

# Chapter 5

## Oil Palm Biomass and Its Kinetic Transformation Properties

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**Abstract** Malaysia generates millions of tons of oil palm biomass from oil palm mills which need a proper waste utilization application. One of the most commonly method used to utilize the wastes is by using pyrolysis method. This chapter discusses some current applications of biomass pyrolysis. Moreover, kinetic transformation properties of biomass, biomass pyrolysis reaction kinetics, and parameter estimation have also been discussed as the purpose of kinetic modeling is to find a good correlation between reaction rate ( $k$ ), conversion rate ( $\alpha$ ), and reaction temperature ( $T$ ). In order to interpret the biomass pyrolysis behavior, activation energy ( $E$ ) and pre-factor ( $A$ ) were needed and calculated based on Arrhenius equation. Last but not least, the recently available kinetic models such as lumped and distributed models are also listed.

**Keywords** Oil palm biomass · Pyrolysis · Kinetics · Modeling

### 1 Introduction

Malaysia is blessed with abundant of agricultural resources. In the previous years, agricultural industry has become the major of few other contributors for Malaysia's economy sector. Malaysia is the world's second major producer of palm oil, after Indonesia, and is one the biggest contributor to the country's economy. In 2016, Malaysia had an increase of 1.7% of total plantation, with total plantation area of 5.74 million hectares compared to 5.64 ha in the previous year. The state of Sabah has the largest total planted area in Malaysia with 1.55 million hectares followed by Sarawak with total hectarage of 1.51 million hectares. Meanwhile, Peninsular Malaysia with the 11 states contributed around 2.68 million hectares of palm

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plantation area (MPOB 2017). Biomass is a popular source of renewable energy, can be converted into fuel, and used to generate electricity or other forms of power. It usually refers to plant-based materials which are used other than for food or feed. This lignocellulosic biomass is often used directly in producing heat and power by combustion, as well as indirectly after it has been converted into biofuel. Lignocellulosic biomass contains three main components; lignin, cellulose, and hemicellulose, followed by other subcomponents; protein, pectin, ash, and extractives.

## 2 Current Application of Oil Palm Biomass in Malaysia

Currently, many researches focused on biomass as another source of power generation. Figure 1 shows some initiatives of using biomass as renewable energy.

### 2.1 Bioproduct

Bioproducts are materials, chemicals, and energy derived from renewable biological resources. Oil palm biomass utilization as bio-fertilizer is a common way to reuse the waste as a beneficial product. For example, shredded OPF and OPT are being returned to the oil palm estate as mulch (Geng 2014). Moreover, Wu et al. (2009) also reviewed the potential application of POME as fertilizer, fermentation media, and live food for animals and aquaculture organism. In POME, high concentrations of carbohydrates, lipids, protein, nitrogenous compounds, and minerals can be found. These compounds could be used as fermentation media for the production of various metabolites such as bio-insecticides, polyhydroxyalkanoates,

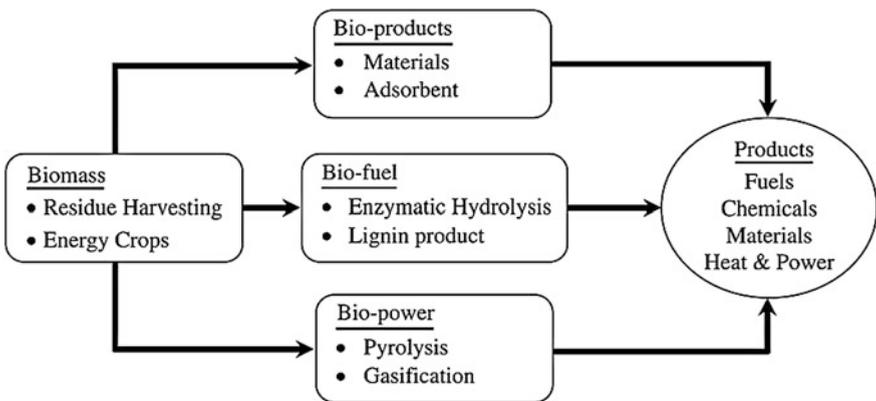


Fig. 1 Biomass initiatives as renewable energy (Sumathi et al. 2008)

antibiotics, organic acids, and enzymes. According to Saidu et al. (2011), mesocarp fiber (MF) of oil palm also served as good substrate for cultivation of oyster mushroom. Last but not least, activated carbon also can be produced from EFB, OPF, and OPT (Alam et al. 2007; Salman and Hameed 2010; Ahmad et al. 2007). They also have been used as adsorbents (Shuit et al. 2009). Moreover, OPF can also be used as a component in the formulation of ruminant animals' feed (Zahari et al. 2003).

## 2.2 Biofuel

A type of fuel that is produced through contemporary biological processes, such as agriculture and anaerobic digestion is known as biofuel. It is a liquid or gaseous fuel that is derived from renewable sources such as biomass and generally used for power plants and transport sectors. The depletion of petroleum source makes biofuel, such as biohydrogen and bio-methanol, a feasible alternative as fuel for the transportation sector. Besides its much cheaper pricing and sustainable supply, biofuel resulted in a near-zero air pollution (Ibrahim et al. 2014). The oil palm biomass can also be converted to bioethanol (Shuit et al. 2009). Bioethanol is one of the products of fermentation from sugar or starch rich biomasses including oil palm. Yamada et al. (2010) stated that oil palm trunk (OPT) has become a promising source of sugars as good feedstock for bioethanol. The sap from OPT core also gives a great potential biofuel and value-added chemical as it can be converted into bioethanol (Wan Asma et al. 2010). Furthermore, utilization of POME with a greater beneficial return to culture microalgae for biodiesel and bioethanol production was discussed by Lam and Lee (2011) in a review study.

Bio-oil contains a huge amount of oxygenated molecules which made it unstable, viscous, and corrosive but it depends on biomass feedstock and pyrolysis condition (Demirbas 2011). There are so many names for bio-oil such as pyrolysis oil, pyroligneous acid, and wood liquids. It has dark-brown color with strong acrid smell (Abnisa et al. 2011). Solid biomass can be converted into liquid bio-oil through pyrolysis, which is easier to transport, store, and upgrade (Demirbas 2011). Pyrolysis of lignocellulosic biomass produced bio-oil which is a complex group of chemical as it contains organic acids, ketones, phenolic compounds, furans, aldehydes, and many other compounds (Chen and Lin 2016). In some previous studies, production of bio-oil from oil palm biomass has concluded that the bio-oil has potential as fuel source and chemical feedstocks (Sukiran et al. 2009; Khor et al. 2009; Abnisa et al. 2013). The generated bio-oil may be directly used for boiler or furnace and also can be considered to be used for vehicles after refinement process (Khor et al. 2009).

Study by Abnisa et al. found that the oxygenated contents of bio-oil from pyrolysis process were quite high (71.40%). High content of oxygenated compounds makes bio-oil less attractive to be used as transport fuels due to decrement of high heating values. This makes it imperative to remove these compounds using

methods such as hydrotreating–hydrocracking process which would not just increase the heating value but also reduce the corrosive properties (Abnisa et al. 2011). According to Sumathi et al. bioethanol and bio-oil can be produced by using EFB as a feedstock through fermentation or hydrolysis, and pyrolysis, respectively (Sumathi et al. 2008). Last but not least, solid by-product generated from pyrolysis also found to be potentially used as alternative fuel for energy production (Salema and Ani 2012).

### 2.3 Bioenergy

Bioenergy or bioenergy is renewable energy made available from materials derived from biological sources and it is the biggest source of national renewable energy (Sumathi et al. 2008). The production of bioenergy from lignocellulosic biomass provides another alternative for biomass conversion. A review on electricity generation in Malaysia by Shafie et al. (2012) stated that oil palm based biomass including EFB, PKS, OPF as well as other biomasses have great potential for this sector. There also a study by Lam and Lee (2011) discovered the potential of POME as an alternative source of biomethane and biohydrogen for renewable energies generation. Furthermore, oil palm biomass also can produce hydrogen gas as renewable energy (Mohammed et al. 2011).

## 3 Kinetic Transformation Properties of Biomass

Biomass is a carbonaceous resource of renewable energy and is abundantly available around the world. The awareness in producing energy from biomass has increased drastically in the past few decades due to environmental issues which is increasing of carbon dioxide content in atmosphere, associated with the depletion of fossil fuel resources. Bio-oil from biomass pyrolysis is a suitable and eligible replacement for the fossil fuels (Asadieraghi and Daud 2015). Pyrolysis is a thermochemical process of decomposition of organic material or biomass such as wood, garbage and industrial waste. It is a most known and promising industrial technology as it efficiently converts biomass into advanced fuels, bio-oil, solid charcoal, and gaseous products (Cai and Liu 2016; Asadieraghi and Daud 2015). Understanding the kinetics of biomass pyrolysis could help in describing the physicochemical phenomena occurred inside the pyrolysis vessel. The kinetics also can predict the products distribution, mass loss behavior, chemistry of the solid decomposition, and thermal transfer between wall of vessel as it provides valuable information for reactor design and optimization of pyrolysis process in industry (Wang et al. 2016; Reverte et al. 2007). The purpose of kinetic modeling is to find a good correlation between reaction rate ( $k$ ), conversion rate ( $\alpha$ ), and reaction temperature ( $T$ ). Thus, a solid understanding of kinetics of biomass pyrolysis is very

crucial in developing design tools for a bigger scale pyrolysis including industrial scale pyrolysis process and reactor design.

## 4 Biomass Pyrolysis Reaction Kinetics and Parameter Estimation

The Arrhenius equation is commonly used in determining the pyrolysis reaction kinetics. Activation energy ( $E$ ), pre-factor ( $A$ ), and kinetic equation or reaction model ( $f(\alpha)$ ) were calculated to interpret the biomass pyrolysis behavior (Wang et al. 2016). A solid body thermal degradation needs solving of heat and mass balance equation in order to calculate the temperature and gas composition at each location inside the material. The calculation of mass and heat source terms comes from the chemical reactions progress which is computed from reaction schemes considering some kinetic parameters (Reverte et al. 2007). Biomass thermal degradation under non-isothermal condition can be represented as follow (Zhang et al. 2006; Khan et al. 2011):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \quad (1)$$

Based on above equation,  $\alpha$ —sample mass fraction reacted,  $T$ —temperature,  $A$ —frequency factor,  $E$ —activation energy,  $R$ —universal gas constant and  $n$ —reaction order.

$\alpha$  can be defined as:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (2)$$

where  $m_0$ —initial weight,  $m$ —actual weight,  $m_\infty$ —final weight.

By integrating Eq. (1), it becomes:

$$\frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (3)$$

In Eq. (3),  $\int_0^T \exp\left(-\frac{E}{RT}\right)$  has no definite solution. Thus, integrating the function by neglecting high order terms, it becomes:

$$\frac{1 - (1 - \alpha)^{1-n}}{(1 - n)} = \frac{ART^2}{\beta E} \left[1 - \frac{2RT}{E}\right] \exp\left(-\frac{E}{RT}\right) \quad (4)$$

Equation obtained below is in logarithmic form:

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[ \frac{ART^2}{\beta E} \left[ 1 - \frac{2RT}{E} \right] \exp \left( -\frac{E}{RT} \right) \right] \quad (5)$$

As  $RT/E \ll 1$ , it can be assumed that  $1 - 2RT/E \sim 1$  (Ahmed and Gupta 2009), so the final form for  $n$ th order reaction can be derived as:

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[ \frac{AR}{\beta E} \right] - \frac{E}{RT} \quad (6)$$

For the first order reaction, the equation becomes:

$$\ln \left[ -\frac{\ln(1 - \alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \right] - \frac{E}{RT} \quad (7)$$

Plotting left-hand side term of Eqs. (6) and (7) against  $1/T$  will get  $n$ th and first order reactions, respectively. The resulting straight line poses a slope of  $E/R$  and intercept of  $\ln(AR/\beta E)$ . Activation energy and frequency factor can be determined using the slope and intercept values (Ahmed and Gupta 2009).

In conjunction with that, it is important to consider some factors such as kinetic model, reaction scheme, and reaction rates before analyzing the kinetic parameters. The kinetic parameters should be distinctive and independent of operating conditions (Reverte et al. 2007). The determination of activation energy, reaction model, and other kinetic parameters such as pre-factor, and reaction order have been discussed by Wang et al. in their research about kinetics of biomass pyrolysis (cellulose, hemicellulose, and lignin) using model-fitting method (Wang et al. 2016). Furthermore, in a previous study by David et al. uses six reaction schemes to analyze thermal degradation of cardboard but it comes out with no conclusion which one is the right scheme (David et al. 2003). Moreover, literature reviews have been made by (Antal and Varhegyi 1995; Conesa et al. 1995) on how many kinetic laws and parameters have been proposed by previous researches about cellulose thermal degradation.

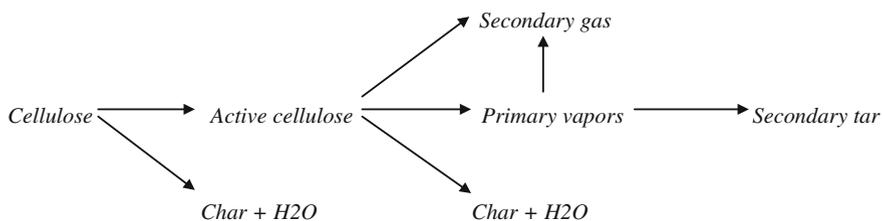
## 5 Kinetic Models

Kinetic models consist of some different types of reaction models developed to differentiate the reaction occurs during biomass degradation. These models can be categorized to two groups based on their mechanism of reaction through pyrolysis process named as lumped and distributed models (Sharma et al. 2015).

### 5.1 Lumped Model

The first group of kinetic models is lumped model where both individual components of biomass and reaction products are lumped into three categories; gas, tar, and char. There were some proposed kinetic schemes respecting the biomass degradation and volatile products. The lumped model is then separated to study the homogeneous species decomposition of biomass and its individual components.

There are some models developed for lignin, cellulose, and hemicellulose decomposition. Bradbury et al. proposed a three-reaction model for the degradation of cellulose through pyrolysis (Bradbury et al. 1979). The model was developed from Broido model which had an assumption that an initiation reaction will lead to active cellulose formation which can decompose two competitive first order reaction (Broido and Nelson 1975; Bradbury et al. 1979). The products of reaction can be classified into two yield types which are char with gaseous fraction and volatiles. The Broido model stated that dehydration reactions will occur at low temperature (493 K) and can cause anhydrocellulose formation which will be converted exothermally into gas and char (Broido and Nelson 1975). Meanwhile, at higher temperature (553 K), depolymerization reactions will occur and may lead to levoglucosan formation which then converted to volatile tars. The three-reaction model for cellulose pyrolysis was affected by two aspects; at low temperatures, the reaction tends to cross-linking and conversion of cellulose into char. Second, at high temperature and low pressure, the reaction favors cellulose cracking reactions to gases (Agrawal 1988). Moreover, a model proposed by Diebold claimed that formation of char, carbon dioxides, and water was due to chain cleavage and active cellulose dehydration (Diebold 1994). But then, active cellulose vaporization may lead to primary vapors formation which undergo dehydration, decarbonylation, decarboxylation, and cleavage reactions afterward forming secondary gases such as CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> higher olefins, and also produce secondary tar (Fig. 2). Lin et al. had another study about the mechanism of cellulose conversion into anhydrosugar and levoglucosan. It was stated that the conversion reaction will further undergoes some series of reactions; polymerization, dehydration, and condensation which may lead to gas and char formation (Lin et al. 2009). Despite that, the model proposed by Diebold seems contradicted to this in terms of energy requirement and product



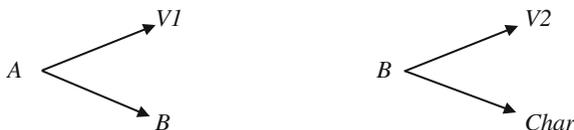
**Fig. 2** Decomposition of cellulose through pyrolysis (Diebold 1994)

formation. This is because majority of char is produced from depolymerization of fragmented species and volatile anhydrosugars instead of active cellulose (Diebold 1994).

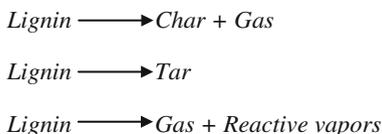
Kinetics of decomposition of hemicellulose (xylan) can be described using two-stage mechanism isothermally. The process was carried out in inert condition. The reaction was illustrated in Fig. 3 as A represents hemicellulose (xylan), B represents intermediate product of reaction with a reduced degree of polymerization, and V1 and V2 represent volatiles formed during reactions (Di Blasi and Lanzetta 1997).

For lignin, Antal et al. have proposed a model named semi-global multistep model. The model stated that at higher temperature above 773 K, there were lignin monomers which may lead to secondary decomposition and condensation reaction (Antal 1983). Furthermore, the lignin also might be converted into reactive gas and vapors at a very high temperature which subsequently led to secondary char formation by condensation. Concurrently, at low temperature below 773 K, char and gas formation occurred caused by dehydration reactions. Caballero et al. in his research has reviewed about the thermal degradation kinetics of lignin as a function of distribution of solid decompositions. Moreover, Adam et al. (2013) came with a lumped model for primary and secondary pyrolysis of Kraft lignin and stated that longer reaction time will trigger the production of lower molecular weight components and decrease the higher molecular weight compounds (Fig. 4).

There are also some models by some researchers (Shafizadeh and Chin 1977; Thurner and Mann 1981; Font et al. 1990; Samolada and Vasalos 1991; Di Blasi and Branca 2001) developed by considering biomass as a homogeneous and heterogeneous mixture separately. Only primary thermochemical degradation of biomass is considered for biomass of homogeneous species. A study by Yang et al. on degradation of cellulose, hemicellulose, and lignin showed that the products of



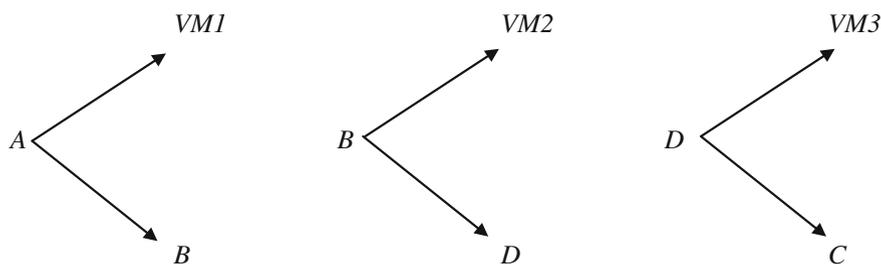
**Fig. 3** Decomposition of hemicelluloses; A—xylan (major component in hemicellulose), B—intermediate reaction product with a reduced degree of polymerization and V1, V2—volatiles produced during reactions (Di Blasi and Lanzetta 1997)



**Fig. 4** Various degradation products from the degradation of lignin through pyrolysis (Antal 1983)

degradation were same which are main gaseous products which are CO, CO<sub>2</sub>, CH<sub>4</sub>, and organics but with different yields for each component (Yang et al. 2007). Moreover, lignin was notably had higher decomposition temperature ranged from 433 to 1173 K. However, Thurner and Mann (1981) with their investigation on kinetics of wood pyrolysis found that gas consists mainly of CO<sub>2</sub>, CO, O<sub>2</sub>, and C<sub>3</sub><sup>+</sup> compounds with a small quantity of CH<sub>4</sub>, C<sub>2</sub>, H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> while tar contains a lot of levoglucosan. A detailed chemistry for the char, liquid, and gaseous formation from pyrolysis process of wood was discussed by Shafizadeh and Chin with their model (Shafizadeh and Chin 1977). The decomposition of lignin and cellulose was found to occur at 523–773 K and 598–648 K respectively while hemicellulose was analyzed to be decomposed at 498–598 K which was the least stable component among others. Besides, it was also discovered that lignin formed a charred residue while hemicellulose and cellulose produced volatile products. Lastly, investigation on product yields variation and kinetic rates by Di Blasi and Branca was mainly because of some aspects such as operating temperatures, experimental setups, and different heating rates (Di Blasi and Branca 2001).

There were also some models developed by assuming biomass as heterogeneous mixture of different components. However, these models neglect the effect of secondary tar degradation mechanism on yield of products. There were many studies regarding calculation of kinetic parameters for devolatilization of components (cellulose, hemicellulose, lignin) from various species of biomass using different heating rates and temperatures via thermogravimetric analysis and nonlinear least square algorithm (Orfão et al. 1999; Grønli et al. 2002; Manya et al. 2003; Mészáros et al. 2004; Branca et al. 2005). Multistep reaction model was proposed by Branca and Di Blasi discovering the mechanism of isothermal wood degradation of cellulose, hemicellulose, lignin, and some extractives in different reaction zones (Branca and Di Blasi 2003). Figure 5 shows the multicomponent mechanism in this model whereas; A represents wood, B and D described as intermediate solid-phase reaction products. VM1, VM2, and VM3 represent volatiles generated in the three stages and final residue of char represents by C.



**Fig. 5** Biomass decomposition mechanism; A—wood, B, D—intermediate solid-phase reaction products, VM1, VM2, VM3—volatiles generated in the three stages and C—the final residue of char (Branca and Di Blasi 2003)

Radmanesh et al. have proposed a three-independent parallel reaction model for biomass components devolatilization by using gas chromatograph and thermogravimetric analysis (Radmanesh et al. 2006). They also analyzed yield of tars and gases based on the heating rates. Moreover, Liden et al. proposed a kinetic model for wood pyrolysis. In this model, flash pyrolysis of wood was assumed according to two-parallel reaction model and stated that the gas yield with char and liquid tar then experienced decomposition by secondary homogeneous reactions as shown in Fig. 6 (Liden et al. 1988).

A kinetic model by Koufopoulos et al. proposed that the small particles (cellulose, hemicellulose, lignin) were pyrolyzed by using summation of their individual reaction rates considering primary and secondary reactions (Koufopoulos et al. 1991). It was found that the volatiles, gases, and char were produced from decomposition of biomass whereas volatiles and gases could react with char afterward to produce different compositions of volatiles, gases, and char. The model is shown in Fig. 7. However, Srivastava et al. have modified the model by Koufopoulos et al. by considering the reaction order of biomass pyrolysis (Srivastava et al. 1996). They concluded that zeroth order has faster pyrolysis and the first order has higher final pyrolysis temperature because linear relationship of time and temperature.

### 5.2 Distributed Model

One type of model in which its pyrolysis products are formed by unlimited independent parallel reactions is generally called distributed model. Those parallel reactions have different activation energies derived using Gaussian distribution

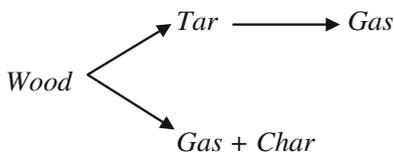


Fig. 6 Primary and secondary wood decomposition through pyrolysis (Liden et al. 1988)

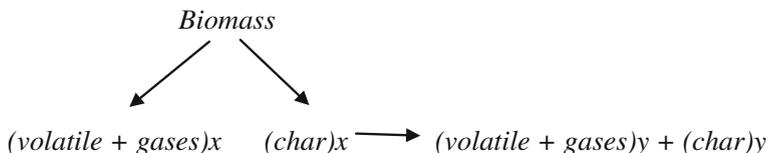


Fig. 7 Mechanism for primary and secondary biomass decomposition (Koufopoulos et al. 1991)

function. A model proposed by Chen et al. about coal pyrolysis was discussed regarding the tar–char formation and gas evolution from pyrolysis of biomass. The model's name was FG-DVC that stands for Functional Group—Depolymerization, Vaporization, Cross-linking (Chen et al. 1998). Nevertheless, the model did not cover some of the following: secondary reactions effect, impact of mineral on kinetics of biomass, and heating rate. Niksa then came with a reaction model that can be used for coal devolatilization. This model was based on polymerization of chain macromolecules mixture into fragments that volatilize into tar, partially decompose into gases, or recombine with the nascent char matrix and the model was named as bio-FLASCHAIN (bio-FC) (Niksa 2000). However, the mechanism is very difficult to be implemented and validating it due to significant gaps in the supporting database. Figure 8 shows the reaction mechanism of distributed activation energy proposed by Niksa.

Moreover, there were some researches made on behavior of biomass components during transformation and their chemical structure under different mechanisms (Sheng and Azevedo 2002; Shen and Zhang 2001). The model is called Chemical Percolation Devolatilization (CPD) model. However, the secondary degradation of tar clusters that yields light gases were not considered. Thus, it leads to digression of results compared to experimental data. Nonetheless, Rostami et al. came with a new model by taking distributed activation energy mechanism (DAEM) for pyrolysis of biomass into account. The model made few changes in kinetic parameters obtained from experimental data could improve the accuracy of

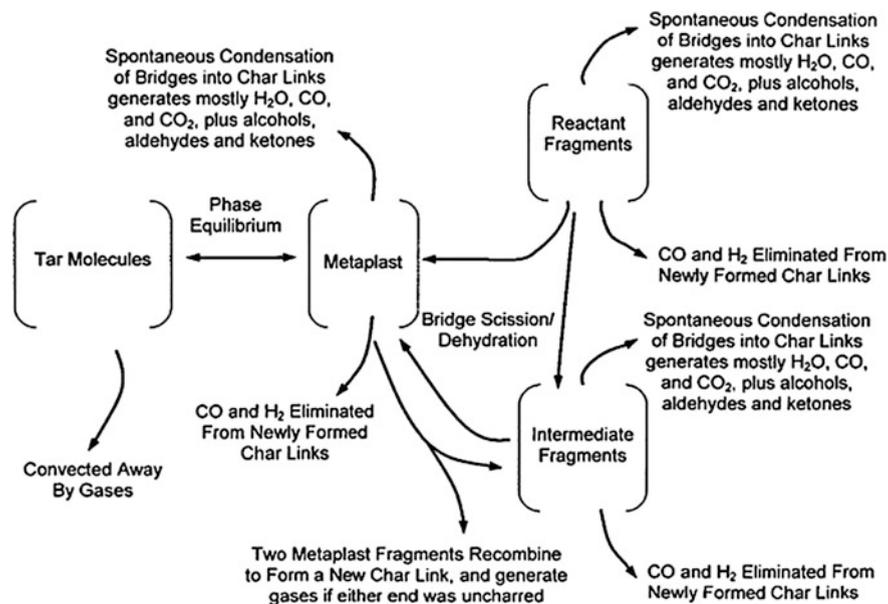
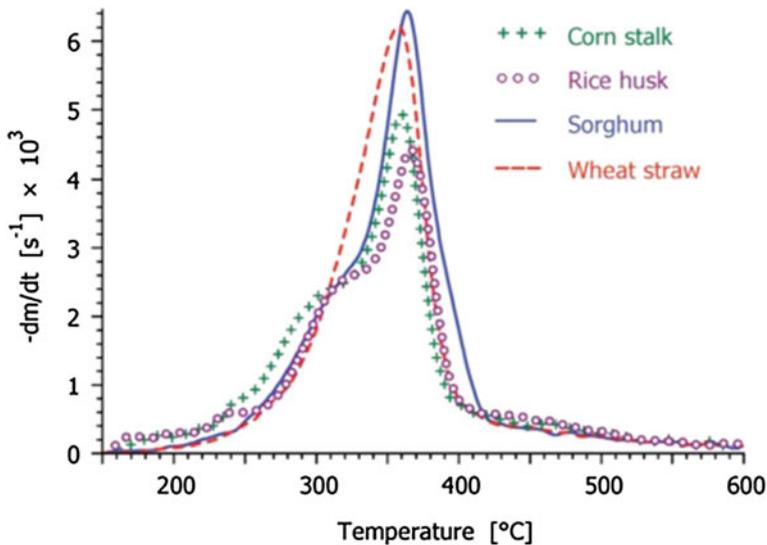


Fig. 8 Reaction mechanism of distributed activation energy (Niksa 2000)



**Fig. 9** Curves of mass loss rate using different biomass samples with eating rate of 40 K/min (Várhegyi et al. 2010)

the model (Rostami et al. 2004). Some other models were proposed by Becidan et al. (2007), Sonobe and Worasuwanarak (2008), Várhegyi et al. (2010) based on thermochemical decomposition that utilize the TG analysis technique for model validation with experimental data. In order to calculate model parameters, these models use the nonlinear least squares algorithm depending on mass loss rate of biomass samples with respect to temperature or time as shown in Fig. 9.

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