

PROFESOR DR. DZULKEFLY KUANG ABDULLAH

# **PALM OIL** Still The Best Choice

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## ABSTRACT

Looking at the development of the palm oil market today it is conceivable that this oil is going to be the world's choice. The continuing high demand for it, as seen in the world market today, reflects the importance of palm oil and the public's awareness of its superiority. Palm oil is extracted from the fruits of oil palm *(Elaeis guineensis)*, the golden crop of Malaysia. Oil from this attractive palm has been used as food and energy source for millennia. Palm oil can be processed to produce various type of solid fats and liquid oils of different physical and chemical properties, while this cannot be done with other vegetable oils. Being *trans* fatty acid free, and possessing significant nutritional and medicinal values, palm oil is chosen for better health. It is packed with nutrients; pro-vitamin A, vitamin E, phytosterol, squalene, coenzyme and lecithin. Probably, the most exciting discovery is that palm oil has shown effective anti cancer activity and is a cholesterol lowering agent. Scientists and nutritionists, backed by extensive published papers agree that **tocotrienols**, found only in palm oil, are effective anti cancer agents and have been shown to inhibit human breast cancer cells whereby gamma-tocotrienol is 3 times more potent in inhibiting the growth of human breast cancer cultured-cells than Tamoxifen (a drug widely used in the treatment of breast cancer). While palm oil has all these beneficial values, none of the other vegetable oils possess similar qualities.

In the current biofuel era, palm oil is touted to be the best choice for biofuel feedstock. Based on its availability and fuel-related properties, today palm oil is the most viable raw material for biodiesel conversion. However, the existing Government policy will restrict future production of palm oil for biodiesel in anticipation of strong world demand for biodiesel raw materials. Since biodiesel production from palm oil will be limited in the future, the Government should look for alternative renewables, probably bioethanol from cassava as a complement to biodiesel, and at the same time explore new technologies

#### Palm Oil: Still The Best Choice

particularly to convert plant celluloses or palm biomass to bioethanol. Being a tropical country, Malaysia has an abundance of plants where celluloses can be extracted and used as raw materials for bioethanol.

## INTRODUCTION

Looking at the development of the palm oil market today, it is conceivable that this oil is going to be the world's choice. The continuing high demand for it, as seen in the world market, reflects the importance of palm oil and the public awareness of its superiority. Palm oil is extracted from the fruits of oil palm *(Elaeis guineensis)*, the golden crop of Malaysia. Oil from this attractive palm, which originated from West Africa, has been used as a food and energy source for millennia. Crude palm oil (CPO) which is orange-red in color is refined, bleached and deodorized to produce the bright golden RBD palm oil. Total world production of palm oil exceeded 35 million tonnes in 2006, thus overtaking production of all other vegetable oils including the soybean oil. This implies strong confidence and trust in the values and quality provided by palm oil from users and traders. The current high demand for palm oil is mainly due to its great impact on food and non-food uses in particular in the emerging biofuel era. Among the exciting recent developments shown by the palm oil sector are:

- Palm oil production in 2006 (35 million tones) exceeded soybean oil production.
- Increase in demand of palm oil in USA by 4.8% (the fourth major importer of Malaysian palm oil) when food manufacturers switched to palm oil in anticipation of *trans*-fats labeling which came into effect in January 2006.
- Highest world consumption (24.4%) compared to soybean oil (23.5%) and rapeseed oil (12.2%)
- Great jump in palm oil prices (the current CPO oil price is about RM 3000.00/tonne compared to RM 1600.00/tonne on average in 2006)

The above scenarios indicate the importance of palm oil and that it is going to be the world's choice of oil.

## PALM OIL GENERATES MORE OILS AND FATS

Palm oil is unique among the vegetable oils as it can be further processed to generate more oils and fats which have various uses. While the major component of palm oil is triglyceride (or oil), it has about 1% of other minor components (non oil materials). Palm oil contains an equal proportion of total saturated fatty acids and unsaturated fatty acids (see Table 1) which means that at room temperature palm oil is a mixture of 50% solid fat and 50 % liquid oil. In contrast, soybean and corn oils are highly unsaturated oils (rich in polyunsaturated acids, C18:2 and C18:3 acids), and thus they exist only in liquid form at room temperature.

Fatty Acid Composition	Corn Oil (%)	Soybean Oil (%)	Palm Oil (%)
C16:0	8-19	7-14	41.8-46.8
C18:0	0.5-4	1.4-5.5	<u>4.2-5.1</u>
C18:1	19-50	19-30	37.3-40.8
C18:2	<u>34-62</u>	<u>44-62</u>	9.1-11.0
C18:3	2 Max	4-11	0.6 Max

 Table 1
 Major fatty acids of significant importance in corn, soybean and palm oils

In comparison to other vegetable oils and fats, in terms of unsaturation, palm oil is in between the two extremes; the saturated solid fats and the highly unsaturated liquid oils (Fig. 1). This means that palm oil can easily be split into two fractions, i.e. solid fat and liquid oil fractions by a fractionation process (see Fig. 3).

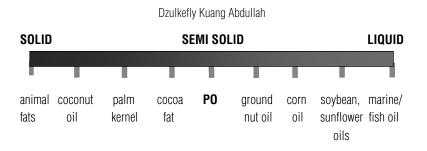
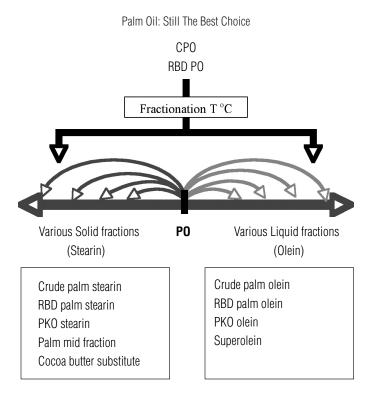


Figure 1 Spectrum of some vegetable oils and fats, based on the degree of unsaturation (or iodine value). Solid animal fats on the left end are highly saturated fat and marine oils on the right end represent highly unsaturated liquid oil. Palm oil which is in the middle is a mixture of both solid and liquid.

By performing a fractionation process at different temperatures, various solid fats (termed as stearin) and liquid oils (termed as olein) of different physical and chemical properties can be separated. This process is always performed on palm oil but rarely performed on other vegetable oils and fats (see Fig. 2). The oils and fats obtained by this process have found various uses in industries.



**Figure 2** Palm oil is fractionated into various solid stearins and liquid olein for various industrial applications by varying fractionation temperatures.

# PALM OIL - VEGETABLE OIL FOR BETTER HEALTH

## 1) Trans Fatty Acid Free-Oil

Palm oil is *trans* fatty acid free. The oil from the palm fruits contains a variety of fats, vitamins and nutrients, but NO *trans* fatty acids. *Trans* fatty acids are normally found pre-dominantly in hydrogenated oils. This is because highly unsaturated oils have to undergo hydrogenation process to make them slightly saturated (reduce unsaturation level) and thus, increase their melting point, making them attractive for baking, and resistant to rancidity. It is interesting to note that food regulations in France do not *permit an oil to be offered for* 

sale for frying if its linolenic acid (unsaturated C18:3 acid) content exceeds 2% (Ordinance of 12 February, 1983) (Berger, 1984). This means that all polyunsaturated oils must be hydrogenated to reduce their unsaturation level. In doing so, the unsaturated fatty acids are rearranged, converting some to the *trans* configuration (Fig. 3). In contrast, palm oil perfectly matches this requirement. Its unsaturation level is well below 2% (Table 1), which means it is relatively stable and does not require hydrogenation, thus, a *trans* fatty acid-free oil.

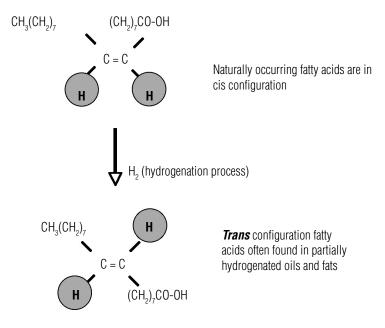


Figure 3 Hydrogenation process to make oils and fats more saturated by adding hydrogen into the doubles.

*Trans* fats are associated with chronic health problems. They are not essential and provide no known benefit to human health. Epidemiological studies since 1990 have identified the risk of consumption of *trans* fats as an elevated risk to coronary heart disease (CHD) (Ascherio, 1999; Mozaffarian *et al.*, 2006; Hu *et al.*,

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1997; Willet and Ascherio, 1994; Willet, 1993; Mozaffarian *et al.*, 2006). All the studies concluded that *trans* fatty acid raises LDL cholesterol (bad cholesterol), lowers HDL cholesterol (good cholesterol), thus, increasing the risk of CHD. *Trans* fats also interferes with the enzyme converting essential fatty acids to biologically active compounds (arachidonic acid and prostaglandins) that are required for functioning of cells (Mahfouz, 1981). Other potential health effects of *trans* fats are (Jorge *et al.*, 2006; Hu *et al.*, 2001; Gosline *et al.*, 2006):

- Increased risk of cancer
- Risk of diabetes
- Increased risk of obesity and
- Risk of infertility



Realizing its bad effects, many countries imposed strict regulations on the sale of food containing *trans* fats such as margarine, pastries, potato chips, french fries, cookies, bread etc. Some even proposed a ban on partially hydrogenated oils. It is recognized that *trans* fats cause thousands of premature deaths in the USA each year. Because of these dangers, the *trans* fats labeling regulation was introduced in the USA recently, in January 2006, which requires Food Labels to clearly list the amount of *trans* fat in the nutrition facts section. This means that food producers have to re-formulate their products to lower or eliminate *trans* fatty acids. This would be possible by employing the benefits of palm oil. The move has resulted in a great jump in palm oil exported to the USA recently as traders are looking for an alternative *trans* fatty acid free oil. **Thus, palm oil is not just an energy source but also the choice for better health.** 

Another interesting finding to note is the work of Professor Csallany and her colleague at the University of Minnesota (Seppanen and Csallany, 2004a,b). They discovered a highly toxic compound called HNE (4-hydroxy-*trans*-2-noneal) in extended or repeated heating of polyunsaturated oils, which include soybean, sunflower and corn oils at frying temperature (185 °C). In addition, heated soybean oil produced an additional three toxic HNE-related compounds (known as HHE, HOE and HDE). HNE, a well known highly toxic compound easily absorbed through diet, causes chronic diseases such as atherosclerosis and stroke, Parkinson disease, liver ailments and even cancer (Science Daily, 2005). Based on these findings, a spokeswoman from the American Dietetic Association stated that

"if a person is concerned about the health aspects of HNE, then my recommendations would be to never heat any oil to the point of smoking and, as far as cooking at home goes, just use the oil one time. And avoid eating fried foods in restaurants" (Mundell, 2006).

HNE has never been discovered in heated palm oil.

## 2) Palm Oil Lowers Plasma And Lipoprotein Cholesterols

For the prevention of heart diseases, surprisingly palm olein is equally as effective as olive, rapeseed and canola oils which are touted to be among the healthiest of the edible oils in maintaining desirable LDL (low density lipoprotein) and HDL (high density lipoprotein) in the human body (Ng *et al.*, 1992; Choudhury *et al.*, 1995; Truswell, *et al.*, 1993). Olive oil is regarded as the gold standard among the edible oils because of its association with a lower incidence of heart disease among the Mediterranean population. The presence of a high amount of monounsaturated oleic acid (C18:1), a well known cholesterol-lowering agent in olive oil is responsible for the cholesterol lowering effects of this oil. In contrast, palm olein with its 47-53% oleic acid shows equal effects in modulating plasma

and lipoprotein cholesterols compared to olive (70% oleic acid), canola (65% oleic acid) and rapeseed (60% oleic acid) oils. The findings suggest that palm olein is a good choice, to replace olive, canola and rapeseed oils, to maintain plasma and lipoprotein cholesterols in the human body.

## 3) Health and Medicinal Values of Palm Oil

Palm oil is a nutrition packed vegetable oil. Its minor components (about 1%) provide both health and medicinal values that are not commonly found in other vegetable oils (Table 2). Carotenoids and vitamin E (tocopherols and tocotrienols) are the most important minor components in palm oil.

Component	Concentration (ppm)	Health/Medicinal Values
Tocols (Vitanin E)	600-1000	Vit E, powerful antioxidant, anti cancer
Carotenoids	500-700	Pro vitamin A, antioxidant
Phytosterols	300-620	Prevent cholesterol absorption
Squalene	250-540	Powerful antioxidant
Coenzyme (Ubiquinones)	10-80	Energy booster
Lecithin (phospholipids)	20-100	Food emulsifier

 Table 2
 Valuable minor components in crude palm oil

Choo et al., 2007; Palm Oil Information Series, 2000

### Carotenoids – pro Vitamin A

Crude palm oil (CPO) is one of the richest sources of carotenoids with a concentration of 500-700 ppm (see Table 3). It has 15 times more retinol-

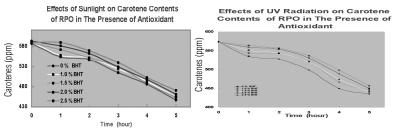
equivalent than carrots and 50 times more than tomatoes. No other vegetable oils and plant sources contain as much carotenoids as CPO. The human body uses carotenoids as vitamin A. Since carotenes dissolve in oil, the bioavailability of carotenes from palm oil is the highest among plant sources. Carotenoids also show antioxidant properties, protecting cells and tissues from free radicals, which could cause cancer (Krinsky, 1993; Ziegler, 1993; Greenberg, 1990). Thus, CPO is the best source of Vitamin A with added anti cancer properties although studies have shown that carotenes are unstable under sunlight (Dzulkefly and Hamdan, 1999; Dzulkefly, 1999c; Hussein *et al.*, 2001). About 24% of carotenes are destroyed by UV radiation in sunlight after 5 hours of exposure (Fig. 4). While carotene supplements are already available in the market, studies to isolate pure carotenes from CPO with high efficiency are still ongoing. In our previous work, we discovered that after transesterification of CPO with methanol, and with the correct amount of added methanol and water, the carotenes float on top of the solution and can easily be siphoned off (Dzulkefly and Abdullah, 2007). This method is simple and can be used to extract carotenes in high yields.

Food	$\mu$ g Retinol Eq/100g E.P
Oranges	21
Bananas	50
Tomatoes	130
Carrots	400
Red Palm Oil	5,000
CPO	6,700

Table 3 Vitamin A content of some selected sources

Souce: Palm Oil Information Series, 2000

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#### Vitamin E – anti ageing and anti cancer

Probably the most exciting thing about palm oil is the presence of 'super' vitamin E comprising of tocopherols and tocotrienols. Tocopherols and tocotrienols (each has four isomers: alpha, beta, gamma and delta) have the same chemical formula but are different in the number of double bonds (Fig. 5). Vitamin E is well known for its powerful antioxidant properties and is capable of neutralizing (quenching) free radicals in biological membranes, thus delaying the ageing process. Free radicals, generated in the body are capable of interacting and destroying body tissues that lead to the aging process. With sufficient presence of the antioxidant, the accelerated aging process can be stopped. In the vitamin E group, alpha-tocopherol is considered to be the more active antioxidant in neutralizing free radicals.

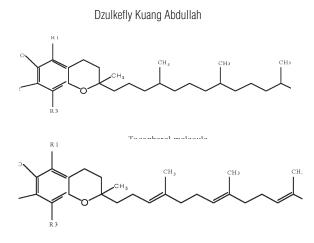


Figure 5 Chemical structures of tocopherol and tocotrienol.

However, recent findings have suggested that tocotrienol is the more powerful antioxidant. This miraculous compound has attracted the attention of researchers worldwide such that studies are constantly revealing more and more benefits of tocotrienols. It is now known that tocotrienols, which are found abundantly only in palm oil (see Table 4), possess both antioxidant and anti cancer properties (Komiyama *et al.*, 1989; Guthrie *et al.*, 1993; Goh et al, 1994; Kato *et al.*, 1985; Kaku *et al.*, 1999). Here are some of the most exciting findings about tocotrienols:

## • Anti Cancer Properties

Scientists and nutritionists, backed by extensive published papers agree that tocotrienols are effective anti cancer agents and have been shown to inhibit human breast cancer cell lines whereby gamma-tocotrienol is 3 times more potent in inhibiting the growth of human breast cancer cultured-cells than Tamoxifen (a drug widely used in the treatment of breast cancer) (Carroll, 1995; Guthrie, 1997a,b; Nesaretnam *et al.*, 1998). Delta-tocotrienol was found to be the most effective in inhibiting human breast cancer and liver cancer cells (Kline, 1999).

## Potent Natural Antioxidant

Alpha-tocotrienol is 40-60 times more potent than alpha-tocopherol as an antioxidant in preventing lipid peroxidation. However, delta-tocotrienol is the most potent antioxidant of all of the commercially available tocopherols and tocotrienols.

## • Anti Aging Agent

Protects skin from damage and aging caused by UV or oxidative rays, by neutralizing the free radicals generated in the skin.

### • Reversing Arteriosclerosis

Palm-based tocotrienols is the first natural compound, as shown by human studies, to have the ability to reverse arteriosclerosis, hence reducing the risk of arteriosclerosis and stroke.

### • Inhibit Platelet Aggregation

Oils & Fats	alpha-T	gamma-T3	Total
	(ppm)	(ppm)	(ppm)
Palm oil	152	439	591
Soybean oil	101	-	101
Cottonseed oil	389	-	389
Olive oil	51	-	51
Peanut oil	130	-	130
Corn oil	112	-	112
Sunflower oil	487	-	487
Coconut oil	5	19	24

 
 Table 4
 alpha-Tocopherol (T) and gamma-Tocotrienal (T3) Content of Some Vegetable Oils

Source: Minyak sawit fakta sebenar, MPOB, 1987

While a combination of tocopherols and tocotrienols, as in CPO, exhibits the

most powerful and effective antioxidant, anti aging and anti cancer properties, the current refining practice in the industry removes almost all of them from the palm oil. Thus, to benefit from the health values of palm oil we should change the norm from using refined oil to crude palm oil in daily cooking.

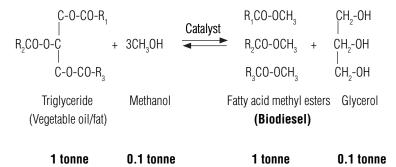
# BIODIESEL- *NATURE'S GIFT TO MALAYSIA, AND MALAYSIA'S GIFT TO THE WORLD*

The current high energy prices and global economic growth combined with the environmental issues have created an environment where biofuels are an increasingly viable alternative to petroleum fuels. Efforts are under way in many countries, particularly in Europe and the USA, to convert vegetable oils into biodiesel as a substitute for petrodiesel. Malaysia has started a biodiesel program with the launching of the National Biofuel Policy in March 2006, and at the same has introduced the new Malaysian-made biodiesel, the so-called Envo Diesel or B5 fuel. Biodiesel is environmentally friendly. Its combustion produces less smoke and less toxic gases, and thus is good for the environment.

## What is biodiesel?

Biodiesel is referred to as methyl esters of long chain fatty acids derived from vegetable oils or animal fats for use in diesel engines (Krawczyk, 1996). It is commonly prepared by transesterification of oils or fats with methanol in the presence of a catalyst to produce fatty acid methyl esters (biodiesel) and glycerol. This process converts approximately 1 tonne of vegetable oil into 1 tonne of biodiesel.

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Research on biodiesel has progressed rapidly in Europe and the USA. Fatty acid methyl esters of soybean (Alcantara *et al.*, 2000, Clark *et al.*, 1984), rapeseed (Korbitz, 1999), sunflower (Mittelbach, 1990), safflower (Isugur, *et al.*, 1994) and palm oil (Choo *et al.*, 2000; Crabbe *et al.*, 2001) are among the most extensively investigated biodiesel for internal combustion engines. There are many ways to convert vegetable oils into biodiesel fuel. Some of these are:

- Chemical methods such as *trans*esterification reaction with methanol to produce methyl ester derivative, amidation reaction using diethylemine, and pyrolysis to obtain paraffin and olefin.
- 2) Physical methods such as blending with diesel fuel, use in pure form (unmodified) and formation of microemulsion with alcohols.
- 3) Enzymatic methods

The success of the biofuel industry depends on many critical factors; among which is the availability of raw materials. Converting vegetable oils into biofuels means converting agricultural outputs into energy. Traditionally, the focus of agriculture is to provide food, and the outputs are usually dependent on demand. Using vegetable oils for biofuel means that for the first time, a major portion of agricultural outputs will not depend on food demand, but will respond to the increasing global need for more energy. Since production of biofuels consume very large quantities of vegetable oils, where approximately

one tonne of vegetable oil is needed to produce one tonne of biodiesel, it is likely that the price of feed stocks will rise substantially. In the case of palm oil for example, the average price of CPO used to be about RM1600 per tonne in 2006 but it has now risen to about RM3000/tonne in the advent of the biodiesel era. For certain vegetable oils, where the production capacity is low, this situation (price increase) is intolerable when considering that the oil is also needed as food. Shane (2007) stated that,

"A critical variable in the viability of biofuels is a plentiful supply of raw materials at a competitive price.....and 80 percent of the cost of producing biodiesel is raw materials cost".

The question now is: is there any <u>viable source</u> with <u>substantial supply</u> of raw materials to meet the growing global demand for biofuels? The answer is yes, palm oil has the advantage over other conventionally used oil crops. There is evidence showing that besides having superior fuel-related properties, palm oil can provide a huge and constant supply of raw materials for the growing biofuel industry.

## Availability - palm oil is a high yield crop

In 2006, Malaysia alone produced more than 15.9 million tonnes of CPO, while world production was more than 35 million tones (see Fig. 6). This drastic increase of palm oil production is due to the fact that oil palm produces a much higher yield than other oil crops in the world. The normal yield of palm oil per hectare in Malaysia is about 3.9 tonnes whereas the average soybean oil yield per hectare in the USA is only about 0.5 tonnes. The yield of other oilseed crops is far below 1.5 tonnes per hectare (see Table 5). Despite competition with food uses, our production of palm oil is still sufficient for biofuel purposes. Thus, palm oil is viable and guarantees a constant supply of feed stock for biodiesel demand.

Palm Oil: Still The Best Choice

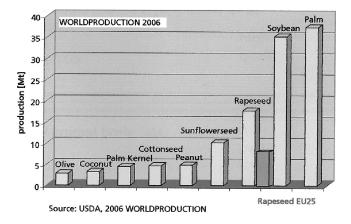


Figure 6 Palm oil leading other vegetable oils in world production in 2006

Crops	Average Oil Yield (tons/hed	
Soybean (USA)	0.38 - 0.46	
Palm oil (Malaysia)	3.74 - 3.93	
Sunflower (Argentina)	0.48 - 0.66	
Rapeseed (Canada)	0.40 - 0.67	
Rapeseed (EU)	1.33	
Cottenseed (USA)	0.14	
Peanut (USA)	0.78	
Jatropha	1.44	

 Table 5
 Average oil yield per hectare of oilseed crops

Choo et al., 2007; Law, 1986

## Competitive Production Cost - Positive Energy Balance

Interestingly, palm oil is still being produced on a positive energy balance (energy output/input ratio), when calculated based on the energy input such as fertilizer, diesel for machinery and other production cost, to produce a unit of

output energy. The energy output/input ratio for palm oil is remarkably high 9:1, compared to only about 4:1 for corn, soybean and rapeseed oils (see Table 6). Therefore, palm oil can be produced on a positive energy balance, compared to other competing vegetable oils. Palm oil is a real energy 'store', whereas other crops have a very low output to input energy ratio. High energy ratio, 9:1 means palm oil is very sustainable and is the most energy-efficient crop. Thus, palm oil is most viable to be produced in large quantity for biodiesel feed stock.

Vegetable oils	Energy Output/Energy Input Ratio
Peanut (USA)	2.26
Soybean(USA)	4.33
Palm (Malaysia)*	9.0
Cotton seed	1.76
Corn	3.95
Sunflower	3.50
Safflower	3.39
Rapeseed (Canada)	4.18

 Table 6
 Energy output/energy input ratios for vegetable oil crops<sup>@</sup>

@Bhattacharyya and Reddy, 1994

\* Yusof Basiron, Symbiosis, October 2006, p. 4

## Fuel-Related Properties of Palm Oil and Palm Oil Products

The fuel-related properties of some vegetable oils are listed in Table 7. Generally, the kinematics viscosity of vegetable oils is relatively high (ranges between 30 to 40 mm<sup>2</sup>/s) compared to petrodiesel. The reason is mainly due to their large molecular mass and chemical structure. The molecular weights of vegetable oils (average 600 to 900) are three or more times higher than that of petrodiesel. As a result, their heat contents are low (39 to 40 MJ/kg) when compared to petrodiesel (about 45 MJ/kg). Nevertheless, for palm oil (Table 7), the heat content and kinematics viscosity are comparable to other vegetable oils, if not to those of petrodiesel.

#### Palm Oil: Still The Best Choice

Vegetable oil	Kinematic Viscosity (mm²/s)	Heat Content (MJ/kg)
Diesel	2.85 - 7.5	45.3
Sunflower	34.9	39.5
Soya bean	33.9	40.9
Winter rapeseed	51.0	39.9
Palm oil	39.6	39.4
Cotton seed	33.5	44.0
Oleic safflower	41.2	39.5
Neem oil	140.3	41.6
Peanut	39.6	39.8

**Table 7** Properties of some vegetable oils compared to diesel fuel

Source: Srivastava and Prasad , 2000; Bhattacharyya and Reddy, 1994

In contrast, if we look at the methyl ester derivatives of vegetable oils (biodiesel), their heat content and kinematics viscosity are almost similar to that of petrodiesel (see Table 8). However, the cetane numbers of biodiesels (45 to 60) are better than that of petrodiesel (42), which means biodiesels have short ignition delay, a criteria for better performance. Palm oil-based biodiesels show superior fuel quality, at least in terms of viscosity, heat content and cetane number. Again, judging from this aspect (fuel properties) palm oil-based biodiesel is a strong candidate to replace petrodiesel compared to other vegetable oils.

Vegetable oil methyl ester	Kinematic Viscosity (mm²/s)	Heating Value (MJ/I)	Cetane Number	Cloud Point (°C)
Peanut Soya bean Palm Crude palm oil Crude palm stearin	4.9 4.5 <b>5.7</b> <b>4.5</b> <b>4.6</b>	33.6 33.5 <b>33.5</b> 40.1 <sup>*</sup> 39.9*	54 45 <b>62</b> 50.0 52.0	5 1 <b>13</b>
Sunflower Babassu	4.6 3.6	33.5 31.8	49 63	1 4

	Table 8	Fuel-related	properties	of vegetable oi	l methyl es	ters (biodiesels)#
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<sup>\*</sup>MJ/kg; <sup>#</sup>Srivastava and Prasad, 2000; Cetane number of diesel fuel is 42

In Malaysia, the production of biodiesel has been progressing rapidly. Extensive studies have been conducted by the Malaysia Palm Oil Board (MPOB) since 1982 to transform palm oil into biodiesel (Choo *et al.*, 2000). This process involves transesterification of crude palm oil into palm oil methyl esters, followed by testing and evaluation of the fuel. Palm methyl esters, either in crude or distilled forms, were used during testing and field trials. While performance of palm biodiesel was found to be better than petrodiesel in terms of exhaust emission, the use of neat crude palm methyl esters as fuel was not encouraging due to the high production cost. Subsequently, unmodified CPO was tested on diesel engines (Ahmad and Salmah, 1995). Again, the overall performance was not encouraging. Combination of high viscosity and low volatility of unmodified CPO led to major problems being encountered during the field trial. Among them were:

- Poor cold-engine start up
- Poor atomization
- Incomplete combustion and
- Misfire and ignition delay

The situation worsens when the crude oil crystallized, particularly in the mornings. The melting temperature of CPO is about 33-39 °C, and it solidifies at ambient temperature (about 29 °C in Malaysia). Further, the use of CPO or crude palm methyl esters as fuel will also cause a great loss of phytonutrients. For every 1 tonne of methyl esters burnt as fuel, we also burn away some amount of phytonutrients (see Table 9).

Phytonutrients	Amount burnt	Cost
Carotenoids	0.6 kg	US 200/kg (30% purity)
Vitamin E	0.8 kg	US 500/kg
Phytosterols	0.5 kg	US 25/kg (Industrial grade)
Squalene	0.4 kg	US 33/kg (Nutraceutical grade)
Phospholipids	0.06 kg	US 25/kg (Nutraceutical grade)

 Table 9
 Market price and amount of phytonutrients burnt for every tonne of methyl esters burnt

Source: Choo et al., 2007

Based on the current market value of the phytonutrients (see Table 9), it is estimated that for every 1 tonne of crude palm oil burnt as fuel, the value of accompanying phytonutrients burnt is about **US 770 (RM 3,400)** (Choo *et al.*, 2007).

It is therefore of great interest to find the best technology to formulate CPO or its products into a stable solution to be used as biodiesel. Currently, Malaysia has produced a biofuel, the so-called Envo Diesel (B5). This new biodiesel is a blend of 5% palm olein with 95% petrodiesel. In contrast, EU's B5 blends 5% methyl ester with 95% petrodiesel. Diesel engine manufacturers prefer the use of palm oil methyl ester blends, as diesel engines are designed to handle 5% neat methyl esters, meeting the EN14214 biodiesel standard, which palm oil cannot meet due to the high production cost of palm methyl

esters. In fact, Malaysia's move to introduce B5 diesel fuel is not so much to save the environment but rather to siphon off excess supply and thus, help stabilize palm oil prices (Yusof Basiron, 2006). Another exciting development in palm-based biodiesel technology is that Malaysia has managed to develop a process to produce low pour point (-21°C - 0°C) palm biodiesel which is suitable for temperate countries (Choo *et al.*, 2007).

Despite various breakthroughs in biofuel technologies, Malaysia is still looking for a cheap, efficient and simple technology for biofuel production in order to remain competitive. We have recently studied microemulsification techniques to formulate palm oil-based biofuel (Dzulkefly et al, 2002 a,b,c). Microemulsion is an isotropic, clear or translucent thermodynamically stable dispersion of oil, water, surfactant and often a small amphiphile or cosurfactant (Schwab *et al.*, 1987). Methanol and ethanol are fuel extenders but less soluble in vegetable oils. Their solubility can be increased substantially when a suitable amphiphile is added to the system forming a microemulsion (Vesala and Rosenholm, 1985; Schwab and Pryde, 1985; Dunn and Bagby, 1994). Microemulsions of methanol or ethanol with vegetable oils can perform as well as diesel fuel (Srivastiva and Prasad, 2000). In our study, methanol or ethanol was solubilised in palm oils (crude palm oil, RBD palm oil, red palm oil and palm olein) in the presence of co-solvents (alkanols,  $C_4-C_{12}$ ) to form microemulsions (see Fig. 7).

Palm Oil: Still The Best Choice

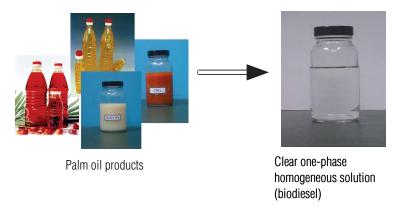
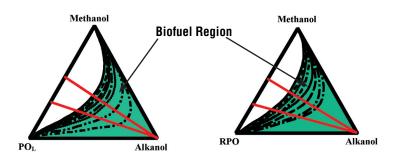


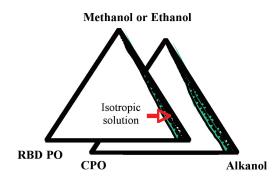
Figure 7 Formation of biofuel by microemulsification process using palm oil products, surfactant, co-surfactant and fuel extenders.

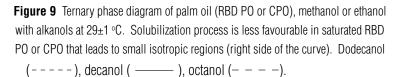
Results have shown that palm olein  $(PO_L)$  and red palm oil (RPO) are easily solubilised in methanol and ethanol forming large microemulsion regions (see Fig. 8). Similar results were obtained when alkanols were replaced with mixed fatty alcohol/alkanol. In contrast, the high viscosity of CPO and RBD PO are difficult to solubilise in methanol or ethanol, thus forming very small microemulsion regions (Fig. 9).





**Figure 8** Ternary phase diagrams of PO<sub>L</sub> and RPO/methanol/alkanol systems showing isotropic regions (rightside of the curve) at 29±1 °C. Dodecanol (-----), decanol (-----), octanol (----), octan-2-ol (------), hexanol (------), pentanol (------), butanol (-------) and t-butanol (------).



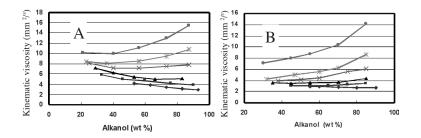


With microemulsion systems the viscosity of PO, and RPO solutions

(measured on the selected points along the lines A and B, Fig. 9) were significantly reduced. In a system containing  $PO_1$ / methanol/butanol (Fig.

10) the kinematics viscosity of PO<sub>L</sub> solution was reduced from 72.7 mm<sup>2</sup>s<sup>-1</sup> to the value allowable for No. 2 diesel fuel, 1.9 - 4.1 mm<sup>2</sup>s<sup>-1</sup> (the range specified by ASTM) (Dunn et al, 1994). Similarly for the RPO system, the kinematics viscosity was reduced from 43.7 mm<sup>2</sup>s<sup>-1</sup> to that of a No. 2 diesel fuel. We have also shown that for the ethanol system the kinematics viscosity was slightly higher than that of the methanol system but the values are still within ranges specified by ASTM.

With respect to isotropic regions and kinematics viscosity, microemulsion systems of PO<sub>L</sub>/methanol/butanol and RPO/methanol/butanol could be developed into a palm based biofuel. The systems are stable down to 15 °C. Production of biofuel by microemulsion technique does not require any heating or chemical reaction, but just physical mixing, and thus it is a low cost process.



**Figure 10** Kinematics viscosities of isotropic solutions at  $29 \pm 1 \, {}^{\circ}$ C for **A**: PO<sub>L</sub>/ methanol/alkanol and **B**; RPO/methanol/alkanol systems at ratio of oil/methanol of 50:50 wt%. Dodecanol, •; decanol, ; octanol, ×; hexanol, **A**; pentanol, **B**; butanol, **•** 

# PALM OIL-CARBOHYDRATE INTERACTIONS: SOLVENTLESS TRANSTERIFICATION TECHNIQUE

Of all the organic compounds in nature, carbohydrates are the most abundant. Among the carbohydrate components, glucose and starch are finding increasing

industrial applications because of the broad range of functional properties they exhibit. To widen their uses, carbohydrate structures need to be modified so as to alter their physical and chemical properties to suit new uses. However, the stability of the glucose ring of carbohydrates and the availability of mutual solvents for both carbohydrate and modifier make modifications difficult. Therefore, we have developed a technique to modify glucose and starch by using a solvent-free transesterification method, for the production of palm based surfactants and a biodegradable plastic filler, using formic acid as a ring activator. The major advantage of this process is that it does not require solvents as the reactant itself (used in excess) behaves like a solvent.

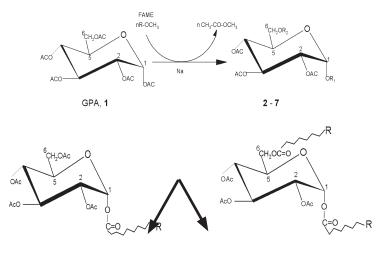
## Palm Glucose Fatty Esters - The Nonionic Surfactants

In our continuing search for new and novel surfactants, we have successfully synthesized food and pharmaceutical grade glucose fatty esters of palm and palm kernel oils through a solvent-free process (Dzulkefly *et al.*, 1999; Obaje *et al.*, 1999; Dzulkefly *et al.*, 2000; Dzulkefly *et al.*, 2001). Glucose fatty esters are good surfactants (Bobalek, 1977; De Luca *et al.*, 1997; Ducret, *et al.*, 1995; Akoh and Swanson, 1990), but the commercial production of these surfactants remain a big challenge. The methods developed, so far, for the production of glucose-based fatty esters, are still facing problems such as:

- (i) Finding a nontoxic mutual solvent for both the fatty acids and the carbohydrate. Commonly used solvents such as formamide, dimethylformamide, pyridine, dimethlyacetamide etc. are toxic and their residues are unsafe for food and pharmaceutical applications.
- (ii) Avoiding caramelization of the glucose at high temperatures.

To overcome these problems, we have developed a one stage solvent-free, low temperature (less than  $100 \,^{\circ}$ C) interesterification process yielding products of up to 80%. The reaction scheme for the interesterification and the two major

products are shown in Figure. 11. The products which are non-cytotoxic, exhibited mild antimicrobial activities and are potential food emulsifiers.



**Product A**: Mono-substituted AGFE (1-O-fattyacyl 2,3,4,6-acetyl  $\alpha$ -D-glucopyranose)

**Product B**: Di-substituted AGFE (1,6-O-fattyacyl 2,3,4-acetyl α-D-glucopyranose)

Figure 11 Reaction scheme for interesterification of fatty acid methyl esters (FAME) of palm oil with glucosepentaacetate and the molecular structures of the major products A and B.

During the course of this work we developed a novel technique for structural elucidation of the reaction products known as Substituent-Induced Changes (SIC) Chemical Shift. The structural elucidation of the reaction products has always remained difficult. The chemical methods employed so far are not straight forward and sometimes lead to ambiguous conclusions. However, by systematically combining the <sup>13</sup>C-NMR technique with heteronuclear shift correlation (HETCO) and heteronuclear multiple bond correlation (HMBC) data to assign the chemical shifts of the pyranosyl ring-proton and carbon atoms, and

those of carbonyl carbon atoms, a novel method was developed (Dzulkefly *et al.*, 1999; Dzulkefly *et. al.*, 2000; Obaje *et al.*, 2000a,b). The method is simple, solely based on physical measurements (NMR data) and provides positive identification of the products. The structures of the interesterification products were assigned as shown in Figure 11. If I may, I would like to share with you one of the comments made by the reviewer:

"The paper reports an interesting method for assigning structures and the composition of mixtures of mono and difatty acid esters of peracetylated  $\alpha$ -D-glucopyranoses. The use of HMBC as a tool to probe the induced shifts on the carbonyl carbon is **very novel**. This work will make an excellent contribution to JAOCS".

## Sago Fatty Esters - A Potential Filler For Biodegradable Plastics

Another interesting finding which resulted from the modification of carbohydrate is the sago fatty esters, filler for biodegradable plastics. The current petroleumbased plastics are resistant to biological degradation and their recycling is not economical. Thus, biodegradable plastic is a solution to the growing problem of disposal of petroleum-based plastics. Starch-based plastics are biodegradable. Microbes in the soil consume starch in the plastic and subsequently cut the plastic into small particles that can easily be degraded.

Blending neat sago starch with plastic material such as PVC resulted in poor mechanical properties (Aburto *et al.*, 1997), due to their immiscibility. Sago starch is a polar compound, whilst PVC is a non-polar material, and thus their blends are incompatible. To overcome this problem we chemically modified the sago starch by a solventless esterification method to produce non-polar sago fatty esters of different degrees of substitution (DS) with yields up to 80% (Dzulkefly *et al.*, 2007a,b; See *et al.*, 2007). The products were sago hexanoate with DS 1.3 (STHC1.3), sago octanoate with DS 1.2 (STOC1.2), sago lauroate

with DS 1.2 (STLC1.2) and sago lauroate with DS 0.6 (STLC0.6). The reaction scheme is shown in Figure 12.

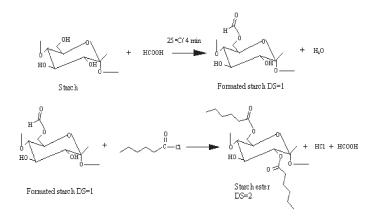


Figure 12 Reaction scheme for preparation of sago fatty esters



Figure 13 Waxy solid sago ester (A) and a biodegradable plastic film formed by sago ester/PVC blend (B).

Blending the products of non-polar sago fatty esters with PVC produces potential biodegradable plastic materials (see Fig. 13). The blends exhibit exciting properties such as:

- Good mechanical property with up to 20 wt % of sago esters content (whereby the blends retained 80% tensile strength of that pure PVC) (Fig. 14)
- Reduced water absorption capacity due to the existence of hydrophobic sago esters in the blends (Fig. 15)
- Good biodegradation properties (Fig. 16)

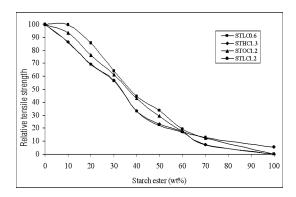


Figure 14 Relative tensile strength of PVC blended with sago fatty esters.

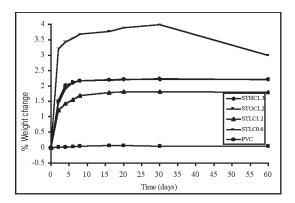
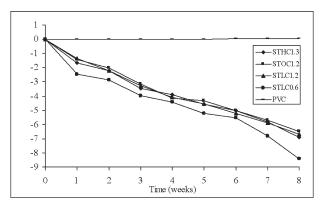


Figure 15 Water absorption of PVC/sago fatty ester blends. All blends are at 50/50 ratio. Water absorption is less than 4%.



**Figure 16** Weight loss of PVC/sago fatty ester blends relative to pure PVC. All blends are at 50/50 ratio. The blends show good biodegradation properties.

# CHALLENGES

# **Meeting Stringent Requirements**

While interest in biodiesel production is expanding rapidly, the biodiesel business is not really as lucrative as every one thinks. Biodiesel producers have to meet strict industry specifications, the European Standard (EN14214) or the USA (ASTM D6751) Standard for fuel-grade biodiesel. For EN14214 standard, the products have to comply with all 26 criteria set up by the European Union, before the fuel can be legally used in transportation vehicles. This ruling only benefits multinational companies and not the small companies which have to bear high costs. Additionally, while the focus is on alternative fuel as a solution to ever increasing oil prices, one tends to forget to take note that even the price of raw materials needed for the production of biodiesel has increased. Indeed, the biodiesel industry is not really beneficial to small Malaysian companies. For the local market, what we really need now is a low-cost biodiesel which can be easily produced and is suitable for use by tractors and other agricultural machineries. This low cost biodiesel can be made, for example, from used oil

and does not have to comply with any Standard Specification, and normally the diesel engines can tolerate small amounts of water that remain in the fuel during production. There is a company in Malaysia which is already supplying "portable biodiesel making machines". With this machine anybody can produce biodisel at home.

# **Biofuel Raw Materials**

Palm oil is used for food and fuel. The success of the biofuel industry very much depends on the availability and sustainability of raw materials. Agricultural outputs are normally associated with food. Using agricultural outputs for fuel, such as palm oil will compete with its other uses. Since biofuel consumes very large quantities of feedstock, converting more palm oil to biofuel will certainly affect the food industries. If the world demands for more biodiesel, palm oil production may not be in a position to meet the requirement. This is because the current Government policy has fixed a temporary quota (40%) on palm oil to be used as fuel to protect the food industries. At the same time, the Government also does not allow cutting down of virgin forests for palm oil production for biodiesel purposes, and thus, limits biodiesel output. The best solution to this constraint and in anticipation of the future high price of palm oil feed stock, is to search for new alternative biofuels with raw materials which are not in competition with other uses.

In Malaysia cassava and plant celluloses are yet to be explored and they are potential raw materials for bioethanol. The Cassava industry in Malaysia is almost disappearing. Cassava grows on any soil and its production is very cost effective and high yielding, with about 22 tonnes per hectare (Shane, 2007). As cassava is not in competition with other uses, the use of cassava for biofuel is very viable and would benefit the cassava industry.

However, it is more challenging to develop a new technology to convert plant cellulose into biofuel. Cellulose is a major component of plants but this natural polymer is resistant to break down. However, with appropriate technology, this polymer can be broken into its component sugars and fermented to produce "cellulosic ethanol". Cellulosic ethanol uses non-food plant materials such as woodchips, sawdust, biomass, agricultural and forestry residues or even municipal waste. While the technology is not yet commercially available, extensive research on cellulosic ethanol is already ongoing in the USA. The US government recently invested more than US\$300 million to develop a technology to convert corn stalks, wheat straw, barley straws, swithgrass and wood waste into bioethanol. Compared to the USA, Malaysia has distinct advantages for production of cellulosic ethanol. Being a tropical country, Malaysia has an abundance of trees where plenty of cellulose can be extracted to be used as raw materials for bioethanol.

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# BIOGRAPHY

**Professor Dzulkefly Kuang Abdullah** was born on 21<sup>st</sup> February 1952 in Jitra, Kedah where he received his primary education before moving to Sekolah Alam Shah, Cheras, Kuala Lumpur from 1968 to 1971 for his secondary education. He continued his tertiary education at Universiti Kebangsaan Malaysia (UKM) in 1972 where he obtained the B.Sc degree (Chemistry) in June 1975. After joining Universiti Putra Malaysia (formerly known as Universiti Pertanian Malaysia) as a tutor in October 1975, he then pursued a Diploma In Advanced Chemistry at North East Wales Institute of Technology (UK) in 1976. After completing his M Sc degree at The University Of Salford (UK) in 1977, he was appointed as a lecturer at The Department of Chemistry, Universiti Putra Malaysia (UPM) in December 1977. He served as a lecturer at the UPM, Sarawak Campus, Sarawak for two years from 1980 to 1982. Professor Dzulkefly obtained his PhD degree in Oils and Fats Chemistry from the University of Salford (UK) in 1988.

Since joining the Department of Chemistry, UPM, he has participated in various activities at both Faculty and University levels. Professor Dzulkefly was involved in the development of the curriculum for the undergraduate program in Chemistry as well as in the general staff development at the department. He actively conducts courses and workshops on Instrumentations and Laboratory Safety to improve competency among the laboratory staff and research community in UPM. His involvement in helping the Government to combat haze pollution from forest fires in 1997 is another great contribution to the Nation. He was among the scientists who conducted a study on "Haze Formation and Impacts", and was responsible to the Ministry of Science, Technology and The Environment Malaysia. Professor Dzulkefly was involved directly in preparing guidelines or recommendations, for installation of water sprinklers to reduce haze on all high-rise buildings in Kuala Lumpur city, which later became a law in Malaysia.

Professor Dzulkefly is also an active researcher. His research interest is in Oils and Fats Chemistry with particular reference to palm oil-based oleochemicals. His research thrust areas include Development of palm-based biodegradable surfactants, Biofuel, Emulsion and microemulsion systems of palm oil, Chemical modification of carbohydrates, Recovery of valuable components from wastes generated by the refining industry and Palm oil-based adjuvant in herbicide formulations. Currently, he is working on a project to convert plant cellulose into bioethanol. This project is aimed at utilizing abundant low-cost raw materials such as wood cellulose for biofuel production. Todate, he has published more than 74 papers in refereed journals and has written over 80 conference papers and articles in proceedings and magazines. He has also developed modules for Laboratory Safety and Instrumentation (GC and HPLC) Courses to be used by the "Unit Latihan Dalam Perkhidmatan, Jabatan Pendaftar, UPM". For his excellent work, Professor Dzulkefly has received many awards. These include Faculty and University Research Awards, The Lever Brothers (USA) Award, the American Oil Chemists' Society Award for outstanding research in biodegradable surfactants and the Excellent Service Award in 1997.

Besides research activities, Professor Dzulkefly lectures on various chemistry courses, inclusive of Industrial Chemistry, Physical Chemistry and Laboratory Safety at undergraduate and post-graduate levels. In addition to teaching, he has also edited papers for journals. He is also a member of The Malaysian Institute of Chemistry and The Malaysian Analyst Society.

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