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Mathematical Modelling of Hydrothermal Carbonization of Biomass Using MATLAB

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Abstract: This paper presents an original reaction kinetics model as a tool for estimating the carbon yield in hydrothermal carbonization (HTC) of biomass. The kinetics model was developed in MATLAB. The reaction pathways described through a model, in which biomass is converted into solid, liquid and gaseous products. Runge-Kutta method was used to solve the 4 equations derived from the reaction suggestion, through the estimation of 6 Arrhenius kinetics parameters (k_1, k_2, k_3, k_4, k_5, and k_6). The HTC reaction pathway was described through a lumped model, in which biomass is converted into three phase, residual solid, liquid and gaseous products. By choosing the values of k_1 and others k values and modelling predictions are in the good of the figure pattern. The k values gave good pattern of figure 3 were k_1 = 0.3, k_2=0.1, k_3=0.3, k_4=0.1, k_5=0.2, and k_6=0.1. They resulted that the biomass conversion was very high about of 90%, carbon content of 39%, liquid content of 24, and gaseous content of 30%.

Key words: HTC, model, kinetics, figure pattern

I. Introduction

Biomass mainly consists of lignin, hemi-cellulose and celluloses. Cellulose shows various unique characteristics such as resistance to chemical or including water, and structural rigidity. It was found that crystalline cellulose underwent transformation to an amorphous state in hot and compressed water, which was followed by complete dissolution (Deguchi, 2007). Cellulose molecules are bound to each other by inter- and intra-molecular hydrogen linkages through their hydroxyl groups, and crystalline cellulose is difficult to decompose. Direct liquefaction of biomass in sub- and super-critical solvents water has proven to be an effective approach to convert lignocelluloses materials into low molecular weight chemicals (Wang, 2009).

Biomass can be converted into smaller molecules in the grade of fuels using thermo-chemical processes. The basic reaction mechanisms of biomass liquefaction can be described: (i) The first step is to dissolved the α-cellulose crystalline into liquid phase. (ii) depolimerization of the α-cellulose (iii) decomposition of the biomass monomers by cleavage, dehydration, decarboxylation and deamination; (iv) recombination of the reactive fragments through condensation, cyclization, and polymerization to form new compounds (Huang, 2011). In the first step cellulose is converted into glucose, hemi-cellulose into xylose, and lignin into polyols. The first step is very important step that influents to the whole reaction. Reaction between α-cellulose crystalline can be derived as a fluid-solid reaction.

Information about the fundamentals of the hydrothermal carbonization model system have been studied using model carbohydrate precursors (e.q. D-Xylose and D-Glucose) and their decomposition products (e.q. furfural and HMF) (Baccile, 2008). Degradation of solid biomass become three fraction namely, residual solid, dissolved liguid and gaseous. Biomass dissolved macrostructures and monomers, by further reaction time degradation continue intermediate and gas reaction included dehydration, hydrolysis, aromatization and polymerization (Pedersen, 2016). Lucian (2018) scheme the reaction of degradation in HTC is described that gas can come from degradation of biomass and liquid. It's resulted in the different model of kinetic.

It was demonstrated that under hydrothermal conditions all hexose become sugars, regardless of their complexity, degrade to a HMF intermediate, which finally condenses to a carbon-like materials having similar morphologies and the same chemical and structural composition, independent of the starting precursor. By contrast, D-xylose dehydrates to furfural, which in turn reacts to provide carbon structures very similar to those obtained from using a pure furfural precursor, which are importantly different from materials derived from the hexose (Baccile, 2009). The hydrothermal carbonization reaction essentially proceeds via three important steps: Dehydration of the carbohydrate to HMF or furfural, Polymerization towards polyfurans, and carbonization via further intermolecular dehydration.

Hu (2010) reported that in direct hydrothermal carbonization biomass compounds were heated in sealed autoclaves in the presence of citric acid at 200 ^{o}C for 16 hours. Interestingly they found two types of carbonaceous materials: soft tissues and hard plant tissues. Soft plant tissues were without extended crystalline cellulose scaffolds of spherical carbonaceous nanoparticles of a very small size and porosity. Hard plant tissues are with structural crystalline cellulose scaffolds, however, they can preserve the shape and large scale features on a macro and micro scale; as a result of considerable mass loss, there arises a significant structural change on a nano-scale resulting in a sponge like continuous carbon network with well-defined meso-porous structures.

II. Materials and Methods

The HTC process was degraded biomass into smaller molecules in the form of residual solid, dissolved liquid, and gaseous. As

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mention above the biomass crystalline was degraded into smaller molecules through several steps as describe by (Huang, 2011). Degradation biomass was complex chemical reaction, it's hard to describe by every singular reaction to define the whole reaction in the degradation process. Simplified the whole reaction in HTC process, reseachers used simulation methods to solve the complexity of reaction (Lucian, 2018; Lucian, 2019).

It's can be imagined that the reaction scheme can be shown in Figure 1.

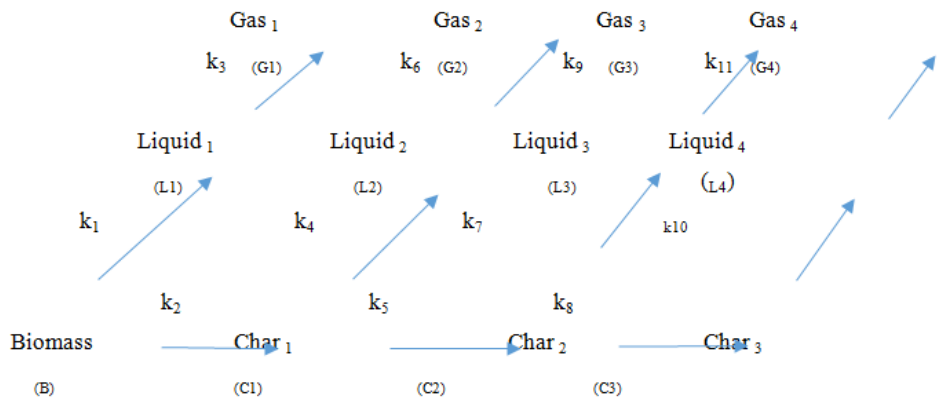

Figure 1. The Schematic of HTC process reaction.

In HTC processes the reaction run simultaneously, in the certain residence time (τ) the scheme can be simplified into single step.

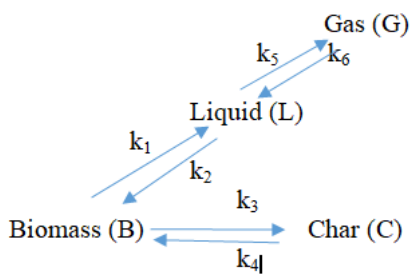

Figure 2. In certain residence time (τ) the HTC process can be simplified in single step.

Mathematical model can be drawn as follows:

1. $\frac{dC_B}{dt} = -k1\ C_B - k2\ CL - k3CB + k4C_C$
2. $\frac{dC_L}{dt} = k1\ C_B\ - k2CL - k5CL + k6\ CG$
3. $\frac{dCC}{dt} = k3\ C_B - k4\ C_C$
4. $\frac{dC_G}{dt} = k5\ C_L - k6C_G$

B= Biomass

C= Char

L= Liquid

G= gas

K value: $ki = ko, i\ e^{\frac{Ea,i}{RT}}$, i= 1,2,3…..6

The kinetics model, developed using MATLAB software.

III. Result and Discussion

The simulation of HTC degradation derive by k value that resulted the figure of degradation products, namely residual solid, liquid and gaseous products. By different k value resulted different of figure patterns. In Figure 3,4, and 5, k values with k_1 = 0.3, 0.4, and 0.5 values of k_2 = 0.1, k_3 = 0.3, k_4=0.1, k_5=0.2. and k_6=0.1 have different pattern of component distribution. In k_1= 0.3 with 10 minutes of running resulted the components distribution were relatively good compared with the k_1 values of 0.4 and 0.5. The component distribution already decreased after 10 minutes run. The carbon component is higher compared to liquid and gas

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components. It,s good results of carbon production (Fig. 3). The biomass conversion was very high about of 90%, carbon content of 39%, liquid content of 24%, and gaseous content of 30%There were a good pattern of conversion and degradation of biomass.

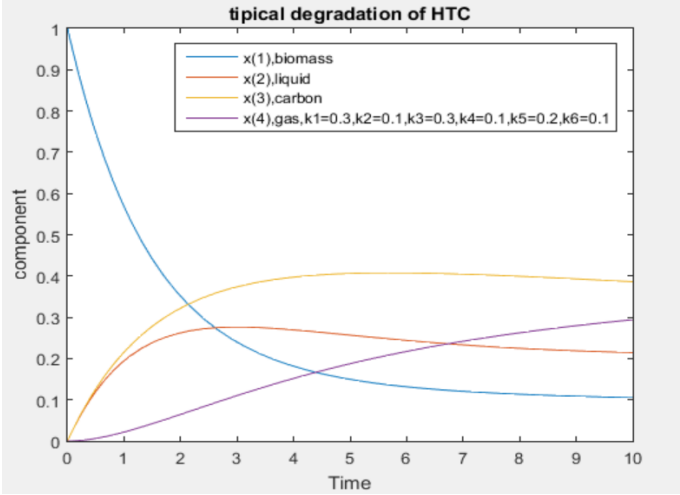

Figure 3. Value of k_1 = 0.3, k_2=0.1, k_3=0.3, k_4=0.1, k_5=0.2, and k_6=0.1

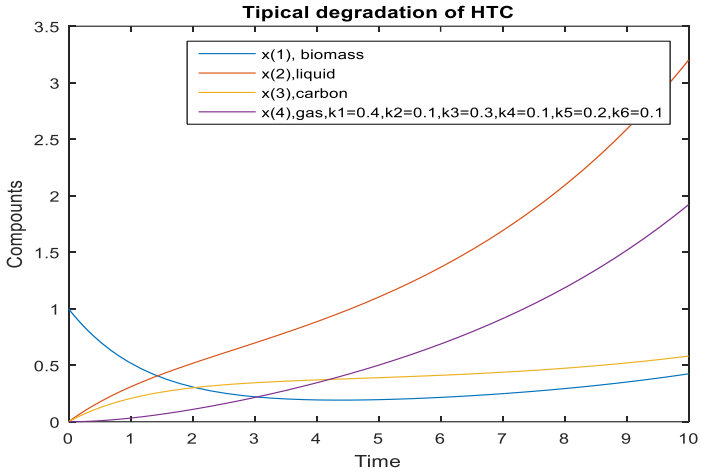

Figure 4. Value of k_1 = 0.4, k_2=0.1, k_3=0.3, k_4=0.1, k_5=0.2, and k_6 =0.1

In figure 4 shown that by k_1 = 0.4 and in ten minutes running gave a pattern of biomass degradation was good enough, biomass degradation was about of 80%, and resulted the carbon content of 50%, liquid content up to 300%, and gaseous content nearly 200%. It's out of prediction. According to the reaction scheme in Figure 4. Increase k_1 from 0.3 to 0.4, there were a different pattern of components distribution in Figure 3 and 4. The liquid and gaseous products rapidly increase, while biomass conversion and carbon products were slowly increase.

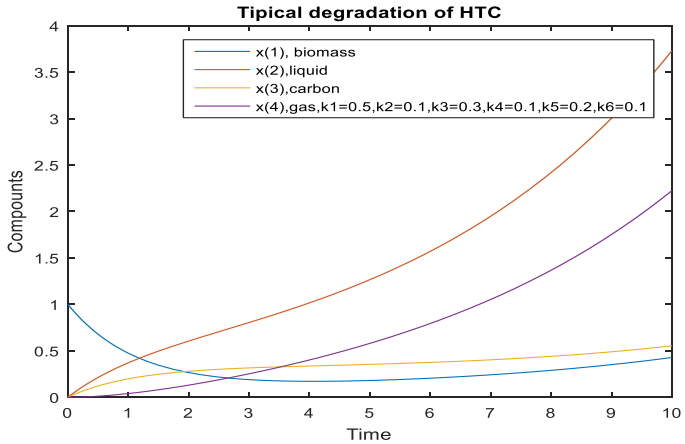

Figure 5. Value of k_1 = 0.5, k_2=0.1, k_3=0.3, k_4=0.1, k_5=0.2, and k_6=0.1

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In figure 5 shown that by k_1 values of 0.5 and 10 minutes of running resulted the components distribution were increased gradually after 10 minutes. It's meant that choosing the value of k_1 = 0.5 were resulted liquid and gaseous products increase rapidly. Biomass degradation was increased after 5 minutes run. The conversion of biomass about of 30%, carbon production was about of 40%, but liquid and gaseous products were very high, it's up 100%, it's out of prediction. While biomass conversion and carbon products were slowly increase.

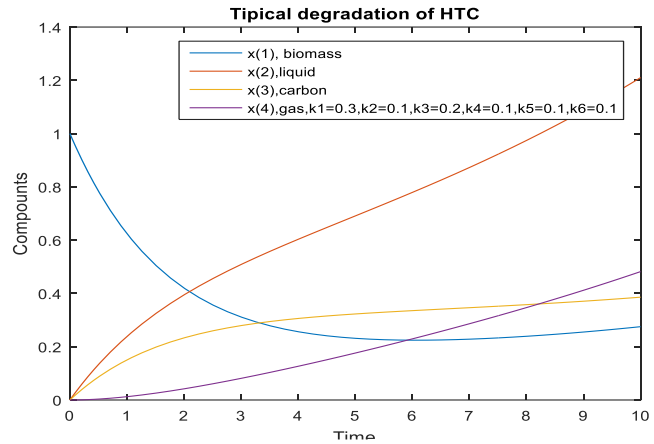

Figure 6. Value of k_1 = 0.3, k_2=0.1, k_3=0.2, k_4=0.1, k_5=0.1, and k_6=0.1

In Figure 6 shown that k_1=0.3, k_3 =0.2 and k_5 = 0.1 resulted degradation component composition. Biomass degradation resulted conversion of 70%, carbon of 40%, gaseous of 50%, and liquid production up to 120% (out of prediction). By the different of k value , there was different pattern of figure between Figure 3 and Figure 6. The k value in Figure 3 were that k_3 = 0.2, k_5=0.2 and in Figure 4 the k value were k_3 =0.2 and k_5 =0.1. There was different pattern of Figure between Figure 3 and Figure 6. In Figure 6 biomass degradation was about 72%, carbon content of 40%, gaseous production was about 48%, while liquid production was about 120% (out of prediction). Reduced the value of k_3 from 0.3 to 0.2 carbon and gaseous production were similar values in Figure 3 and 6. Liquid production completely different, in Figure 3 liquid production was 24% and in Figure 6 was about 120%.

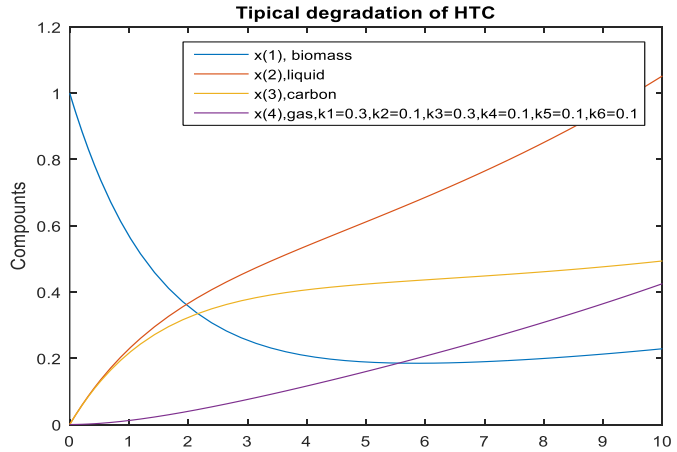

Figure 7. Value of k_1 = 0.3, k_2=0.1, k_3=0.3, k_4=0.1, k_5=0.1, and k_6=0.1

In Figure 7 shown that by different value of k_5 in Figure 3 k_5 = 0.2 and Figure 7, k_5 = 0.1, there were different pattern of components distribution. In Figure 7 resulted biomass conversion of 80%, carbon conversion of 48%, gaseous conversion of 42%, and liquid conversion of 105%. The liquid result is to high.

V. Conclusions

The simulation can be concluded that after several run resulted different figures of degradation biomass become solid residue, liquid and gaseous. Each run with different k value gave a typical pattern of figure that presentation of the degradation composition. The good pattern of the figure is in figure 3, with the value of k_1 = 0.3, k_2=0.1, k_3=0.3, k_4=0.1, k_5=0.2, and k_6=0.1. It was resulted biomass degradation about 80%, carbon content of about 40%, liquid content about of 30% and gaseous content of about 39%. It was a good results that closed to the real laboratorium works.

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