Energy Conversion and Management 153 (2017) 48–59

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Genetically engineered hybrid poplars for the pyrolytic production of bio-oil: Pyrolysis characteristics and kinetics

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ARTICLE INFO

Keywords:
TGA
Pyrolysis
Hybrid poplar
Model-free method
Reaction network
Kinetic model

ABSTRACT

In this study, hybrid poplars were genetically engineered to increase their biomass volume and change their biochemical composition to improve the pyrolytic production of bio-oil. Wild-type hybrid poplars (WT) and genetically engineered hybrid poplars (TP) were comparatively investigated with regard to their pyrolysis characteristics and kinetics via thermogravimetric analysis (TGA) and isothermal pyrolysis within a micro-tubing reactor. Model-free methods were used to determine the activation energy for the thermal decomposition of the WT and TP samples. The results showed that the activation energy of the WT sample was always greater than that of the TP sample at the same level of conversion. Isothermal pyrolysis experiments of the two biomass samples were performed at various temperatures (360–400 °C) and durations (1–5 min) using a micro−tubing reactor. The pyrolytic product distributions and chemical compositions were compared. The obtained results showed that the TP sample yielded a higher quantity of bio-oil compared to the WT sample under the same conditions with different chemical compositions. A reaction network and quantitative kinetic model were proposed for pyrolysis of the WT and TP samples. Kinetic parameters were obtained through an optimization function and used to explore the parameter space in order to predict product yields as a function of reaction time and temperature for both WT and TP feedstocks.

1. Introduction

Woody biomass, the most abundant naturally occurring resource, has gained popularity as an environmentally friendly, renewable, and sustainable resource for the production of biofuel. In particular, lignocellulosic biomass, composed primarily of cellulose, hemicelluloses, and lignin, is considered to be an economical and eco-friendly energy source, due to the fact that it is available in large quantities and that it does not compete with the food chain [1]. Pyrolysis of lignocellulosic biomass has attracted considerable interest specifically for the production of liquid bio-oil [2]. Research with regard to the thermal decomposition of lignocellulosic biomass as well as each component of lignin, hemicellulose, and cellulose has been extensively conducted for many years. Most studies have focused on the pyrolysis characteristics of biomass via TGA and the construction of a prediction model to allow for the ability to correctly capture the experimental TG curves during the pyrolysis of biomass [3–11]. Some other studies have focused on reaction pathways for the pyrolysis of biomass compositions. Dong et al. [12] reported possible pyrolytic pathways for the decomposition of lignin based on analyses of the products obtained from the pyrolysis of poplar wood. Shen and Gu [13] proposed a pyrolytic pathway for cellulose-derived pyrolytic products obtained from the degradation of pure cellulose compounds. Demirbaş [14] reported a pyrolysis mechanism for individual lignin, hemicellulose, and cellulose based on the relationship between these macromolecules and the pyrolytic products obtained through biomass decomposition. However, a systematic study has not yet been performed with regard to developing a quantitative kinetic model allowing for the ability to evaluate the contribution of each biochemical composition into a pyrolytic product.

Among the most promising lignocellulosic biomass resources, poplar trees (native cottonwood, aspen species, and its hybrids) are considered to be a valuable biomass feedstock because they can grow very fast and are also suitable candidates for genetic improvement with regard to bioenergy feedstock production due to their modest genome size [16,17]. Genetic modification could be a promising method to improve the characteristics of hybrid poplars through an increased growth rate, biomass volume, or change in its biochemical composition [18–20]. Van Doorsselaere et al. [19] produced a transgenic hybrid poplar (*Populus trichocarpa* × *P. deltoides*) by modified 5–hydroxyferulic acid O-methyltransferase (COMT) enzyme. The lignin of

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http://dx.doi.org/10.1016/j.enconman.2017.10.001
Received 9 August 2017; Received in revised form 20 September 2017; Accepted 2 October 2017

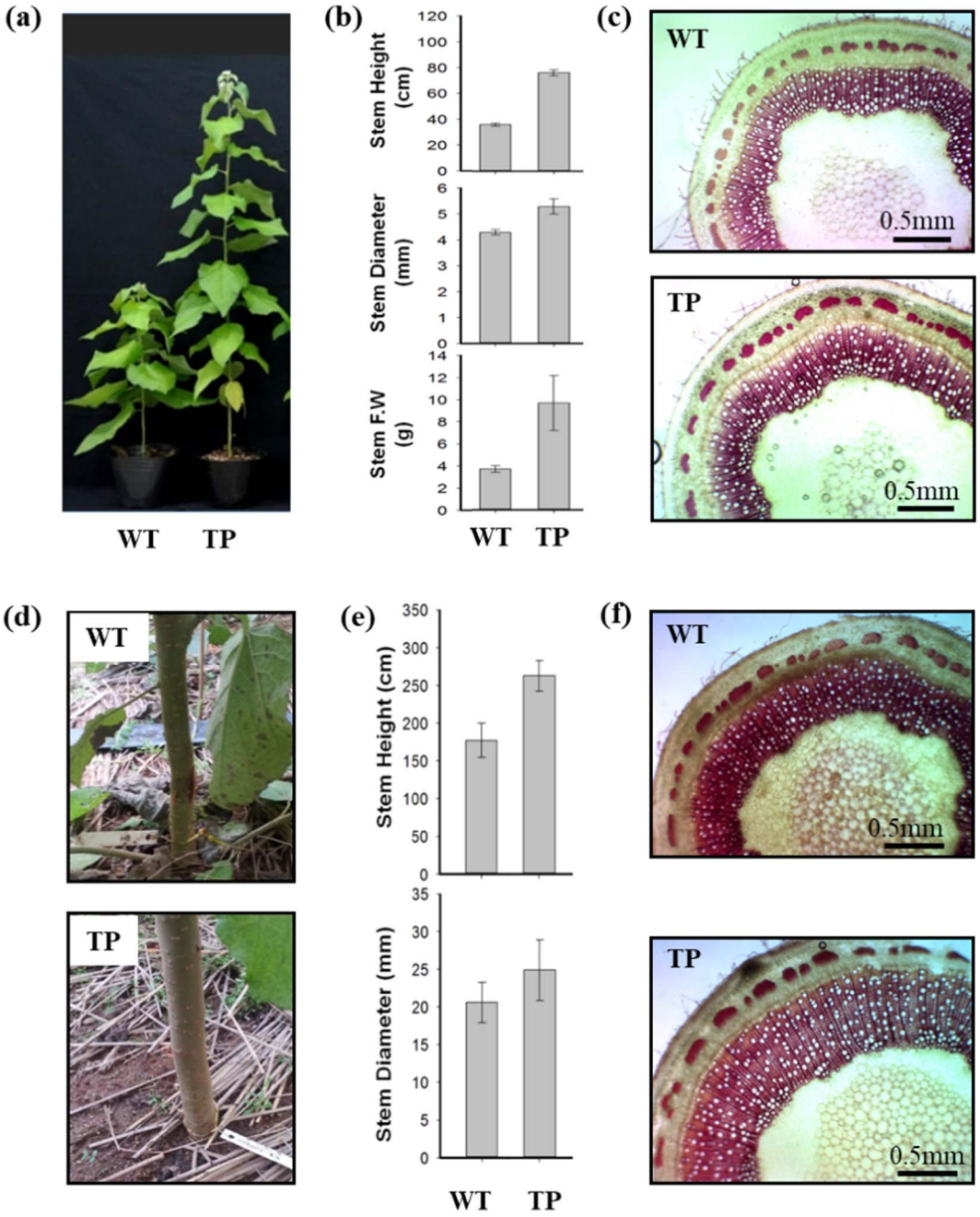

Fig. 1. Growth and histological characteristics of transgenic poplars (TP) compared to wild type poplars (WT) in two different growing conditions: (a–c) 60 days in pots, and (d–f) 3 months in LMO sites.

COMT down-regulated lines (ASB2B and ASB10B) presented about 85% decrease in syringyl/guaiacyl ratio as compared to the wild-type line, whereas their total lignin content was equal to that in the wild-type line [19]. Meyermans et al. [20] generated a transgenic poplar with 12% reduced Klason lignin content and 11% increased syringyl/guaiacyl ratio in the noncondensed lignin fraction by reducing 10% of Caffeoyl-coenzyme AO-methyltransferase (CCoAOMT) methylates, a precursor in monolignol biosynthesis *in vitro*. In our previous work, we demonstrated biotechnological improvement of woody biomass by employing developing xylem (DX)-preferential production of gibberellin (GA), a phytohormone that positively regulates stem growth [18]. The resulting transgenic poplar trees (DX15::PdGA20ox1) showed a dramatic increase in biomass, up to 300%, with accelerated stem growth and xylem differentiation [18]. However, pyrolysis utilization of those genetically modified biomass has not been investigated extensively yet. Since specific genetic modification of lignin composition, for example, is possible in hybrid poplar, the production strategies of specialty chemicals possessing a high economic value can be steered [21]. Very recently, Toraman et al. [2] reported the pyrolytic production of bio-based guaiacyl and syringyl lignin-derived phenolic compounds by using genetically engineered hybrid poplars.

Pyrolysis of hybrid poplar trees has attracted considerable attention in recent years. Özyurtkan et al. [22] investigated the effects of carbonization conditions of hybrid poplars such as the heating rate, particle size, and sweep gas flow using TGA method. The experimental results indicated that biochar yields decreased with an increased heating rate and sweep gas flow rate, but increased with an increase in particle size. Additionally, the kinetic parameters were also determined separately for the carbonization of cellulosic and lignin components of hybrid poplars. Xiang et al. [17] studied the kinetic mechanism with