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Elimination of arsenic-containing emissions from gasification of chromated copper arsenate wood

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HIGHLIGHTS

- Bench-scale gasification tests of CCA wood.
- Product gas cleaning system for removing arsenic using a hot filter.
- Equilibrium modeling of arsenic behavior using combined thermodynamic database.

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ABSTRACT

The behavior of arsenic in chromated copper arsenate containing wood during gasification was modeled using thermodynamic equilibrium calculations. The results of the model were validated using bench-scale gasification tests. It is shown that over 99.6% of arsenic can be removed from the product gas by a hot filter when the gas is cooled below the predicted condensation temperature.

1. Introduction

Gasification of biomass and recycled fuels is of particular interest for efficient production of power and heat, as well as allowing for the possibility of liquid biofuel and chemical production. Wood materials treated with special chemicals can be used in certain purposes, such as railway sleepers. The chemical treatments often contain toxic elements which can complicate the disposal of the wood. Generating energy by using a thermochemical process, such as combustion and gasification is one option. Elevated contents of some inorganic chemicals containing toxic species, such as arsenic, makes direct combustion of the material difficult due to possible toxic emissions in the flue gases.

Chromated copper arsenate (CCA) containing wood is one such chemically treated material. Helsen et al. [1] has thoroughly reviewed the possible disposal methods for CCA wood, focusing on thermochemical conversion methods. In the review the authors point out that gas cleaning for removal of arsenic is the key obstacle for gasification of CCA woods.

A review about gasification of fuels containing elevated levels of heavy metals was presented in Konttinen et al. [2]. Considering Arsenic-containing species in gasification product gas, Diaz et al. [3,4] indicated that they are volatile at temperatures of the gasification process and they are condensed at a temperature range of 200–500 °C. The results of gasification of waste-type solid fuels by Konttinen et al. [2] indicated that Arsenic-containing species are condensed at temperatures below 500 °C. The condensation temperature of the heavy metal species in gasification product gases is dependent on the fuel used and other process conditions, such as type of the gasification process and the operating pressure. The railway sleepers of this study contain such high amounts of arsenic that the results of heavy metal condensation in earlier studies may not be applicable.

Konttinen et al. [2] also presented a method and a process to remove inorganic species and elements from the gasification

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product gases by cooling the gases to a certain temperature, thus the harmful inorganic are condensed and removed by the fly ash in the particulate filter. The idea of removing inorganic species from fly ashes in connection with gasification of waste has also been commercially demonstrated in the 160 MWth WtE gasification plant in Lahti, Finland.

The objective of this work has been to investigate the use of CCA containing wood as feedstock to a gasification process for energy generation. It has been of particular interest to prove that the vaporized heavy metals species, such as those containing arsenic, can be removed by condensation from the gasification product gas, even in the case of high heavy metals contents of the fuel. The chemistry and phase changes of inorganic species in the product gas can be investigated using thermodynamic equilibrium modeling. The calculation system and its principles are the same as those presented earlier in Konttinen et al. [2]. The modeled results are also validated experimentally by using a bench-scale gasification setup.

2. Methods

2.1. Equilibrium modeling of As behavior

Thermodynamic equilibrium calculations were performed using the Excel-interface ChemSheet [5] which uses ChemApp [6] for Gibbs energy minimization of the chemical system to find the equilibrium solution. The thermodynamic database used for the calculations was developed by selecting thermodynamic data for 29 elements and their compounds from several different databases and combining the results together. A database was formed, including data from gas, solid and liquid phases (and liquid solutions), for the elements and their compounds that are relevant in reducing gasification conditions [7]. A total of 199 gas compounds were included as well as 505 solid and liquid phases. This method of combining several databases was used previously by Konttinen et al. for modeling the behavior of trace elements in biomass gasification [2]. A complete list of the arsenic containing compounds included in the equilibrium calculations is given in Table 1.

The equilibrium modeling was done for six conditions. Cases A1, A2 and A3 are modeling the conditions inside the gasifier, at temperature 850 °C. Cases B1, B2 and B3 model the conditions after the gas cleaning, where the product gas has been cooled from the gasification temperature to 260 °C. The inputs for B cases are taken as the output gas composition from the corresponding A case (e.g. the output from A1 is used as the input for B1). The elements included in the equilibrium calculations were increased stepwise. For cases A1 and B1 the main ash elements of the biomass were excluded. For cases A2 and B2 the main ash elements are included, but Ca, Al and Si are still excluded. For cases A3 and B3 all fuel ash components were included as well as the bed material feed. The bed material used was dolomite and had a measured chemical composition of 21.23% calcium, 12.01% magnesium and 12.74% carbon on a weight basis, which is generally consistent with the nominal dolomite composition. The inputs values for the equilibrium calculations were based on the measurements of the fuel properties and feed rates for the experimental measurements described below and are given in Tables 2–4.

Table 1
The arsenic containing compounds which included in the thermodynamic database used in the equilibrium calculations.

Gas	Liquid	Solid
As	As	As_2O_3 arsenolite
As_2	As_2O_3	As_2O_3 claudetite
As_2S_3	As_2S_2	As_2O_5
As_3	As_2S_3	As_2S_2 realgar
As_4		As_2S_3 orpiment
As_4O_{10}		As rhombohedral
As_4O_6		$Ca_3(AsO_4)_2$
As_4O_7		$Cd_3(AsO_4)_2$
As_4O_8		$Co_3(AsO_4)_2$
As_4O_9		$Cu_3(AsO_4)_2$
As_4S_4		$Ni_3(AsO_4)_2$
$AsCl_3$		$Zn_3(AsO_4)_2$
AsH		
AsH_2		
AsH_3		
AsO		
AsO_2		
AsS		

Table 2
Ultimate analysis of the treated (dried, crushed and pelletized) CCA-wood sample.

Property	wt% dry basis
Carbon	46.95
Hydrogen	5.46
Nitrogen	0.14
Sulfur	0.08
Oxygen (as balance)	37.25
Ash	9.4
Moisture (wt% wet)	8.4

Table 3
Ash composition of the CCA wood ash.

Ash component	mg/kg ash
Al	8070
As	72,100
B	470
Ba	1160
Be	0.25
Ca	70,300
Cd	920
Co	33
Cr	57,500
Cu	66,400
Fe	60,600
K	10,300
Mg	11,000
Mn	3832
Mo	18
Na	5780
Ni	150
P	2630
Pb	1030
S	8260
Sb	270
Se	55
Sn	25
Ti	330
V	23
Zn	6010

Table 4
Targeted operating conditions.

Temperature, °C	850
Pressure, bar	1.72
Solids feed rate, kg/h	0.45
Steam/feed ration, kg/kg	0.35
Steam feed rate, m^3/h	0.22
Oxygen/feed ration, kg/kg	0.13
Air flow rate, m^3/h	0.14