

ARASTIRMA MAKALESİ / RESEARCH ARTICLE

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UPGRADING OF LIGNITES BY FAST PYROLYSIS AND HIGH DENSITY DRY MAGNETIC SEPERATION

ÖZ

In this study, fast pyrolysis followed by high intensity dry magnetic (HIDM) separation experiments were conducted to obtain liquid and solid fuels from Çayırhan region lignites. First pyrolysis experiments were performed in a well-swept resistively heated fixed-bed reactor in a nitrogen atmosphere, and pyrolysis temperature and heating rate were studied. Afterwards, pyrolysis, oil, solid and gas products were obtained and characteristics of the oil were determined by elemental analysis and ¹H NMR. The highest oil yield (17.58%) was obtained at a pyrolysis temperature of 500°C and heating rate of 350°Cmin⁻¹. Under these conditions total sulphur removal and weight yield of char were obtained as 17.24% and 59.21%, respectively. HIDM separation experiments were then carried out by using the char of fast pyrolysis experiments to enable the use of char as a solid fuel by reducing ash and sulphur contents. In the HIDM separation experiments, roller speed, feed rate and angle of back splitter were optimized. After HIDM separation, solid product was analysed for ash, sulphur and higher heating value. At optimum conditions, ash was reduced to 46.72% while total sulphur was not reduced due to lack of size liberation.

Keywords: : Lignite; Fast pyrolysis; Pyrolysis oil; Char; Magnetic Separation; Sulphur

LİNYİTLERİN HIZLI PİROLİZ YÖNTEMİ VE YÜKSEK YOĞUNLUKLU KURU MANYETİK AYIRMA İLE İYİLEŞTİRİLMESİ

ABSTRACT

Bu çalışmada, Çayırhan bölgesi linyitlerinin önce hızlı pirolizi, ardından elde edilen katı ürünün yüksek yoğunluklu kuru manyetik (HIDM) ayırma ile zenginleştirilerek, sıvı ve katı yakıt eldesi amaçlanmıştır. Hızlı piroliz deneyleri, azot atmosferi altında, sürüklenmeli sabit yatak reaktörde gerçekleştirilmiş ve piroliz sıcaklığı ve ısıtma hızının etkileri incelenmiştir. Piroliz sonrasında elde edilen sıvı ürünün yapısı elementel analiz ve ¹H NMR ile belirlenmiştir. Hızlı piroliz deneylerinde en yüksek sıvı ürün verimi %17.58 değeri ile 500°C piroliz sıcaklığı ve 350°Cmin⁻¹ ısıtma hızında elde edilmiştir. Bu piroliz koşullarında katı ürün verimi %59.21 ve elde edilen katı ürünün kükürt giderimi %17.24 olarak belirlenmiştir. Pirolizden elde edilen katı ürünün, kül ve kükürt içeriğinin azaltılarak, katı yakıt olarak kullanılmasını sağlamak için HIDM zenginleştirme deneyleri gerçekleştirilmiştir. HIDM deneylerinde tambur hızı, besleme hızı ve bıçak açısı optimize edilmiş ve en uygun koşullardaki katı ürünün kül, kükürt ve üst ısıl değerleri belirlenmiştir. Optimum koşullarda katı ürünün kül oranı %46.72 değerine azalırken, toplam kükürt oranında tane serbestleşmesi gerçekleşmediği için azalma görülmemiştir

Anahtar Kelimeler: Linyit; Hızlı Piroliz; Piroliz sıvı ürünü; Katı ürün; Manyetik ayırma; Kükürt

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1. INTRODUCTION

Coal is the most abundant and dominant fossil fuel energy source readily available to the world. However, many coal reserves contain substantial amounts of sulphur and inorganic materials, and consumption of these reserves cause global warming and atmospheric pollution. It is estimated that about 90% of SO₂ in the atmosphere and acid rain are due to coal combustion. Because of the growing international concern for preserving the environment and eliminating air pollution, high sulphur and high inorganic content coal reserves are unsuitable for direct use.

Lignite has the biggest share, with 37.6% in total primary energy production in Turkey (dektmk.org.tr). Turkish lignites typically have high sulphur, moisture and ash contents and low heating value; if used for direct combustion they lead to serious environmental pollution by particulate matter and SO_x emissions (Ateşok, 2009). These emissions have to be reduced to acceptable levels imposed by domestic governments and international organizations. A feasible strategy for utilization of such quality lignites is to apply desulphurization and deashing methods. It is possible to clean lignites by physical, chemical and biological methods prior to combustion (Aksoy et al., 2014). Chemical and biological cleaning methods are currently under investigation and could be expensive (Aytar et al., 2014). Physical methods are preferred to clean lignites because of their low operational costs. On the other hand, physical methods highly depend on the particle size of materials and may not be effective for separating finely dispersed minerals as well as coarse particles (Aytar et al., 2014).

It has been suggested that pyrolysis technology could be an effective method for comprehensive utilization of low-rank lignites (Li et al., 2015, Hanson et al., 2002). Pyrolysis can also be used efficiently for desulphurization of lignites by both removal of organic sulphur species and pyrite decomposition prior to combustion. (Erşahan et al, 1997). Heat treatment under oxygenless conditions increases magnetic susceptibility of mineral matters and pyrites in lignite (Koca et al., 2000). It was claimed in literature that in pyrolysis experiments, pyrite transforms various sulphides such as pyrrhotite at temperatures above 350°C (Koca et al., 2007). Coal is diamagnetic while pyrrhotite is

ferromagnetic, therefore magnetic separation can be applied to clean char after pyrolysis.

The cleaning of coal by pyrolysis followed by magnetic separation appears to be the most promising lignite cleaning process. Pyrolysis is considered not only a promising technology to produce liquid, gaseous and solid carbonaceous fuels, but also a fundamental step for fuels and chemicals which may be combusted directly or refined for recovery of certain chemicals such as benzene, phenol, naphthalene, anthracene, and other compounds.

Çayırhan lignite deposit, the subject of this study, is located in the mid-north region of Turkey. It has over 350 million tonnes of reserves and Park Teknik Lignites Company produces over 3 million tonnes of lignite from mechanized underground pits annually. Run-of-mine lignites are fed to a washing plant before utilization in the nearby power plant for electricity generation.

The objective of the present study is to determine the pyrolysis conditions required to obtain a maximum oil yield and desulphurization tendency. For this purpose, the effects of pyrolysis temperature and heating rate on the pyrolysis products were determined. Solid product, char, was further processed by magnetic separation method to increase the possibility of the utilization of char as a solid fuel.

2. EXPERIMENTAL

2.1. Materials

The sample was kindly supplied by Park Teknik Lignites Company from Çayırhan Region lignites. The sample was crashed and wet sieved into two size fractions: -1+0.55 and -0.55 mm. Coarse fraction was used in the all experimental work. The analysis of the studied sample is given in Table 1.

2.2. Experiments

2.2.1. Pyrolysis Experiments

The fast pyrolysis experiments were conducted in a nitrogen atmosphere in a well-swept resistively heated fixed-bed reactor with a length of 90 cm and an inner diameter of 8 mm, made of 310 stainless steel. The first group of experiments was performed to determine the effect of pyrolysis temperature and heating rate on the product yields. Five grams of air-dried sample was placed in the reactor and sweep gas velocity with a flow rate of 5cm³sec⁻¹ was

controlled and measured by a rotameter. In order to establish the effect of the pyrolysis temperature, the sample was placed in the reactors and heated to final temperatures of either 400, 500, 600 or 700°C with heating rate of 350°Cmin⁻¹ and held at that temperature for 10 min or until no further significant release of gas was observed. In the second group of experiments, the temperature was raised from room temperature to final pyrolysis temperature of 500°C by heating rates of 100, 350 or 800°Cmin⁻¹. After pyrolysis, char yield was determined from the overall weight losses of the reactor tube. The liquid phase was collected in a glass liner located in a cold trap maintained at about 0°C. Water was determined by refluxing the toluene solution in a Dean and Stark method. Gas yield was determined by overall material balance.

All the experiments were carried out at least three times in order to determine the variability of the results and to assess the experimental errors. In this way, the mean results were calculated, and the standard deviations for the oil yields were 0.2. Results were illustrated in terms of pyrolysis yield in the dry ash free basis, and volatile matter, total sulphur (ASTM D3177-75) and sulphur reduction in the char on dry basis.

2.2.2. Magnetic Separation Experiments

Magnetic separation experiments were carried out by using the char of pyrolysis experiments. A laboratory type Permanent Magnetic Roll Separator (PERMROLL), which has a 19000 gauss magnetic field strength, was used to separate magnetic and non-magnetic

fractions. Feeding rate, roller speed and splitter angle were varied to determine the optimum conditions of High Intensity Dry Magnetic Separation. Obtained fractions were analysed for ash, total sulphur and heating value.

2.3. Analysis

The elemental composition and higher heating value (HHV) of the samples were determined using a LECO TruSpec CHN Elemental Analyser and IKA C200 calorimeter, respectively. Total sulphur analysis was performed with an Eltra CS-530 analyser (Eltra, Germany) with an infrared absorption detection procedure (ASTM D4239).

The pyrolysis oil and char analysed in this study were obtained in the experimental condition that has given maximum oil yield. The ¹H NMR of the oils was obtained at an H frequency of 500 MHz using a Bruker BioSpin GmbH instrument. The samples were dissolved in chloroform-d. XRD spectra of solid samples were recorded by using a Rigaku Rint 2200 diffractometer (40 kV, 30 mA). The experiments were operated in the 2θ range of 10–80 degrees.

3. RESULTS AND DISCUSSION

Experiments were carried out in two series. The first was to determine the effect of fast pyrolysis on oil yield and desulphurization of lignites. In the second group of experiments, char obtained from the pyrolysis was subjected to further cleaning by high intensity dry magnetic separation.

Table 1. Proximate and elemental analysis of the materials

<i>Proximate analysis</i> (wt.%, on dry)	<i>Lignite</i>	<i>Elemental analysis</i> (wt.%, on dry ash free)	<i>Lignite</i>	<i>Oil</i>	<i>Char</i>	<i>Magnetics</i>
Moisture	5.26	C	63.93	80.61	79.49	73.99
Volatile	47.91	H	5.17	9.98	1.67	1.95
Fixed C	6.08	N	4.21	1.92	3.19	4.09
Ash	40.75	S	12.35	0.83	11.49	12.83
		O ^a	14.34	6.66	4.16	7.14
		H/C molar ratio	0.97	1.49	0.25	0.32
		Heating value (MJkg ⁻¹)	9.65	40.55	8.95	9.45

^aBy difference

3.1. Pyrolysis experiments

Pyrolysis temperature was varied from 400°C to 700°C and the heating rate was set as 350°Cmin⁻¹ in fast pyrolysis. Effects of the temperature on the oil yield are shown in Figure 1. Oil yield increased up to 500°C and then gradually decreased with increasing temperature. The decrease in oil yield may be a result of its poor flow ability, which could lead to less volatiles released from lignite at higher temperatures. That is, the pyrolysis of lignite was affected by two primary factors, including heating transfer and mass transport processes in the temperature range of this study. The highest oil yield was obtained at 500°C as 17.58 %. At low pyrolysis temperature, the oil yield was low because the temperature increase was not enough for complete pyrolysis to take place, thus yielding less liquid product.

The effects of pyrolysis temperature on char yield are also shown in Figure 1. As can be seen from Figure 1, at low pyrolysis temperature (400°C), the char yield was 62.41 % and afterwards sharply decreased with increasing temperature. As expected, as the temperature increases, the carbonaceous part of lignite decomposes in liquid and gas products.

It is noteworthy to point out that gas yield is also increased with increasing temperature. The increase in gaseous products is thought to be predominantly due to secondary cracking of the pyrolysis vapours at pyrolysis temperatures of higher than 500°C. However, the secondary decomposition of the char at higher temperatures may also yield noncondensable gaseous products.

The ash, volatile matter, total sulphur and sulphur reduction in the char as a function of pyrolysis temperature are given in Figure 2. As can be seen in Figure 2, the volatile matter and total sulphur content of char were decreased

while sulphur reduction and ash content were increased with increasing temperature. The results show that at the low temperature, sulphur reduction is negligible, but it increased up to the final temperature of 700°C. Figure 2 shows that total sulphur, volatile matter and ash content of solid product were obtained as 5.52%, 12.14% and 51.96%, respectively at optimum conditions of 500°C pyrolysis temperature. At this point 17.24% total sulphur reduction was obtained.

The effects of heating rate on pyrolysis product yields were systematically studied with heating rates of 100, 350 and 800°Cmin⁻¹ and pyrolysis temperature set as 500°C. The results are shown in Figure 3. The increase in heating rate of particles occurred more gradually and led better heat transfer to the inner portions of the particles than low heating rates. The maximum rate of decomposition increases with increasing heating rate, and the oil yield reached a maximum value of 17.58% with a heating rate of 350°Cmin⁻¹, at the final pyrolysis temperature of 500°C. This value was about 12.6 wt. % higher than that of 100°Cmin⁻¹. At heating rate of 850°Cmin⁻¹, the oil yield decreased to 15.82%. Char yield was decreased slightly while gas yield and water did not change significantly with increasing heating rate.

The effects of heating rate on the ash, volatile matter and total sulphur content of char were studied at heating rates of 100, 350 and 800°Cmin⁻¹ in fast pyrolysis (Figure 4). Total sulphur reduction and ash content of the char increased while total sulphur and volatile matter in the char decreased with increasing heating rate. The results indicate that high heating rate is favourable for increased desulphurization, but unfavourable for char recovery.

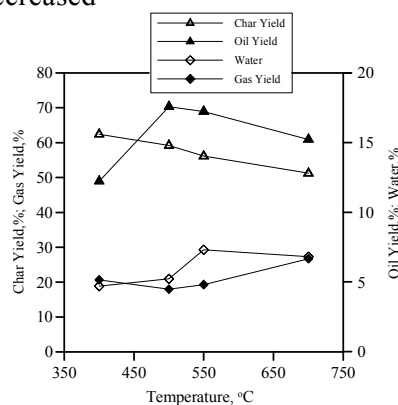


Figure 1. The effect of temperature on pyrolysis product yields.

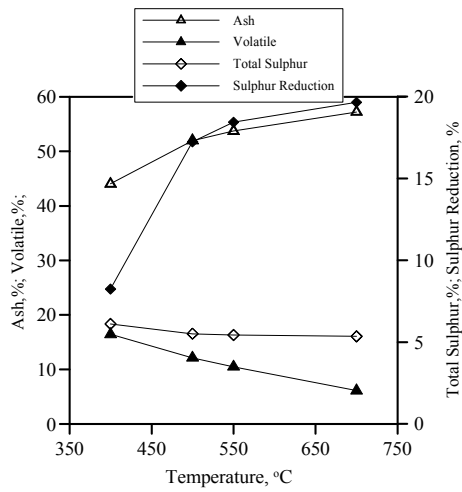


Figure 2. The effect of temperature on char

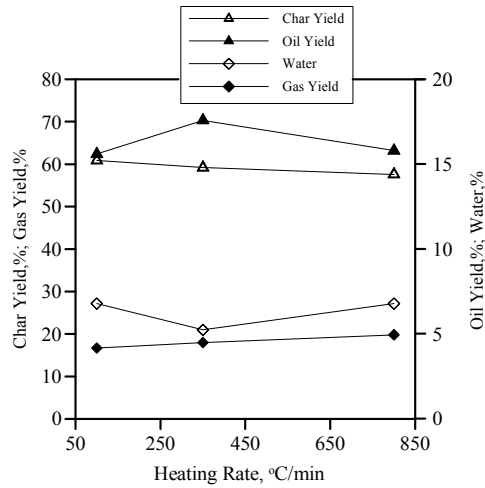


Figure 3. The effect of heating rate on pyrolysis product yields.

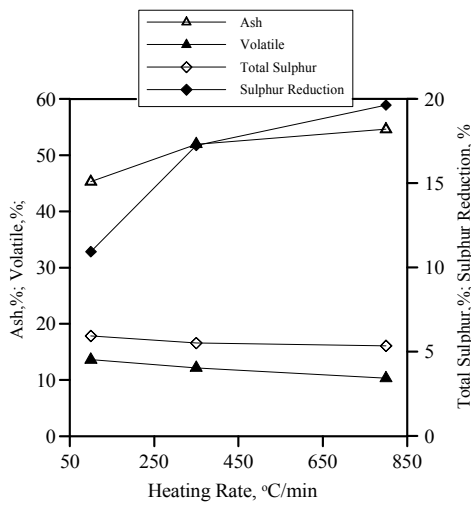


Figure 4. The effect of heating rate on char.

3.2. Magnetic Separation Experiments

As mentioned earlier, pyritic sulphur in lignite decomposes to iron sulphide and is converted to pyrrhotite in the range of 350-650°C. As pyrrhotite shows strong magnetic susceptibility, a PERMROLL magnetic separator was used to obtain a clean solid product from the char of the pyrolysis experiments. Two products, non-magnetics and magnetics, were obtained after each experiment. The effects of process parameters on ash, total sulphur content and combustible recovery of the products were evaluated under the following conditions.

Roller speed: 50, 100, 150 rpm
 Feed rate: 56, 113, 178 gmin⁻¹
 Angle of back splitter: 86°, 100°, 114°

Three sets of magnetic separation experiments were carried out to determine the optimum conditions of separation. The feed rate, roller speed and angle of back splitter of the PERMROLL magnetic separator were optimized in each set. The optimum conditions for feed rate, roller speed and angle of back splitter were determined as 56 gmin⁻¹, 150 rpm, and 86°, respectively. The best results obtained under the above condition are summarized in Table 2.

As indicated in Table 2, ash content of the magnetics fraction decreased to 46.72% with a combustible recovery of 73.07%. Under optimum conditions, total sulphur and heating value of the magnetic fraction were obtained as 6.84% and 9.45 MJkg⁻¹ respectively. It should be noted that the magnetics fraction includes diamagnetic lignites along with ferromagnetic pyrrhotites, attributable to the particle size of the lignites. It has previously been shown that pyrite

particles are disseminated finely in Çayırhan Lignites (Sönmez and Giray, 2001). Therefore particle size liberation was not obtained at the particle size of -1.0+0.55 mm. and unliberated diamagnetic lignite particles were dragged to the magnetics fraction along with ferromagnetic pyrrhotite particles.

3.3. Characterization of Products

The char of pyrolysis was further analysed to determine the structure of sulphide minerals by X Ray Diffraction Spectrometer. XRD patterns of head sample, char and magnetic fraction are illustrated in Figures 5, 6 and 7, respectively. XRD spectra for head sample was dominated by pyrite, and no pyrrhotite existence was traced. XRD patterns of pyrolysis char and magnetics fraction showed that conversion of some pyrite to pyrrhotite occurred. Pyrrhotite formation can be clearly seen in Figures 6 and 7.

Table 1 represents the elemental composition and HHV (MJkg⁻¹) of pyrolytic oil and char. As can be seen in Table 1, a significant decrease in oxygen content of the pyrolytic oil compared to the original feedstock is obtained, that causes the stability and heating value of oil to increase. The heating value of pyrolytic oil was found to be 40.55 MJkg⁻¹.

Results of the ¹H NMR analysis given in Figure 8 show that the pyrolysis oil contains 15.97% aromatics (peak in 6.3–9.3 ppm chemical shift range), 34.82% aliphatic adjacent to aromatic-alkene group (peak in 1.8-3.3 ppm chemical shift range) and 49.21% other aliphatic, bonded to aliphatic only (peak in 0.41.8-3.3 ppm chemical shift range).

Table 2. The summarized results of magnetic separation experiments (on dry basis)

<i>Products</i>	<i>Ash %</i>	<i>Total sulphur %</i>	<i>Combustible recovery %</i>
Magnetics	46.72	6.84	73.07
Non-magnetics	62.08	2.97	26.93
Feed	51.96	5.52	100

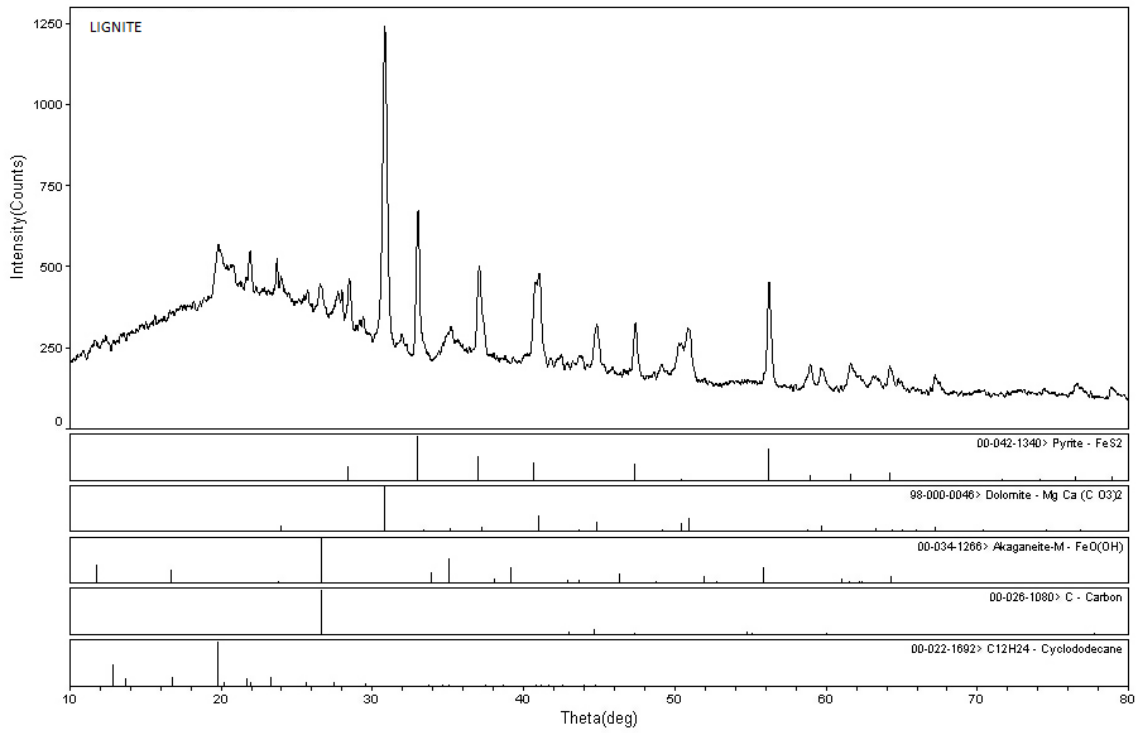


Figure 5. XRD spectra of lignite

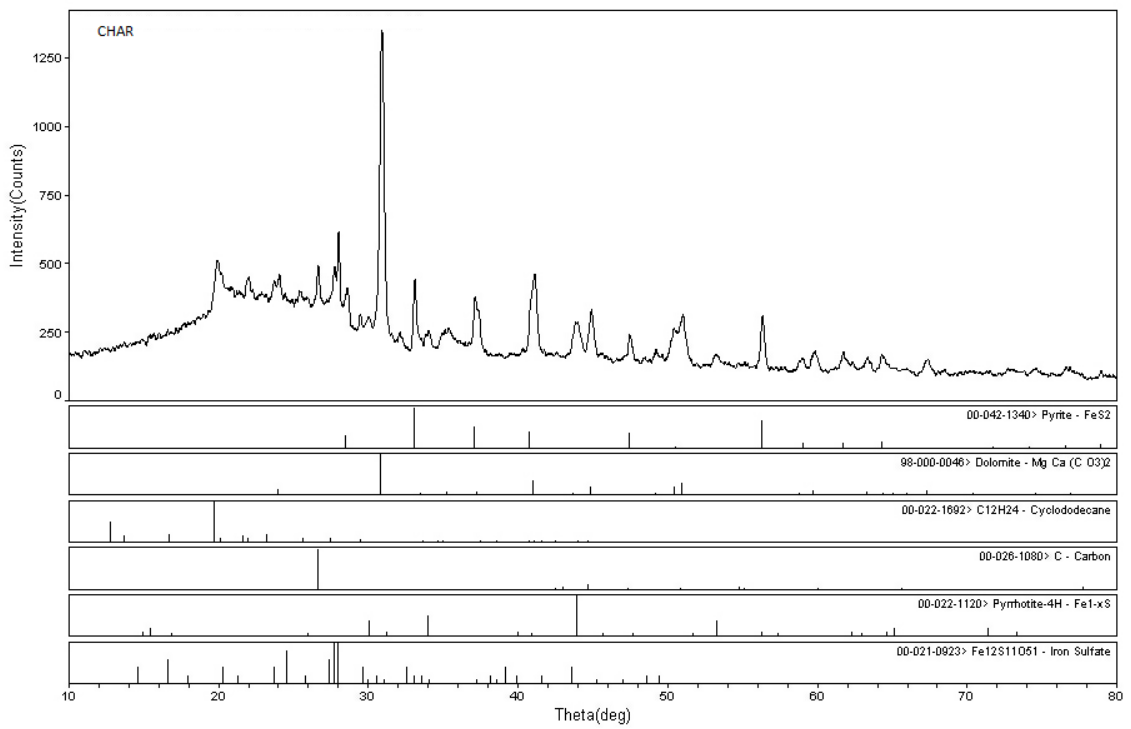


Figure 6. XRD spectra of pyrolysis char.

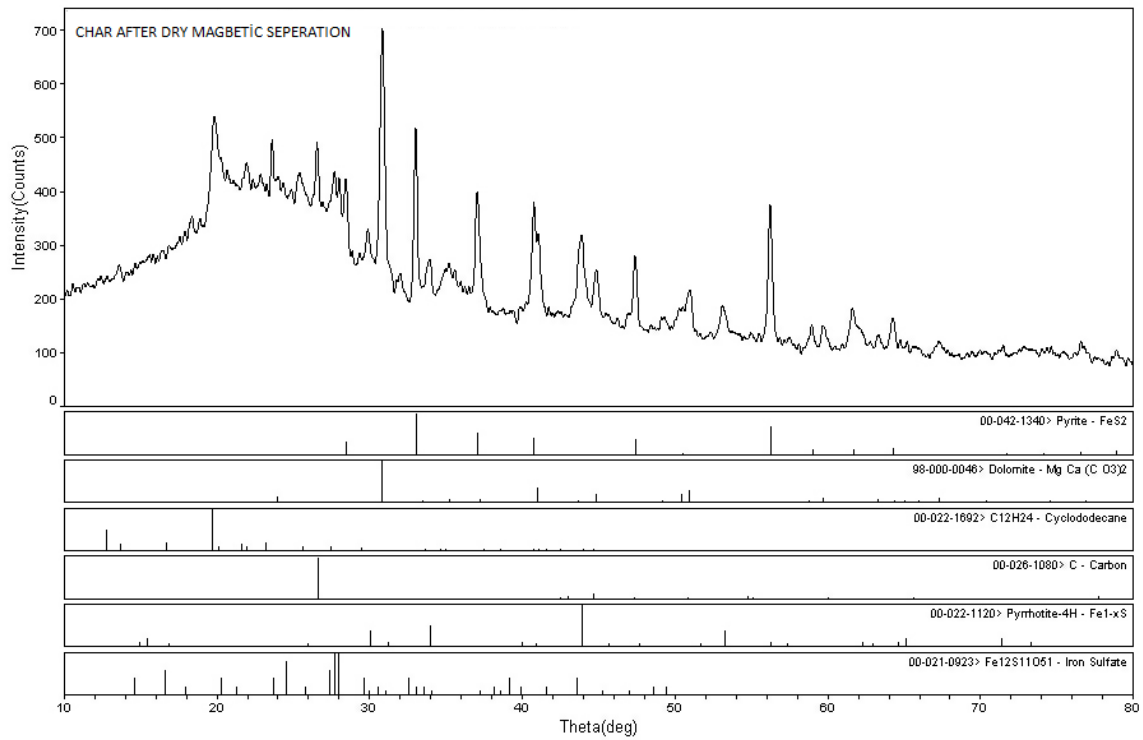


Figure 7. XRD spectra of magnetics fraction.

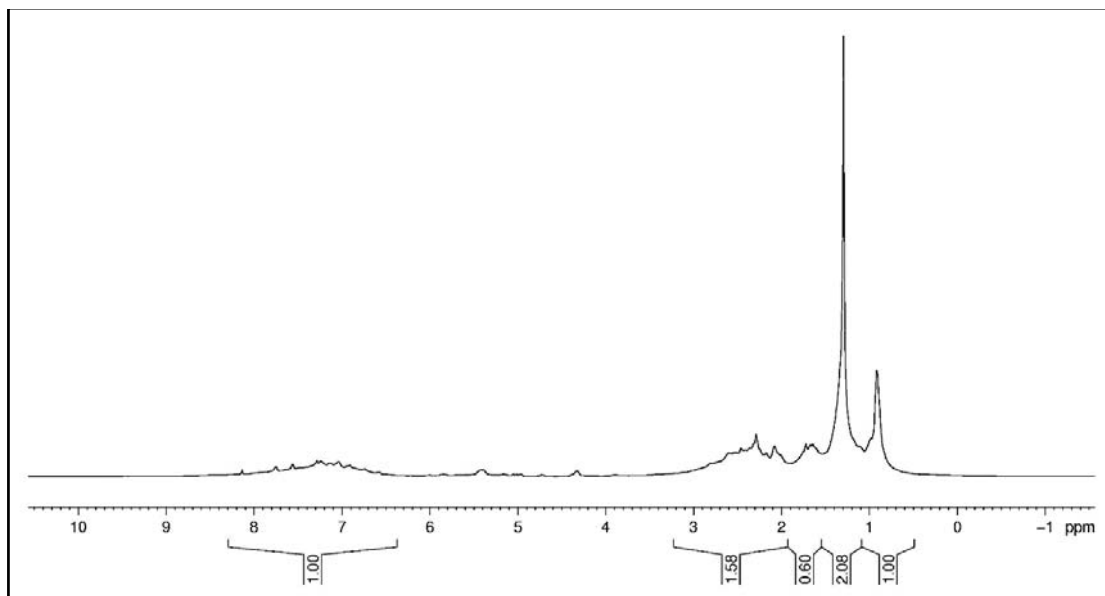


Figure 8. ¹H NMR results of pyrolysis oil.

4. CONCLUSION

Extensive research has indicated that conversion of Çayırhan region lignites into liquid and solid fuels was efficiently obtained by means of pyrolysis followed by High Intensity Dry Magnetic Separation. The structure of the pyrolysis oil is similar to crude oil and can be directly fed to petroleum refining plants.

Conversion of pyrite to pyrrhotite was obtained at the 500°C pyrolysis temperature and heating rate of 350 °Cmin⁻¹. The XRD patterns showed that char contained pyrrhotite after pyrolysis. Particle size liberation was not obtained in the studied size fraction, therefore lignites were reported to the magnetics fraction with pyrrhotite particles. At optimum conditions, ash reduction of 10.01% was obtained with 73.07% combustible recovery. Total sulphur content of the sample was increased to 6.84% due to lack of size liberation.

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