A comparative analysis of heat recovery and product stabilization in fluid-bed and ablative pyrolysis systems

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Abstract. Nearly all existing commercial pyrolysis technologies employ single-step rapid condensation of vapours from 500 ºC to 50 ºC using sprays of cold bio-oil or liquid hydrocarbon as a quench fluid. This approach produces raw bio-oil, a non-homogenous mixture of hundreds of oxygenated organic compounds including organic acids and water. Single-step quench also results in loss of high quality heat to the ambient. In this work, a novel 3-stage fractional condensation approach has been proposed. The intent is to produce targeted stable products for value added applications as well to enhance the overall efficiency of pyrolysis processes. The first phase of this research involved modelling and simulation of staged condensation of pyrolysis vapours using Pro/2 process software. A comprehensive pyrolysis model with 13 representative compounds was developed and validated. The Pro/2 model is able to simulate complex condensation of lignin and sugar fractions at high temperatures. Multiple cases involving staged condensation in ablative and fluid bed pyrolysis systems were investigated. In each case, there was a trade-off between high-quality heat recovery and early separation of lignin and sugars from organic acids. Results demonstrated that dew point depression adds additional complexity and limits heat recovery. However, judicious selection of condenser temperatures offers opportunity for early isolation of sugars and lignin from acids, thereby improving product stability.

1 Introduction

Pyrolysis is the endothermic decomposition of complex biomass materials at high temperatures in the absence of air or oxygen. Pyrolysis produces solid (bio-char), pyrolysis liquids and gaseous streams. Although polar and nearly immiscible with conventional crude oil fractions, pyrolysis liquids are widely labelled bio-oil as they carry the potential to be converted into transportation fuels e.g. gasoline and diesel etc. [1].

Heat transfer rates play an important role for qualitative and quantitative distribution of solid and liquid yields in pyrolysis processes. Rapid biomass heating and rapid vapour

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quenching to reduce vapour residence time have been the essence of fast pyrolysis to maximize the yield of bio-oil [2,3].

In last few decades, many new reactor configurations have been proposed for rapid heating of biomass particles in fast pyrolysis [2,3]. These configurations include shallow moving beds or transported beds (vacuum pyrolysis), auger reactors, fluid beds and ablative reactors. While the fluid bed reactor achieve high heat transfer rates by using very small biomass feed size entrained by heated inert gases, the ablative systems use relative motion of biomass feed and a heated surface creating ablation and high heat transfer coefficients [3-5]. Nearly all of the existing pyrolysis technologies employ single step rapid condensation of pyrolysis vapours from 500 °C to 50 °C using sprays of cold bio-oil (or liquid hydrocarbon) as a quench fluid (See Fig. 1).
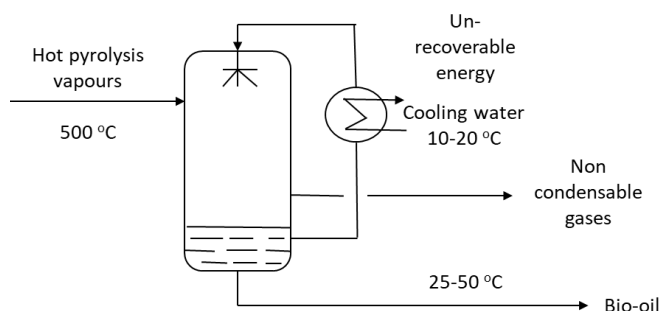

Fig. 1 Current practice of single step quench of pyrolysis vapours

While single step rapid quench helps maximize the quantity of the liquid product obtained, this liquid product becomes a non-homogenous mixture of hundreds of oxygenated polar compounds and contains large fraction of water and acids. It is widely considered that aging process in bio-oil is initiated by acid-catalysed sugar decomposition forming reactive compounds such as hydroxymethyl furfural. This aging process can be slowed down if acids can be isolated from sugars in the bio-oil [6]. In addition to chemical instability of bio-oil, the conventional one-step quench also leads to loss of high quality heat to the surroundings (primarily cold water utility or ambient air) with no possibility to recover or recycle this energy back to upstream heat requirements for rapid heating.

Table 1. Bio-oil representative compounds for Pro/2 simulations

Functional group	Model compound	Functional group	Model compound
Acids	$C_2H_4O_2$	Low MW lignin derived compound B	$C_{12}H_8O$
Alcohols	$C_6H_6O_2$	Extractives	$C_{20}H_{30}O_2$
Ketones	$C_3H_6O_2$	High MW lignin derived compound A	$C_{16}H_{22}O_4$
Aldehydes	$C_8H_8O_3$	High MW lignin derived compound B	$C_{10}H_6O_8$
Guaiacols	$C_7H_8O_2$	Nitrogen compounds	$C_8H_{11}N$
Sugars	$C_{12}H_{22}O_{11}$	Sulfur compounds	$C_{12}H_8S$
Low MW lignin derived compound A	$C_{14}H_{12}O_2$		

Recently, some researchers have initiated exploring the possibility of staged condensation [7-11]. However, their focus has been to remove water and other low boiling by reducing

condenser temperatures in the range of 150 – 4 °C. These low condenser temperatures not only limit any useful heat recovery but also incur more energy loss because of cooling utility requirements for temperatures lower than ambient.

The objective of this study is to develop a preliminary process model for heat recovery and product stabilization in biomass fast pyrolysis processes and simulate multistage condensation and product fractionation for ablative and fluid-bed pyrolysis systems. The intent is to separate lignin and sugars from acids to enhance product stability and quality produce targeted stable products for value added applications as well enhance the overall efficiency of pyrolysis processes.

2 Materials and methods

Pro/2 simulation software (Schneider Electric®) was used to develop the pyrolysis model. Pro/2 is also capable of modelling solids, a desired feature for incorporating biomass and char in simulations. Since biomass, char and bio-oil are
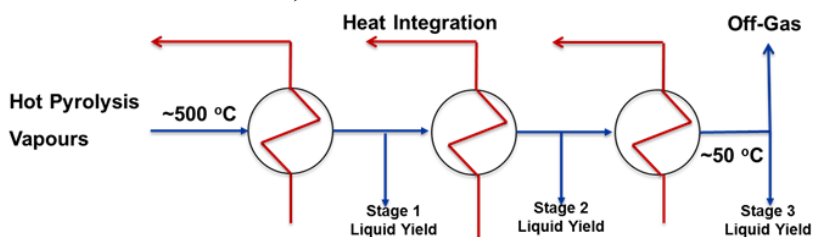

Fig.2. 3-stage fractional condensation concept for heat recovery and product stabilization.

complex materials and are not defined in Pro/2's chemical library, it was necessary to identify representative compounds in Pro/2's chemical library which could simulate key functional compounds in bio-oil. Our laboratory (CanmetENERGY-Ottawa) had previously
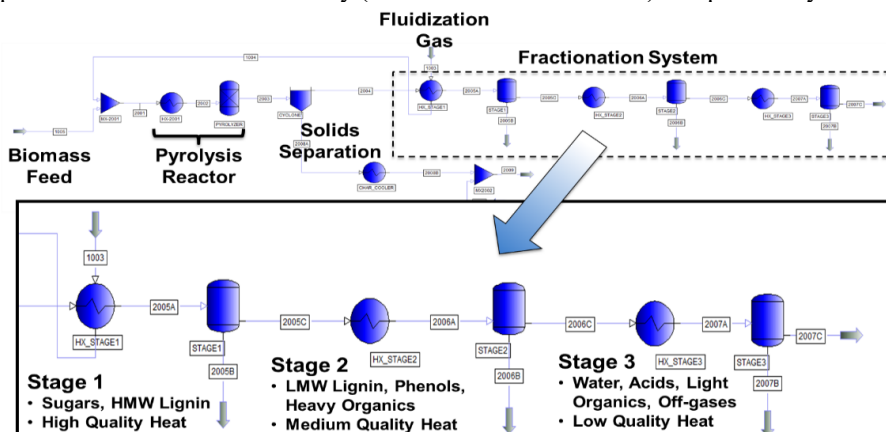

Fig. 3. A Pro/2 process model for biomass pyrolysis with three-stage condensation.

developed a Pro/2 process model using 10 representative compounds [12]. The previous pyrolysis model used single step quenching and considered bio-oil as a simple fluid. Model compounds considered in previous model, did not adequately represent the physical properties or complexity of bio-oil condensation. For example, in the previous model, ethyl phenol which represented phenolic monomers, was the compound with highest melting point (46 °C). Whereas in the literature, common compounds in bio-oil such as pyrolytic lignin (approximately 20 wt. % of bio-oil) and sugars (approximately 30 wt. % of bio-oil) have been

reported to have a melting point in the range of 180 – 220 °C [1,13]. Lack of adequate compounds representing sugars and lignin, in previous model was found to be unsuitable for simulating condensation of high melting sugars and lignin in multistage quenching.

Subsequently, a pyrolysis model with 13 representative compounds was developed. For the purpose of simulating condensation process, representative compounds were chosen from Pro/2 library to have as close as possible molecular structures as well the phase behaviour (melting and boiling points) as the key functional groups in bio-oil as shown in Table 1.

3 Results and discussions

The three-stage condensation concept (as shown in Fig. 2) targeted to bring down pyrolysis temperatures from 500 to 50 °C offering three different qualities of heat available for recovery. Fig. 3 shows sample Pro/2 process model used for simulating this three stage concept.
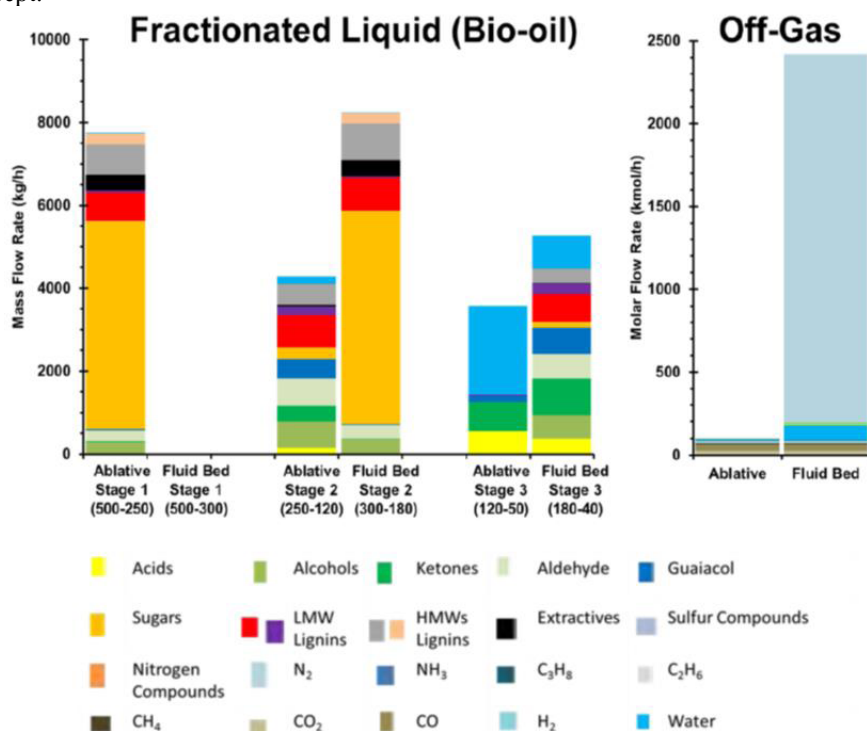

Fig.4. A comparative analysis of 3-staged condensation in ablative and fluid bed systems

The revamped model with representative compounds shown in Table 1 was able to effectively simulate lignin and sugar condensation. Prior to conducting simulations on pyrolysis vapour condensations, model results were verified with NREL's 2013 model [14].

Multiple cases involving staged condensations in ablative and fluid bed pyrolysis systems were investigated. These two system represented low and high carrier gas to biomass ratios, respectively. In each case, the intent was to reach a trade off between high quality heat recovery and early separation of lignin and sugars with that of acids to enhance product stability and quality. Fig. 4 shows striking differences between ablative and fluid bed systems. For example, high amounts of fluidization gas causes dew point depression in the product vapours. As a result, pyrolysis vapours containing HMW lignin, LMW lignin and extractives that typically exit the system as liquid in Stage 1 of an ablative process, remain

vapours in fluid bed process. At around 250 °C, almost (95%) of high melting sugar and HMW lignin as well extractives are condensed early in the first stage while most of the acids and water are discarded in the third stage. As lignin and sugar are very distinctive in chemical properties and in term of energy density (33 MJ/kg and 17 MJ/kg respectively – See Fig. 5a), their early recovery and isolation from acid catalyzing reactions offers additional opportunities for their immediate applications or for their further selective upgrading.

In the fluid bed system, in the first stage, no condensation occurs when the condenser temperature is around 300 °C. This is disappointing from fractionation perspective. However, this also negates any change of fluid state in first stage, thus offering more flexibility for fouling-free heat recovery. The effect of dew point depression can be further noticed in stage 3 and in off gas.

Compared to ablative pyrolysis, large fractions of water and acid vapours slip through in the off gases, which also contain significant amount of inert fluidization gases. High relative
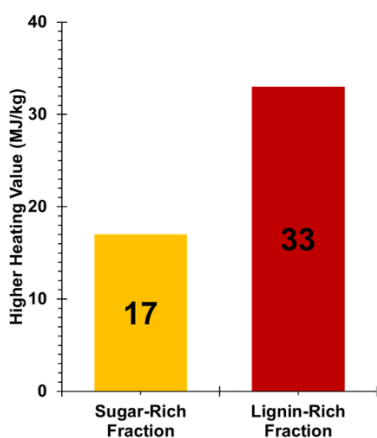

Fig.5a. Relative higher heating values of sugar rich and lignin rich fractions in stage 1 of ablative pyrolysis unit.
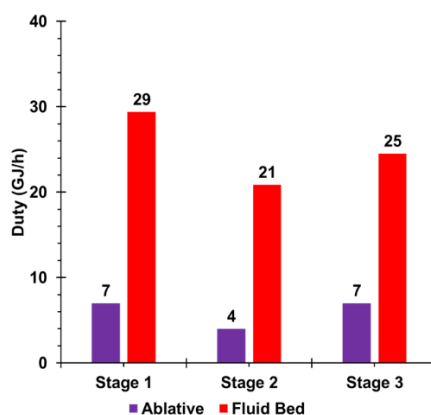
Fig. 5b. Relative recoverable heat available for 3 staged vapour condensation in ablative and fluid bed systems.

volume of fluid bed gases could be a matter of concern as any gas recycle strategy will require larger equipment and larger plant footprints. Thus, need for heat recovery in fluid bed is much more intense than in ablative systems (See Fig. 5b).

4 Conclusions

This work provided first of a kind simulation study on advanced pyrolysis processes with a focus on heat recovery and product stabilization. In this work, a Pro/2 pyrolysis model with 13 representative compounds was used to model bio-oil. This model was used to compare fluid bed and ablative pyrolysis systems. The outcome demonstrated that staged condensation and heat recovery offer better product selectivity and better process efficiency than single-step pyrolysis vapour condensation. Judicious selection of condenser temperature configurations offers opportunity for early isolation of sugars and lignins from acids, thus reducing instability of product stream. Quality of product fraction and heat recovery are dependent on type of reactor. Given the high ratios of fluidization gas to biomass ratio in fluid bed pyrolysis, heat recovery and recycle are very crucial for these systems.

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