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Thermogravimetric analysis of the combustion of dry distiller's grains with solubles (DDGS) and pyrolysis char under kinetic control

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ABSTRACT

The combustion behavior of dry distiller's grains with solubles (DDGS) and the corresponding pyrolysis char using a thermogravimetric system is studied. Comparison with beech wood indicates that DDGS devolatilization occurs with a slower rate and the char consists of two fractions with different reactivity. Thermogravimetric curves, obtained with heating rates between 2.5 and 20 K/min, are used to develop a multi-step global reaction mechanism. The description of DDGS devolatilization requires four reactions, representative of the evolution of lumped classes of components, with activation energies of 95, 107, 106 and 100 kJ/mol, which are lower than those typically associated with wood devolatilization. DDGS char combustion is well described by two reaction steps with activation energies of 137 and 153 kJ/mol that again barely touch the lower limit of the typical range of values reported for lignocellulosic chars.

1. Introduction

Apart from sugars directly fermentable, the main source of ethanol is currently starch from corn, wheat and barley. Enzymatic hydrolysis is applied to transform starch into sugars which are then fermented by yeasts to produce ethanol, corresponding to about 50% of the grain's energy [1]. The solid residues of this process are indicated as dry distiller's grains with solubles (DDGS). For a dry-grind process [2], the whole stillage (water and solids remaining after distillation of ethanol, comprised primarily of water, fiber, protein, and fat) is centrifuged to separate coarse solids from liquid. The liquid, called thin stillage, goes through an evaporator to remove additional moisture resulting in condensed distiller's solubles (syrup) which contain approximately 30% dry matter. Condensed distiller's solubles, combined with the coarse solids fraction and dried, give rise to DDGS. This residue contains mainly proteins, cellulose, hemicellulose and lignin from the original cereal, with the addition of residual starch and yeast [3]. It is mainly used as a source of protein and energy for ruminants but its increasing production in recent years has motivated the search of alternative uses such as thermal and chemical conversion for bio-energy and bio-fuels. Therefore, for an efficient exploitation, thermo-chemical characterization is needed.

Thermogravimetric analysis, based on integral (TG) and differential data (DTG), is widely recognized as an excellent means to examine the chief characteristics of the conversion process under a controlled environment and is often associated with kinetic modeling. In particular the heterogeneous reaction rates of biomass and char conversion are needed to formulate both empirical rules and kinetic mechanisms that should be coupled with the mathematical description of heat, mass and momentum transfer, to provide advanced tools for combustor/gasifier design and optimization. Therefore, the intrinsic rate, that is, the rate of the reaction step free from heat and mass transfer limitations should be investigated [4]. On the other hand, in commercial thermogravimetric systems the sample temperature is not directly measured or controlled, so that the high exothermicity of the combustion reactions may result in significant deviations between the programmed and the actual sample temperature [5–7]. Moreover a shift from kinetic to diffusion control occurs when the temperature, the heating rate, the sample mass and/or the particle sizes are increased above certain limits [4]. Although numerous studies have been made to investigate the thermogravimetric behavior of biomass under oxidative conditions, kinetic models have been developed only in a relatively few cases [8–21], which can be considered potentially correct. Indeed, they are based on measurements carried out at different heating rates with multiple curve evaluation leading to invariant kinetic parameters. This approach has not yet been applied for DDGS combustion which has until now received scarce consideration.

DDGS thermogravimetric curves in inert atmosphere show three distinct peaks [22–24], in addition to that caused by moisture evaporation, and the attainment of char yields around 20–25%. In air, the devolatilization stage is followed by char combustion [25,26]. Moreover, the dynamic TGA analysis of DDGS char in oxidizing environment at moderate heating rates [23,27] indicates a multi-step process. Devolatilization kinetics in inert atmosphere are described using multiple experiments by means of a distributed activation energy method (25 parallel first order reactions) [22] or using a single experiment

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modeled with two global reactions [23]. Global one-step combustion kinetics is proposed in Ref. [26] for the sequential devolatilization of DDGS and combustion of char with parameters dependent on the heating rate and thus not representative of intrinsic kinetics. Moreover a single experiment is used in Ref. [23] to model char combustion. Instead both isothermal and dynamic data of DDGS char combustion, obtained by varying heating rate and final temperature, are used in Ref. [27]. Unfortunately, however, some of the measurements show incongruities most likely as a consequence of serious mass (oxygen) transfer limitations and probably thermal runaway, due to the rather severe thermal conditions employed, so also affecting the results of the kinetic analysis.

The brief analysis of the state of the art shows that, although mechanisms representative of the intrinsic kinetics of heterogeneous combustion are available for lignocellulosic fuels and a unified treatment has been recently proposed [20], accurate kinetic models are not available for DDGS combustion. Accurate kinetic mechanisms are needed for incorporation into advanced models aimed at optimizing practical conversion systems and also for improving the understanding of experimental results generally obtained from chemical reactors dominated by heat and mass transfer, such as for instance, for various thermochemical processes [1,28–32]. In this study, thermogravimetric curves are measured by means of a previously developed system, which permits precise measurement and control of the sample temperature. Moreover not only the reactions take place under exactly known thermal conditions but also the sample mass and particle sizes are accurately determined so as there is no limitation from the rate of oxygen diffusion. Measurements are made for both DDGS and DDGS char samples in air by varying the heating rate. The TG and DTG data are used to formulate a kinetic mechanism with the evaluation of the related parameters. Previous results obtained for beech wood samples are used for comparison.

2. Materials and methods

2.1. Materials

The DDGS sample has been provided in the framework of the European project BRISK from the same batch previously used [22], obtained by the company Abengoa from a plant in Spain converting barley seeds (Hordeum Vulgare) into ethanol with a dry-grind process. The elemental composition of the sample, listed in Table 1, is also that previously reported [22]. For comparison purposes, beech wood data are also enclosed. The C and H contents of DDGS are comparable to those of wood but the N and S contents are higher. The reported ash content of 7.1% [22] is also much higher than that of beech wood (around 0.4% [33]). According to literature [23], the DDGS ash contains large quantities of P, K, Na and Mg that imply a fouling tendency and also a possible catalytic action on the reaction rates.

In general, there is not agreement in relation to the chemical composition of DDGS which is scarcely investigated, although it highly affects the conversion rate. It can be expected that it is in same way dependent on the origin fuel and the conversion process. According to [34], corn-originated DDGS composition consists of: water extractives 24.7%, ether extractives 11.6%, crude protein 24.9%, glucan (cellulose and starch) 21.2%, xylan and arabinan 13.5%, and ash 4.5% (dry matter 88.8%). Instead for the wheat-originated DDGS [23] a total contribution of the main biomass components around 33% is reported (hemicellulose, about 22%, is the most abundant because harder to ferment compared to cellulose, 7.6% cellulose and 2.88% lignin) with a protein content around 10%.

Table 1
Elemental composition of the DDGS and DDGS char samples (data for beech wood and beech wood char are also included for comparison; oxygen by difference).

	DDGS	Beech wood	DDGS char	Beech wood char
C	49	48.3	59.3	78
H	6.3	6.02	2.64	3.2
N	4.5	0.30	6.20	0.25
S	0.4	<0.05	n.a.	n.a.
O	39.8	45.3	31.9	18.6

Table 1 also lists the ultimate analysis of DDGS and beech wood char samples obtained at a pyrolysis temperature of 800 K following the procedure described below. Apart from the obvious increase in the C content for both cases with respect to the origin fuels, it can be noticed that a lower value is shown by the DDGS char.

2.2. Experimental details

Two different sets of tests are carried out with the scope of investigating 1) the thermogravimetric behavior of DDGS and DDGS char combustion and producing weight loss curves to be used for kinetic analysis and 2) the morphological structure of char produced from DDGS pyrolysis, studied by means of Scanning Electron Microscope (SEM), and the char samples to be used for the thermogravimetric tests. The first set of experiments is made in air using DDGS or DDGS char pellets previously milled to powder (particle sizes below 80 μm) and pre-dried for 10 h at 373 K. The second set of experiments is made in nitrogen using single DDGS pellets with no pretreatment apart from pre-drying as above.

The thermogravimetric tests are made using a non-commercial system already extensively applied to study solid conversion under conditions of kinetic control [8,11,20,21,35–40], where the pulverized sample is settled in the shape of a layer extending over a surface of 4 mm × 20 mm and exposed to a nominal air velocity of 30 mm/s. The temperature of the sample layer, whose thickness is the characteristic size of the process, is measured, by a close-coupled thin thermocouple, and controlled using the intensity of the applied radiative heat flux as the adjustable variable. In this way it is possible to carry out the tests under exactly determined thermal conditions of the sample. For both DDGS and DDGS char, it has been observed that sample layer thicknesses up to 150 μm allow a good temperature control to be achieved and avoid heat and mass transfer limitations. In fact, given maximum heating rates of 40 K/min and a final temperature of 950 K, thermogravimetric curves remain unchanged when the layer thickness is further reduced. Hence, the tests are made for sample layers about 110 μm thick (5 mg mass) using a final temperature of 950 K and heating rates of 2.5–20 K/min (2.5, 5, 10 and 20 K/min for DDGS; 5, 10 and 15 K/min for DDGS char). Each thermogravimetric test is made in triplicate, showing good repeatability (maximum deviations between the measured weight loss curves are always in the range 0.1–0.3%).

The second set of experiments is carried out for the pyrolysis of single DDGS pellets (length 20 mm and diameter 6 mm), instantaneously suspended in a pre-heated (isothermal) cylindrical stainless reactor [36,40] at the temperature of 800 K. Each pyrolysis test is made in triplicate, showing an excellent reproducibility in relation to the char yield (standard deviation of 0.1%). Good reproducibility is also obtained for the time profile of the pellet center temperature with maximum deviations of ± 2 K. The same deviations are also observed for beech wood pellets, of the same size and subjected to pre-drying as the DDGS pellets, used for comparison. The center pellet temperature profile is the same for both DDGS and beech wood at low temperatures (below 600 K). However, during the reaction period, the temperature dynamics of beech wood pellets are clearly affected by reaction heat effects as already discussed in the previous work [41]. Instead, for DDGS, the shape of the temperature profile does not bring any evidence directly related to exothermicity during pyrolysis. As expected, the final temperature reached by the two char samples is the same (about 20 K below the heating temperature). Finally, the DDGS char yield is 27 wt.% (versus 20% of beech wood).