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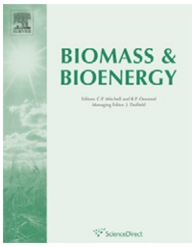

Kinetics of CO release from bark and medium density fibreboard pyrolysis

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ABSTRACT

The apparent rate of CO release during pyrolysis, from bark and Medium Density Fibreboard (MDF) particles was measured. The method used was a pre heated wire grid technique. Experiments were performed under ambient nitrogen and at atmospheric pressure conditions over a temperature range 620–940 K. The temperature history of each pyrolysis experiment has been recorded. The CO release was monitored using a tunable diode laser set to a single infrared absorption line of 2082 cm^{-1}. The release followed a typical growth curve in time to a steady state level. Curves were fitted using a simple first order kinetic analysis and Arrhenius parameters were extracted. Both uncertainties in applied temperature and release rate were taken into account. The calculated apparent activation energies E_a were 64 ± 6 kJ mol^{-1} for bark and 71 ± 6 kJ mol^{-1} for MDF, uncertainties are determined on a very conservative basis. A single apparent rate seems to be a fair description although two time scales can be identified.

1. Introduction

In recent years there has been a renewed emphasis on the use of sustainable forms of energy to replace, at least in part, dwindling fossil fuel resources. However it is not solely on account of economic factors that this upsurge in interest is happening but also due to a widespread awareness of the harmful impact our reliance on fossil fuel is having on our environment. With this in mind, European governments have set targets for increasing the relative contribution from sustainable energy to national power output over the coming years ([1]).

One of the major forms of sustainable energy is biomass, a source that can be reaped and replenished in reasonably short time scales and is considered CO_2 neutral. Research and development in this area has received intermittent emphasis over the years, (e.g. [2]), however, the topic is now in a period of more sustained growth. The by-products of the wood processing industry make a significant contribution to total biomass stocks. This is, therefore, a major source of renewable energy for adapted or purpose built electricity generating plants. An electricity generating plan that is adaptable to variable fuel loads is a more viable economic investment. A variable feedstock means fluctuating levels of CO released from the fuel layer during the pre-combustion, thermal decomposition of the fuel particle or pyrolysis. Pyrolysis is a process whereby a material is thermally decomposed in the absence of an oxidant. In the case of biomass (or coal) the result is the formation of char, tar and gas. Interest is ongoing in the development of kinetic models to accurately describe the release of CO, amongst other species, from the fuel layer (e.g. the European OPTICOMB project, [3,4]). In the study of Albrecht et al., [5], a correlation based on quite coarse experimental observations is used for the volatile release from a fuel bed, to investigate the gaseous combustion in a grate furnace with computational fluid dynamics. For developing

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good design tools also the fuel layer has to be taken into account and thus kinetics has to be known explicitly.

In this study, the feedstock fuels examined were pine bark (*Pinus sylvestris*) and Medium Density Fibreboard or MDF. These materials are high volume by-products of industrial wood processing. Bark has a quite different composition compared to interior wood (40–45% cellulose, 15–30% lignin and 20–35% hemicellulose). Its cellulose content may range from 16 to 41%, lignin 38–58% and hemicellulose, 9–23% ([6]). Furthermore it contains extractives and polyesters and a very peculiar form of lignin. Mainly a by-product of the wood processing industry it is usually disposed of by on site combustion or as landfill, [4]. MDF is a wood based composite material that is used for the production of architectural mouldings. Processing of this material produces a fine, powdery waste with particle sizes lower than 1 mm. The composition varies only slightly between manufacturers, 85% mixed softwoods, 10% Urea Formaldehyde, 4.5% water and 0.5% paraffin wax ([7]).

It was not possible to find experimental kinetic data for a direct comparison however some comments can be made. Owing to the difficulties involved in measuring individual species release kinetics, most investigators have relied on the application of thermal analysis techniques and obtained global pyrolysis kinetics based on weight loss determinations. However, reported activation energies ranging from 14 to 227 kJ mol^{-1} for wood and other cellulosic materials reflect the diverse experimental conditions employed, [8]. The next paragraphs provide a short overview of relevant measurements and is certainly not meant to be comprehensive.

Kinetics based on fast pyrolysis of cellulose and wood decomposition were measured by Simmons and Lee, [9]. Finely powdered Douglas Fir wood and cellulose samples were dropped onto a mesh in a preheated tube with infra red analysis of evolved CO. On the basis of a proposed kinetic model using two parallel reactions it was shown that for cellulose in the temperature range studied, 600–700 K approximately, the activation energy was 41 kJ mol^{-1}. Evidence is presented suggesting the two separate decomposition rates for cellulose and hemicellulose. Aspects of the experimental methodology are similar to this work. Firstly, similar quantities of fine particle size were dropped into a preheat zone minimizing transport effects. Secondly, gas evolution times are of the same order of magnitude to this work.

An analysis of the production kinetics of CH_4, CO_2 and CO from the pyrolysis of poplar bark was performed by Kumar and Mann, [10]. Evolved gases were monitored by GC between 573 and 1023 K using a vertical preheated tube reactor into which a sample approximately 1 g of bark was dropped. It was observed that at approximately 920 K production of CO as well as CH_4 peaked. The reported activation energy was 43,5 kJ mol^{-1}. There are similarities between the technique used by Kumar and Mann, [10] and the grid reactor technique used here. Firstly, both techniques rely on a preheated zone onto which the sample is dropped. Secondly, the temperature range over which the experiments were performed is similar to that used here. A post weight loss rate-limiting step was postulated as a possible reason for higher activation energies reported elsewhere.

Results collected from the pyrolysis of wood in a furnace were presented by Thurner and Mann, [11]. The time resolved production of chars, tars and gases based on the weight loss method was presented in the temperature range 573–673 K. A first order kinetic model was applied to the data and yielded activation energies of 88, 113 and 107 kJ mol^{-1} for gas, tar and char, respectively.

The TGA weight loss technique was applied and a kinetic model developed by Tran and Ray, [8], for the pyrolysis, catalyzed and non-catalyzed, of Douglas Fir Bark. Experiments were performed in the temperature range 520–1000 K. The reported activation energy, ranging from 102 to 202 kJ mol^{-1}, was based on a conversion ranging from 0 to 70%, and was found to have a linear dependence on the extent of conversion.

A fluidized bed technique was used by Chen, [4], to study the slow pyrolysis of pine bark between 1023 and 1123 °C. The conversion kinetics and first order model were developed based on the weight loss approach. An activation energy of 37 kJ mol^{-1} was reported.

The Functional Group-Depolymerization Vaporization cross-linking or FG-DVC code was developed by Advanced Fuel Research ([12]) to model the pyrolysis of coal, e.g. Solomon et al. ([13]). In a modified version of the code the DVC part has been de-emphasized in favor of the FG part to account for the relatively higher quantities of volatiles released by biomass as opposed to coal. This has then been applied to TG-FTIR data on biomass pyrolysis based on first order kinetics with a distributed activation energy model by Chen et al., [14] and De Jong et al., [15,16].

Chen et al., [14], calculated an activation energy of approximately 180 kJ mol^{-1} for CO release, based on weight loss curves of various biomass samples including a higher set of values for lignin ranging from 190 to 315 kJ mol^{-1} at heating rates between 3 and 100 °C/min and adjusted it to fit individual species release rates for temperatures up to 1100 °C. The reported validation attempt with literature data acquired at higher heating rates of 10^3 °C showed good agreement between overall weight loss and model. However, CO yields were underpredicted. A similar approach was used by De Jong et al., [15], who presented a kinetic analysis of species release rates, including CO, from the flash pyrolysis of *Miscanthus* and wood pellets with heating rates between 10 and 100 °C/min to a final temperature of 900 °C. Fitting requirements meant the use of three different sets of kinetic parameters to adequately describe the release of CO. The lowest of the three activation energy values with the smallest distribution presented is 169 kJ mol^{-1}. Species yield underprediction was again noted and rationalized by underlining the model inability to account for light gas release from tar.

The development of accurate, predictive models for thermal decomposition rely not only on a good understanding of heat and mass transfer processes but also on the complicated decomposition and product formation kinetics involved. There exist large deviations in the pyrolysis kinetics reported in literature. This is symptomatic of the difficulties involved in measurements of this type. The majority of kinetic pyrolysis experiments on bark and other cellulosic materials have used a slow pyrolysis technique of which the most widely used are both Thermo-Gravimetric Analysis or TGA