CHAPTER II
LITERATURE REVIEWS

2.1 Chemical and physical compositions in *Jatropha curcas* oil

Jatropha curcas Linn. (physic nut or purging nut) is a drought-resistant shrub or tree belonging to the Family *Euphorbiaceae*, which is cultivated in Central and South America, south-east Asia, India and Africa (Schmook & Seralta-Peraza, 1997). The *Jatropha curcas* (*J. curcas)* plant, which can easily be propagated by cuttings, is widely planted as a hedge to protect fields, as it is not browsed by cattle or other animals. Like many other *Jatropha* species, *J. curcas* is a succulent that sheds its leaves during the dry season. It is well adapted to arid and semi-arid conditions and often used for prevention of soil erosion (Heller, 1996). The seeds of *J. curcas* are a good source of oil, which can be used as a diesel substitute. They are also used in medicines, and soap and cosmetics manufacture in various tropical countries. Although the seed meal, after extraction of oil, is rich in protein, it is toxic to rats, mice and ruminants and therefore cannot be used as an animal feed. Several cases of *J. curcas* nut poisoning in humans after accidental consumption of the seeds have been reported with symptoms of giddiness, vomiting and diarrhea and in the extreme conditions even death has been recorded (Becker & Makkar, 1998). The meal has high trypsin inhibitor and lectin activities, which could be inactivated by heat treatment. In addition, high concentration of the antimetabolic, metal-chelating and heat-stable factor, phytic acid, has been reported in *J. curcas* meal (Makkar, Aderibigbe, & Becker, 1998). Apart from these, phorbolesters that are present at high levels in the kernels have been identified as the main toxic agent responsible for toxicity (Adolf, Opferkuch, & Hecker, 1984; Makkar, Becker, Sporer, & Wink, 1997). After removing the toxic and heat-stable factors through solvent extraction, using 92% methanol, the extracted meal was found to be non-toxic to rats (Makkar & Becker, 1997). The defatted meal has been found to contain a high amount of protein in ranged between 50% and 62%. Except for lysine, all other essential amino acids in *J. curcas* meal protein have been reported to be in higher concentrations than those of

the FAO reference pattern suggested for pre-school children (Makkar, Becker, & Schmook, 1998). In addition to the more common toxic varieties, a non-toxic variety of *J. curcas* seeds, that contained negligible amounts of phorbol esters, but similar levels of trypsin inhibitors, lectin activity and phytic acid compared to the toxic variety, has been reported from the Papantla region of Veracruz State in Mexico (Makkar & Becker, 1999). The non-toxic seed kernels are consumed by local people after roasting. The hydrothermally processed defatted meal of the non-toxic variety did not show any toxicity to rats (Makkar & Becker, 1999). However, the growth rates of fish fed diets containing heated *Jatropha* meal were found to be lower than the unheated *Jatropha* meal group (Makkar & Becker, 1999). The decrease of growth rate was also related to increase in the time of heat treatment. Though various processing techniques have been attempted, no treatment has been successful in completely eliminating the antimetabolic factors and toxic principles of defatted *Jatropha* kernel meal of non-toxic and toxic varieties.

Figure 2.1 Characteristics of *Jatropha curcas* plant

In 2000, Pathama and coworkers studied fatty acid composition and properties of *Jatropha* seed oil and its methyl ester. *Jatropha* seeds (as shown in Figure 2.2) were analyzed for their proximate composition. The decupled seeds contained lipid as a major component (46.3%). The efficiency of oil extraction examined and the maximum yield of oil (94.6%) was obtained by extracting with hexane for 3 hr at room temperature and increasing extraction time did not improve extraction efficiency. The oil fraction predominantly contained 78.4% unsaturated fatty acids mainly oleic acid (42.4%) and linoleic acid (35.2%) and 21.7%. Saturated fatty acids mainly consisted of palmitic acid (14.7%) and stearic acid (6.9%). The chemical properties of *Jatropha* oil including acid value, peroxide value, iodine value and saponification value were also evaluated. *Jatropha* seed oil was subjected to transesterification process in which the oil was reacted with methanol and sodium hydroxide was used as a catalyst to produce methyl esters. The yield of methyl esters was 80.45%. The preliminary results presented serve as a basic knowledge regarding oil contents, composition of fatty acids as well as physico-chemical characteristics of methyl esters derived from *Jatropha curcas* oil are shown in Table 2.1-2.3.

Figure 2.2 Characteristics of *Jatropha curcas* seeds

Table 2.1 Physical properties of *Jatropha curcas* oil

Properties	Value	Units
Viscosity at 30 °C	46.6	cSt
Density at 15 °C	0.903	g/cm^3
Sulfate ash	0.0078	% wt
Total glycerol	-	% wt

(Gubitz et al., 1999)

Table 2.2 Chemical characteristics of *Jatropha curcas* oil

Properties	Value	Units
Acid value	2.13	mg KOH/g
Free fatty acid (as oleic acid)	1.07	%
Peroxide value	1.31	meq/kg
Iodine value	97.17	g Iodine/100 g
Saponification value	189.87	mg KOH/g
Calculated saponification value	184.05	mg KOH/g
Unsaponifiable matter	5.01	%

(Gubitz et al., 1999)

Table 2.3 Fatty acid composition of crude *Jatropha curcas* oil

Fatty acid	Formula	Systemic name	Structure	% wt
Myristic	$C_{14}H_{28}O_2$	Tetradecanoic	14:0	0-0.1
Palmitic	$C_{16}H_{32}O_2$	Hexadecanoic	16:0	4.1-15.3
Palmitoleic	$C_{16}H_{30}O_2$	*cis*-9-Hexadecenoic	16:1	0-1.3
Stearic	$C_{18}H_{36}O_2$	Octadecanoic	18:0	3.7-9.8
Oleic	$C_{18}H_{34}O_2$	*cis*-9-Octadecenoic	18:1	34.3-45.8
Linoleic	$C_{18}H_{32}O_2$	*cis*-9,*cis*-12-Octadecedianoic	18:2	29.0-44.2
Linolenic	$C_{18}H_{30}O_2$	*cis*-6,*cis*-9,*cis*-12-Octadecatrienoic	18:3	0-0.3
Arachidic	$C_{20}H_{40}O_2$	Eicosanoic	20:0	0-0.3
Behenic	$C_{22}H_{44}O_2$	Docosanoic	22:0	0-0.2

(Gubitz et al., 1999)

2.2 Transesterification of *Jatropha curcas* Linn oil

J. curcas plant has high agro-industrial potential in Mexico because of its various potentially beneficial products. The oil extracted from the seeds can be used as a substitute of diesel after transesterification. Biodiesel has currently high demand in the United States and Europe and is being promoted in a big way in countries such as India. The residual protein-rich seed cake, remaining after extraction of the oil, could form a protein-rich ingredient in feeds for poultry, pigs, cattle and even fish if it could be detoxified. The plant itself is very sturdy and can be an excellent candidate for regreening of eroded zones, and for those lands that are not suitable for culture of more sensitive and demanding crops (Martinez-Herrera et al., 2006)

Amish et al. (2009) studied the production of biodiesel though transesterification of *Jatropha* oil with methanol in heterogeneous system, using alumina loaded with potassium nitrate as a solid-based catalyst. Followed by calcination, the dependence of the conversion of *Jatropha* oil on the reaction variables such as the catalyst loading, the molar ratio of methanol to oil, reaction temperature, agitation speed and the reaction time was studied. The conversion was over 84%

under the conditions of 70 ^{0}C, methanol/oil mole ratio of 12:1, reaction time for 6 h, agitation speed at 600 rpm and catalyst amount (catalyst/oil) of 6% by weight.

Production of glycerine residue from transesterification of *Jatropha curcas* oil. *Jatropha curcas* oil (200 ml) was studied Foidl et al. (1996). It was performed with a solution of 2 g NaOH in 44.5 g methanol to produce fatty acid methyl esters and glycerol. The mixture was stirred gently at 70 ^{0}C for 6 hour and allowed to cool overnight without stirring. Two layers were formed; the bottom layer was glycerol and the top layer was the methyl ester.

2.3 Purification of glycerine

The research of Hass & Patterson (1941) has been reported the purification of glycerol residue by crystallization. The artifices ordinarily was used for starting crystallization in the absence of seed crystals were all tried without success pure glycerine produced to crystals with liquid air at prolonged cooling and bringing gradually to 0 ^{0}C. After standing for a few hours at 0 ^{0}C, the crystals have grown enough to resemble sucrose in general appearance. After 2 days at 10 ^{0}C, the crystallization was completed.

The purification of glycerol residue from glycerol refining in the production of palm kernel methyl ester was reported by Yong et al. (2001). The crude fatty acids were isolated from the glycerol residue by conventional acid hydrolysis followed by phase separation. These dissolved fatty and methyl esters then reacted with excess sodium hydroxide in the subsequent neutralization to re-form soap which concentrated in the glycerol residue after the distillation in refining. Twelve samples of glycerol residue, GR1 to GR12, showed large variation in the contents of glycerol, ash, moisture, MONG and crude fatty acids. Salt (64.3%), glycerol (20.2%), and fatty acids (6.6%, present as soap) were the three main valuable components of glycerol residue, accounting for 91.1% of the residue. The main fatty acids were C12:0 (40.8%), C8:0 (30.3%) and C10:0 (9.4%).

The research of Ooi et al. (2001) has been studied the purification of glycerine residue obtained from a local oleochemicals company, the waste from glycerine refining in a palm kernel oil methyl ester plant. Initially, glycerine residue was carried out by acidified using sulfuric acid to split the soap and neutralize the residual NaOH

contained in them. The charred substances produced were filtered off. Subsequently, they were evaporated to concentrate the glycerine solutions. The salt crystallizing out was removed by decanting. To purify and concentrate the solutions further, they were solvent extracted and filtered to remove the residual salt. Finally, they were evaporated to obtain the crude glycerine. The average composition of the recovered crude glycerine were glycerol 51.4%, ash 13.8%, water 8.9% and matter organic non-glycerol (MONG) 25.9%.

In addition, Yong et al. (2001) has been applied the glycerine residue obtained from refining the crude glycerine by simple vacuum distillation and characterization of the distilled glycerine. The crude glycerine was distilled at 120 – 126 ^{0}C and 4.0 x 10^{-2} mbar pressure. The pH for the distillation was kept < 5 to avoid foaming. The characteristics of the distilled glycerine were 96.6 % glycerol, 0.03 % ash, 1% water, 2.4 % matter organic non-glycerol (MONG) and pH 3.5.

Beside, the research of Hazimah et al. (2003) has been studied the purification of glycerol pitch that one of the wastes generated by the Malaysian Oleochemicals Industry. The technique which involved an acid-based extraction was developed in which the pitch was separated into three components crude glycerine containing diglycerine, fatty acid and inorganic salts. After that crude glycerine was subjected to vacuum distillation to produce pure glycerine. The results are shown that the glycerol pitch comprised of 55 - 65% glycerine, 15 - 25% diglycerine, and less than 10% each of fatty acids and inorganic salts.

However, the research of Ooi et al., (2004) has been studied isolation of glycerine residue (GR1 to GR12) obtained from a local oleochemical company. The soap in the crude glycerine was removed in the soap splitting step where the glycerine was acidified with diluted hydrochloric acid. The excess hydrochloric acid was removed by subsequent neutralization step where the hydrochloric acid was neutralized by diluted sodium hydroxide solution. In this step, a considerable amount of sodium chloride was formed in the glycerine solution. The acidified and neutralized glycerine solution was then concentrated in a drying process before it was subjected to distillation to produce distilled glycerine and glycerol residue. The results showed that the average weight percentage of isolated crude fatty acids was 6.6%.

The main components of crude fatty acids were C 8:0 (30.3%), C 10:0 (9.4%) and C12:0 (40.8%).

Furthermore, Piyanat (2004) has been worked on the purification of glycerine obtained from transesterification of vegetable oils by 4 step included 1) evaporation of methanol 2) removal of base-catalysts by neutralization using sulfuric acid and extraction impurity by organic solvent 3) vacuum distillation 4) decolorization and deordorization using activated charcoal. The glycerine obtained from purification in all step have been resulted concentrated of glycerine 98% by weight and properties of glycerol following the international industry.

Otherwise, development in glycerol purification processes was done by Aiken (Aiken, 2006). The reaction mixture was sparged with nitrogen to remove water and low molecular weight alcohol, which driven the transesterification reaction toward glyceride formation. A wash water stream may also be added to the recovered glycerin stream from biodiesel production. Either before or following the transesterification reaction, an oil layer can be separated from the recovered glycerin stream by reducing the pH of the stream to below 7. Following separation of the oil layer and transesterification the glycerin stream was distilled to separate glycerin from water, salts, and glycerides.

2.4 Identification of biodiesel obtained from transesterification

2.4.1 Analysis of biodiesel by gas chromatographic technique

Numerous analytical techniques have been used for the pure biodiesel (B 100) determination, including a Gas Chromatograph couple with a flame ionization detector (Fausto et al., 2003; Christina & Eberhard; 1995; Coen, 2001).

2.5 Characterization of purified glycerine

2.5.1 Fourier Transform infrared spectroscopy (FTIR) for analysis of glycerine

Crude glycerine was determined by Ooi et al., 2001; Yong et al., 2001; Hazimah et al., 2003; Su and Wei, 2008 using a Fourier transform infrared (FTIR) spectra. The liquid samples were investigated as liquid films (neat) and solid samples using potassium bromide (KBr) pellets.

2.5.2 The determination of free glycerol content in the reaction mixture by Ultraviolet-Visible (UV-Vis) Spectroscopy

Some researchers such as Su & Wei, 2008; Bondioli & Della Bella, 2005, determined free glycerol in biodiesel by using a PDA UV-VIS Spectrophotometer. Formaldehyde is also generated by reaction between free glycerol in biodiesel and the reaction between acetyl acetone and the generated formaldehyde lead to formation of the 3, 5-diacetyl 1,4-dihydrolutidine that was yellow complexes. As these complexes were generated proportionally the amount of glycerol in the sample. Glycerol was then determined by measuring these complexes that have specific absorption band at 410 nm.

2.5.3 Determination of purified glycerine compositions in purification process

Crude glycerine has been determined several researchers (Yong et al., 2001; Ooi et al., 2001; Yong et al., 2001; Hazimah et al., 2003) by using the International Organization for Standardization method as following,

Moisture: ISO 2089-1972

Glycerol: ISO 2879-1975

Ash: ISO 2098-1972

Acidity: ISO 1615-1976

MONG: Standard method ISO 2464-1973.