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A novel chemical looping partial oxidation process for thermochemical conversion of biomass to syngas

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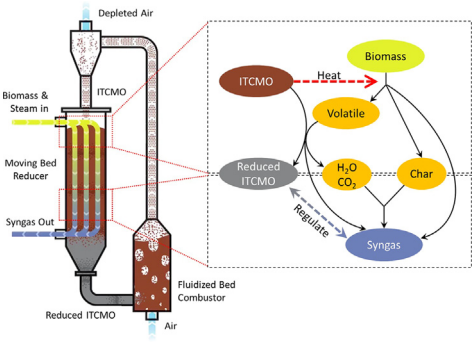
HIGHLIGHTS

- Demonstrated chemical looping process using moving bed for biomass gasification.
- Experimentally verified syngas production at high purity from woody biomass.
- Proved multiple syngas conditioning units are not required for BTS process.
- Process simulation shows significant reduction in biomass and water consumption.
- The new process shows the potential to reduce renewable energy production cost.

GRAPHICAL ABSTRACT



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ABSTRACT

The Biomass-to-Syngas (BTS) chemical looping process is an advanced thermochemical biomass conversion process for the production of sustainable fuels and chemicals. The BTS process is novel in that it converts biomass feedstock to high purity syngas with adjustable H_2:CO molar ratio without needing an air separation unit (ASU), a tar reformer, a steam reformer, or a water-gas-shift (WGS) reactor. In the BTS process, biomass feedstock is partially oxidized to produce syngas by oxygen carriers in a reducer that is operated in a co-current gas-solid moving bed contact mode. The reduced oxygen carriers are regenerated in a fluidized bed combustor via the oxidation reaction with air. The BTS process uses the iron-titanium composite metal oxide (ITCMO) material as the oxygen carrier, which is capable of cracking the volatiles produced in biomass pyrolysis as well as regulating the syngas composition. The co-current moving bed reducer eliminates back-mixing, channeling, or bypassing of solid and gas reactants, resulting in a syngas composition that is close to the thermodynamic equilibrium. In this paper, the rationale of a successful BTS process is discussed along with the thermodynamic characteristics of the ITCMO oxygen carrier, that can effectively react with a woody biomass feedstock, analyzed based on an ASPEN Plus model. Bench scale moving bed reducer experiments are presented, indicating the conversion of wood pellets to syngas with a H_2:CO ratio of 2, which is suitable for methanol or liquid fuel synthesis. The gas and solid composition produced in the bench scale reducer matches the prediction from the ASPEN Plus thermodynamic model. This model is further used to analyze the performance of the BTS process under autothermal conditions for methanol production, with a comparison with a baseline indirectly heated gasification process. The results indicate that the BTS process significantly reduces the biomass and steam

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consumption and appreciably improves the biomass conversion efficiency over that obtained from the baseline process.

1. Introduction

The utilization of biomass as an energy source dates back to the beginning of human history. In an effort to reduce fossil fuel consumption and address growing concerns of greenhouse gas emissions, biomass is growing as an important sustainable fuel source due to its renewable and carbon neutral characteristics and abundant availability [1–3]. The technologies for biomass conversion to fuels and chemicals being developed are categorized into biochemical and thermochemical methods [4–6]. The former include processes that convert biomass to fuels and chemicals via fermentation and/or enzyme-based reactions at mild conditions (lower than 250 °C in most cases). The latter processes convert biomass to products via chemical reactions at elevated temperatures (usually higher than 400 °C). Compared to biochemical methods, thermochemical methods generally have faster reaction rates, which is favorable for developing continuous, large-scale operation systems necessary for commercial power generation and commodity chemical production. In addition, biochemical methods are restricted to specific feedstock conditions that maximize carbohydrates or oil input and, as such, may require additional biomass conditioning, or pretreatment, steps prior to being fed to the biochemical reactor.

Biomass gasification is a type of thermochemical conversion method for the production of CO and H_2, or syngas, a chemical intermediate for a variety of products. Techniques for converting syngas into liquid fuels, hydrogen, methanol, acetic acid, and other high value chemicals have been developed and applied in the chemical industry [7–10]. To date, the syngas generation from biomass feedstock has been realized using multiple gasification technologies [5,6,11–14]. In 1998, the THERMIE demonstration project in Lahti, Finland started commercial operation of a directly heated gasification process to convert biomass into syngas using Foster Wheeler's Atmospheric Circulating Fluidized Bed Gasification (ACFBG) reactor [12]. Air is directly used in this process to gasify the biomass. The syngas produced from the ACFBG process is limited to heat and electricity generation due to the nitrogen dilution from the air supply stream. If chemical production is desired from the gasified biomass, an air separation unit (ASU) must be used in order to produce a high purity syngas stream required for the downstream catalytic conversion units. The use of an ASU for biomass gasification will substantially increase the parasitic energy and capital costs requirements of the chemical plant, resulting in product production costs uncompetitive with the current market value. Battelle developed the indirectly heated gasification technology and demonstrated it at the pilot scale [14]. In contrast to the ACFBG process, the indirectly heated gasifier circulates a heat carrier solid where the heat from the combustion of residual char is used to gasify majority of the biomass with steam avoiding the use of an ASU. In both directly and indirectly heated gasification processes, a substantial portion of the gaseous product from the gasifier consists of light hydrocarbons and tars [11]. Thus, these processes require the use of a catalytic tar reformer and/or steam reformer to increase the syngas purity, resulting in additional capital costs and reduced process efficiencies. Further, in order to adjust the syngas H_2:CO composition for downstream chemical synthesis units, a water-gas-shift (WGS) reactor may also be required.

Steam-only gasification process was developed to produce syngas with high H_2 content. This process requires a large amount of high temperature steam as the gasifying agent to maintain a suitable gasifier temperature for the endothermic gasification reactions, which decreases the overall process energy efficiency [15–17].

In recent efforts, researchers are studying the application of the chemical looping concept for biomass gasification [5,6,18–26]. Chemical looping intensifies indirectly heated gasification process by circulating CaO as a CO_2 carrier between the gasifier and the combustor, which is known as calcium looping gasification or sorption-enhanced reforming [5,6]. CaO absorbs CO_2 in the gasifier to produce a high purity syngas with high H_2 mole fraction. However, experimental studies showed a CH_4 mole fraction of up to 20% in the gas product, indicating the inefficient hydrocarbon conversion in this process [18,19]. Further research is also required to overcome the deactivation and attrition issue of the CO_2 carrier material.

Chemical looping partial oxidation processes are investigated for direct biomass gasification. As illustrated in Fig. 1, chemical looping partial oxidation for direct biomass gasification consists of cyclic reduction-oxidation reactions with recycling metal oxides to produce syngas from biomass and air. In the reducer, the biomass feedstock is partially oxidized via the lattice oxygen in the metal oxides to produce syngas. The reduced metal oxides are transferred into the combustor where they are subsequently regenerated by air and then recycled back to the reducer. The metal oxide serves as an oxygen carrier intermediate separating the air source from the fuel, avoiding the dilution of the syngas product with the nitrogen present in air. Thus, chemical looping gasification processes can produce high purity syngas without the need for ASUs. The concept of chemical looping has been applied to the conversion of gaseous fuels to syngas, which was sometimes referred to as chemical looping reforming [26–30]. The production of high purity syngas from CH_4 was reported by multiple researchers [26–30]. However, the conversion of biomass in chemical looping systems brings additional challenges due to the solid nature of the fuel. Initial demonstrations of biomass gasification using the chemical looping concept with iron ore as the oxygen carrier in a dual fluidized bed reactor system design were reported [21–24]. From the experimental results, 5–15% of the syngas produced from these systems consisted of unconverted hydrocarbons, such as CH_4. This high hydrocarbon concentration in the syngas stream would require additional processing with a steam reformer prior to syngas cleanup and catalytic processing steps for chemical synthesis. When the operating temperature of the chemical looping reactor system was raised in order to increase the conversion of the hydrocarbons in the biomass, the CO and H_2 purity in the syngas product stream decreased due to over conversion to CO_2 and H_2O. The limitations of these chemical looping reactor systems are, in part, due to the use of a fluidized bed reducer reactor and the inability of this reactor design to provide an environment thermodynamically favorable for high CO and H_2 yield.

In this paper, we investigate the application of the Biomass-to-Syngas (BTS) chemical looping process using a co-current moving bed

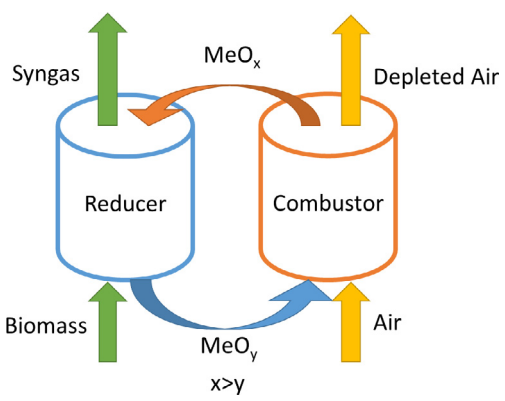

Fig. 1. The concept of chemical looping.