



Fractionation of liquid products from pyrolysis of lignocellulosic biomass by stepwise thermal treatment

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ARTICLE INFO

Article history:

Received 27 February 2018

Received in revised form

23 April 2018

Accepted 25 April 2018

Available online 26 April 2018

Keywords:

Pyrolysis

Biomass

Bio-oil

Stepwise

Fractionation

ABSTRACT

The thermal properties of cellulose, hemicellulose and lignin can be utilized to improve the characteristics of pyrolysis liquids. In this study, a concept of stepwise pyrolysis to fractionate the liquid based on the thermal properties of the biomass constituents was investigated. Lignocellulosic biomass was thermally treated in two steps: 200–300 °C followed by 550 °C. Derived liquids were studied for GC/MS analysis, water content, acid concentration and a solvent extraction method. Pyrolytic liquid derived from 550 °C after treatment at lower temperatures have a higher relative composition of phenolic compounds compared to one-step pyrolysis (increased from 58 to 90% of GC/MS peak area). Also, compounds known to promote aging, such as acids and carbonyl compounds, are derived at lower temperatures which may suppress aging in the liquid derived downstream at 550 °C. For liquids derived at 550 °C, the total acid number was reduced from 125 in one-step treatment to 14 in two-step treatment. Overall, no significant difference in the total liquid yield (sum of the liquids derived in separated treatments) nor any variations in their collective composition compared to one-step treatment at 550 °C was observed, i.e. stepwise pyrolysis can be utilized for direct fractionation of pyrolytic vapors.

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1. Introduction

Pyrolysis can be applied to produce renewable liquids for production of chemicals and fuels. This is conventionally performed by introducing biomass to a heated reactor for treatment at fixed temperature conditions followed by quenching of hot vapors [1]. The derived liquid is a complex mixture of molecules derived from the depolymerization of lignocellulosic biomass constituents: mainly cellulose, hemicellulose and lignin. Even though this liquid is considered as an alternative to fossil resources it has several properties that complicates its applicability: a high oxygen content, a high water content, and being acidic [2]. Also, such pyrolytic liquid is a complex mixture of hundreds of compounds which complicates the refining processes to maximize its economic value [3]. Additionally, the polar characteristics of the liquid make it immiscible with fossil crude oil which limits the potential blending of feedstocks in existing refineries [4]. Another technical issue regarding liquid derived from conventional pyrolysis is aging, which is caused by the liquid not being at thermodynamic

equilibrium when quenched. During storage this leads to changes to its chemical and physical properties such as viscosity, density, water content, as well as its temperature under adiabatic conditions due to aging reactions. Aging reactions are mainly promoted by the presence of acids, aldehydes and other carbonyl compounds, which react with each other and/or with other compounds, such as phenols [5–7].

Lately, different approaches to fractionate the pyrolytic liquid have been investigated. One approach is to introduce multiple condensers downstream the pyrolyzer operating at different temperatures [8]. Another approach could be to pyrolyze biomass in several steps in series with increasing temperature. Such stepwise thermal treatment may also reduce the severity of secondary pyrolysis reactions compared to single step pyrolysis [9]. Previous studies on pyrolysis in several steps have identified the potential of this approach. De Wild et al. proved the concept based on thermogravimetry and two-staged thermal degradation of coniferous, deciduous and herbaceous biomass [10]. Based on studies on pine wood, Westerhof et al. concluded that the yields of char and liquid, as well as the liquid composition, are similar for two-step treatment and one-step treatment when heating the material up to 290 °C followed by 530 °C in a fluidized bed. For the intermediate

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temperatures, a mechanism is proposed for competing char forming reactions and depolymerization [11]. By studying the polymeric structure and the thermal properties of the biomass constituents, it is possible to understand their contributions to the pyrolytic liquids. The least thermally stable of them is hemicellulose (220–315 °C) from which the main part of acids and carbonyls are derived. Cellulose and its crystalline structure is more stable (315–400 °C), while the amorphous structure of lignin is decomposed over a wide temperature range (160–900 °C) [12–14]. The main condensable derivatives from hemicellulose and cellulose are anhydrosugars, furans and light carbonyls [15] while lignin contributes with phenols and guaiacols [16]. By thermally treating biomass in several steps with increasing temperature, the composition of derived liquids can be dependent on the thermal stability of its constituents. This approach could result in liquids of increased chemical stability and reduced complexity compared to the liquid from conventional pyrolysis performed in one step. However, little is known about the behavior of different biomass feedstocks in stepwise pyrolysis and the choice of different reactors. Additionally, the utilization of stepwise pyrolysis to overcome technical issues previously mentioned (aging, immiscibility with crude oil etc.) has not been addressed in previous studies.

The aim of this work is to evaluate pyrolysis in several steps in order to identify its potential to fractionate condensable compounds based on the choice of temperature. A lignin-rich feedstock (palm kernel shells) [17] was used because of the essentiality of aromatic hydrocarbons in the petrochemical industry and for lignin being the most abundant aromatic-based polymer in nature [18]. A fixed-bed reactor was used compared to previous studies, which results in a reduced heating rate of biomass and a longer residence time of vapors. Derived liquids were analyzed in terms of water content, acid concentration and organic composition.

2. Materials and methods

2.1. Materials

PKS supplied by a Malaysian palm oil production plant was used as raw material in this study. Its particle size was 2–3 mm. Proximate and ultimate analyses of the material are presented in Table 1. Fig. 1 presents the thermal decomposition behavior of the material, conducted from thermogravimetric analysis. Analytical methods used are presented in Table 2.

2.2. Experimental setup

Pyrolysis experiments were performed in a tubular three-heating zone fixed bed pyrolyzer with 60 cm length and 5 cm inner diameter. An illustration of the pyrolyzer is presented in Fig. 2. The setup allows batch-wise pyrolysis at a specific temperature and time. Biomass is firstly placed in a basket made of stainless steel

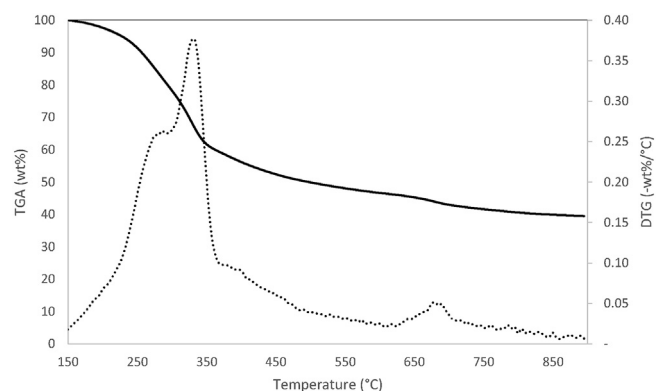


Fig. 1. TGA and DTG analysis of PKS performed in inert atmosphere and heating rate of 10 °C/min.

Table 2

Methods used for biomass characterization.

Characteristic test	Method
Ash content	SS-EN ISO 18122:2015
Volatile matter	SS-EN ISO 18123:2015
Elemental composition (C, H, N, S)	SS-EN ISO 16948:2015/16994:2016
Elemental composition (O)	Calculated by difference
Thermal degradation behavior	TGA

mesh, and kept in a water-cooled section during heating of the furnace (position 1). When the furnace has reached the target temperature, the basket is introduced to the hot zone as a fixed bed (position 2). A constant gas flow of nitrogen is used as carrier gas. Pyrolytic vapors are continuously quenched in a condenser (cooling bath) operating at –15 °C.

2.3. Pyrolysis experiment procedure

Temperatures for the two-step treatment of PKS were decided based on the thermogravimetric analysis presented in Fig. 1 together with previous works on pyrolysis of the individual biomass constituents and the irreversible charring reactions observed by Westerhof et al. in stepwise treatment [10,11,14]. From the DTG in Fig. 1 it can be seen that the peak for thermal degradation of hemicellulose occurs at 280 °C, whereas for cellulose the peak of degradation is at 330 °C. Treatment at lower temperatures were investigated in the range of 200–300 °C (similar as torrefaction [19]) followed by treatment at 550 °C. Table 3 presents the different cases and specific temperatures investigated. Also, a reference case of one-step pyrolysis was performed at 550 °C for comparison.

For each case, 60 g of pre-dried PKS (kept at 105 °C for 24 h) was treated at the lower temperature, cooled to room-temperature followed by treatment at the higher temperature. For the lower temperature treatment between 200 and 300 °C, PKS was kept in the heated zone for 45 min. Thereafter, the solid and liquid products were collected for analysis followed by treatment at 550 °C for 15 min. In the reference case, 60 g of PKS was directly pyrolyzed at 550 °C.

2.4. Analysis of pyrolysis products

The yields of the solid and liquid products were measured by weighing. The liquid product was analyzed in terms of water content, total acid number, GC/MS, and through a solvent extraction scheme developed by VTT [20]. In this scheme pyrolysis oil is

Table 1

Ultimate and proximate analysis of PKS (presented on dry basis).

Characteristics	wt%
Volatile matter	64.4
Ash content	8.5
C	51.7
O ^a	33.8
H	5.6
S	0.03
N	0.4

^a Oxygen is calculated by difference.

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