Estimation of Kinetic Parameters for *Imperata Cylindrica* Flash Pyrolysis

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Abstract
Flash pyrolysis of biomass has been identified as a viable Thermochemical process of converting biomass to biooil (Tar). A new biomass (*Imperata cylindrica*) under consideration as all the characteristic of an energy crop, with the ability to burn even when green. It is abundantly available in South-East Asia, however, as farmers' nightmare weed. In this paper a model was developed for flash pyrolysis of *Imperata cylindrica* in a batch transported bed reactor. The model developed was used to further understand the kinetic behavior of *Imperata cylindrica* pyrolysis as a lignocellulosic biomass. The kinetic analysis is based on a modified Broido-Shafizadeh kinetic mechanism and expressed as a first-order reaction of 6-lump model. The 8-paired kinetic parameters generated from the Arrhenius equation (frequency factor k_0 and activation energy ($\boldsymbol{E_a}$) were estimated by optimizing the kinetic model using the laboratory measured data and order of magnitude analysis. Using the estimated kinetic parameters the model predicts the biomass consumption and biooil production within the average deviation of ±10% of the experimental data.

Keywords: Lalang; Biomass; Transported Bed; 6-Lump; Model; Tar; Char; Lignocellulose

Introduction

Pyrolysis of biomass has been identified of having viable commercial potentials in meeting the energy needs of the future, as well as in cleaning up the environment. Pyrolysis reduce bulk biomass of solid waste to manageable energy packed materials. Some of these materials has also been known to be chemicals with specific high quality for added-value applications (Van de Velden *et al.*, 2010). Pyrolysis is a very important process in thermochemical conversion of biomass, in fact, it is the first stage in all thermochemical conversions such as combustion, torrefaction and gasification (Bridgwater, 2011; Basu, 2010). Pyrolysis was defined by Basu (2010) as a thermochemical decomposition of biomass into a range of useful products, either in the total absence of oxidizing agents or with a limited supply that does not permit gasification to an appreciable extent. Furthermore, pyrolysis occurs at a temperature range between 300 to 650 °C with products lumped into three (3) phases of liquid (Biooil or Tar), gas (Bio-gas or Gas) and solid (Char).

Pyrolysis product's proportion is dependent on the following operating conditions:

- Reaction temperature
- Residence time of vapour

- Rate of cooling of the vapour
- Heat transfer to reaction surface
- Rate of particle heating

However, the desired product in pyrolysis is the biooil and it is favoured by moderate temperature 500 ±10 °C, vapour (volatile) short residence time of less than two seconds, high heat transfer and small particle size of less than 3 mm. Research has shown that flash pyrolysis a type of pyrolysis which occurs within 450 to 600 °C with vapour residence time of 30 to 1500ms and rapid cooling of vapour favors biooil yield of 70 to 75% with subsequent char and gas yield of 10% and 15%, respectively, when there is a high heat transfer to the surface of the biomass (Basu, 2010; Bridgwater, 2012).

The interest in biomass as a source of energy and chemicals is in that they are renewable, sustainable and environmental friendly unlike fossil fuel. Several categories of biomass over time has been identified and used as feedstock from agricultural produce, which competes with man food to agricultural wastes and now energy grasses such as Miscanthus and Switchgrass. Exploiting grasses that don't compete with man's food supply for energy is laudable, but taking advantage of a grass that have been documented to compete and adversely affect food supply is more than impressive and one of such is *Imperata cylindrica*.

Imperata cylindrica is a farmer's nightmare grass. A native of Southeast Asia and commonly known as Lalang, Cogon-grass or Speargrass. It is a perennial grass of about 0.6 - 3 m in height with sharp pointed leaves of about 2 cm wide at the plant base, see Figure 1. It propagates through a network of rhizomes and secretes substance that inhibits germination of other plants. The plant also shows the characteristic of being flammable by burning even when green. This ability to burn even when green could make it a suitable energy crop.

Fig. 1. Field of Growing *Imperata Cylindrica*.

In this paper the kinetic parameters, namely the Activation energy $(\boldsymbol{E_a})$ and the pre-exponential factor $(\boldsymbol{k_0})$ Of *Imperata Cylindrica* pyrolysis reaction in a transported bed pyrolyzer was determined, using the experimental yields obtained for Tar, Gas and Char.

Pyrolysis is a complex process with a series of complex reactions (Prakash and Karunanithi, 2009). However, the understanding of the science involve in the reactions will consequently lead to optimal design of the process. In the determination of the kinetic parameters a major step is in selecting the kinetic mechanism or model of interest. The kinetic mechanism could be grouped into the well-established one-component and multi-component decomposition mechanisms. The products of the both classifications are lumped into three products, classes of Tar, Gas and Char, as shown in Figure 2 and 3 (Di Blasi, 2008; Basu and Kaushal, 2009). However, many new kinetic studies are considering individual species in the lumped products (Greenhalf *et al.*, 2012; Aysu and Küçük, 2014).

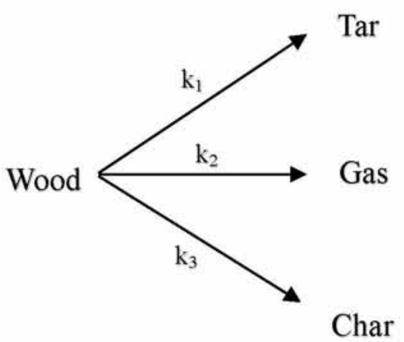

Fig. 2. One-component mechanism of pyrolysis by Shafizadeh and Chin (1977)

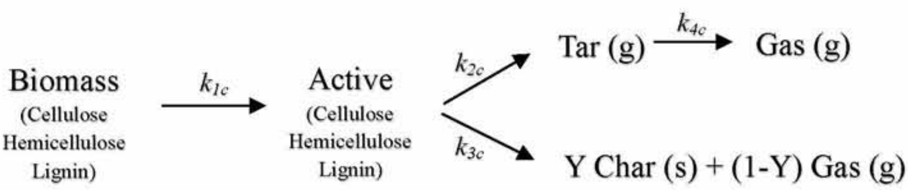

Fig. 3. Multi-component mechanism of pyrolysis by Miller and Bellan (1997)

Many researchers have studied and determined the kinetic parameters of different biomass pyrolysis using the two kinetic models shown in Fig. 1 and 2 above, with their kinetic constants as stated in Table 1.

Table 1: Kinetic Parameters for one component mechanism (Di Blasi, 2008)

Feedstock	Experimental System	Tr	Kinetic constants: E_a (kJ/mol), k_0(s-1)	Author (Ref)
Oak, 650mm	Isothermal tube furnace	573-673K	$k = 2.47 \times 10^6 \exp(-106.5/RT)$ $k_1 = 4.12 \times 10^6 \exp(-112.7/RT)$ $k_2 = 1.43 \times 10^4 \exp(-88.6/RT)$ $k_3 = 7.4 \times 10^5 \exp(-106.5/RT)$	(Thurner and Mann, 1981)
Harwood, 300-	Isothermal	677-	$k = 1.483 \times 10^6 \exp(-89.52/RT)$	(Gorton and

350 μm	entrained-flow reactor	822 K		Knight, 1984)
Almond shells, 300-500 μm	Pyroprobe 100	733-878 K	$k = 1.885 \times 10^6 \exp(-121/RT)$ $k_1 = 5.85 \times 10^6 \exp(-119/RT)$ $k_2 = 1.52 \times 10^7 \exp(-139/RT)$ $k_3 = 2.98 \times 10^3 \exp(-73/RT)$	(Font *et al.*, 1990)
Pine, 100-125 μm	TGA Drop tube	553-673 K 773-873 K	$k = 1.4 \times 10^{10} \exp(-150/RT)$ $k_1 = 9.28 \times 10^9 \exp(-149/RT)$ $k_2 = 1.11 \times 10^{11} \exp(-177/RT)$ $k_3 = 3.05 \times 10^7 \exp(-125/RT)$	(Wagenaar *et al.*, 1993)
Beech, < 80 μm	Tube Furnace	573-708 K	(a) $k = 2.4 \times 10^5 \exp(-95.4/RT)$ (b) $k = 4.4 \times 10^9 \exp(-141/RT)$ $k_1 = 1.1 \times 10^{10} \exp(-148/RT)$ $k_2 = 4.4 \times 10^9 \exp(-153/RT)$ $k_3 = 3.3 \times 10^6 \exp(-112/RT)$	(Di Blasi and Branca, 2001)

Despite the fact that many biomass pyrolysis kinetic parameters have been determined. The kinetic constants shows that every biomass decomposes uniquely. Therefore, the need to determine the kinetic parameters for the novel biomass *Imperata Cylindrica*. The one component kinetic mechanism was selected for this paper, with the aim of determining the kinetic parameters of each pyrolysis product.

2. Transported Bed Process Description

A simplified diagram of lab-scale setup for flash pyrolysis of Imperata cylindrica is presented below in Figure 4. The biomass feedstock and sand (heat source) are fed simultaneously into the reactor, thus the volatile gases released are rapidly condensed into a collector.

The mixture of biomass (Imperata cylindrica) and sand in the ratio of 1:2 by weight was put into the screw feed vessel (B) and likewise the sand to be used as heat carrier was packed into tank A. The pyrolysis reactor (C) and the sand in vessel (A) were heated and maintained in the desired pyrolysis temperature range between 450 – 650 °C by an electric heater. Nitrogen N2, at the rate of 20ml/min and 10 ml/min for 15 min was allowed to flow into the reactor (C) and biomass vessel (B) respectively to purge the system of Oxygen O2. After the removal of Oxygen O2, the reaction was allowed to proceed. At the desired temperature both the sand and biomass were opened to allow the flow of biomass feed (Biomass + Sand) and hot sand by gravitational force into the reactor at the desired mass flow rates. After 5 minutes the vacuum pump assists in gas product flow out of the pyrolysis reactor to the condenser. The reaction was ran till no visible gas release from the reactor.

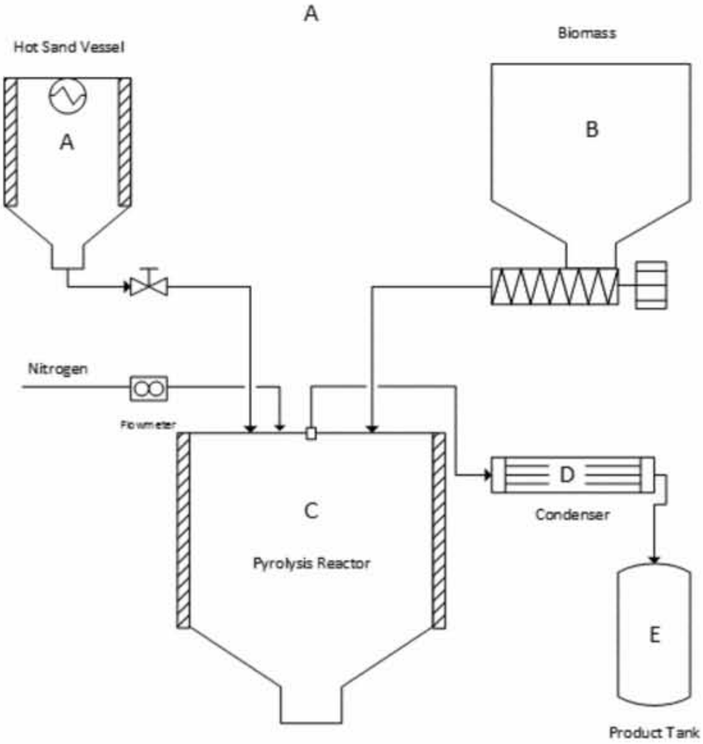

Fig. 4. Transported Bed Schematic Diagram

Table 2, below show feedstock, heat source, sweeping gas and the transported bed reactor operating conditions.

Table 2. Experimental Variable

Feedstock	90 g
I. Cylindrica	30 g
Sand	60 g
I. Cylindrica size	0.5125 mm
Feed rates	
I. Cylindrica	1.750 g/s
Hot Sand	2.224 g/s
Sweeping Gas	35ml
Pressure	1 atm
Batch time	900 s

3. Kinetic Modelling and Analysis

The single or one component kinetic mechanism shown in Fig. 2 was selected for consideration in this study. It has been applied to many biomass feedstocks with main focus on the final yield of the main products namely Tar, Gas and Char from the decomposition of biomass without detailed consideration of the secondary or intermediate reactions.

The rate equations in mass fractions (X_i) for the solid state primary decomposition reactions of biomass feedstocks could be formulated as Eqn. 3.1 (Hattingh *et al.*, 2013; Van de Velden *et al.*, 2008):

$$\frac{dX_i}{dt} = k_i X_i \qquad 3.1$$

In equations 3.1 X_i represent the mass faction and k_i is the kinetic rate constant for each species involved in the reactions. The kinetic rate constant k_i, could further be express in equation 3.2 as the Arrhenius equation, which contain the pre-exponential factor, k_0 and the activation energy, E_a.

$$k = k_0 \exp\left(-E_a/RT\right) \qquad 3.\ 2$$

Furthermore, equation 3.1 and 3.2 could be combined and expressed in terms of the kinetic parameter as:

$$\frac{dX_i}{dt} = k_{0,i} \exp\left(-E_{a,i}/RT\right) X_i \qquad 3.3$$

The equation 3.3 could explicitly be expressed for each species of Biomass (B), Tar (T), Gas (G) and Char(C) in the parallel reactions in equations 3.4 – 3.7:

$$\frac{dX_B}{dt} = -\left[\left(k_{0,1} \exp\left(-E_{a,1}/RT\right)\right) + \left(k_{0,2} \exp\left(-E_{a,2}/RT\right)\right) + \left(k_{0,3} \exp\left(-E_{a,3}/RT\right)\right)\right] X_B \qquad 3.4$$

$$\frac{dX_T}{dt} = k_{0,1} \exp\left(-E_{a,1}/RT\right) X_B \qquad 3.5$$

$$\frac{dX_G}{dt} = k_{0,2} \exp\left(-E_{a,2}/RT\right) X_B \qquad 3.6$$

$$\frac{dX_C}{dt} = k_{0,3} \exp\left(-E_{a,3}/RT\right) X_B \qquad 3.7$$

The evaluation of the kinetic parameters for each species required the numerical solution of system ordinary differential equations 3.4-3.7 with the application of an explicit Runge-Kutta formula, by using the appropriate algorithm and the *expint* function in MATLAB R2013a. For parameter estimation, the objective function (OBF) was set up as the sum of squared error, SSE, as given in equation 3.8 and was minimized by varying the values of k_0 and E_a. The optimization of equation 3.8 was performed by multidimensional nonlinear least square analysis.

$$OBF = \sum_{i=1}^{N_i} \sum_{n=1}^{N_n} \left[\left(\frac{dX_i}{dt}\right)_{exp,i,m} - \left(\frac{dX_i}{dt}\right)_{calc,i,m} \right]^2 \qquad 3.8$$

The flowchart of the algorithm in MATLAB used in estimating the kinetic parameters is presented in Figure 5.

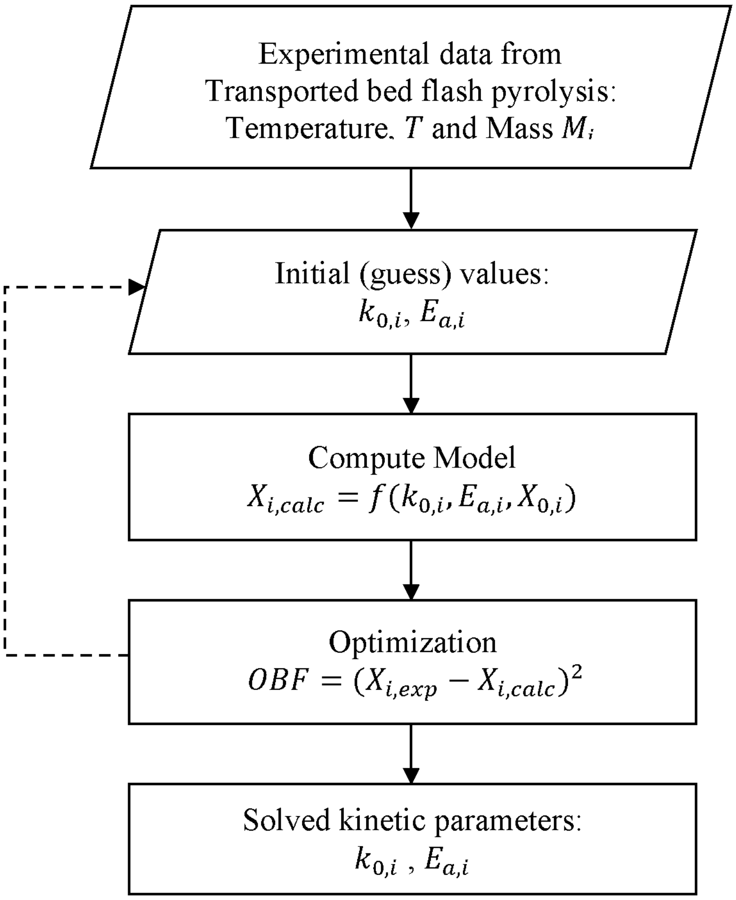

Fig. 5. MATLAB algorithm used for kinetic parameter estimate

4. Results and Discussion

4.1. Experimental Result

The laboratory experiment was conducted as described in the transported bed process description section. The process temperature was varied from 450-650 °C at the step of 50 °C and the resulting weight of Tar, Gas and Char are shown in Table 3 and the weight percent in yield in Figure 6.

Table 3. Experimental Result

Temperature (°C)	Biomass (g)	Tar (g)	Gas (g)	Char (g)
450	0	2.076	19.174	8.750
500	0	3.843	18.617	6.920
550	0	5.400	17.020	7.580
600	0	5.415	17.665	6.920
650	0	5.010	18.610	6.380

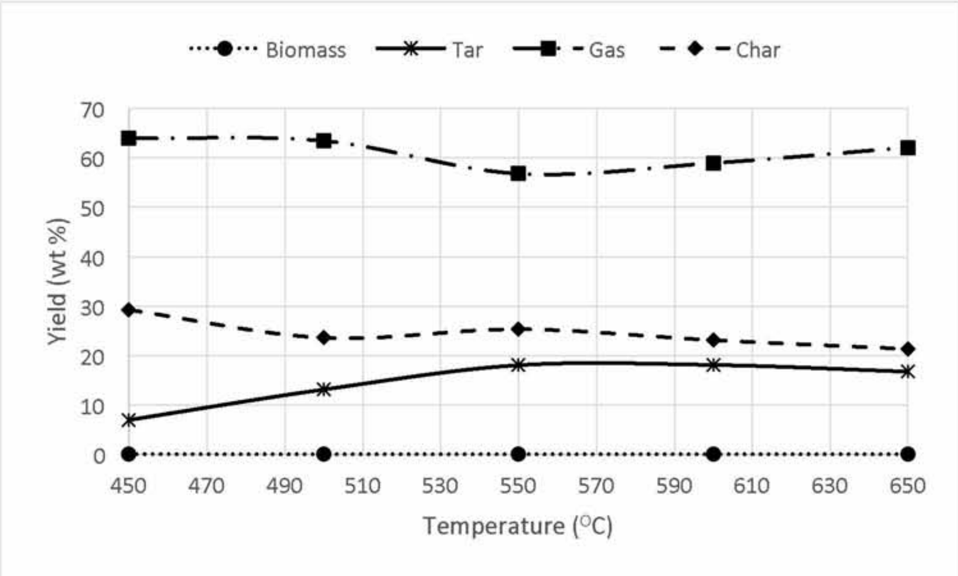

Fig. 6. Pyrolysis products with Temperatures

From Fig. 6 there was a steady increase in Tar production with an increase in temperature from 6.92% at 450°C to the maximum of 18.05% at 600°C, follow with a slight decrease to 16.70% at 650°C. The increase in Tar production was due to increase in heat transfer to the biomass particle (Lehto *et al.*, 2014; Bridgwater, 2012). The graph also shows that the Gas production varies inversely with Tar production. At low temperatures when there was a steady increase in Tar, Gas reduces until 600°C, after which the Gas yield increases from 58.88 % at 600° C to 62.03% at 650°C the highest incremental step. Furthermore, the Char yield decreases with increase in temperature, probably because of secondary cracking of char. The Gas product has the highest yield among the products at all temperatures, followed by Char then Tar, this is typical for pyrolysis reactors with less effective heat transfer rate to the biomass particle surface especially in fixed bed pyrolyzer (Di Blasi, 2009).

4.2. Kinetic Modelling and Curve fitting

The kinetic model and curve fitting for the kinetic parameter estimate was carried out based on the algorithm shown in Fig. 5. The experimental values were combined with the kinetic model developed in section 3 and curve fitted to obtain the pre-exponential factor (k_0) and activation energy (E_a) for the transported bed flash pyrolysis. The initial values for the Six (6) kinetic parameters were randomly generated by the system to allow unbiased selection. Subsequently the generated values were passed to the Trust- Region- Reflective algorithm for optimizing the functions. The Trust- Region- Reflective algorithm was selected above Levenberg-Marquardt algorithm because it allows lower and upper bound constraint of the solution. Table 4 summarises the obtained kinetic parameter values with their sum of square error and the corresponding bound.

Table 4. Kinetic Parameters for transported bed flash pyrolysis

	ko (s^{-1})	Ea (J/g)	ko (s^{-1})	Ea (J/g)
1	1.8032	10669.43	5437.21	13516.29
2	1.3100	2621.73	4390.57	5627.51
3	0.2931	35.69	1000.87	3121.09

SSE	5.818022		5.821245	
Lower	-	-	1e3	1e3
Upper	-	-	1e8	1e6

The estimated kinetic parameters were used in the kinetic model and the simulated Tar, Gas and Char products were plotted with the experimental data and shown in Figure 7.

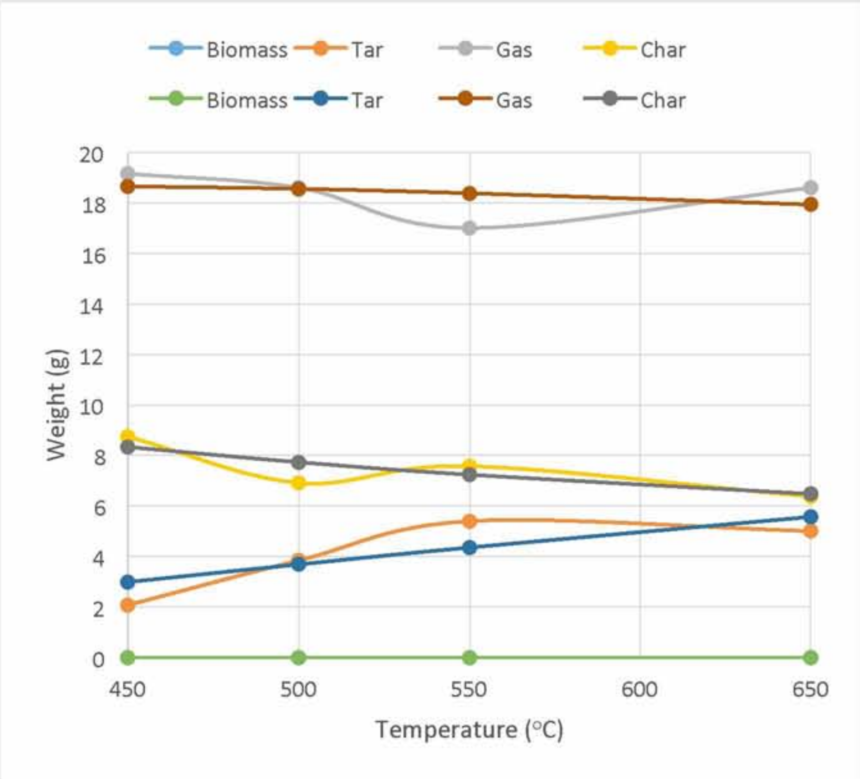

Fig. 7. Experiment and Model Curve

The fitted value is acceptable since the sum of square error, 5.8, is close to zero, and the average deviation for simulated value from experimental value are $\pm 0.67, \pm 0.65$ and ± 0.42 for Tar, Gas and Char respectively

4.3. Simulating the Effect of Temperature on Yield

The estimated kinetic parameters for transported bed flash pyrolysis of Imperata cylindrica was used in the kinetic model simulation to study the effect of temperature on the yield of Tar, Gas and Char. The input variable as outline Table 2 remain unchanged, but the temperature range start from 150-2000°C at the rate of 10 °C. The temperature range is well below and above identified pyrolysis temperatures. However, one of the major problems of pyrolyzer similar to fixed bed is heat transfer to biomass particle, therefore the effective heat transfer are lower than the system heat. Fig. 8, below show the simulated yields and temperatures.

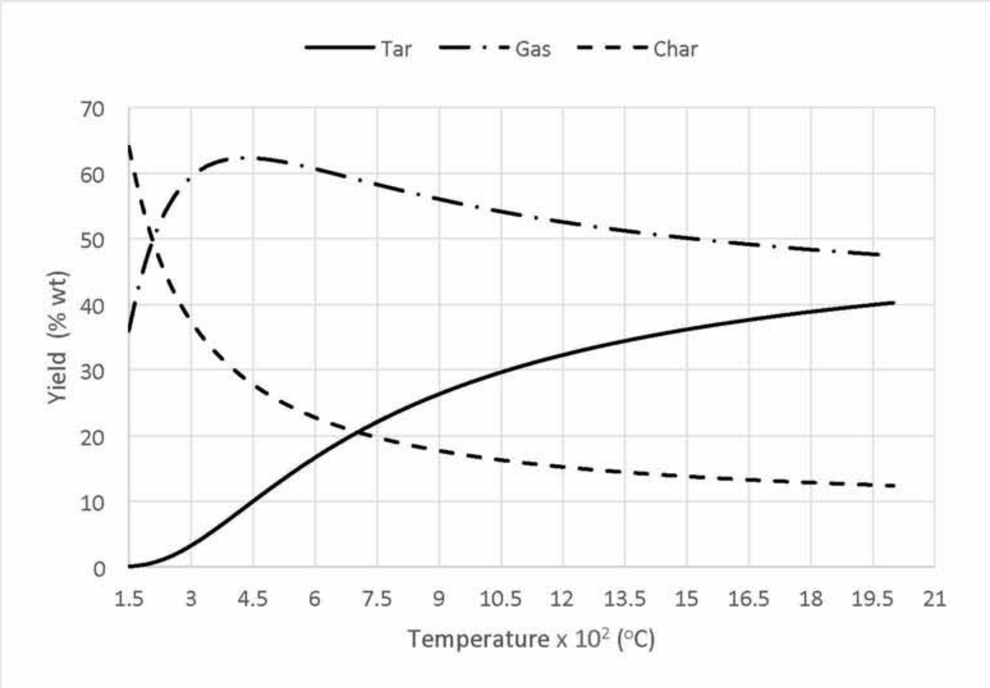

Figure 8. Simulate yield of Tar, Gas and Char with temperature

The graph of the effect of temperature on Tar production shows that Tar increases rapidly with increase in temperature, until temperature of about 870 °C and equivalent yields of 25.53%. The subsequent increase in tar yield with increase in temperature are negligible. The corresponding yields at 870 °C for Gas and Char were 56.42 % and 18.05%.

5. Conclusion

The determination of kinetic parameters (pre-exponential factor, (k_0) and activation energy (Ea) for Imperata cylindrica a novel biomass in a transported bed flash pyrolysis, was achieved by curve fitting the experimental results obtained from the weight of Tar, Gas and Char, at temperatures of 450-650 °C with the aid of kinetic model and non-linear regression. The kinetic model is based on the one component mechanism with three parallel reactions to Tar, Gas and Char products. The sum of squares error an indicator for quality of fit was 5.81 which is close to zero, and zero being value for perfect fit. The simulation average deviation from experimental data was computed for Tar, Gas and Char and found to be $\pm0.67, \pm0.65$ and ±0.42 respectively. Further investigation was carried out on the effect of temperature on biomass product yield using the estimated kinetic parameters and 870 °C was identified as the temperature for optimal Tar yield.

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