



CHAPTER I

INTRODUCTION

There is a need for novel markers which are particularly suitable for water immiscible organic liquids such as petroleum fuels. These needs arise primarily from differing price or tax structures of different fuels or even the same fuel used for different purposes. For example, grades of oil are used interchangeably for heating oil or for diesel motor fuel. Fuels are sometimes mixed for the purpose of adulterating a higher priced product with a lower priced product, or for purpose of evading taxation by the addition of low-taxed light heating oil to highly taxed diesel.

These situations can lead to abuse to the tax laws and cheating by unscrupulous persons. There is also a need for marked fuels and to distinguish such marked liquid from the otherwise identical but unmarked substances, especially diesel fuel which is the biggest volume of fuel consumed in Thailand. Currently, there is no way to distinguish the taxed and untaxed products. Therefore, it is very important to find some markers for diesel fuel which enable authorized government organizations to differentiate between legal and illegal products.

There are several classes of diesel marker available on the market. This research will concentrate on a new potential type of markers based on palm oil and derivatives of palm oil. Since palm oil is a cheap, renewable resource and it has been tested as diesel fuel substitute for sometime, therefore, markers based on palm oil and its derivatives should be very interesting. It can be blended very well

with diesel fuel and it has high boiling point range that could be modified to match that of diesel fuel. Moreover, fatty acid profile in palm oil or its derivatives should give rise to unique finger print of markers and it can be used both for qualitative and quantitative analysis.

OBJECTIVE AND SCOPE OF RESEARCH :

The objective and scope of this research are :

1. To synthesize ester derivatives of palm oil as diesel fuel markers.
2. To characterize those ester derivatives using chemical, chromatographic and spectroscopic methods.
3. To evaluate the potential of using those esters as diesel marker by developing detection methods for both field test and laboratory confirmation.

1.1 DIESEL FUEL[1-3]

Diesel fuel is obtained from crude oil, which is a mixture of hydrocarbons such as benzene, pentane, hexane, heptane, toluene, propane and butane, which form crude oil vaporize at different temperatures. Diesel fuel has range boiling point at 150-360 °C.

Diesel fuel has two types, high speed diesel(Automotive Diesel Oil(ADO)), gas oil or solar oil, used in buses, pickups, trucks and low speed diesel(Industrial Diesel Oil(IDO)) used in water crafts and submarines.

1.2 MARKERS [4.7]

1.2.1 Characteristics of markers for petroleum fuels and other liquids

A marker is defined herein as a substance which can be dissolved in a liquid to be identified, then subsequently detected by performing a simple chemical or physical test on the tagged liquid.

The important characteristics of certain desirable markers for petroleum and other liquids :

1. are entirely foreign to the liquids.
2. can be supplied as highly concentrated solutions in compatible solvents.
3. are easily detected by a simple field test.
4. are not obscured by unstable natural components of the liquids.
5. are stable over the anticipated storage life of the tagged liquid (usually to six months).
6. have identities which can be confirmed by laboratory methods.

1.2.2 Markers for fuels

Markers are needed to clearly distinguish liquid chemically or physically. Fuels are dyed or tagged to provide visually distinctive brand and grade denomination for commercial and safety reasons. For example, some lightly taxed products are tagged to distinguish them from higher taxed, deter fraudulent adulteration of premium grade products with low grade products, such as by blending kerosene, stove oil, or diesel fuel into regular grade gasoline.

Identification of particularly batches of bulk liquids for protection against theft is another valuable function of markers and dyed, particularly for identifying fuels owned by large government, military or commercial consumers.

Example markers for fuels :

Quinizarin and diphenylamine are fairly sensitive marking materials, with simple detection, but have disadvantage of poor solubility in nonpolar materials (less than 1 %).

Furfural has previously been used as a marker for middle distillate fuels. It is extracted by a 10 % solution of aniline in acetic acid to form a strongly colored bluish-red complex in the lower layer, this test has disadvantage. First, the slightest contamination of the fuel by residual furfural. Second, furfural is unstable in oil after storage period of three to six months. Third, middle distillate fuels tend to discolor appreciably during storage.

The markers[4] is added to a petroleum fuels in a concentration of about 12 part per million, in which it dissolves without imparting any color to the fuel or otherwise indicating its presence to the naked eye. Detection procedure may be confirmed by extracting the aqueous acidic. The aqueous phase containing the marker is treated with a small of diazotized 2-chlor-4-nitroaniline whereupon a characteristic pink coloration develops instantly. Testing of markers are to be performed by enforcement officers, an effective diazo reagent must be stable for lengthy periods under an ambient temperature condition.

The marker compounds[5] are typically added to liquids to be tagged at a concentration from about 1 ppm to about 15 ppm. However, fuels containing the minimum detectable and visible concentration of the pure tagging compound (less than 1 ppm). The amount tagging compound is not critical, provided that it is dissolved or stably suspended in the solvent and is as concentrated as its solubility permits. Two reagents for use herein are disclosed. The alkaline, fuel immisible reagent is specific to these markers and it is bluish red.

Liquid petroleum products are tagged with marker of the general class of chemicals described as phenylazophenol[6]. Marker at levels of about 0.25 ppm above are added, detected by extraction with alkaline aqueous solution (NaOH or KOH). The marker reacted by alkaline producing color.

The marker[7] which are invisible in liquid petroleum products but that provide a distinctive fluorescence and/or colors when extracted form the petroleum product with an appropriate developing reagent. The esters markers of the present invention may be added to any liquid petroleum products such as fuels, lube oils and greases. Their presence is detected by strong base such as an alkali metal hydroxide or quaternary ammonium hydroxide. The base hydrolyses the esters and prompt formation of highly fluorescent.

1.3 PALM OIL[8,9]

The palm oil, *Elaeis guineensis*. The oil palm fruit is unusual in that it yield two distinct oils : palm kernel oil differs from the kernel and palm oil from the pulp (about 50 %). Palm oil is deep orange-red by large amount of carotene. It is used

in making vegetable, margarine, soap, and a small amount is used in marking thin plate and in aluminium sheet rolling.

1.3.1 Fatty acid composition of palm oil

Palm oil has saturated and unsaturated fatty acids with palmitic and oleic acids are the main component acids. More than 85 % of unsaturated fatty acids are located at the 2-position of the glycerol nucleus of triglyceride composition of palm oil. Both the glyceride structure and the FFA content affect the melting and plastic properties of palm oil.

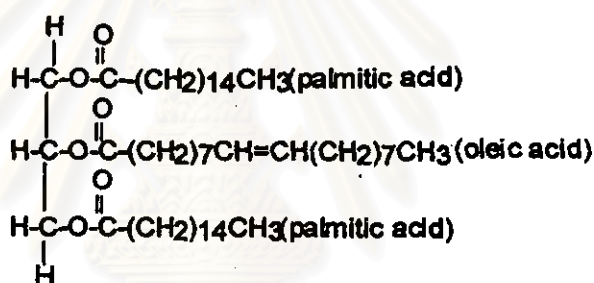
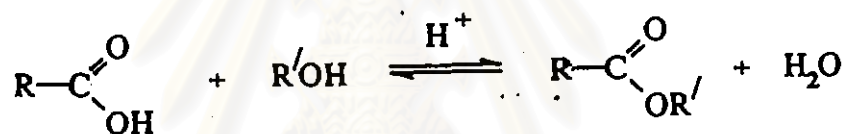


Table 1 Composition of fatty acid in palm oil

Common name	Synematic name	Formula	%
<u>Saturated</u>			
Myristic acid	tetradecanoic	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	0.6-1.6
Palmitic acid	hexadecanoic	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	32-45
Stearic acid	octadecanoic	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	3.7-5.5
<u>Unsaturated</u>			
Oleic acid	cis-9-octadecanoic	$ \begin{array}{c} \text{H} \quad \text{H} \\ \backslash \quad / \\ \text{C}=\text{C} \\ / \quad \backslash \\ \text{CH}_3(\text{CH}_2)_7 \quad (\text{CH}_2)_7\text{COOH} \end{array} $	39-42
Linoleic acid	cis-9,cis-12-ocdecanoic	$ \begin{array}{c} \text{H} \quad \text{H} \\ \backslash \quad / \\ \text{C}=\text{C} \\ / \quad \backslash \\ \text{CH}_3(\text{CH}_2)_3-\text{CH}_2 \quad (\text{CH}_2)_7\text{COOH} \\ \left[\quad \quad \quad \right]_2 \end{array} $	6-9

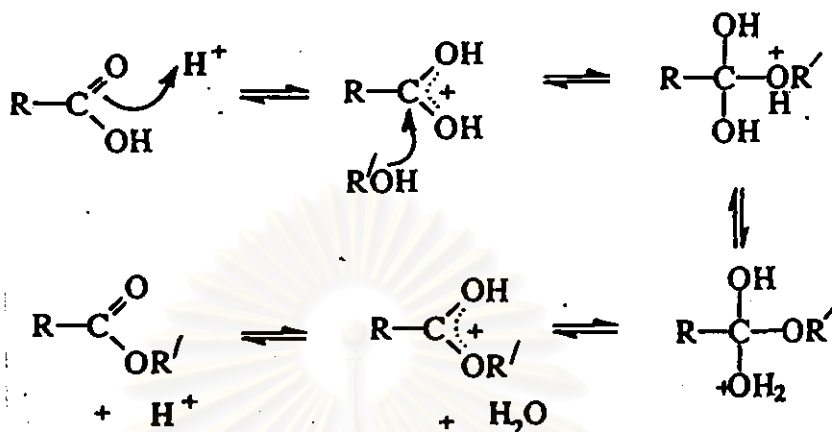
1.4 ESTERIFICATION[10-12]

The most usual method for the preparation of esters is the reaction of carboxylic acid and alcohol with elimination of water. Esters are also formed by a number of other reactions, including the use of acid anhydrides, acid chlorides, amides, nitriles, unsaturated hydrocarbons, ethers, aldehydes and ketones, and by dehydration of alcohols. For esters are prepared by alcoholysis and acidolysis(ester interchange). Esterification is a reversible reaction, but is driven to completion by using of excess alcohol and removal of water as it forms by azeotroping agent, e.g. toluene.



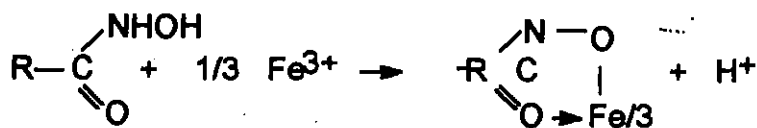
The uncatalysed reaction is usually too slow to be useful. The acid and alcohol can be reacted thermally, usually in the presence of a catalyst in an esterification reactor. Possible catalysts include sulfuric acid, *p*-toluene sulphonic acid, tetra alkyl titanate, anhydrous sodium hydrogen sulfate, phosphorous oxides and stannous octanoate.

For acid-catalyzed esterification



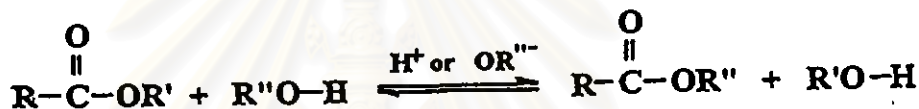
1.4.1 Determination of Esters[21,22]

The determination of esters, $RCOOR'$, is of importance because they occur in so many natural and manufactured products. The common method of determining esters is to heat sample with alkali hydroxides. It is designated a saponification. Another methods, especially adapted to hte determination of small amounts of esters, is the colorimetric one based on their reaction with hydroxylamine to form hydroxamic acid, which in turn reacts with ferric ion to form a red-colored complex.



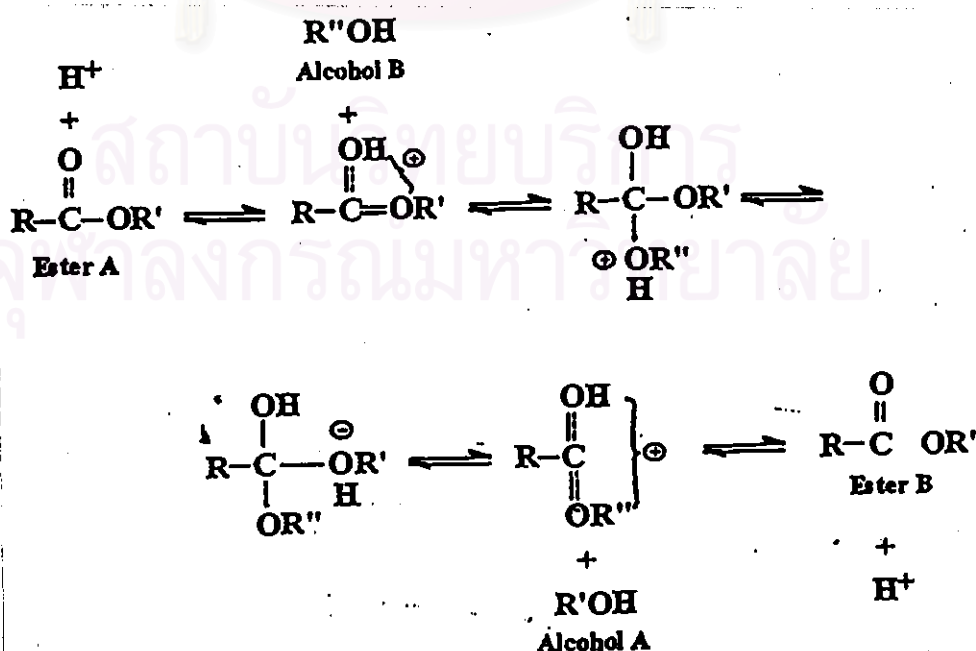
1.5 ESTER INTERCHANGE[14]

Ester interchange (re-, trans-, or interesterification) may be defined as a reaction between an ester and another compound, characterized by an exchange of alkoxy groups or of acyl groups, and resulting in the formation of different ester. In the transesterification of an acid, an alcohol acts as a nucleophilic reagent, in the hydrolysis of an ester, an alcohol is displaced by a nucleophilic reagent. Knowing this, we are not surprised to find that one alcohol is capable of displacing another alcohol from an ester.

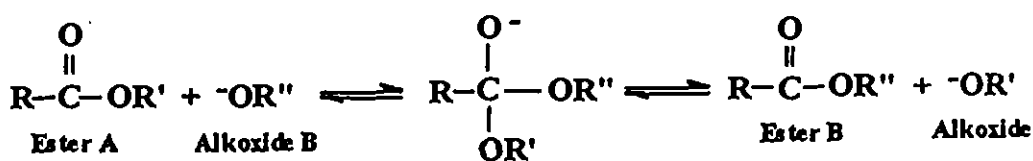


Transesterification is catalyzed by acid (H_2SO_4 or dry HCl) or base (alkoxide ion). The mechanism of these two reactions are exactly analogous to those we have already studied.

For acid-catalyzed transesterification



For base-catalyzed transesterification



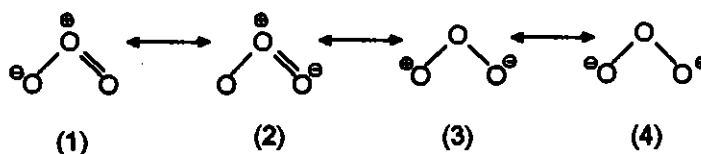
Transesterification is an equilibrium reaction. To shift the equilibrium to the right, it is necessary to use a large excess of the alcohol whose ester we wish to make, or to removed one of the products from the reaction mixture.

1.6 OZONIZATION REACTION[15-17]

1.6.1 Properties of Ozone

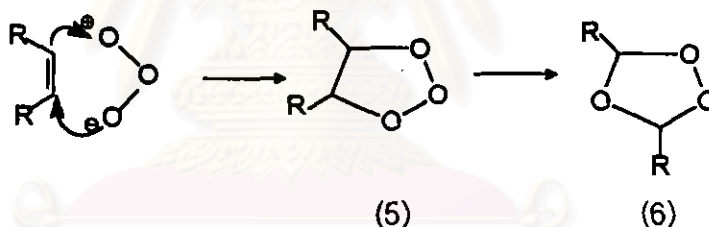
Ozone occurs in the atmosphere, but its concentration its too low for the atmosphere to be a practical source. Ozone is a colorless gas and dark blue liquid. It has characteristic sharp odor which is detected by the nose at levels that provide warning of toxic exposure. Ozone(O₃) is a powerful oxidizing agent. The value of ozone as an oxidant of olefins was established by Harries.

The ozone molecule is nonlinear with a bond angle of 116°. Ozone is best viewed as a resonances species with four contributions. In contrast to oxygen, it is not paramagnetic and the resonance forms that contribute to its structure posses paired eletrons. Forms (1) and (2) with a coordinate bond to the third oxygen might be expected to make a greater contribution but (3) and (4) each posses a terminal oxygen with only six electrons which account for the electrophilic nature of ozone exhibited in many of its reactions.

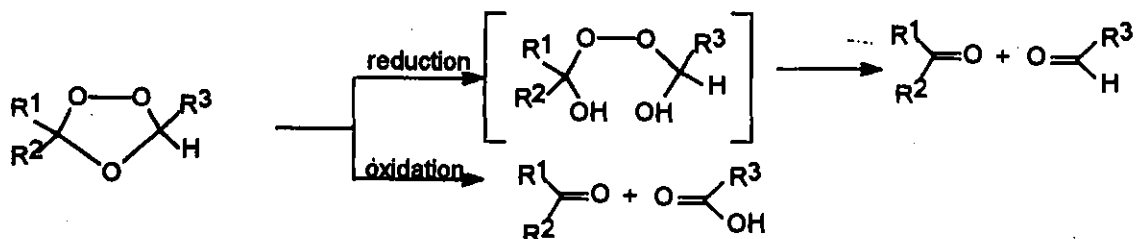


1.6.2 Reaction of Ozone

Since most application of ozonization have involved the oxidation of carbon-carbon double bond. Contributors (3) and (4) are important in reaction of alkene via 1,3-dipolar addition to give 1,2,3-trioxolane(5) and rapid rearranges to 1,2,4-trioxane better known as an ozonide(6).



An ozonide can be decomposed by four methods: 1) reduction, 2) hydrolysis, 3) oxidation, and 4) thermolysis.



The decomposition of ozonides and other ozonolysis products by oxidation leads to the formation of ketones or carboxylic acids. Dull studied such oxidizing agents as chromic acid, nitric acid, permanganate, hydrogen peroxide, Caro's acid, as well as catalytic oxidation. He concluded that alkaline permanganate and hydrogen peroxide were the best with the substrates studied. Permanganate has disadvantages with many substrates. Peroxycarboxylic acids have been introduced since Dull's studies and have been widely used.

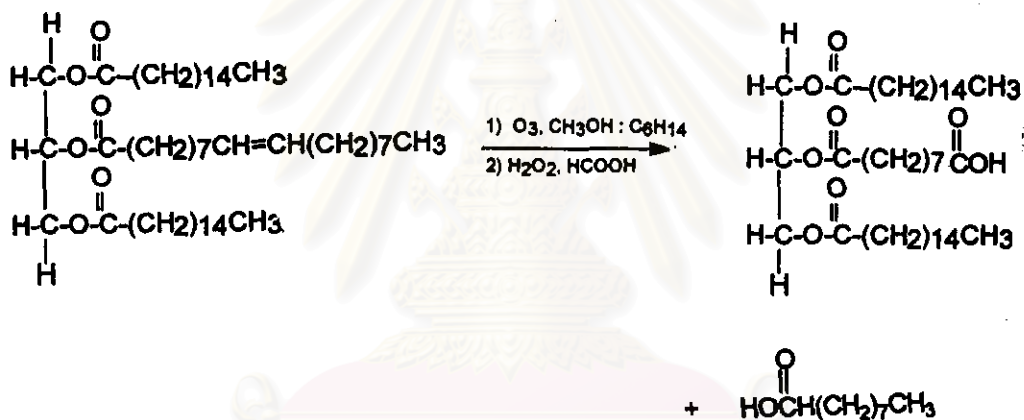
Bailey's method[18] for preparation of adipic acid by ozonolysis from cyclohexene. Oxidative decompositions in formic acid medium were the most satisfactory.

Frémery's method[19] for Emulsion Ozonization of Cycloolefins in Aqueous Alkaline Hydrogen Peroxide. This method was explored with cyclic mono- and polyolefins and condensed. Cyclic polyolefins by controlled ozonization gave olefinic dicarboxylic acids. The reaction involved two steps, the formation and accumulation of the ozonide in an inert solvent and the oxidation of the ozonide by peracid.

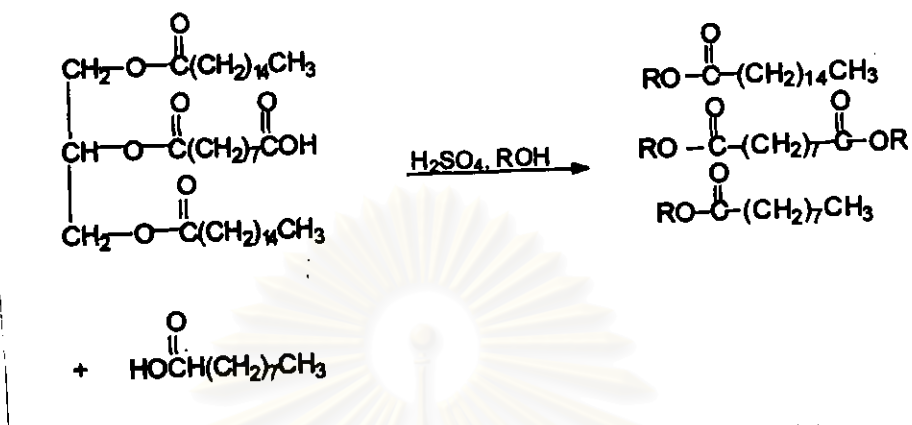
Albert L. and Philip Hill's method[20] for the preparation of aldehydes, ketones, and acids by ozone oxidation. Oxidation with ozone can be adapted to a practical preparation of aldehydes, ketones, and acids in good yields.

In this research, ester compounds will be synthesized via two steps, reacting carboxylic acids from palm oil after cleavage by ozonization and oxidation reaction, with alcohols by esterification and transesterification reactions. The products will be purified by column chromatography and characterization using FT-IR, NMR, GC-MS and GC.

First step



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Second step

ROH = CH₃OH, CH₃CH₂OH, CH₃CHOHCH₃, CH₃(CH₂)₂OH,
 CH₃CH₂CH₂CH₂(CH₂CH₃)CHCH₂OH

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