

MOLECULAR BEAM MASS SPECTROMETRIC CHARACTERIZATION OF BIOMASS PYROLYSIS PRODUCTS FOR FUELS AND CHEMICALS¹

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ABSTRACTS

Converting biomass feedstocks to fuels and chemicals requires rapid characterization of the wide variety of possible feedstocks. The combination of pyrolysis molecular beam mass spectrometry (Py-MBMS) and multivariate statistical analysis offers a unique capability for characterizing these feedstocks. Herbaceous and woody biomass feedstocks that were harvested at different periods were used in this study. The pyrolysis mass spectral data were acquired in real time on the MBMS, and multivariate statistical analysis (factor analysis) was used to analyze and classify Py-MBMS data into compound classes. The effect of harvest times on the thermal conversion of these feedstocks was assessed from these data. Apart from sericea lespedeza, the influence of harvest time on the pyrolysis products of the various feedstocks was insignificant. For sericea lespedeza, samples harvested before plant defoliation were significantly different from those harvested after defoliation. The defoliated plant samples had higher carbohydrate-derived pyrolysis products than the samples obtained from the foliated plant. Additionally, char yields from the defoliated plant samples were lower than those from the foliated plant samples.

INTRODUCTION

The U.S. Department of Energy has embarked on a major program to explore alternate energy sources including biomass. Biomass is an attractive alternative energy source because if energy crops are managed sustainably, a fuel cycle results that will contribute little or no net greenhouse gases to the earth's atmosphere. Biomass feedstocks vary considerably in source and composition and some examples of biomass feedstocks are waste woods from the pulp, paper and lumber industries; demolition wood from urban areas; and agricultural residues and cultivated herbaceous and woody energy crops. It is projected that biomass energy could contribute 11 quads of the United States' energy requirement if all the biomass resources are fully developed [1].

To embark on a large scale production of biomass energy, the quality of the feedstock, that may be influenced by the time of harvest, must be assessed. Seasonal variations give rise to changes in nitrogen, minerals and carbohydrate content of the plants [2]. These changes in turn influence the pyrolysis pathways of the biomass feedstocks. Low alkali metal content of biomass species promotes cellulose decomposition pathways that favor levoglucosan formation whereas the high ash content of biomass favors hydroxyacetaldehyde and char formation reactions [3]. Similarly, a high nitrogen content of biomass favors char formation because of interaction between the amino acids and carbohydrate decomposition products [4]. Thus by judiciously selecting the harvest time of the biomass, it may be possible to influence the pyrolysis products of the feedstock.

In addition to feedstock quality, the conversion technology is equally important for a successful biomass energy program. Several technologies including pyrolysis, gasification, liquefaction and biochemical conversion are currently under development. Fast pyrolysis technologies are receiving considerable attention because they can produce a more dense and easily transportable fuel compared to the original feedstock. The pyrolysis oils can conceivably be used as a chemical feedstock for other processes.

Efficient pyrolytic conversion of biomass to fuels and chemicals requires a thorough understanding of the pyrolysis process and an efficient tool for analyzing the pyrolysis products. The molecular beam mass spectrometer (MBMS) is a unique tool that is capable of analyzing biomass pyrolysis products in real time. However, the MBMS alone offers only qualitative and semiquantitative capability, but when combined with multivariate statistical analysis, it offers a powerful tool to analyze biomass and other pyrolysis products.

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In this paper, we discuss the application of MBMS and multivariate statistical technique in the classification and analysis of biomass feedstocks harvested at different periods. The influence of harvest time on the pyrolysis products of the feedstocks is discussed. The goal of the study is to develop a rapid method for characterizing biomass and other feedstocks pyrolysis products.

MATERIALS AND METHODS

Pyrolysis of Biomass Feedstocks

The biomass feedstocks used in this study were supplied by subcontractors of the National Renewable Energy Laboratory (NREL), Biofuels Program. The following feedstocks (harvested in various parts of the contiguous USA) were used in this study: hybrid poplar (*Populus deltoides x nigra* var. *Caudina*), sericea lespedeza (*Lespedeza cuneata* var. *Seralata*), black locust (*Robinia pseudoacacia* L.), and switchgrass (*Panicum virgatum* L.). Hybrid poplar samples were harvested from section #11 of Rocksbury Township, Pennington County, MN in November 1991 and March 1992; sericea lespedeza samples were harvested in October and December 1992 and black locust samples were harvested from 9-year-old plants at the Hind's Research Farm near Ames, IA in the fall of 1991 and spring 1992. Switchgrass samples were harvested from a 6-year-old stand located on the Koemel ranch 7 km south of Stephenville, TX in October 1991 and August 1992. About 1kg of each feedstock was shipped to NREL where they were prepared for pyrolysis. The feedstocks were air-dried at room temperature for 4-7 days to facilitate milling because wet samples tend to heat up during milling. The samples were milled in a Wiley mill (Model 4) until all the material passed through a 2 mm screen. The ground materials were then sieved to -20/+80 mesh size and riffled to homogenize them. We stored the sieved samples in freezers until such time the analysis were performed. The moisture content of the feedstocks prior to pyrolysis was 5-7%.

Biomass samples (20-30 mg) were weighed in quartz boats in triplicates and pyrolyzed in a quench pyrolysis reactor. The reactor consisted of a quartz tube (2.5 cm inside diameter) with helium flowing through at 5 L/min (at STP). The reactor tube was interfaced with the orifice of the molecular beam mass spectrometer (MBMS), Extrel™ Model TQMS C50, for pyrolysis vapor analysis (see detailed description of the MBMS in [5]). The reactor was electrically heated and its temperature maintained at 550 ± 5 °C. The temperature profile of the biomass samples once introduced into the reactor, is unknown, although the pyrolysis reaction was completed in 50 s. Total pyrolysis time was 90 s (including the time the quartz boat heats up to 550°C), but the residence time of the pyrolysis vapors in the reactor pyrolysis zone was ~75 ms and this prevented secondary cracking reactions. The pyrolysis vapors were sampled through the MBMS orifice in real time. During the sampling process, the pyrolysis vapors underwent free-jet expansion during their passage through the orifice and this sufficiently cooled the pyrolysis vapors to prevent secondary reactions or condensations. The cooled pyrolysis vapors passed through a skimmer to form a molecular beam that was fed to a 22.5 eV electron impact ionization triple quadrupole mass spectrometer for real time analysis. Mass spectral data for 15-300 Da were acquired on a Teknivet Vector 2™ data acquisition system.

Multivariate Analysis of Data

Mass spectral data acquired from the pyrolysis process were analyzed by multivariate statistical techniques. The data were first normalized to the total ion current to account for the sample size variation. Data reduction and resolution were carried out on the normalized data using the Interactive Self-modeling Multivariate Analysis (ISMA) program. The correlation around the mean matrix was used to select the significant number of factors for resolution of the mass spectral data into compound classes (see details of this methodology in [6]). In this method, the data set was mean-centered by subtracting the mean from each mass variable. Each variable was weighted by its standard deviation so that all masses (both large and small) were equally important. This method was used to show the differences between the pyrolysis products of the biomass species and the influence of harvest time on the samples. On the other hand, the correlation around the origin matrix was used to extract the relative fractional concentration of compound classes in the biomass pyrolysis products. In performing factor analysis around the origin, the absolute magnitude of the relative abundance for each mass variable was also factor analyzed. However, each variable is weighted by the standard deviation so that each mass is equally important in this method as well. This is in contrast to factor analysis around the mean where only the differences between samples are used for factor analysis. The latter technique is used when only differences between samples are needed, while the former is used when fractional concentrations of components are to be determined. This can be confusing to the reader who is accustomed to factor analysis around the mean and viewing plots of factor score 1 versus factor score 2. When factor analysis around the origin is used, this same information is contained in factor scores 2 and 3, and factor score 1 contains the information about the mean of each variable. The number of factors selected for the analysis was limited to significant factors (eigenvalues >1). Factor scores from the analysis were presented in two-dimensional plots to show compositional differences between various biomass materials. Materials with similar mass spectral intensities form clusters in the factor space. The factor analyzed data were resolved into three components corresponding to lignin, hexosans and pentosans. These resolved pyrolysis products of the biomass

feedstocks were used to determine the influence of storage time on the composition of the biomass.

RESULTS AND DISCUSSION

Pyrolysis-molecular beam mass spectra (Py-MBMS) for the different biomass materials (hybrid poplar, black locust, sericea lespedeza, and switchgrass) that were harvested at two different times of the year show visual similarity for all the species except sericea lespedeza. The Py-MBMS spectra can be divided into three main classes representing pentosans with typical m/z 43, 85, 96, and 114; hexosans with typical m/z 31, 60, 73, 97, 126, 144, and 162; and lignins with typical m/z 124, 137, 150, 154, 167, 180, 194, 210, and 272. A small region, which is typical of phenolic esters and phenylpropane lignins (m/z 94, 120, and 150), is prominent in the switchgrass pyrolysis mass spectra.

The influence of harvest time cannot be readily discerned from visually inspecting most of the spectra of the feedstocks (see Figure 1a and 1b) except by multivariate statistical analysis. In the case of sericea lespedeza, the Py-MBMS from the two harvests are visually discernible (see Figure 2a and 2b). In Figure 2b, the pyrolysis products that derive from the carbohydrates are higher for the December harvest compared to the October harvest.

The Py-MBMS spectral data were further analyzed using the ISMA program to highlight the differences between the harvests. The analysis of the mass spectral data using the correlation around the mean matrix indicated that 87% of the variance in the data set could be explained using four factors. The four factors were used to perform factor analysis using a correlation around the origin matrix. The factor-score plot (Figure 3a) showed four main groups corresponding to hardwoods, switchgrass, the October sericea lespedeza harvest, and the December sericea lespedeza harvest. The repeatability of the pyrolysis runs is indicated by the triangles in the factor score plot. The variance diagram in Figure 3b also confirms the clusters in the factor score plot.

The different clusters shown in the factor space for the two sericea lespedeza harvests suggests that the pyrolysis products of these two feedstocks are different. The major difference between the pyrolysis products of the two harvests is the carbohydrate component of the feedstocks. The resolution of the pyrolysis spectra showed a relatively high concentration of carbohydrate component in the December harvest of the sericea lespedeza compared to the October sericea lespedeza harvest. This observation is similar to the seasonal carbohydrate cycles noted in deciduous trees in the temperate climate. Carbohydrate contents of stems and branches of deciduous trees are maximized near the time of leaf fall and start to decrease in late winter [2]. Although sericea lespedeza is technically not a tree, it is a woody shrub that defoliates in the fall like the deciduous trees. It is probable that the total reserve carbohydrate accumulation in this shrubby species follows a similar cycle to those observed for the trees.

In addition to the high carbohydrate content of the December sericea lespedeza harvest, the char produced during the pyrolysis was lower ($16.2 \pm 1.0\%$) than that for the October sericea lespedeza harvest ($21.4 \pm 1.0\%$). The difference in char yields was attributed to the significant differences between the nitrogen and ash contents of the two harvests. The October sericea lespedeza harvest had a high leaf to stem ratio (0.26) and consequently a high nitrogen content ($1.14 \pm 0.10\%$) compared to the December sericea lespedeza harvest that was defoliated and had a nitrogen content of $0.75 \pm 0.10\%$. The ash contents of the October and December sericea lespedeza harvests were 2.1 ± 0.3 and $1.3 \pm 0.4\%$ respectively. Both the nitrogen and ash components of the biomass are known to promote char formation. Nitrogen compounds are known to react with carbohydrate decomposition products during the pyrolysis process resulting in char [4].

For switchgrass samples, although the repeatability triangles do not overlap, the differences between the pyrolysis products of the two harvests appear to be very small and statistically insignificant. The factor analysis of the data indicates that the switchgrass samples have a higher concentration of components that are rich in m/z 120 and 150 compared to the sericea lespedeza and the woody species. These masses derive from phenolic ester units known to occur in grass lignins. Nitrogen (0.59 ± 0.08 and $0.56 \pm 0.066\%$) and ash (5.2 ± 0.4 and 4.8 ± 0.2) contents of the two harvest were similar, and hence char yields from both harvests were very similar (18.6 ± 0.3 and $18.4 \pm 1.4\%$).

Py-MBMS and factor analysis of the woody biomass species (black locust and hybrid poplar) indicated that there are no significant differences in the yield of pyrolysis products because of harvest time. The repeatability triangles overlap as shown in Figure 3a. The variance diagram also indicates that the hardwoods are richer in lignin components compared to the non-woody species (switchgrass and sericea lespedeza). The woody species have very strong peak intensities at m/z 138, 154, 167, 180, 194, and 210 which are typical lignin decomposition products. Nitrogen and ash contents of the woody species from the two harvests were very similar and hence the char yields were also very similar. Although seasonal variations in minerals, nitrogen, and reserved carbohydrates contents have been reported for hardwoods,

the influence of these changes on the pyrolysis products of the woody biomass feedstocks analyzed by our method appear to be minimal.

CONCLUSIONS

The multivariate analysis of the biomass feedstocks studied shows that the influence of harvest time on the composition of the biomass pyrolysis products is only significant for the herbaceous biomass feedstock (*sericea lespedeza*). The pyrolysis products of woody biomass feedstocks appear to be less affected by the time of harvest. Thus, for fuel production from *sericea lespedeza* this factor must be taken into account. Small changes in the biomass feedstocks can be detected by MBMS and their subsequent influence on converting the feedstocks to fuels and chemicals can be assessed. The Py-MBMS technique for analyzing biomass feedstocks has some advantages over conventional chemical analysis in that sample preparation is minimal, very small samples are required for analysis, pyrolysis time is very short, and the pyrolysis data is acquired in real time. This technique may also find application in coal and other fossil fuel analysis.

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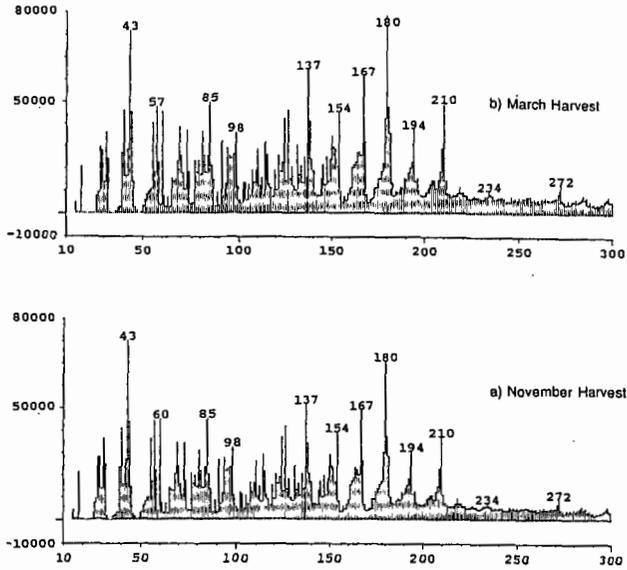


Figure 1. Pyrolysis mass spectra of hybrid poplar. Note the strong similarity in the spectra of a) the November harvest, and b) the March harvest.

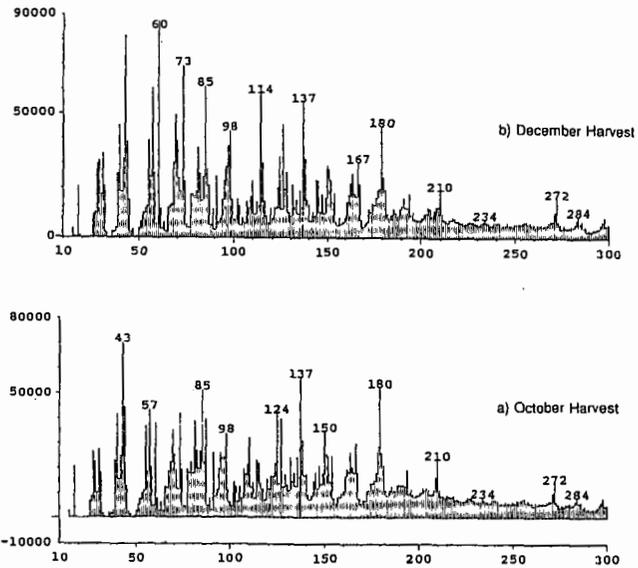


Figure 2. Pyrolysis mass spectra of sericea lespedeza. Notice the difference in the intensity of the low mass peaks (e.g., m/z 60, 73 and 114) in a) the October harvest, and b) the December harvest.

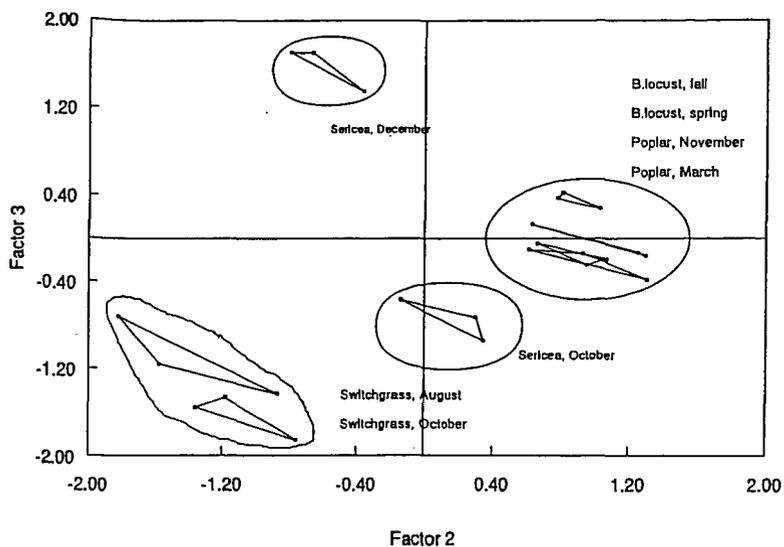


Figure 3a. Factor-score plot of Factor 2 versus Factor 3 of the different harvests of sericea, black locust, hybrid poplar, and switchgrass showing the clusters of the similar biomass samples in the factor space. The triangles show the repeatability of the pyrolysis runs.

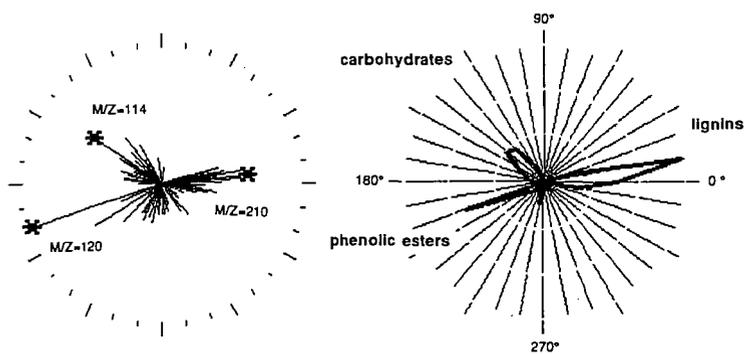


Figure 3b. Variance diagram of factor 2 versus factor 3 of the Py-MBMS of the biomass feedstocks showing compound classes in the spectra.