Industrial Crops and Products 58 (2014) 230–237

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Willow biomass as feedstock for an integrated multi-product biorefinery

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ARTICLE INFO

Article history:
Received 31 October 2013
Received in revised form 4 April 2014
Accepted 17 April 2014

Keywords:
Willow biomass
Thermophysical properties
Chemical and elemental composition
Biorefinery

ABSTRACT

Biomass has enormous potential for use in the chemical industry. It is a source of a large number of chemical components and manufactured products. Lignocellulosic biomass can be a source of high-value products produced on an industrial scale in a profitable way.

The aim of this study was to determine the chemical composition of seven varieties and clones of willow grown in the moderate climate of Europe and to choose cultivars which can provide a sufficient quantity of feedstock to operate an integrated multiproduct biorefinery. The biomass of the willow cultivars under study had good thermophysical compositions and they contained only small amounts of undesirable components (ash, sulphur, chlorine). The average higher heating value and lower heating value of willow biomass was 19.50 MJ kg^{-1} d.m. and 8.38 MJ kg^{-1}, respectively. The content and yield of cellulose and hemicelluloses in biomass of the UWM 006 and UWM 043 clones of *Salix viminalis* L. makes them highly useful for an integrated multi-product biorefinery, based on lignocellulosic raw material.

1. Introduction

The global consumption of energy, which is generated mainly from fossil fuels, is increasing. Fossil fuels are also the main feedstock in use by the chemical industry. The constant increase in their consumption and their shrinking resources are making them increasingly expensive (IEA, 2012). For example, the average price of oil supplied by OPEC countries increased from 23 to almost 110 USD per barrel between 2001 and 2012 (OPEC, 2013). Moreover, their production and use causes greenhouse gas emission, with a consequent increase in the greenhouse effect. The atmospheric concentrations of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) have all increased since 1750 due to human activity. In 2011, the concentrations of these gases exceeded the pre-industrial levels by about 40%, 150% and 20%, respectively. At the same time, global average temperatures have increased, each of the past three decades being warmer than previously (IPCC, 2013). These changes will have serious environmental effects: they will increase droughts, coral bleaching and influence crop productivity. Moreover, they have a dramatic effect on ice melting in polar zones and, consequently, rising sea levels and frequent occurrences of abnormal weather conditions (Watson and Albritton, 2001). Global efforts have been made to slow climate change and growing interest has been focused on using renewable resources to replace non-renewable products of the chemical and energy industry, which have an adverse impact on the environment.

Biomass has enormous potential for use in the chemical industry. It is a source of a large number of chemical components and products manufactured around the world. Lignocellulosic biomass can be a source of high-value products, such as: speciality cellulose and vanillin. Importantly, they can be produced on an industrial scale in a profitable way (Sjöde, 2013).

Lignocellulosic biomass is frequently obtained from forest wood and from wood industry waste. Directive 2009/28/EC introduced the minimum requirements for the sustainability of solid biomass, such as a ban on the production or acquisition of biomass in protected areas of unique natural value, primeval forests or areas of high biodiversity (European Commission, 2009). The European Union also intends to implement sustainability standards for solid biomass and to devote more attention to wood products originating outside its borders (Simmet, 2013). Since the forest resources in the EU are limited and its use is frequently unsustainable (e.g.

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http://dx.doi.org/10.1016/j.indcrop.2014.04.033
0926-6690/

long-distance transport), lignocellulosic biomass produced in agriculture is of increasing interest. Apart from agricultural residues, energy crops can also be used as feedstock in energy generation. Such crops with a stable yield and well-developed cultivation technology include: herbaceous plants (e.g. *Miscanthus giganteus*, giant reed, Virginia mallow) as well as short rotation trees and coppice (e.g. willow, poplar, black locust) (Angelini et al., 2009; Borkowska and Molas, 2012; Dini-Papanastasi, 2008; Wang and MacFarlane, 2012).

Trees and coppice of genus willow (*Salix* L.) can be grown in a short-rotation system. Such cultivation produces a high yield of dry biomass, which ranges from 10 to 20 Mg ha^{-1} year^{-1}. Among the characteristic features of willow crops are: uniform chemical composition and small amounts of contaminants and undesirable components (Stolarski et al., 2013b). Therefore, willow is a high quality uniform material, which can be harvested and subsequently stored before delivery to a biorefinery as needed. Therefore, wood can be successfully used as feedstock in an integrated multiproduct biorefinery (García et al., 2014; Krzyżaniak et al., 2013; Liu et al., 2012; Röser et al., 2011).

Many studies have been conducted worldwide on integrated multiproduct biorefineries. Among them there are research projects, advanced pilot installations and operating biorefineries. Eurobioref is a research project within which pilot installations are developed (FitzPatrick et al., 2010; Menon and Rao, 2012; Rødsrud et al., 2012; Star-COLIBRI, 2013; Thomsen et al., 2013). The project will develop a new highly-integrated and diversified concept, including multiple feedstocks (including lignocellulosic biomass), multiple processes (chemical, biochemical, thermochemical) and multiple products (aviation fuels and chemicals). This flexible approach will widen biorefinery implementation to the full geographical range of Europe and will offer opportunities to export biorefinery technology packages to more local markets and feedstock hotspots (EuroBioRef, 2013). Biorefineries set up as part of the project will use material obtained from oil crops, biowaste and lignocellulosic crops. The choice of feedstock will be suited to the local conditions.

The aim of this study was to determine the chemical composition of seven varieties and clones of willow grown in the moderate climate of Europe and to choose cultivars which could provide a sufficient quantity of feedstock to operate an integrated multiproduct biorefinery.

2. Material and methods

2.1. Field research

A willow plantation was established between the 11th and 20th of April 2010 at the Educational and Research Station in Łężany, owned by the University of Warmia and Mazury in Olsztyn. It is located in north-eastern Poland near Samławki village (53°59′N, 21°05′E). The main factor in the field experiment are three varieties and four clones of willow, all of them created by the Department of Plant Breeding and Seed Production of the University of Warmia and Mazury in Olsztyn: *Salix viminalis* varieties Start, Tur, Turbo; *Salix viminalis* clones UWM 006, UWM 043; clone UWM 035 *Salix pentandra*; clone UWM 155 *Salix dasyclados*.

The plant density was 18,000 per ha. A strip planting system was applied, in which 2 rows in a strip were arranged at an inter-row distance of 0.75 m, with an inter-row of 1.50 m for separation from the next 2 rows in a strip (with an inter-row distance of 0.75 m, etc.) and the distance between the plants in a row was 0.50 m.

After the third year of growth, in December 2012, willow plants were harvested with a Jaguar-Claas harvester. The harvester transported the chips on a tractor trailer. The trailer with chips from different cultivars was subsequently weighed and the yield of fresh biomass was calculated (Mg ha^{-1}). Next, the yield of dry biomass, (Mg ha^{-1}) was calculated from the moisture content and the fresh biomass yield. Biomass samples of seven willow varieties were collected for laboratory analyses. Fresh chips were collected from a tractor trailer. Subsequently, chips were transported on a tractor trailer, from which 10 one-litre primary samples of chips were taken from random places. Then, 10 primary samples were poured into one container, yielding an average sample. After this was mixed, a 3-litre laboratory sample was taken and transported to the laboratory of the Department of Plant Breeding and Seed Production of the UWM in Olsztyn. Subsequently, in the laboratory, analytical samples were made and each attribute was determined in triplicate.

2.2. Laboratory analyses

The biomass moisture content was determined in fresh willow chips in a laboratory, with the drying and weighing method according to PN 80/G-04511. The biomass was dried at 105 °C until a constant mass was achieved. After drying, the biomass samples were ground in an IKA KMF 10 basic analytic mill using a 0.25 mm sieve. The ash content was determined in the prepared analytical samples at 550 °C in an ELTRA TGA-THERMOSTEP automatic thermogravimetric analyser with the standard methods as follows: ASTM D-5142, D-3173, D-3174, D-3175, PN-G-04560:1998 and PN-ISO 562. Moreover, the higher heating value of dry biomass was determined in an IKA C 2000 calorimeter using the dynamic method, in accordance with the PN-81/G-04513 standard. The lower heating value of the fresh biomass was calculated on the basis of the higher heating value and moisture content of the biomass (Kopetz et al., 2007). The carbon, hydrogen and sulphur content were also identified by means of an ELTRA CHS 500 automatic analyser, according to PN/G-04521 and PN/G-ISO 35 standards. The nitrogen content was determined with the Kjeldahl method, using a K-435 unit and a B-324 BUCHI distiller and the chlorine content using the Eschka mixture. All of the analyses were performed in three replications.

The biomass for chemical analyses was prepared in accordance with PN-92/P-50092. Samples were ground in a laboratory mill (Fritsch type 15) using a sieve with 1.0 mm square screens. The material was passed through brass sieves to separate the 0.5–1.0 mm fraction. The chemical composition was determined with standard methods applied for wood chemical analysis. Before determination of the cellulose, lignin and holocellulose contents, extraction in 96% ethyl alcohol was performed in a Soxhlet apparatus according to TAPPI T 204 cm-07 (Baeza and Freer, 2000; Fengel and Wegener, 1989). Subsequently, the material was dried under laboratory conditions and the extracted substances (lipids, waxes, resins and others) were dried at 103 ± 2 °C and the contents of the following substances was determined: cellulose (with the Seifert method) (according to PN-92/P-50092), lignin with the Tappi T 222 om-06 method, using 72% H_2SO_4, pentosans (with Tollen's method) (TAPPI 223 cm-01), holocellulose (using sodium chlorite, according to PN-75/50092) (Rowell, 2005), base-soluble substances (1% aqueous solution of NaOH) according to TAPPI T 212 om-07, and the content of substances soluble in cold and hot water (TAPPI T 204 cm-07). Hemicellulose content was calculated as the difference between the content of holocellulose and cellulose. However, it must be stressed that this is a calculated, theoretical value. Additionally, pH was assessed according to PN-Z-15011-1. First, 50 g of the resource material was mixed in a conical flask with 200 cm^3 of distilled water. The flask, tightly closed, was put into a shaker and shaken for 0.5 h. It was then left for 1 h and the contents were stirred prior to the pH measurement. All of the tests were repeated