



Full Length Article

Cu-impregnated alumina/silica bed materials for Chemical Looping Reforming of biomass gasification gas



Martin Keller^{a,*}, Jason Fung^b, Henrik Leion^a, Tobias Mattisson^c

^a Department of Chemical and Biological Engineering, Chalmers University of Technology, S-412 96 Göteborg, Sweden

^b University of Strathclyde, Glasgow, United Kingdom

^c Department of Energy and Environment, Chalmers University of Technology, S-412 96 Göteborg, Sweden

ARTICLE INFO

Article history:

Received 1 October 2015

Received in revised form 27 January 2016

Accepted 6 April 2016

Available online 20 April 2016

Keywords:

Tar reforming

Chemical-looping reforming

Gasification

Copper catalyst

Alumina

ABSTRACT

Raw gas derived from low-temperature biomass gasification usually contains condensable hydrocarbons referred to as “tars” as well as other hydrocarbons such as ethylene and other olefins. Reforming of these compounds via Chemical Looping Reforming has been recently proposed. In this work Cu supported on four different Al₂O₃/SiO₂-based porous support materials were investigated for reforming of ethylene. The investigated particles were manufactured by incipient wetness impregnation of the porous support with a copper nitrate solution followed by calcination, and then tested in a small-scale fluidized bed reactor at temperatures between 600 °C and 850 °C. The ethylene conversion was found to be strongly inhibited by the presence of aromatics in the gas. However, it was found that Cu supported on commercial PURALOX transition alumina catalyst exhibited superior properties, with high degrees of ethylene conversion achievable even in the presence of aromatic compounds. Under the experimental conditions in this work, up to 90% ethylene conversion was obtained at $T = 850$ °C in the presence of high concentrations of benzene. For the other prepared materials, the ethylene conversion was drastically reduced when monoaromatic compounds were present in the feed.

© 2016 Published by Elsevier Ltd.

1. Introduction and background

Gasification of biomass presents a promising route to generate carbon-neutral synthesis gas (CO + H₂), which can then be further processed into valuable gaseous and liquid fuels [1–3]. Apart from the desired major syngas compounds CO and H₂, raw gasification gas usually contains impurities and contaminants such as sulfur compounds, ammonia, non-condensable hydrocarbons and condensable hydrocarbons usually referred to as tars [4]. The high condensation temperature of the tar compounds causes them to condense in downstream equipment which may lead to fouling and blocking [5]. Other hydrocarbons than tars commonly found in raw gasification gas include methane, olefins such as ethylene and monoaromatic compounds such as benzene, toluene and xylene (BTX). The concentration and, in particular, the fraction of

the total energy content of these hydrocarbons can be significant, especially when the biomass gasification is conducted at low temperature in an indirect gasification process. For example, Rabou and Van Der Drift conducted measurements of hydrocarbons in the raw gasification gas from the MILENA indirect gasifier. They found concentrations of CH₄, C₂ hydrocarbons and BTX of 13, 4.8 and 1.1 vol.% (dry), corresponding to fractions of 27%, 16% and 9% of the total energy content of the gas, respectively [6]. When Substitute Natural Gas (SNG) is the desired main product to be synthesized in a downstream methanation process, CH₄ should be retained in the gasification gas. Olefins and BTX are problematic compounds since they easily give rise to coke formation on Ni-containing methanation catalysts [7]. It could either be attempted to reform them entirely, or they could be considered as useful products that could potentially be separated and sold as byproducts [6]. The separation of olefins from the gasification gas stream is complex and costly as cryogenic distillation would likely be required [8]. Therefore, it appears more promising to attempt to reform them into compounds that can be utilized in the methanation reaction. BTX compounds, however, could be separated from the gas with relative ease, and thus present an opportunity to generate revenue as byproducts [9]. In any case, comprehensive gas

Abbreviations: BET, Brunauer–Emmett–Teller; BTX, Benzene Toluene Xylene; CLR, Chemical Looping Reforming; FCC, Fluid Catalytic Cracking; FT-IR, Fourier Transform Infrared; SNG, Substitute Natural Gas; XRD, X-Ray Diffraction.

* Corresponding author.

E-mail address: kellerm@chalmers.se (M. Keller).

Nomenclature

γ	conversion of hydrocarbon
φ	degree of gas oxidation
$\Delta\omega$	mass of oxygen transported per gram of bed material, g g^{-1}
K_{eq}	equilibrium constant of water–gas shift reaction
M	molar mass, g mol^{-1}
m	mass of bed material, kg
\dot{n}	molar flow rate, mol s^{-1}
Q	reaction quotient of water–gas shift reaction

t	elapsed time, s
x	molar fraction

Subscripts

in	gas flowing into the experimental reactor
out	gas flowing out from the experimental reactor

cleaning and conditioning is necessary before the raw gasification gas can be utilized in a methanation process.

It has been suggested to reform tars, lighter hydrocarbons and other contaminants by hot catalytic gas cleaning [4,10]. Such a catalytic hot gas conditioning can be realized in various reactor configurations and many different catalytically active bed materials have been proposed and tested [11]. Many of the investigated catalytically active bed materials suffer from deactivation due to coke formation or sulfide formation on their surface [12,13]. Recently, reactor configurations have been proposed that circumvent this problem by continuously regenerating the catalyst in air in a similar way as in a Fluid Catalytic Cracking (FCC) unit [14]. This is achieved by circulating the bed material between a reformer, in which the bed material is contacted with the raw synthesis gas, and a regenerator, in which the bed material is regenerated by oxidizing coke deposits with air. This process is illustrated in Fig. 1 and referred to as Chemical Looping Reforming (CLR).

In recent work it was observed that supported perovskitic $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ and spray-dried $\text{CuO/MgAl}_2\text{O}_4$ are able to convert ethylene effectively in a CLR unit. The supported perovskitic $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ material was furthermore found to be able to convert BTX compounds. The spray-dried Cu-based material was, however, not able to convert monoaromatic compounds. In fact, the conversion of ethylene was even inhibited by the presence of BTX compounds. The selective conversion of olefins and the preservation of monoaromatic compounds over Cu-based bed materials is nonetheless a very interesting property that could be exploited in a process configuration where the objective is not to convert BTX compounds, but instead to separate them and sell them as byproducts, as has been discussed previously.

The previously investigated spray-dried $\text{CuO/MgAl}_2\text{O}_4$ bed material exhibits only a limited active Cu surface area due to the use of micrometer-sized CuO powder as a precursor. The prepara-

tion of catalytically active bed materials by the impregnation of porous, Al_2O_3 -based support material with aqueous solution of Cu salts could potentially generate materials with more favorable properties due to a higher dispersion of Cu. The aim of this work is thus to investigate the suitability of various Al_2O_3 -based support materials for the preparation of Cu-impregnated catalysts for their use as a bed material in a CLR unit for hot gasification gas conditioning. To this end, the conversion of benzene and ethylene over four different Cu-impregnated support materials, both low-cost naturally occurring minerals and commercially available catalyst supports, are investigated in this work.

2. Experimental

2.1. Experimental setup and procedure

Experiments were conducted in a small-scale fluidized bed reactor and the experimental setup is illustrated in Fig. 2. A detailed description of this experimental setup can be found in a previous publication [15]. Experiments were conducted with 9 g of bed material sieved to a size range of 125–250 μm . Additionally, empty reactor experiments were conducted to determine the extent of homogeneous gas phase reactions which could not be attributed to the bed material. To emulate the circulation of the bed material between the regenerator and the reformer of a continuous CLR unit as described in Fig. 1, the bed material was alternately exposed to reducing and oxidizing conditions in a cyclic manner. In between these exposures, the reactor was flushed with N_2 for 180 s. Reducing conditions in the reformer were emulated by a synthetic gasification gas flow of 1 $\text{L}_\text{N}/\text{min}$ for 1000 s. The composition of these gas mixtures is shown in Table 1. For some experiments the concentration of benzene was varied between 0 and 1.4 mol.%. After the exposure of the bed material to the reducing gas, the reactor was flushed with N_2 and then the bed material was exposed to a flow of 0.6 $\text{L}_\text{N}/\text{min}$ of synthetic air (consisting of 20.9% O_2 in N_2) for 360 s in order to emulate the oxidizing conditions in the regenerator and to achieve full reoxidation and regeneration of the bed material. The system was operated at atmospheric pressure and the temperature was varied between 600 °C and 850 °C. Experiments were repeated three times to ensure reproducibility. Unless indicated otherwise, the data presented here are averages of the three experiments.

2.2. Gas analysis

The wet effluent gas was transported in heated lines to a Thermo-Scientific iS50 FT-IR analyzer equipped with a heated gas cell. The FT-IR analyzer was carefully calibrated for the quantification of the concentration of CO , CO_2 , H_2O , CH_4 , C_2H_4 , C_2H_6 , and C_6H_6 by conducting calibration experiments with both pure gases diluted in N_2 and various wet and dry gas mixtures. In total, over

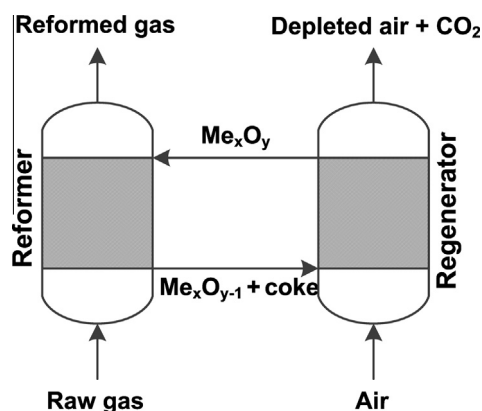


Fig. 1. Schematic of the Chemical Looping Reforming process for gas conditioning of biomass raw gasification gas.

Download English Version:

<https://daneshyari.com/en/article/6633798>

Download Persian Version:

<https://daneshyari.com/article/6633798>

[Daneshyari.com](https://daneshyari.com)