Enerbio Ph.D. thesis

Exothermic reactions runaway of biomass torrefaction

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SUMMARY

This work mainly focuses on the Anhydrous Weight Loss (AWL) due to mild thermal treatment (torrefaction) of the main components of lignocellulosic biomass which are cellulose, xylan, glucomannan and lignin. It is shown that kinetic models as the one developed by Lanzetta and Di Blasi [1] for biomass pyrolys is are not accurate enough for AWL predictions at lower temperatures. The Distributed Activation Energy Method (DAEM), initially developed for coal pyrolysis, allows good data fitting to be obtained.

INTRODUCTION

The BTL process (Biomass To Liquid) described in figure 1, allows gas oil to be obtained from woody biomass or agricultural residues.

Figure 1 : BTL principle scheme.
Gasification is one of the key steps of the chain, as it allows to produce syngas (H₂ + CO) from solid biomass. In the case of an Entrained Flow Reactor (EFR), lignocellulosic biomass needs to be pulverized before injection into the gasifier. However, the physical properties of ground biomass are not good enough for pneumatic transportation, and a thermal pretreatment before grinding becomes essential.

Torrefaction is a mild thermal treatment of biomass in a temperature range of 200°C-300°C under inert atmosphere. Even if it leads to an important mass loss, grinding of torrefied biomass gives powders which have better fluidization properties than those of untreated biomass. However, some exothermic reactions occur during torrefaction which may act as a trigger for other exothermic reactions, and generate a temperature overshoot. This overshoot may increase the total mass loss (then decreasing process efficiency) and even lead to complete carbonization, compromising the process safety in the case that too high temperatures were reached.

The aim of this PhD thesis is to find a model able to predict the mass loss and the heat flux during torrefaction. The work presented here deals with the weight loss simulation of the main lignocellulosic biomass components which are cellulose, xylan, glucomannan and lignin.

**Lignocellulosic biomass structure**

The lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin. Cellulose is a linear chain of D-glucopyranose linked by a β 1-4 bound. The hemicellulose is a polysaccharide with side chains, which is mainly composed of 4-O methyl glucuronoxylan (more commonly called xylan) and glucomannan. Lignin is a complex structured polymer; it is accepted to consider it as the combination of three monomers which are coumarylic alcohol, sinapinic alcohol and coniferilic alcohol.

**Experimental set-up for weight loss measurements**

Anhydrous weight loss (AWL) measurements have been carried out using an ATG-DSC device from Setaram (Sensys-Evo 3D), which measures both the mass loss and the heat flux. The ATG measurement is given with a resolution of 0.02 µg which means in our case an accuracy of 0.01 % ; the DSC measurement is given with a resolution of 0.35 µW (1 % accuracy).

**Method**

Samples are first dried at 100°C for 2 hours. Then, they are submitted to a temperature profile which is shown in figure 2 (the drying phase is not shown here). Three levels of temperature (210, 250 and 290°C) have been tested.

Table 1 presents a summary of the main kinetic models found in the literature. We suppose that all reactions are first order and that kinetic constants kᵢ follow the Arrhenius’s law. However, the AWL observed during the heating phase cannot be neglected. This point makes it impossible to solve differential equations analytically. Consequently, it has been chosen to solve those equations numerically.

Finally, the parameters of the Arrhenius’s law are determined by using an inverse method.
RESULTS

Table 1 : Main kinetic model found in literature.

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The AWL of cellulose at 210°C is too low and has not been taken into account. Then, a test run has been realised at 270°C to replace the one at 210°C. Model B has been adopted for xylan, cellulose and glucomannan, while model C has been used for lignin.

![Figure 3](image) Figure 3 : temperature profiles, experimental and modeled AWL for the 4 samples.

In order to validate the kinetic parameters, some other tests with different heating rates have been carried out. Figure 4 shows the comparison between measurements made with a heating rate of 5°C/min and the prediction of model B with parameters identified with a heating rate of 20°C/min in the case of xylan. This figure shows that model B cannot predict the AWL whatever the heating rate.

![Figure 4](image) Figure 4 : Same legend presented in Figure 3

The same observation is made for all other samples, which can be explained by the fact that the chemical reactions which occur during torrefaction, and more precisely the fastest of them, are unknown for now. We have then used another kind of kinetic model, the Distributed Activation Energy Model (DAEM), which consist to consider the torrefaction of a sample as a group of several first order reactions, with a number of reactions high enough to suppose a distribution of activation energy [4]. The AWL prediction is written as follows :

\[
\text{AWL prediction} = \exp\left(\frac{-E_a}{RT}\right)
\]

where:
- \(E_a\) is the activation energy,
- \(R\) is the gas constant,
- \(T\) is the temperature.

The predictions obtained with this model are shown in Figure 5. The figure indicates that the distribution of activation energy accurately predicts the AWL for all samples, except for lignin at 270°C.

![Figure 5](image) Figure 5 : Distribution of activation energy model predictions for the 4 samples.
\[ 1 - \frac{V}{V_{\infty}} = \int_0^\infty \Phi(T,E)f(E)dE \] with \[ \Phi(T,E) = \exp \left( -\frac{A E_0}{RT} \exp \left( \frac{-E}{RT} \right) dt \right) \] and \[ f(E) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{(E - E_0)^2}{2\sigma^2} \right) \]

Where \( V \) is the mass of released gas and \( V_{\infty} \) is the total mass of volatile which could be released. Figure 5 shows the comparison between the AWL measurements and predictions using the DAEM. Figure 6 shows that it is possible to predict the AWL of any sample and so whatever the heating rate or the final temperature.

**CONCLUSIONS AND ACKNOWLEDGMENTS**

This work highlights that torrefaction of cellulose, xylan, glucomannan and lignin cannot be explained using such simple kinetic models as those presented in table 1. It has been shown that the best way to predict the AWL of our samples is to use the Distributed Activation Energy Model. Future work will be focused on the capacity of this method to simulate the measured heat flux.

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**REFERENCES**


