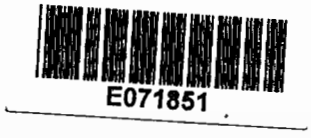
KETONE WAX FROM RENEWABLE FATTY ACID



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ABSTRACT

Lubricant from renewable fatty acids was formed by ketonization reaction with various type of catalysts, ratio of reactant to catalyst and condition of reaction. The three different catalysts are cerium oxide, zirconium oxide and cerium-zirconium oxide.

Zirconium oxide and cerium oxide were prepared by calcinations at the same temperature at 600°C for 3 hours, cerium-zirconium oxide catalyst was prepared by co-precipitation method and calcinations at 600°C for 3 hour then checked with X-ray diffraction technique (XRD). The experiment was done by packing the palmitic acid and each type of catalyst with the ratio of 1:1 and 2:1 (catalyst : palmitic acid) in the close system and then heat up to 350-450°C. The characterization shows that, the main factor of ketonization to produce the highest yield and conversion are the type of catalysts and temperature which cerium-zirconium oxide at 350°C is the best condition to produce the highest yield and conversion.

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Nowadays, lube consumption has been rapidly increased. Lubricating products are generally produced from petroleum feedstock that is non-renewable resource. From the current petroleum exploration, it was found that petroleum and natural gas reserves are depleting. Hence, research on renewable raw material for lube production is increasingly important to preserve the use of petroleum. With this view, animal fats and vegetable oils could be alternative resource that can be used for lube production. Animal fats and vegetable oil contain fatty acids that are aliphatic monocarboxylic acids which derived from, or contained in etherified form. Natural fatty acids commonly have a chain of 4 to 28 carbons (usually unbranched and even numbered), which may be saturated or unsaturated chain [1]. Among these fatty acids, palmitic acid, $CH_3(CH_2)_{14}COOH$ (hexadecanoic acid) [2] is one of the most common saturated fatty acids found in animals and plants. It is also a major component of the oil from palm trees (palm oil and palm kernel oil).

Ketonization of fatty acid can be used to produce a ketone wax or lubricating oil by subsequent hydrotreating. In ketonization, carboxylic acid can interact with adjacent carboxylic over various types of catalysts forming longer ketone apparently on the surface of catalysts. Upon heating, carbon dioxide and water were obtained as co-products. An appropriate catalyst should

be provided high yield of ketone wax without cracking of the long chain hydrocarbon to light hydrocarbon. The ketonization of fatty acid is shown below;

In this project, ketonization of palmitic acid to produce a ketone wax will be investigated over various metal oxide catalyst namely cerium (IV) oxide, zirconium oxide and cerium zirconium oxide. The effects of temperature at 350°C, 400°C and 450°C with different mole ratio of catalyst to palmitic acid which are 1:1 and 2:1 will be also evaluated.

1.2 OBJECTIVE

1.2.1 To obtain a ketone wax from ketonization of palmitic acid.

1.2.2 To compare the activity and selectivity of catalyst in ketonization

1.2.3 To obtain appropriate reaction conditions for ketonization with reasonable catalyst stability.

1.3 SCOPE OF THIS STUDY

1.3.1 Catalyst preparations, Calcinations of zirconium oxide and cerium oxide at 600 °C for 3 hours and 500°C for 1 hour, respectively. Cerium-zirconium oxide was prepared by co-precipitation method and then calcined at 600°C for 3 hours.

1.3.2 Characterization of $CeZrO_2$ by X-ray diffraction (XRD) and Scanning electron microscope (SEM).

1.3.3 The ketonization of palmitic acid is carried out at temperature range from 350 -450°C over

ZrO_2, CeO_2 and $CeZrO_2$ with different mole ratio of catalyst to palmitic acid (1:1 and 2:1).

1.3.4 Study on thermal degradation of palmitic acid.

1.3.5 Analysis and quantification of ketone wax by thermogravimatric analysis (TGA) and Fourier Transform Infrared Spectroscopy (FT-IR)

1.3.6 Analysis of residue using thermogravimatric analysis (TGA)

1.4 EXPECTED RESULTS

Long chain ketone wax from ketonization reaction of palmitic acid over three different catalysts can be obtained. This reaction could be potential process for ketone wax production from the renewable sources.

CHAPTER 2

RELATED LITERATURE

2.1 REACTANT

2.1.1 Palmitic acid $CH_3(CH_2)_{14}COOH$

Palmitic acid is also known as Hexadecanoic acid ($C_{16}H_{32}O_2$) in IUPAC name, is one of the most saturated fatty acid, which found in animals and plants. As its name indicates, it is a major component of the oil from palm trees (palm oil and palm kernel oil) [3]. In this special project, it is white flake solid which has molecular weight equal to 256.42 g/mol. The melting point is 61-62.5°C, boiling point is 271.5°C and it is insoluble in water [4].

Figure 2.1 Palmitic acid

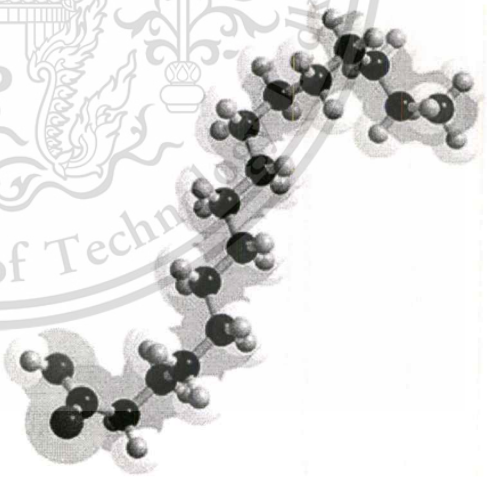


Figure 2.2 Structure of Palmitic acids

2.2 CATALYST

2.2.1 Zirconium (IV) Oxide (ZrO_2)

Zirconium (IV) Oxide, sometime known as Zirconia, is commercial metal oxide catalyst, which is seen as white crystalline oxide of Zirconium. It is commonly found in nature as mineral tazheranite (Zr, Ti,Ca)O_2. At the room temperature, pure ZrO_2 has monoclinic crystal structure and transitions to tetragonal and cubic at increasing temperatures [5].

Zirconium dioxide is stable at a wide temperature range. It possesses both acidic and basic centers. Its properties enable surface processes as a mechanism of bi-functional acid–base catalysis. The number of acidic and basic centers can be changed using proper preparations in ZrO_2 synthesis. Zirconium dioxide can have three crystallographic forms depends on the temperature: at 1200 °C a stable variety is a monoclinic form, at 1200 to 1900 °C it crystallizes as a tetragonal form and over 1900 °C to the melting point at 2670 °C the regular structure is stable. There is also a metastable tetragonal structure to 650 °C. Its appearance is usually explained by the influence of impurities or crystallites effect. The stability ranges for the structural varieties can be modified introducing various admixtures. All polymorph types of ZrO_2 are used in catalysis [6].The zirconium oxide has many application such as Ceramic material, Diamond simulate and etc.

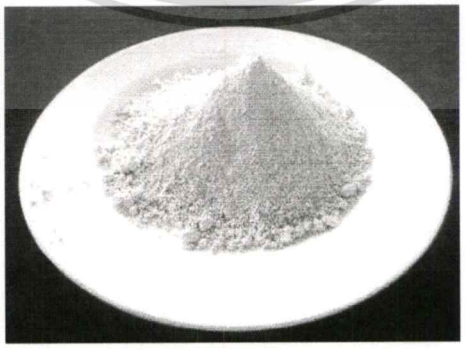


Figure 2.3 Zirconium (IV) Oxide Powder

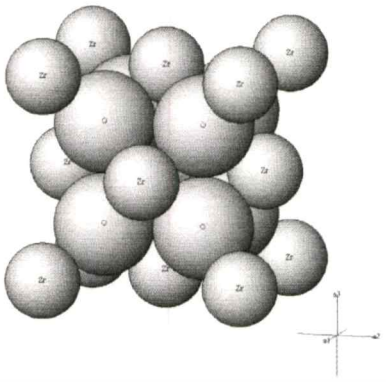


Figure 2.4 Structure of Zirconium (IV) Oxide

2.2.2 Cerium (IV) Oxide: (CeO_2)

Cerium (IV) Oxide is also known as ceria, cerium oxide or cerium dioxide, is an oxide of the rare earth metal cerium. It is a pale yellow powder with the chemical formula CeO_2.

The application of cerium oxide is used in ceramics, to sensitize photosensitive glass, as a catalyst support and also catalyst in auto motive application [7]. Stubenrauch et al. studied the ketonization of acetic acid over the single crystal surface of CeO_2. A difference in the catalytic activity was found between the (1 11) and (1 0 0) planes ofCeO_2: propanone is formed only on theCeO_2 (1 11) plane in the ketonization of acetic acid, whereas the CeO_2 (1 0 0) plane does not catalyze the ketonization, indicating that the catalytic activity depends on the crystal plane. Various metal oxides including CeO_2 are active catalysts for the ketonization [8].

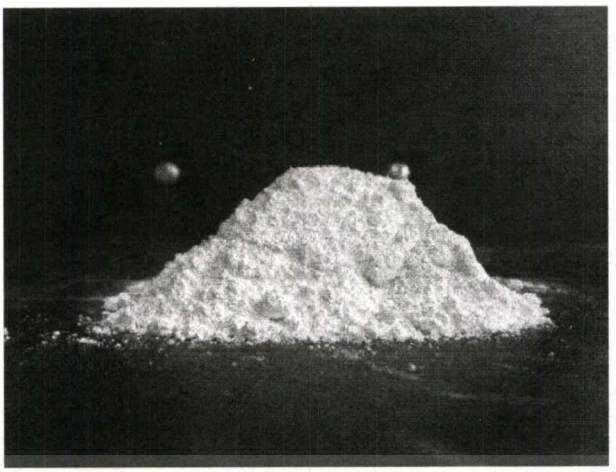


Figure 2.5 Cerium (IV) Oxide Powder

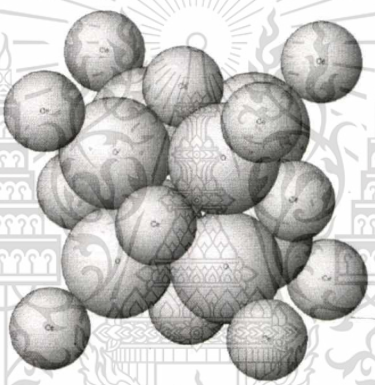


Figure 2.6 Structure of Cerium (IV) Oxide

2.2.3 Cerium Zirconium Oxide ($CeZrO_2$)

Both of the mentioned metal oxides can be applied in the catalysis as a single unit or as a component of compound catalysts and is also a very good support for catalysts or an additive to supports, which improves their properties.

Many articles have been devoted to catalytic properties of pure ZrO_2. It is a material of weak basic and acidic centers, in some conditions showing very good catalytic properties, e.g. the

acidic properties of ZrO_2 are used for the synthesis of ketones from aldehydes, alcohols and carboxylic acids [9].

Moreover, the articles, which mention about the better properties of $CeZrO_2$ with the 0.5mol%CeO_2 and 0.5mol%ZrO_2 were published with the small reactant, such as Hexanoic, Pentanoic and etc. [10, 11]

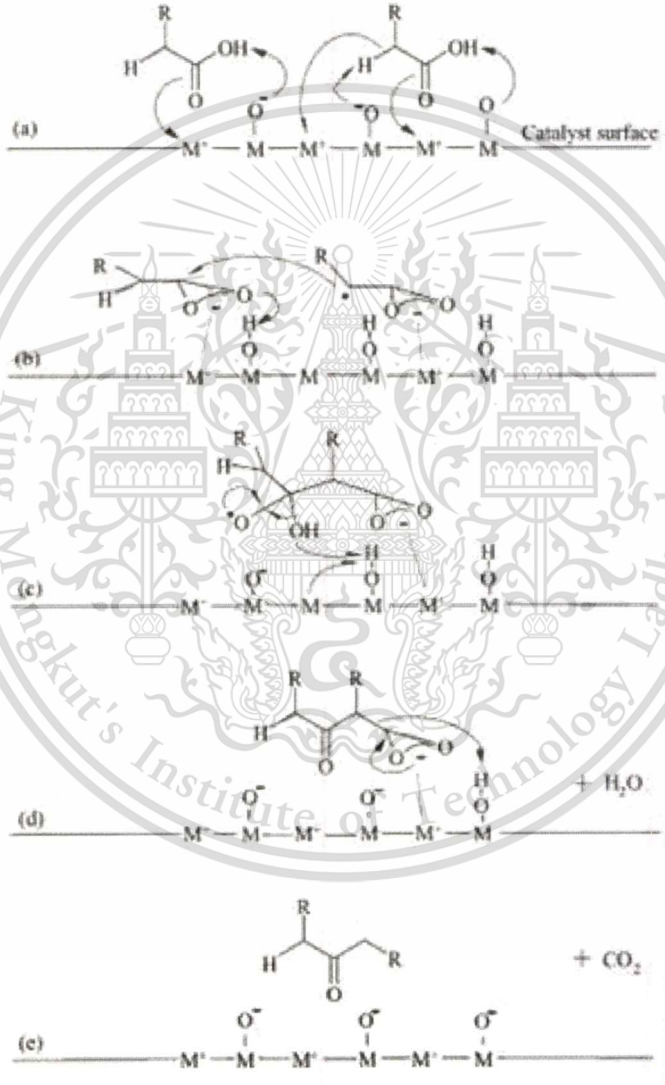


Figure 2.7 Mechanism of ketonization on the surface of catalyst

2.2.3.1 Catalyst Preparations

A) Ball Mill:

The catalysts that are CeO_2 andZrO_2 were mixed with 1:1 mol ratio. Ball Mill equipment was filled by the mixture of metal oxide then grinds them together. Finally, the metal catalyst was characterized by XRD to check the reaction [12].

B) Co-Precipitation:

Cerium (III) Chloride Heptahydrate and Zirconium Tetrachloride were dissolved in water. The solutions of Cerium and Zirconium were mixed together. Addition of Ammonium Hydroxide would form the precipitate of Cerium Zirconium Hydroxide. Then the precipitate was washed by DI water. After that, dry it in the oven over night. Finally, the sample powder was calcined at 500C for 1hour to remove hydroxyl group [13].

2.3 REACTION

2.3.1 Ketonization

Ketonization is an irreversible reaction forms the compound of ketone which is the desirable product from the renewable fatty acid reactant or carboxylic acid via the coupling of 2molecules of acid on metal oxide catalyst at the range of temperature 350-450°C. The co-products are carbon dioxide and water [14].

2.3.2 Side Reactions

A) Catalytic and Thermal Cracking:

This type of side reaction produces smaller compound such as Methane, Alcohol and etc, from reactant and product.

B) Catalytic Reforming:

The reforming reaction would maintain the number of carbon atoms in new compound but different structure was appeared.

C) Polymerization:

The larger co-product would perform by this reaction.

2.4 CHARACTERIZATION

2.4.1 Fourier Transform Infrared Spectroscopy (FT-IR)

-Introduction

Fourier Transform Infrared Spectroscopy is most useful for identifying chemicals that are either organic or inorganic. It can be utilized the quantities of some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FT-IR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FT-IR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments.

-Qualitative Analysis

FT-IR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FT-IR is perhaps the most powerful tool for identifying types of chemical

bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum.

By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FT-IR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds.

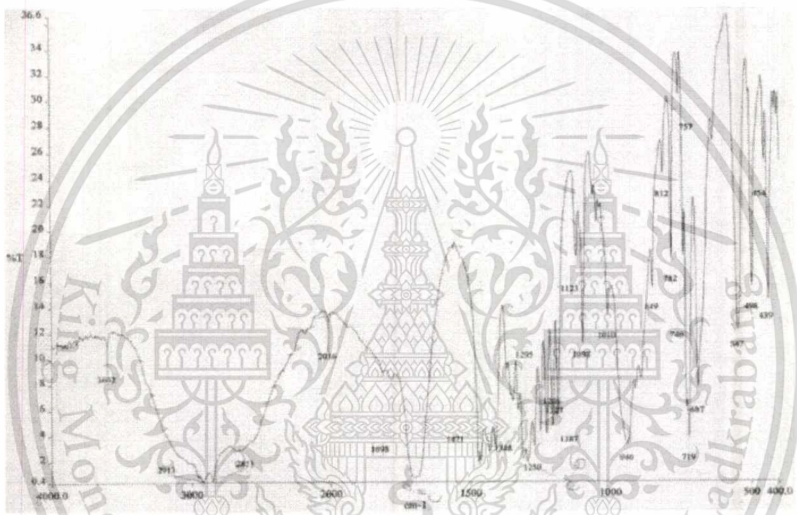


Figure 2.8 Spectrum of pure palmitic acids

-Quantitative Analysis

Because of the absorption strength is the proportional to the concentration; FT-IR can be used for some quantitative analyses. Usually these are rather simple types of tests in the concentration range of a few parts per million up to the percent level.

-Physical Principles

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E_0) and the first excited state (E_1)]. The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole that corresponds to the infrared portion of the electromagnetic spectrum. [15]

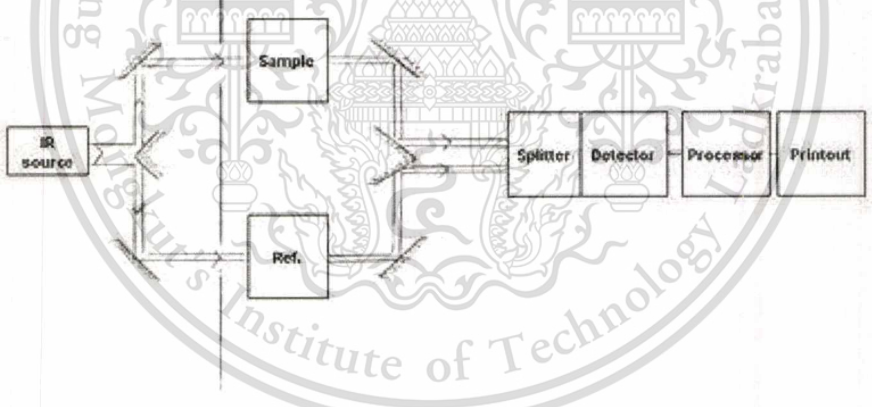


Figure 2.9 Conventional apparatus

2.4.2 Thermogravimetric analyses

Thermal Gravimetric Analysis (TGA) is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. [16]

-Characteristics or Properties Measured

Drying, structural water release, structural decomposition, carbonates decomposition, gas evolution, sulfur oxidation, fluoride oxidation, and re-hydration.

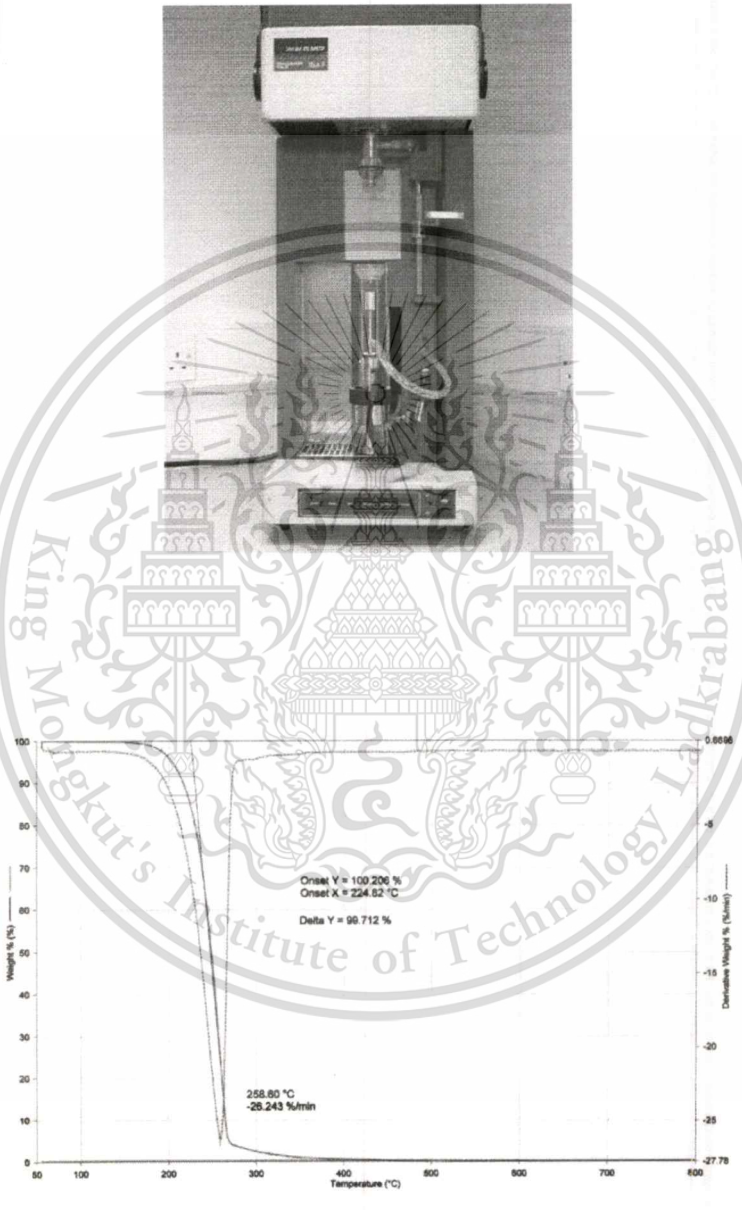


Figure 2.10 Upper: Machine of TGA and Lower: TG curve

-Principle of Operation

A sample material is placed into a high alumina pan that is supported on, or suspended from an analytical balance located outside the furnace chamber. The balance is zeroed, and the sample cup is heated according to a predetermined thermal cycle. The balance sends the weight signal to the computer for storage, along with the sample temperature and the elapsed time. The TGA curve plots the TGA signal, converted to percent weight change on the Y-axis against the reference material temperature on the X-axis.

2.4.3 X-ray diffraction techniques (XRD)

X-ray diffraction (XRD) finds the geometry or shape of a molecule using X-rays. X-ray diffraction techniques are based on the elastic scattering of X-rays from structures that have long-range order. The most comprehensive description of scattering from crystals is given by the dynamical theory of diffraction. [17]

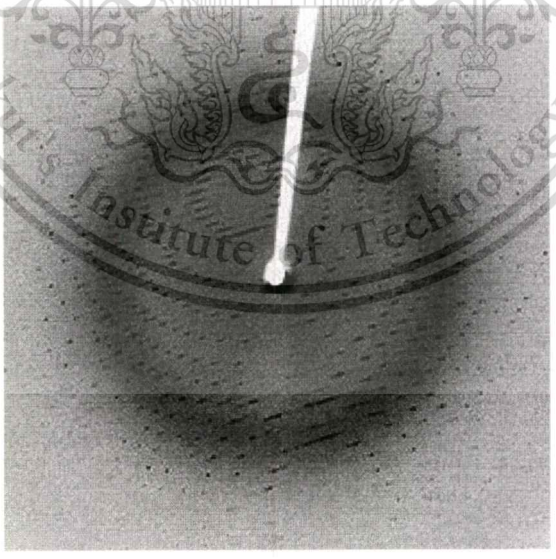


Figure 2.11 X-ray diffraction pattern formed when X-rays are focused on a crystalline material, in this case a protein. Each dot, called a reflection, forms from the coherent interference of scattered X-rays passing through the crystal.

Single-crystal X-ray diffraction is a technique used to solve the complete structure of crystalline materials, ranging from simple inorganic solids to complex macromolecules, such as proteins. Powder diffraction (XRD) is a technique used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. Powder diffraction is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data. It may also be used to characterize heterogeneous solid mixtures to determine relative abundance of crystalline compounds and, when coupled with lattice refinement techniques, such as Riveted refinement, can provide structural information on unknown materials. Powder diffraction is also a common method for determining strains in crystalline materials. An effect of the finite crystallite sizes is seen as a broadening of the peaks in an X-ray diffraction as is explained by the Scherer Equation.High-resolution X-ray diffraction is used to characterize thickness, crystallographic structure, and strain in thin epitaxial films. It employs parallel-beam optics.

2.4.4 Scanning electron microscope (SEM)

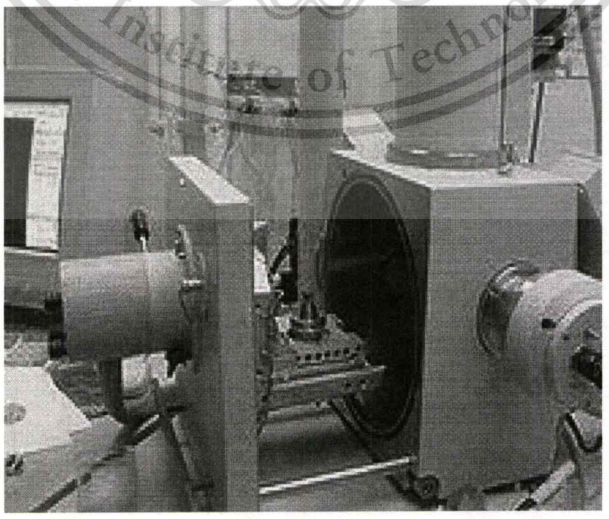


Figure 2.12 SEM opened sample chamber

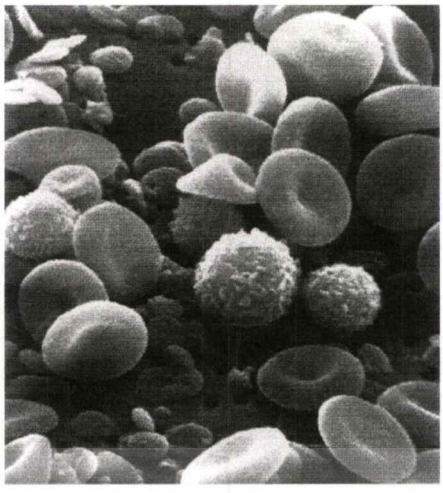


Figure 2.13 SEM image of normal circulating human blood.

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEM, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details in range of less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, from about 10 times to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal goldimmuno-labels of 5 or 10 nm diameter, which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

-Scanning process and image formation

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapor pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB6) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and field emission guns (FEG), which may be of the cold-cathode type using tungsten single crystal emitters or the thermally-assisted Schottky type, using emitters of zirconium oxide. The electron beam, which typically has an energy ranging from a few hundrede V to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the

interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronized with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor.

-Magnification

Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. Unlike optical and transmission electron microscopes, image magnification in the SEM is not a function of the power of the objective lens. SEM may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen. Provided the electron gun can generate a beam with sufficiently small diameter, a SEM could in principle work entirely without condenser or objective lenses, although it might not be very versatile or achieve very high resolution. In a SEM, as in scanning probe microscopy, magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x, y scanning coils, or the voltage supplied to the x, y deflector plates, and not by objective lens power.

-Sample preparation

All samples must also be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Several models of SEM can examine any part of a 6-inch (15 cm) semiconductor wafer, and some can tilt an object of that size to 45°. For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Nonconductive specimens tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. They are therefore usually coated with an ultrathin coating of electrically conducting material, commonly gold, deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. Conductive materials, which are used for specimen coating: such as gold, platinum and graphite. Coating prevents the accumulation of staticelectric charge on the specimen during electron irradiation. Two important reasons for coating, even when there is more than enough specimen conductivity to prevent charging, are to maximize signal and improve spatial resolution, especially with samples of low atomic number (Z). Broadly, signal increases with atomic number, especially for backscattered electron imaging. The improvement in resolution arises because in low-Z materials, that are materials with low atomic number such as carbon, the electron beam can penetrate several micrometers below the surface, generating signals from an interaction volume much larger than the beam diameter and reducing spatial resolution. Coating with a high-Z material such as gold maximizes secondary electron yield from within a surface layer a few nm thick, and suppresses secondary electrons generated at greater depths, so that the signal is predominantly derived from locations closer to the beam and closer to the specimen surface than would be the case in an uncoated, low-Z material. These effects are particularly, but not exclusively, relevant to biological samples.

-Resolution of the SEM

The resolution of the SEM depends on the size of the electron spot, which in turn depends on both the wavelength of the electrons and the electron-optical system which produces the scanning beam. The resolution is also limited by the size of the interaction volume, or the extent to which the material interacts with the electron beam. The spot size and the interaction volume are both large compared to the distances between atoms, so the resolution of the SEM is not high enough to image individual atoms. The SEM has compensating advantages, though, including the ability to image a comparatively large area of the specimen; the ability to image bulk materials (not just thin films or foils); and the variety of analytical modes available for measuring the composition and properties of the specimen. Depending on the instrument, the resolution can fall somewhere between less than 1 nm and 20 nm. By 2009, the world's highest SEM resolution at high beam energies (0.4 nm at 30 kV) is obtained with the Hitachi S-5500. At low beam energies, the best resolution (by 2009) is achieved by the Magellan system from FEI Company (0.9 nm at 1 kV). [18]

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 CHEMICALS

Table 3.1 Show the chemicals used in the reaction

	Chemicals	Grade of purity	Manufactures
3.1.1	Ammonium hydroxide	30%	CARIO ERBA
3.1.2	Cerium chloride	99%	ACROS
3.1.3	Cerium(IV) oxide	99.9%	ALDRICH
3.1.4	Distilled water	-	-
3.1.5	*n*-Hexane	95%	Fisher Scientific
3.1.6	Nitrogen gas	-	TIG
3.1.7	Palmitic Acid	>98%	Fluka
3.1.8	Zirconium(IV) oxide	99%	Fluka
3.1.9	Zirconyl chloride	>99%	Fluka

3.2 APPARATUS.

- Buchner flask
- Set of reactors
- Buchner funnel
- Catalytic testing rig
- Differential Scanning Calorimeter (Bruker AG, Scientific Instrument Service Centre, KMITL)
- Furnace (Vecstar Furnaces)

- Gas adsorption analyzer (Autosorb-1C, Quantrachrome)
- Gas chromatography (Buck scientific, model 910)
- Heating Tape
- Hotplate
- Laboratory glassware
- Magnetic stirrer
- Oven
- Thermogravimetric Analyzer (Pyris 1 TG, Perkin Elmer, Scientific Instruments Service Centre, KMITL)
- Vial
- Wash bottle
- X-ray Fluorescence Spectrometer (SRS 3400, Bruker AG, Scientific Instrument Service Centre, KMITL)
- X-ray Powder Diffractometer (D8 Advance, Bruker AG, Scientific Instrument Service Centre, KMITL)

3.3 EXPERIMENT PROCEDURE.

3.3.1 Preparation of catalysts.

- **Single oxide catalysts (CeO_2 and ZrO_2)**

The samples of ZrO_2 (>98%, FLUKA, Inc.) and CeO_2 (99.9%, ALDRICH, Inc.) were prepared by calcinations using air at 600°C, heating rate 1 °C/min for 3 hour in a tube furnace.

- **Mixed oxide catalyst ($CeZrO_2$)**

The $CeZrO_2$were synthesized by the co-precipitation method. An aqueous solution of cerium chloride and zirconyl chloride were prepared with 50 mol% $CeO_2$and 50 mol% ZrO_2($Ce_{0.50}Zr_{0.50}O_2$). Then, the CeZrOH were co-precipitated by the addition of an excess of ammonium hydroxide. Finally, the precipitate was washed with distilled water and then dried in oven at 110°C. After that, the sample would be calcined in the same manner as single oxide catalyst. The flowchart was shown below:

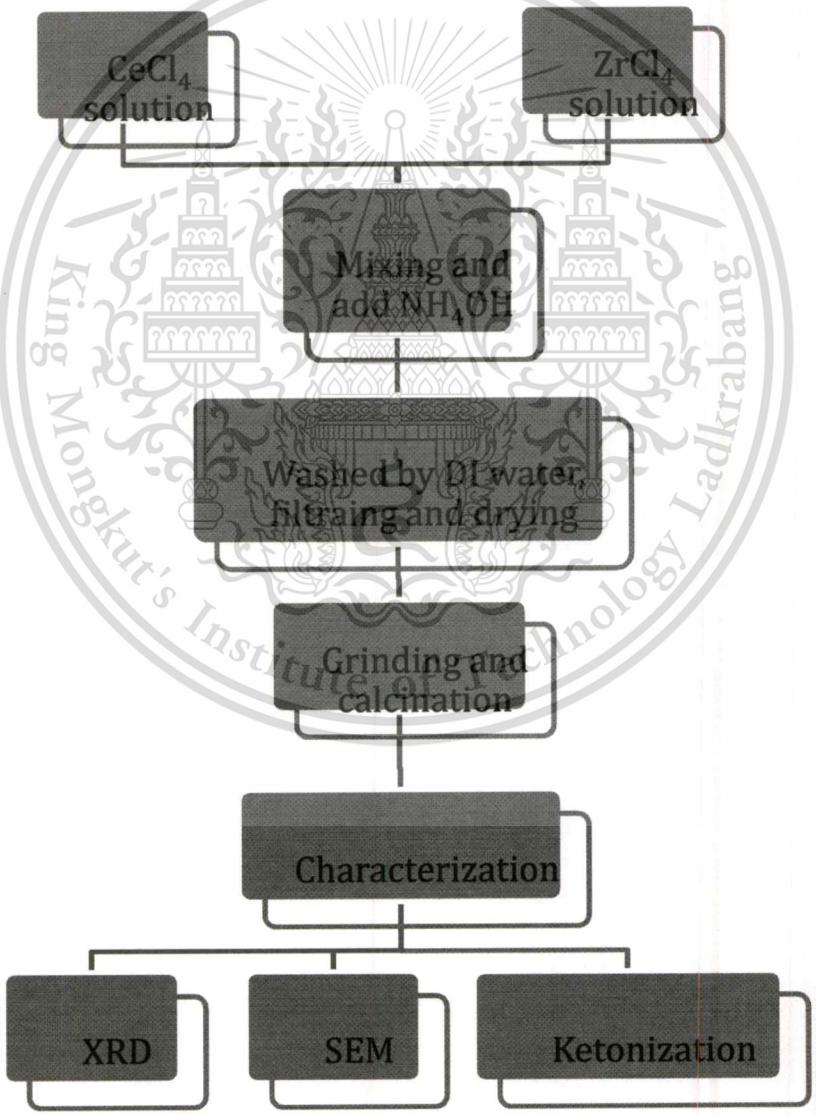


Figure 3.1 Show the stages of $CeZrO_2$ preparation

3.3.2 Characterization of catalysts

In order to consider the physical properties of catalysts, XRD (X-Ray power diffraction, D8 Advance, Bruker AG, Scientific Instrument Service Centre, KMITL) and SEM (Scanning Electron Microscope) were used.

- **X-ray diffraction Analysis**

The X-ray diffraction technique was performed to determine their crystallinity of single oxide catalysts and also structure of them by comparing with the standard. The sample was finely grinded to a permit packing of the sample into an XRD sample holder. The XRD pattern was obtained by scanning over the angle range from 2Θ = 5 to 60° with a step angle of 0.04 degree per step and detection time 1.0 seconds. The X-ray source was Cu-Kαgenerated at a voltage of 40 kV, 40 mA. Moreover, the catalyst with high intensity would have high crystallinity.

- **Scanning Electron Microscope**

The scanning electron microscope was required to observe the morphology and particle size of the catalyst which should relate to XRD pattern.

3.3.3 Ketonization

Table 3.2 Show the amount of palmitic and catalysts in each batch

Type of catalyst	Temperature	Mole ratio (catalyst : palmitic)	Weight of catalyst	Weight of palmitic
CeO_2	350°C	1:1	3.959	5.888
		2:1	7.918	
	400°C	1:1	3.959	
		2:1	7.918	
	450°C	1:1	3.959	
		2:1	7.918	
ZrO_2	350°C	1:1	2.839	
		2:1	5.678	
	400°C	1:1	2.839	
		2:1	5.678	
	450°C	1:1	2.839	
		2:1	5.678	
$CeZrO_2$	350°C	1:1	3.400	
		2:1	6.800	
	400°C	1:1	3.400	
		2:1	6.800	
	450°C	1:1	3.400	
		2:1	6.800	

- **Condition : heating rate 20°C/min, residence time 3 hours and nitrogen gas flow**

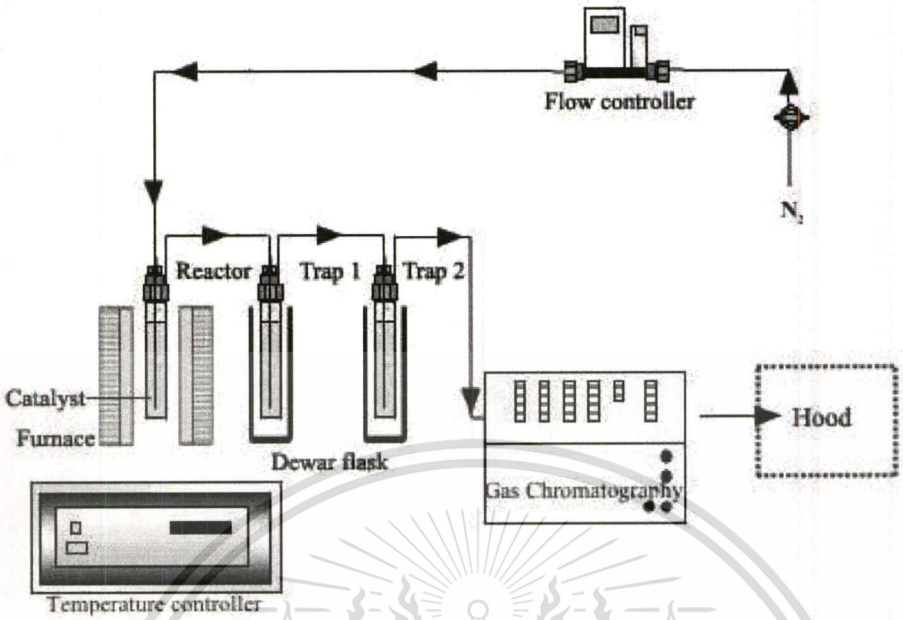


Figure 3.2 Semi-Batch Reactor

Ketonization was performed by using the condition from Table 3.2 in the semi-batch reactor which is shown in Figure 3.2. The sample was contained in the reactor that could be prepared by mixing pure plamitic acid and catalyst. Nitrogen gas (TIG, Inc) was used as the carrier. Then, the leakages at every connected position were checked. Next, the reactor was heat up to the temperature (350°C, 400°C or 450°C) with a heating rate of 20°C/min for 3 hours. Flow rate of nitrogen gas was controlled by mass flow controller. The gas entered to the top of reactor and exited from the side of the reactor then, the pipeline that joined between the reactor and trap1 must be covered with heating tape to prevent plugging.

While the co-products went out of the reactor with nitrogen gas, they were trapped in trap 1 and 2. Then, the lighter gas mixture flowed to hood. After the reaction was completed, hexane extraction was used in the process which hexane was used as a solvent. From this stage the residues and extracted solids were collected. The residues were dried in the oven overnight and the hexane in the extracted solid was removed by the rotary evaporator and vacuum oven for 24

hour. Finally, characterization of both residues and extracted solids were needed. The flowchart of the experimental process was shown below:

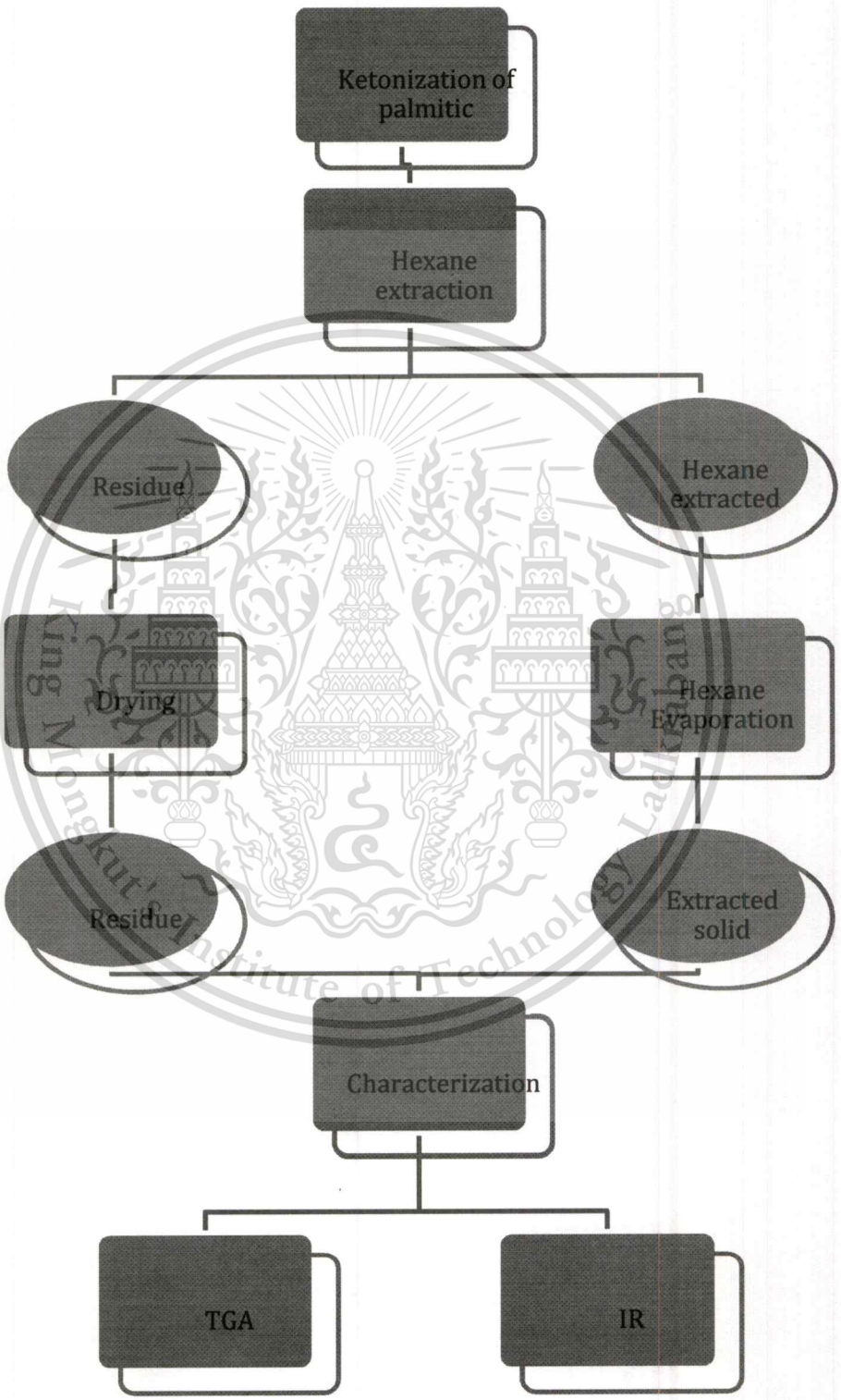


Figure 3.3 Flowchart of the experimental process

3.1.10 Characterization of residues and extracted solids

- **Fourier Transform Infrared Spectroscopy (FT-IR)**

Residues and extracted solids from the reactor would be checked by Fourier Transform Infrared Spectroscopy (FT-IR) to confirm that the ketonization occurred. Spectrums of the samples were recorded in the range of 4000–400 cm^{-1} with an Infrared spectrophotometer, KBr being employed to obtain the background spectrum.

- **Thermogravimetric analysis**

Thermogravimetric analysis (TGA) is a technique which examines the mass change of a sample as a function of temperature. TGA is used to characterize the composition of products and the amount of each product. This technique can be used because every organic compound always has only one value of decomposition temperature.

After residues and extracted solids were performed with the TGA, the TG curves of them show many components in each sample. Thus, the decomposition temperature of pure palmitic acid (un-reacted reactant) must be performed to use as a reference. The other peaks which appear in the TG curve would be characterized as products. The process was done by nitrogen gas flow at the range of temperature 50 $^{\circ}C$ to 800 $^{\circ}C$ and a heating rate of 10 $^{\circ}C$ /min. The reason that the nitrogen gas must be used instead of oxygen gas was to prevent the oxidizing reaction.

As the above mentioned, TG curve could be used to calculate the amount of ketone wax and un-reacted reactant. Thus, the calculation could be divided into two parts which were:

1. **Calculation from TG curve of extracted solids.**

In a TG curve of extracted solid was contained the peak of un-reacted reactant and ketone wax hence the amount of them would be evaluated.

- **For un-reacted reactant (palmitic left)**

% of palmitic left was shown in TG curve at the temperature range about 250°C – 260°C multiplied with the weight of extracted solid and then, divided by 100. So, the amount of palmitic left in extracted solid could be evaluated. The formula was shown as:

$$\text{Weight of palmitic left} = \frac{\%\ of\ palmitic\ left}{100} \times \text{Weight of extracted solid}$$

Note: weight of palmitic left in extracted solid is W_7 in Appendix A.

-. **For ketone wax**

Total % of the other peaks in TG curve at the other temperature out of range 250°C – 260°C were assumed as ketone wax, multiplied with the weight of extracted solid then, divided by 100. So, the amount of ketone wax in extracted solid could be evaluated. The formula was shown as:

$$\text{Weight of ketone wax} = \frac{\%\ of\ ketone\ wax}{100} \times \text{Weight of extracted solid}$$

Note: weight of ketone wax in extracted solid is W_6 in Appendix A.

2. **Calculation from TG curve of residues.**

The reason why we must to characterize the residues was the catalyst's weight changed. Thus, it could be concluded that some of ketone wax and un-reacted reactant left in catalyst after the hexane extraction.

- **For un-reacted reactant (palmitic left)**

The calculation was the same manner as calculation of the palmitic left's weight in extracted solid (W_7) but should be multiplied with weight of residue instead weight of extracted solid. The formula was shown as:

$$\text{Weight of palmitic left} = \frac{\%\ of\ palmitic\ left}{100} \times \text{Weight of residue}$$

Note: weight of palmitic left in residue is W_4 in Appendix A.

- **For ketone wax**

The calculation was the same manner as calculation of the ketone wax's weight in extracted solid (W_6) but should be multiplied with weight of residue instead weight of extracted solid. The formula is shown as:

$$\text{Weight of ketone wax} = \frac{\%\ of\ ketone\ wax}{100} \times Weight\ of\ residue$$

Note: weight of ketone wax in residue is W_3 in Appendix A.

After that, the weight of the same component in both extracted solid and residue would be combined together before verifying. Finally, the calculation of conversion and yield must be evaluated to compare the efficiency factors which are temperature, amount of catalysts and type of catalysts.

1. **Conversion**

The definition of this term is the amount of converted reactant to anything such as gas, liquid, wax and etc. by the ketonization. The conversion was calculated in term of percentage by following formula.

$$\% \text{ Conversion} = \frac{Initial\ weight\ of\ palmitic - Total\ weight\ of\ palmitic\ left}{Initial\ weight\ of\ palmitic} \times 100$$

Note:T*otal weight of palmitic left = W.of palmitic left in extracted solid + W.of palmitic left in dried catalyst*

2. **Yield**

The definition of yield is the amount of desirable products (ketone wax) which were created by the ketonization. Unfortunately, the molecular weight of ketone wax does not exist. So, the carbon balance was used instead of the basic calculation which calculated only the molecule that contained carbon atom.

From the above chemical reaction found that palmitic, ketone wax and carbon dioxide are the molecules that contained carbon atom hence they were used in calculation. First stage, the conversion factor which is constant value must be evaluated to determine the ratio of produced ketone wax to amount of the reactant. The formula of conversion factor is:

$$\text{Conversion factor} = \frac{M.W.of\ 2\ moles\ palmitic - M.W.of\ carbon\ dioxide}{M.W.of\ 2\ moles\ palmitic}$$

Note: M.W. is molecular weight

Second stage, weight of ketone wax from theory which was going to use in the calculation of %yield would be calculated by:

$$Weight\ of\ ketone\ wax\ from\ theory = Conversion\ factor\ x\ Initial\ weight\ of\ palmitic$$

After that the calculation of % yield would be performed by the following formula:

$$\%\ \text{yield} = \frac{Weight\ of\ ketone\ wax\ from\ experiment}{Weight\ of\ ketone\ wax\ from\ theory} \times 100$$

Note:$W.ketone\ wax\ from\ experiment = W.of\ ketone\ wax\ in\ extracted\ solid + W.of\ ketone\ wax\ in\ dried\ catalyst$

Conversion and yield were plotted to compare the efficiency factors which are temperature, amount of catalyst and type of catalyst.

\

CHAPTER 4

RESULTS AND DISCUSSION

The objective of this project was to produce ketone wax from palmitic acid via ketonization. The performance of ketonization depended on three factors which are the temperature of reaction (350°C, 400°C and 450°C), amount of catalyst (2 mole of catalyst: 1 mole of palmitic and 1 mole of catalyst: 1 mole of palmitic) and the metal oxide catalysts (ZrO_2, CeO_2 and $CeZrO_2$).

4.1 Characterization of catalysts

- X-ray Diffraction

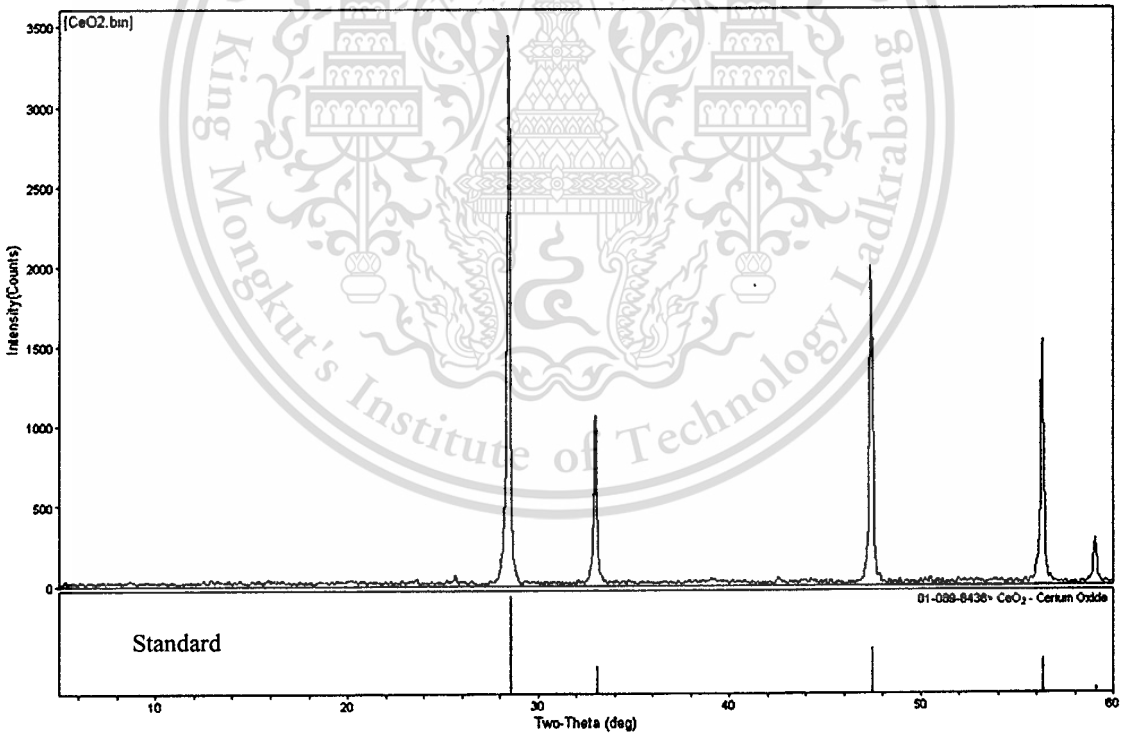


Figure 4.1 XRD pattern of CeO_2

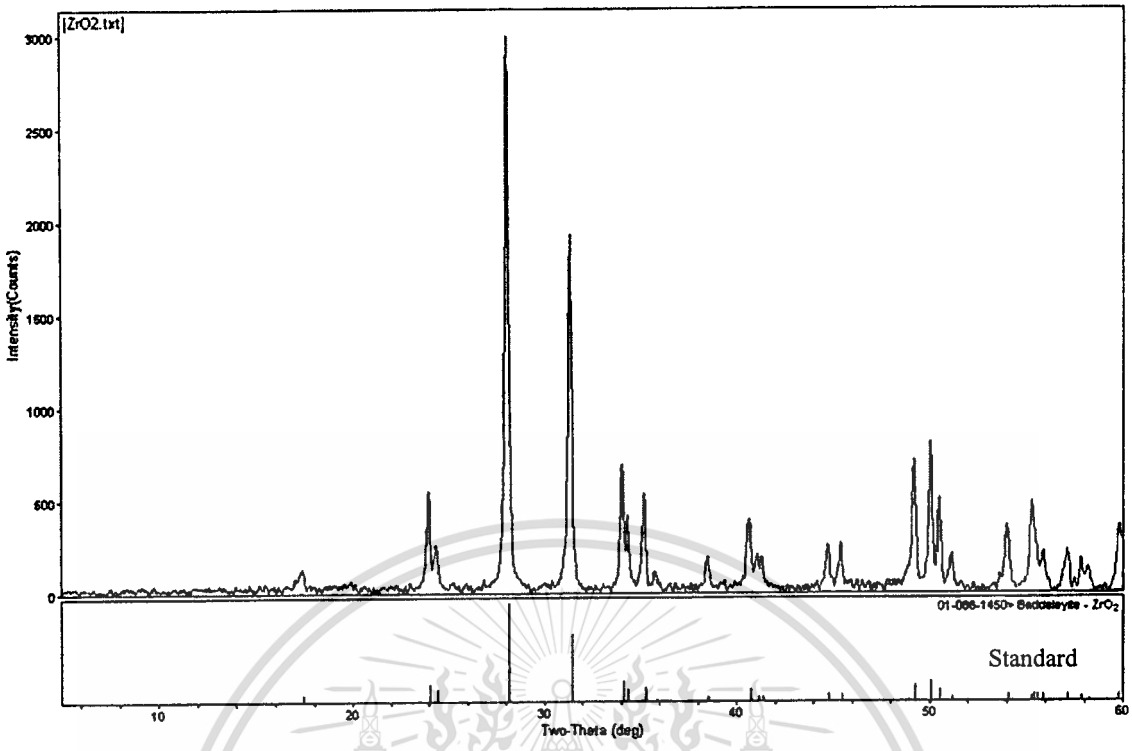


Figure 4.2 XRD pattern of ZrO_2

For single oxide catalysts (ZrO_2 and CeO_2), they were compared with the standards to confirm them and also see their intensity to determine their crystallinity. From the Figure 4.1 and 4.2, the catalysts in the experiment were the same as the standard and the related literature (CeO_2 [18], ZrO_2 [6]).

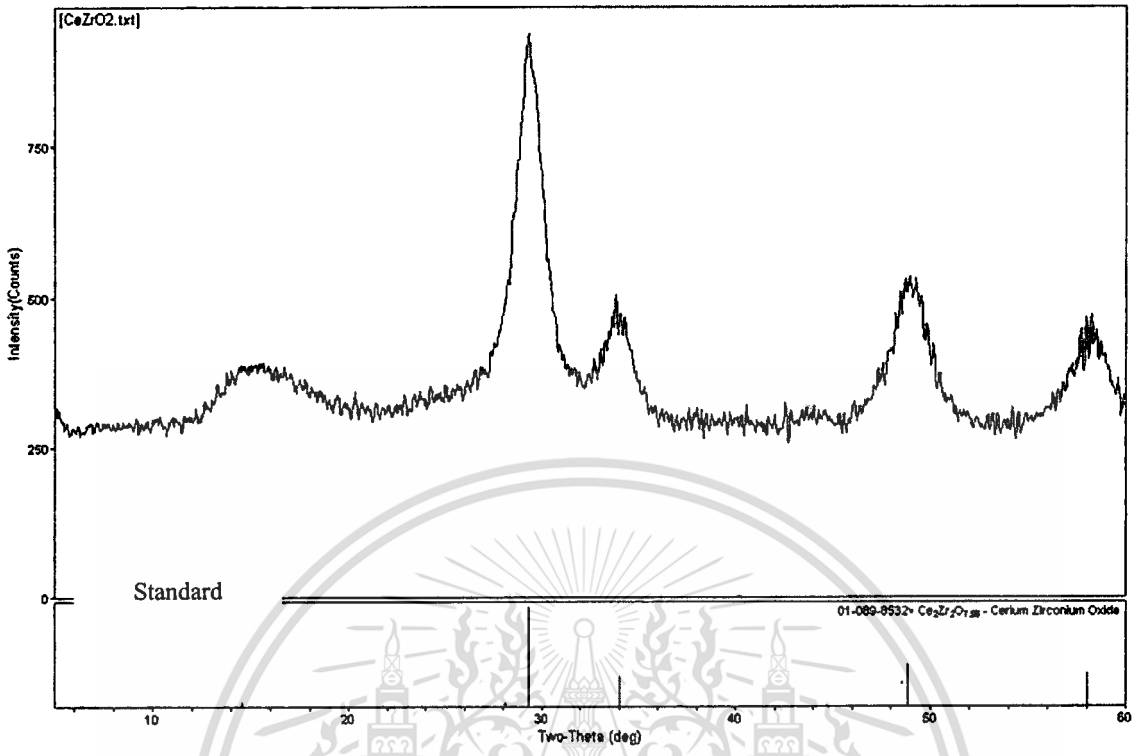
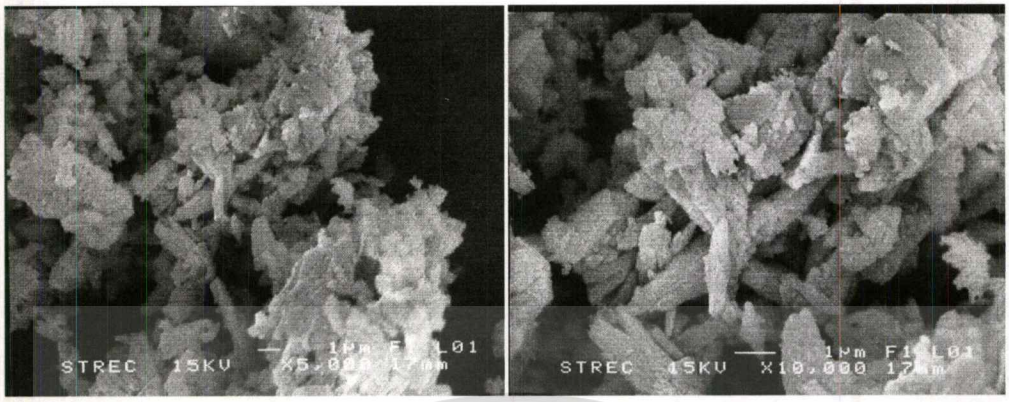


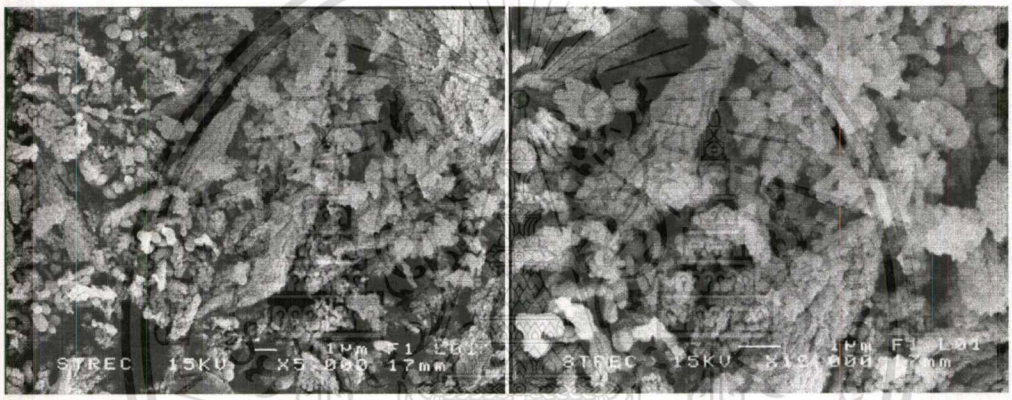
Figure 4.3 XRD pattern of $CeZrO_2$

In case of mixed oxide catalyst which is $CeZrO_2$ in Figure 4.3, the comparison between XRD pattern of $CeZrO_2$ and CeO_2 found that, they have the same peaks' position. But the pattern of $CeZrO_2$ has the broader peak and lower intensity due to the additional of zirconium particle to the structure of CeO_2. This could be confirmed by the other literature [9]. Moreover, the related literature [9] reported the additional of zirconium particles could increase the oxygen vacancies which are the active site for ketonization.

- Scanning Electron Microscope Test Results



(a1) CeO_2 at Magnification= 5,000x (a2) CeO_2 at Magnification=10,000x



(b1) ZrO_2 at Magnification= 5,000x (b2) ZrO_2 at Magnification=10,000x

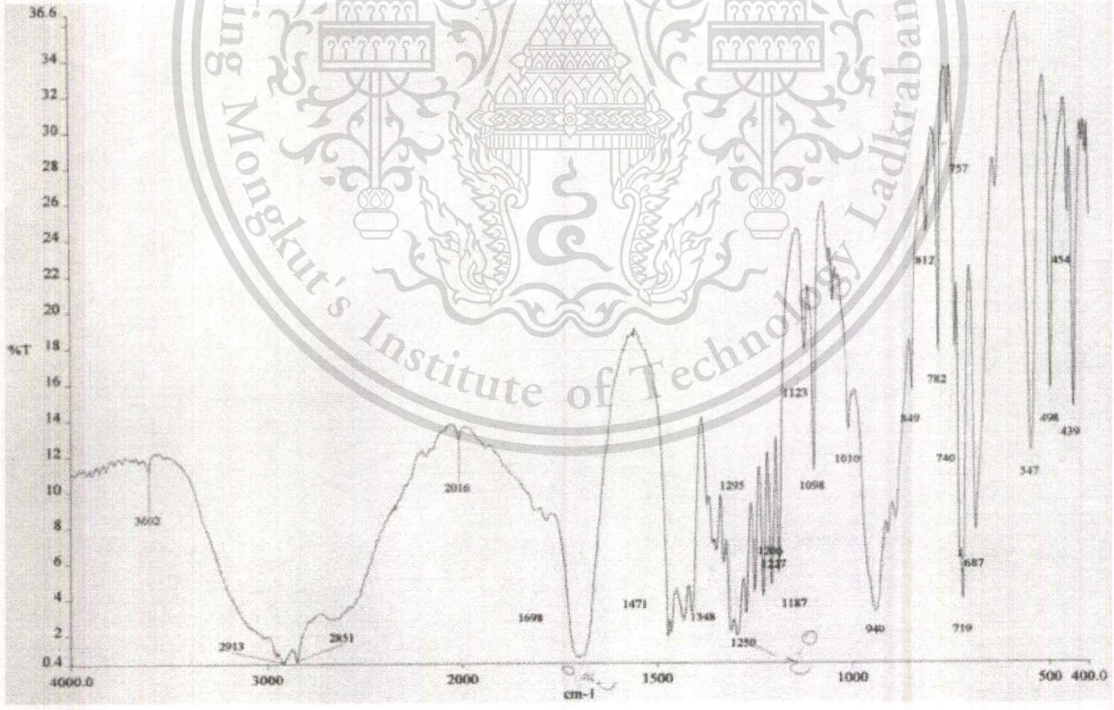
(c1) $CeZrO_2$ at Magnification= 5,000x (c2) $CeZrO_2$ at Magnification=10,000x

Figure 4.4 SEM image of (a1) CeO_2 at Magnification= 5,000x, (a2) CeO_2 at Magnification=10,000x, (b1) ZrO_2 at Magnification= 5,000x, (b2) ZrO_2 at Magnification=10,000x, (c1) $CeZrO_2$ at Magnification= 5,000x and (c2) $CeZrO_2$ at Magnification=10,000x

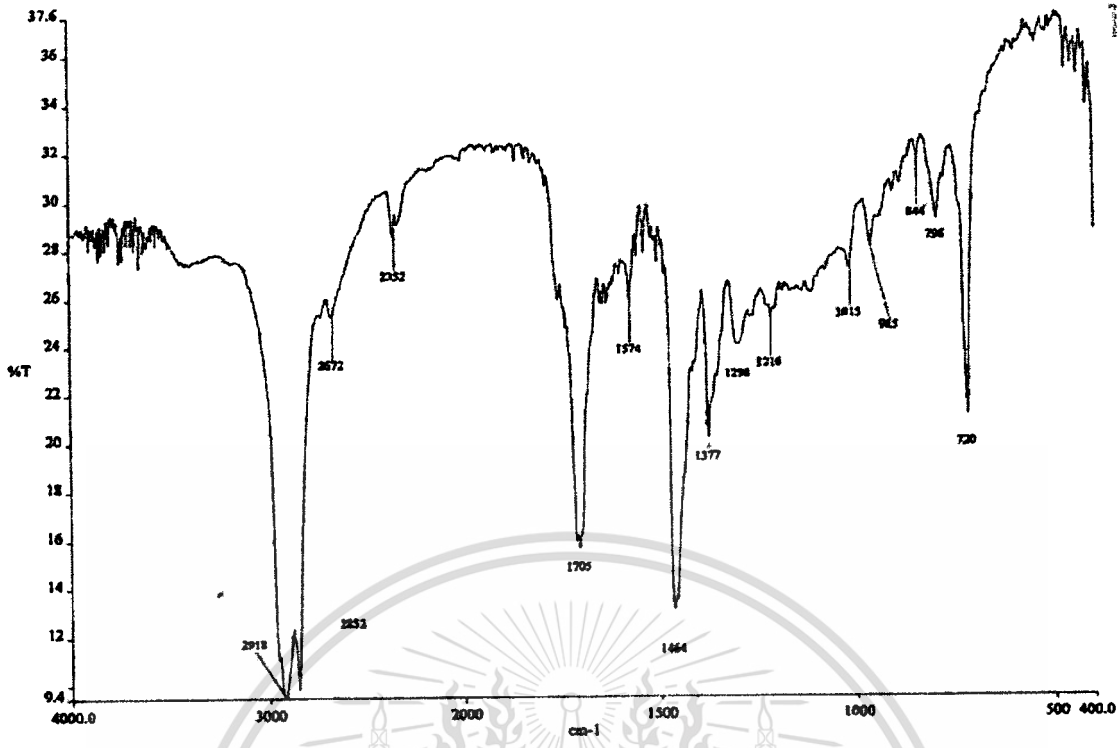
From Figure 4.4, The SEM image of $CeZrO_2$ is totally different from the other two catalysts in term of particle size. The order of particle size is $CeZrO_2 > CeO_2 > ZrO_2$ and the related literature [9] reported that the large particle size (low surface area) is suitable for ketonization.

4.2 Product characterization

Both extracted solids and residues in the mixture from the reactor could be separated by hexane extraction which used hexane as a solvent. Then, the confirmation was needed to confirm that the reactions were the same as our hypothesis. Fourier Transform Infrared Spectroscopy (FT-IR) is a common technique used to identify the functional group. Hence, the spectrum of pure palmitic acid must be performed to used as a reference in comparison with the spectrum of extracted solids which show that the ketonization occured in the reaction system.



(a) Spectrum of pure palmitic acid



(b) Spectrum of extracted solid of 1:1 at 400° C, $CeZrO_2$

Figure 4.5 Spectrum data (a) Spectrum of pure palmitic acid (b) Spectrum of extracted solid of 1:1 at 400° C by use $CeZrO_2$ as a catalyst.

The spectrum of pure palmitic acid and extracted solid were compared. Figure 4.5(a) indicated the spectrum of pure palmitic acid that is an aliphatic carboxylic acid. The distinct peak are peak in the range of 3500-2500 cm^{-1} for O-H stretching of –COOH, peak in the range of 2980-2880 cm^{-1} for C-H stretching of $–CH_3$, $-CH_2-$, the peak at 1710 cm^{-1} for C=O stretching of RCOOH, and peak in the range of 1220-1250 cm^{-1} for C-O stretching of –COOH. Figure 4.5(b) indicated the spectrum of extracted solid that it has some distinct peaks such as the peak at 1710 cm^{-1} for C=O stretching of R_2CO, the peak at 1470 cm^{-1} for C-H bending of $–CH_3$, $-CH_2-$, and peak in the range of 2925-2870 cm^{-1} for C-H stretching of $–CH_3$, $-CH_2-$. They were noticed that no carboxylic acid in extracted solid and the peak of ketone of extracted solid was stronger than pure palmitic acid. So, it could be concluded that after the ketonization occurred, the COOH was reduced.

Secondly, the TG curve was used to calculate the weight of ketone wax and un-reacted reactant. Then the weight of them would be calculated for conversion and the yield by the equation in chapter3.

- **Conversion**

The percentage conversions of each catalyst at the different temperatures and different amount of catalysts are shown in the graph below.

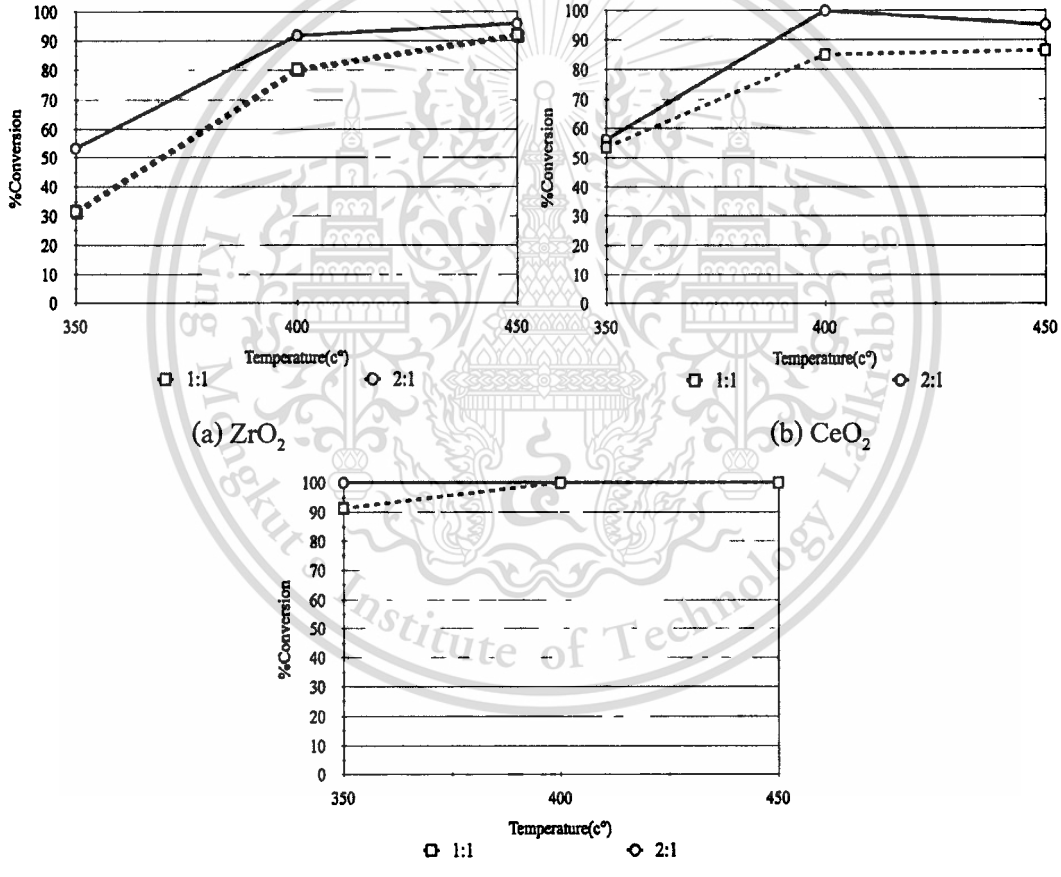


Figure 4.6 Show the effect of temperature and mole ratio (Catalyst: Palmitic) of all catalysts: (a) ZrO_2 (b) CeO_2 (c) $CeZrO_2$

From the Figure 4.6, the main factors which induced to the higher conversion for single oxide catalyst were the temperature and the amount of catalyst while the mixed oxide catalyst did not show much different because its conversion was mostly 100%.

In case of single oxide catalyst, the higher the temperature, the higher the reaction rate. This is because higher temperature gives higher the energy and if this energy is higher than the activation energy (E_A) the molecules will collide together, then the more reactant would be converted.

In addition, the more amount of catalyst (more contact time) would be increased the conversion because there was more active site for the reaction. However, the high percentage conversion was not the most important because we concerned about ketone wax production hence the plot of yield versus time was needed to support the conclusion.

- **Yield**

The effect of temperature and amount of catalyst which shown in Figure 4.7 are not the same as Figure 4.6. The dropped yield at the higher temperature was the result from the cracking of the sample because the cracking is the endothermic reaction which needs high temperature to provide it. The higher temperature would crack the reactants and products to small hydrocarbon which called secondary reaction or thermal cracking.

In term of the amount of catalysts, the result was similar to the temperature's effect which was too much catalysts would reduced the yield of products due to the increasing of the active site with the amount of catalysts. So, either reactants or products inside the reactor had more chance to react on the catalyst's active site and produce undesirable products. This type of secondary reaction was known as catalytic cracking.

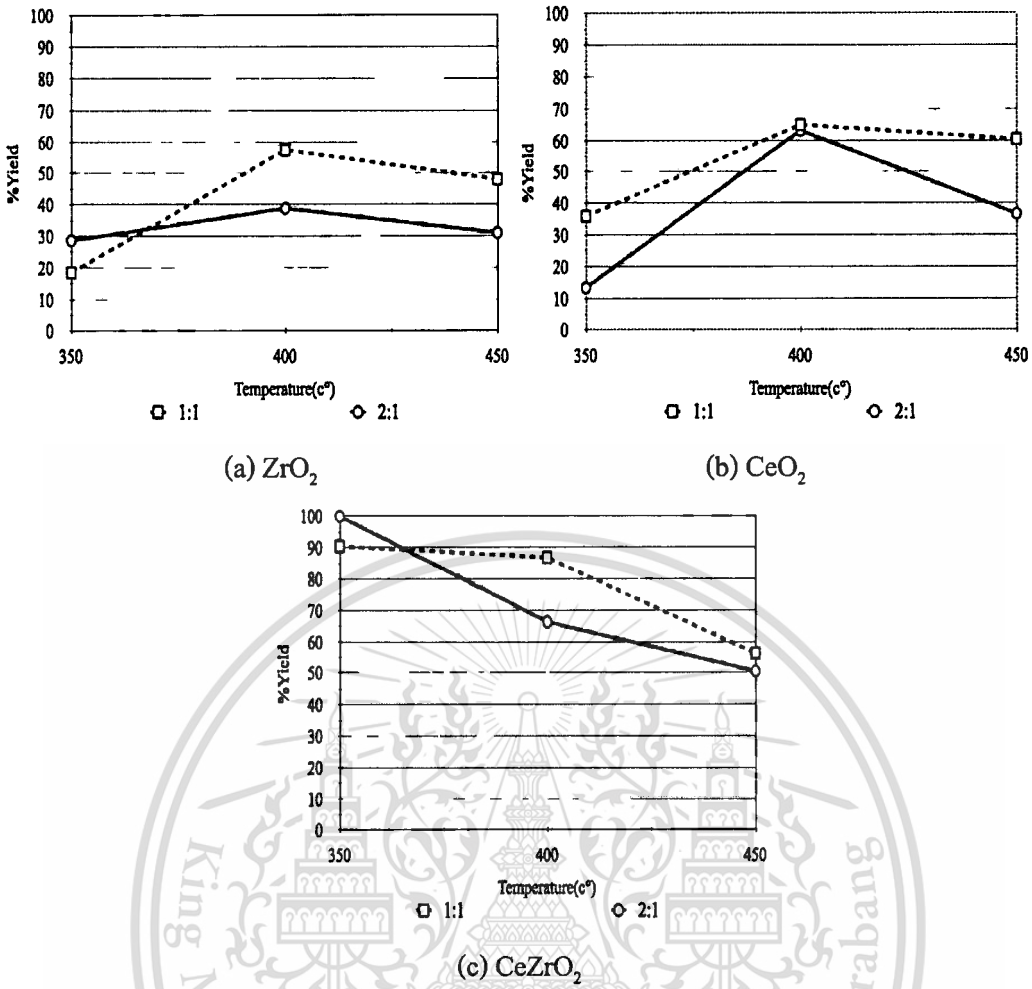


Figure 4.7 Show the % yield of extracted solid from different catalyst.

(a) ZrO_2 (b) CeO_2 (c) $CeZrO_2$

From the Figure 4.7, the most effective factor to the ketonization was the type of catalyst which was the $CeZrO_2$ because it has large particle size and high oxygen vacancies which suitable for ketonization. But, the yield's results of $CeZrO_2$ and ZrO_2 at 350°C do not relate to the theory which the more amount of catalysts would be increased contact time which produces more secondary reaction (catalytic cracking) and lower the yield. This is because of the larger particle size of them could prevent the catalytic cracking. Anyway the increasing of temperature would indicate to the other type of secondary reaction which is thermal cracking.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This project produced ketone wax from renewable fatty acid via ketonization reaction. Three different catalysts are ZrO_2, CeO_2 and $CeZrO_2$ and three different temperatures are 350°C, 400°C and 450°C were varied. The experiment was done by packing the palmitic acid and each type of catalysts with the ratio of 1:1 and 2:1 (catalyst: palmitic acid) in the close system reactor and then heat up to each temperature for 3 hours. So, the reaction was effected by temperature, type of catalysts, and amount of catalysts.

The effect of temperature was shown that the conversion increase due to an increasing in temperature because the higher the temperature, the higher the energy given to the reaction. For the yield which used to determine the desirable product would effected from temperature also. Unfortunately, the yield of product is not as high as the conversion because some secondary reaction such as thermal cracking could be occurred by the higher temperature.

Next, the effect of type of catalysts, the amount of oxygen vacancies has been concerned because higher amount of oxygen vacancies mean higher active sites on the surface of catalyst for ketonization. The outstanding of ZrO_2 is Lewis acid. CeO_2 that can provides oxygen vacancies by itself however it could be provided only at high temperature but $CeZrO_2$ has higher oxygen vacancies than CeO_2 due to the addition of Zirconium to the CeO_2 structure could increase the sites of oxygen vacancies. Hence, $CeZrO_2$ give high conversion and yield. The order of amount of oxygen vacancies would be:

$$CeZrO_2 > CeO_2 > ZrO_2$$

Finally, the effect of amount of catalyst was shown that the higher the amount of catalysts, the higher the active sites to react with reactants. From comparison of % conversion and % yield of three different catalysts found that the result of an increase in amount of catalysts was an increase in the % conversion for all three catalysts but for the yield is not because secondary reaction such as catalytic and thermal cracking would be taken place. Thus, the amount of catalysts would be not the main effect to % yield

Therefore, the conclusion could be the main factors of the ketonization to produce the best yield and conversion are the type of catalysts and the temperature. The best condition of this special project is the reaction with $CeZrO_2$ that has high oxygen vacancies at low temperature as 350 °C, it could be potential condition for ketone wax production from the renewable sources.

5.2 Recommendation

1. Find the way to separate the type of products.
2. From the conclusion, $CeZrO_2$ is the best catalyst hence, the different ratio of Cerium and Zirconium should be varied.

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Appendix A

Calculation

Example 1: Calculation of ketone wax from TG curve

- Ketone wax in extracted solid from TG curve
- Ketone wax in residue from TG curve

Example 2: Calculation of palmitic left from TG curve

- Palmitic left in extracted solid from TG curve
- Palmitic left in residue from TG curve

Example 3: Calculation of amount of gas from the reaction

Example 4: Calculation of % conversion

Example 5: Calculation of % yield by carbon balance

- Calculation of % yield of ketone wax
- Calculation of % yield of liquid
- Calculation of % yield of gas

Example 6: Calculation of % selectivity

Example 1: Calculation of ketone wax from TG curve

- **Ketone wax in extracted solid from TG curve**

Example ZrO_2 1:1 350°C

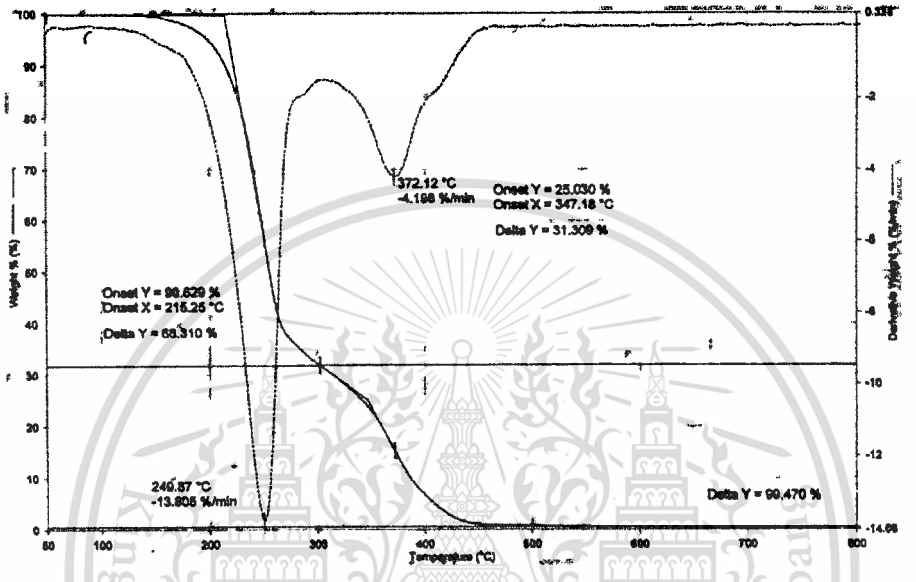


Figure A.1 TG curve of extracted solid of ZrO_2 1:1 at 350°C

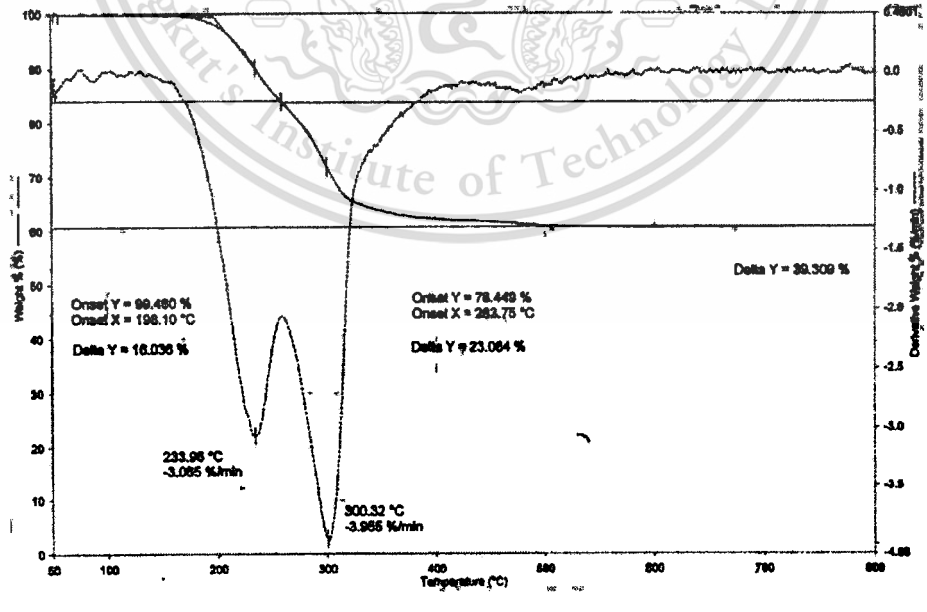


Figure A.2 TG curve of residue of ZrO_2 1:1 at 350°C

Data

W' (Beginning weight of palmitic)	5.888 g
W_0 (Beginning weight of catalyst)	2.839 g
W_1 (Weight of extracted solid)	2.992 g
W_2 (Weight of residue)	4.315 g
$\%T_w$ (% TGA of ketone wax in extracted solid)	31.309 %
$\%R_w$ (% TGA of ketone wax in residue)	23.064 %

So, weight of ketone wax in extracted solid from TG curve (W_6)$= \frac{\%Tw \; x \; W1}{100}$

$= \frac{31.309\% \; x \; 2.992}{100}$

$W_6 = 0.937$ g

- **Ketone wax in residue from TG curve**

So, weight of ketone wax in residue from TG curve (W_3) $= \frac{\%R\,w \; x \; W2}{100}$

$= \frac{23.064 \; x \; 4.315}{100}$

$W_3 = 0.995$ g

Example 2: Calculation of palmitic left from TG curve

- **Palmitic left in extracted solid from TG curve**

Example ZrO_2 1:1 350°C

Data

W' (Beginning weight of palmitic)	5.888 g
W_o (Beginning weight of catalyst)	2.839 g
W_1 (Weight of extracted solid)	2.992 g
W_2 (Weight of residue)	4.315 g
$\%T_P$ (% TGA of palmitic left in extracted solid)	68.310 %
$\%R_P$ (% TGA of palmitic left in residue)	16.036 %

So, weight of palmitic left in extracted solid from TG curve(W_7) $= \frac{\%Tp \; x \; W1}{100}$

$= \frac{68.310\,\% \; x \; 2.992}{100}$

$W_7 = 2.044$ g

- **Palmitic left in residue from TG curve**

So, weight of palmitic left in residue from TG curve (W_4) $= \frac{\%Rp \; x \; W2}{100}$

$= \frac{16.036\,\% \; x \; 4.315}{100}$

$W_4 = 0.692$ g

Example 3: Calculation of amount of gas from the reaction

Example ZrO_2 1:1 350°C

Data

Weight of trap 1	0.169 g
Weight of trap 2	0.045 g
Weight of ketone wax in residue from TG curve (W_3)	0.995 g
Weight of palmitic left in residue from TG curve (W_4)	0.692 g
Weight of ketone wax in extracted solid from TG curve (W_6)	0.937 g
Weight of palmitic left in extracted solid from TG curve (W_7)	2.044 g

From $W' = W_3 + W_4 + W_6 + W_7 +$ weight of liquid +amount of gas

$5.888 = 0.995 + 0.692 + 0.937 + 2.044 + 0.2132 +$ amount of gas

$5.888 = 4.881 +$ amount of gas

So, amount of gas = 1.007 g

Example 4: Calculation of % conversion

Example ZrO_2 1:1 350°C

Data

W' (Beginning weight of palmitic)	5.888 g
Weight of palmitic left in residue from TG curve (W_4)	0.692 g
Weight of palmitic left in extracted solid from TG curve (W_7)	2.044 g

$$\% \text{ conversion} = \frac{[W' - (W7 + W4)]}{W'} \times 100$$

$$= \frac{[5.888 - (2.044 + 0.692)]}{5.888} \times 100$$

$$= 53.533\ \%$$

So, % conversion = 53.533 %

Example 5: % yield by carbon balance

- **% yield of ketone wax**

Example ZrO_2 1:1 350°C

Data

Conversion factor $= \frac{512 - 44}{512} \times 100$

$= 91.41\ \%$

Weight of ketone wax from theory $= \frac{91.41\% \times 5.888}{100}$

$= 5.382\ g$

Weight of ketone wax from experiment $0.937 + 0.995 = 1.932\ g$

$$\% \text{ yield} = \frac{Weight\ of\ ketone\ wax\ from\ experiment}{Weight\ of\ ketone\ wax\ from\ theory} \times 100$$

$= \frac{1.932}{5.382} \times 100$

$= 35.897\ \%$

So, % yield of ketone wax $= 35.897\ \%$

- **% yield of liquid**

Data

Weight of trap 1 0.169 g

Weight of trap 2 0.045 g

Weight of ketone wax from theory $= \frac{91.41\% \times 5.888}{100}$

$= 5.382\ g$

$$\% \text{ yield of liquid} = \frac{0.169 + 0.045}{5.382} \times 100$$

$$= \frac{0.214}{5.382} \times 100$$

So, % yield of liquid = 3.976 %

- **% yield of gas**

Data

Amount of gas = 1.007 g

$$\text{Weight of ketone wax from theory} = \frac{91.41\% \, x \, 5.888}{100}$$

= 5.382 g

$$\% \text{ yield of gas} = \frac{Amount\ of\ gas}{Weight\ of\ ketone\ wax\ from\ theory} \times 100$$

$$= \frac{1.007}{5.382} \times 100$$

So, % yield of gas = 18.711 %

Example 6: Calculation of % selectivity

Example ZrO_2 1:1 350°C

Data

% conversion	53.533 %
% yield of ketone wax	35.897 %

$$\% \text{ selectivity} = \frac{\% \textit{ yield of ketone wax}}{\% \textit{ conversion}} \times 100$$

$$= \frac{35.897\ \%}{53.533\ \%} \times 100$$

$$= 67.056\ \%$$

So, % selectivity = 67.056 %

Appendix B

Result

Table B.1 show the amount of liquid and gas at every temperature of all catalysts

- For ZrO_2

Temperature	1:1			2:1		
	Amount of liquid		Amount of gas	Amount of liquid		Amount of gas
	Trap 1	Trap 2		Trap 1	Trap 2	
350°C.	0.169	0.045	1.007	0.160	0.011	2.423
400°C	0.585	0.067	0.124	0.482	0.475	1.533
450°C	0.735	0.078	1.028	0.665	0.068	2.901

- For CeO_2

Temperature	1:1			2:1		
	Amount of liquid		Amount of gas	Amount of liquid		Amount of gas
	Trap 1	Trap 2		Trap 1	Trap 2	
350°C.	0.212	0.027	0.636	0.167	0.031	1.402
400°C	0.471	0.106	1.075	0.584	0.083	2.659
450°C	0.970	0.175	1.701	0.481	0.004	2.485

- For $CeZrO_2$

Temperature	1:1			2:1		
	Amount of liquid		Amount of gas	Amount of liquid		Amount of gas
	Trap 1	Trap 2		Trap 1	Trap 2	
350°C.	0.339	0.004	0.173	0.218	0.002	0.292
400°C	0.588	0.008	0.621	0.261	0.001	2.059
450°C	2.461	0.007	0.400	2.672	0.009	0.490

Appendix C

Experimental Equipment

C-1 Direction of reaction process

1. Put the added chemical reactor and traps to the sites.
2. Connect the $N_{2(g)}$ line to the top of the reactor.
3. Connect the reactor from its side to the top of trap 1 with metal tube.
4. Wrapped the metal tube by heating tape and then turn it on the number 2.
5. Connect the trap 1 from its side to the top of trap 2 with rubber tube, and then connect to the waste gas line.
6. Put Dewar with cold water at trap 1 (Let the trap immerse in the water).
7. Put Dewar which is fulfill with $N_{2(l)}$ at trap 2 (Do not immerse the trap in $N_{2(l)}$) .
8. Open the tank of $N_{2(g)}$ and apply pressure.
9. Slowly turn on the valve of $N_{2(g)}$ at the rig, the gas will pass through the mass flow to measure the amount of them before get into the reactor.
10. Set up the furnace for the reaction conditions which are temperature (350°C, 400°C or 450°C) and heating rate (20°C/minute).
11. Waiting for 3 hours after the temperature reach to the setting and then cool down the system to the condition which are temperature (80°C) and heating rate(30°C/minute).
12. Turn off the furnace, heating tape, gas and then remove the reactor and traps rapidly.

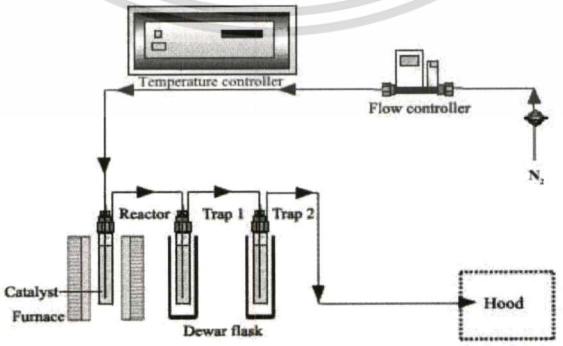


Figure C.1 Schematic of Semi-Batch Reactor System

C-2 Direction of Rotary Evaporator

1. Open the rotary evaporation machine and turn valve of cooler then wait until the temperature go down about 6-9°C.
2. Put a fuse in the pressure meter.
3. Open the digital water bath and set the temperature at S, L, H parameters.
4. Adjust the pressure from 756 mm hg to 250 mm hg and gradually decrease down to separate hexane out.
5. Turn the rotary valve to adjust the speed of rotation.
6. Pour the sample to at bottom flask and joint it rotary evaporator.
7. Joint a bottom shape at the bottom of the rotary evaporator.
8. Click "start end" button and open the cooler. Then, the process is progressive.

Figure C.2 Rotary Evaporator

(http://www.imlab.com/buchi/Rotavapor_R-215%20ADVANCED.jpg)

C-3 Direction of vacuum oven

1. Connect the reactor with vacuum oven and pump which a reactor must be trapped by liquid nitrogen.
2. Open the vacuum oven and make sure that both valves of vacuum and purge are closed.
3. Click “set”, “sp”, “temp.”, “set”, “ pump ”, “ increase ”, “ on ”, “ set ” respectively.
4. Open the vacuum valve slowly.
5. Then, procession will be progress about 45 minutes. Next, close the vacuum valve and release the process about 24 hour.
6. Close the vacuum oven and then open the purge valve to purge gas into the vacuum oven.

Figure C.3 Vacuum oven

(http://www.scientificdealers.com/ggtech/images/vacuum-oven-rectangular.jpg)

C-4 Direction of Thermalgravimetric Analyzer

1. Open valve of N_2 gas and air
2. Open valve at the TGA machine and adjust the pressure by turn the black button to 20 Psi for purging.
3. Open TGA machine and open computer.
4. Set up the condition that use for processing such as temperature, rate of an increasing temperature (degree Celsius/minutes).
5. Put the sample into the pan (weight of the sample should not over than 100 mg)
6. Click " Raise Furnace " in the computer for raise the furnace up.
7. Click " go to temperature " in the computer and wait until the temperature go to Initial temperature.
8. Click " Get sample weight " in the computer.
9. Click " Start / Stop a method " to raise the temperature up.

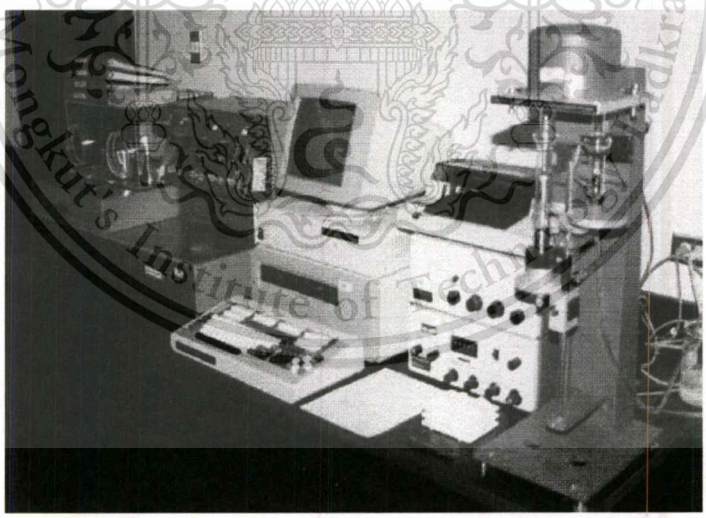


Figure C.4 Thermogravimetric Analyzer (http://teton.if.uidaho.edu/TGA-DSC.jpg)

C-5 Direction of Fourier Transform infrared spectrometer

1. First of all, sample must be prepared by paint the sample on the plate.
2. Open computer. Then, click on the spectrum program and click "OK".
3. Click "scan background", "initialize", and click "yes" to scan the air inside the machine.
4. Calibrate the machine by use polystyrene film.
5. Scan sample. Click "instrument", "scan sample", and put the sample in the machine.
6. Then we will get the peak of product and can adjust the peak by click "process", "smooth" and click "auto smooth".
7. Adjust the base line by click "baseline correction" and then click "automatic connection".
8. Adjust the scale of graph by click "peak" and click "Vcursor".

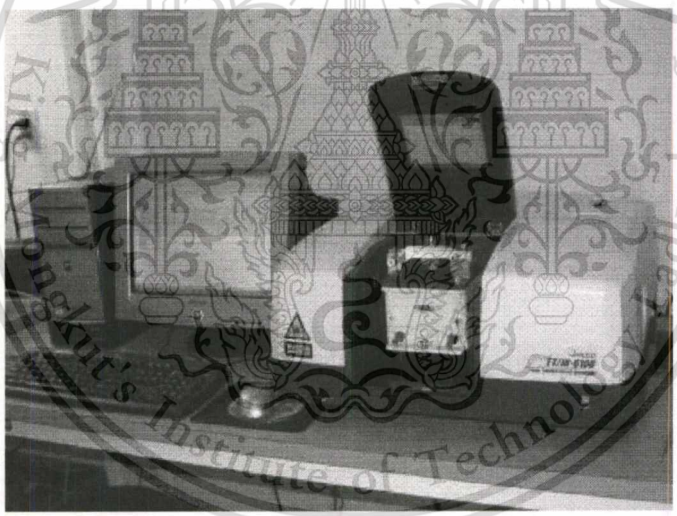


Figure C.5 Fourier Transform infrared spectrometer
(http://www.andersonmaterials.com/images/ftir.jpg)

C-6 Direction of X-ray Diffraction Analyzer Bruker type D8 Advance

1. Prepare the sample by grind the sample and then pack it into a plate.
2. Put the sample into the X-ray Diffraction machine. In this stage, we can determine times that use to measure intensity of the ray.
3. Analyze the sample by EVA program
   then compare with the standard pattern so, we can classify the composition of sample.

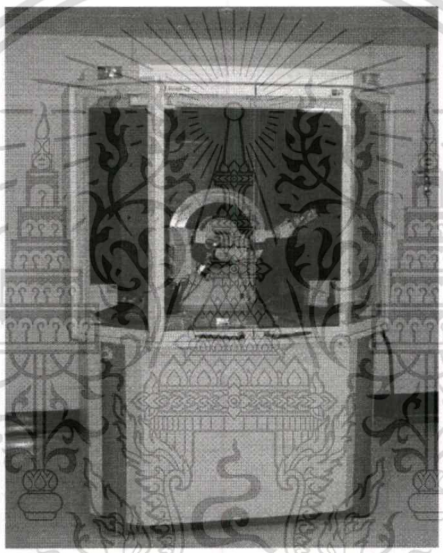


Figure C.6 X-ray Diffraction Analyzer
(http://www.uq.edu.au/nanoworld/images/equip/XRD.jpg)

C-7 Direction of Scanning Electron Microscope

1. Prepare the sample first by mounting it on the sample holder (called stub).
2. SEM samples need to be conductive therefore coating the sample by a conducting material, such as gold or carbon.
3. Put the samples in the chamber of the sputter coater.
4. Put the coated samples inside the SEM chamber.
5. Observe the operator acquires SEM image of your samples.
6. Observe SEM images when the operator tilts the samples.
7. Observe the difference between images from secondary electrons (SE) and back-scattered electron (BSE).
8. Get the X-ray patterns of your samples by using EDS (Energy Dispersive Spectrometer).

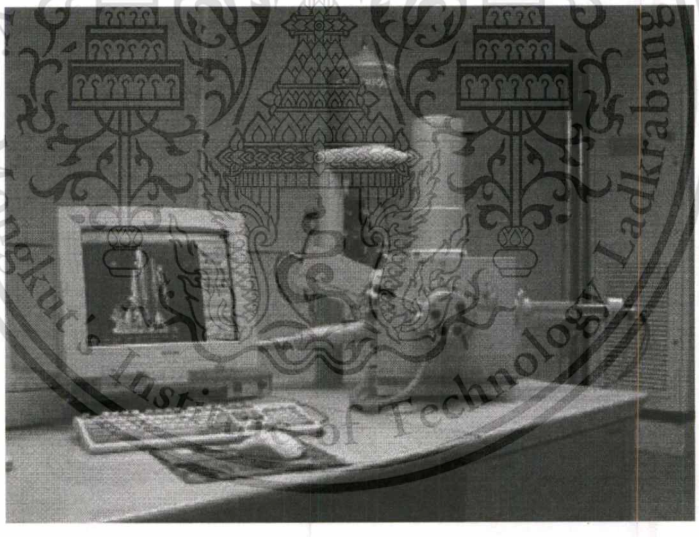


Figure C.7 Scanning electron microscope (http://www.geos.ed.ac.uk/facilities/sem/newsem.jpg)

Appendix D

Characterization Results

Figure D.1 Show TG curve of extracted solid and residue of ZrO_2 1:1 at 350°C

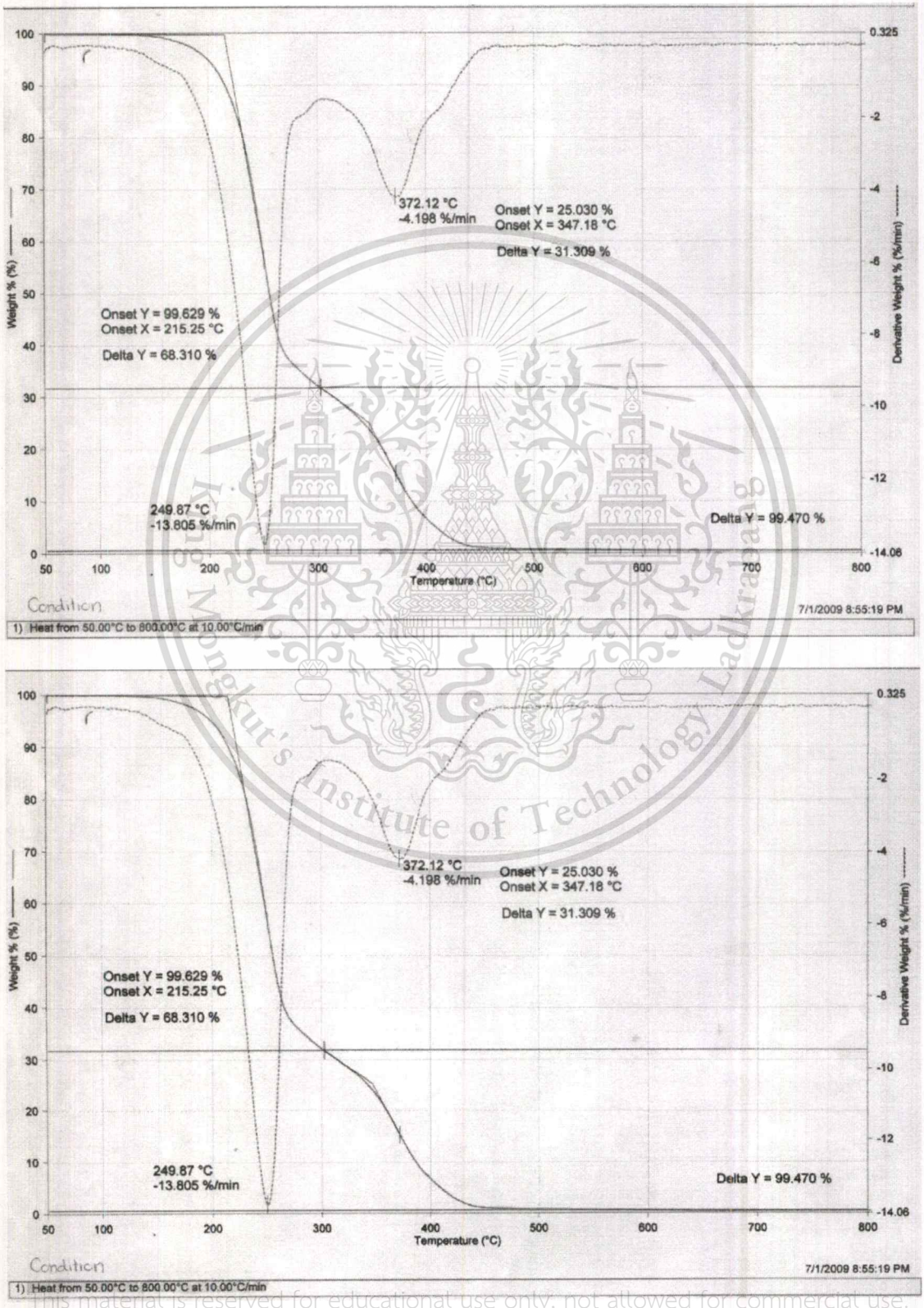
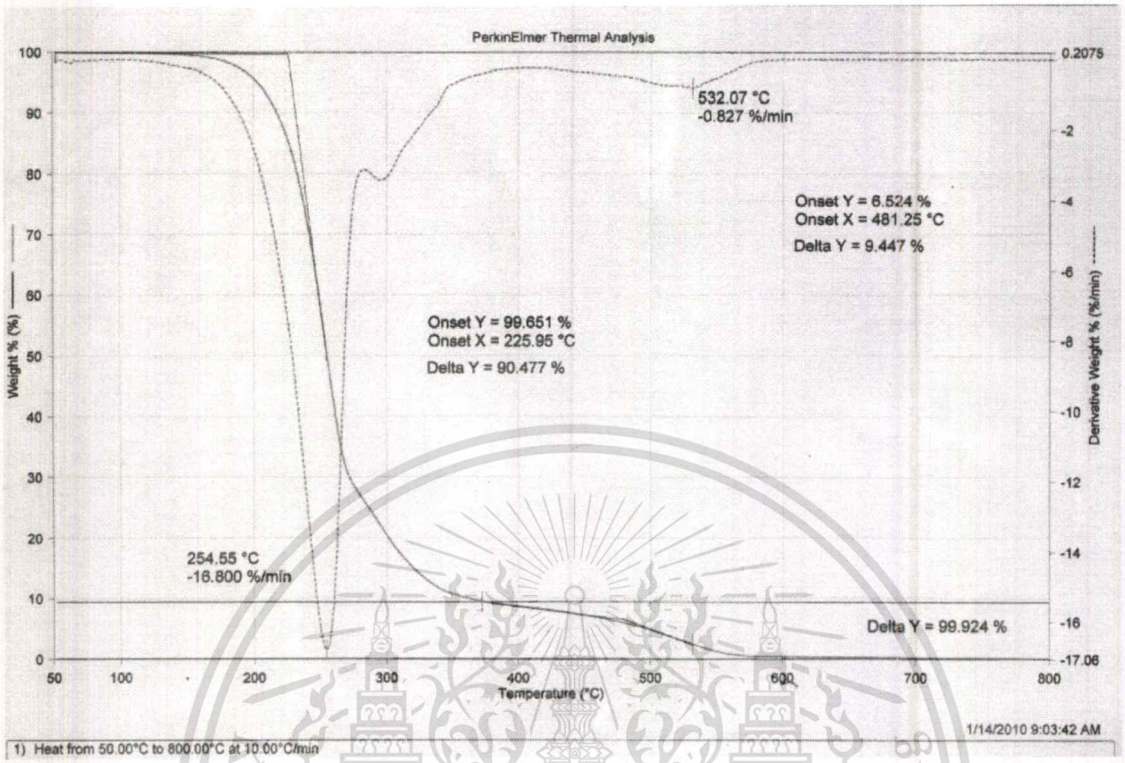


Figure D.2 Show TG curve of extracted solid and residue of ZrO_2 2:1 at 350°C



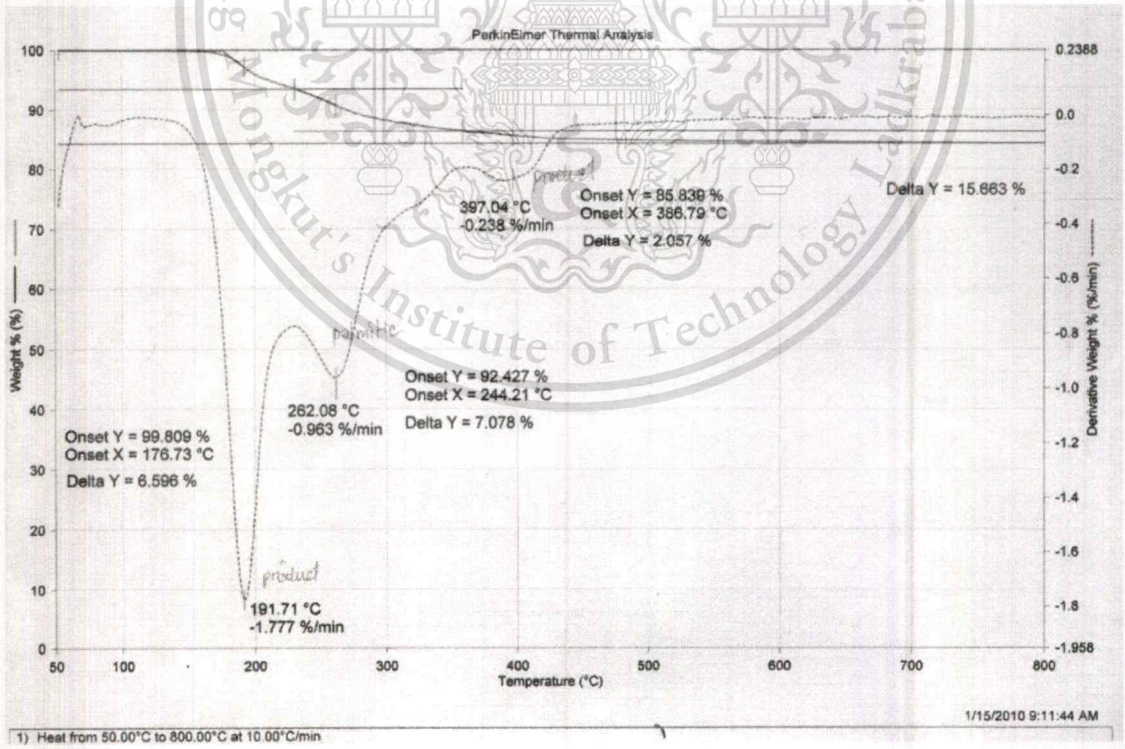
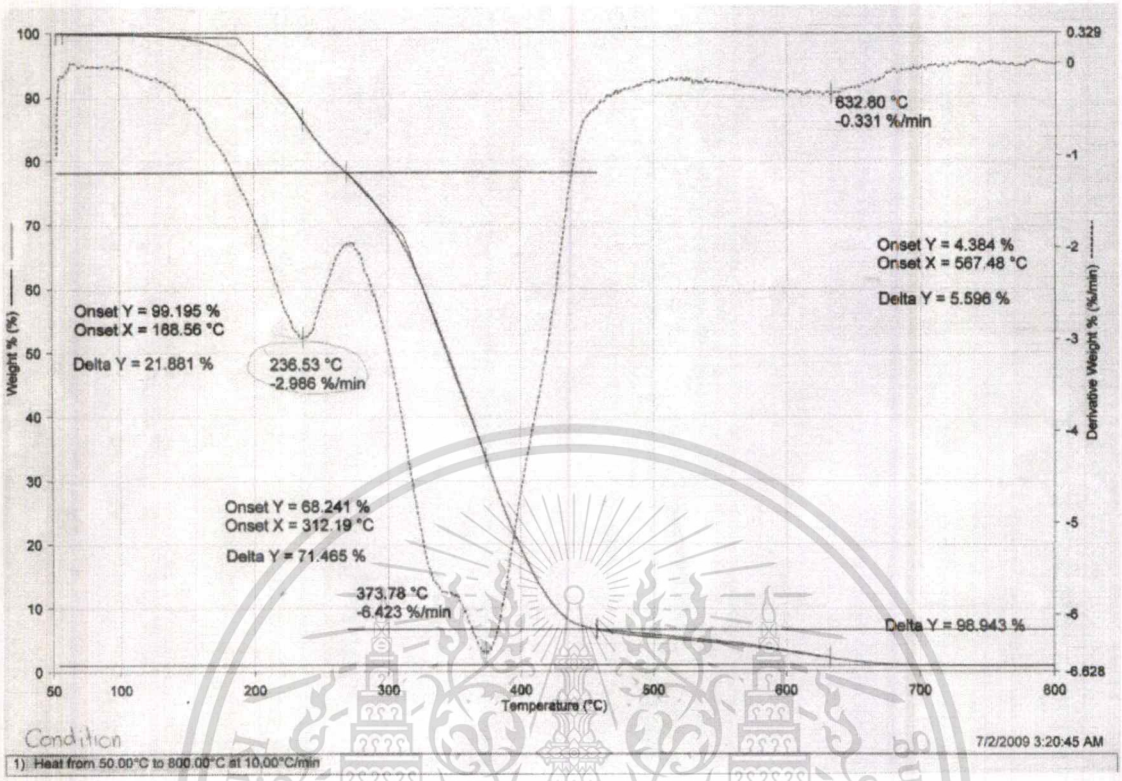


Figure D.3 Show TG curve of extracted solid and residue of ZrO_2 1:1 at 400°C



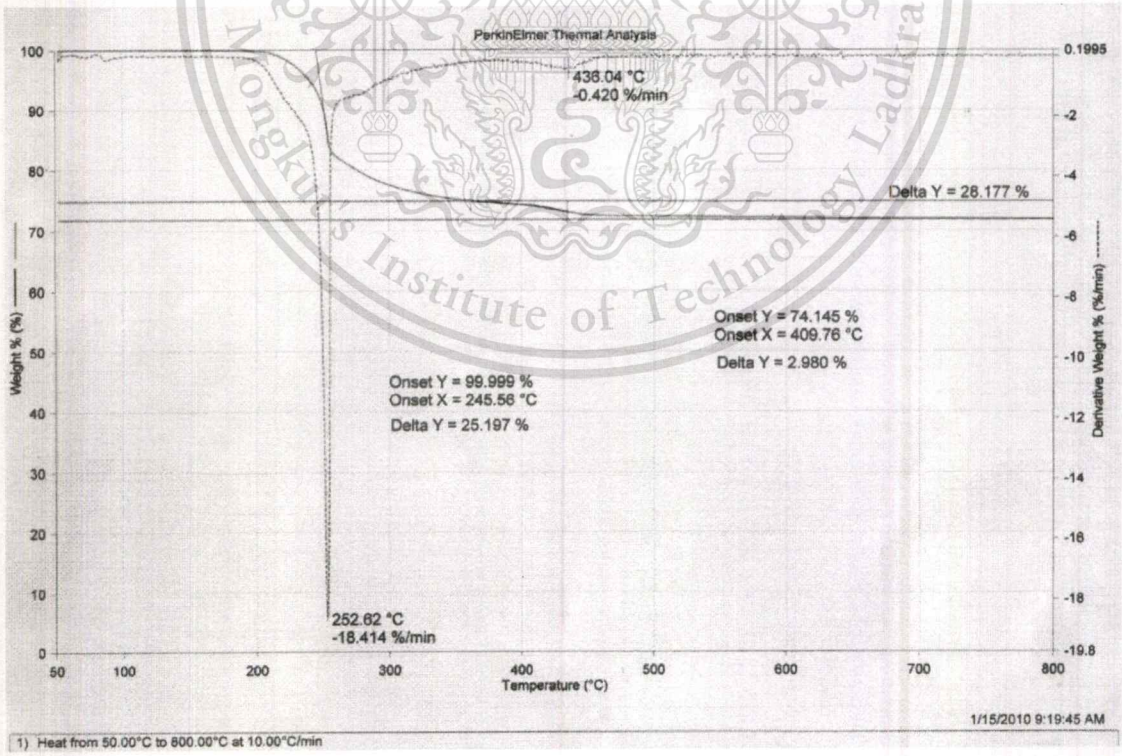
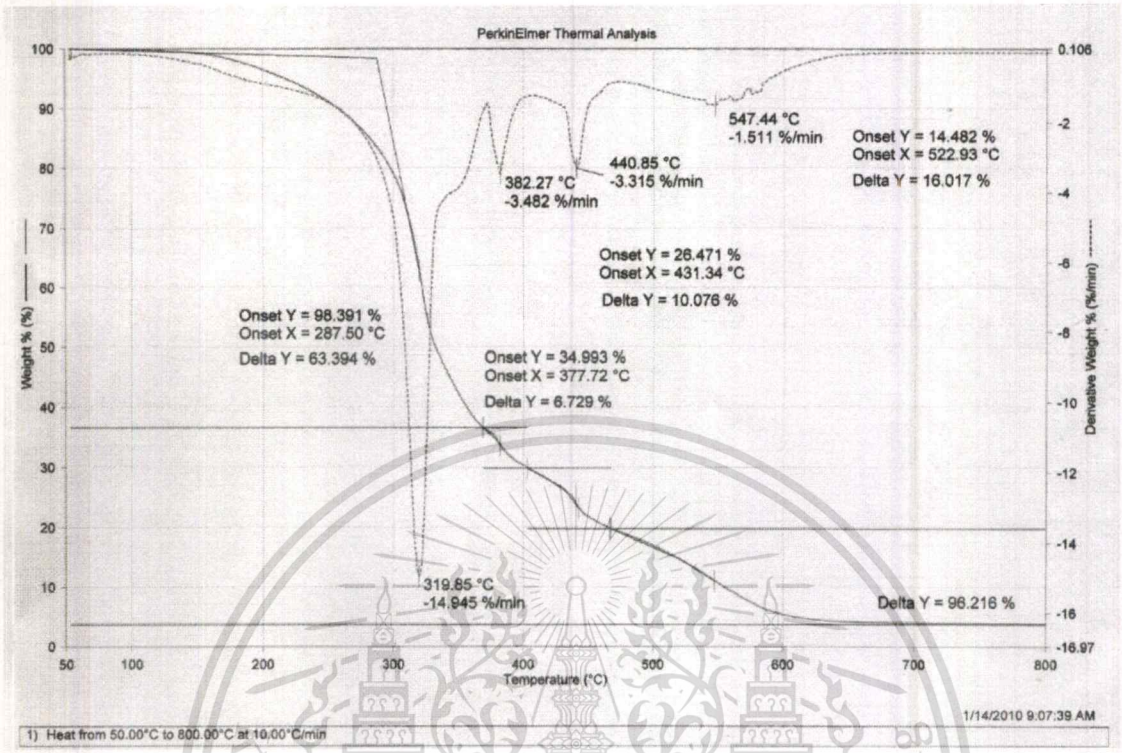


Figure D.4 Show TG curve of extracted solid and residue of ZrO_2 2:1 at 400°C



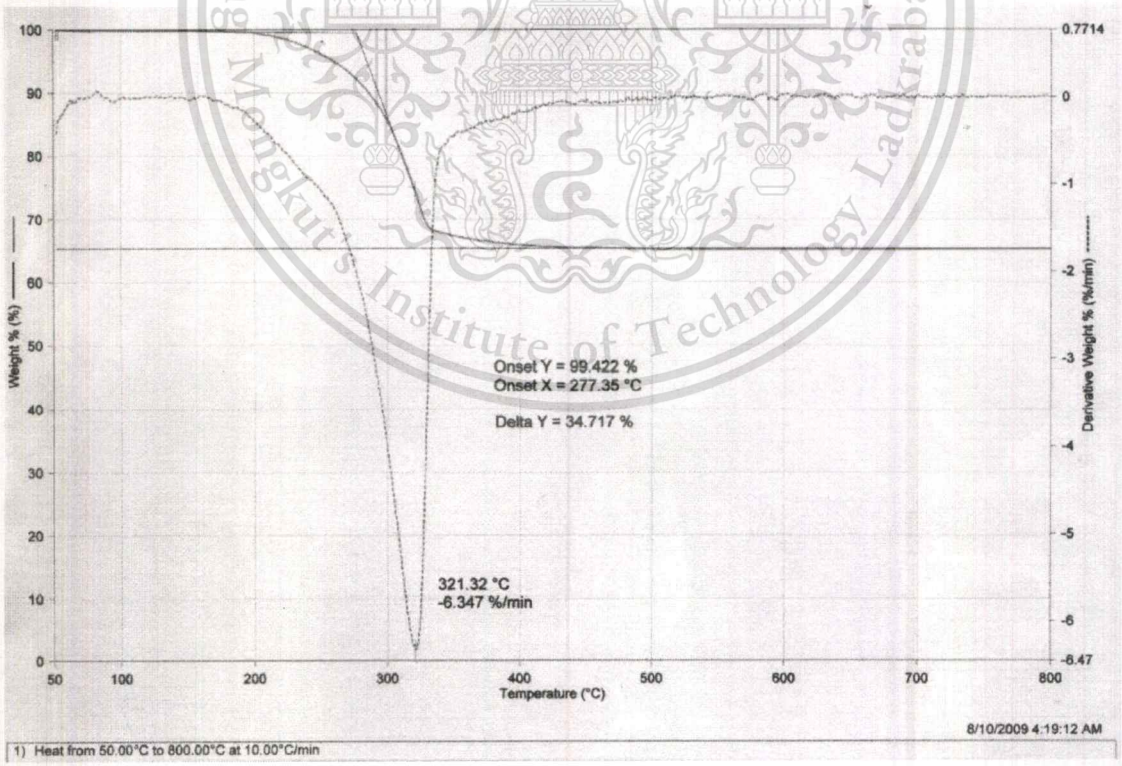
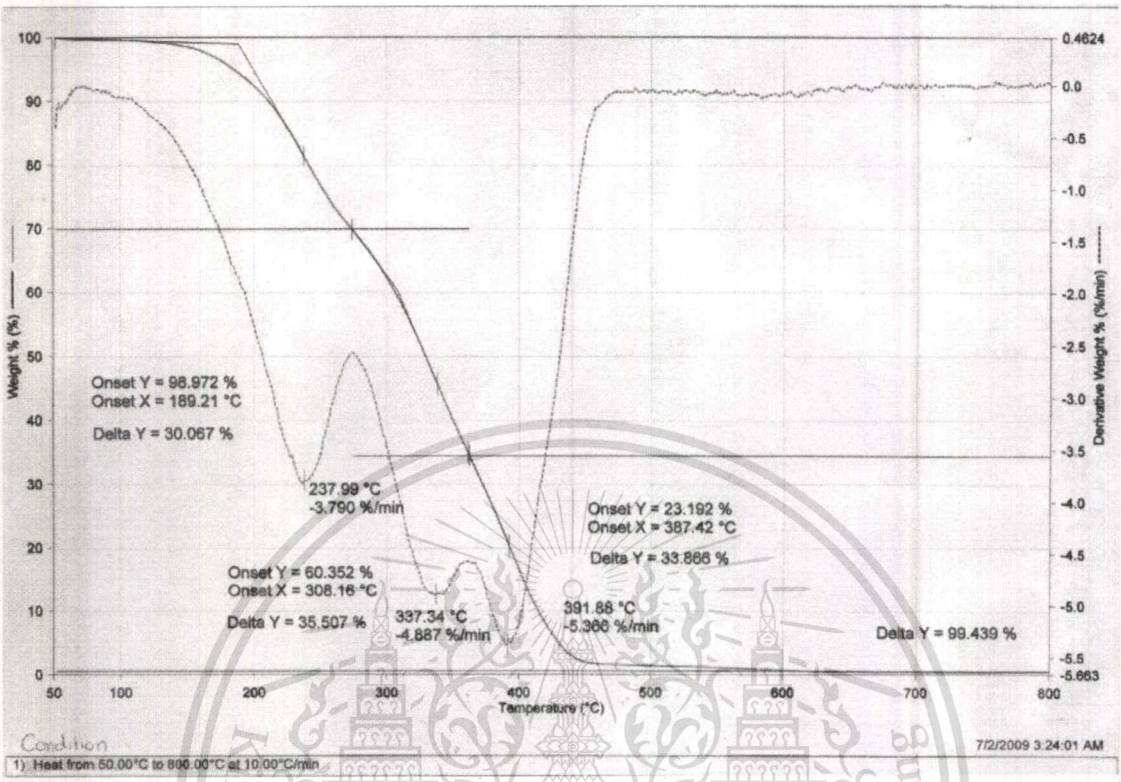


Figure D.5 Show TG curve of extracted solid and residue of ZrO_2 1:1 at 450°C



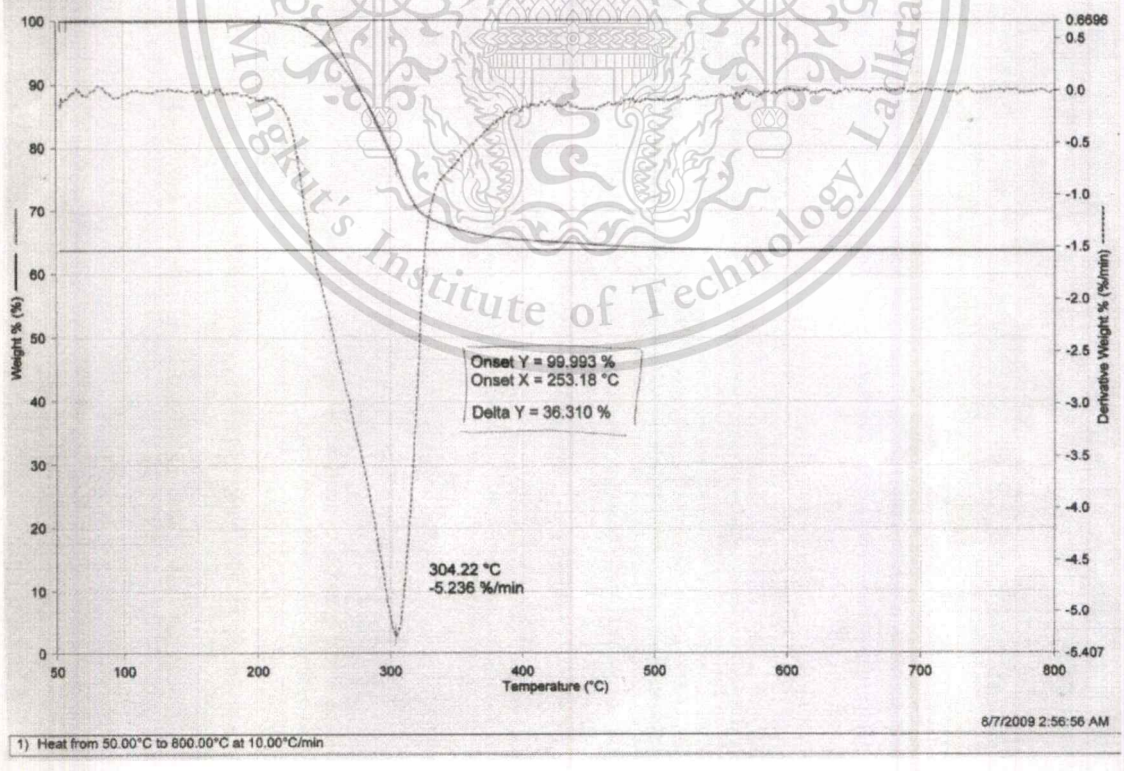
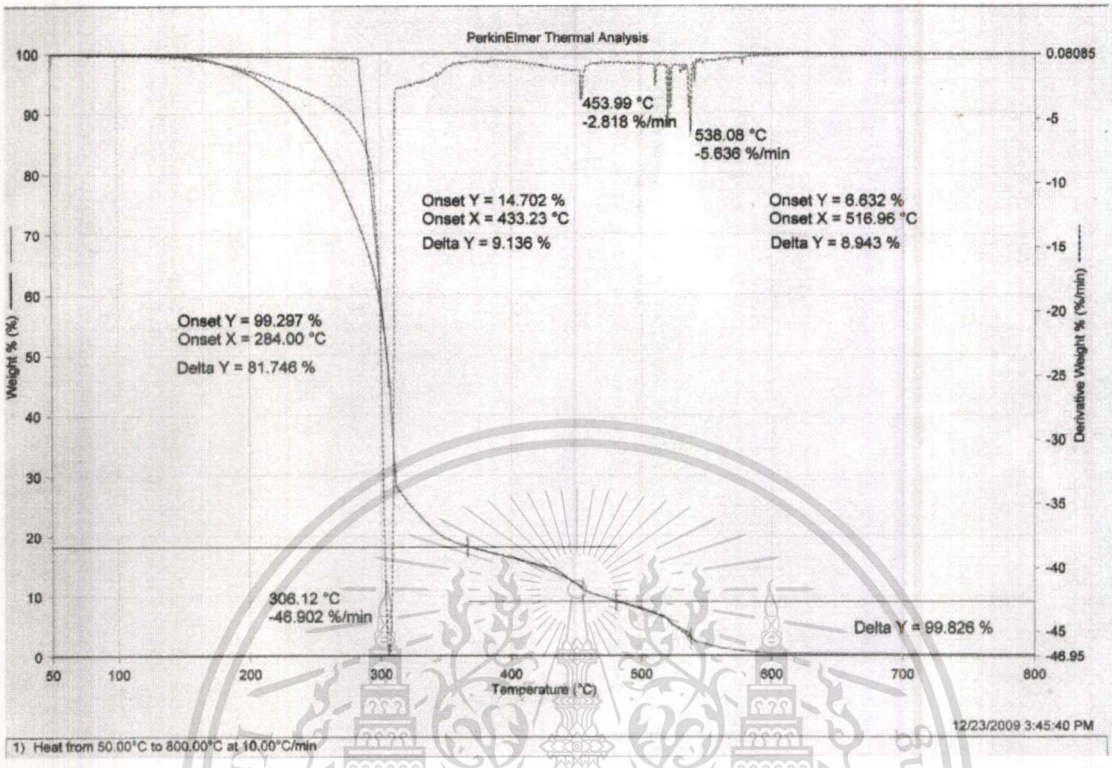


Figure D.6 Show TG curve of extracted solid and residue of ZrO_2 2:1 at 450°C



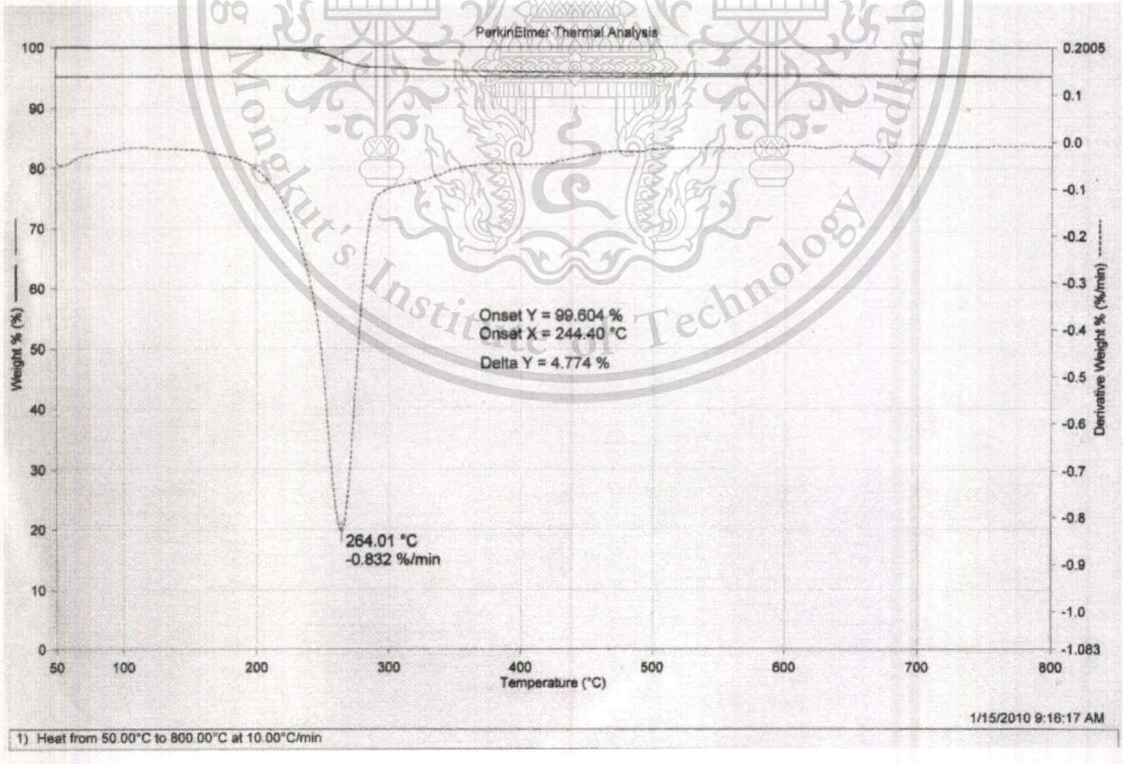
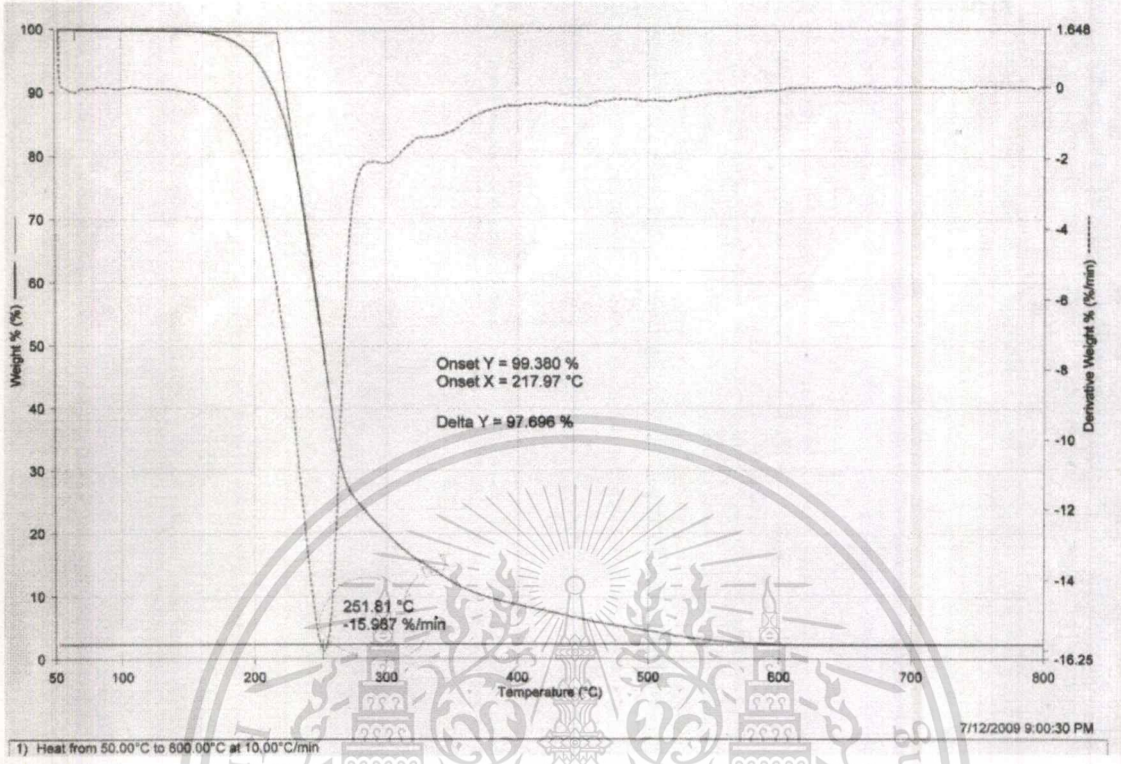


Figure D.7 Show TG curve of extracted solid and residue of CeO_2 1:1 at 350°C



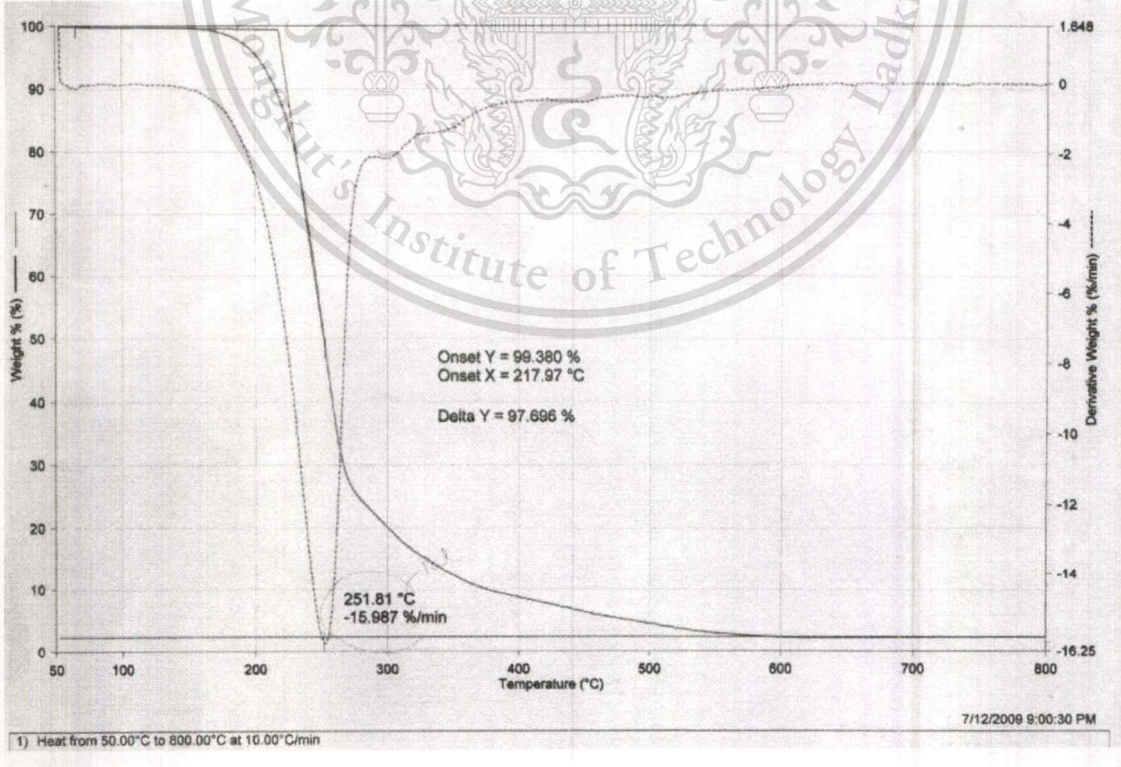
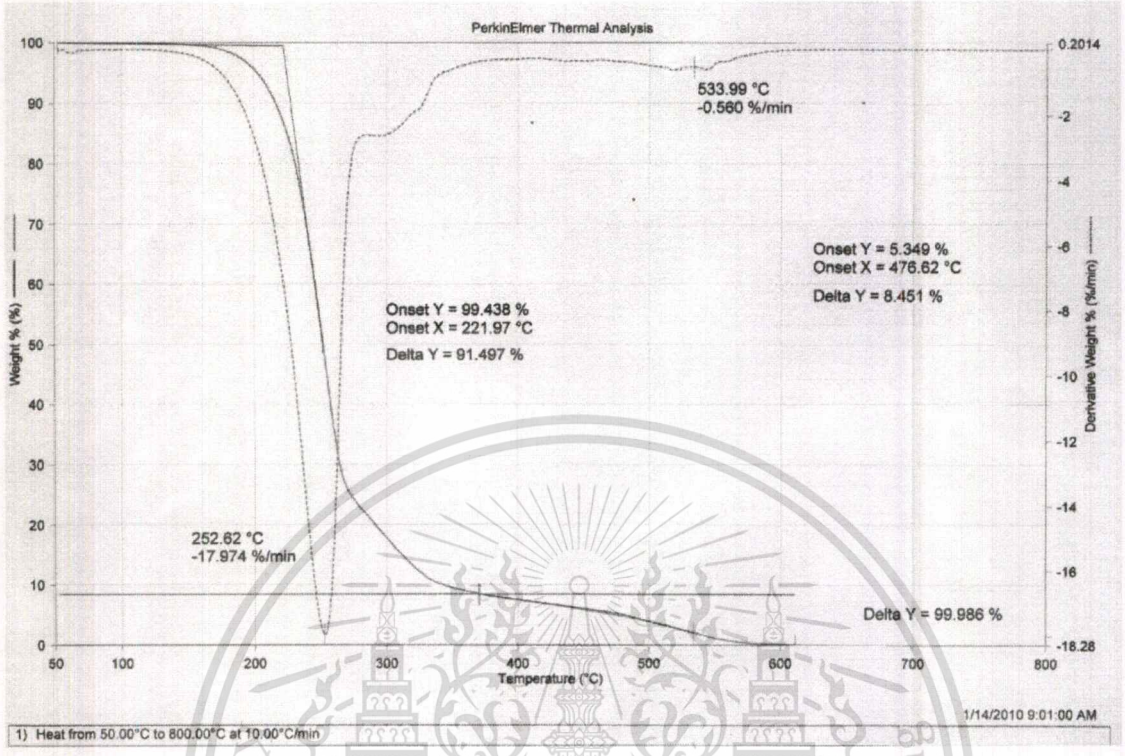


Figure D.8 Show TG curve of extracted solid and residue of CeO_2 2:1 at 350°C



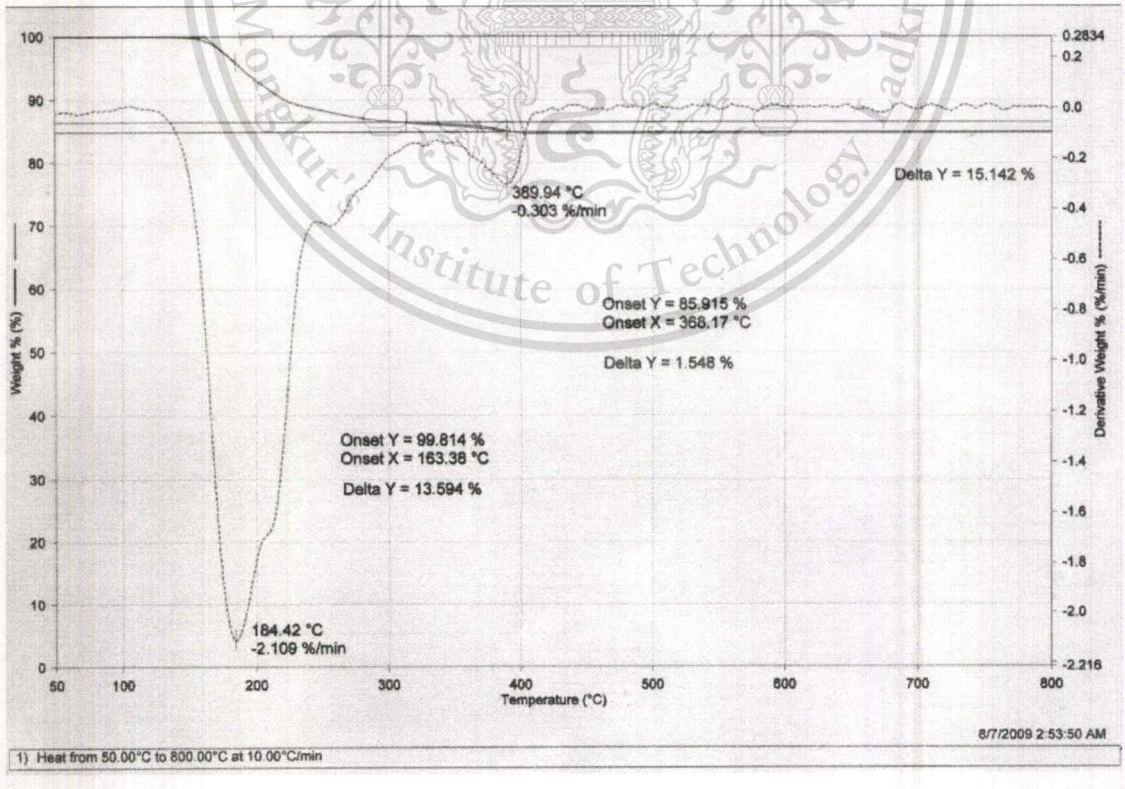
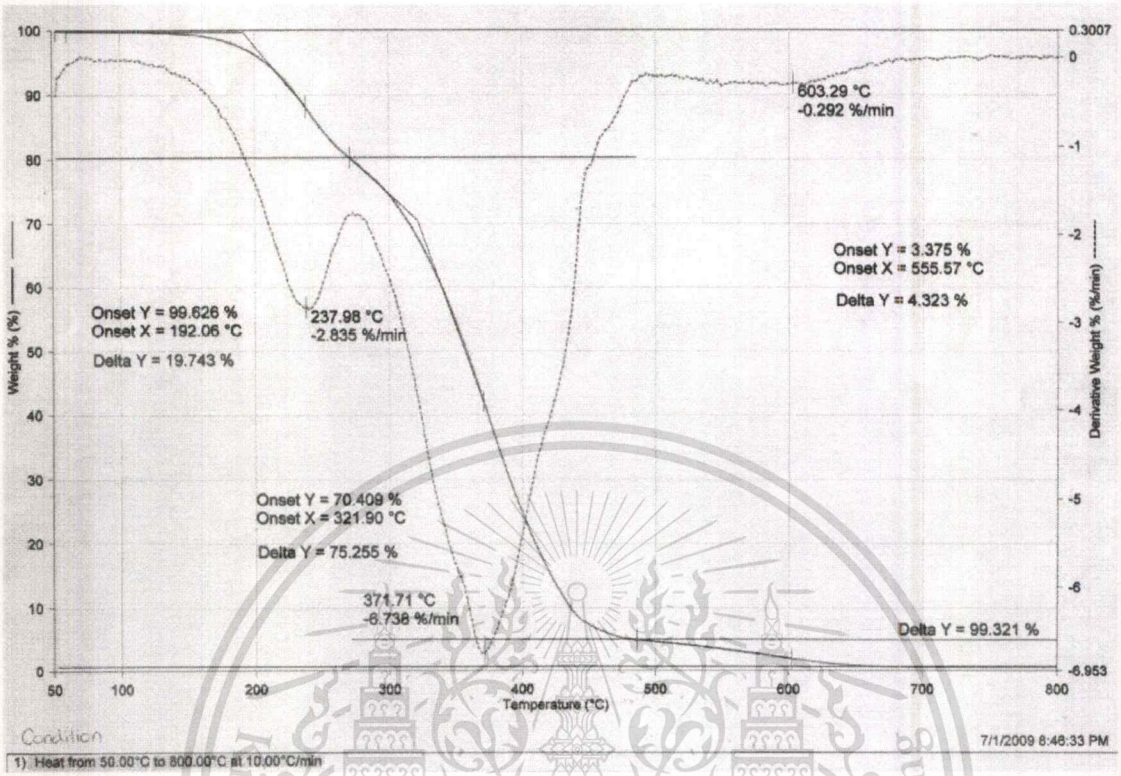


Figure D.9 Show TG curve of extracted solid and residue of CeO_2 1:1 at 400°C



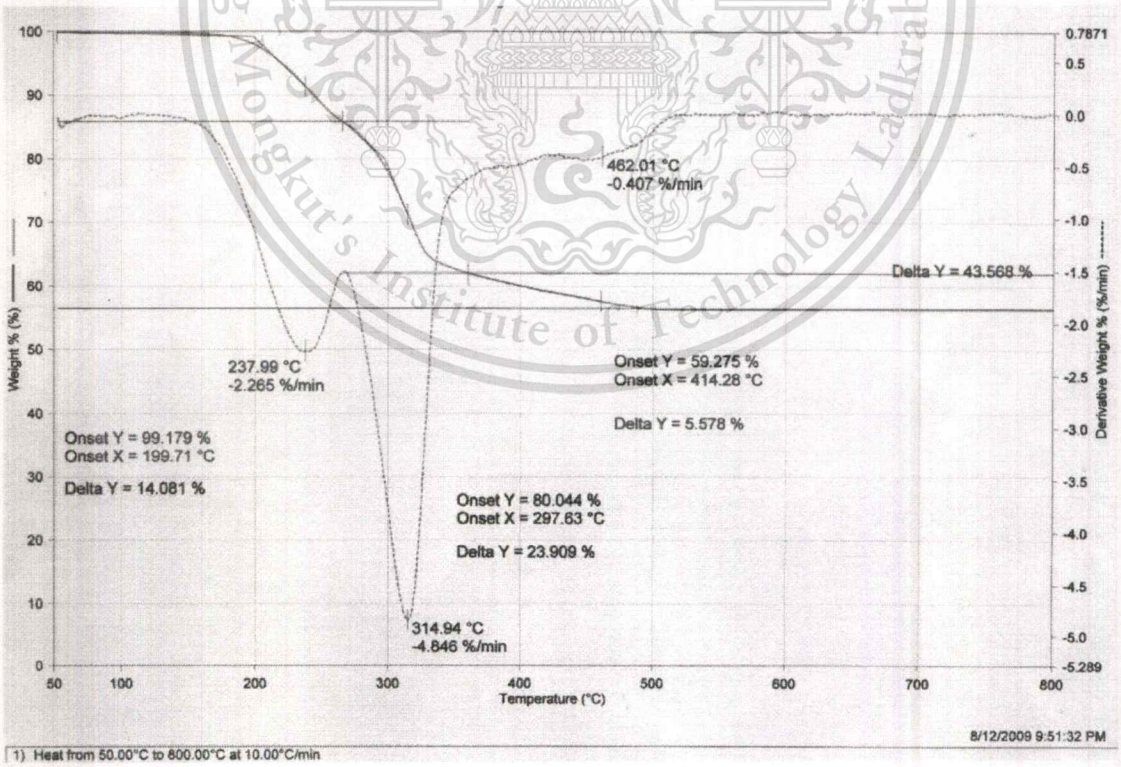
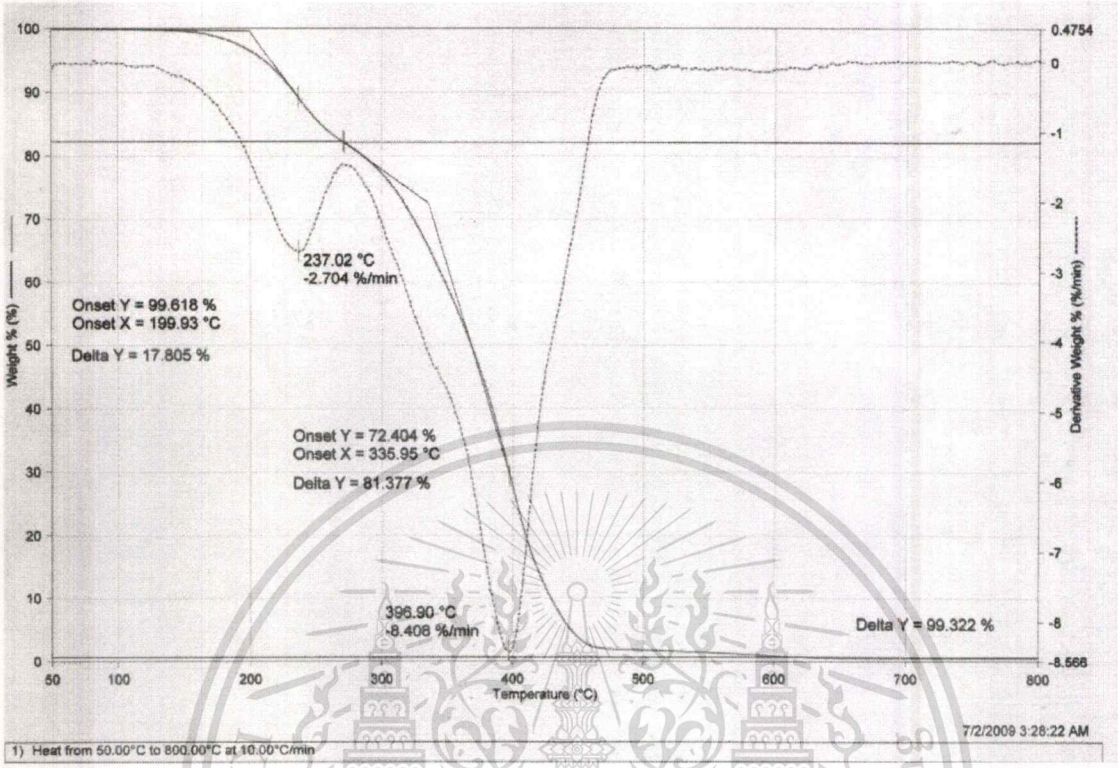


Figure D.10 Show TG curve of extracted solid and residue of CeO_2 2:1 at 400°C



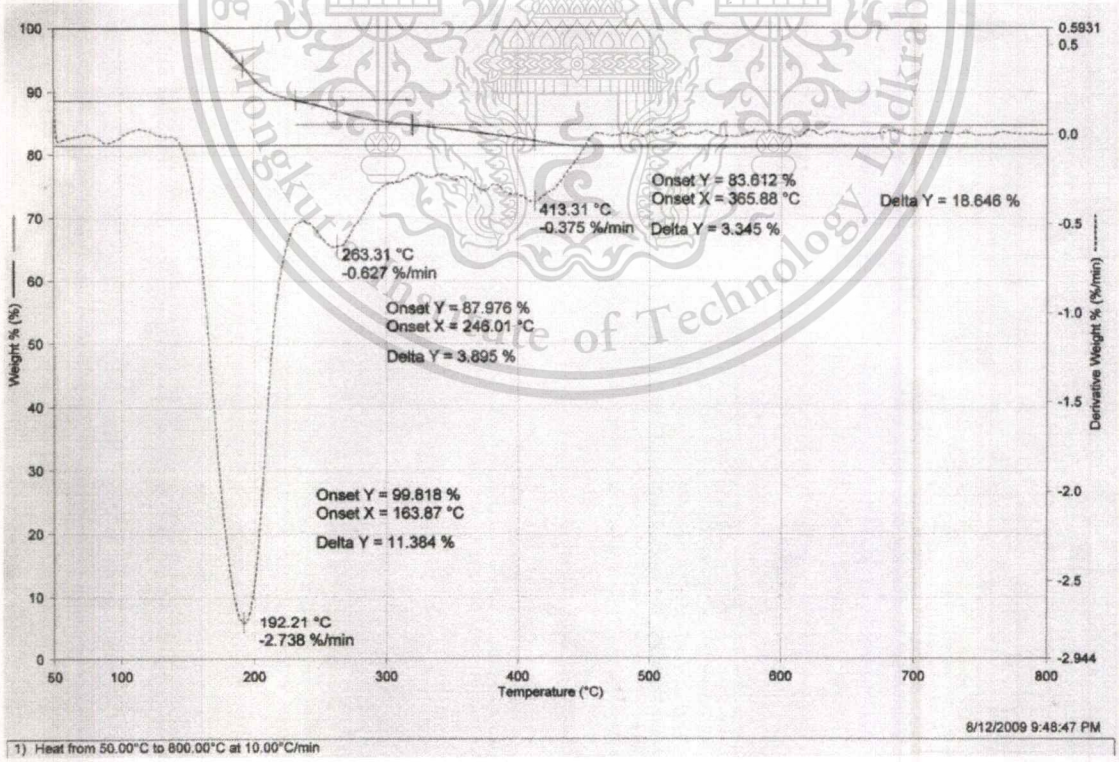
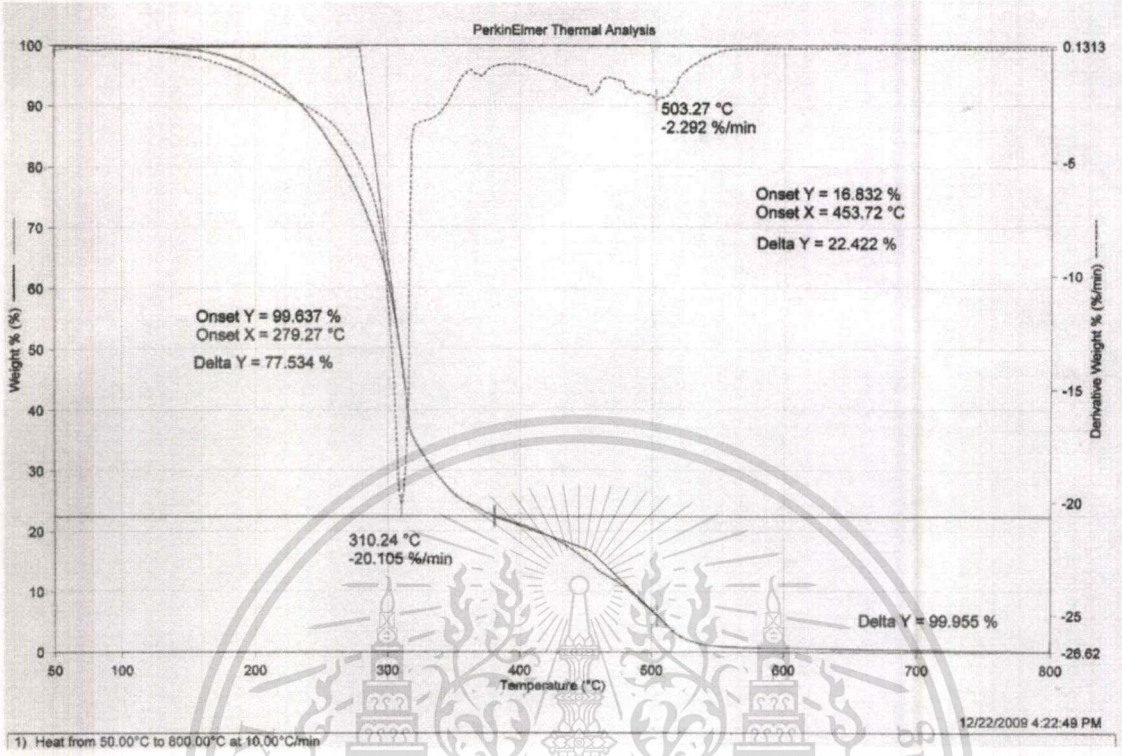


Figure D.11 Show TG curve of extracted solid and residue of CeO_2 1:1 at 450°C



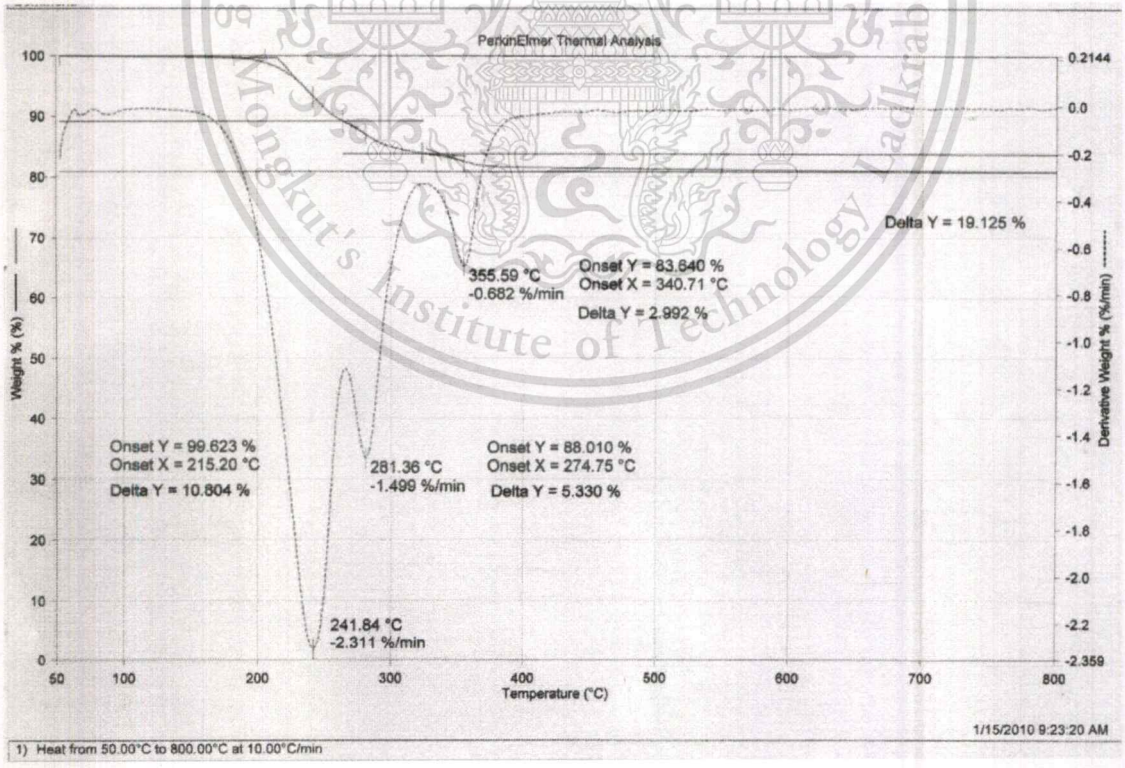
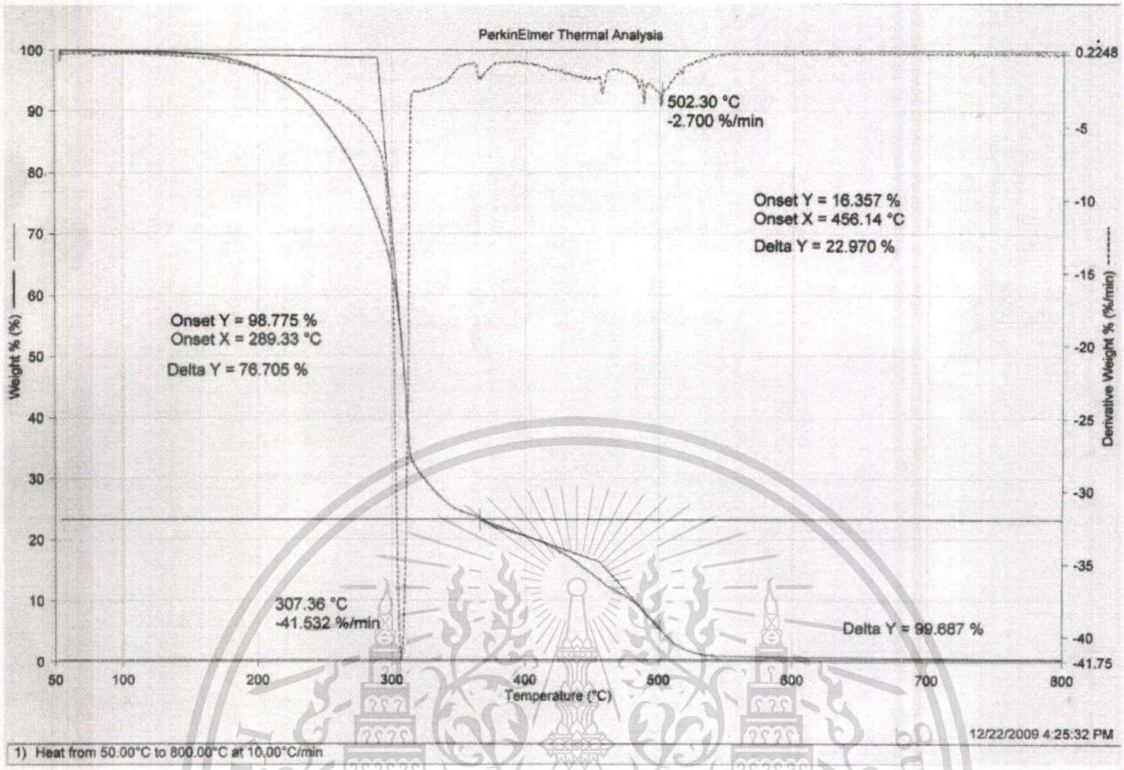


Figure D.12 Show TG curve of extracted solid and residue of CeO_2 2:1 at 450°C



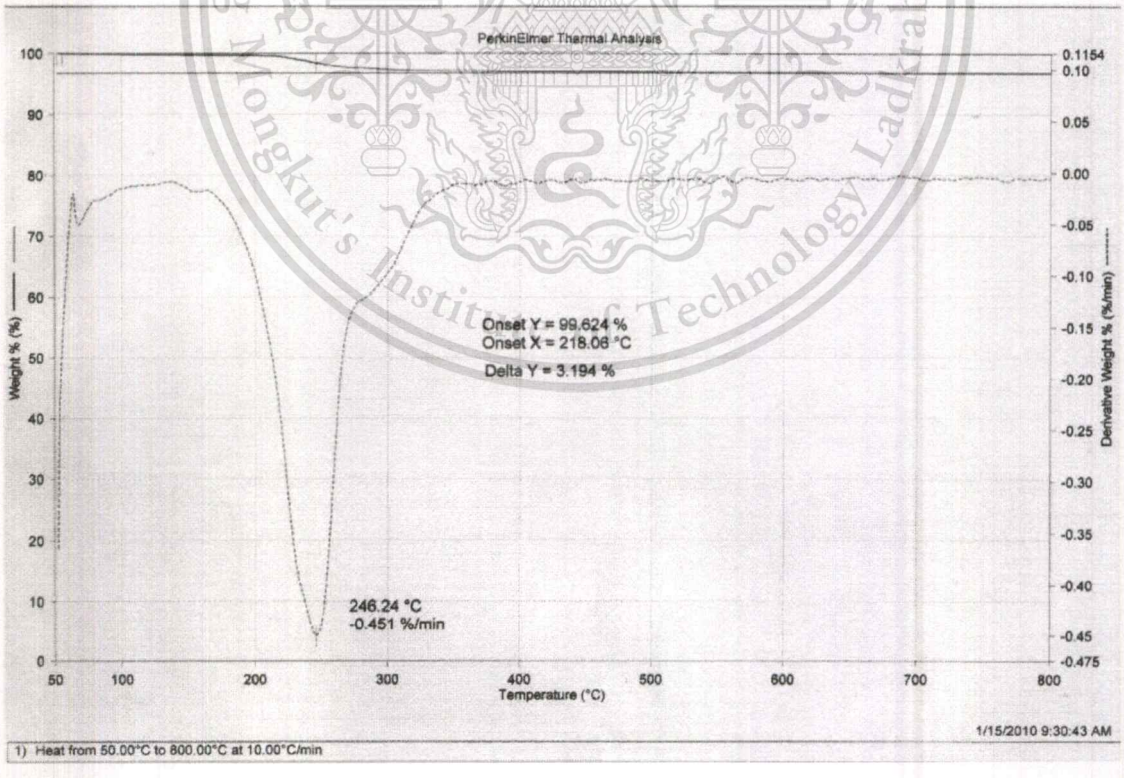
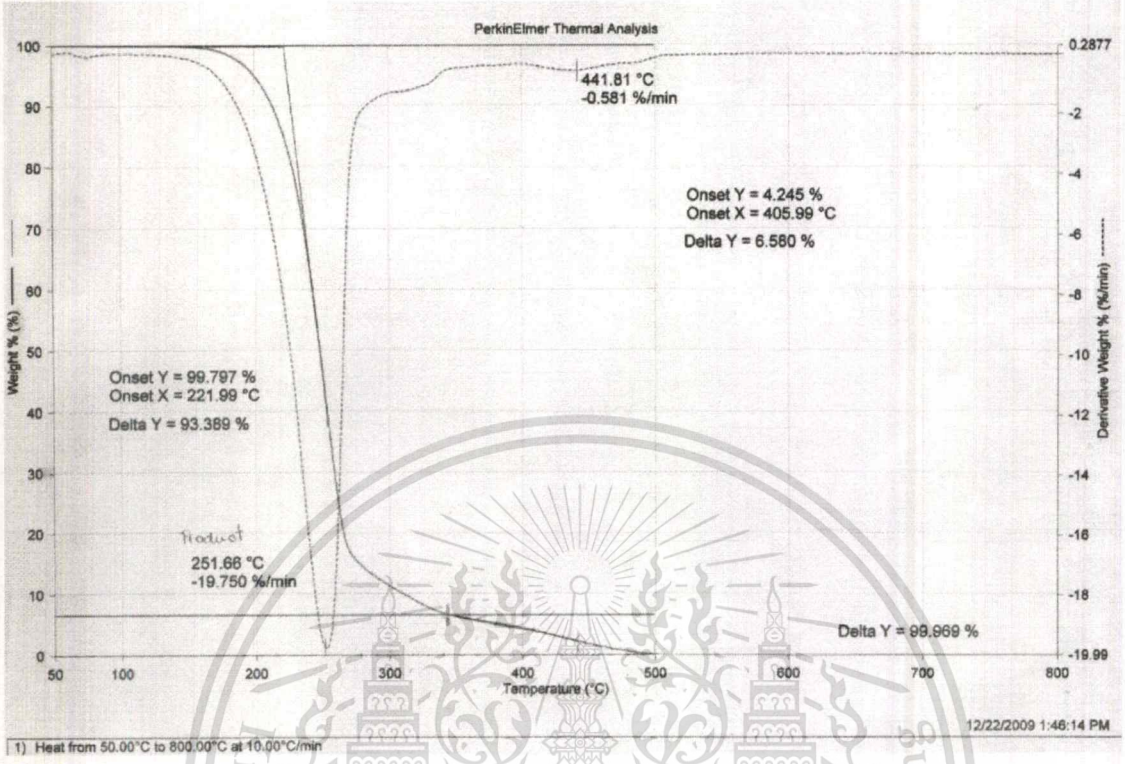


Figure D.13 Show TG curve of extracted solid and residue of $CeZrO_2$ 1:1 at 350°C



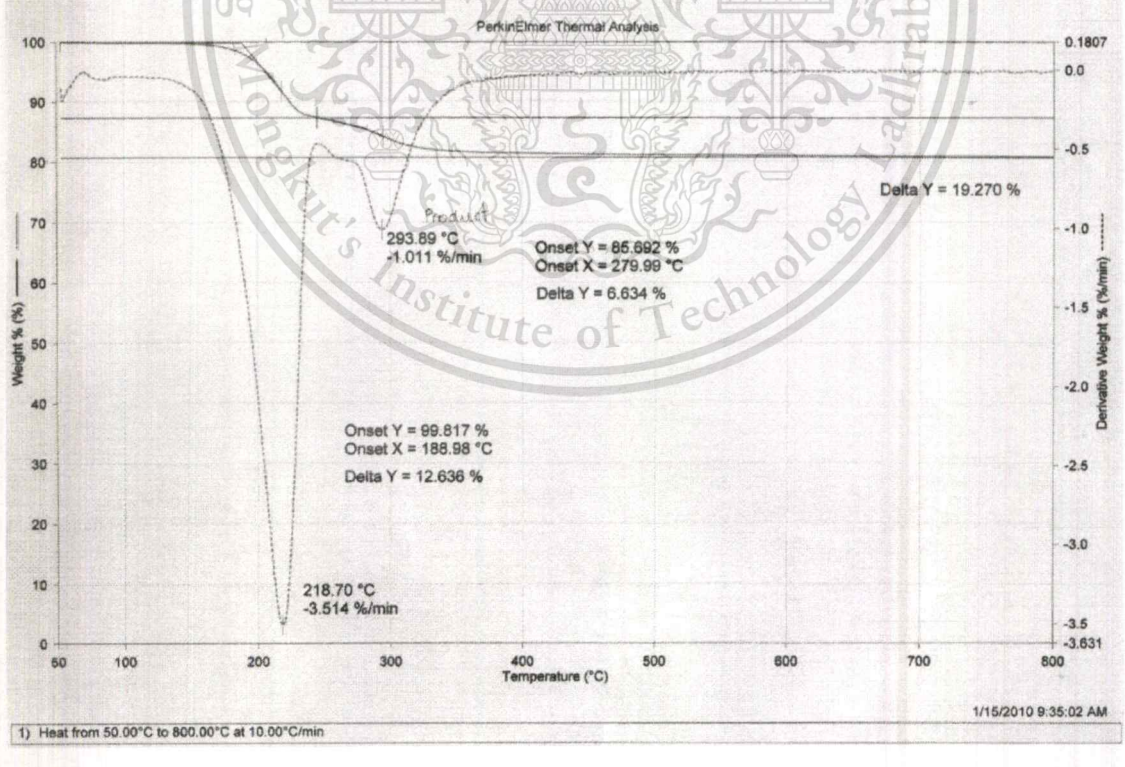
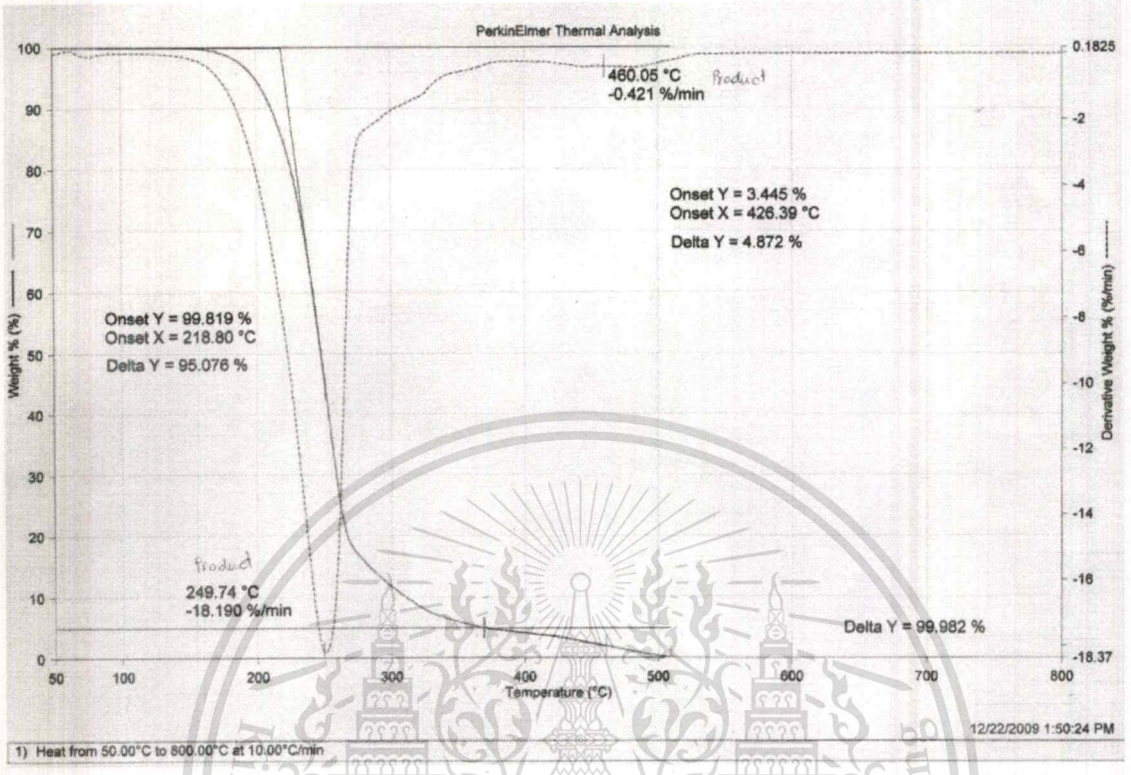


Figure D.14 Show TG curve of extracted solid and residue of $CeZrO_2$ 2:1 at 350°C



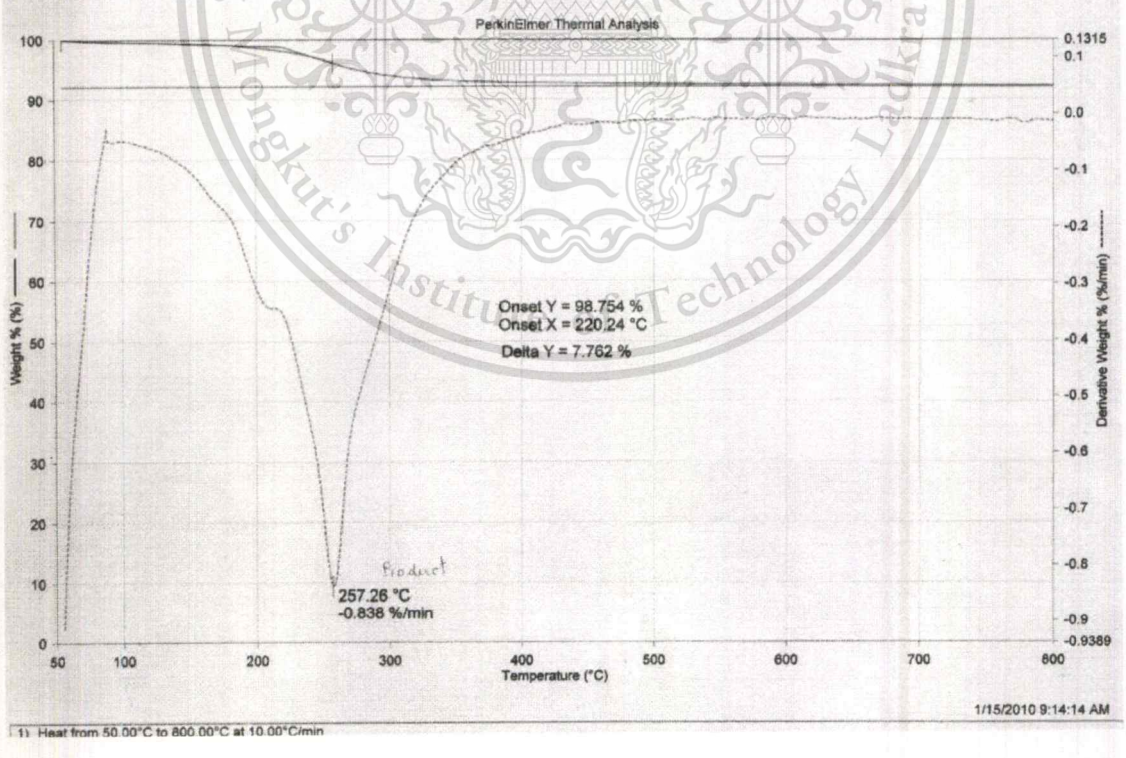


Figure D.15 Show TG curve of extracted solid and residue of $CeZrO_2$ 1:1 at 400°C

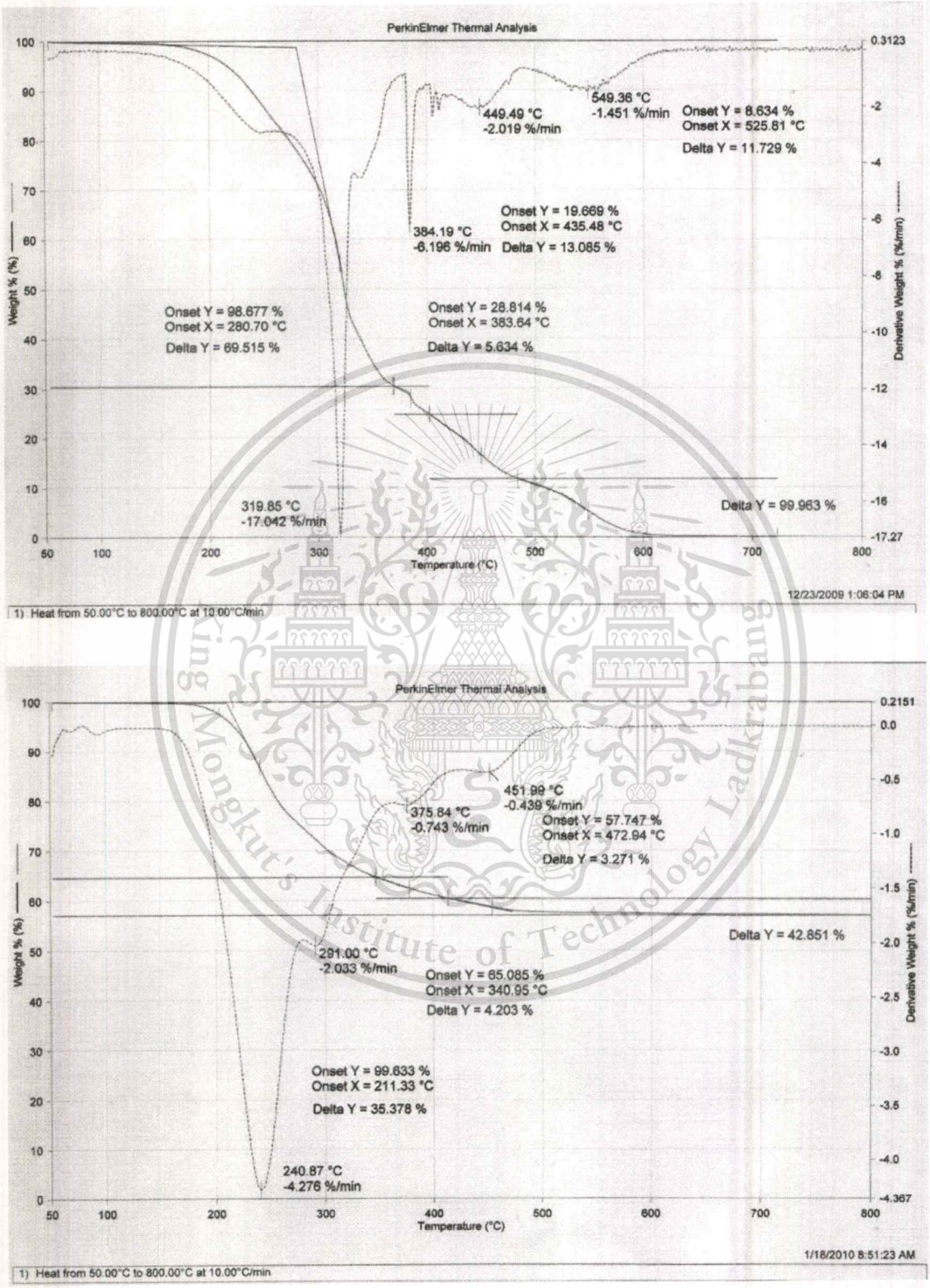
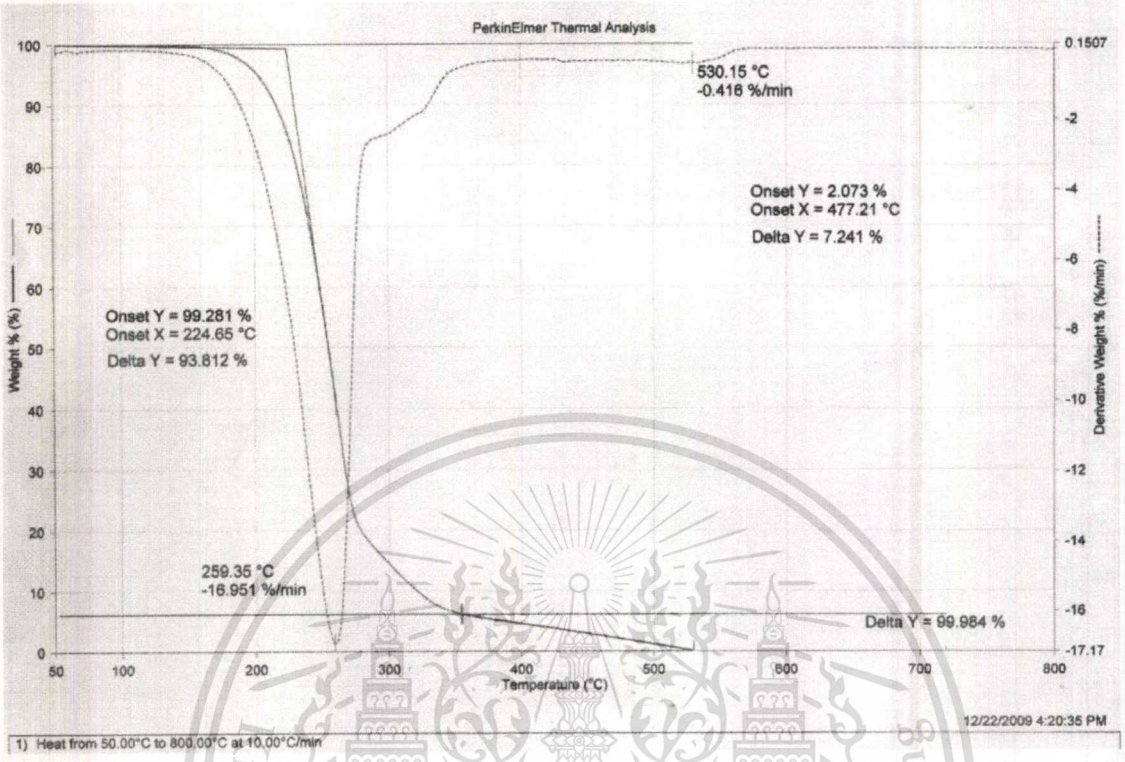


Figure D.16 Show TG curve of extracted solid and residue of $CeZrO_2$ 2:1 at 400°C



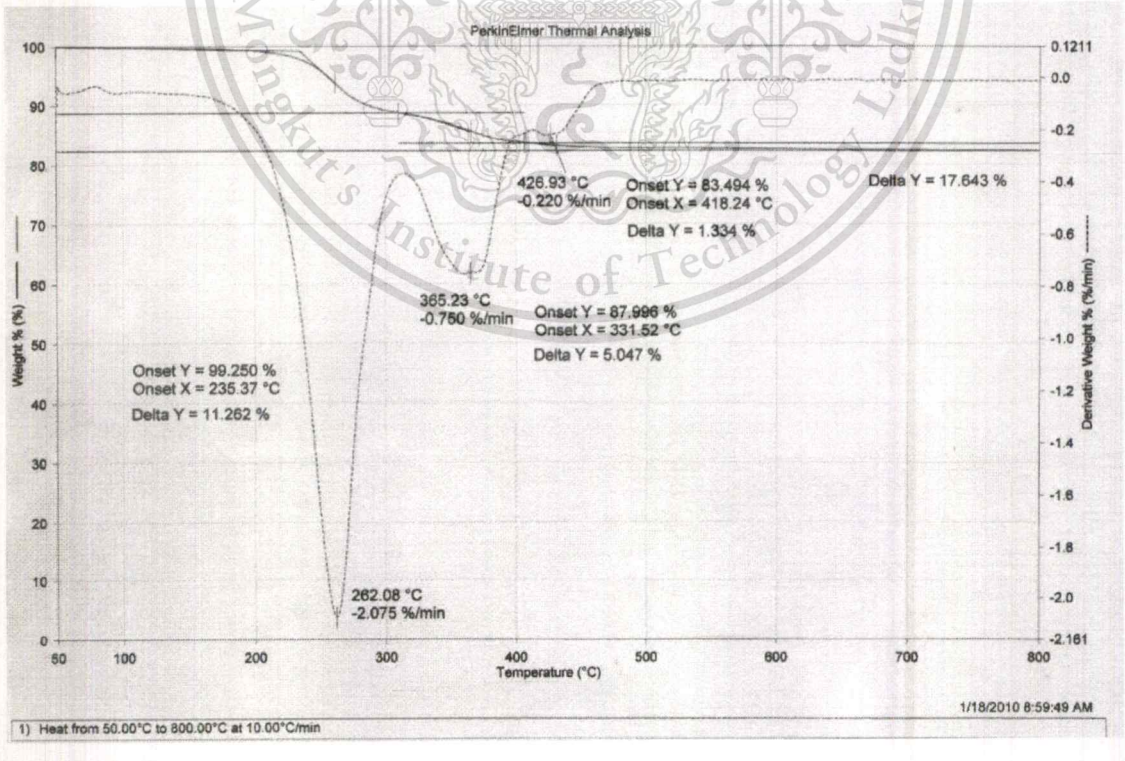
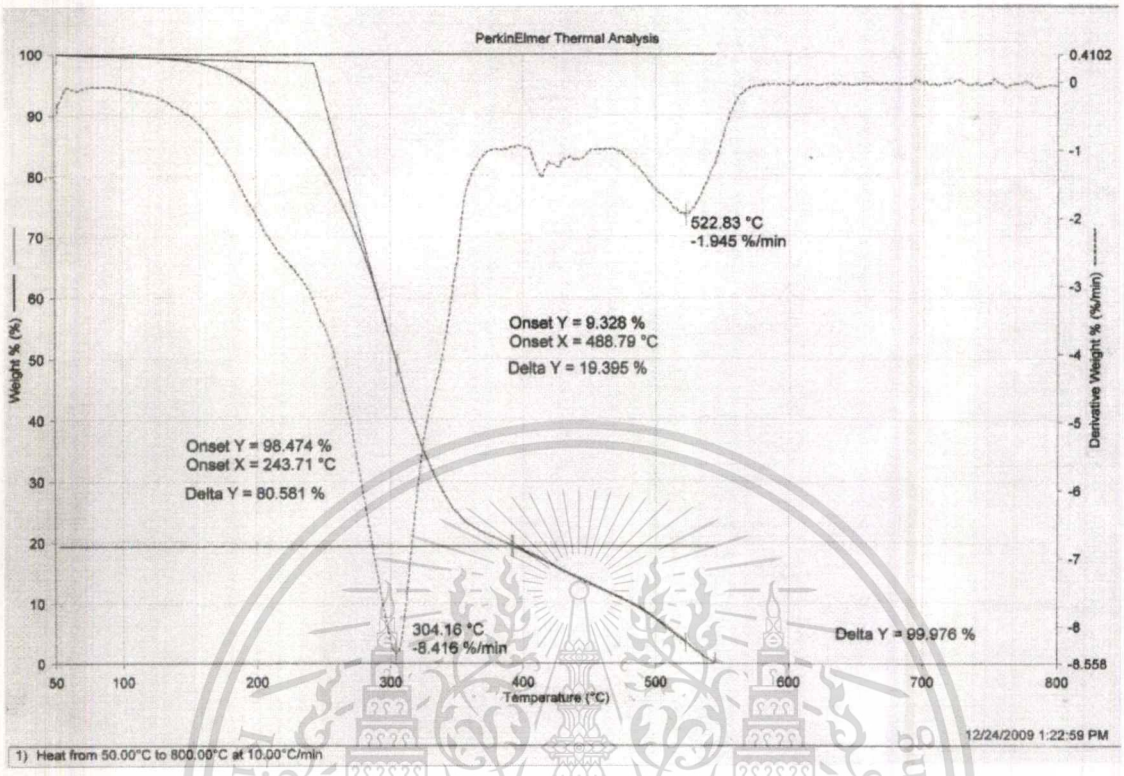


Figure D.17 Show TG curve of extracted solid and residue of $CeZrO_2$ 1:1 at 450°C



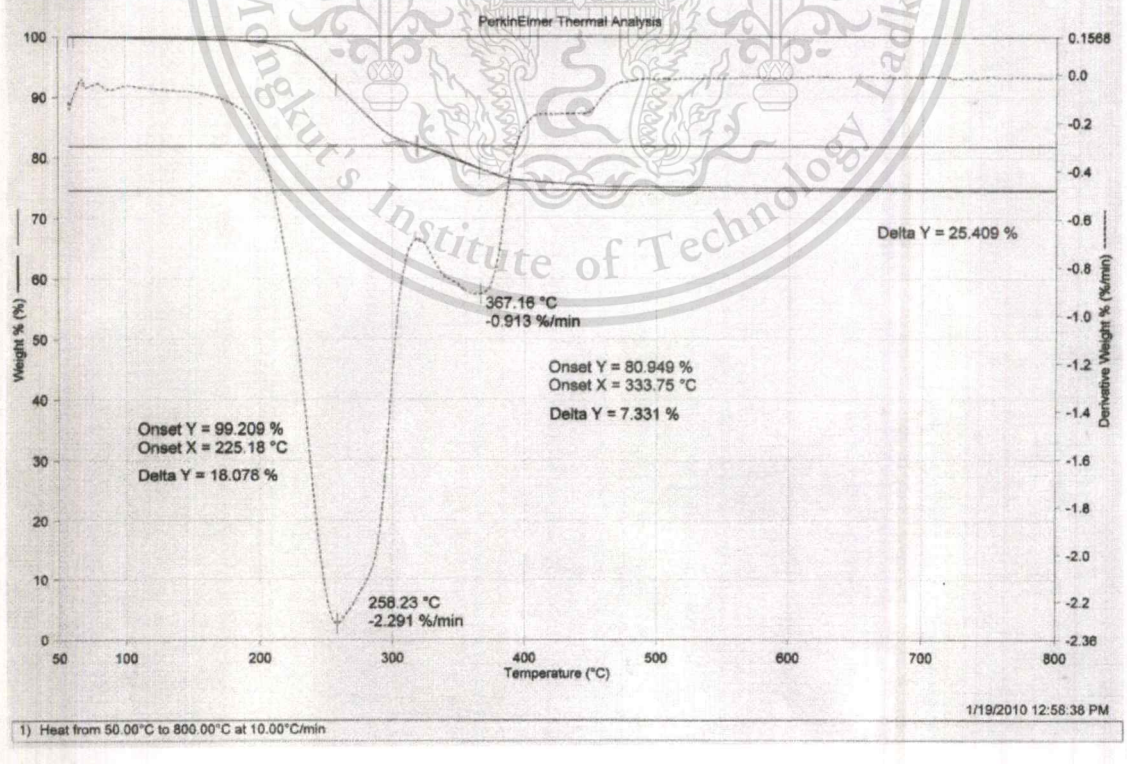
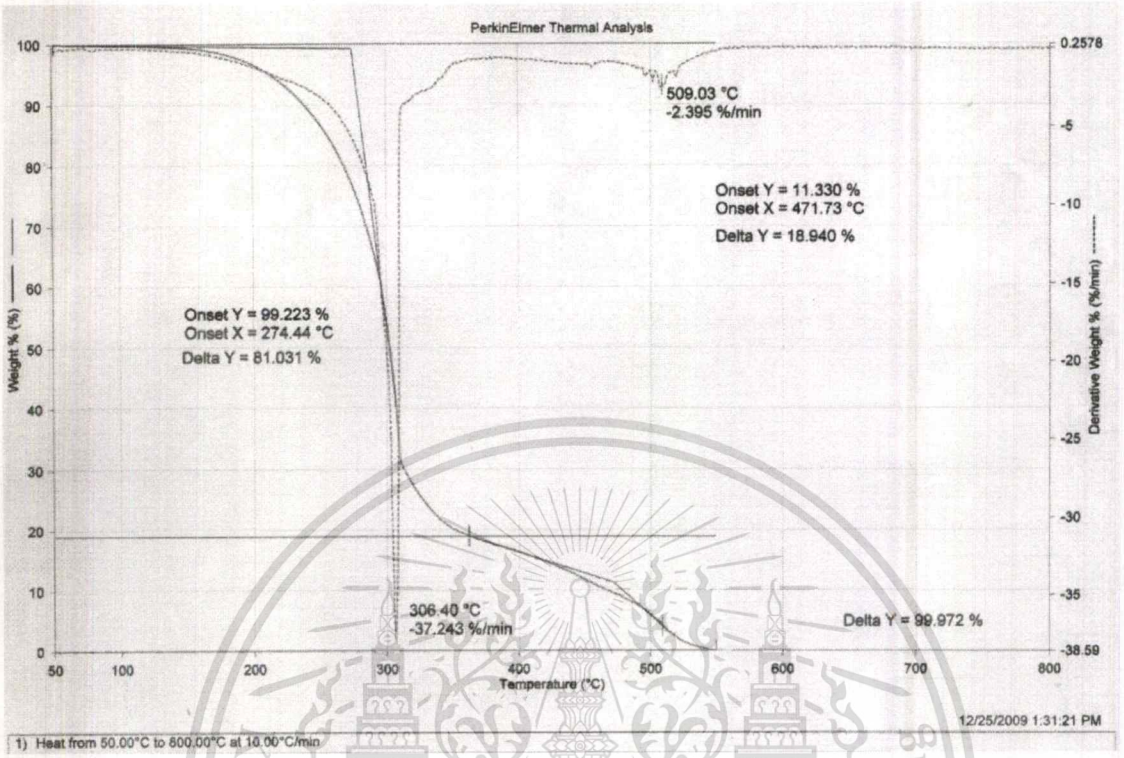


Figure D.18 Show TG curve of extracted solid and residue of $CeZrO_2$ 2:1 at 450°C



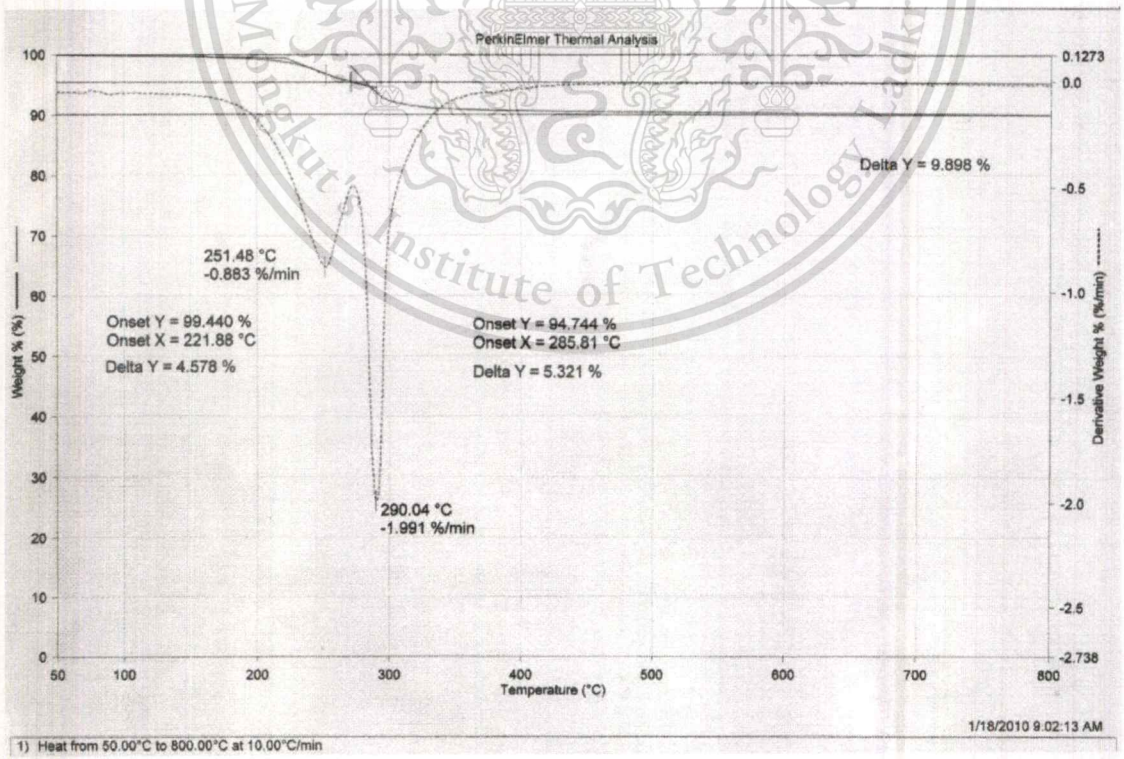


Figure D.19 Show spectrum of extracted solid of ZrO_2 1:1 and 2:1 at 350°C

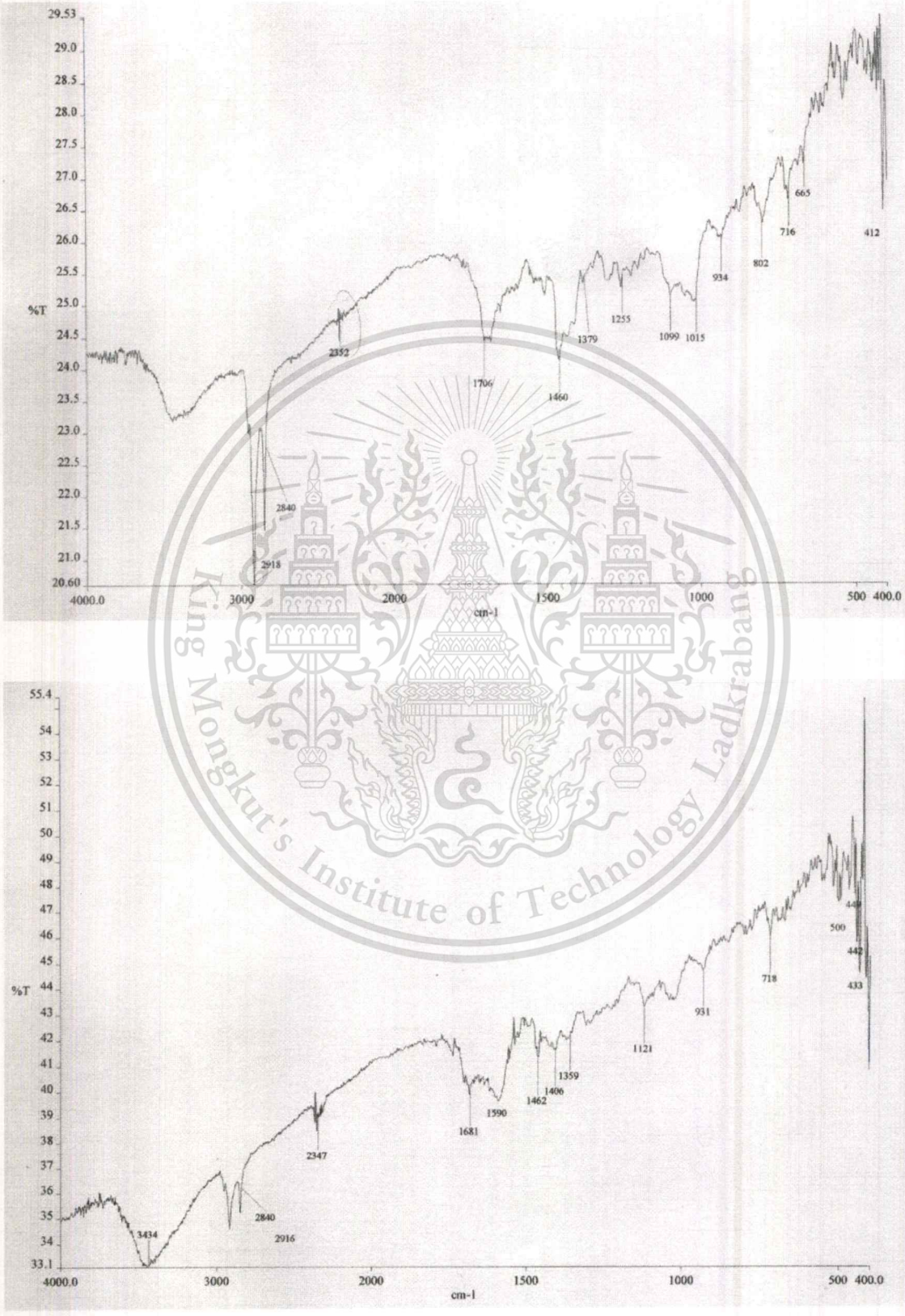
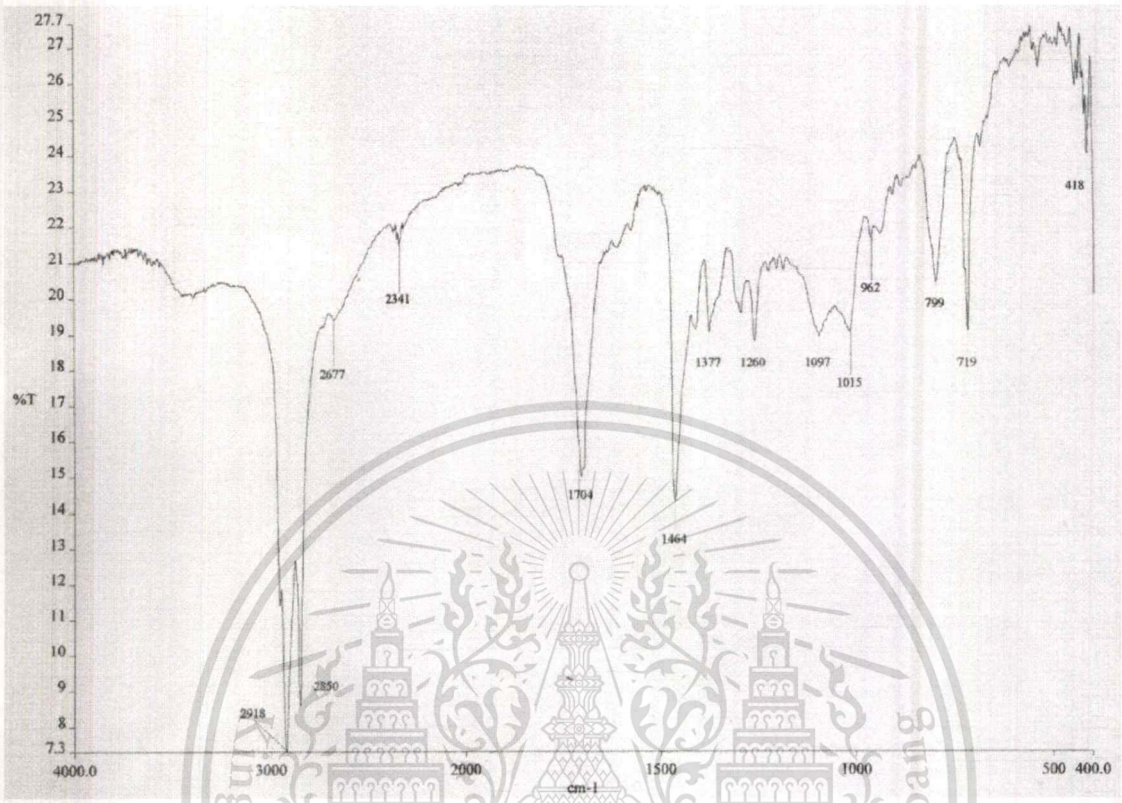


Figure D.20 Show spectrum of extracted solid of ZrO_2 1:1 and 2:1 at 400°C



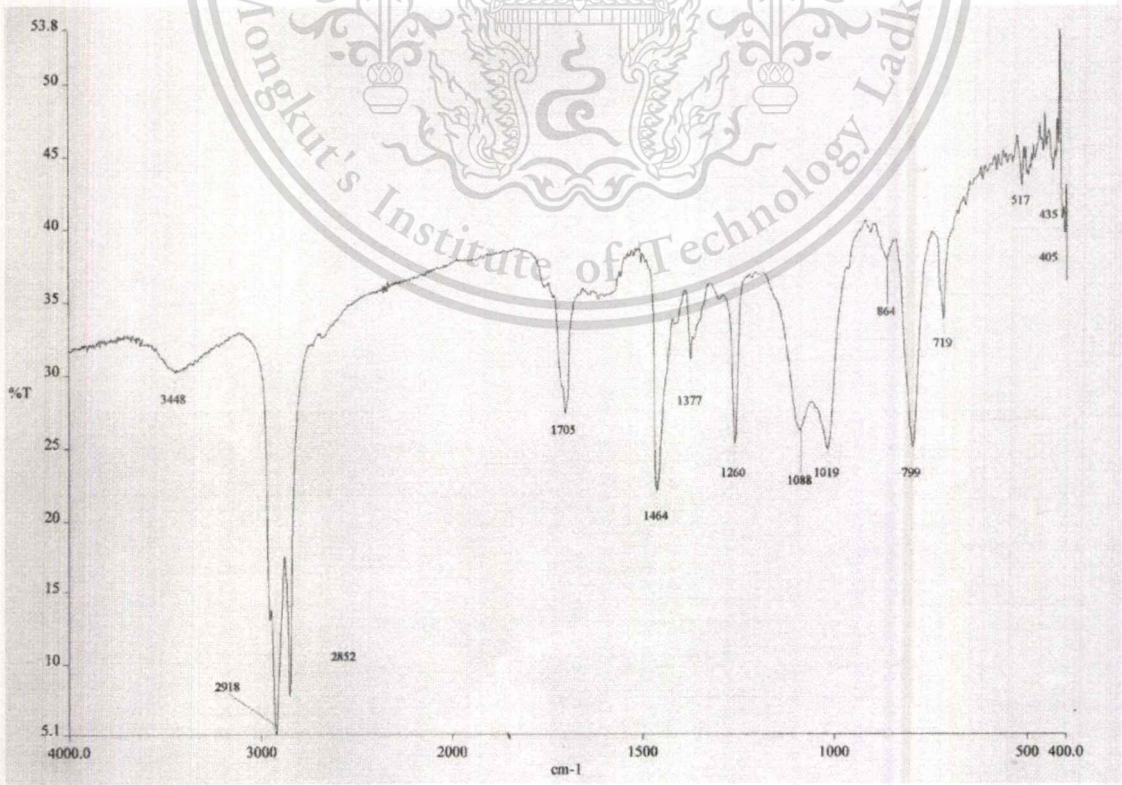
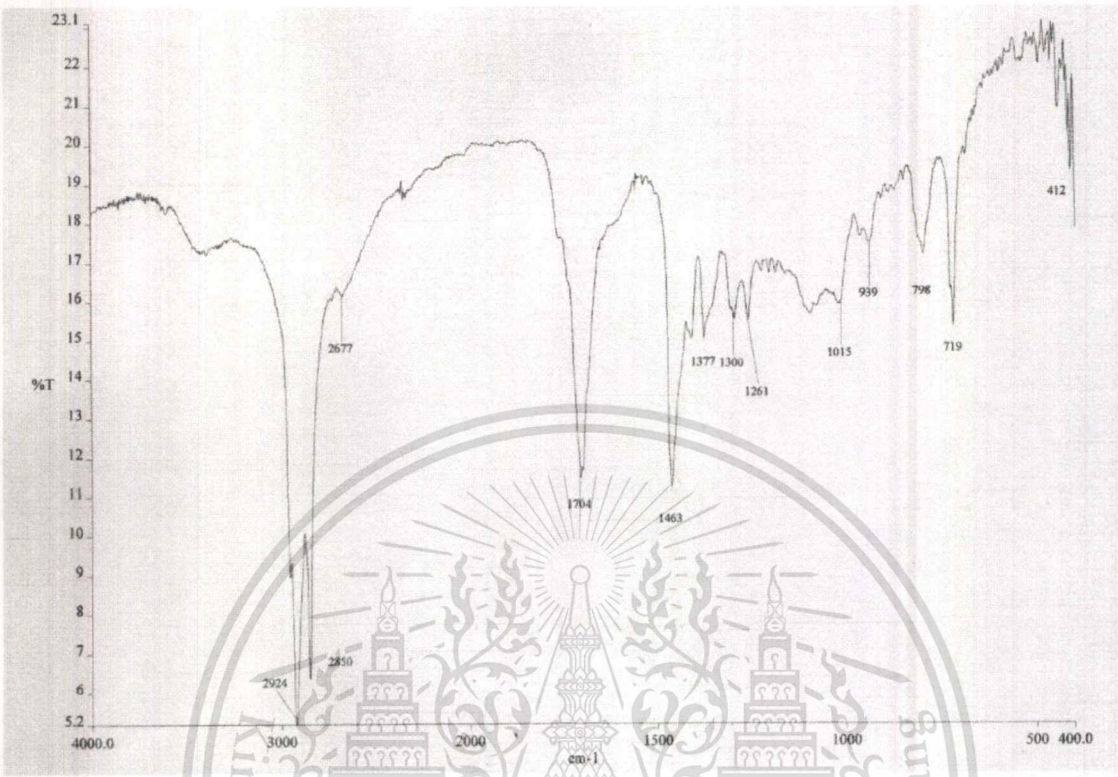


Figure D.21 Show spectrum of extracted solid of ZrO_2 1:1 and 2:1 at 450°C



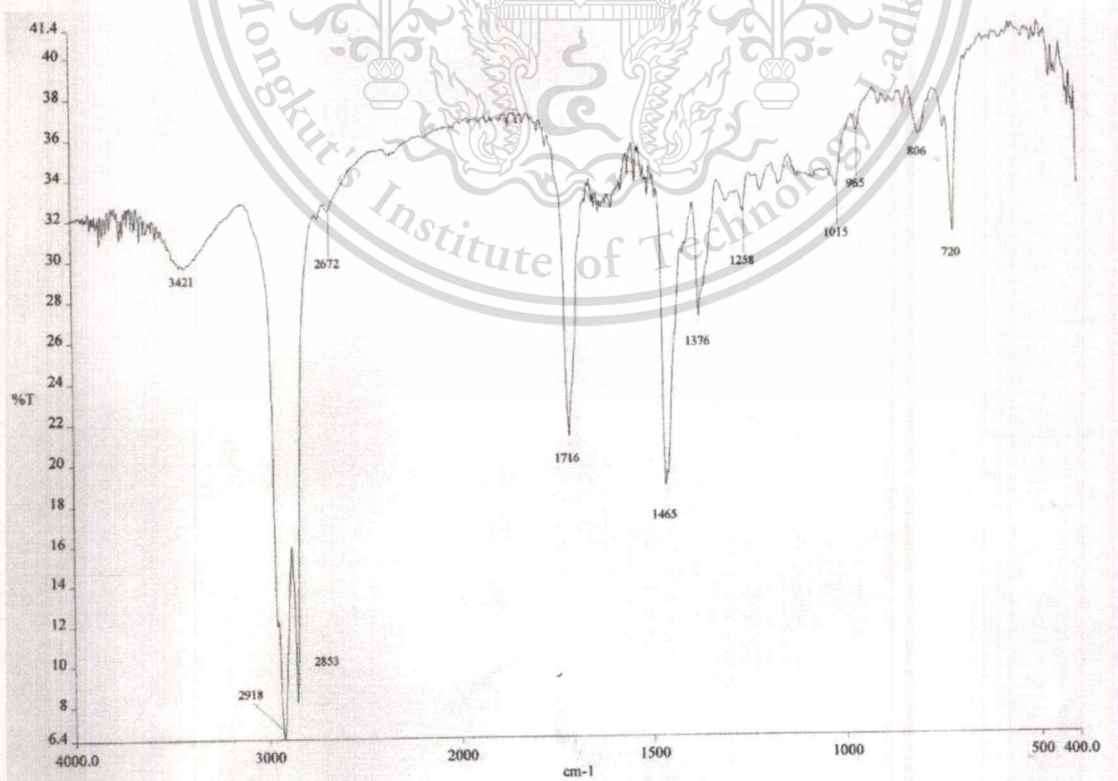
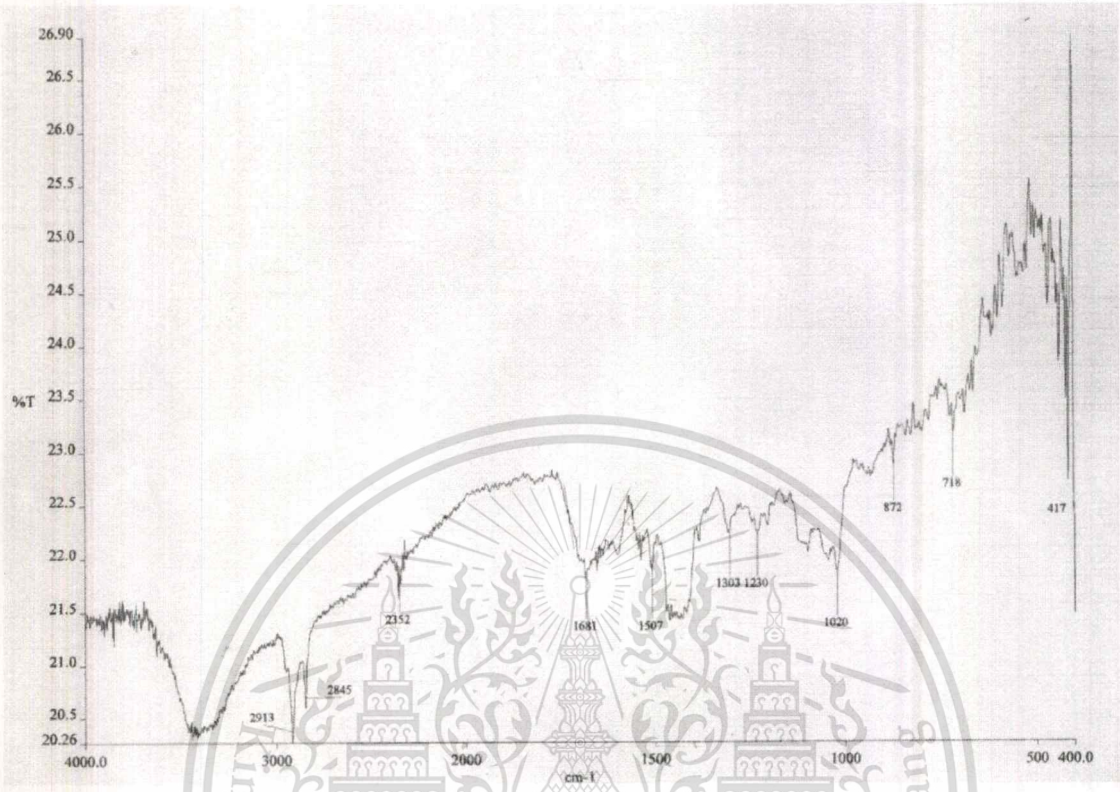


Figure D.22 Show spectrum of extracted solid of CeO_2 1:1 and 2:1 at 350°C



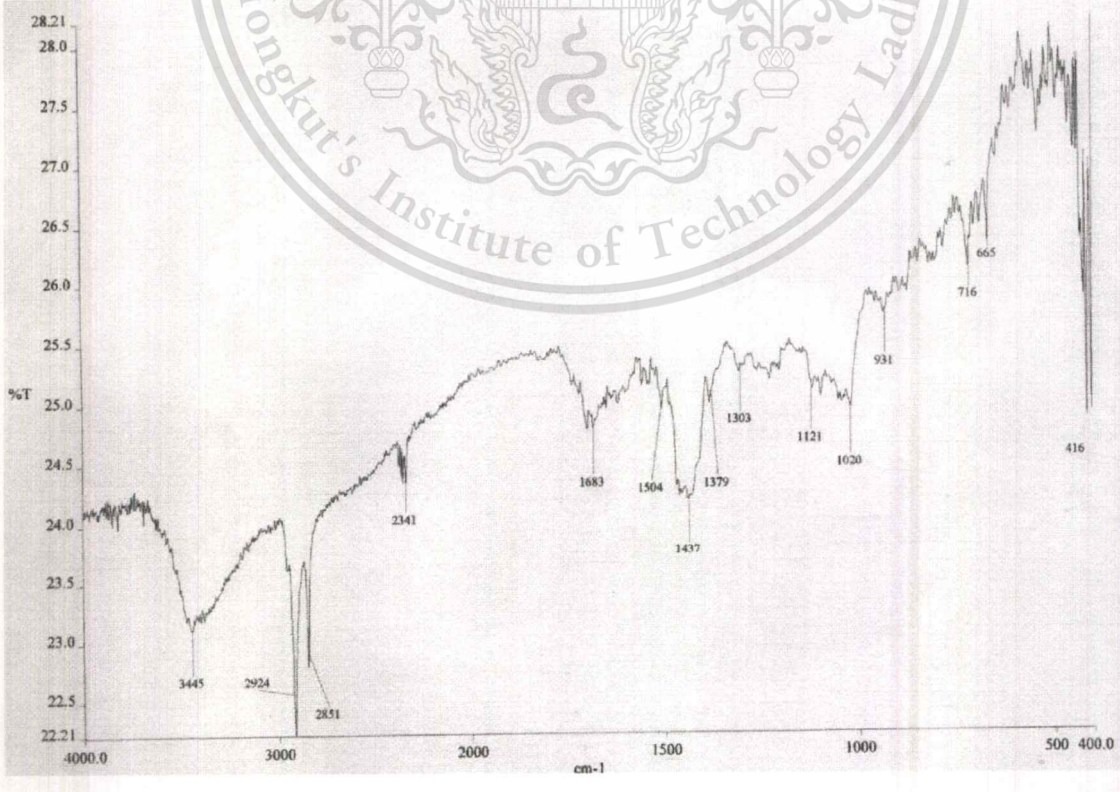
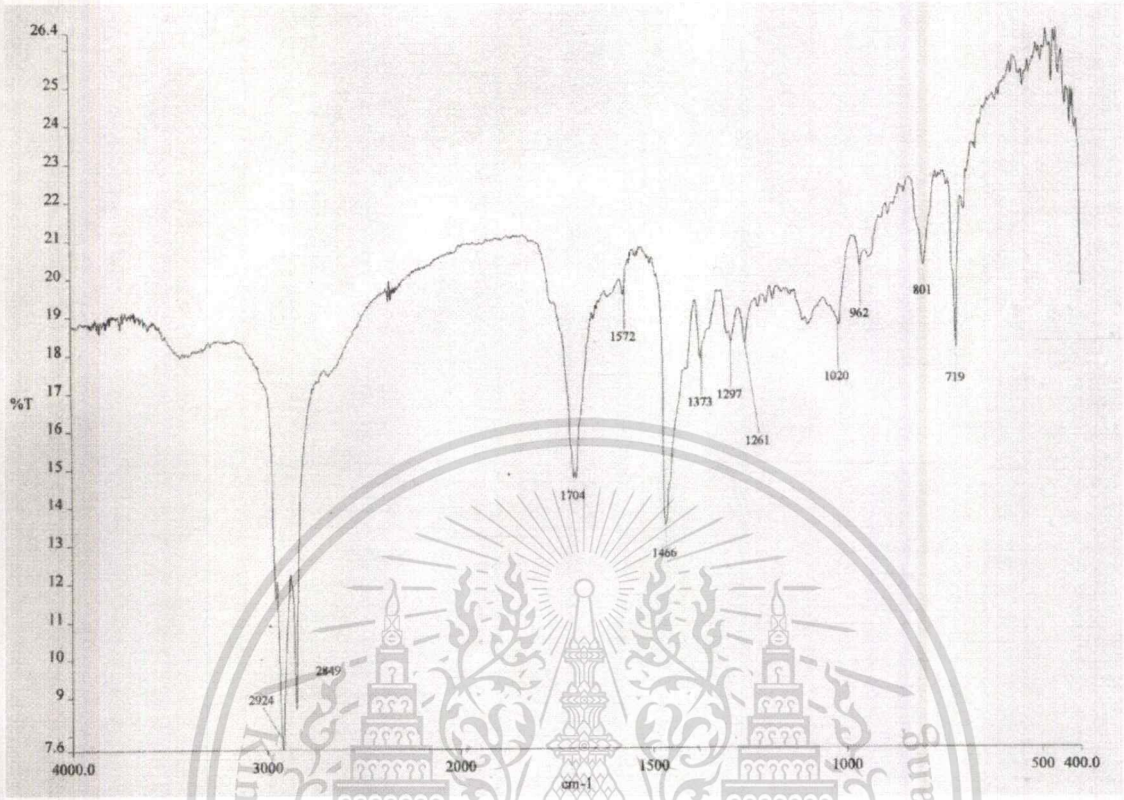


Figure D.23 Show spectrum of extracted solid of CeO_2 1:1 and 2:1 at 400°C



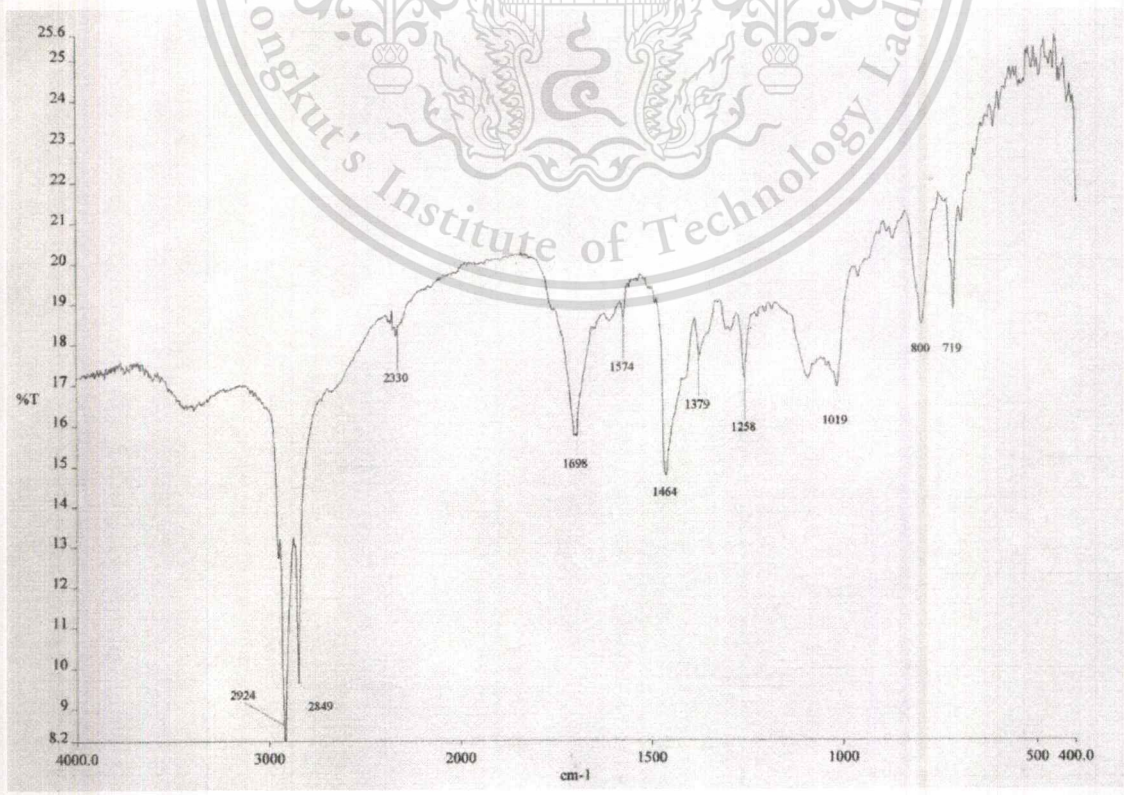
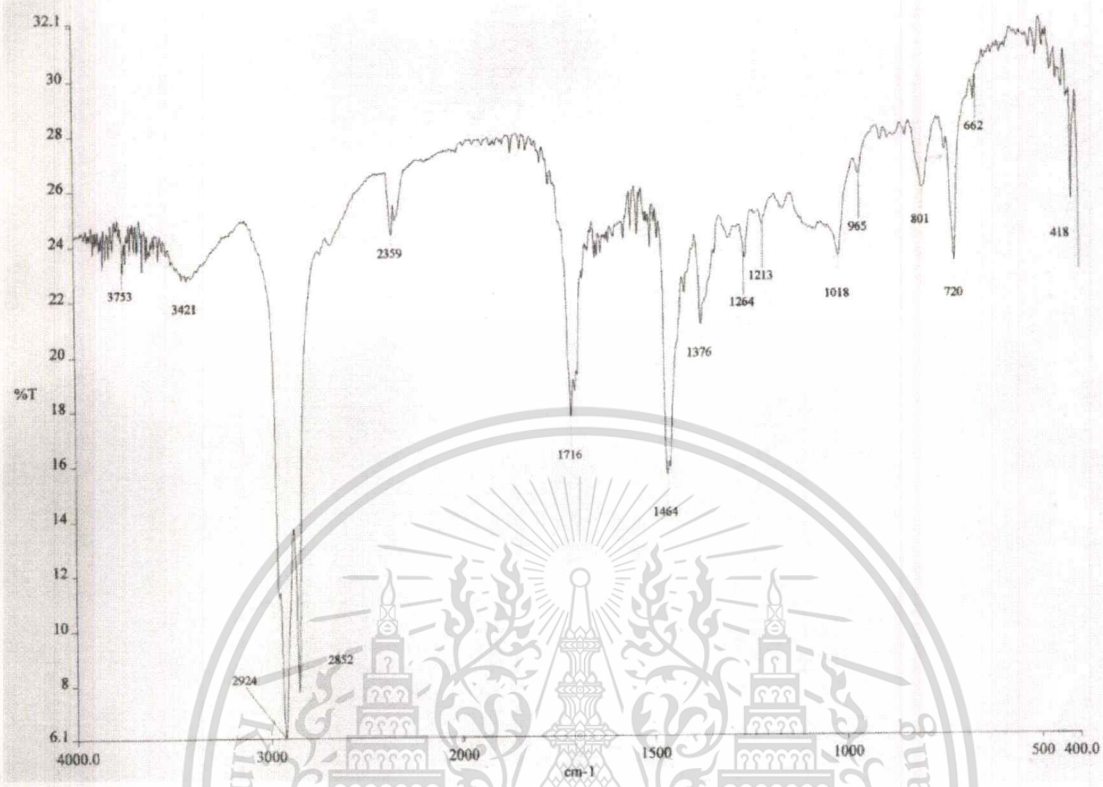


Figure D.24 Show spectrum of extracted solid of CeO_2 1:1 and 2:1 at 450°C



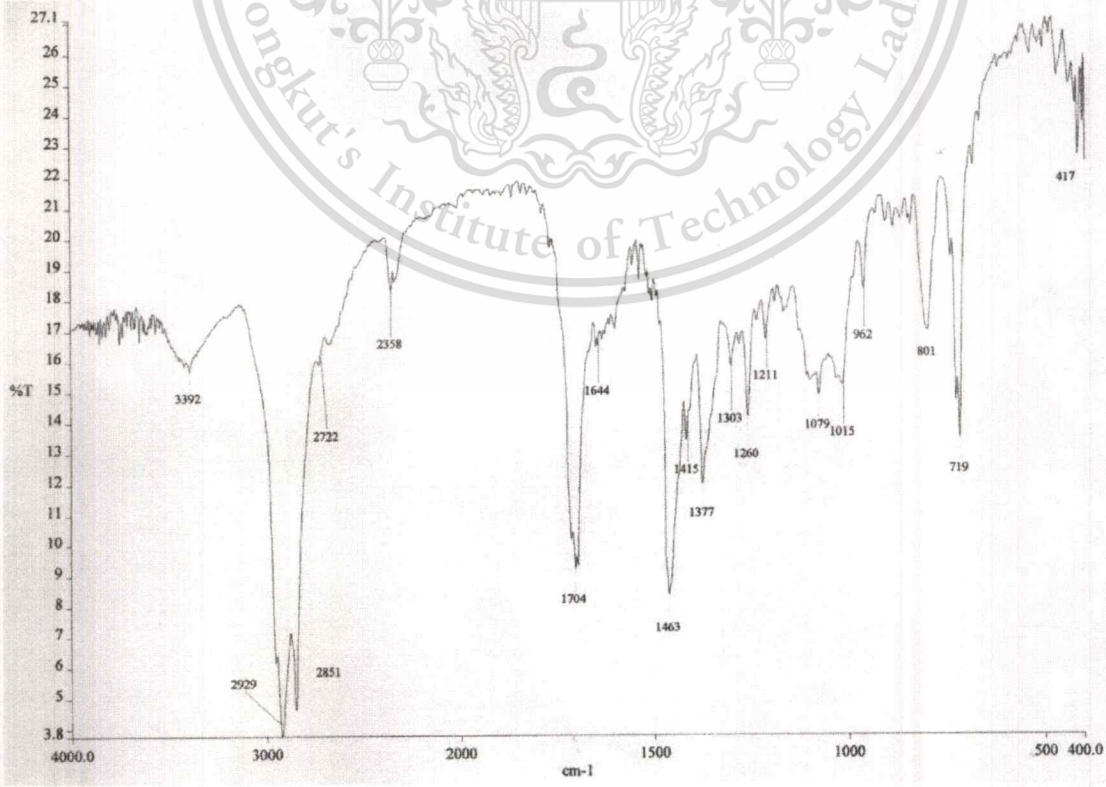


Figure D.25 Show spectrum of extracted solid of $CeZrO_2$ 1:1 and 2:1 at 350°C

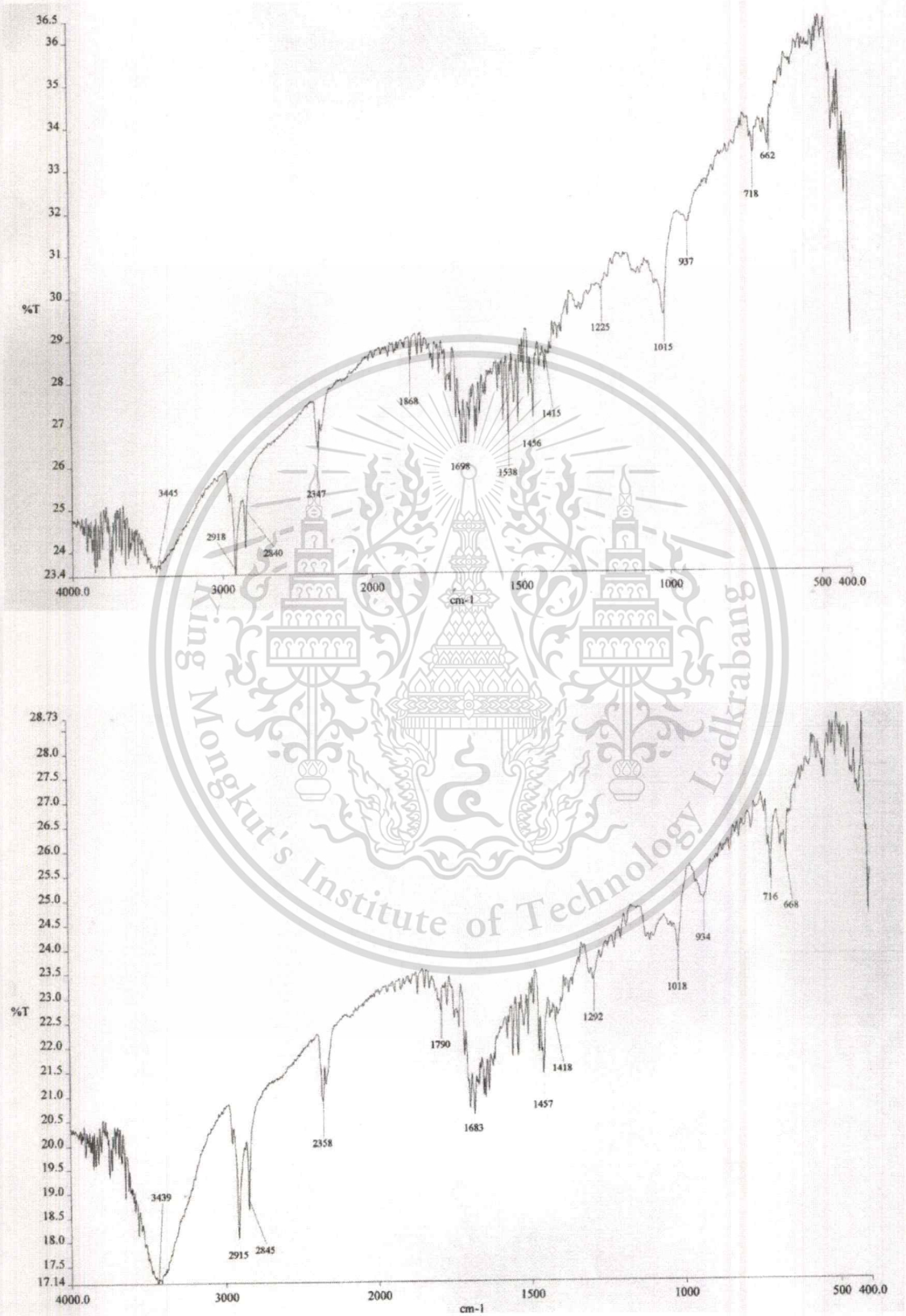
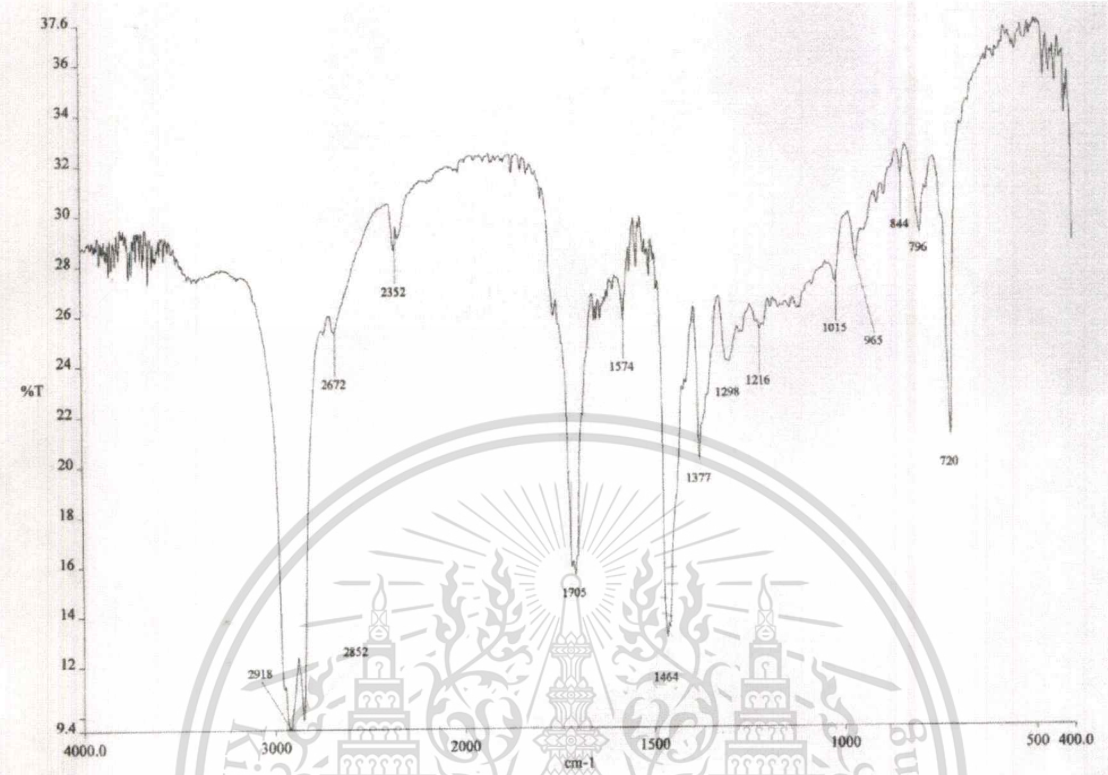


Figure D.26 Show spectrum of extracted solid of $CeZrO_2$ 1:1 and 2:1 at 400°C



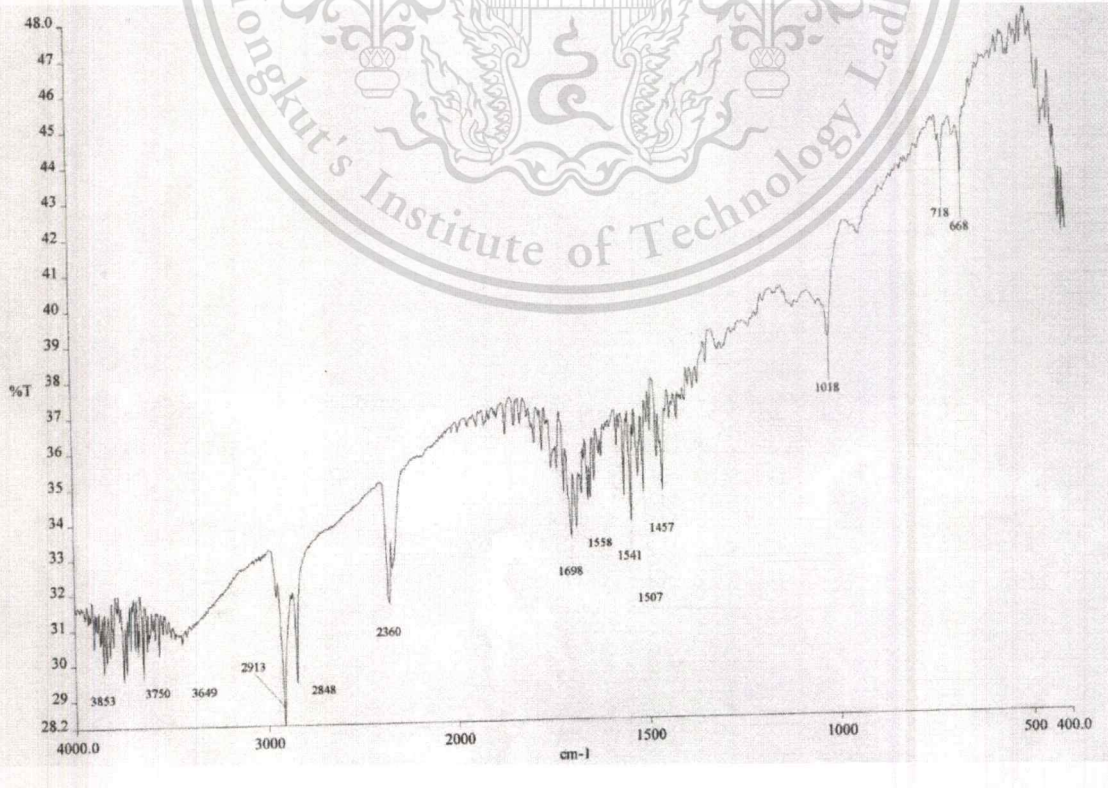


Figure D.27 Show spectrum of extracted solid of $CeZrO_2$ 1:1 and 2:1 at 450°C