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Full Length Article

Distribution and comparing of volatile products during slow pyrolysis and hydropyrolysis of Turkish lignites

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ABSTRACT

Lignite samples obtained Ermenek and Uzunköprü coal plants in Turkey have been pyrolysed under specific conditions and the temperature effect on the final product distribution was elucidated by the use of GC and TGA. The temperature has been found to have a remarkable effect on the product distribution and evolution rate. The pyrolysis was carried out with the use of a fixed bed reactor equipped with a special sampling system to collect the organic volatile products to be analyzed by capillary gas chromatography (GC). The maximum product formation rate was found to be about 440 °C for both of the samples. The formation rate of n-paraffins was higher than that of 1-olefines at each temperature employed. The hydrocarbons obtained by pyrolysis of lignite from Ermenek and Uzunköprü coal plants were observed to contain 43 wt% and 40 wt% n-paraffins at the maximum formation rate, respectively. The 1-olefins determined at the maximum product formation rate were found to be 15 wt% for both lignite samples. Additionally, the effect of temperature on pyrolysis product distribution of Turkish lignites has been compared with those hydropyrolysed at different pressures and temperatures. The formation curves of hydropyrolysis differed from those obtained under inert pyrolysis conditions. Hydrogen was found to have an appreciable effect on pyrolytic decomposition especially at high temperatures and pressures. There were higher tar formation and less gas yield at higher hydrogen pressures.

1. Introduction

The pyrolysis of solid fuels especially coal plays an important role in most conversion processes such as carbonization, liquefaction, combustion, and gasification. The first stage of coal combustion is known as devolatilization or pyrolysis. Currently, coal is mainly used of as a source of energy by direct combustion. Combustion of coal in unprocessed form causes environmental problems. The amount of emission of harmful products depends on the efficiency of combustion process and the quality of the combusted fuels. Pyrolysis is defined as the thermal decomposition or recombination of the coal macromolecules in the absence of oxygen. It has been widely used for converting coals and another solid fuels into valuable liquid hydrocarbons, gases, and solid char. The thermal decomposition of coal has been the subject of many investigations [1–5].

Pyrolysis products are influenced by the type or rank of coal, by the temperature and by the contact time of evolved vapors with the heated surfaces within the reactor. Structural properties of coal obviously control devolatilization behavior. The decomposition of volatile products proceeds in two steps: the primary decomposition of gaseous vapors takes place at moderate temperatures and the secondary decomposition of vapors at higher temperatures. The pyrolysis behavior of coal is dependent upon particle size, coal type, pressure, heating rate and temperature. Low rank coals such as lignite release a relatively large amount of light gases and less tar during devolatilization.

As a developing country the energy and chemical raw material needs of Turkey are of critical importance. The crude oil and natural gas reserves of the country not adequate and the primary potential energy resources are solid fuels such as lignite, bituminous coal and oil shale. There are 1.3 billion tons of bituminous coal reserves in five areas in Turkey. Lignite, the most dominant source of energy produced in Turkey, is mainly used (about 75%) for power generation in thermal plants. Turkey has very abundant lignite reserves with a total of 14 billion tons. Lignite deposits are widespread all over Turkey. Lower heat values vary from 1100 to 4500 kcal kg^{-1}, some are even higher. 73% of Turkish lignite has a heat value under 2000 kcal kg^{-1}, 22% of it has a heat value between 2000 and 3000 kcal kg^{-1} and 5% total lignite has a heat value over

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Table 1
Proximate and ultimate analysis of samples.

	Ermenek lignite	Uzunköprü lignite
Proximate analysis		
Moisture (wt%)	14.5	9.0
Ash (wt%)	21	17.5
Volatile matter (wt%, daf)	44.5	26
Elemental analysis (wt%, daf)		
C	73.6	70.5
H	4.9	4.6
N	0.5	0.5
S	3.8	2.4
O	17.2	22.0
BET surface area ($m^2\,g^{-1}$)	6.5	2.3

4000 kcal kg^{-1}. The annual lignite production of Turkey is about 75 million tons and nearly 75% of the indigenous lignite it's burned in thermal power plants for electricity generation [6]. The demand for raw chemicals and especially electricity is growing rapidly due to economic and social development of country. Most of the Turkish lignite (approximately 68%) are poor quality containing considerable amount of sulphur. That is why the conversion of lignite into valuable liquid and gaseous compounds is of crucial importance. Pyrolysis is regarded as an additional method of producing of liquids from lignite besides gasification. But there are limited investigations about importance of lignite as a chemical feedstock in Turkey. Most of pyrolysis studies with Turkish lignites were concerned with co-pyrolysis, gasification, supercritical extraction and kinetics of pyrolysis processes [7–11]. Knowledge of the lignite pyrolysis is very important in the design and control of pyrolysis reactor, since the volatile yield, gas and liquid product composition as well as the calorific value of the lignite is strongly dependent upon the pyrolysis behavior of lignite in a fixed bed reactor [12].

Lignite is the most abundant and important energy source of Turkey, which is why it is very important to understand the pyrolysis behavior of lignites from the significant lignite deposits in Turkey. This paper is related to the slow pyrolysis of the less studied low rank lignites from Turkey (Ermenek and Uzunköprü) and investigates the effect of temperature and thermal behavior of the lignites during pyrolysis as the main parameters. In this study, the temperature programmed pyrolysis of lignites was investigated by using an efficient technique. The volatile product distribution profile and product evolution rate were determined by using a simple and special sampling technique for collecting pyrolysis products eluted from the reactor at different desired temperatures and times. The paper also aims at the elucidation of the temperature at which product evolution rate is maximum and the distribution of n-paraffins and 1-olefines in the pyrolysis product at different temperatures. n-Paraffins and 1-olefines are classified by carbon number at each desired temperature. Also, the formation rates of volatiles and the product yields of hydropyrolysis of Turkish lignite under similar conditions were compared with those of pyrolysed under inert atmosphere.

2. Experimental

2.1. Materials

Two lignite samples investigated in this study were obtained from Uzunköprü/Edirne (U) and from Ermenek/Karaman (E) in Turkey. The ultimate and proximate analyses of these samples are presented in Table 1. The content of volatile products of Uzunköprü lignite is very low. Kılıckalkan et al. has been found the similar data for this lignite [13]. The in air dried lignite samples were grounded in a jaw mill until desired particle size was obtained. The samples were homogenized and sieved to obtain a 0.1–1.0 mm fraction. Than the lignite samples were dried at 105 °C under nitrogen atmosphere. The dried particles were kept in tightly closed vessels until the pyrolysis experiments. Some experimental results of a Turkish lignite subjected to slow pyrolysis under pressure and to hydropyrolysis procedure were also used for comparison purposes.

Table 2
FT-IR spectrums of the Ermenek lignite and its pyrolysis liquids.

Wave number cm^{-1}	Spectrums			Bond type and functional groups
	Ermenek lignite	Liquid product at 400 °C	Liquid product at 500 °C	
3600–3200	s, i	s	w	O—H, S—H, N—H stretching
3080–3020	–	w	i	C—H stretching (aromatic)
2980–2900	n	i	n	C—H stretching (aliphatic)
2300–2200	i	n	i	C≡N stretching
1610–1550	i	n	i	C=C stretching (aliphatic, aromatic)
1460–1450	i	n	i	C—H bending
1280–1250	w	w	–	C—O stretching
1250–1020	i	w	–	Aliphatic and aromatic ether
850–700	w	n	i	C—H bending (aromatic compound)

s: splayed, i: intensive, n: normal, w: weak.

Table 3
FT-IR spectrums of the Uzunköprü lignite and its pyrolysis liquids.

Wave number cm^{-1}	Spectrums			Bond type and functional groups
	Uzunköprü lignite	Liquid product at 400 °C	Liquid product at 500 °C	
3600–3200	s	s	n, w	O—H, S—H, N—H stretching
3080–3020	i	i	i	C—H stretching (aromatic)
2980–2900	i	i	i	C—H stretching (aliphatic)
2300–2200	n	n	s	C≡N stretching
1610–1550	i	n	i	C=C stretching (aliphatic, aromatic)
1460–1450	n	i	s	C—H bending
1280–1250	o	w	w	C—O stretching
1250–1020	n	n	i	Aliphatic and aromatic ether
850–700	i	i	i	C—H bending (aromatic compound)

s: splayed, i: intensive, n: normal, w: weak.