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Variability in pyrolysis product yield from novel shrub willow genotypes☆

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ABSTRACT

Fast pyrolysis is becoming a more attractive conversion option for the production of biofuels, due to the potential for directly producing hydrocarbon fuels seamlessly compatible with petroleum products (drop-in fuels). Dedicated bioenergy crops, like perennial grasses and short-rotation woody crops, will be among the major sources of biomass for fast pyrolysis. To aid in the advancement of fast pyrolysis conversion and to identify appropriate feedstock crops, novel genotypes of shrub willow recently bred for high yield were evaluated for pyrolysis product yield using pyrolysis-gas chromatography-mass spectroscopy (py-GC/MS). The goal of this study was to understand how variations in biomass composition impact pyrolysis conversion efficiency and pyrolysis oil (bio-oil) quality by analyzing the composition of the pyrolysis vapors by py-GC/MS. The results of the py-GC/MS analysis showed significant differences in products from both non-catalytic and catalytic pyrolysis carried out over zeolite catalyst (HZSM-5), which were correlated with differences in biomass composition. For non-catalytic conversion, the most significant relationships were between the syringyl:guaiacyl (S:G) ratio in the biomass and phenolic monomers, in addition to levoglucosan yields and cellulose content. Production of phenols, guaiacols, and syringols were largely independent of total lignin content, but were strongly related to the S:G ratio. Willow genotypes with low ash content and high cellulose content produced more liquid products and higher levels of deoxygenated aromatics following catalytic pyrolysis. These results demonstrate that it is possible to breed for improvements in biomass compositional traits that can ultimately lead to improvements in bio-oil yield and quality.

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1. Introduction

Petroleum-based technology has been the major contributor to the world's economic growth within the past century. However, the extraction, transportation, and use of petrochemicals have put a huge stress on the environment. The production of biofuels and renewable feedstocks from locally grown agricultural crops and forest products and residues could help alleviate these problems. Conversion of biomass resources and dedicated energy crops can be accomplished through a number of processes including biochemical conversion and thermochemical conversion processes such as pyrolysis. Fast pyrolysis is a promising thermochemical conversion technology, in which the main product is bio-oil (pyrolysis oil), an energy dense liquid that can be refined to hydrocarbon fuel [1]. Examining the effects of feedstock type and upstream pretreatments on the chemical pathways of the conversion process could lead to improvements in bio-oil quality.

Biomass resources consist of multiple feedstocks from different plant materials and species. The diversity of feedstocks can prove challenging in the development of new conversion technologies due to the heterogeneity of the feedstock material (physical and chemical) and inconsistencies in supply. Understanding how chemical composition impacts pyrolysis oil yield and quality can be an added advantage to improving the overall performance and efficiency of the pyrolysis process and the downstream quality improvements, such as upgrading. Fast pyrolysis methods have been tested on a large number of feedstock types ranging from various grasses to woody plant material [1]. In general, herbaceous feedstocks have higher ash content and lower lignin content compared with woody feedstocks, which can lead to lower bio-oil yield [2].

In addition to differences among feedstock crop species, there are genotypic (within species) effects on pyrolysis product yields that must also be considered. Research in this area is limited, but the development of new cultivars through breeding has led to the characterization of many novel genotypes with regard to their conversion efficiency. Analysis of different *Miscanthus* species and genotypes revealed a relationship between cell wall compositional changes and pyrolysis product yield and the potential for new breeding strategies for *Miscanthus* cultivars [3]. Similar results were also achieved by examining fast pyrolysis products among near-isogenic brown midrib lines of maize [4]. Jeffrey et al. [4] suggest that it might be possible to predict phenolic compounds in the bio-oil based on cell wall composition, and that bio-oil quality improvements can be achieved through breeding.

These prior studies suggest that shrub willow (*Salix*), an emerging bioenergy crop in the US, could be tailored for its pyrolysis products through selective breeding. Shrub willow is an established energy crop in Europe [5–7], and breeding of shrub willow in the US, which began in NY in the mid-1990's, has led to the selection and commercialization of over 10 cultivars with production on marginal land typical of the northeast US [8]. Yields of current commercial cultivars average 11.5 Mg ha^{-1} yr^{-1} [9], while yield of new pre-commercial cultivars has exceeded 16 Mg ha^{-1} yr^{-1} [10]. Shrub willow is also being grown, harvested, and utilized as fuel in power plants in northern NY under the USDA Biomass Crop Assistance Program. In the region, its high yield on marginal land and ease of management make it a preferred crop from production of biomass feedstock.

The breeding and selection of shrub willow has produced new hybrid genotypes through intraspecific crosses, leading to significant improvements in biomass yield and pest and disease resistance, while maintaining a high level of genotypic variation in biomass quality traits, including wood density and cellulose and lignin content [11]. Many of the new progeny that have recently been evaluated display hybrid vigor associated with interspecific triploidy [10,12]. In addition, it has been shown that biomass traits are improved in these high-yielding willow triploids [12]. The chemical composition of plant biomass is highly variable and is dependent on genetic and environmental factors and the interaction of the two. Differences in chemical composition can have a significant impact on the quality of bio-oil produced through fast pyrolysis. In shrub willow, there is significant variation in biomass chemical composition that could easily be exploited in a breeding program selecting for these biomass traits, such that improvements in the bio-oil yield are realized [11–13]. To continue the improvement of this bioenergy crop it is imperative to evaluate new cultivars and genotypes with regard to their conversion efficiency and to identify biomass quality traits suitable for biofuels production.

The goal of this project was to evaluate how genotypic variation in shrub willow biomass composition impacts pyrolysis product yield and bio-oil composition by analysis of pyrolysis vapors through pyrolysis-gas chromatography-mass spectroscopy (py-GC/MS). This will allow for the identification of new genotypes most suitable for fast pyrolysis and bio-oil production. Pyrolysis product yields from non-catalytic and catalytic pyrolysis over popular zeolite catalyst, HZSM-5, were compared with the following biomass traits: cellulose content (%wt), lignin content (%wt), ash content (%wt), specific gravity (g cm^{-3}), and syringyl:guaiacyl content (S:G molar ratio). In addition, py-GC/MS product yields were used to develop predictive models for the determination of the S:G ratio in the lignin component in the willow biomass. In contrast to grasses, shrub willow biomass is similar to other angiosperm hardwoods in terms of lignin composition, consisting of mostly syringyl (S) and guaiacyl (G) units [14,15]. Hydroxyphenyl (H) units are present in most hardwoods, but in very small percentages, compared to grasses. These three units differ by methoxylation on the phenolic ring, with H units having no methoxyl groups, G units with one methoxyl group, and S units with two.

2. Materials and methods

2.1. Source material and tissue collection

The plant material obtained for analysis in this study consisted of 75 genotypes of shrub willow planted in a replicated trial (2008 Selection Trial) at Cornell University's New York State Agricultural Experiment Station in Geneva, NY (42°52′48″

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