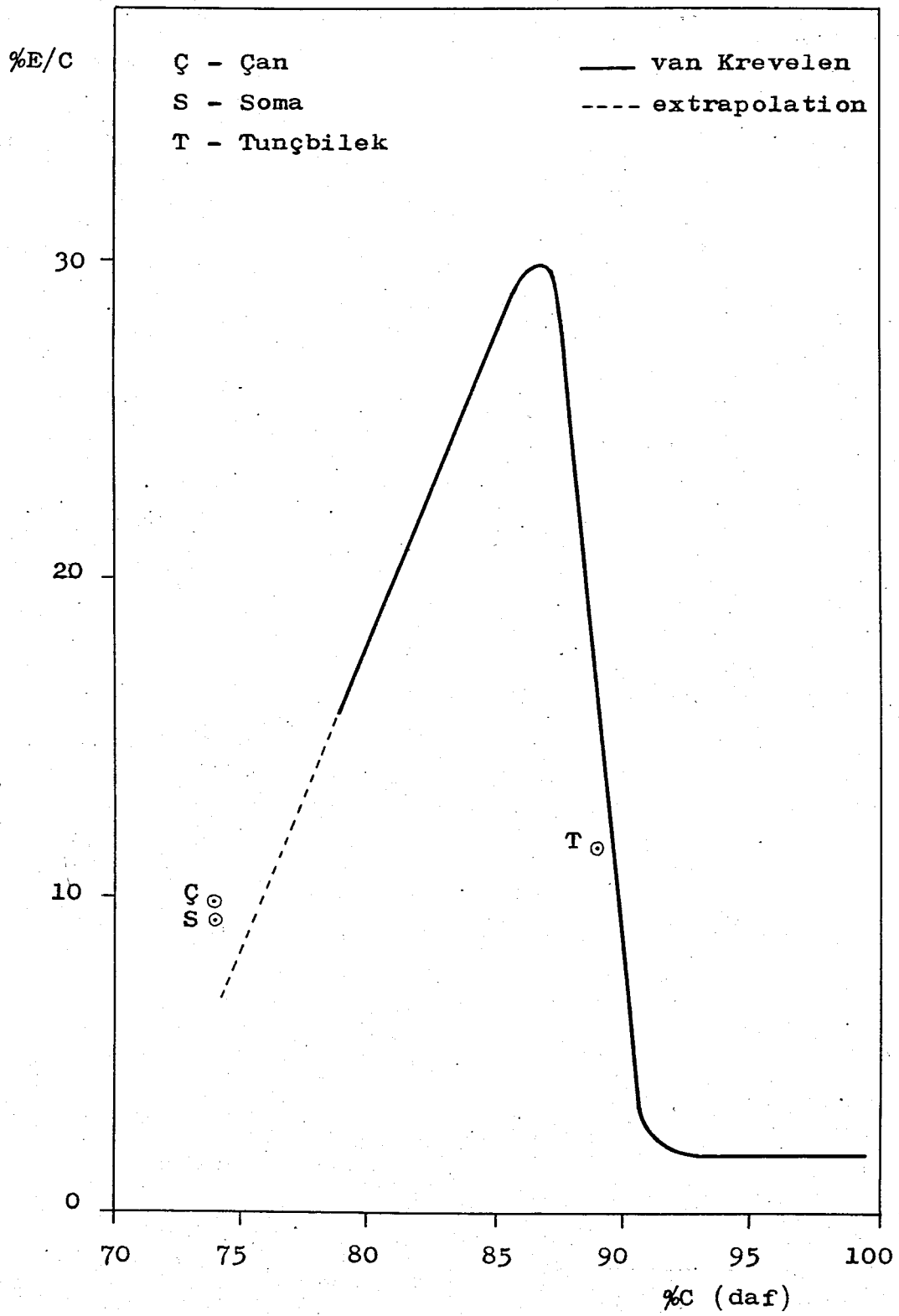


Figure 4.4 Extraction yields with pyridine
(van Krevelen, 1961)

The effects of other solvents on extraction yields are shown in Fig. 4.5.

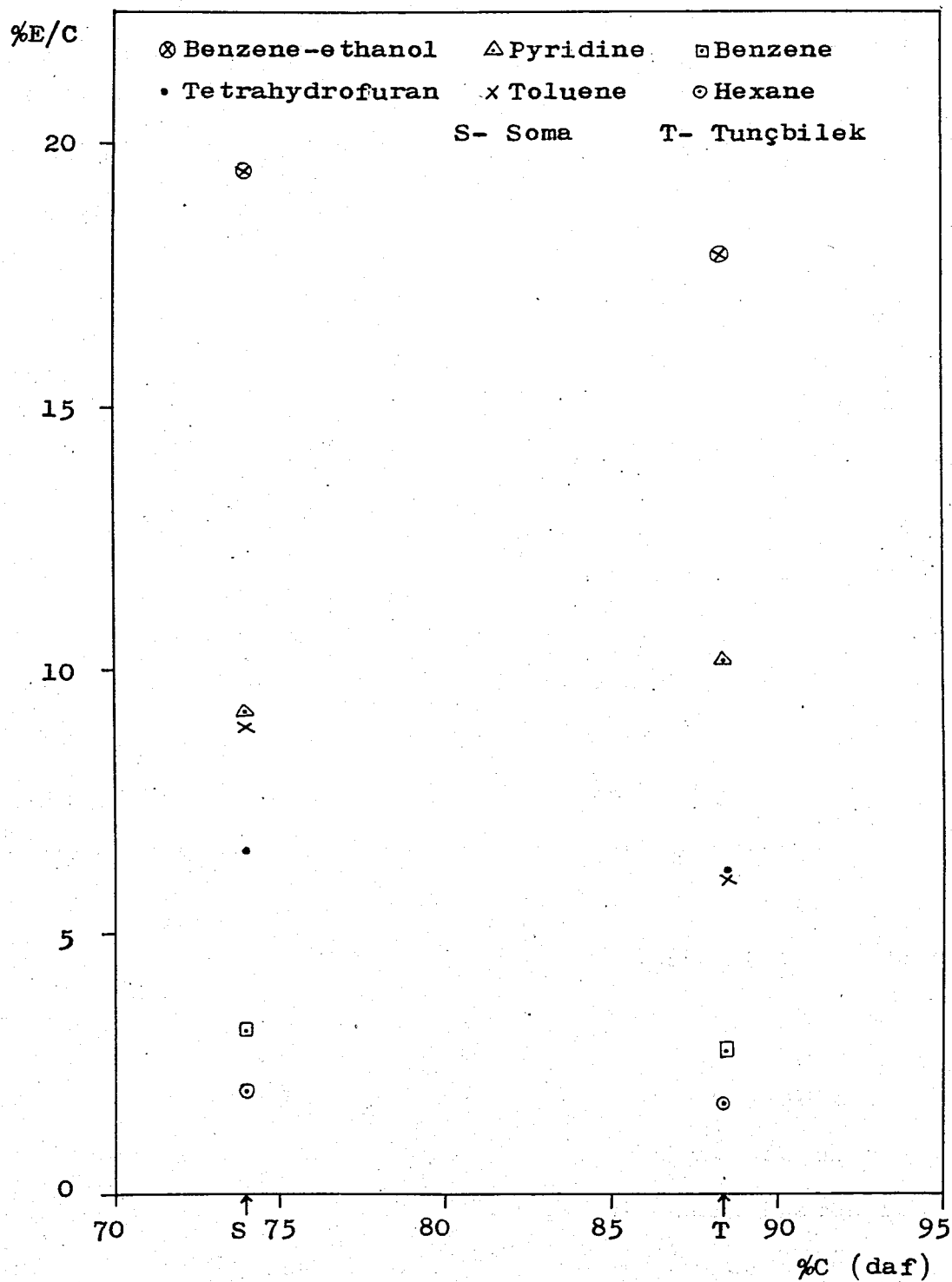


Figure 4.5 Effect of solvents on extraction yields as a function of %C

It is seen that hexane, benzene and toluene are not effective solvents but pyridine is a good one. Pyridine effectiveness increases as %C increases (from 73.97 to 88.48%). Just the contrary can be observed for all the other solvents. Figure 4.6 illustrates the effect of solvents on extraction yields as a function of H/C ratio. Yield increases when H/C increases. (with exception of pyridine). Benzene extraction yields varied in the range of 2.56 to 3.11 % (run 25, 26, 27, TABLE 4.2). These low yields agree with the results given in literature (vanKrevelen, 1961).

Figure 2.7 shows that ethanolamine is a good solvent for low rank coals. Ethanolamine extraction has been attempted but attack of the thimble by this solvent was observed during the extraction done in runs 34, 35 and 36 (TABLE 4.2). Also, a great retention of solvent in the residue and extract was observed. This is the reason for such high yields obtained in runs 34 and 36. Run 35 has been attempted but for each time destruction of thimbles was observed and the run couldn't be continued. However, decrease in yield with increase in %C in lignite is reported in literature (Dormans, 1960; vanKrevelen, 1965).

The duration of runs 16 through 36 (TABLE 4.2) was determined by the period required to obtain a colorless extract, a criteria which has been used by many others (Farcasiu, 1976; Ōuchi, 1965; Darlage, 1976). The extract as removed from Soxhlet apparatus varied from dark brown (extraction with pyridine) to

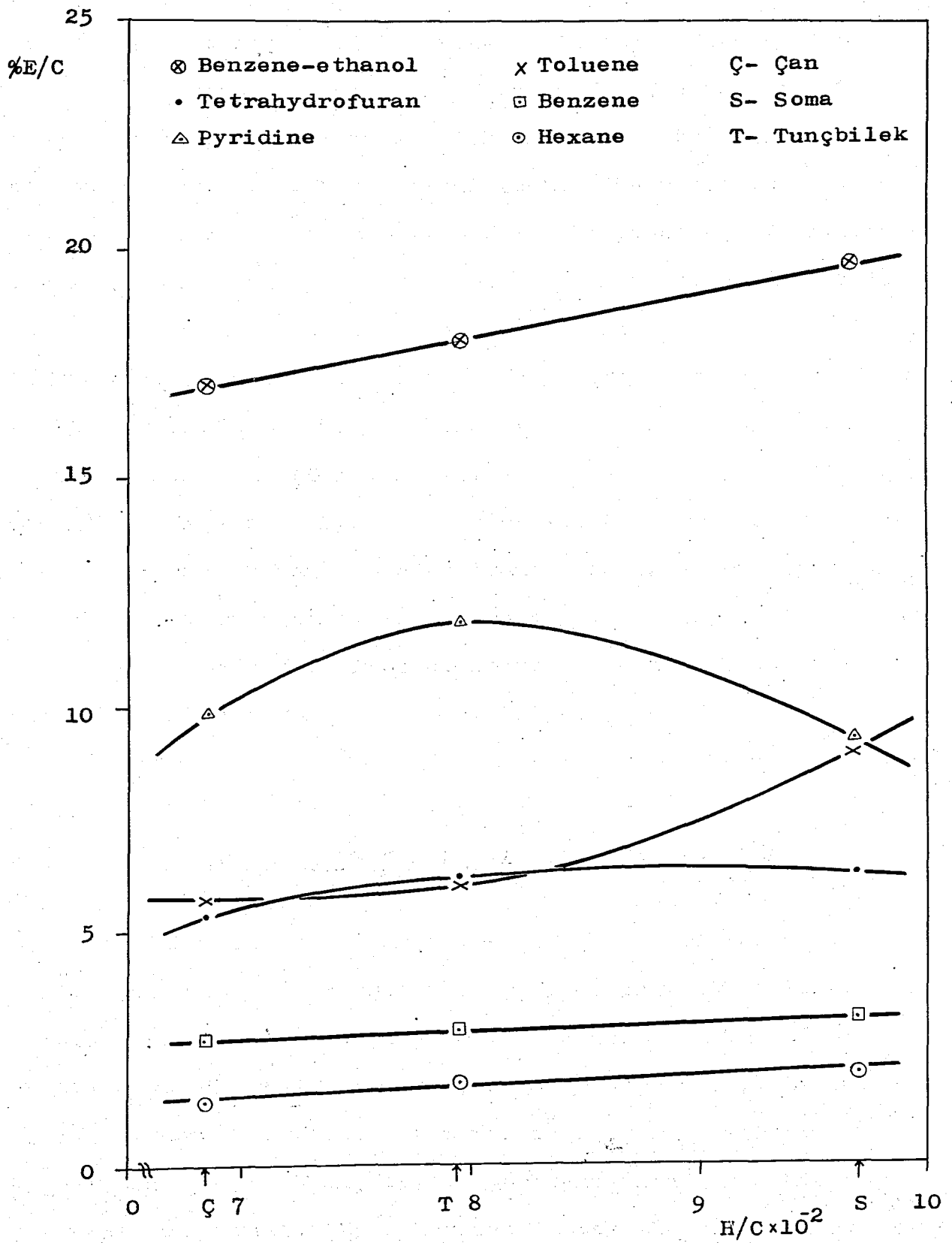


Figure 4.6 Effect of solvents on extraction yields as a function of H/C ratio

colorless (extraction with hexane) solutions. Examination of pyridine extract solution showed presence of a very small amount of colloidal material which showed visible signs of precipitate formation after several weeks. The precipitate formation in solutions is attributed to the presence of free radicals in the coal (Dormans, 1960). The extract and insoluble residue shows affinity for the solvent. It was reported that in the application of solvents like pyridine, a surplus of 10 to 15 percent in the weight balance based on the original coal is not exceptional (Oele, 1951). As it is seen in TABLE 4.2, $\%(C-R)/C$ values and $\%E/C$ values for the same run do not agree because of the entrapment of solvent molecules both in porous structure of coal and extract. Prolonged heating of extraction residues and extracts produced no weight changes, as it is also observed in literature (Darlage, 1975).

4.2 AUTOCLAVE EXTRACTION AND HYDROLIQUEFACTION

The extraction in autoclave were performed using tetralin under a) N_2 pressure and b) H_2 pressure. The lignite samples from Çan (Çanakkale), Soma (Manisa) and Tunçbilek (Tavşanlı) used in previous work, were also used here. Although it is reported that hydrogen transfer is better at temperatures higher than $400^\circ C$ (Wise, 1971), the temperature in this work was kept constant at $325^\circ C$ because it was the maximum safe temperature that could be used in the reactor. The effects of rank,

reaction time, solvent to lignite ratio and pressure on the %E/C and %(C-R)/C values for the experiments carried out in the autoclave using N₂ gas are shown in TABLE 4.3.

TABLE 4.3 RESULTS OF TETRALIN EXTRACTION OF LIGNITE
SAMPLES UNDER A) N₂ , B) H₂ PRESSURE

Run	Gas	Lignite	Time (min)	S/L	Pressure at 325 °C (atm)	%E/C	%(C-R)/C
1	N ₂	Ç	60	10	119	21.76	13.28
2	N ₂	S	60	10	119	19.43	6.73
3	N ₂	T	60	10	119	11.03	- 2.17
4	N ₂	T	60	7	119	9.89	- 4.43
5	N ₂	T	60	4	119	7.52	- 8.95
6	N ₂	T	60	2	119	4.32	- 9.23
7	N ₂	T	60	10	92	10.75	- 2.36
8	N ₂	T	60	10	59	10.72	- 4.19
9	N ₂	T	60	10	4	10.60	- 7.15
10	N ₂	T	45	10	119	10.90	-11.38
11	N ₂	T	30	10	119	10.40	-12.73
12	N ₂	T	15	10	119	9.75	- 5.96
13	H ₂	Ç	60	10	119	23.15	20.20
14	H ₂	S	60	10	119	19.83	14.89
15	H ₂	T	60	10	119	12.51	10.01
16	H ₂	S	60	10	131	20.11	15.22

Ç- Çan, S- Soma, T- Tunçbilek

Effect of rank is observed at the end of the first three runs in TABLE 4.3. It can be seen that decrease in yield occurs with the increase in rank. The %C content of Tunçbilek is given as 88.48% (see TABLE 3.3). It is reported in literature that the yields decrease quite abruptly for coals with carbon contents between 87 and 90% (vanKrevelen, 1961). Here, Tunçbilek lignite falls into this region. The results given in runs 1, 2 and 3 of TABLE 4.3 are plotted in Fig. 4.7.

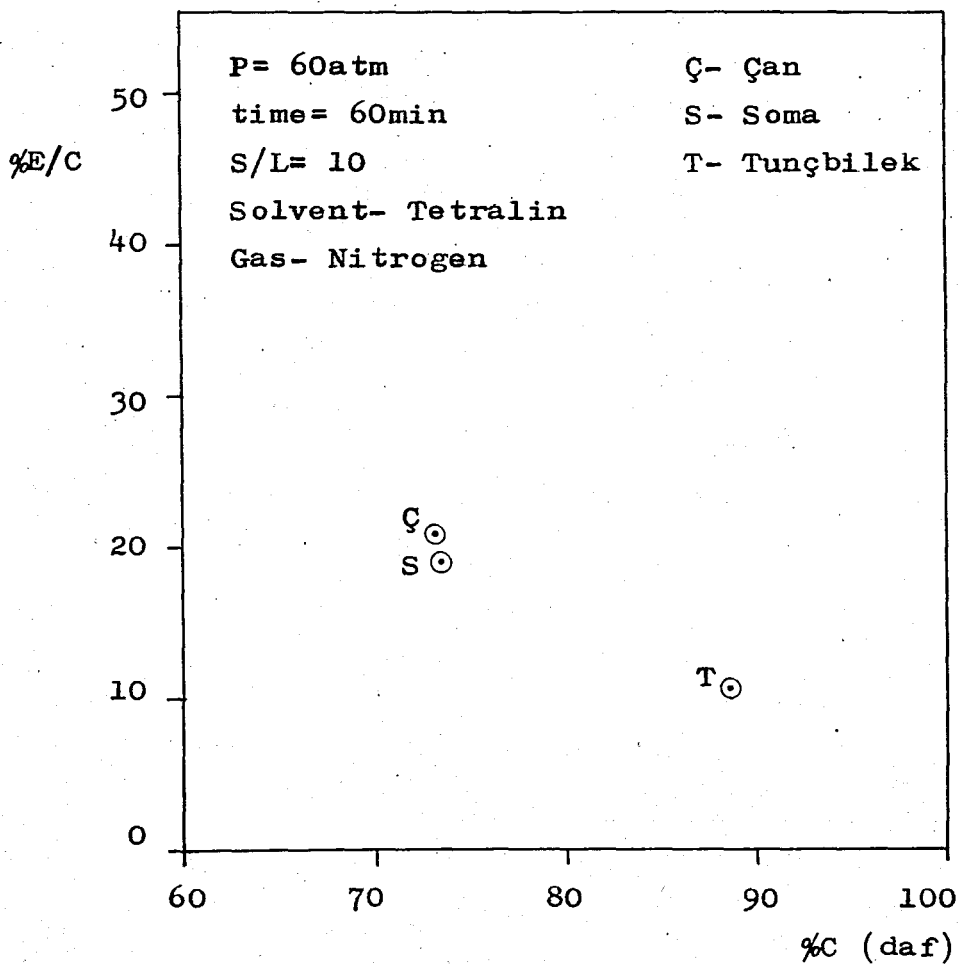


Figure 4.7 Effect of rank on extract yield

The results obtained in this work, shown in runs 3, 4, 5 and 6 of TABLE 4.3, disagree with the observation of Neavel (1976) (see Section 2.2.3.2) but agree with that of Severson et al. (1977) who reported that yields increase with increasing solvent to coal ratio. From the shape of the curve given in Fig. 4.8 it can be deduced that beyond solvent to lignite ratios greater than 10:1, yield will not significantly increase.

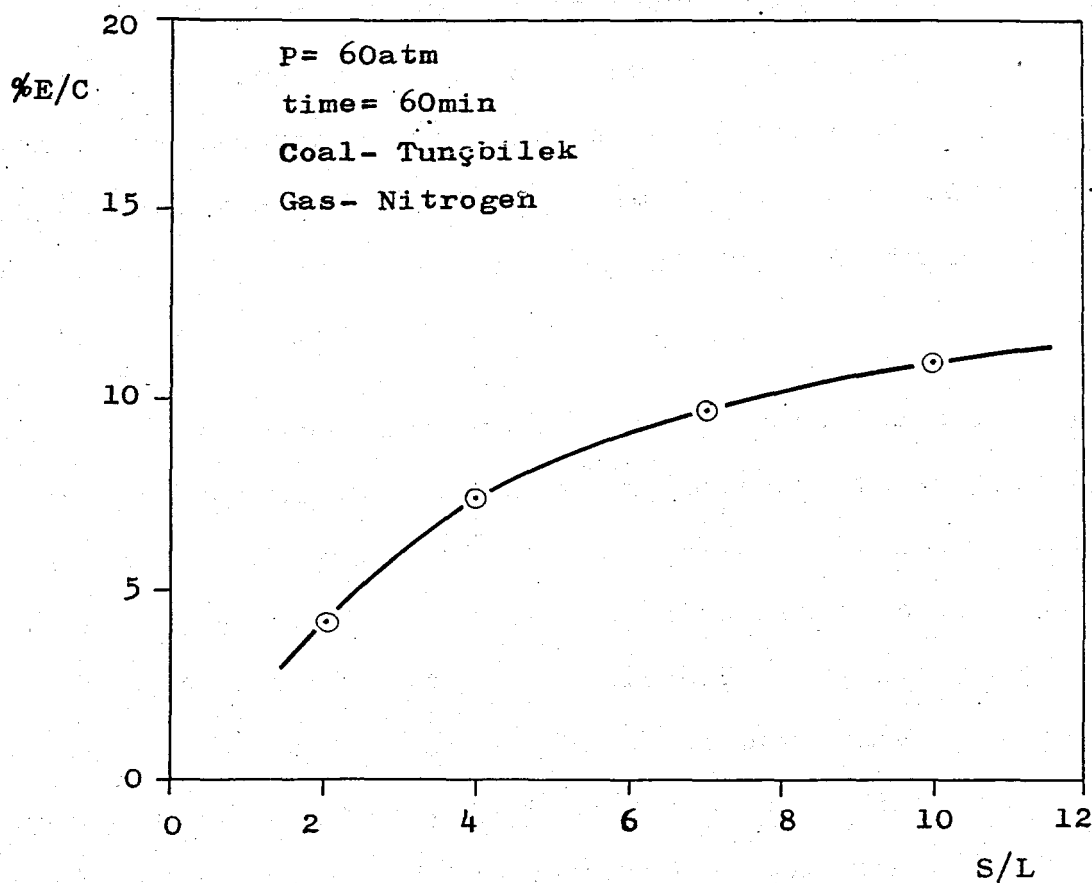


Figure 4.8 Effect of tetralin to lignite ratio on extract yield

Negative values for $\%(C-R)/C$ are obtained as seen in TABLE 4.3. This means that the weight of residues are higher than those of dry lignite samples. This is because of entrapment of tetralin in the residue. The entrapment is observed (see TABLE 4.3) to decrease (smaller absolute values of $\%(C-R)/C$) with increase in solvent to lignite ratio. Because of the higher yield and the lower solvent entrapment, the solvent to lignite ratio for the rest of experiments was fixed to 10:1.

Pressure is also an important parameter in extraction. Increasing pressure resulted in increased yields (see TABLE 4.3) as reported also in literature (Lurgi, 1978). The extraction yields are plotted against pressure at the reaction temperature (325°C) and the curve obtained shows that increasing pressure beyond the pressures used in this study, will increase the yield further (see Fig. 4.9).

Reaction time was also varied and its effect on yield is presented in Fig. 4.10. Further increase in time would not affect the yield much, so reaction time was safely fixed to 60 min. Comparing the $\%(C-R)/C$ results given in runs 3, 10, 11 and 12 of TABLE 4.3, it can be deduced that entrapment of tetralin is lowest for run 3, which was performed at reaction time of 60 min. Fixing the reaction time of the rest of experiments to 60 min, is again justified by this result.

In the experiments where H_2 gas was used, pressure and temperature were set to fixed values of 60atm (measured at

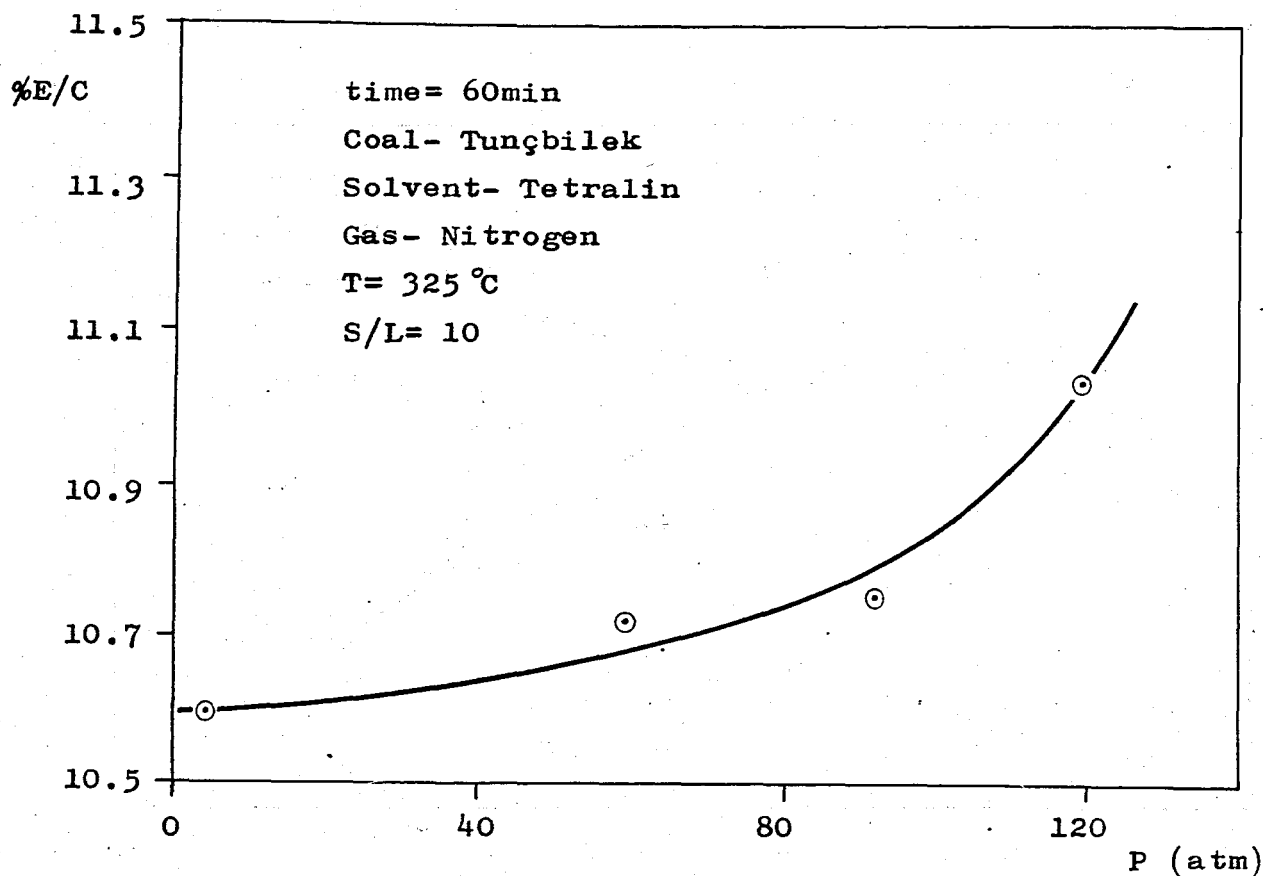


Figure 4.9 Effect of pressure on extract yield

room temperature) and 325 °C, respectively. The yields given in runs 13, 14, 15 of TABLE 4.3 show the same trend observed with N₂ gas: they decrease as the %C of coal increases. The yields are slightly higher when H₂ gas is used instead of N₂ gas. It is reported in literature that hydrogen effect is not very important when reaction temperatures are low for intensive bond breakage to occur (Ignasiak, 1980). Increase of 1.39, 0.40 and 1.48% in yields were obtained for Çan, Soma and Tunçbilek lignite samples, respectively, when H₂ gas was used instead of N₂

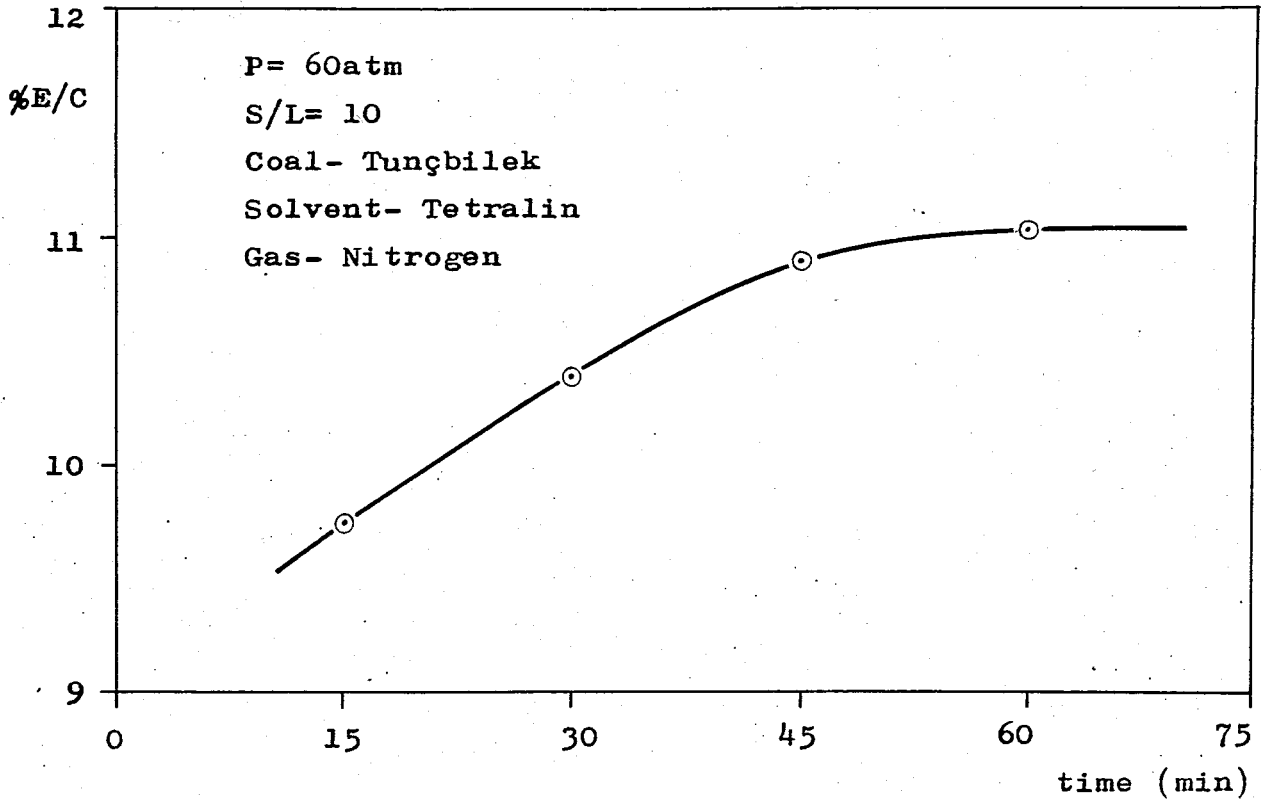


Figure 4.10 Effect of reaction time on extract yield

gas (see Fig. 4.11).

Run 16 in TABLE 4.3 was performed at 75 atm (measured at room temperature) and 325°C using Soma (Manisa) lignite. The extract yield obtained was slightly higher than that obtained at 60 atm (see run 14, TABLE 4.3). The residue of this run was extracted with hexane, benzene and pyridine in a Soxhlet apparatus. The results given in TABLE 4.4 compare the oil, asphaltene, asphaltol and residue yields of lignite extracted in Soxhlet apparatus with yields of residue of lignite reacted with tetra-

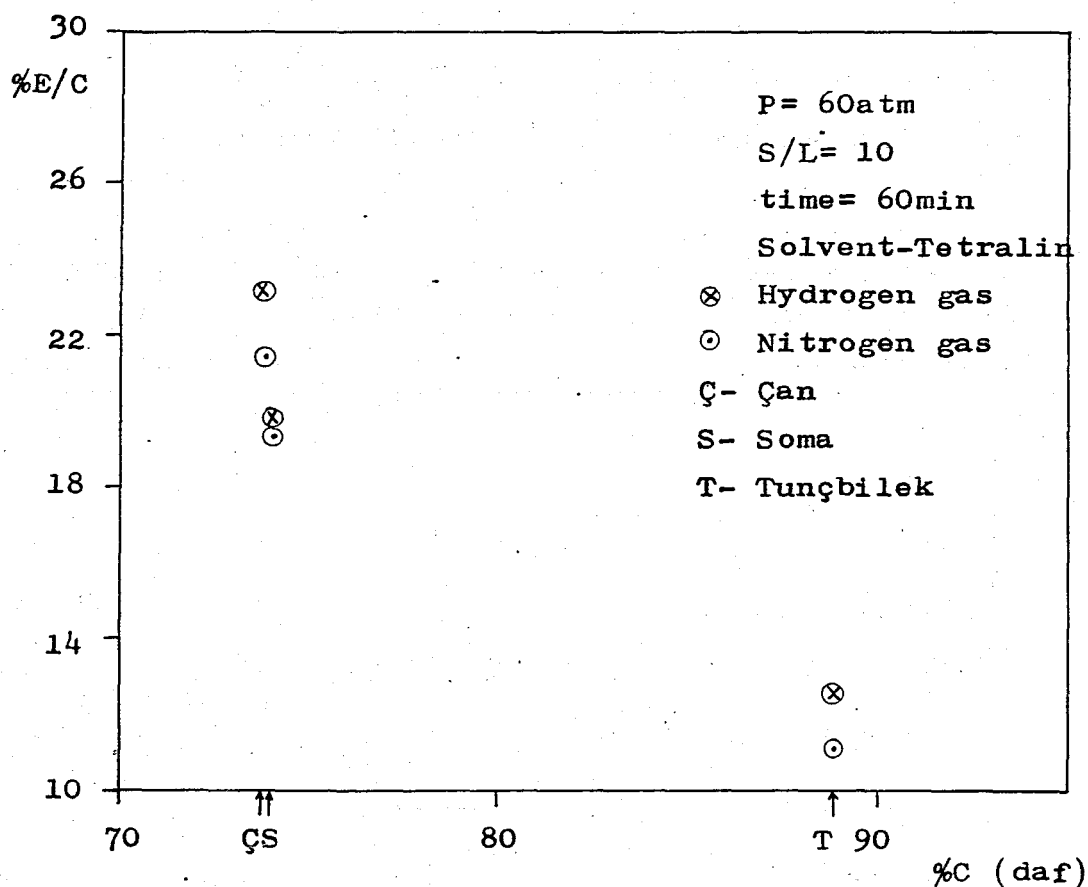


Figure 4.11 Effects of hydrogen pressure on the yield as a function of %C

lin in autoclave at 325 °C and under hydrogen pressure of 75atm. The % oils, % asphaltene, % asphaltol and % residue results tabulated in the first column of TABLE 4.4 are calculated using the results obtained by Soxhlet extraction of Soma lignite using hexane, benzene and pyridine (see runs 23, 26, 32 of TABLE 4.2) and keeping in mind that oils are hexane solubles, asphaltenes are hexane insoluble but benzene soluble, asphaltols are benzene insoluble but pyridine soluble and the residue is pyridine insoluble.

TABLE 4.4 OIL, ASPHALTENE, ASPHALTOL AND RESIDUE YIELDS OF SOMA (MANISA) LIGNITE SAMPLE AT 325 °C

<u>% with respect to lignite sample used</u>	<u>Lignite extracted in Soxhlet apparatus</u>	<u>Lignite extracted with tetralin in autoclave</u>
Oils	2.02	4.51
Asphaltenes	1.09	5.89
Asphaltols	6.17	30.55
Residue	94.63	39.09
Tetralin extract	—	20.11
	103.91*	100.15

} **

* Higher than 100 because residue could have trapped solvent in it

** Using the residue left after hydroliquefaction

Gas product of the same run was analyzed in an Orsat apparatus for carbon dioxide, oxygen and carbon monoxide contents. The results are shown in TABLE 4.5.

The main sources of error in autoclave work are associated with the transfer of liquid and solid products from the autoclave. Also, coal liquefaction experiments conducted

TABLE 4.5 ORSAT ANALYSIS OF GASES FROM RUN 16 OF
TABLE 4.3

	<u>CO₂</u>	<u>O₂</u>	<u>CO</u>
Volume %	2.5	1.4	5.7

in autoclave required long periods of heat-up (65 min) and cool down (overnight) during which, reactions could have occurred. However, all the runs were performed in the same manner to provide uniformity.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The tendency of extraction yields obtained in this study agree in general with literature. The Soxhlet extraction yields increased as the size of particles of lignite samples, the siphon number, the lignite to solvent ratio and the %C in lignite sample increased. In general, increased extraction yields were observed for extraction with solvents of higher boiling points.

The autoclave extraction yields, using N_2 gas and tetralin, increased as the reaction time, the solvent to lignite ratio and the pressure increased, but they decreased as the %C of lignite samples increased. The autoclave extraction yields using H_2 gas and tetralin show a similar trend, but they are slightly higher than those obtained using N_2 gas and tetralin. The yields of oil, asphaltene and asphaltol products obtained from extraction of residue of hydroliquefied Soma lignite are higher than those obtained from Soxhlet extraction of lignite sample itself.

5.2 RECOMMENDATIONS

1) Attack of thimbles by ethanolamine was observed during Soxhlet extraction. Therefore, the digestion method should be used for this type of extraction. By this method the lignite is extracted in a batch reactor at the boiling temperature (or higher) of solvent. This shortens the time of extraction but the increase in yield thus obtained will be small (Dormans, 1960),

2) The solvent removal should be done only with rotary evaporator. Simple distillation unit is inefficient to remove significant amounts of solvent,

3) A more efficient method should be developed for the transfer of solid and liquid products from autoclave,

4) Prehydrogenation of H-donor solvent may increase its hydrogen donor activity. Guin's (1978) results show that 20% additional coal dissolution occurs in prehydrogenated solvent,

5) Reaction should be performed, if possible, at higher temperatures,

6) Higher pressures may be applied to increase the yield,

7) Reactions under carbon monoxide pressure should be tried in autoclave. Results of Oelert et al. (1975) show that yield with carbon monoxide is almost twice of that obtained under hydrogen pressure,

8) More elaborate gas analysis should be done to determine

the constituents of gas formed in the autoclave,

9) More developed product characterization methods need to be employed. In general, clay-gel chromatographic methods can separate and assign reasonable structures to products. The fractionation of coal products by successive elution in solvents on a silica gel column causes separation into chemically different fractions. Also, high resolution mass spectrometry can in general separate and identify the formula of almost all heteroatomic components containing one or more O, S and N atom per molecule. Different analysis methods applicable to coal solutions are given in literature (Farcasiu, 1977; Liphard, 1980; Mair, 1978; Schiller, 1977). It is reported that mass spectrometry can be applied directly to unseparated samples but better results are obtained when it is combined with other separation methods and spectrometric methods such as GC, IR and NMR (Farcasiu, 1977; Aczel, 1977).

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APPENDIX

App.1 COSTRUCTION OF DRYING CURVES FOR LIGNITE SAMPLES

The weight of coal sample changes with time when dried in air oven at 105 °C, due to loss in weight of sample resulting from loss of moisture. After a while, the dried coal reacts with the oxygen in atmosphere and the weight loss of sample decreases. Finally, the oxidation products are released and the weight difference increases. Therefore, the time required for drying of coal is the time corresponding to the appearance of the first peak of drying curve. The drying times of lignite samples from Çan, Soma and Tunçbilek were determined to be 20 min, 40 min and 40 min respectively (see Figs. A.1.1, A.1.2 and A.1.3).

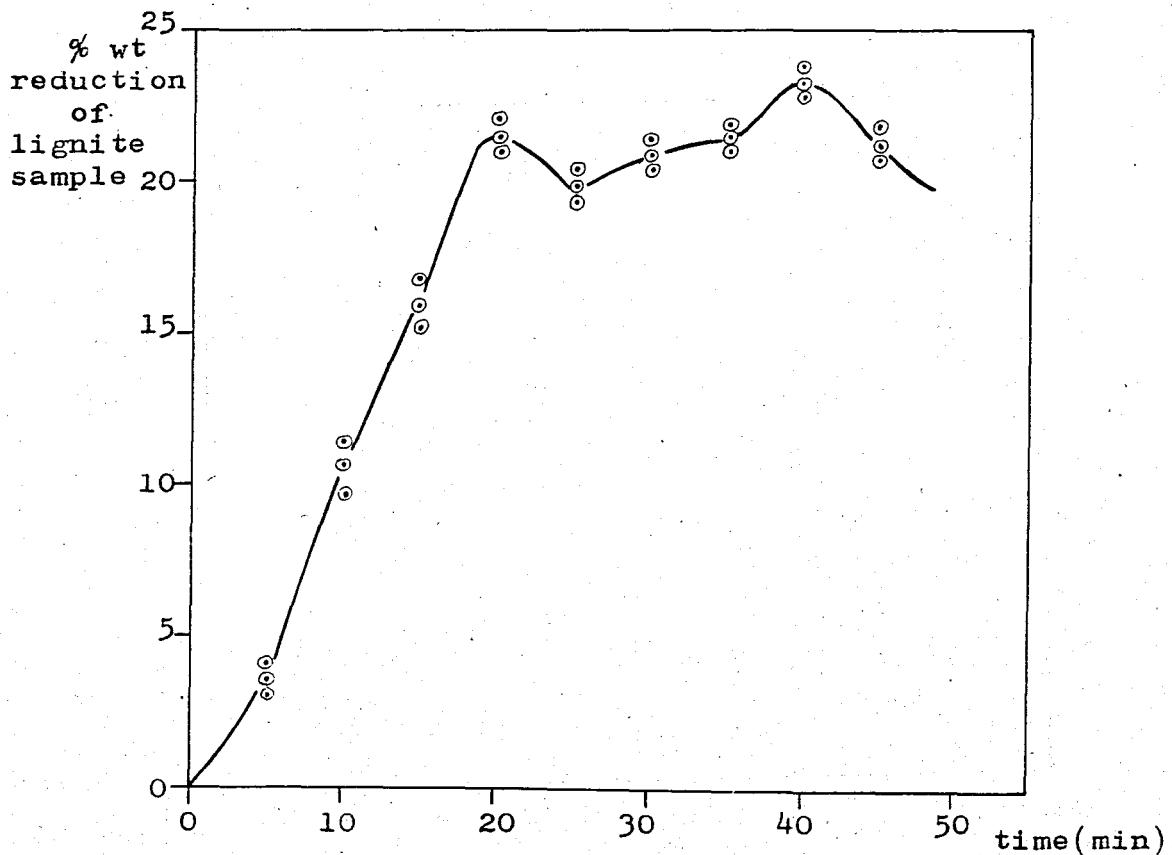


Figure A.1.1 Drying curve of lignite sample from Çan

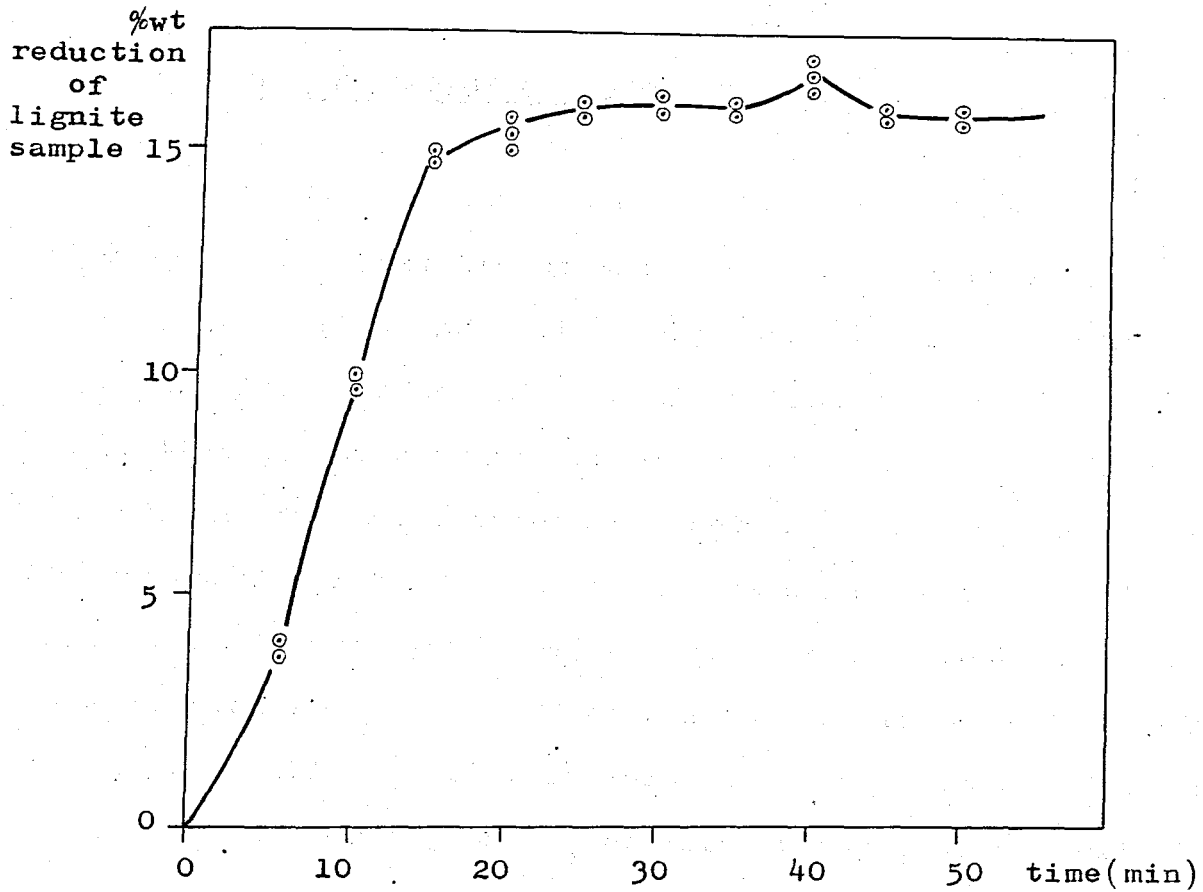


Figure A.1.2 Drying curve of lignite sample from Soma

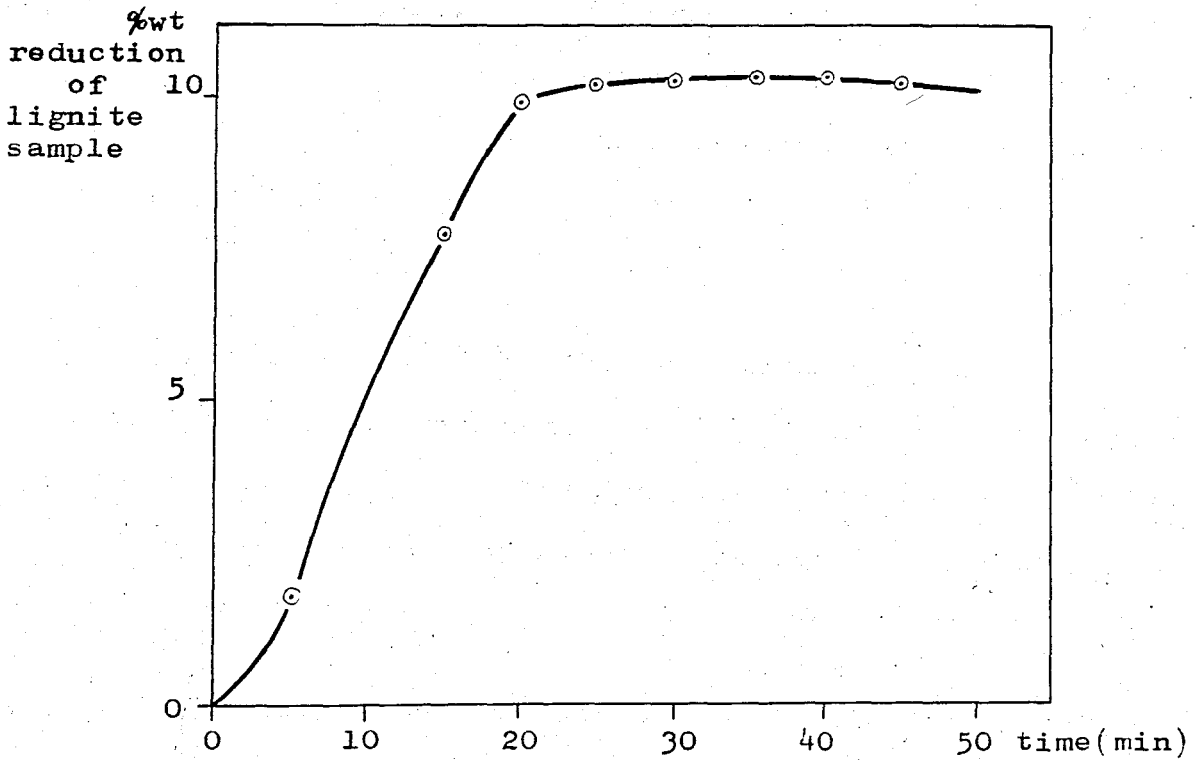


Figure A.1.3 Drying curve of lignite sample from Tunçbilek

App.2 DETERMINATION OF AUTOCLAVE CONTROLLER SETTINGS

Tests were done to determine the optimum controller settings. The adjustable controls were proportional band (X_p), maximum power (M_p) and limit alarm (Limit). The proportional band was slowly reduced from maximum (fully clockwise) until no cycling of temperature above and below set point was obtained. The optimum response was obtained at 5% X_p . This value for proportional band is also suggested in the instruction manual as satisfactory in most cases. Alarms could be set to operate between 1% and 10% of scale span away from the set point by means of this control. In this work the Limit value was adjusted to 1%. Turning the M_p control anti-clockwise, will limit the maximum power that can be applied. The test runs were carried out in autoclave containing only tetralin in nitrogen gas at atmospheric pressure. Temperatures were recorded as a function of time, and different curves were obtained. From Fig. A.2.1 it can be observed that time necessary for heating the autoclave to 275°C is quite long because of low value of M_p setting.

Figure A.2.2 shows the temperature versus time curve obtained for the test run done with 75% M_p at the same temperature set value of 275°C. The required temperature was reached in a time period of only 45 minutes and no fluctuations in temperature were observed.

The temperature at which the autoclave was operated

in this work was 325 °C. For this reason, another test was done at the same controller settings but with the set temperature of 325 °C. The results are shown in Fig. A.2.3. The required temperature was attained in a short time interval without any fluctuations.

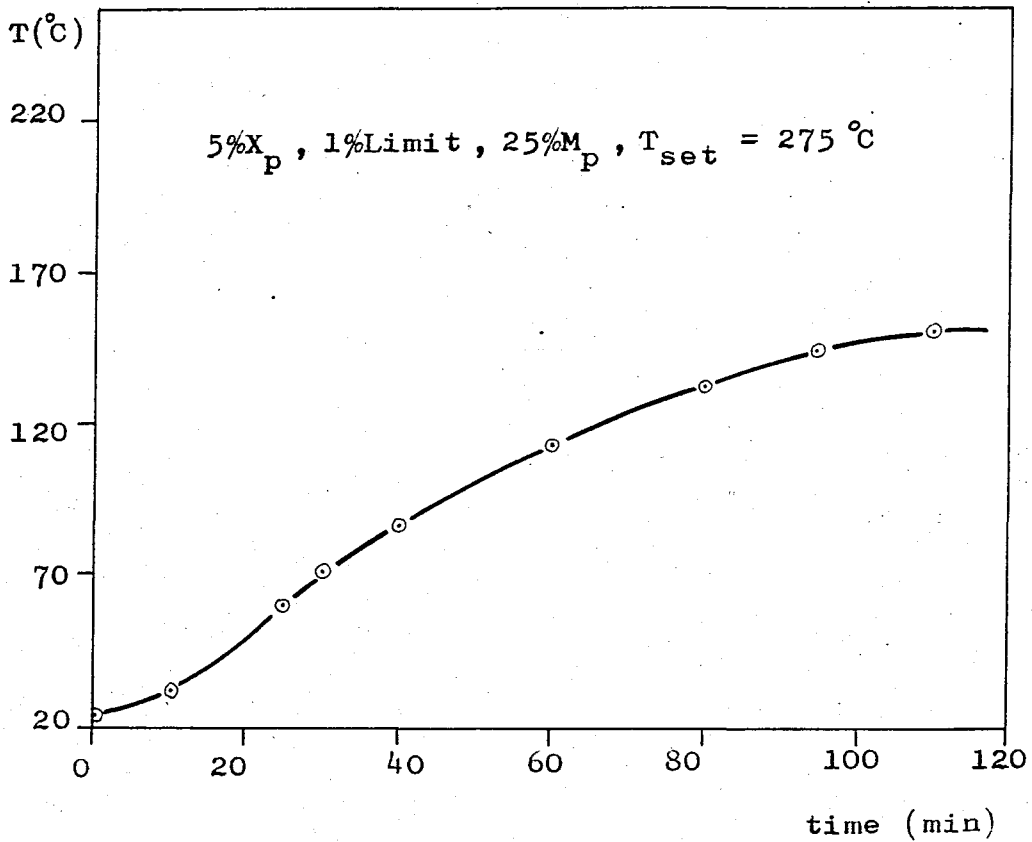


Figure A.2.1 Test results of controller settings (I)

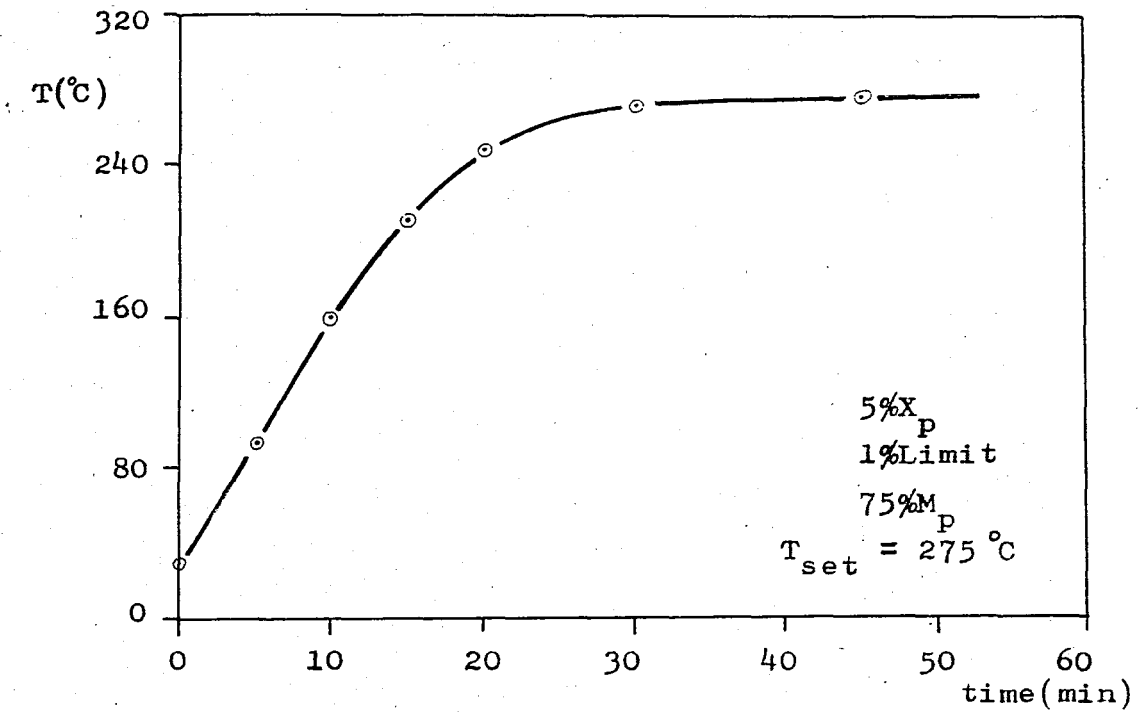


Figure A.2.2 Test results of controller settings (II)

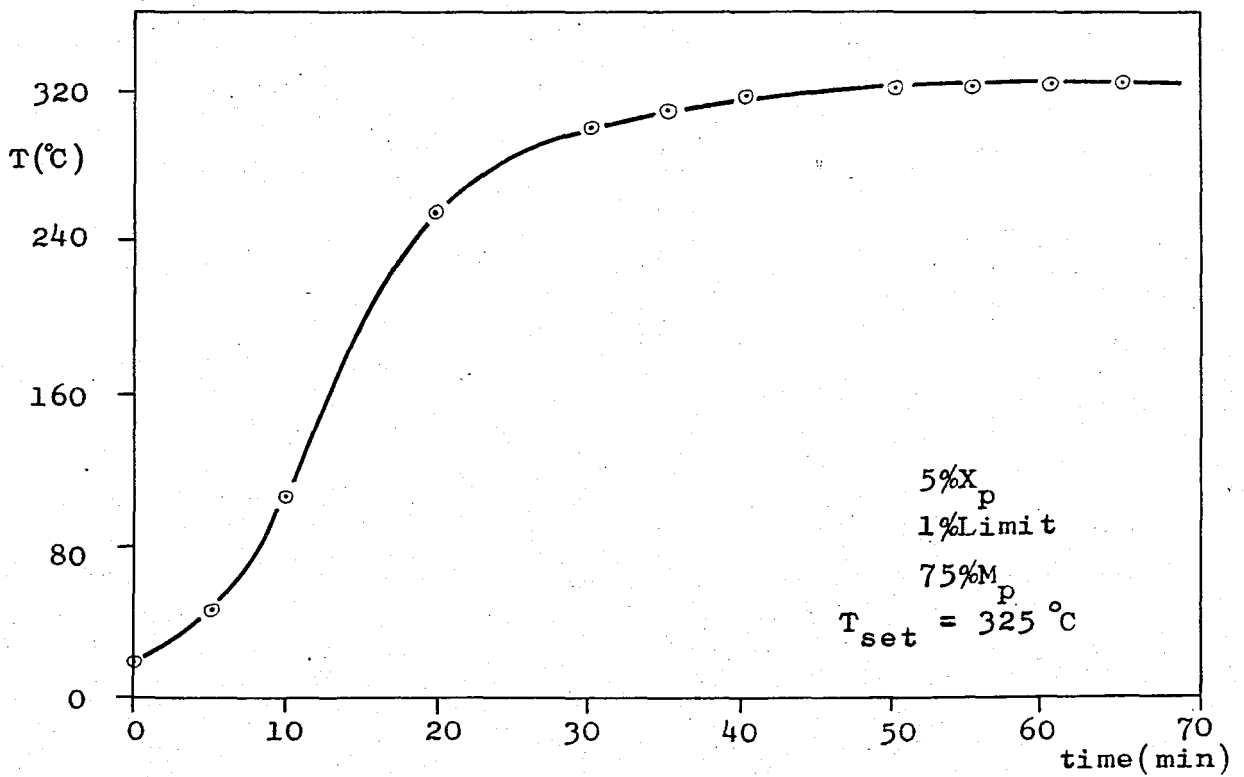


Figure A.2.3 Test results of controller settings (III)