Energy 64 (2014) 1002–1025

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Biomass pyrolysis in a fixed-bed reactor: Effects of pyrolysis parameters on product yields and characterization of products

Tevfik Aysu*, M. Maşuk Küçük

Yuzuncu Yil University, Educational Faculty, 65080 Van, Turkey

ARTICLE INFO

Article history:
Received 29 June 2013
Received in revised form
7 October 2013
Accepted 19 November 2013
Available online 16 December 2013

Keywords:
Energy
Biomass
Pyrolysis
Bio-oil
Giant fennel
Ferula orientalis L.

ABSTRACT

Slow pyrolysis of eastern giant fennel (*Ferula orientalis L.*) stalks has been performed in a fixed-bed tubular reactor with (ZnO, Al_2O_3) and without catalyst at six different temperatures ranging from 350 °C to 600 °C with heating rates of 15, 30, 50 °C/min. The amounts of bio-char, bio-oil and gas produced, as well as the compositions of the resulting bio-oils were determined by FT-IR and GC–MS. The effects of pyrolysis parameters such as temperature, catalyst and ratio of catalyst, particle size (D_p) and sweeping gas flow rate on product yields were investigated. According to results, temperature and catalyst seem to be the main factors effecting the conversion of *F. orientalis* L. into solid, liquid and gaseous products. The highest liquid yield (45.22%) including water was obtained with 15% zinc oxide catalyst at 500 °C temperature at a heating rate of 50 °C/min when $0.224 > D_p > 0.150$ mm particle size raw material and 100 cm^3/min of sweeping gas flow rate were used.

1. Introduction

In recent years, interest in renewable energies has increased due to environmental concerns about global warming and air pollution and the increasing demands of energy by the world. Among renewable energies, biomass is one of the most plentiful and well-utilised source in the world [1]. Biomass is defined as the plant material derived from the reaction between CO_2 in the air, water and sunlight by photosynthesis process which produces carbohydrates, the building blocks of biomass. Biomass resources include woody plants, herbaceous plants, aquatic plants and manures [2]. The obtaining of energy from biomass can be achieved in a number of ways which include production of crops, burning solid wastes, landfill gas and bio-oil production. In recent years, converting biomass to energy was centered mainly to biochemical and thermochemical processes. Of them, thermochemical processes can be subdivided into gasification, pyrolysis, carbonization, and direct liquefaction. Amongst the thermochemical processes, pyrolysis has received much more attention than others as its conditions could be optimized to produce high energy density pyrolytic oils as well as the derived biochar and gas [3]. Pyrolysis is defined as the thermal decomposition of biomass by heat in the absence of oxygen which produces solid (bio-char), liquid (bio-oil) and gaseous products. According to operating conditions, pyrolysis processes are generally divided into three sub-classes: conventional or slow pyrolysis, fast pyrolysis and flash pyrolysis. Conventional or slow pyrolysis is performed under the conditions of slow heating rates, low temperatures and, lengthy gas and solids residence times. This type of pyrolysis results in the production of solid, liquid, and gaseous products in significant amounts. If the aim is the production of mainly liquid and gaseous products, the preferred technology is fast or flash pyrolysis at high temperatures with very short residence times [4].

Biomass feedstocks, such as wood, agricultural and forest residues, energy plants, urban and solid industrial wastes, lumber and municipal wastes have attracted great attention as renewable energy sources in the worldwide. Turkey has high potential of agricultural renewable source with diverse crops production in 25 million hectares of arable land [3]. Numerous types of plants grow in the lands of Turkey and they could be used as a source of biomass for production of clean energy or chemicals [5–9]. One of them, commonly named as "eastern giant fennel", is *Ferula orientalis* L. is a perennial plant which grows in eastern region of Turkey with 2 m tall massive stalks and numerous clusters of yellow flowers. Essential oils of leaves and flowers of *F. orientalis* L. are used in folk medicine in a wide range. However, there is no single study of evaluation of its stalks which go dormant by midsummer and no value in terms of industrial respect in the literature. As one of the

* Corresponding author. Tel.: +90 432 225 17 02; fax: +90 432 225 13 69.
E-mail addresses: tevfikaysu@hotmail.com, tevfikaysu@gmail.com (T. Aysu).

0360-5442/$ – see front matter
http://dx.doi.org/10.1016/j.energy.2013.11.053

Table 1
Main characteristics of the *Ferula orientalis* L.

Components	
Moisture (%)	5.66
Proximate analysis[a] (%)	
Ash	4.85
Lignin	26.11
Cellulose	41.28
Hemicellulose	22.57
α-Cellulose	45.60
Soxhlet extractives (40–60 °C petroleum ether)	0.87
Ultimate analysis[b] (%)	
Carbon	44.408
Hydrogen	6.7357
Nitrogen	1.3257
Oxygen[c]	47.5306
H/C molar ratio	1.82
O/C molar ratio	0.81
Empirical formula	$CH_{1.82}N_{0.025}O_{0.81}$
Higher heating value (MJ/kg)	
Dulong's formula	16.16

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

abundant and fast growing plants found in many parts of Turkey, *F. orientalis* L. has been chosen with the idea of bio-oil and bio-char or chemical feedstock production from its stalks. Therefore, in this work, considering it as one of the promising species for bio-oil and bio-char production, we have performed the catalytic (ZnO, Al_2O_3) and non-catalytic slow pyrolysis of its stalks at six different temperatures between 350 and 600 °C. Effects of pyrolysis parameters such as temperature, types of catalyst, ratio of catalyst, heating rate were investigated. Furthermore, characterization of some of the selected products (bio-chars and bio-oils) obtained from pyrolysis has been carried out elemental, Fourier transform infrared spectroscopy (FT-IR), gas chromatography/mass spectrometry (GC–MS).

2. Materials and methods

2.1. Materials

F. orientalis L. plants were collected in an agricultural zones between the countries of Hamur and Tutak in Ağrı province of Turkey. They were harvested in May and the stems cleaned from leaves and tops and dried naturally in open air and then were ground, milled, and screen-sieved. Samples of different particle size ranging between 0.150 and 0.85 mm were used to in this study.

Ultimate and proximate analyses of the *F. orientalis* L. were performed. Ultimate analysis of the sample was carried out using an Elemental analyzer (LECO CHNS 932). The tests for determining the main characteristics of the *F. orientalis* L. were performed according to Tappi Test methods [10] . Lignin was determined according to Tappi T222. Hollocellulose and cellulose contents were determined using the chloride method [11] and Tappi T202 method. Ash and moisture contents were determined by Tappi T211 and Tappi T264 respectively. Higher heating value was calculated by Dulong's Formula. Fourier transform infrared (FT-IR) analysis of the *F. orientalis* L. was also carried out using a Varian model Scimitar 2000 to identify structural groups using potassium bromide as transparent pellets. The results of ultimate and proximate analyses of *F. orientalis* L. are given in Table 1. FT-IR spectra of raw material are given in Fig. 1. The raw *F. orientalis* L. was characterized by FT-IR in the middle region, including the wave

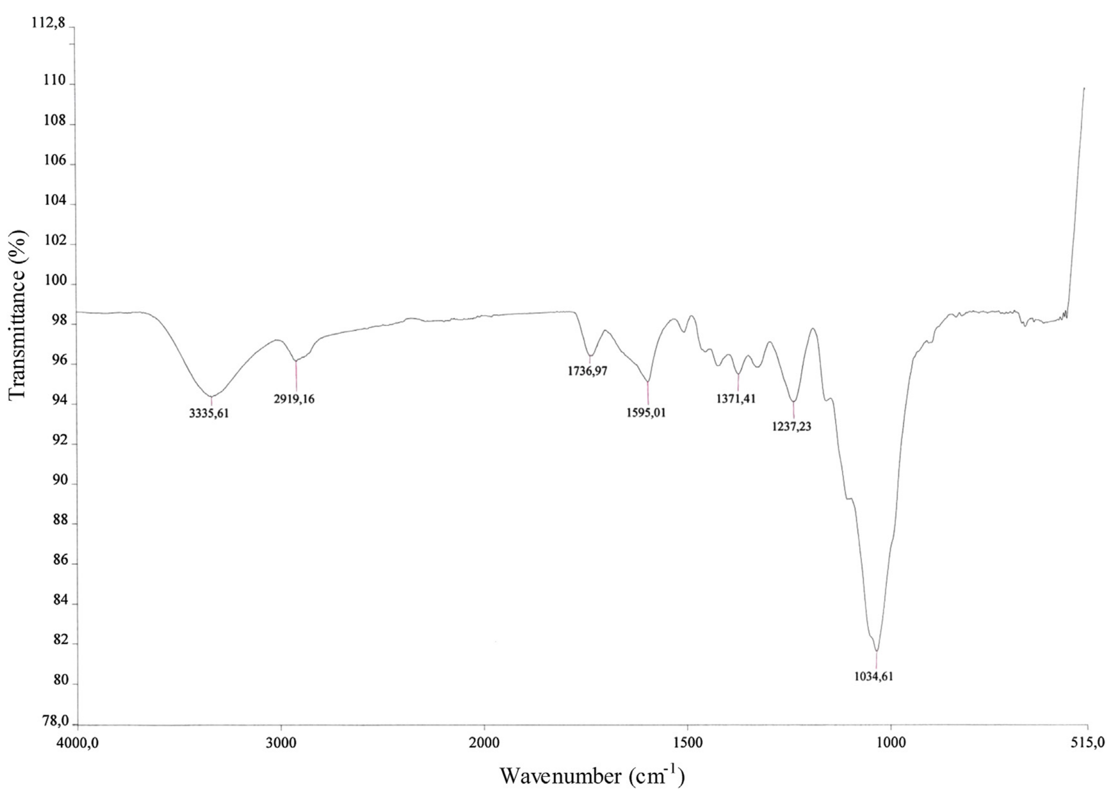

Fig. 1. FT-IR spectra of raw material (*Ferula orientalis* L.).