PRODUCING CARBONACEOUS PRODUCTS FROM *EUPHORBIA RIGIDA* BY PYROLYSIS

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Abstract

An arid land plant, euphorbia rigida was pyrolysed in a fixed bed reactor to obtain valuble solid and liquid products. Pyrolysis temperature, heating rate, sweeping gas flow rate were chosen as 550^{o}C, 10^{o}C/min and 50 cm^{3}/min respectively. Under these conditions, liquid product yield was attained to be 25 % whereas char yield was 20 %. Both liquid and solid products were characterized for their possible uses. Column chromatography was applied to liquid product to separate it into its aliphatic, aromatic and polar sub fractions. GC-MS chromatogram of liquid product was also taken to identify the chemical constituents of bio-oil and the presence of aliphatic, olefinic and phenolic compounds was observed. FTIR spectra of bio-oil and its subfractions were taken to specify functional groups. The chemical composition of the liquid product was also characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy. For the characterization of solid product, ultimate and proximate analyses were done and FTIR spectrum was taken. Thermo gravimetric analysis was carried out to monitor the thermal behavior of the char. Surface area and pore volume of the char was estimated by using BET and t-plot methods when nitrogen adsorption and desorption isotherms were taken at 77 K and surface morphology was obtained by SEM and EDX.

Introduction

The disposal of solid wastes such as biomass, industrial and municipal wastes is one of the main problems of the world and it is necessary to find out new ways to reuse this great potential as raw materials to produce advantageous products. Pyrolysis is one of the primary thermo chemical conversion methods to convert biomass into valuable products, namely; solid char, liquid and gas product yields and compositions of which depend on pyrolysis conditions [Bridgwater, A.V. and Grassi G., 1991; Mc Kendry P., 2002a; Mc Kendry P., 2002b]. Solid product, char, can be used as a fuel either directly as briquettes or as char-oil or char-water slurries since it has a high calorific value or it can be used as feedstock to prepare activated carbons [Suarez-Garcia F. et al., 2002; Encinar J.M. et al., 2000]. The liquid product, pyrolytic oil, approximates to biomass in elemental composition, and is composed of a very complex mixture of oxygenated hydrocarbons. It is useful as a fuel, may be added to petroleum refinery feedstock or upgraded by catalysts to produce premium grade refined fuels, or may have a potential use as chemical feedstock. Bio-oils are generally preferred products because of their high calorific values, their ease of transportation and storage, their low nitrogen and sulphur content and their opportunity to be converted into chemicals. The third product gas having a high calorific value may also be used as a fuel [Bridgwater, A.V. and Grassi G., 1991; Williams P.T. and Beşler S., 1993; Antal M.J., 1983].

There are a number of biomass feedstock such as forest residues, low-grade plants, agricultural residues and municipal solid wastes that can be utilised for energy purposes [Ates, F. et al., 2004]. The economics of biomass pyrolysis are generally considered to be most favorable for plants that grow abundantly and require little cultivation in arid lands. One group of plants is Euphorbiaceae, which are characterized by their ability to produce milky latex, an emulsion of 30wt% terpenoids in water. *Euphorbia rigida* (Euphorbiaceae family) is found around the Mediterranean from Morocco through Portugal to Turkey and Iran. It is known that 80 species of Euphorbia are found in Turkey. Previous studies showed that some species of this family have been identified as promising candidates for renewable fuels and chemical feedstock for the future [Ates, F. et al., 2005; Pütün, A.E. et al., 1996; Pütün, A.E. et al., 2001].

Objectives of this study are to characterize the liquid and solid products from the pyrolysis of *Euphorbia rigida* and to improve the quality of solid product for its possible utilization as carbon source.

Methods

Raw Material

The samples of Euphorbia rigida were collected from southwest Anatolia. Prior to the experiments,the sample was dried, ground in a high speed rotary cutting mill to obtain mean particle size. Proximate analysis was performed on the *Euphorbia rigida* sample to determine the weight fraction of volatile, ash, and fixed carbon contents. The weight fractions of carbon, hydrogen and nitrogen were determined; using Carlo Erba, EA 1108, and the weight fraction of oxygen was calculated by the difference. 13 C solid state NMR was also applied to raw material using Bruker BioSpin GmbH 300 MHz solid NMR spectrometer

Pyrolysis

Pyrolysis experiments were performed in a fixed-bed reactor, details were given in the previous studies [17, 18]. Pyrolysis temperature, heating rate and nitrogen gas flow rate were chosen as 550^{o}C, 10^{o}C/min and 50 cm^{3}/min respectively. After reaching the final pyrolysis temperature the reactor was set to cool to room temperature. Pyrolysis product yields were determined gravimetrically by weighing the three products. The liquid phase was collected in cold traps maintained at about 0^{o}C using salty ice. The liquid phase consisted of aqueous and oil phases were separated and weighed. Solid product, char, was removed from the reactor and weighed. The gas yield was calculated by the difference.

Bio-oil Characterisation

Elemental analysis was carried out with Carlo Erba, EA 1108 for CHNO determination. Chemical class compositions of the oil were determined by liquid column chromatographic fractionation. Bio-oil was separated into two fractions according to its pentane solubility. Silica-gel that was pre-treated at 105^{o}C for two hours prior to use was the packing material for the column. Pentane soluble part was further separated into aliphatic, aromatic and polar fractions using 200 ml of each pentane, toluene and methanol respectively. Each fraction was dried and weighed.

The FT-IR spectra of the oil and its aliphatic, aromatic and polar sub fractions were recorded using a Bruker Tensor 27 FT-IR analyser. GC-MS analysis of the bio-oil was performed using a Hewlett-Packard 6890 Model gas chromatograph equipped with a 5973 mass selective detector using HP 5 column. ^{1}H MNR and ^{13}C NMR measurements were carried out with Bruker BioSpin GmbH 500 MHz liquid NMR spectrometer.

Char Characterisation

The thermal behaviour of produced char (ERC) to 1050^{o}C was studied using Linseis Thermowaage L 81 thermogravimetric analyzer. The surface characteristics of the char was analysed using Scanning Electronic Microscope SEM EVO 50. Char was mounted on an aluminium stub using carbon film and coated with a thin layer of gold and palladium using Agar Sputter Coater.

To improve the quality of the produced char three different processes were applied. For this purpose ERC was mixed with either distilled water, 1 M HCl or 1 M NaOH and agitated for 24 hours at room temperature. Chars were filtered and washed with hot distilled water until pH 7 was reached. Processed chars were renamed as ERCW (water), ERCHCl (hydrochloric acid) and ERCNaOH (sodium hydroxide). The elemental analyses of all chars were performed with a Carlo Erba 1108 elemental analyzer. The BET surface areas of the carbons was obtained from N2 adsorption isotherm at 77 K with Quantachrome Autosorb 1. Outgassing was applied to about 50 mg of material for 15 hours at 130^{o}C.

Results and Discussion

Raw Material

The results for the proximate analysis of *Euphorbia rigida* are given in Table 1. Using elemental analysis results calorific value of *Euphorbia rigida* was calculated as ~16.7 MJ/kg from Du-Long's formula [Harker JH and Backhurst JR, 1981].

^{13}C CPMAS NMR spectrum of Euphorbia rigida sample is shown in Figure 1. Since biomass samples consist of mainly hemicellulose, cellulose and lignin, the presence of these structures can be seen from the figure. J.C.C. Freitas et al., 2001 have studied 13 C NMR of rice hulls and indicated that the main resonance lines occuring at about 105 ppm is for C-1; about 70-75 ppm is for C-2,3,5. From figure 1, it can be seen that slight resonance peaks between 110 and 156 ppm are due to aromatic carbons that might come from the presence of lignin.

Table 1. Properties of Euphorbia rigida

Analysis	**(wt %)**		**Component**	**(wt % daf)**
Moisture	3.0		C	53.6
Volatiles	76.2		H	8.3
Ash	6.5		N	2.2
Fixed carbon	14.3		O*	35.9

*Calculated from difference

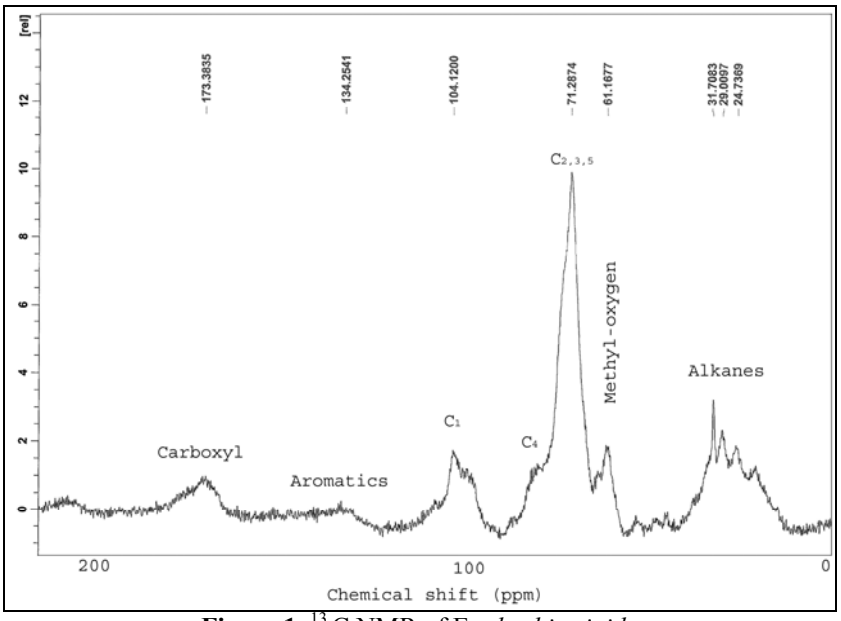


Figure 1. ^{13}C NMR of E*uphorbia rigida*

Pyrolysis

It is known from literature and previous studies that pyrolysis temperature plays an important role on product distribution and previous pyrolysis experiments with different types of biomass samples showed that highest bio-oil yield is reached at about 500 and 550^{o}C [Ates, F. et al., 2005;Özbay, N. et al., 2001; Putun A.E., et al., 2002]. Having this knowledge, pyrolysis of Euphorbia rigida under nitrogen atmosphere was held at 550^{o}C. Calculations for the product yields showed that 25 % of Euphorbia rigida was converted to bio-oil, 20 % to char, 20% to water and 35 % to gaseous products.

Bio-oil Characterisation

Biomass pyrolysis oils contain a very wide range of complex organic chemicals [Bridgwater, A.V. and Grassi, G., 1991] Elemental composition of bio-oil was determined to be 72.1 % carbon, 8.9 % hydrogen, 1.8 % nitrogen and the rest being oxygen. Bio-oil is characterised with a higher calorific value than the original biomass sample.

GC-MS chromatogram of the bio-oil is given in Figure 2. Library report for this chromatogram shows that this bio-oil is consist of mostly aliphatic, olefinic and phenolic compounds.

^{1}H-NMR and 13 C NMR spectroscopes were applied to bio-oil and the results are given in Tables 2 and 3. Both results were in consistency with each other, indicating that total aliphatics is the main part of the bio oil produced.

For characterization, bio-oil that obtained at 550^{o}C was taken and column chromatography was applied to separate it into its sub fractions. Chemical class fractionation of the oil; showing aliphatic, aromatic and polar fractions; are found to be 30.5 %, 26.5 % and 43 % respectively.

FT-IR spectra representing functional groups, of the bio-oil at 550^{o}C and its subfractions are given in Figure 5. The O-H stretching vibrations between 3200 and 3400cm^{-1} indicate the presence of phenols and alcohols. It is not surprising that these vibrations do not exist in aliphatic fraction since this fraction contains no highly oxygenated compounds. The C-H stretching vibrations between 2800 and 3000 cm^{-1} and C-H 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} and 875 and 950 cm^{-1} represent C=C stretching vibrations, and are indicative of alkenes.

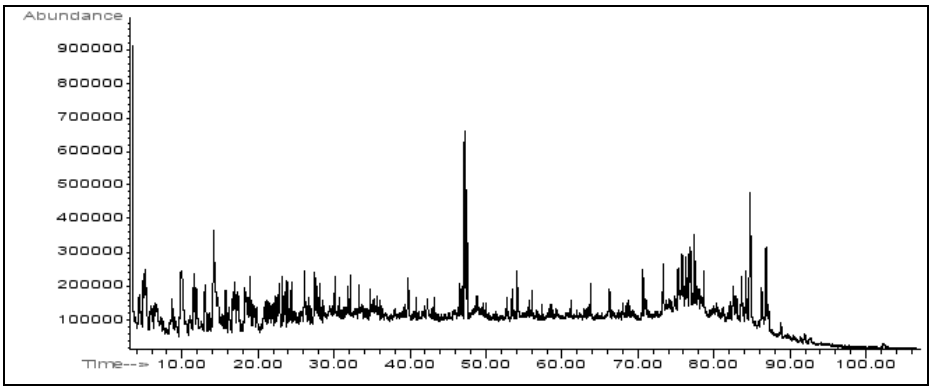


Figure 2. GC-MS chromatogram of bio-oil

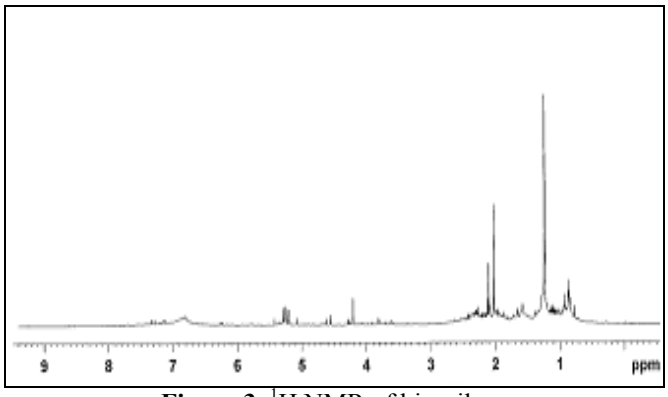


Figure 3. ^{1}H NMR of bio-oil

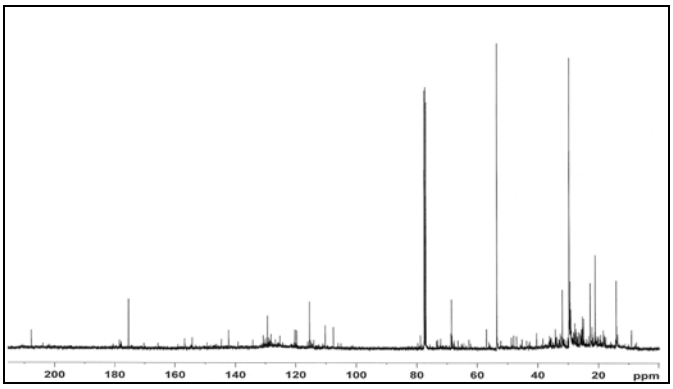


Figure 4. ^{13} C NMR of bio-oil

Table 2. Results of ^{1}H-NMR

Type of hydrogen	Chemical shift (ppm)	Bio-oil (%)
Aromatics or conjugated olefins	9.0-6.0	15.9
Phenolic (OH) and unconjugated olefins	6.0-4.0	6.4
Hydroxyl groups or ring-join methylene (Ar-CH_2-Ar)CH_3.CH_2 and CH α to an aromatic ring	4.0-3.0	3.3
Aliphatics (total)	3.0-0.5	74.4

Table 3. Results of ^{13}C-NMR

Type of carbon	Chemical shift (ppm)	Bio-oil (%)
Ketones or aldehydes	215-195	0.55
Esters	175-164	1.41
Aromatics or alkenes	156-104	11.11
Acetylenes	96-75	19.13
Methyl-Oxygen	56-44	18.77
Methyl, methylene, alkanes	42-4	49.02

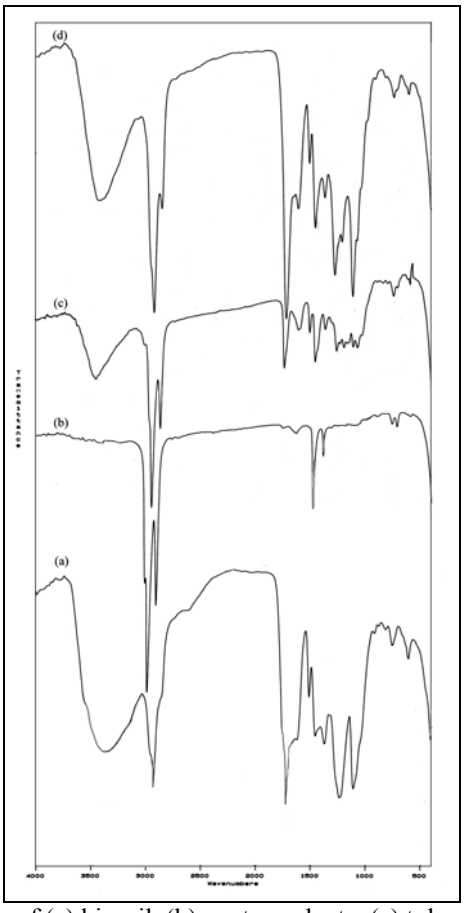


Figure 5 . FT-IR spectra of (a) bio-oil, (b) pentane eluate, (c) toluene eluate, (d) methanol eluate

Char Characterisation

Many analytical techniques can be applied to characterize the chars, looking for their possible uses. In this study char obtained from *Euphorbia rigida* (ERC) was characterised. To have information about the thermal behaviour of ERC, thermo gravimetric analysis was applied. As shown in Figure 6, a slight weight loss appeared initially that could be due to the elimination of water (~5.0 %). Second weight loss corresponds to main volatilization process, giving the volatile content of the sample as 71.50 %. After this major weight loss, there is essentially no further loss of weight. TG and DTG data showed that initial mass loss gives its maximum peak at about 100^{o}C. Second major weight loss starts at about 660^{o}C, having its first maximum as a shoulder at 722^{o}C and finishes at about 1050^{o}C.

For the characterization of chars, one of the important parameters is surface area or surface morphology. The surface area of char is important because, like other physico-chemical characteristics, it may strongly affect the reactivity and combustion behaviour of the char. BET surface area of ERC was found to be about 1.16 m^2/g and this value is very low when compared with other biomass chars. For this reason further processes were applied to char to get larger surface areas. Figure 7 gives the results of BET surface areas of ERC and processed chars versus their carbon content. From that figure, it can be seen that ERHCl having the highest carbon content gave the highest surface area as 33.59m^2/g. This means that hydrochloric acid treatment had the maximum influence to the increment of surface area. Sodium hydroxide treatment also affected the carbon content (67.1 %) and surface area (18.3 m^2/g) but when compared with water treated ERC there is no significant difference in the carbon contents and BET areas and hence it is not so proper to use sodium hydroxide as the activating agent for ERC.

SEM micrographs and EDX of ERC are given in Figure8. From the photograph, it can be said that porosity of the char is very low. EDX results showed that ERC contains mostly carbon, oxygen, magnesium, potassium and calcium. Inorganic elements are responsible for ash content of ERC. Since raw material contains 6.5% ash, it is not surprising to see that produced char contains significant amounts of inorganics.

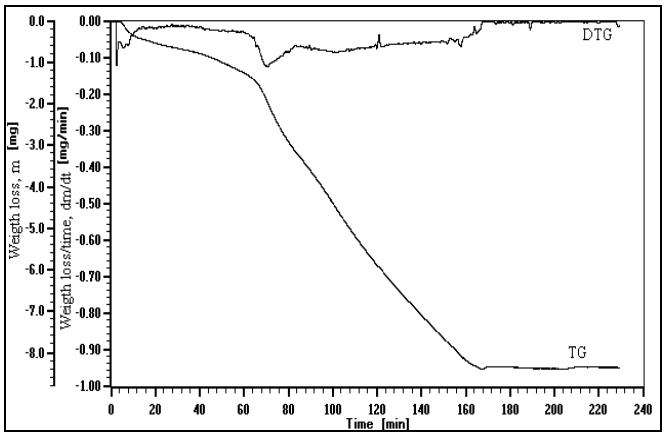


Figure 6. Thermal behavior of char obtained from pyrolysis of *Euphorbia rigida*

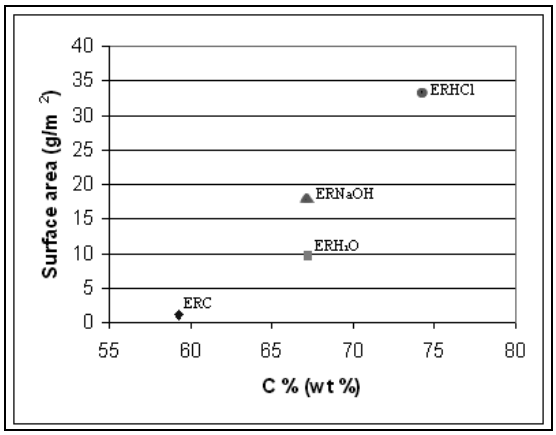
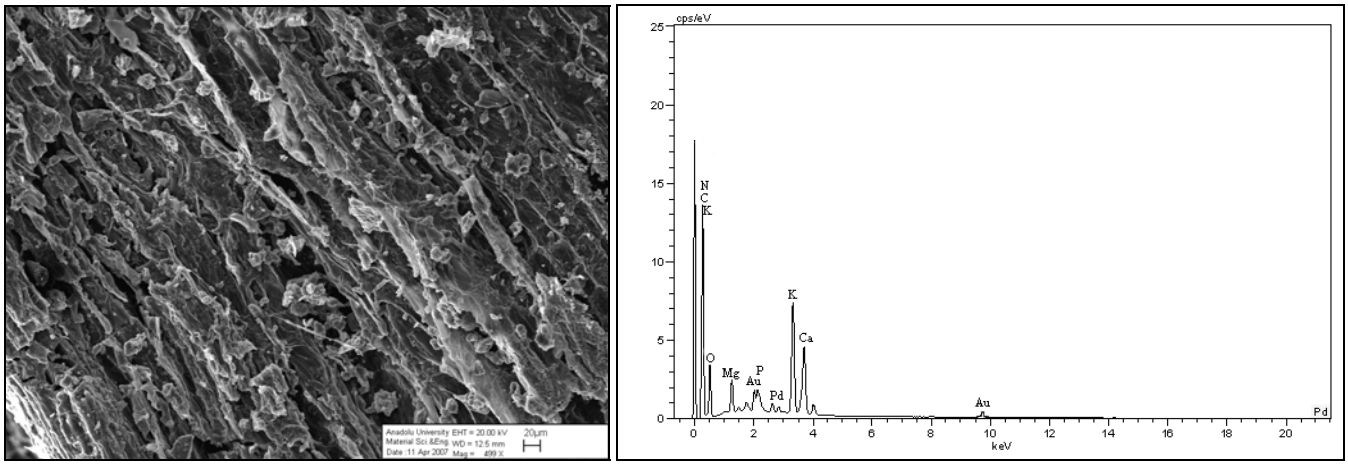


Figure 7. Surface area vs. carbon content of produced chars



(a) (b)

Figure 8. (a) SEM image, (b) EDX spectrum of char

Conclusion

In this study *Euphorbia rigida* samples were taken as the biomass for the pyrolysis experiments performed in a fixed-bed reactor with a heating rate of 10°C/min to 550°C when nitrogen gas was used as the sweeping gas. Under these conditions it was found that bio-oil yield was 25 %, char yield was 20 %, water yield was 20% to water and gas product yield was 35 %.

Characterization of the bio-oil has showed that it contains mainly aliphatic structures, and also contains hydrocarbons in aromatic and phenolic forms. Also according to elemental analysis results bio-oil has higher amounts of carbon then the original biomass sample.

Acidic basic and neutral treatments to improve the quality of the produced char were applied and experimental results gave that acidic media had great effect for the surface area and carbon content, whereas basic or neutral media had similar effects for carbon content. Hydrochloric acid treatment increased the carbon content of the produced char 25 %.

As a result producing carbonaceous liquid and solid products from an arid land plant, *Euphorbia rigida,* seems to be applicable when pyrolysis was applied.

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