



Full Length Article

Continuous solvent liquefaction of biomass in a hydrocarbon solvent



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ARTICLE INFO

Keywords:

Solvent liquefaction
Biomass
Lignocellulosic
Pilot plant
Fractionation

ABSTRACT

Solvent liquefaction (SL) of biomass is a promising technology for the conversion of biomass to renewable fuels and chemicals. Liquid-phase thermal deconstruction of biomass in the presence of hydrocarbon-based hydrogen-donating solvents can result in bio-oils with low moisture and low oxygen content. These oils are thermally stable and highly miscible with hydrocarbon streams, which make them a promising biorenewable blendstock for petroleum refineries. We have developed a 1 kg hr⁻¹ continuous SL pilot plant to evaluate the performance of SL of southern yellow pine in a hydrocarbon solvent. The process development unit (PDU) was also designed to evaluate several unit operations critical to large-scale operations. Online solids removal was conducted with inline wire mesh barrier filters with separation efficiency of over 99%. Acetone injection was used to aid in solids removal, and an online recovery system was demonstrated with greater than 97% acetone recovery. Continuous online bio-oil fractionation was also demonstrated using a distillation column to separate approximately 93 wt% of the initial solvent from the biomass-derived products.

1. Introduction

Direct liquefaction thermally decomposes solid carbonaceous feedstocks into predominantly liquid products using a liquid solvent. It is generally carried out at moderate temperatures and pressures, typically ranging from 200 to 400 °C and 20 to 200 bar, respectively. The operating pressure of a given direct liquefaction system is largely dictated by the vapor pressure of the solvent, but it can be impacted by the vapor pressures of the products, as well. Direct liquefaction is a broad category that includes several subcategories delineated by the primary solvent employed. Hydrothermal liquefaction, in which water is the primary solvent, and solvent liquefaction (SL), which employs non-aqueous solvents (e.g. tetralin, phenol, γ -valerolactone), are the most common.

The products of SL vary widely based on the reaction conditions and the solvent employed. The mixture of solubilized products are generally referred to as bio-oil, although they have historically also been termed proto-oil [1]. Bio-oils produced from SL closely resemble the products of fast pyrolysis.

The choice of solvent can have a strong impact on product distribution and yield [2,3]. For example, recent studies suggest that

certain solvents can lower the apparent activation energy for cellulose depolymerization [4,5].

There are several key attributes of SL bio-oils that are advantageous for use as renewable chemical and fuel precursors. For instance, SL bio-oils tend to have lower oxygen content than fast pyrolysis bio-oils due mild deoxygenation of the product molecules. Deoxygenation can be promoted several ways, but one of the most common is through the use of a hydrogen-donor solvent (HDS) which provides hydrogen to the process [6]. Formic acid, light alcohols such as 2-propanol, and hydrocarbons such as tetralin are among the most common HDSs studied in the literature [6–8]. HDSs are also effective at stabilizing thermal decomposition products. This has a net effect of reducing repolymerization of products [6,8]. In addition to HDS capabilities, the solvent dilutes the products improving their thermal stability [9].

Thermal stability of bio-oil is defined as resiliency against changes in chemical and physical properties upon exposure to elevated temperatures. Bio-oils are generally regarded as having poor thermal stability due to the presence of compounds with reactive oxygenated functionalities such as aldehydes and carboxylic acids [10]. As a result, attempts to fractionate bio-oil through distillation have largely been unsuccessful [11–13].

Abbreviations: PERC, Pittsburgh Energy Research Center; LCO, light cycle oil; mGC, micro gas chromatograph; HDS, hydrogen donor solvent; SL, solvent liquefaction; PDU, process development unit; PTFE, polytetrafluoroethylene; AF, ash-free; MF, moisture-free

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Although these solvent effects are beneficial, the addition of solvent represents a considerable operating cost in commercial operations [3]. For this reason, the development of solvent recycle is very important for the economic viability of SL.

The origins of continuous SL can be traced back to the Bergius process, which was developed early in the 20th century to convert bituminous coal to synthetic fuels. However, it was not until the latter half of the century that continuous SL of biomass was investigated in earnest, largely due to the energy crisis of the 1970s. At that time several processes were developed to produce a bio-based product that resembled crude petroleum. The foremost effort originated with the Pittsburgh Energy Research Center (PERC) of the Bureau of Mines. Researchers developed a process that reacted Douglas fir (*Pseudotsuga menziesii*) in recycled wood oil at 350–370 °C and 270 bar [14]. It became known as the PERC Process. This effort culminated with the construction of a 3 ton day⁻¹ demonstration unit located in Albany, Oregon [15]. Unfortunately, the facility was plagued with technical difficulties, and was ultimately abandoned due to poor economics. A principle problem was the inability to feed biomass slurries greater than 8 wt% dry solids [14]. Despite this setback, research related to the PERC Process was continued at both the Lawrence Berkeley Laboratory and the University of Arizona.

Researchers at the University of Arizona employed a modified single-screw extruder feeder instead of more conventional positive displacement pumps to convey slurries up to 60 wt% wood flour [16]. They demonstrated continuous wood flour liquefaction at pressures up to 25 MPa and temperatures up to 400 °C in the presence of wood oil vacuum bottoms taken from the Albany facility, mixed with steam and carbon monoxide [17]. This work produced bio-oil with an oxygen content of approximately 6–10 wt%, with relative yields at 80–100% of the maximum theoretical yields, or absolute yields of 48–58% [18].

Liquefaction of carbonaceous materials has also been explored in industry. The Exxon donor-solvent coal liquefaction process was developed in the 1970s by the Exxon Research and Engineering Company. This technology was modeled after the Bergius process, and was scaled up to a 1 bone-dry ton day⁻¹ plant. Over the nearly 10 year span of the project, research efforts explored the impact of HDSs, solvent recycle, and product separation techniques [19]. Similar coal liquefaction processes were subsequently explored and patented by Chevron Research Company [20] and Mobil Oil Corporation [21]. Comprehensive review articles on continuous SL have been published by Chornet & Overend [14], Elliott et al. [18], and van Rossum et al. [3].

Despite the long history of SL, the technology faces many practical technology barriers. Thus, the goal of this study was to evaluate several technical barriers pertaining to continuous SL of biomass in a hydrocarbon solvent. In order to study continuous SL at a scale relevant to industrial development, a 1 bone-dry kg hr⁻¹ (a SL process development unit (PDU) was constructed at Iowa State University. Three separate experiments, each more than twelve hours long, were conducted using the SL PDU. The product yields and quality were determined for each experiment. Furthermore, three unit operations were explored in this study. These were continuous solids separation using barrier filters, continuous acetone injection and recycle, and continuous online bio-oil fractionation. To our knowledge, research on continuous solids separation and acetone recycle for SL of biomass has not yet been published.

The studies on bio-oil fractionation have two goals. The first is to demonstrate a bio-oil fractionation system that can continuously separate and recover a stream suitable for use as a recycle solvent. This should be achieved without significantly impacting the product quality and composition. Thus the thermal stability of the product stream entering the bio-oil fractionation system was extensively evaluated.

The second goal is to investigate the thermal stability of the resulting bio-oil. It was hypothesized the bio-oil would have improved thermal stability due to its reduced oxygen content and the presence of the thermally stable hydrocarbon solvent. Improvement on the thermal

Table 1
Southern yellow pine feedstock proximate and ultimate analyses (uncertainty reflects the standard error of the mean).

Proximate Analysis (wt%)	
Moisture (AF)	2.99 ± 0.35
Volatiles (MF)	81.24 ± 0.21
Fixed Carbon (MF)	15.05 ± 0.34
Ash (MF)	3.71 ± 0.13
Ultimate Analysis (wt% AF/MF)	
C	52.77 ± 0.37
H	5.33 ± 0.12
N	0.19 ± 0.04
S	0.01 ± 0.01
O (by difference)	41.70 ± 0.32
AF – ash free	
MF – moisture free	

stability of pyrolysis oils by the presence of a co-solvent has been well documented [23,24].

2. Materials and methods

2.1. Biomass feedstock

Southern yellow pine sawmill residue was acquired from Weyerhaeuser Co. (Seattle, WA) and shipped to Iowa State University in polymer drums. The material consisted primarily of heartwood, but did contain trace amounts of bark. No pine needles were included. The biomass was dried in Fisher Scientific Isotemp ovens from the as-received moisture content of approximately 55 wt% down to 4 wt% or less. All drying was conducted at 105 °C for a minimum of 12 h. Moisture content was periodically measured with an Ohaus MB 25 moisture analyzer to monitor progress. After drying, the material was sieved with a 6.4 mm (0.25 in) square weave screen. Only the material that passed through the screen was kept as feedstock. The combined results of proximate and ultimate analysis of the dried and sized biomass are shown in Table 1. All proximate and ultimate analyses were conducted in duplicates on a Mettler-Toledo TGA/DSC 1 thermogravimetric analyzer and a Elementar vario MICRO cube, respectively.

2.2. Solvent feedstock

The solvent was a blend of two hydrocarbon liquids. The majority of the solvent was comprised of commercially available naphthalene-depleted heavy aromatic solvent (CAS # 64742-94-5). The hydrogen donor solvent was a proprietary cut of light cycle oil (LCO) (CAS # 64741-59-9) that was specially hydrotreated. As much as 25 wt% of the solvent mixture was comprised of the hydrotreated LCO. Higher blend ratios were limited by the economics of providing hydrogen to the process in this manner.

2.3. Feed system

An illustration of the feed system and reactor are shown in Fig. 1. Biomass feeding was done in a two-stage process to feed the solids into a pressurized reactor. The first stage (FDR-1) was an Acrison Weight-Loss-Differential Weigh Feeder model 406 operating at atmospheric pressure. This feeder consisted of a 15 L hopper on top of a single-screw auger capable of metering up to 12.7 L hr⁻¹ of solids. A biomass feed rate of 0.7 kg hr⁻¹ was held constant across all tests.

The second stage (EXT-1) was a Coperion ZSK-26 custom twin-screw compounding extruder. The extruder consisted of two co-rotating intermeshed screws that extended through the middle of 14 stainless steel blocks that collectively make up the extruder barrel. Electric cartridge heaters were inserted into each block to provide heat. Each screw was comprised of 126 individual elements each measuring about 19 mm in

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