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Continuous hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation

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HIGHLIGHTS

- Biocrude compounds from woody biomass can be classified into two groups: cyclopentenones and oxygenated aromatics.
- Biocrude quality can be predicted based on the feedstock model compound composition.
- Elemental composition is almost invariant to feedstock composition.
- Reaction scheme from model compound, through intermediates, to biocrude is proposed.
- Residual oxygen in the biocrude is mainly positioned in ketones and phenolic alcohols.

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ABSTRACT

Hydrothermal liquefaction is a promising technology for the conversion of a wide range of bio-feedstock into a biocrude; a mixture of chemical compounds that holds the potential for a renewable production of chemicals and fuels. Most research in hydrothermal liquefaction is performed in batch type reactors, although a continuous and energy-efficient operation is paramount for such process to be feasible. In this work an experimental campaign in a continuous bench scale unit is presented. The campaign is based on glycerol-assisted hydrothermal liquefaction of aspen wood carried out with the presence of a homogeneous catalyst at supercritical water conditions, 400 °C and 300 bar. Furthermore, in the experimental campaign a water phase recirculation step is incorporated to evaluate the technical feasibility of such procedure. In total, four batches of approximately 100 kg of feed each were processed successfully at steady state conditions without any observation of system malfunctioning. The biocrude obtained was characterized using several analytical methods to evaluate the feasibility of the process and the quality of the product. Results showed that a high quality biocrude was obtained having a higher heating value of 34.3 MJ/kg. The volatile fraction of the biocrude consisted mostly of compounds having number of carbon atoms in the C_6–C_{12} range similar to gasoline. In terms of process feasibility, it was revealed that total organic carbon (TOC) and ash significantly accumulated in the water phase when such is recirculated for the proceeding batch. After four batches the TOC and the ash mass fraction of the water phase were 136.2 [g/L] and 12.6 [%], respectively. Water phase recirculation showed a slight increase in the biocrude quality in terms on an effective hydrogen-to-carbon ratio, but it showed no effects on the product gas composition or the pH of the water phase. The successful operation demonstrated the technical feasibility of a continuous production of high quality biocrude.

1. Introduction

Hydrothermal conversion of biomass in hot-compressed water is a viable, scalable, and energy-efficient thermo-chemical route for converting biomass into synthetic solid, liquid, or gaseous fuels and chemicals. At near and supercritical water conditions, biomass fragments into a bulk liquid phase, better known as biocrude. It consists of low molecular weight and deoxygenated chemical species compared to the original biomass macromolecules. The biocrude may be further processed into platform chemicals or infrastructure-compatible fuels. Hydrothermal conversion of

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biomass has been widely studied experimentally, mostly in batch reactors and less so in continuous systems, and has been reviewed in the many process aspects, such as near-critical water synthesis properties [1,2], the effects of various process conditions [3], effects of biomass composition [4–7], process developments [8–10], and upgrading of the biocrude [11–13].

Although the vast majority of research is carried out in batch reactors, development of continuous operation and technology upscaling of near-critical water technologies has been ongoing since the mid-seventies – but has not yet reached commercialization [9]. The continuous process was first demonstrated at a bench scale system at the Pittsburgh Energy Research Center (PERC) which was later scaled to the Albany plant, Oregon [14]. The production facility utilized a recycle concept in which wood (Douglas fir) was slurried in recycled process water and initially in anthracene oil and eventually in recycled biocrude as it became available. The following three aspects of the process were identified as critical: (1) the energy intensive pre-drying and grinding step required for wood flour preparation, (2) wood–biocrude–water slurries could not be fed at concentrations greater than 10% without causing system plugging, (3) high recycle ratios of biocrude (up to 19:1) required excessive heat [15]. Many process improvements have since been done, and it is believed that the critical aspects can be overcome or greatly reduced to an extent for the process to become feasible. One aspect of the process optimization is to maximize the biocrude whilst decreasing the amount of solid byproducts. During liquefaction, reactive biomass fragments rearrange to biocrude compounds through condensation, cyclization, and re-polymerization, and for prolonged process severity a solid fraction insoluble in most solvents is formed, which is generally termed char.

In a lignocellulosic context, char formation results primarily from two counteracting mechanisms; (1) dehydration reactions of free sugars favored at intermediate temperatures, high feed concentrations [16], and acidic conditions [17] and (2) radical formation during lignin degradation leading to retrogressive char formation [18]. Char formation from carbohydrates can be suppressed by applying high heating rates to reach high reaction temperatures, preferably above supercritical conditions, and alkaline conditions [16,19,20]. Lignin radical formation purely a thermal effect, hence supercritical conditions tends to enhance lignin char formation [21]. Means of overcoming these counteracting thermal effects includes the addition of a reducing agent such hydrogen or carbon monoxide, or by the addition of a stabilizing co-solvent acting as a radical scavenger through hydrogen donation. Alcohols may undergo thermal scission causing hydrogen abstraction in the form of ·H, ·OH, or ·CH_2OH radicals, amenable to cap lignin radicals and hence preventing lignin repolymerization [22–24]. Low molecular weight co-solvents such as phenol [25], propanol [26], ethanol [27,28], methanol [29], and glycerol [30,31] have been applied, and are preferable in order to obtain low molecular weight product compounds, when transport fuel precursors are targeted.

Among co-solvents, glycerol is of particular interest since it is already produced in large quantities. Today, glycerol is mainly a refined bio-based by-product from biodiesel production, and its market value has been declining since the market entry of biodiesel production, making it economically interesting. Xiu et al. investigated in batch the potential of utilizing crude glycerol, the unrefined by-product, as a co-substrate in hydrothermal processing of swine manure. It was found that crude glycerol enhanced both the yield and the quality of the biocrude based on the elemental composition [32–37]. In the same studies it was attempted to understand the conversion chemistry involved through model studies using pure glycerol, methanol, and fatty acids as model co-substrates, but the reaction mechanisms of the different organic compounds in the crude glycerol on the biocrude production were not fully established. Moreover, in house, but yet unpublished, model studies in batch reactors have shown that by hydrothermally liquefying aspen wood in the presence of glycerol or crude glycerol, char formation can be significantly reduced whilst maintaining a high yield of high quality biocrude [38].

The objective and novelty of the present study is to investigate and demonstrate continuous co-liquefaction at bench scale conditions of aspen wood and glycerol as a co-solvent as a viable route to process lignocellulose at high organic concentrations in the feed. The technical feasibility of process water phase recirculation is incorporated to evaluate benefits and eventual complications of such procedure. The process is evaluated based on system performance, recirculation effects on phase characteristics, and a product assessment to examine the quality of the obtained biocrude.

2. Materials and methods

2.1. Materials

Supercritical co-liquefaction of aspen wood and glycerol was demonstrated in the continuous bench scale reactor unit (CBS1) at the Department of Energy Technology, Aalborg University. In total, four batches of approximately 100 kg of feed each were processed, all prepared from the same recipe. Table 1 shows the properties of the aspen wood. Glycerol (99.5%), potassium carbonate (K_2CO_3), and carboxymethyl cellulose (CMC) were purchased from Brenntag Nordic A/S.

2.2. Process feed composition

Table 2 shows the feed composition used in the experimental campaign. Aspen wood and glycerol were mixed in nearly 50/50 ratios in recycled water phase together with K_2CO_3 and CMC. In the absence of product water phase, the feed for Batch #1 was prepared using distilled water.

2.3. Description of the Continuous Bench-Scale Unit (CBS1)

A process flow diagram (PFD) of the CBS1 is presented in Fig. 1. Pretreatment and feed slurry preparation is done in a stand-alone mixer, where aspen wood, glycerol, water phase and catalyst are mixed. Steady state conditions at the preset operating conditions are reached by circulating hot-compressed water (HCW) through

Table 1
Elemental and chemical analysis of aspen wood used in continuous hydrothermal liquefaction.

Elemental and chemical analysis[a] *(%, daf)*	
C	50.39 (±0.86)
H	6.19 (±0.08)
N	0.19 (±0.02)
S	N.D.
O (by difference)	43.23 (±0.08)
Fibre mass composition (%, db)[b]	
Cellulose	47.14 (±0.86)
Hemicellulose	19.64 (±0.11)
Lignin	22.11 (±0.17)
Extractives (by difference)	6.63 (±0.01)
Ash[c]	0.46 (±0.02)

daf = dry, ash-free. N.D. = Not Determined.

[a] Ultimate analysis was carried out in a Perkin Elmer 2400 Series II CHNS/O system.

[b] Fibre composition was determined by the Van Soest method in a FOSS Fibertec M6 unit.

[c] Ash content measured by heating a sample to 850 °C and held isothermally for 2 h.