Proceedings of the Seventh IASTED International Conference
POWER AND ENERGY SYSTEMS
August 29–31, 2007, Palma de Mallorca, Spain
ISBN Hardcopy: 978-0-88986-689-8 / CD: 978-0-88986-690-4

THE EFFECT OF MIXING RATIO ON CO-PYROLYSIS OF LIGNITE AND RAPESEED

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ABSTRACT

The biomass and coal mixtures were subjected to fast pyrolysis process to produce biooil. The biooil yield was in the range of 11.573.1wt%. depending on the percentage of biomass and coal in the mixture. On the other hand, considerable synergetic effects were observed during the copyrolysis in a fixed bed reactor leading to increase in oil yield. Maximum pyrolysis oil yield of 73.1% was obtained with 5wt% of lignite mixed with rapeseed, as compared to the expected ones, calculated as the sum of oil fractions produced by pyrolysis of each separated component. The obtained oils are characterized by FTIR, ^{1}H NMR, and elemental analysis.

KEY WORDS

Co-pyrolysis; Bio-oil; Rapeseed; Lignite

1. INTRODUCTION

The development of new technologies and increase of population make the search for new energy sources a major concern. Traditional energy resources have diminished in the last decades, and in consequence, there is a big interest in the production and use of renewable energy sources. Among the latter, biomass is one of the most important [1].

Co-utilization of biomass and coal fuels has been popular in recent years because of its potential benefits for both the environment and the economics of power generation. On one hand, biomass is considered CO2 neutral and can inherently reduce the net CO2 production when it is used with the primary fuels. On the other hand, if the biomass processing cost can be well-controlled, the total fuel costs can also be greatly reduced [2].

Coal is dominant energy sources in Turkey. Lignite has the biggest share in total primary energy production at 43%. Total lignite reserves are estimated at 8075 million tons, of which 7339 million tons are economically feasible. The electricity generation sector represents the major energy consuming sector in Turkey's lignite consumption [3].

Turkey also has a large potential for renewable energies. Turkey's geographic location has several advantages for extensive use of most of the renewable energy sources. The annual biomass potential of Turkey is approximately 32 million tones oil equivalents (Mtoe). The total recoverable bioenergy potential is estimated to be about 16.92 Mtoe [4]. Turkey's geographic and climatic conditions are suitable for growing field crops. Based on the total production of field crops (45 million tons) and oil-seeds (2.5 million tons) it is estimated that 5760 million tons of agricultural residues are produced annually in Turkey [5].

Pyrolysis of biomass can be described as the direct thermal decomposition of the organic matrix in the absence of oxygen to obtain an array of solid, liquid and gas products. The pyrolysis method has been used for commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feedstocks. Conventional pyrolysis consists of the slow, irreversible, thermal decomposition of the organic components in biomass. Slow pyrolysis has traditionally been used for the production of charcoal. Short residence time pyrolysis (fast, flash, rapid, ultrapyrolysis) of biomass at moderate temperatures has generally been used to obtain high yield of liquid products. Fast pyrolysis is characterized by high heating rates and rapid quenching of the liquid products to terminate the secondary conversion of the products [67]. In view of the biomass and coal, their thermochemical co-conversion seems to be an attractive way of use and utilization. Several works on the copyrolysis of biomass and coal have been done recently [812].

To our knowledge, there are no investigations on the copyrolysis of rapeseed and lignite, the yield and the chemical structure of the liquid products. The primary objective of this study was to determine the influence of lignite on the yield and chemical structure of biooil produced from rapeseed during fast pyrolysis.

2. EXPERIMENTAL

2.1 Materials

The rapeseed (Brassica napus L.) and lignite sample investigated in this study has been taken from vicinity of Erzurum and KutahyaSeyitömer region, was located in east and central Anatolia, respectively. Prior to use, the sample was air dried, grounded in a highspeed rotary cutting mill. Particle size range was between +0.51.0 mm for lignite and +0.60.85 mm for rapeseed. Some characteristics of the used rapeseed and lignite are given in Table 1.

Table 1. Main characteristics of the rapeseed and lignite

Characteristics	**Lignite**	**Rapeseed**
Proximate analysis *(wt.%,as received)*		
Moisture	11.2	5.3
Volatile	32.7	81.2
Fixed C	16.5	7.9
Ash	39.6	5.6
Elemental analysis *(wt%, daf.basis)*		
Carbon	35.6	63.1
Hydrogen	3.1	9.3
Nitrogen	-	3.7
Sulphur	0.6	-
Oxygen *(by difference)*	60.7	23.9
Empirical formula	$CH_{1.05}N_{0.0}O_{1.28}$	$CH_{1.77}N_{0.05}O_{0.28}$
H/C molar ratio	1.05	1.77
O/C molar ratio	1.28	0.28
Calorific value(MJ/kg)	6.6	30.45

Rapeseed, lignite and their mixtures were pyrolysed in a wellswept resistively heated fixedbed reactor with a length of 90 cm and an inner diameter of 8 mm, made of 310 stainless steel. Three grams of airdried sample, was placed in the reactor (bed height: 11 cm) and sweep gas velocity of 100 $cm^3 min^1$ was controlled and measured by a rotameter. The temperature was raised 300°$Cmin^1$ to the final temperature of either 400, 500, 550, 600 or 700°C and held at that temperature for 10 min. Heating rate and pyrolysis temperature were controlled by a PID controller. The flow of gas released was measured using a soap film for the duration of the experiments. 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. The weight gains for the liquids trap were corrected for the amounts of water present to give the actual oil yields. Water was determined by refluxing the toluene solution in a Dean& Stark method. Gas yield was determined by overall material balance. This reactor has been described previously [1314]. For these experiments %50 blending ratio of rapeseed (weight of rapeseed in the blend expressed as a percentage of the total sample weight) was used.

In order to establish the effect of blending ratio on the pyrolysis yields, experiments were conducted at a range of blending ratios (weight of coal in the blend expressed as a percentage of the total sample weight) between 0% and 100% (w/w). For all these experiments the final pyrolysis temperature and the heating rate were 550°C and 300°$Cmin^1$, respectively.In this study, all the yields are expressed on a dry ash free (daf) basis and the average yields of at least three experiments within the experimental error of less than ±1%.

2.2 Characterization

A proximate analysis was carried out on the rapeseed. The carbon, hydrogen and nitrogen contents of the rapeseed and pyrolysis biooils were determined using a Fisions, EA 1108 Elemental Analyzer. The oxygen content of the rapeseed and biooils was found by difference. The calorific value of the rapeseed and pyrolysis biooils was determined. The values reported are the gross heat of combustion at constant volume. Functional group compositional analysis of the oils after removal of water was carried out using Fourier transform infrared spectrometry. A Perkin Elmer FTIR Spectrometer Spectrum 2000 was used which had data processing and spectral library search facilities. A small amount of the oil was mounted on a KBr disc which had been previously scanned as a background. The infrared spectra of the sample were then taken. The ^1H NMR of the oils was obtained at an H frequency of 500 MHz using Bruker BioSpin GmbH instrument. The sample was dissolved in chloroform-d.

3. RESULTS AND DISCUSSION

The influence of pyrolysis temperature on the products yields has been studied using mixtures of 50% blending ratio of rapeseed. Fig.1 shows that the conversion degree increases slightly with the temperature in the studied range (400700°C). The main effect of temperature increase is higher amounts of gas and oil, whilst the yields of char continuously decrease. As the pyrolysis temperature increased to e level of 550°C the liquid product yield reached the highest value of 37.9wt%, but further increasing the temperature to 700°C the oil yield decreased and gas yield increased. The obtained results could be explained by the cracking of oil from coal and biomass to gas at temperature above 550°C.

The influence of biomass/coal composition on the co-pyrolysis products yield was investigated at 550°C. The productions of char, oil and gas yields were plotted against the blending ratio of coal in Fig.2.

It can be seen that the yields of both conversion and oil increase with the biomass concentration. But distribution between conversion and oil strongly depends on the blending ratio. In that case, the maximum yield of oil is obtained for 5% blending ratio of coal (73.1wt.%). Clearly, the yield of oil is higher, as compared to the expected ones (dashed line, Fig.2.) calculated as the sum of oil fractions produced by pyrolysis of each separated component.

At pyrolysis temperature of 550°C the copyrolysis of rapeseed and coal leads to production of more than 11% (in mass) of oil for 5% blending ratio of coal, whatever the origins of studied raw materials.

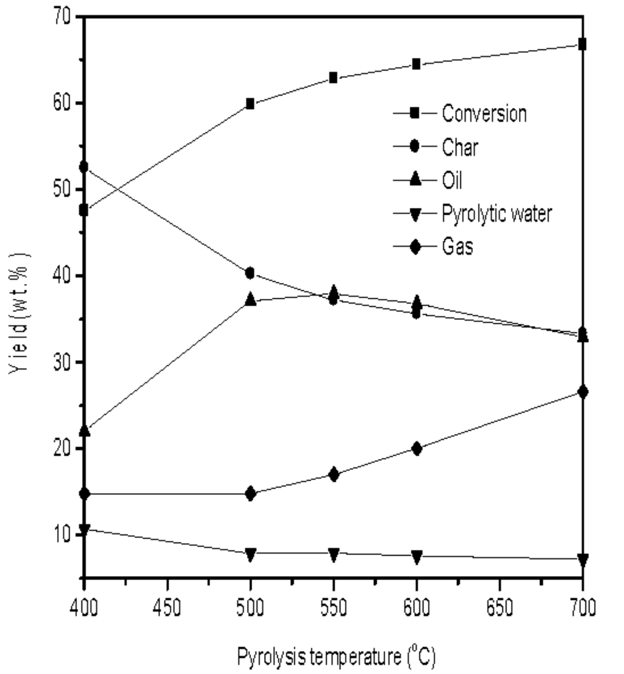

Fig.1. Effects of pyrolysis temperature on the copyrolysis products at 50%(w/w) blending ratio of rapeseed

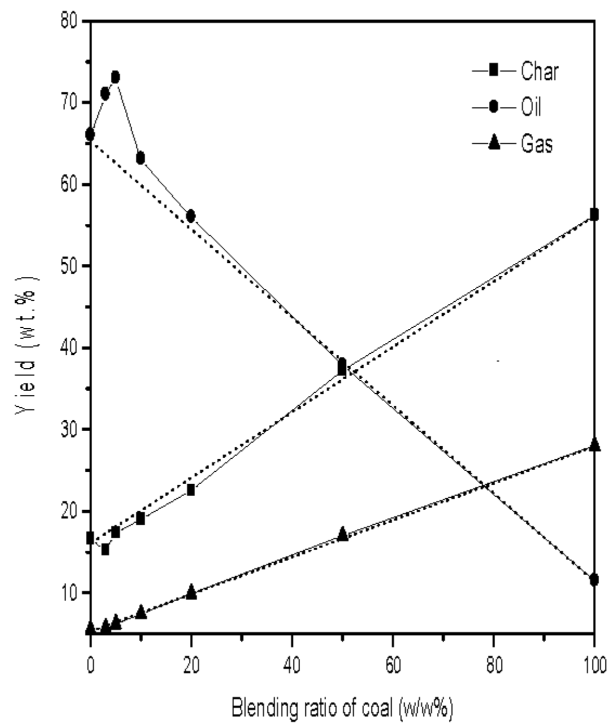

Fig.2. Effects of blending ratio of coal and rapeseed on the production of the copyrolysis products at pyrolysis temperature of 550°C. The dashed lines represent the theoretical additive evolutions of the products.

Table 2. The elemental compositions and calorific values of pyrolysis oils

Elemental analysis[a]	Lignite	5% Lignite	Rapeseed
C	80.1	77.7	73.1
H	11.2	11.9	11.5
N	0.5	2.3	4.7
S	0.6	-	-
O[b]	7.6	8.1	10.7
H/C molar ratio	1.68	1.84	1.89
Calorific value (MJkg^{1})	41.9	42.0	39.4

[a] Weight percentage on dry ash free basis
[b] By difference

The properties of oils are given in Table 2. As it can be seen in Table 1 and 2, oils contain less amounts of oxygen content than that of the original feedstock. The significant decrease in oxygen content of the oil compared to the original feedstock is important, because the high oxygen content is not attractive for the production of transport fuels. Further comparison of H/C ratios with conventional fuels indicates that H/C ratios of the oils obtained in this study lie between those of light and heavy petroleum products. It can be seen in Table 2, 5% blending ratio of coal at the copyrolysis conditions in removing the oxygen from the biomass derived pyrolysis oils is evident from the much reduced oxygen content of the oils.

Functional group compositional analysis was determined by FTIR spectrometry and results are shown in Fig 3.The OH stretching vibrations between 3200 and 3400 cm^{1} indicate the presence of phenols and alcohols. The CH stretching vibrations between 2800 and 3000 cm^{1} and CH deformation vibrations between 1350 and 1475 cm^{1} indicate the presence of alkanes. The C=O stretching vibrations with absorbance between 1650 and 1750 cm^{1} indicate the presence of ketones or aldehydes. The absorbance peaks between 1575 and 1675 cm^{1} represent C=C stretching vibrations indicative of alkenes and aromatics.

The ^{1}H NMR spectra of the oils and hydrogen distributions are given in Table 3. Results of the ^{1}H NMR analysis show that the oils mainly contain aliphatic protons at carbon atoms bonded to other aliphatic carbon atoms. The amount of aliphatic adjacent to oxygen decreased with copyrolysis. On the contrary, the co-pyrolysis oils contained more concentration of single ring aromatic compound than biomass pyrolysis oil.

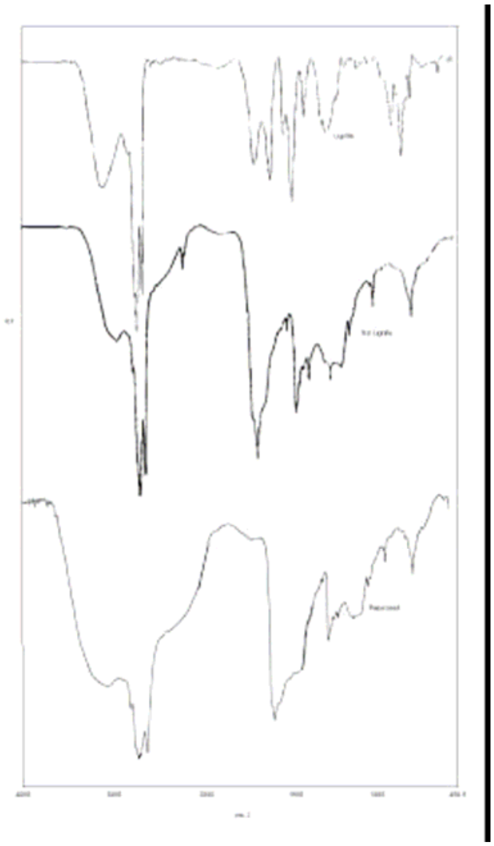

Fig. 3. The IR spectra of the pyrolysis oils

Table 3. ^{1}H NMR results of pyrolysis oils

Hydrogen environment	Range (ppm)	Sample (% in weight)		
		Rapeseed	5% Lignite	Lignite
Aromatic	6.3-9.3	1.1	3.9	14.8
Alkene	4.5-6.3	2.1	3.6	0.6
Aliphatic adjacent to oxygen	3.3-4.5	6.9	0.9	0.8
Aliphatic adjacent to aromatic-alkene group	1.8-3.3	14.4	19.3	21.3
Other aliphatic (bonded to aliphatic only)	0.4-1.8	75.5	72.3	62.5

4. CONCLUSION

In the present work, mixtures of rapeseed and coal can be radically converted to liquid products by pyrolysis under self pyrolysis atmosphere in Heinze retort. At pyrolysis temperature of 550°C the maximum yield of oil is watched. At this temperature, the most important parameter for the oil production is the blending ratio in feedstocks. For the experiments with coal less than 10wt.%, additive phenomena occur, leading to higher oil production. The yield of oil goes to a maximum of about 73.1wt.% for 5% blending ratio of coal in the experimental conditions used.

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