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Investigation of the Liquefaction Possibility of Ermenek Lignite as an Alternative Clean Energy Source

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ABSTRACT

Coal liquefaction: can be defined as the transformation of coal into products that have a high energy density, can be easily stored and transported and do not create environmental pollution, to meet both fuel and chemical raw material requirements. This study was carried out to determine the yields of the products formed as a result of the liquefaction of Konya-Ermenek lignite in the N_2 atmosphere and under non-catalytic conditions. Proximate and ultimate analysis of the obtained solid and liquid products was made. The composition of the oil product was determined by GC-MS. As a result of liquefaction, the char yield was 71.37%, the preasphaltene yield was 12.24%, the asphaltene yield was 2.23% and the oil + gas yield was 14.16%. It was determined that the higher heating value of 4199 kcal/kg in raw lignite is twice as high in liquefaction products. It was determined that the sulfur content of 3.94% in raw lignite decreased to 1.54%, 0.85% and 0.44% in char, preasphaltene and oil, respectively.

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1. INTRODUCTION

Due to the organic and inorganic compounds found in coal, it is important not only for meeting energy needs but also for being a source of chemical raw materials. For this reason, various processes such as pyrolysis and liquefaction are tried to produce solid and liquid fuels or chemical raw materials from coal. In liquefaction, first of all, under high temperature and pressure conditions, the coal is broken down into free radicals by using hydrogen donor solvent and catalyst. Later, these radicals are saturated with hydrogen and both liquid fuel and chemical raw materials are produced [1]. The products obtained as a result of the liquefaction of coal are divided into three main groups as oils, asphaltenes and preasphaltenes. Such grouping is made according to the dissolution state of the soluble products in various solvents. Soluble in pentane (C_5H_{12}) or hexane (C_6H_{14}) are oils; those that are insoluble in pentane or hexane but soluble in benzene (C_6H_6) or toluene (C_7H_8) are asphaltenes (AS); those that are insoluble in benzene or toluene but can be soluble in tetrahydrofuran (THF) (C_4H_8O) are called preasphaltene (PAS) [2].

Oils are the most desired group among coal liquefaction products. The molecular weight ranges from 100-300. Oils are generally composed of ethers, thioethers, polynuclear compounds and non-basic nitrogen compounds. Asphaltenes with a molecular weight of 300-700 are mainly composed of monofunctional compounds such as phenols, basic nitrogen compounds and ethers. The preasphaltenes with a molecular weight of 400-2000 consist of multi-functional compounds [2].

The liquefaction of coal is affected by the degree of carbonization of the coal. Since coals with a carbon content of more than 88% generally contain large amounts of aromatic rings and low amounts of reactive hydrogen and functional groups, it is difficult to liquefaction them. Since lignites have low aromatic carbon content and high oxygen content, they cause large amounts of hydrogen consumption. However, their reactivity during liquefaction is quite high [3].

There are some studies in the literature on lignite coal liquefaction. Gül et al. (2004) was carried out catalytic liquefaction experiments of Bolu Mengen and Sivas Kangal coals in solvent (tetralin) and solvent-free conditions at 400°C and 450°C and examined the product distribution. They determined that when tetralin is used as a solvent during liquefaction, the formation of oil + gas, asphaltene and preasphaltene is higher [4]. Yıldız et al. (2006) studied the catalytic/non-catalytic liquefaction of Elbistan lignite and various biomass types (waste plastic, waste paper, waste sludge and molasses). They investigated the effect of particle size, catalyst type, liquid/solid ratio, reaction time and reaction temperature on liquefaction yields. As a result of the experiments, they determined that the particle size did not have a significant effect on the liquefaction of coal. They calculated the total conversion as 79% under non-catalytic conditions and 92% under catalytic conditions [5]. Rahman et al. (2015) was carried out liquefaction experiments at 4 MPa hydrogen pressure, 4°C/min heating rate, 350°C-450°C temperature range, solvent/coal ratio 2/1 and for 30 minutes and investigated the effects on liquid product quality. They determined that as the reaction time increased at 350°C, the liquid quality of the coal decreased. They also observed that the concentration of nitrogen-containing components in the coal liquid increased with increasing temperature and reaction time [6]. Kanca et al. (2016) was studied the liquefaction of Tunçbilek lignite. They determined that the sulfur content, which was 5.4% in raw lignite, decreased to 0.5% in the solid and liquid products they obtained as a result of the liquefaction experiments [7].

In recent years, converting and using coal into the most suitable product according to its properties has emerged as a modern approach. With technologies such as pyrolysis and liquefaction, it is possible to use coal without creating environmental pollution by reducing the sulfur and ash contents. In this way, it will be possible to evaluate low-quality lignite coals economically. There are many studies on this subject in the literature [8-14]. In this study, the product yields and characterization of Konya-Ermenek lignite as a result of liquefaction were determined.

2. MATERIAL AND METHOD

The Konya-Ermenek lignite used in the study was obtained from the Central Anatolia Region of Turkey. Proximate analysis and ultimate analysis were carried out to determine the characteristic properties of the lignite sample. For liquefaction experiments, lignite was ground to below 106 microns. Basic chemicals used in liquefaction experiments; tetralin-$C_{10}H_{12}$ (Merck, 98% purity) and nitrogen (N_2) gas (Habaş, 99.99% purity). Auxiliary chemicals; Hexane-C_6H_{14} (Riedel-de Haen, 95% purity), toluene-C_7H_8 (Riedel-de Haen, 99.7% purity) and tetrahydrofuran-C_4H_8O (Merck, 99.0% purity). The physical properties of the main solvents used in the liquefaction experiments are given in Table 1. The PARR 4575/482 reactor given in Figure 1 was used for liquefaction.

30 g lignite sample was put into an autoclave and closed with a 1/3 ratio of 90 ml tetralin ($C_{10}H_{12}$). First, the gas inlet and outlet valves were opened and the reactor was purged with N_2 gas for 30 minutes. Then, gas outlet valves were closed and N_2 gas was fed into the reaction medium until the initial pressure was 20 bar. By turning on the heater and stirrer, the autoclave was heated at a rate of approximately 3-4°C/min until the selected reaction temperature (400°C) was reached. It was left at 400°C for 2 hours. It was stirred at a constant speed of 400 rpm during both the heating and the reaction. After waiting for 1-2 hours for the autoclave temperature to cool to ambient temperature, the autoclave was opened and the solid + liquid products inside were poured into a beaker. Solid + liquid products were separated from each other by filtration. Soxhlet extraction was performed with tetrahydrofuran (THF) (C_4H_8O) into the solid products to separate the coal liquefaction products trapped in the solid products.

Table 1. Physical properties of solvents used in liquefaction experiments

Solvents	Chemical composition	Molecular weight	Melting point (°C)	Density (g/cm^3)	Boiling point (°C)
Tetralin	$C_{10}H_{12}$	132	-31	0.973	206
Tetrahydrofuran	C_4H_8O	72	-65	0.888	65
Hexane	C_6H_{14}	86	-94	0.659	69
Toluene	C_7H_8	92	-95	0.866	110.8

Figure 1. The batch reactor used in liquefaction experiments

Equations used in the calculation of liquefaction products and conversion rates are given in (1) - (5).

Char yield:

$$\%\text{Char} = \frac{\text{Char (g)}}{\text{Total sample(g)}} \times 100 \quad (1)$$

Total conversion rate (Liquefaction products + gases):

$$\%Total\ conversion = 100 - \%\text{Char} \quad (2)$$

Preasphaltene (PAS),

$$\%\text{Preasphaltene} = \frac{\text{PAS (g)}}{\text{Total sample(g)}} \times 100 \quad (3)$$

Asphaltene (AS),

$$\%\text{Asphaltene} = \frac{\text{AS (g)}}{\text{Total sample (g)}} \times 100 \quad (4)$$

Oil+Gas,

$$\%(\text{Oil} + \text{gas}) = \%\text{Total conversion} - \%\text{PAS} - \%\text{AS} \quad (5)$$

Proximate and ultimate analyzes of the products obtained as a result of liquefaction were made and their higher heating values (HHV) were determined. GC-MS analyzes were performed at Inonu University Scientific and Technological Research Center (IBTAM) with the Agilent 890 GC 5973 MS device. Since the molecular weight of the compounds in the preasphaltene and asphaltene groups, which are among the soluble product groups, are very high and their volatility is very low, only oils can be analyzed by gas chromatography. Thus, qualitative analysis of oil samples was made by using the retention times of known compounds. GC-MS analysis conditions are given in Table 2.

Table 2. GC-MS analysis conditions

Column	**HP-INNOWAX Capillary nominal column**
Film thickness	0.25 µm
Length	60 m
Diameter	0.25 µm
Carrier gas (Helium)	5 ml/min
Sample quantity	2 ml
Detector	MS
Detector temperature	250 °C
Initial temperature	60°C (1 min isothermal)
Final temperature	250°C (10 min isothermal)
Heating rate	25°C/min
Solvent	Hexane (C_6H_{14})
Residence in the column	98 min

Table 3. Proximate analysis results of the raw lignite and chars (air-dried)

	Raw lignite	**Char**
Ash (%)	18.15	7.11
Volatile matter (%)	39.75	26.23
Moisture (%)	6.20	-
Fixed C* (%)	35.90	66.66

3. RESULTS AND DISCUSSION

The proximate analysis results of the raw lignite and the char are given in Table 3. According to Table 3, raw lignite contains 18.15% ash, 39.75% volatile matter, and 35.90% fixed carbon (on an air-dried basis). It was determined that the char ash content decreased to 7.11% whereas the fixed C increased to 66.66%. As a result of the liquefaction process, there was an increase of about 31% in the C content of the solid.

Ultimate analysis and HHV values of raw lignite and its liquefaction products (char, PAS, oil) are given in Table 4. Due to the difficulty of removing AS from glass systems and the small amount of material, their elemental analysis and calorific values could not be determined.

It can be seen from Table 4 that the C content of approximately 39% in raw lignite is 61%, 76% and 78% in char, PAS and oil, respectively. The sulfur content was reduced from 3.94% to 1.54% in the char. The lowest sulfur content (0.44%) was found in the oil product. Considering the C and S contents of the products, it can be said that liquefaction has a positive effect. HHV increased about two times compared to raw lignite. HHV, which was 4199 kcal/kg in raw lignite, was determined as 8326 kcal/kg in the char.

Table 4. Ultimate analysis results of raw lignite and liquefaction products

(%)	Raw lignite	Char	Preasphaltene	Oil
C	39.49	61.29	76.16	77.66
H	5.32	6.49	6.59	6.85
N	0.90	1.35	1.21	1.19
S	3.94	1.54	0.85	0.44
O	50.35	29.33	15.19	13.86
HHV (kcal/kg)	4199	8326	8729	8826

In Table 5, the yields and total conversions of the products obtained as a result of liquefaction of lignite under non-catalytic conditions are given. As seen in Table 5, the product yields obtained as a result of liquefaction were calculated as approximately 71% for char, 12% for PAS and 14% for oil + gas. The total conversion is about 33%. Since the char yield (71%) and HHV (8326 kcal/kg) are high and the S content (1.54%) is low, it will be very important both economically and environmentally.

Table 5. Product yields and total conversion were obtained as a result of the liquefaction of lignite.

	Char	PAS	AS*	Oil+Gas	Total conversion
Yield (%)	71.37	12.24	2.23	14.16	33.19

*by difference

The main purpose of coal liquefaction is to be able to produce a new liquid fuel and raw material chemicals. For this purpose, quantitative and qualitative analyzes of oils obtained as liquefaction products were made by GC-MS analysis. GC-MS results are shown in Table 6.

When Table 6 is examined, as stated in the literature, saturated n-alkanes, isoprenoid, branched alkanes, n-alkyl cyclohexane, terpan and other aromatic structures were observed in the structure of oils obtained as a result of coal liquefaction [15-20]. As a result of liquefaction, it has been determined that the carbon structures in lignite are destroyed and this carbon constitutes the main structure of liquefaction products. According to Table 6, the most abundant compounds in the oil product obtained as a result of liquefaction are Naphthalene (51.41%), Azulene (33.47%) and Toluene (7.48%). These products are precious chemicals and can be used in various industries.

Table 6. GC-MS analysis results of the oil product obtained as a result of liquefaction of lignite under non-catalytic conditions

Residence in the column (min)	Possible compound name	Amount in total (Abundance %)
7.201	Toluene	7.48
25.495	Naphthalene, 1,2,3,4-tetrahydro-	51.41
31.273	Azulene Naphthalene	33.47
32.739	Naphthalene ,1,2,3,4-tetrahydro-1-propyl	0.94
37.205	Naphthalene , 2-methyl- Naphthalene , 1-methyl-	1.21
38.300	Butylhydroxy toluene	1.09
62.785	Benzene,1,3-Diethyl-5-Methyl	0.82
88.683	2,2'- binaphtalene , 1,1',2,2',3,3',4,4'-oktahydro-	1.11
93.797	7,8,9,10,11,12-hexa hydro benzo [a]pyrene	1.19

4. CONCLUSIONS

From the liquefaction experiments of Ermenek lignite, it was determined that the char yield was 71.37%, the PAS yield was 12.24%, the AS yield was 2.23% and the oil + gas yield was 14.16%. The total conversion amount is calculated as 33.19%.

The ash content of the char was calculated as 7.11%, the volatile matter content as 26.23% and the constant C content as 66.66%. Compared to the ash content of raw lignite (18.15%), the ash of the char decreased more than half, and the fixed C amount increased from 35.90% to 66.66%. It has been observed that there is a 2.40% reduction in sulfur content. The HHV of the liquefaction products are 8326 kcal/kg, 8729 kcal/kg and 8826 kcal/kg for char, preasphaltene and oil, respectively. It was observed that the HHV of the liquefaction products was approximately twice higher than the HHV of raw lignite (4199 kcal/kg).

According to the GS-MS analysis results of the oils obtained as a result of liquefaction, it was determined that a significant amount of azulene and its derivatives, naphthalene and its derivatives, butylhydroxytoluene consisted of hydrocarbon compounds.

As a result, it is thought that transforming lignite with low calorific value into more valuable products will contribute both to the national economy and the reduction of environmental pollution caused by combustion. However, the economics of the theoretically and practically possible liquefaction method should be investigated.

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AUTHOR CONTRIBUTIONS

Aydan Aksoğan Korkmaz contributed 100% at every stage of the study.

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