ALKYD RESINS FROM WASTE COOKING OIL

UBOLRAT WEERAWATSOPHON

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ABSTRACT

The purpose of this research was to prepare oil-modified alkyd resins using an alcoholysis process. Waste cooking oil as monobasic acid, glycerol as polyhydric alcohol, phthalic anhydride as dibasic acid and a mixture of NaOH, H_2O and glycerol as the catalyst were used. Important properties of oil such as acid value, iodine value and composition of fatty acids were investigated. The reaction trend was also studied at various times from the acid value of the mixture. Functional groups of the reactants and products were analyzed using FT-IR spectroscopy. The important properties such as acid value, viscosity and non-volatile matter were characterized by a standard method. The results were compared with alkyd resins from palm olein oil which use TISI 618-2529 (1986) as the standard for selecting suitable conditions. In addition, all data were statistically analyzed by 2 independent samples tests; Mann-Whitney Tests, at a 95% confidence interval.

Based on the results received, it can be concluded that waste cooking oil can be utilized as a raw material for alkyd resin production. The optimum condition was at 35%w/w oil with the reaction time of 160 min. These alkyd resins have a acid value, viscosity and non-volatile matter of 13.28 mg.KOH/g., 17.60 stoke and 59.05 %w/w, respectively. For alkyd resins from palm olein oil, they have an optimum condition at 35 %w/w oil, with 100 min. of reaction time. These alkyd resins have acid value, viscosity and non-volatile matter of 11.25 mg.KOH/g., 17.60 and 59.17 %w/w, respectively. Although alkyd resins from waste cooking oil (AR_WCO) used more reaction time than alkyd resins from palm olein oil (AR_PO), AR_WCO is more friendly environmentally than AR_PO because it is recycled waste. Therefore, it is reasonable to assume that waste cooking oil is a considerably better alternative for oil-modified alkyd resin production.

KEY WORDS: ALKYD RESIN/ ALCOHOLYSIS PROCESS/ BINDER/ WASTE UTILIZATION/ WASTE COOKING OIL/ PALM OLEIN OIL

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อัลคีดเรซินจากน้ำมันประกอบอาหารที่ใช้แล้ว (ALKYD RESINS FROM WASTE COOKING OIL)

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บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาถึงวิธีเตรียมออยล์โมดิไฟด์อัลคีดเรซินจากกรรมวิธีแอลกอฮอล์ไลซิส โดยมีน้ำมันประกอบอาหารที่ใช้แล้วเป็นกรดโมโนเบสิก กลีเซอรอลเป็นโพลิไฮดริกแอลกอฮอล์ พทาลิกแอนไฮไดรด์เป็นกรดไดเบสิก และมีของผสมระหว่างโซเดียมไฮดรอกไซด์ น้ำ และกลีเซอรอลเป็นตัวเร่งปฏิกิริยา โดยได้ศึกษาถึงสมบัติต่างๆ ที่สำคัญของน้ำมัน ได้แก่ ค่าของกรด ค่าไอโอดีน ชนิดและปริมาณของกรดไขมัน และได้ศึกษาถึงแนวโน้มของการเกิดปฏิกิริยาจากค่าของกรดของของผสม ณ เวลาต่างๆ และนำอัลคีดเรซินที่เตรียมได้มาวิเคราะห์หาหมู่ที่แสดงสมบัติเฉพาะตัว และสมบัติต่างๆ ได้แก่ ค่าของกรด ความหนืด และปริมาณสารที่ไม่ระเหย จากนั้นเปรียบเทียบผลที่ได้กับอัลคีดเรซินที่เตรียมจากน้ำมันประกอบอาหารที่ยังไม่ผ่านการใช้งาน โดยอาศัยมาตรฐานผลิตภัณฑ์อุตสาหกรรมสารยึดสำหรับสีและวาร์นิช:อัลคีดเรซิน (มอก.618-2529) เป็นเกณฑ์ในการกำหนดสภาวะที่เหมาะสม สำหรับการวิเคราะห์ข้อมูลใช้ Two Independent Samples Tests; Mann-Whitney Test ที่ระดับความเชื่อมั่น ร้อยละ 95

จากผลการทดลองสรุปได้ว่า น้ำมันประกอบอาหารที่ใช้แล้วสามารถนำมาใช้เป็นวัตถุดิบในกระบวนการผลิตอัลคีดเรซินได้ โดยมีสภาวะที่เหมาะสมคือที่ปริมาณน้ำมัน 35%w/w ระยะเวลาที่ใช้ในการทำปฏิกิริยา 160 นาที อัลคีดเรซินที่เตรียมได้มีค่าของกรด ความหนืดและปริมาณสารที่ไม่ระเหยเท่ากับ 13.28 มก.KOH/ก. 17.60 สโตกส์ และ 59.05 %w/w ตามลำดับ ในขณะที่อัลคีดเรซินที่เตรียมได้จากน้ำมันประกอบอาหารที่ยังไม่ผ่านการใช้งาน มีสภาวะที่เหมาะสมที่ปริมาณน้ำมัน 35%w/w เช่นเดียวกัน แต่มีระยะเวลาในการทำปฏิกิริยาที่ 100 นาที โดยมีค่าของกรด ความหนืดและปริมาณสารที่ไม่ระเหยเท่ากับ 11.25 มกKOH/ก. 17.60 สโตกส์ และ 59.17%w/w ตามลำดับ แม้ว่าอัลคีดเรซินจากน้ำมันประกอบอาหารที่ใช้แล้วจะใช้ระยะเวลาในการทำปฏิกิริยามากกว่า แต่ก็น่าที่จะส่งผลดีต่อสิ่งแวดล้อมมากกว่า เนื่องจากเป็นการนำของเสียมาใช้ให้เกิดประโยชน์ ดังนั้น น้ำมันประกอบอาหารที่ใช้แล้วจึงเป็นกรดโมโนเบสิกอีกทางเลือกหนึ่งในกระบวนการผลิตออยล์โมดิไฟด์อัลคีดเรซิน

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CONTENTS

Page

ACKNOWLEDGEMENTS ……..……. iii

ABSTRACT ……..……..……..……. iv

LIST OF TABLES ……..…… viii

LIST OF FIGURES ……..... ix

CHAPTER

1. INTRODUCTION

1.1 State of the problem ……..... 1

1.2 Objectives ……..... 3

1.3 Scope of the study ……..……..… 3

1.4 Conceptual framework 4

1.5 Expected results ……..... 4

2. LITERATURE REVIEWS

2.1 Oils ……..……. 5

2.2 Alkyd resins …..……..……..…… 9

2.3 Classification of alkyd resin …….. 10

2.4 Raw materials ……..... 10

2.5 Alkyd resins processing ……..……... 13

2.6 Polymerization theory …… 14

2.7 Modified alkyd resins 18

2.8 Applications of alkyd resins …….. 18

2.9 Standard for binders for paints and varnishes: alkyd resins 22

3. MATERIALS AND METHODS

3.1 Experimental procedure ……..…. 24

3.2 Equipments and chemical reagents ……..…. 26

3.3 Experimental methods ..……..... 27

CONTENTS (CONTINUED)

Page

4. RESULTS AND DISCUSSION

4.1 Oil properties …..... 30

4.2 Synthesis results of alkyd resins …….....……..….. 32

4.3 Characteristic of functional group by FT-IR spectroscopy …... 36

4.4 Properties of alkyd resins ….……..... 38

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusions ……..……..… 43

5.2 Recommendations ……..…… 44

REFERENCES 45

APPENDIX 49

BIOGRAPHY 62

LIST OF TABLES

Page

2-1 Composition of fatty acid in palm olein oil ……..……...…. .. 8
2-2 Modified alkyd resins ……..... 18
2-3 Characteristic of alkyd resin type 1 ……..…. 23
2-4 Characteristic of alkyd resin type 2 …….. 23
2-5 Characteristic of alkyd resin type 3 …….. 23
3-1 Experimental condition ….……..... 24
3-2 Proportion of reactants ……..…. 28
4-1 Various properties of WCO and PO comparing with those of the TISI 288-2535 (1992) standard …….. 31
4-2 IR spectrum of oils and alkyd resins ……..... 37
4-3 Effect of oil content to acid value of alkyd resins from waste cooking oil and palm olein oil ……..…… 38
4-4 Effect of oil content to non-volatile matter of alkyd resins from waste cooking oil and palm olein oil …… 40
4-5 Viscosity of alkyd resins from waste cooking oil and palm olein oil ……... 41

LIST OF FIGURES

Page

1-1	Conceptual framework ……..…..…	4
2-1	Composition of oils …..……...……	5
2-2	Molecular structure of polyhydric alcohol ……..…...……...	11
2-3	Molecular structure of dibasic acid …..…….…….….....	12
2-4	Polymerization reaction of alkyd resin from alcoholysis process ……...…	14
2-5	Polymerization reaction of anhydride and alcohol …….....	15
2-6	The formation of a three-dimensional network, or gel ……..…..	16
3-1	Flow diagram of experiment procedure ……..…….....	25
3-2	Equipment for preparation alkyd resins ……..…….....	28
4-1	Reaction trend of alkyd resins from waste cooking oil ……..……	32
4-2	Reaction trend of alkyd resins from palm olein oil ……..…..…….	33
4-3	Effect of reaction time to acid value of alkyd resins from waste cooking oil and from palm olein oil …….……..…….....	34
4-4	Appropriate time of reaction ending ……..……..…....	35
4-5	FT-IR spectrum of alkyd resins ……..…..……..….....	36
4-6	FT-IR spectrum of oils ……...…..……..….....	36

CHAPTER 1
INTRODUCTION

1.1 State of the problem

Waste cooking oil (WCO), also known as used cooking oils resulting from food cooking by manufacturing and catering establishments such as restaurants and all kitchens. In Thailand, there are a lot of fried foods that cause a huge amount of WCO. They are presently an important waste due to arising environmental problem in terms of waste disposal. In addition, according to food safety standard, cooking oil should not be repeatedly used so many time as frying oil. Utilization of WCO is, therefore, a suitable environmental management alternative.

Various attempts have been made for WCO utilization with value added such as production of dish washing cream [1], biodegradable polyurethane [1, 2] and modified bio-diesel [3-8] etc. In addition, previous works revealed that general cooking oil could be used as raw material for alkyd resins production process [9-11]. More importantly, alkyd resins are extensively produced for surface coating industry. It is usually used as main component of paints, lacquers and varnishes in which it is functional as binder of surface coating in order to protect the coated material from erosion and to increase the beauty of materials. In addition, it is also an important ink binder apart from being used as adhesives and plasticizer [9-10], the material used to increase elasticity of other polymers [12].

Alkyd resin is polyester resulting from the condensation polymerization of polyhydric alcohol and dibasic acid. Glycerol is the traditional polyhydric alcohol used in alkyd resin production because it is easily accessible and low cost [10]. Phthalic anhydride is preferable dibasic acid because of its low cost, stability at synthetic varnish's temperature and good resistance to ultraviolet ray [10], which are important to make film of alkyd resin having a good weathering tolerance [10].

If polyhydric alcohol reacted with dibasic acid, prepared alkyd resin would be brittle and subsequently, the resin was less useful for surface coating. This is due to the occurrence of crosslinking structure that decreases the solubility of alkyd. However, this problem can be solved by using some long chained monobasic acid to modify the alkyd structure. In general, natural oils contain a number of monobasic acid (fatty acids) therefore the alkyds prepare from oils are called as oil-modified alkyd resin [10].

An alcoholysis process or monoglyceride process is widely used for alkyd resin production because removal of fatty acid from oil by hydrolyzation is unnecessary during the monoglyceride process oil was heated with polyhydric alcohol such as glycerol giving monoglyceride which will be polymerized to alkyd resin after addition of dibasic acid i.e. phthalic anhydride into the reactor [10].

Currently, surface coating industry is at need of a large amount of vegetable oil for alkyd resins production process causing more imported oil [13] especially linseed oil [10]. In addition, most research revealed that the oil used in alkyd resins production process are linseed oil [14], Nahar seed oil [15], rubber seed oil [13, 16-20], soybean seed oil [11], peanut seed oil [11], sunflower seed oil [11], rice bran oil [11], and castor oil [10, 21-22] etc. Different kinds of oil used in alkyd resin production, the different drying properties are received depending on unsaturated fatty acid in oil, which is able to be determined by iodine value [4, 10]. Results from previous works showed that iodine value of castor oil was - g.I_2/100g [21] and it was classified as non-drying oil [4]. Although castor oil was non-drying oil, it can be used as raw material for alkyd resin [21]. It is important to note that WCO is also non-drying oil for which its iodine value of was primarily measured as 50.13 g.I_2/100g [Table 4-1 in Chapter 4]. Therefore, it may be possible to use WCO as raw material to prepared alkyd resin.

As discussed above, if WCO is used as raw material for alkyd resin production instead of using pure oil, the waste could become a value added product. Also it is an alternative way for WCO disposal management.

Therefore, it is reasonable to investigate the possibility of using WCO as a raw material for oil-modified alkyd resins production using alcoholysis process by condensation polymerization of glycerol and phthalic anhydride as polyhydric alcohol

and dibasic acid [10, 21] together with WCO and palm olein oil (PO) as monobasic acid. The received alkyd resins from both two oils should be further analyzed for functional group [23] acid value [24], viscosity [24] and non-volatile matter [25]. Then all the received results should be compared with Industrial Products Standard for binders for paints and varnishes: alkyd resins; TISI 618-2529 (1986), Ministry of Industry [26].

1.2 Objectives

1.2.1 To prepare alkyd resin from waste cooking oil.

1.2.2 To investigate the properties of alkyd resins prepared from waste cooking oil and palm olein oil.

1.2.3 To compare the properties of alkyd resins with the Industrial Products Standard TISI - (1986

1.3 Scope of the study

1.3.1 This work has been carried out only on laboratory scale.

1.3.2 The process used in this work is alcoholysis process [10, 21].

1.3.3 Oils used as monobasic acid are waste cooking oil of palm olein oil denote as WCO and ready-to-use palm olein oil denote as PO which were collected from Kun Amara' s shop at the Faculty of Science (Payathai), Mahidol University.

1.3.4 Polyhydric alcohol used in this work is glycerol because of its cheap cost [10, 21].

1.3.5 Dibasic acid used is phthalic anhydride because of its cheap cost, stability at synthetic varnish's temperature and high resistance to ultraviolet ray [10, 21].

1.4 Conceptual Framework

Conceptual framework of this work is as follows:

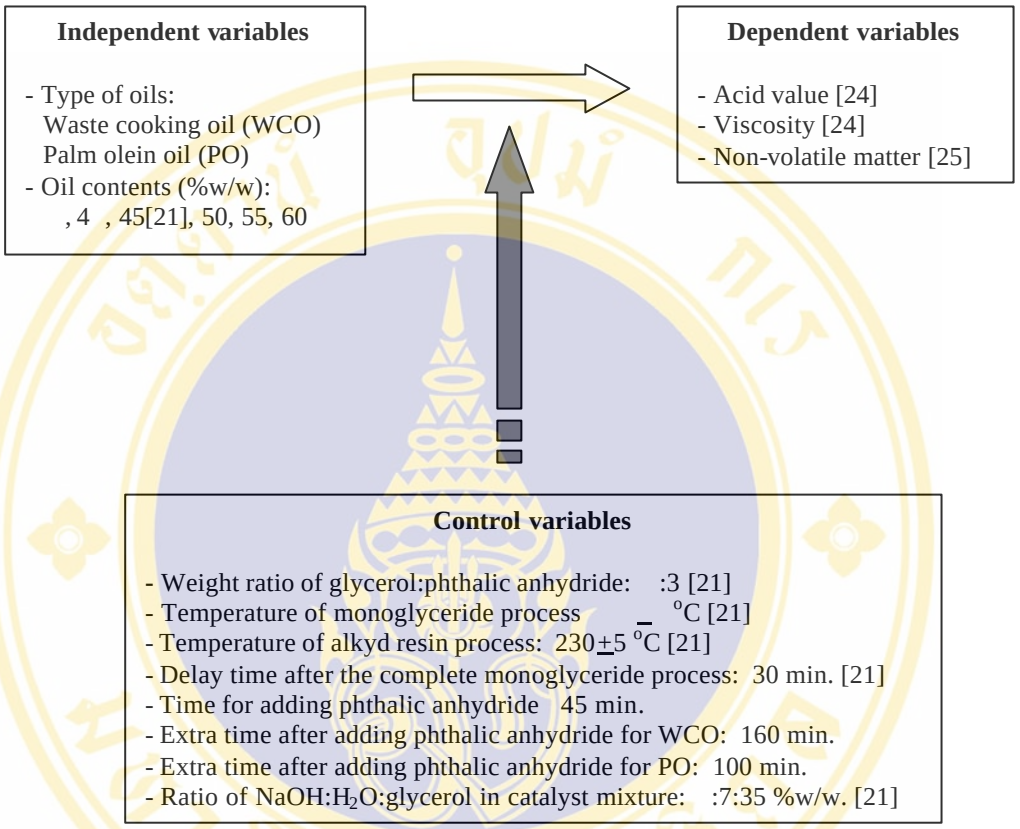


Figure 1-1: Conceptual framework

1.5 Expected results

1.5.1 Increase of an alternative to for waste cooking oil disposal.

1.5.2 Transformation waste cooking oil to a value added product.

1.5.3 Replacement of pure oil in alkyd resin production and reduction of amount of vegetable oil imported.

1.5.4 The alkyd resin with good properties for suitable applications.

CHAPTER 2
LITERATURE REVIEWS

2.1 Oils

In the past, oils have been used as binder in the surface coating industry, However, using oil as binder is presently less, oil usage as an ingredient of some varnishes or surface coating such as improving film flexibility or solubility etc [10] are more interesting. Oils used in surface coating industry are usually come from vegetable oils [11, 13, 15-21, 27] and marine oils in which the majority are of fish oils.

2.1.1 Compositions of oil

Oil is triglyceride compound. It is triester of glycerol and fatty acid, as shown in Figure 2-1 [10]. This reaction is reversible reaction. If oil (or triglyceride) hydrolyzed, it gives glycerol and free fatty acid. If triglyceride is liquid at room temperature called oil, but it is solid at room temperature called fat.

R^1, R^2 and R^3 are chain of fatty acid (C_9 - C_{22})

Figure 2-1: Composition of oils

2.1.2 Fatty acid

The properties of oil are depending on fatty acid in oil, which affect to dry property of oil [10]. Fatty acid comprise of carboxyl group connected to hydrocarbon chain of 9 to 22 carbon atoms, while carbon atoms are mostly presented. They are classified into two groups as follows:

1) Saturated fatty acids: it is fatty acid with no double bond in molecular structure. Each carbon on molecular chain is attached to at least two atoms of hydrogen. By these reasons, oils with only saturated fatty acids such as stearic acid and palmitic acid etc have non-dry properties.

2) Unsaturated fatty acid: it is fatty acid with double bond in carbon chain. However, different position of double bond will also give rise to different kind of fatty acid. As shown below, having a single bond alternately with double bond the structure, they called conjugated double bond. Others called isolated double bond.

-CH=CH-CH=CH-CH= is conjugated double bond

-CH=CH-CH_2-CH=CH- is isolated double bond

Double bond in fatty acid are most affecting to drying property of oil, due to drying reaction of oil is the reaction of oxygen and double bond in oil. Therefore, more double bonds in the structure are the more rapidly dried are presented. In addition, positioning of double bond in the structure are also affecting to the drying property, conjugated double bond structure can give rise to more rapidly dry than isolated double bond. For instance, unsaturated fatty acids are oleic acid and linoleic acid etc.

2.1.3 Oil types

Three kinds of oil are classified by drying property as follows: [4, 10, 22]

1) Drying oils: They are fastest dried oil due to oxidation reaction that changing liquid to dry film, which are insoluble in oil-solvent, and are durable to chemicals and moisture penetration. This oil is mostly composing of fatty acid, which have double bond more than three. For example, linseed oil and tung oil etc [10]. Alkyd resin produced from these oils type would have a water resistance property, the

latter changes are always occurred as alkyd resin film have losses their gloss and broken faster than the others producing from lower unsaturation [22]. Usually, these oil have an iodine value of - g.I_2/100g., it is therefore giving more polymerization reaction.

2) Semi-drying oils: It is able to absorb lesser oxygen from the air, resulting film is more slowly dried than from drying oil. Fatty acids in this kind of oil have two double bonds and usually have been used as the ingredient in non-yellowing alkyd. For example of these oils type are tall oil soybean oil, dehydrated castor oil, sunflower oil and wordfiber oil etc [10]. Usually, this oil has iodine value of 120-160 g.I_2/100g., that can give a moderate polymerization reaction.

3) 1 RQ-GU ILQ oils: This oil cannot be dried by themselves, composing of subjective amount of saturated fatty acid. It can be used as plasticizer for binder in lacquer. For examples, castor oil and palm oil etc [10]. They are usually has iodine value of <120 g.I_2/100g., causing low polymerization reaction.

.4 Natural palm oil

The oil palm, *Elaeis guineensis*, [8] is the oil that has very much of the saturated fatty acid [28] which come from two parts of palm fruit namely:

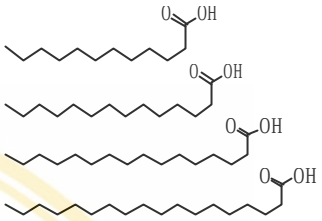
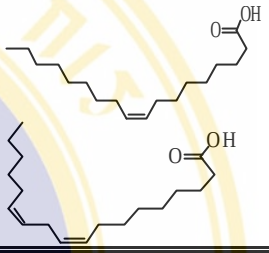
1) Seed (kernel): It is called that palm kernel which have the chemical properties resembles with coconut oil, having high saturated fatty acid. It is not suitable to be consumed.

2) Palm meat (mesocarp): It is called that palm olein oil (PO). It has a high oleic acid, which is necessary kind of fatty acid. However, it is suitable to be consumed.

Palm oil, unlike other vegetable oils, contains equal amounts of saturated and unsaturated fatty acids [8]. Crude palm oil is chemically composed of the following substances [8]:

- % of saturated fatty acid (palmitic acid and stearic acid)
- % of monounsaturated fatty acid (oleic acid)
- Vitamin E (tocopherols and tocotrienols)
- Vitamin A (beta-carotene)

Table 2-1: Composition of fatty acid in palm olein oil

Common Name	Systematic Name	Structure
Saturated fatty acid		
Lauric acid	didecanoic	
Myristic acid	tetradecanoic	
Palmitic acid	hexadecanoic	
Stearic acid	octadecanoic	
Unsaturated fatty acid		
Oleic acid	*cis* – 9 - octadecanoic	
Linoleic acid	*cis* – 9, *cis* – 12 - octadecanoic	

Source: [8]

1.5 Waste cooking oil (WCO)

The physical and the chemical property of WCO has been modified from palm olein oil [see Table - in Chapter 4], during to oxidation as well as interaction between oil, water and food components. These reactions produce a variety of physical and chemical changes in the oil, some of which are visible. These include darkening of the color, thickening, foaming and smoking of the oil. The odor and flavor of frying oil as well as fried food are also changed. However, invisible changes also occurred. In addition, waste coking oil can be used for a longer time without loosing its quality if the given advices are followed [8]:

? Frying temperature should be 160-180 ^{o}C (320-356 ^{o}F). At low temperatures, the products can absorb more fat than the high temperatures in which the fat deteriorates more quickly.

? Keep a constant level of oil in the fryer. Fry a small amount of food at a time to keep the temperature as even as possible.

? Avoid salting or seasoning fried food over the fryer. Salt and seasoning can accelerate breakdown of the fat.

? Use a separate fryer if possible for potatoes. The fat deteriorates more rapidly when meat or fish are fried than when only potatoes are fried.

? Lower the temperature when not frying and cover the fat to protect it from light.

? All fat in the fryer should be changed before it smokes or foams. Use tests such as Food Oil Sensor or Ox frit Test to indicate when it is time to change.

? Solid material and detergent residues can accelerate breakdown of the fat. Strain the fat to remove solid material. Clean the fryer once daily and rinse carefully after cleaning to remove all traces of detergent. Store the strained fat at room temperature or at lower temperatures in a covered stainless steel vessel. If iron pots are used, they should be rinsed only with hot water. Detergents remove the protective film of polymerized fat that builds up during use [8].

Numerous researches on WCO utilization have been reported [1-8]. They are utilized as biodiesel, soap and biodegradable polyurethane. However, there was no report on alkyd resin shown.

2 Alkyd resins

Alkyd came from **al** (**al**cohol) and **cid** (phthalic a**cid**). It combines **alcid** Then I pronounce to be similar to the word that acid It has changed to alkyd. The some people producer calls that **glyptal** [**gly**cerol + **p** (h) **t** (h) **al**ic] [9].

Alkyd resins are literally, polyester that are made by condensation polymerization of polyhydric alcohol, dibasic acid and monobasic acid. The largest use of alkyd resins is for surface coating (paints, enamels, lacguers and varnishes) in which the resins function as binders, forming a tough, continuous film that adheres to the object coated. Alkyd resins are the most versatile of coating binders and they are used extensively in all major categories of coating such as architectural, industrial and special purpose. It is estimated that about one third of all organic coating applied worldwide use alkyd resins as a primary binder and perhaps another one fourth of all coating contain smaller amounts of alkyd resins. Alkyd resins are also important ink binders. Other uses include caulks, adhesives and plasticizers [9].

2.3 Classification of alkyd resin

2.3.1 Classified from type of oil

Alkyd resins classified from type of oil are as follows: [9]

1) Drying alkyds: Drying alkyds are alkyd resins containing enough unsaturated fatty acids to make curing by oxygen possible.

2) Nondrying alkyds: Nondrying alkyds are alkyd resins containing lower levels of unsaturated fatty acids and are not polymerized appreciably with oxygen.

2.3.2 Classified from oil content

Alkyd resin classified from oil content are as follows: [26]

1) Short-oil alkyds: As alkyds contain oil less than %.
   Classified to two types as:
   - ? Drying oil is the components.
   - ? Nondrying oil is the components.
2) Medium oil alkyd resin: As alkyds contain oil as -60 %.
3) Long oil alkyd resin: As alkyds contain oil more than 6 %.
   Classified to two types as:
   - ? It have a non-volatile matter 70 %w/w.
   - ? It have a non-volatile matter 75 %w/w.

4 Raw materials

The main raw material had been use in alkyd resins production are given as follows. [22]

4 Polyhydric alcohol

1) Glycerol is the traditional alcohol used in alkyd resin production. It is a trihydric alcohol containing two primary and one secondary hydroxyl groups, as shown in Figure 2-2.

2) Pentaerythritol is the main polyhydric alcohol used in long oil alkyds today. It posses four primary hydroxyl groups, as shown in Figure 2-2, which

confer the potential for building more complex molecules than with trihydric alcohols, hence its alkyd derivatives are characterized by higher viscosity, faster dry and superior water resistance. In practical terms, this allows the development of long oil alkyds with freer brushing properties for the same drying times. However, the high reactivity of pentaerythritol limits its use in short oil alkyds, where it can cause gelation unless its functionality is lowered by the use of dihydric alcohols and/or monobasic acid such as rosin or benzoic acid. Blends of pentaerythritol and ethylene glycol lead to lower cost alkyds than those made on glycerol and produce short oil alkyds of excellent durability.

Figure -2: Molecular structure of polyhydric alcohol [22]

Although prepared alkyd resin from pentaerythritol has a better properties than glycerol, but most of research work [11, 15-17, 21, 27] are still using glycerol as polyhydric alcohol because it is easy to buy and also cheap. As we can see from the past in 1847, Berzelius is the first one who produced polyester from condensation polymerization of tartaric acid and glycerol [22]. Later in 1901, Watson Smith prepared a glycerol-phthalic anhydride polymer but it is a brittle resin [22]. In 1921, General Electric Company was attempting to decrease a brittle property with adding fatty acid from oil, glycerol-phthalic anhydride-fatty acid polymer was then prepared [22]. For this reason, glycerol is able to be used as polyhydric alcohol in this work.

4 Dibasic acid

1) Phthalic anhydride has traditionally been the leading dibasic acid used for alkyd production.

2) Isophthalic acid produces alkyd resins of higher viscosity and slightly faster drying, but the batch conditions for cooking vary from the phthalic

anhydride cook, because isophthalic acid is not soluble in oil at low temperatures, and batch temperarure must be high enough to eliminate “isophthalic haze”.

3) Maleic anhydride undergoes a Diels-Alder reaction across the unsaturation of the oil to produce alkyds of high viscosity and fast dry. However, its functionality is high and early gelation may occur if maleic anhydride is used alone. It is often employed in very small amounts as a viscosity controller.

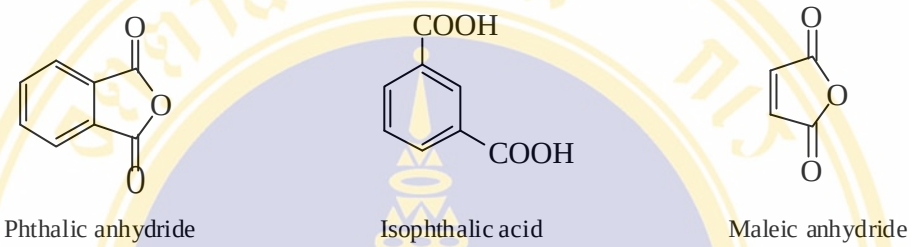


Figure -3: Molecular structure of dibasic acid [22].

In case of dibasic acid, phthalic anhydride is the most favorite used because its low cost, stable at synthetic varnish’ s temperature and good resistance to ultraviolet ray [10, 21]. Then, phthalic anhydride are always use for preparing to alkyd resin in most of research works [11, 14-17, 20-21, 27]. However, using maleic anhydride as dibasic acid is appeared in some work [15]. Form history of phthalic anhydride usage it was rather the same as glycerol because both substances were used as raw material for alkyd resin at the same time [22].

4 Monobasic acid

While the preparation of alkyd resins involves hydroxyl and carboxylic acid groups, the cross-linking reaction may depend on excess of these functionality groups. Thus, monobasic acid from fatty acid of oil in nature are used for decrease reactivity of polyhydric alcohol.

The natural oils used as monobasic acid are soybean [11], sunflower seed oil [11], peanut seed oil [11], rice bran oil [11], rubber seed oil [13, 16-20], linseed [14], Nahar seed oil [15] and castor oil [21] etc.

2.4.4 Solvents

Types of solvents used for alkyd resin dilution are also classified using oil content as follows: [9, 10, 22]

1) Short-oil alkyds: suitable solvent for aromatic solvent such as xylene [16-17, 20-21] and toluene.

2) Medium-oil alkyds: suitable solvent for aliphatic solvent or a mixture solvent of aliphatic and aromatic solvent such as a mixture solvent of white spirit and toluene.

3) Long-oil alkyds: have a suitable solvent as aliphatic sovent such as white spirit [27].

5 Alkyd resin processing

Various production processes of alkyd resin have been reported, but only 2 processes are practically well known[9-10, 21-22] as follows:

2.5.1 Fatty acid process

Free fatty acid from hydrolysis of oil is mixed by glycerol and phthalic anhydride. They have been heat at _ ^{o}C and flushed with nitrogen gas for eliminate oxygen gas. Alkyd resins were prepared to have a light color.

2.5.2 Alcoholysis process

Glycerol and oil were heated at T_1 = _ ^{o}C [21], which is temperature of monoglyceride process and flushed with nitrogen gas, and has the alkaline as catalyst. Products were prepared as diglyceride and monoglyceride. Next, it was cooled to T_2 = _ ^{o}C [21], which is alkyd resin process, and added phthalic anhydride, as the reaction shown in Figure -4 [21].

However, the alcoholysis process is more favorite than fatty acid process [11, 13-21, 27], because oil can be used as monbasic acid without fatty acid separation from oil.

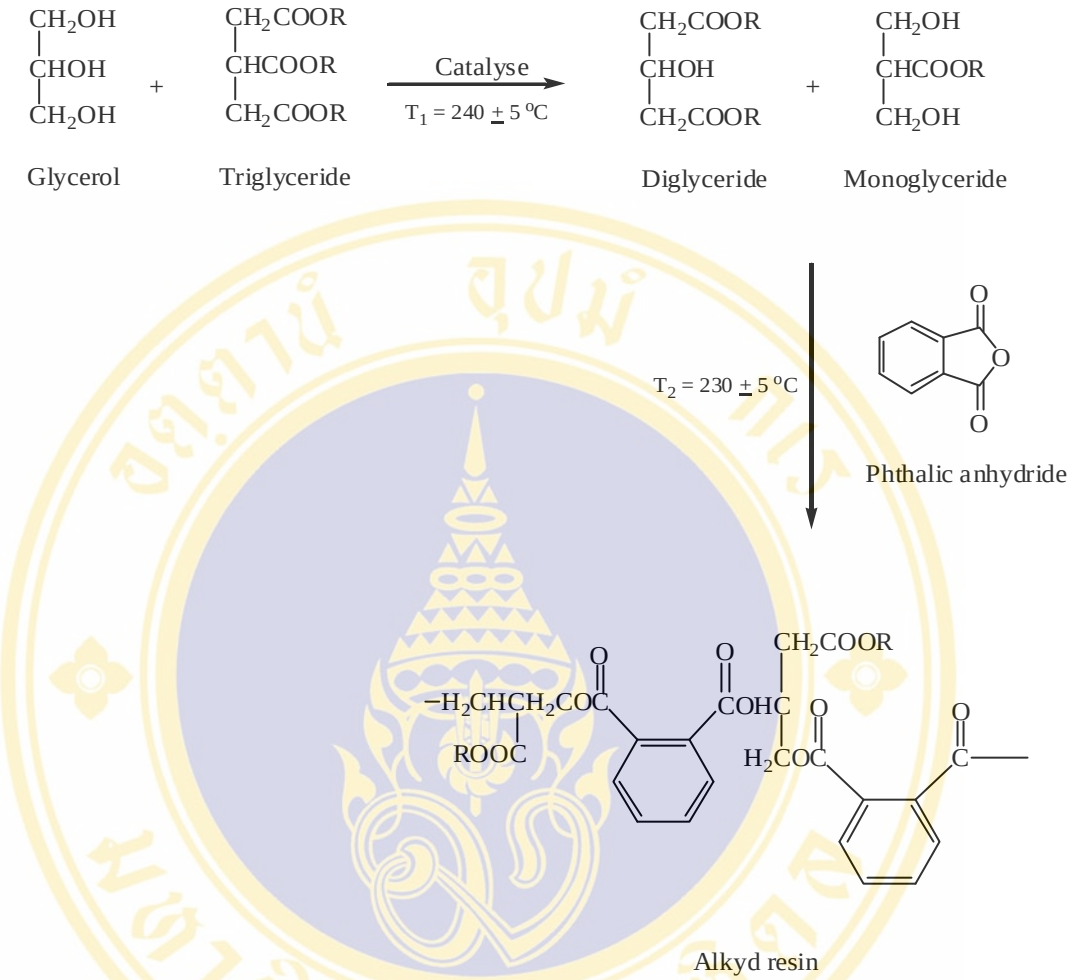


Figure 2-4: Polymerization reaction of alkyd resin from alcoholysis process

6 Polymerization theory

When a difunctional acid or anhydride (AA) and a difunctional alcohol (BB) are heated together, a stepwise reaction occurs that builds up liner chain moleculars: [9]

Compositions containing short chains (3 to about 20 monomer units per chain) are called “oligomers”. Those containing long chains are “polymers”. Under ideal conditions polymer chains containing thousands of monomer units can be made. Conditions necessary for formation of very high molecular mass chains include the following:

Figure 2-5: Polymerization reaction of anhydride and alcohol

? The mixture must be heated long enough to complete the reaction.

? Equimolar quantities of AA and BB must be present.

? No alternative reactions may be possible.

? AA and BB must contain no monofunctional reactive impurities.

The average molecular mass can be deliberately held at lower levels by altering any of the above ideal conditions, for example:

$$9\,AA + 8\,BB \xrightleftharpoons{-16H_2O} AA\text{-}(BB\text{-}AA)_8 \qquad (2.1)$$

$$9\,AA + 10\,BB + 2\,A \xrightleftharpoons{-20H_2O} A\text{-}(BB\text{-}AA)_9\text{-}BB\text{-}A \qquad (2.2)$$

A represents a monofunctional acid. Of course the actual products of such reactions are mixtures of various chain lengths.

If a trifunctional monomer, BBB is added, chain branching occurs:

$$4\,AA + 2\,BB + BBB \xrightleftharpoons{-6H_2O} \begin{array}{l} AA\text{-}BBB\text{-}AA\text{-}BB\text{-}AA \\ \qquad\quad | \\ \qquad\quad AA\text{-}BB \end{array} \qquad (2.3)$$

If substantial amounts of BBB are present, continued polymerization leads to formation of a three-dimensional network, or gel:

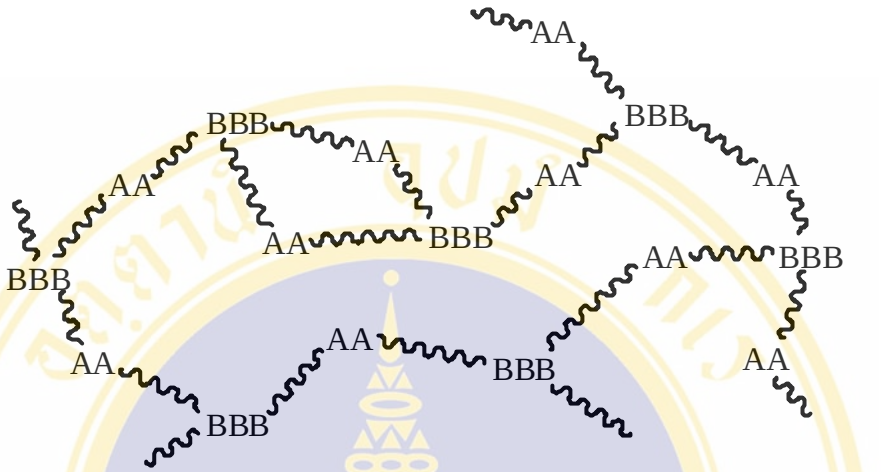


Figure 2-6: The formation of a three-dimensional network, or gel

One of the goals in alkyd resin synthesis is to prepare structures that are branched but are not quite gelled. A fairly close approach to gelation is needed to form a polymer which readily forms cross-linked networks after application as a coating. However, gelation in the reactor causes a total loss of materials and a difficult clean-up job.

Many researches have been directed toward understanding polymerization and developing general principles to help the alkyd formulator achieve the desired degree of polymerization and to optimize properties. Early theories of polymerization were developed by Carothers and by Kienle and co-workers. Carothers hypothesized a uniform, stepwise polymerization process. In his model, gelation occurs as the polymer molecular mass approaches infinity. The condition for gelation would be:

$$P_g = \frac{2}{F_{AV}} \quad (2.4)$$

when

P_g is the extent of reaction at the gel point.
F_{AV} is the average functionality of the monomer mixture.

According to this equation pure difunctional monomers can never be gel but a mixture of glycerol and phthalic anhydride ($F_{AV} = 2.5$) would gel at $P_g = 0.8$; that is, it would gel when 80% of the functional groups have reacted.

In practice, gelation usually occurs at lower P_g than predicted by this theory. To explain this fact Flory and co-workers proposed a probabilistic theory: gelation occurs when a relatively small proportion of the monomer molecules first become bonded into a three-dimensional network. Flory's theory is satisfactory for predicting polymerizations of the chemically straightforward monomers used to make polyesters. However, alkyd formulators must deal with monomers that are far from straightforward. Complications include [9]:

- Variable starting materials
- Competing side reactions
- Reaction reversibility
- Differential reactivity of the functional groups
- Differential solubility effects
- Nonuniform process conditions

Gradual progress has been made toward a general and reliable theory of alkyd formation by several authors. A completely precise theory is unlikely, mainly because alkyd polymerizations probably are not homogeneous during the late stages of reaction. Most alkyds contain small, soft gel particles as well as soluble material and these gel particles are in some cases essential to the attainment of optimum properties. Despite this difficulty, certain alkyd polymerizations can be accurately modeled with the aid of computers and advanced statistical techniques. Such theoretical methods offer considerable help and insight to the alkyd formulator. They can reduce reliance on empirical trial and error but they will not completely eliminate it for the foreseeable future.

2.7 Modified alkyd resins

Table 2-2: Modified alkyd resins

Modified alkyd resins	Advantage	Disadvantage	Application
Chain-stopped alkyds	Fast dry, hard film	Brittle film	Traffic-control striping
Styrenated alkyds	Hardness, very fast lacquer dry characteristics, chemical resistance	If it has high levels of styrene reduce weather ability and toughness	
Acrylated alkyds	Sunlight-resistance	Expensive cost	
Other olefinic monomers	Very fast lacquer dry characteristics		Enamel, aerosol paint
Silicone alkyds	Resistance to heat and weather		Stove enamel, petroleum storage tank, coil-applied coating
Thixotropic alkyds			Bridge paint, marine paint
Uralkyds	Outstanding toughness, water-resistance, abrasion resistance	Skin irritation	Gymnasium floor
Epoxy esters	Toughness, adhesion, corrosion resistance, easy application		Auto body primers
Phenolic modified alkyds	Hardness, moisture resistance		
Rosin and resin ester (natural resins)		Inferior weather ability, film yellow with age	Wall primers

2.8 Applications of alkyd resins

Alkyd resins are polyester-based materials that are normally modified with oil or fatty acids. These products may be further modified with a variety of other chemical materials. Various polybasic acid, polyhydric alcohol, oils, fatty acid and modifying agents may be combined to produce alkyds with specially desighed properties. The precise combination of the ingredients used, together with the careful control of the

reaction, influences the final properties of the alkyd produced. For this reason, many alkyds are available to the coating formulator. In considering the applications of alkyd resins, it is convenient to take them in order of decreasing oil length [22].

2.8.1 Long oil alkyds : (>60 %oil)

Long oil length is usually prepard from drying and semi-drying oils, with pentaerythritol being the preferred polyhydric alcohol. The most common oils used are linseed and the semi-drying oils, soya, safflower, sunflower and tall oil.

All the resins in this range are soluble in low odor aliphatic solvents, permitting excellent brushing properties with good flow characteristics and easy brush cleaning. Their main use is in architecture and maintenance as brushing enamels, undercoats and primers and also marine paints. Their slowness to dry and lack of response to force drying has prevented their use in industrial finishes.

In these resins, linseed oil gives the best drying properties, but is prone to yellowing away from direct sunlight, the main use, therefore, is restricted to primers and exterior finishing coats and in dark colors. Many people still use linseed-oil-based alkyds for roof paints but since a high degree of flexibility is required, it is normal to add additional quantities of linseed oil to paint.

Most architectural high gloss enamels for the consumer market are formulated on long oil soya-based alkyds. Safflower-oil-based alkyds give slightly better drying and non-yellowing properties but safflower is normally considerably more expensive than soya oil and its use is restricted. Sunflower-oil-based alkyd has properties in between those of soya and safflower but again its use is restricted by its price, which is normally higher than that of soya oil. Tall-oil-based alkyds give good non-yellowing properties with reasonable drying time. They are increasingly used in architectureal enamels, particularly when favourably priced against soya oil.

Topside marine paints are generally based on enamels similar to architectural high gloss materials but additional oil is frequently added to undercoats to ensure adequate flexibility. Also, as marine paints, these alkyds may be fortified with chlorinated rubber.

Siliconized long oil alkyds have improved resistance to chalking. They are somewhat prone to checking on long term exposure but this can be overcome,

provided properly formulated undercoats are used. Because of their high cost, they have only found limited acceptance in high performance areas. In the USA they are extensively used in topside marine paints.

Rosin additions are not normally made to long oil alkyds since gloss and color retention are downgraded. These alkyds do give better flow and speed of set and rosin modified alkyds are used in architectural undercoats. In these cases, if the undercoat is to be used externally, it is advisable to add linseed oil to improve flexibility.

Long oil alkyds modified with polyamide resins are used to produce thixotropic architectural paints. These resins are also used in fairly high proportions in some undercoats, where they show excellent non-penetrating properties and ease of brushing. Polyamide modified long oil alkyds are frequently blended at lower levels into a variety of paints to produce a slight degree of thixotropy, thereby improving anti-settling and application properties.

2.8.2 Medium oil alkyds : (40-60 %oil)

Products in this range are probably the most versatile of all the alkyds. In general, all-round durability is better than among their longer or shorter relations. They still maintain solubility in low boiling aliphatic solvents, enabling brushing paints to be prepared but they can also be produced in faster evaporating solvents for industrial spray applications.

The most commonly used unmodified medium oil length alkyds are based on linseed oil. Color retention is not a problem since they are generally used in exterior situations. Alkyds of this type are extensively used in anti-corrosive primers and in general maintenance painting applications. Fish oil based medium oil length alkyds are also employed in such paints.

Medium oil linseed and soya alkyds are used in automotive refinishing and implement enamels. In these cases, they are frequently modified with shorter oil alkyds, the extent depending on the individual application. If durability is the prime requirement, then the extent of modification is usually small; where some loss of durability can be tolerated, then higher levels are used with resultant faster drying

properties. Medium oil length alkyds for these applications are sometimes chain-stopped to achieve faster set times without significant loss of durability.

A specific application for medium oil length alkyds is in flat wall paints. These are highly polymerized products cut in hydrocarbon solvents of low solvency power. Under these conditions, the formation of a large number of resin aggregates leads to products with excellent non-penetrating properties over a variety of porous surfaces.

Medium oil length alkyds dissolved in toluol are used in conjunction with chlorinated rubber for road marking paints. Rosin and phenolic modifications are frequently made to medium oil length alkyds, to give them excellent hard drying properties, with improved resistance to abrasion, water and alkali. They are extensively used in maintenance paints, industrial primers and marine primers. They form the basis of conventional paving paints. Some non-drying medium oil length alkyds are produced in the range 40 to 60 % for use in exterior nitrocellulose lacquers.

Medium oil length alkyds can be made water-dilutable by trimellitic anhydride modifications. Although suggested as the basis for architectural enamels and undercoats, they have only limited acceptance, mainly because of poor drying under humid conditions. They perform somewhat better in industrial situations, particularly where force drying can be employed.

2.8.3 Short oil alkyds : (<40 %oil)

Unmodified short drying oil alkyds are typically made of linseed, soya or dehydrated castor oils. The linseed-based alkyds are used in automotive refinishing enamels and in general purpose industrial air drying enamels. They also perform well in force dry and low bake situations. Soya and dehydrated castor oils can be used in air drying system but they tend to be too slow-drying for most applications. They perform well in force drying and baking system, either with metal driers or when modified with amino resins. In these cases, they have good baking properties with excellent film characteristics; their color retention is only fair and they are not used in light colored paints that are liable to be overbaked. Low-rosin-containing tall oil alkyds have good color retention on baking with amino resins and are used as the basis for most industrial baking enamels where high durability is not required.

Non-drying, short oil alkyds are generally based on castor or coconut oils. They are used with nitrocellulose for exterior lacquers. Coconut oil alkyds give the best exterior durability. Castor oil lacquers have the best film properties. In combination with melamine-formaldehyde resins these alkyds give baking enamels with excellent resistance to yellowing and good exterior durability. For many years they were used as the basis for automotive finishing enamels and still find some limited use in this application.

Both the semi-drying and non-drying short oil alkyds can be used with urea-formaldehyde resins for acid-catalysed room-temperature-curing enamels and lacquers. When they are modified with nitrocellulose and have weak acid catalysts, they can be supplied as one-component finishes. These acid catalysed finishes are used in clear and pigmented system for timber furniture.

Rosin and phenolic modification of short drying-oil alkyds is frequently carried out. These modifications considerably speed up drying, improve hardness and adhesion, and impart aliphatic solvent solubility. They find extensive use in general-purpose, air-drying industrial enamels, drum paints and shop primers. They show good compatibility with medium oil alkyds and are used in blends to speed drying.

Most styrenated alkyds fall into the category of short oil alkyds. They are extremely fast drying with excellent toughness. Their poor re-coating properties and fair durability, however, limit their applications. Mainly they are used as one coat finishes for small articles, hammertone finishes being a typical outlet. Modification with acrylic monomers improves durability at the expense of toughness and drying properties. These find limited applications as automotive refinishing enamels. Acrylated and styrenated short oil alkyds are used in baking systems as metal decorating enamels. Chain stopping of short-oil-alkyds is also carried out. They have better durability than other fast-drying alkyds but like vinylated alkyds, have recoating problems.

2.9 Standard for binders for paints and varnishes : alkyd resins

The Thailand Industrial Standard Institute, Ministry of Industry has fixed the standard for binders for paints and varnishes: alkyd resins, TISI 618-2529(1986), As shown in Table 2-3, 2-4 and 2-5. [26]

Table 2-3: Characteristic of alkyd resin type 1*

No.	Characteristic	Standard		Test method
		Kind 1**	Kind 2***	
1	Acid value (mg.KOH /g.) not more than	10	10	ASTM D 1639 [24]
2	Viscosity at 25 ^{o}C by gardner bubble viscometer	W - Z_4 (10.7-63.4 stoke)	W - Z_4 (10.7-63.4 stoke)	ASTM D 1545 [24]
3	Non-volatile matter (%w/w)	60 $\pm$ 1	60 $\pm$ 1	TISI 285(6) – 2524 (1981) [25]

*Remarks: * is shot–oil alkyds which have oil contents less than 40 %w/w.*
*** is alkyd resin which have semi-drying oil as component.*
**** is alkyd resin which have non-drying oil as component.*

Table 2-4: Characteristic of alkyd resin type 2*

No.	Characteristic	Standard	Test method
1	Acid value (mg.KOH /g.)	5 - 12	ASTM D 1639 [24]
2	Viscosity at 25 ^{o}C by gardner bubble viscometer	Z - Z_7 (22.7-388 stoke)	ASTM D 1545 [24]
3	Non-volatile matter (%w/w)	60 $\pm$ 1	TISI 285(6) –2524 (1981) [25]
4	Period of drying		TISI 618-2529 (1986) [26]
	- Surface drying (hr.) not more than	2	
	- Stick drying (hr.) not more than	5	

*Remarks: * is medium–oil alkyds which have oil contents between 40-60 % w/w.*

Table 2-5: Characteristic of alkyd resin type 3*

No.	Characteristic	Standard		Test method
		Kind 1**	Kind 2***	
1	Acid value (mg.KOH /g.)	5 – 10	5 - 10	ASTM D 1639 [24]
2	Viscosity at 25 ^{o}C by gardner bubble viscometer	Z - Z_4 (22.7-63.4 stoke)	U – Z (6.27-22.7 stoke)	ASTM D 1545 [24]
3	Non-volatile matter (%w/w)	70 $\pm$ 1	75 $\pm$ 1	TISI 285(6) – 2524 (1981) [25]
4	Period of drying			TISI 618-2529
	- Surface drying (hr.) not more than	4	4	(1986) [26]
	- Stick drying (hr.) not more than	7	7	

*Remarks: * is long–oil alkyds which have oil contents more than 60 %w/w.*
*** is alkyd resin which have non-volatile matter as 70 %w/w.*
**** is alkyd resin which have non-volatile matter as 75 %w/w.*

CHAPTER 3
MATERIALS AND METHODS

3.1 Experimental Procedure

This work has been carried out in laboratory scale in order to prepare oil-modified alkyd resins by alcoholysis process. It is a condensation polymerization between glycerol as polyhydric alcohol, phthalic anhydride as dibasic acid [10, 21] and a palm olein oil as monobasic acid. The oils used in this research are waste cooking oil of palm olein oil, denoted as WCO and ready-to-use palm olein oil, denoted as PO. All experiments were repeated twice to ensure reproducibility. From literature review [11, 14-17, 20-21, 27] it was found that types and content of a vegetable oil, ratio of glycerol and phthalic anhydride including reaction time and temperature are important parameters which affect the properties of prepared alkyd resin. Consequently, in this work, experimental conditions are carefully controlled, as shown in Table 3-1.

Table 3-1: Experimental condition

Controlled parameters	Values
Oil contents (%w/w)	35, 40, 45 [21], 50, 55 and 60
Weight ratio of glycerol and phthalic anhydride	2:3 [21]
Temperature: monoglyceride process (^{o}C)	240$\pm$5 [21]
Temperature: alkyd resin process (^{o}C)	230$\pm$5 [21]
Delay time after the complete monoglyceride process (min.)	30 [21]
Time for adding phthalic anhydride (min.)	45
Extra time after adding phthalic anhydride for WCO (min.)	160
Extra time after adding phthalic anhydride for PO (min.)	100
Ratio of NaOH : H_2O : Glycerol in catalyst mixture (%w/w)	8:7:35 [21]

Majority of works including synthesis, acid measurement and non-volatile matter quantitative study have been carried out at Faculty of Environment and Resource Studies, Mahidol University, Salaya Campus, Nakornpathom Province. The functional groups of reactants and alkyd resins prepared from WCO and PO were confirmed using FT-IR Spectroscopy [23] at Faculty of Science (Payathai); Mahidol University, whereas the measurement of iodine value of oils were done at Thailand Institute of Scientific and Technological Research. In addition, the free fatty acid content of oils were examined at Department of Agriculture and viscosity of the prepared alkyd resins were determined using Gardner-Holdt Bubble Viscometer at Department of Science Service. Importantly the acid value, viscosity and percentage of non-volatile matter of the alkyd resins were compared with those corresponding to TISI 618-2528 (1986) [26]. The general procedures of this work were described below and it is schematically outlined in Figure 3-1.

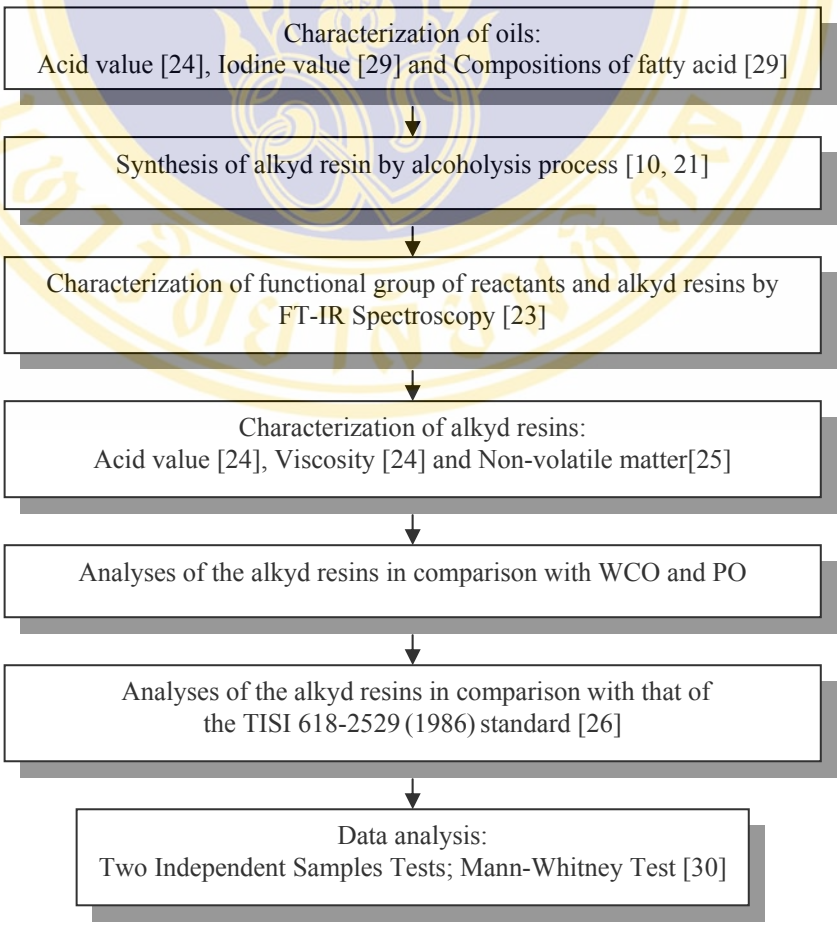


Figure 3-1: Flow diagram of experiment procedure

3.2 Equipments and Chemical Reagents

All equipments used in this work are listed as below:

1) 3-neck round bottom flask
2) Condenser
3) Erlenmeyer flasks
4) Beakers
5) Cylinders
6) Droppers
7) Thermometer 0-300 ^{o}C
8) Pipettes
9) Stirring rods
10) Volumetric flasks
11) N_2 gas inlet
12) N_2 gas
13) Burette
14) Suction rubber
15) Stand and Clamp
16) Spatula
17) Magnetic bar
18) Alumenium foil
19) Heating mantle
20) Cooling apparatus
21) FT-IR spectrometer (spectrum GX Perkin Elmer, USA)
22) Gardner-Holdt Bubble Viscometer

All chemicals were commercially supplied and the details of each were given.

1) Glycerol (analytical 99.5 %v/v, Univar)
2) Phthalic anhydride (purum ≥97% (NT), Fluka)
3) NaOH (pro analtysi ≥99 % min. anhydrous pellets, Merck)
4) Ethanol (absolute GR for analysis 99.9 % (GC), Merck)
5) Potassium hydroxide (ACS-ISO-for analysis 85 % min. pellets, Carlo erba reagent)

6) Isopropanol (AR (ACS) 100 %, Mallinckrodt)
7) Diethylether (analytical 99.5 %, LAB-SCAN)
8) Phenolphthalein standard (AG >99 % (NT), Fluka)
9) Xylene (analytical reagent (AR) 98.0 %, LAB-SCAN)
10) Catalyst solution (mixture of NaOH : H_2O : Glycerol = 8:7:35 %w/w)
11) Distilled water

3.3 Experimental methods

3.3.1 Characterization of oils

Various properties of WCO and PO such as acid value, iodine value and composition of fatty acid were analyzed by standard test method ASTM D 1639 [24], IUPAC (1979) 2.205 [29] and IUPAC (1979) 2.301-2.302 [29] respectively.

3.3.2 Synthesis of alkyd resins

1) Alkyd resins from waste cooking oil (AR_WCO)

A three-necked round-bottomed flask equipped with a heating mantle, thermometer 0-300 ^{o}C, condenser and a nitrogen gas inlet were equipped as shown in Figure 3-2, for the preparation of the alkyd resins. Waste cooking oil and glycerol were added into the flask and the reactor was flushed with nitrogen gas throughout the reaction. When the temperature of the mixture reached 115 ^{o}C [21], a drop of catalyst solution, a mixture of NaOH: H2O: glycerol (8:7:35 %w/w) [21] was added. The mixture was further heated up to 240$\pm$5 ^{o}C [21] then it was taken to test for being monoglyceride by solubility test with ethanol (the mixture : ethanol = 1:2 %v/v [21]). If the mixture was soluble, the reaction temperature would be kept constantly for 30 min.[21], and phthalic anhydride (39%w/w of the whole mixture) was slowly added within 45 min. The proportion of all reactant; oil, glycerol and phthalic anhydride are summarized in Table 3-2. When addition of phthalic anhydride was complete, the temperature of mixture was adjusted to 230$\pm$5 ^{o}C [21]. Then the acid value [24] of the mixture was determined every 20 min. for 160 min. [Table A-1 in Appendix A]. After that the reaction was immediately terminated.

Figure 3-2: Equipment for preparation alkyd resins

Table 3-2: Proportion of reactants

Alkyd resins	Oil (%w/w)	Glycerol; Gly (%w/w)	Phthalic anhydride; PA (%w/w)	Gly / PA (by weight) [21]
AR_35	35	26	39	0.67
AR_40	40	24	36	0.67
AR_45	45	22	33	0.67
AR_50	50	20	30	0.67
AR_55	55	18	27	0.67
AR_60	60	16	24	0.67

2) Alkyd resins from palm olein oil (AR_PO)

The AR_PO samples were prepared using the same method of preparing the AR_WCO samples but PO was used instead of WCO and the reaction was kept for 100 min. [Table A-2 in Appendix A] after adding phthalic anhydride, instead.

3.3.3 Characterization of alkyd resin

Various properties of the products from 3.3.2 were determined as follows:

Characterization of function groups of the sample were conducted on a Perkin Elmer model PE 2000- FT-IR spectrometer in the wave number region of 400-

4000 cm^{-1}. The spectra were measured with 40 scans with resolution of 4.0 cm^{-1}. IR measurements all liquid samples were carried out at room temperature using the Neat technique [23]. In order to record IR spectra of the alkyd, a small amount of the sample was dissolved with chloroform and a drop of the mixture was then spread on BaF_2 windows. For phthalic anhydride, IR spectrum was obtained using the KBr pellet for which a small amount of the powder sample was ground then mixed with KBr powder and pressed into pellet under hydraulic press.

The acid value, viscosity and non-volatile matter of the alkyd samples were analyzed by the standard method; ASTM D 1639 [24], ASTM D 1545 [24] and TISI 285(6)–2524(1981) [25] respectively.

3.3.4 Data analysis

Two independent samples tests; Mann-Whitney Test was used to determine an appropriate time for reaction ending, acid value, viscosity and non-volatile matter content of alkyd resins prepared from waste cooking oil (AR_WCO) to those of alkyd resins from palm olein oil (AR_PO) at 95 % confidence interval [30]. All data were analyzed using the package program of SPSS for Window version 11.5.

CHAPTER 4
RESULTS AND DISCUSSION

This research has been carried out on producing oil-modified alkyd resins from waste cooking palm olein oil (AR_WCO) and that from ready-to-used palm olein oil (AR_PO) using alcoholysis process. Glycerol and phthalic anhydride had been used as polyhydric alcohol and dibasic acid [10, 21]. The important properties of oil such as acid value [24], iodine value and non-volatile matter [29] were determined. Note that iodine value is used to indicate drying property of the oils [4, 10]. The completion of reaction was followed by measuring the acid value of reactant mixture in a function of time. The functional groups of received alkyd resins were characterized using FT-IR Spectroscopy [23]. In this study, the properties of alkyd resins such as acid value, viscosity [24] and non-volatile matter [25] were compared with standard for binders for paints and varnishes: alkyd resins; TISI 618-2529 (1986), Ministry of industry [26]. The experimental results can be explained as follows:

4.1 Oil properties

The properties of waste cooking oil (WCO) and palm olein oil (PO) are shown in Table 4-1; the results showed that WCO has acid value greater than that of PO. Also, the acid value of WCO, 1.00 mg.KOH/g., is exceeding the standard value that it is limited at the level of less than 0.60 mg.KOH/g. [31]. On the other hands, it was found that PO has acid value of 0.17 mg.KOH/g. only, being within the standard limit. This indicates that WCO is questionable on its purity and quality for consumers.

Nevertheless, the iodine value of WCO, 50.13 g.I_2/100 g. is slightly different from that of PO, 52.94 g.I_2/100 g., both are still have the values lower than the standard limit; 55.00–60.00 g.I_2/100 g. [31]. In general iodine value indicates drying properties of oils [4,10] implying the content of unsaturated fatty acid in the oils. If the iodine value is high, oil drying is fast [32] during oxidation reaction between oil and

oxygen in air or drier [10]. As shown in Table 4-1, WCO and PO are classified as non-drying oil because both have iodine value less than 120 g.I_2/100 g. [4]. It should be note that the less of unsaturated fatty acid the worse nutrition [28].

As mentioned above, WCO and PO have small amount of unsaturated fatty acid when comparing with the standard limit for edible palm olein oil [31]. As seen in Table 4-1, the oil content essentially 39.03 %w/w unsaturated fatty acids comprising mainly of oleic acid (32.53 %w/w) and linoleic acid (6.50 %w/w), being less than the standard value. In PO the oil content with 43.91 %w/w unsaturated fatty acid composing mainly of oleic acid (35.46 %w/w) within the standard range [31]. However, PO has linoleic acid of 8.45 %w/w, less than the standard value [31]. These results have shown that WCO has the unsaturated fatty acid content lower than that of PO in agreement with the iodine values. From previous reports a number of vegetable oils are suitable for the synthesis of polymeric resins such as castor and Nahar seed oils. Although the iodine values of WCO and PO are lower than that of castor oil (80-90 g.I_2/100 g.) [21] and Nahar seed oil (89.26 g.I_2/100 g.) [15], they may have a potential for preparation of alkyd resin due to their non-drying property as well as that of castor and Nahar seed oils.

Table 4-1: Various properties of WCO and PO comparing with those of the TISI 288-2535 (1992) standard

Properties	Waste cooking oil (WCO)	Palm olein oil (PO)	TISI 288 – 2535 (1992)*
Acid value (mg.KOH/g.)	1.00	0.17	Not more than 0.60
Iodine value (mg.I_2/100 g.)	50.13	52.94	55.00 – 60.00
Saturated fatty acid (%):	60.97	56.09	
C 12:0 Lauric acid	6.98	1.08	Not more than 1.20
C 14:0 Myristic acid	2.94	1.67	0.50 – 5.90
C 16:0 Palmitic acid	48.85	50.24	32.00 – 59.00
C 18:0 Stearic acid	2.20	3.10	1.50 – 6.00
Unsaturated fatty acid (%):	39.03	43.91	
C 18:1 Oleic acid	32.53	35.46	35.00 – 52.00
C 18:2 Linoleic acid	6.50	8.45	10.00 – 16.00

*Remarks: * is standard for edible palm olein oil, Thailand Industrial Standard Institute, Ministry of Industry [31].*

4.2 Synthesis results of alkyd resins

Polymeric oil-modified alkyd resins were synthesized with varying the oil concentration 35, 40, 45, 50, 55 and 60 %w/w. The pretest experiments reported in Appendix A show that in order to have the polymerization complete the reactants must been kept at a specific temperature after adding phthalic anhydride for 160 minutes using WCO but only 100 minutes using PO. It should be pointed out that WCO has acid value greater than that of PO and this may be the reason why longer reaction time is needed. The initial acid value was measured after adding phthalic anhydride every 20 minutes until the reaction is ended. All the samples show a high initial acid value but the value decrease gradually indicating the moderate kinetic of the reaction. The acid value changed occurring during the reaction were observed throughout the preparation of AR_WCO and AR_PO. The results are explained as follows:

4.2.1 Trend of reaction

Trend of reaction of prepared alkyd resins from waste cooking oil (AR_WCO) were shown as Figure 4-1

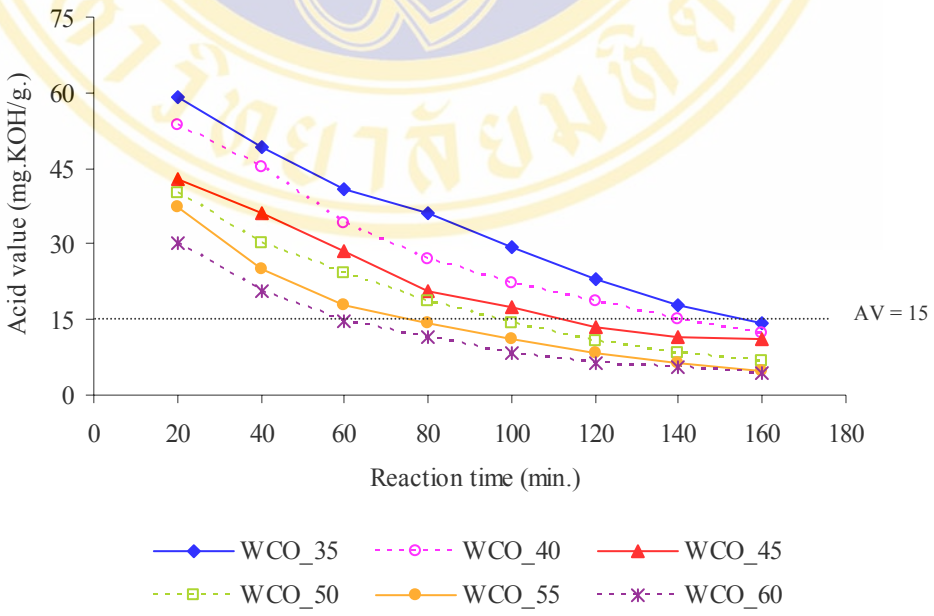


Figure 4-1: Reaction trend of alkyd resins from waste cooking oil (AR_WCO)

Figure 4-1 has shown that the acid value of reactant mixture of all compositions decreased with increasing of reaction times. The slope of reaction curves tend to decrease as the time increased indicating faster reaction at the beginning. The initial mixture has a high acid value due to high concentration of phthalic anhydride. By varying the oil concentration, it is the greater oil content the less acid value of the alkyd mixtures. Again, the acid value is directly related to the concentration of phthalic anhydride, in agreement with the composition of reactants as seen in Table 3-2. For in case of prepared alkyd resins from palm olein oil (AR_PO), they have the same trend of reaction with AR_WCO, but AR_PO uses reaction time ending only 100 minutes. The results were shown as Figure 4-2:

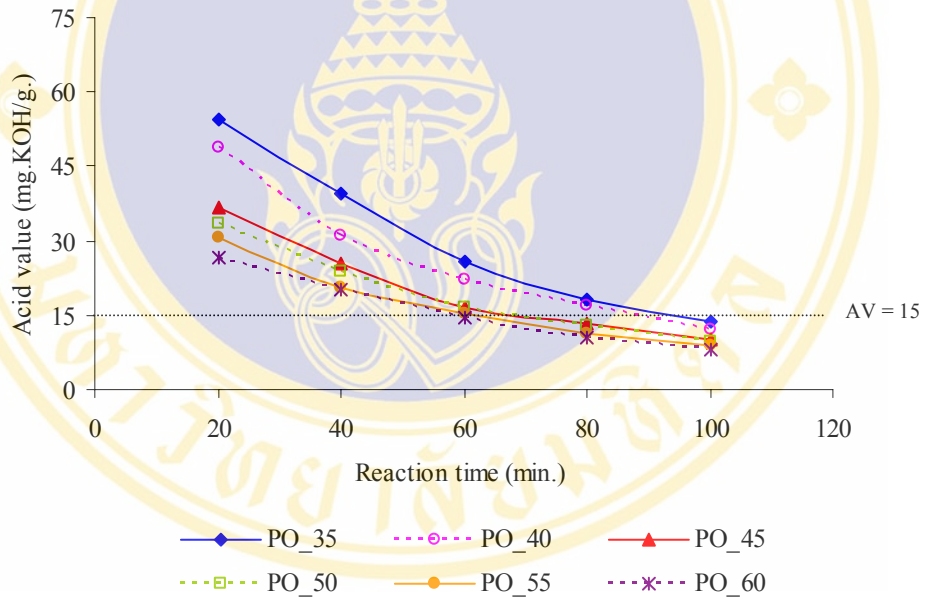


Figure 4-2: Reaction trend of alkyd resins from palm olein oil (AR_PO)

In addition, it appeared that by using the same experimental condition e.g. reaction time and oil concentration, WCO always give higher acidic alkyd mixtures as shown in Figure 4-3.

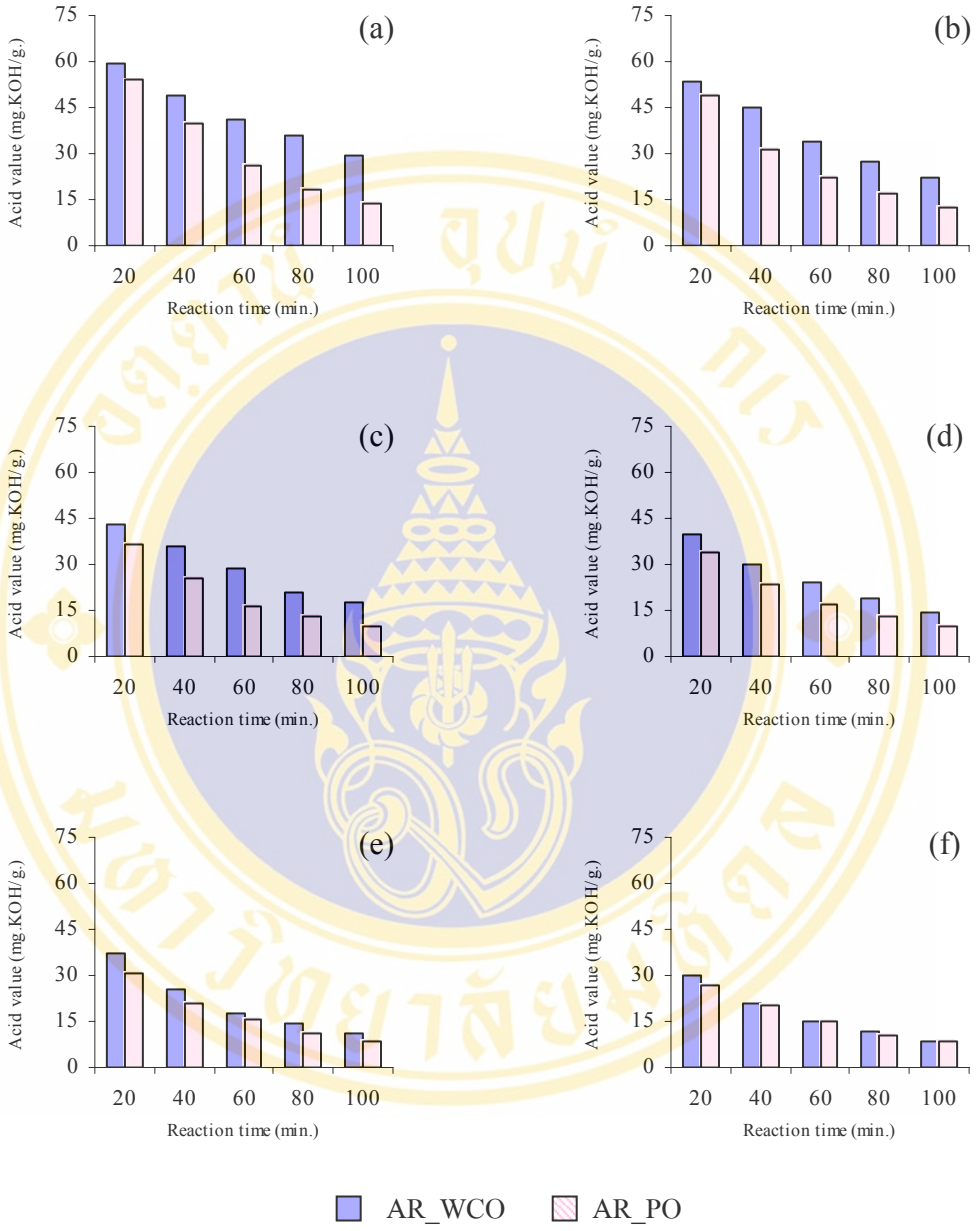


Figure 4-3: Effect of reaction time to acid value (AV) of alkyd resins from waste cooking oil (AR_WCO) and from palm olein oil (AR_PO) at the same oil content (a) Oil_35 (b) Oil_40 (c) Oil_45 (d) Oil_50 (e) Oil_55 (f) Oil_60

From Figure 4-1, 4-2 and 4-3 have shown that reaction time, oil content and oil type effect to acid value of prepared alkyd resins.

4.2.2 The appropriate time of reaction ending

The experimental procedure in this work has designed to obtain a general protocol to synthesized the polymeric alkyd resin from the oil of any concentration. Thus, the extra time after adding phthalic anhydride was fixed at 160 minutes for preparing of AR_WCO and at 100 minutes for that of AR_PO. In fact, one has reported that the reaction could be stopped once the acidity of alkyd mixture reach the value less than 15 mg.KOH/g.[21]. The acid values of all alkyd mixture at all step of reaction were reported in Table B-1 and B-2 in Appendix B. Figure 4-4 has shown the appropriate time to stop the reaction following the reported criteria.

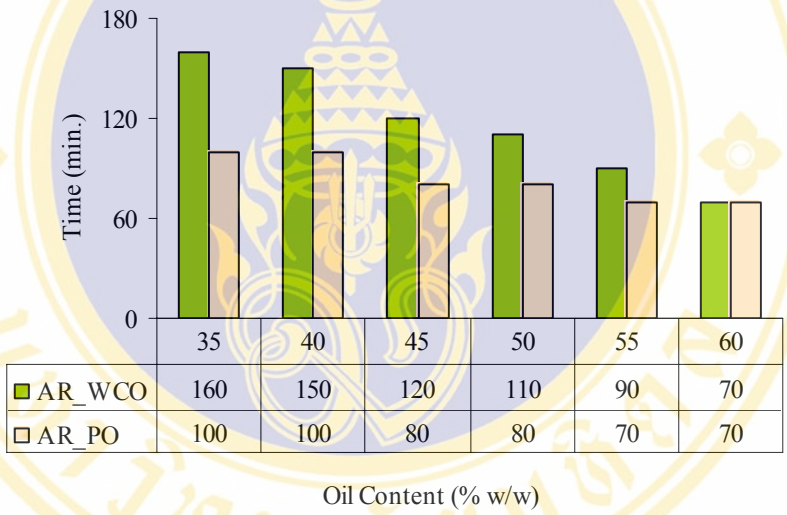


Figure 4-4: Appropriate time of reaction ending

This study has shown that the reaction time can be reduced by increasing the oil content. However, the alkyd mixture with high oil content would have less phthalic anhydride [Table 3-2], resulting less acidity of the alkyd mixture as well as less reaction times. Furthermore, with oil concentration of 35-50 %w/w, the appropriate time of producing AR_WCO are significantly different at 95% confidence interval [Table C-1 in Appendix C] from that of AR_PO. Regarding to the alkyd resin prepared from at 55 and 60 %w/w oil (AR_55, AR_60), there is no significantly different [Table C-1 in Appendix C] between the appropriate times to produce the resins. Nevertheless, in this work the reaction temperature can not be strictly

controlled due to the limitation of instruments, which may affect the reaction rates as well as the acid value changes.

4.3 Characteristic of functional group by FT-IR spectroscopy

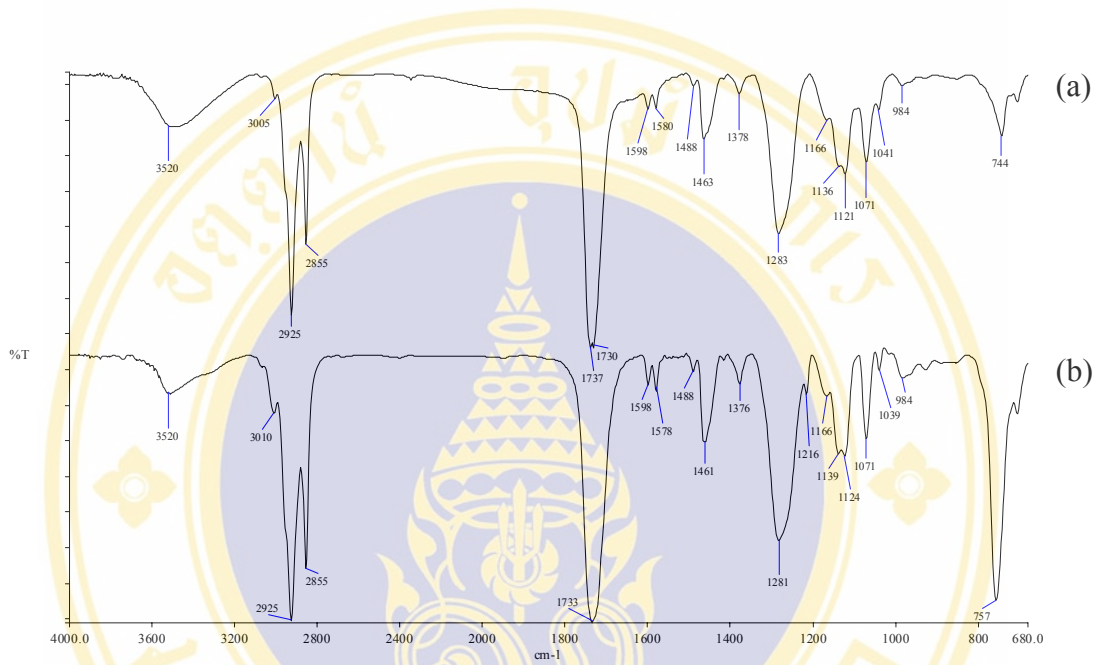


Figure 4-5: FT-IR Spectrum of alkyd resins (a) from waste cooking oil at 60 %w/w (WCO_60) and (b) from palm olein oil at 60 %w/w oil (PO_60)

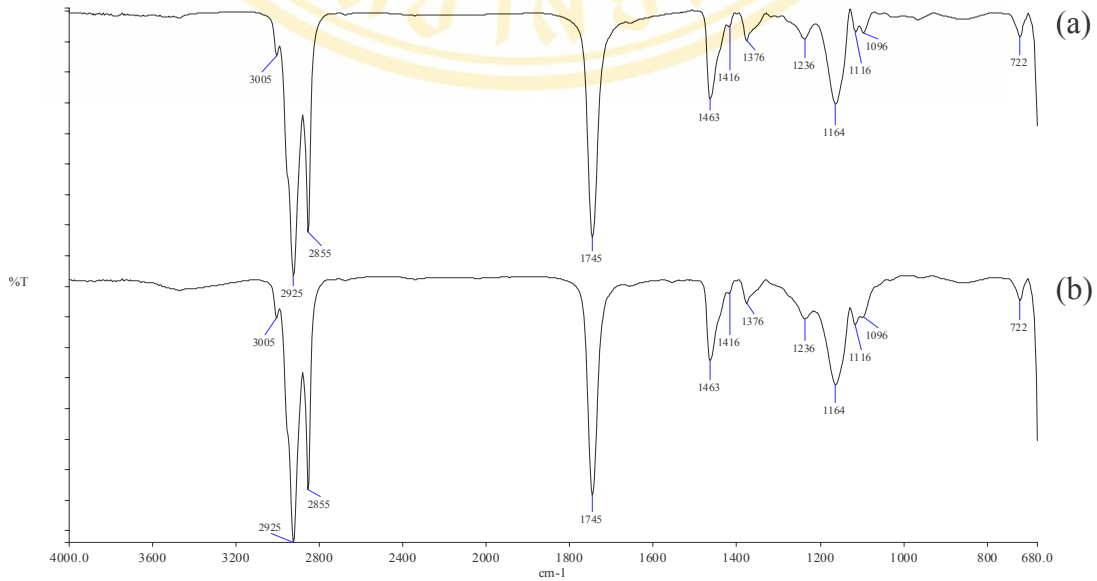


Figure 4-6: FT-IR Spectrum of oils (a) Waste cooking oil (WCO) and (b) Palm olein oil (PO)

Table 4-2: IR spectrum of oils and alkyd resins

Peak (cm^{-1})				Functional groups [15, 23]
Oils		Alkyd resins		
WCO*	PO*	WCO_60**	PO_60**	
-	-	3520	3520	O-H Stretching
3005	3005	3005	3010	=C-H Stretching of alkene
2925	2925	2925	2925	C-H Vinyl
2855	2855	2855	2855	C-H Aliphatic
1745	1745	1737, 1730	1733	C = O of ester
-	-	1598, 1580	1598, 1578	C = C Stretching of ring
1463, 1416	1463, 1416	1463	1461	CH_2
1376	1376	1378	1376	CH_3
1236	1236	1283	1281	C- O Stretching of ester
1164, 1116, 1096	1164, 1116, 1096	1136, 1121	1139, 1124	C- O– C Stretching
-	-	984	984	C = C-H Out of plane C-H bend
-	-	744	757	= C-H Out of plane bending of aromatic
722	722	-	-	CH = CH (isomer)

Remark: * *WCO and PO are waste cooking oil and palm olein oil.*
** *WCO_60 and PO_60 are alkyd resin from waste cooking oil and palm olein oil at oil content 60 %w/w.*

As shown in Figure 4-5 and Table 4-2, IR-spectra of alkyd resins from waste cooking oil (AR_WCO) and palm olein oil (AR_PO) are almost identical, indicating the same functional groups. These IR spectra compose of peaks corresponding to ester, which is the important functional group of alkyd resin. For example of those peaks of carbonyl group of ester at 1737 cm^{-1} and 1730 cm^{-1} for AR_WCO, and at 1733 cm^{-1} [see Table 4-2], and peak of C-O stretching of ester at 1283 cm^{-1} for AR_WCO and 1281 cm^{-1} for AR_PO. Besides, this IR-spectra of alkyd resins also compose of the other important peak such as peak of O-H group at 3520 cm^{-1} and peak of aromatic group at 1598 cm^{-1}, 1580 cm^{-1}, 1136 cm^{-1}, 1121 cm^{-1}, 984 cm^{-1} and 744 cm^{-1}, as seen in Figure 4-5 and Table 4-2. These functional groups are consistent with the molecular structure of alkyd resins [Figure 2-4]. IR experiments confirm that the oil-modified alkyd resins were successfully produces because the IR spectra of alkyds are substantially different from those of the oils [Figure 4-6]. Moreover, there is no evident of remained phthalic anhydride in the alkyd mixture. Although the IR spectra obtained from alkyd samples are slightly complicated, the aromatic =C-H plane blending peak corresponding to the modified alkyd is clearly observed. The IR spectra

of the glycerol, phthalic anhydride, catalyst solution and a various oil contents of prepared alkyds are shown in Appendix D.

4.4 Properties of alkyd resins

The properties of prepared alkyd resins from waste cooking oil (AR_WCO) and palm olein oil (AR_PO) were systematically analyzed. Various important properties used for describing of grades and prizes of the alkyds are acid value, viscosity and non-volatile matter. These properties of AR_WCO and AR_PO were taken for making a comparison with that of a standard for binders for paints and varnishes: alkyd resins; 618-2529 (1986), Ministry of industry [26]. The property details are given:

4.4.1 Acid value (AV)

The acid values of alkyd samples should be measured also at room temperature (Tr). The measured acid value of AR_WCO and AR_PO are from the reaction time at 160 minutes (t_{AR_WCO}) [Table A-1 in Appendix A] and 100 minutes (t_{AR_PO}) [Table A-2 in Appendix A]. The analytical results are presented in Table 4-3.

Table 4-3: Effect of oil content to acid value (AV) of alkyd resins from waste cooking oil (AR_WCO) and palm olein oil (AR_PO)

Oil (%w/w)	Acid value (mg.KOH/g.)				TISI 618 – 2529 (1986)**
	AR_WCO		AR_PO		
	at t_{AR_WCO}*	at Tr	at t_{AR_PO}*	at Tr	
35	14.22	13.28	13.74	11.25	≤ 10***
40	12.42	11.51	12.15	9.33	
45	10.94	9.97	9.95	7.53	
50	6.59	6.09	9.61	7.51	5-12****
55	4.95	4.22	8.73	6.46	
60	4.33	3.26	8.21	6.11	

Remarks: * *are acid values being measured at time to stop reaction for AR_WCO and AR_PO.*
** *Standard for binders for paints and varnishes: alkyd resins, Thailand Industrial Standard Institute, Ministry of Industry [26].*
*** *TISI 618 – 2529 (1986) type 1 [26].*
**** *TISI 618 – 2529 (1986) type 2 [26].*

It was found that the values changed slightly from what have been measured at the time to stop the reaction [see Table B-1 and B-2]. The acid values measured at room temperature of the alkyd samples prepared from WCO and PO varying the oil content are reported in Table 4-3. It is appeared that, in this plot, the acid value of AR_WCO are not necessarily greater than of AR_PO. This is because the acid value depends upon oil type, oil concentration and the appropriate time to end the reaction for each condition, described in section 4.2. In regards to previous work done by Kaekai Chaiyawong and Piti Nithipakron [21] preparing a castor oil modified alkyd resin using the oil content of 45 %w/w, the obtained alkyd has acid value of 17.00 mg.KOH/g. Comparatively, the acid value of WCO_45 and PO_45 are only 9.97 and 7.53 mg.KOH/g., resulting from the difference of reaction time used. Since Kaekai Chaiyawong and Piti Nithipakron chose to stop the reaction when the acid value of the alkyd mixture reach the limit of 15 mg.KOH/g., to prepared WCO_45 and PO_45 under such criteria the reaction time of 100 and 60 minutes [Table B-2 in Appendix B] must be used in each case.

The comparison of the acid value of alkyd resin prepared in this work with that TISI 618-2529 (1986) [26] is given in Table 4-2.

It can be seen that the acid value of the alkyd prepared in this study are sometime out of the standard limit for example WCO_35, WCO_55, WCO_60 and PO_35. Note that these values can be adjusted by changing reaction time in order to meet the standard limit.

From statistical calculation to investigate difference of the acid value of the alkyd prepared from WCO and PO, the result shows a significant difference at 95% confidence interval [Table C-2 in Appendix C].

4.4.2 Non-volatile matter (NVM)

The NVM containing in alkyd resin may be either solid or liquid, which is the remaining residue after the solvent, evaporation. Therefore, NVM is in fact the alkyd resin. In case of usage, it should be diluted to liquid because the alkyd resin with exceeded NVM would also have an exceeded viscosity. Thus a suitable solvent must be chosen in to consideration. Since solvents are always cheap relatively to other raw material, they are increasingly required for reducing capital cost. Nevertheless, repeat

coating on a material for a required thickness cost of can be also of expensive process. In order to meet the same standard of producing materials and industrial production line follow the regulation of Thailand Industrial Standard Institute (TISI), Ministry of industry [26]. The characteristic details of alkyd resin are divided into 2 types namely alkyd resin type 1 [see Table 2-3] and alkyd resin type 2 [see Table 2-4] which both types have NVM of 60 $\pm$ 1 %w/w [26]. Then, alkyd resins this work must be dissolved in suitable solvent for instance xylene [9-10, 14, 21-22], in order to obtain NVM are within the standard value, as shown in Table 4-4.

Table 4-4: Effect of oil content to non-volatile matter (NVM) of alkyd resins from waste cooking oil (AR_WCO) and palm olein oil (AR_PO)

Oil (% w/w)	Non-volatile matter (%w/w)		
	AR_WCO	AR_PO	TISI 618 – 2529 (1986)*
35	59.05	59.17	60 $\pm$ 1
40	59.26	59.32	
45	59.30	59.36	
50	59.43	59.39	
55	59.49	59.59	
60	59.71	59.67	

Remarks: * *Standard for binders for paints and varnishes: alkyd resins, Thailand Industrial Standard Institute, Ministry of Industry [26].*

According to Table 4-4, it is found that the NVM containing in the alkyd resins prepared from two kinds oil are relatively increased with oil content. Typically, oil is non-volatile in normal condition. Therefore, adding more oil to prepare alkyd resins is an NVM increasing in the modified alkyd resin.

In case of WCO_45 and PO_45, oil content as 45 %w/w, they have lower NVM (59.30 %w/w and 59.36 %w/w) than alkyd resin from castor oil (64.25 %w/w) [21]. The dilution of using 40 %w/w xylene [26] was used to prepared WCO_45 and PO_45, while 35.75 %w/w xylene was used in the case of castor oil [21].

It can be seen that all alkyd resin obtained from this work have NVM of 59.05 – 59.71 %w/w, and they are within the standard limit (60 $\pm$ 1 %w/w) [see Table 2-3 and Table 2-4] [26]. When the statistic are applied, it is appeared that these results were significantly different at 95 % confidence interval [Table C-3 in Appendix C],

except for NVM of WCO_60 and PO_60 which there were no significantly different at 95 % confidence interval [Table C-3 in Appendix C].

4.4.3 Viscosity

The prepared alkyd resins from waste cooking oil (AR_WCO) and palm olein oil (AR_PO) are of high viscosity. Therefore, if we want to compare these viscosity with the standard value for binders for paints and varnishes: alkyd resins; 618-2529 (1986) which refer to non-volatile matter of 60 $\pm$ 1 %w/w, the dilution of alkyd resin is necessary. For this work, xylene is selected as solvent because it is suitable for alkyd resin with oil content ranging from 35-60 %w/w [9-10, 14, 21-22]. To make the dilution of alkyd resin to that with 60 $\pm$ 1 %w/w of non-volatile matter, 40 %w/w of xylene was used. The analytical results are presented in Table 4-5.

Table 4-5: Viscosity of alkyd resins from waste cooking oil (AR_WCO) and palm olein oil (AR_PO)

Oil (% w/w)	Viscosity at 40 % Xylene (stoke)		
	AR_WCO	AR_PO	TISI 618 – 2529 (1986)*
35	17.60	17.60	10.70 – 63.40**
40	5.50 – 6.27	6.27	22.70 – 388.00***
45	2.80	2.50 – 2.80	
50	0.85	0.85	
55	0.65	0.65 – 0.85	
60	0.50	0.50	

Remarks: * *Standard for binders for paints and varnishes: alkyd resins, Thailand Industrial Standard Institute, Ministry of Industry [26].*

** *TISI 618 – 2529 (1986) type 1 [26]*

*** *TISI 618 – 2529 (1986) type 2 [26]*

Table 4-5 illustrates that the viscosity of alkyd samples decreased with increasing the oil content used. Because molecules of oil enter to insert between chains of alkyd resin, results to each chains of the alkyds can be easy slip. Thus, alkyds prepared from high oil content have a viscosity less than alkyds prepared from low oil content. However, it was found that by using the same amount of oil, the viscosity of AR_WCO is very similar to that of AR_PO. It shown that a type of the oil is not affect

to viscosity of alkyd resins at the same oil content, which it has consistence with IR spectra of WCO and PO. The IR spectra of the oils are very similar [see Figure 4-6]. These the results show that WCO and PO have not difference of chemistry. Then, modifiability of the oils is equable.

The viscosity of WCO_45 and PO_45 are of 2.80 stoke and 2.50-2.80 stoke, which less than viscosity of alkyd resin from Nahar seed oil (544 p or 553 stoke) [15]. This is due to the viscosity of alkyd resin from this work use of 40 %w/w xylene, while the viscosity of alkyd resin from Nahar seed oil use of 0 %w/w xylene [15]. Consequently, alkyd resin from this work has less viscosity than alkyd resin from Nahar seed oil.

In addition, it can be also seen that viscosity from using AR with oil content 35 %w/w, WCO_35 and PO_35 are equal at 17.60 stoke, which is within the standard limit of 10.70-63.40 stoke. Apart from AR_35, the viscosities of AR with oil content at 40-60 %w/w are lower than the standard value. However, all the obtained viscosity can be adjusted as required, by changing proportion of solvent, reactant, type of reactant, or even reaction time, depending on its application.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 Conclusions

From this study, it is found that waste cooking palm olein oil (WCO) has acid value of 1.00 mg.KOH/g. [Table 4-1], which is exceeding the standard limit; TISI 288-2535 (1992) [31]. This oil is, therefore, not appropriate for being reused. In addition, the iodine value of WCO is 50.13 g.I_2/100 g., which it is classified as non-drying oil [4] similar to castor oil [21] and Nahar seed oil [15]. However, the experiments in the research showed that WCO can be used as a raw material for preparing alkyd resin. The conclusions from this work can be drawn as follows:

5.1.1 Alkyd resins from waste cooking oil (AR_WCO)

The appropriate condition of producing alkyd resins from waste cooking oil (AR_WCO) are the condition that use of oil content at 35 %w/w (WCO_35), because the received alkyd resin can give rise to the viscosity value of 17.60 stoke and non-volatile matter of 59.05 %w/w in which both value are within the standard limit; TISI 618-2529 (1986) [26]. However, its acid value of 13.28 mg.KOH/g. is exceeding the standard limit [26], but the acidity can be adjusted by increasing reaction time (>160 minutes) after adding phthalic anhydride.

5.1.2 Alkyd resins from palm olein oil (AR_PO)

Using palm olein oil (PO) of 35 %w/w also gives an appropriate condition for alkyd resin production. The received alkyd resin (PO_35) has the viscosity value of 17.60 stoke and non-volatile matter of 59.17 %w/w, for which both are within the standard TISI 618-2529 (1986) [26]. However, its acid value of 11.25 mg.KOH/g., is also exceeding the standard score [26], but adjusting can also be preformed by increasing reaction time (>100 minutes) after adding phthalic anhydride.

It can be seen that introduction of 35 %w/w of oils into the reaction gives the optimum condition to obtain both AR_WCO and AR_PO. The viscosity and non-volatile matter of the received alkyd resin are similar for both cases, within the standard limit. Although preparing of AR_WCO spend longer reaction time than that of AR_PO, it can be concluded that utilizing of WCO for AR_WCO production is an alternative environmental management and also gives rise value added WCO.

5.2 Recommendations

As the results mentioned above, the recommendation can be given as follows:

5.2.1 The received alkyd resins from WCO this reaction are of non-drying type because of the non-drying property of the oil. Thus, the alkyd resin prepared in this work is more suitable to be used as plasticizer than surface coating.

5.2.2 In order to be used as surface coating, drying properties of these alkyd resins from waste cooking oil are necessary to be improved by mixing with drying oil such as linseed oil or drier.

5.2.3 Comparison of the properties of alkyd resins prepared and the standard limit; TISI 618-2529 (1986) [26] was made to yield the optimum conditions only. To produce an alkyd resin with desirable properties, one can change the preparation steps in numerous ways.

5.2.4 From this study, it can be concluded the waste cooking palm olein oil have an excellent potential for preparation of industrial alkyd resin for plasticizer such as binder in lacquer.

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APPENDIX

APPENDIX A
PRETEST

Table A-1: Acid value of alkyd resins from waste cooking oil (AR_WCO)

Sampling	Time (min.)	Acid value (mg.KOH / g.)					
		WCO_35	WCO_40	WCO_45	WCO_50	WCO_55	WCO_60
1	20	58.94	56.42	49.11	42.95	40.01	28.50
2	40	48.06	44.81	41.25	37.06	33.56	18.89
3	60	40.01	31.47	29.25	24.01	17.73	14.26
4	80	37.23	29.50	19.71	18.23	16.84	
5	100	28.62	22.51	14.97	14.62	14.80	
6	120	23.88	18.49				
7	140	17.24	14.68				
8	160	13.08					

Remark: Acid value which less than 15 mg.KOH/g. indicate to appropriate time to ending of polymerization reaction because it is completed [14, 20-21].

Table A-2: Acid value of alkyd resins from palm olein oil (AR_PO)

Sampling	Time (min.)	Acid value (mg.KOH / g.)					
		PO_35	PO_40	PO_45	PO_50	PO_55	PO_60
1	20	56.19	51.43	42.50	34.66	31.43	25.01
2	40	41.64	36.96	27.87	25.98	20.27	21.98
3	60	28.60	24.75	18.51	17.12	16.27	14.44
4	80	18.51	17.27	15.25	13.79	11.73	
5	100	14.01	13.63	12.33			

Remark: Acid value which less than 15 mg.KOH/g. indicate to appropriate time to ending of polymerization reaction because it is completed [14, 20-21].

APPENDIX B
DATA RECORD

Table B-1: Acid value of alkyd resin from waste cooking oil (AR_WCO) at various time

Oil (% w/w)	Time (min.)	Acid value (mg. KOH / g.)		
		#1	#2	Average
35	20	59.11	59.26	59.19
	40	49.62	48.73	49.18
	60	39.81	41.76	40.79
	80	34.44	37.39	35.92
	100	29.90	29.16	29.53
	120	23.26	22.76	23.01
	140	17.81	17.89	17.85
	160	14.53	13.91	14.22
40	20	52.88	54.50	53.69
	40	43.47	47.10	45.29
	60	32.65	35.63	34.14
	80	27.48	26.73	27.11
	100	21.81	22.48	22.15
	120	17.52	19.96	18.74
	140	13.91	16.61	15.26
	160	11.05	13.78	12.42
45	20	44.85	41.24	43.05
	40	35.89	36.49	36.19
	60	27.47	29.31	28.39
	80	19.97	21.27	20.62
	100	16.13	18.80	17.47
	120	12.84	14.03	13.44
	140	10.83	12.18	11.51
	160	10.06	11.81	10.94
50	20	40.96	39.18	40.07
	40	32.44	27.96	30.20
	60	25.24	23.17	24.21
	80	18.23	19.16	18.70
	100	13.30	15.13	14.22
	120	10.36	10.79	10.58
	140	8.10	8.51	8.31
	160	6.60	6.58	6.59
55	20	38.36	36.36	37.36
	40	25.65	24.56	25.11
	60	18.07	17.67	17.87
	80	13.17	15.51	14.34
	100	9.60	12.99	11.30
	120	7.34	8.94	8.14
	140	5.61	7.10	6.36
	160	4.67	5.22	4.95
60	20	28.85	31.08	29.97
	40	19.27	22.17	20.72
	60	14.09	15.27	14.68
	80	10.82	12.12	11.47
	100	8.02	8.45	8.24
	120	6.67	6.03	6.35
	140	5.33	5.66	5.50
	160	4.53	4.12	4.33

Remark: Acid value was less than 15 mg. KOH / g. indicate to end point of reaction because reaction is completed at this time [14, 20-21].

Table B-2: Acid value of alkyd resin from palm olein oil (AR_PO) at various time

Oil (% w/w)	Time (min.)	Acid value (mg. KOH / g.)		
		#1	#2	Average
35	20	52.24	56.53	54.39
	40	36.61	42.67	39.64
	60	24.66	27.07	25.87
	80	17.51	19.11	18.31
	100	13.87	13.60	13.74
40	20	47.58	49.60	48.59
	40	31.94	30.28	31.11
	60	22.07	22.61	22.34
	80	16.18	17.57	16.88
	100	11.18	13.12	12.15
45	20	38.25	35.43	36.84
	40	26.33	24.10	25.22
	60	17.59	15.28	16.44
	80	14.31	12.33	13.32
	100	10.08	9.81	9.95
50	20	32.48	34.71	33.60
	40	22.43	25.01	23.72
	60	15.93	17.52	16.73
	80	12.74	13.06	12.90
	100	9.21	10.01	9.61
55	20	31.00	30.61	30.81
	40	22.28	19.11	20.70
	60	16.08	14.75	15.42
	80	11.74	10.94	11.34
	100	8.73	8.73	8.73
60	20	27.08	25.88	26.48
	40	19.72	20.93	20.33
	60	15.13	14.27	14.70
	80	11.26	9.89	10.58
	100	8.28	8.13	8.21

Remark: Acid value was less than 15 mg. KOH / g. indicate to end point of reaction because reaction is completed at this time [14, 20-21].

Table B-3: Temperature of alkyd resin from waste cooking oil (AR_WCO) at various time

Oil (% w/w)	Time (min.)	Temperature of mixture (°C)		
		#1	#2	Average
35	20	208	204	206
	40	206	204	205
	60	208	208	208
	80	220	210	215
	100	220	220	220
	120	227	226	227
	140	232	230	231
	160	232	230	231
40	20	205	204	205
	40	213	210	212
	60	218	215	217
	80	220	220	220
	100	223	222	223
	120	229	229	229
	140	232	231	232
	160	236	234	235
45	20	212	210	211
	40	218	216	217
	60	223	222	223
	80	229	227	228
	100	232	232	232
	120	232	230	231
	140	231	229	230
	160	230	229	230
50	20	220	224	222
	40	218	230	224
	60	232	226	229
	80	236	224	230
	100	239	230	235
	120	235	234	235
	140	228	230	229
	160	225	224	225
55	20	216	217	217
	40	222	222	222
	60	226	228	227
	80	228	229	229
	100	230	229	230
	120	233	231	232
	140	233	232	233
	160	232	231	232
60	20	221	221	221
	40	228	226	227
	60	231	231	231
	80	230	231	231
	100	232	232	232
	120	233	232	233
	140	232	232	232
	160	226	230	228

Table B-4: Temperature of alkyd resin from palm olein oil (AR_PO) at various time

Oil (% w/w)	Time (min.)	Temperature of mixture (°C)		
		#1	#2	Average
35	20	212	212	212
	40	221	218	220
	60	230	227	229
	80	236	236	236
	100	240	240	240
40	20	218	216	217
	40	224	224	224
	60	228	228	228
	80	234	232	233
	100	233	232	233
45	20	222	224	223
	40	227	229	228
	60	230	233	232
	80	232	232	232
	100	232	230	231
50	20	225	222	224
	40	232	227	230
	60	235	231	233
	80	234	232	233
	100	230	232	231
55	20	224	224	224
	40	224	227	226
	60	227	229	228
	80	230	230	230
	100	232	232	232
60	20	219	221	220
	40	223	223	223
	60	221	221	221
	80	224	226	225
	100	224	228	226

Table B-5: Appropriate time to ending of reaction of alkyd resin from waste cooking oil (AR_WCO)

Oil	Time (min.)		
(% w/w)	#1	#2	Average
35	160	160	160
40	140	160	150
45	120	120	120
50	100	120	110
55	80	100	90
60	60	80	70

Table B-6: Appropriate time to ending of reaction of alkyd resin from palm olein oil (AR_PO)

Oil	Time (min.)		
(% w/w)	#1	#2	Average
35	100	100	100
40	100	100	100
45	80	80	80
50	80	80	80
55	80	60	70
60	80	60	70

Table B-7: Acid value at room temperature of alkyd resin from waste cooking oil (AR_WCO)

Oil	Acid value at room temperature (mg. KOH / g.)		
(% w/w)	#1	#2	Average
35	14.35	12.21	13.28
40	10.85	12.17	11.51
45	9.53	10.41	9.97
50	6.05	6.13	6.09
55	3.82	4.61	4.22
60	3.43	3.08	3.26

Table B-8: Acid value at room temperature of alkyd resin from palm olein oil (AR_PO)

Oil	Acid value at room temperature (mg. KOH / g.)		
(% w/w)	#1	#2	Average
35	11.32	11.17	11.25
40	8.81	9.84	9.33
45	7.79	7.26	7.53
50	7.42	7.60	7.51
55	6.38	6.53	6.46
60	6.16	6.06	6.11

Table B-9: Non volatile matter (40% Xylene) of alkyd resin from waste cooking oil (AR_WCO)

Oil (% w/w)	Non volatile matter (40% Xylene) (% w/w)		
	# 1	# 2	Average
35	59.00	59.09	59.05
40	59.27	59.25	59.26
45	59.31	59.29	59.30
50	59.44	59.41	59.43
55	59.50	59.47	59.49
60	59.68	59.73	59.71

Table B-10: Non volatile matter (40% Xylene) of alkyd resin from palm olein oil (AR_PO)

Oil (% w/w)	Non volatile matter (40% Xylene) (% w/w)		
	# 1	# 2	Average
35	59.16	59.18	59.17
40	59.33	59.30	59.32
45	59.35	59.36	59.36
50	59.39	59.39	59.39
55	59.63	59.54	59.59
60	59.69	59.65	59.67

Table B-11: Viscosity (40% Xylene) in various units of alkyd resin from waste cooking oil (AR_WCO)

Oil (% w/w)	Viscosity (40% Xylene)					
	Gardner			Stoke		
	#1	#2	Average	#1	#2	Average
35	Y	Y	Y	17.60	17.60	17.60
40	T-U	T-U	T-U	5.50-6.27	5.50-6.27	5.50-6.27
45	K	K	K	2.80	2.80	2.80
50	C	C	C	0.85	0.85	0.85
55	B	B	B	0.65	0.65	0.65
60	A	A	A	0.50	0.50	0.50

Table B-12: Viscosity (40% Xylene) in various units of alkyd resin from palm olein oil (AR_PO)

Oil (% w/w)	Viscosity (40% Xylene)					
	Gardner			Stoke		
	#1	#2	Average	#1	#2	Average
35	Y	Y	Y	17.60	17.60	17.60
40	U	U	U	6.27	6.27	6.27
45	J-K	J-K	J-K	2.50-2.80	2.50-2.80	2.50-2.80
50	C	C	C	0.85	0.85	0.85
55	B-C	B-C	B-C	0.65-0.85	0.65-0.85	0.65-0.85
60	A	A	A	0.50	0.50	0.50

APPENDIX C

STATISTICAL RESULTS

Table C-1: Different analysis of appropriate time to ending of reaction between alkyd resin from waste cooking oil (AR_WCO) and alkyd resin from palm olein oil (AR_PO) at various oil content
Mann-Whitney Test

Oil content (% w/w)	Mann-Whitney Test	Results
35	.000	Difference
40	.000	Difference
45	.000	Difference
50	.000	Difference
55	.500	No difference
60	2.000	No difference

Remarks : If Mann-Whitney Test ≤ .05 The mean difference is significant at the .05 level.
If Mann-Whitney Test > .05 The mean no difference is significant at the .05 level.

Table C-2: Different analysis of acid value at room temperature between alkyd resin from waste cooking oil (AR_WCO) and alkyd resin from palm olein oil (AR_PO) at various oil content
Mann-Whitney Test

Oil content (% w/w)	Mann-Whitney Test	Results
35	.000	Difference
40	.000	Difference
45	.000	Difference
50	.000	Difference
55	.000	Difference
60	.000	Difference

Remarks : If Mann-Whitney Test ≤ .05 The mean difference is significant at the .05 level.
If Mann-Whitney Test > .05 The mean no difference is significant at the .05 level.

Table C-3: Different analysis of non-volatile matter (40 % Xylene) between alkyd resin from waste cooking oil (AR_WCO) and alkyd resin from palm olein oil (AR_PO) at various oil content
Mann-Whitney Test

Oil content (% w/w)	Mann-Whitney Test	Results
35	.000	Difference
40	.000	Difference
45	.000	Difference
50	.000	Difference
55	.000	Difference
60	1.000	No difference

Remarks : If Mann-Whitney Test ≤ .05 The mean difference is significant at the .05 level.
If Mann-Whitney Test > .05 The mean no difference is significant at the .05 level.

Table C-4: Different analysis of viscosity (40 % Xylene) between alkyd resin from waste cooking oil (AR_WCO) and alkyd resin from palm olein oil (AR_PO) at various oil content
Mann-Whitney Test

Oil content (% w/w)	Mann-Whitney Test	Results
35	2.000	No difference
40	.000	Difference
45	.000	Difference
50	2.000	No difference
55	.000	Difference
60	2.000	No difference

Remarks : If Mann-Whitney Test ≤ .05 The mean difference is significant at the .05 level.
If Mann-Whitney Test > .05 The mean no difference is significant at the .05 level.

APPENDIX D

FTIR Spectrum

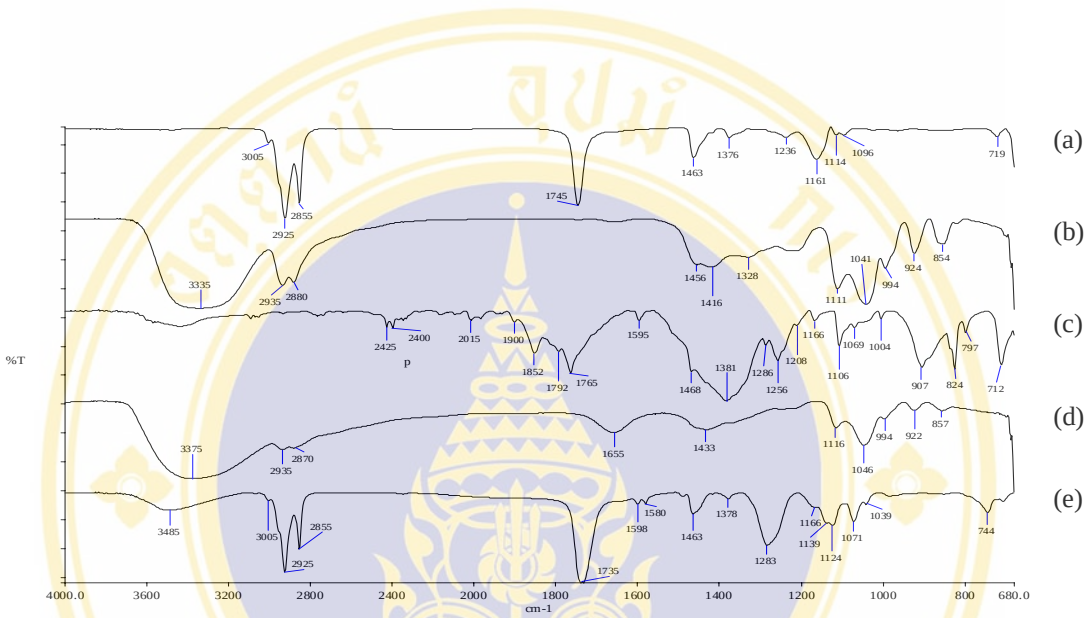

Figure D-1: FTIR Spectrum of reactant and product of waste cooking oil modified alkyd resin (a) Waste cooking oil (b) Glycerol (c) Phthalic anhydride (d) Catalyst (e) WCO_60

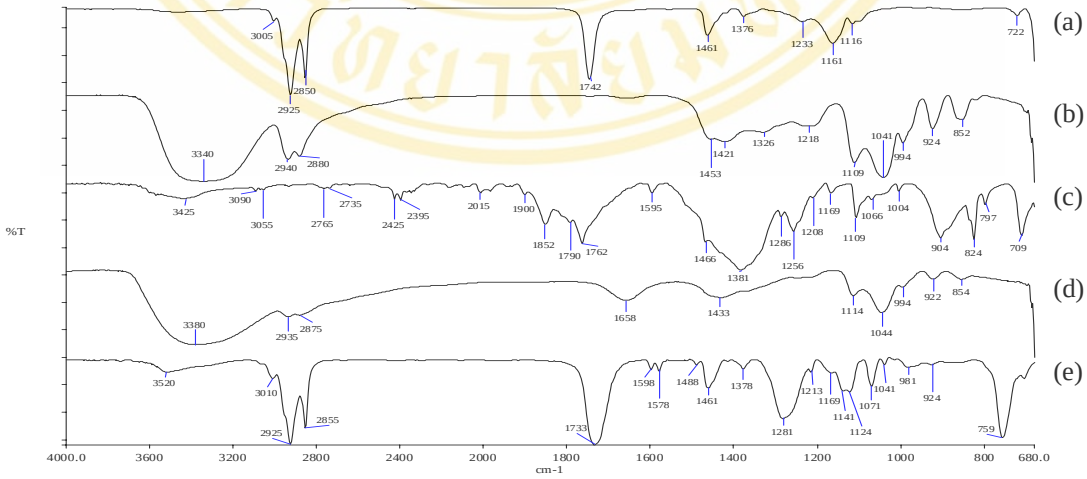

Figure D-2: FTIR Spectrum of reactant and product of palm olein oil modified alkyd resin (a) Palm olein oil (b) Glycerol (c) Phthalic anhydride (d) Catalyst (e) PO_60

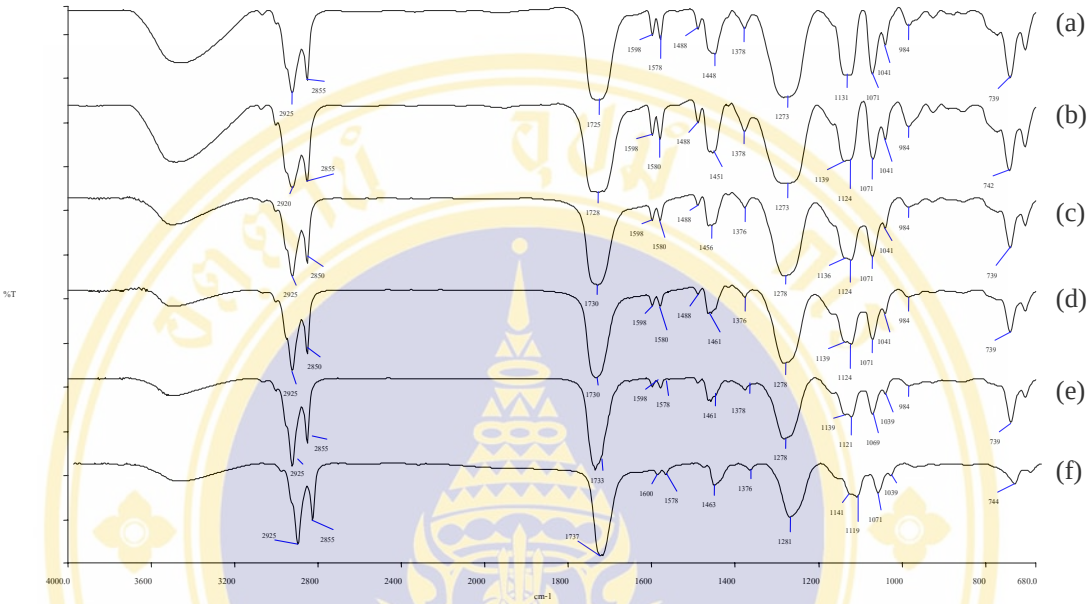

Figure D-3: FTIR Spectrum of waste cooking oil modified alkyd resin (a) WCO_35 (b) WCO_40 (c) WCO_45 (d) WCO_50 (e) WCO_55 (f) WCO_60

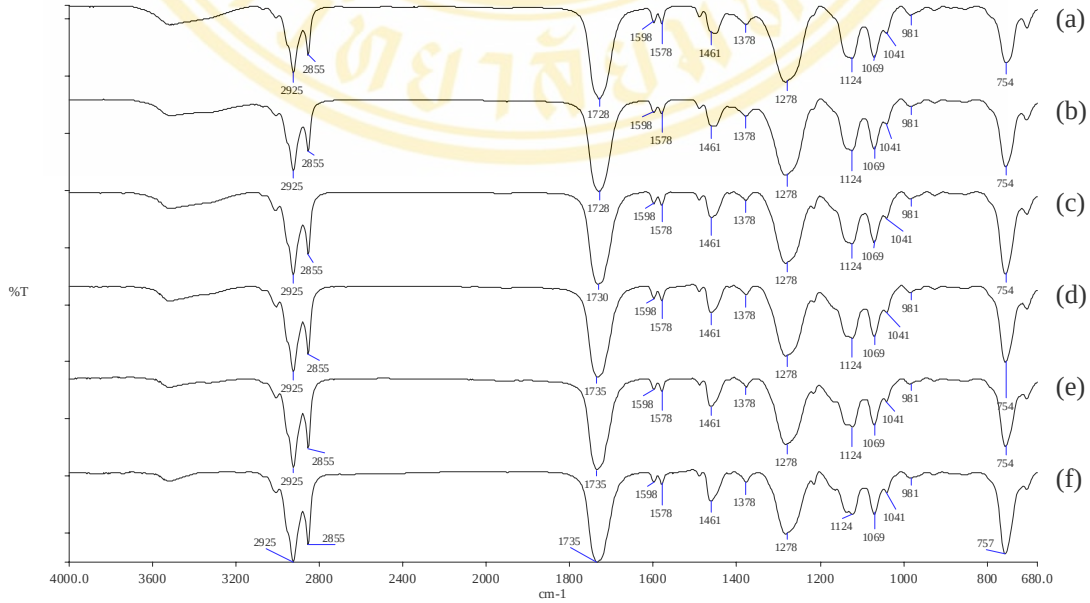

Figure D-4: FTIR Spectrum of palm olein oil modified alkyd resin (a) PO_35 (b) PO_40 (c) PO_45 (d) PO_50 (e) PO_55 (f) PO_60

APPENDIX E

OIL-MODIFIED ALKYD RESINS

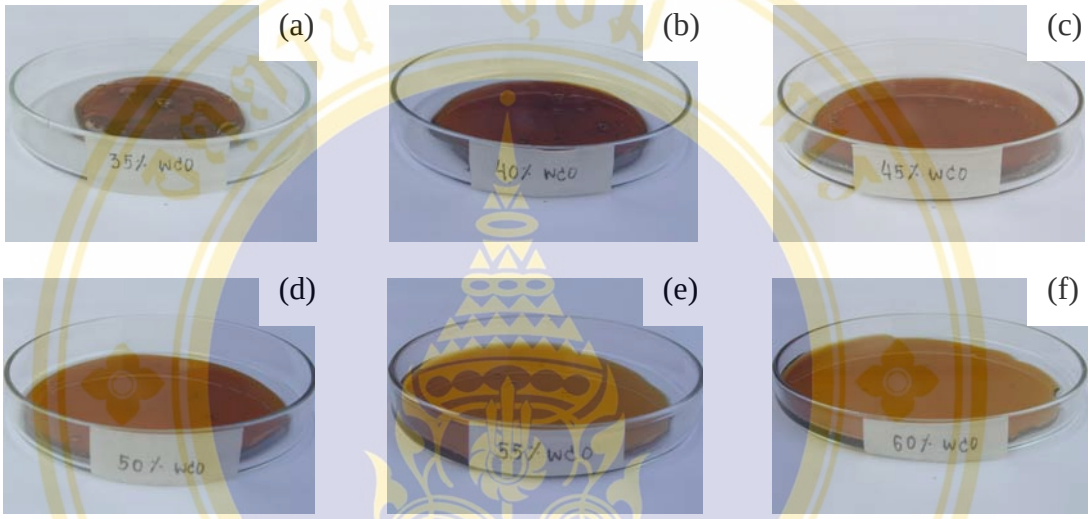

Figure E-1: Alkyd resins from waste cooking oil (AR_WCO) (a) WCO_35 (b) WCO_40 (c) WCO_45 (d) WCO_50 (e) WCO_55 (f) WCO_60

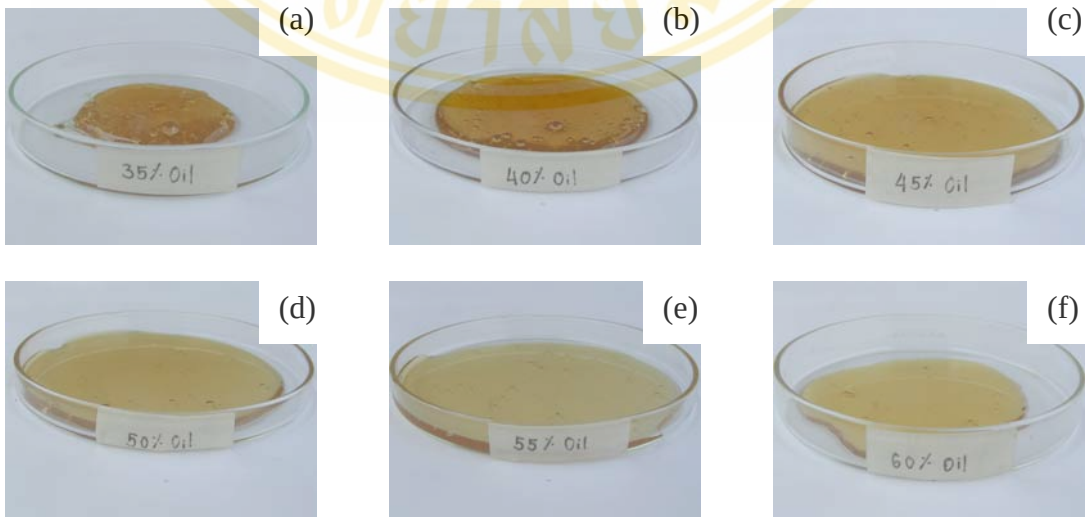

Figure E-2: Alkyd resins from palm olein oil (AR_PO) (a) PO_35 (b) PO_40 (c) PO_45 (d) PO_50 (e) PO_55 (f) PO_60

BIOGRAPHY

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