



A study of thermal pyrolysis for castor meal using the Taguchi method[☆]



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ABSTRACT

Castor beans are one of the world's top ten oil crops, with approximately 50% castor oil and 50% castor meal being obtained after a two-stage pressing process (cold and hot pressing). Nevertheless, castor meal still contains a significant amount of residual oil, due to the mechanical limitations of current pressing technology, and this can be further extracted from by means of thermal pyrolysis. In the study, the Taguchi method is performed to optimize the thermal pyrolysis of castor meal in order to maximize the yield of pyrolytic oil.

The effects of different parameters on castor meal pyrolysis are investigated, namely the pyrolytic temperature, residence time, heating rate and nitrogen flow rate. The pyrolysis control factors were selected and categorized into three levels. Based on the Taguchi design concept, an L_9 orthogonal array was chosen for the experiments. The results show that the maximum yield of 19.61% (g-pyrolytic oil/g-castor meal) pyrolytic oil is obtained when the castor meal is subjected to a pyrolytic temperature of 400 °C, residence time of 120 min, heating rate of 20 °C/min, and the nitrogen flow rate of 200 mL/min. The effective sequence of different parameters on castor meal pyrolysis is the nitrogen flow rate, pyrolytic temperature, residence time and heating rate, respectively. The results of the experiment confirm that there were some differences between the theoretical and experimental yields because of certain assumptions in the Taguchi method and the non-uniformity of castor meal. As to the external energy input for castor meal pyrolysis, a preliminary assessment of electric power consumption was 3.27 kW-hr for the treatment of 1 kg castor meal at 400 °C for a period of 60 min.

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1. Introduction

The amount of carbon dioxide in the atmosphere has rapidly increased over the last century, due mainly to the consumption of fossil fuels. In addition to pollution, this is also causing many problems related to climate change, and thus there is an urgent need to develop clean forms of alternative energy. Hoffert et al. [1] proposed that future energy demands will mainly be met by the following sources: (1) solar energy, (2) wind energy, (3) solar energy from the satellites, (4) biomass energy, (5) nuclear energy, and (6) fossil fuels without carbon. Renewable energy sources, such as solar energy, hydro energy and wind energy, are inexhaustible and

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do not cause any pollution, and thus many countries have invested considerable sums in research related technologies. However, even after years of development such methods sources still face the challenges of high costs and low energy conversion efficiency. Biomass energy is different from other forms of renewable energy, because the resources it relies on require land and time to grow. Through photosynthesis, plants use carbon dioxide and water to transform solar energy into chemical energy, and the resulting biomass energy can be artificially converted into different forms. After biomass has been used, the carbon dioxide that it once contained is released back to the atmosphere, and so the net carbon emission of this form of energy is zero [2].

In order to avoid jeopardizing the food supply, the United Nations has stated that food crops cannot be used as raw materials for biofuels. The current second-generation biofuels are mainly non-edible lignocellulosic feedstocks, including agricultural and forestry wastes or residues, and these also enable to more complete use of otherwise non-cultivable, barren land for planting crops [3]. Among the various raw materials that can be converted to biomass

Nomenclature

BCC	biochemical conversion
DSC	differential scanning calorimetry
DTG	differential of thermo gravimetry
M.S.D.	mean-square deviation
NTB	nominal the best
S/N	the ratio of the signal to the noise
SEM	scanning electron microscopy
STB	smaller the better
TCC	thermochemical conversion
TG	thermo gravimetry
TGA	thermogravimetric analysis
<i>L</i>	orthogonal array matrix
LTB	larger the better

energy, castor and jatropha have attracted much attention due to their vitality, ability to grow in barren land, and excellent soil and water conservation abilities.

Castor matures in six months, and can be harvested two or three times a year. The oil content of castor beans is more than 50%, and the annual output of castor oil can reach 10–15 tons per hectare. In contrast, jatropha seeds require 2.5 years to be harvested and their oil content is approximately 30%. Therefore, from an economic point of view, planting castor has considerable advantages over planting jatropha. Castor is currently one of the world's top ten oil crops, and its main distribution areas include Africa, South America, Asia and Europe, with the castor seed production of India, China and Brazil accounting for 81.2% of world production [4]. Castor oil is an important industrial raw material, with the international market mainly concentrated in North America, Europe and China. After the oil has been pressed out of the castor beans, the remaining residue, known as castor meal, accounts for about 50% of the original biomass (as shown in Fig. 1).

There are two broad approaches to transform biomass to bio-fuels. One is TCC (thermochemical conversion), and the other is BCC (biochemical conversion). TCC conversion can be further divided into direct combustion, gasification, pyrolysis and liquefaction [5], and the resulting materials can be directly applied for use as fuels, specialty chemicals or electricity precursors. TCC has



Fig. 1. Photograph of castor meal.

the following benefits: (1) it does not require a large area, (2) it is easy to replenish the required nutrients, (3) it reduces harmful emissions, (4) it is fast, (5) it can handle a wide variety of raw materials, and (6) it can use heat to remove the active compounds or pathogens [6]. In contrast, BCC is the use of fermentation and other biological conversion processes to produce bio-fuels. For instance, waste cooking oil is used to produce biodiesel by transesterification, while starchy crops are used to produce bio-ethanol by fermentation. Bio-fuels can be used in engines, power generators, fuel cells, and so on.

Among the various TCC methods for biomass, thermal pyrolysis is the most promising with regard to liquid products. In addition to handling a broad range of materials in a short time, it also obtains the high yield of pyrolysis liquid. Pyrolysis refers to thermal decomposition that occurs with little oxygen or in an oxygen-free environment. Depending on mode of pyrolysis used, the heating temperature is generally between 290 °C and 750 °C. Lower heating temperatures and longer residence times promote the production of charcoal, while higher temperatures and longer residence times increase the production of gas, and moderate temperatures and short residence times are optimum for producing liquids [7,8].

Based on the conditions of heating temperature, residence time and heating rate, pyrolysis processes can be divided into various different modes. These include gasification to generate gas, liquefaction to generate oil, and carbonization to form char [9]. Since biomass is composed of cellulose, hemicellulose and lignin, the composition of lignocellulosic biomass directly affects the pyrolysis conversion rate and the distribution of the gas, liquid, and solid phase products.

Due to the high pyrolysis temperature and the complex composition of raw materials, the related reaction processes involve phase changes and are therefore quite complicated. McNeill [10] proposed that the main reactions of thermal pyrolysis processes are as follows: (1) random chain scission, (2) depolymerization, (3) elimination, (4) cyclization, and (5) crosslinking. Koufopoulos [11] described the following three-step pyrolysis process:

- [1] Primary reaction: When exposed to heat, organic structures dehydrate and undergo volatile reactions. These reactions begin to occur when the temperature exceeds 300 °C.
- [2] Secondary reaction: This reaction generally occurs when the temperature rises to more than 500 °C. Here, the volatile substances in the biomass undergo cracking, dehydration, dehydrogenation, polymerization, and catalyst reactions, thus breaking down into smaller molecules.
- [3] Gasification: This reaction occurs at temperatures of over 700 °C. At this stage, the organic materials decompose to produce char, steam, hydrogen, carbon dioxide and other substances.

Castor oil is generally obtained by the squeezing castor beans, and this process can be divided cold and hot pressing. With cold pressing the castor oil is derived without the aid of steam heating. With this approach, the resulting castor oil is not affected by exposure to high temperatures, and thus its medicinal properties can be preserved for medical applications. In contrast, with hot pressing method the castor oil is obtained derived with the aid of steam heating. A slow heating treatment can reduce the viscosity of the residual castor oil, and thus make it possible to extract oil that could not be obtained by the use of cold pressing alone [11]. However, conventional squeezing methods have some limitations. According to the results of our preliminary study, castor meal still retains a certain amount of oil although there are few works that examine how to obtain this. Therefore, in the current study the

residual castor oil in castor meal is extracted by thermal pyrolysis, and the Taguchi method is used to establish the optimal operating conditions for the maximum yield of castor oil. The characteristics of the resulting pyrolysis products are also discussed.

2. Experimental method

2.1. Experimental setup

Fig. 2 shows the experimental apparatus for thermal pyrolysis. In the experiment, 50 g of castor meal was packed in the cylindrical metal holder. The holder was made of stainless steel 316, with high resistance to pitting and crevice corrosion, and thus no chemical reactions occurred with the pyrolytic product during the procedure. The holder was placed in a tube furnace, which was vacuumed by a vacuum pump (MZ 2C, Vacuubrand), and then filled with nitrogen to ambient pressure. The furnace was heated up to the target temperature, and then kept at this for a preset length of time. A high-temperature volatile gas was generated by this procedure, and delivered to a condensing system to form the liquid product. A separatory funnel was used to separate the pyrolytic oil from the aqueous product. The gaseous remainder which could not be condensed was discharged through the exhaust system. After the furnace cooled down, the material that remained in the holder was castor meal char.

Thermal analysis (TA Instruments, SDT Q600) was utilized to simultaneously carry out TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry), and the related device was connected to an FTIR (Bruker, Tensor 27) for synchronization. The temperature range for the thermal analysis was set to 50–1000 °C, with the corresponding heating rate of 10 °C/min. The testing sample was placed in a 90 µL platinum crucible, and the flow rate of nitrogen or air in the environment was set to 100 mL/min. The process of the scans at FTIR was set to 64, and the wave number ranged from 4000 to 650 cm⁻¹, with the resolution of 1 cm⁻¹. The standard procedure is to perform thermal analysis of castor meal and qualitative analysis of the pyrolytic gas products, as this helps to delineate the pyrolysis mode of castor meal.

Scanning electron microscopy (SEM (scanning electron microscopy), FEI Quanta 400F) was also used to investigate the surface structure of castor meal char generated by various pyrolytic temperature conditions. At the same time, FTIR (Fourier transform infrared spectroscopy) (Nicolet, Magna-IR 560 Spectrometer) was used to examine the qualitative analysis of the liquid sample. The process of the scans was set to 64, and the scanning ranged from 4000 to 5002 cm⁻¹ with the resolution of 22 cm⁻¹. The liquid sample was dropped on a KBr plate, and then placed in the spectrometer for detection. An element analyzer (EL III) was also used to examine the castor meal char, and the results of the quantitative analysis of the carbon, hydrogen, oxygen, nitrogen, and sulfur contents were obtained as gravimetric percentages.

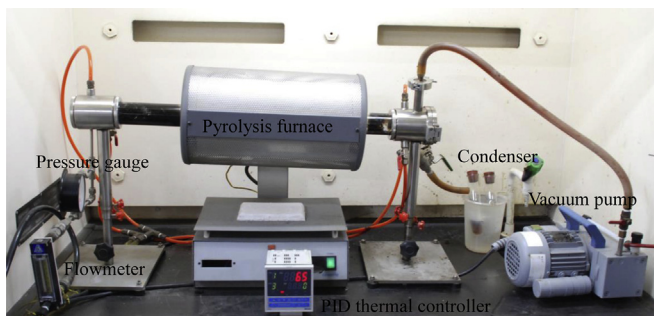


Fig. 2. The experimental setup for thermal pyrolysis.

An energy assessment of the thermal pyrolysis process was also performed by detecting the upstream AC (alternating current) of the tube furnace with a clamp meter (HIOKI 3284), which could detect the AC with a true RMS (root-mean-square) measurement. The data thus collected was imported into a PC (Personal computer) via the data acquisition system with a 10 Hz sampling rate, and the average current was then calculated and stored in the PC's database. The data acquisition system was a data acquisition card (PCI-6023E, National Instruments) and the LabVIEW software. The required voltage for the tube furnace was 110 V. The voltage was multiplied by the measured current, and the product was integrated over time. Based on this, the electrical consumption of the tube furnace can be evaluated.

2.2. Taguchi method

Dr. Genichi Taguchi developed a new method of conducting the design of experiments (Taguchi method). The most important feature of the Taguchi method is the use of an orthogonal array. The orthogonal array stipulates the way of conducting the minimal number of experiments which could give the full information of all the factors that affect the performance parameter. Although the Taguchi method is not a full factorial one that can pinpoint the exact optimal conditions, it can obtain the best trend using less experimental data, and thus in practice is more feasible than a full factorial approach. In addition to the main effect of each factor, the Taguchi method can also study the interactions between the factors to optimize the output response. It is thus a widely used strategy for the optimization of industrial processes.

In the Taguchi method, the term “signal” (S) represents the desired value for the output characteristic, while “noise” (N) represents an undesirable value for the output characteristic. The S/N ratio is thus the ratio of the signal to the noise, and the Taguchi method uses this to measure how a specific quality characteristic deviates from the desired value [12]. The S/N ratio is defined as

$$S/N = -10 \log(\text{M.S.D}) \quad (1)$$

where M.S.D. is the mean-square deviation for the output characteristic.

The S/N ratio characteristics can be divided into three categories, i.e. NTB (nominal is the best characteristic), the STB (smaller the better), and the LTB (larger the better) [13]. To obtain the maximum yield of pyrolytic oil, the larger the better is used in the study, and the related S/N ratio can be expressed as follows:

$$S/N_{LB} = -10 \log \left[\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right] = -10 \log \left[\frac{1}{y^2} \left(1 + \frac{3s^2}{y^2} \right) \right] \quad (2)$$

where n is the number of tests and y_i is the value of the yield of pyrolytic oil in the i th test.

The design of an experiment by Taguchi method involves the following steps

1. Selection of the output response
2. Selection of S/N ratio characteristics
3. Selection of independent variables
4. Selection of number of level settings for each independent variable
5. Selection of orthogonal array
6. Assigning the independent variables to each column
7. Conducting the experiments
8. Analyzing the data
9. Conducting confirmation experiments

In the Taguchi method, the most important step is the use of orthogonal arrays, which are created on the basis of the statistical approach developed by C.R. Rao in 1947. Orthogonal arrays are mainly used to design experiments [14], and these are matrices related to the experimental factors and levels of interest. Because all the columns in such matrices are independent from each other, they are called orthogonal arrays. The key advantage of these is that they can reduce the number of experiments that are needed to obtain the optimal condition, and thus significantly reduce the costs of the analysis. The orthogonal array in Taguchi method is often labeled as follows:

$$L_a(b^c) \quad (3a)$$

where a is the total experiment number, b is the level number of each factor and c is the number of control factor. L represents the orthogonal array matrix comes from the Latin square. For each control factor with two levels, commonly used orthogonal arrays are $L_4(2^3)$, $L_8(2^7)$, $L_{16}(2^{15})$ and $L_{32}(2^{31})$. For each control factor with three levels, commonly used orthogonal arrays are $L_9(3^4)$ and $L_{27}(3^{13})$. Therefore, in the choice of the orthogonal array, the number of control factor must be considered in combination with the level. In the study, four control factors with three levels are selected and an $L_9(3^4)$ orthogonal array is used.

3. Results and discussion

Singh et al. studied the effects of temperature on the pyrolysis of castor beans with the aim of achieving the maximum liquid yield [15]. They carried out thermal pyrolysis of castor beans in a semi-batch reactor made of stainless steel at temperatures ranging from 450 °C to 600 °C, and the heating rate was 20 °C/min. The maximum yield of oil, 64.4% by weight, was obtained at a temperature of 550 °C. However, while Sing et al. used castor beans, the raw material for thermal pyrolysis in the current study is the remaining castor meal after pressing, and various parameters are investigated with regard to their effects, such as pyrolytic temperature, residence time, heating rate and nitrogen flow rate. The optimal operational conditions are then found using a Taguchi experimental design method.

3.1. Thermo gravimetric analysis of castor meal

Biomass is mainly composed of cellulose, hemicellulose and lignin, and the ratio of these three substances will have significant effects on biomass pyrolysis. In slow heating conditions, thermal pyrolysis of cellulose occurs at a temperature range between 325 and 375 °C. For hemicellulose, the temperature is between 200 °C and 300 °C, and it is between 280 and 500 °C for lignin. Therefore, in the first derivative of the TGA curves, the peak located at the lower temperatures is mainly attributed to the pyrolysis of hemicellulose, and the peak at higher temperatures is usually attributed to the pyrolysis of cellulose and lignin [16].

Fig. 3 shows the TGA thermograph of castor meal at a heating rate of 20 °C/min and a nitrogen flow rate of 100 mL/min. The green (in the web version) curve is TG (thermo gravimetry), the blue (in the web version) curve is DTG (differential of thermo gravimetry), and the red (in the web version) curve is DSC (differential scanning calorimetry). There are two distinct peaks in the DTG curve. The main one occurs between 200 and 500 °C, while the other occurs below 100 °C, which represents the removal of moisture from the castor meal. With regard to the TG curve, three stages of weight loss can be seen in the temperature range between 50 and 550 °C. The first stage represents a weight loss of 8.98%, due to the water inside the castor meal being removed. In the second stage, 52.22% of the

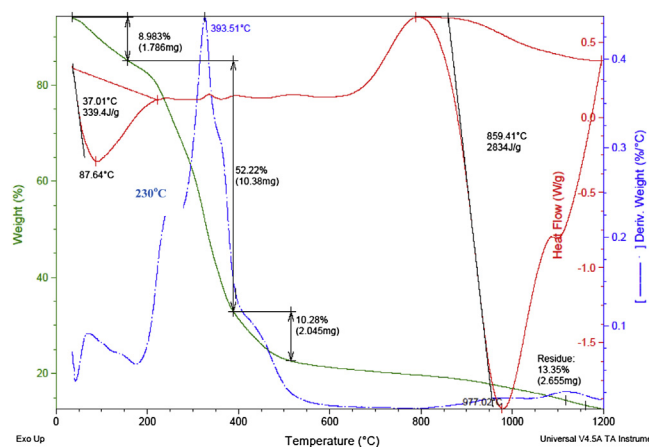


Fig. 3. Thermo gravimetric analyses for castor meal (N_2 flow rate: 100 mL/min, heating rate: 10 °C/min).

original weight of the castor meal is lost. This is because of the thermal instability of the biomass, and thus the aliphatic group is destroyed to form volatile gases and smaller molecules (mainly carbon monoxide and carbon dioxide). In the third stage, a further 10.28% of the initial weight is lost, and this is mainly due to pyrolysis of the residual hydrocarbons. At the temperature of 230 °C, there is a small weight loss, which is mainly due to decomposition of lipids and hexane extract in the castor meal. Babich et al. also found a similar peak at 230 °C for the thermal pyrolysis of *Chlorella* [17].

The TGA is connected to an FTIR to analyze the composition of the pyrolytic gas. Light gases, such as CO_2 , CO, H_2O and CH_4 , can be easily detected. However, for more complex compounds, such as hydrocarbons, phenols, acids, and carbon-based compounds (acids, aldehydes and ketones), only special functional groups can be identified. The characteristic wave numbers of the main volatile products are listed in Table 1 [18].

Fig. 4 shows a 3D image of the FTIR signal. The wave number of 3711 cm^{-1} at the beginning represents the removal of water vapor. Pyrolytic gas is mainly produced before 3000 s, when the pyrolysis temperature is less than 550 °C. The pyrolytic gas mainly contains hydrocarbons, carbon dioxide, carbon monoxide and methane, accompanied by a small amount of phenols, acids and carbon compounds. After 3000 s, the temperature exceeds 550 °C, and secondary pyrolysis occurs, which is the further decomposition of char or volatile substances. The pyrolytic gas that is produced here includes carbon monoxide, methane and light hydrocarbons. Fig. 4 shows that CH_4 is generated at both high and low temperature ranges.

Table 1
Infrared band positions and assignments of the main volatile products.

Wave number (cm^{-1})	Assignment	Compound
3711	O–H stretching	H_2O
3141	C–H stretching	CH_4
2955	C–H stretching	Hydrocarbons
2388	C=O stretching	CO_2
2109	C–O stretching	CO
1777	C=O stretching	Carbonyl compound
1278	O–H bending	Phenol
1192	C–O stretching	Acids

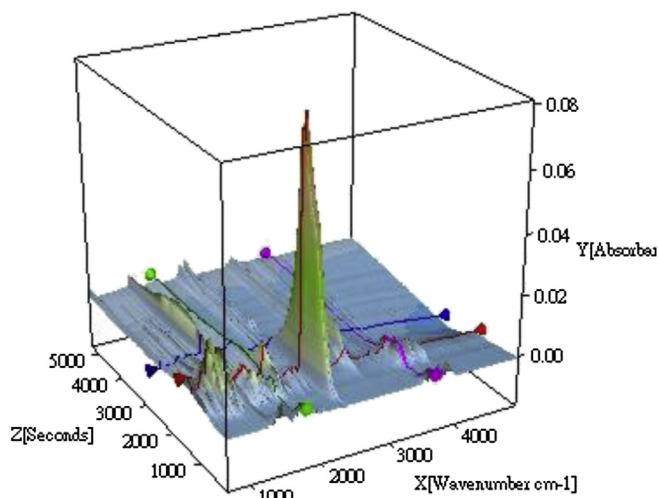


Fig. 4. FTIR signal for pyrolytic gas of castor meal.

3.2. Optimization of the pyrolysis parameters for castor meal

3.2.1. The effect of nitrogen flow rate on the production of pyrolytic oil

It is very common to introduce non-oxygen gases into the reactor during the pyrolysis process, with nitrogen, helium and carbon dioxide often being used. These gases have two main effects. One is to maintain the system in a state without oxygen, and the other is to take the volatiles out of the system in order to avoid them condensing, which also helps in the collection of pyrolytic products. Pütün et al. (2010) examined the effect of the nitrogen flow rate on pyrolysis products, and found that a lower residence time can be obtained for the gas products when this flow rate is higher, thus minimizing the secondary reactions for coke formation [19].

Fig. 5 shows the effect of the nitrogen flow rate on the collection of pyrolytic oil, and the conditions are set at a pyrolysis temperature of 300 °C, heating rate of 20 °C/min, and the residence time of 30 min. The amount of pyrolytic oil that is collected increases with the nitrogen flow rate in the range of 50–200 mL/min. However,

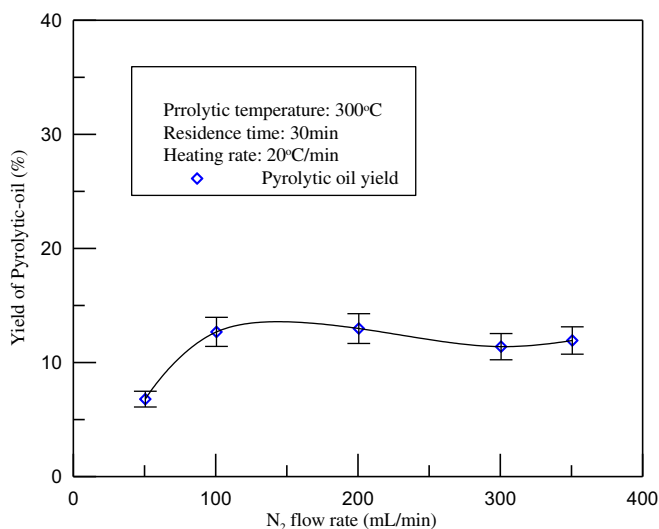


Fig. 5. The effect of nitrogen flow rate on the yield of pyrolytic oil (pyrolysis temperature: 300 °C, heating rate: 20 °C/min and the residence time: 30 min).

Table 2
Pyrolysis control factors and their levels.

	Level 1	Level 2	Level 3
Temperature (°C)	300	400	500
Heating rate (°C/min)	10	20	50
Residence time (min)	30	60	120
N ₂ flow rate (mL/min)	50	100	200

when the nitrogen flow rate is over 200 mL/min, the amount of pyrolytic oil that is obtained remains at roughly a constant value, and no longer changes with the flow rate. Therefore, the nitrogen flow rate was set between 50 and 200 mL/min in the current work.

3.2.2. The optimization of pyrolysis conditions

This study uses the Taguchi method to find the optimal pyrolysis conditions for castor meal in order to produce maximum yield of pyrolytic oil. Table 2 gives the pyrolysis control factors and the settings (i.e., levels) using in this work. The four pyrolysis control factors are pyrolysis temperature, heating rate, residence time and nitrogen flow rate. These factors are assumed to be independent of each other, and each factor has three levels. If the selected factor has significant effects on the product, then it may be better to choose among the low, middle and high values, instead of only the low and high ones.

Based on the number of factors and the related levels, an $L_9(3^4)$ orthogonal array is used in this work, as it is suitable for four factors with three levels. The experimental layout using an $L_9(3^4)$ orthogonal array is shown in Table 3. The original 81 experiments with different conditions are significantly reduced to nine experiments, as this is a more efficient way to learn the effects of the various parameters on the production of pyrolytic oil, thus optimizing the operating conditions. In order to increase the reliability of experimental results, each experiment was repeated several times and the results were averaged.

Table 4 shows the experimental results for the yield of pyrolytic oil and the corresponding S/N ratio based on equation (2). Since the experimental design is orthogonal, it is possible to separate out the effects of each pyrolysis factor at different levels. For example, the mean S/N ratio for the pyrolytic temperature at levels 1, 2 and 3 can be calculated by averaging the S/N ratios for the experiments 1–3, 4–6, and 7–9, respectively. The mean S/N ratio for each level of the other pyrolysis parameters can be computed in a similar manner. The mean S/N ratio for each level of the pyrolysis factors is summarized, and Table 5 shows the S/N response table for the maximum yield of pyrolytic oil. In addition, the total mean S/N ratio for the nine experiments is also calculated, and the results are shown in Table 4.

Based on the results for the production yield and S/N ratio, the optimal operation conditions can be obtained, which are shown in Table 5 and Fig. 6. In this study, the pyrolytic temperature is marked

Table 3
Experimental layout using an $L_9(3^4)$ orthogonal array.

Experiment no.	Pyrolysis temp. (°C)	Heating rate (°C/min)	Residence time (min)	N ₂ flow rate (mL/min)
1	300	10	30	50
2	300	20	60	100
3	300	50	120	200
4	400	10	60	200
5	400	20	120	50
6	400	50	30	100
7	500	10	120	100
8	500	20	30	200
9	500	50	60	50

Table 4
Experimental results and S/N ratio.

Experiment no.	Yields of pyrolytic oil	S/N ratio
1	0.100525325	−19.95449032
2	0.154050704	−16.24672627
3	0.158726683	−15.9870012
4	0.179932041	−14.89782989
5	0.169841174	−15.39914031
6	0.136952791	−17.26858228
7	0.154962668	−16.1954583
8	0.145564373	−16.73889813
9	0.087233321	−21.1863519
Average	0.143087675	−16.88795544

as “A”, heating rate as “B”, residence time as “C”, and nitrogen flow rate as “D”. As can be concluded from the results, the optimal set of conditions for the maximum yield of the pyrolytic oil are A2, B2, C3 and D3, which are a pyrolytic temperature of 400 °C, heating rate of 20 °C/min, residence time of 120 min, and nitrogen flow rate of 200 mL/min. In addition, the order of significance is D, A, C and B, that is, the nitrogen flow rate is the most significant variable, followed by the pyrolytic temperature and then residence time, and finally the heating rate.

3.2.3. Confirmation experiment

The confirmation experiment is the final step, and is carried out to validate the yield of pyrolytic oil based on the previously evaluated optimal conditions. The predicted S/N ratio using the optimal levels of the parameters can be calculated as:

$$S/N_{\text{opt}} = S/N_{\text{AV}} + (A2 - S/N_{\text{AV}}) + (B2 - S/N_{\text{AV}}) + (C3 - S/N_{\text{AV}}) + (D3 - S/N_{\text{AV}}) = -13.544 \quad (3b)$$

where S/N_{AV} is the total mean of the S/N ratio, while S/N_{opt} is the mean of the S/N ratio at the optimal level.

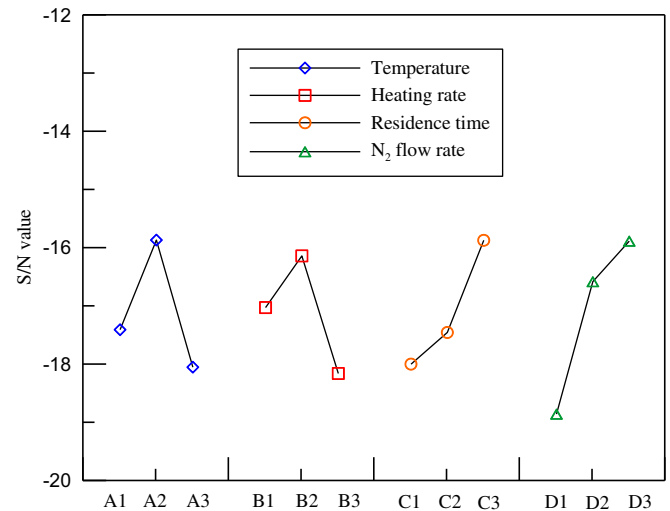
From the results of the standard $L_9(3^4)$ orthogonal array experiments, the optimal process conditions to obtain the maximum yield of pyrolytic oil from castor meal are A2, B2, C3, and D4. The theoretical optimized S/N value is −13.544, so the theoretical yield of pyrolytic oil is 0.22474 g/g-castor meal. The real yield of pyrolytic oil is 0.196141 g/g-castor meal. There 0.03 g/g-castor meal difference between the theoretical and real cases may be due to the following reasons. First, the heating rate will affect the residence time. Second, the effects of the various pyrolysis factors are different. Third, the amount of residual oil in the castor meal is not uniform.

3.2.4. The effect of pyrolysis temperature on the pyrolytic products

Pyrolysis of biomass can be divided into two stages. The first stage is called primary pyrolysis and occurs at a temperature of about 300 °C. This ends at the temperature of 700 °C, and thermochemical decomposition of biomass during this first stage produces tar, coke and volatiles. The second stage occurs at a higher temperature range (>400 °C), and the primary reactions relate to cracking and transformation of tar, including decarboxylation, dehydrogenation, cyclization, aromatization and polymerization.

Table 5
S/N response table for pyrolytic oil.

	L1	L2	L3	Max	Min	Max–min	Mark	Rank
Temperature	−17.396	−15.855	−18.04	−15.855	−18.04	2.18505	A	2
Heating rate	−17.016	−16.128	−18.147	−16.128	−18.147	2.01906	B	4
Residence time	−17.987	−17.444	−15.861	−15.861	−17.987	2.12679	C	3
N ₂ flow rate	−18.847	−16.57	−15.875	−15.875	−18.847	2.97208	D	1

**Fig. 6.** S/N response figure for pyrolytic oil.

Raising the thermal decomposition temperature can alter the extent of these reactions [20].

The results of the Taguchi method show that the pyrolysis temperature is the most significant operating parameter. Fig. 7 shows the effects of different pyrolysis temperatures on the pyrolytic products. The blue (in the web version) column represents the yield of pyrolytic liquid, and the orange (in the web version) column represents the yield of pyrolytic gas. In addition, the red (in the web version) symbol represents the yield of castor oil. Fig. 7 shows the yield of castor meal char decreases with the increase in pyrolysis temperature, and this is particularly significant when the temperature is higher than 500 °C, due to further pyrolysis of the char. As for the pyrolytic liquid, the yield increases as the pyrolysis temperature rises. However, after the temperature exceeds 500 °C, it tends to a constant value. The yield of pyrolytic gas also increases as the pyrolysis temperature rises. Pyrolytic oil has a higher yield between 350 °C and 400 °C, and the maximum yield occurs at the pyrolysis temperature of 400 °C. This confirms the results of the Taguchi method that the best operating conditions occur at a pyrolysis temperature of 400 °C. This is due to the secondary reaction of the pyrolytic liquid. In this, the pyrolytic oil breaks bonds at high temperature, forming small and uncondensed gases or volatiles. The yield of pyrolytic oil thus decreases, while that of pyrolytic gas increases.

3.2.5. The effect of residence time on pyrolytic liquid production

The results of the Taguchi experiment method show that the residence time is the second important parameter that affects the yield of pyrolytic oil, and this is also closely related to the cost of the process. Fig. 8 shows the effect of pyrolysis residence time on the yield of pyrolytic liquid, with the other operating conditions being a pyrolytic temperature of 400 °C, heating rate of 20 °C/min and nitrogen flow rate of 200 mL/min. The green (in the web version) symbols represent the pyrolytic liquid and the blue (in the web

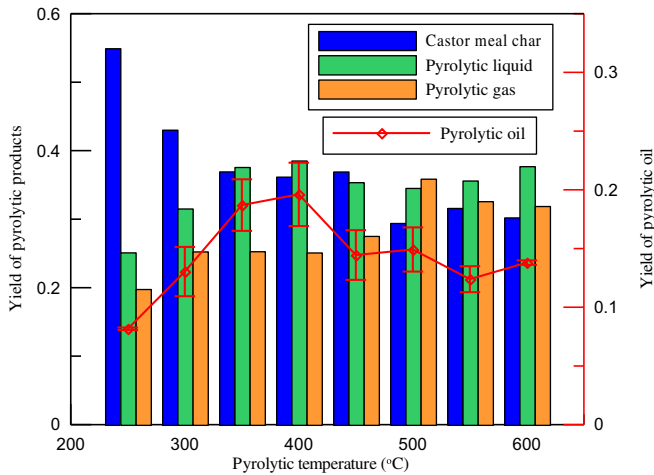


Fig. 7. The effect of pyrolysis temperature on pyrolytic products.

version) ones represent the pyrolytic oil. The yield of pyrolysis liquid increases with the residence time, being about 30% for 30 min, and approximately 37% for 120 min. However, increasing the residence time has a limited effect on the yield of pyrolytic oil, with the primary effect being to increase the pyrolysis products of the aqueous phase. Since the yields of pyrolytic oil are almost the same at 60 and 120 min, setting a residence time of 60 min can significantly accelerate the pyrolysis process and reduce costs.

3.2.6. The estimation of electric power consumption

Fig. 9 shows the accumulated electric power consumption at different pyrolysis temperatures. In the current study, the laboratory scale system is operated in batch mode and the maximum amount of castor meal that can be treated in each run is 0.15 kg. The power consumption is 3.27 kW*hr for 1 kg castor meal at a pyrolytic temperature of 400 °C for 60 min, 2.21 kW*hr/kg-castor meal at 300 °C for 60 min, and 4.12 kW*hr/kg-castor meal at 500 °C for 60 min.

It should be noted that the above results are just a preliminary estimation of the energy consumption of a small batch mode system, and the consumption is relatively high for the following reasons. First, only a small amount of feedstock is treated, because of the laboratory scale system. Second, not all of the electricity is used

to heat the castor meal. Moreover, the power consumption can be dramatically decreased in a large-scale system, and the resulting pyrolytic gas or char can also be reused as heat sources for pyrolysis.

3.3. Analysis of pyrolytic products

3.3.1. Surface structure of castor meal char

Bonelli et al. investigated changes in chemical and surface characteristics of Brazil Nut shells due to pyrolysis at different temperatures [21]. They found noticeable changes in the shells' structure with different pyrolytic temperature. There is progressive destruction of the cell lumen as the pyrolytic temperature increases. The original cellular structure remained almost the same at 600 °C, whereas the char at 850 °C shows signs of structural destruction and walls rupture.

Pyrolysis also causes significant changes in the structure of castor meal char. Fig. 10 shows the surface microstructures of castor meal chars, as obtained by scanning electron microscopy (SEM), when the pyrolytic temperature is 25 °C, 350 °C, 550 °C, and 750 °C. As the temperature increases, there are obvious variations in the surface structure. The original fibers become flaky, and these are then gradually destroyed to produce many pores at higher temperatures. These porous structures then collapse, and the remaining skeleton has a relatively high surface area.

3.3.2. FTIR analysis of pyrolytic oil

FTIR is a fast, accurate and non-destructive method of analysis for pyrolytic oil. It is thus used in this study to analyze the functional groups of the pyrolytic oil obtained from castor meal, with the results shown in Table 6 and Fig. 11. In the figure there is a broad peak related to the OH stretching vibration in the wave number range of 3600–3300 cm^{-1} , which means that the pyrolytic oil obtained from castor meal has alcohol and phenolic groups. The peaks in the wave number ranges of 2950–2800 cm^{-1} and 1480–1370 cm^{-1} are related to the stretching and bending vibration of the CH functional group, respectively, indicating that the pyrolytic oil has alkene groups and methyl structures. The peak in the wave number range of 1700–1680 cm^{-1} is related to the C=O functional group, and shows that the pyrolytic oil has aldehydes, ketones and esters. The peak in the wave number range of 1680–1550 cm^{-1} is related to the C=C stretching vibration of functional groups, which means that the pyrolytic oil of castor meal has an alkene structure. The peak in the wave number range of 820–690 cm^{-1} shows the

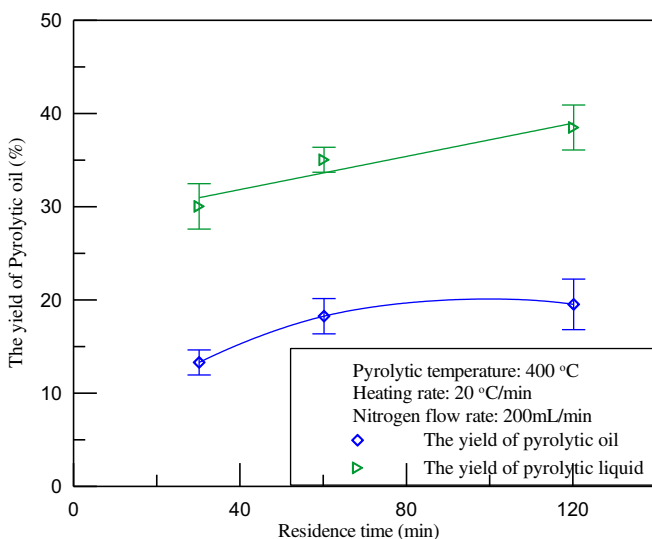


Fig. 8. The effect of pyrolysis residence time on the yield of pyrolytic liquid.

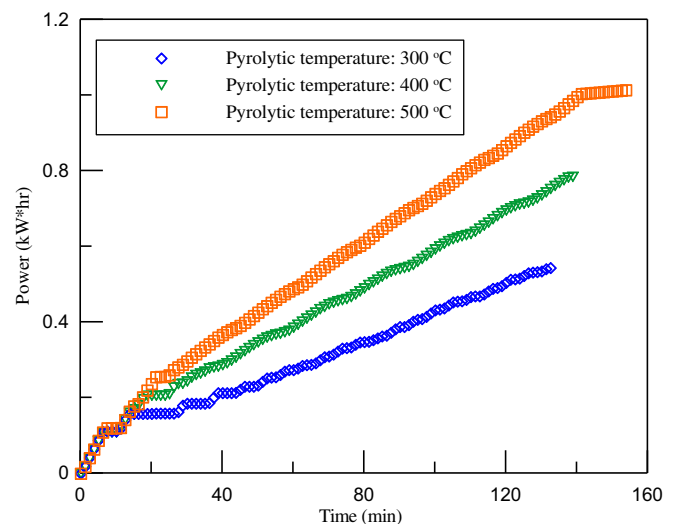


Fig. 9. The accumulated electric power consumption at different pyrolysis temperature.

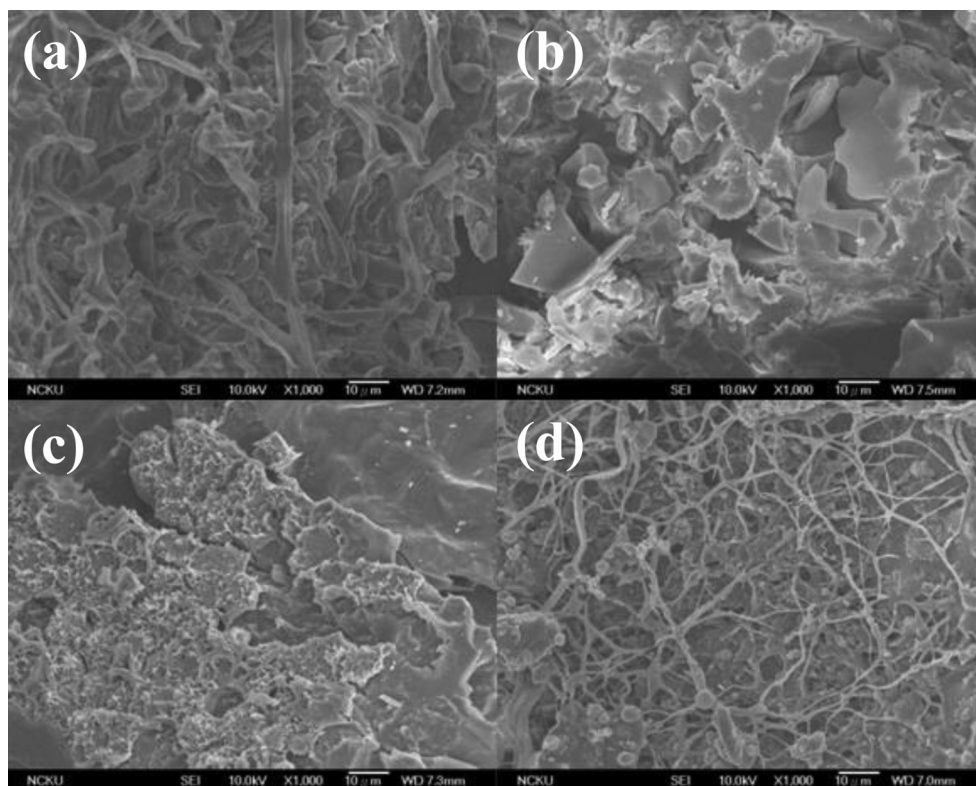


Fig. 10. SEM analysis for pyrolytic char of castor meal ($\times 1000$) at: (a) room temperature, (b) pyrolytic temperature: 350 °C, (c) pyrolytic temperature: 550 °C, and (d) pyrolytic temperature: 750 °C.

pyrolytic oil has aromatic and phenolic groups. These results show that the pyrolytic oil obtained from castor meal is primarily a hydrocarbon coupled with a small amount of the phenol group and the carboxyl group, and is thus suitable for use as a fuel.

3.3.3. Elemental composition and heating values of the pyrolysis products

The heating value is an important parameter with regard to the quality of biomass fuel. The heating values of the pyrolytic oil and pyrolytic char are calculated using the results of the elemental analysis and an empirical formula. The following, often cited equation for coal data was developed by Boie [22]

$$\text{Calorific value(Boie, kcal/Kg)} = 83.2C + 224.2H + 25S + 15N - 25.8O \quad (3c)$$

Lloyd and Davenport [23] developed a regression model with 138 compounds representative of the substances found in fossil fuel liquids.

$$\text{Calorific value(Lloyd – Davenport, kJ/kg)} = 357.77C + 917.58H - 84.51O - 59.38N + 111.87S \quad (4)$$

Table 7 shows the elemental composition and the heating value for the pyrolytic char and pyrolytic oil obtained from castor meal at different pyrolytic temperatures. The castor char has a high proportion (more than 50%) of the C elements. In addition, as the pyrolytic temperature is raised, the variations in the amount of the H element are not obvious. The O elements are released as carbon monoxide and carbon dioxide from the secondary reaction of decomposition, so the percentage of O elements will decrease. More specifically, the percentage of O elements falls from 22.78% at

350 °C to 21.56% at 550 °C. The percentage of C elements increases from 51.69% at 350 °C to 55.53% at 550 °C. Nitrogen is supplied as the carrying gas at high temperature, and the proportion of N elements also increases along with the temperature. The heating value of castor char increases as the pyrolytic temperature is raised, being 22.569 MJ/kg at 350 °C and 23.892 MJ/kg at 550 °C.

In Table 7, the heating value of castor char is 22.569 MJ/kg at the pyrolytic temperature of 350 °C. Based on the TGA thermal analysis of castor char, the integration of the DSC signal curve can obtain a heating value of 22.564 MJ/kg. The heating value of pyrolytic char obtained from the integration of the DSC signal is consistent with the empirical estimation. Therefore, Boie's empirical formula is an accurate, reliable and time-saving method to estimate the heating value of castor char. Substituting the elemental composition of pyrolytic oil into equation (4) can obtain heating value of 22.277 MJ/kg, which is quite close to that of castor char. In addition, the effective measurement range of the elemental analyzer used in this study for sulfur is 0.03–6 mg, with the error range of $\pm 0.39\%$. In Table 7, the concentration of sulfur is so small that it cannot be detected in the pyrolytic products of castor meal. Therefore, the use of pyrolytic oil and pyrolytic char will not produce SO_x and so these substances are very environmentally friendly.

Table 6
The corresponding functional groups for pyrolytic oil obtained from castor meal.

Functional group present	Wave number (cm^{-1})
Broad –OH stretching vibrations, presence of alcohol group	3600–3300
Sp^3 C–H stretching vibration, presence of alkene group	2950–2800
C=O (carbonyl) aldehydes, ketones and esters	1700–1680
C=C stretching vibration, presence of alkene group	1680–1550
C–H bending vibration, CH_2 , CH_3 bending vibration	1480–1370
Aromatic and phenolic	820–690

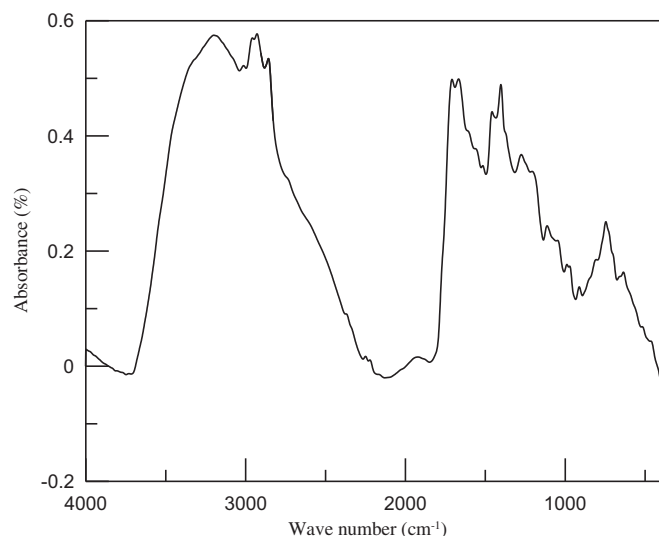


Fig. 11. FTIR signal for pyrolytic oil obtained from castor meal.

4. Conclusions

The Taguchi method was used in this study to optimize the process of thermal pyrolysis for castor meal, with the aim of producing the maximum yield of pyrolytic oil. The effects of pyrolytic temperature, residence time, heating rate and nitrogen flow rate on castor meal pyrolysis are thus investigated, and the following findings are obtained.

1. From the TGA analysis of castor meal, the pyrolysis reaction primarily occurs between 200 °C and 500 °C. In addition, the yield of pyrolytic oil increases along with the nitrogen flow rate in the range of 50–200 mL/min.
2. From the results of the Taguchi method, the effective order of pyrolytic parameters with regard to the yield of pyrolytic oil is nitrogen flow rate > pyrolytic temperature > residence time > heating rate. Of these, the nitrogen flow is a system variable, while the others are operating variables.
3. From the results of the method, the best pyrolysis operating conditions for castor meal are a pyrolysis temperature of 400 °C, residence time of 120 min, heating rate of 20 °C/min, and nitrogen flow rate of 200 mL/min. Under these conditions, the maximum yield of pyrolytic oil is 0.196141 g/g-castor meal, while the estimated maximum yield from the Taguchi method is about 0.22474 g/g-castor meal. It is speculated that the difference may be due to the simplifying assumptions of the Taguchi method used in this study, and the uneven distribution of the remaining oil in the castor meal.
4. The pyrolysis reactor used in this study is laboratory scale and operated in batch mode, so the power consumption was high. A preliminary estimation shows that under the best operating

conditions (pyrolysis temperature of 400 °C and residence time of 60 min), the energy consumption is about 3.27 kW*hr/1 kg-castor meal.

5. The heating values of the pyrolytic oil and pyrolytic char obtained from castor meal can be calculated by using the elemental analysis results and an empirical formula. The heating value of pyrolytic char obtained from the integration of the DSC signal is consistent with the empirical estimation. In addition, the concentration of sulfur is very small in the pyrolytic products of castor meal, and thus the use of pyrolytic oil and pyrolytic char will not produce SO_x, and so these substances are very environmentally friendly.

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Table 7

The elemental analysis and heating values for pyrolytic char and pyrolytic oil obtained from castor meal.

Pyrolytic temperature (°C)	N (%)	C (%)	H (%)	O (%)	Heating value (MJ/kg)
250	4.83	51.69	6.31	22.78	22.071 (char)
350	4.92	52.95	6.32	22.27	22.569 (char)
450	5.41	55.13	6.11	21.8	23.167 (char)
550	5.87	55.33	6.83	21.56	23.892 (char)
400	4.88	52.34	6.24	22.3	22.277 (oil)