Process activated ilmenite as catalyst for cleaning of biomass producer gas

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Abstract:

Catalytic tar cleaning has been identified as a promising technology for upgrading a raw gas originating from biomass gasification. In this work, ilmenite previously collected in the fly-ash from the Chalmers 12 MW circulating fluidized bed boiler was used as a catalyst for producer gas upgrading. The experiments were conducted in a bench scale bubbling fluidized bed reactor fed with a raw gas stream from the Chalmers 2-4 MW indirect biomass gasifier, in which silica sand was the bed material. This reactor is operated in a batch mode and after reduction on raw gas, the catalyst is regenerated using nitrogen diluted air. This study is an extension of earlier experiments using fresh ilmenite and where the concept was proven. Here, the ilmenite particles were exposed to actual process conditions and the possibility to control the operation more accurately is intended to yield kinetics on the tar decomposition but also give hint for a later process up-scaling. The effect of the ilmenite on both tar decomposition and gas composition was evaluated at 800°C and different gas-solid contact times by either varying the flowrate of raw gas or the quantity of ilmenite. Despite an expected short time-on-stream in the boiler at 900°C, the reduced ilmenite fines showed a significant effect on adjusting the gas composition with an H_2/CO ratio increased from 1 in the raw gas to lightly higher than 3 in the reformed gas, a ratio potentially interesting for downstream methane synthesis. More importantly, at the contact time of 1.1s, the tar removal efficiency was as high as 52% on a tar-to-reformed gas basis, and up to 90% if benzene is excluded. Branched hydrocarbons and phenol were almost completely reformed while naphthalene, a stable molecular compound, decreased by 37% although the decomposition of branched tar compounds could contribute to the accumulation of this stable component.

1. Introduction:

Biomass gasification in which biomass is thermochemically converted into gaseous fuel has recently appeared as a promising technology for reducing the CO_2 emissions and the dependency on fossil fuels. The raw gas produced from the gasification process mainly consists of permanent gas components such as H_2, CO, CO_2, CH_4, and light hydrocarbons. However, an unacceptable amount of condensable hydrocarbons, so-called tar, is also formed [1-3]. The condensation of the tar starts around 350°C, usually resulting in a blockage of the downstream systems and an inhibition of the raw gas applications. Consequently, removal of these hydrocarbons plays an important role in the raw gas upgrading process. Among the potential tar cleaning techniques, hot gas cleaning using catalysts seems particularly attractive. With this technique, not only the tar concentration in the producer gas is reduced, but the gas composition can also be adjusted, facilitating the following upgrading steps.

Extensive research on hot conditioning of biomass gasification product gas with various catalytic materials has been performed. Less expensive and environmentally friendly materials have raised attention, especially those naturally originating. Ilmenite, an inexpensive natural iron - titanium ore processing a high attrition resistibility, is one of interest. This material has previously been identified as a promising catalyst for tar cleaning application downstream the gasifier [1-3]. Larsson et al. [4] revealed that ilmenite showed the catalytic effect on decreasing the yield of the tar when it was employed as a bed material in a dual fluidized bed gasifier. The batches of ilmenite used in the current experiments were collected from the fly-ash exiting the Chalmers 12 MW bed boiler operated at approximately 900°C where the alternating redox conditions have enhanced the preliminary activation step of the ilmenite catalyst and possibly exposed them to alkali. Here, the fraction used in the experiment was in the range 45-90 µm. The focus of this study was directed onto the tar reforming properties of the processed ilmenite, particularly in relation with the gas - solid contact time or residence time. The experiments were conducted using a slip stream of raw gas from the Chalmers 2-4 MW indirect biomass gasifier. This stream has a high steam content, approximately 60%. The reactor temperature was kept at 800°C.

2. Concept and methodology:

This work is an extension to previous investigations in a dual-fluidized bed system where the proof of concept, Chemical-Looping Reforming of tars from a biomass-derived raw gas (CLR), was established [1-3]. Here though, the tests in this bench scale bubbling bed reactor can be performed in a more controlled manner and the effect of oxygen transport and actual catalysis decoupled. Moreover, it is possible to change the bed height and adjust the inlet raw gas flow more accurately, which is expected to give hints on the reactions kinetics for the tar decomposition and mechanisms. The idea behind the tar reforming concept is to convert the high molecular weight hydrocarbons into useful gas components. The process is facilitated in the presence of the catalyst at high temperature, demonstrated by ilmenite in the current work. During the time-on-stream in the boiler, the oxygen transport ability of ilmenite was induced because of the exposure to the alternating oxidizing and reducing conditions [5]. Therefore, during the initial stage contacting with the raw gas in the reforming reactor, oxygen carried by ilmenite particles is released to combust hydrocarbons, CO and H_2 available in the raw gas. The oxidized ilmenite is subsequently reduced, resulting in reduced iron oxide and iron metal which will act as catalysts for light hydrocarbons/tar reforming as well as water-gas shift reaction in the high steam content environment.

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