



Nickel cerium olivine catalyst for catalytic gasification of biomass

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ABSTRACT

A nickel cerium modified olivine was used as a fluidized bed material in a biomass gasifier and the impact of the modification on biomass conversion, product gas composition, and tar speciation at different temperatures of oak gasification was measured. The experiments were conducted in the pyrolysis mode, without additional input of steam or oxygen (e.g., from air) into the system. In both plain and modified olivine, carbon- and hydrogen-based yields in light gases produced increased as temperature increased from 600 to 800 °C. Using modified olivine resulted in significant improvement in carbon- and hydrogen-based yields and substantial reduction in tars and methane. With modified olivine, the biochar produced at 800 °C was 40% less than that with plain olivine. Characterization of the fresh and post-reaction catalyst showed that a fraction of the NiO was reduced in situ in the gasifier by the syngas. In addition, the catalyst was also contributing oxygen to the environment inside the gasifier in a chemical-looping like mode, resulting in less char and coke formation than that of gasification of biomass without an additional oxygen source. Statistical analysis of molecular beam mass spectrometry data provided detailed tar speciation information under different gasification conditions. At both 650 and 800 °C, the modified olivine was effective in producing more syngas either through conversion of hydrocarbon rich tars into syngas or blocking the pathway for hydrocarbon rich tar formation. However, the impact of the modified olivine in converting oxygenates (that are primarily derived from deconstruction of biomass) into deoxygenated compounds was probably minimal.

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1. Introduction

To reduce green house gas emissions and to ensure a source of long-term, reliable renewable transportation fuels, there is great interest in developing economical and efficient biomass to bio-fuel technologies. Gasification of biomass to syngas is a promising route, as the syngas can be used to produce liquid biofuels through Fisher–Tropsch synthesis [1,2]; to produce dimethyl ether (DME) [3] which can be used as a diesel substitute; or to produce alcohol and advanced biofuels through microbial conversion [4]. During gasification, secondary reactions can produce tars, components that condense at 400–500 °C, resulting in problematic downstream processing as well as loss of carbon efficiency (since the production of tar corresponds to a decrease in CO production, a major component of syngas) [5,6]. There has been extensive research on catalytic tar removal downstream of the gasifier [7–12] and the approach has been found effective and ready for commercial pilot testing.

Though less frequently investigated, several literature reports have indicated that catalytic gasification can significantly reduce or eliminate tar content in the product gas generated from biomass gasification [13–18]. García et al. studied the catalytic pyrolysis (no steam added) and gasification (steam or CO₂ added) of biomass using co-precipitated nickel aluminate catalysts at 650–850 °C [13,19–23]. For catalytic pyrolysis at 650 °C, most of the replicates show gas phase carbon yields in the 50–60% range [20], depending on the catalyst to biomass ratio, the calcination temperature of the catalyst, and whether the catalyst was reduced in situ [20,22]. Increasing the temperature to 700 °C in their catalytic pyrolysis experiments did not significantly impact the gas phase carbon yield [21]. At 700 °C with steam added, the gas phase carbon yield averages 80% for all the runs reported, with the yield closer to 100% for the earlier runs [13]. Garcia et al. concluded that at 700 °C, the addition of steam to the gasification process increases H₂ and CO₂ production primarily through the effect of the catalyst on the water gas shift reaction [13].

The Zaragoza group and another research group at the University of Twente [17,24] further conducted extensive research on the gasification of pyrolysis oil. The two-stage pyro-gasification process offers additional process control and inorganic reduction but does

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require both a pyrolyzer and a gasifier in the biomass conversion process.

Several research groups have reported that iron in olivine, a mineral often used as the fluidizing material in biomass gasifiers, may have catalytic activity. They also endeavored to modify olivine to impart further catalytic activities to the material. Some of the modified olivines were tested for gas phase reforming reactions (no biomass present) while others were tested for catalytic gasification with biomass. Courson et al. impregnated olivine with nickel and tested the catalysts for dry and steam reforming of methane [25,26]. Swierczynski et al. conducted extensive characterization of olivine and nickel-impregnated olivine and used methane and toluene as model compounds to investigate the tar-reforming activity of the modified catalyst [15,27]. The Gas Technology Institute and Ohio State University conducted a detailed study of the impact of thermal vs. aqueous impregnations on the structure and property of several different types of nickel modified olivine and the use of the modified olivine for tar reforming and catalytic gasification [28,29]. To improve the attrition resistance of the catalytic material further, researchers at the Gas Technology Institute also investigated the synthesis and use of glass-ceramics that incorporates NiO as an active component [30,31] as a tar-reforming catalyst.

Rapagna et al. enriched olivine with 10 wt.% iron and reported that steam gasification of biomass with the Fe-enriched olivine reduced tar content by 60% and improved gas yield by 40% [32]. Recently, Virginie et al. used Fe-enriched olivine for biomass gasification in a dual fluidized bed, i.e., the catalyst is cycled between a combustor and a gasifier [18]. They concluded that the Fe-olivine can act as a catalyst for tar and hydrocarbon reforming, as well as an oxygen carrier that transfers oxygen from the combustor to the gasifier, with part of the oxygen used to burn volatile compounds.

In addition to catalytic gasification, Dauenhauer et al. used a rhodium catalyst operating in a combination of partial oxidation and flash volatilization mode to convert biomass into gas [33]. The gas stream produced consists of H₂, CO, CO₂, and light hydrocarbons. The carbon selectivity was quantified, with approximately 65% selectivity for CO₂ and 29% selectivity for CO.

Corella et al. compared the use of olivine and dolomite as fluidized bed material [34,35] and quantified the relative merits of using dolomite in a downstream reactor (downstream-dolomite) vs. in the gasifier itself (in-bed dolomite) [36]. By comparing gas and tar yields of the two different configurations, they concluded that “down-stream-dolomite” only confers slight advantage than “in-bed-dolomite”. They hypothesized that the contact between gas-phase tar molecules and dolomite is better in a “downstream-dolomite” configuration because there are no char and biomass particles in a downstream reactor, though they also concluded that a second bed of dolomite is not necessary if the gasifier bed is well designed and operated. The authors also hypothesized that the observed relatively high tar reduction efficiency of “in-bed dolomite” compared to “downstream dolomite” may be due to “nascent tars” in the gasifier that are less refractory than the types of tars in secondary reactor [36]. Detailed tar composition analysis in both the gasifier and downstream reactor would be useful to test the hypothesis.

In a number of studies the quantity of tar was determined by mass balance (difference between raw biomass and the sum of light gas and char formed) or impinger sampling. Speciation of the type of tars via impinge sampling has to be conducted off-line, e.g., collection of the tars followed by GC-MS analysis [18]. Rapagna et al. used a HPLC/UV method to study tar composition [32]. The HPLC/UV method has been used extensively for identification and quantification of polycyclic aromatic hydrocarbons.

Molecular-beam mass spectrometry (MBMS) is a method that allows universal detection of a large number of species from biomass pyrolysis and gasification, including oxygenates, linear

Table 1

Composition of white oak used in catalytic gasification experiments.

Loss on drying (wt.%)	5.28
Elemental analysis (wt.%, dry and ash free)	
C	50.1
O	43.3
H	5.5
N	0.3
S	0.2
Ash (wt.%, dry)	0.5

hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs). The advantage of this method is that the hot gases flow over the sampling orifice, creating an expansion at the outlet that is nearly adiabatic and isentropic. This yields effective quenching of further chemical reactions of the gas stream before it passes through a skimmer to generate a molecular beam. This beam is ionized with a relatively low energy (22.5 eV) electron beam to minimize fragmentation of the sampled products. Details of the species detected via pyrolysis and tar species determination using MBMS are reported in the literature [37–40]. The use of MBMS for measurement of gases released during catalytic gasification thus allows us to determine the type of tar species present under different experimental conditions. The detailed data on the types of tar molecules present can be incorporated into detailed modeling of the chemical kinetics inside the gasifier and can also be useful in catalytic mechanism investigation.

In this work, we build upon the previous research, but pursue a new catalyst composition, and several new data collection and analysis methods to advance the state of the art in this area and to elucidate new information. For this research we used a nickel-cerium-based catalyst without preliminary reduction; we conducted the gasification experiments in a 4" fluidized bed reactor with on-line MBMS analysis to speciate syngas tars; and used statistical analyses to quantify the impact of the catalyst on tars and oxygenate molecules. We interpreted the gas and char yield data using thermodynamic modeling of the gas composition and evaluated the potential impact of the material both as a catalyst and an oxygen source that reduces coke formation in the system.

2. Experimental

2.1. Material synthesis and material properties determination

The white oak feedstock used in this work was sieved to 18–40 mesh (sieve sizes 1.0 mm and 0.42 mm) fractions, with the average particle size being 0.7 mm. The composition of the white oak is shown in Table 1. The olivine used in the gasifier and used for the catalyst preparation was supplied by AGSCO. Inductively coupled plasma analysis of the olivine indicates that there is 4.4% Fe and 0.25% Ni in the as-received material. The particle size distribution of the olivine is 80–1000 μm, as determined with a Mastersizer 2000 particle size analyzer (Malvern Instruments). Water was used as a dispersant in the measurements using a Hydro 2000G accessory for the particle analyzer.

A nickel-cerium on olivine catalyst was synthesized for this research using incipient wetness impregnation. The catalyst was prepared by drop-wise addition of a solution saturated in nickel and cerium nitrate to an olivine support. The salts used in the aqueous solution preparation are nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, CAS # 13478-00-7, Alfa Aesar stock number 12222) and cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, CAS # 10294-41-4, Alfa Aesar stock # 11329). A saturated solution of nickel and cerium nitrate was prepared by dissolving 250 g Ni(NO₃)₂·6H₂O and 38.8 g Ce(NO₃)₃·6H₂O in water that was kept at 80 °C, with the final solution volume being 200 ml. The prepared

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