Article

Kinetics on Biomass Conversion of Terminalia Catappa L. Shell through Isothermal Pyrolysis

Yuniarti[1,2], Bardi Murachman[2], Suryo Purwono[2], and Himawan Tri Bayu Murti Petrus[2,*]

1 Department of Oil and Gas Processes Technology, STT Migas Balikpapan, KM.8, Karang Joang, Balikpapan Utara, Kalimantan Timur 76127, Indonesia
2 Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Jl. Grafika 2 Yogyakarta 55281, Indonesia
*E-mail: bayupetrus@ugm.ac.id (Corresponding author)

Abstract. Lignocellulose decomposition in the pyrolitic process are affected by several factors, mainly temperature and reaction time. Conducting isothermal pyrolisis on Terminalia Catappa L., this study aims to determine the reaction mechanism and to justify the kinetics. Powder sample of Terminalia Catappa L. was prepared by grounding it to certain particle size. The temperature was varied and kept constant at 350°C, 400°C, 450°C, 500°C, and 550°C with time interval of 30, 60, and 90 minutes. For kinetics study, data were obtained by measuring the liquid and gas products every 5 minutes. While the solid yield can be calculated using MATLAB simulation program based on the mass balance conception. The results showed that the increase of temperature accelerates the pyrolitic reaction rate increasing the liquid and gas products yield but decreasing the solid product yield. Furthermore the kinetics model of Terminalia Catappa L. pyrolysis was verified to understand the reaction mechanism. It was found that the pyrolysis reaction of Terminalia Catappa L. seed shells refers to the secondary decomposition reaction with the reaction kinetics parameter value of char for 488 min^{-1} for the exponential factor. , and the reaction kinetics parameter value of Tar 0.38 min^{-1} for the exponential factor. The primer and secondary decomposition reaction with the reaction kinetics parameter value of tar 71 min^{-1} for the exponential factor, 0.43 min^{-1} for the exponential factor, respectively.

Keywords: Isothermal pyrolysis, Terminalia Catappa L. seed shells, reaction mechanism, kinetics.

Nomenclature

A : Arrhenius constant (1/sec)
E_A : Activation energy (kJ/mol)
k : Reaction rate Constant (1/sec)
k_{app} : Total reaction rate constant, (1/sec)
MW : Molecular weight, (gram/mol)
m_B : Biomass weight, (gram)
m_C : Char weight, (gram)
m_G : Gas weight, (gram)
m_P : Solid weight, (gram)
R : Ideal gas constant, L.atm/(mol.K)
t : Reaction time, (sec)
T : Temperature (^{0}K)

1. Introduction

Energy plays an important role in supporting human lives. Along with the increasing population worldwidely, the need of energy is getting higher. Somehow the production of primary energy from non-renewable sources such as fossil fuel is not always proportional to the need for energy with the latter always exceeding the former. In adition there is environmental issue related to the gas emitted from the energy production from fossil fuel [1-2]. Thus it has been a worldwide acts to reduce the dependency on fossil fuel. The energy mix policy of Indonesia, stated in Presidential Regulation no. 5 2006, shows the good will to increase the renewable energy from 4.79% in 2011 to 17% in 2025 while the expectation of the energy mix for renewable energy is 25% in 2025 as depicted in Fig. 1.
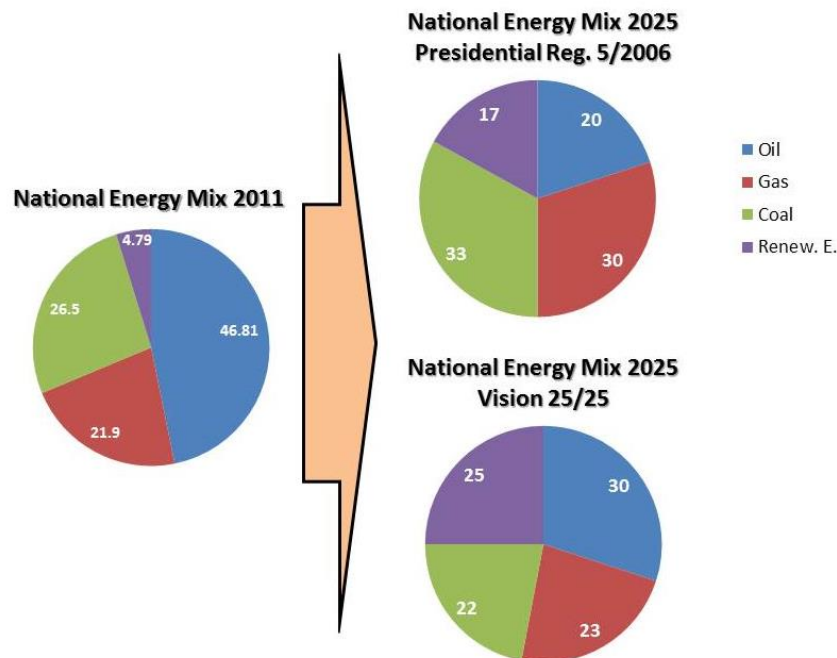

Fig. 1.   Indonesia Energy Mix 2025.

One of the alternatives to reduce the dependency on primary energy has been done in the form of renewable energy through the conversion of biomass. The utilization of biomass, especially those that are still unused is an area that is very promising and come into interest due to the neutral carbon consideration for energy generated from biomass. Energy and environmental problems can both be solved simultaneously by utilizing waste that virtually has no economic value and converting it into a new source of energy. Some research have been conducted related to the waste/unused biomass utilization, i.e.; Agriculture biomass [3-14], animal and human waste [5, 15-17], industrial waste [7, 18-20], and aquatic biomass [21-23].

Indonesia as an agricultural country has enormous potential in utilizing biomass as a source of energy as it has an abundant amount of biomass available from its agriculture activity. One of the most promising process that can convert biomass into valuable products such as energy that can be applied in Indonesia is a thermochemical process.

Terminalia Catappa L. is a plant that is native to Southeast Asia and is ubiquitous in almost all regions in Southeast Asia including Indonesia. This plant is also commonly grown in Australia, India, Madagascar, Central America, and South America. Terminalia Catappa L. tree favoured low land areas such as coast up to 500 meters above sea level as its habitat. Terminalia Catappa L. will mostly bear fruit in 3-5 years after planting and will bear fruit regularly once to twice a year. Terminalia Catappa L. tree can produce 5 kg of seeds per tree in one harvest which can double given the appropriate soil and climate condition [24-25]. Due to its potential as an unused biomass, Terminalia Catappa L. Seed shells can be converted to energy. Only few references have been found dealing with Terminalia Catappa L.related to biomass conversion [26]. Thus, we would like to conduct

comprehensive study on Terminalia Catappa L. seed shells conversion through isothermal pyrolysis.

This experiment aims to study the effect of temperature and reaction time on the kinetics of pyrolysis reaction of Terminalia Catappa L. seed shells. In this study, three mathematical models were formulized based on the reaction mechanism proposed by Turner and Mann [27].

Pyrolysis is the first step in the treatment of wide variety of biomass using heat [28]. The main gas constituent of the result of pyrolysis is CO, H_2, CO_2, CH_4 and other light hydrocarbons [29-30].

The study of pyrolysis reaction kinetics can involve more than one hundred intermediate products depending on the reaction mechanism. Ideally, the kinetics model used should consider the kinetics of decomposition reaction of primary and secondary decomposition. But until now, the models used are generally based on the main decomposition reaction. However, there are some cases where the mechanism of reaction resulted in the model must involve the secondary reactions.

Reaction mechanism suggested by Shafizadeh and Chin [31] incorporates the production of gas, tar, and char in three parallel reactions, and the broke down of tar into gas and char in two parallel reaction. Whereas Turner and Mann [27] suggested that this complex reaction can be simplified into only the former three parallel reactions, with each reaction occurs independently from each other. On the other hand, the reaction mechanism developed by Koufupanos [32] consists of both series and parallel reactions. The Turner and Mann model over a rather narrow temperature range while the model proposed by Koufupanos wider a temperature range. These two models are used because of the mass degradation mechanism of biomass occur before reach the setting temperature

2. Kinetic Models of Isothermal Pyrolysis

Three reaction mechanism models are proposed. The first model is the reaction mechanism from Thurner and Mann [27], the second model is a modified Koufopanos mechanism [32], and the third model is the modified combination of the first and second model that is generated in this study.

2.1. Model I

As the reaction kinetics in pyrolysis is used as process control variable, it can be formulated using a simple model and is widely used for the pyrolysis kinetics modelling. The reaction mechanism that is used in this model is based on Three Lumps Model used by Shafizadeh and Chin [31] as well as Thurner and Mann [27]. This model stated that in the pyrolysis reaction, the material breaks down into three groups of products, namely gas, liquid and solid in the form of charcoal [33-34]. The mechanism of the first model is shown in Fig. 2.
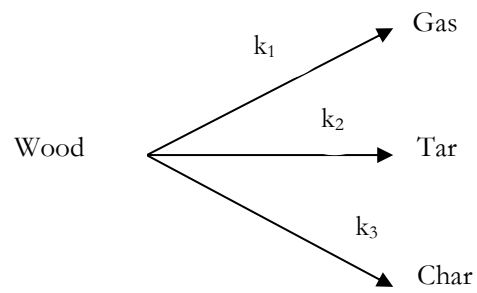

Fig. 2.   Pyrolysis reaction mechanism of Model I.

In the pyrolysis of biomass containing lignocellulose compound such as wood, the number of mol of the solid compound at any times (m_B) changes because it can decompose into gas and liquids. If the initial mol of solid is, then the mass balance of the reaction for the batch reaction can be described as follows:

$$\frac{dm_B}{dt} = -k_{app}m_B \tag{1}$$

with: $k_{app} = k_1 + k_2 + k_3$

$$\frac{dm_G}{dt} = k_1 m_B \tag{2}$$

$$\frac{dm_C}{dt} = k_2 m_B \tag{3}$$

$$\frac{dm_P}{dt} = k_3 m_B \tag{4}$$

2.2. Model II

The second model used is a modification of the reaction mechanism proposed by Koufupanos [32] which is also used by Erawati [35]. The reaction mechanism of the second model can be seen in Fig. 3.
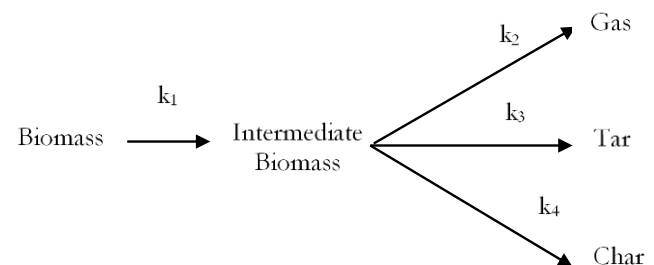

Fig. 3.   Pyrolysis Reaction Mechanism of Model II.

The mass balance is as follows:

$$\frac{dm_{B1}}{dt} = -k_1 m_{B1} \qquad (5)$$

$$\frac{dm_{B2}}{dt} = k_1 m_B - k_{app} m_{B2} \qquad (6)$$

with : $k_{app} = k_2 + k_3 + k_4$

$$\frac{dm_G}{dt} = k_2 m_{B2} \qquad (7)$$

$$\frac{dm_C}{dt} = k_3 m_{B2} \qquad (8)$$

$$\frac{dm_P}{dt} = k_4 m_{B2} \qquad (9)$$

2.3. Model III

The third model is formulized by combining and modifying the first and second model. The reaction mechanism for the third model can be seen In Fig. 4.
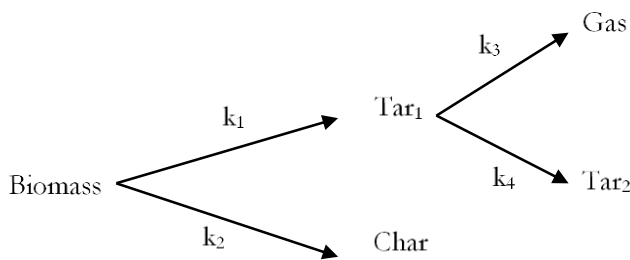

Fig. 4. Pyrolysis reaction mechanism of Model III.

The mass balance is as follows:

$$\frac{dm_B}{dt} = -\left(k_1 + k_2\right) m_B \qquad (10)$$

$$\frac{dm_{C1}}{dt} = k_1 m_B - \left(k_3 + k_4\right) m_{C1} \qquad (11)$$

$$\frac{dm_{C2}}{dt} = k_4 m_{C1} \qquad (12)$$

$$\frac{dm_G}{dt} = k_3 m_{C1} \qquad (13)$$

$$\frac{dm_P}{dt} = k_2 m_B \qquad (14)$$

In the experiment, the initial mass of biomass used was 500 grams. The mass of liquid was measured every 5 minutes, while the mass of gas was calculated using Eq. (15).

Gas content data was used to calculate the mass of gas using equation as follows:

$$GasMass(G) = \frac{PV_G}{RT} \times \overline{MW} \qquad (15)$$

Gas pressure (P) was measured using a manometer, and the gas volume (V_G) was measured based on the volume of water overflowing from the gas capture apparatus.

The reduction of biomass sample weight shows that the sample was converted into liquid product and gaseous product. The mass fraction of the biomass sample that has been converted (m_x) can be calculated using equation formulized by Gasparovic et al. [36] which described m_x as follows:

$$m_x = \frac{m_0 - m_t}{m_0 - m_f} \qquad (16)$$

where m_0 is the initial mass of the biomass sample, m_t is the mass of biomass sample at an observed time, and m_f is the mass of remaining solids after the reaction. The mass of the observed biomass sample (mt) was measured at the time the reaction was stopped the sample was removed from the pyrolysis equipment which was regulated and weighed outside by balance.

Mass ratio remains can be calculated using equation as follows:

$$1 - m_x = 1 - \frac{m_0 - m_t}{m_0 - m_f} = \frac{m_t - m_f}{m_0 - m_f} \qquad (17)$$

Using the approach in the three models described, the value of reaction rate constant (k) can be calculated. Arrhenius equation was used to calculate the value of reaction rate constant in the described equations which can be formulized as follows:

$$k = A\left(\exp\left[-\frac{E_A}{RT} \right] \right) \qquad (18)$$

$$\ln k = \ln A - \frac{E_A}{RT} \qquad (19)$$

The value of parameters obtained from calculation of the mathematical model was optimized using minimization of the sum of squared error (SEE). The SSE was calculated using equations as follows:

$$SSE = \Sigma \left(m_{C(data)} - m_{C(calc)} \right)^2$$
$$+ \Sigma \left(m_{G(data)} - m_{G(calc)} \right)^2$$
$$+ \Sigma \left(m_{S(data)} - m_{S(calc)} \right)^2 \qquad (20)$$

3. Materials and Method

3.1. Materials and Reagents

Terminalia catappa seed shells, as it can be seen in Fig. 5, were collected from several places in the city of Yogyakarta, for example at Universitas Gadjah Mada and Tempel. Collected Terminalia Catappa L. seed shells were then ground and analyzed for its content in Chem-Mix Pratama Laboratory in Yogyakarta.

Fig. 5.   Terminalia Catappa L.; a) trees, b) fruits, and c) dried fruits and seed shells.

3.2. Experimental Apparatus

The apparatus (Fig. 6) consisted of the reactor as the combustion chamber which was made of metal pipe with its upper part sealed with perpak. The external surface of the reactor was coted with furnace insulator (asbestos tape). The reactor was put into a furnace, and the outside surface of the furnace was covered with Nikelin insulator. The temperature inside the reactor was measured using a thermocouple. The liquid discharged from the reactor was cooled using a straight pipe condenser. Non-condensable gases from the reactor entered into a container filled to the brim with 19 liters of water. The exit gas was captured by the water inside the container. The volume of water overflowed from the container is equal to the volume of gas captured. The overflowed water was collected and observed in the final container.
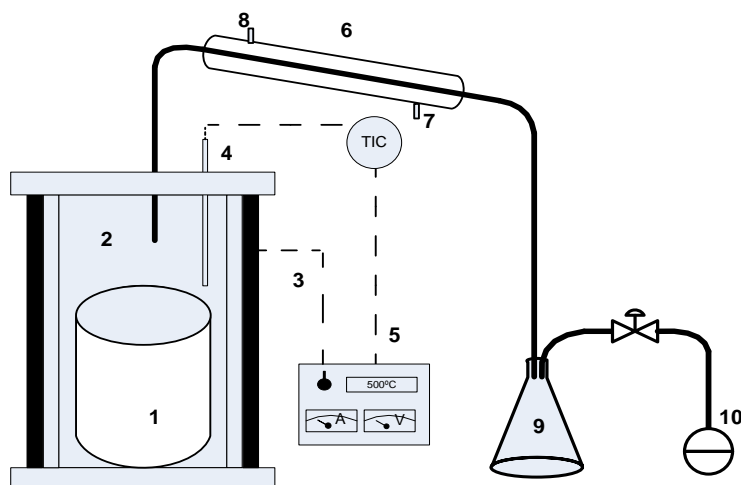
Fig. 6. Pyrolysis apparatus set.

Note:
1. Sample holder
2. Reactor
3. Electrical Heater
4. Thermocouple
5. Temperature sensor
6. Condenser

7. Cooling water inlet
8. Cooling water outlet
9. Liquid product container
10. Liquid product container
11. Manometer

3.3. Experimental Variables

The variables observed in this experiment were:
    a. Independent variable:
       A 500 g sample was placed in the center of reactor and the heating rate were programmed at 0,3 °C/min.
    b. Dependent variable:
- Temperature variation = 350 °C, 400 °C, 450 °C, 500 °C, and 550 °C
- Time variation = 30 minutes, 60 minutes and 90 minutes (the time was counted from the moment the pyrolysis temperature was reached)

4. Results and Discussion

The decomposition of lignocellulose compounds to produce three main products which are solid (charcoal), liquid (bio-oil) and gas. In the decomposition reaction, compounds with low molecular weight will turn into gas at room temperature. The majority of those compounds, however, condense and form a liquid called bio-oil. Observation of liquid and gas products in this experiment was made to observe the kinetics of the reaction in the pyrolysis process.

In the pyrolysis reaction, temperature and time are two of the most important operating conditions and is highly influential to the product yield. To know the significance of the influence of those two variables, the experiment was carried out with varying temperature of 350 °C, 400 °C, 450 °C, 500 °C, and 550 °C and varying duration of pyrolysis at 30 minutes, 60 minutes and 90 minutes after the sample reached the pyrolysis temperature. At high temperatures, the mechanism of biomass degradation occurs before reaching the setting temperature. Gas, liquid and solid results that occur due to degradation of biomass are calculated as mass at 0 minutes or when it reaches the setting temperature

4.1. The Effect of Temperature and Time on Product Yield

Lignocellulose compounds in the biomass samples in this experiment were decomposing at different temperatures which make temperature as an important factor in the pyrolysis process. The lowest temperature variation used in this experiment were 350 °C, and the highest was at 550 °C. It was expected that in that temperature range, all lignocellulose compounds have decomposed. The effect of temperature and time on the yield of solid, liquid, and gas products are shown in Fig. 7.
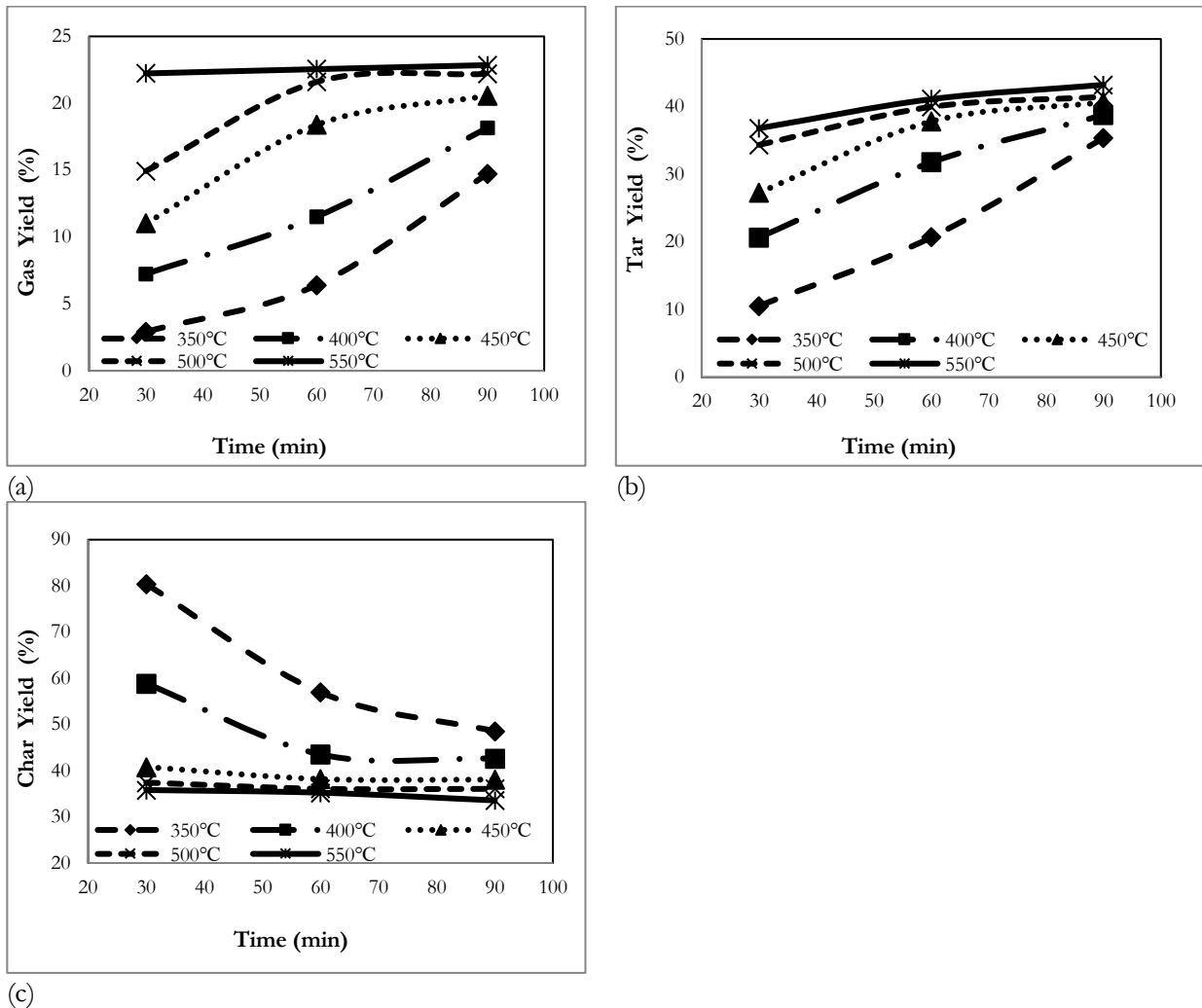
Fig. 7.   The yield of pyrolysis; a) gas product, b) liquid product, and c) solid product, at varying temperature and time.

Figure 7(a) shows that with higher temperature and longer time of pyrolysis, more gas product was obtained. The maximum gas yield produced was 22.85%. These results consisted with the statement of Balci [34] which stated that the production of gas in the pyrolysis process could reach 20-25% of the total products. The gas production at temperatures below 450 °C increased significantly after 60 minutes of pyrolysis. At a temperature above 450 °C, the rate of production of gas started to decrease one hour after that start of pyrolysis. At the temperature of 550 °C, from 30 minutes to 90 minutes, the amount of gas produced is stable and shows virtually no change. This means that if the process were continued at the temperature of 550 °C, there would be no more gas produced.

In this experiment, the liquid product made up most of the product yield produced by the pyrolysis reaction. Figure 7(b) shows that the maximum yield obtained for the liquid product was 43.22%. Fagbemi [29] stated that the production of liquid in the pyrolysis reaction depends heavily on the type of biomass used. In the experiment by Balci [34] for material containing alpha cellulose, the product obtained was mostly liquid at room temperature

which was tar with 60-65% yield, while sawdust made up only 30% of the total product of pyrolysis.

Balci [34] stated that the product of pyrolysis which is solid (char) is a non-volatile solid residue which is rich in carbon. Figure 7(c) shows that with higher temperature and longer time, the lower mass of the sample and the faster the reduction rate would be. The significant mass reduction was observed for the pyrolysis at 350 °C and 400 °C. This was caused due to the high temperature of the experiment, the heating of the sample required a shorter time and causes the particle of biomass was fast pyrolysis [37]. The yield of solid product at the temperature of 550 °C for 90 minutes of pyrolysis was 33.55%. As reported by Yang [38], the decomposition of cellulose ends at the temperature of 400 °C, the decomposition of hemicellulose stops at the temperature of 315 °C and the decomposition of lignin halts at very high temperature. The time of pyrolysis begins after reaching the desired temperature, so for experiments at 450 ° C, 500 ° C, and 550 ° C, cellulose and hemicellulose completely degraded long before, and only the thermal decomposiiton of lignin is left to be studied.
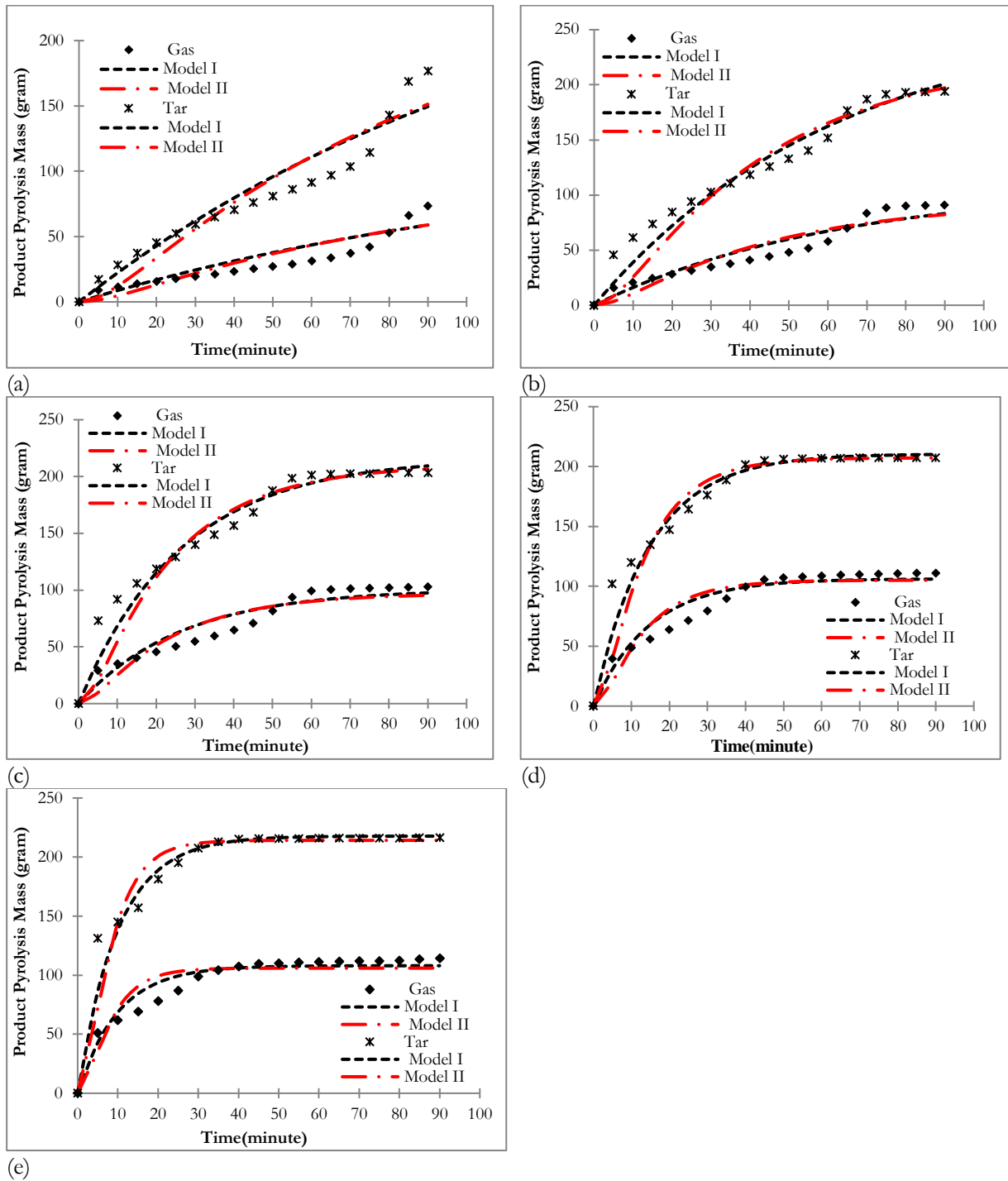
Fig. 8. The model I and II calculation for gas and liquid yield at; a) 350 ᵒC, b) 400 ᵒC, c) 450ᵒC, d) 500 ᵒC, and e) 550 ᵒC, over time using MATLAB.

4.2. Pyrolysis Reaction Kinetic

The reaction mechanism proposed the first model follows the kinetic reaction model proposed by Thurner and Mann [27]. The second model assumes that biomass is transformed into intermediate biomass before decomposes into gas, liquid and solid products.

The reaction mechanism for this experiment was made in the temperature range of 350-550 ᵒC for three reactions that occurred simultaneously. Those three reactions were gas-forming reaction, liquid forming

reaction and the formation reaction of solid. Assumption was made in this experiment was that the activation energy for the formation reaction of solid was the same as the sample weight reduction reaction. Reference data for this calculation were obtained from previous researches including the liquid mass data and the volume of gas formed which were taken periodically during pyrolysis reaction that occurred at the isothermal condition.

4.2.1. Determining reaction rate constant

Data obtained from the experiment were processed using MATLAB to calculate the pyrolysis reaction rate constant of Terminalia Catappa L. seed shells. The program was designed so that by inputting data of gas and liquid yield over time, the value of constant for each model at every temperature could be obtained. Results of the calculation for model I and II are plotted in Fig. 8. At the high temperature, volatile components much decomposed before 30 minute. This process causes the amount of gas produced is stable and shows virtually no change at the temperature of 550°C, from 30 to 90 min. It causes the biomass have been degradation long time before 30 minute, especially the volatile component.

From the calculation results of the gas and liquid yields data in Fig. 8 which was based on the minimization of the value of SSE with the overall data, correction was done by evaluating the R^2 value. The R^2 illustrated how adaptable these models were in describing the mechanism of pyrolysis reaction. Table 1 provides a listing of R^2 value. R^2 determine from SSE/SST. In model I, it was found that the value of R^2 is in the range of 0.8-0.96 as shown in Table 1. Thus, it was concluded that the first model was more accurate than the second model for the data obtained in this experiment.

Compared to the second model, the first model showed better accuracy and the resulting calculation was closer to the experimental data. But, from the experiment data and the result of calculation alone, it cannot be concluded without a doubt that the reaction mechanism proposed in the model I was the reaction mechanism that occurred in the experiment. Thus, the third model was formulized as a comparison to give better insight into the accuracy of the first model. The third model was formulized by combining and modifying the first and second model. In the third model, biomass did not have intermediate reaction step, but there is a secondary reaction after the first pyrolysis reaction which occurred after the formation of the first liquid product. The secondary reaction produced liquid and gas products. The comparison of experimental data of the model I and III are shown in Fig. 9.

From the value of R^2 obtained in Fig. 9 shows that the average value of R^2 in model III is better than model I. The result of data simulation for mathematical model of gas and liquid yield compared to the experimental data in Fig. 9 for model III shows that the calculation data has little deviation when compared to the experimental data.

Additionally, the simulation was conducted to evaluate the value of reaction rate constant (k) from the data obtained in the experiment. By correlating the value of ln k and $1/T$, the value of E_A and A were also obtained as listed in Table 2.

The value of activation energy of pyrolysis reaction according to model III calculation is 65.0602 kJ/mol. This activation energy value is not that different compared to the value of model I. The activation energy for the pyrolysis of Terminalia Catappa L. seed shells is lower than that of cashew, pistachio and walnut which have activation energy higher than 100 kJ/mol, but still does not deviate greatly from almonds (42.4-99.7 kJ.mol), Brazil nut (47.2-82.0 kJ.mol), coconut (58.9-114.8 kJ/mol) or peanut (44.3-71.5 kJ/mol). [39]. The effect of the pyrolysis temperature on the final mass of char (solid residue) is clearly observed (see Fig. 10). The higher the temperature, the lower the mass of charcoal. The time lag of mass loss was observed significantly for pyrolysis at 300, 350 and 400 °C

Table 1. R^2 value.

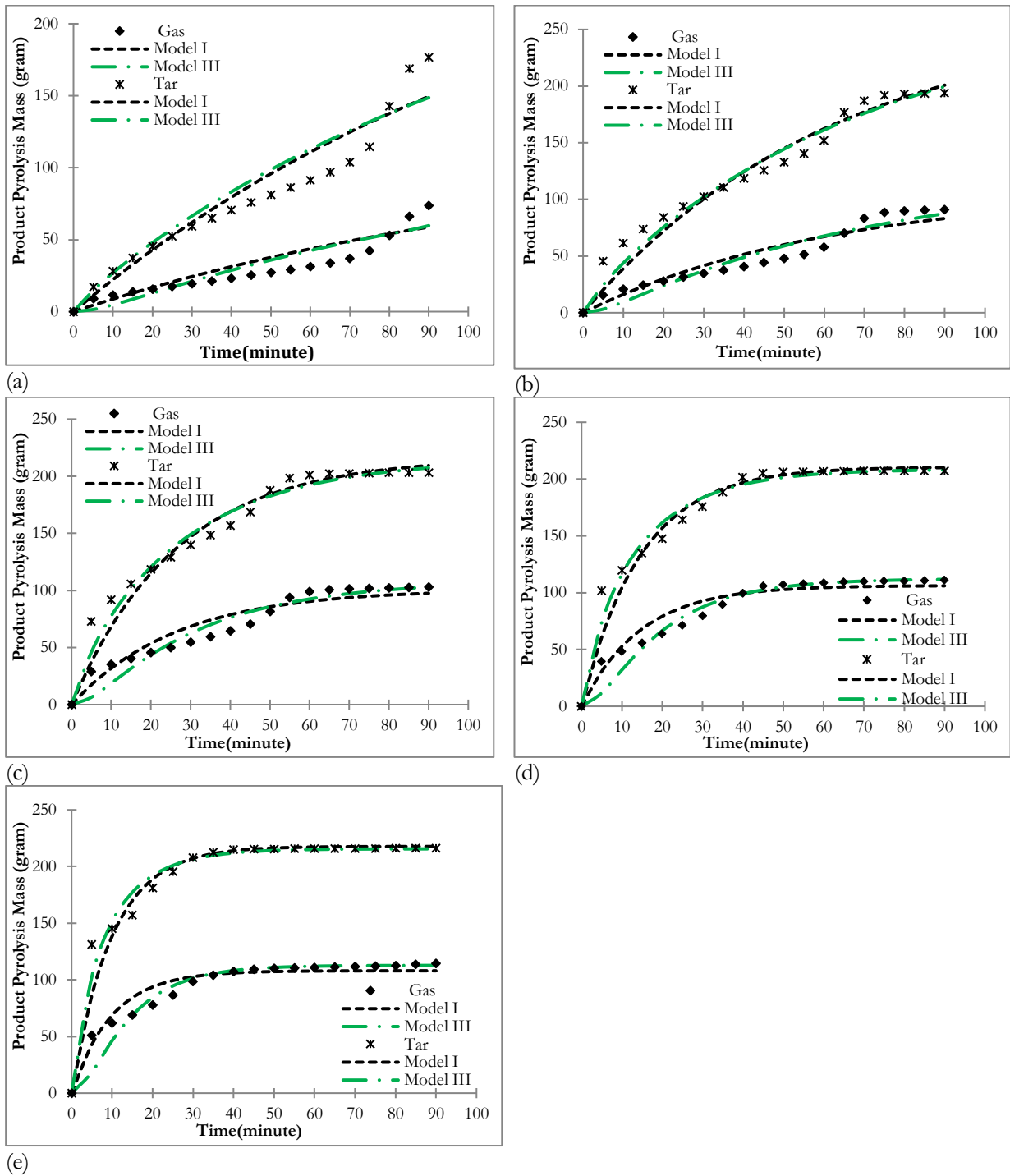| Temperature	I		II		III	
	Gas	Tar	Gas	Tar	Gas	Tar
350	0,80	0,91	0,80	0,89	0,82	0,89
400	0,90	0,96	0,88	0,91	0,92	0,97
450	0,92	0,96	0,89	0,91	0,92	0,97
500	0,94	0,96	0,90	0,90	0,93	0,97
550	0,94	0,95	0,88	0,91	0,91	0,97
R^2	0,924		0,887		0,93	

Fig. 9. The model I and III calculation for gas and liquid yield at; a) 350ºC, b) 400ºC, c) 450ºC, d) 500ºC, and e) 550ºC, over time using MATLAB.

Table 2. Parameters of model I, II, and III kinetics.

(a) Model I

Constant rate of reaction minutes⁻¹)	Equation	A_0(minutes⁻¹)	Ea(kJ/mol)
k_1	$k_1 = 68{,}1697 \exp\left(\frac{-6591}{T}\right)$	68,1697	54,8
k_2	$k_2 = 56{,}9971 \exp\left(\frac{-5895}{T}\right)$	56,9971	49,0134
k_3	$k_3 = 1487{,}7200 \exp\left(\frac{-8579}{T}\right)$	1487,7200	71,3292

(b) Model II

Constant rate of reaction (minutes⁻¹)	Equation	A_0(minutes⁻¹)	Ea(kJ/mol)
k_1	$k_1 = 734{,}3605 \exp\left(\frac{-6934}{T}\right)$	734,3605	57,6520
k_2	$k_2 = 2{,}9952 \exp\left(\frac{-2974}{T}\right)$	2,9952	24,7270
k_3	$k_3 = 2{,}4695 \exp\left(\frac{-2269}{T}\right)$	2,4695	18,8654
k_4	$k_4 = 7{,}1635 \exp\left(\frac{-3194}{T}\right)$	7,1635	26,5562

(c) Model III

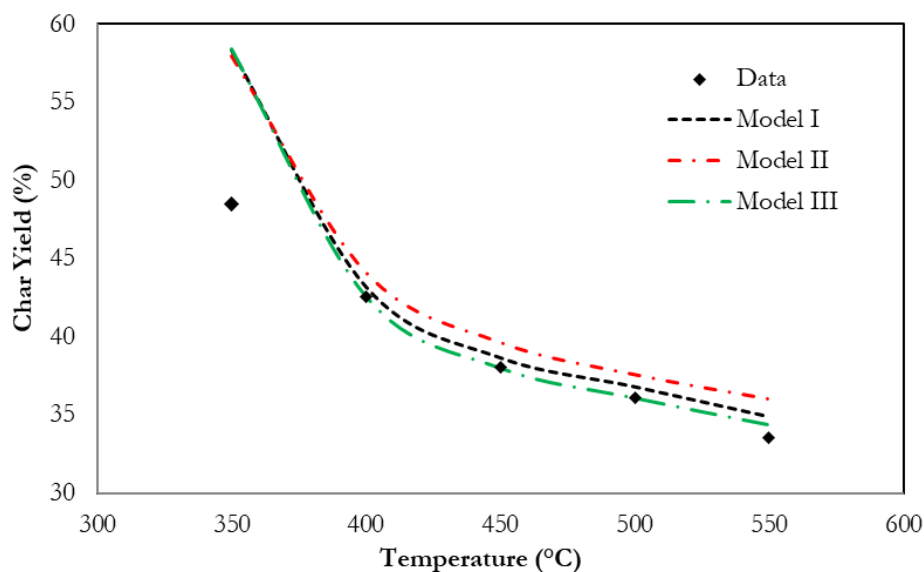| Constant rate of reaction (minutes⁻¹)	Equation	A_0(minutes⁻¹)	Ea(kJ/mol)
k_1	$k_1 = 71{,}3073 \exp\left(\frac{-5818}{T}\right)$	71,3073	48,3731
k_2	$k_2 = 487{,}8461 \exp\left(\frac{-7825}{T}\right)$	487,8461	65,0602
k_3	$k_3 = 0{,}3821 \exp\left(\frac{-766}{T}\right)$	0,3821	6,3688
k_4	$k_4 = 0{,}42870 \exp\left(\frac{-1361}{T}\right)$	0,42870	11,3159

Fig. 10. Mass reduction in pyrolysis reaction at various temperature.

4.2.2. Solid reduction

From the results of the mathematical model simulation, the reduction of solid mass in the pyrolysis for each temperature over time can be calculated. The calculation data for the yield of solid for all three models is shown in Fig. 10. Among the three models evaluated, model III gave the calculation results with the smallest deviation compared to the experiment data. From Fig. 9, it is shown that the biggest deviation of yield occurred at 350 °C. At higher temperature, solid yield calculated from the model approaches the experiment data. Solid reduction yield decreases sharply for the pyrolysis temperature between 350 °C and 450 °C. From Fig. 9, this phenomenon can be explained that with different temperature, the required reaction time will be different. The higher the pyrolysis temperature, the shorter the reaction time would be. This difference can be seen from the decrease of sample weight at a temperature between 350 °C and 550 °C. At 350 °C, mass loss tends to be slower until 90 minutes with a steady decrease of reduction rate. The weight of the sample at the temperature of 550 °C decreased sharply between 0 and 40 minutes and stabilized after that which means the reaction has already finished at 40 minutes.

At high temperature, the cellulose and hemicellulose will decompose before the beginning of the heating process which makes the mass fraction of solid decreased rapidly. Although cellulose and hemicellulose will decompose, lignin exhibits different behaviour to temperature. Due to the wide temperature range of lignin decomposition, lignin will continue to decompose after cellulose and hemicellulose decompose completely which leads to a slow decrease of solid.

Along with the formation of liquid and gas during the pyrolysis reaction, solid yield in the form of charcoal was formed as well. Mass of solid left in the reactor was the accumulation of biomass which has already undergone pyrolysis and turned into charcoal and its unreacted residue.

4.3. Gas Analysis

To find out the composition of the gas product of the pyrolysis reaction, the gas product was analyzed using gas chromatography (GC) at Instrumental Analysis Laboratory of Chemical Engineering Department, Universitas Gadjah Mada. Sampling was performed twice at the temperature of 450 °C and 550 °C. The analysis result of the gas composition analysis is shown in Table 3.

Yang et al. [38] stated that the gas product of pyrolysis mainly contains CO_2, CO, CH_4, H_2 and other organic compounds. In Table 3, it can be seen that the largest constituent of the gas product of pyrolysis is CO_2 which made up 50% of the gas followed by CO at about 25%. CO_2 and CO are the product of the pyrolysis of hemicellulose and cellulose. With a carboxyl group

(RCOOH) more pronounced than cellulose, hemicellulose produced more CO_2 than cellulose. Further thermal decomposition of cellulose would result in carboxyl and carbonyl (C=O) group of cellulose be split into CO gas. This is the cause of the lower yield of CO gas in the gas product when compared to CO in the gas product at the temperature range of 450-550°C.

It was reported by Yang et al. [38] that CO_2 and CH_4 gas is produced at the temperature range of 400-600 °C, while H_2 gas is produced at a temperature more than 400 °C. At 450 °C, the yield of H_2 gas was only 0.635% which increased sharply to 550 °C to 5.847%. CH_4 gas exhibited the same behaviour as H_2 gas, at 450 °C, the yield was 3.656% which increased sharply at 550 °C to 11.651%.

With a chemical structure that contains an aromatic ring and methoxyl group (CH_3O), the decomposition of lignin at high temperature will produce more H_2 and CH_4 than other lignocellulose compounds. Because lignin decomposes at high temperature, it can be concluded that the higher the temperature of pyrolysis, the higher the H_2 and CH_4 gas yield.

5. Conclusion

The conclusions that can be drawn from this experiment are:

1. Higher temperature and longer time of pyrolysis will raise the yield of liquid and gas product but lower the yield of solid product. Maximum yield for the liquid product was 43.22%, and for gas, product was 22.85%. The maximum yield for the solid product was 33.55%. With a higher temperature, the rate of mass loss will be faster.

2. At the temperature range of 350-550 °C, Arrhenius equation is corrected by using a pyrolysis reaction mechanism model. The most suitable model for this experiment is model III. Model III predicted that with higher pyrolysis reaction temperature, the value of reaction rate constant would increase. The rate of reaction equation for solid in this experiment is:

$$k_2 = 487.8461 \exp\left(\frac{-7825}{T}\right)$$

$$E_A = 65.0602 \, \text{kJ/mol}$$

3. The most substantial gas component in the gas product was CO_2 which made up to 52.39% of the gas product. By increasing the pyrolysis temperature, H_2 and CH_4 production will increase.

Acknowledgement

Table 3.   Gas product composition analysis result.

ID#1.Compound Name: Carbon Dioxide						
Sample Name	Ret.Time (sec)	Area (mm)	Height (mm)	Mark	Dilution Factor	Conc.(%)
SGY_A_450°C	15.976	140389	2853	V	1.000.000	52.739
SGY_A_550°C	16.036	136915	2773	V	1.000.000	51.434
ID#1.Compound Name: Carbon Monoxide						
Sample Name	Ret.Time (sec)	Area (mm)	Height (mm)	Mark	Dilution Factor	Conc.(%)
SGY_A_450°C	4.790	62806	3672	V	1.000.000	28.407
SGY_A_550°C	4.812	56004	3224	V	1.000.000	25.330
ID#1.Compound Name: Methane						
Sample Name	Ret.Time (sec)	Area (mm)	Height (mm)	Mark	Dilution Factor	Conc.(%)
SGY_A_450°C	7.766	8192	352	V	1.000.000	3.656
SGY_A_550°C	7.758	26108	1099	V	1.000.000	11.651
ID#1.Compound Name: Hydrogen						
Sample Name	Ret.Time (sec)	Area (mm)	Height (mm)	Mark	Dilution Factor	Conc.(%)
SGY_A_450°C	3.836	12285	497	V	1.000.000	0.635
SGY_A_550°C	3.865	113130	4436	V	1.000.000	5.847

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