PROJECT DESCRIPTION

"DETERMINATION OF ACTIVE SITES DURING GASIFICATION OF BIOMASS CHAR"

1. BACKGROUND

The use of biomass as a renewable energy source has gained attention as a mean to mitigate fossil fuel depletion, climate change and other environmental problems caused by the traditional energy conversion systems. By gasification of biomass a raw syngas principally consisting of H_2, CO, CO_2, CH_4, light hydrocarbons and some impurities is produced. After cleanup and conditioning, a syngas suitable for further processing is obtained [1,2].

Biomass char gasification is a complex heterogeneous reaction that is strongly influenced by the physico-chemical properties of the char surface and the catalytic activity of the ash. Although the production and properties of biomass chars have been extensively studied and a high amount of kinetic expressions have been generated using thermogravimetral analysis [3], less attention has been paid to the fundamental understanding of the sequence of reactions and the role of the chemical and physical characteristics of the char [4]. Char chemical properties affecting reactivity are related to the active sites and the surface functional groups, as well, as to the presence of catalytic minerals. Physical properties include total internal surface area, porosity and pore size distribution, as well as char carbonaceous structure and ordering [5].

CO_2 or H_2O gasification of char follows an oxygen exchange mechanism that involves dissociative chemisorption of the gasification agent in an active site on the surface followed by desorption and formation of a new active site. In most cases however, the gasification reaction is dominated by the catalytic influence of ash components, mainly alkali and alkaline earth metallic species (AAEM) [7,8]. In this case, the metal undergoes a redox cycle with participation of an active site on the char surface [9,10]. K, Ca and Mg enhance the presence of active sites for char gasification. Other species such as Si and P inhibit the reaction. Some authors found correlations between the concentration of K, Ca, Mg and Si and char reactivity [5], however a comprehensive mechanism of the catalytic influence has not been proposed yet.

The Fuel Technology Division of the Engler-Bunte-Intitute (EBI ceb) of the Karlsruhe Institute of Technology (KIT) together with the Research Group on Biomass and Optimization of Thermal Processes (BIOT) of the National University of Colombia (Unal) have been working since 2015 regarding the investigation of the influence of physical and chemical properties of biomass char during gasification. Until now the research activities concentrate on the development of an experimental methodology that allows for the determination of both non-

catalytic and catalytic active sites on the char surface based on the Temperature-Programmed-Desorption (TPD) technique proposed by Lizzio et al. [6].

During gasification, active sites are occupied by oxygen surface complexes that desorb yielding in CO and CO_2 during TPD. However, catalytic active metals decompose during TPD yielding the same gases. The desorption temperatures of the gases evolving from both origins are similar and therefore the individual contributions are difficult to distinguish. This causes that the original methodology proposed by Lizzio et al. [6] must be modified and the research must be supplemented using complementary techniques for determination of oxygenated surface complexes on the surface, determination of the level of dispersion of the metals on the surface and the measurement of physical properties and its change during gasification.

2. OBJECTIVE

The present project is located within the framework of the cooperation activities currently carried out between BIOT-Unal and EBI-ceb. The main goal is to gain understanding of the phenomenological changes during biomass char gasification that can be applied in the establishment of reliable kinetic expressions describing the course of the reaction.

The objective of the present project is to perform a TPD study on partially gasified biomass char samples with the implementation of variations on the conventional methodology in a way that it is possible to differentiate between non-catalytic and catalytic sites on the char surface. The gasification will be performed using CO_2 as gasification agent on beech wood char.

3. METODOLOGY AND ACTIVITIES

On a first preparatory stage the student will be introduced in the specific knowledge related to the mechanisms of biomass char gasification reaction with CO_2, char physico-chemical characterization and existent experimental techniques. This will be performed in the Unal in Bogotá under the supervision of Prof. Rincón who is the coordinator of the project in the Unal.

At EBI ceb the work of the student will be supervised by Dipl.-Ing. Schneider who is responsible for the project at EBI ceb.

Experimental work at EBI ceb begins with training regarding sample preparation and operation as well as handling of the TPD-MS facility. This includes calibration the mass flow controller (MFC) and the mass spectrometer (MS). A first set of test experiments for checking the repeatability of the experimental results and to standardize the calculations for evaluating of the obtained data will be carried out.

The experimental plan includes following sets of experiments:

i) Experiments with variation of heating rate during TPD in order to quantify the extent of secondary reactions of released gases during TPD.

ii) Experiments aimed to establish the origin of the different peaks of released CO_2 and CO during TPD. Based on the results obtained until now on partially gasified samples (using 80 % CO_2 in Ar at 820 °C) at different conversion levels following parameter variation during TPD measurements will be performed:

- Use of constant temperature ramps to divide the occurrence of desorption and decomposition reactions of ash components.
- Determination of BET (Brunauer-Emmett-Teller) surface area by single-point BET measurement using the function of the TPD-MS facility.
- CO_2 chemisorption experiments at low temperatures.
- TPD decomposition experiments of the individual main of ash components. These results will allow determining their decomposition temperatures and correlating its behavior with the obtained spectra of the partially gasified samples.

iii) Finally TPD experiments of samples submitted to CO_2 gasification using different temperatures will be performed. CO_2 concentration is maintained constant at 80 vol.-% in Ar.

Results obtained during the stay will be continuously discussed with Prof. Rincón and Dipl. Ing. Schneider coordinator of the project at EBI ceb and during programed meetings with Prof. Kolb, head of EBI ceb.

The student must present a final report and make a presentation of the results of the project at the EBI seminar.

4. TIME SCHEDULE

The activities am EBI ceb are planned to be performed on a period of six months between 01.04.2019 and 30.09.2019 according to following schedule:

	April	May	June	July	August	September
Training in sample preparation and handling of the TPD-MS facility						
Calibration and set-up of the TPD-MS facility						
Test experiments with variation of heating rate (set of experiments i)						
TPD measurements with parameter variation (set of experiments ii)						
TPD of samples submitted to gasification at different temperatures (set of experiments iii)						
Compilation and analysis of results						
Elaboration of the final report and presentation on EBI seminar						

The dates of the research stay correspond to the dates of the summer semester at KIT so that the student will be able to enroll at the university and can take part of some of the courses offered at KIT. For example the course Thermal Waste Treatment which is offered at EBI ceb and taught in English.

5. LITERATURE

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