Tars from air blown fluidized bed biomass gasification: identification, characterization, classification and lump kinetic modeling

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Introduction

Fluidized bed thermal gasification of biomass is an effective route that results in 100 % conversion of the fuel. In contrast to chemical, enzymatic or anaerobic methods of biomass treatment, the thermal conversion leaves no contaminated residue after the process. The products of solid fuel thermochemical conversion can be classified into three different categories: gases, tars and char. Among these the tars are of a special interest in both pyrolysis and gasification processes. During pyrolysis the tars are the main products hence their amount and quality must be studied thoroughly. In gasification the tars are undesired products that can cause problems such as sooting, plugging and deposit formation. The severity of the problems is dependent on the characteristics of the tar species and on the way the product gas is treated. In pressurized IGCC systems based on hot gas cleaning tars are not problematic since they can be kept in gaseous form through the all process steps, from gasifier to the gas turbine [1]. The problem becomes more evidence for systems, where the gas must be cooled down before the final usage. Examples are atmospheric IGCC systems, IC, gas engine and fuel cell applications. For these applications the minimizing of the tars is a crucial step and the extensive research work in this area [2-5] shows the importance of the subject. Up to now the studies on formation and cracking of the tars has been limited to study the single compounds or the entire tar species as a single compound. Our study has shown that tar species can be divided into 5 different lumped groups based on their problematic nature i.e. solubility and condensability. A mathematic model based on the theory of the reaction in continuous mixture is used to predict the formation and cracking of the tars as a function of parameters such as residence time, oxygen availability and temperature. The results of the model will be validated by experiments in a 10 kW^{th} bubbling fluidized bed gasifier.

Tar classification

The aim of the classification is to simplify studying the behavior of different tar species from biomass gasifiers in cold gas cleaning applications. In cold gas cleaning the water from the process will be in condensed form, hence the water soluble tar species will be captured in the process water. The condensation of different tar species will be dependent on their quantity in the gas and also to the gas cleaning temperature. To keep the volumetric heating value of the product gas a low gas cleaning temperature is preferable. However for practical and economical reasons this temperature is going to be above the ambient temperature and below 100°C. In this conditions the main tar categories and their solubility/condensability can be described as follows:

a) Hetrocyclic aromatics: Have generally a high water solubility hence will cause contamination of the waste water.
b) Light aromatic hydrocarbons such as benzene and toluene: Although are found in high concentrations in the product gas, due to their low dew point will stay in the gas phase.
c) Light polyaromatic hydrocarbons consisting of two and three rings: At low concentrations these compounds are in the gas phase but will cause plugging and deposition at high concentrations.
d) Heavy polyaromatic hydrocarbons comprising more than 3 rings: Even at very low concentrations (ppm level) condensation of these compounds will occur at discussed gas cleaning temperatures.
e) GC, GC/MS undetectable tar fraction: Consists probably of unreacted fuel fragments, can be problematic even at very high temperatures.

This classification includes all tar components for which the data about solubility and condensability was available in the literature.

Lumped kinetic model

A computer model for studying of lumped kinetics during biomass thermal conversion has been developed in cooperation between TNO and University of Twente [6]. The model is based on theory of reaction in continuous mixtures, presented by Prasad et.al [7]. The chemical composition of the fuel (C and O content), residence time for the fuel particles and reaction temperature are the input parameters in the model. The model predicts the initial formation and also cracking of the different product lumps as function of fuel composition, residence time and temperature, and calculates the weight fraction for each lumped group at any process conditions. C and O content, and molecular weight are the parameters that are used for dividing the products into different lumped categories. To be able to incorporate the results from the model to tar species, problematic properties of these must be expressed as a function of their C and O content, or molecular weight.

As a first approach the condensability for tar species is described by their boiling point, and more accurately by their partial pressure, which are calculated by using Antoine or Clausius-Clapeyron equations. The paper shows the mathematical expressions for describing the condensation behaviour for all tar compounds having a molecular weight between benzene and coronene and for which Antoine or Clausius-Clapeyron constants were available in the literature (more than 60 compounds).

Experimental validation of mathematical model

The experimental work will be carried on in a 10 kW^{th} bubbling fluidized bed gasifier (L= 1 m, ID= 0.12m) at Laboratory of Thermal Engineering . The gasifier is equipped with isothermal sampling lines at 10 different heights along the reactor; first one located 25 mm above the biomass feeder. At different reactor heights the gas produced will be analyzed on line by GC, IR and FID to determine the concentration of permanent gases, water and light and linear aromatic hydrocarbon. Equivalence Ratio (ER) and the temperature will be varied independently from each other. In combination with the variations in residence time enough information will be achieved for calculation of the kinetic parameters for formation or cracking of different tar species. Two different tar sampling methods will be employed: Solid Phase Adsorption (SPA) for collecting the components within the tar classes **a-c**, and condensation method for groups **d** and **e**. The quantification will be done by using both GC/MS and gravimetric analyses. In previous work a total number of 80 different components has been identified in the tars from biomass gasifiers [8]. These compounds will be grouped within the above mentioned tar classes and lumped kinetic parameters for formation and cracking of each group will be determined for each group.

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