LINEAR LONG CHAIN HYDROCARBONS FROM DEOXYGENATION OF PALMITIC ACID OVER CALCINED HYDROTALCITE

PURACHET PATTAMASINGH
SUPHAWIT MANKONG

A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIRMENT FOR THE DEGREE OF BACHELOR OF SCIENCE
IN PETROCHEMICAL TECHNOLOGY
FACULTY OF SCIENCE
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG

Project Title	Linear long chain hydrocarbons from deoxygenation of palmitic acid over Calcined-hydrotalcite
Students	Purachet Pattamasingh Suphawit Mankong
Degree	Bachelor of Science
Program	Petrochemical Technology (International)
Project Advisor	Assoc. Prof. Dr. Tawan Sooknoi

ABSTRACT

Calcined-hydrotalcites were synthesized at different Mg/Al ratio (2 and 3) and hydrothermal temperature (120 and 160 °C) by co-precipitation method of the $MgSO_4$ and $Al_2(SO_4)_3$ solution. From BET, the calcined-hydrotalcites possess higher surface area than that of bulk MgO. From XRD, the calcined-hydrotalcite R3T160 and R2T120 have a relative crystallinity higher than that of R3T120 and R2T160. The deoxygenation of palmitic acid was carried out in a semi-batch reactor at 460°C, 6 hours, and N_2 as carrier gas using synthetic calcined-hydrotalcites and bulk MgO as a catalyst at catalyst:palmitic acid ratio of 0.8:1.0, 1.0:1.0, and 1.2:1.0. Major products were linear long chain α-olefins (C_{14} and C_{15}) and linear paraffinic hydrocarbons (C_{14} and C_{15}) from decarboxylation and deacetylation reaction. The catalysts activity of calcined-hydrotalcite is generally higher than that of bulk MgO. It was found that the crystallinity of the hydrotalcite phase of the calcined-hydrotalcite catalyst can be affected to the liquid hydrocarbon yield and also prevent the formation of high molecular weight ketone due to coupling reaction when the mol ratio of catalyst:palmitic is increased to 1.2:1.0. While bulk MgO give significant extent of the coupling reaction. From TGA of residue showed that no metal carbonate was formed after the reaction. Carbon dioxide was released to the gas phase during the reaction.

ACKNOWLEDGEMENT

The authors wish to express their deep gratitude to Assoc. Prof. Dr. Tawan Sooknoi for continuous supports, encouraging guidance, advices, and helpful suggestions that substantially contributed for completion of this project.

Sincere thanks to Asst. Prof. Dr. Vanchat ChuenChom and Asst. Prof. Dr. Montre Thongkam for serving as committee and their valuable comments.

Apart from that we would like to extend this sincere appreciate to our senior mentor, Mr. Assawin Krachonwong and all other seniors especially Mr. Tanasak Solos for their grateful supports and guidance over the year. We also would like thank all of my friends and our research group for their encouragement and support.

Without instruments, chemicals and facilities of Department of Chemistry, Faculty of Science, this project would not be completed.

Finally, the authors would like to dedicate this project to our parents and beloved family for the encouragement and continuous support.

Purachet Pattamasingh

Suphawit Mankong

CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

CHAPTER 1

INTRODUCTION

1.1Motivation

In the recent years, the fuel price has been increased due to the depletion of petroleum. Therefore, scientists try to find the renewable source that could be used to produce fuel, in particular the diesel, as it is the main fuel for logistic system. Recently, the biodiesel has been considered as the alternative source for diesel fuel but later the scientists found that it could cause some problems with the combustion engine as it is an oxygenate compound. Hence, the fatty acid from hydrolysis of animal fat and vegetable oil that can be used as alternative source for production of the long chain hydrocarbon via deoxygenation reaction.

The deoxygenation of fatty acid can separate into 2 types of reactions, decarboxylation and hydrodeoxygenation reaction. In this project, the investigation of decarboxylation reaction of fatty acid at relatively milder condition, as compared to hydrodeoxygenation that need high partial pressure of hydrogen as co-feed [1]. In addition, the hydrocarbon product has many advantages over the petrofuel since it has no presence of sulfur and metal content [2].

The fatty acid can react with the basic catalyst forming carboxylate intermidiate due to neutralization reaction. When heating this salt, as in the general case, it undergoes deoxygenation reaction bearing the long chain hydrocarbon and metal carbonate as show in Figure 1.1

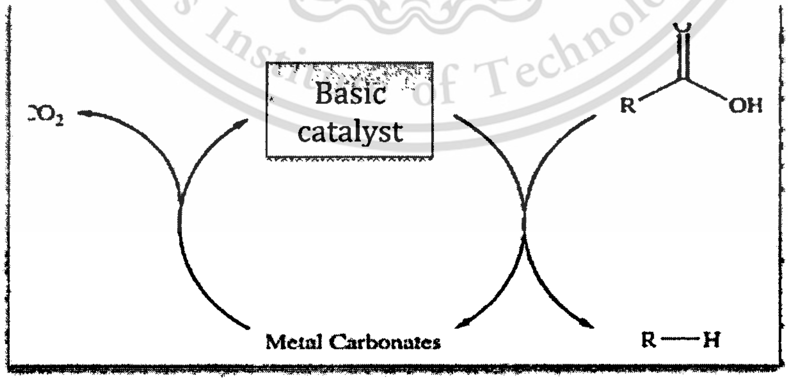


Figure 1.1 Catalytic cycle of decarboxylation of fatty acid over basic catalyst

The metal carbonate formed that can be regenerated by heating to release carbon dioxide and active basic catalyst [3] can be recovered.

From the previous research, various type of metal oxide were used as catalysts for deoxygenation of fatty acid, the results showed that the metal oxide such as MgO have a lower catalyst activity when compared with the other metal oxide such as barium oxide. However, barium oxide required a high regeneration temperature (>1000 °C) [4]. As discussed earlier, the MgO is appropriate catalyst for the further studies by improve the catalyst activity of that MgO. Therefore, this research seek for other types MgO catalysts that could increase the activity, selectivity for longchain hydrocarbon and does not formed stable $MgCO_3$ during the reaction. This includes the Mg hydrotalcite catalyst that contains more basicity and higher surface area as compared to the bulk magnesium oxide catalyst. The hydrothermal temperature and ratio of Mg/Al was studied that both factor can be effected the crystallinity and surface area of the catalyst.

1.2 Objectives

1.2.1 To synthesis the Mg hydrotalcite catalyst.

1.2.2 To obtain a mixture of hydrocarbons from deoxygenation of palmitic acid over hydrotalcite catalysts.

1.2.3 To understand the effect of the surface area, basicity, and crystallinity on activity and selectivity long chain hydrocarbon.

1.3 Scope of work

1.3.1 Synthesis hydrotalcite catalyst with the mole ratio of M^{2+}/M^{3+} of 2 and 3 with hydrothermal temperature of 120 and 160 °C for 6 h and calcination temperature at 500 °C for 3 h.

1.3.2 Characterization of each catalyst by using X-ray diffraction (XRD), Gas adsorption analysis (BET), Thermogravimetric analysis (TGA).

1.3.3 Study the degradration of palmitate salt by using Thermogravimetric analysis (TGA)

1.3.4 Investigation of the decarboxylation reaction of each catalyst in semibatch reactor at 460 °C with mol ratio of catalyst:palmitic acid of 1.2:1.0, 1.0:1.0, and 0.8:1.0.

1.3.5 Analysis of the product with gas chromatography and residue with Thermogravimetric analysis (TGA).

1.4 Expected results

It is expected that a Mg hydrotalcites catalyst can give higher activity and selectivity for long chain hydrocarbon than MgO catalyst and this new technology could be further develop for the future energy.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Fatty acid

Fatty acid is a carboxylic acid with a long aliphatic tail (chain), which is either saturated or unsaturated [5]. Most naturally occurring fatty acids have a chain of an even number of carbon atoms, from 4 to 28.

Fatty acid chains can be categorized as short, medium, or long. Short-chain fatty acids (SCFA) are fatty acids with aliphatic tails of fewer than six carbons (i.e. butyric acid).

Medium-chain fatty acid (MCFA) are fatty acids with aliphatic tails of 6–12 carbons, which can form medium-chain triglycerides.

Long-chain fatty acid (LCFA) are fatty acids with aliphatic tails longer than 12 carbons. Very long chain fatty acid (VLCFA) are fatty acids with aliphatic tails longer than 22 carbons[5]

Fatty acids are usually derived from triglycerides or phospholipids of animal fat(e.g., beef, butter) or vegetable oil(e.g., palm oil, coconut oil)[6].

Saturated fatty acid is fatty acid that do not contain any double bonds and other functional group such as palmitic acid.

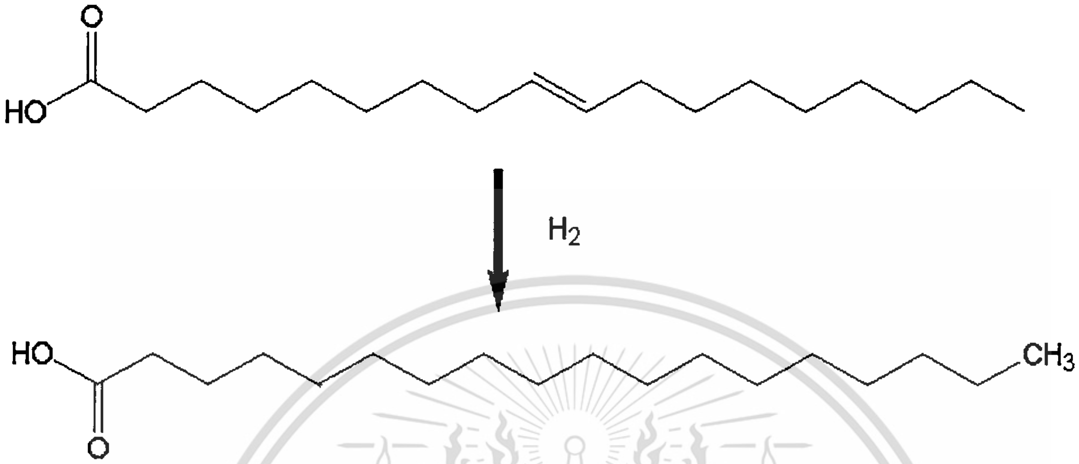
Unsaturated fatty acid is fatty acids that have one or more double bonds between carbon atoms. The two carbon atoms in the chain that are bound next to either side of the double bond can occur in a *cis* or *trans* configuration. The example of unsaturated fatty acid such as oleic acid or linoleic acid.

2.1.1 Reaction of fatty acid

2.1.1.1 Hydrogenation

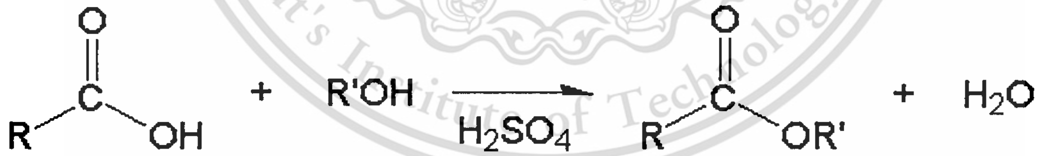
Hydrogenation is the chemical reaction between hydrogen and unsaturated compound ordinarily in the presence of a catalyst. The reaction may be one in which hydrogen simply adds to a double or triple bond connecting two atoms in the structure of the molecule. For non-catalytic hydrogenation take place at very high pressure [7].

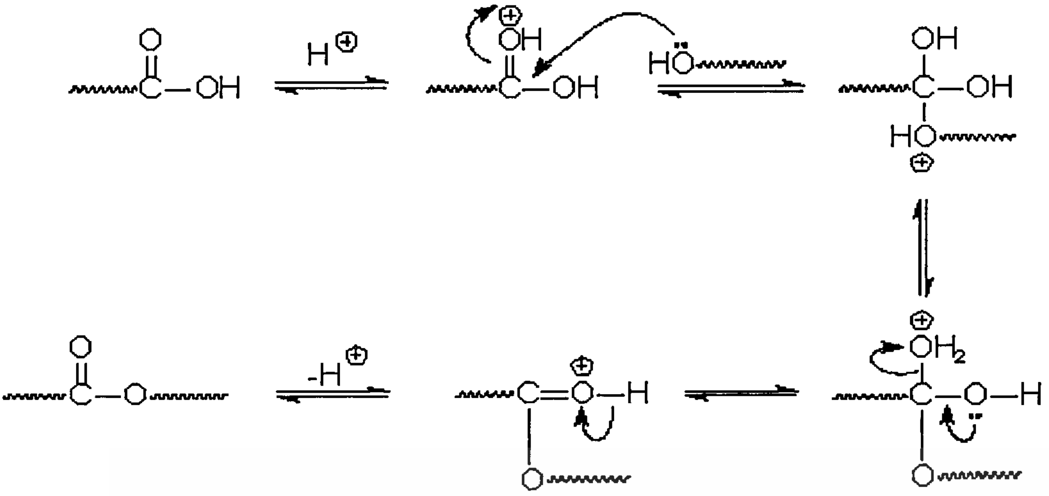
For example, titania-supported monometallic ruthenium catalyst prepared by impregnation method is more active and selective for the hydrogenation of oleic acid to the saturated stearic acid[8].



2.1.1.2 Esterification

Fatty acid is also have the same functional group as carboxylic acid, then it mean that they can undergo esterification and acid-base reaction. Esterification is a chemical reaction of alcohol and carboxylic acid forming ester compound[9-10].





Each step of esterification is reversible but in the presence of large excess of the alcohol, the equilibrium point of reaction is displaced so that esterification proceed virtually to completion.

2.1.1.3 Decarboxylation

Decarboxylation is a chemical reaction that releases carbon dioxide (CO_2). Usually, decarboxylation refers to a reaction of carboxylic acids, removing a carbon atom from a carbon chain in form of carbon dioxide[11].

The example of decarboxylation is the catalytic liquid phase decarboxylation of fatty acids and ester over Pd/C catalyst for the production of linear hydrocarbon has been investigated in semi-batch reactor[12].

The initial reaction in the decarboxylation of stearic over catalyst at 300 °C under helium with a total pressure of 6 bar in dodecane. The selectivity to the desired product, n-heptadecane was very high under this condition (98 %) and other heptadecene is about 3 %.

2.1.1.4 Hydrodeoxygenation

Hydrodeoxygenation is a hydrogenolysis process removing oxygenated compounds from fast pyrolysis or hydrothermal liquefaction derived bio-oil using commercial hydrotreating catalysts in the form of water [13].

Hydrotreating catalyst commonly used are nickel-molybdenum or cobalt-molybdenum on gamma alumina, zeolites (ZSM-5), palladium on carbon and platinum on carbon as well as alumina.

$$C_{18}H_{37}OH \xrightarrow[\text{[-}H_2O\text{]}]{+H_2} n\text{-}C_{18}H_{38}$$

2.2 Basic catalyst

2.2.1 Solid base

2.2.1.1 Definition of acids and bases

There are two main definitions of acids and bases, is bronsted and lewis acid or base. According to bronsted acids are substances that donate a proton to another molecule or ion, while bronsted base are substances that accept a proton to another molecule or ion.

$$AH + B^- \longrightarrow A^- + BH$$

AH is an acid and B^- is base. In reverse reaction BH is a conjugated acid and A^- is base. The reaction between AH and A^- is called conjugated. Thus, AH is a conjugated acid of A^- and A^- is a conjugated base of AH. Similarly, B^- is a conjugated base of BH and BH is a conjugated acid of B^-. Then AH and BH are called bronsted acids, while A^- and B^- are called bronsted acid.

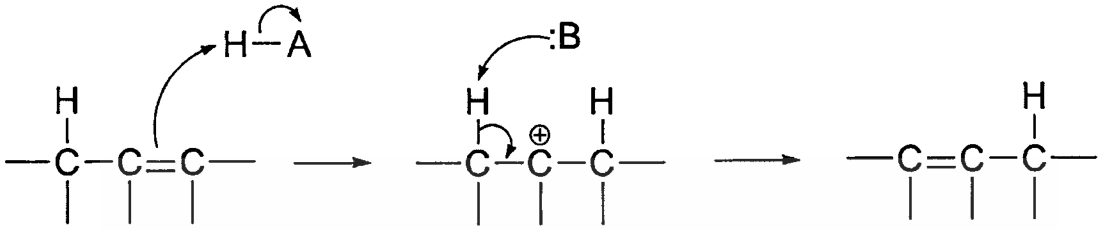
According to lewis acid are substances that accept an electron pair to form a covalent bond, while lewis base are substance that donate an electron pair to another molecule or ion.

$$BF_3 + :NH_3 \longrightarrow F_3B\cdots NH_3$$

Following above reaction, NH_3 is a lewis base and FB_3 is a lewis acid.

2.2.1.2 Solid base and basic sites

Solid base are defined as solid that serve as base by either definition of bronsted or lewis acid. On the surface of solid base consist of specific sites or centers that it function as base. This sites are called basic sites. For example, isomerization of alkene.



Hence, basic site :B on the solid surface act as a bronsted base. The example of lewis base is reaction of ketone [14]

Hence, the basic site B^- on the solid surface act as lewis base. It should be noted that the same surface sites could either serve as bronsted and lewis base depend on the nature of the adsorbate.

2.2.2 Basic strength of basic sites

H_ acidity function is defined as a measure of the ability of the basic solution to abstract a proton from an acidic solute.

$$H\_ = pK_a - \log(\{AH\}/[A^-])$$

To determine the H_ value, the concentration of AH and A^- have to measure accurately. It was proposed that the H_ scale can be used as the measurement of basic strength of solid base, then basic sites of solid base is express by mean of H_ value equated to the highest among the pK_a Value of adsorbate from which the basic sites is able to abstract proton.

2.2.3 Solid base material

2.2.3.1 Hydrotalcite and hydrotalcites-like-compound.

Hydrotalcite is a magnesium–aluminum hydroxycar- bonate, naturally occurring mineral of chemical composition $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H2O$ exhibiting a layered crystal structure, which is comprised of positively charged hydroxide layers and interlayer composed of carbonate anions and water molecules [15], as shown in figure 2.1

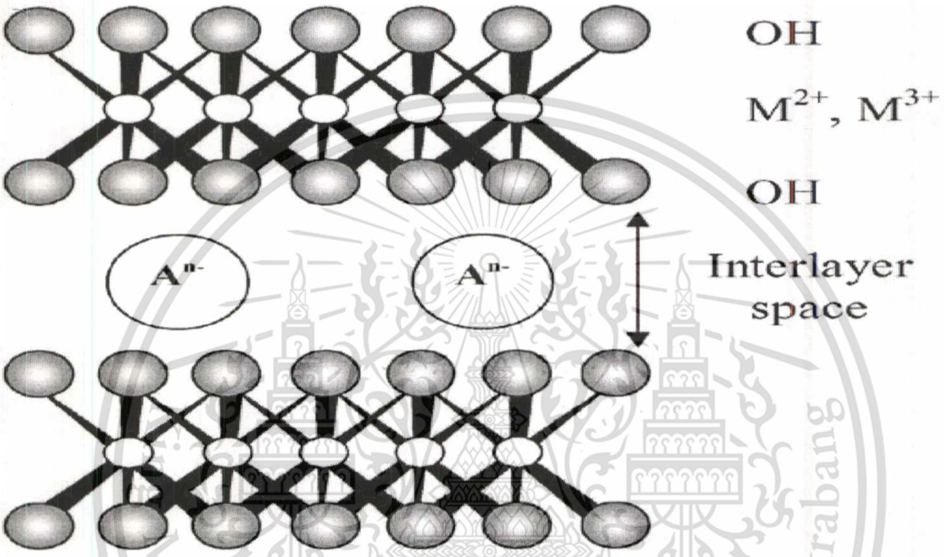


Figure 2.1 Structure of hydrotalcite

The ordering of hydroxide layers is similar to that of brucite, $Mg(OH)_2$, where each Mg^{2+} cation is octahe-drally surrounded by six OH^- anions and the different octahedra $[Mg(OH)_6]^{4-}$ share edges to form infinite sheets. In the hydrotalcite, the Mg^{2+}/Al^{3+} isomorphous substitution in octahedral sites of the hydroxide sheet results in a net positive charge, which has to be neutralized by interlayer anionic species. The brucite-like sheets can stack one on the other with two different symmetries, rombohedral or hexagonal. Rombohedral symmetry have mainly been found in nature; the hexagonal polytype may be the high temperature form of the rombohedral one [16].

Hydrotalcite-like compounds is isomorphous compounds, with chemical composition $[M(II)_{1-x}\ M(III)_x(OH)_2]^{X+}(A^{n-})_{x/n} \cdot\ mH_2O$ containing various M(II) and M(III) metal cations in hydroxide layers and various interlayer anions. They are used in heterogeneous catalysis as catalysts, catalyst precursors and support materials, as neutralizing agents and halogen scavengers in polymer processing or in pharmacy.

There are 4 factors that affected on chemical composition of hydrotalcite. First, M(II) and M(III) ions which can be accomodated in the holes of the close packed configuration of OH groups in the brucite-like layers should have an ionic radius not too different from that of Mg^{2+}or Al^{3+} .Second, value of x, it is possible to obtain pure HTlcs only for $0.2<x<O.33$. For x values outside the above range either the pure hydroxides or other compounds with different structures have been obtained such as For higher x, the $Al(OH)_3$ may be obtain .In the other hand, For lower x, the $Mg(OH)_2$ .Third, the nature of anion. Fourth, the values of m, Water molecules are localized in the interlayer in those sites which are not occupied by the anions. Usually, the amount of water is determined by thermogravimetric measurements of weight loss. The most common method applied to preparation of hydrotalcite-like compounds is co-precipitation by constant pH at low supersatuation.

Hydrothermal treatment is thermal treatment in the presence of water vapour at temperatures which do not exceed the decomposition temperature of the hydrotalcite -like compound in the autoclave that can improve the crystalinity and crystalize size of hydrotalcite-like compound and also increase the hydrotalcite content [15].

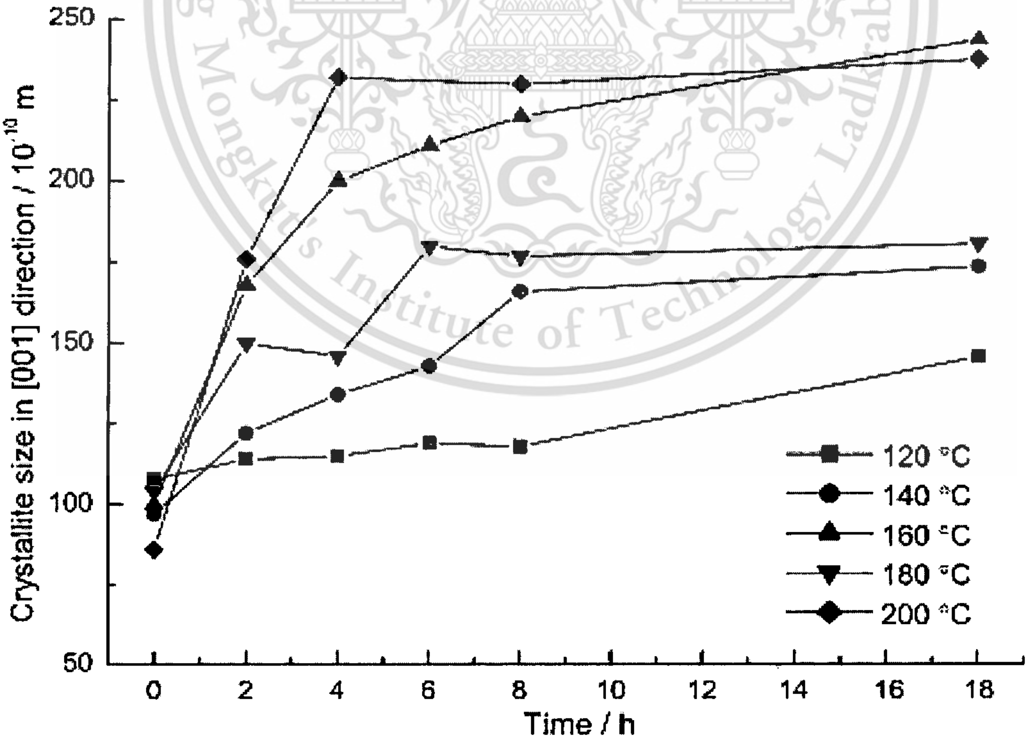


Figure 2.2 The affect of hydrothermal temperature on crystallite size

From the Figure, If hydrothermal temperature increase,the crystallize size always increase. After the hydrotalcite was calcined the structure change from M(lI)M(IlI)A-HTlc to spinel $M(II)M(III)_2O_4$ together with free M(II)O. We shall deal with the four main properties of the oxides and mixed oxides formed by calcination of hydrotalcite-like compound consist of basic property, paracrystalliity, formation of non-stoichiometric spinels, and memory effect. For the example of basic property can be explain by the catalysis activity of calcined hydrotalcite ($MgAlCO_3$-HT) on polymerization of propylene oxide, the result show that the polymer yield as a function of the calcination temperature. The uncalcined HT and the one treated at the temperature at which only the water of crystallization is lost (533K) were not active, while the maximum activity was found for the HT calcined at 723 K[16].

For the $MgAlCO_3$-HT system, the modifications of some HT properties (surface area, pore volume, X-raypattern) according to the temperature of calcination as shown in figure 2.3. The main transformations occurred between 570 and 670 K, where the d values of reflections for MgO began to appear in the X-ray pattern. Between 670 and 770 K small variations in porosity and weight loss were observed, and at further, higher temperatures no other modifications apparently occurred ($MgA1_20_4$ forrned at even higher temperatures). High surface area MgO and, possibly, amorphous phases containing aluminium ions are the products of $MgAlC0_3$-HT decomposition.

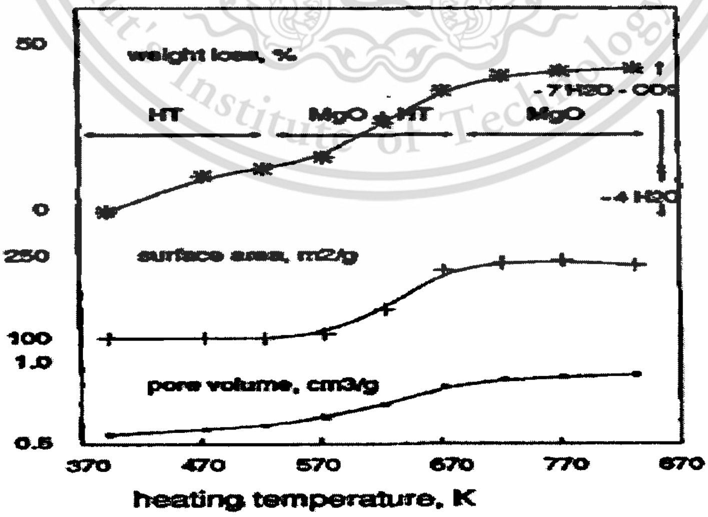


Figure 2.3 Modification of some HT properties as a function of the calcination temperature

The nature of basic property of MgO from the decomposition of $MgAlCO_3$-HT was investigated. The basic properties of MgO have been recognized for a long time, and have been attributed to O^{2-} surface basic sites (strong basic sites), O^- located near hydroxyl groups (medium strong sites), and to OH groups (weak basic sites).

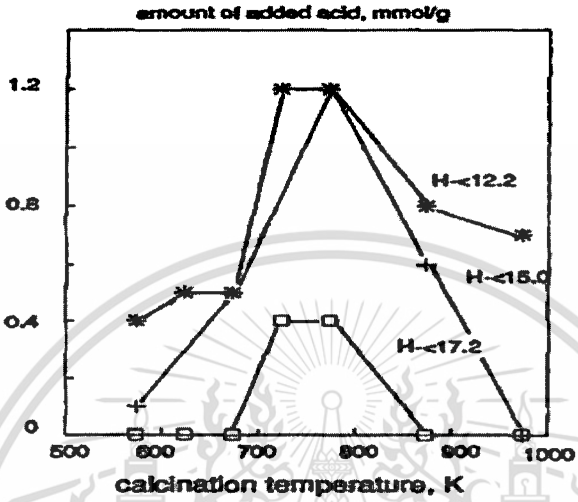


Figure 2.4 Shows the basic strength of the products of HT calcination at different temperatures

The basic strength was measured by titration with different indicators, in order to determine the number of basic sites in correspondence with different maximum basic strengths. It is shown that there is a maximum in the number of active sites when the HT is calcined at 773K. The other factor that can affect the basic sites of calcined hydrotalcite is Mg/Al ratio, when the Mg/Al ratio increase, the number of basic site increase [16].

2.3 Fuels

Most liquid fuels used currently are produced from petroleum. The fuel products feature gasoline, kerosene, and diesel oil provides fuel for vehicle and generates electricity. The constant demand for products, such as liquid fuels, is the main driving force behind the petroleum industry. Other products such as lubricating oils, waxes, and asphalt. Now a day the main part of the petroleum industry was inspired by the development of the automobile and the continued demand for gasoline and other fuels. Such a demand has been accompanied by the demand for other products: diesel fuel for engines, lubricants for engine and machinery parts, fuel oil to provide power for the industrial complex, and asphalt for roadway.

2.3.1 Kerosene

Kerosene, also called paraffin oil, is a flammable pale-yellow or colorless oily liquid with a characteristic odor. It is obtained from petroleum and used for burning in lamps and domestic heaters or furnaces, as a fuel or fuel component for jet engines, and as a solvent for greases and insecticides. Kerosene is also defined petroleum distillate that has a flash point of about 25 °C (77 °F) and is suitable for use as an illuminant when burned in a wide lamp. The term kerosene is also too often incorrectly applied to various fuel oils, but a fuel oil is actually any liquid or liquid petroleum product that product that produces heat when burned in a suitable in container or that produces power when burned in an engine. Kerosene originated as a straight-run petroleum fraction that boiled between approximately 205 and 260 °C (400-500 °F). Chemically, kerosene is usually consists of about 10 different hydrocarbons each containing from 10 to 16 carbon atoms per molecule; the constituents include n-dodecane (n-$C_{12}H_{26}$), alkyl benzenes, and naphthalene and its derivatives [16-17]. Kerosene, because of its use as burning oil, must be free aromatic and unsaturated hydrocarbons, as well as free of the more obnoxious sulfur compound. It is stable product, and not required the additive to improve the quality. Apart from the remove of excessive quantities of aromatics by the Edeleanu process, kerosene fractions may need only a lye wash or a doctor treatment if hydrogen sulfide is present to remove Mercaptans. The essential properties of kerosene are flash point, fine point, distillation rang, burning sulfur content, color, and cloud point. In the case of the flash point, the minimum flash temperature is generally placed above the prevailing ambient temperature; fine point determines the fire hazard associated with its handling and use. The boiling rang is of less importance for kerosene than for gasoline, but it can be taken as an indication of the viscosity of the product. The ability of kerosene to burn steadily and cleanly over an extended period is an important property and gives some indication of the purity or composition of the product. The significance of the total sulfur content of a fuel oil varies greatly with the type of oil and the use to which it is put. Sulfur content is of great importance when the oil to be burned produces sulfur oxides that contaminate the surroundings. The color of kerosene is of little significance, but a product darker than usual may have resulted from contamination or aging and in fact a color dark than specified may be considered by some users as unsatisfactory. Finally, the cloud point of kerosene gives indication of the temperature at which the wick may become coated with wax particles, thus lowering the burning qualities of the oil.

2.3.2 Diesel

Diesel is also a distillate fuel oil. In general, it is a blend of straight-run gas oil and cracked gas oil to produce a produce a product boiling in the 175-345°C (350-650°F) rang. Diesel fuel oil is essentially the same as furnace fuel oil, but the proportion of cracked gas oil is usually less since the high aromatic content of the cracked gas oil reduces the cetane value of the diesel fuel [18]. Cetane number is a measure of the tendency of a diesel fuel to knock in a diesel engine. The scale is based upon the ignition characteristics of two hydrocarbons n-hexadecane (cetane) and 2, 3, 4, 5, 6, 7, 8-heptamethylnonane. Cetane has a short delay period during ignition and is assigned cetane number of 100; heptamethylnonane has a long delay period and has been assigned a cetane number of 15. Just as the octane number is meaningful for automobile fuels, the cetane number is a means of determining the ignition quality of diesel fuels and is equivalent to the percentage by volume of cetane in the blend with heptamethylnonane, which matches the ignition quality of the test fuel. The boiling range, carbon atom and phase of petroleum products are shown in Table 2.1.

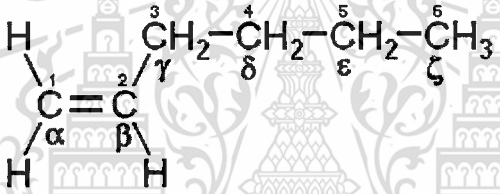
Table 2.1 Property of petroleum products

Product	Boiling range, °C	Phase	Carbon atoms
Gas petroleum	<10	Gas	1-4
Gasoline	30-185	Liquid	4-13
Kerosene	170-250	Liquid	10-14
Diesel	175-350	Liquid	14-19
Lubricant	350-500	Liquid	19-35
Wax	350-500	Solid	19-35
Fuel oil	>500	Liquid	>35
Bitumen	>500	Solid	>35

2.4 Linear alpha olefins

The term 'olefin', also known as alkenes, refers to a large number of compounds that contain carbon and hydrogen and have at least one double bond in their structure. Short-chain olefins, like ethylene, are cracked from naphtha or natural gas. Ethylene is then oilgomerised into longer chain linear alpha olefins, ranging from 6 to 30 carbons in length. Alpha olefins are characterized by their high purity, high degree of linearity, and a double bond uniformly positioned between the first and second carbon. For drilling fluid applications, alpha olefins in the C14 to C18 range are used because they have the right mix of physical properties like viscosity, pour point and flash point. Internal olefins are then produced from linear alpha olefins by catalytically moving the double bond to different locations in the molecule. As a result, the pour point of the fluid decreases significantly, thus enabling these materials to be used successfully in deep-water applications. Internal olefins used as base fluids for drilling muds typically have carbon chain lengths in the C15 to C18 range [19].

Linear Alpha Olefins (LAO) or Normal Alpha Olefins (NAO) are olefins or alkenes with a chemical formula C_xH_{2x}, distinguished from other mono-olefins with a similar molecular formula by linearity of the hydrocarbon chain and the position of the double bond at the primary or alpha position.



1-hexene, a typical linear alpha-olefin

Linear alpha olefins are a range of industrially important alpha-olefins, including 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and higher blends of C_{20}-C_{24}, C_{24}-C_{30}, and C_{20}-C_{30} ranges.

2.5 Literature reviews

The decarboxylation of palmatic acid is produced the long chain hydrocarbon by basic catalyst. Catalytic decarboxylation is a well-established chemical reaction in organic processes that has been widely applied in organic synthesis. It has been studied in a broad reaction condition and over various types of catalysts, but works on fatty acid over metal oxide as catalyst are rather limited.

From the previous research, various type of metal oxide were used as catalyst for decarboxylation of palmatic acid, the results show that the metal oxide such as magnesium oxide did not give a high activity for liquid hydrocarbon. However some metal oxides such as barium oxide gave a high activity for liquid hydrocarbon [4]. In our research we investigate the hydrotalcite catalyst in the decarboxylation reaction as it contains more basicity and higher surface area than metal oxide catalyst.

The studied the crystallization of synthetic hydrotalcite. Various studies were molar ratio of magnesium per aluminuim [20] and temperature of hydrothermally treated at temperatures from 120 to 200 °C for 2-18 hours [20].

The studied the activity and percentage of conversion of decarboxylation reaction when various the ratio of palmitic acid per hydrotalcite catalyst but same temperature of reaction, flow rate of the carrier gas [4].

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Reagent

1. Acetone (ZEN POINT), Commercial-grade
2. Aluminium sulphate (Ajax Finechem), AR-grade
3. Hexane (Fisher Scientific), AR-grade
4. Hydrogen gas (TIG)
5. Liquid nitrogen (TIG)
6. Magnesium oxide powder (Fluka), ≥ 98%
7. Magnesium sulphate (APS Finechem), AR-grade
8. Methanol (Fisher Scientific), HPLC-grade
9. Nitrogen gas (TIG)
10. Nonane (Fulka), AR-grade
11. Palmitic acid (Fluka), ≥ 97%
12. Paraffin oil (Fisher Scientific)
13. Sodium hydroxide pellets (CARLO ERBA), AR-grade
14. Sodium carbonate anhydrous (APS Finechem), AR-grade
15. Tetrahydrofuran (J.T Baker), AR-grade

3.2 Apparatus

1. Autoclave
2. Clamp
3. Dewar
4. Filter paper
5. Furnace
6. Heating tape
7. Hot plate
8. Laboratory glassware
9. Oven
10. Reactor

11. Trap condenser
12. Vial
13. Water bath
14. X-ray Powder Diffractometer (D8 Advance, Bruker AG, Scientific Instrument Service Centre, KMITL)
15. Thermal Gravimetric Analyzer (Perkin-Elmer, Scientific Instrument Service Centre, KMITL)
16. Gas adsorption analyzer (Autosorb-1C, Quantrachrome)
17. Gas chromatography (Varian 3800)

3.3 Experiment

3.3.1. Synthesis of hydrotalcite

Hydrotalcite was prepared by coprecipitation from aqueous solution of $MgSO_4$ and $Al_2(SO_4)_3$ with Mg/Al molar ratio equal to 2 (total metal ion concentration of 1.2 mol/L). The $MgSO_4$ (88.56 g) was dissolved in 225 mL distilled water. And $Al_2(SO_4)_3$ (59.94 g) was dissolved with the same amount of distilled water. The aqueous solution of $MgSO_4$ and $Al_2(SO_4)_3$ were added dropwise into 500 mL of 1 M Na_2CO_3 under vigorous stirring. During synthesis temperature was maintained at 75 °C and pH 10 was adjusted by addition of 10 M NaOH. After all solution was mixed the solution was left at 75 °C with stirring for another 1 hours. Precipitate formed was filtered and washed with hot distilled water. The precipitate was resuspended in 1000 ml of hot distilled water, filtered, and washed again with hot distilled water to remove all residues SO_4^{2-}. Filtration cake was resuspended in distilled water to obtain a suspension containing about 10 wt% of solid. The mixture (30 mL) was transferred into autoclave and hydrothermally treated at temperatures 120 °C and 160 °C for 6 hours. The product was filtrated and dried at 130 °C for 24 hours. Calcinations the dry product by temperature 500 °C 3 hours

The hydrotalcite with Mg/Al molar ratio 2 was increased to ratio 3 using the same procedure. The weight of $MgSO_4 \cdot 7H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$ was changed to 99.63 g and 44.955 g respectively.

Table 3.1 Type of hydrotalcite

Type of hydrotalcite	Molar ratio of Mg/Al	Hydrothermal temperature (°C)
R2T120	2	120
R2T160	2	160
R3T120	3	120
R3T160	3	160

3.3.2. Characterization of hydrotalcite

3.3.2.1Investigation of the metal oxides structure using X-rays powder diffractometer (XRD)

The structure of catalyst can be determined by X-ray diffractometer (D8 Advance, Bruker, Scientific Instruments Service Centre, KMIT'L). The sample is prepared by packing the catalyst in the sample holder. CuK∝ X-ray beam is used for analysis at 30 kV, 30 mA. The sample is scanned from 2θ angle 5° to 60° with 1 second/step time and 0.04 2θ/step increment. X-ray diffraction pattern of the sample can be compared with the X-ray diffraction pattern of standard catalyst for structure determination.

3.3.2.2 Determination of specific surface area using gas adsorption analyzer

Surface area of the catalysts can be determined by gas adsorption analysis (Autosorb-1, Quantachrome). Approximaly 0.02-0.04 grams of sample can be loaded into a cleaned and dried sample cell. The sample is degassed at out-gas station at 350° C for 24 hours. Then, nitrogen is filled and the sample cell is moved to the analysis station. The adsorption isotherm is measured in a pressure range of 0.05-0.30 P/P_0 .at 70 K.

3.3.2.3 Thermal decomposition of metal oxides, fatty acids and fatty acids salt using thermal gravimetric analyzer (TGA)

The thermal decomposition of metal oxides, fatty acids and fatty acids salt was investigated by Thermogravimetric Analyzer. Approximately 10 mg of sample was placed in a platinum pan hanging from a microbalance and nitrogen was introduced as a carrier gas. The sample was then heated under oxygen (50 ml/min) for %weight loss from 50°C to 800°C at a heating rate of 15°C/min.

3.3.3. Reaction of decarboxylation

For the palmitate salt preparation, the palmitic acid was melted at 180 °C in paraffin oil. When the palmitic acid became a clear solution, hydrotalcite was added into the solution and maintained temperature at 180 °C until it become the palmitate salt. The reactor was installed onto the catalytic test rig which was located inside a temperature-regulated furnace. After that it was heated to the reaction temperature under stream of nitrogen at the flow rate of 27 ml/min. The product mixture is carried from the reactor to a series of trap condenser. The heavy product will be condensed to liquid an ice trap condenser (0 °C). The light hydrocarbon will be condensed in the cryogenic of liquid nitrogen trap (-70 °C). In order to prevent condensation of products before trapping, the line after reactor is heated at 180°C by heating tape. The schematic diagram of the experimental setup is shown in Figure 3.1.

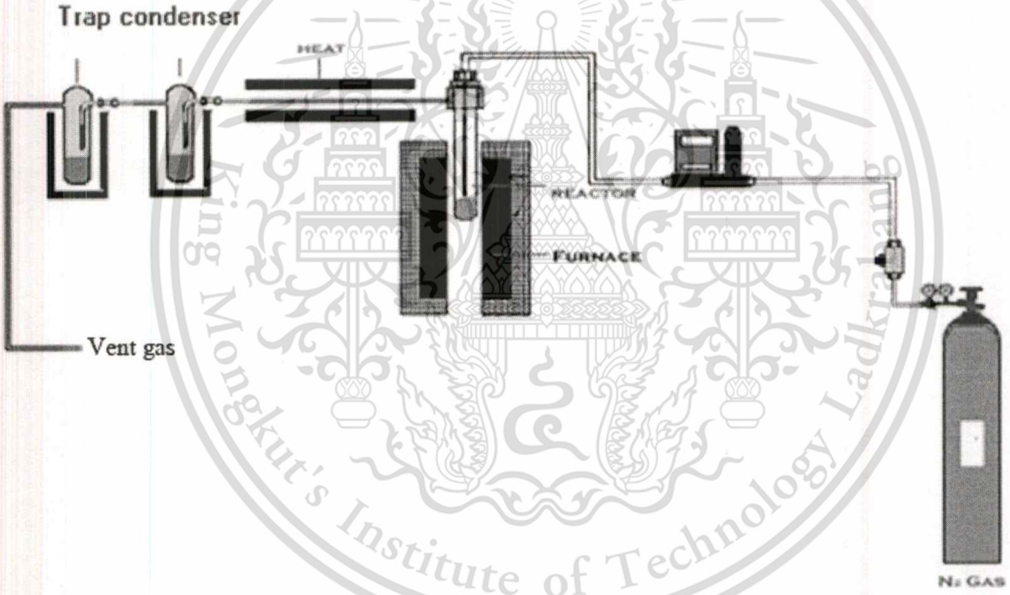


Figure 3.1 The catalytic test rig

The liquid products were analyzed by a gas chromatograph (Varian 3800) equipped with flame ionization detector (GC-FID) and a capillary column HP-5 (length, 30 m; internal diameter, 0.53 mm; film thickness, 0.88 um). The following temperature program was used for the analysis of liquid hydrocarbon: 50 °C hold for 2 min, then ramp at 12 °C/min to 280 °C and hold at this temperature for 40 min. The structures of products were confirmed by gas chromatography-mass spectrometry (GC-MS).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Thermal stability of palmitic acid

The palmitic acid was characterized with TGA, weight loss of palmitic acid was determined in the nitrogen gas as shown in Figure 4.1.

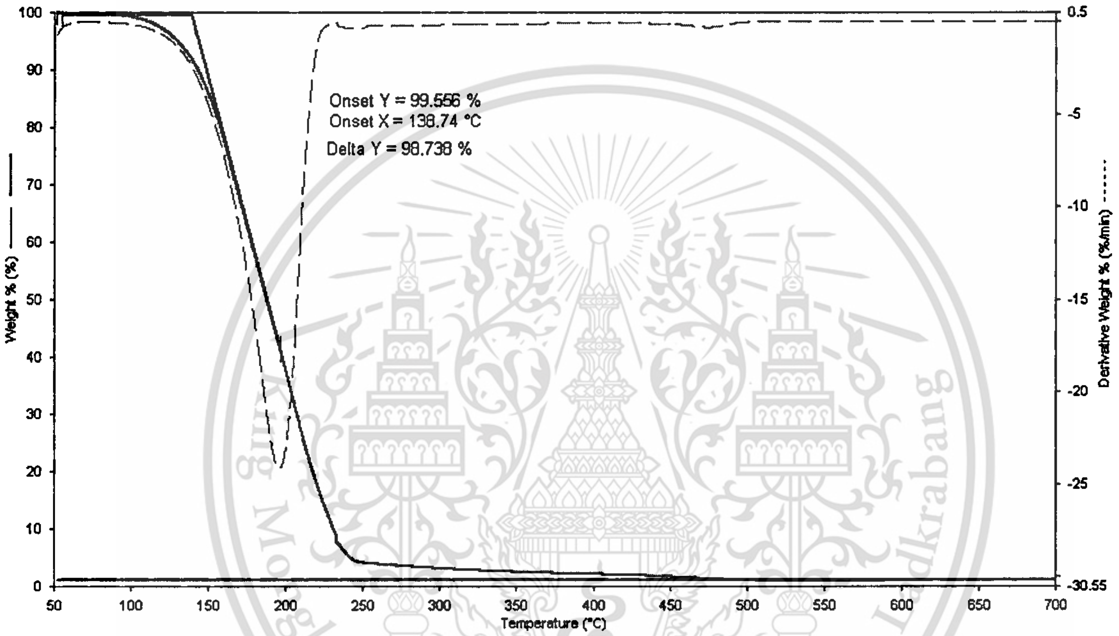


Figure 4.1 Thermogravimetric analyzer of palmitic acid

It can be seen that a significant weight loss of palmitic acid is singly obtained at 100-250°C which is lower than the boiling point of palmitic acid (350°C). It could be suggested that the weight loss was due to the evaporation of palmitic acid under flow of N_2 gas.

4.2 Catalyst characterization

4.2.1 X-ray diffraction (XRD)

The crystallinity and phases of catalysts were characterized by diffraction pattern in Figure 4.2

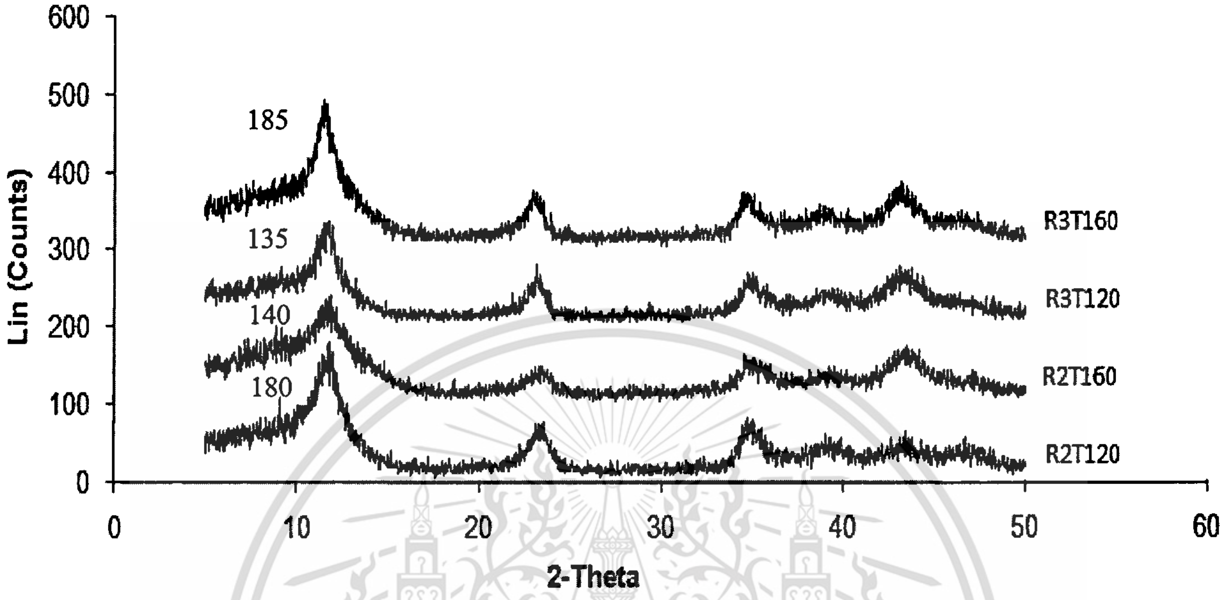


Figure 4.2 Diffraction pattern of calcined-hydrotalcites

From XRD result, all of the hydrotalcite catalysts consist of both hydrotalcites and Magnesium oxide phase as shown in Table 4.1

Table 4.1 Phase of Mg-Al hydrotalcitecatalyst from diffraction pattern

Phase	Pattern(2θ)
Hydrotalcites	11.5,23,34.5,38.5,46
Magnesium oxide	43
$MgAl_2O_4$	19,31,37

There is no $MgAl_2O_4$ phase can be observed in the XRD result because the $MgAl_2O_4$ phase ocuur only at the calcination temperature higher than 700°C.

It can be seen that a hydrotalcite phase, the intensity of 11.5°indicated R3T160 and R2T120 have the relative crystallinity of hydrotalcite phase higher than that of R2T160 and R3T120. It can be explained that for the calcined-hydrotalcite with Mg/Al ratio of 3, the higher hydrothermal temperature can lead to higher crystallinity of hyydrotalcite phase. However, in case of Mg/Al ratio of 2, the higher hydrothermal temperature can lead to lower crystallinity of hyydrotalcite phase. This is probably due to the basicity of suspended precipitate for hydrotalcite synthesis with Mg/Al ratio equal to 3 is higher than that of suspended precipitated for hydrotalcite synthesis with Mg/Al ratio equal to 2 because the Mg content of hydrotalcite (Mg/Al ratio is 3) is higher than hydrotalcite (Mg/Al ratio is 2). Hence the higher basicity of suspended precipitate preferably crystallizes at higher hydrothermal temperature. The MgO phase is formed after the hydrotalcite was calcined at temperature higher than 250°C. All of four catalysts have the intensity of 43° that indicated the MgO phase is nearly equal because the same calcination temperature (500°C) was employed for all of four hydrotalcite catalysts.

4.2.2 X-ray fluorescence (XRF)

The composition of the catalysts were characterzed by XRF as shown in Table 4.2

Table 4.2 Elemental analysis and surface area of the catalyst

Catalyst	Elemental analysis			Specific Surface Area (m^2/g)
	MgO (%)	Al_2O_3 (%)	SO_3 (%)	
R3T160	71.7	25.7	2.48	260
R3T120	69.1	27.8	3.16	230
R2T160	65.1	31.8	2.99	268
R2T120	64.4	31.6	3.96	223
Bulk MgO	100	-	-	90

It can be seen that higher hydrothermal temperature result in higher Mg composition. This can be explained that Mg can be better cooperated in the solid phase than Al at higher hydrothermal temperature [16].

4.2.3 Gas adsorption analysis

The specific surface area of each calcined-hydrotalcite and bulk MgO were determined by BET measurement using gas adsorption analyzer with nitrogen gas as shown in Table 4.2

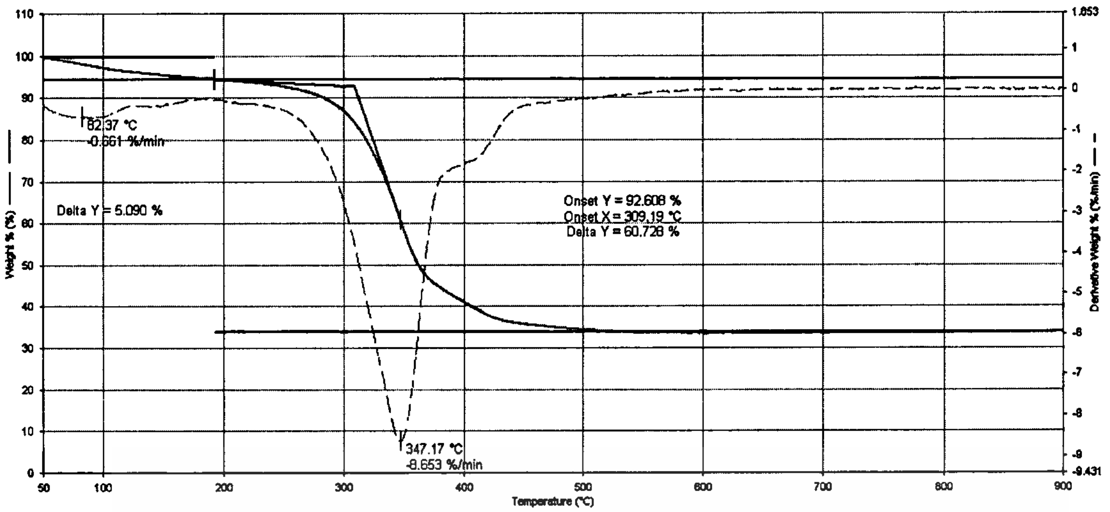
It can be seen that all of calcined-hydrotalcite posses surface area higher than that of bulk MgO. This can be explained that bulk MgO have a non-porous structure but calcined-hydrotalcite have a porous structure because the porous system was developed during the transformation of CO_3^{2-} to CO_2in the calcination step. For calcined-hydrotalcite, as the hydrothermal temperature increase, the surface area also increases. It can be suggested that higher hydrothermal temperature can lead to higher hydrotalcite content [2] that can improved the transformation of CO_3^{2-} to CO_2in the calcination step resulting in higher surface area of calcined-hydrotalcites.

4.3 Decomposition of palmitic acid over calcined-hydrotalcites and bulk MgO

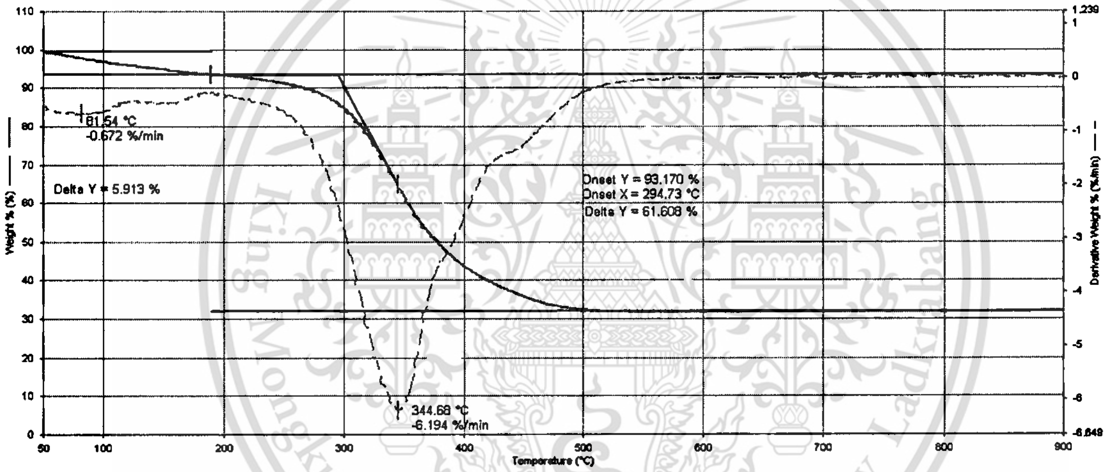
Decomposition of palmitic acid over hydrotalcites and bulk MgO were examined by TGA. The catalyst initially reacted with palmitic acid to form palmitate salt due to neutralization reaction. Upon heating palmitate salt could decompose to long chain hydrocarbon as shown in Table 4.3 and Figure 4.3

Table 4.3 Decomposition of palmitic acid over calcined-hydrotalcites and bulk MgO

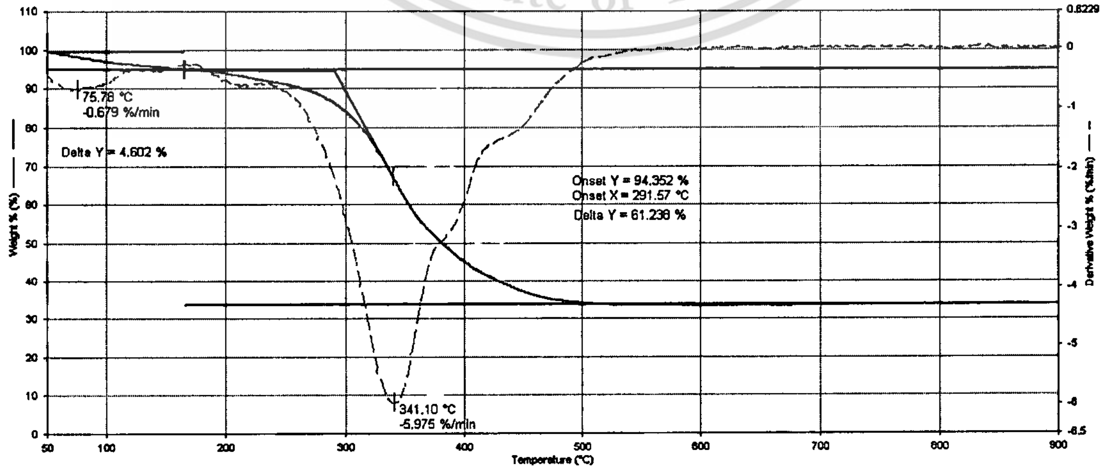
Catalyst	TGA of palmitate salt decomposition temperature (°C)	
R3T160	347.17	~410 (small derivative weight loss)
R3T120	344.68	~410 (small derivative weight loss)
R2T160	341.10	~410 (small derivative weight loss)
R2T120	338.04	~410 (small derivative weight loss)
Bulk MgO	320 [4]	


110
100
90
80
70
60
50
40
30
20
10
0
Weight % (%)
50
100
200
300
400
500
600
700
800
900
Temperature (°C)
1.653
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-9.431
Derivative Weight % (%/min)
82.37 °C
-0.661 %/min
Delta Y = 5.090 %
Onset Y = 92.608 %
Onset X = 309.19 °C
Delta Y = 60.728 %
347.17 °C
-8.653 %/min

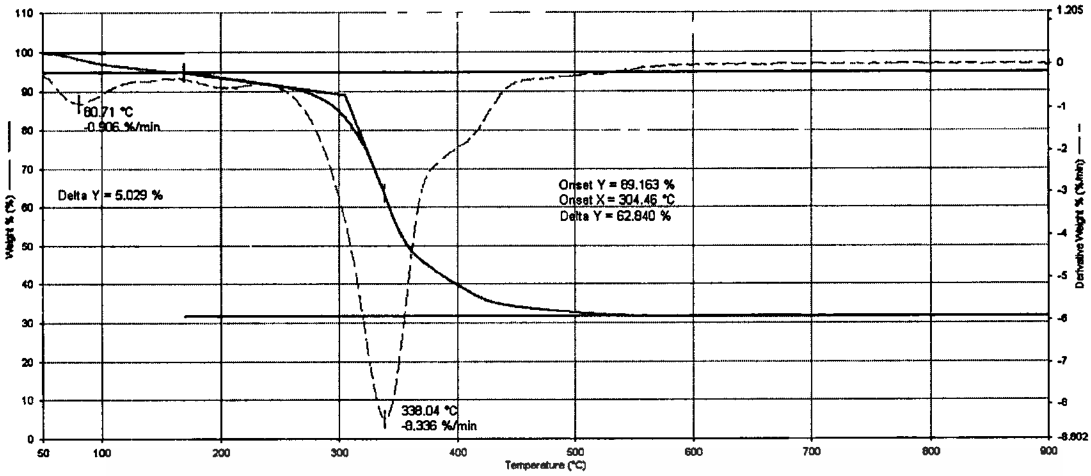
(a)


110
100
90
80
70
60
50
40
30
20
10
0
Weight % (%)
50
100
200
300
400
500
600
700
800
900
Temperature (°C)
1.239
1
0
-1
-2
-3
-4
-5
-6
-6.649
Derivative Weight % (%/min)
81.54 °C
-0.672 %/min
Delta Y = 5.913 %
Onset Y = 93.170 %
Onset X = 294.73 °C
Delta Y = 61.608 %
344.68 °C
-6.194 %/min

(b)


110
100
90
80
70
60
50
40
30
20
10
0
Weight % (%)
50
100
200
300
400
500
600
700
800
900
Temperature (°C)
0.6229
0
-1
-2
-3
-4
-5
-6
-6.5
Derivative Weight % (%/min)
75.78 °C
-0.679 %/min
Delta Y = 4.602 %
Onset Y = 94.352 %
Onset X = 291.57 °C
Delta Y = 61.238 %
341.10 °C
-5.975 %/min

(c)



(d)

Figure 4.3 Thermogravimetric analyzer of palmitate salt (a)R3T160, (b)R3T120, (c)R2T160, (d)R2T120

The palmitate salt was decomposed at evaluated temperature, as compared to the palmitic acid alone (200°C). This is due to the interaction between basic catalyst with palmitic acid. It was believed that when hydrotalcites reacted with palmitic acid at temperature about 180 °C resulting in palmitate salt due to neutralization reaction as shown in Figure 4.4

$$CH_3(CH_2)_{14}COOH + Mg^{2+}O^{2-} \longrightarrow Mg(CH_3(CH_2)_{14}COO)_2 \text{ (palmitate salt)}$$

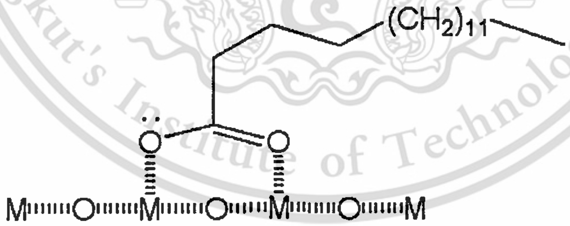


Figure 4.4 The interaction between the palmitic acid and the basic catalyst (palmitate salt).

The oxygen molecules of carboxylic group formed strong bond with the metal surface of the active site, as the metal ion preferably donated electron while oxygen atom possess high electron negativity (EN).

It can be seen that two derivative weight loss peaks can be observed in the TGA result as shown in Figure 4.3. First derivative peak appears at temperature about 340°C that is possibly derived from decomposition of palmitic acid that interacts with hydrotalcite phase of calcined-hydrotalcite catalyst. The second derivative peak appears at temperature about 410°C presumably due to the decomposition of palmitic acid that interacts with magnesium oxide phase present in the calcined-hydrotalcite catalyst. This suggests that interaction of palmitic acid and catalyst depends on basic strength on the surface of the catalysts [3]; i.e. the stronger basic strength, the higher decomposition temperature. As the decomposition temperature of palmitic acid that interact with magnesium oxide phase is higher than that of the hydrotalcite phase. It can be suggested that the magnesium oxide phase possess basic strength stronger than that of hydrotalcite phase. However, the hydrotalcite (340°C) and magnesium oxide (410°C) phase of calcined-hydrtalcite catalysts show a decomposition temperature of palmitate salt higher than that of bulk MgO. (320°C) From the result it clearly shows that calcined-hydrotalcite catalyst possess basic strength stronger than that of bulk MgO.

Comparing hydrotalcites sample, the basic strength of hydrotalcite phase of calcined-hydrotalcite catalyst as estimated from decomposition temperature of palmitate salt is in the order of R3T160 > R3T120 > R2T160 > R2T120. It can be suggested that increase the hydrothermal temperature and ratio of Mg/Al can be increase basic strength. However, in the case of Mg/Al ratio, the basic strength can be limited because at very high Mg/Al ratio, the formation of hydrotalcite would be contaminated with brucite [$Mg(OH)_6$) [15]

4.4 Deoxygenation of palmitic acid over calcined-hydrotalcites and bulk MgO

The deoxygenation of palmitic acid over calcined-hydrotalcite and bulk MgO were studied in semi-batch reactor. The reaction were investigated using 0.8:1.0 catalyst:palmitic acid ratio at the appropriate temperature at 460 °C 6 hours, using 27 ml/min of nitrogen gas as carrier gas. Hydrocarbon product was shown in Figure 4.5 that can separate well by gas chromatography as shown in figure 4.6

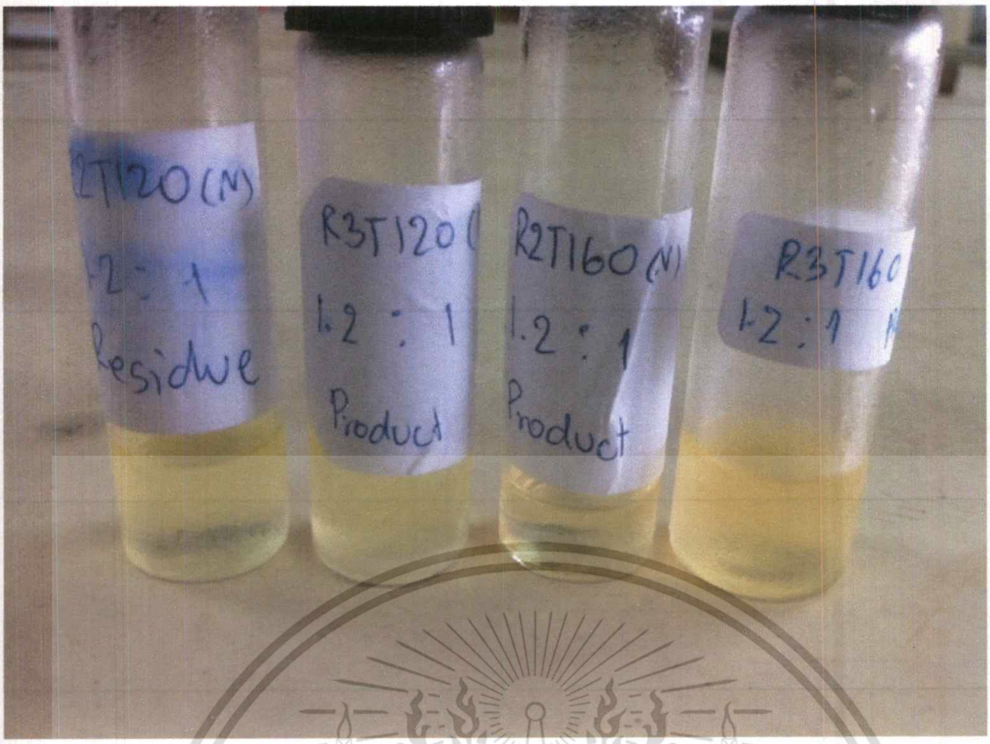


Figure 4.5 The hydrocarbon product

The color of the hydrocarbon products is pale yellow

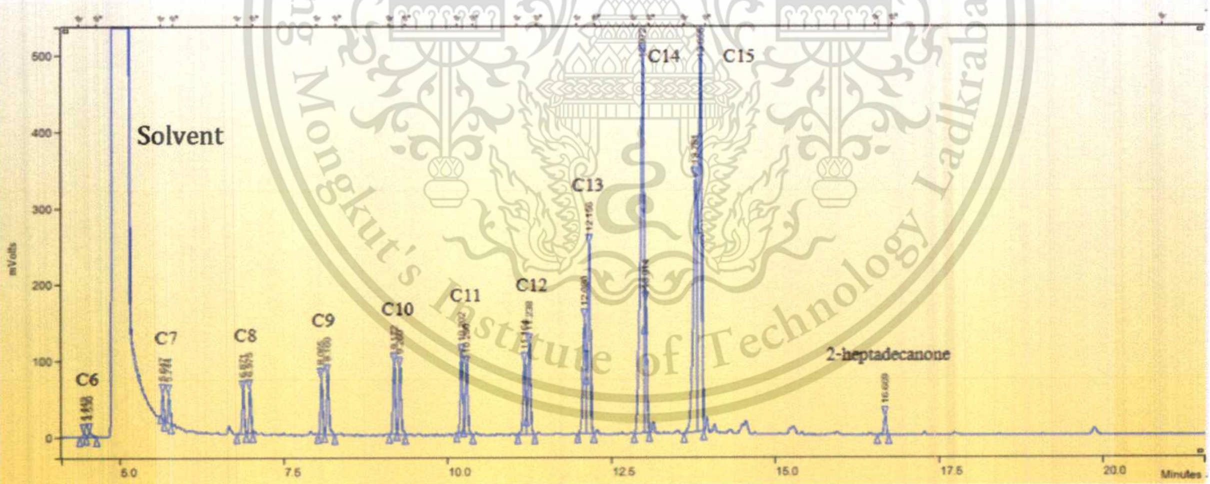


Figure 4.6 Chromatogram of liquid hydrocarbon products.

%Yield of liquid hydrocarbon and product selectivity obtain over each calcined-hydrotalcite and bulk MgO are shown in Table 4.4.

Table 4.4 %yield of deoxygenation reaction and product selectivity over each Calcined-hydrotalcite and bulk MgO with mol ratio of Catalyst:palmitic acid equal to 0.8:1

0.8:1 Reaction										
Catalyst	R2T120		R2T160		R3T120		R3T160		MgO	
% Yield	66.61		60.89		56.92		65.22		28.79	
Product selectivity (%)										
	Uns.	Sat.	Uns.	Sat.	Uns.	Sat.	Uns.	Sat.	Uns.	Sat.
C6	0.19	0.22	0.31	0.40	0.30	0.35	0.26	0.30	0.21	0.23
C7	0.71	1.27	0.93	3.58	1.01	1.12	0.79	0.86	0.78	0.88
C8	1.55	1.67	1.74	1.76	1.77	1.82	1.52	1.47	2.09	2.05
C9	2.12	2.36	2.33	2.79	2.29	2.73	2.15	2.56	3.04	3.43
C10	3.14	3.49	3.07	2.92	3.12	3.21	2.79	2.91	4.58	4.06
C11	3.92	3.71	3.71	3.19	4.06	3.37	3.85	3.17	5.64	4.16
C12	3.86	5.29	3.66	4.75	3.73	4.67	3.66	4.57	4.20	5.49
C13	6.42	10.05	5.91	9.23	6.58	9.52	6.05	9.67	5.01	13.46
C14	14.97	8.05	14.68	6.84	17.61	6.32	17.87	6.69	11.33	6.78
C15	5.97	21.07	6.78	19.07	7.01	19.29	7.42	21.22	22.16	
2- heptadecanone	n/a		2.35		0.11		0.15		0.11	

As the palmitate salt were heat to temperature higher than 350 ^{o}C, it undergo deoxygenation and bearing long chain hydrocarbon (both saturated and unsaturated) and carbon dioxide as confirmed by GC-MS.

The main product was C_{15} hydrocarbon (~25-30%yield), it would be obtained from direct decomposition of carboxylic group of palmitate salt to form C_{15} radical and CO_2, (decarboxylation). The C_{15} radical could abstract hydrogen atom on surface to form C_{15} saturated hydrocarbon (~20% yield) or hydrogen elimination to formed C_{15} unsaturated hydrocarbon (~8% yield) as shown in Figure 4.7

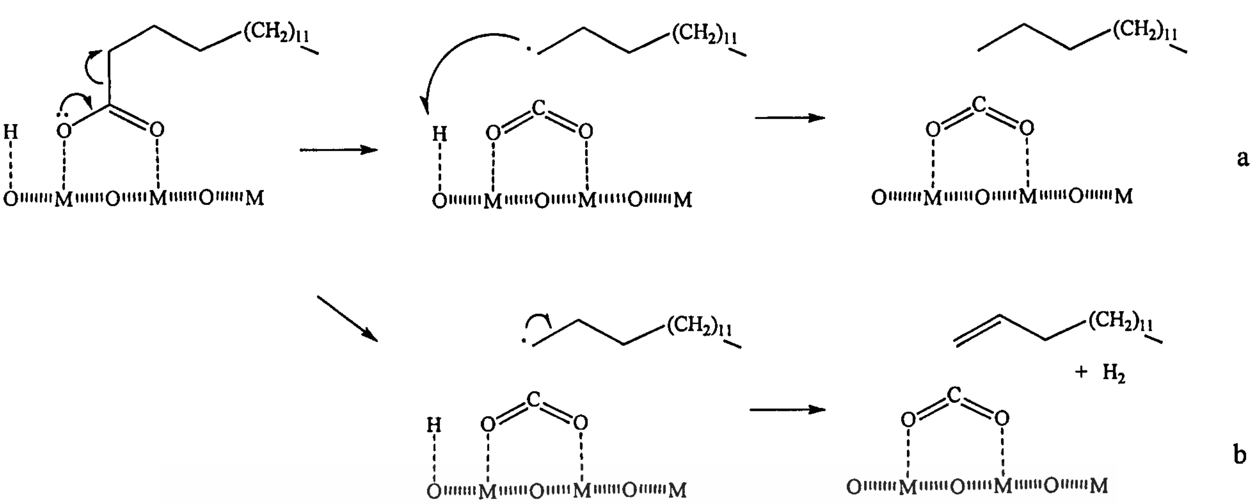


Figure 4.7 Decarboxylation of alkaline earth palmitate(a) C_{15} saturated hydrocarbon; (b) C_{15} unsaturated hydrocarbon

The other main product was C_{14} hydrocarbons (~22% yield), with mainly C_{14} unsaturated compound (∼19%). While yield of C_{14} saturated hydrocarbon was relatively lower (3%yield). It was proposed that the palmitate salt undergoes deacetylation by cleavage of β carbon-carbon bond in palmitate species to form C_{14} unsaturated hydrocarbon (Figure 4.8, a) and acetate species remained on the catalyst surface. Besides, C_{14} unsaturated hydrocarbon can abstract hydrogen atom on surface of catalyst to form C_{14} saturated hydrocarbon.

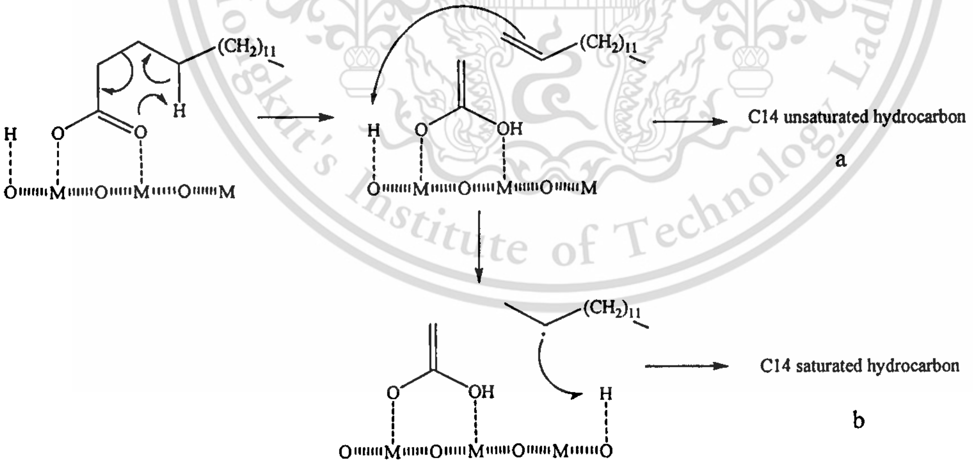


Figure 4.8 Deacetylation of alkaline earth palmitate(a) C14 unsaturated hydrocarbon; (b) C14 saturated hydrocarbon

After deacetylation the acetate species remained on the catalyst surface could decompose to CO and H_2O. The methyl group remains on the surface of catalyst as methoxy species. This was concluded from the observed yield of 2-heptadecanone as co-product. It was suggested that palmitate salt was ketonized with methoxy group on surface catalyst that retained on the surface from the decetylation, forming 2-heptadecanone(ketone with one methyl group) as shown in Figure 4.9

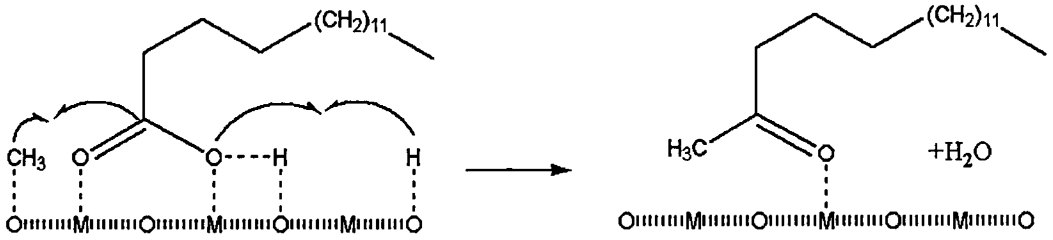
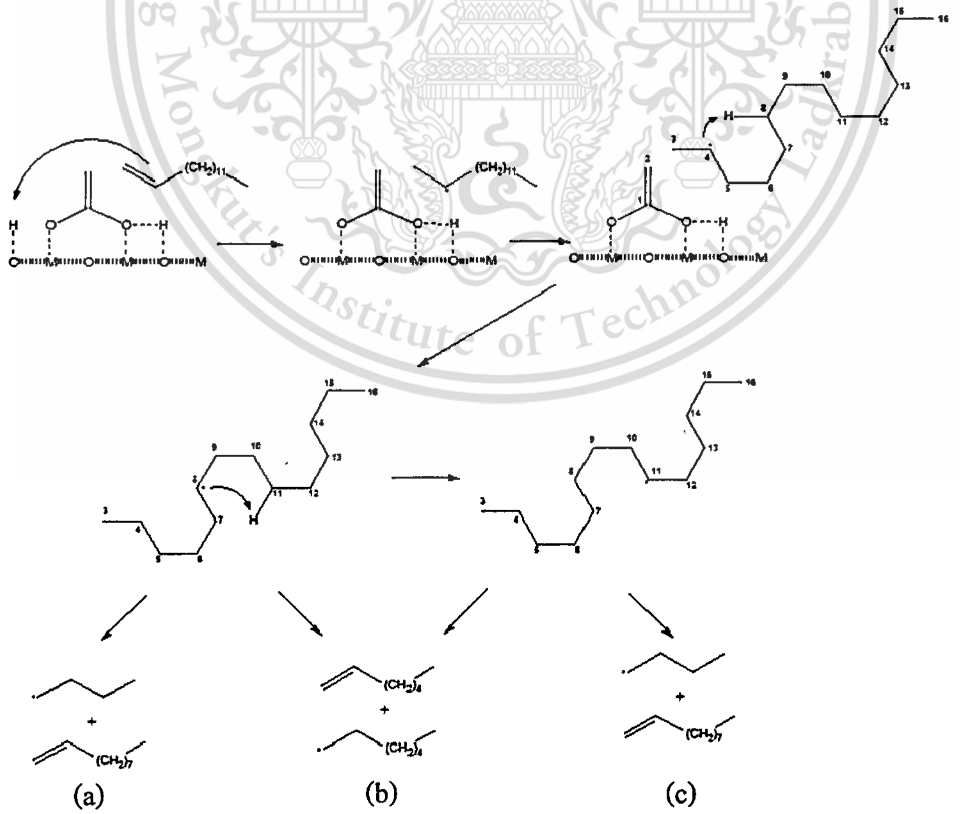


Figure 4.9 Ketonisation of palmitate salts with methoxy group

Moreover, thermal cracking of palmitates salts, and other hydrocarbons product could be expected at high temperature. For example, C_{14} radical would be abstract hydrogen atom within its own hydrocarbon chain, forming a new hydrocarbon radical (most likely at C_8 position) that would crack at β position to form C_{10} unsaturated hydrocarbon and C_4 radical. This inner radical (C_8 position) can also either crack at C_9-C_{10} position to form C_7 hydrocarbons. The C_7 hydrocarbon could also obtain from other inner radical (C_{11} position) in a manner similar to that discussed earlier. Hence, a number of C_7 hydrocarbons were largely produced from cracking of these inner radical (C_8 and C_{11} position) as shown in Figure 4.10



(a) (b) (c)

Figure 4.10 Product from cracking reaction of C_{14} radical; a) C_{10} unsaturated hydrocarbon and C_4 radical; b) C_7 unsaturated hydrocarbon and C_7 radical c); C_{10} unsaturated hydrocarbon and C_4 radical

From the product distribution, it could be concluded that the C_{15} hydrocarbons derived from decarboxylation. While the C_{14}, C_{10} and C_7 hydrocarbons results in form of deacetylation. It could be seen from Table 4.4 that the catalytic with basic sites promoted predominantly decarboxylation, and deacetylation and partly cracking.

As the result at catalyst:palmiticacid ratio is 0.8:1.0, it can be seen that the liquid hydrocarbon yield of bulk MgO (~28%) is much lower when compared with that of calcined-hydrotalcite catalyst (~60%). As discussed earlier the calcined-hydrotalcite catalyst possesses higher basic strength and surface area as compared to those of MgO. This suggested that calcined-hydrotalcite catalyst provide adequated number of active sites for the deoxygenation reaction at even lower catalyst:palmitic acid ratio.

Catalyst activity of each calcined-hydrotalcites was in the following order R3T160~R2T120 > R2T160 > R3T120. These are corresponding to the XRD results that show both R3T160 and R2T120 have a relative crystallinity of hydrotalcite phase higher than R2T160 and R3T120, it can be suggested that the crystallinity of hydrotalcite phase can merely affect the yield of liquid hydrocarbon in the deoxygenation of palmitic acid.

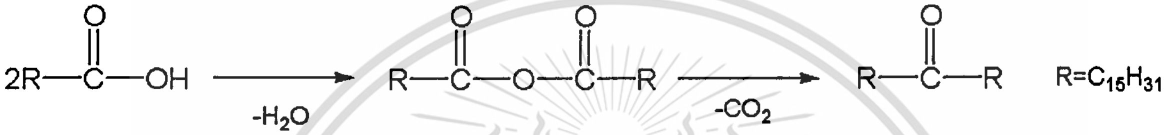
4.5 Effect of catalyst/palmitic acid ratio

The effect of catalyst/palmitic acid ratio was studied at 460°C, reaction time at 6 hours. The catalyst: palmitic acid ratio was varied from 0.8:1.0, 1.0:1.0, and 1.2:1.0 as shown in Table 4.5

Table 4.5 Liquid yield of hydrocarbon over various catalysts: palmitic acid ratio

Catalyst	Liquid hydrocarbon yield (%)		
Catalyst:palmitic acid ratio	0.8 : 1.0	1.0 : 1.0	1.2 : 1.0
R3T160	65.22	78.56	83.64
R3T120	56.92	68.73	67.81
R2T160	60.89	72.52	71.35
R2T120	66.61	78.85	80.71
Bulk MgO	28.79	71.82	68.85

It can be seen that, for R3T160 and R2T120 catalyst, yield of liquid hydrocarbon increase as catalyst: palmitic acid ratio is increased. For example, yield of liquid hydrocarbon of R3T160 increase from 65.22 to 78.56 and to 83.64 as mole ratio of catalyst: palmitic acid increase from 0.8:1.0, 1.0:1.0, and 1.2:1.0, respectively. This is due to the higher number of active sites as discussed earlier. However for R3T120 and R2T160 yield of liquid hydrocarbon slightly decrease when the catalyst: palmitic acid ratio is increase from 1.0:1.0 to 1.2:1.0. The decreasing of liquid hydrocarbon yield is possible from the ketonization (coupling) of palmitic acid take place forming larger oxygenated compound retained in the used catalyst. When the catalyst: palmitic acid ratio is increase, the palmitic acid can be absorbed in closely proximate. The fatty acid on the adjacent site can then undergo dehydration to form acid anhydride. At high temperature, such acid anhydride can be readily decarboxylated to form symmetrical ketone [4] as shown in Figure 4.11



$$2R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-H_2O]{} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow[-CO_2]{} R-\overset{O}{\overset{\|}{C}}-R \qquad R=C_{15}H_{31}$$

Figure 4.11 Ketonization(coupling) reaction of two palmitic acid molecules to from palmitone (31)

In consistent with above hypothesis, the larger oxygenated compound retained in the used catalysts were examined by TGA as shown in Figure 4.12

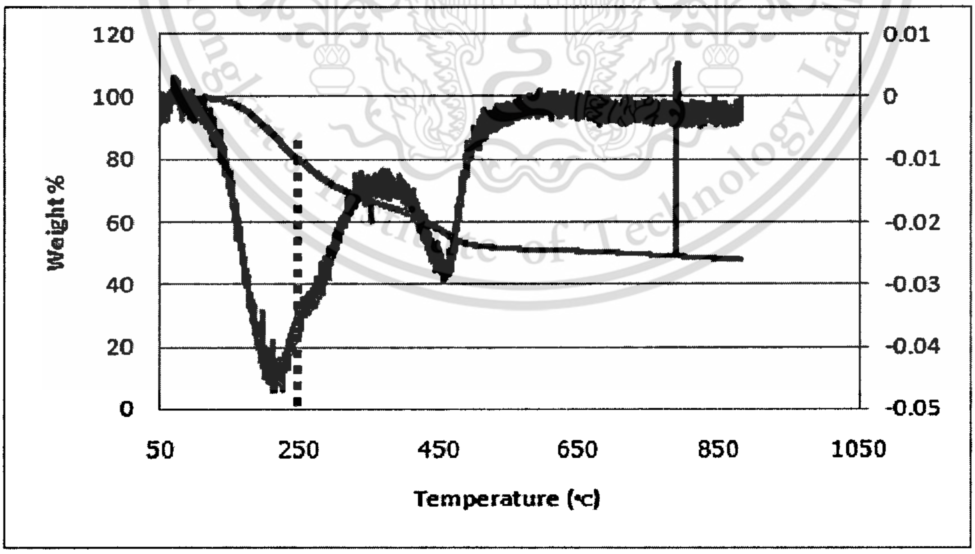


Figure 4.12.aThermogravimetric analyzer of residue (R3T120)

(Mole ratio of Catalyst:palmitic is 1.0:1.0)

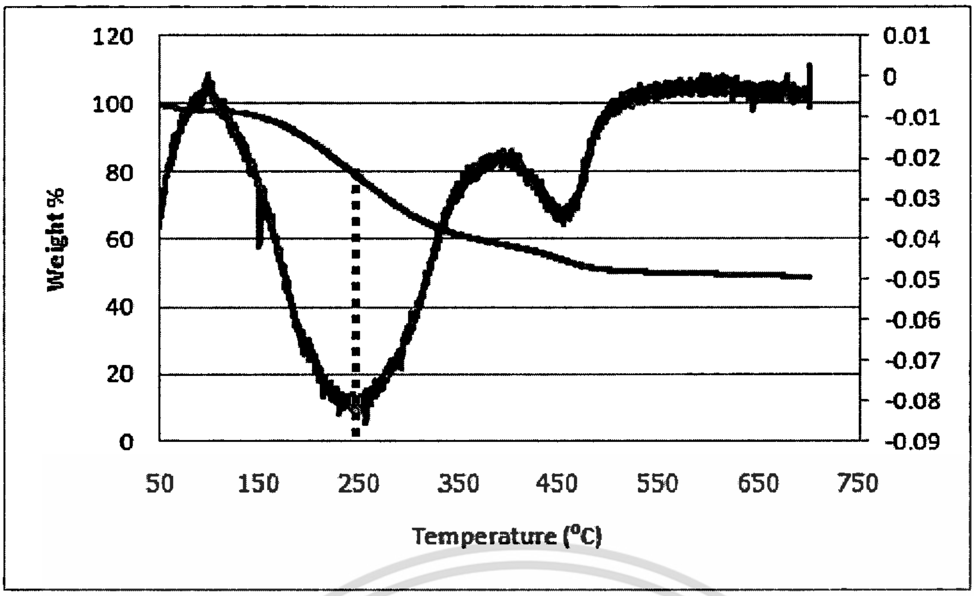


Figure 4.12.bThermogravimetric analyzer of residue (R3T120)

(Mole ratio of Catalyst:palmitic is 1.2:1.0)

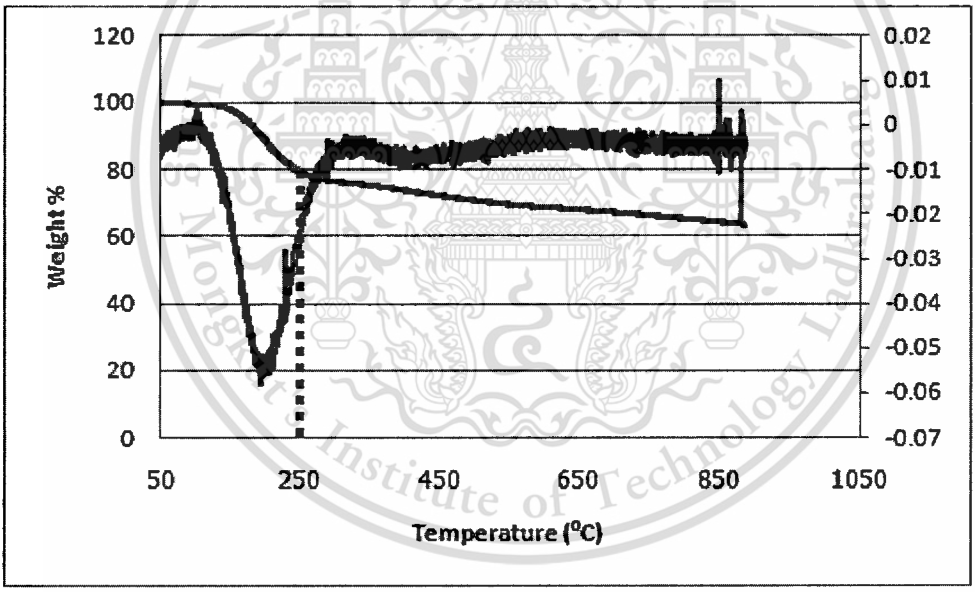


Figure 4.12.cThermogravimetric analyzer of residue (R3T160)

(Mole ratio of Catalyst:palmitic is 1.0:1.0)

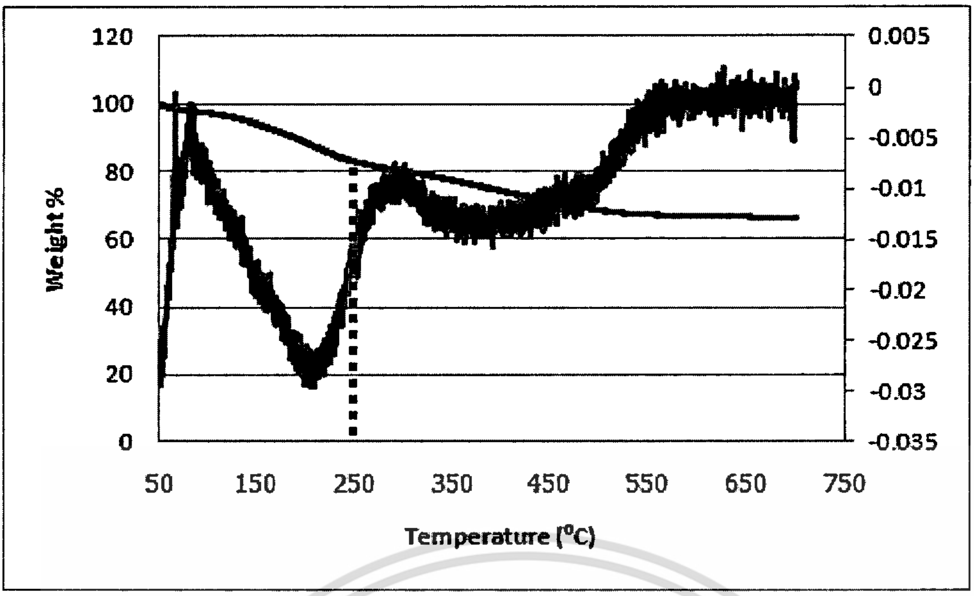


Figure 4.12.d Thermogravimetric analyzer of residue (R3T160)

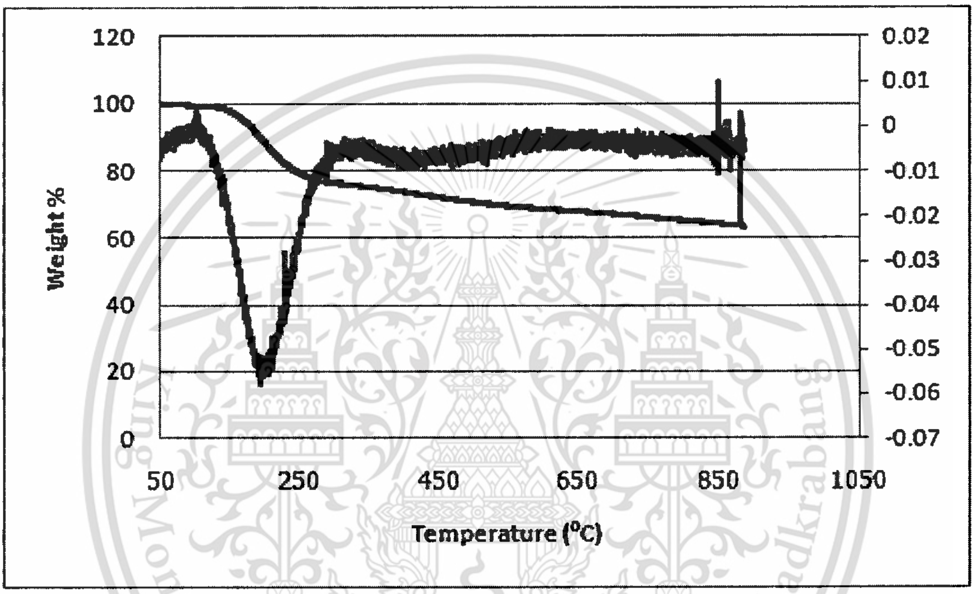
(Mole ratio of Catalyst:palmitic is 1.2:1.0)

It can be seen from the residue of R3120 at catalyst:palmitic acid ratio of 1.2:1.0 (Figure 4.12.b) that the derivative weight loss is relative broad as compared to that of R3120 at catalyst:palmitic acid ratio of 1.0:1.0 (Figure 4.12.a). The additional derivative weight loss at about (250-300°C) is derived from the formation of palmitone [4] in the residue which decomposes at temperature higher than the unreacted palmitic acid (~200°C). However, TGA ofresidue of R3T160 with catalyst:palmitic acid ratio of 1.2:1.0 (Figure 4.12.d) , such derivatve weight loss at (250-300°C) cannot be observed indicating that the coupling reaction did not take place as discussed previously. Moreover, R3T160 and R2T120 have a relative crytallinity of hydrotalcite phase higher than R2T160 and R3T120. It can be suggested that higher crystallinity of hydrotalcite phase can prevent the ketonization of palmitic acid. This is because the layer structure in the pore of the hydrotalcite phase can decrease the interaction between each palmitic acid.

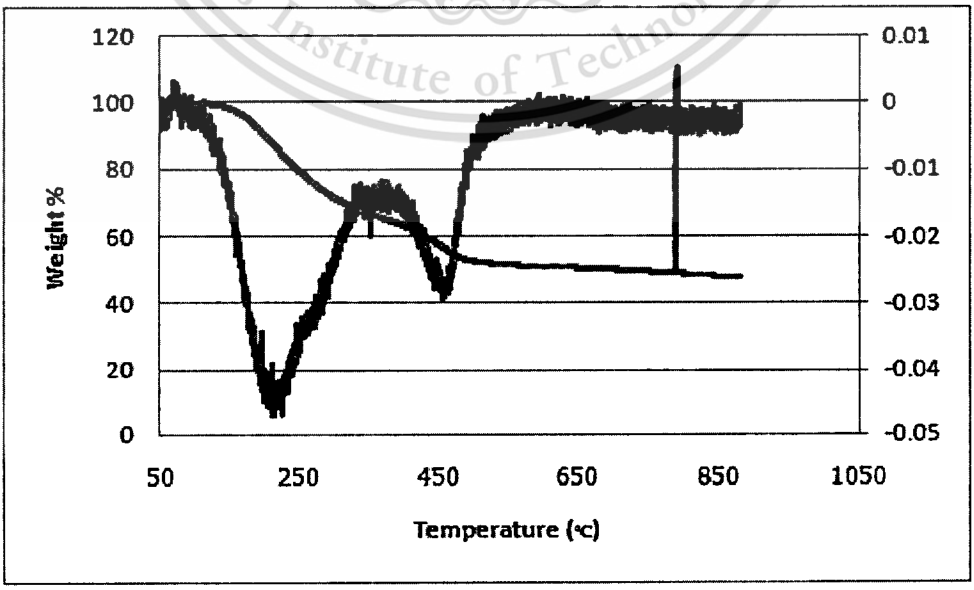
In case of bulk MgO, the yield of liquid hydrocarbon decreased as ratio of catalyst:palmitic acid is increased from 1:1 to 1.2:1. This manner is due to the coupling reaction of palmitic acid because the reaction of bulk MgO catalyst occurs only on the surface (dense active site) that is relatively low surface area (90 m^2/g). From this surface reaction of MgO, the interaction between two adjacant palmitic acid on surface is higher than that over calcined-hydrotalcites (layer-pored structure). For bulk MgO, it can be suggested that the coupling reaction can be readily promoted, leading to lower liquid hydrocarbon yield.

4.6 Study on the metal oxide-carbonate interconversion

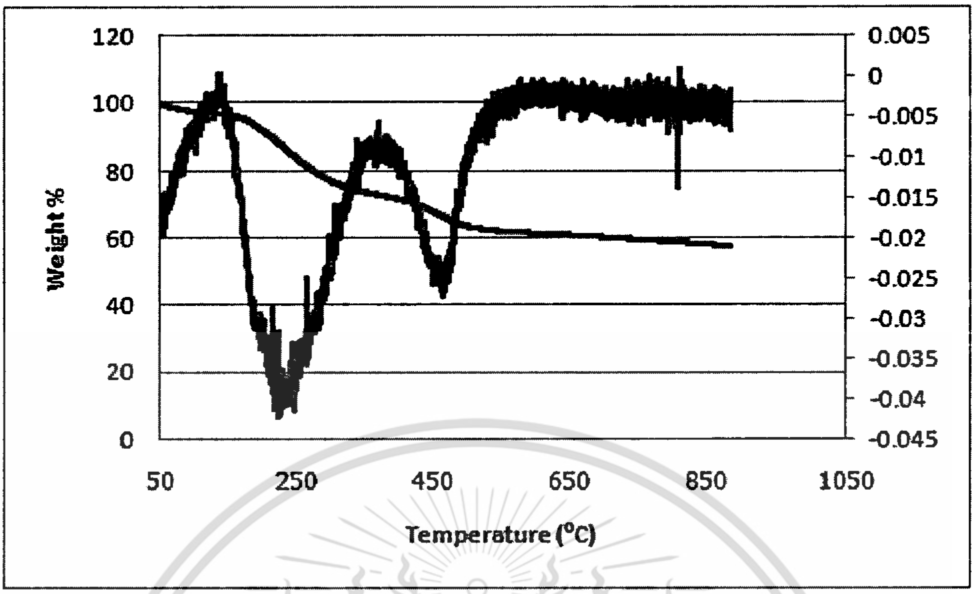
In the deoxygenation of palmitate salt, carboxylic group of palmitate salt was adsorbed on the catalyst surface and bearing of long chain hydrocarbon and carbon dioxide at the temperature higher than 350 °C. In general, carbon dioxide product can react with the metal oxide forming metal carbonate which leads to the deactivation of the catalyst. Since the metal carbonate can deactivate the catalyst, it should not form after the reaction. This can be investigated by the Thermogravimetric Analyzer TGA of residue as shown in Figure 4.13



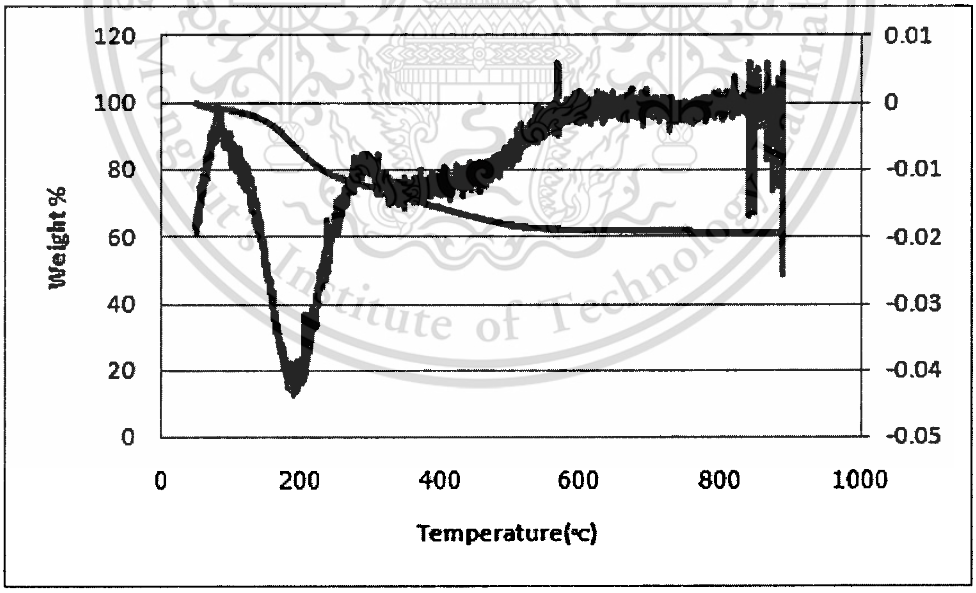
(a)



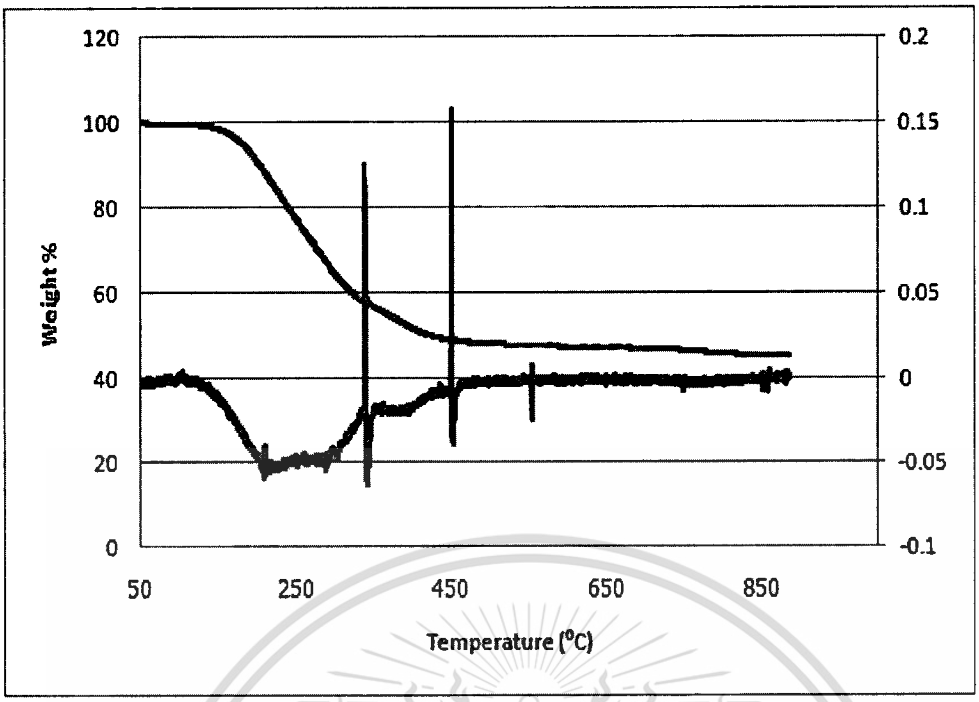
(b)


120
100
80
60
40
20
0
Weight %
0.005
0
-0.005
-0.01
-0.015
-0.02
-0.025
-0.03
-0.035
-0.04
-0.045
50
250
450
650
850
1050
Temperature (°C)

(c)


120
100
80
60
40
20
0
Weight %
0.01
0
-0.01
-0.02
-0.03
-0.04
-0.05
0
200
400
600
800
1000
Temperature(°c)

(d)



(e)

Figure 4.13 Thermogravimetricanalyzer of residue (a)R3T160, (b)R3T120, (c)R2T160, (d)R2T120, (e)MgO

The decomposition of CO_2 cannot be observed since there is nothing decomposes at temperature higher than 500 °C. It was suggested that no metal carbonate is formed after the reaction and CO_2 is released to gas phase during the reaction as shown in Figure 4.13.

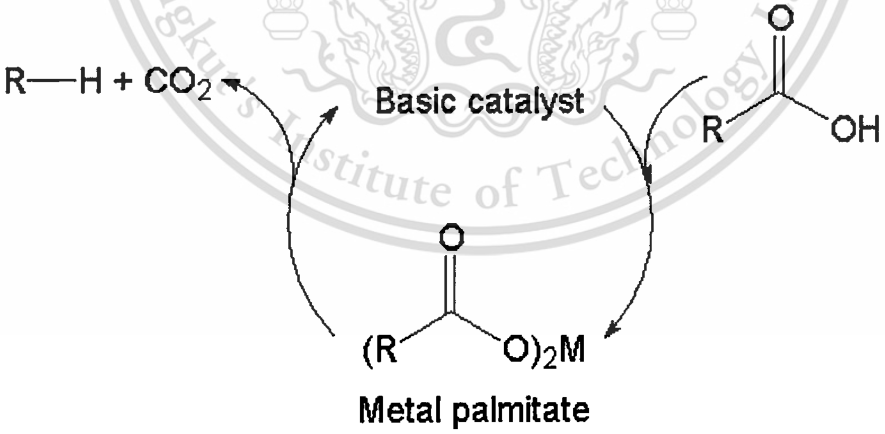


Figure. 4.14 The catalytic cycle of the deoxygenation of palmitic acid.

As palmitic acid that did not react completely with the basic catalyst and remain on the residue, as evaporated at 200-320 °C and higher molecular hydrocarbon; i.e. coke that retained on the used catalyst is decomposed at 350-480 °C. The unreacted palmitic acid and higher molecular hydrocarbon (coke) from the TGA result can be used to calculate the %conversion of palmitic acid and %coke as shown in the Table 4.6

Table4.6 Conversion of palmitic acid over each catalyst at ratio of catalyst:palmitic acid equal to 1

Catalyst	Conversion (%)	% Coke	% Liquid hydrocarbon yield
R3T160	93.07	2.15	78.56
R3T120	90.74	3.58	68.73
R2T160	92.835	3.38	72.52
R2T120	91.31	4.95	78.85
Bulk MgO	n/a	n/a	71.82

All of calcined-hydrotalcite show high conversion >90% and %coke varies from 2-5% but for conversion and %coke of bulk MgO cannot be calculated due to the unreacted palmitic acid peak and higher molecular hydrocarbon peak are overlapped. It can be seen that at higher hydrothermal temperature will lead to higher conversion and lower %coke.

However, in case of R2T120, the conversion is less than R2T160 but the liquid hydrocarbon yield is higher than R2T160, This suggests that at ratio of Mg/Al equal to 2, higher hydrothermal temperature of calcined-hydrotalcite lead to increase thermal cracking of palmitate salt to produce lower hydrocarbon (<C_5) or hydrocarbon gas. This is because the surface area of R2T160 is higher than that of R2T120. Since the thermal cracking of palmitate salt take place at the surface of catalyst. It can be suggested that the higher surface area could have a better heat transfer on the surface, hence increase the thermal cracking of palmitate salt.

CHAPTER 5

CONCLUSION AND SUGGESTION

5.1 Conclusion

Cacined-hydrotalcite consists of 2 phase. Hydrotalcite phase and MgO phase that have higher basic strength than the hydrotalcite phase. It posses high surface area and basicity.

The calcined-hydrotalcite and bulk magnesium oxide are active(basic) catalyst for deoxygenation of palmitic acid to produce linear long chain hydrocarbons in a batch reactor at reaction time 6 hr; reaction temperature 460 °C. The catalyst primarily react with palmitic acid to form palmitate salt. After that, palmitate salt can be decarboxylate, deacethylate and thermal crack into mainly C_{14}-C_{15}, lower hydrocarbons and carbon dioxide. No metal carbonate was formed during the reaction.

Comparing between calcined-hydrotalcites and bulk MgO, there are two advantages of calcined-hydrotalcites over bulk MgO. First, the catalyst activity of deoxygenation of palmitic acid over calcined-hydrotalcite is higher than that of bulk MgO at lower mol ratio of catalyst: palmitic acid (0.8:1). This is because calcined-hydrotalcite possess higher surface area and basic strength as compared to bulk MgO. Second, the layer structure in the pore of calcined-hydrotalcite can prevent the ketonization (coupling) reaction of palmitic acid.

R3T160 and R2T120 give highest yield of liquid hydrocarbon due to it have a relative crystallinity higher than the R2T160 and R3 T120. As mole ratio of catalyst:palmitic acid is increased from 1:1 to 1.2:1, the liquid hydrocarbon yield of R3T160 and R2T120 are increase while the liquid hydrocarbon yield of R2T160 and R3T120 are slightly decrease. This can be concluded that the crystallinity of hydrotalcite phase can increase the liquid hydrocarbon yield and also can prevent the ketonization(coupling) reaction of palmitic acid.

5.2 Suggestion for further studies

5.2.1 The yield of liquid hydrocarbon of deoxygenation of palmitic acid over calcined-hydrotalcite should be improved by further study on the higher hydrothermal temperature and time to increase the crystallinity of hydrotalcite phase or study on the higher calcination temperature that lead to increase amount of MgO phase in the calcined-hydrotalcite catalyst.

5.2.2 Saturated hydrocarbon products from deoxygenation reaction of palmitic acid with calcined-hydrotalcites are raw material for gasoline production. The unsaturated hydrocarbon products could be hydrogenated to saturated hydrocarbon. However, the property of hydrocarbon that we obtained should be investigated such as pour point, flash point, and octane/cetane number.

REFERENCES

[1] J. G. Na, B. E. Yi, J. N. Kim, K. B. Yi, S. Y. Park, J. H. Park, J. N. Kim, C. H. Ko, "Hydrocarbon production from decarboxylation of fatty acid without hydrogen" **Catalysis Today**, vol. 156, 2010. pp 44–48.

[2] K. Iva, S. Mathias, E. Kari, A. M. Paivi and M. Y. Dmitry. "Hydrocarbons for diesel fuel via decarboxylation of vegetable oils" **Catalysis Today**, vol. 106, 2005. pp. 197–200.

[3] Z. Aihua, M. Qisheng, W. Kangshi, L. Xicai, S. Patrick and T. Yongchun. "Naphthenic acid removal from crude oil through catalytic decarboxylation on magnesium oxide" **Applied Catalysis A: General,** vol. 303, 2006. pp. 103–109

[4] T. Suppawat. "Linear long Chain Hydrocarbon From Deoxygenation Of Palmitic Acid Over Metal Oxides"

[5] Cigaro Pizarro. "Fatty Acid" [Online] : http://en.wikipedia.org/wiki/Fatty_acid

[6] Andi baca. "Animal fat as fuel alternative " [Online]: http://www.polimerieuropa.com/200Page.lasso.html,2001

[7] G.C. Bruce. **Catalytic Chemistry.** New York : John Wiley & Sons, Inc. 1992

[8] M.J. Mendes, O.A.A. Santos, E. Jordao, and A.M. Silva." Hydrogenation of oleic acid over ruthenium catalysts" **Applied Catalysis A: General,** vol. 217, 2001. pp. 253–262.

[9] Stiki. "Esterification " [Online] : http://en.wikipedia.org/wiki/Ester

[10] Chem424. "Esterification mechanism" http://chem.chem.rochester.edu/~chem424/pemech.htm

[11] Cluebot NG. "Decarboxylation" http://en.wikipedia.org/wiki/Decarboxylation

[12] S. Mathias, K. Iva, A. M. Paivi, E. Kari and M. Y. Dmitry. " Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel" **Industrial Engineer Chemistry Research,** vol. 45, 2006. pp. 5706-5715.

[13] Auntof6. "Hydrodeoxygenation" http://en.wikipedia.org/wiki/Hydrodeoxygenation

[14] A. Saadi, Z. Rassoul and M.M. Bettahar "Reduction of benzaldehyde on alkaline earth metal oxides" **Journal of Molecular Catalysis A: Chemical,** vol, 258, 2006. pp. 59–67

[15] F. Kovandaa, D. Kolousek, Z. Cılova, V. Hulınsky. "Crystallization of synthetic hydrotalcite under hydrothermal conditions" **Applied Clay Science,**Vol. 28, 2005. pp. 101–109

[16] F. Cavani, F. Trifirb, A.Vaccari "HYDROTALCITE-TYPE ANIONIC CLAYS: PREPARATION, PROPERTIES AND APPLICATIONS" **Catalysis Today**, vol. 11, 1991. pp. 173–301.

[17] A.G. Olah and A. Molnar. Hydrocarbon Chemistry. New York: John Wiley & Son, Inc. 1995.

[18] L.W. Nelson. Petroleum Refinery Engineering. 4th Ed. New York: Megraw-Hill book company.1985.

[19] J. J. Sheehan, J. A. Dufield, R. B. Codon and V. J. Camobreco. " Life –cycle assessment of biodieel versus petroleum diesel fuel" 1996.

[20] George Lappin (ed.) (1989). "Alpha Olefins Applications Handbook" [Online] http://en.wikipedia.org/wiki/Linear_alpha_olefin

[21] Frantisˇek Kovanda[a],*, David Kolousˇek[a], Zuzana C´ılova´[b], Va´clavHul´ınsky´ b , Crystallization of synthetic hydrotalcite under hydrothermal conditions , [a]Department of Solid State Chemistry, Institute of Chemical Technology, Technicka´ 5, 166 28 Prague, Czech Republic , [b]Department of Glass and Ceramics, Institute of Chemical Technology, Prague, Czech Republic. Applied Clay Science 28 (2005) 101–10.

APPENDICES

APPENDIX A

CALCULATION

Calculations of catalytic parameters Yield

Yield of each product is defined as percentage of molar ratio of particular product obtained and the reactant fed during a certain period of time.

EX. *Deoxygenation of R3T160.*

Sample hydrotalcite(R3T160) + Palmitic acid (1:1 mol)

R3T160	1.000 g
Palmitic acid	4.588 g
Total	5.588 g.

Proceed

Residue in reactor	1.347 g
Trap condenser 1	2.909 g
Trap condenser 2	0.077 g
Total	4.333 g

Calculate % Yield

Palmitic acid	4.588 g
MW Palmitic acid	256.42 g/mol
MW Oil ($-CO_2$)	=256.42-44 =212.42 g/mol

$$\text{Theoretical weight oil} \quad \frac{4.588\ \text{g}}{256.42\text{g/mol}} \times 212.42\ \text{g/mol} = 3.801\ \text{g}$$

$$\%\ \text{Yield} \quad = \frac{(2.909+0.077)\text{g}}{3.801\text{g}} \times 100 \quad = 78.56\%$$

Calculation % unreacted palmitic acid

Delta Y (from TGA) 23.614 %

Weight of residue 1.347 g

$$\text{Unreacted palmitic} = \frac{23.614 \times 1.347}{100}$$

$$= 0.318 \text{ g}$$

$$\text{\% Unreacted palmitic acid} = \frac{0.318}{4.588} \times 100 = 6.93 \%$$

Calculation % of coke

Delta Y (from TGA) 7.3249 %

Weight of residue 1.347 g

$$\text{Unreacted palmitic} = \frac{7.3249 \times 1.347}{100}$$

$$= 0.0986 \text{ g}$$

$$\text{\% Coke} = \frac{0.0986}{4.588} \times 100 = 2.15 \%$$

Calculation % of conversion

$$\text{\% of conversion} = 100 - \text{\% unreacted palmitic acid}$$

$$= 100 - 6.93$$

$$= 93.07 \%$$

APPENDIX B

REACTION DATA

Table B1 Liquid product of deoxygenalation between palmitic acid over each hydrotalcite (1:1.2 by mol, 460°C, 6 hours)

Type of hydrotalcite	R2T120		R2T160		R3T120		R3T160		Bulk MgO	
Weight of palmitic acid (g)	4.122		4.173		4.430		4.588		6.361	
Weight of product (g)	2.755		2.57		2.508		3.179		3.627	
% Liquid yield	80.71		71.35		67.81		83.64		68.85	
Product selectivity %	Unsaturated	Saturated	Unsaturated	Saturated	Unsaturated	Saturated	Unsaturated	Saturated	Unsaturated	Saturated
C6	0.3679	0.4472	0.0581	0.0665	0.2481	0.2947	0.3126	0.2947	0.2469	0.2823
C7	1.0369	2.3806	2.6369	0.3709	0.8056	0.9954	0.8984	0.9190	.9784	0.9641
C8	1.8676	2.0122	0.4262	0.4765	1.6639	1.8687	1.2565	1.3996	1.3902	1.2702
C9	2.1975	2.5726	0.9827	1.2893	2.4711	2.9849	2.0234	2.3658	1.8463	1.8745
C10	2.9221	2.9131	2.1258	2.6120	3.4769	3.6748	2.5847	2.9316	2.5543	2.8284
C11	4.1087	3.6435	3.0596	3.0342	4.4067	3.9316	3.4199	2.7987	3.0629	2.5338
C12	3.6942	4.8622	3.1878	4.5798	4.1056	5.4927	3.1762	4.3962	2.9411	3.8162
C13	6.0797	9.3916	5.7862	9.8017	6.3053	10.2184	5.6058	8.5758	6.3841	7.4413
C14	16.7463	6.0175	18.0351	9.0775	15.3550	7.1341	18.8914	5.4191	21.9353	6.5186
C15	7.8994	18.6842	8.3058	23.9211	5.1247	19.4417	10.4315	21.8487	30.8368	
2-heptadecanone	0.1650		0.2664		n/a		0.4506		0.3844	

Table B2 Liquid product of deoxygenation between palmitic acid over each hydrotalcite (1:1 by mol, 460°C, 6 hours)

Type of hydrotalcite	R2T120		R2T160		R3T120		R3T160		MgO	
Weight of palmitic acid (g)	4.122		4.173		4.430		4.588		6.361	
Weight of product (g)	2.691		2.507		2.543		2.986		3.784	
% Liquid yield	78.85		72.52		68.73		78.56		71.82	
Product selectivity %	Unsaturated	Saturated	Unsaturated	Saturated	Unsaturated	Saturated	Unsaturated	Saturated	Unsaturated	Saturated
C6	0.1713	0.2828	0.1388	0.2306	0.1437	0.2941	0.1749	0.257	0.2079	0.2763
C7	0.5706	0.8467	0.5509	0.7882	0.7755	0.9088	0.629	0.8293	0.7092	0.7568
C8	1.5279	1.5468	1.5538	1.4857	1.7207	1.6224	1.4686	1.3949	1.3545	1.2361
C9	2.024	2.1406	2.1651	2.4362	2.231	2.5763	1.8071	2.1503	1.6462	1.6582
C10	2.7386	2.6012	2.8359	2.6762	3.0131	2.9613	2.3819	2.4087	2.3063	2.1493
C11	3.4684	2.9954	3.3165	2.6626	3.626	3.1011	2.8851	2.3921	2.8599	2.0378
C12	3.4889	4.3525	3.5913	3.9221	3.6867	4.3153	2.9734	3.4002	2.7641	2.8764
C13	5.9668	8.941	6.4558	8.1696	6.7249	8.0096	5.5634	7.896	5.0281	7.1835
C14	19.6371	4.9827	20.9037	4.6387	18.9348	5.1211	21.2807	3.6165	20.9877	3.2305
C15	9.4527	22.0366	13.3545	17.6755	9.9076	20.0961	16.1239	19.6465	12.6915	27.4146
2-heptadecanone	0.2274		0.4483		0.23		0.7206		0.6251	

Table B3 Liquid product of deoxygenation between palmitic acid over each hydrotalcite (1:0.8 by mol, 460°C, 6 hours)

Type of hydrotalcite	R2T120		R2T160		R3T120		R3T160		MgO	
Weight of palmitic acid (g)	4.122		4.173		4.430		4.588		6.361	
Weight of product (g)	2.274		2.105		2.106		2.479		1.591	
% Liquid yield	66.61		60.89		56.92		65.22		28.79	
Product selectivity %	Unsaturated	Saturated	Unsaturated	Saturated	Unsaturated	Saturated	Unsaturated	Saturated	Unsaturated	Saturated
C6	0.1883	0.2217	0.3077	0.4005	0.3038	0.3537	0.2628	0.3032	0.2094	0.2332
C7	0.7072	1.2717	0.9258	3.5820	1.0055	1.1179	0.7985	0.8633	0.7816	0.8806
C8	1.5463	1.6692	1.7402	1.7610	1.7652	1.8286	1.5249	1.4749	2.0907	2.0542
C9	2.1162	2.3576	2.3283	2.7880	2.2920	2.7325	2.1518	2.5625	3.0432	3.4292
C10	3.1366	3.4864	3.0684	2.9224	3.1209	3.2117	2.7958	2.9096	4.5767	4.0611
C11	3.9172	3.7079	3.7132	3.1927	4.0581	3.3688	3.8467	3.1736	5.6382	4.1577
C12	3.8576	5.2934	3.6648	4.7525	3.7296	4.6696	3.6693	4.5765	4.2002	5.4936
C13	6.4187	10.0496	5.9120	9.2314	6.5822	9.5224	6.0507	9.6696	5.0094	13.4603
C14	14.9718	8.0459	14.6786	6.8394	17.6087	6.3208	17.8762	6.6914	11.3293	6.7794
C15	5.9691	21.0674	6.7765	19.0719	7.0109	19.2916	7.4233	21.2226	22.1616	
2-heptadecanone	n/a		2.3475		0.1058		0.153		0.4104	

APPENDIX C

GAS CHROMATOGRAM

Analysis liquid product from gas chromatography

The liquid products were analysed by GC-FID.

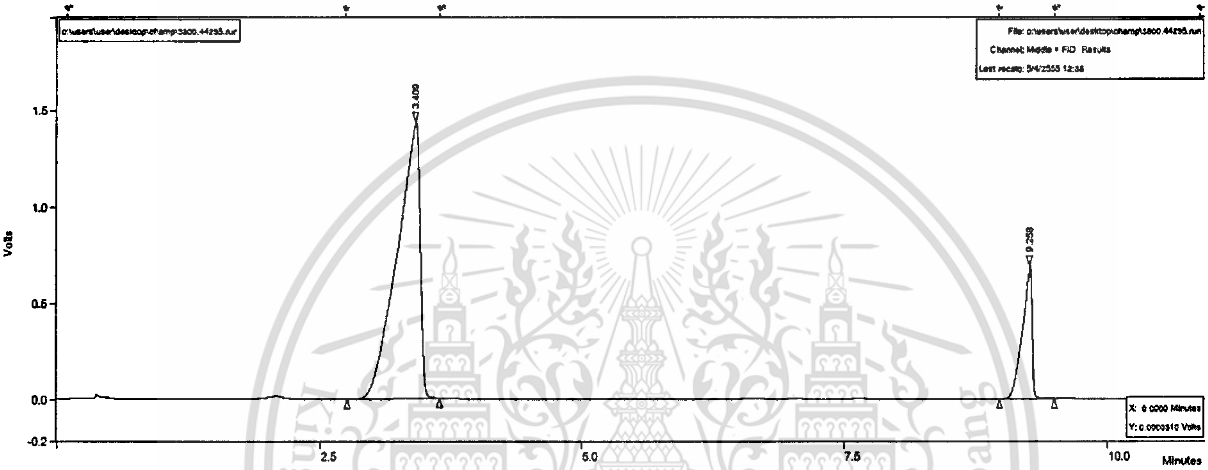


Figure C1 Gas chromatogram of standard nonane with tetrahydrofuran

Table C1 Chromatogram of standard nonane and tetrahydrofuran

Retention time (min)	Hydrocarbon
5.72	Tetrahydrofuran (solvent)
9.26	Nonane (standard C9 hydrocarbon)

The GC-FID of liquid hydrocarbon from of reaction palmitic acid over hydrotalcite catalyst

The liquid hydrocarbon product from deoxygenation of palmitic acid react over R2T120 (1:1.2 by mol, 460°C, 6 hours)

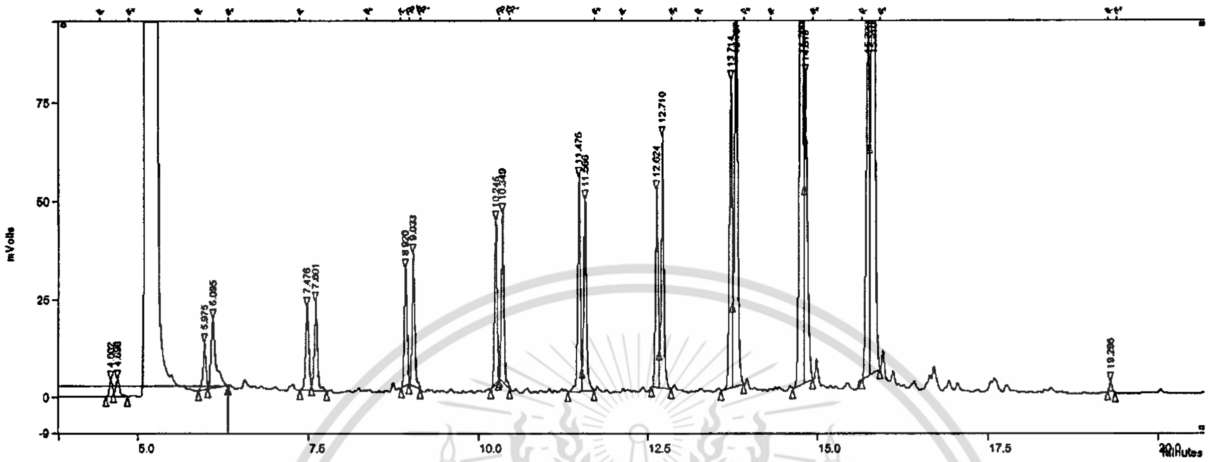


Figure C2 Chromatogram of liquid hydrocarbon product from palmitic acid over R2T120 (1:1.2 by mol, 460°C, 6 hours)

Table C2 Chromatogram of liquid hydrocarbon product from the deoxygenation of palmitic acid

Retention time (min)	Hydrocarbon	Retention time (min)	Hydrocarbon
4.602	2-Hexene	12.624	1-Dodecene
4.698	Hexane	12.710	Dodecane
6.975	2-Heptene	13.714	1-Tridecene
6.095	Heptane	13.797	Tridecane
7.476	2-Octene	14.769	2-Tetradecene
7.601	Octane	14.818	Tetradecane
8.920	1-Nonene	15.728	1-Pentadecene
9.033	Nonane	15.810	Pentadecane
10.246	1-Decene	19.295	2-Heptadecanone
10.349	Decane		
11.475	Cyclopropane		
11.566	Undecane		

The liquid hydrocarbon product from deoxygenation of palmitic acid react over R2T120 (1:1 by mol, 460°C, 6 hours)

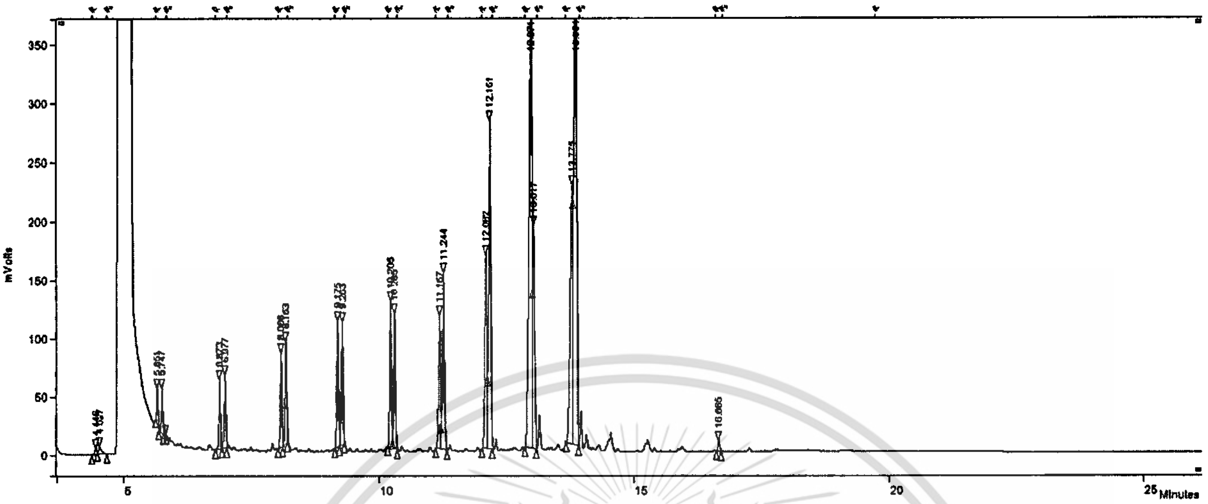


Figure C3 Chromatogram of liquid hydrocarbon product from palmitic acid R2T120 (1:1 by mol, 460°C, 6 hours)

Table C3 Chromatogram of liquid hydrocarbon product from deoxygenation of palmitic acid

Retention time (min)	Hydrocarbon	Retention time (min)	Hydrocarbon
4.446	2-Hexene	11.167	1-Dodecene
4.527	Hexane	11.244	Dodecane
5.651	2-Heptene	12.082	1-Tridecene
5.747	Heptane	12.161	Tridecane
6.873	2-Octene	12.971	2-Tetradecene
6.977	Octane	13.017	Tetradecane
8.066	1-Nonene	13.775	1-Pentadecene
8.163	Nonane	13.854	Pentadecane
9.176	1-Decene	16.665	2-Heptadecanone
9.263	Decane		
10.205	Cyclopropane		
10.285	Undecane		

The liquid hydrocarbon product from deoxygenation of palmitic acid react over R2T120 (1:0.8 by mol, 460°C, 6 hours)

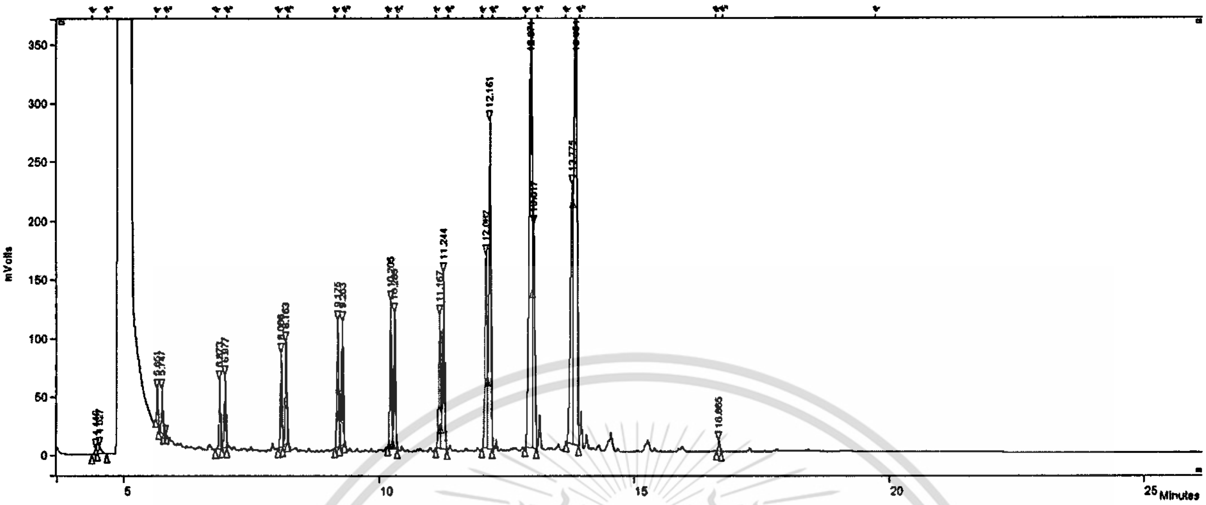


Figure C4 Chromatogram of liquid hydrocarbon product from palmitic acid using R2T120 hydrotalcite (1:0.8 by mol, 460°C, 6 hours)

Table C2 Chromatogram of liquid hydrocarbon product from deoxygenation of palmitic acid

Retention time (min)	Hydrocarbon	Retention time (min)	Hydrocarbon
4.609	2-Hexene	12.626	1-Dodecene
4.706	Hexane	12.713	Dodecane
5.981	2-Heptene	13.716	1-Tridecene
6.101	Heptane	13.800	Tridecane
7.481	2-Octene	14.759	2-Tetradecene
7.604	Octane	14.824	Tetradecane
8.922	1-Nonene	15.729	1-Pentadecene
9.036	Nonane	15.815	Pentadecane
10.248	1-Decene	19.426	2-Heptadecanone
10.351	Decane		
11.476	Cyclopropane		
11.568	undecane		

APPENDIX D

CHARACTERIZATION DATA

The X-ray diffraction patterns of hydrotalcite

Ratio of Magnesium per Aluminium is 2 and hydrothermal treating at 120 °C

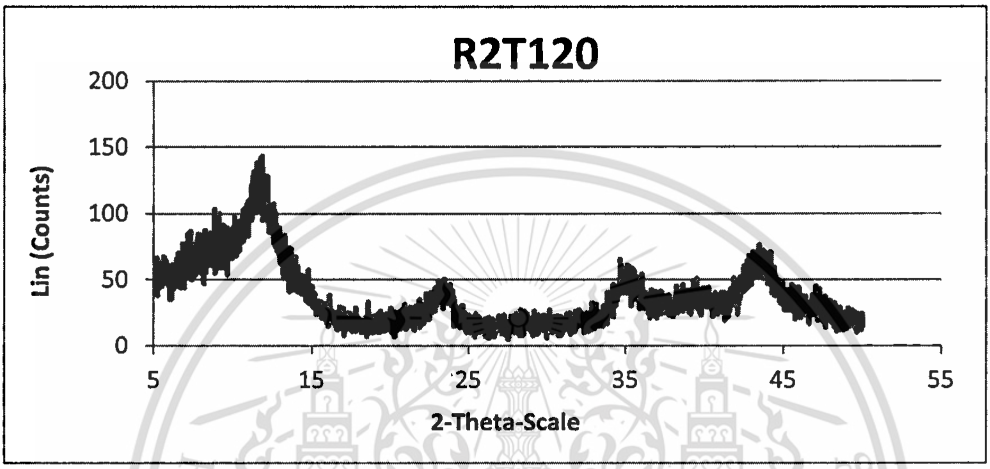


Figure D1 X-ray diffraction patterns of R2T120

Ratio of Magnesium per Aluminium is 2 and hydrothermal treating at 160 °C

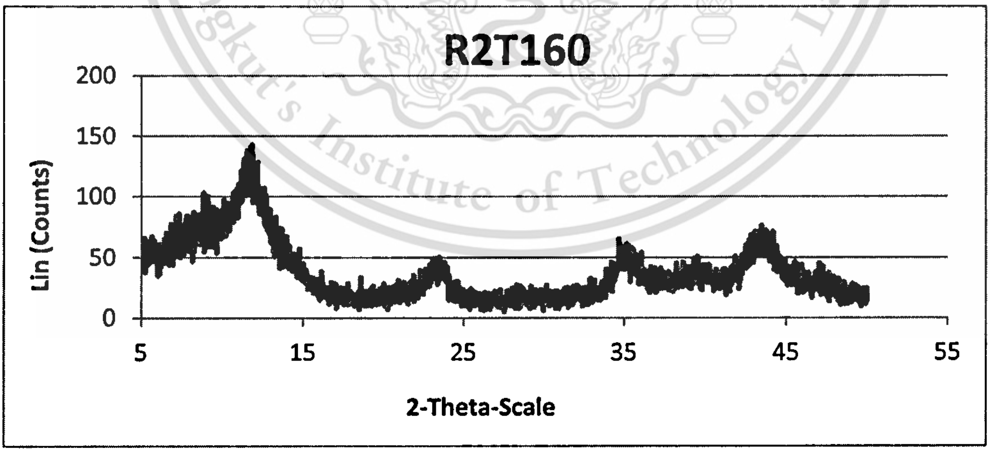


Figure D2 X-ray diffraction patterns of R2T160

Ratio of Magnesium per Aluminium is 3 and hydrothermal treating at 120 °C

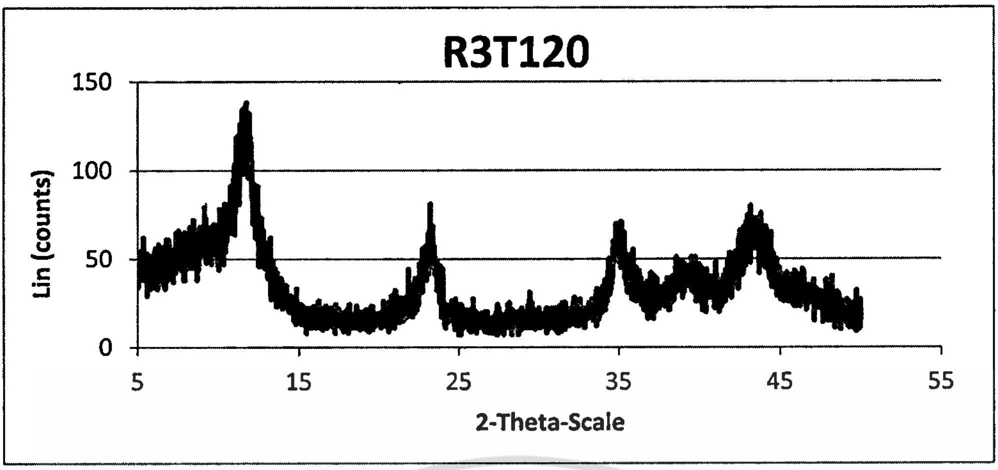


Figure D3 X-ray diffraction patterns of R3T120

Ratio of Magnesium per Aluminium is 3 and hydrothermal treating at 120 °C

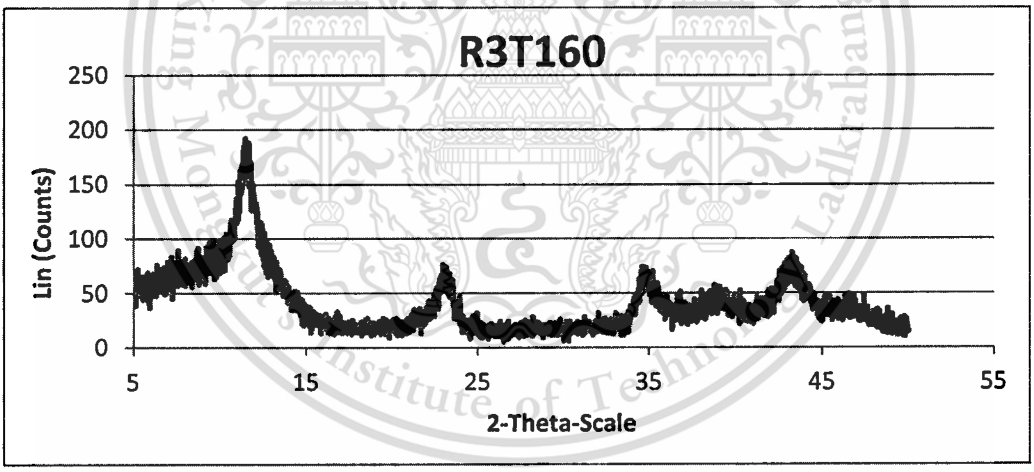


Figure D4 X-ray diffraction patterns of R3T160

Isotherm of hydrotalcite by gas adsorption analyzer

Ratio of Magnesium per Aluminium is 2 and hydrothermal treating at 120 °C

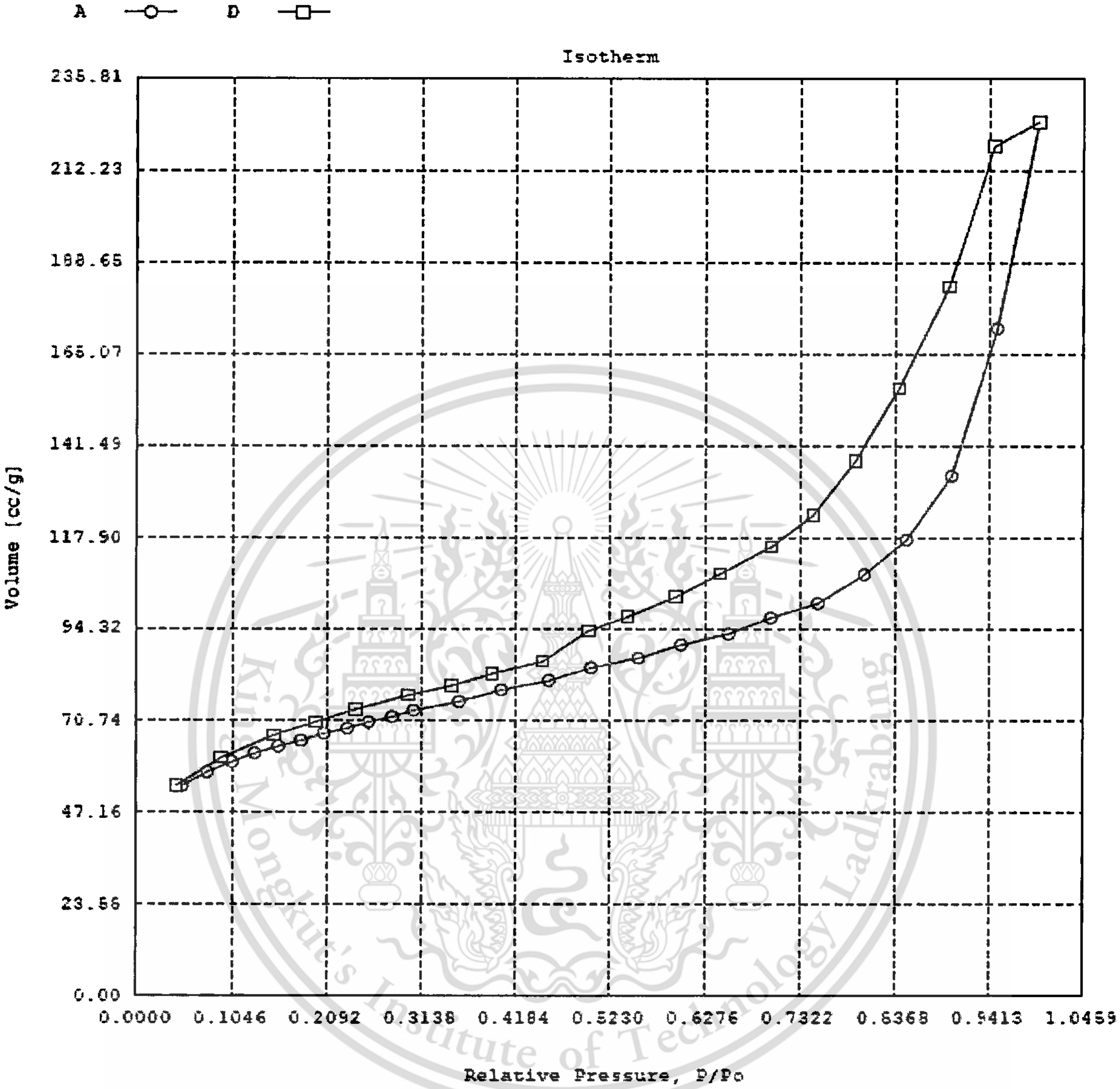


Figure D5 Isotherm of R2T120

Ratio of Magnesium per Aluminium is 2 and hydrothermal treating at 160 °C

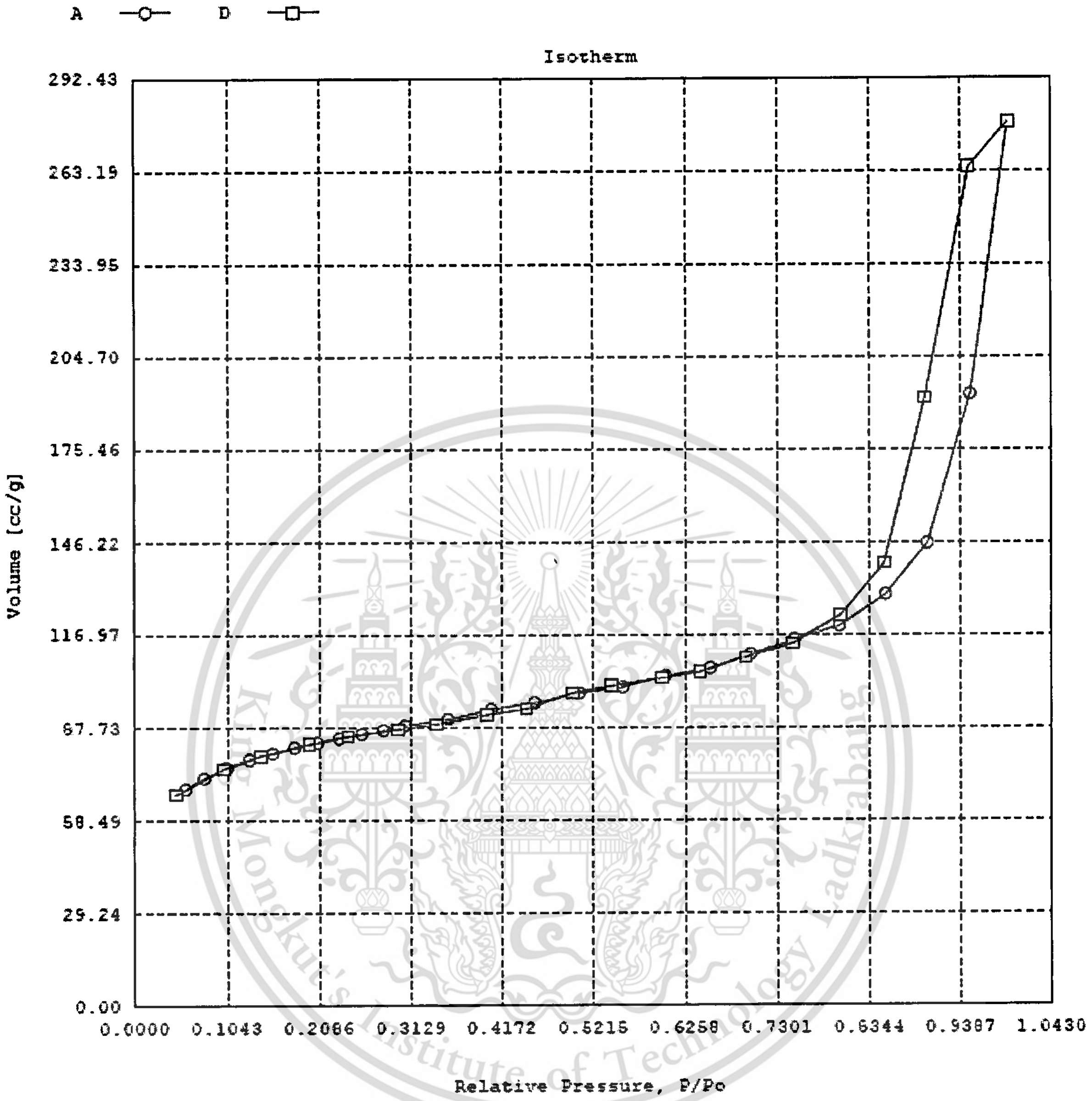


Figure D6 Isotherm of R2T160

Ratio of Magnesium per Aluminium is 3 and hydrothermal treating at 120 °C

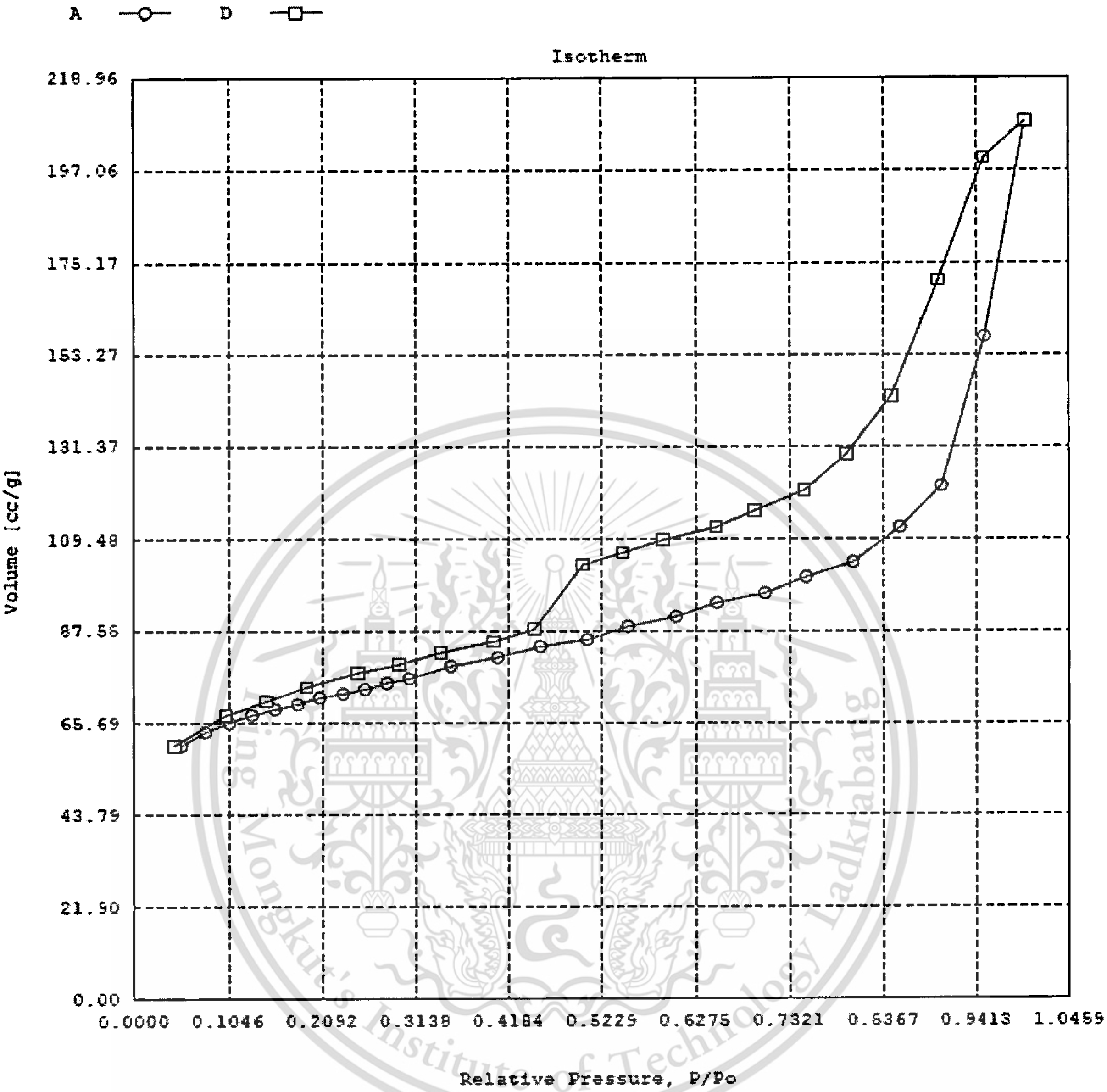


Figure D7 Isotherm of R3T120

Ratio of Magnesium per Aluminium is 3 and hydrothermal treating at 160 °C

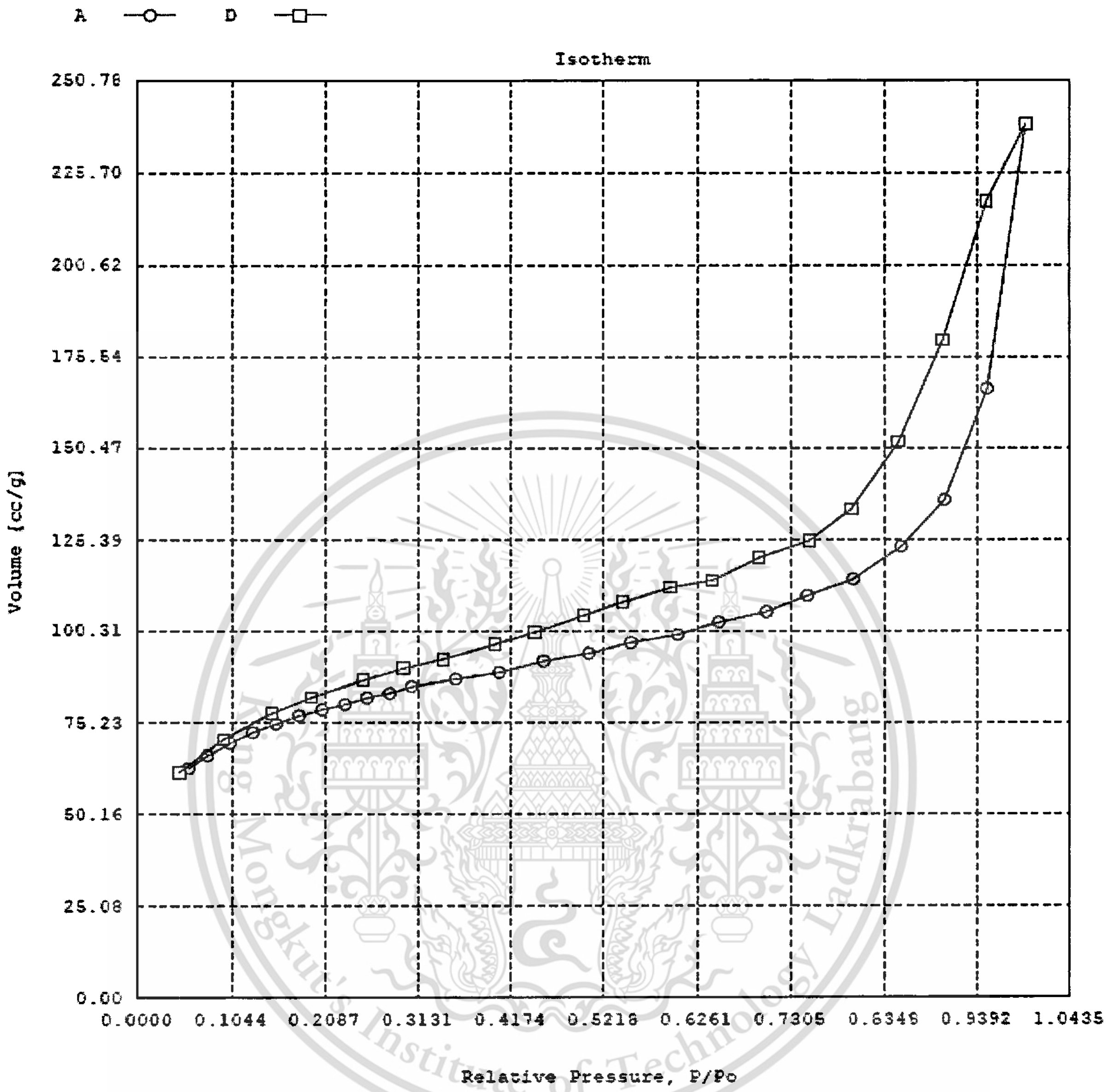


Figure D8 Isotherm of R3T160

Thermal gravimetric analysis

Palmitate salt of palmitic acid with R2T120

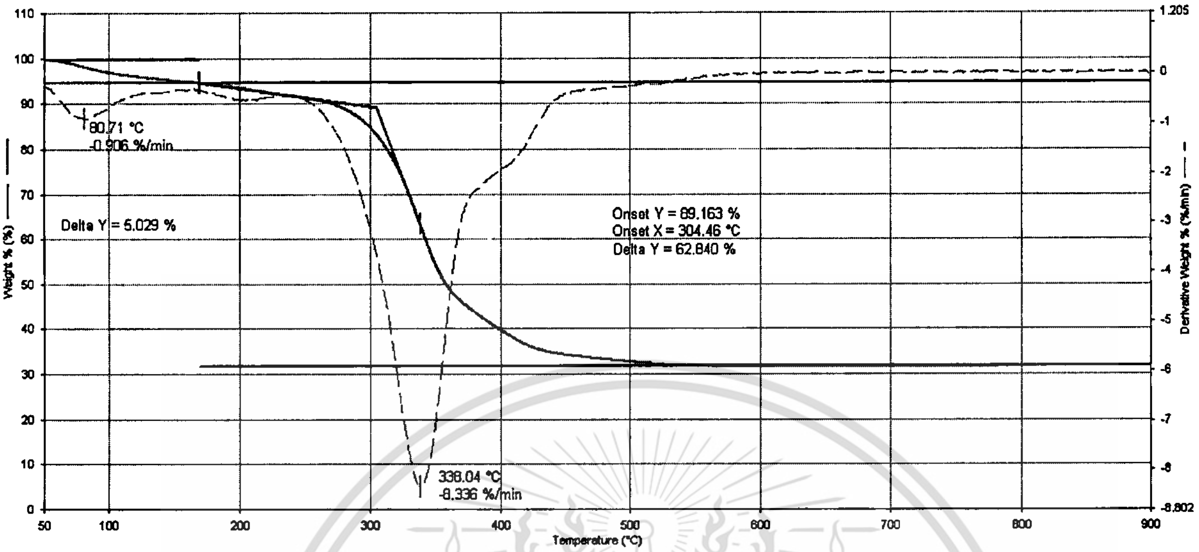


Figure D13 Thermal gravimetric analyzer of palmitric acid with R2T120

Palmitate salt of palmitic acid with R2T160

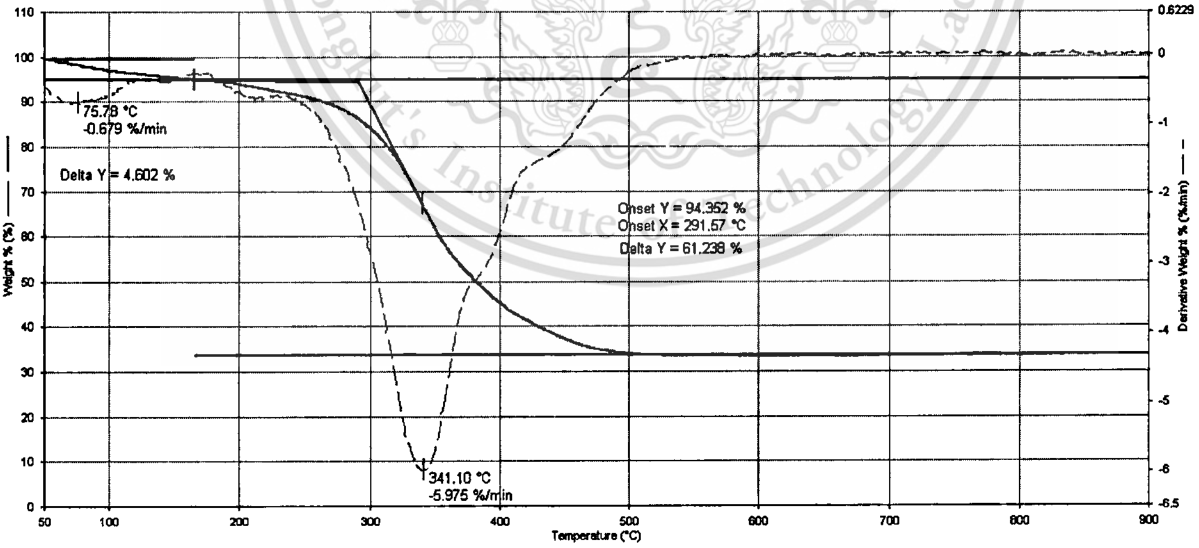


Figure D14 Thermal gravimetric analyzer of palmitric acid with R2T160

Palmitate salt of palmitic acid with R3T120

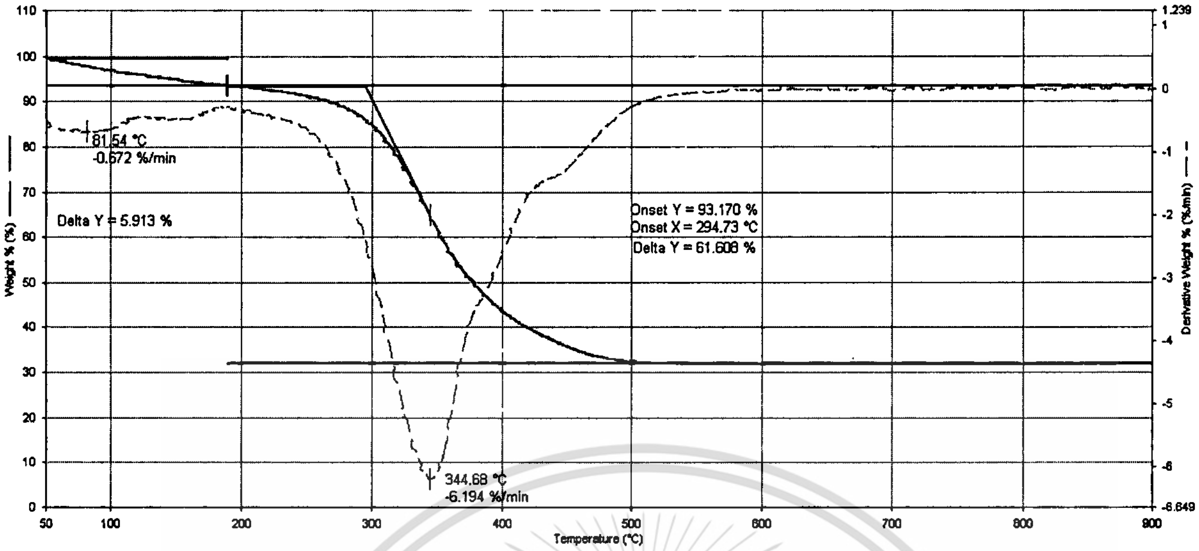


Figure D15 Thermal gravimetric analyzer of palmitric acid with R3T120

Palmitate salt of palmitic acid with R3T160

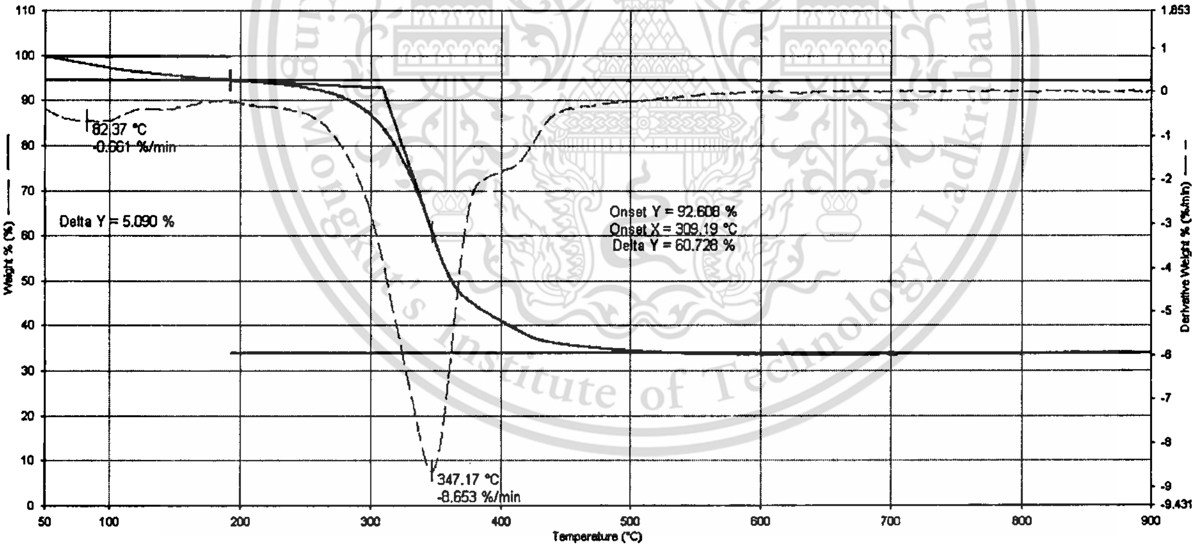


Figure D16 Thermal gravimetric analyzer of palmitric acid with R3T120

Residue from deoxygenation of palmitic acid over R2T120 (1:1.2 by mol)

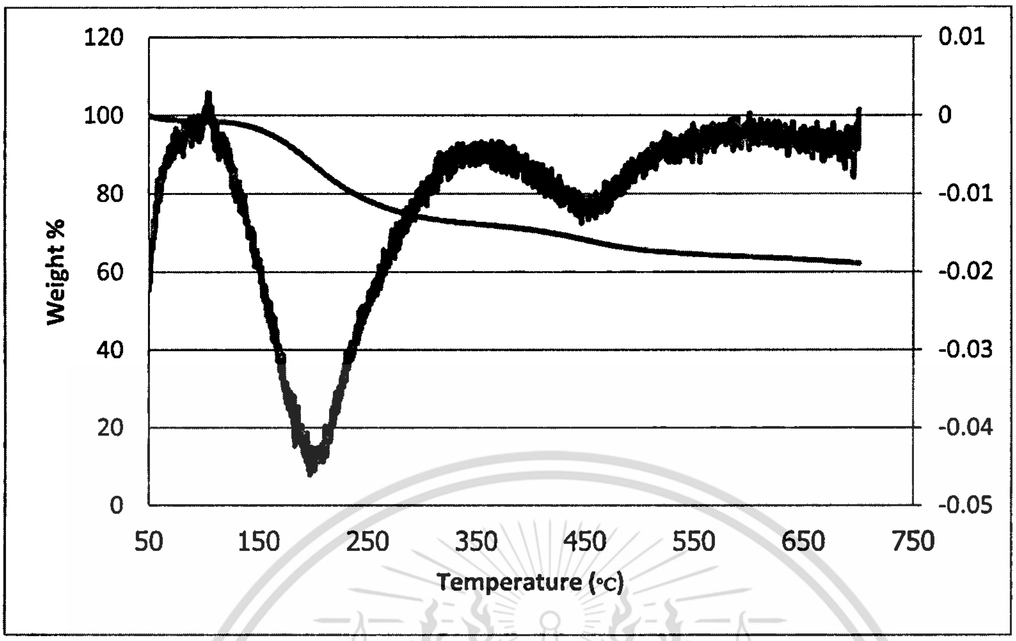


Figure D17 Thermal gravimetric analyzer of residue of R2T120 (1:1.2 by mol)

Residue from deoxygenation of palmitic acid over R2T160 (1:1.2 by mol)

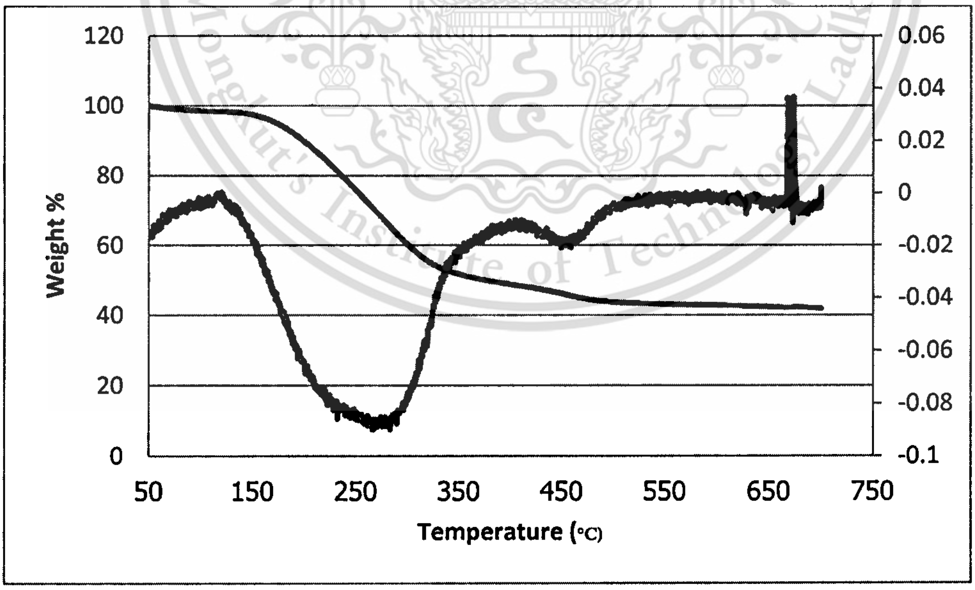


Figure D18 Thermal gravimetric analyzer of residue of R2T160 (1:1.2 by mol)

Residue from deoxygenation of palmitic acid over R3T120 (1:1.2 by mol)

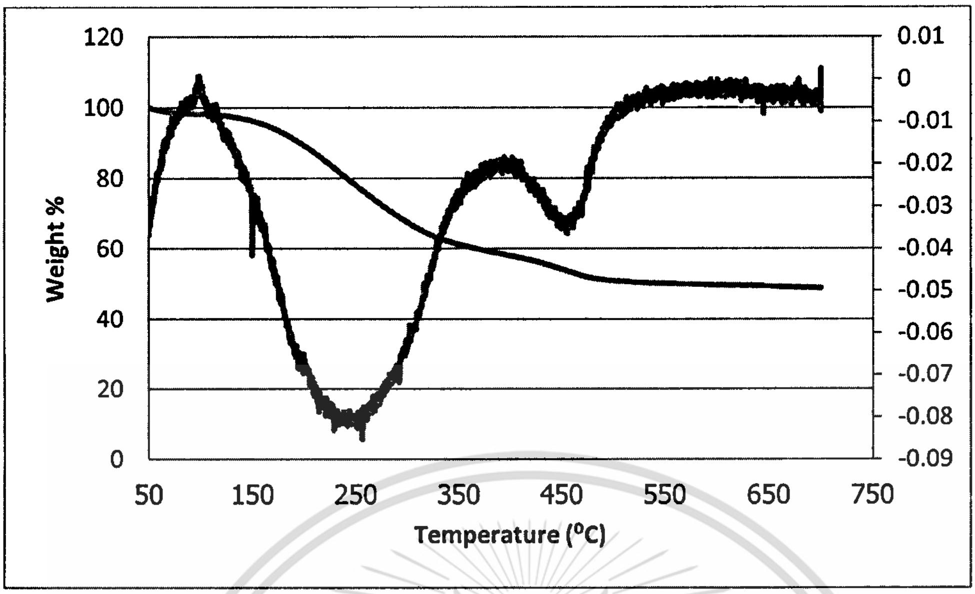


Figure D19 Thermal gravimetric analyzer of residue of R3T120 (1:1.2 by mol)

Residue from deoxygenation of palmitic acid over R3T160 (1:1.2 by mol)

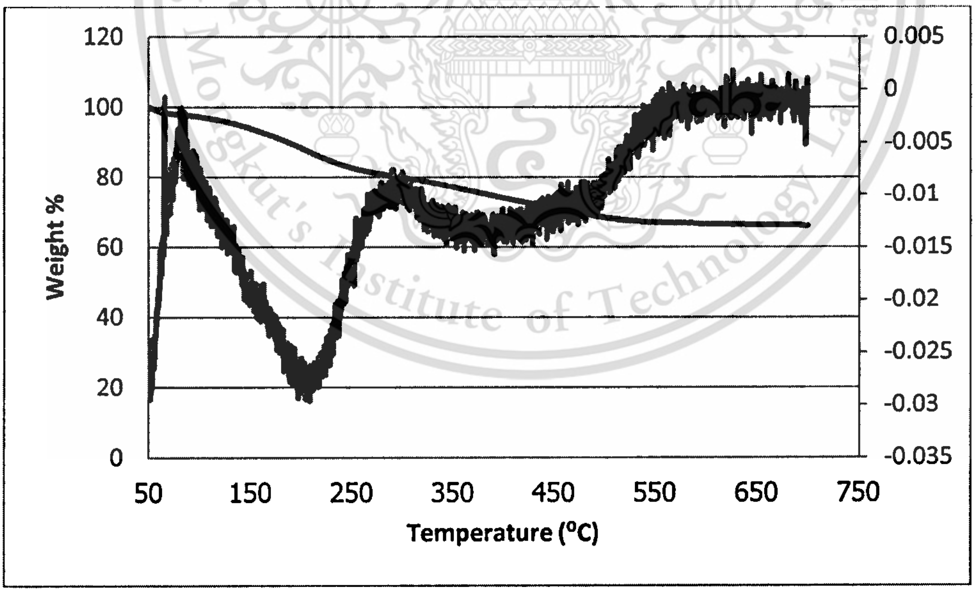


Figure D20 Thermal gravimetric analyzer of residue of R3T160 (1:1.2 by mol)

Residue from deoxygenation of palmitic acid over R2T120 (1:1 by mol)

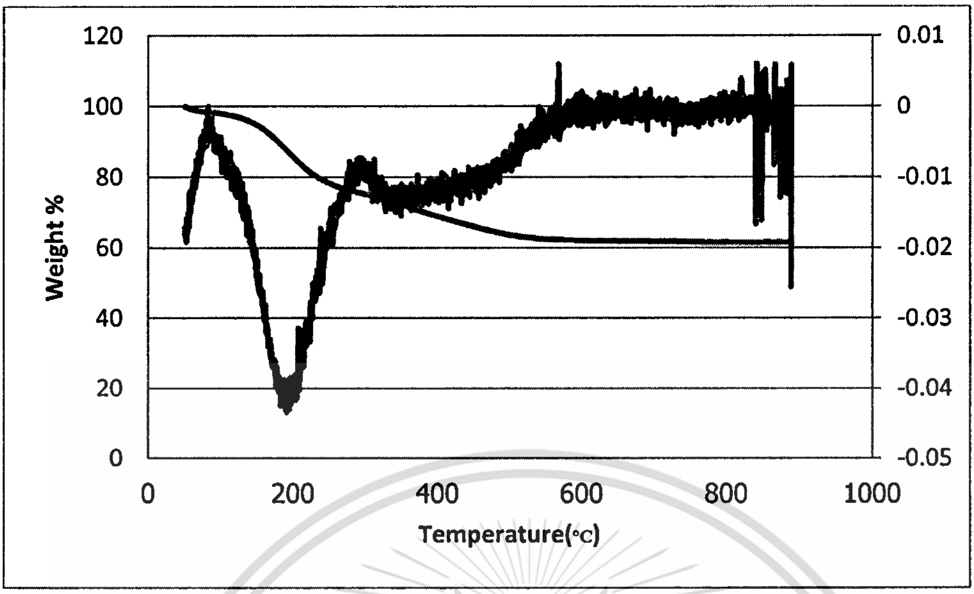


Figure D21 Thermal gravimetric analyzer of residue of R2T120 (1:1 by mole)

Residue from deoxygenation of palmitic acid over R2T160 (1:1 by mol)

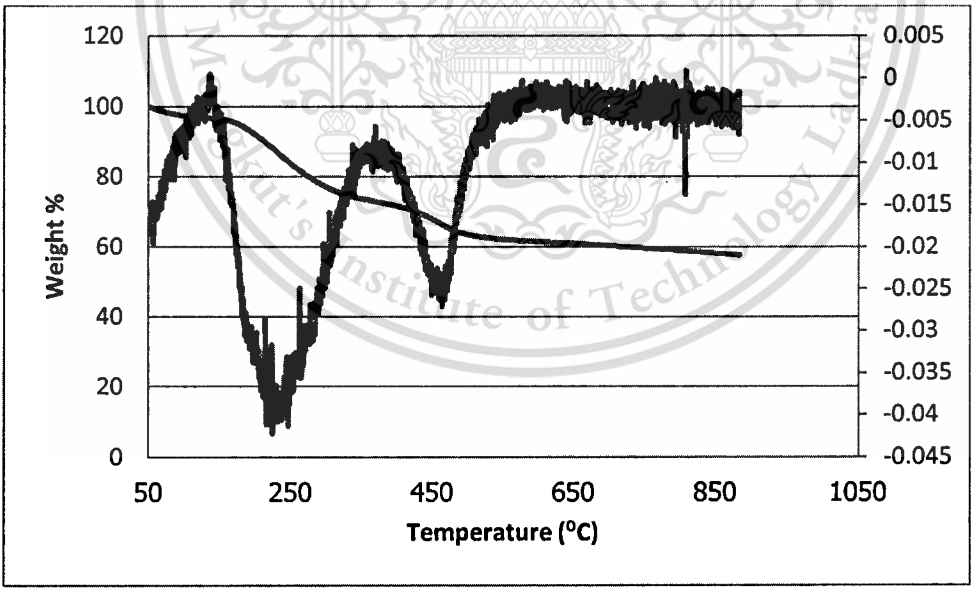


Figure D22 Thermal gravimetric analyzer of residue of R2T160 (1:1 by mol)

Residue from deoxygenation of palmitic acid over R3T120 (1:1 by mol)

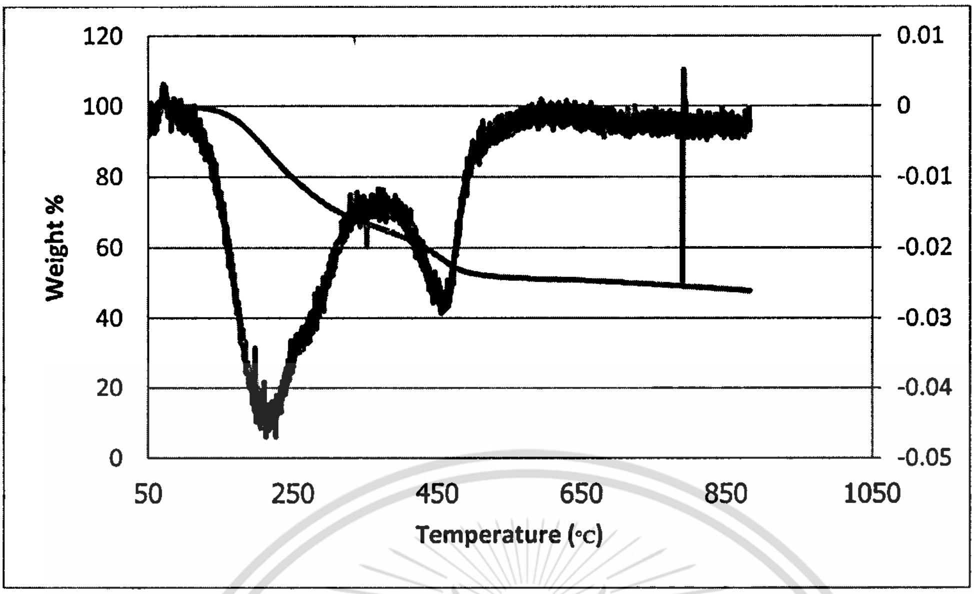


Figure D23 Thermal gravimetric analyzer of residue of R3T120 (1:1 by mol)

Residue from deoxygenation of palmitic acid over R3T160 (1:1 by mol)

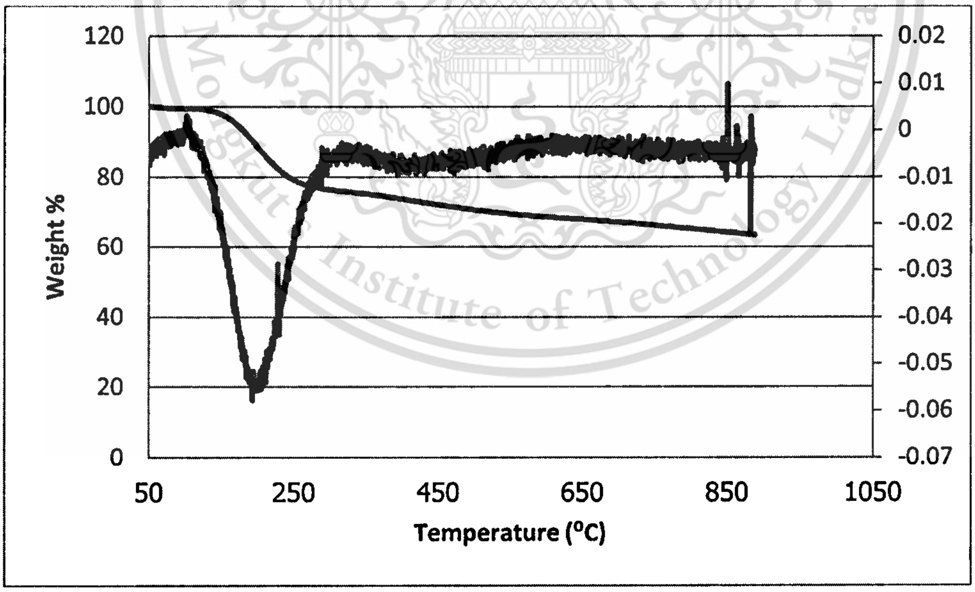


Figure D24 Thermal gravimetric analyzer of residue of R3T160 (1:1 by mol)

Residue from deoxygenation of palmitic acid over bulk MgO (1:1 by mol)

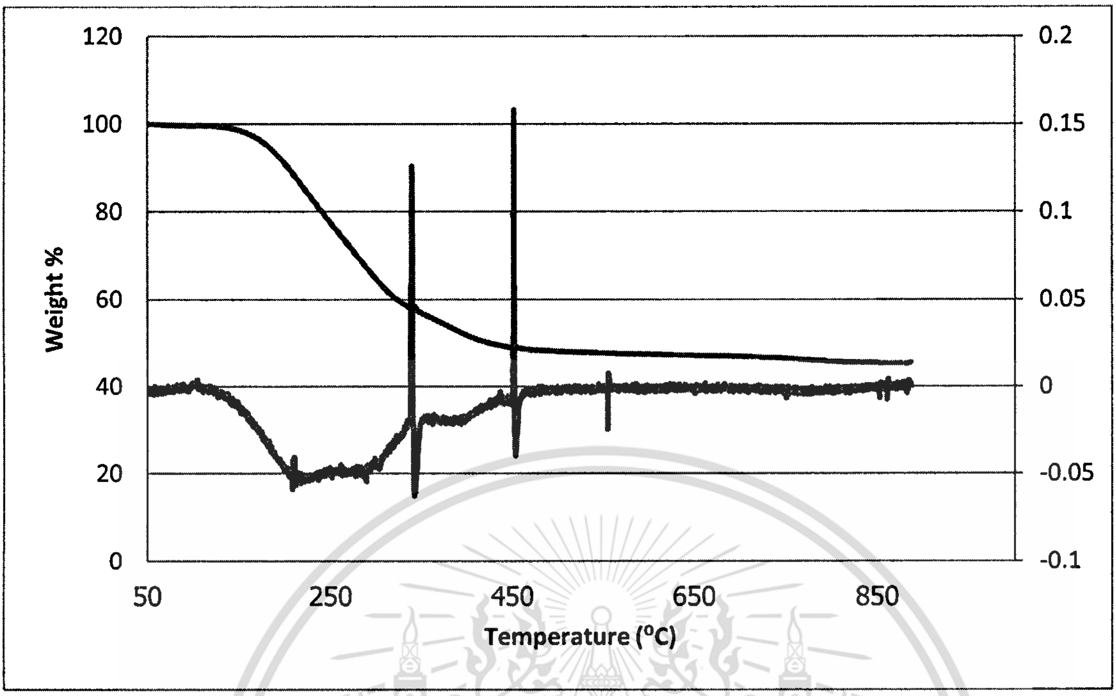


Figure D25 Thermal gravimetric analyzer of residue of bulk MgO (1:1 by mol)

Residue from deoxygenation of palmitic acid over R2T120 (1:0.8 by mol)

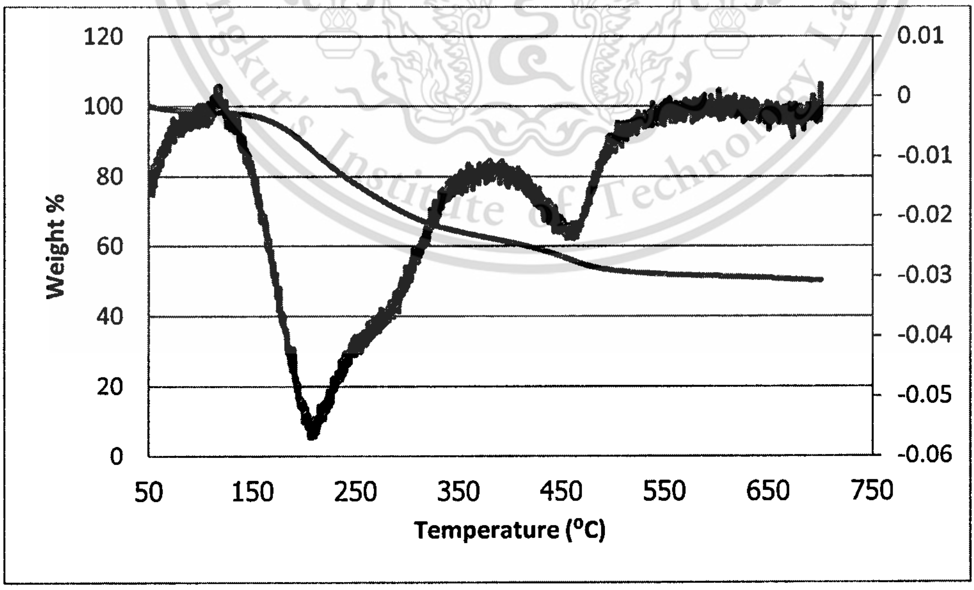


Figure D26 Thermal gravimetric analyzer of residue of R2T120 (1:0.8 by mol)

Residue from deoxygenation of palmitic acid over R2T160 (1:0.8 by mol)

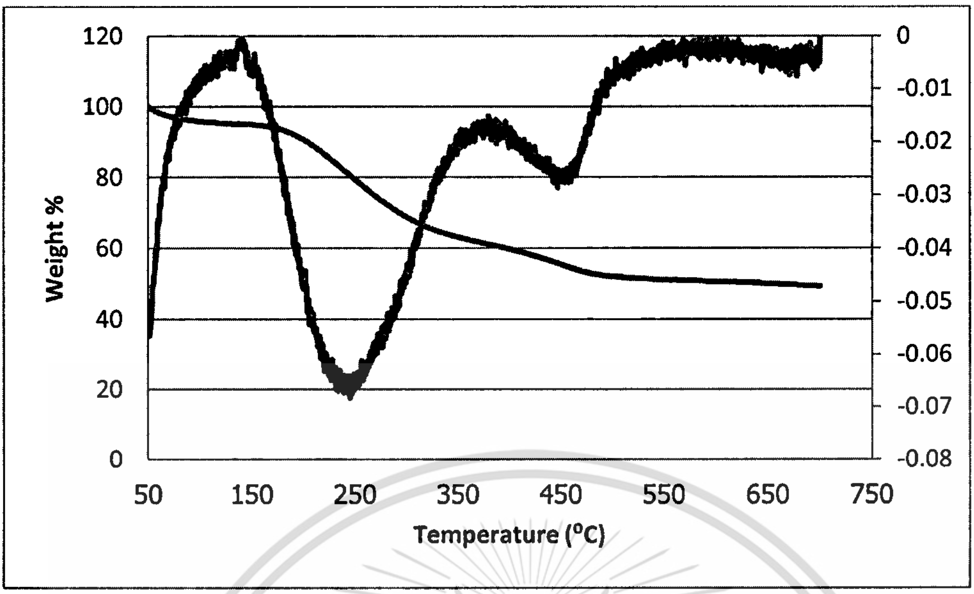


Figure D27 Thermal gravimetric analyzer of residue of R2T160 (1:0.8 by mol)

Residue from deoxygenation of palmitic acid over R3T120 (1:0.8 by mol)

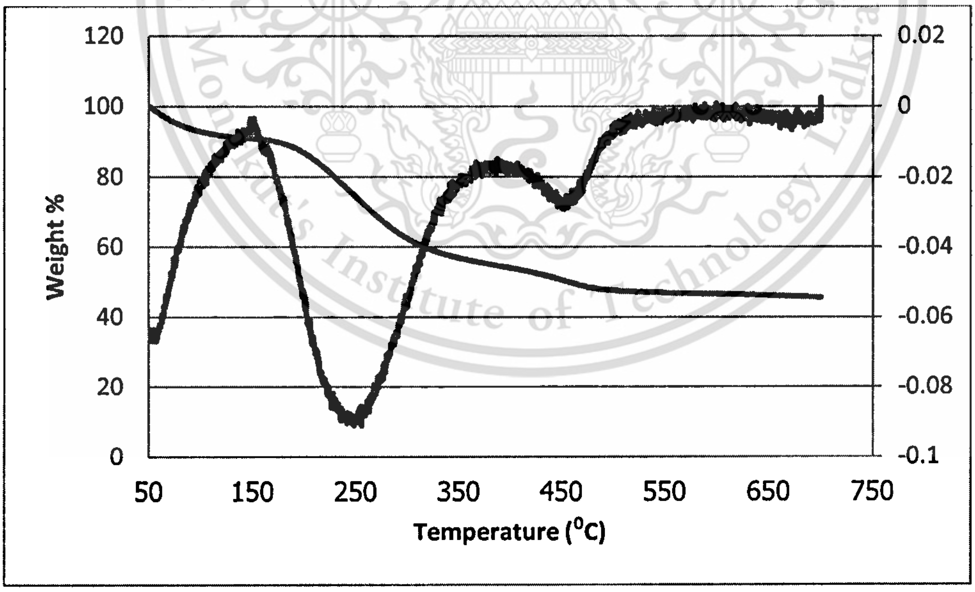


Figure D28 Thermal gravimetric analyzer of residue of R3T120 (1:0.8 by mol)

Residue from deoxygenation of palmitic acid over R3T160 (1:0.8 by mol)

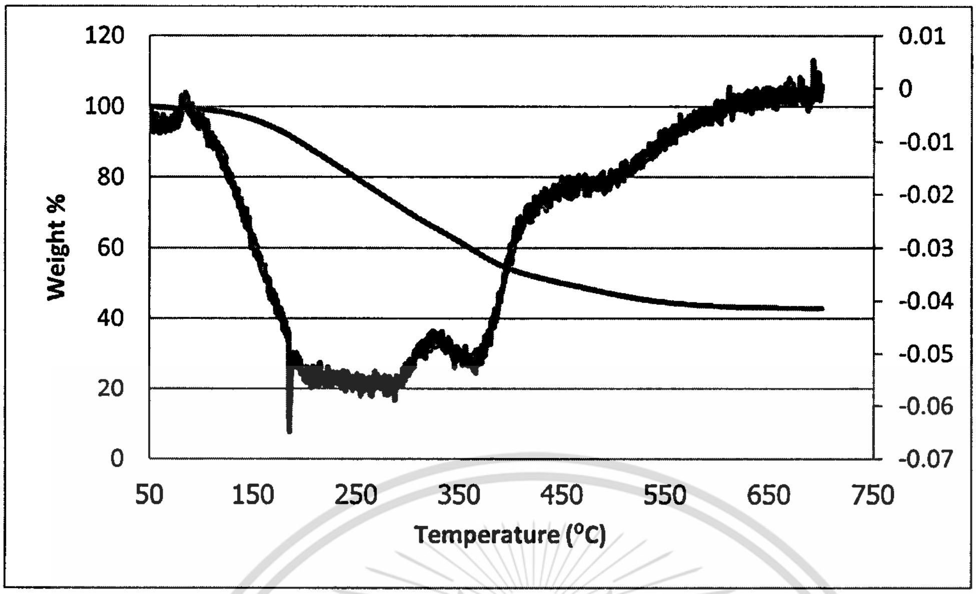


Figure D29 Thermal gravimetric analyzer of residue of R3T160 (1:0.8 by mol)

Residue from deoxygenation of palmitic acid over bulk MgO (1:0.8 by mol)

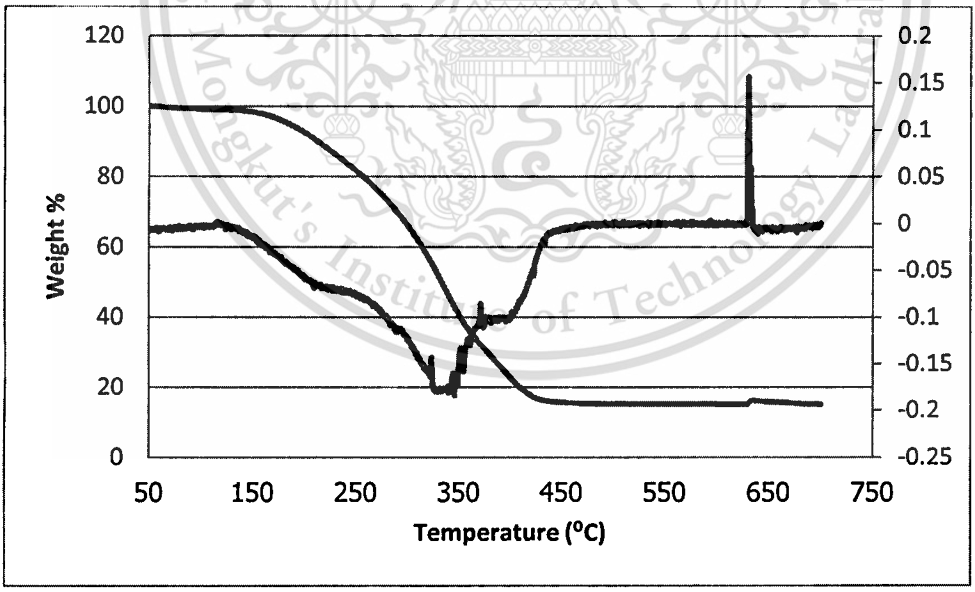


Figure D30 Thermal gravimetric analyzer of residue of bulk MgO (1:0.8 reaction)