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Modelling pyrolysis with dynamic heating

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ABSTRACT

In literature, the reaction kinetic of pyrolysis process is often determined and modelled under constant heating rates. In reality, the heating rate of an industrial pyrolysis process is difficult or often not necessary to be kept constant. The variation of heating rate at different reaction stages, termed "dynamic heating", governs the pyrolysis performance such as production rate, energy consumption, product quality, etc. In this work, pyrolysis progress with dynamic heating is being studied. The rate and reaction heat of tyre pyrolysis at different heating rates are obtained experimentally. A transient model considering the effect of dynamic heating was then developed and compared with the conventional static heating model. Results show that a higher heating rate favours the production of volatiles and shifts the overall pyrolysis heat flow to more endothermic. The significance of the dynamic heating model was observed for processes with large feed size and/or with high heating rate.

1. Introduction

Pyrolysis is the thermal decomposition of organic materials at elevated temperatures in the absence of oxygen. It yields carbonaceous residues, liquid hydrocarbons and combustible gases. These products can be used as fuel substituent, precursor for producing activated carbon and for the extraction of useful bio-chemicals (Mohan et al., 2006). By using waste materials like waste biomass and waste tyre as feedstock, pyrolysis is a way to utilize these wastes. Pyrolysis is a complex process. Its performance and outcome are determined by the choice of feedstock and the pyrolysis conditions such as temperature, pressure, heating rate, vapour residence time and feed size. Therefore, a lot of works have been carried out to correlate the pyrolysis conditions with the pyrolysis output in light of predicting the pyrolysis performance (Arabiourrutia et al., 2007; Font and Williams, 1995; González et al., 2001; Leung et al., 2002; Park et al., 2010; Rofiqul Islam et al., 2008; Wang et al., 2007; Williams and Besler, 1996; Williams et al., 1990).

The influence of heating rate on the pyrolysis performance has been studied by many works (Arabiourrutia et al., 2007; Font and Williams, 1995; González et al., 2001; Leung and Wang, 1998; Park et al., 2010; Wang et al., 2007; Williams and Besler, 1996; Williams et al., 1990). As mentioned by Park et al. (2010), there is a competition between gas, char, and oil yield during wood pyrolysis depending on the heating conditions. In waste tyre pyrolysis, Williams et al. (1990) suggested that the effect of heating rate on the product yield is relatively small, but more prominent in the characteristics of primary vapours and the surface area of char. In a similar study by them on biomass (Williams and Besler, 1996), it shows a general trend, similar to that in waste tyre, that an increase in the heating rate slightly reduces the char yield and increases both the oil and gas yield. This change in the product distribution has also been noticed by some other works (González et al., 2001; Wang et al., 2007). Quek and Balasubramanian (2009) also pointed out that tyres exhibit different kinetics behaviour under different heating rates. In thermogravimetric analysis (TGA) study, it is common to observe that there is a shift of the mass loss curve to higher temperature when the heating rate increases (González et al., 2001; Leung and Wang, 1998; Quek and Balasubramanian, 2009; Williams and Besler, 1996). These observations suggest that possibly, the pyrolysis mechanism is modified when the heating rate varies.

Experimental investigations usually accompany with modelling works. The development of mathematical models to describe pyrolysis phenomena can greatly assist the large scale development and optimization of pyrolysis process (Di Blasi, 2008). It includes the prediction of reactor performances, the understanding of pollutant emission, the examination of effective control strategies, the development of energy minimization strategies and the optimization of product yield. Of these models, quite a number of them describe biomass particle pyrolysis (Babu and Chaurasia, 2003; Grieco and Baldi, 2011; Koufopanos et al., 1991; Park et al., 2010; Yang et al., 1995).

Pyrolysis is overall endothermic that involves both exothermic and endothermic processes. In biomass pyrolysis, it is suggested

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that endothermic reactions first occur and later followed by exothermic reactions (Koufopanos et al., 1991). The endothermic process is attributed to the primary cracking reactions, while the exothermic process is caused by the secondary reactions between the vapour phase and the solid phase. In tyre rubber pyrolysis, it is believed to be successively exothermic and endothermic reactions (Yang and Roy, 1996).

The influence of exothermic and endothermic nature in pyrolysis is often ignored or simplified in modelling work. In most of the particle pyrolysis models, the heats of reaction are assumed to be constant under different pyrolysis conditions being studied or to be limited to the conditions in which the pyrolysis experiments were performed. In some cases, an overall heat of pyrolysis reactions was considered to lump all the reaction enthalpy changes together disregarding of the existence of both exothermic and endothermic enthalpy changes during pyrolysis. Since the reaction heat flow of pyrolysis plays a key role in altering the heating rate of the pyrolysis feed, which in term influences the pyrolysis performance, such simplification together with the neglect of the effect of varying heating rate possess great uncertainties in modelling pyrolysis.

Slow pyrolysis, which is characterized as having a small heating rate and is usually the case for larger shred of feed, is our subject of study. A transient tyre particle pyrolysis model that integrates tyre pyrolysis kinetics and heat flow has been developed in our previous works (Cheung et al., 2011a, 2011b). Thermal analysis techniques, thermogravimetric analysis (TGA) and differential thermal analysis (DTA), were used to determine the mass loss kinetics and heat flux during tyre pyrolysis under specific heating rates by Yang and Roy's mass-difference baseline method (Yang and Roy, 1996, 1999). The known thermal behaviour information was then used to construct a tyre particle pyrolysis model. Considering also the exothermic and endothermic heat flow, the pyrolysis progress and the process heat flow for bulk tyre particle can then be described transiently.

Experimental thermal analysis only makes use of milligram size of sample and the heating rates of the bulk environment and within the sample are well-controlled and quite steady. On the other hand, in industrial pyrolysis, such steady heating rate condition does not exist. Therefore, to further our work, this work aims to integrate the varying tyre pyrolysis characteristics under different heating rates, termed dynamic heating, into the tyre particle pyrolysis model to account for the difference in the pyrolysis path undergoing at different radial position of the tyre particle because of the difference in the local heating profile. Previous works (Cheung et al., 2011a, 2011b) consider the pyrolysis progress within the tyre particle to be static, i.e. the pyrolysis kinetics and the heat of reactions in every parts of the particle are governed by the constant bulk heating rate instead of the local heating rates. In this work, the effects of heating rate on the mass loss and the heat flux are first examined. A comparison between the old static heating model and the new dynamic heating model is then made.

2. Methodology

Common thermal analysis techniques, thermogravimetric analysis (TGA) and differential thermal analysis (DTA), were employed to examine the thermal behaviour of cotton tyre, which is reinforced by fibre cord, under pyrolysis condition using TGA/DTA 92 Seteram II. Milligram size of the sample was pyrolysed under nitrogen purge environment from ambient temperature to 600 °C with controlled heating rates of 2, 5, 10 and 20 °C/min.

A least squares sum regression approach is used to fit the TGA data. A least squares sum function of the following form is used:

$$S_{TGA} = \sum_{x=1}^{n_{exp}} \sum_{y=1}^{n_x} (\alpha_{T_{x,y,reg}} - \alpha_{T_{x,y,exp}})^2 / n_x^2 \quad (1)$$

where S_{TGA} is the objective function to be minimized for fitting TGA data, $\alpha_{T_{x,y,reg}}$ and $\alpha_{T_{x,y,exp}}$ are the regressed overall mass loss fraction and the experimental overall mass loss fraction, respectively, at a particular temperature and experimental heating rate, n_{exp} is the number of experimental sets performed at different heating rates and n_x is the number of points regressed in an experimental set.

Yang and Roy's mass-difference baseline method (Yang and Roy, 1996, 1999) was utilized to model the pyrolysis heat flow from the DTA data. Similar to fitting the TGA data, a least squares sum function of the following form is used:

$$S_{DTA} = \sum_{x=1}^{n_{exp}} \sum_{y=1}^{n_x} (Q_{T_{x,y,reg}} - Q_{T_{x,y,exp}})^2 / n_x^2 \quad (2)$$

where S_{DTA} is the objective function to be minimized for fitting DTA data, and $Q_{T_{x,y,reg}}$ and $Q_{T_{x,y,exp}}$ are the regressed overall heat flow and the experimental heat flow, respectively, at a particular temperature and experimental heating rate. The obtained kinetics parameters and heat flow parameters were then used to construct the pyrolysis model.

3. Model description

With the kinetics parameters and heat flow parameters obtained from thermal analysis by the Yang and Roy's (1996, 1999) approach, a tyre particle pyrolysis model is constructed. The model aims to predict the pyrolysis progress of a tyre particle. It integrates the mass loss and heat flow characteristics of tyre pyrolysis at different heating rates. The kinetics parameters, the heat flow parameters and some physical properties, mentioned later in Section 5, serve as the model parameters. By inputting the bulk heating profile and the particle size as model variables, the model simulates the pyrolysis transiently and outputs the temperature profiles and the mass loss profiles during pyrolysis. These profiles can indicate the overall energy usage, the completion time and the final residue mass of tyre pyrolysis under the specified pyrolysis conditions.

The model consists of a kinetic model and a heat transfer model. Finite difference method (FDM) is used as the numerical method to discretize the heat equation involved. The following assumptions are made in the model:

(i) Pyrolysing tyre is spherical in shape.
(ii) No shrinking of the tyre particle occurs during pyrolysis.
(iii) Intraparticle heat transfer is by conduction only.
(iv) Heat transfer between bulk environment and particle surface is by convection only.
(v) Temperature gradients are along radial position only.
(vi) Volatiles leave the particle to the pyrolysis environment without directly interfering the progress of pyrolysis.
(vii) The bulk environment has a uniform temperature at any given time.

The pyrolysis of the particle is illustrated in Fig. 1. A particle with radius R is heated by the bulk environment with temperature T_{bulk}. When the bulk temperature T_{bulk} is higher than the particle surface temperature T_R, heat is transferred from the bulk to the particle by convection. In most of the time, the surface temperature is higher than the inner particle temperature. Heat is conducted from the particle surface toward the particle centre along the temperature gradient. At the particle layer with radius r, it receives heat from the outer layer (q_{r+dr}) and at the same time, heat further conduct into the inner layer (q_r). The temperature T_r at the layer determines the pyrolysis progress within that layer. The pyrolysis progress in term determines the reaction heat