CHAPTER I
INTRODUCTION

1.1 Rationale and backgrounds

Diesel fuel is largely utilized in the transport, agriculture, commercial, domestic and industrial sectors for the generation of power/mechanical energy. Of the alternative fuels, biodiesel obtained from vegetable oils and animal fats holds good promises as an eco-friendly alternative to diesel fuel. Biodiesel has recently attracted huge attention in different countries all over the world because of its availability, renewability, non-toxicity, better gas emissions, and its biodegradability. Moreover, it can be used as a substitution for petroleum diesel without the need for diesel engine modification. Because of biodiesel is also essentially free of sulfur and aromatics, therefore it produces lower exhaust emissions than conventional gasoline whilst providing similar properties in terms of fuel efficiency (Demirbas, 2009; Lang et al., 2001; Ghadge & Raheman, 2005). Biodiesel production from vegetable oil has been extensively studied in recent years. One kind of plants deserving special attention for biodiesel production is *Jatropha curcas* Linn.

Jatropha curcas Linn or physic nuts are a drought-resistant shrub or tree belonging to the family *Euphorbiaceae* and classified as one of the plant oil similar to palm oil. It has cultivated in Central and South America, south-east Asia, India and Africa. Besides, it can easily be propagated by cuttings (Martinez-Herrera et al., 2006). This plant is well adapted to arid and semi- arid conditions and can be grown in most regions of Thailand, especially in the North-eastern area. Depending on the variety, *Jatropha* seeds contain 43-59% of oil used for many purposes such as lighting, lubricant and making soap. It has good burning potential as the seeds burn and emit energy for a considerable period of time. Since *Jatropha* oil cannot be used for nutritional purposes without detoxification, its use as an energy source for biodiesel presently becomes more attractive (Canakci et al., 2001; Dorado et al., 2002; Wool et al., 2000). Generally *Jatropha* 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 consists of palmitic acid (14.7%) and stearic acid (6.9%)

(Gan et al., 1995). It's oil may be used directly with slow speed diesel engine or upgrade via transesterification to conventional biodiesel.

Many researchers have reported the biodiesel production in several ways (Demirbas, 2002; Freedman et al., 1986; Pryde et al., 1984; Ma et al., 1998; Rashid & Anwar, 2008). There are four basic routes to biodiesel production from oils and fats: Base-catalyzed transesterification; direct acid-catalyzed transesterification; enzyme catalytic (Fukuda et al., 2001; Iso et al., 2001; Nelson et al., 1996; Nie et al., 2002; Shimada et al., 2005) conversion of the oil into its fatty acids and then into biodiesel, and non-catalytic transesterication using methanol (Antolin et al., 2002) or methanol/co-solvent (Han et al., 2005).

In conventional process, biodiesel or fatty acid methyl ester is manufactured by the transesterification of vegetable oils or animal fats with alcohol (methanol or ethanol) in the presence of catalysts, such as alkali (KOH or NaOH) or their corresponding alkoxides as shown in Figure 1.1 (Freedman, et al., 1984; Alan Holser & Harry-O Kuru, 2006; Ikwuagwu, et al., 2000; Jitputti, et al., 2006; Leung & Guo, 2006; Ma & Hanna, 1999; Siler-Marinkovic & Tomasevic, 1998). The by-product of this reaction is glycerol, which is a trivalent alcohol.

Glycerol is a clear, odorless, viscous liquid with a naturally sweet taste. It is derived from both natural and petrochemical feedstocks. The name glycerol is preferred for the chemical, but commercially the product is usually called glycerin, glycerine, 1,2,3-propanetriol, propanetriol, 1,2,3-trihydroxy propane, trihydroxy propane, glycyl alcohol, glyceritol, which has structure and physicochemical properties as shown in Figure 1.2 and Table 1.1, respectively.

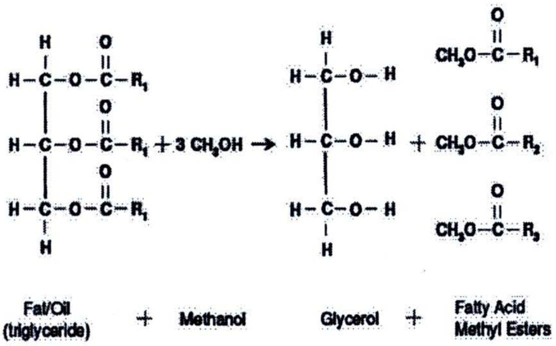

Figure 1.1 Reaction schematic of transesterification of triglycerides to biodiesel (Pagliaro & Rossi, 2008)

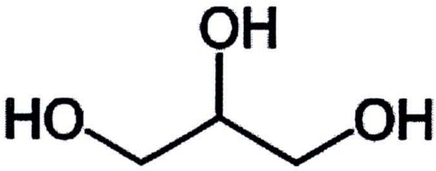

Figure 1.2 Structure of glycerine

Table 1.1 Physicochemical properties of glycerine at 20 ^{0}C

Chemical formula	$C_3H_5(OH)_3$
Molecular mass	92.09382 g mol^{-1}
Density	1.261 g cm^{-3}
Viscosity	1.5 Pa.s
Melting point	18.2 ^{0}C
Boiling point	290 ^{0}C
Food energy	4.32 k cal g^{-1}
Flash point	160 ^{0}C (closed cup)
Surface tension	64.00 m Nm^{-1}
Temperature coefficient	-0.0598 mN $(mK)^{-1}$

(Pagliaro & Rossi, 2008)

In addition, glycerine contains three hydrophilic alcoholic hydroxyl groups, which are responsible for its solubility in water and is hygroscopic nature. It is a highly flexible molecule forming both intra- and intermolecular hydrogen bonds (Pagliaro & Rossi, 2008).

Glycerine currently has over 1500 known uses in many different industries such as foods, pharmaceuticals, and cosmetics (USP grade glycerin), coatings and other industrial types of applications (technical grade glycerine). Crude glycerine is 70-80% pure and is often concentrated and purified prior to commercial sale to 95.5-99% purity (Pagliaro & Rossi, 2008). However, glycerine as chemical, glycerine is widely used as a solvent or drug carrier in pharmaceutical and medicinal products, as humectants in cosmetics, toiletries and other personal care products. Glycerine is also used in the making of paper alkaline or acid condensation catalyst. The use of glycerol and polyglycerol for manufacturing of urethane foam is on the increase. Foams made from glycerol derivatives are flexible, resilient and age well in humid conditions. Furthermore, the products are 1,3-propanediol (Himmi et al., 1999; Papanikolaou & Aggelis, 2003; Papanikolaou & Aggelis, 2000; Zeng et al., 1997; Xiu et al., 2004; Menzel et al., 1997; Wang et al., 2001) hydrogen (Ito et al., 2005; Wood, 2002; Hirai et al., 2005; Huber et al., 2003) succinic acid (Lee et al., 2001), propylene glycol (Dasari et al., 2005), 1,2 propanediol (Perosa & Pietro, 2005), dihydroxyacetones (Garcia et al., 1995; Kimura, 2001; Bauer et al., 2005), polyesters (Stumbe & Bruchmann, 2004; Pramanick & Ray, 1988; Alksnis et al., 1976; Nagata et al., 1996), Polyglycerols (Clacens et al., 2002) and Polyhydroxyalkanoates (Koller et al., 2005). Despite the wide applications of pure glycerine in many other industries, it is too costly to refine the crude glycerine to a high purity, especially for medium and small biodiesel producers. Crude glycerine derived from biodiesel production very low value because of the impurities. Further refining of the crude glycerine will depend on the economy of production scale and the availability of a glycerine purification facility.

The conventional process for glycerine purification comprises of the following steps: pretreatment, concentration, purification and refining. The pretreatment step is used to remove colour and odour matters as well as any remaining fat components from crude glycerine. In the pretreatment step sodium hydroxide is used for the removal of fat components by saponification reaction where as activated carbon is used for bleaching purpose. All of them involve soap splitting followed by two main separation steps: salt removal and methanol removal. Some of the separation techniques should involve vacuum because glycerol is a heat sensitive compound that splits into water and decomposes at 180 ^{0}C (Pagliaro & Rossi, 2008). However, purification of glycerine by conventional method to make many steps which will spend much time, furthermore, it will be lost glycerine in purification step.

In this work, the improved method for purification of residue glycerine from transesterification of *Jatropha curcas* oil extracted was investigated by using cation/anion exchange chromatography. The characterization of standard glycerine, residue glycerine and purified glycerine obtained was monitored by using UV-VIS spectrophotometry, FT-IR spectrophotometry. Moreover, the composition of standard glycerine, residue glycerine and purified glycerine was determined following the International Organization for Standardization method. This improved method may be applied for glycerine purification from other biofuel production and can increase purity of residue glycerine for use in industry in the future.

1.2. Objectives of the research

1.2.1 To produce residue glycerine from transesterification process of *Jatropha curcas* oil extracted.

1.2.2 To purify residue glycerine from transesterification of *Jatropha curcas* oil by both conventional method and improved method.

1.2.3 To investigate some optimized conditions for purification of residue glycerine by improved method using ion exchange chromatography.

1.2.4 To characterize standard glycerine, residue glycerine and purified glycerine by using Fourier transform infrared spectroscopy (FT-IR) and ultraviolet-visible spectroscopy (UV-VIS).

1.2.5 To determine the compositions of standard glycerine, residue glycerine and purified glycerine based on the International Organization for Standardization method.

1.3. The scope and limitations of the research

1.3.1 Production of residue glycerine from transesterification of *Jatropha curcas* oil extracted by using methyl alcohol and NaOH as a catalyst.

1.3.2 Purification of residue glycerine from transesterification of *Jatropha curcas* oil by conventional method and improved method.

1.3.3 The optimized conditions for glycerine purification by improved method using ion exchange chromatography.

1.3.4 Characterization of standard glycerine, residue glycerine and purified glycerine by Fourier Transform infrared spectroscopy (FT-IR), and ultraviolet-visible spectroscopy (UV-VIS).

1.3.5 Determination of the compositions of standard glycerine, residue glycerine and purified glycerine in the terms of glycerine content, ash content, moisture content and acidity followed by the International Organization for Standardization method.

1.4 The anticipated outcomes

1.4.1 The residue glycerine was obtained from transesterification of *Jatropha curcas* oil.

1.4.2 The purified glycerine was achieved from conventional method and modified method.

1.4.3 The optimum conditions of improved method by ion exchange chromatography for purification of residue glycerine were obtained.

1.4.4 The characteristics and physicochemical properties of purified glycerine by conventional method and modified method was investigated by using ion-exchanger.