NEW INSIGHTS INTO CELLULOSE FAST PYROLYSIS KINETICS USING ADVANCED ANALYTICAL TECHNIQUES

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Abstract

A novel micropyrolyzer setup has been designed to study the intrinsic kinetics of biomass fast pyrolysis, using cellulose as a model compound. A detailed product distribution has been obtained by coupling GC × GC-FID/TOF-MS to the micropyrolyzer reactor of which a large number were never reported earlier in the literature. A customized GC, also coupled to the reactor, has enabled the analysis of water and permanent gases simultaneously. Glucose pyrolysis yielded about 8 wt.% of levoglucosan, which is in agreement with the literature. However, the yields of products such as methyl glyoxal and glycolaldehyde were found to increase due to advanced analytics. About 70 product species could be identified and quantified using this novel setup. The effect of two different cellulose particle sizes gave substantial differences in the measured bio-oil. Cellulose with 15 μm particle sizes resulted in nearly 3 times lower levoglucosan yields than that of 50 μm particles. Simultaneously, a significant increase in the yields of furan species was also observed. Further investigation into this could improve the current mechanistic understanding of cellulose fast pyrolysis.

Introduction

Fast pyrolysis of lignocellulosic biomass has proven to be a potential route to generate alternative fuels and fine chemicals. Understanding the kinetics of fast pyrolysis is very essential to design a suitable reactor and optimize the process. Over the years, researchers have been able to elucidate some of the key reactions governing biomass pyrolysis through its model compounds such as cellulose. (SriBala et al., 2018) It is the most abundant homopolymer found in biomass. A range of cellulose samples and particle sizes, along with model compounds such as cellobiose, and glucose have been used in the past to comprehend the influence of temperature, pressure, sample amounts on the product distribution. When subjected to pyrolysis, cellulose yielded about 60-70 wt.% of levoglucosan (LVG) at 400 – 500 °C. (Zhou et al., 2014) However, the experimental studies which were used to validate suffer from issues such as water quantification and mass balance closures. Importantly, 1D GC utilized in these studies led to lumping of many low molecular weight species (C3-C6) due to the superimposition of their boiling points. Further, a recent study on thin-film cellulose pyrolysis suggests a drastic decrease in the production of LVG, with a decrease in film thickness at 400 – 500 °C. (Maduskar et al., 2018) A detailed study on cellulose pyrolysis with different particle sizes along with comprehensive analysis of its products using advanced analytics is very much needed to address these anomalies.

This work extensively focusses on the fast pyrolysis kinetics of cellulose (15 and 50 μm particles) and model compounds such as cellobiose, glucose and LVG at 400 – 600 °C. The intrinsic kinetics of solid-to-gas transformation of cellulose are studied by performing experiments on a novel setup, wherein a micropyrolyzer is coupled with a GC × GC and a customized GC for the simultaneous detection of low molecular weight products (LMWPs), permanent gases and water. The detailed product profiles obtained for both types of cellulose particles along with model compounds will be interpreted with mechanistic information found in the literature to address the new findings of this work.

Materials and methods

The first reactor of double shot tandem micropyrolyzer obtained from Frontier labs is directly connected to the injector port of the Trace GC (Thermo scientific). The injector port is held at 300 °C to avoid condensation of products. The GC is equipped with a cold-trap that is cooled cryogenically up to -196 °C for 5 min, up to which the reactor is heated, to refocus the product molecules. The molecules are then released based on their boiling points during the cold-trap heating. Further, the product vapors are split for their analysis in a customized GC and a GC × GC-FID/MS. The gases such as CO, CO_2 are analyzed using a

customized GC equipped with a Haysep-N and Molsieve-5A columns connected to TCD and PDD detectors. Water is analyzed using a Rtx-5 capillary column connected to a TCD detector. Rest of the products are analyzed using GC × GC-FID/TOF-MS with Rtx-1 PONA and BPX-5 column combination. Soft ionization feature of the TOF-MS enables accurate identification of the product molecules.

About 100- 150 µg of sample was taken in the standard eco-cup supplied by Frontier labs. A known amount of fluoranthene was also added to the sample cup (20 - 40 µg) as an internal standard and plugged the cup with 200 µg of quartz wool. The loaded sample cups were introduced into the pyrolyzer and flushed with helium for 0.5-1 min. The samples are dropped into the pre-heated reactor (400 – 600 ˚C). A split flow of 210 ml/min with a split ratio of 100:1 is maintained to sweep the product vapors from the reactor. LMWPs are quantified using the internal standard method proposed by Pyl et al.,(2011) while other products are quantified using absolute calibrations.

Results and discussions

Pyrolysis of cellulose model compounds

Initially, LVG was pyrolyzed at 600 ˚C to confirm the absence of its secondary reactions. LVG remained intact at fast pyrolysis conditions and appears to be a single peak on GC × GC-FID/TOF-MS. This observation is in agreement with literature. Further, 100-150 µg of glucose was pyrolyzed at 500 ˚C. The product distribution of a few important species generated from glucose was compared with the data reported by Zhou et al., (2014) shown in Table 1. The yield of LVG from glucose pyrolysis match reasonably-well with the values reported in literature. However, much more glycolaldehyde has been recovered in this study due to the better resolution in 2D GC, as shown in the Figure 1. Nearly 70 LMWPs were identified and quantified for glucose pyrolysis, some of which were never reported in the literature. The total mass recovered from the GC analysis is about 60-65 wt.%. The missing mass can be attributed to unreacted glucose based on the elemental balances.
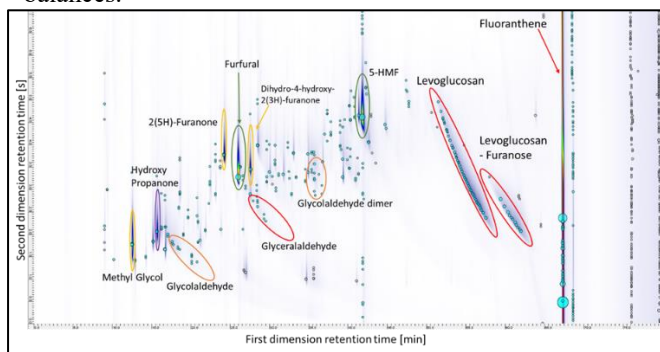

Figure 1. A GC × GC-FID chromatogram showing the product spectrum of glucose pyrolysis at 500 ˚C

Pyrolysis of cellulose particles

Preliminary experiments of cellulose pyrolysis with 15 µm particles reveal that the product distribution is very different than that of 50 µm particles. A comprehensive analysis of the product species suggests a shift in LVG formation towards furan species as the cellulose particle size shifts from 50 µm to 15 µm. The yields of LVG have been reduced by a factor of three, approximately. While the profile of LVG evolution from 50 µm cellulose particle size is in agreement with the literature, the yields are lower than those commonly reported. Besides LVG, many other anhydro- and dianhydro- sugars have been identified during cellulose pyrolysis.

Table 1 A comparison of the yields of major products of glucose pyrolysis with literature

Compound	This work wt.%	Zhou et al. (2014) wt.%
Formaldehyde	0.47	0.41
Acetaldehyde	0.05	0.61
Furan	0.12	0.15
Propenal	0.05	0.18
Methyl glyoxal	2.29	1.50
Glycolaldehyde	8.13	5.21
Acetol	0.31	0.59
Dihydroxyacetone	2.62	0.11
Furfural	1.81	0.96
Levoglucosenone	0.46	0.61
Levoglucosan	8.44	8.10
Levoglucosan-furanose	4.13	3.96

Conclusions

Fast pyrolysis of cellulose using a micropyrolyzer setup illustrates its potential to study intrinsic kinetics. A large number of products species have been identified and quantified, which were never reported in the literature. The reason behind significant drop in LVG by reducing particle sizes from 50 to 15 µm will be investigated in future. The experimental data gathered in this work can be utilized to fine-tune the existing mechanistic models available in the literature to better predict the product distribution of cellulose pyrolysis.

Acknowledgments

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