High temperature thermochemical processing of biomass and methane for high conversion and selectivity to H$_2$-enriched syngas

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HIGHLIGHTS

- Hybrid biomass-methane steam processing was studied in the range 1600–1800 K.
- Syngas yields, CGE, and carbon conversion were determined for three bio-feedstocks.
- Production of CO was shown to be kinetically limited relative to H$_2$ production.
- Gasifier efficiency and yields favored allothermal over autothermal operation.

ARTICLE INFO

ABSTRACT

Hybrid thermochemical processes show promise to increase plant performance with respect to fungible hydrocarbon production as a substitute to petroleum-based transportation fuels. Biomass, methane, and steam were reacted in a high temperature, indirectly heated reactor to determine the effects of biomass type (microalgae, rice hulls, cotton stalk), temperature (1600–1800 K), and reactant ratios (α = 0–2.0; β = 1.0–4.8) on carbon conversion, cold gas efficiency, and syngas composition. This hybrid co-feed system was shown to achieve high H$_2$-content syngas with CO selectivity >0.90 and carbon conversion of both biomass and methane >0.90. Temperature was the dominant factor on the yields of CO, CO$_2$, and CH$_4$, while reactant ratios could be used to fine-tune the syngas composition. H$_2$ yield was only slightly dependent on temperature and excess steam. CO formation was highly kinetically-limited for this temperature range. Biomass type slightly affected gasifier performance, most likely due to total char and soot yield from devolatilization. Allothermal reactor design results in comparable gasifier efficiencies depending on steam input and thermal efficiency; a solarthermal reactor would negate 1.3–1.6 kgCO$_2$/kgC processed and represents the recommended configuration for this type of process operation.

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1. Introduction

Liquid transportation fuels in the U.S. accounted for 28% of the total energy consumed in 2011 according to the EIA, adding up to a total of 27 quads that resulted in 1845 MMt CO$_2$ emitted [1]. Concern for domestic energy security and a volatile oil market have spurred interest in producing fungible transportation fuels from domestic resources such as coal, natural gas, shale oil, and biomass. Fuels produced from these resources can be synthesized and/or refined to be compatible with the existing refining, distribution, and storage infrastructure; also, without having to modify point-of-use internal combustion engines. Indeed, the technology within these areas has benefited from 100+ years of innovation

and advancement since petroleum based fuels first became mass produced. Their high energy density and established infrastructure keep liquid hydrocarbons relevant to the national energy picture. Thus, it is likely that fungibility of alternative fuels will remain of high importance, especially for short- and mid-term outlooks. Addressing all issues surrounding conventional transportation fuel sources may imply commercial scale adoption of biomass-to-liquid (BTL) technologies with emphasis on decreased well-to-wheel emissions as it is believed that biomass can at least be partially, if not wholly, renewable and sustainable [2–4].

Unfortunately, BTL technologies for fungible hydrocarbon fuels have limited implementation into the national supply chain, representing less than 0.1% of the total liquid fuels consumed in the U.S., not including ethanol and biodiesel, which are oxygenated and have limited blending compatibility at the refinery stage [5]. Other noteworthy hurdles include high delivered cost of biomass ($4–9/MMBtu) [6–8], small economical delivery radius (∼35 miles)

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[6,7], high initial capital investments required [9–12], and high compositional variability among types and between species-specific varieties [13,14].

From a conversion standpoint, biomasses are highly heterogeneous and oxygenated, typically composed of about 35–50% oxygen by dry weight, indicating that up to half of the feedstock will not be incorporated into the end-product hydrocarbon fuel. As a direct consequence of their oxygenation, biomasses have relatively low heating values compared to natural gas and coal, meaning that more biomass will need to be "upgraded" to form a kilogram of liquid fuel with an energy content equivalent to those that can be produced from fossil fuel resources. To further exacerbate the problem of low mass conversion, liquid hydrocarbon fuels commonly contain hydrogen-to-carbon ratios around 2.1–2.5 whereas this ratio in biomass is about 1.3–1.7, limiting theoretical maximum carbon conversions to 75–85% and further decreasing the maximum total mass conversion unless additional hydrogen is added to the process [15–21].

Perhaps as a result of both high feedstock sensitivity and low mass conversion, hybrid processes have been conceived and analyzed to leverage costs and compositions from two (or more) carbonaceous feedstocks, increasing end-product yield per kilogram of total feedstock [8]. Since natural gas has recently undergone domestic production expansion due to advanced recovery methods from shale it can be used as a hydrogen donor to offset the high oxygen content of biomass in BGTL processes and high carbon content in coal in CGTL processes. From the literature, CGTL and BGTL processes remain a niche area of research and are primarily studied through process design scenarios in software packages such as ASPENPlus™. Little work has been done to experimentally verify operational performance and technical feasibility. Interestingly, most process variations employ gasification as the central conversion unit of the solid fuel. For gasification-based processes where at least one of the target products was liquid fuels, there are three conceptual configurations to convert natural gas and biomass (or coal) to syngas: parallel, sequential, and co-feed. In all scenarios there is remarkable improvement on carbon conversion and liquid fuel yield compared to conventional gasification processes [22–26].

Co-feed processes thermochemically convert the solid and natural gas in the same reactor system. The total number of unit operations is minimized and blending occurs before the inlet of the primary reactor. Studies that include process design show similar results to parallel configurations: increased product yields, carbon-to-fuel conversion, and energy efficiency all with the added benefit of reduced operational greenhouse gas emissions [8,23,25,27,28]. Sudiro and Bertucco studied configurations that included heat contributions from concentrated solar energy in an indirectly heated reactor design [29], representing one of the few attempts to incorporate an externally heated gasifier. Both autothermal [30,31] and allothermal [29,32] configuration gasifiers have been considered resulting in high carbon conversion efficiencies and high selectivity to an H_2-enriched syngas. Autothermal designs, though, require four reactants: biomass, natural gas, oxygen, and steam where it is likely that an air separation unit must be constructed to avoid dilution of syngas products with nitrogen. The energy penalty for generating pure oxygen from air using cryogenic separation techniques is high, representing up to 70% of the total onsite energy consumption [11,12,33,34].

Allothermal designs offer simpler operation based on blending of three reactants where external energy is converted directly to chemical energy via endothermic steam-reforming and steam-gasification reactions [35–37]. The products of combustion, then, do not degrade the value of the product syngas. This is exemplified in, but not limited to, solarthermal reactor systems, operating at high temperatures while avoiding emissions from combustion reactions [37]. Since allothermal designs would require more energy input per mass of feedstock processed, concentrating solar radiation may negate this extra energy penalty and potentially allow for a net-zero lifecycle emissions for the primary conversion reactor.

Recent advances in solarthermal reactor design have enabled high temperature operation in cavity-style receivers achieving temperatures in the range of 1300–2000 K atop power towers centered within fields of solar-tracking heliostats. In the lab, central power towers can be approximated using solar simulators. Receivers have been designed and operated in particle-flow configurations under simulated and 'on-sun' conditions specifically for metal oxide dissociation or water splitting [38–40], methane decomposition [41–43], and steam-gasification of carbon [35,44–47]. Reactor designs are dichotomized into categorizations where the reacting media is either directly or indirectly irradiated, the latter employing absorbers to transfer heat conductively such as in the case of a multiple tubular reactor where the absorbers are opaque and composed of a refractory material able to withstand high temperatures and large temperature gradients [37]. In the presence of oxidizers such as steam, the absorbers are typically formed from sintered silicon carbide or alumina and exhibit maximum long-term operating temperatures around 1923 K. Unfortunately,
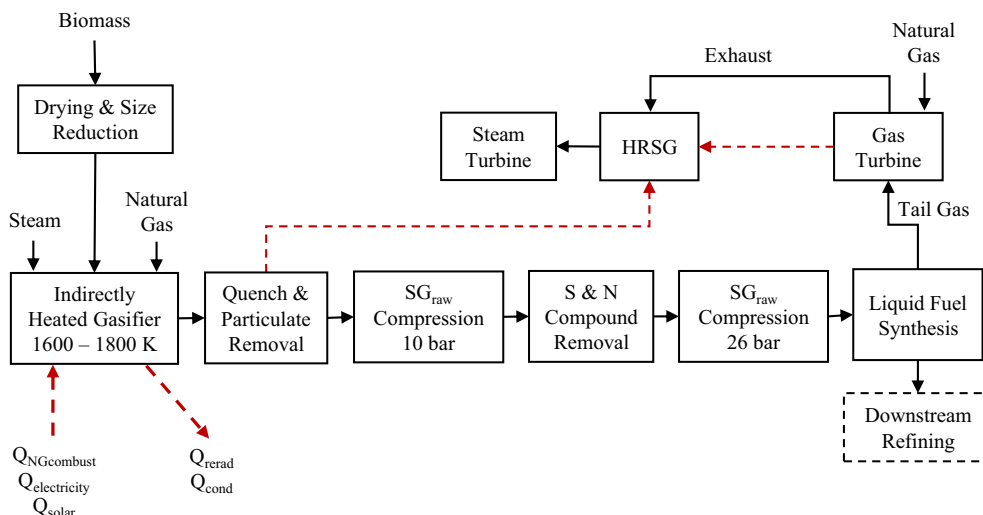

Fig. 1. Example process flow diagram using a co-feed BGTL thermochemical reactor as the primary conversion step in a biorefinery.