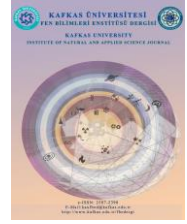




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Investigation of Swelling Properties and Liquefaction of Solid Fuels

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Abstract: In this study, the effect of various parameters on the swelling of Edirne Uzunköprü, Edirne Keşan Çanakkale Yeniçirpılar and Bursa Mustafa Kemal Paşa lignites was investigated. In the first part of the study, swelling processes were applied to the lignites. Swelling measurements were made in closed glass tubes using 10 different solvents. Swelling ratios of lignite samples treated with solvents were determined and the dependence of these ratios on the properties of the solvent was examined. In the second part, the original lignite samples, swollen with various solvents, were subjected to soxhlet extraction with THF and the liquid product yields obtained from each sample were determined. Then, the same samples were extracted with toluene under supercritical conditions, and the effects of temperature, pressure, and pre-expansion on the extract yield were investigated. Extract yields of lignite samples swollen with solvents such as THF, TBAH, DMSO, DMF, and EDA were found to be higher than those of other solvents. The common features of these solvents are that they have atoms containing unpaired electrons such as N, O, etc. In addition, it was thought that the high extract yields of solvents with a large and positive difference in the number of donors and acceptors may be related to the breaking of the cross-links in the lignites by the solvent.

Katı Yakıtların Şişme Özelliklerinin İncelenmesi ve Sıvılaştırılması

Anahtar Kelimeler:

Linyit,
çözücü ile şişirme,
katalizör,
kritik üstü ekstraksiyon

Özet: Bu çalışmada Edirne Uzunköprü, Edirne Keşan Çanakkale Yeniçirpılar ve Bursa Mustafa Kemal Paşa linyitlerinin şişirilmesine çeşitli parametrelerin etkisi incelenmiştir. Çalışmanın ilk bölümünde, linyitlere şişirme işlemleri uygulanmıştır. Şişme ölçümleri ağzı kapalı cam tüplerde 10 ayrı çözücü kullanılarak yapılmıştır. Çözücülerle işlem gören linyit örneklerinin şişme oranları belirlenmiş ve bu oranların çözücünün özelliklerine bağlılığı irdelenmiştir. İkinci bölümde ise orjinal linyit, çeşitli çözücülerle şişirilmiş linyit örnekleri, THF ile soxhlet ekstraksiyonuna tabi tutulmuş ve her bir örnekten elde edilen sıvı ürün verimleri belirlenmiştir. Daha sonra aynı örnekler toluen ile süperkritik koşullarda ekstrakte edilerek sıcaklığın, basıncın ve ön şişirme işleminin ekstrakt verimine etkisi incelenmiştir. THF, TBAH, DMSO, DMF ve EDA gibi çözücülerle şişirilen linyit örneklerinin ekstrakt verimlerinin diğer çözücülerinkinden yüksek olduğu bulunmuştur. Bu çözücülerin ortak özellikleri yapısında N gibi O gibi ortaklanmamış elektron bulunduran atomlara sahip olmalarıdır. Ayrıca donör sayısı – akseptör sayısı farkı büyük ve pozitif olan çözücülerin ekstrakt verimlerinin büyük olmasının linyitlerdeki çapraz bağların çözücü tarafından koparılmasıyla ilişkili olabileceği düşünülmüştür.

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1. INTRODUCTION

Until the second half of the 20th century, coal was used as the sole raw material source for synthetic liquid fuels and especially for aromatic basic materials for about a century. Coal has been an important source of energy for people for a long time and enabled the rapid development of the industry (Song et al., 1993). Tar, which is formed as a by-product during the production of coke, which is necessary for the steel industry, formed the basis of chemicals extracted from coal. By processing the tar, dyestuffs, drugs, and chemicals are obtained (Franck et al., 2012). Although it lost its former importance for a while as a result of the rapid progress of the petrochemical industry, it has gained great importance again in recent years due to the continuous increase in energy consumption and the evaluation of new energy sources (Gür et al., 2018). However, it is difficult to make a long-term economic evaluation of energy, and the limited total oil reserves have led researchers to work on the liquefaction of coal and lignites in recent years (Xie et al., 2010). Such studies aim to produce liquid fuels from coal, which can replace oil or at least reduce dependence on oil. In addition, it is known that coal is more than enough to meet the need for energy and chemical raw materials for a longer period compared to oil, and it has a more homogeneous distribution compared to oil in the world (Şimşek, 1997). Since solar, geothermal, and nuclear energy sources do not reach an efficient or safe level of use, the most suitable liquid fuel to replace oil is liquid hydrocarbon mixtures obtained from coal. The continuation of the existing systems following the use of liquid fuel will only be possible in this way (Lee, 2012).

In 1980, the Sasol II process in South Africa and the NEDO (later NEDOL) pilot plant, which tested the suitability of lignite and bituminous coals for liquefaction, were commissioned in Japan. In the same year, the H-Coal process was started to be applied in the USA. Research and development programs continue in different countries, especially in Canada, Japan, China, America, England, and Germany (Asaro et al., 2013; Dingbang et al., 2021). In 1986, a joint transaction working group (US-DOE) was established with these countries, including France, Portugal, and Spain (Wiser et al., 2008). The structure of coal is different from that of oil, and the main difference here is that the H/C ratio in coal is smaller than that of oil. It is thought that the complex organic structure of coal has a polymeric character and consists of macromolecules (Peppas et al., 1984). The most widely accepted one among the hypothetical coal models put forward by using the average structure parameters is the aromatic/hydroaromatic structure model. According to this model, aromatic ring groups carrying alkyl, hydroaromatic and functional groups and condensed to varying degrees are connected by heteroatom of methylene bridges. As a result of the breaking of these bridges, it seems possible to convert coal into soluble products or liquid products. After the decomposition process, hydrogen should be added to this hydrogen-poor structure or carbon should be reduced. It was observed that higher liquid product yields were obtained from coals that were pre-expanded with some solvents before the liquefaction process compared to the original coals (Eaves, 2004).

In this study, 4 different lignite samples taken from different regions of Turkey were pre-inflated with various organic solvents, then supercritical gas extraction and soxhlet extraction were applied to these lignites. The yields of the obtained extracts were compared and the effects of swelling were tried to be investigated.

2. MATERIAL AND METHOD

It is possible to summarize the experiments in this study, which were carried out to examine the swelling properties of solid fuels and the liquid product obtained as a result of soxhlet extraction and supercritical extraction of swollen samples with some organic solvents. Lignite samples from 4 different regions obtained from MTA laboratories (The name of the organization is MTA, there is no abbreviation.) were ground to 0.2 mm-1 mm dimensions and used in the experiments. The thermal decomposition of lignite samples was investigated by heating them to 1000 °C in a thermogravimetric analyzer. Then, these samples were swelled by treating them with organic solvents with different properties and swelling measurements were made. Extraction efficiencies of all inflated samples and untreated lignite samples were compared by soxhlet extraction. Extraction efficiencies were found by supercritical gas extraction of all inflated samples and untreated lignite samples.

2.1. Lignite Samples Used in Experiments

In this study, MTA is solid fuel. obtained from the laboratories of the General Directorate of Lignite sample from Bursa Mustafa Kemal Paşa region, Lignite sample from Edirne Uzunköprü region, Lignite sample from Çanakkale Yeniçirpılar region, and Lignite sample from Edirne Keşan Yenimuhacir region were used.

2.2. Sample Analysis

Moisture, ash, and volatile matter analyses of lignite samples were carried out following the relevant Turkish Standards. Moisture determination was made according to TS 690, ash determination according to TS 1042, and volatile matter determination according to TS 711.

2.3. Swelling Tests

Swelling experiments were carried out to select the pre-expansion solvents and to determine the relations between the characteristic properties of the solvents and the swelling ratio. Swelling experiments, which have the advantage of being simple and can be applied in a short time, were carried out volumetrically in graduated glass tubes with a height of 10 cm and a diameter of 1.3 cm. For the experiment, 1 g of lignite sample, dried in an oven, was placed in a glass tube, the tube was centrifuged for five minutes and the first h_1 height of the lignite layer was measured. After this process, 5 cm³ of solvent was added and the tube was centrifuged again and the h_2 height of the layer was read. After shaking the tube vigorously, it was kept closed overnight and the h_2 height was read again after centrifugation. This process was continued until a constant h_2 height was achieved. The swelling ratio (Q) and the % swelling value are calculated from equations 1 and 2 below;

$$\text{Swelling ratio} = Q = \frac{h_2}{h_1} \quad (1)$$

$$\% \text{ Swelling} = \% S = \frac{h_2 - h_1}{h_1} \cdot 100 \quad (2)$$

Each percent swelling value is the average of the result found in at least three experiments at room temperature. The samples to be subjected to the pre-expansion process and then to be used in the studies of obtaining liquid product by soxhlet and supercritical gas extraction were prepared as follows. 30 g of oven-dried lignite and 75 cm³ of solvent were placed in a 500 cm³ graduated glass container, and the container was closed and waited for 3 days at room temperature. Then the solvent was filtered and the remaining solvent in the pre-expanded lignite was removed under vacuum in a rotary evaporator. The samples obtained by applying the pre-expansion process in this way were subjected to soxhlet extraction with THF and supercritical gas extraction with toluene.

2.4. Soxhlet Extraction

The Soxhlet extractor consists of a grinding glass balloon, a reflux cooler, and a lignite chamber. A certain amount of solvent is placed in the glass flask and heated from the bottom. The evaporated solvent rises and condenses in the refrigeration unit and collects in the coal section. Here it dissolves the substances it can extract in lignite. After the chamber is filled, it empties back into the balloon with the substances it has dissolved from the lignite sample by making a siphon. This process is continued until the solvent coming into the chamber is colorless, that is until there is no substance to be extracted from the lignite. After the extraction is complete, the solvent is removed from the extractant with a rotary evaporator and the amount of extract is determined. The extract yield is calculated from Equation 3 below.

$$\% \text{ Yield} = \% n = \frac{A}{B} \cdot 100 \quad (3)$$

Here, A shows the amount of extract (g), and B shows the amount of dry lignite (g). THF was used as the solvent in these experiments.

2.5. Super Critical Gas Extraction

The experimental system in which the supercritical gas extraction is carried out consists of three main parts:

- 1- Reactor made of stainless steel.
- 2- An oven whose temperature can be controlled and used to heat the reactor.
- 3- Temperature control unit.

The reactor has a volume of 1 L and the highest working pressure is 150 atm. The lid of the reactor is closed by tightening with 6 nuts and there are inlet and outlet valves for liquid or gas when necessary and a manometer capable of measuring up to 300 atm. In addition, the safety valve is

located on the cover for sudden pressure increases. With the temperature control system, the temperature of the oven can be kept constant at the desired value. Toluene was used as a solvent in supercritical gas extraction experiments. The critical temperature of toluene is 318.6 °C and its critical pressure is 41.1 atm. For each experiment, 15 g of lignite with a grain size of 0.2 mm⁻¹ mm was put into the reactor and 150 g of toluene was added, with a solvent/lignite ratio of 10/1 used in similar studies in the literature. The reactor was started to be heated after the lid was closed using a torque wrench. It was kept at 450 °C, a temperature above the critical temperature of toluene, for 60 minutes. At this temperature, the pressure of the system was measured as 80 atm. After 30 minutes, the heating process was terminated and the system was left to cool. The lid of the reactor, which was cooled by spraying external air on it until about laboratory temperature, was opened and the solvent containing the extract was separated from the solid part by filtration. This mixture was evaporated in a rotary evaporator under a vacuum and the solvent was removed. The remaining extract was weighed and the extract yield was calculated from equation 4 below.

$$\% \text{ Extract yield} = \frac{A}{B} \cdot 100 \quad (4)$$

Here, A is the extract amount (g), and B is the dry ashless lignite amount (g).

3. RESULTS AND DISCUSSIONS

3.1. Soxhlet Extraction

Moisture, ash, and volatile matter amounts in the lignite samples used in the experiment were determined according to TS 690, TS 1042, and TS 711, respectively. The results are given in Table 1.

3.2. Swelling Tests

Based on the literature information, 12 different solvents were selected for swelling the lignite samples to cover a wide range of solubility parameters. The solubility parameters of the solvents vary between 8.9 (cal cm⁻³)^{1/2} and 12.9 (cal cm⁻³)^{1/2}. The solvents used, their donor (DS) and acceptor (AS) numbers, and solubility parameters (δ) are shown in Table 2.

A concept called donor number has been developed for solvents to relate properties such as solubility, redox potential, and ionization degrees of substances in various solvents. Here, solvents are considered as Lewis bases and their electron-pair donor affinities are compared. V. Gutmann in 1966 defined the donor number of a base (solvent) as the negative enthalpy (kcal/mol) of the reaction of that base with antimony pentachloride as a reference acid.

The number of donors shows the solvent's tendency to bond with the solute (acid) by donating an electron pair (Gutmann et al., 1966). Mayer and Gutman (1975) proposed a similar concept for acidic solvents. In this concept called acceptor number, the solvent is this time the electron pair acceptor.

Table 1. Results of short analysis and elemental analysis of lignite samples

Lignite Sample	Air Dried Base			Dry, Ashless, Base			
	Moisture, %	Ash, %	Volatile substance, %	C	H	N	S
Bursa MKP	11.8	19.6	24.2	61.0	5.9	1.7	4.8
Edirne Keşan	9.5	18.5	22.5	62.4	5.7	1.9	3.8
Çanakkale Yeniçirpılar	10.6	20.4	23.6	58.3	5.4	1.5	2.6
Edirne Uzunköprü	9.0	17.5	21.7	60.2	5.3	1.6	3.5

The determination of the acceptor number was based on the amount of change caused by the interaction in the P-NMR (nuclear magnetic resonance) chemical shift of the base. Et₃PO was used as the reference base. The acceptor number of a solvent is proportional to the change in the P-NMR chemical shift of the reference base. To use the relative values, the acceptor number of hexane, which does not cause any change in the chemical shift, is taken as 0 and the acceptor number of antimony pentachloride in dichloroethane is taken as 100. In this chart, the acceptor numbers of the solvents are calculated relative to the change caused by the P-NMR chemical shift of Et₃PO (Mayer et al., 1975). Compared to Figure 1a, THF, pyridine, DMF, EDA, and DMSO give higher swelling rates. Apart from TBAH, which shows the highest swelling effect for all lignite samples, a high swelling ratio is also obtained with DMF and EDA. Here, due to the structural properties of lignite, the effect of these solvents is slightly more than the others.

According to the literature, if the solubility parameter of the solvent used and the solubility parameter of the lignite are close to each other, greater swelling and ultimately more extract can be obtained with these lignites. From this, it can be said that the solubility parameter of Edirne Uzunköprü lignite is closer to those of DMF and EDA. A graph (Q-DS) was drawn to determine the relationship of swelling ratios with the number of donors (DS) of the solvent (Figure 2a). Accordingly, as DS increases, the swelling ratio also increases. Swelling is smaller, especially in solvents with a donor number of 0-20. The swelling ratios obtained with solvents with 20-55 donor numbers are greater. Similar results were obtained in the studies conducted by Szeliga and Marzec (1983) (Szeliga et al., 1983).

On the other hand, while there was no regular relationship between swelling and acceptor number (AS), a significant change was observed between the swelling ratio and DS-AS as in Figure 3a. Greater swelling ratios are achieved with solvents with a positive DS-AS value. According to Figure 3a, higher swelling ratios were obtained in the same lignite sample with THF, pyridine, EDA, DMSO, and DMF solvents compared to other solvents. The common feature of these solvents is that the difference between DS and AS is large. This situation was expressed by Marzec (1979) as “solvents with a large difference between DS and AS are suitable solvents for extraction” (Marzec et al., 1979). The relationship between the solvent properties and the swelling properties of Edirne Keşan lignite is shown in Figures 1b, 2b, and 3b. When these graphs are examined, it can be said that Uzunköprü and Keşan lignites show similar properties to solvents.

The solvents with a DS value greater than 20 are more likely to interact with lignite: Again, it can be seen from these

figures that the larger the DS-AS difference, the higher the swelling and effect of the solvent on the lignite.

In the same conditions, the relationship between the solvent properties used in the swelling test of the samples used as a result of the swelling experiments with Çanakkale Yeniçirpılar and Bursa Mustafa Kemal Paşa lignites are shown in Figure 1c, 1d, 2c, 2d, 3c, and 3d respectively.

When the results obtained from the swelling tests with solvents of four different lignite samples used are compared, i) It is seen that the solvents behave according to their properties in terms of affecting and penetrating the lignite, ii) In different lignite samples, especially solvents with high donor numbers such as THF, NMP, EDA, DMSO, DMF, TBAH, pyridine and having unpaired electrons in atoms such as N and O in their structure show almost the same interaction, iii) The observed small swelling differences appear to be related to the differences in the pore structure of the lignites, iv) It is also seen that solvents with low donor numbers interact less with lignites. In Figure 4, the swelling percentages of all lignite samples with solvents are shown comparatively. According to Figure 6, it is seen that the amount of swelling depends more on the physical and chemical properties of the solvent than the structural properties of the lignites.

3.3. Soxhlet Extraction

Soxhlet extraction was carried out by incorporating soluble compounds in the original lignite and blowing lignites into a solvent at atmospheric pressure with THF. Then, the solvent (THF) was separated from the extract by evaporation in a rotary evaporator and the extract yield was calculated. In Table 3, the yields of the samples obtained from Edirne Uzunköprü, Edirne Keşan, Çanakkale Yeniçirpılar and Bursa MKP lignites as a result of pre-expansion with solvents from soxhlet extraction with THF are shown. Lignites swollen with TBAH, THF, NMP, DMSO, DMF, EDA, pyridine, toluene, and benzene were used in these experiments.

As can be seen from the extract yields in Table 4, the extract yields of lignites pre-blown with NMP, TBAH, THF, DMF, DMSO, and pyridine solvents are considerably higher than the original lignite yields.

The yields of other solvents were either lower or close to the original lignite yield. The common features of solvents with high yields are that the donor number is greater than 20 and the DS-AS difference is greater than 15. These solvents probably change the pore structures with the pre-expansion process, and the extraction solvent enters the macromolecular structure of the lignite more easily, increasing the extraction efficiency by allowing the compounds soluble in the lignite to be taken out of the pores more easily.

Table 2. Properties of solvents used in swelling tests (Çalışkan, 1992)

Solvent	DS	AS	DS-AS	$\delta(\text{cal cm}^{-3})^{1/2}$	Cross-sectional area (nm ²)
Methanol	19.0	41.3	-22.3	12.9	0.16
Toluene	0	-	-	8.9	0.31
Benzene	0.1	8.2	-8.1	9.2	0.27
dichloromethane	0	20.4	-20.4	9.9	0.22
Tetrahydrofuran (THF)	20.0	8.0	12.0	9.1	0.26
Pyridine	33.1	14.2	18.9	10.4	0.25
dioxane	14.8	10.8	4	9.8	0.268
Ethylene diamine (EDA)	55.0	20.9	34.1	11.5	0.228
Dimethylformamide (DMF)	26.6	16.0	10.6	11.5	0.24
Dimethylsulfoxide (DMSO)	29.8	19.3	10.5	12.8	0.237
N-methyl-2 pyrrolidine (NMP)	27.3	13.3	14.0	-	-
Tetrabutylammoniumhydroxide	49.0	18.0	29	12.27	-

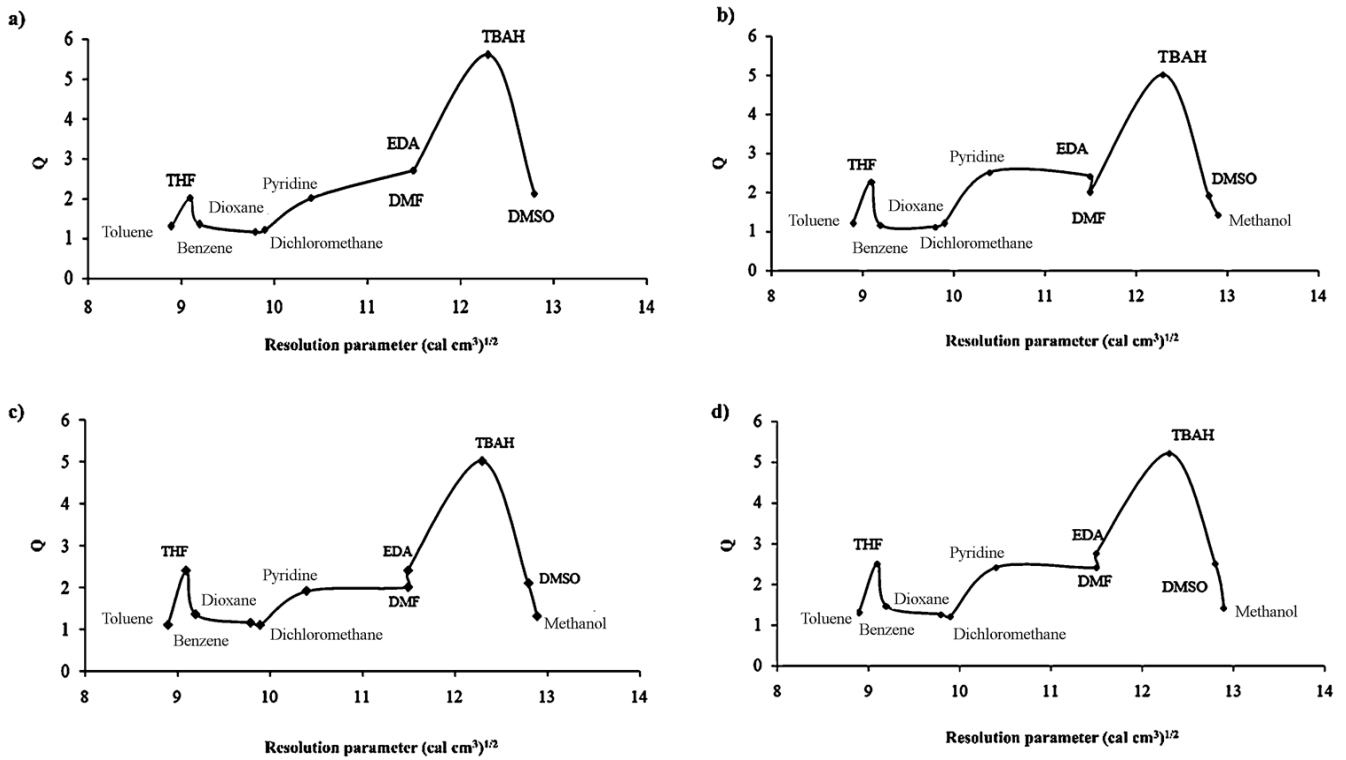


Figure 1. a) variation of swelling ratio with a solubility parameter of Edirne Uzunköprü lignite, b) variation of swelling ratio with a solubility parameter of Edirne Keşan lignite, c) variation of swelling ratio with a solubility parameter of Çanakkale Yeniçırpılar lignite, d) variation of swelling ratio with a solubility parameter of Bursa Mustafa Kemal Paşa Lignite

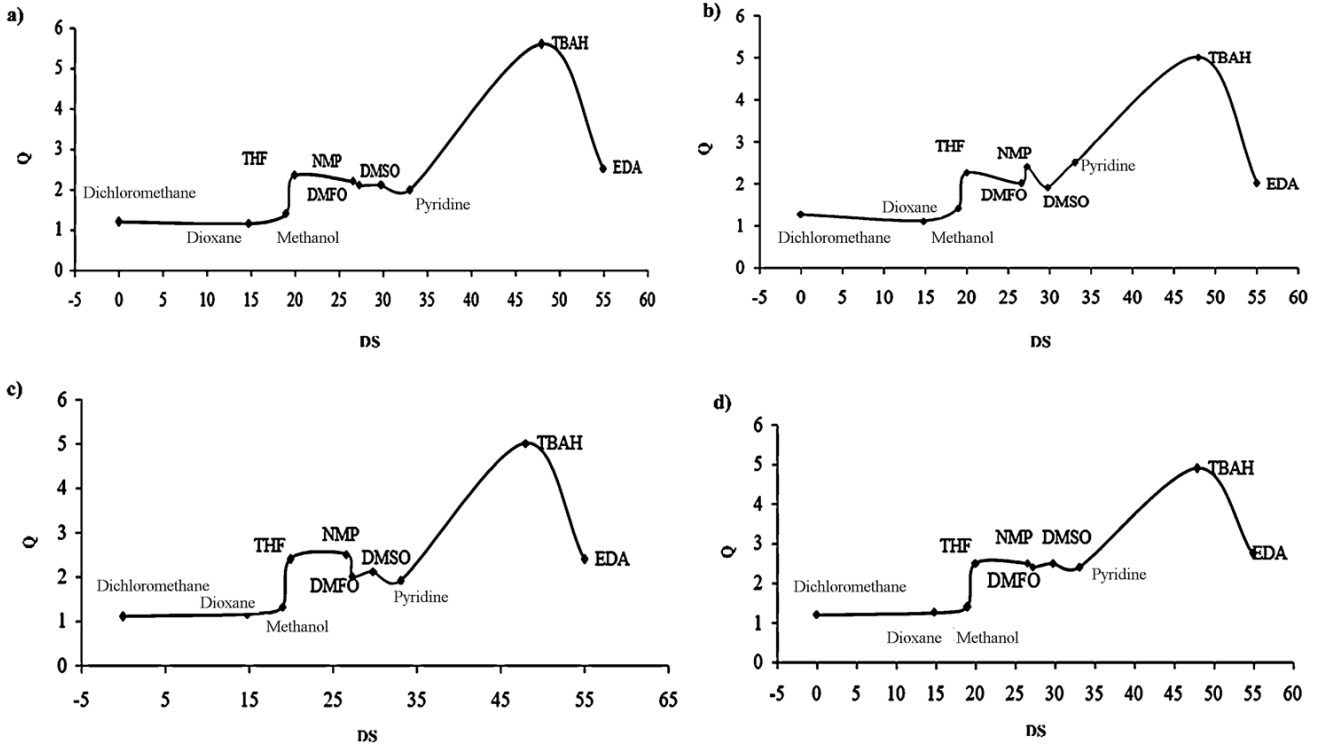


Figure 2. a) variation of swelling ratio with a number of donors of Edirne Uzunköprü lignite, b) variation of swelling ratio with the number of donors of Edirne Keşan lignite, c) variation of swelling ratio with DS of Çanakkale Yeniçırpılar lignite, d) variation of swelling ratio with the number of donors of Bursa Mustafa Kemal Paşa Lignite

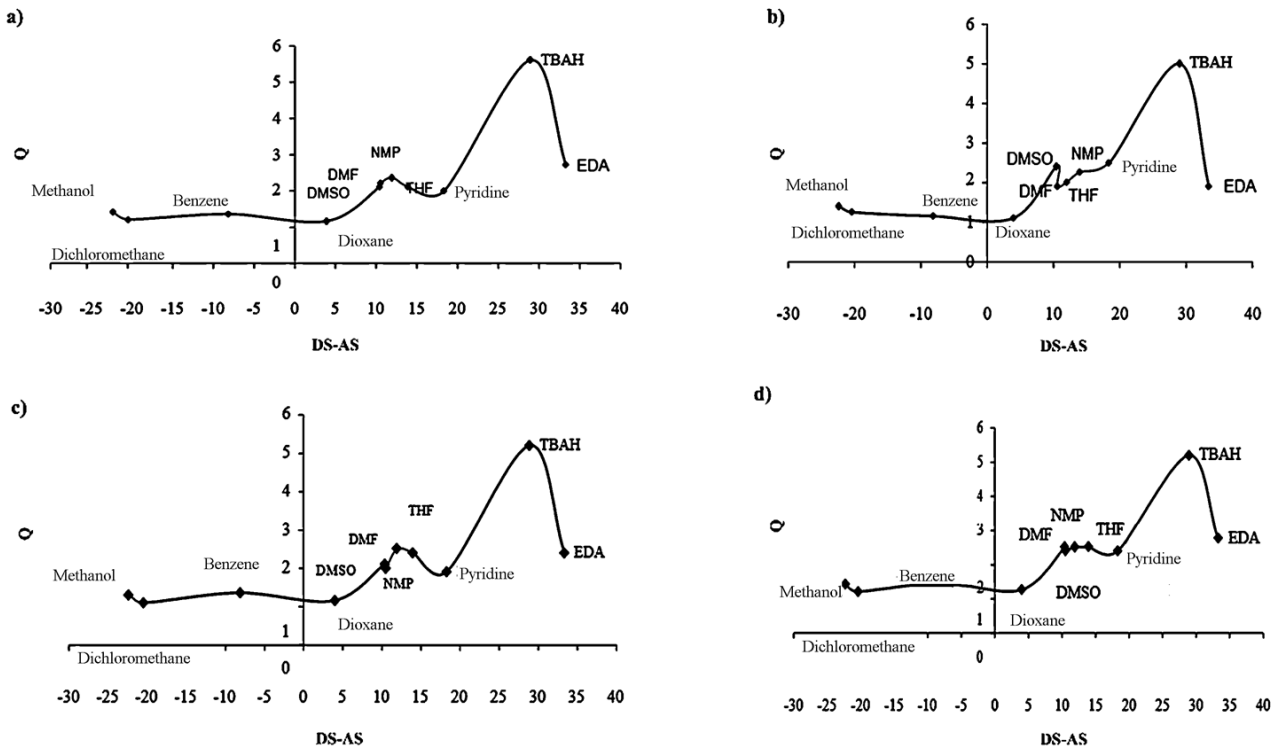


Figure 3. a) variation of swelling ratio with DS-AS values of Edirne Uzunköprü lignite, b) variation of swelling ratio with DS-AS values of Edirne Keşan lignite, c) variation of swelling ratio with DS-AS of Çanakkale Yeniçırpılar lignite, d) variation of swelling ratio with DS-AS values of Bursa Mustafa Kemal Paşa Lignite.

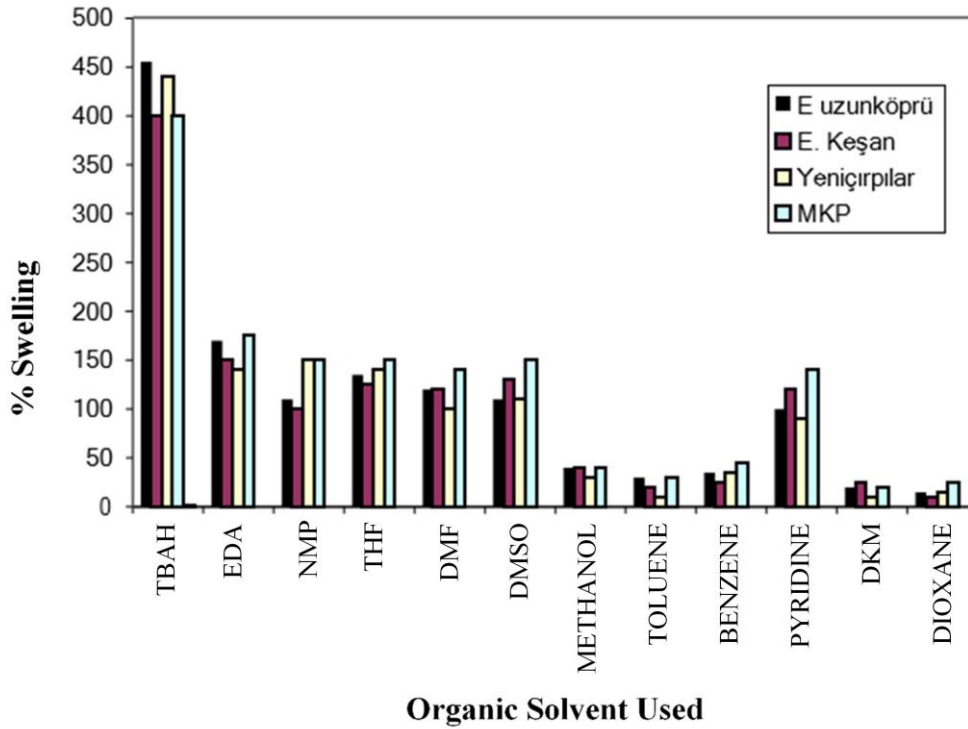


Figure 4. Dependence of the percentage of swelling of lignites on the kind of solvent.

Table 3. Extract yields obtained from the original and solvent-blown lignite samples used in Soxhlet extraction

Lignite Sample	% Extract yields			
	Edirne Uzunköprü	Edirne Keşan	Çanakkale Yeniçirpılar	Bursa MKP
Original lignite	7.5	9.0	8.0	8.5
Lignite has blown with TBAH	13.0	12.0	14.0	16.0
EDA blown lignite	11.0	16.0	18.5	13.0
Lignite has blown with NMP	15.5	17.5	16.5	14.5
Lignite has blown with THF	18.6	18.0	14.5	15.8
DMF blown lignite	16.5	18.5	17.5	16.5
Lignite has blown with DMSO	17.0	16.5	18.5	15.0
Lignite has blown with methanol	7.0	8.0	6.5	7.5
Lignite has blown with toluene	8.5	7.5	7.0	6.5
Lignite has blown with benzene	6.5	8.0	7.0	7.0
Lignite has blown with pyridine	15.0	16.0	14.0	16.5

These results are also consistent with the statement of Szeliga and Marzec (1983) that "solvents with 15-30 donor numbers are the most suitable solvents for extraction" (Szeliga et al., 1983).

3.4. Soxhlet Extraction

The lignite samples used in this study were extracted with toluene under supercritical conditions in an autoclave, at 450 °C and 80 atm pressure. Extractions using toluene as solvent were carried out with original lignites, DMSO, EDA, DMF, NMP, THF, TBAH, and preblown lignites with pyridine, methanol, and benzene. In this way, it is aimed to determine whether the swelling process affects the extraction under supercritical conditions. In Table 4, the extract yields obtained by extraction with toluene under supercritical

conditions from samples of lignite samples swollen with different solvents are shown. Figure 5a-5d shows the variation of the extract yields found by supercritical extraction experiments with the number of donors of various swelling solvents.

The fact that the extract yield of lignite pre-inflated with TBAH, DMSO, EDA, and DMF is greater than the extract yield of the original lignite sample under the same conditions can be explained by the following situations: i) these solvents transform the lignite into a more porous structure during the blowing process. ii) After the removal of the pre-swelling solvent by evaporation, toluene molecules in supercritical conditions enter the pores more easily, increasing the extract yield. This increase in extract yield is in agreement with

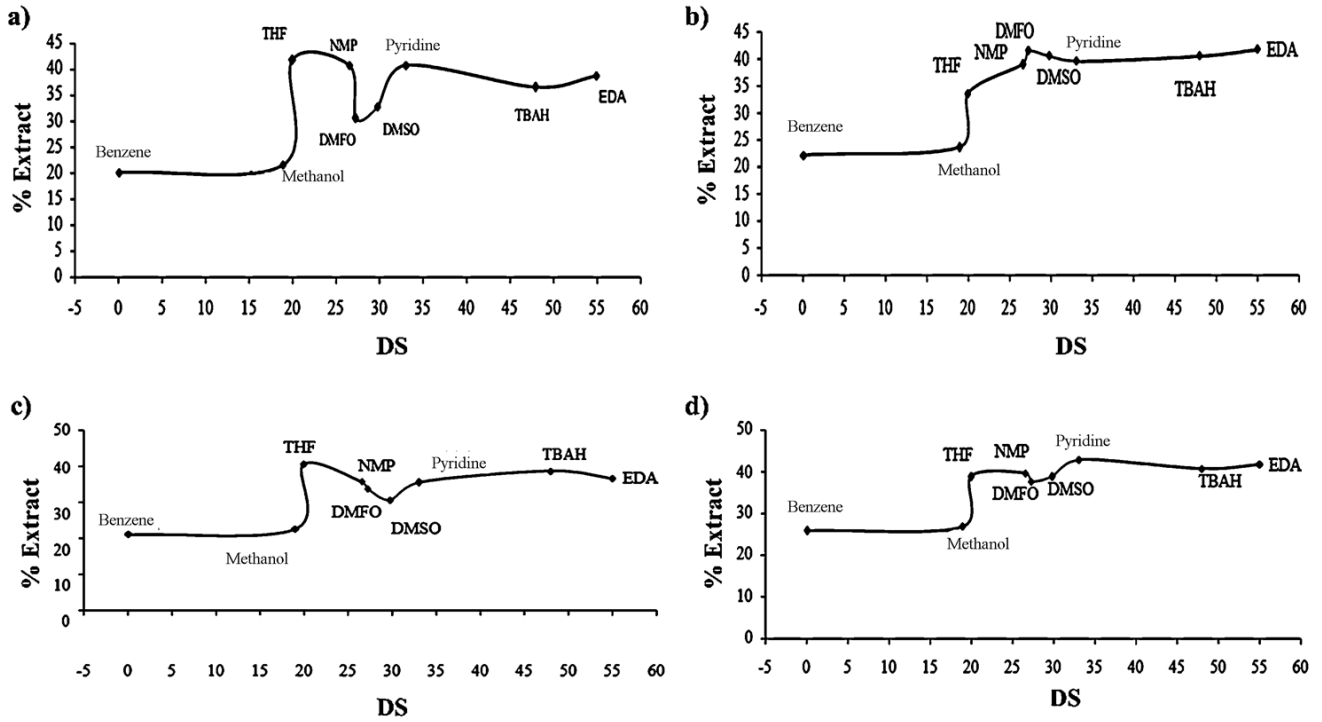


Figure 5. a) The relationship between the supercritical gas extraction efficiency of Edirne Uzunköprü lignite and DS, b) The relationship between the supercritical gas extraction efficiency of Edirne Keşan lignite and DS, c) The relationship between the supercritical gas extraction efficiency of Çanakkale Yeniçirpılar lignite and the DS, d) Bursa MKP The relationship between the supercritical gas extraction efficiency of lignite and DS.

Table 4. Yields of supercritical extraction of lignite samples with toluene

Lignite Sample	% Extract yields			
	Edirne Uzunköprü	Edirne Keşan	Çanakkale Yeniçirpılar	Bursa MKP
Original lignite	19.0	23.2	20.5	25.7
Lignite has blown with TBAH	36.5	40.5	38.6	43.8
EDA blown lignite	38.6	41.7	36.5	40.5
Lignite has blown with NMP	40.6	38.9	35.6	44.4
Lignite has blown with THF	41.7	33.5	40.5	38.7
DMF blown lignite	30.5	41.4	33.6	39.0
Lignite has blown with DMSO	32.6	40.5	30.5	38.7
Lignite has blown with methanol	21.5	23.5	22.5	26.7
Lignite has blown with toluene	24.5	25.0	23.5	28.6
Lignite has blown with benzene	20.0	22.0	21.0	25.8
Lignite has blown with pyridine	40.6	39.5	33.5	42.7

Table 5. Coal Properties of Various Ranks (Tsai S.C., Fundamentals of Coal Beneficiation and Utilization, Elsevier, New York 1982)

Rank (Degree of Carbonization)	VOLATILE CONTENT % Mass (Wet – Ashless)	CARBON CONTENT % Mass (Wet – Ashless)	THERMAL VALUE kcal/kg (without ash)	MOISTURE CONTENT % Mass
1. LIGNITE	69 – 44	76 – 62	4.611 – 3.500	52 – 30
2. SUB BITUMINOUS	52 – 40	80 – 71	6.390 – 4.611	30 – 12
3. BITUMINOUS				
a) High Volatile - B	50 – 29	86 – 76	7.222 – 5.833	15 – 2
b) High Volatile - C	-	-	-	-
c) High Volatile - A	49 – 31	88 – 78	7.778	5 – 1
d) Medium Volatile	31 – 22	91 – 86	7.778	5 – 1
e) Düşük Uçuculu	22 – 14	91 – 86	7.778	5 – 1
4. ANTHRACITE	14 – 2	-	7.778	5 – 1

similar studies in the literature, and the change in structure is explained as follows: It is known that some of the molecules in coals blown with active solvents such as TBAH, DMSO, EDA, and DMF separate from each other and make a new arrangement with lower free enthalpy (Nishioka, 1990; Larsen et al., 1990). Solvents used in blowing break weak bonds and provide macropore formation in coal. Macropores facilitate the penetration of liquid molecules used in extraction into the pore, and the reactivity of coal increases with the contribution of active centers formed by breaking some bonds (Suuberg et al., 1993). This change in the structure of the coal remains after the solvent is removed, that is, the structure of the coal after the swelling process is different from the structure of the original coal. Therefore, depending on the solvent used, lignite samples, whose pore structure and the number of active centers change with pre-expansion, are extracted with toluene. In this case, as a result of macropore formation, the factors that prevent the diffusion of toluene into the pore are reduced and more material can be taken out of the lignite structure by solvent-lignite interaction in possible new active centers. The results obtained in the literature studies are given for comparison purposes (Table 5).

4. CONCLUSION

The chemical compositions of the lignites used and the amounts of ash and volatile matter they contain are close to each other. When the thermal effect and degradation temperatures of lignites were compared, Edirne Uzunköprü lignite was affected the least by the temperature change, and Bursa MKP lignite was the most affected. It has been observed that the fastest degradation temperature in lignites is between 420-440 °C. It is the lowest in supercritical gas extraction of Uzunköprü lignite, where thermal degradation is the least active. Mustafa Kemal Paşa lignite has the highest extract yield. Accordingly, the temperature has a similar effect during both pyrolysis and extraction. With the increase in temperature, the separation of small molar mass fractions from the main structure as a result of disintegration directly affects the extract yields. When the used lignite samples are swollen with different solvents, some properties of the solvent, such as the solubility parameter and the number of donors, are important in terms of interaction with lignite and penetration into the pores of the lignite. The swelling obtained with solvents with less than 20 donors is smaller. It has been determined that solvents with a large and positive DS-AS difference cause greater swelling because they interact more easily with lignite. Apart from the solvent used here, it affects the applied pressure. With the increase in pressure, the entry of the solvent into the pores becomes easier, the residence time of the solvent in the pore increases, and the increased solvent-solute interaction increases the extract yield. The extract yields obtained from the extraction of pre-expanded lignites with toluene under supercritical conditions are greater than the extract yields of the original lignites under the same conditions. When the lignite is swelled with a suitable solvent, the extract yield increases because the solvent can enter the swollen pores and the solvent-solute mixture can easily back-diffuse from the same pores.

5. REFERENCES

- Asaro M., and Smith R.M. (2013) in *Fossil Energy*. Springer, 389-442.
- Caliskan S. (1992). *Effect of Swelling of Lignites on their Solubility*. Master Thesis, A.U.F.F. Department of Chemical Engineering.
- Dingbang C., Cang C., Qing C., Lili S., Caiyun C. (2021). Does new energy consumption conducive to controlling fossil energy consumption and carbon emissions?-Evidence from China. *Resources Policy*, 74, 102427.
- Eaves D. (2004). *Handbook of polymer foams*. iSmithers Rapra Publishing.
- Franck H.G. and Stadelhofer J.W. (2012). *Industrial aromatic chemistry: raw materials· processes· products*. Springer Science & Business Media
- Gutmann V., Wychera E.J.I. (1966). Coordination reactions in non aqueous solutions-The role of the donor strength. *Inorganic and Nuclear Chemistry Letters*, 2(9), 257-260.
- Gür T.M. (2018). Review of electrical energy storage technologies, materials and systems: challenges and prospects for large-scale grid storage. *Energy & Environmental Science*, 11 (10), 2696-2767.
- Larsen J.W., and Mohammadi M. (1990). Structural changes in coals due to pyridine extraction. *Energy Fuels*, 4, 107
- Lee D.H. (2012). Toward the clean production of hydrogen: Competition among renewable energy sources and nuclear power. *International Journal of Hydrogen Energy*, 37 (20), 15726-15735.
- Marzec A., Juzwa M., Betlej K. and Sobkowiak M. (1979). Bituminous coal extraction in terms of electron-donor and-acceptor interactions in the solvent/coal system. *Fuel Processing Technology*, 2(1), 35-44.
- Mayer U., Gutmann V. and Gerger W. (1975). The acceptor number — A quantitative empirical parameter for the electrophilic properties of solvents. *Monatshefte für Chemie / Chemical Monthly*, 106(6), 1235-1257.

- Nishioka M., and Larsen, J.W. (1990). Association of aromatic structures in coals. *Energy & Fuels*, 4, 100.
- Peppas N.A., and Lucht L.M. (1984). Macromolecular structure of coals. I. The organic phase of bituminous coals as a macromolecular network. *Chemical engineering communications*, 30(3-5), 291-310.
- Song C., and Schobert H.H. (1993). Opportunities for developing specialty chemicals and advanced materials from coals. *Fuel Processing Technology*, 34 (2), 157-196.
- Suuberg E. M., Otake Y., Yun Y., Deevi S.C. (1993). Role of moisture in coal structure and the effects of drying upon the accessibility of coal structure. *Energy & fuels*, 7(3), 384-392.
- Szeliga J., and Marzec A. (1983). Swelling of coal in relation to solvent electron-donor numbers. *Fuel*, 62 (10), 1229-1231.
- Şimşek E. (1990). Effect of Pre-inflating Lignites on their Extraction. Master Thesis, A.Ü.F.F. Department of Chemical Engineering.
- Wiser R., Bollinger M., Barbose G., Belyeu K., Hand M., Heimiller D., Lew D., Milligan M., Mills A., and Moreno A. (2008). Annual report on US wind power installation, cost, and performance trends: 2006.
- Xie K., Li W. and Zhao W. (2010). Coal chemical industry and its sustainable development in China. *Energy*, 35(11), 4349-4355.