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Production of Fischer–Tropsch hydrocarbons via oxygen-blown gasification of charred pinewood pellets

Nazim Muradov *, Amit Gujar, Jong Baik, Ali T-Raissi

Florida Solar Energy Center, 1679 Clearlake Road, Cocoa, FL 32922, USA

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ABSTRACT

Thermochemical conversion of biomass to petroleum-equivalent liquid fuels is of particular practical interest since this approach would require practically no changes in existing engine technology and transportation infrastructure. This paper presents results of experimental studies aimed at the producing liquid hydrocarbons (C7+) via a two-step process: gasification of charred pinewood pellets (CPP) followed by Fischer–Tropsch (FT) synthesis. The gasifier was operated in a semi-continuous updraft mode using a steam-oxygen mixture (in the range of $[H_2O]/[O_2] = 2.2–4.4$ mol/mol) as an input oxidizing gas. The effect of gasification parameters, including the rate of oxygen flow and steam/oxygen molar ratio on the syngas yield and composition was determined. It was found that increasing oxygen flow rate into the gasifier (by a factor of 2.3) resulted in higher (by 32%) H_2/CO ratio while it had a minor effect on the CO/CO_2 ratio in the syngas. Increasing the steam/oxygen ratio led to higher H_2/CO ratio in the syngas (up to 2.1 mol/mol) with slight decrease in the gasification rate of CPP. The water consumption rate was significantly reduced at higher steam/oxygen ratios (by almost half at $[H_2O]/[O_2]$ ratio of 4.4 mol/mol). The syngas from the gasifier was scrubbed of particulate matter and traces of oxygen and dried before it was directed to a FT synthesis reactor. FT synthesis reactor packed with cobalt-based catalyst featuring novel radial-flow design with improved heat-transfer characteristics was employed in this work. The integrated operation of the gasifier and FT reactor yielded mainly C7–C28 straight-chain hydrocarbons. The chain propagation probability (α) of the FT-hydrocarbon products estimated according to Anderson–Schulz–Flory (ASF) distribution model was about 0.8.

1. Introduction

The thermochemical conversion of biomass to biofuels has gained significant momentum recently mostly due to environmental and energy security concerns. The “Billion Ton Study” conducted jointly by the U.S. Department of Energy (DOE) and Department of Agriculture (USDA) concluded that biomass has the potential to displace over 30% of US annual petroleum consumption and that the 1 billion tons of the biomass required can be sustainably obtained from forest and agricultural lands [1]. Of particular interest is the conversion of biomass to petroleum-equivalent fuels such as liquid hydrocarbons since this approach would require practically no changes in engines or existing transportation infrastructure. In principle, biomass can be converted to liquid hydrocarbon fuels (LHF) by at least four thermochemical pathways as follows:

- Gasification of biomass to syngas followed by Fischer–Tropsch (FT) synthesis of LHF (biomass-to-liquid, BTL, technology)
- Pyrolysis of biomass to bio-oil, followed by its catalytic hydrodeoxygenation (CHD) to LHF
- Hydropyrolysis of biomass to LHF.
- Sub- or supercritical hydrothermal liquefaction of biomass to bio-oil (at 250–420 °C and 10–250 atm pressure) followed by its CHD to LHF.

Among the above-listed options, BTL is the most promising route because it is based on two well-established technologies: gasification and FT synthesis. Gasification of biomass produces syngas (mixture of H_2, CO and CO_2) that can be catalytically converted to infrastructure-ready liquid hydrocarbons via FT synthesis [2]. FT synthesis is carried out at the temperature range of 225–365 °C and pressures from 0.5 to 4.0 MPa over transition metal catalysts, predominantly, iron, cobalt, and ruthenium based catalysts [3–6]. Typically, lower range of temperatures and higher pressures favor the formation of heavier hydrocarbons (including waxes), while lighter hydrocarbons (gases

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Abbreviations: ASF, Anderson–Schulz–Flory; ASU, air separation unit; BTL, biomass-to-liquid; CHD, catalytic hydrodeoxygenation; CPP, charred pinewood pellets; CTL, coal-to-liquid; DOE, US Department of Energy; EDX, Energy Dispersive X-ray (EDX) Spectroscopy; FSEC, Florida Solar Energy Center; FT, Fischer–Tropsch; GC, gas chromatograph; GC–MS, gas chromatography mass-spectrometry; GTL, gas-to-liquid; LHF, liquid hydrocarbon fuels; OD, outside diameter; USDA, US Department of Agriculture.

* Corresponding author.

E-mail address: muradov@fsec.ucf.edu (N. Muradov).

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and gasoline range hydrocarbons) are preferentially formed at higher range of temperatures. It should be noted that FT-synthesized hydrocarbons are in many ways superior to petroleum-derived fuels (gasoline, jet and diesel) because they are entirely free of sulfurous and nitrogenous compounds, and contain very few aromatics or other harmful impurities, which results in lower emission levels.

Recently, BTL technology has received intensive developmental efforts involving process analysis and optimization of different technical options and evaluation of FT-fuels' potential to displace petroleum-based transportation fuels [7]. It should be noted that in many ways, the BTL technology is akin to coal-to-liquid (CTL) and gas-to-liquid (GTL) technologies [8,9]. Detailed techno-economic analyses of LHF production from biomass via gasification–FT synthesis have been conducted by several researchers [10–14]. Swanson et al. [11] have shown that the FT hydrocarbons can be produced at the cost of $4–5 per gallon of gasoline equivalent (2007 U.S. dollars). Zhu et al. [14] reported the cost of liquid fuel production by biomass gasification–FT process at $6.75 per gasoline gallon equivalent (2007 U.S. dollars). We have estimated the cost of diesel fuel produced by FT synthesis of the syngas generated by gasification of pine wood to be about $7 per gallon (2005 U.S. dollars) [15].

Despite the fact that extensive data is available in the literature on such aspects of BTL technology development as process modeling, biomass gasification, gas clean-up and FT synthesis, experimental studies of the fully-integrated biomass gasification–FT synthesis systems are rather scarce. For example, Hanaoka et al. [16] described liquid fuel production from woody biomass by means of a downdraft gasifier and a slurry-bed FT reactor utilizing cobalt based catalyst. Folkedahl et al. [17] have developed a process for conversion of coal and biomass to fuels that employed a pressurized fluidized bed gasifier paired with a fixed bed FT reactor using iron based catalyst. It was emphasized in several studies (e.g., [18]), that in order to reduce many problems associated with handling, utilization and processing (e.g., combustion, gasification) of raw biomass, the latter would require substantial pretreatment. Among promising approaches to biomass pretreatment are torrefaction, flash-pyrolysis and charring, which involve thermal treatment of biomass at different levels of severity [18]. For example, during the torrefaction process raw biomass is heated at 200–320 °C in the absence of oxygen resulting in the partial decomposition of biopolymers (mainly, cellulose and hemicellulose) and release of various types of volatiles [19] (note that during the process, biomass loses about 20% of its mass and 10% of its heating value). It has been shown that torrefaction of biomass improves its stability, transportability and makes it easier to process and feed it to gasifiers (using existing coal-processing equipment and infrastructure) [18].

At the Florida Solar Energy Center (FSEC), we have been developing a process for converting biomass (aquatic as well as lignocellulosic) to LHF via an integrated gasification — FT synthesis process [15,20,21]. Oxygen-blown gasifiers were used in our experiments. Use of O_2, instead of air prevents dilution of syngas with N_2, and, thus, allows using smaller reactors and gas-handling equipment. One novelty aspect of our work relates to the use of a water electrolyzer (preferably powered by renewable and inexpensive off-peak electricity) as a source of oxygen and hydrogen for the process. The advantages of using an electrolyzer instead of air separation unit (ASU) are two-fold: 1) due to their modular configuration electrolyzers can be easily scaled up or down depending on the required capacity (in contrast, ASUs are cost-effective only at very large capacities), 2) H_2 produced during water electrolysis can be utilized in a number of operational stages of the biofuel plant. Since, in most cases, H_2/CO ratio in biomass-generated syngas is relatively low for the efficient operation of the FT reactor, H_2 from the electrolyzer can be supplied to the FT reactor to adjust the required H_2/CO ratio in the FT feed stream and ensure its optimal performance. Electrolytic H_2 could also be used in the post-treatment of raw FT hydrocarbons, e.g., in the hydrocracking process, especially, if the FT synthesis yields a product stream with excessive amounts of waxy hydrocarbons. Alternatively, the liquid and waxy hydrocarbon products of the process could be directly introduced into the refinery units for co-processing with petroleum-derived fractions.

This paper aims at demonstrating the feasibility of operating an O_2/steam biomass gasifier integrated with an FT synthesis reactor using charred pinewood pellets (CPP) as a feedstock for the process. The CPP were selected as a feedstock for this study in order to identify and resolve the operational issues of the integrated process without having to deal with additional complicating factors that arise when excessive amounts of tars, pyrolysis gases, particulates, sulfurous compounds are present (the use of whole-biomass feedstock will be the next step in the process development). A pressurized updraft steam-oxygen gasifier coupled with a system of condensers and scrubbers allowing for the efficient post-treatment of the synthesis gas (before it enters FT reactor) was designed and fabricated. Although this type of gasifier is favorable for the feedstocks with relatively high moisture content (which is not the case with CPP), it was used in the experiments to demonstrate the feasibility of the concept and its potential applicability to a variety of biomass feedstocks, including the ones with high moisture content. There are very few studies on gasification of torrefied biomass (e.g., [22]), and, as far as we know, no experimental investigation of the conversion of torrefied biomass to liquid fuels via FT synthesis has been reported in the literature. A novel radial flow tubular FT reactor featuring improved heat-transfer characteristics was designed, fabricated and operated in this work (the novelty aspects of the radial flow FT reactor are explained in more details in the Materials and Methods section). The performance data for the integrated operation of the gasifier and FT reactor were collected and analyzed.

2. Materials and methods

2.1. Feedstock

The feedstock used in this work was CPP prepared by devolatilizing (or charring) virgin pinewood pellets as follows. The fresh pine wood pellets (2.5 cm in length and 0.8 cm in diameter) were obtained from Green Circle Bioenergy Inc. (Cottondale, Florida). The charring vessel (drum) consisted of a cylindrical riser sleeve that was filled with pine wood pellets. A nozzle for air/oxygen flow was placed below the riser sleeve. Initially, a red hot piece of charcoal briquette was placed on the top of the pine pellets with oxygen flowing up from the bottom. The flow was then switched to air so that only pyrolysis vapors were emitted without flaming combustion. The pinewood pellets were stirred from time to time so as to allow homogenous devolatilization of the pellets. The CPP were removed from the vessel when the pellets appeared completely charred. The smoldering CPP were placed in a metal bucket and covered with a lid (cutting off the air supply), thus stopping further reactions. The proximate analysis of charred pinewood pellets used in this study is shown in Table 1.

2.2. Materials and catalysts

20% Co–SiO_2 catalyst was prepared by a conventional incipient wetness method described by Lögdberg [23]. 40 g of Davisil 635 silica gel powder (60–100 mesh) was placed in a drying oven at 110 °C overnight to remove excess water. The cobalt nitrate solution was prepared

Table 1
Proximate analysis of charred pinewood pellets used as a feedstock.

Composition	Mass, %
Moisture	1.11
Primary volatiles (120–650 °C)	16.1
Secondary volatiles (650–950 °C)	17.2
Total volatiles (120–950 °C)	33.4
Fixed carbon	65.5
Ash	2.62