Research article

Fast devolatilization characteristics of 'low cost' biomass fuels, wood and reed. Potential feedstock for gasification

K. Anastasakis *, I. Kitsiou, W. de Jong

Faculty of Mechanical, Maritime and Materials Engineering, Process and Energy Department, Delft University of Technology, Leeghwaterstraat 39, Delft, 2628 CB, The Netherlands

ABSTRACT

Fast devolatilization of woody (mixture of softwoods) and herbaceous (reed) biomasses has been studied in a heated foil reactor coupled to an FTIR spectrophotometer. Biomass fuels were chosen based on their potential for contributing to power generation on an industrial scale through gasification in The Netherlands. Heating rate (600 °C/s) and holding time (10 s) at peak pyrolysis temperature were chosen to correspond to conditions encountered in industrial processes. The effect of peak pyrolysis temperature on pyrolysis products was investigated. Particular emphasis was given to tar collection, and subsequent gravimetric quantification. The results indicated a strong total weight loss increase with temperature, to reach an asymptote char yield of 16.7 wt.% at 800 °C and of 32.4 wt.% at 700 °C for wood and reed, respectively. Reed primary devolatilization reactions ceased at lower temperatures compared to wood. The latter was confirmed by the lower activation energy of reed (32.1 kJ/mol) compared with that of wood (38.4 kJ/mol) during extrapolation of kinetic data from the fast devolatilization experiments. CO_2 dominated the gaseous products released at lower temperatures (<700 °C) while CO became predominant at higher pyrolysis temperatures (>700 °C) reaching a maximum of 19.1 wt.% and 18 wt.% for wood and reed, respectively, at 1000 °C. Maximum tar yields of 38.8 wt.% (d.b.) of dry wood and 23.3 wt.% (d.b.)of dry reed were able to be recovered at 600 °C. An overall mass balance of approximately 90 wt.% (d.b.) for both biomass fuels was obtained at high (900–1000 °C) pyrolysis peak temperatures.

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1. Introduction

Gasification of biomass is an attractive option as a renewable energy conversion process. During gasification, biomass is converted into a gaseous fuel, the syngas, composed mainly of CO, CH_4, CO_2 and H_2. Syngas, after cleaning, can be directly used in gas engines/turbines for combined heat and power generation, as a feedstock for the production of synthetic liquid fuels via the Fischer–Tropsch process or for the production of methanol, synthetic natural gas and hydrogen. While being one of the promising thermochemical conversion technologies for biomass, commercialization of this technology poses some challenges. These challenges include the supply of biomass feedstock, the type of gasifier and its operating variables as well as the gas cleaning from tars and other contaminants [1].

One of the key aspects in both selection of suitable biomass feedstock and design of gasifiers is the investigation of the primary devolatilization (pyrolysis) process. During devolatilization, biomass is decomposed into gases (CO_2, CO, CH_4, H_2, H_2O, C_xH_y), condensable volatiles (tar) and a solid residue (char) which then undergo the gasification reactions. Reproducing industrial scale conditions is fundamental to generate reliable data for implementing into models for the design of a suitable

reactor. In this context, but as a separate thermochemical process as well, pyrolysis has received extensive investigation over the last 40 years.

Knowledge of the yields and composition of the main devolatilization products as a function of process conditions is crucial for the development and optimization of industrial thermal conversion applications. Hence, substantial focus has been directed towards studying the involved phenomena both in large and small scale setups. Up to now, biomass devolatilization carried out on a small scale has been studied in a variety of different setups including thermogravimetric analyzers (TGA), curie-point reactors, drop tube furnaces and heated grid reactors [2]. Among the different equipments, the heated foil (also named wire mesh, screen heater or heated grid reactor) setups are distinguished by their unique characteristics. The main advantage of this reactor type is that it is possible to reproduce similar conditions to industrial processes by employing very high heating rates (10^3–10^5 °C/s) and temperatures. Moreover, secondary reactions are minimized, since volatiles are immediately swept by some inert gas (i.e. helium or nitrogen) and condensed.

The heated foil reactor setups were initially used for studying coal pyrolysis [3]. However, research has also been carried out on various types of biomass in a number of works. An overview of the previous studies on fast devolatilization of biomass and biomass components in heated foil reactor setups is presented in Table 1. As it can be seen from the table, operating temperatures vary from 250 to 1300 °C and heating rates used are up to 15,000 °C/s. Holding times applied are

* Corresponding author.
E-mail addresses: K.Anastasakis@tudelft.nl, kanastasakis@gmail.com (K. Anastasakis).

Table 1
Overview of heated foil reactor setups used for fast pyrolysis experiments of biomass.

Year	Feedstock	T (°C)	Heating rate (°C/s)	Holding time (s)	Reference
1979	Kraft lignin	400–700	250	5–120	[4]
1982	Cellulose	300–1100	100–15,000	0–30	[5]
1985	Sweet gum hardwood	327–1127	1000	0	[6]
1991	Sugarcane bagasse, silver birch	300–900	1–1000	0–100	[7]
1993	Cellulose	400–1100	1000	0–5	[8]
1994	Pine wood	400–600	1–1000	10	[9]
1994	Sugarcane bagasse	300–1100	200–10,000	0–30	[10]
1996	Sugarcane bagasse, silver birch	300–900	0.1–1000	0–100	[11]
2008	Olive kernel	300–600	200	1.5	[12]
2008	Rapeseed residues	480–790	48	–	[13]
2009	Corn cob and corn stalk	360–730 / 380–680	52 / 45	–	[14]
2009	Olive kernel	300–600	200	1.5	[15]
2009	Pine wood	500–700	300–600	7–20	[16]
2009	Chicken litter, MBM	500–1300	600–1000	1–10	[2]
2010	DDGS, PKC	500–1200	600	10	[17]
2011	Pine wood	500–700	300–600	7–20	[18]
2011	MDF, bark pine, Avicel cellulose	435–1100	300–500	0–50	[19]
2012	Pine wood and model compounds	250–700	50–7000	1	[20]

BGS: brewer spent grains, MBM: meat &bone meal, DDGS: dry distiller grains with solubles, PKC: palm kernel shells, MDF: medium density fibreboard.

between 0 and 120 s to approach complete conversion. Even though research using those setups focused on several aspects of biomass devolatilization, and product yields as well as compositions were determined by various techniques, only a few of the works have dealt with determination of the produced tar. A common practice to determine tar content is by the difference of the other quantified phases (gases and char) from the initial mass. Hence, limited information on the effect of operating conditions on tar formation is available. Furthermore, the aim of most of the studies was to maximize liquid (tar) yields as the scope was to examine pyrolysis as a standalone process for the production of liquid fuels (pyrolysis oil). Therefore in many studies very high heating rates, short residence times and rapid quenching of the reactor have been employed.

The aim of this work is to investigate the devolatilization behaviour of some selected biomass fuels under conditions simulating industrial processes such as gasification and combustion. More specifically, the present study investigates the pyrolytic conversion behaviour of woody (mixture of softwoods) and herbaceous (reed) biomass fuels. The selected biomass fuels were chosen according to their availability and price in The Netherlands (for large scale utilisation). An attempt to quantify all product streams (including tar) and to close the mass balance is made. The effect of pyrolysis temperature on product yields (char, gas and tar) is under examination. Experimental data obtained by the present study are used to obtain kinetic parameters for total conversion and rates of gaseous species evolution under fast heating rate conditions. While there is a substantial amount of literature on fast pyrolysis of different types of wood biomass, literature data on fast pyrolysis of reed are scarce. The main objective of this study is to provide both experimental and kinetic data under fast heating rate conditions in order to advance the understanding of fast pyrolysis of the specific feedstocks and provide with data to be implemented in models for predicting thermochemical reaction behaviour.

2. Materials & methods

2.1. Proximate ultimate and biochemical analysis of the fuels

The biomass fuels under investigation were supplied by the Dutch company Synvalor, currently employing research on the development and deployment of a novel gasification reactor. More specifically, a mixture of waste softwoods from a furniture company and whole reed (leaves and stems) harvested from Dutch wetlands, used as feedstock for the gasifier, were under investigation. Harvesting reed from Dutch wetlands is a common practice occurring every 1–2 years in order to

avoid formation of forests, by removing nutrients from the ground. Prior to the experiments the biomass specimens were ground and sieved to powder with a particle size between 250 and 425 μm. In this way the soil particles present in reed samples could be removed. Subsequently the 250 and 425 μm particle size fraction was further ground and sieved to powder with particle size <90 μm. Proximate analysis of the fuels was performed by thermogravimetry. Thermogravimetric (TGA) and differential thermal (DTG) analysis were performed in nitrogen atmosphere using a TA-Instruments SDTQ600. A typical sample mass of 12–15 mg was heated to 900 °C at a ramp rate of 10 °C/min in a total flow rate of 100 ml/min. When the desired temperature (900 °C) was reached the atmosphere was switched from inert to oxidative in order for the burnout of any remaining carbon in the residue and thus ash determination. The C, H, N, S contents of the fuels were provided by the TLR international laboratories. For the calculation of the HHVs of the fuels the correlation provided by Channiwala and Parikh [21] was used. The proximate and ultimate analysis of the fuels is presented in Table 2. Wood was found to have a significantly higher calorific value than reed (20.6 MJ/kg and 11.4 MJ/kg, d.b., respectively) reflecting its higher volatile matter and lower ash content. Biochemical composition of the selected biomass fuels was determined according to the standard procedure for determination of structural carbohydrates and lignin in biomass (NREL/TP-510-42618) [22]. Extractives present in reed fuel were determined according to the standard procedure for determination of extractives in biomass (NREL/TP-510-42619) [23]. The biochemical composition along with the neutral sugars content of the fuels is presented in Table 3. Wood was found richer in cellulose and lignin while reed was richer in hemicellulose and extractives.

Table 2
Proximate and ultimate analysis of wood and reed fuels.

	Wood			Reed		
	a.r.	d.b.	daf	a.r.	d.b.	daf
Moisture[a] (wt.%)	7.9	–	–	8.8	–	–
Ash[a] (wt.%)	0.7	0.8	–	19.4	21.3	–
VM[a] (wt.%)	72.1	78.3	78.9	57.9	63.5	80.6
FC[a] (wt.%)	19.3	21.0	21.1	13.9	15.2	19.4
C (wt.%)	45.6	49.5	49.8	30.5	33.4	42.5
H (wt.%)	3.8	4.1	4.1	3.8	4.1	5.3
N (wt.%)	0.5	0.5	0.5	0.2	0.2	0.3
S (wt.%)	0.04	0.04	0.04	0.06	0.07	0.08
O[b] (wt.%)	41.6	45.1	45.5	37.2	40.8	51.9
HHV (MJ/kg)	16	17.7	17.9	10.8	12.3	16.1

[a] Calculated by TGA.
[b] Calculated by difference.