

OPTIMIZATION OF JATROPHA OIL EXTRACTION AND ITS BY-PRODUCT  
UTILIZATION BY PYROLYSIS METHOD

A Thesis

by

JINJUTA KONGKASAWAN

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Approved by:

Chair of Committee,	Sergio C. Capareda
Committee Members,	Patricia K. Smith
	Jorge L. Alvarado
Head of Department,	Stephen W. Searcy

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## ABSTRACT

Since the price of fossil fuel has increased, petroleum resources have been restricted and the environmental effects have been of great concern. Biofuel has been considered to be a good solution because it is a clean, non-pollutant and a renewable energy. Biodiesel is one alternative energy that plays a major role in the energy industry. So, the development of biofuel process is more interesting. *Jatropha curcas* L. is considered as an alternative energy source in order to help solve the energy crisis.

The purpose of this research is to investigate the optimum condition of *Jatropha* seed extraction via a screw press and its by-product utilization by a pyrolysis method for achieving the maximum mass conversion and energy recovery. In this study, *Jatropha* seeds were first extracted by a screw press with different discharge aperture sizes, namely, number 4 (4.0 mm), 8 (7.0 mm), and 10 (10.5 mm). The by-product obtained from a screw press was then performed pyrolysis runs at the operating temperatures of 400, 500, and 600 °C.

Results revealed that the optimum condition was achieved when using discharge aperture number 8 (7.0 mm) for a screw press and performing the pyrolysis of the by-product at 500°C. The mass conversion efficiency of 35.8% refined oil, 21.8% bio-char, 14.6% bio-oil, and 11.7% syn-gas were obtained. Therefore, the utilization of by-product using a pyrolysis can enhance the effectiveness of *Jatropha* oil extraction with only 16% mass losses occurred. In addition, the gross heating values of the products were observed as 39.6 MJ/kg for the refined oil, 35.1 MJ/kg for the bio-oil, 27.5 MJ/kg for the bio-char,

and 2.1 MJ/kg for the syn-gas. Due to a high mass conversion efficiency and energy content of Jatropha products, Jatropha has the potential to serve as an alternative energy source.

## DEDICATION

To my wonderful parents, Malee and Suwit Kongkasawan and super brother, Thanit Kongkasawan, who have been my constant sources of inspiration...

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## NOMENCLATURE

ANOVA	Analysis of Variance
AOCS	American Oil Chemists' Society
ASTM	American Society for Testing and Materials
BETA Lab	Bio-Energy Testing and Analysis Laboratory
EERE	Energy Efficiency and Renewable Energy
EIA	Energy Information Administration
FC	Fixed Carbon
GC	Gas Chromatography
HID	Helium Ionization Detector
LSD	Least Significant Difference
NTP	Normal Temperature and Pressure
PPO	Pure Plant Oil
TCD	Thermal Conductivity Detector
VCM	Volatile Combustible Matter

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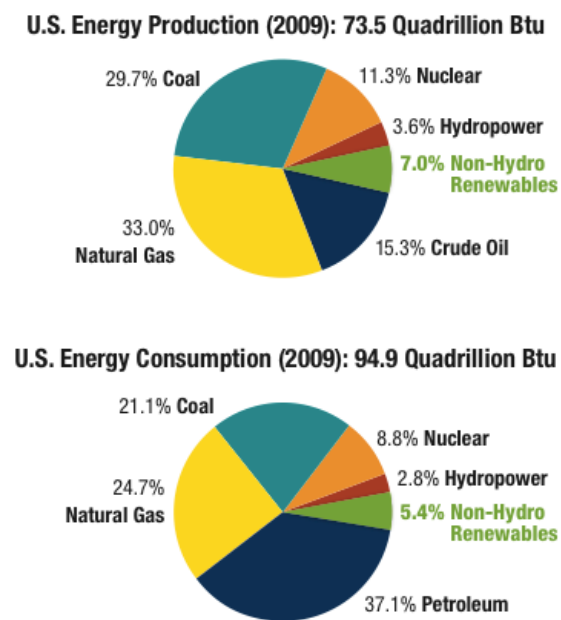
## CHAPTER I

### INTRODUCTION

The U.S. Department of Energy Information Administration (EIA, 2011a) defines fossil fuel as “an energy source formed in the Earth's crust from decayed organic material. The common fossil fuels are petroleum, coal, and natural gas.” Fossil fuels play a crucial role in global energy consumption. The energy generated from fossil fuel remains the primary source of energy. According to the 2009 report of the U.S. Department of Energy (EERE, 2010) on the energy production and consumption, the U.S. energy consumption is mainly based on the petroleum, which is about 37% of the total energy consumption. However, the U.S. energy supply of the crude oil seems not to be sufficient for the demand of petroleum, since the crude oil production is only 15% of the total energy production (Figure 1). Therefore, the restriction of petroleum resources has been of concern and it is important to discover the new sources of energy that can address the energy crisis problem.

Alternative energy, such as solar, wind, tides, biomass etc., has been considered the good alternative because it is clean, non-pollutant and renewable. Therefore, many researchers have been working on developing alternative energy to be used effectively and widely. Nevertheless, the investments in renewable energy development always include external costs and benefits that need to be considered if the large scale of the investments is performed. There are also some external effects that should be taken into

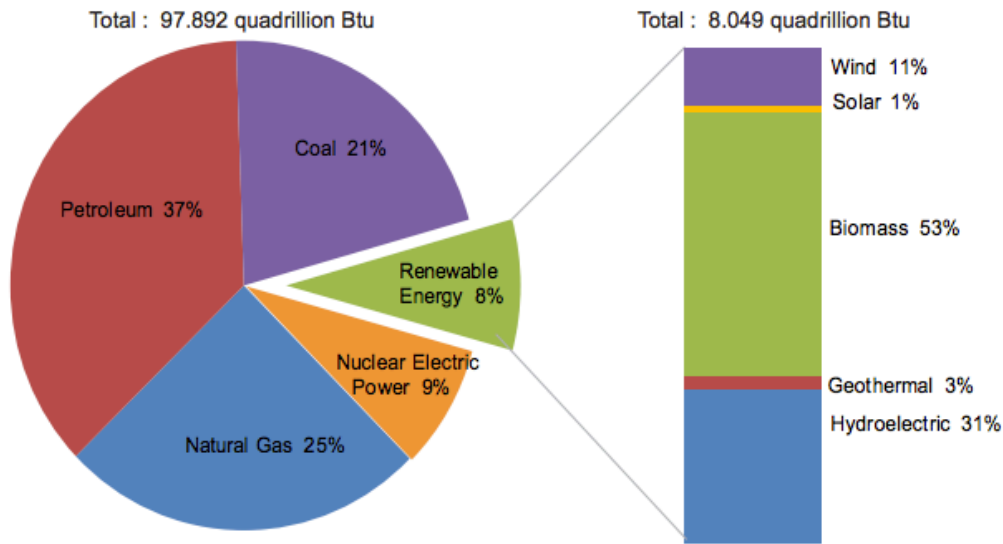
account such as landscape quality, wildlife, air quality and the welfare implications of alternative investment strategies for employment and electricity (Bergmann et al., 2006). Although the renewable energy appears to be a small part of total energy production and consumption in both the world and the United States, the established renewable energy scale increased by more than three times from 2000 to 2009 (EERE, 2010).



**Figure 1. U.S. energy production and consumption in 2009. (EERE, 2010)**

Biomass refers to a form of living species like plants and animals that is still alive or recently dead. Biomass does not take a very long time to replenish as a fossil fuel; for that reason, it is regarded as a renewable source (Basu, 2010). According to the

Renewable Energy Consumption and Electricity Preliminary Statistics 2010 report of the Energy Information Administration (EIA, 2011c), the U.S. renewable energy consumption between 2009 and 2010 increased by 6 percent to about 8 quadrillion Btu, which is approximately 8 percent of total energy consumption in the U.S. Remarkably, more than 50 percent of renewable energy comes from biomass, followed by hydroelectric, wind, geothermal and solar, respectively (Figure 2).



**Figure 2. Renewable energy consumption in the nation's energy supply, 2010. (EIA, 2011c)**

Biofuel is a production from biomass, which is considered to be more environmental friendly than a petroleum-based fuel. Biodiesel is one form of biofuels that is an alternative to petroleum diesel. Biodiesel is non-toxic and made from oil crops

such as corn, soybeans, flaxseed, rapeseed, sugar cane, palm oil and *Jatropha* (Speight, 2008). Due to the multipurpose use of *J. curcas* L., it has been investigated by many researchers for its medicinal utilizations, agricultural purposes, and energy production. Even though *Jatropha* cannot be used as human food because of its toxicity, it provides highly nutritious and protein sources for animal feed if the toxins are removed (Kumar and Sharma, 2008). *Jatropha curcas* L. is one of the oilseed crops that are widely used for biodiesel production. Openshaw (2000) stated that the *Jatropha* oil is considered as a possible fuel alternate. Although *Jatropha* oil contains high number of carbons atom per molecule, which results in a high viscosity and lower ignition quality (or cetane number), the transesterification process of the oil into biodiesel will decrease the viscosity and increase the cetane number.

Various methods of extracting *Jatropha* oil have been performed, whether by thermo-chemically processing, mechanically using a press or chemically extracting with solvents. Many studies have been done to evaluate the optimal condition for *Jatropha* oil extraction. However, different extraction methods have affected the maximum oil produced. Mechanical screw pressing seems to be the popular method to extract the oilseeds because of low initial and operation investments, a simple operation, and a solvent free method (Beerens, 2007). Previous studies indicate that the engine driven screw press gives a high yield of oil extracted with the efficiency ranges between 75 – 90% of available oil (Achten et al., 2008; Henning, 2000; Ofori-Boateng et al., 2012).

Since the extraction efficiency of the mechanical press cannot reach one hundred percent, there is still some oil left in the seed cake after the oil extraction by the screw

press. To increase the extracting efficiency of Jatropha oil extraction, the pyrolysis method is taken into consideration. Therefore, the focus of this research is to enhance the effectiveness of Jatropha oil extraction by using the pyrolysis to obtain the recovery oil in the by-product from a pressing machine.

### 1.1 Objectives

This research will contribute to improve the oil extracting efficiency of *Jatropha curcus* L. seed kernels and reduce the cost-effectiveness of the extracting process. Generally, the Jatropha oil is first extracted by screw-pressing machine but there still some oil remained in the by-product. We expect to use pyrolysis to obtain the remaining oil in the by-product that will enhance the effectiveness of Jatropha oil extraction. Our objectives are as follows:

- a. Investigate the effects of the pressed cake discharge aperture size of the screw press machine on the Jatropha oil yield.
- b. Investigate the effects of pyrolysis operating temperature on the Jatropha oil recovery and pyrolysis products.
- c. Evaluate the mechanical pressing and pyrolysis operating condition for achieving maximum oil yield.
- d. Determine the energy and mass balance of Jatropha seed and energy potential in oil and by product.

In order to accomplish the main objectives, five chapters are included in this thesis. The literature review on Jatropha production, oil extraction methods, and



extraction efficiency will be provided in the next chapter (chapter two). In the third chapter, we will present the methodology to carry out the experiments and describes all the experimental set-up applied in this work. The experimental results, data analysis and discussions will be provided in chapter four. Finally, the last chapter summarizes the achievements of this research and further development for future work.

## CHAPTER II

### LITERATURE REVIEW

In order to investigate the optimum condition for the extraction of oil from *Jatropha* and its by-product utilization, it is important to understand the science behind the processes and concepts that this research is proposing. Therefore, the next few sections will provide some background and related studies associated with *Jatropha* production and characterization, oil extraction methods, and extraction efficiency.

#### **2.1 Background on *Jatropha***

*Jatropha* is a drought-resistant tropical tree, with a minimum necessity of water compared to other fruit trees, and it can produce seed yield with an acceptable quality. It is spread in the wild and agricultural tropical zone of Central America, South America, Africa, India, South Eastern Asia, and Australia. *Jatropha* is likely to grow in an area with intensive sunshine as found in a savanna or desert region (Carels, 2009). The trees shed the leaves in dry season and blossom in wet season. Two flowering peaks often appear during summer and autumn. It will take approximately 3 – 4 months after blooming to seed maturity. The seeds are black with the seed weighing about 1,375 seeds per kilogram (Kumar and Sharma, 2008).

In one *Jatropha* tree, the annual seed production can range from 0.2 kg to above 2 kg. The seed yield also depends on the nature of the crop area such as rainfall levels, soil

type and soil fertility. With the yearly rainfall of 700 – 800 mm, the total seed yield is approximately around 3.2 tonnes per hectare, which lead to about 1.5 tonnes of oil per hectare (Carels, 2009). Henning (2000) reported that the yields of *Jatropha* production in Nicaragua and Mali were 5 and 2.8 tonnes per hectare per year, respectively. For semi-arid areas and cultural wasteland, Heller (1996) found that the seed production could be at least 2 – 3 tonnes per hectare per year. However, if the good soil areas with an average annual rainfall of 900 – 1200 mm were considered, the seed production was up to 5 tonnes of dry seed per hectare per year (Achten et al., 2008).

#### *2.1.1. Properties of Jatropha Seed and Oil*

Many studies have been carried out to determine the physical, mechanical and chemical properties of *Jatropha curcas* L. fruits, seeds and kernels (Garnayak et al., 2008; Karaj and Muller, 2010; Openshaw, 2000; Pradhan et al., 2009; Sirisomboon et al., 2007). Their studies examined physical and mechanical properties such as unit mass, fruit part fraction, seed dimension, surface area, density, rupture force, hardness, and energy used for rupture. Sirisomboon (2007) found the 1000-unit mass (kg) of *Jatropha* fruit, nut and kernel, which were approximately 14, 1.3 and 0.69 kg, respectively. Openshaw (2000) also reported the fraction of the *Jatropha* whole nut, which is composed of 34% shell and 66% kernel.

Karaj and Muller (2010) investigated the chemical properties of *Jatropha* seeds and kernels at different fractions of unit mass. The results of moisture content, protein content, ash content, gross calorific value, and oil content were shown in Table 1,

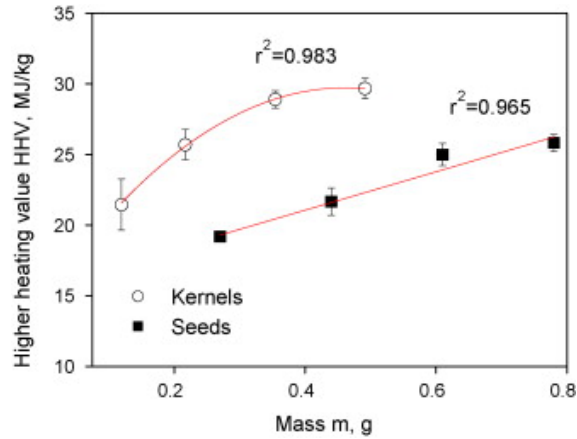
Figure 3, and Figure 4. The heaviest fraction of seeds and kernels gave the highest oil content and gross calorific value. The moisture content of the kernel decreased along with the increase of the unit mass. Openshaw (2000) also reported that dehulling the coat from the fruit would increase the energy value by 20%, from approximately 21 to 25.5 MJ/kg. However, if one would throw away the coat, there would be a total energy loss about 15%.

**Table 1. Chemical properties of *Jatropha curcas* seeds and kernels. (Karaj and Muller, 2010)**

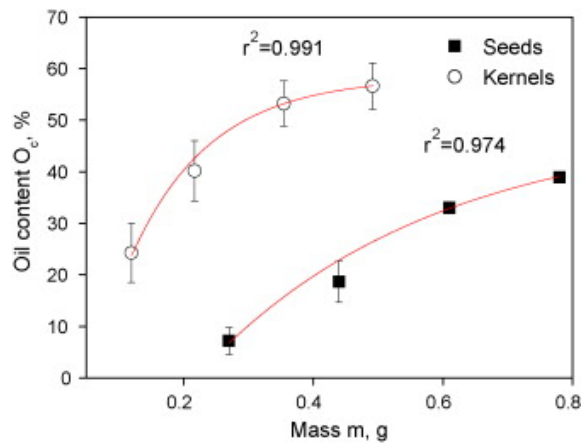
Fraction	Moisture content MC (% w.b)	Crude protein C <sub>p</sub> (% in DM)	Ash content A <sub>c</sub> (% m/m)
<b>Seeds</b>			
I	8.0 ± 1.4 <sup>a</sup>	12.26 ± 0.83 <sup>a</sup>	5.42 ± 0.26 <sup>a</sup>
II	5.5 ± 3.7 <sup>b</sup>	15.08 ± 0.89 <sup>b</sup>	5.06 ± 0.14 <sup>b</sup>
III	4.4 ± 3.2 <sup>cb</sup>	17.51 ± 1.09 <sup>c</sup>	4.48 ± 0.09 <sup>c</sup>
IV	5.2 ± 0.9 <sup>db</sup>	18.15 ± 0.45 <sup>cd</sup>	4.17 ± 0.18 <sup>cd</sup>
<b>Kernels</b>			
I	7.5 ± 0.3 <sup>a</sup>	29.36 ± 0.58 <sup>a</sup>	9.65 ± 1.09 <sup>a</sup>
II	5.4 ± 0.1 <sup>b</sup>	26.89 ± 1.56 <sup>b</sup>	6.37 ± 0.50 <sup>b</sup>
III	4.2 ± 0.4 <sup>c</sup>	25.48 ± 1.10 <sup>cb</sup>	4.62 ± 0.08 <sup>c</sup>
IV	4.1 ± 0.2 <sup>cd</sup>	24.93 ± 0.09 <sup>dbc</sup>	4.15 ± 0.13 <sup>dc</sup>

A *Jatropha* seed contains a high fraction of oil compared to other oil plants. In previous work, the oil composition in *Jatropha* seeds can vary from 30 - 50% by weight of non-edible oil and 45 -60 wt.% for its kernel (Pramanik, 2003). Gubitz's studies (1997) confirmed that there was approximately 55 wt.% of oil contained in the *Jatropha* seed. Koh and Ghazi (2011) also reported the percentage of oil content in *Jatropha* seeds that was about 50 - 60 wt.% non-edible oil. The effect of *Jatropha* shells on the oil

content was studied by Karaj and Muller (2010). They found that by removing the shell, the oil content of *Jatropha* seeds increased from 36% to 55% (Figure 4).



**Figure 3. Gross calorific value of *Jatropha curcas* seeds and kernels vs. unit mass. (Karaj and Muller, 2010)**



**Figure 4. Oil content of *Jatropha curcas* seeds and kernels vs. unit mass. (Karaj and Muller, 2010)**

The properties of *Jatropha* crude oil were also investigated by several researchers. Achten et al. (2008) summarized the overview of the *Jatropha* crude oil properties from the available information at that time as shown in Table 2. They also suggested that the broad range in the values of the free fatty acids, unsaponifiables, acid number, and carbon residue indicated that the oil quality was affected by the environmental conditions and *Jatropha* genetics. The seed oil consisted of more than 70% unsaturated fatty acids with a higher fraction of oleic acid than linoleic acid (Akintayo, 2004; Augustus et al., 2002). Augustus et al. added that the high content of monounsaturated oleic acid represented the semi-drying property, which could be applied to the industrial surface coating.

**Table 2. *Jatropha* oil characteristics and composition. (Achten et al., 2008)**

	Range	Mean	S.D.	n
Specific gravity (g cm <sup>-3</sup> )	0.860–0.933	0.914	0.018	13
Calorific value (MJ kg <sup>-1</sup> )	37.83–42.05	39.63	1.52	9
Pour point (°C)	–3			2
Cloud point (°C)	2			1
Flash point (°C)	210–240	235	11	7
Cetane value	38.0–51.0	46.3	6.2	4
Saponification number (mg g <sup>-1</sup> )	102.9–209.0	182.8	34.3	8
Viscosity at 30 °C (cSt)	37.00–54.80	46.82	7.24	7
Free fatty acids % (kg kg <sup>-1</sup> *100)	0.18–3.40	2.18	1.46	4
Unsaponifiable % (kg kg <sup>-1</sup> *100)	0.79–3.80	2.03	1.57	5
Iodine number (mg iodine g <sup>-1</sup> )	92–112	101	7	8
Acid number (mg KOH g <sup>-1</sup> )	0.92–6.16	3.71	2.17	4
Monoglycerides % (kg kg <sup>-1</sup> *100)	nd–1.7			1
Diglycerides % (kg kg <sup>-1</sup> *100)	2.50–2.70			2
Triglycerides % (kg kg <sup>-1</sup> *100)	88.20–97.30			2
Carbon residue % (kg kg <sup>-1</sup> *100)	0.07–0.64	0.38	0.29	3
Sulfur content % (kg kg <sup>-1</sup> *100)	0–0.13			2

S.D. = standard deviation; n = number of observations used; nd = no data.

Due to the high gross heating value of Jatropha oil, it is considered to serve as an energy source. Pure Jatropha oil can be used directly in a diesel engine without converting into biodiesel. In comparison with an ordinary diesel, using the pure plant oil (PPO) will lower the emission of sulfur oxides, carbon monoxides, poly-aromatic hydrocarbons, smoke, particle matter and noise. However, the PPO has a high viscosity, which results in the pumping and fuel spray problem. In addition, the high acidity of pure Jatropha oil can lead to damage in rubber engine parts (Beerens, 2007).

### *2.2.2. Potential of Jatropha Oils for Biofuels Production*

Biofuels refer to transportation fuels similar to ethanol and biodiesel. Biofuels are derived from biomass feedstock and usually blend with gasoline or diesel fuel, but they can also be used directly on the engines (EIA, 2011b). One can categorize the biofuels by their source and type. Biofuels may be obtained from forest, agricultural waste and by-products from the agro-industry. Biofuels can be in any form such as solid charcoal; or liquid biodiesel; or gaseous biogas (Nigam and Singh, 2011).

Vegetable oils are one of the promising feedstock for biofuel production due to their high energy, lower sulfur and aromatic content, and capabilities of renewing and biodegrading (Agarwal and Agarwal, 2007; Koh and Ghazi, 2011). Triglycerides, the main component in vegetable oils, consist of three fatty acid molecules bonded to a glycerin. The bulk energy in triglycerides has made these molecules an interesting supply for biodiesel manufacture (Lu et al., 2011). Both edible and non-edible vegetable

oils such as canola, soybean, corn, madhuca indica and Jatropha curcas are appropriate for diesel substitution.

Biodiesel has already been verified as suitable fuel for diesel engines. Biodiesel from vegetable oils are produced via a transesterification process. Transesterification is the chemical reaction of triglycerides with alcohol in the presence of a catalyst. A catalyst is a supplement for the reaction, which helps the reaction to be completed in a short time. Typically, methanol is selected for biodiesel production because of its low price. The products from a successful transesterification process are crude glycerol and mono-alkyl ester, as we called it biodiesel (Koh and Ghazi, 2011).

Jatropha oil has been considered by many researchers as a prospective fuel substitution, due especially to its ability to be cultivated in dry and marginal lands (Pandey et al., 2012). In contrast with other oil plants, Jatropha oil has low acidity, good oxidation stability compared to soybean oil, low viscosity compared to castor oil, and well cooling properties compared to palm oil (Augustus et al., 2002; Pandey et al., 2012). Numerous researches on Jatropha as a potential feedstock for biodiesel production have been conducted. Foidl et al. (1996) studied the possibility of Jatropha curcas L. as a source for biofuel production in Nicaragua. They concluded that the jatropha crude oil was suitable for biodiesel making. The biodiesel obtained from transesterification process had high qualities that reached the standards for vegetable oil-based fuels and could be used in diesel engines without modifications.

Diwani et al. (2009) performed the transesterification process of Jatropha oil on both bench and pilot scales. The physical and chemical properties of produced biodiesel



on both scales were compared to the petroleum diesel as presented in Table 3. The comparison showed that these properties were in agreement with the international standards biodiesel. However, using 100% Jatropha oil may contribute to the problem of gum formation, lubricating oil thickening, inadequate atomization and incomplete combustion, resulting in the reduction of engine life. These problems are related to the high viscosity of Jatropha oil. Therefore, it has been investigated by many researchers that blending Jatropha oil with mineral diesel can reduce its viscosity and make it suitable for a diesel engine (Agarwal and Agarwal, 2007; Forson et al., 2004; Pramanik, 2003).

**Table 3. Produced Jatropha biodiesel properties compared to petroleum diesel. (Diwani et al., 2009)**

Property	Jatropha biodiesel			Diesel
	Bench scale	Pilot scale		
Viscosity at 20 °C (m pas.s)	5.01	5.20		3-5
Flash point °C	160	162		68
Pour point °C	-9	-6		-20
Cloud point °C	6	0		-
Carbon residue (% wt.)	Nil	Nil		0.17
Acid value (mg KOH/g)	0.26	0.30		-
Calorific value (M J/kg)	40.59	39.44		42

## 2.2 Mechanical Extraction

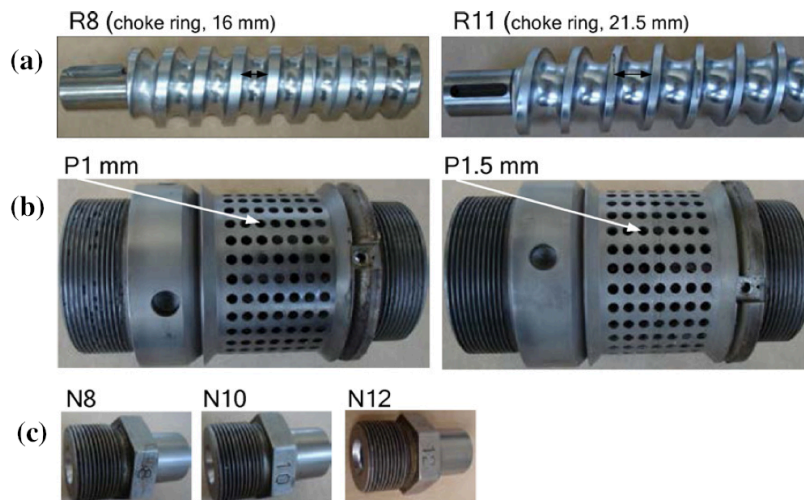
Early mechanical extraction technologies were developed by Romans in 184 B.C. Examples of these technologies were edge runner mills and screw, and wedge presses, which combined animal power and leverage to operate milling and oil extraction. In 1800s, the animal power was replaced by water and wind power to aid the

oil extraction. After that the hydraulic press machine and screw press machine were invented by J. Bramah of England in 1795 and Valerius D. Anderson in 1900, respectively. The screw press machine was used broadly over the hydraulic press at that time due to its abilities to handle large amounts of materials and allow continuous oil extraction. (Kemper, 2005)

Mechanical pressing was the common method used for oil extraction before the 1940s because of its simplicity and low investment cost (Adriaans, 2006). Either a manual ram press or an engine screw press was used, with the extracting efficiency of 75–80% of the available oil for an engine screw press and only 60-65% of the available oil for a manual ram press (Achten et al., 2008). Forsan et al. (2004) conducted the mechanical extracting method upon the assumption of 55% oil content by weight. The extraction efficiency of approximately 39%, corresponding to 71% of the available oil in seed, was achieved.

Several studies have been carried out to improve the efficiency of mechanical oil extraction whether by doing seed pretreatment, adjusting the operating conditions, or modifying the press designs. Seed pretreatments such as dehulling, water soaking, drying, and cooking, along with the seed moisture content were proved to effect the oil yield of screw press machine (Bargale and Singh, 2000; Beerens, 2007; Singh and Bargale, 1990). Beerens (2007) concluded that seed moisture content appeared to be the strongest effect on the oil recovery. For *Jatropha*, he found that the optimum oil yield obtained with natural moisture content of seed was around 6.7 wt % w.b.

Willems et al. (2008) studied the operating condition of hydraulic pressing, including pressure, temperature and pressing rate on the amount of oil yield. Their results showed that using a high pressure ( $>45$  MPa) improved the oil yield by up to 15 wt%. Karaj and Muller (2011) modified the design parameters of a mechanical screw press by changing the sizes of screw choke ring, press cylinder pore, and discharge aperture as demonstrated in Figure 5. These adjusting parameters enhanced the efficiency of oil recovery and lowered the oil remaining in the press cake. The maximal oil yield was achieved when using a screw press with 16 mm choke ring size, 1.5 mm cylinder pore size and 8 mm discharge aperture size.



**Figure 5. Design parameters of mechanical screw press (a) choke ring, (b) press cylinder and (c) discharge nozzle with different sizes. (Karaj and Muller, 2011)**

### 2.3 Pyrolysis

Pyrolysis or thermal cracking refers to the decomposition of organic materials by heating in the lack of oxygen at a specified rate to a maximum temperature, called pyrolysis temperature, and keeping it at that temperature for a specified time. Pyrolysis converts a biomass into solid bio-char, liquid bio-oil and syn-gas product, which consists of CO, CO<sub>2</sub> and H<sub>2</sub>. Pyrolysis is considered an innovative option among the thermo-chemical methods due to its simple operation, its suitability as fuel for energy production and its uncomplicated reproduction (Basu, 2010; Manurang et al., 2009; Speight, 2008).

The yield and properties of pyrolysis product are strongly influenced by pyrolysis reactor design, reaction conditions (temperature, heating rate, residence time, pressure, and catalyst), and feedstock type, and characteristics (particle size, structure, and shape) (Capunitan and Capareda, 2012). Pyrolysis can be categorized into fast, intermediate and slow pyrolysis. Generally, each type of pyrolysis results in different compositions of liquid, char and gas products as demonstrated in Table 4 (Aquino, 2007).

**Table 4. Typical product yields (dry wood basis) at different pyrolysis modes. (Aquino, 2007)**

Mode	Conditions	Liquid (%)	Char (%)	Gas (%)
Fast	Moderate temperature, around 500°C, short hot vapor residence time ~ 1 s	75	12	13
Intermediate	Moderate temperature, moderate hot vapor residence time ~ 10–20 s	50	20	30
Slow	Low temperature, around 400°C, very long residence times	30	35	35

### *2.3.1 Pyrolysis of By-Products*

Agricultural and industrial residues such as husk, rice bran, bagasse, and de-oiled seed cakes can be utilized by the biomass to energy conversion processes (Agrawalla et al., 2011). Utilization of by-products is substantially required because it reduces waste products that may harmful to environment, increases the economic profit from the use of whole product chain, and is appropriate for the development of bio-based economies (Manurang et al., 2009). Pyrolysis is considered to be a potential option for a waste management since the products obtained from a pyrolysis can be used as feedstocks to produce hydrocarbons, which are the primary energy source for petroleum refineries or biorefineries (Kim et al., 2012).

The pyrolysis of oilseed by-product has been investigated by many researchers. Oilseeds such as hazelnut, groundnut, olive, sunflower, rapeseed and *Jatropha* were first extracted by a mechanic press. The de-oiled cakes were then used to perform a pyrolysis process at a pyrolysis temperature in the range of 450 – 550 °C with the liquid product yield about 40 – 60 wt%. The properties of produced bio-oil were in an acceptable quality fuels. Furthermore, the bio-oil generated from a pyrolysis had a considerably high gross calorific value, which enabled it to be used as a fuel after a proper treatment (Agrawalla et al., 2011; Demiral and Sensoz, 2008; Gercel, 2002; Raja et al., 2009; Ucar and Ozkan, 2008).

*Jatropha* residues from a press machine are an interesting feedstock for a pyrolysis process since they still have a high composition of volatile matter and reasonable gross energy value. The studies from Kim et al. (2012) revealed that *Jatropha*

de-oiled cake contained 79.80 wt % of volatile matter and a gross calorific value of 20.80 MJ/kg. After the pyrolysis of Jatropha cake, the pyrolytic oil was produced with the gross heating value increased to 30.2 MJ/kg. Raja et al. (2009) performed the fluidized bed flash pyrolysis to study the effects of the pyrolysis temperature, particle size, and nitrogen flow rate on pyrolysis yield. The optimum oil produce of 64.25% is obtained at a pyrolysis temperature of 500 °C, particle size of 0.7-1.0 mm and nitrogen flow rate 1.75 m<sup>3</sup>/hr. Manurung et al. (2009) also conducted the flash pyrolysis of Jatropha nut shell conversion to pyrolysis oil at 480 °C and atmospheric pressure, resulting in 50 wt.% oil yield, 23 wt.% char, 17 wt.% gas and ash.

## CHAPTER III

### METHODOLOGY

All experiments of this study were performed at the Bio-Energy Testing and Analysis Laboratory (BETA Lab) of the Biological and Agricultural Engineering Department at Texas A&M University. The outline of the processes associated with this study is demonstrated in Figure 6. Details of each process will be provided in the next sections.

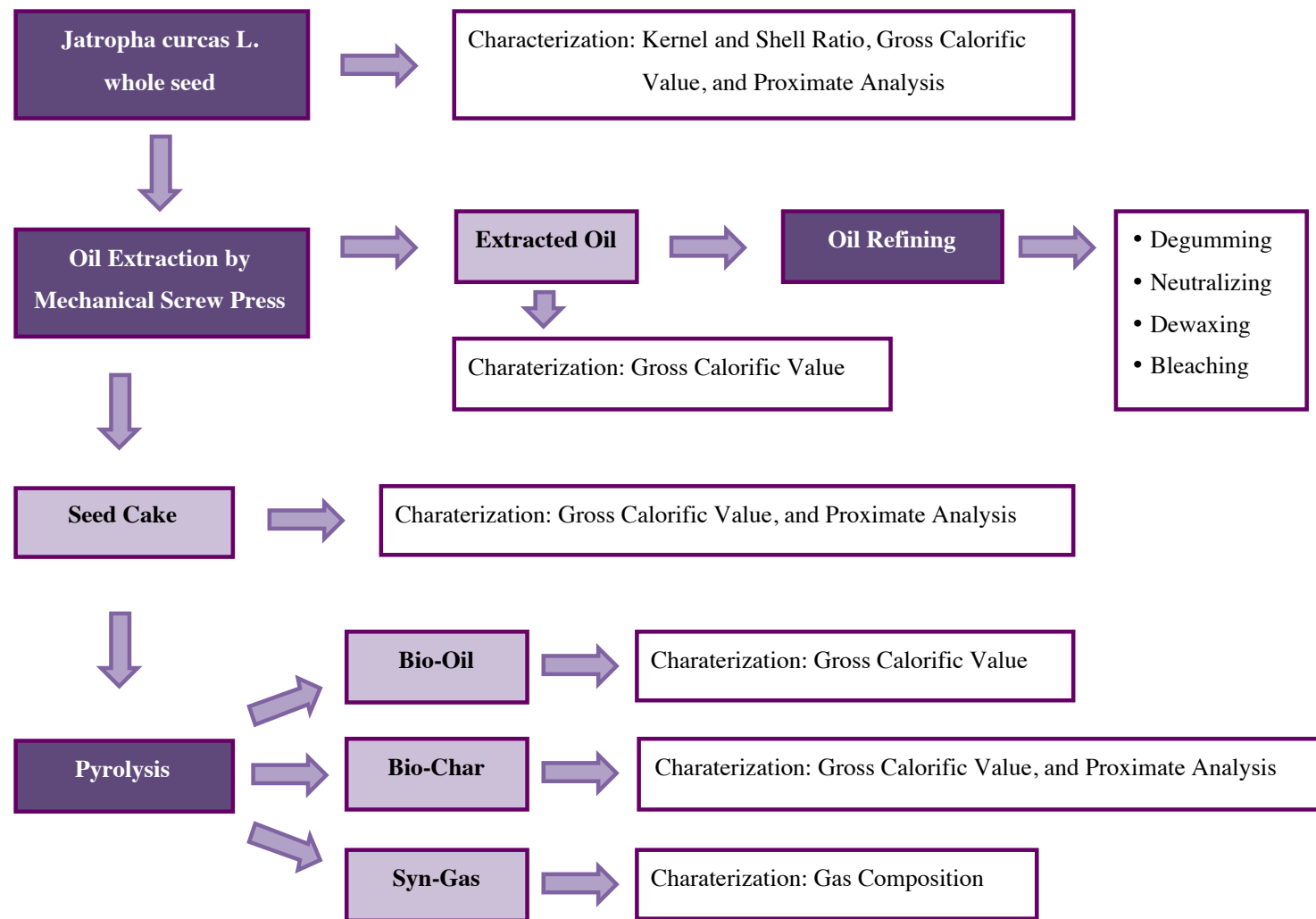
#### **3.1 Mechanical Oil Extraction**

##### *3.1.1 Raw Material Preparation*

*Jatropha curcas* L. seeds were obtained from the BETA Lab. The chemical and physical properties of a *Jatropha* seed were determined through the ratio of the kernel and the shell, proximate analysis and calorific value.

##### *3.1.2. Extraction of Oil*

The *Jatropha* seeds were used for the first-stage oil extraction by using a screw press machine (HFG 505 WN) at the BETA Lab. This screw press can operate with a rated capacity of 5-8 kg/hr. The screw press has different diameters of discharge aperture ranging from number 4 to number 10. Note that the diameter proportionally depends on the number labeled: i.e., the lesser number indicated, the smaller aperture size.



**Figure 6. Experimental outline involved in this study.**



The dependent variable of interest in this experiment was the percent oil recovery with a discharge nozzle diameter as an independent variable. The effect of press cake discharge aperture size was investigated for achieving the maximum oil yield. The experiments were conducted by using three sizes, namely number 4 (4.0 mm), 8 (7.0 mm) and 10 (10.5 mm), of press cake discharge aperture. In each replicate, 300 g of raw seeds were placed into the feeding chamber. The operating temperature was selected at 140 °C since it was the condition that the maximum percent oil extracted was achieved (Santos, 2009).

The extracting times of each replicate were recorded. The oil extracted and the press cakes were weighed after the process was completed. All experiments were repeated three times for each discharge aperture size; the mean and standard deviation values were then calculated. The percent of oil extracted and residues can be obtained using formulas shown in Equation 1 and 2:

$$\% \text{ oil extracted} = \frac{\text{Wt. of oil extracted}}{\text{Initial wt. of sample}} \times 100 \quad (1)$$

$$\% \text{ residues} = \frac{\text{Wt. of press cake}}{\text{Initial wt. of sample}} \times 100 \quad (2)$$

The extracted oil that resulted from the optimal condition was filtered using a 25 µm fiberglass filter membrane. This filtered oil was then used for the refining process.

### *3.1.3. Oil Refining*

The oil refining processes of *Jatropha* was conducted in the same way as Santos' work (2009). The details of oil refining procedures including degumming, neutralization, dewaxing, and bleaching were provided in the next sections.

#### **3.1.3.1. Degumming and Neutralization**

The objective of the degumming process is to remove the phosphorus-based compounds, mainly lecithin and cephalin from the fresh oil before converting it into biodiesel. The removed substance is called “gums.”

The filtered oil was heated to 60 - 70 °C and de-ionized water (2% by weight of the oil) was added. Then an additional 2% (by weight of the oil) of phosphoric acid was added to enhance the degumming process. The mixer was agitated for 1 hour with the temperature maintained at 60 - 70 °C. The hydrated gums were removed by centrifugation. Finally, the gums and the oil were separated, weighed and the results were recorded.

For the neutralization process, the degummed oil was mixed with sodium hydroxide (NaOH) aqueous solution. The amount of NaOH used was based on the free fatty acid content of *Jatropha* oil. Free fatty acids determination was done by following the AOCS Official Method Ca 5a-40 (AOCS, 1997). A contacting time of 30 minutes for the soap formation was allowed, and the mixture was separated by centrifugation. The neutralized oil was washed with a de-ionized water twice to make sure that all traces of

soap were eliminated. Then we used the centrifuge to separate the oil and water. The oil and recovered soap were recorded.

### **3.1.3.2. Dewaxing and Bleaching**

Vegetable oils usually contain high amount waxes that lead to the cloud when refrigerated. Therefore, the waxes must be removed during a biodiesel conversion process.

The oil from obtained from a neutralization process was mixed with a 5% (by weight of the oil) of NaOH aqueous solution and a 5% (by weight of the oil) of a de-ionized water in a covered flask and place in a chiller setting at 5 °C. The mixture was agitated for 4 hours. The soapy water wetted the waxes, which moved from oil to water phase. The waxes were then removed by centrifugation. The oil and the waxes were separated, and recorded their weights.

A bleaching procedure was done in order to remove the colored substances and oxidation products. After this process, the oil will be nearly colorless with a peroxide value of zero.

For a bleaching process, the dewaxed oil was heated to 100 °C under constant agitation. Fuller's earth was added (1% by weight of the oil) to the heated oil, and the mixer was continued agitating for 30 minutes. While it was hot, using the centrifuge to separate the oil from the clay. Finally, the weights of oil and oxidation product were recorded.

## **3.2 Pyrolysis of Jatropha By-products**

### *3.2.1. Sample Preparation*

Jatropha residues from the screw press machine with the maximum oil yield condition were used for a pyrolysis process. The Jatropha de-oiled cakes were ground through a Wiley mill (Arthur A. Thomas Co., Philadelphia, PA) filtered with a 1.0 mm screen and dried in a 104 °C oven for 24 hrs before performing a pyrolysis.

### *3.2.2. Experimental Set-up*

Pyrolysis runs were carried out using a batch pressure reactor (4540 HP/HT Reactors, Parr Instrument Company, Moline, IL) with automatic temperature control. This pyrolyzer operated with temperatures ranging from 300 to 1200 °C and a heating rate up to 3 °C/min. The operating rate of each run was 200 – 600 g/min. The batch reactor was equipped with a condenser connected directly to the head of the reactor. A condensed bio-oil was stored in a collecting cylinder, which was attached under the condenser. The volume of gas produced was measured by a gas flow meter connected at the gas outlet of the reactor.

Approximately 200 g of sample was placed in the reactor. Before starting each run, the reactor was purged with nitrogen for 15 minutes to make sure that the process would operate in the absence of oxygen. The reactor controller and heater were then turned on with a specified temperature. The operating temperatures of pyrolysis for this study were chosen at 400, 500 and 600 °C. The reactor was heated until it reached the desired temperature.

During the heating process, the outlet valve of the reactor was closed until the reactor pressure approached 100 psi. As the pressure increased above 100 psi due to the gas production, the outlet valve was gently opened to maintain the pressure. When a setting temperature was achieved, the process continued to run for 20 minutes, and the gas produced was collected in a sampling bag for the gas composition analysis. After that, the reactor was allowed to cool down and the products were collected and weighed. The liquid product (bio-oil) was collected from the cylinder below the condenser and the bio-char was collected from the reactor for further analyses. Each pyrolysis temperatures were conducted in triplicate.

### **3.3 Product Characterization**

The products obtained from both screw press and pyrolysis were then analyzed for their characteristics as explained in the following sections. Each analysis was made in three replicates; the mean and standard deviation values were then calculated.

#### *3.3.1. Gross Calorific Value*

The gross calorific value of the oil extracted, seed cake, bio-oil, and bio-char were determined according to ASTM D5865 Standard Test Method for Gross Calorific Value of Coal and Coke by bomb calorimeter (6200 Isoperibol Calorimeter, Parr Instrument Company, Moline, Illinois). Solid products were ground with a Wiley mill using a 2 mm screen prior to the bomb calorimeter operation.

### *3.3.2. Moisture Content and Proximate Analysis*

The moisture content of the feedstock was ensured to be less than 10% before performing the pyrolysis process. Moisture content was determined according to the ASTM E1756 Standard Test Method for Determination of Total Solids in Biomass. The *Jatropha* seed, the residues from pressing machine, and bio-char were also characterized by proximate analysis using ASTM D3172 Standard Practice for Proximate Analysis of Coal and Coke, and ASTM E1755 Standard Test Method for Ash in Biomass. All products were hammer ground before conducting an analysis.

### *3.3.3. Gas Composition*

The syn-gas collected at different pyrolysis temperatures was then analyzed for its composition by an SRI Multiple Gas Analyzer #1 (MG#1) gas chromatograph (SRI GC, Torrance, CA). The detectors used in the analyzer were helium ionization detector (HID) and thermal conductivity detector (TCD). The columns for the syn-gas analysis were 6' Molecular Sieve 13X and 6' Silica Gel, with helium as the carrier gas. The calibration gas standard mixture consisted of H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> (Praxair Specialty Gases, Austin, TX) with an analytical accuracy of  $\pm 5\%$ .

## **3.4 Mass and Energy Balance**

Mass and energy balance for all the processes were determined. These processes were divided into two parts: (1) Mass and energy distribution for the pyrolysis at

different operating temperatures and (2) Mass and energy distribution for all Jatropha extraction process including the screw press machine and pyrolysis.

The yields of products from both the screw press machine and the pyrolysis process were expressed as a weight percent (wt%). The quantity of gas produced was measured in the form of gas volume; therefore the mass of gas was calculated after the gas composition was determined. Equation 3 was used for the mass of gas calculation under the assumption that the gas was collected at normal temperature and pressure (NTP). The densities of each gas were obtained from the Handbook of Natural Gas Engineering (Katz et al., 1959).

$$M = \frac{D \times V \times x}{100} \quad (3)$$

Where: M is the mass of each gas, kg

D is the gas density of each gas, kg/m<sup>3</sup>

V is the total gas produced, m<sup>3</sup>

x is the gas fraction obtained from gas composition analysis, %

According to the initial biomass input and the weights of the products, mass balance for the pyrolysis at different temperatures, as well as the oil extraction process and by-product utilization was determined. The efficiency of biomass conversion into the products namely “%Mass Conversion”, and %Mass Losses were calculated using the following equations:

$$\% \text{ Mass conversion} = \frac{W_{prod}}{W_{biomass}} \times 100 \quad (4)$$

$$\% \text{ Mass Losses} = 100\% - \sum (\% \text{ Mass Conversion of all products}) \quad (5)$$

Where:  $W_{\text{biomass}}$  is the initial weight of biomass, kg

$W_{\text{prod}}$  is the weight of product, kg

For the energy distribution, the energy input to the system was computed based on the biomass gross calorific value. Energy output was a summation of energy from oil extracted by screw press, de-oiled cake, bio-oil, bio-char and syn-gas acquired from a bomb calorimeter (refer to section 3.3.1 for heating value determination). Gross heat values of each gas were referenced from the Handbook of Natural Gas Engineering (Katz et al., 1959). The amount of energy recovery in the product and energy losses were calculated in terms of percentage using the following equations:

$$\% \text{ Energy Recovery in Product} = \frac{W_{\text{prod}} \times HV_{\text{prod}}}{W_{\text{biomass}} \times HV_{\text{biomass}}} \times 100 \quad (6)$$

$$\% \text{ Energy Losses} = 100\% - \sum (\% \text{ Energy Conversion of all products}) \quad (7)$$

Where:  $W_{\text{prod}}$  is the weight of product, kg

$W_{\text{biomass}}$  is the initial weight of biomass, kg

$HV_{\text{prod}}$  is the gross heat value of the product, MJ/kg

$HV_{\text{biomass}}$  is the gross heat value of of the biomass, MJ/kg



CHAPTER IV  
RESULTS AND DISCUSSION

**4.1 Physical and Chemical Properties of *Jatropha Curcas* L. Seeds**

The chemical and physical properties of *Jatropha* whole seeds, kernels, and shells were determined. The ratio of the kernel and the shell, moisture content, proximate analysis and calorific value are presented in Table 5.

**Table 5. Properties of *Jatropha curcas* L. seeds.**

Properties	<i>Jatropha curcas</i> L. seeds		
	Whole seed	Kernel	Shell
Ratio (%)	-	61.2 ± 0.91	38.2 ± 0.71
Moisture content (%)	7.5 ± 0.12	4.8 ± 0.43	9.1 ± 0.09
Volatile matter (%d.b.)	83.4 ± 1.03	91.1 ± 0.46	71.1 ± 0.45
Fixed carbon (%d.b.)	10.2 ± 0.57	4.3 ± 0.35	24.0 ± 0.19
Ash (%d.b.)	6.4 ± 0.59	4.6 ± 0.15	4.9 ± 0.46
Calorific value (MJ/kg)	24.0 ± 0.24	28.3 ± 0.54	19.9 ± 0.38

The values of the kernel and shell fraction, moisture content, percent ash and gross heating value obtained from the experiments were comparable to that reported by Openshaw (2000) for a *Jatropha* whole nut, kernel and shell. The proximate analysis of *Jatropha* showed that it had a high amount of volatile combustible matter (VCM) and

low ash content. High VCM was the key factor to generate low NO<sub>x</sub> combustion conditions in flames and also helped in easier ignition. Low ash content resulted in less unburned product after heating. The fixed carbon (FC) content indicated the solid combustible residue that remained after the volatile matter was discharged. Fixed carbon was also used as estimation for calorific value; i.e., the higher FC content would increase the gross heating value of a product. The heating value referred to the amount of energy contained in biomass, which was quite high for a *Jatropha* seed. Based on the results, the *Jatropha* was potentially suitable for energy conversion.

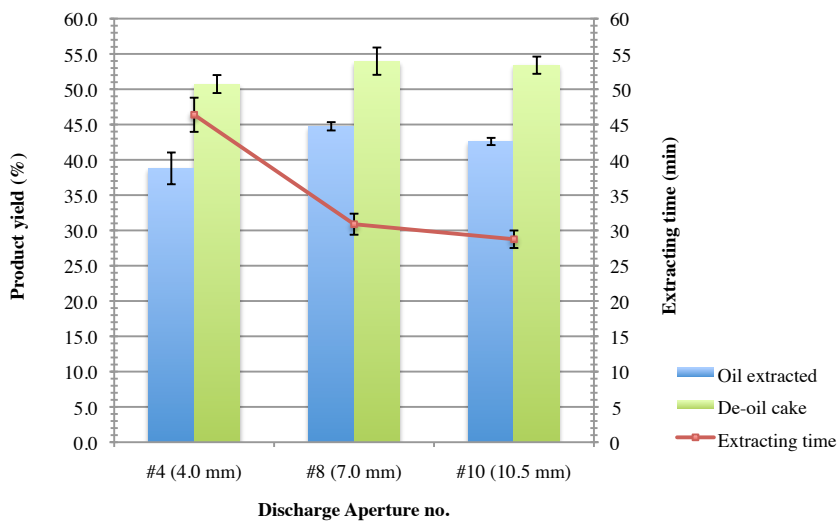
## **4.2 Mechanical Extraction**

### *4.2.1. Effect of Discharge Aperture Sizes on Oil yield*

*Jatropha curcas* L. seeds were first extracted using a screw press machine with three different discharge aperture sizes, namely 4.0 mm, 7.0 mm, and 10.5 mm. The percent oil extracted and extraction time of each aperture size was obtained. Figure 7 represents the relationship among the product yield, operating time, and discharge aperture sizes.

Based on the graph, the highest oil recovery of 44% and de-oiled cake of 54% from *Jatropha* oil extraction were achieved when using discharge nozzle number 8. The statistical analysis by Analysis of Variance (ANOVA) showed that the size of discharge nozzle had an effect on the product yields and extracting time. As the size of discharge aperture increased, the pressure required to force the press cake passing out of the nozzle decreased, resulting in the ability of press cake to move out more quickly. Thus, the

extraction time decreased with the increasing of discharge aperture size. However, the Fisher's least significant difference (LSD) test indicated that the de-oiled cake yield and the extracting time of using discharge nozzle number 8 were not significantly different from number 10. Therefore, the optimum condition of oil extraction via the screw press was achieved when using the discharge nozzle number 8 (7.0 mm).



**Figure 7. The effect of discharge aperture size on product yield (%) and extracting time (min) of *Jatropha curcas* L.**

#### 4.2.2. *Extracted Oil and Press Cake Characterization*

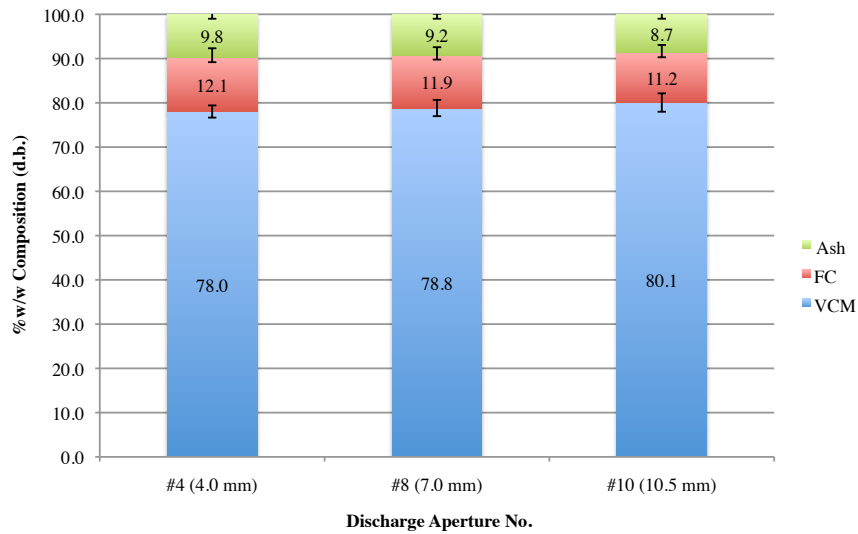
After extracting the *Jatropha* seeds by a screw press, the extracted oil and de-oiled cake were then analyzed for their characteristics. The gross calorific values of the products obtained from the screw press at different discharge diameters are shown in

Table 6. The gross heating values of oil obtained from all discharges aperture sizes were around 39.5 – 39.6 MJ/kg with no significant difference among the treatments. These values were similar to those of Achten et al. (2008) and Pramanik (2003).

**Table 6. Gross heating value of product from screw press at different discharge aperture sizes.**

	Discharge Aperture		
	#4 (4.0 mm)	#8 (7.0 mm)	#10 (10.5 mm)
Calorific Value of Oil (MJ/kg)	39.6	39.6	39.5
Calorific Value of De-oiled Cake (MJ/kg)	19.3	20.5	21.5

The gross heating values of the de-oiled cake obtained from all discharge aperture sizes approximately ranged between 19 – 22 MJ/kg. The maximum heating value was acquired from the discharge nozzle number 10 (10.5 mm), but it was not significantly different from number 8 (7.0 mm). The de-oiled cakes still had a high energy value due to some un-extracted oil left in the seed cakes. The proximate analysis of the de-oiled cake from different discharge aperture number is represented in Figure 8. The value of VCM component of the press cake was quite high and not far lower than the VCM of the feedstock. The FC composition was around 12%, which was still high. This content also influenced the gross energy of the press cake.



**Figure 8. Proximate analysis of de-oiled cake (dry basis) after screw press extraction.**

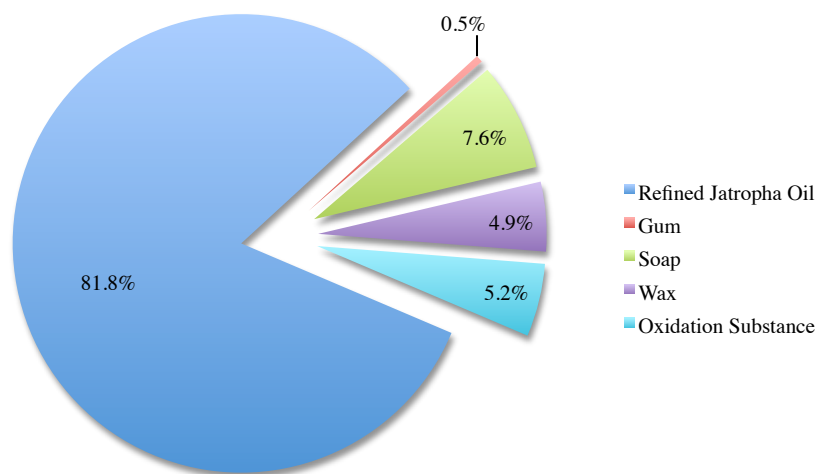
The moisture content of de-oiled cakes obtained from discharge nozzle number 4, 8, and 10 were 6.51%, 5.85%, and 6.01%, respectively. The result from ANOVA at the 95% confidence level indicated that the size of discharge aperture significantly affected the moisture content. However, the Fisher's LSD test showed that there was no significant difference in means among the pairs of treatments for each composition of proximate analysis, except that the ash content of de-oiled cake from the discharge aperture number 4 showed a significant difference from number 10.

According to the results, it can be seen that the use of discharge aperture number 8 provided the maximum yield of products (the oil and the press cake). The de-oiled cake obtained from this aperture also had low moisture content with high values of gross energy and VCM content. For that reason, the press cake received from the using of

discharge nozzle number 8 (7.0 mm) was selected to perform the pyrolysis runs at different operating temperatures.

#### *4.2.3. Oil Refining*

The Jatropha oil extracted from a screw press was then carried through a refining process, including degumming, neutralization, dewaxing, and bleaching. According to Figure 9, approximately 82% of Jatropha refined oil was obtained with only 0.5% gum, 8% soap, 5% wax, and 5% oxidation substance. The acid number indicated the amount of free fatty acid in the oil; i.e., the higher acid value, the higher free fatty acid content. The acid value of the crude Jatropha oil was 12.3 mg KOH/g, corresponding to 6.2% of free fatty acid, which was higher than the 1% limit for the transesterification reactions to occur. High free fatty acid composition would result in large amount of soap by-product in a neutralization process, which reduced the yield of biodiesel conversion (Koh and Ghazi, 2011).



**Figure 9. Percent composition of products from Jatropha oil refining process.**

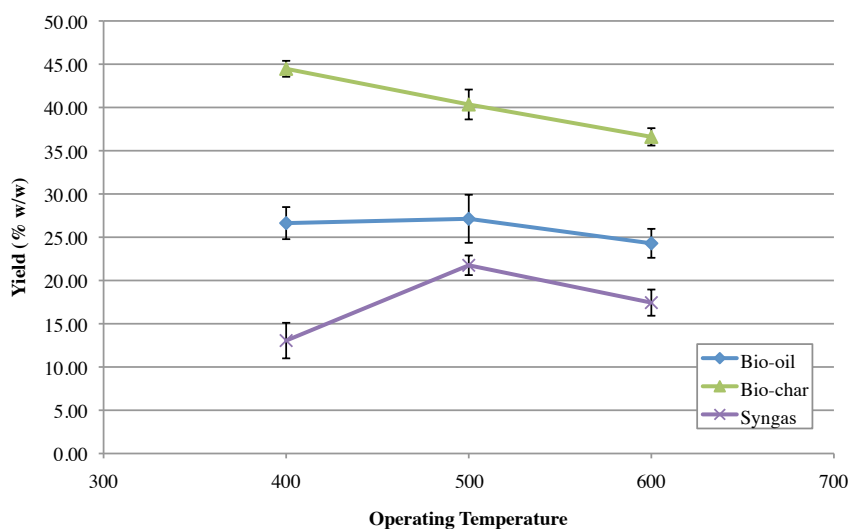
### 4.3 Pyrolysis of Jatropha By-products

#### 4.3.1. Effect of Operating Temperature on Pyrolysis Yields

Pyrolysis runs of Jatropha residues received from a screw press using the discharge aperture number 8 (7.0 mm) were conducted. To investigate the effect of temperature on pyrolysis product yields, the operating temperatures were chosen at 400, 500 and, 600 °C. The product yields at different temperatures are shown in Figure 10. Based on the graph, the general trends revealed that the amount of bio-char decreased with an increase of the temperature, while the bio-oil and syn-gas increased from temperature range of 400 – 500 °C, then decreased when the temperature increased from 500 – 600 °C. The peaks of bio-oil and syn-gas yields were detected at 500 °C. However, the statistical analysis by ANOVA proved that at the 95% confidence level, the operating temperature significantly influenced the yield of bio-char and syn-gas, but not the liquid product. Among the products at all operating temperatures, Bio-char had the

highest yield of 37 – 44%, followed by the bio-oil product (24 – 27%) and syn-gas product (12 – 22%).

Similar trends for the pyrolysis yields of different feedstock were obtained by many researchers (Aquino, 2007; Capunitan and Capareda, 2012; Kim et al., 2012; Raja et al., 2009). The increase of gas yields and reduction in bio-oil and bio-char at higher pyrolysis temperatures could be explained by the secondary reaction of volatile liquids and the deterioration of the char particles that occurred while the temperature was increasing (Raja et al., 2009). Aquino (2007) also explained about the increase of gaseous products when the pyrolysis temperature increased that was due to the secondary thermal cracking of volatiles, which decomposed the biomass into non-condensable compounds.



**Figure 10. Yields of bio-oil, bio-char, and syn-gas of Jatropha pyrolysis at different operating temperatures.**



The highest amount of bio-char could be explained as follows. During the heating process of pyrolysis, the gas produced from biomass was allowed to stay in the reactor to maintain the pressure at 100 psi, resulting in the secondary cracking reactions of pyrolytic gas. Therefore, this led to the production of bio-char like carbonaceous substances left in the reactor (Capunitan and Capareda, 2012). At a lower temperature, a high yield of char and a low yield of liquid and gas products occurred due to the incomplete pyrolysis reaction. As the temperature increased, primary thermal decomposition and a secondary reaction of biomass caused the releasing of more volatiles, leading to the reduction of the bio-char yield (Kim et al., 2012).

#### *4.3.2. Pyrolysis Products Characterization*

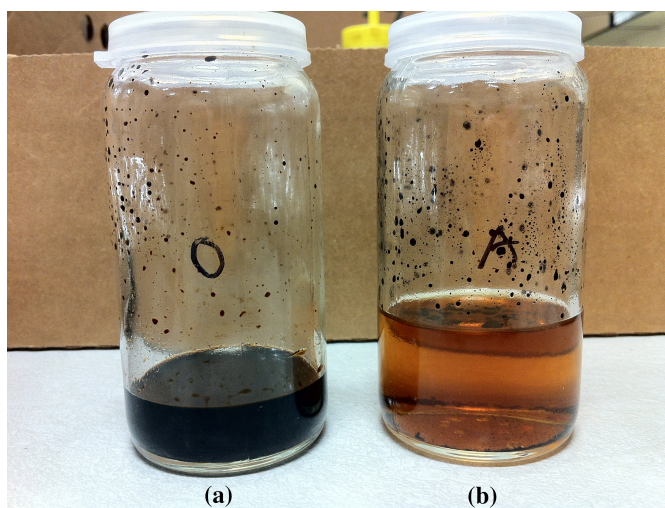
The products commonly obtained from a pyrolysis process were bio-oil, bio-char, and syn-gas. The physical and chemical properties, such as appearance, color, energy content, moisture content, and proximate analysis, were explained in the following sections.

##### **4.3.2.1. Bio-Oil**

The gases released from the biomass during the pyrolysis process were condensed, and formed the liquid product with some solid matters that were transported by the moving gases. Therefore, the liquid product (bio-oil) obtained from all operating temperatures, was combined of two phases in separated layers, namely, aqueous phase and bio-oil phase. The bio-oil was a black viscous smoky oil and had a very strong

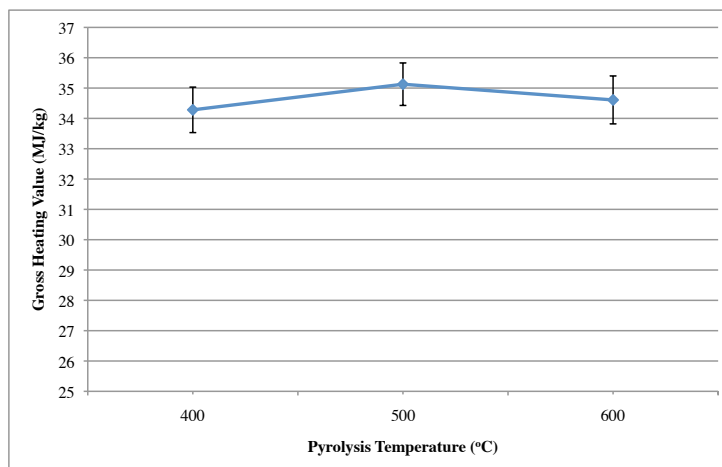
irritable smell, while the aqueous product was a slightly cloudy yellow-brown solution as illustrated in Figure 11. However, these physical properties were observed as the same for all pyrolysis liquid products derived from biomass feedstock (Aquino, 2007; Capunitan and Capareda, 2012)

It had been reported that the amount of aqueous solution in a liquid product had an effect on its energy content. The water content in bio-oil came from the tar decomposition, which contributed to the production of  $H_2$ ,  $CO$ , and some light hydrocarbons. This finally resulted in the formation of  $H_2O$ . Low heating value of the bio-oil was due to high amount of water content in it. Therefore, the separation of aqueous solution from the bio-oil would result in higher energy value.



**Figure 11. The liquid product obtained from pyrolysis of Jatropha residue (a) bio-oil and (b) aqueous solution.**

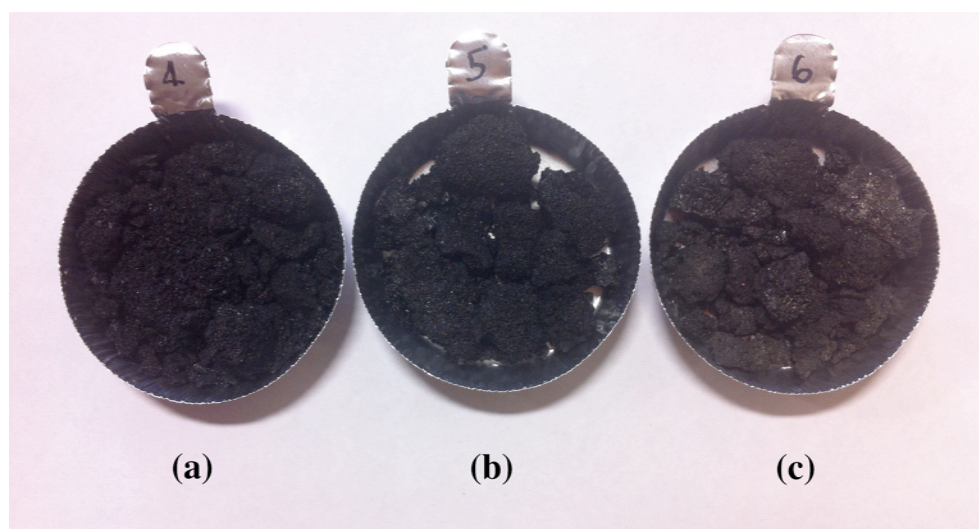
The gross heating values of bio-oil (separated from aqueous solution) obtained at pyrolysis temperatures ranging between 400 – 600 °C were around 34 – 35 MJ/kg as provided in Figure 12. The pyrolysis temperature at 500 °C presented the optimum gross calorific value of 35.1 MJ/kg. However, the result from statistical analysis by ANOVA indicated that at the 95% confidence level, the pyrolysis temperature did not have an effect on the gross heating value of the bio-oil. This gross energy of the bio-oil was not much different from the oil extracted via the screw press (39 MJ/kg), but was considerably higher than the de-oiled cake (19 – 21 MJ/kg). The gross heating values of the bio-oil obtained from this experiment were rather higher than some values reported in the literature for *Jatropha* residue bio-oil (Kim et al., 2012; Raja et al., 2009) and other biomass bio-oil such as corn stover, palm residue, olive waste, and straw (Capunitan and Capareda, 2012; Kim et al., 2012; Zanzi, 2002).



**Figure 12. Effect of pyrolysis temperature on gross calorific value of pyrolytic oil.**

#### 4.3.2.2. Bio-Char

Bio-char is the solid product that remained in the reactor after the completed pyrolysis process. Figure 13 represents the bio-char obtained from pyrolysis of Jatropha de-oiled cake, which was a black compact solid with a strong smell. The bio-char obtained from a low pyrolysis temperature was fairly darker than the one from a high temperature because the longer burning time of biomass at higher pyrolysis temperature led to more ash production in bio-char, which made the bio-char appeared more colorless.



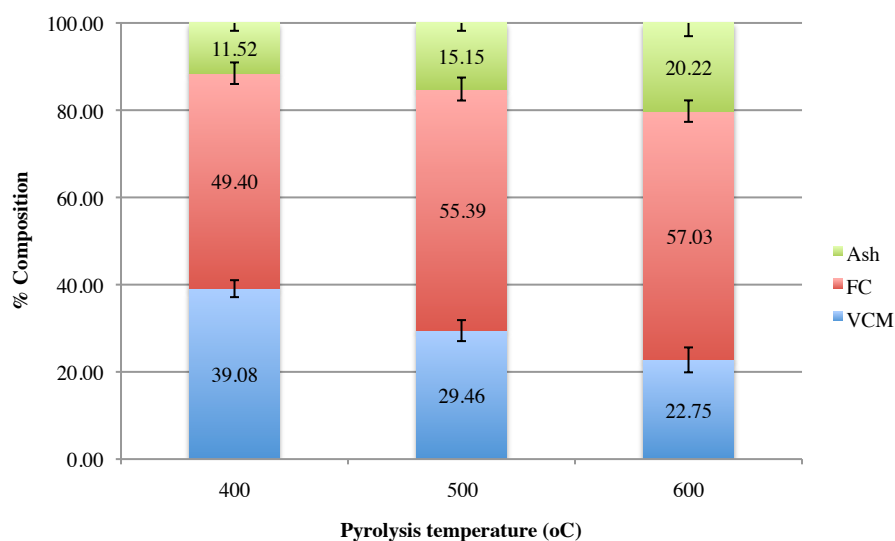
**Figure 13. Bio-char obtained from pyrolysis at different operating temperature (a) 400 °C (b) 500 °C and (c) 600 °C.**

The proximate analysis of dry bio-char at different pyrolysis temperatures was conducted in order to determine for their elementary constituents, such as VCM, FC and

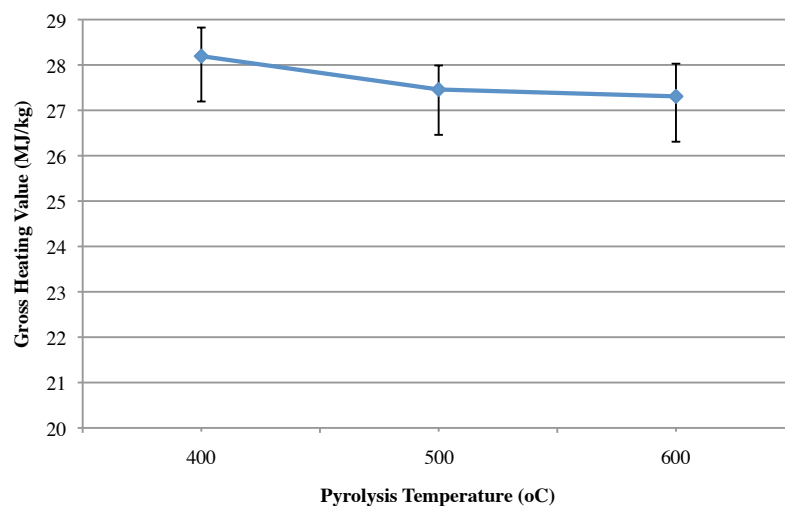
ash. Figure 14 demonstrates the proximate analysis of bio-char obtained from different pyrolysis temperatures. From the graph, as the pyrolysis temperature increased from 400 to 600 °C, the VCM decreased from 39% to 23%. The VCM content of bio-char diminished at a high pyrolysis temperature for the reason that the biomass released more volatiles at high temperatures. FC referred to the remaining solid combustible residues after volatile matter was released. Therefore, the increasing of FC from 49% at 400 °C to 57% at 600 °C was due to the reduction of VCM in bio-char. According to the result, there was a significant change in FC composition of bio-char (49% to 55%) when the pyrolysis temperature increased from 400 °C to 500 °C. On the other hand, a small change in FC composition of bio-char was observed when the pyrolysis temperature increased from 500 °C to 600 °C. This could be explained by the difficulty of FC to vaporize at pyrolysis temperature above 500 °C (Asadullah et al., 2007). Ash content also increased with the increase of pyrolysis temperature. The statistical analysis by ANOVA confirmed that at the 95% confidence level, the pyrolysis temperature had an effect on the VCM, FC, and ash content of bio-char. A trend of proximate analysis for *Jatropha* bio-char, which obtained from different pyrolysis temperatures, was also similar to other feedstock such as cotton-gin trash (Aquino, 2007), corn stover (Capunitan and Capareda, 2012), and nutshells (Demirbas, 2006).

The bio-char samples were also analyzed for their gross calorific value using bomb calorimeter. Figure 15 shows the gross heating value of bio-char at different pyrolysis temperature. Based on the graph, the heating value was decreased slightly with the increase of pyrolysis temperature, specifically, from 28.2 MJ/kg at 400 °C to 27.3

MJ/kg at 600 °C. At a high pyrolysis temperature, the increase in ash content probably lowered the energy value of the bio-char. However, the statistical analysis by ANOVA proved that at the 95% confidence level, the pyrolysis temperature did not affect the heating value of bio-char. The gross calorific value of bio-char was considerably higher than that of the de-oiled cake obtained from a screw press. This could be explained by the carbonization in pyrolysis process of organic materials, which left a solid residue abundant in carbon content, or bio-char. The carbon, which formed the bio-char, was called fixed carbon (FC). Therefore, the higher FC composition of the bio-char (49% - 57%) than the de-oiled cake (11% - 12%) resulted in higher energy content of the bio-char.



**Figure 14. Proximate analysis of dry bio-char at different pyrolysis temperatures.**



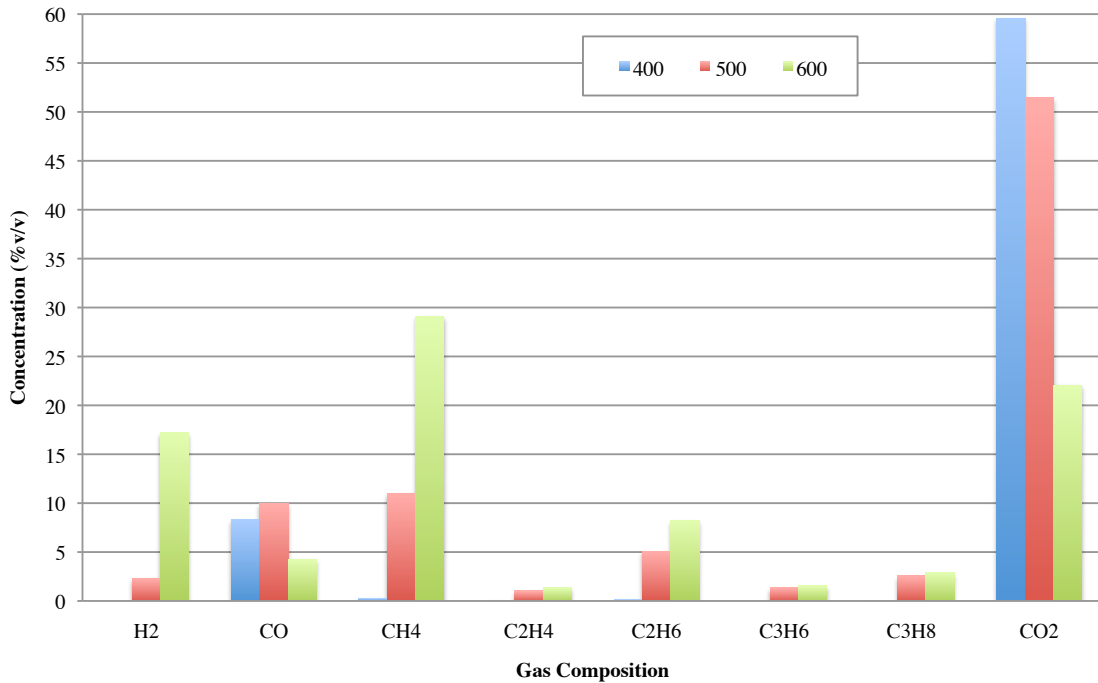
**Figure 15. Effect of pyrolysis temperature on gross calorific value of bio-char.**

#### 4.3.2.3. Syn-gas

The gaseous product collected from pyrolysis at different operating temperatures was characterized for its composition using the GC. Combustible gases such as hydrogen, carbon monoxide, and hydrocarbons were produced from the pyrolysis process. Figure 16 represents the components of syn-gas obtained at different pyrolysis temperatures.

According to the graph, carbon dioxide appeared to be the main composition of the syn-gas product. The amount of carbon dioxide produced also decreased with the increase of pyrolysis temperature because carbon dioxide was rather unleashed at low temperature. Hydrogen and hydrocarbon gases, such as methane ( $\text{CH}_4$ ), ethylene ( $\text{C}_2\text{H}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), propene ( $\text{C}_3\text{H}_6$ ), and propane ( $\text{C}_3\text{H}_8$ ), were considerably released at high temperature due to the secondary thermal cracking of volatiles (Capunitan and Capareda,

2012). It was also observed that the yield of lower-molecular weight hydrocarbons was notably increased with temperature while there was no significant change in the yield of higher-molecular weight as the temperature varied.

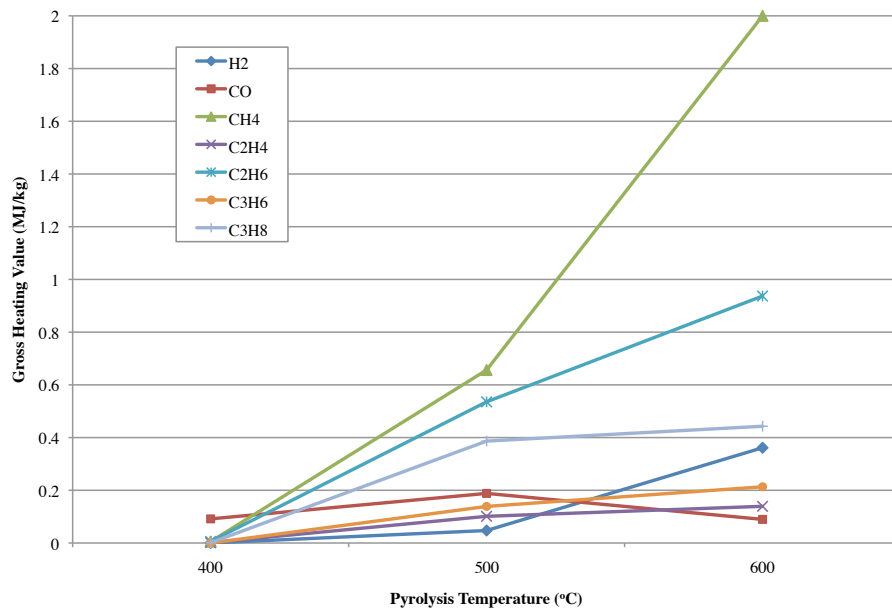


**Figure 16. Syn-gas compositions produced at different pyrolysis temperatures.**

The gross heating values of each syn-gas composition were computed based on the calorific values of H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub>, which were obtained from the Handbook of Natural Gas Engineering (Katz, 1959). Figure 17 demonstrates the relationship between the pyrolysis temperature and gross heating value of syn-gas



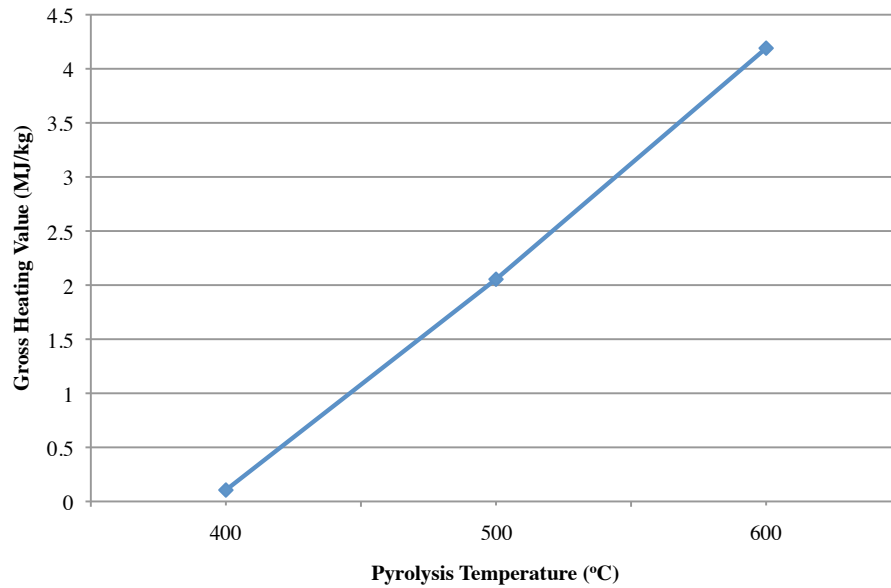
compositions. General trend indicated that the gross calorific value of each gas component increased when the pyrolysis temperature increased. The possible reason for this is that the H<sub>2</sub> and the hydrocarbon gases, which had high gross calorific values, were likely to discharge at high pyrolysis temperatures.



**Figure 17. Gross heating value of each syn-gas component at different pyrolysis temperatures.**

The total gross calorific value of syn-gas produced at different pyrolysis temperature is shown in Figure 18. The total energy value of syn-gas significantly increased from 0.1 MJ/kg at 400 °C to 4.2 MJ/kg at 600 °C. The small energy content at lower pyrolysis temperatures came from the deficient pyrolysis reaction, which resulted

in lower amount of combustible gases released. However, at the pyrolysis temperature around 500 – 600 °C, almost 50% of total energy of syn-gas came from methane (CH<sub>4</sub>), which yielded highest energy content for all pyrolysis temperatures.



**Figure 18. Total gross heating value of gaseous product at different pyrolysis temperatures.**

## **4.4 Mass and Energy Balance**

### *4.4.1. Mass and Energy Distribution for Pyrolysis*

Mass and energy balance for pyrolysis at different operating temperatures were examined based on the weights of initial biomass and final product, and their heating values. The mass and energy distribution for pyrolysis at different operating

temperatures are provided in Figure 19 and Figure 20. On the average, mass conversion and energy recovery of pyrolysis process were around 85% for mass conversion and 75% for energy recovery.

Bio-char presented the highest mass and energy conversions for all pyrolysis temperatures. The pyrolysis temperature of 500 °C appeared to yield the smallest amount of losses for both mass and energy conversions. The energy recovery for syn-gas significantly increased with the temperature due to more combustible gases generated at higher temperatures. On the other hand, the energy conversion of bio-char decreased when the pyrolysis temperature increased because the quantity of bio-char decreased at higher temperatures. Based on the overall mass and energy distributions, the pyrolysis temperature of 500 °C yielded the highest effectiveness for *Jatropha* residues utilization due to their highest values of mass and energy conversion, namely, approximately 90% for mass conversion and 80% for energy recovery.

#### *4.4.2. Mass and Energy Distribution for All Jatropha Extraction Processes Including the Screw Press Machine and Pyrolysis*

Mass and energy balance for the whole process of Jatropha oil extraction, including oil extraction via a screw press and de-oiled cake utilization by pyrolysis, are demonstrated in Figure 21 and Figure 22. The highest contents of mass and energy conversions came from the extracted oil obtained from a screw press (43.8% for mass conversion and 66% for energy recovery), followed by the bio-char product obtained from pyrolysis process (approximately 22% for both mass conversion and energy conversion). The bio-oil and syn-gas presented small energy portions in comparison to bio-char and oil extracted from a screw press, since there was a little amount of bio-oil and syn-gas produced during the pyrolysis process. However, by combining two extraction methods (mechanical extraction and pyrolysis), the total mass and energy losses were significantly lower than the losses from the pyrolysis process only.

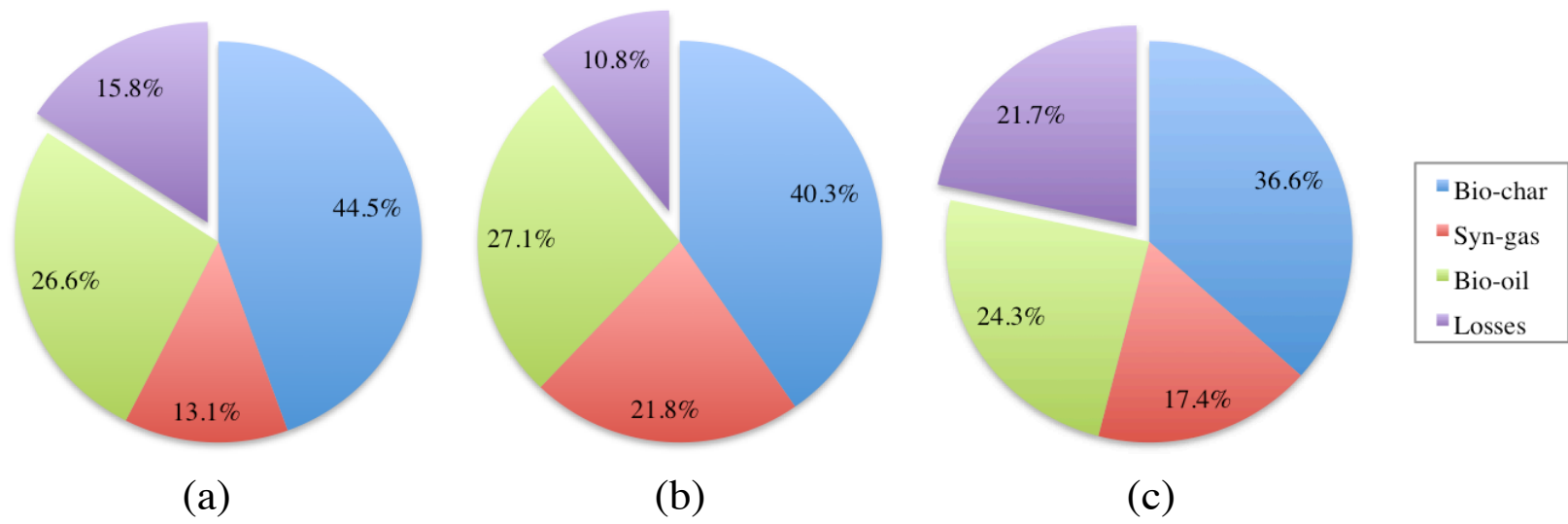
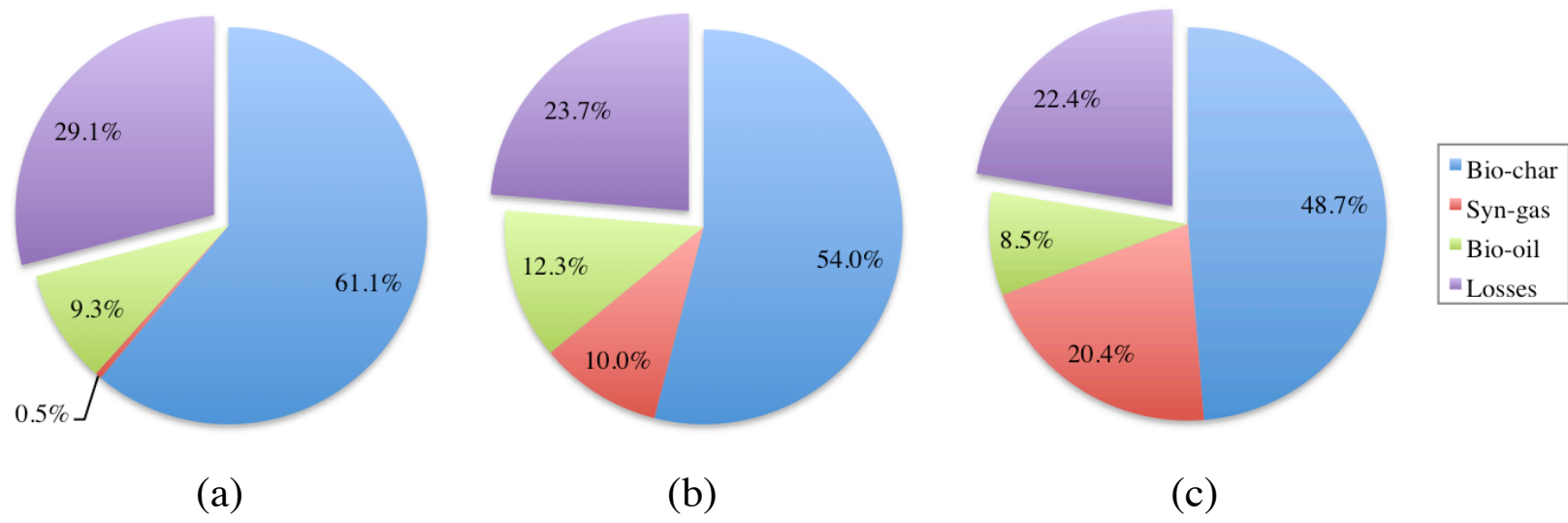
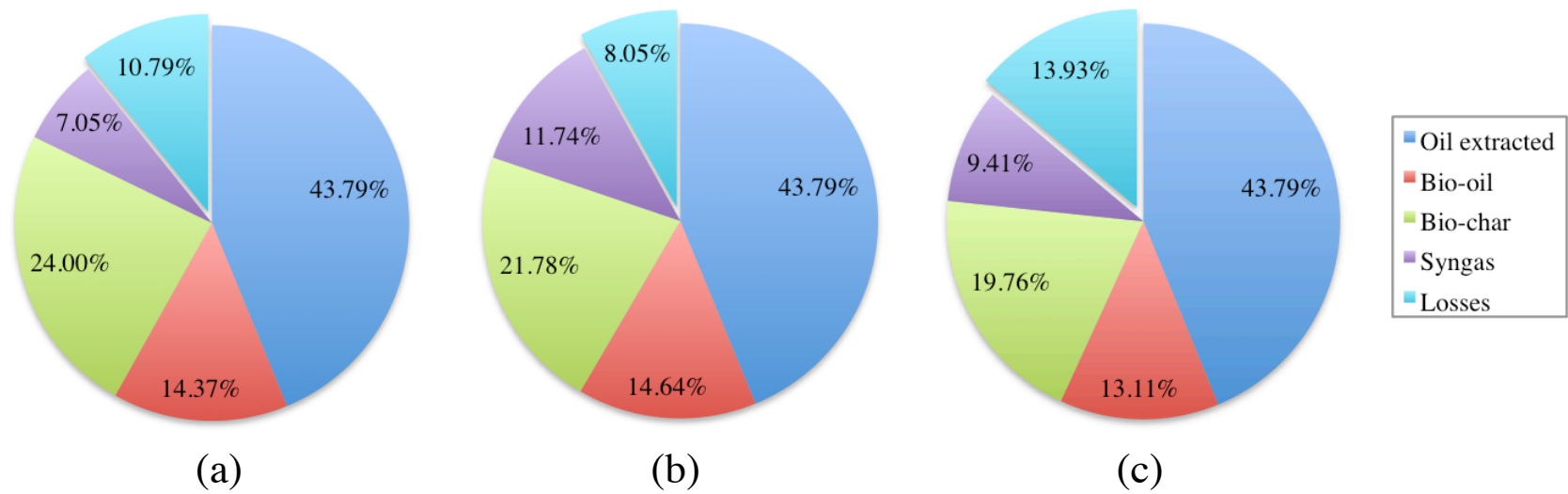


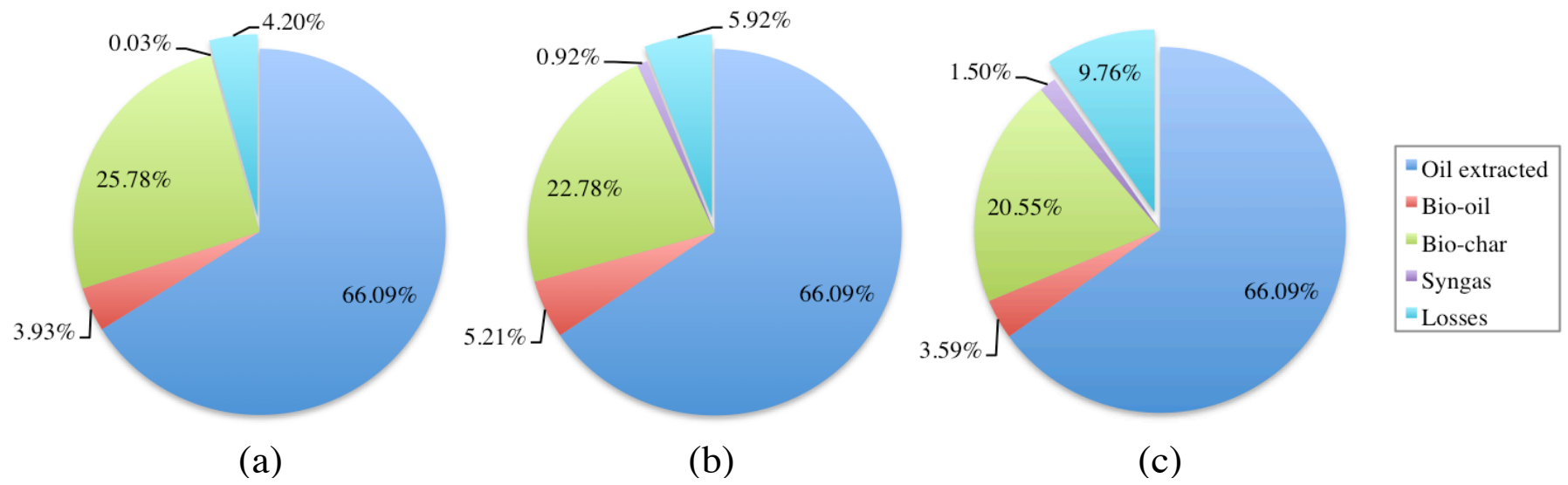
Figure 19. Mass balance for pyrolytic products at different operating temperatures (a) 400 °C (b) 500 °C and (c) 600 °C.



**Figure 20. Energy distribution for pyrolytic products at different operating temperatures (a) 400 °C (b) 500 °C and (c) 600 °C**



**Figure 21. Mass balance for overall process of Jatropha extraction by a screw press and pyrolysis at (a) 400 °C (b) 500 °C and (c) 600 °C.**



**Figure 22. Energy balance for overall process of Jatropha extraction by a screw press and pyrolysis at (a) 400 °C (b) 500 °C and (c) 600 °C.**

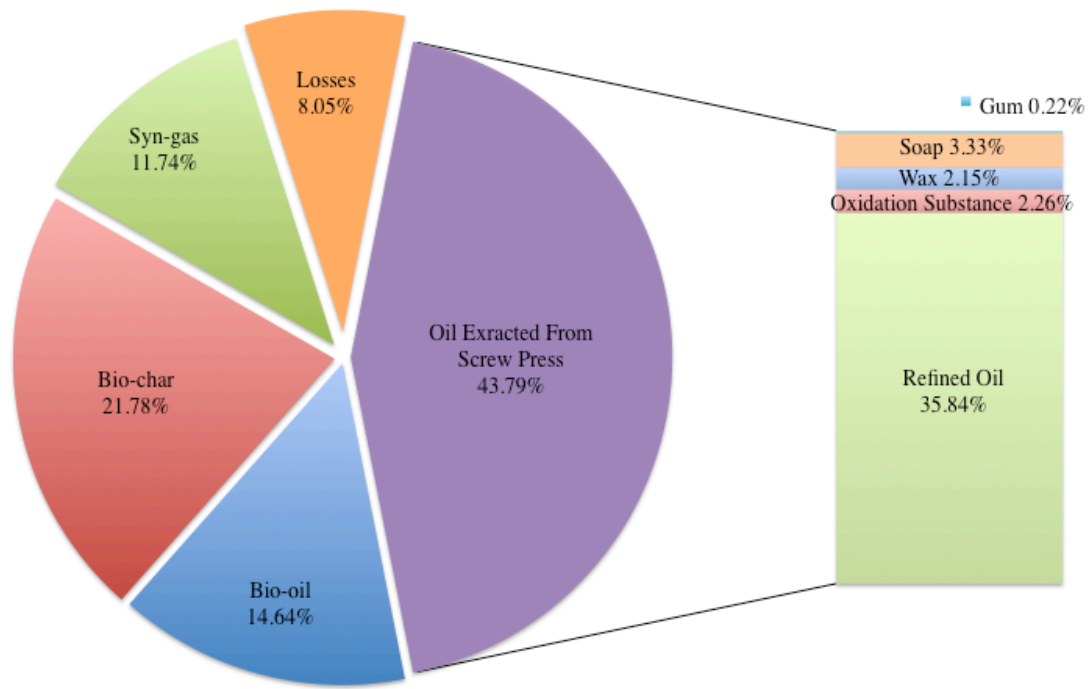


#### 4.5 Potential of Jatropha Seeds As an Alternative Energy Source

Jatropha plant has been reported as a multipurpose oil seed crop since it can be used as a hedge, fertilizers, animal feed, medicines, and an energy source. Many researchers are interested in using Jatropha as an alternative energy (Achten et al., 2008; Beerens, 2007; Diwani et al., 2009; Foild et al., 1996; Koh and Ghazi, 2011; Kumar and Sharma, 2008; Openshaw, 2000). According to this study, the Jatropha seeds were investigated for two steps of extraction processes, including, the oil extraction of raw seeds via a screw press and utilization of residues by pyrolysis. The experiments were performed at different operating conditions by modifying the discharge aperture size of a screw press, and varying the pyrolysis operating temperatures, in order to find the condition for achieving maximum product yields. The summary of percent product yields and their gross heating values obtained from the optimum condition is provided in Figure 23 and Table 7.

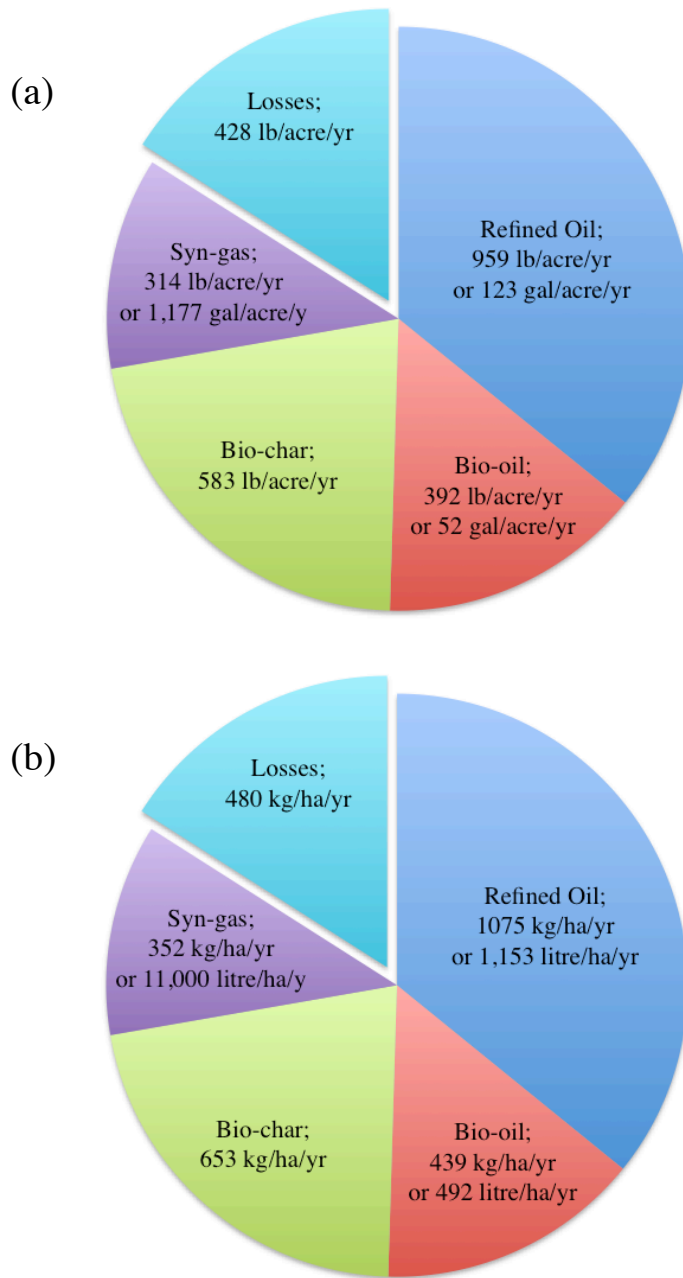
**Table 7. Summary of gross heating values of all products from Jatropha extraction at optimum condition.**

Products	Gross Heating Value (MJ/kg)
Refined Oil	39.6
Bio-oil	35.1
Bio-char	27.5
Syn-gas	2.1

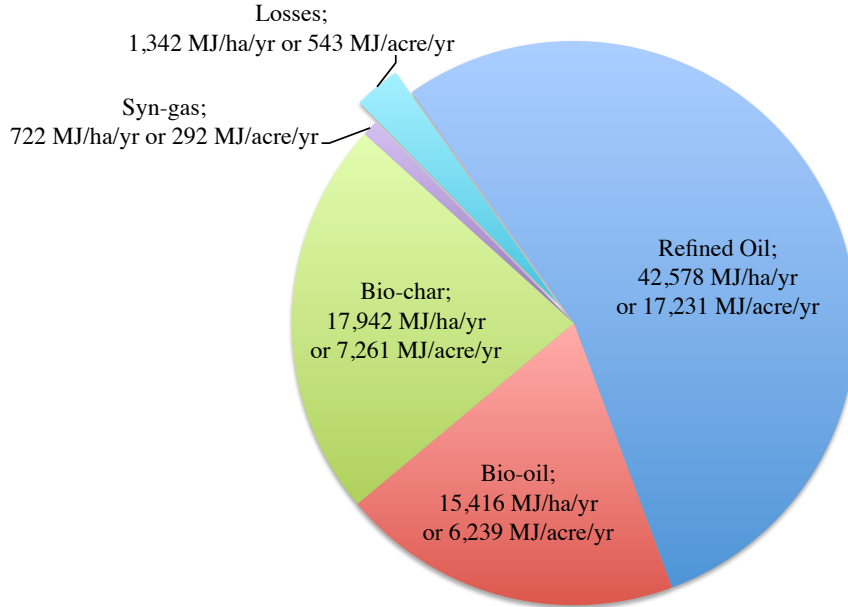


**Figure 23. Summary of percent mass conversion of Jatropha extraction at optimum condition.**

Based on the assumption that the seed production of Jatropha was three tonnes per hectare per year (Carels, 2009; Heller, 1996; Henning, 2000), the mass conversion of Jatropha seeds into other energy products and energy contents of Jatropha products in the unit of per hectare per year were calculated as shown in Figure 24 and Figure 25. According to the percent mass conversions and gross heating values obtained from optimum condition of this study, the 3,000 kg/ha/yr of seed production would correspond to the 78,000 MJ/ha/yr of input energy of biomass feedstock



**Figure 24. Estimation of annual Jatropha seeds conversion into other energy products (a) English unit system and (b) metric unit system.**



**Figure 25. Estimation of annual energy contents received from Jatropha seeds extraction.**

After the completed two steps of extraction processes (a screw press and pyrolysis), Jatropha seeds were transformed into refined oil, bio-oil, bio-char, and syn-gas. The refined oil gave the highest content in both mass and energy conversion, followed by bio-char, bio-oil, and syn-gas, respectively. If the conversion efficiency of refined oil into biodiesel were assumed at 100%, the biodiesel production of 1,153 litre/ha/yr (123 gal/acre/yr) with the energy content of 42,578 MJ/ha/yr (17,231 MJ/acre/yr) would be achieved. The bio-char also presented the large portions in both mass and energy balance i.e., 653 kg/ha/yr (583 lb/acre/yr) for mass conversion and 17,942 MJ/ha/yr (7,261 MJ/acre/yr) for energy content. Furthermore, only 480 kg/ha/yr (428 lb/acre/year) of mass losses and 1,342 MJ/ha/yr (543 MJ/acre/yr) of energy losses

were observed. Hence, this was very small portion compared to the initial mass and energy input. Therefore, the optimum condition of Jatropha extraction processes obtained from this study proved to be an effective way for Jatropha seeds utilization as an alternative energy source.

## CHAPTER V

### SUMMARY AND CONCLUSION

In this study, the oil extraction of *Jatropha* seeds via a screw press and its residue utilization by a pyrolysis method were conducted. The experiments were conducted under different operating conditions in order to achieve the highest efficiency of mass conversion and energy recovery of the biomass feedstock. It was found that the size of the discharge aperture had an effect on the amounts of the oil extracted and the de-oiled cake. Discharge aperture number 8 (7.0 mm) yielded the highest percent mass conversion of 44% for the oil extracted and 54% for the residues. The refining process yielded the conversion efficiency of 82% of refined oil. *Jatropha* seeds had the gross calorific value of 24.0 MJ/kg. However, the heating value of *Jatropha* oil obtained from a screw press was around 40 MJ/kg, which was much higher than the energy content of the raw seeds.

From observation, the gross heating value of the residues from a screw press was not much lower than that of the raw seeds. Therefore, a pyrolysis method was carried out for the utilization of the residues. Pyrolysis of the *Jatropha* residues was performed at different operating temperatures, which resulted in different yields of pyrolytic products; i.e., bio-oil, bio-char, and syn-gas. The general trend found was that the amount of bio-char decreased with an increase of temperature, while the bio-oil and syn-gas yields increased when the operating temperature was increased from 400 – 500 °C, then

decreased at the temperatures above 500 °C. The optimum condition that yielded the highest mass conversion efficiency (40% bio-char, 27% bio-oil and 22% syngas) was observed at the pyrolysis temperature of 500 °C. In addition, it was observed that the pyrolysis temperatures did not affect the gross calorific values of bio-oil and bio-char. The highest energy contents obtained from the pyrolytic products were 35.1 MJ/kg for bio-oil, 27.5 MJ/kg for bio-char, and 4.2 MJ/kg for syn-gas. However, the maximum energy recovery of 54% bio-char, 12.3% bio-oil, and 10% syn-gas was achieved exactly at the pyrolysis temperature of 500 °C.

In regards to the entire *Jatropha* extraction process, including a mechanical press and a pyrolysis method, the total mass and energy losses were lower than the losses in the pyrolysis process only. The highest contents of both mass and energy conversion came from the oil extracted by a screw press, followed by bio-char, bio-oil, and syn-gas obtained from the pyrolysis process. The optimum condition was achieved when using the discharge aperture number 8 (7.0 mm) for a screw press and conducting the pyrolysis of the de-oiled cake at 500°C. The best condition yielded the mass conversion efficiency of 35.8% refined oil, 21.8% bio-char, 14.6% bio-oil, and 11.7% syn-gas. Therefore, the utilization of *Jatropha* residues using a pyrolysis can enhance the effectiveness of *Jatropha* oil extraction with only 16% mass losses obtained. At the optimal condition, the gross heating values of the products were obtained as 39.6 MJ/kg for the refined oil, 35.1 MJ/kg for the bio-oil, 27.5 MJ/kg for the bio-char, and 2.1 MJ/kg for the syn-gas.

It was assumed that there was 3,000 kg/ha/yr of *Jatropha* seed production, according to the works of Carels (2009), Henning (2000), and Heller (1996). Based on

this study, the completed two steps of extraction processes (the mechanical press of Jatropha seeds and the pyrolysis of its residue) would transform the Jatropha seeds into refined oil, bio-oil, bio-char, and syn-gas. If the assumption that 100% conversion efficiency of refined oil into biodiesel was made, the optimum extracting condition obtained from this study would yield the biodiesel production of 1,153 litre/ha/yr, corresponding to the energy content of 42,578 MJ/ha/yr. The bio-char also occupied a large part in both mass and energy distribution, i.e., 653 kg/ha/yr for a mass conversion and 17,942 MJ/ha/yr for an energy recovery. In comparison to the initial mass and energy input, a very small amount of mass and energy losses (480 kg/ha/yr for mass losses and 1,342 MJ/ha/yr for energy losses) was observed after the completed extracting processes. Finally, this study revealed that the mass and energy conversion efficiency obtained from the optimum condition had proved the potential of Jatropha seeds as an alternative energy source.

Further possible research may employ the elemental composition or ultimate analysis of the bio-oil and bio-char samples for the detail in a carbon and hydrogen content. Bio-oil compound may also be examined using a gas chromatography-mass spectrometry. These characterization results are useful for a product upgrading in the future research.



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APPENDIX A

**Table A.1. Density and gross calorific value of Hydrocarbon gases. (Katz et al., 1959)**

Compound	Formula	Gas Density at 60°F, 14.696 psia		Gross Calorific Value at 60°F	
		lb/ft <sup>3</sup>	kg/m <sup>3</sup>	Btu/ft <sup>3</sup>	MJ/kg
Hydrogen	H <sub>2</sub>	0.0053	0.0849	324	142.35
Oxygen	O <sub>2</sub>	0.0844	1.3520	-	-
Nitrogen	N <sub>2</sub>	0.0739	1.1837	-	-
Carbon monoxide	CO	0.0738	1.1822	321	10.13
Methane	CH <sub>4</sub>	0.0424	0.6785	1012	55.64
Carbon dioxide	CO <sub>2</sub>	0.1167	1.8694	-	-
Ethyne (acetylene)	C <sub>2</sub> H <sub>2</sub>	0.0686	1.0989	1472	49.96
Ethene (ethylene)	C <sub>2</sub> H <sub>4</sub>	0.0739	1.1839	1600	50.41
Ethane	C <sub>2</sub> H <sub>6</sub>	0.0799	1.2794	1783	51.98
Propene	C <sub>3</sub> H <sub>6</sub>	0.1109	1.7759	2333	49.00
Propane	C <sub>3</sub> H <sub>8</sub>	0.1180	1.8910	2557	50.44

## APPENDIX B

### Statistical Analysis by SPSS

#### 1. Jatropha seeds extraction via a screw press

##### 1.1. Effect of discharge aperture size on extracting time and product yields

**ANOVA**

		Sum of Squares	df	Mean Square	F	Sig.
oil	Between Groups	54.679	2	27.340	14.404	.005
	Within Groups	11.389	6	1.898		
	Total	66.068	8			
de_oiled_cake	Between Groups	17.932	2	8.966	3.926	.081
	Within Groups	13.702	6	2.284		
	Total	31.634	8			
time	Between Groups	555.736	2	277.868	86.866	.000
	Within Groups	19.193	6	3.199		
	Total	574.928	8			

**Multiple Comparisons**

LSD

Dependent Variable	(I) diameter	(J) diameter	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
oil	4.00	8.00	-5.96098*	1.12490	.002	-8.7135	-3.2085
		10.00	-3.81098*	1.12490	.015	-6.5635	-1.0585
	8.00	4.00	5.96098*	1.12490	.002	3.2085	8.7135
		10.00	2.15000	1.12490	.105	-.6025	4.9025
	10.00	4.00	3.81098*	1.12490	.015	1.0585	6.5635
		8.00	-2.15000	1.12490	.105	-4.9025	.6025
de_oiled_cake	4.00	8.00	-3.23867*	1.23388	.039	-6.2579	-.2195
		10.00	-2.66773	1.23388	.074	-5.6869	.3515
	8.00	4.00	3.23867*	1.23388	.039	.2195	6.2579
		10.00	.57093	1.23388	.660	-2.4483	3.5901
	10.00	4.00	2.66773	1.23388	.074	-.3515	5.6869
		8.00	-.57093	1.23388	.660	-3.5901	2.4483
time	4.00	8.00	15.50000*	1.46032	.000	11.9267	19.0733
		10.00	17.63333*	1.46032	.000	14.0601	21.2066
	8.00	4.00	-15.50000*	1.46032	.000	-19.0733	-11.9267
		10.00	2.13333	1.46032	.194	-1.4399	5.7066
	10.00	4.00	-17.63333	1.46032	.000	-21.2066	-14.0601
		8.00	-2.13333	1.46032	.194	-5.7066	1.4399

\*. The mean difference is significant at the 0.05 level.

1.2. Effect of discharge aperture size on gross heating value of the products

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
HV_oil_extracted	Between Groups	.040	2	.020	1.896	.230
	Within Groups	.063	6	.011		
	Total	.104	8			
HV_deoil_cake	Between Groups	7.023	2	3.512	6.378	.033
	Within Groups	3.304	6	.551		
	Total	10.327	8			

Multiple Comparisons

LSD

Dependent Variable	(I) aperture number	(J) aperture number	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
HV_oil_extracted	4.00	8.00	-.05583	.08399	.531	-.2614	.1497
		10.00	.10520	.08399	.257	-.1003	.3107
	8.00	4.00	.05583	.08399	.531	-.1497	.2614
		10.00	.16103	.08399	.104	-.0445	.3666
	10.00	4.00	-.10520	.08399	.257	-.3107	.1003
		8.00	-.16103	.08399	.104	-.3666	.0445
HV_deoil_cake	4.00	8.00	-1.18257	.60586	.099	-2.6651	.2999
		10.00	-2.16063*	.60586	.012	-3.6431	-.6781
	8.00	4.00	1.18257	.60586	.099	-.2999	2.6651
		10.00	-.97807	.60586	.158	-2.4606	.5044
	10.00	4.00	2.16063*	.60586	.012	.6781	3.6431
		8.00	.97807	.60586	.158	-.5044	2.4606

\*. The mean difference is significant at the 0.05 level.



1.3. Effect of discharge aperture size on moisture, VCM, FC, and ash content of the de-oiled cake

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
MC	Between Groups	.719	2	.359	90.372	.000
	Within Groups	.024	6	.004		
	Total	.743	8			
VCM	Between Groups	6.516	2	3.258	1.010	.419
	Within Groups	19.353	6	3.226		
	Total	25.869	8			
FC	Between Groups	1.340	2	.670	.181	.839
	Within Groups	22.220	6	3.703		
	Total	23.560	8			
Ash	Between Groups	1.885	2	.942	3.431	.102
	Within Groups	1.648	6	.275		
	Total	3.533	8			

Multiple Comparisons

LSD

Dependent Variable	(i) aperture	(j) aperture	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
MC	4.00	8.00	.66333*	.05150	.000	.5373	.7893
		10.00	.50333*	.05150	.000	.3773	.6293
	8.00	4.00	-.66333*	.05150	.000	-.7893	-.5373
		10.00	-.16000*	.05150	.021	-.2860	-.0340
	10.00	4.00	-.50333*	.05150	.000	-.6293	-.3773
		8.00	.16000*	.05150	.021	.0340	.2860
VCM	4.00	8.00	-.80000	1.46641	.605	-4.3882	2.7882
		10.00	-2.06667	1.46641	.208	-5.6549	1.5215
	8.00	4.00	.80000	1.46641	.605	-2.7882	4.3882
		10.00	-1.26667	1.46641	.421	-4.8549	2.3215
	10.00	4.00	2.06667	1.46641	.208	-1.5215	5.6549
		8.00	1.26667	1.46641	.421	-2.3215	4.8549
FC	4.00	8.00	.20000	1.57127	.903	-3.6448	4.0448
		10.00	.90000	1.57127	.588	-2.9448	4.7448
	8.00	4.00	-.20000	1.57127	.903	-4.0448	3.6448
		10.00	.70000	1.57127	.672	-3.1448	4.5448
	10.00	4.00	-.90000	1.57127	.588	-4.7448	2.9448
		8.00	-.70000	1.57127	.672	-4.5448	3.1448
Ash	4.00	8.00	.60000	.42791	.210	-.4471	1.6471
		10.00	1.12000*	.42791	.040	.0729	2.1671
	8.00	4.00	-.60000	.42791	.210	-1.6471	.4471
		10.00	.52000	.42791	.270	-.5271	1.5671
	10.00	4.00	-1.12000*	.42791	.040	-2.1671	-.0729
		8.00	-.52000	.42791	.270	-1.5671	.5271

\*. The mean difference is significant at the 0.05 level.

## 2. Pyrolysis of the de-oiled cake

### 2.1. Effect of operating temperature on pyrolysis product yields

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
bio_oil	Between Groups	13.746	2	6.873	1.477	.301
	Within Groups	27.924	6	4.654		
	Total	41.670	8			
bio_char	Between Groups	92.860	2	46.430	28.748	.001
	Within Groups	9.691	6	1.615		
	Total	102.551	8			
syn_gas	Between Groups	138.903	2	69.452	16.027	.004
	Within Groups	26.001	6	4.334		
	Total	164.904	8			

Multiple Comparisons

LSD

Dependent Variable	(i) pyrolysis temp	(j) pyrolysis temp	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
bio_oil	400.00	500.00	-.49833	1.76144	.787	-4.8084	3.8118
		600.00	2.33667	1.76144	.233	-1.9734	6.6468
	500.00	400.00	.49833	1.76144	.787	-3.8118	4.8084
		600.00	2.83500	1.76144	.159	-1.4751	7.1451
	600.00	400.00	-2.33667	1.76144	.233	-6.6468	1.9734
		500.00	-2.83500	1.76144	.159	-7.1451	1.4751
bio_char	400.00	500.00	4.12333*	1.03765	.007	1.5843	6.6624
		600.00	7.86500*	1.03765	.000	5.3260	10.4040
	500.00	400.00	-4.12333*	1.03765	.007	-6.6624	-1.5843
		600.00	3.74167*	1.03765	.011	1.2026	6.2807
	600.00	400.00	-7.86500*	1.03765	.000	-10.4040	-5.3260
		500.00	-3.74167*	1.03765	.011	-6.2807	-1.2026
syn_gas	400.00	500.00	-9.62291*	1.69971	.001	-13.7819	-5.4639
		600.00	-4.84571*	1.69971	.029	-9.0047	-.6867
	500.00	400.00	9.62291*	1.69971	.001	5.4639	13.7819
		600.00	4.77720*	1.69971	.031	.6182	8.9362
	600.00	400.00	4.84571*	1.69971	.029	.6867	9.0047
		500.00	-4.77720*	1.69971	.031	-8.9362	-.6182

\*. The mean difference is significant at the 0.05 level.

2.2. *Effect of operating temperature on gross heating value of pyrolysis products*

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
HV_biooil	Between Groups	3.274	2	1.637	.586	.564
	Within Groups	67.056	24	2.794		
	Total	70.330	26			
HV_biochar	Between Groups	4.048	2	2.024	.969	.394
	Within Groups	50.141	24	2.089		
	Total	54.189	26			

2.3. *Effect of operating temperature on VCM, FC, and ash content of the bio-char*

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
VCM	Between Groups	1008.435	2	504.217	46.548	.000
	Within Groups	259.971	24	10.832		
	Total	1268.406	26			
FC	Between Groups	243.823	2	121.912	14.720	.000
	Within Groups	198.764	24	8.282		
	Total	442.587	26			
Ash	Between Groups	292.011	2	146.005	24.259	.000
	Within Groups	144.444	24	6.018		
	Total	436.455	26			

Multiple Comparisons

LSD

Dependent Variable	(I) pyrolysis temp	(J) pyrolysis temp	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
VCM	400.00	500.00	9.61817*	1.55149	.000	6.4160	12.8203
		600.00	14.74340*	1.55149	.000	11.5413	17.9455
	500.00	400.00	-9.61817*	1.55149	.000	-12.8203	-6.4160
		600.00	5.12523*	1.55149	.003	1.9231	8.3274
	600.00	400.00	-14.74340*	1.55149	.000	-17.9455	-11.5413
		500.00	-5.12523*	1.55149	.003	-8.3274	-1.9231
FC	400.00	500.00	-5.98908*	1.35662	.000	-8.7890	-3.1892
		600.00	-6.70068*	1.35662	.000	-9.5006	-3.9008
	500.00	400.00	5.98908*	1.35662	.000	3.1892	8.7890
		600.00	-.71160	1.35662	.605	-3.5115	2.0883
	600.00	400.00	6.70068*	1.35662	.000	3.9008	9.5006
		500.00	.71160	1.35662	.605	-2.0883	3.5115
Ash	400.00	500.00	-3.62910*	1.15648	.004	-6.0160	-1.2422
		600.00	-8.04277*	1.15648	.000	-10.4296	-5.6559
	500.00	400.00	3.62910*	1.15648	.004	1.2422	6.0160
		600.00	-4.41367*	1.15648	.001	-6.8005	-2.0268
	600.00	400.00	8.04277*	1.15648	.000	5.6559	10.4296
		500.00	4.41367*	1.15648	.001	2.0268	6.8005

\*. The mean difference is significant at the 0.05 level.