

Catalytic pyrolysis of biomass in inert and steam atmospheres

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Abstract

The objective of this study was to investigate thermal conversion of a perennial shrub, *Euphorbia rigida* biomass sample with catalyst in inert (N₂) and steam atmospheres. Experimental studies were conducted in a well swept fixed bed reactor with a heating rate of 7 °C/min to a final pyrolysis temperature of 550 °C and with a mean particle size of 0.55 mm in order to determine the effect of different atmospheres with various catalyst ratios on pyrolysis yields and characteristics. The catalyst ratios were 5%, 10% and 20% (w/w) under nitrogen atmosphere with flow rates of 50, 100, 200 and 400 cm³/min and steam atmosphere with well-swept velocities of 12, 25 and 52 cm³/min. The optimum oil yield was obtained as 32.1% at the nitrogen flow rate of 200 cm³/min, while it was obtained as 38.6% at steam flow rate of 25 cm³/min when a 10% catalyst by weight according to the biomass was used. Higher oil yields were observed when biomass sample was treated in steam atmosphere than in inert (N₂) atmosphere. The oil composition was then analysed by elemental analyses techniques such as IR and GC–MS. The oil products were also fractionated by column chromatography. The bio-oils obtained at both atmospheres contain mainly *n*-alkanes and alkenes, aromatic compounds; mainly benzene and derivatives and PAHs, nitrogenated compounds and ketones, carboxylic acids, aldehydes, phenols and triterpenoid compounds. More oxygenated compounds and less substituted alkanes and alkenes were obtained in catalytic pyrolysis of *E. rigida* in the steam atmosphere. The experimental and chemical characterisation results showed that the oil obtained from perennial shrub, *E. rigida* can be used as a potential source of renewable fuel and chemical feedstock.

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1. Introduction

Renewable sources of energy are constantly examined as alternatives for fossil fuels. Biomass is one of the main renewable energy sources which are available, readily [1]. They have complex compositions, similar to petroleum. Its primary separation into the main groups of substances is appropriate. Subsequent treatment and processing of those substances leads to a whole palette of products. An important difference is that petroleum is obtained by extraction, whereas biomass already exists as product

mostly that of an agricultural substantial conversion process [2].

Pyrolysis is the thermochemical process that converts organic materials into usable fuels. During pyrolysis the successive reactions like cracking, isomerization, dehydrogenation, aromatization, and coking occurs, and gaseous products like H₂O, H₂, CO, CO₂, CH₄, C₂H₄, char, some organic compounds and liquids come into existence [3].

According to Babu and Chaurasia [4] a pyrolysis phenomena occurs in five steps: in the first step of the pyrolysis, the heat transfer occurs from a heat source, leading to an increase in temperature inside the fuel; in the second step, the volatiles released and char forms due to increased temperature; in the third step, due to the heat transfer between the hot volatiles and cooler unpyrolysed fuel volatiles outflow; in the next step, some of the volatiles condense to

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produce tar and in the final step due to these interactions autocatalytic secondary pyrolysis reactions occur.

Many pyrolysis conditions such as particle size, temperature, heating rate, residence time, catalyst, different atmospheres, biomass type and so on, strongly affect the yield and properties of products [5].

There is an extensive literature on pyrolysis of biomass. The objective of most of those studies, were obtaining alternative liquid fuels by decomposing of biomass samples at different pyrolysis conditions and the obtained chemicals were also investigated by various instrumental techniques [6–11]. According to the product yields and composition of the chemicals, it has been found that the most effective parameters for the pyrolysis process are pyrolysis temperature, reactor configuration, biomass type, catalyst and heating rate.

Wang et al., investigated effect of the low pyrolysis temperature (400–700 °C) and low heating rate (5–20 °C/min) on the pyrolysis characteristics of oil sludge in a horizontal quartz reactor. They have found that the optimum oil fraction conditions obtained at a pyrolysis temperature of 500 °C, retention time of 20 min at 400 °C and a heating rate of 10 °C/min. Three additives used in their work as catalyst did not improve oil product quality markedly although they promoted pyrolysis conversion significantly [7].

The *in situ* upgrading of biomass pyrolysis vapors with two mesoporous aluminosilicate materials assembled from zeolite Beta seeds was tested in another study [9], in comparison to conventional mesoporous aluminosilicate (Al-MCM-41) and to non-catalytic biomass pyrolysis. The experiments were performed on a fixed-bed reactor, and pyrolysis temperature was 500 °C in nitrogen atmosphere. Total organics and total liquid products in the Al-MCM-41 catalyst using system were greater than the non-catalytic system. Obtained products were analyzed using GC–MS while the hydrocarbons and heavy compounds were reduced, PAH's were increased in the Al-MCM-41 using system with respect to the non-catalytic system.

Influence of temperature (300–900 °C) and low heating rate (2–14 °C/min) on the fixed-bed pyrolysis of meat and bone meal was determined [10]. It was found that the effect of the final pyrolysis temperature is more important than the effect of heating rate and around 120 compounds have been detected in the tar obtained.

In another study, pyrolysis of southern pine, red oak and sweet gum sawdust was carried out in an inert atmosphere [6] and gas and liquid pyrolysis products were identified by GC–MS. Below 538 °C, the major liquid components were ketones, alcohols and cresols; however almost no hydrocarbons were present.

The pyrolysis studies which are conducted at steam atmosphere mainly focused on active carbon production [12,13]. Also obtained bio-oil product yields were compared with other bio-oil product yields produced in different atmospheres [14,15]. In these studies, bio-oil yields obtained under three different atmospheres (static, inert

and steam) were compared and the results showed that the bio-oil yields at the steam atmosphere were the greatest among those atmospheres.

For this purpose; at first stage of this study in inert and steam atmospheres with catalyst, the bio-oil yields were compared each other. In previous studies which are conducted at steam atmosphere, obtained bio-oil components have not been examined, especially. Because of this reason, the second stage of the study has been conducted to fill this gap.

Terpene hydrocarbons are high energy capacity hydrocarbons. Because of this they could be used as an engine fuel and as chemical feedstock. The most known terpenoid biomass is *Euphorbiaceae* family. Due to the growing of *Euphorbia rigida*, a member of *Euphorbiaceae*, on the arid lands of Middle Anatolia in abundant quantities and without any requirement of special labor, this has made this plant attractive as a new energy source. To date several studies have already been done on pyrolysis of this plant [16–20].

Consequently, the objective of this study was to investigate, by means of experimental studies, elemental analysis, IR, GC–MS and column chromatography, the influences of inert and steam atmospheres on the product yields and chemical characteristics of the oils and to compare the results obtained with each other.

2. Experimental

2.1. Materials

Fresh samples of *E. rigida* have been taken from southwest Anatolia. Before the experiments, the sample was dried, milled, sieved and then separated in fractions. Mean particles of biomass with a size of 0.55 mm were used. The main characteristics of the biomass sample pyrolysed: their proximate, ultimate (Carlo Erba, EA 1108) and component analyses were discussed detailed in our previous study [21].

Alumina was used as catalyst in the experiments. For its activation, the catalyst was calcinated at 400 °C for 3.5 h and kept in a desiccator for the experiments.

2.2. Pyrolysis

The pyrolysis experiments were performed using a fixed bed reactor. A detailed description of the pyrolysis experiments has already been reported elsewhere [21] and a schematic diagram of the unit is presented in Fig. 1. The 316 stainless steel reactor had a volume of 400 cm³ (70 mm ID) and was externally heated by an electrical furnace in which the temperature is measured by a thermocouple inside the bed. The connecting pipe between reactor and the trapping system was heated to 400 °C to avoid condensation of tar vapour.

The experiments were carried out under two different conditions: inert gas (N₂) and steam atmospheres.

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