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Review

A review on condensing system for biomass pyrolysis process

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ABSTRACT

Pyrolysis oil (py-oil) produced via the pyrolysis of waste biomass is an alternative sustainable source of both bioenergy and valuable biochemical. Py-oil produced from woody biomass typically has water content between 15 and 30 wt%, a heating value between 16 and 19 MJ/kg and high acidity, limiting application as a fuel. The fuel quality could be improved by optimizing the downstream condensing systems to separate the light organic acid and water from the py-oil. However there has been limited research in this area, instead the work on enhancing oil quality has focussed on the reactor or upgrading the condensed oil. Typical biomass pyrolysis condenser systems include single condenser systems with single liquid product, multi-stage condensers with a single liquid product, and multi-stage condensers with multiple liquid products. This paper reviews published information on biomass pyrolysis condensing systems, from lab to pilot to commercial scale, and subsequent impacts of the condensing system on py-oil quality and yield. The review includes energy required, wastes generated, and chemicals/utilities used. The review proposes fractionation condensing based system could improve the quality of the py-oil, increasing heating value, decreasing the water content and acidity.

1. Introduction

Biomass is a source of bioenergy and biochemicals, through conversion via thermochemical, biological, chemical, and physical processes [1]. Thermochemical and biochemical conversion technologies are common methods to convert lignocellolosic biomass to bio-based energy/chemicals [2]. Both are viable options depending on the nature of the biomass, location of the feedstock, and regional/market needs with respect to energy and potential for value added chemicals. The focus of this paper is the pyrolysis oil (py-oil) produced via fast pyrolysis, a liquid fuel which can be used as a heating oil and/or marine fuel. The py-oil is also a source of biochemicals that could be used as alternatives/blends feedstock for petroleum based chemicals. Fast pyrolysis converts 50–75% of woody biomass to py-oil at temperatures between 400 and 600 °C, and a bio-char and non-condensable gas. Py-oil is a complex mixture of chemicals including acids, ketones, furans, phenols, hydro sugars and other oxygenates [3–5]. The pyrolysis process consists of two main sections, the furnace/reactor, which converts biomass to bio-products (i.e. volatile vapour [6–9], non-condensable gas and char [10,11]), and a condensing system, which recovers the condensable gases as a liquid product. While the reactor conditions are the main drivers in py-oil yield and quality, the condenser design impacts the oil quality with respect to composition. Condenser systems typical in biomass pyrolysis include traditional single condenser and multi-condenser systems for bulk separation of water and non-condesables to produce one liquid and fractional systems, where more than one liquid product is generated.

Fractional methods used in py-oil separation include liquid chromatography, extraction, centrifugation, fractional condensation, molecular distillation and precipitation by adding water. Liquid chromatography, extraction, and centrifugation are not cost-effective for large scale recovery of the oil [12]. Molecular distillation can be challenging due to the thermal instability of compounds in the py-oil and requires significant energy and time to overcome the instability, for example in order to avoid coking or polymerization the temperature must be ramped up slowly [13–15]. Using condensers to fractionally separate the py-oil is less energy intensive and potentially produces higher fuel quality liquids and product streams that can be further refined to recover high value chemicals such as methanol. There has been limited study of biomass pyrolysis condensing system, as the bulk of the work has focussed on the reactor operation and design [16–20] and upgrading after the oil is condensed. The reactor is important, however, there is a limit to py-oil quality enhancement that can be accomplished solely by optimizing the reactor and upgrading “after the fact” introduces another unit operation (i.e. increased energy use and waste generated). The primary objective of this work is to review the impact of the operation and design of the condensing system on py-oil quality and yield to inform the design of a more effective pyrolysis vapour

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Table 1
Properties of pyrolysis oil, diesel, and heavy crude oil [22–25].

Properties	Soft/hardwood oil	Diesel	Heavy fuel oil
Water content (wt%)	13–33 wt%	0.05*	0.1
TAN (g KOH/g oil)	56–120	–	–
Solid Content	0.2–3.2	–	1
pH	2.2–4.1	5	–
Density (g/cm^3)	1.13–1.24	0.84	0.94
Viscosity (cSt)	33–38 (20 °C)	2–4 (20 °C)	180(50 °C)
HHV (kJ/kg)	15.8–21.9	42	40
Flash point (°C)	55	–	–
Pour point (°C)	−25	–	–

* v/v%.

recovery system.

The physical, thermal, and chemical py-oil properties ultimately determine the end use of the oil and are compared as a function of various pyrolysis systems.

2. Py-oil physicochemical properties

Py-oil properties compared to heavy fuel oil and diesel are outlined in Table 1. Water, present in the initial biomass and chemically produced from the dehydration reactions impacts the heating value, viscosity and phase separation (should the water exceeds 30 wt%) of the light polar components in the aqueous phase, and heavy non-polar components the oily phase are present [21]. Py-oil is acidic due to carboxylic acids (10–15 wt%, predominantly acetic and formic acids), resulting in possible corrosion issues in use. As such, the removal of water and some light carboxylic acids from raw py-oil can improve fuel quality.

Table 2 summarizes the normal boiling point and molecular weight of groups of identified chemicals. Boiling points range from 250 K to > 550 K, and molecular weights range from 31.4 to 1050 g/mol, resulting in a complex mixture of compounds. Chemicals with a molecular weight lower than 62 g/mol and boiling point lower than 390 K constitute the “light” group, compounds from 390 to 550 K boiling point are the “middle” boiling point group, and large molecules with a molecular weight > 150.9 g/mol and boiling point > 550 K are in the heavy group. The removal of the light group of chemicals, which includes water and a bulk of the light acids, could enhance the fuel quality of the remaining oil [26].

In addition to the temperatures of inlet and outlet fluids, the mass flow rates of the fluids and the heat transfer surface area are key factors in controlling the outlet pyrolysis vapour temperature:

$$Q = m_H C_{p,H}(T_{H,in} - T_{H,out}) = m_C C_{p,C}(T_{C,in} - T_{C,out}) \quad (1)$$

where, Q (W) is the heat transfer rate, m_H (kg/s)and m_C (kg/s) are the mass flow rate of hot and cold fluid respectively; C_p ($J/K.kg$) heat capacity of vapours and T (K) is temperature. Further,

$$Q = UA\Delta T_{lm} \quad (2)$$

U ($W/(m^2K)$) is the overall heat transfer coefficient, $A(m^2)$ is the surface area, and ΔT_{lm} (K) is the log mean temperature. The mass flow rate of cold fluid or the heat transfer surface area can be optimized via these equations however, the thermodynamic properties (e.g. heat capacity) of the vapours as a function of temperature is not well characterized due to the complex composition of the uncondensed vapours.

The narrow boiling point ranges of the py-oil compounds make the separation into individual components challenging and therefore separation into light, middle and heavy groups more achievable (see Table 2). Assuming vapour-liquid equilibrium is attained:

$$y_i P\varphi_i = x_i P_i^* \gamma_i \quad (3)$$

where, y_i is vapour composition, x_i is the liquid composition, P is total pressure, φ_i is the fugacity coefficient in the vapour phase, P_i^* is the saturation pressure and γ_i is the activity coefficient in liquid phase. Total pressure, composition of pyrolysis vapour, and temperature determine separation, modifying vapour composition and pressure is challenging. Condenser temperature is the most easily adjusted and therefore work has focussed on controlling temperature in fractional condensation [26,28–33].

The VLE behaviour of select pyrolysis products of a specific pyrolysis oil composition are shown in Fig. 1 [19]. It should be noted that the interactions between azeotropes or other intermolecular interactions have been not taken into account in this analysis (Fig. 1). The intersection of the VLE curves and partial pressure of the compounds in mixture give the dew points.

For this particular pyrolysis oil, water will start to condense at 50 °C, levoglucosan at 200 °C, and phenol at 80 °C. It should be noted that the partial pressure of vapour compounds are also a function of composition which is depends on feedstock type and reactor operating conditions and therefore the dew point will change for different pyrolysis oil compositions. In addition to liquid recovery, the solids (char) must also be separated from the pyrolysis product.

3. Char removal system

Volatile vapours, formed from the pyrolysis of biomass, pass through a char separator(s) to remove solid particles. Char removal designs differ depending on the overall process, typically there are one [34] or two gas-solid cyclones [35] alone or connected to a hot ceramic filter [36]. (e.g. Fig. 2). Fine char in condensable vapours is difficult to separate and therefore an insoluble lignin and fine char can combine to

Table 2
Normal boiling point and average molecular weight for organic components of py-oil obtained from forestry residue pyrolysis [27].

Components	Group	Normal boiling point (K)	Average molecular weight (g/mol)
Formaldehyde, acetaldehyde	Lights	250–300	31.4
Propionaldehyde, glycolic acid, glyoxal, acetone	Lights	300–330	65.4
Methanol, 2-oxobutanoic acid, ethanol, MEK, 2-propanol, (5*H*)-furan-2-one	Lights	330–360	48.4
Formic acid, hydroxyacetaldehyde, 5-hydroxymethylfurfural acetic acid, butanol, lactic	Lights	360–390	61.6
Acid, 4-propylguaiacol, propionic acid, acrylic acid, acetol	Middles	390–420	71.0
Isobutyric acid, 2-hydroxy-2-cyclopentene-1-one, 2-hydroxy-1-methyl-1-cyclopentene-3-one, 1-hydroxy-2-butanone, furfural, methacrylic acid, *n*-butyric acid, coniferylaldehyde	Middles	420–450	105.8
Phenol, crotonic acid, valeric acid, 3-hydroxypropanoic acid, *o*-cresol, tiglic acid, 4-methylpentanoic acid, *p*-creosol, *m*-creosol, hexanoic acid, guaiacol, 4-hydroxybenzaldehyde, 4-methylguaiacol, vinylguaiacol	Middles	450–500	125.3
4-ethylguaiacol, 1,2-benzendiol, levulic acid, benzoic acid, eugenol, syringol, vanillin, isoeugenol (cis + trans)	Middles	500–550	150.9
Levoglucosan, glucose, xylose, cellobiosan, hydroquinone, …	Heavies	∞	160
Components in sugar constituent group	Heavies	∞	320
Components in low molecular mass lignin group	Heavies	∞	450
Components in extractives group	Heavies	∞	460
Some components in high molecular mass lignin group	Heavies	∞	1050

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