

Full Length Research Paper

Biodiesel production from *Euphorbia tirucalli* L.

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Demand of renewable and clean energy to replace diesel world is big and urgent. However, edible crop oil as raw material is limited and its price is expensive and unstable. We want to look for new suppliers of raw materials, which should be cheap and supply stable to replace edible oil such as rapeseed and euphorbia extract. This study shows, the best candid for this purpose is *Euphorbia tirucalli*. It can be feasible and efficient to produce biodiesel in plant as stocks which contains terpenoids. Based on economic situation of oriental (Iran, UAE, Oman), several suggestions have been listed for development and promotion of biodiesel from *E. tirucalli*. These lands can be used to grow biodiesel feed stocks plant and to produce non-food biodiesel feedstocks for the domestic energy market to diminish imports. Biodiesel is non toxic and environmental friendly as it produces substantially less carbon monoxide and 100% less sulfur dioxide emissions with no unhurt hydrocarbons and consequently it is ideal fuel for heavily polluted cities. Biodiesel reduces serious air pollutants such as particulates and air toxicity. This material can be used directly by a diesel-powered car. Also, biodiesel extends the life of diesel engines.

Key word: *Euphorbia tirucalli*, biodiesel, energy, air toxicity, engine.

INTRODUCTION

Biodiesel refers to a non-petroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, made by transesterification of vegetable oil or animal fat (tallow), which can be used (alone, or blended with conventional petro diesel) in unmodified diesel-engine vehicles (Figures 1 and 2, Goering et al., 1982). Biodiesel is distinguished from the straight vegetable oil (SVO) (sometimes referred to as "waste vegetable oil", "WVO", "used vegetable oil", "UVO", "pure plant oil", "PPO") used (alone, or blended) as fuels in some converted diesel vehicles (Chang et al., 1997). Biodiesel is standardized as mono-alkyl ester and other kinds of diesel-grade fuels of biological origin are not included (Peterson et al., 1992). Chemically, transesterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids (Feuge and Gros, 1949). The most common form uses methanol (converted to sodium methoxide) to produce methyl esters as it is the cheapest

alcohol available, though ethanol can be used to produce an ethyl ester biodiesel and higher alcohols such as isopropanol and butanol have also been used (Hopia et al., 1986). Using alcohols of higher molecular weights improves the cold flow properties of the resulting ester, at the cost of a less efficient transesterification reaction (Freedman et al., 1984).

A lipid transesterification production process is used to convert the base oil to the desired esters. Any free fatty acids (FFAs) in the base oil are either converted to soap or removed from the process, or they are esterified (yielding more biodiesel) using an acidic catalyst (Canakci et al., 1999). After this processing, unlike straight vegetable oil, biodiesel has combustion properties very similar to those of petroleum diesel, and can replace it in most current uses (Culshaw et al., 1993). Despite the widespread use of fossil petroleum-derived diesel fuels, interest in vegetable oils as fuels in internal combustion engines is reported in several countries during the 1920 and 1930's and later during World War II. Some operational problems were reported due to the high viscosity of vegetable oils compared to petroleum

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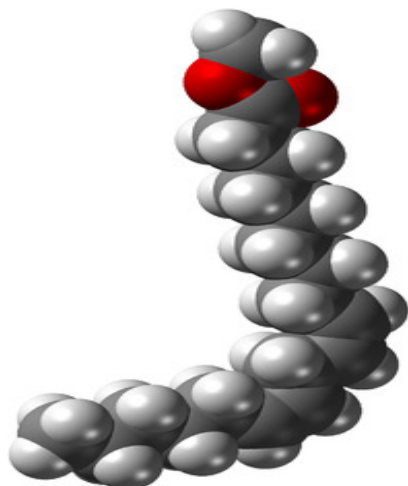


Figure 1. Space-filling model of methyl linoleate, or linoleic acid methyl ester, a common methyl ester produced from soybean or canola oil.



Figure 2. Space-filling model of ethyl stearate, or stearic acid ethyl ester, an ethyl ester produced from soybean or canola oil and ethanol.



Figure 3. Biodiesel feedstock soybean seeds.

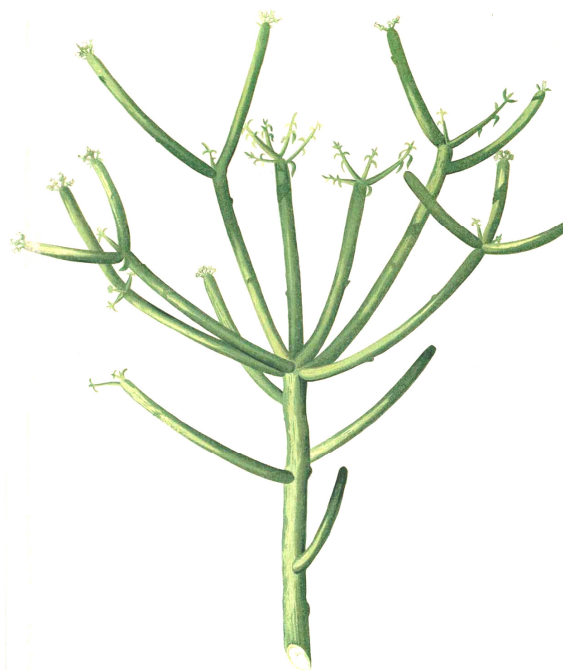


Figure 4. *E. tirucalli*.

diesel fuel, which result in poor atomization of the fuel in the fuel spray and often leads to deposits and coking of the injectors, combustion chamber and valves. Attempts to overcome these problems included heating of the vegetable oil, blending it with petroleum-derived diesel fuel or ethanol, pyrolysis and cracking of the oils. It was demonstrated with a diesel engine running on peanut oil (Figure 3). *Euphorbia tirucalli* L. is a shrub that grows in semi-arid tropical climates. Milk bush produces poisonous latex which can, with little effort, be converted to the equivalent of gasoline (Garg et al., 1989). Milk bush is also used in traditional medicine in many cultures (Figure 4). It has been used to treat cancers, excrescences, tumors, and warts in such diverse places as Brazil, India, Indonesia and Malaysia (Garg et al., 1989). It has also been used as an application for asthma, cough, earache, neuralgia, rheumatism, toothache, and warts in India. There is some interest in milk bush as a cancer treatment. Biodiesel is commonly produced by the transesterification of the vegetable oil or animal fat feedstock (Pandey, 1986). There are several methods for carrying out this transesterification reaction including the common batch process, supercritical processes, ultrasonic methods, and even microwave methods. Blends of biodiesel and conventional hydrocarbon-based diesel are products most commonly distributed for use in the retail diesel fuel marketplace. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix: fuel containing 20% biodiesel is labeled B20, while pure biodiesel is referred to as B100. Blends of 20% biodiesel

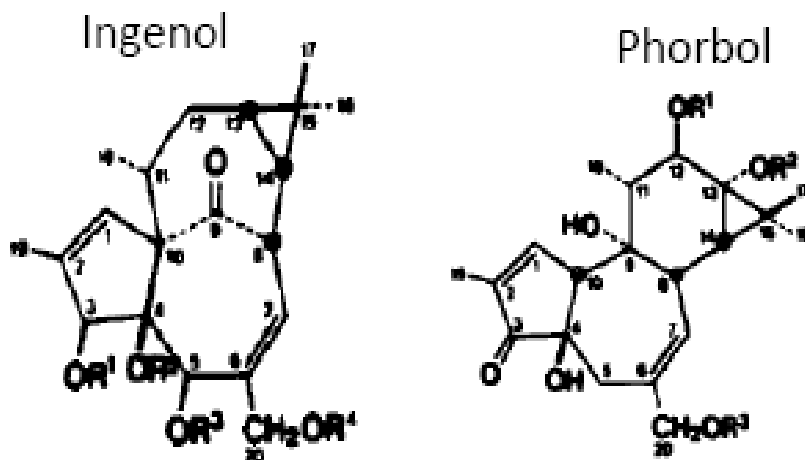


Figure 5. Diterpenes from *E. tirucalli* extract.

with 80% petroleum diesel (B20) can generally be used in unmodified diesel engines. On August 31, 1937, G. Chavanne of the University of Brussels (Belgium) was granted a patent for a 'procedure for the transformation of vegetable oils for their uses as fuels'. This patent described the alcoholysis (often referred to as transesterification) of vegetable oils using ethanol (and mentions methanol) in order to separate the fatty acids from the glycerol by replacing the glycerol with short linear alcohols (Feuge et al., 1945). This appears to be the first account of the production of what is known as 'biodiesel' today. Biodiesel can be used in pure form (B100) or may be blended with petroleum diesel at any concentration in most modern diesel engines (Wang et al., 2000). Biodiesel can also be used as a heating fuel in domestic and commercial boilers, sometimes known as bioheat. During the biodiesel research suggested that B20 biodiesel could reduce environmental household CO₂ emissions by 1.5 million tons per year (McCormick et al., 1997). Biodiesel is often more expensive to purchase than petroleum diesel but this is expected to diminish due to economies of scale and agricultural subsidies versus the rising cost of petroleum as reserves are depleted. Biodiesel has better lubricating properties than today's lower viscosity diesel fuels. Biodiesel addition reduces engine wear increasing the life of the fuel injection equipment that relies on the fuel for its lubrication, such as high pressure injection pumps, pump injectors (also called unit injectors) and fuel injectors.

A variety of oils can be used to produce biodiesel. These include: Virgin oil feedstock; rapeseed and soybean oils are most commonly used. It also can be obtained from field pennycress and *Jatropha*, other crops such as mustard, flax, sunflower, palm oil, hemp (Culshaw et al., 1993). Waste vegetable oil (WVO), animal fats including tallow, lard, yellow grease, chicken fat, and the by-products of the production of Omega-3 fatty acids from fish oil (Feuge et al., 1945). Algae, which

can be grown using waste materials such as sewage and without displacing land currently used for food production. Oil from halophytes such as *Salicornia bigelovii*, which can be grown using saltwater in coastal areas where conventional crops cannot be grown, with yields equal to the yields of soybeans and other oilseeds grown using freshwater irrigation (Hopia et al., 1986). Biodiesel production capacity is growing rapidly, with an average annual growth rate from 2002 to 2006 of over 40% (Martinot, 2007). For the year 2006, the latest for which actual production figures could be obtained; total world biodiesel production was about 5 to 6 million tonnes, with 4.9 million tonnes processed in Europe (of which 2.7 million tonnes was from Germany) and most of the rest from the USA. In 2007 production in Europe alone had risen to 5.7 million tonnes (Martinot, 2007). The capacity for 2008 in Europe totaled 16 million tonnes. This compares with a total demand for diesel in the US and Europe of approximately 490 million tonnes (147 billion gallons). Total world production of vegetable oil for all purposes in 2005/06 was about 110 million tonnes, with about 34 million tonnes each of palm oil and soybean oil (Clark et al., 1984; Martinot, 2007). Feedstock yield efficiency per acre affects the feasibility of ramping up production to the huge industrial levels required to power a significant percentage of national or world vehicles. *E. tirucalli* L. fuel yields have not yet been accurately determined, but it may be that it yielded more amount energy per acre than land crops such as soybeans. Because of their size is bigger, its plump tissue and also yields are highly dependent on climatic and soil conditions (Figure 5). It is grown in the UAE, Iran, Oman, is drought-resistant. It is well-suited to semi-arid lands and can contribute to slow down desertification, according to its advocates. The aim of this study is to survey advantages of *Euphorbia* that can be grown on non-arable land such as deserts, petroleum area or in marine environments, and may be the potential oil yields

are much higher than from forests.

MATERIALS AND METHODS

Procedure for the transformation of vegetable oils for their uses as fuels is described in the alcoholysis (often referred to as transesterification) of vegetable oils using methanol and ethanol in order to separate the fatty acids from the glycerol by replacing the glycerol by short linear alcohols. This appears to be the first account of the production of what is known as "biodiesel" today." All solvent and buffer were prepared from Merck, Darmstadt, Germany. Thin layer chromatography (TLC) plate was obtained from Whatman (Florham Park, USA). All chemical material; Acetonitril, Ethanol and Methanol (Merck) were of analytical grade and used without further purification. All solutions were also prepared with double distilled water and were kept at RT before use. There are several methods for carrying out this transesterification reaction including the common batch process, supercritical processes, ultrasonic methods, and even microwave methods. In this study we are down with TLC, high performance liquid chromatography (HPLC) with conventional column (C18 column, Shimatsu, Japan) and IR methods for separation and known the active material of Euphorbia (Liu et al., 1994; Lezerovich, 1986).

RESULTS

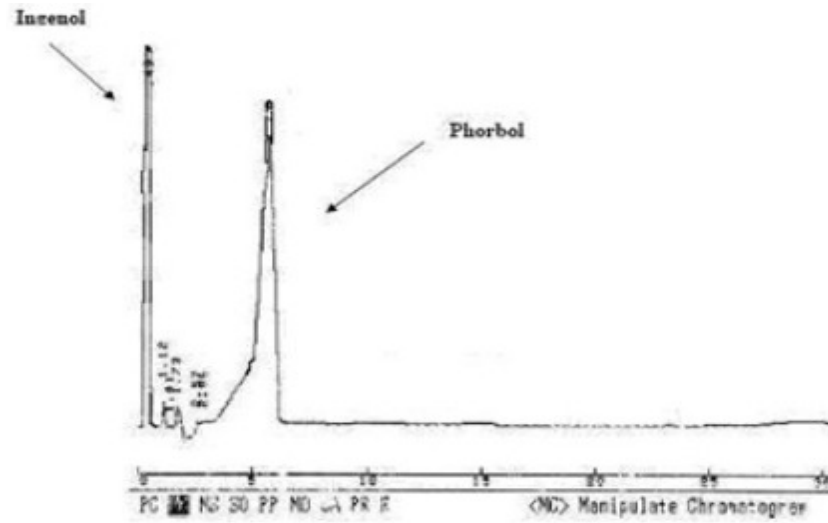
E. tirucalli is a shrub that grows in semi-arid tropical climates. Milk bush produces a poisonous latex which can, with little effort, be converted to the equivalent of gasoline. It is particularly appealing because of the ability of milk bush to grow on land that is not suitable for most other crops (Figure 4). Euphorbia is a liquid which varies in color between golden and dark brown as well as biodiesel feedstock. It is immiscible with water, has a high boiling point and low vapor pressure. Generic biodiesel material safety data sheet (MSDS) has been shown that the flash point of biodiesel (>130°C, >266°F) is significantly higher than petroleum diesel (64°C, 147°F) or gasoline (-45°C, -52°F). Also biodiesel has a density of ~ 0.88 g/cm³, less than that of water. A variety of oils are included *E. tirucalli* Latex. We extract and purified two compound "Phorbol and Ingenol" on latex by TLC and HPLC techniques (Figure 6), which are much more amount than feedstock vegetable oils. Milk bush *E. tirucalli* produces poisonous latex which can, with little effort, be converted to the equivalent of gasoline (Figures 3 and 5).

DISCUSSION

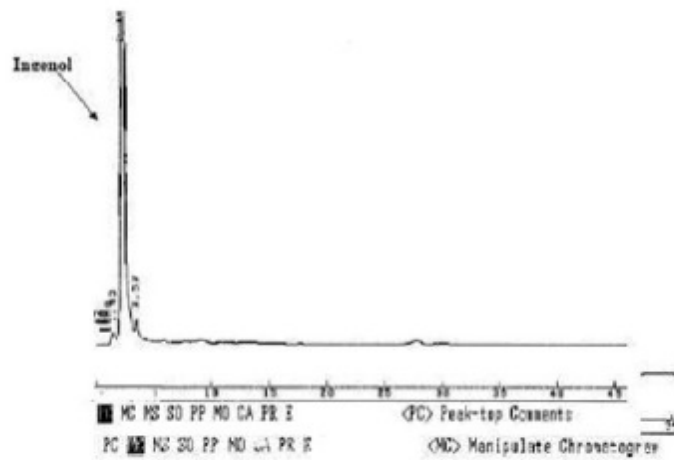
Biodiesel is becoming of interest to companies interested in commercial scale production as well as the more usual home brew biodiesel user and the user of straight vegetable oil or waste vegetable oil in diesel engines (Goering et al., 1982). Homemade biodiesel processors are many and varied. One of the main drivers for adoption of biodiesel is energy security. This means that a nation's dependence on oil is reduced, and substituted with use of locally available sources, such as coal, gas,

or renewable sources (Mittelbach et al., 1988). Thus a country can benefit from adoption of biofuels, without a reduction in greenhouse gas emissions. Whilst the total energy balance is debated, it is clear that the dependence on oil is reduced. The surge of interest in biodiesels has highlighted a number of environmental effects associated with its use. These potentially include reductions in greenhouse gas emissions, deforestation, pollution and the rate of biodegradation. However many of the nation (USA, European and Africa) use vegetable oil as a biodiesel and also biofuel suggested that nations in oriental could use this natural facility as well as others. *E. tirucalli* fuel yields have not yet been accurately determined, but there is reported as saying that algae and non edible vegetable yield have more times energy per acre than land crops such as soybeans and also yields are highly dependent on climatic and soil conditions (Mittelbach and Tritthart, 1988). *E. tirucalli* is well-suited to semi-arid lands and can contribute to slow down desertification, according to its advocates "UAE, Iran and Oman". The production of Euphorbia to harvest oil for biodiesel has not yet been undertaken on a commercial scale, but feasibility studies have been conducted to arrive at the enough yields with suitable commercial grade estimate. In addition to its projected high yield, agriculture unlike crop-based biofuels does not entail a decrease in food production, since it requires neither farmland nor fresh water. It is possible to set up some bio-reactors for various purposes (Valcent, 2008), including scaling up biodiesel production to commercial levels from *E. tirucalli*. There are some that say using food crop for fuel sets up competition between food in poor countries and fuel in rich countries. In some poor countries the rising price of vegetable oil is causing problems. Some propose that fuel only be made from non-edible vegetable oils like *E. tirucalli* as well as camelina, jatropha or seashore mallow which can thrive on marginal agricultural land where many trees and crops will not grow, or would produce only low yields (Hall et al., 1998). Others argue that the problem is more fundamental. Farmers may switch from producing food crops to producing biofuel crops to make more money, even if the new crops are not edible. However, these are not enough to show whether such a change makes economic sense. Additional factors must be taken into account, such as: the fuel equivalent of the energy required for processing, the yield of fuel from raw oil, the return on cultivating food, the effect biodiesel will have on food prices and the relative cost of biodiesel versus petrodiesel (Roy et al., 1996). The cultivatives of *E. tirucalli* dissolved these problems which can be grown using saltwater in coastal areas where conventional crops cannot be grown, with yields equal or even more than to the yields of soybeans and other oilseeds grown using freshwater irrigation (Clark et al., 1984).

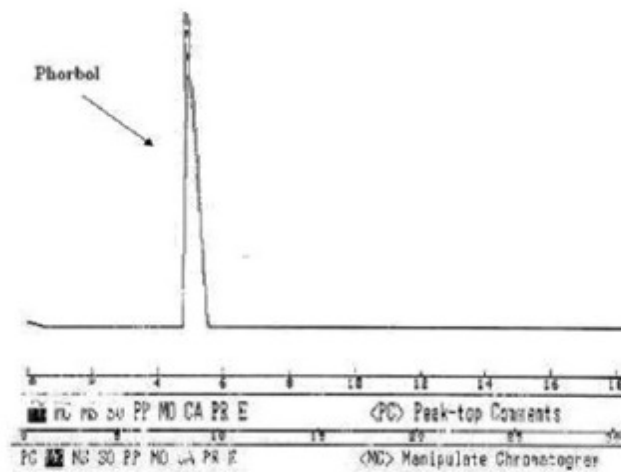
There is ongoing research into finding more effective and improving *E. tirucalli* oil yield. Using the biodiesels current yields of edible vegetable, vast amounts of land



(A)



(B)



(C)

Figure 6. High performance liquid chromatography from euphorbia extract (A) Chromatogram shows two peak (ingenol and phorbol), (B) Chromatogram shows purified Ingenol, (C) Chromatogram shows purified phorbol.

and fresh water would not be to produce enough oil to completely replace fossil fuel usage. Therefore *E. tirucalli* biodiesel, unlike straight vegetable oil, could have combustion properties very similar to those of petroleum diesel, and can replace it in most current uses.

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