

## Kinetic study on ferulic acid production from banana stem waste via mechanical extraction

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**Abstract.** Banana is the tropical plants associated with lots of medicinal properties. It has been reported to be a potential source of phenolic compounds such as ferulic acid (FA). FA has excellent antioxidant properties higher than vitamin C and E. FA also have a wide range of biological activities, such as antioxidant activities and anti-microbial activities. This paper presents an experimental and kinetic study on ferulic acid (FA) production from banana stem waste (BSW) via mechanical extraction. The objective of this research is to determine the kinetic parameters in the ferulic acid production. The banana stem waste was randomly collected from the local banana plantation in Felda Lepar Hilir, Pahang. The banana stem juice was mechanically extracted by using sugarcane press machine (KR3176) and further analyzed in high performance liquid chromatography. The differential and integral method was applied to determine the kinetic parameter of the extraction process and the data obtained were fitted into the 0th, 1st and 2nd order of extraction process. Based on the results, the kinetic parameter and  $R^2$  value from were 0.05 and 0.93, respectively. It was determined that the 0th kinetic order fitted the reaction processes to best represent the mechanical extraction.

### 1. Introduction

Banana is one of the tropical fruits that well known to be associated with many medicinal properties [1]. This fruit has been reported to be the potent source of phenolic compounds which is the ferulic acid (FA). FA has excellent antioxidant properties which are higher than those of vitamin C and E that makes it as an important ingredient in the industry. Thus, it have a wide range of biological activities, such as antioxidant activities, protection against coronary heart diseases, anti-inflammatory, anti-tumour, anti-mutagenic, anti-carcinogenic and anti-microbial activities that will be helpful in pharmaceutical industry [2]. FA also an important ingredient in the cosmetic industries as skin moisturizer, UV light protection, and has the ability to inhibit melanin formation.

FA can be extracted from different sources using several methods such as solvent extraction, enzymatic reaction, mechanical extraction and chemical reaction [3]. Solvent extraction was commonly used due to its simplicity, efficiency and also it wide applicability. The yield of the chemical extraction depends on the type of solvents used such as methanol and ethanol [4]. However, this extraction method has its drawbacks because the extractant may contain some non-phenolic substances such as sugar, organic acids and fats. For mechanical extraction, the sugar cane press machine was used to extract the FA from the banana stem waste. The sugar cane press machine is a well establish equipment in the plant material processing that were used to extract the sugar from



sugar cane and fresh oil palm frond (OPF) particularly [5]. Previous researcher reported that this method was easy to handle since it does not involve any chemicals. The mechanical extraction also takes shorter time than other method of extraction and high yield since the sugarcane press machine doing the mechanical press on the banana stem waste and produce high amount of juice in a shorter time. The mechanical extraction was cheaper than solvent extraction since it does not involve any chemicals and catalysts [6]. The purposes of kinetic study were to determine the factors that could control the fermentation process, increasing the productivity, determine the quality of the product, reducing the operating costs and eliminate disturbances. The factor was the kinetic parameter which was the reaction rate constant ( $k$ ). However, to determine the reaction rate constant the reaction order of the extraction process must be determined whether it is 0th, 1st or 2nd order reaction by using integral and differential method [7].

The objectives of this research were to extract the banana stem juice containing FA from banana stem waste via mechanical extraction and to determine the value of reaction rate constant ( $k$ ) in the FA production. There were several scopes of study need to be done in order to achieve the objectives of this research. Based on the data obtained from the quantification of FA in the juice, the reaction rate constant ( $k$ ) and the order of the reaction will be determined whether the extraction was following 0th, 1st or 2nd order. This research also studied the effect of the storage time on the reaction order and the reaction rate constant ( $k$ ).  $R^2$  was calculated using linear regression method.

## 2. Materials and Methods

### 2.1 Banana stem collection

Banana stem was collected randomly on October during a normal day from local banana plantation located near Felda Lepar Hilir. The outer stem and the pith of banana stem were separated from each other and cut into four parts with dimension of 66.0 cm (length) x 5.5 cm (width).

### 2.2 Extraction processes

The cut banana stems were pressed using the sugar cane press machine (KR3176) with three rotating cylinder rolling for juice extraction. The juice contained of FA was centrifuged at 15,000 rpm for 15 minutes at 4°C (Thermo Fisher Scientific) and the supernatant was filtered using nylon membrane filter with the pore size 0.45  $\mu\text{m}$  (Cole Parmer) [6].

### 2.3 Analysis of FA using HPLC

High Performance Liquid Chromatography (HPLC) was applied to separate and quantify the ferulic acid in banana stem juice, following method by [6]. A simple stability-indicating HPLC-DAD method was validated for the determination of ferulic acid (FA) in polymeric microparticles. Chromatographic conditions consisted of a RP C18 column (250mm  $\times$  4.60 mm, 5  $\mu\text{m}$ , 110 ° A) using a mixture of methanol and water pH 3.0 (48: 52 v/v) as mobile phase at a flow rate of 1.0 mL/min with UV detection at 320 nm. The developed method was validated as per ICH guidelines with respect to specificity, linearity, limit of quantification, limit of detection, accuracy, precision, and robustness provided suitable results regarding all parameters investigated [8].

### 2.4 Kinetic study of the mechanical extraction of banana stem

The purpose of this study was to determine the reaction rate constant ( $k$ ). Here two methods were adopted which were the integral method and the differential method. For integral method, the rate equation was determined from the method of initial rates. The rate was normally verified by comparing the concentrations measured over extended time with the integrated form of the rate equation [7]. Equation 1-3, shows the integral method:

$$C_A = C_{A0} - kt \quad (0^{\text{th}} \text{ order extraction process}) \quad (1)$$

$$\ln C_A/C_{A0} = kt \quad (1^{\text{st}} \text{ order extraction process}) \quad (2)$$

$$1/C_A - 1/C_{A0} = kt \quad (2^{\text{nd}} \text{ order extraction process}) \quad (3)$$

The next three equations (Equation 4-6), shows the differential method:

$$dC_A/dt = -k \quad (0^{\text{th}} \text{ order extraction process}) \quad (4)$$

$$dC_A/dt = -kC_A \quad (1^{\text{st}} \text{ order extraction process}) \quad (5)$$

$$dC_A/dt = -kC_A^2 \quad (2^{\text{nd}} \text{ order extraction process}) \quad (6)$$

where,

$C_A$  = Concentration of FA

$k$  = reaction rate constant

$C_{Ao}$  = initial concentration of FA

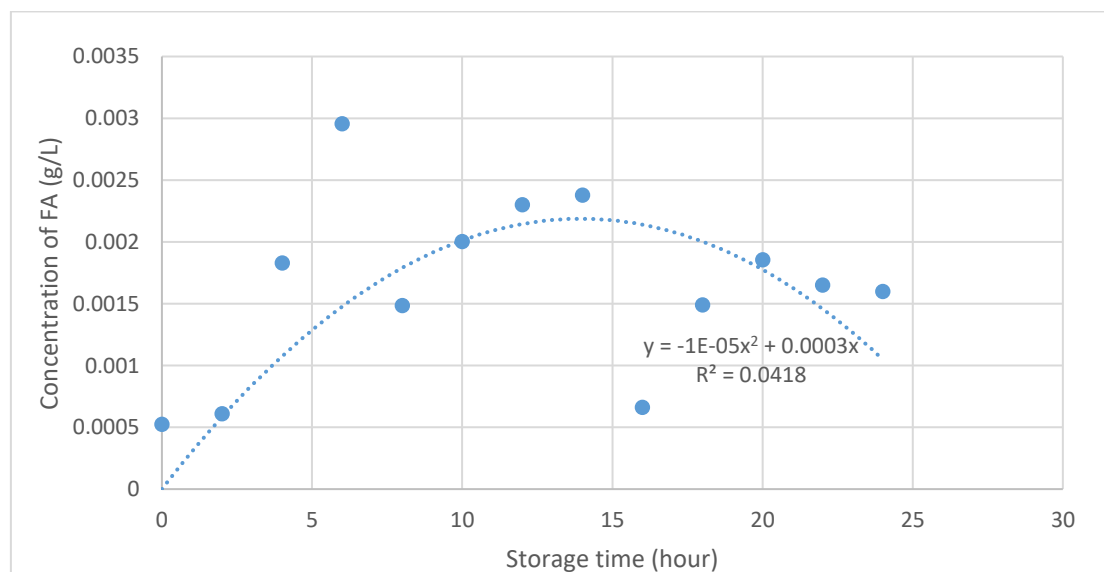
$t$  = storage time

The initial concentration of FA was obtained from the banana stem juice right after it was mechanically extracted. After being extracted, the final concentration of FA was observed based on the optimum condition of the FA. The optimum condition of FA was determined based on the temperature of the pre-treatment and the storage time of FA. Based on the previous study, the optimum condition of the extraction of FA were at 25°C of pre-treatment temperature and 24-hour storage time. The value of reaction rate constant can be calculated after all parameter (the storage time, initial and final concentration of ferulic acid) was determined. After that, the order of the reaction was determined whether the extraction process is following 0<sup>th</sup>, 1<sup>st</sup>, or 2<sup>nd</sup> order.

### 3. Results and Discussion

#### 3.1 FA profile from mechanical extraction

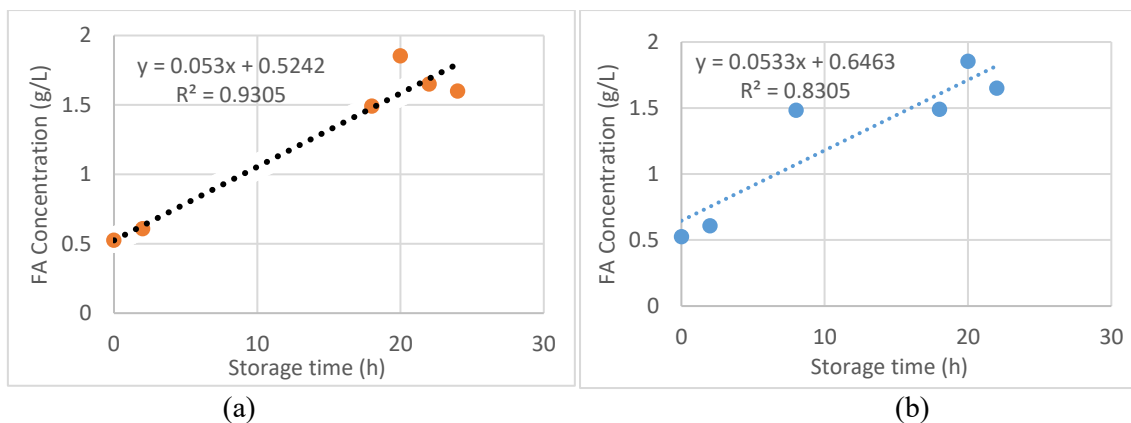
The graph of the average concentration of FA against storage time (Figure 1) shows that the concentration of FA increases from the beginning to 14 hour of storage time. The concentration decreases afterwards until 24 hour. Storage time is referring to the sampling time after the juice was extracted from the banana stem waste. The graph was observed following the quadratic trend. From Figure 1, the maximum and the minimum of FA concentration was at 14 hour and at initial condition (0 hour) which was 0.0024 g/L and 0.00052 g/L, respectively. Based on the graph trend, the FA concentration increased as the storage time increased and started to decrease after reached a certain value. This is due to the FA was exposed to the surrounding temperature.



**Figure 1.** Graph of Average Concentration of FA against Storage time.

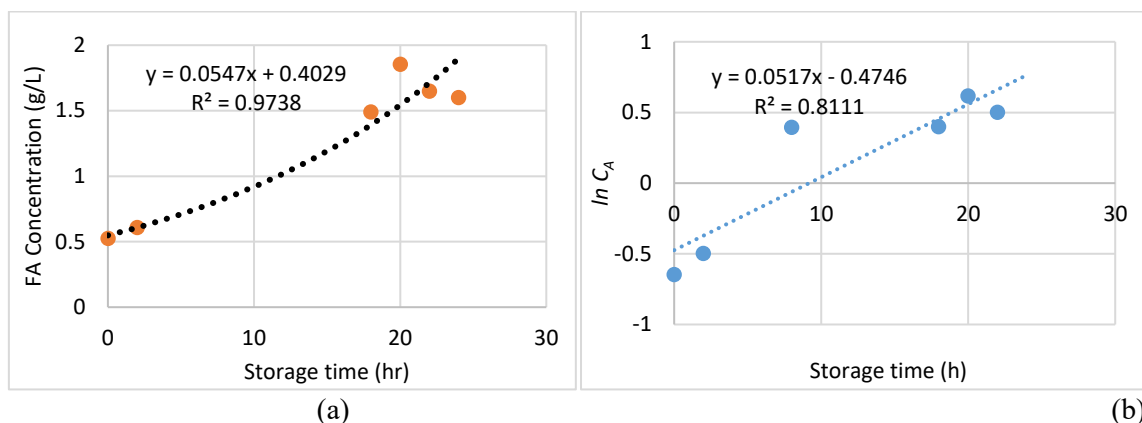
### 3.2 Solution of kinetic constant

**3.2.1 Fitting to 0<sup>th</sup> order equation by using integral and differential method.** The graph of FA concentration against storage time was fitted into three different equations of integral and differential methods. For the 0<sup>th</sup> order, both methods show a linear trend (Figure 2a & b). It was observed that FA concentration was increased linearly from the beginning to 24 hour of storage time.  $R^2$  values for differential and integral method were calculated to be 0.9305 and 0.8305, respectively. The kinetic parameter values determined from here were 0.053 (for differential) and 0.0533 (for integral), respectively. Based on the literature, both differential and integral methods followed the general trend of the 0<sup>th</sup> order reaction in which the rate was independent of concentration [7]. Therefore, in this research the trend of the graph does not depend on the ferulic acid (FA) concentration since no chemicals were used in addition to raw materials as reactant.



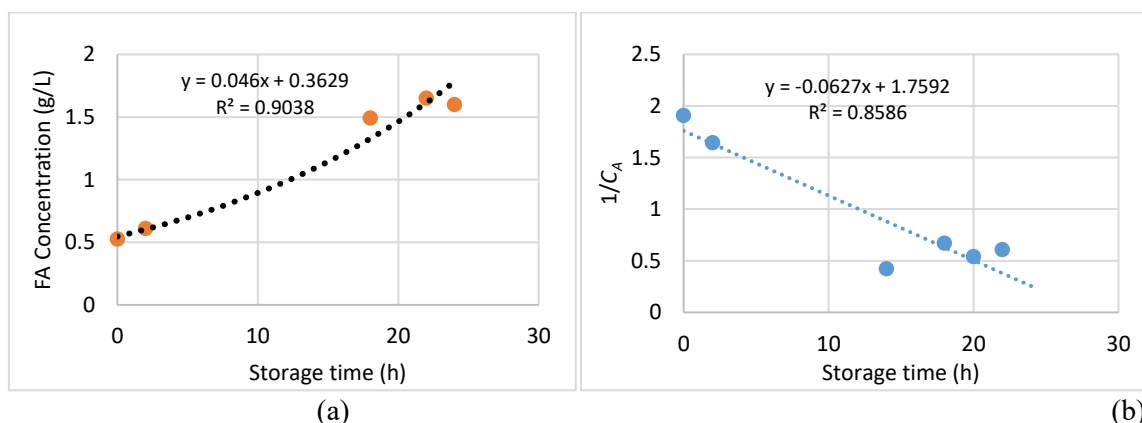
**Figure 2.** The trend of FA concentration against storage time for 0<sup>th</sup> order reaction using (a) integral method, (b) differential method.

**3.2.2 Fitting to 1<sup>st</sup> order equation by using integral and differential method.** For 1<sup>st</sup> order equation, the result for both differential (Figure 3a) and integral (Figure 3b) methods show an increasing trend. FA concentration was increased in both methods from 0 hour to 24 hour. The values of  $R^2$  for both methods were 0.8727 and 0.811, respectively. The kinetic parameter values for 1<sup>st</sup> order extraction process were 0.05317 (integral method) and 0.0517 (differential method), respectively. In a 1<sup>st</sup> order reaction, the reaction is directly proportional to one of the reactants concentration [7]. However, this research was an extraction process and does not using any chemicals as reactants. Therefore, the nature of the extraction process in this work cannot be represented by the 1<sup>st</sup> order reaction.



**Figure 3.** The trend of FA concentration against storage time for 1<sup>st</sup> order reaction using (a) integral method, (b) differential method.

**3.2.3 Fitting to 2<sup>nd</sup> order equation by using integral and differential method.** Using the 2<sup>nd</sup> order equation, the trend for differential method (Figure 4a) shows a smooth exponential trend, while the integral method (Figure 4b) shows a negative linear trend. For differential method, the FA concentration increased exponentially from 0 hour to 24 hour while for integral method, the  $1/C_A$  was decreased linearly from 0 hour to 24 hour. The  $R^2$  for both methods were 0.8375 and 0.8586, respectively. The kinetic parameter values for 2<sup>nd</sup> order extraction were 0.0627 and 0.0567, respectively. In general, the simplest type of second-order reaction has a reaction rate proportional to the square of one reactant concentration. Another type of second-order reaction has a reaction rate that is proportional to the product of two reactants concentration [7]. For this research, the 2<sup>nd</sup> order extraction process does not follow any of these general trends for both differential and integral method.



**Figure 4.** The Graph of FA concentration against time by using differential method (a) and using integral method (b).

### 3.3 Selection of the reaction order

In order to determine the kinetic value, an analysis must be done to select which reaction order gives the best result by comparing its kinetic value with the value of  $R^2$ . Table 1 shows the comparison of reaction order using different solving method with its kinetic value. Based on the table, suitable reaction order for this research was 0<sup>th</sup> order since the graph follows the general trend for both differential method and integral method. For 1<sup>st</sup> and 2<sup>nd</sup> order reaction, both differential and integrals method does not follow the general trend of the graph. This was due to this research was merely an extraction process without involving any chemicals as reactant or catalyst. Thus, the nature of the

extraction process for both reactions cannot be represented and the reactions were not suitable to be selected. Comparing the three reaction order ( $0^{\text{th}}$ ,  $1^{\text{st}}$  and  $2^{\text{nd}}$ ),  $0^{\text{th}}$  order reaction was the most suitable one. Thus, the  $0^{\text{th}}$  order reaction was selected for this research with its kinetic parameter and  $R^2$  values were 0.05 and 0.93, respectively by using differential method.

**Table 1.** Comparison of reaction order on different solving method.

Reaction order	$R^2$ value		Kinetic parameter	
	Differential method	Integral method	Differential method	Integral method
$0^{\text{th}}$	<b>0.9305</b>	0.8305	<b>0.0530</b>	0.0533
$1^{\text{st}}$	0.8727	0.8111	0.05317	0.0517
$2^{\text{nd}}$	0.8375	0.8586	0.0567	0.0627

### 3.4 Comparison with other research

Table 2 shows the comparison on different types of extraction and its reaction order, respectively. In this research, the type of extraction used was the same with Sabarish et al. (2016) which was the mechanical extraction, but differ on the type of machine used. The raw material used for this research was banana stem waste while for Sabarish et al. (2016) used rubber seed. In this research, the extraction was performed to extract the ferulic acid (FA) without using any chemicals as a reactant or catalyst to facilitate the extraction process. However, Sabarish et al. (2016) used methanol as reactant and sulphuric acid as catalyst in order to extract the oil from rubber seed followed by acid esterification of the extracted rubber seed oil. From the experimental results, the extraction order of this research was  $0^{\text{th}}$  while Sabarish et al. (2016) was  $1^{\text{st}}$  order for the forward reaction and  $2^{\text{nd}}$  order for the reverse reaction.

**Table 2.** Comparison with different type of extraction and raw material with other researchers.

Research	Type of extraction	Raw material	Reaction order
This research	Sugarcane press machine	Banana stem waste	$0^{\text{th}}$ order
Sabarish et al., 2016	Hydraulic press	Rubber seed	$1^{\text{st}}$ order
Adnadjovic et al., 2017	Conventional and microwave heating	Guarana seed	$1^{\text{st}}$ order
Patil & Akamanchi, 2017	Microwave assisted process intensification	<i>Nothapodytes nimmoniana</i>	$2^{\text{nd}}$ order
Zhang et al., 2016	Ultrasound-assisted extraction	Chinese chive	$1^{\text{st}}$ order

In studied by [10], conventional heating and microwave heating were used to extract tanine from guarana seed. They compared the kinetic analysis of isothermal extraction of caffeine from guarana seed under conventional heating and microwave heating. In their experiment, chemicals were used as solvents which were water extract, hydrochloric acid (HCl) solution, lead acetate ( $\text{Pb}(\text{CH}_3\text{COO})_2$ ) solution and sulphuric acid. They found out that the reaction order for both conventional heating and microwave heating were following 1<sup>st</sup> order with kinetic parameters of 4.11 (1/min) and 6.6 (1/min), respectively.

[11] used microwave assisted process intensification to extract camptothecin from *Nothapodytes nimmoniana* plant. They made an attempt to fit the extraction kinetics data with different kinetic models such as 2<sup>nd</sup> order rate model, power law model and two site kinetic models. From the experimental results, the 2<sup>nd</sup> order rate model appears to be the best fit to explain the microwave assisted kinetics.

[12] adopted the ultrasound-assisted extraction (UAE) for polysachharide extraction from Chinese chive. They developed a modified kinetic model since the traditional kinetic models cannot reflect the real extraction process of Chinese chive polysaccharide. They compared the performance of the UAE with the conventional hot-water extraction. Phenol-sulphuric acid method was used to determine the content of the polysaccharides for each experiment. From the experimental results, the reaction order for both ultrasound-assisted extraction (UAE) and hot-water extraction was following the 1<sup>st</sup> order extraction process.

The reaction order (0<sup>th</sup>, 1<sup>st</sup>, 2<sup>nd</sup>, ...n<sup>th</sup>) will depends on the condition of the extraction processes. Some extraction processes used chemicals as reactants or catalyst in order to facilitate and improve the efficiency of the process. The usage of these chemicals affected the extraction process so as the reaction order of the extraction process itself.

#### 4. Conclusion

The kinetic parameter of ferulic acid production from banana stem waste via mechanical extraction has been determined in this study. Based on the results, the kinetic parameter and  $R^2$  value were 0.05 and 0.93, respectively. In this research, it was found out that the 0<sup>th</sup> order extraction process was the most suitable reaction orders to represent the behavior of this extraction process.

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