PREPARATION AND CHARACTERIZATION OF CATALYST FROM LOCAL INDUSTRY WASTE, RED GYPSUM FOR BIODIESEL SYNTHESIS

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SUPERVISOR'S DECLARATION

I hereby declare that I have read this dissertation and in my opinion this thesis is sufficient in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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STUDENT’S DECLARATION

I declare that this thesis entitled “*Preparation and characterization of catalyst from local industry waste, red gypsum for biodiesel synthesis*” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Dedicated especially to my beloved Mother, Siblings, Lecturers, Friends and the ones who gave me inspiration and support to ensure the success of the research.

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PREPARATION AND CHARACTERIZATION OF CATALYST FROM LOCAL INDUSTRY WASTE, RED GYPSUM FOR BIODIESEL SYNTHESIS

ABSTRACT

Red gypsum, a reddish brown semi-solid mud is a waste product of local industry in Malaysia which is formed during the extraction of titanium (IV) oxide from the ilmenite ores and they are accumulating in landfill and polluting the environment.The total accumulation of red gypsum in Malaysia is at least 340,000 tons per year. This research is done to find an end use for red gypsum waste that has been land filling and polluting the environment. At the same time there is a crucial need to find an alternative fuel in fulfilling energy demand to replace fossil fuels which are undergoing drastic depletion. The best option is biodiesel which shows almost same properties like fossil fuels and most importantly it is environmental friendly. The major composition of red gypsum are CaSO4.2H2O (70 wt %), Fe2O3 (30 wt %) and small amount of Al2O3 is a potential source for catalyst production which later can be used as solid base catalysts in biodiesel production. The objectives of this research are to produce and characterize catalyst from waste red gypsum and study the activity of catalyst for esterification of FFA. Preparation of catalyst from red gypsum through heat treatment in furnace using activated carbon as reducing agent was investigated in this work. Characterization of the catalyst produced is done using X-Ray Diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX) and Field Emission Scanning Electron Microscopy (FESEM). The performance of the activity of the catalyst produced is studied by esterification of oleic acid with ethanol in a 1:6 molar ratio. Different amount of catalyst is used ; 5%,3% and 1% weight catalyst of oleic acid to find the free fatty acid, FFA conversion and the catalyst activity is studied based on the result obtained.

PENYEDIAAN DAN PENCIRIAN PEMANGKIN DARI SISA INDUSTRI TEMPATAN, GIPSUM MERAH UNTUK SINTESIS BIODIESEL

ABSTRAK

Gipsum merah, lumpur separa pepejal bewarna merah, adalah produk sisa industri tempatan di Malaysia yang terbentuk semasa pengekstrakan oksida titanium (IV) dari bijih ilmenit dan mereka terkumpul di tapak pelupusan dan mencemarkan persekitaran.Jumlah pengumpulan gipsum merah di Malaysia adalah sekurang-kurangnya 340,000 tan setahun. Kajian ini dilakukan untuk mencari penggunaan akhir bagi sisa gipsum merah yang telah mengisi tanah dan mencemarkan alam sekitar. Pada masa yang sama, terdapat keperluan penting untuk mencari bahan api alternatif dalam memenuhi permintaan tenaga untuk menggantikan bahan api fosil yang sedang menjalani pengurangan drastik. Pilihan yang terbaik adalah biodiesel yang menunjukkan ciri-ciri yang hampir sama seperti bahan api fosil dan yang paling penting ia adalah mesra alam. Komposisi utama gipsum merah ialah CaSO4.2H2O (70% berat), Fe2O3 (30% berat) dan sedikit Al2O3 dan ia merupakan satu sumber yang berpotensi untuk pengeluaran pemangkin(catalyst) yang kemudiannya boleh digunakan sebagai pemangkin asas yang kukuh dalam pengeluaran biodiesel. Objektif kajian ini adalah untuk menghasilkan dan mencirikan pemangkin dari sisa gipsum merah dan mengkaji aktiviti pemangkin dalam esterifikasi 'Free Fatty Acid' (FFA). Penyediaan pemangkin dari gipsum merah melalui rawatan haba di dalam relau menggunakan karbon diaktifkan sebagai agen penurunan telah disiasat dalam kajian sebelum ini. Pencirian pemangkin dihasilkan dilakukan menggunakan X-Ray Diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX) and Field Emission Scanning Electron Microscopy (FESEM). Prestasi aktiviti pemangkin yang dihasilkan dari gipsum merah dikaji dengan pengesterifikasi asid oleik dengan etanol dalam nisbah molar 1:6. Jumlah mangkin yang berbeza digunakan, 5%, 3% dan berat 1% pemangkin asid oleik untuk mencari konversi FFA dan aktiviti pemangkin dikaji berdasarkan keputusan yang diperolehi.

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^{o}C - Temperature

l - Length

ρ - Density

s - Time (hour)

M - Mega

g - Gram

Wt - Weight Percent

CHAPTER 1

INTRODUCTION

1.1 Background of study

The process of extraction of titanium (IV) oxide from the ilmenite ores, red gypsum is produced as a by-product. Red gypsum, a reddish brown semi-solid mud that is predominantly produced as by-product in this industry have been causing problems such as storing and environmental pollution. The total accumulation of red gypsum in Malaysia is at least 340,000 tons per year. The major composition of red gypsum are $CaSO_4.2H_2O$ (70 wt %), Fe_2O_3 (30 wt %) and small amount of Al_2O_3.

The search for alternatives to energy source basically for petroleum-based fuel has led to the development of biofuels from various sources, including renewable feedstock likely fats and oils. This ‘biofuels’ term refers to liquid, gas and solid fuels predominantly produced from biomass. Biofuels include biodiesel, bioethanol, biomethanol and biohydrogen. According to a study conducted by U.S Department of Energy, production and use of biodiesel, compared to petroleum diesel, resulted in a

78.5% reduction in carbon dioxide emissions. Biodiesel defined as monoalkyl ester of vegetable oils or animal fats. It is an attractive alternative fuel because it is environmental friendly and can be synthesized from edible and non-edible oils. Biodiesel is produced by transesterification in which oil or fat is reacted with a monohydric alcohol in the presence of a catalyst.

Many researches have been carried out on biodiesel production using different oils as the raw material, different alcohols and different catalyst. Recent research has focused on the application of heterogeneous catalysts to produce biodiesel, because of their environmental and economic advantages compared to homogeneous catalysts which cannot be reused and requires tedious washing and separating steps. To date, many solid base catalysts have been developed for biodiesel production, such as basic zeolites, alkaline earth metal oxides and hydrotalcites. Among all the solid base catalysts, calcium oxide, CaO have attracted much attention due to their relatively high basic strength, low solubility in methanol and can be synthesized from cheap sources like limestone and calcium hydroxide.

Investigation of the reductive decomposition of $CaSO_4$ with H_2, C, and CO has been undertaken to generate SO_2 for the production of sulfuric acid as well as the regeneration of lime from sulfated absorbent. However, it was found that the unfavorable product CaS and CaO were formed during the reductive decomposition of $CaSO_4$. Further investigation on reductive decomposition of $CaSO_4$ was carried out under a CO—CO_2 atmosphere and was found proportion of CaO in the products increased as the concentration ratio of CO/CO_2 decreased. Thermal reduction study illustrates that gypsum can be reduced to calcium sulphide, CaS with reducing agents like activated carbon in a tube furnace operating at 1100 ºC. The study showed the addition of carbon to gypsum at 1:1 moles ratio showed that only 13 % of gypsum was converted to CaS while CaO conversion of 38 % is obtained. The percentage conversion results further explain that CaO formation is favored by a carbon ratio used. Red gypsum which mainly contains $CaSO_4.2H_2O$ (70 wt %), Fe_2O_3 (30 wt %) and small amount of Al_2O_3 is a potential source for catalyst production which later can be used as solid base catalysts in biodiesel production.

1.2 Problem Statement

Red gypsum is a waste product of local industry in Malaysia which is formed during the extraction of titanium (IV) oxide from the ilmenite ores and they are accumulating in landfill and polluting the environment. This Accumulation in landfill and emission of harmful gas such as hydrogen sulfide, H_2S (Satoshi Okumura, et. al., 2003). These concerns have increased the effort to find an end use for the red gypsum industrial waste. At the same time there is a crucial need to find an alternative fuel in fulfilling energy demand to replace fossil fuels which are undergoing drastic depletion. The best option is biodiesel which shows almost same properties like fossil fuels and most importantly it is environmental friendly. Red gypsum which mainly contains $CaSO_4.2H_2O$ (70 wt %), Fe_2O_3 (30 wt %) and small amount of Al_2O_3 is a potential source for catalyst production which later can be used as catalyst in biodiesel production.

1.3 Research objectives

To produce and characterize catalyst from local industry waste, red gypsum for biodiesel synthesis

1.4 Scopes of study

For the purpose of achieving the objective, the scopes of studies are stated as below:

I. Study the ways to synthesize catalyst from red gypsum ($CaSO_4.2H_2O$)

II. Choose the best method to prepare catalyst from red gypsum ($CaSO_4.2H_2O$).

III. To characterize the catalyst prepared from red gypsum ($CaSO_4.2H_2O$).

IV. To study the activity of the catalyst prepared by esterification of Free Fatty Acid (FFA) produced from oil.

1.5 Rationale and significance of study

The rationale of this research is to provide empirical evidence that catalyst can be produced or prepared from waste Red Gypsum. The result of this research would signify the performance and efficiency of the catalyst produced in biodiesel synthesis. The identification of this process of preparing catalyst from red gypsum will be one of the steps to reduce the environmental issue cause by this waste.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

There is a crucial need to find end uses for the industrial waste of local industry, red gypsum which is formed during the extraction of titanium (IV) oxide from the ilmenite ores. Red gypsum which mainly contains $CaSO_4.2H_2O$ (70 wt %), Fe_2O_3 (30 wt %) and small amount of Al_2O_3 is a potential source for catalyst production which later can be used as solid base catalysts in biodiesel production. This chapter of literature review comprises of three major themes discussing on red gypsum and reductive decomposition of red gypsum to catalyst, biodiesel and catalyst in biodiesel production.

2.2 Red Gypsum

Many studies have been carried out to find proper end uses for red gypsum which causes problems such as storing and environmental pollution. I. Fauziah, et. al., 1996, investigated on land application of red gypsum because of its potential use as a soil amendment in Malaysia. According to them, red gypsum, a reddish brown semi solid mud, is a waste product from an industrial process which extracts titanium (IV) oxide from the ilmenite ores and it is commonly known as 'red' gypsum because of the iron content of ilmenite. They further explain on the extraction of titanium (IV) oxide from ilmenite by digestion of sulphuric acid and neutralization of the spent acid produces waste product gypsum.

In 2007, Rose Aini Kamarudin and Mohd. Shahir Zakaria carried out a research to utilize the red gypsum in production of glaze. They found out that the total accumulation of red gypsum in Malaysia is at least 340,000 tons per year after having personal communications with the local industry. Their examination on red gypsum waste composition revealed that it major composition are CaSO4.2H2O (70 wt %), Fe2O3 (30 wt %) and small amount of Al2O3 which can form a glassy phase after sintering. It was found that the addition of up to 36 % of the RG waste was possible in the production of glazes.

2.2.1 Reductive Decomposition of Red Gypsum to Calcium Oxide, CaO

Waste gypsum has been a major problem as it is causing storage issue due to the shortage of landfill sites. In order to achieve a sustainable and greening the environment, recycling and utilization of Ca-based solid waste is considered as a promising undertaking in proper management of waste gypsum. Investigations on reductive decomposition of $CaSO_4$ in CO atmosphere have been actively conducted by many researches in this several decades. Hull et et al., 1957, investigated the reductive decompostion of CaSO4 depended on the reaction temperature as well as CO and CO2 concentrations. Wheelock et al., 1960, Gruncharov et al., 1985, and Kuusik et al., 1985, found that the proportion of CaO in the products increased as the concentration ratio of CO/CO2 decreased in their respectives study on for the reductive decomposition of CaSO4 in a CO-CO2 atmosphere. In addition Wheelock et al., 1986 stated that CaO and CaS generated by CaSO4 decomposition via Equation (2.1) and (2.2),

$$CaSO_4 + CO \longrightarrow CaO + SO_2 + CO_2 \quad (2.1)$$

$$CaSO_4 + 4CO \longrightarrow CaS + 4CO_2 \quad (2.2)$$

Gruncharov et al., 1985, further reported on the strong effects of admixtures of Fe_2O_3, SiO_2 and $Al2O_3$ on the kinetics decomposition of $CaSO_4$. Meanwhile, Chen and Yang, 1979, stated that there are two consecutive steps in the regeneration of CaO from $CaSO_4$ proceeded through equation (2) and (3). They added that the reaction of $CaSO_4$ with CaS expressed by equation (2.3) was the rate-determining step at relatively low temperatures. Years after, Oh JS and Wheelock TD (1990) further explain a two-step mechanism of $CaSO_4$ decomposition by proposing equation (2.4) and (2.5) assuming the presence of intermediate product $CaSO_3$.

$$CaS + 3CaSO4 \longrightarrow 4CaO + 4SO2 \qquad (2.3)$$

$$CaSO4 + CO \longrightarrow CaSO3 + CO2 \qquad (2.4)$$

$$CaSO3 \longrightarrow CaO + SO2 \qquad (2.5)$$

In 2003, Satoshi Okumura et al., studied the recovery of CaO by reductive decomposition of spent gypsum in a $CO\text{-}CO_2\text{-}N_2$ atmosphere. This study was crucial as large amount of waste gypsum were discarded in Japan causing environmental problem due to the emission of harmful gas such as H_2S from waste gypsum from landfill sites. Initially, the investigation on the reductive decomposition of $CaSO_4$ with H_2, C, and CO is to generate SO_2 for the production of sulfuric acid and to generate lime from the sulfated absorbent. Satoshi Okumura et al., (2003), used a packed-bed reactor to regenerate an alternative CaO sorbent. Various process conditions were used to operate the reactor including an increasing CO concentration, CO/CO_2 concentration ratio (0.067-1), and temperature (1123- 1273 K) which in all cases N_2 was used as a balancing gas. The $CO\text{-}CO_2\text{-}N_2$ atmosphere found to be most effective for the regeneration of CaO from $CaSO_4$ and influenced by the CO/CO2 concentration ratio. On the other hand, in a $CO\text{-}N_2$ atmosphere, CaS was predominantly produced confirming Wheelock et al., 1960, stated that the ratio of unfavorable product CaS to CaO depended on the reaction temperature as well as CO and CO2 concentrations. They added that, the SO_2 absorption capacity of CaO regenerated from CaSO4 was higher than that of limestone-calcined CaO and larger pore diameter of the regenerated CaO was considered to be responsible for the higher SO_2 absorptivity. Satoshi Okumura et al., 2003, pointed out several equations to illustrate the reactions of the reductive decomposition of $CaSO_4$ with CO.

$$CaSO_4 + CO \longrightarrow CaO + SO_2 + CO_2 \qquad (2.6)$$

$$CaSO_4 + 4CO \longrightarrow CaS + 4CO_2 \qquad (2.7)$$

$$CaSO_4 \longrightarrow CaO + SO_3 \qquad (2.8)$$

$$CaS + 3SO_3 \longrightarrow CaO + 4SO_2 \qquad (2.9)$$

$$CaSO_4 \longrightarrow CaO + SO_2 + 1/2O_2 \qquad (2.10)$$

$$CaSO_4 + 1/3CaS \longrightarrow 4/3CaO + 4/3SO_2 \qquad (2.11)$$

$$CaSO4 + CO \longrightarrow CaSO_3 + CO_2 \qquad (2.12)$$

$$CaSO_3 \longrightarrow CaO + SO_2 \qquad (2.13)$$

2.2.2 Reductive Decomposition of Red Gypsum to Calcium Sulphide, CaS

In 2009 *N.R. Mbhele* et al., done a research in a respond to gypsum waste disposal sites which are the main reason for the leaching of saline water into surface and underground water and create airborne dust. They mentioned gypsum waste is not only an environmental problem but has measurable economic value in which valuable/saleable byproducts like sulphur and calcium carbonate be recovered from the low quality gypsum. A research in the process for converting waste gypsum into sulphur is done in which the process evaluated consists of the following stages: reduction of gypsum to calcium sulphide; stripping of the sulphide with CO_2 gas and the production of sulphur. Thermal reduction study showed that gypsum can be reduced to calcium sulphide, CaS with activated carbon in a tube furnace operating at 1100 ºC. Their studies shows that reducing agents like coal and activated carbon can be used to reduce gypsum to CaS in a furnace. Based on the study we know that the addition of carbon to gypsum at 1:1 moles ratio showed that only 13 % of gypsum was converted to CaS while CaO conversion of 38 % is obtained. The percentage conversion results further showed that CaO formation is favoured by a carbon. In another research Hongjing Tian et al., 2010, shows that the mole fraction of CaS is higher than CaO when the reacting temperature is below 1000 °C and that the direct reductive products after the reduction of $CaSO_4$ were merely CaO in the temperature range from 900 to 1180 °C.

2.3 Biodiesel

The search for alternatives to energy source basically for petroleum-based fuel has led to the development of biofuels from various sources, including renewable feedstock likely fats and oils. This ‘biofuels’ term refers to liquid, gas and solid fuels predominantly produced from biomass. Biofuels include biodiesel, bioethanol, biomethanol and biohydrogen. Biodiesel defined as monoalkyl ester of vegetable oils or animal fats. It is an attractive alternative fuel because it is environmental friendly and can be synthesized from edible and non-edible oils.

According to N.N.A.N. Yusuf, S.K. Kamarudin et al., 2010, biodiesel is the monoalkyl esters of vegetable oils or animal fats which is an attractive alternative fuel because of its environmental friendly characteristic and can be predominantly produced from both edible and non-edible oils. Biodiesel primarily produced from food crops which are mostly oil seeds (Teresa M. Mata et. al., 2009). Gui et. al., 2008 stated that 95% of the world biodiesel production is from edible oils which are easily available on large scale from the agricultural industry. This agricultural industry supplies conventionally grown edible oils such as rapeseed, soybean, sunflower and palm for biodiesel production, thus lead to food versus fuel issues (Mustafa Balat, 2010).

Teresa et al., 2009, stipulates on development of second generation biodiesel which is produced from non-edible oils is highly concerned as the first generation biodiesel, primarily produced from edible oils have limited ability to achieve targets for biodiesel production. They added, biodiesel which is produced from non-food feedstock have high potential in offering utmost opportunities in a longer term. Improper planning in continuous and large scale production of biodiesel from edible oils may have negative impact to the world, for instance depletion of food source consequently lead to economic crisis (Gui et. al., 2008).

2.3.1 Production of biodiesel from edible oils

Previous study on biodiesel production from edble oils were done by many researchers. Among those, Rathore (2007) studied the synthesis of biodiesel from edible oils such as palm oil and groundnut oil and also from crude non-edible oils which are Pongamia pinnata and Jatropha curcas. The oils were investigated in supercritical methanol and ethanol without using any catalyst.

Biodiesel fuel (BDF) is said to be the alternative of diesel fuel with promising future. Currently, palm oil in southeastern Asia, edible oil such as soybean oil in USA and rapeseed oil in Europe has been used to produce biodiesel (Azam et al., 2005). However, the rise in both cost and demand for edible oils makes it difficult to be used in production of BDF. In addition, in numerous countries, government does not encourage research done on biodiesel production from edible oils. Therefore, waste vegetable oil, non-edible oils and animal fats such as salmon oil, beef tallow, poultry fat, and greases are seen as future promising alternative feedstocks production of biodiesel. The search for other low cost feedstock is also in demand nowadays (Guana and Kusakabe, 2012).

2.3.2 Production of biodiesel from non-edible oils

Gui et. al. (2008) production of second generation biodiesel from non-edible oils is highly concerned with high free fatty acid (FFA) content which has caused conventional transesterification reaction especially the alkaline-catalyzed process not feasible. They added that the reaction between the FFA with alkaline catalyst produces soap thus inhibit the separation of ester and glycerin. They mentioned that the best method to extract biodiesel from non-edible oils as suggested by several researchers is a two-step transesterification process.

A further explanation by them is specifically on the two steps process which starts with the initial step of reduction of the FFA content in the oil by acid-catalyzed esterification process followed by the second step where the oil and methanol is converted to methyl ester and glycerol in an alkaline-catalyzed process. Even though the disadvantage of this process is the high production cost as pointed out by Gui et. al., 2008 meanwhile Saka S., 2005, stressed on the advantage in which this two step process was found to be highly effective as the yield of biodiesel in the overall process reaching up to above 90%.

With regard to Ritesh Kumar et. al., 2011, study there are five parts in this microwave assisted transesterification process which are the chemicals, extraction of oil, microwave assisted transesterification itself, separation and purification of biodiesel, ester content and fuel properties of biodiesel. First, the chemical used in the experiment were analytical reagent grade and were used without purification and the rubber seed oil was extracted using a mechanical oil expeller which later on filtered and kept in an air tight container undisturbed for three to four days for the suspended particles to settle.

Microwave assisted transesterification carried out using two alkali catalysts namely sodium hydroxide(NaOH) and potassium hydroxide(KOH) where the reaction was timed as soon as the desired transesterification temperature (60°C) was achieved. Next the reaction was continue for few different times, suggested 3, 5, 7 and 10 minute in which for each reaction the experiment was repeated for four times and their average value was obtained. Separation and purification of biodiesel undergo few processes in which the first process is capturing the reaction by immersing the glass reactor in an ice bath and as the reaction stopped, the product was kept in separating funnel over night for separating biodiesel and glycerol. The next part was calculation of biodiesel yield relative to the initial amount rubber seed oil by weight the biodiesel purity was determined according to the relative methyl ester content obtained by gas chromatography (GC) analysis. (GC) analysis is done to determine the amounts of products (Yang et al., 2011) and using equation as below:

$$\text{Yield} = \frac{Actual\ \ amount\ \ of\ biodiesel\ (g)}{Theoretical\ \ amount\ \ of\ biodiesel\ (g)} \times 100(\%) \tag{2.14}$$

Finally ester content and fuel properties of biodiesel were determined using ASTM (D6751) standards as shown in Table 3.2. The experimental results indicates that the transesterification of rubber seed oil can be done in 5 to 10 minutes, as compared to conventional heating where approximately 3 hours is required for the reaction. Thus use of microwave will help in considerable time and cost saving (Ritesh Kumar et. al., 2011).

Parameters	Palm oil	ASTM standard for 100% biodiesel	German biodiesel standard DIN V51606
Viscosity(Cst)	-	1.9 - 6.0(40°C)	3.5-5.0(40°C)
Acid value (mgKOH/gm)	-	0.80 max	0.5
Flash point (°C)	-	130 min	100 min
Sulfated ash (wt%)	-	0.020 max	0.01

Table 2.1 Fuel parameters of Palm Oil, ASTM[a] and German Biodiesel standard[a]

2.3.3 Esterification

Esterification process occurs between carboxylic acids found in vegetable oils with methanol or ethanol. This reaction produces esters and water and is a method commonly applied in production of biofuel (Nascimento et al, 2011). Conversions of fatty acids to esters are usually done by reaction using an acid catalyst (Scrimgeour, 2005). In current transportation sector, esterification is seen as a promising way to convert free fatty acids (FFA) into Fatty Acid Ethyl Ester (FAEE). FAEE, in addition, is an alternative currently used as energy source to replace fossil fuel in the factor (Lopez et al., 2008).

According to Oliveira (2010), a wide reserve of vegetable oils, ethanol, low-priced lipid feedstock and even waste are some of the promising resources which can utilized as reagents in a more environmental friendly, industrially and cheaper approach. Among these choices, ethanol is preferable as it has low toxicity compared to methanol, butanol, few other larger chain alcohols and even methanol. High-grade biodiesel could be obtained by esterification of oleic acid, which is one of the fatty acids component of the triglycerides of vegetable oils with short chain aliphatic alcohols (methanol or ethanol) (Zong et al., 2007).

There are two methods in which esterification process can be performed, which is batch reaction and continuous reaction by using packed bed reactor. Powder-type catalyst is being used in batch reaction, as powdered form possess higher surface area as compared to pellet-type catalyst. On the other hand, pellet type catalyst is preferable for packed bed reactor. This is due to the possibility of catalyst being lost and pressure drop while using the powder-type catalyst. Although continuous reaction is highly beneficial in mass production, conversion of FFA is found could be minimal compared to batch reaction. Hence, to maximize the catalyst activity and conversion of FFA, optimization of pellet-size catalyst together with batch reaction is crucial (Park et al., 2008).

2.4 Catalyst in biodiesel production

In early years, homogeneous catalyst was used widely because of several reasons; able to catalyze reaction at low reaction temperature and atmospheric pressure, high conversion can be achieved in a minimal time and widely available and economical (Lotero et al., 2005). Currently, researchers have shifted their focus to heterogeneous-catalyzed transesterification as the homogeneous catalyzed transesterification consumes more energy and requires a costly product separation process (Z. Helwani et al., 2009). According to Fukuda et al., 2001, Kulkarni and Dalai, 2006, the rate for base-catalyzed reaction would be 4000 times faster compared to acidic catalyst but the use of this catalyst is limited only for refined vegetable oil with less than 0.5 wt. % free fatty acid (FFA), (Wang et al., 2006) or acid value less than 1 mg KOH/g (Felizardo et al., 2006). Nag, 2008, Yan et al., 2009, Kulkarni and Dalai, 2006, states that, if an oil or fat containing high FFA content homogeneous catalyst will react typically with FFA to form soap consequently deactivate the catalyst from accelerating the transesterification reaction. They added that, excessive soap in the products can drastically reduce the fatty acid methyl ester (FAME) yield and inhibit the subsequent purification process of biodiesel, including glycerol separation and water washing.

2.4.1 CaO as Catalyst in Biodiesel Production

To date, many solid base catalysts have been developed for biodiesel production, such as basic zeolites, alkaline earth metal oxides and hydrotalcites. On top of that, alkaline earth metal oxides especially calcium oxide, CaO have attracted much attention due to their relatively high basic strength, low solubility in methanol and can be synthesized from cheap sources like limestone and calcium hydroxide (Zabeti et al., 2009). Kouzu et al. (2008a) reported that CaO obtained from calcinations of pulverized limestone, CaCO3 at 900 °C for 1.5 h in the flow of helium gas exhibited substantially good result in transesterification of refined soybean oil.

The yield of FAME was 93% after 1 hour reaction time at methanol reflux temperature andmethanol to oil ratio 12:1. A portion of the catalyst changed into calcium soap by reacting with the FFAs adsorbed, resulting in low recovery of catalyst. Kouzu et al., further reported that the concentration of Ca in reaction product was 3065 ppm which exceeded the basic standard of biodiesel, the concentration of mineral matter should be below 200 ppm (Kouzu et al., 2008a).

In addition, some researchers also pointed out that soluble substance from CaO can leached out during transesterification. Gryglewicz (1999) stated in his paper that calcium oxide slightly dissolves in methanol. Lopez et al. conducted transesterification of sunflower oil with methanol in which a slight amount of calcium oxide was found to dissolved in the reaction product (Granados et al., 2007). Kouzu et al. (2008b) further identified the soluble substance as calcium diglyceroxide in which CaO reacted with glycerol during transesterification of soybean oil with methanol. Thus, an extra purification step is needed such as ion-exchange resin to remove the soluble content in the biodiesel (Kouzu et al., 2009).

Apart from that, Granados et al. (2007) used activated CaO as a solid base catalyst in the transesterification of sunflower oil to investigate the role of water and carbon dioxide on the deterioration of the catalytic performance upon contact with air for different period of time. The study showed that CaO was rapidly hydrated andcarbonated in the air. It was further reported that the active sites of CaO were poisoned due to chemisorption of carbon dioxide and water on the surface sites to form carbonates and hydroxyl groups, respectively. However, the catalytic activity of CaO can be regenerated if CaO is subjected to an activation treatment at 700 °C in order to remove the main poisoning species (the carbonate groups) from the surface. However, leaching of the catalyst was still observed in the transesterification reaction although prior thermal treatment was employed.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

The purpose of this chapter is to state the materials that will be used in this experiment and describe the process flow of the project and how it will be conducted. Specifically the process flow starts with red gypsum itself, in which it is obtained followed by the preparation and characterization of the catalyst generated from it. Finally, the catalyst activity in esterification process is studied.

3.2 Material

3.2.1 Reagents and Raw Materials

Red gypsum, Activated carbon Ethanol, Oleic acid, Phenolphthalein, Sodium Hydroxide(NaOH).

3.2.2 Equipments

X-Ray Diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX), Field Emission Scanning Electron Microscopy (FESEM), Centrifuge, Glass Furnace, Hot plate, Weighing machine, Three neck round bottom flask, Volumetric flask, Mortar and pestle, Crucibles, Beaker, Vials, Magnetic stirrer, Thermometer, Burette, Pipette, Scott bottle, Centrifuge container, Micro pipette, Aluminium foil, Dropper, Conical flask.

3.3 Procedures

3.3.1 Preparation of catalyst from Red Gypsum

Red gypsum obtained from local industry was used in this research. A batch of activated charcoal and red gypsum were ground using pestle and mortar. In detail, 5 g of red gypsum (RG) and 5 g of activated charcoal was initially crushed and mixed using few drops of deionized water. The prepared batch was then placed in 4 crucibles to maximize the surface area. All the crucibles were then placed in furnace to undergo heat treatment for an hour at a temperature 200°C. The catalyst produced from the process is stored in vials then characterizes using XRD. Finally the steps were repeated for glass furnace at various temperatures of 400 ºC (1 hour), 800 ºC (2 hours) and 1050 ºC (5 hours) as shown in Table 3.1.

Sample	Temperature, ºC	Duration, hour
A	200	1
B	400	1
C	800	2
D	1050	5

Table 3.1 Sample preparation of catalyst

3.3.2 Esterification

The mole ratio of ethanol/oleic acid used in this research was 6:1. Initially 20 g of oleic acid was weighed on a weighing machine. Based on the 20 g of ethanol with 99% purity was weighed. Face mask and glove were worn throughout the process to ensure safety. 1% catalyst weight of 20g oleic acid which was 1g of the catalyst prepared from red gypsum earlier is weighed. A three neck flask was set up with a condenser and a magnetic stirrer. Oleic acid was then poured into the three neck flask. The catalyst was added into the flask as the temperature reached 50 ºC followed by ethanol at 70 ºC and this marked the time when the reaction started. The reaction temperature was maintained 70-75 ºC. In order to obtain the initial FFA value of oleic acid and ethanol, 1ml of the solution was pipetted out from the three neck flask and titration was done using 0.1M of sodium hydroxide solution. The initial FFA value was calculated using equation (3.1), with M is the molarity of NaOH used , V is the volume of NaOH used to titrate the solution, Mw is the molecular weight of oleic acid (282.46g/mol) and W is the weight of sample used.

$$\text{Initial FFA value, Ai}= \frac{\mathrm{M}\times\mathrm{V}\times\mathrm{Mw}}{W} \tag{3.1}$$

After 1 hour the sample 3ml of the solution was pipetted out and placed in centrifuge container and centrifuged for 5 min at 10000rpm. Then 1ml of the sample was titrated and FFA value at time t, is calculated using the same formula. Next FFA conversion was calculated using the equation:

$$\mathrm{x}_{\mathrm{ffa}} = \frac{Ai-At}{Ai} \tag{3.2}$$

The result was then tabulated and sample was continuously taken for time interval 2 hour, 3 hour, 4 hour 5 hour and 6 hour. Steps 1- 11 was repeated twice excluding step 4 in which % weight catalyst used is increased to 3% and 5% respectively. The final product was collected and stored in Scott bottle for future use.

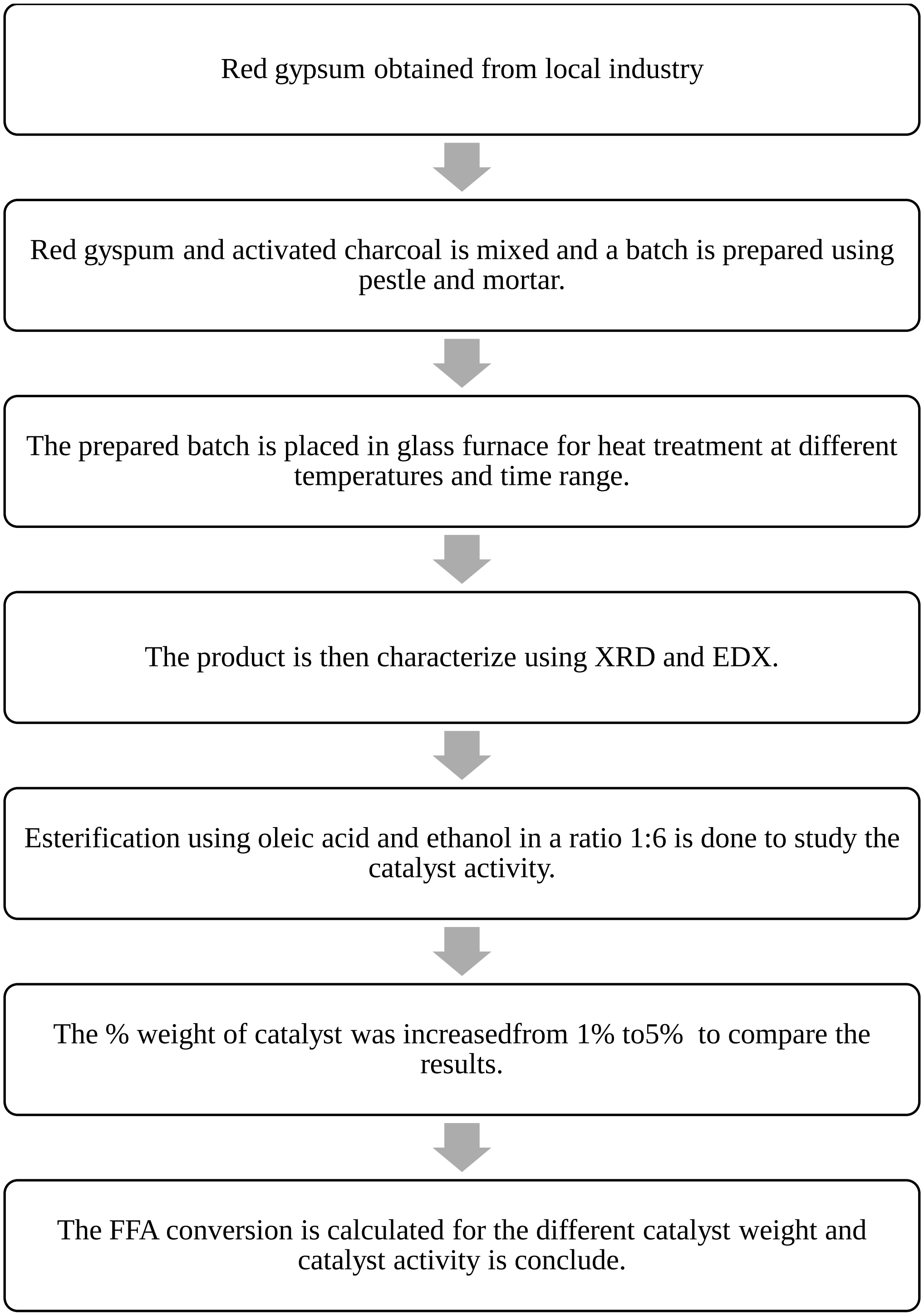


Figure 3.1 Flow chart of overall method of preparation and characterization of catalyst for biodiesel synthesis.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

This research is done to be able to recover catalyst from waste red gypsum and to measure and compare the physical characteristics and chemical analyses of the performance of the catalyst in the esterification process of FFA.

4.2 Catalyst Preparation from Red Gypsum

Sample	Initial weight of red gypsum(5g) + activated charcoal(5g)	Final weight of product	Percentage of weight loss in product
A	10g	9.25g	7.5%
B	10g	6.1g	39%
C	10g	3.55	64.5%
D	10g	2.85g	71.5

Table 4.1 Sample and final weight of product

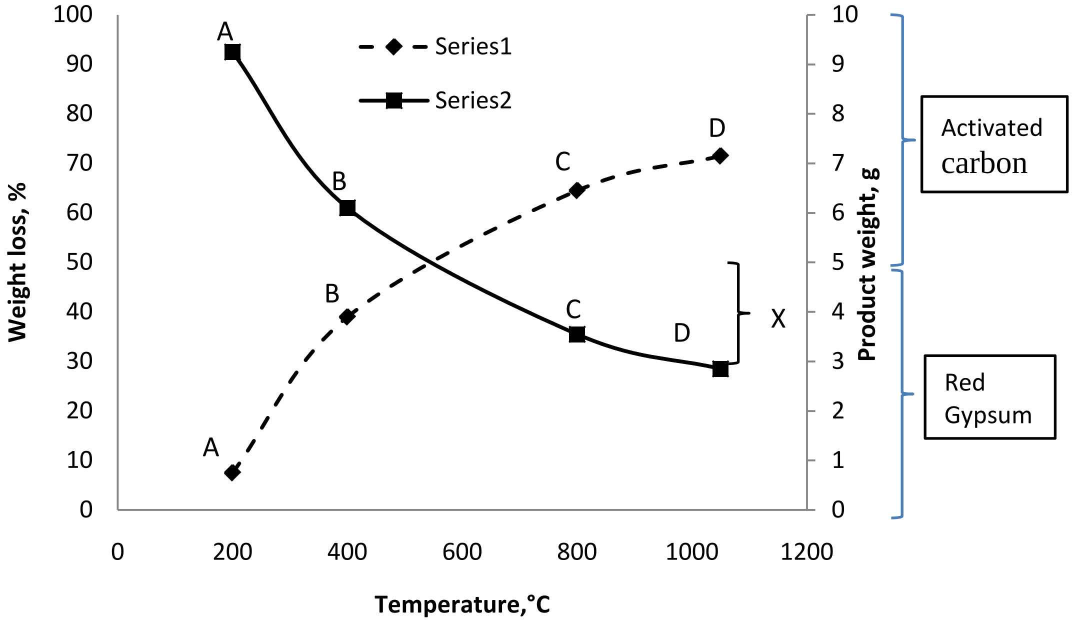


Figure 4.1 Graph of weight loss and final product weight, % vs temperature, ºC

Based on Figure 4.1, the graph shows series 1 which is the graph of weight loss versus temperature and series 2 which is the graph of product weight versus temperature. Series 1 show that the weight loss is increasing as the temperature of furnace increases while series 2 shows that the product weight is decreasing as the temperature is increased. Both this graph explains that more activated carbon is being burn as the temperature increases. Activated carbon is a form of carbon processed to be riddled with small, low-volume pores that increase the surface area available for adsorption or chemical reactions usually used as reducing agents.

Initially a total of 10g consist of 5g of activated carbon and 5g of red gypsum is mixed. The decrease in the weight of product shows that the carbon is burned in the process. There is still a decrease in the product weight shown in the graph by symbol X after all the carbon is burned and this explain the sulphur reduction in red gypsum in the form of sulphur dioxide, SO_2 which will be discussed in the EDX analyses part.

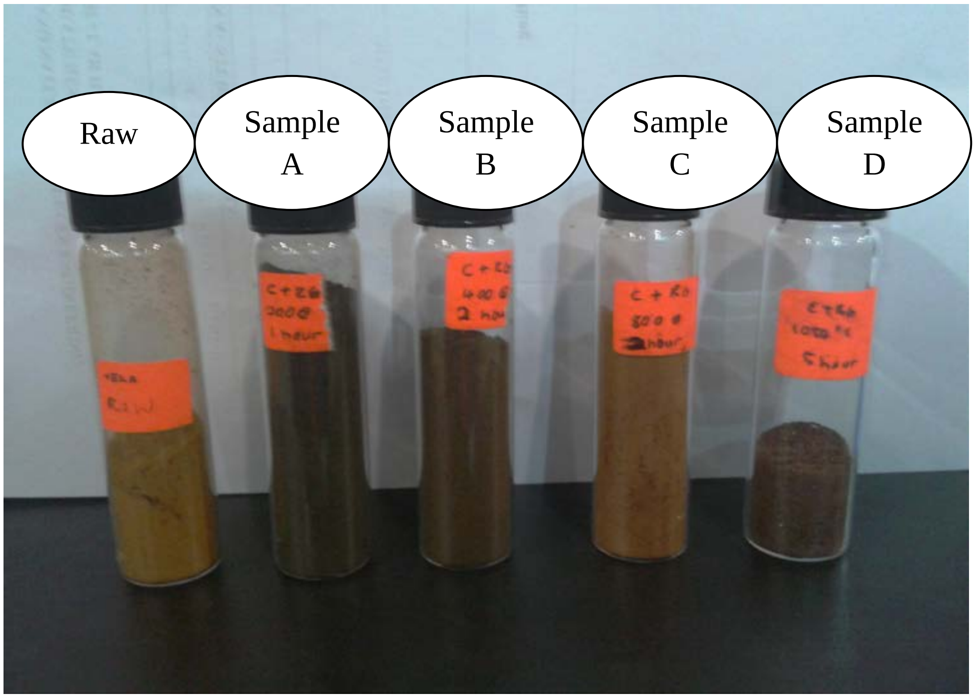


Figure 4.2 Final product obtained after heat treatment

The raw red gypsum displays a light orange colour. The product at 200 ºC(1 hour- Sample A) is dark black in color resembles the activated carbon which still present in large amount in the product and at 400ºC (1hour- Sample B) the product colour changes to grayish-black which shows reduce in activated carbon in the product. At 800 ºC(2 hour –Sample C) the colour is totally change to almost red gypsum original colour showing more carbon been burnt and finally at 1050 ºC(5 hour- Sample D) a dark brown color is observed showing literally that the reaction has takes place and heat is being consumed. The weight decrease shows similarly that reaction has take place and the most of the carbon is been consumed in the heat treatment.

4.3 EDX results

4.3.1 Raw (Red Gypsum)

Element	Weight%	Compd%	Formula
C K	6.66	24.41	CO2
Mg K	0.90	1.50	MgO
Al K	0.74	1.39	Al2O3
Si K	1.13	2.42	SiO2
S K	8.39	20.94	SO3
Ca K	10.65	14.91	CaO
Ti K	4.47	7.46	TiO2
Fe L	20.96	26.97	FeO
O	46.09		
Totals	100.00		

(a) Sample – Raw(Red Gypsum)

Element	Weight%	Compd%	Formula
C K	19.15	70.15	CO2
Mg K	0.23	0.38	MgO
P K	1.46	3.35	P2O5
S K	1.72	4.29	SO3
Ca K	2.69	3.76	CaO
Fe L	14.05	18.07	FeO
O	60.71		
Totals	100.00		

(b) Sample D

Element	Weight%	Compd%	Formula
C K	15.96	58.47	CO2
P K	2.21	5.06	P2O5
S K	0.62	1.55	SO3
Ca K	3.21	4.49	CaO
Ti K	1.09	1.81	TiO2
Fe L	22.24	28.62	FeO
O	54.67		
Totals	100.00		

(c) Sample C

Element	Weight%	Compd%	Formula
C K	5.75	21.08	CO2
Al K	0.76	1.44	Al2O3
Si K	2.34	5.00	SiO2
P K	1.91	4.37	P2O5
S K	0.55	1.37	SO3
Ca K	20.76	29.05	CaO
Ti K	10.45	17.43	TiO2
Fe K	15.76	20.27	FeO
O	41.73		
Totals	100.00		

(d) Sample D

Figure 4.3 Tabulated analysis of EDX

EDX analyses were only carried out on sample raw (red gypsum), sample B, sample C and sample D as the weight decrease in Sample A showed less significance.

Figure 4.3 shows the weight percentage of elements present in the samples analyzed. The carbon weight percentage is more in sample B compared to in raw red gypsum as sample B is the product which contains the mixture of red gypsum and activated carbon which undergone heat treatment in the glass furnace. However in sample C and sample D there is less carbon weight percentage as compared to sample B.

The carbon weight percentage was decreased as the sample B, sample C and sample D undergone heat treatment at temperature 400 ºC, 800 ºC and 1050 ºC respectively. This shows, as the temperature of the heat treatment is increased, the carbon weight percentage decreased. These results agree with Oh and Wheelock (1990) which stated that carbon dioxide, CO_2 is emitted through heat treatment. Activated carbon supplied to the red gypsum in the beginning of the process was released as CO_2 through the equation (2.4) proposed by Oh and Wheelock (1990) which was discussed earlier in literature review.

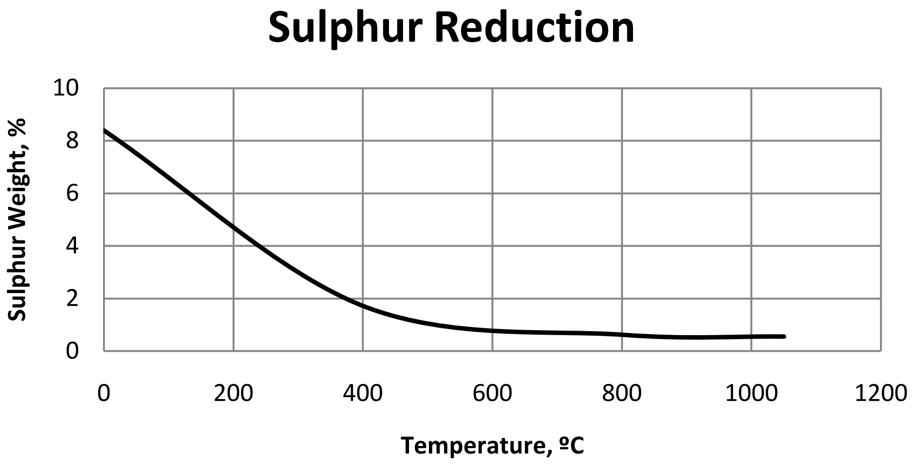
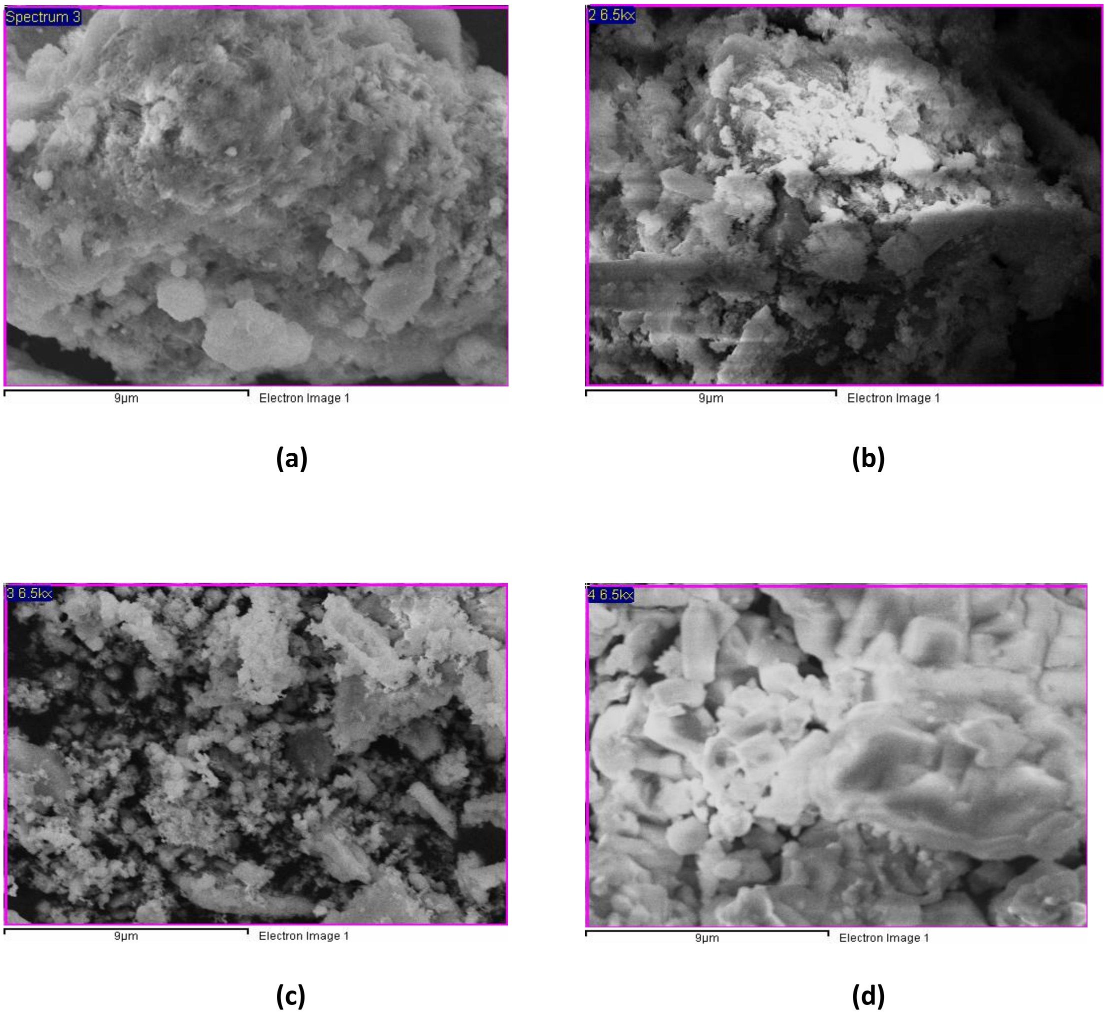


Figure 4.4 Sulphur content versus temperature, ºC.

Results obtained from EDX also depicted the sulphur content in the samples which is shown in Figure 4.4. The trend of results for sulphur content in sample raw, B, C and D show similarity with the carbon reduction as in Figure 4.3. Initially, the raw red gypsum contained 8.39% of sulphur. This amount decreases as the temperature of heat treatment is increased. In sample D which was treated at 1050 ºC, the amount of sulphur was 0.55%. The sulphur content in sample B and C were 1.72% and 0.62%. The sulphur was emitted as sulphur dioxide, SO_2 as the temperature was increased. As temperature increases more sulphur was converted and released and thus the weight of the final product was lesser compared to initial red gypsum (Oh and Wheelock, 1990). This supports the weight results discussed in section 4.2.

4.4 FESEM results



(a) (b)

(c) (d)

Figure 4.5 Image of the product of (a) raw, (b) sample B, (c) sample C and (d) sample D

Based on the Figure 4.5(a) , the sample of raw red gypsum exhibit a less crystalline structure which explain the nature of the red gypsum that contain mainly $CaSO_4.2H_2O$ which contain anion water and hydrogen bonding. Sample B and C show formation of crystalline structure as the crystal lattice loses its liquid water molecule due to the heat supplied. A significant solid crystalline structure can be observed in sample D as the red gypsum loses more liquid water molecule and form minerals such as CaO, Ca_2(Fe2O5) and Fe_2O_3 discussed in the XRD part.

4.5 XRD results

XRD analysis is done on sample A, sample B, sample C and sample D because the composition of raw red gypsum is known. Initially the red gypsum contain $CaSO_4.2H_2O$ (70 wt %), Fe_2O_3 (30 wt %) and small amount of Al_2O_3.

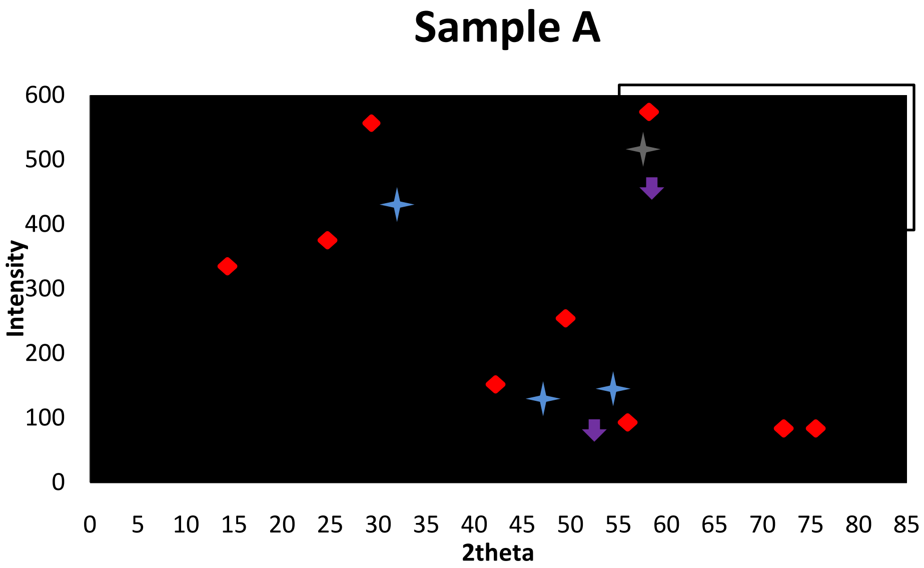


Figure 4.6 XRD analysis of Sample B

The XRD results on sample A shows the present of $CaSO_{4,}$ $CaSO_3$ and CaS. This is possible formation as proposed by Satoshi Okumura, et al., (2003) discussed in literature review through equation (2.7) and (2.12) discussed in chapter literature review.

The formation of the $CaSO_3$ as an intermediate is earlier proposed by Oh and Wheelock (1990) through the same equation (2.2) and (2.4). The temperature supplied was only 200 ºC which was not sufficient enough to reduce the initial composition which proved in the final product weight of sample A of 9.25g from initial 10g, discussed in section 4.2.

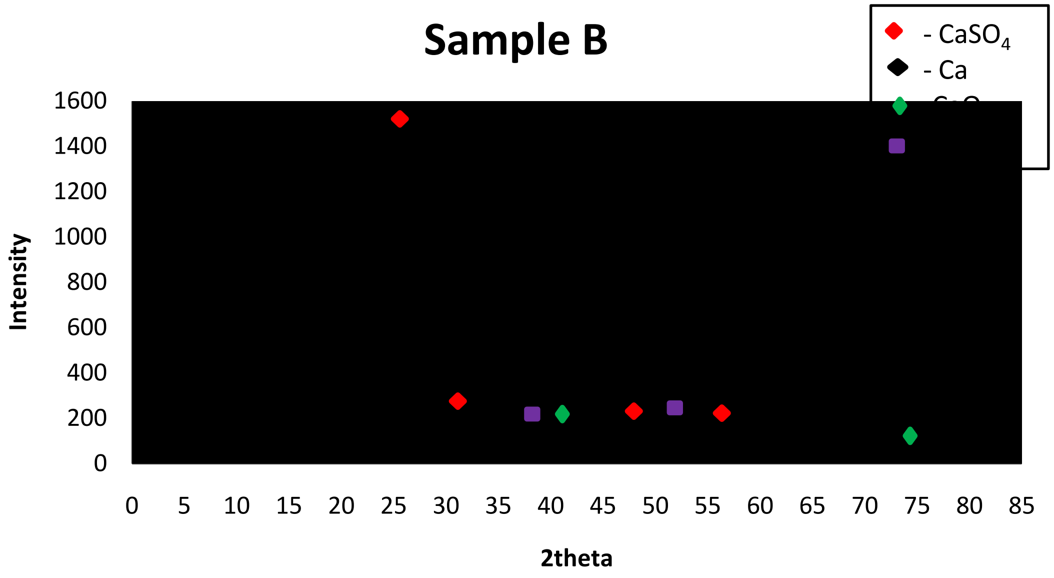


Figure 4.7 XRD analysis of Sample B

XRD analysis on sample B (400 ºC) shows the disappearance of $CaSO_3$ and CaS while there is presence calcium oxide, CaO. This is explained by the proposed reaction that happened by and Oh and Wheelock (1990) in equation (2.1), (2.3) and (2.5) and Satoshi Okumura et al. (2003) through the equations (2.6), (2.11) and (2.13) in chapter two. These reactions must have took place correspond to the disappearance of the intermediate $CaSO_3$ and the formation of CaO and SO_2. This sulphur dioxide, SO_2

emission cause the reduction in weight of the final product as discussed in section 4.2 and sulphur reduction in section 4.3.

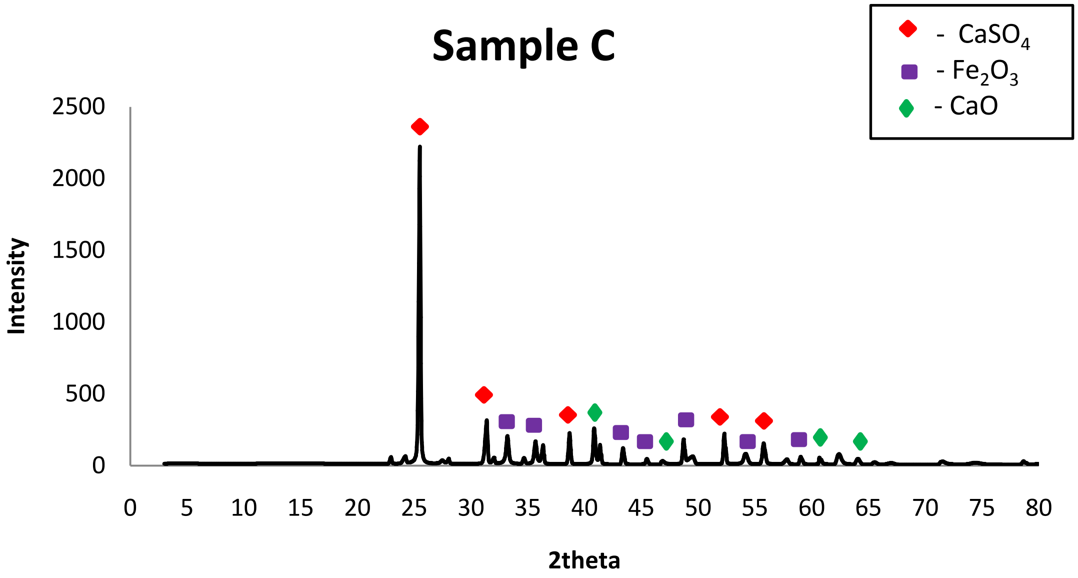


Figure 4.8 XRD analysis of Sample C

As more heat was supplied for sample C (800) °C more reactions occur to form CaO. The temperature increases favor in the production of CaO as mentioned by (Hongjing Tian et al., 2010). This XRD results on sample C suggest that the reduction of initial $CaSO_4$ and the intermediate product $CaSO_3$ and CaS to CaO.

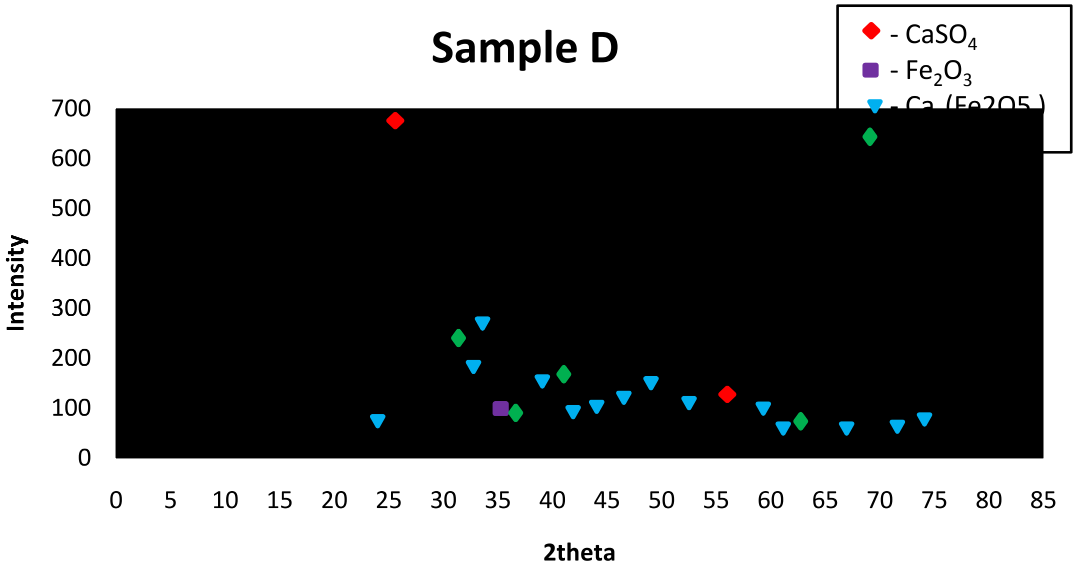


Figure 4.9 XRD analysis of Sample D

Figure 4.9 shows the XRD analysis on sample D which was carried out at 1050 ºC. There is reduction in $CaSO_4$ and formation of new compound, calcium ferrite, $Ca_2(Fe_2O5\ )$ as shown in the result. Reductive decomposition of red gypsum has been taken place even though the CaSO4 remained in all samples. This CaSO4 is the major compound of red gypsum and present in large amount initially. As the temperature of the catalyst production through reductive decomposition of CaSO4 increased from 200 ºC - sample A to 1050 ºC – sample D there was no calcium sulphide, CaS formed. Calcium oxide, CaO present at certain peak together with CaSO4. New compound/element such as CaSO3, Fe2O3 and Ca2 (Fe2O5) were also show peak and thus can conclude that reaction has taken place.

4.6 Esterification

Esterification was done in this research to study the product obtained, as a catalyst after the thermal reduction. This esterification process was carried out using sample D which undergone thermal reduction at 1050 ºC. This is mainly because of the EDX and XRD results of sample D which shows the formation of CaO and Ca2 (Fe2O5) abundantly. Oleic acid and ethanol was used with the temperature of the esterification reaction was maintained at 70-75ºC to avoid the ethanol from vaporized. The FFA conversion of the oleic acid was tabulated with time corresponds to the weight percentage of catalyst used ranging 1-5% as show in tables below.

Time	FFA conversion, X_{ffa}
1 hour	10.4%
2 hour	39.2%
3 hour	73.6%
4 hour	84%
5 hour	88.8%
6 hour	95.2%

Table 4.2 FFA conversion for 1% weight catalyst

Time	FFA conversion, X_{ffa}
1 hour	16%
2 hour	56%
3 hour	80%
4 hour	90.4%
5 hour	96%

Table 4.3 FFA conversion for 3% weight catalyst

Time	**FFA conversion, X_{ffa}**
1 hour	24%
2 hour	67.20%
3 hour	92%
4 hour	95.2%

Table 4.4 FFA conversion for 5% weight catalyst

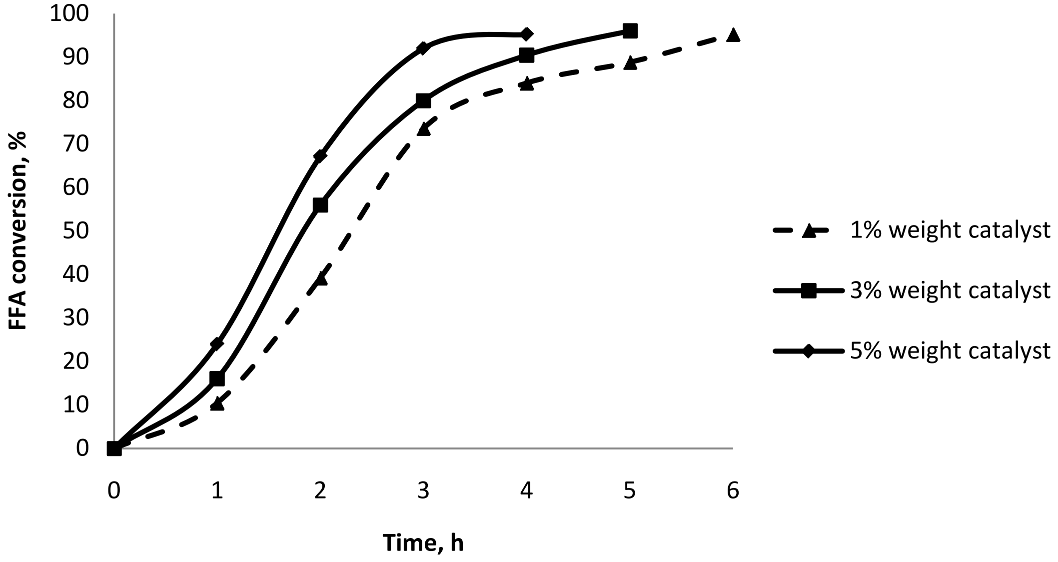


Figure 4.10 Graphs of FFA conversion versus time

Based on the Figures 4.10, for 1% weight catalyst, 95.2% conversion of FFA was achieved within six hours of the reaction time. Figures 4.9 and Figures 4.10 shows that 96% of FFA conversion was obtained within 5 hours, using 3% weight catalyst while only 4 hours was needed to achieve a conversion of 95.2% of FFA using 5% weight catalyst respectively. The three graphs line shows similar trend which is gradually increasing. As the time of reaction was increased, the higher the conversion of FFA obtained. This shows the catalyst prepared through the heat treatment is performing efficiently in the esterification reaction.

Overall, for 5% weight catalyst, FFA conversion was above 95% conversion after 4 hour, for 3% weight catalyst, FFA conversion was above 95% conversion after 5 hour and for 1% weight catalyst, FFA conversion was above 95% conversion after 6 hour. This shows that as the amount of catalyst decreased, the time for FFA conversion to reach 95% increases. This shows the catalyst prepared from red gypsum is effective in esterifiction process and thus can be used in biodiesel synthesis.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This research is done to find an end use for red gypsum waste that has been landfilling and polluting the environment. Many research has be done to find a end use for this waste such as glaze from red gypsum, land application, sulfur recovery from the red gypsum and reductive decomposition of red gypsum to form CaO or CaS. Based on the previous study done, information was gathered to find new end use of this red gypsum. At the same time there is a crucial need to find an alternative fuel in fulfilling energy demand to replace fossil fuels which are undergoing drastic depletion.

The best option is biodiesel which shows almost same properties like fossil fuels and most importantly it is environmental friendly. Many researches have been carried out on biodiesel production using different oils as the raw material, different alcohols and different catalyst. To date, many solid base catalysts have been developed for biodiesel production, such as basic zeolites, alkaline earth metal oxides and hydrotalcites. On top of that, alkaline earth metal oxides especially calcium oxide, CaO have attracted much attention due to their relatively high basic strength, low solubility in methanol and can be synthesized from cheap sources like limestone and calcium hydroxide

Based on the study done for red gypsum disposal, it is found that the red gypsum can be reduce thermally into compound such as CaS , S and CaO using reducing agents like activated carbon. These make an option for the catalyst production from red gypsum (waste) for biodiesel synthesis (alternative environmental fuel). Grinding the activated carbon and red gypsum produce a batch that undergone heat treatment to produce catalyst which perform efficiently in esterification of oleic acid with ethanol in mole ratio of 1:6 and weight catalyst range 1-5%. The catalyst have been characterize using EDX and XRD and it is found that the red gypsum is successfully reduce to compound such as CaO, CaSO3, Fe2O3 and Ca2 (Fe2O5). Thus overall this project has met the research objective in preparing and characterizing the catalyst produced from red gypsum for biodiesel synthesis.

There are several suggestions and recommendation to improve this project results. Firstly use different mass ratio of activated carbon and red gypsum. As previous studies show red gypsum can be reduce to CaO in different atmosphere research can be carried out to improve the results obtained by maximizing Ca) produced. CaO is a catalyst desired for biodiesel synthesis. Find a different reducing agent and compare the results. Find out the optimum temperature of furnace for a catalyst can be produce and the catalyst prepared can be use for transesterification. Biodiesel produce can be sent for Gas Chromatography Mass Spectrometry (GCMS) for further analysis.

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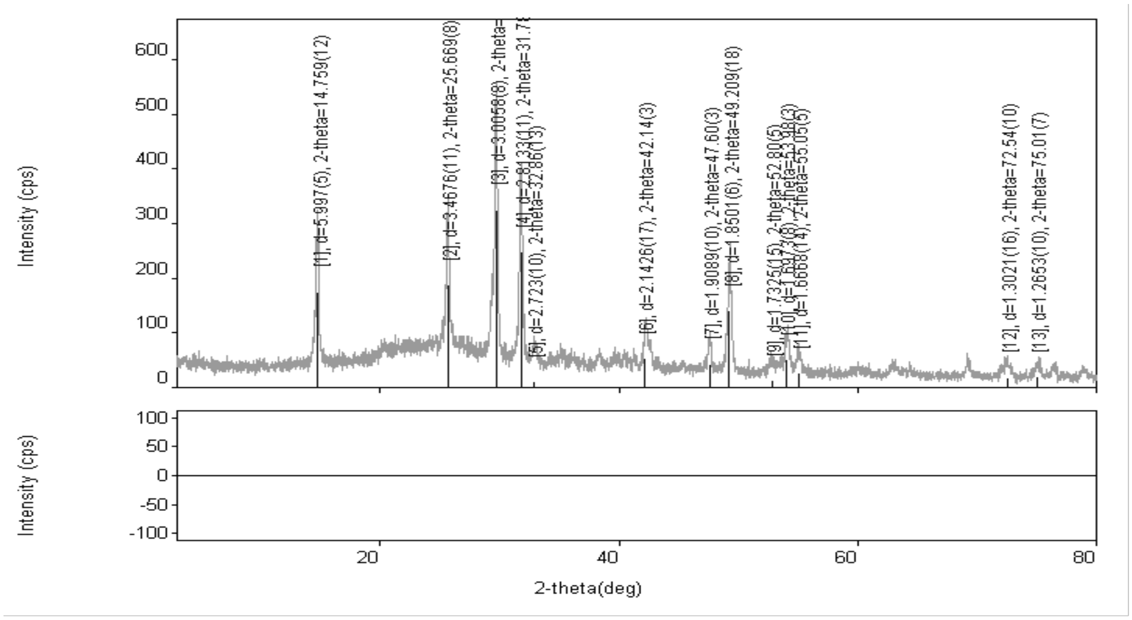
APPENDIX A.1 - XRD RESULT SAMPLE A

General Information

Analysis date	1/7/2013 2:57:01 PM		
Sample name	XRD Analysis	Measured time	1/4/2013 3:50:10 PM
File name	1.raw	Operator	administrator
Comment	FKKSA		

Measurement profile



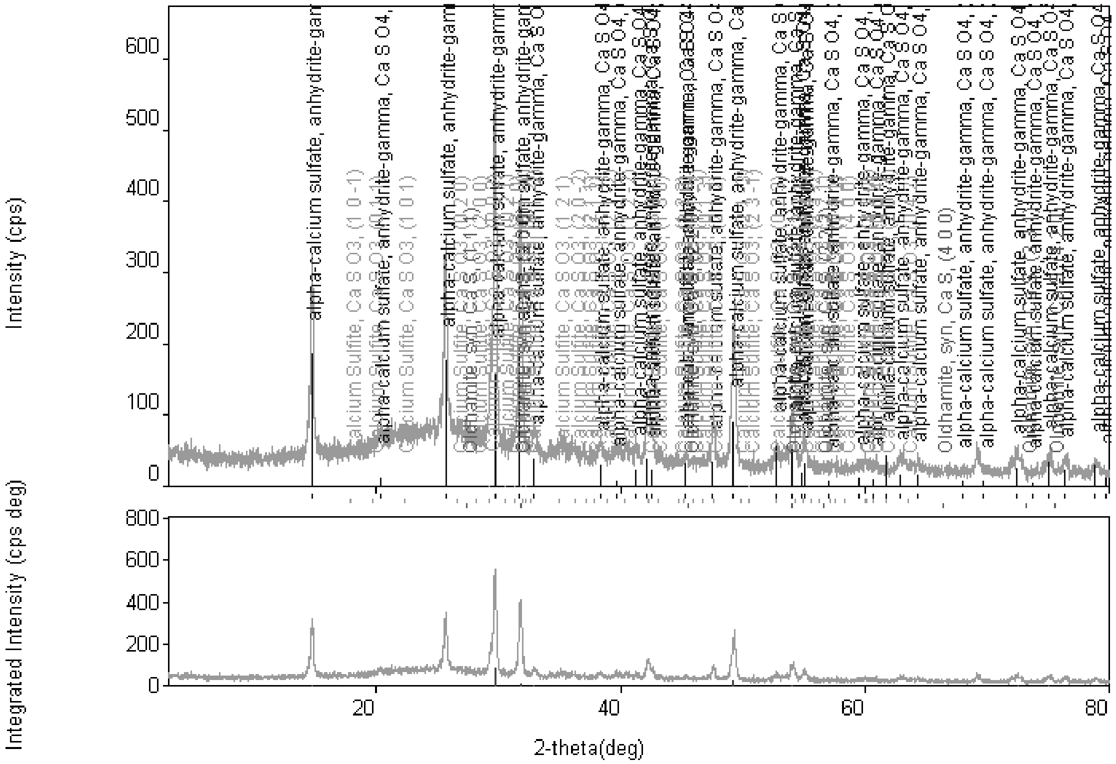
Measurement conditions

XG	Cu/30 kV/15 mA	Duration time / Scan speed	1 deg/min
Goniometer		Step / Sampling step	0.02 deg
Attachment	-	Measurement axis	2ƒÆ/ƒÆ
K-beta filter	-	Scan range	3-80 deg
Incident	-	Incident slit	-
Receiving	-	Vertical divergence	-
Counter	-	Receiving slit #1	-
		Receiving slit #2	-

Qualitative analysis results

Phase name	Formula	Figure of merit	ICDD
alpha-calcium sulfate,	Ca S O4	0.7376150252679471	430606 (ICDD)
Calcium Sulfite	Ca S O3	1.68432823596935	440517 (ICDD)
Oldhamite, syn	Ca S	2.877548759849249	10714760 (ICDD)

Phase name	Formula	Space group	ICDD
alpha-calcium sulfate,	Ca S O4	147 : P-3	430606 (ICDD)
Calcium Sulfite	Ca S O3	10 : P12/m1,unique-b	440517 (ICDD)
Oldhamite, syn	Ca S	225 : Fm-3m	10714760 (ICDD)



Peak list

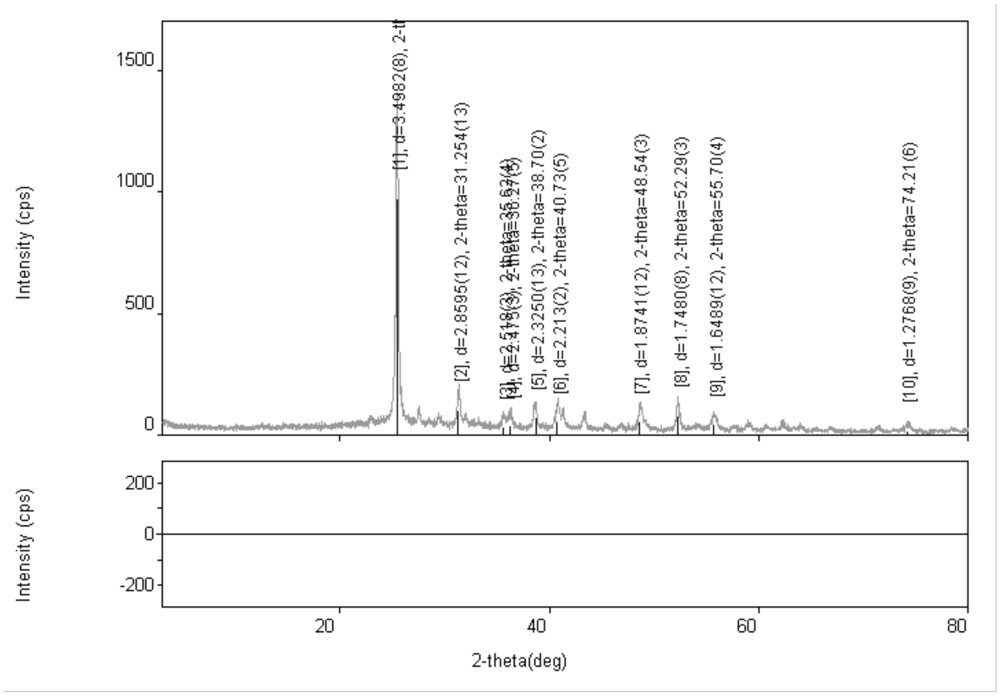
2-theta (deg)	d (ang.)	Height (cps)	Int.I(cps¥deg)	FWHM(deg)	Size	Phase name
14.759(12)	5.997(5)	175(13)	68.3(14)	0.267(12)	313(14)	alpha-calcium sulfate, anhydrite-gamma, (1,0,0)
25.669(8)	3.4676(11)	187(14)	69.2(16)	0.241(14)	353(20)	alpha-calcium sulfate, anhydrite-gamma, (1,1,0)
29.697(8)	3.0058(8)	325(18)	123(3)	0.270(9)	318(11)	alpha-calcium sulfate, anhydrite-gamma, (2,0,0), Calcium Sulfite, (0,0,2)
31.780(12)	2.8133(11)	248(16)	80(2)	0.260(9)	331(12)	alpha-calcium sulfate, anhydrite-gamma, (1,0,2), Calcium Sulfite, (2,1,0)
32.86(13)	2.723(10)	11(3)	8.7(12)	0.64(16)	136(33)	alpha-calcium sulfate, anhydrite-gamma, (2,0,1), Calcium Sulfite, (2,1,-1)
42.14(3)	2.1426(17)	53(7)	26.8(17)	0.42(4)	212(19)	alpha-calcium sulfate, anhydrite-gamma, (2,1,1)
47.60(3)	1.9089(10)	43(7)	13.3(9)	0.25(3)	361(39)	alpha-calcium sulfate, anhydrite-gamma, (3,0,1), Calcium Sulfite, (0,1,3)
49.209(18)	1.8501(6)	140(12)	57.6(15)	0.335(16)	272(13)	alpha-calcium sulfate, anhydrite-gamma, (2,1,2)
52.80(5)	1.7325(15)	13(4)	24(3)	1.7(2)	53(7)	alpha-calcium sulfate, anhydrite-gamma, (2,2,0), Calcium Sulfite, (2,3,-1), Oldhamite, syn, (3,1,1)
53.98(3)	1.6973(8)	51(7)	17.6(13)	0.32(3)	287(23)	alpha-calcium sulfate, anhydrite-gamma, (3,0,2), Calcium Sulfite, (0,2,3)
55.05(5)	1.6668(14)	26(5)	10.9(12)	0.40(5)	235(27)	alpha-calcium sulfate, anhydrite-gamma, (2,2,1)
72.54(10)	1.3021(16)	19(4)	13.9(15)	0.66(8)	157(19)	alpha-calcium sulfate, anhydrite-gamma, (2,1,4)
75.01(7)	1.2653(10)	20(5)	8.9(12)	0.34(10)	303(90)	alpha-calcium sulfate, anhydrite-gamma, (3,2,2)

APPENDIX A.2 - XRD RESULT SAMPLE B

General Information

Analysis date	1/7/2013 2:59:29 PM		
Sample name	XRD Analysis	Measured time	1/4/2013 1:16:02 PM
File name	2.raw	Operator	administrator
Comment	FKKSA		

Measurement profile



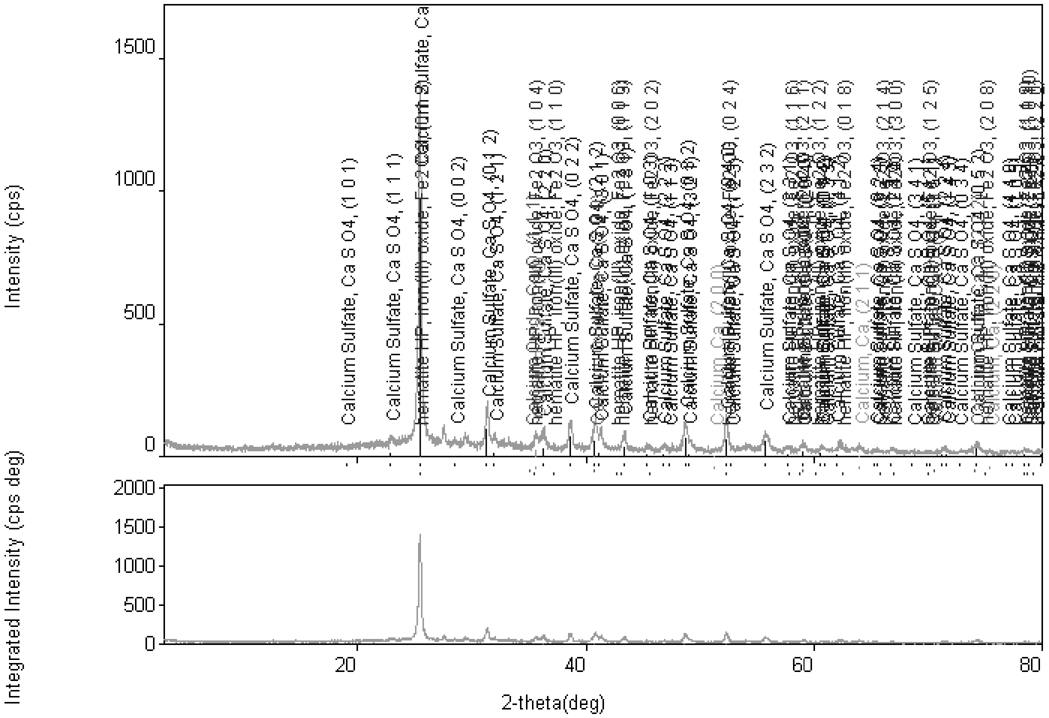
Measurement conditions

XG	Cu/30 kV/15 mA	Duration time / Scan speed	1 deg/min
Goniometer		Step / Sampling	0.02 deg
Attachment	-	Measurement axis	2ƒÆ/ƒÆ
K-beta filter	-	Scan range	3-80 deg
Incident	-	Incident slit	-
Receiving	-	Vertical	-
Counter	-	Receiving slit #1	-
		Receiving slit #2	-

Qualitative analysis results

Phase name	Formula	Figure of merit	ICDD
Calcium Sulfate	Ca S O4	0.5811613691336254	10700909 (ICDD)
Calcium	Ca	1.740317474535331	10714107 (ICDD)
Calcium Oxide	Ca O	1.517458950109851	10777243 (ICDD)
hematite HP,	Fe2 O3	1.625124586237674	10726232 (ICDD)

Phase name	Formula	Space group	ICDD
Calcium Sulfate	Ca S O4	63 : Bmmb	10700909
Calcium	Ca	200 : Pm-	10714107
Calcium Oxide	Ca O	225 : Fm-3m	10777243
hematite HP,	Fe2 O3	167 : R-	10726232



Peak list

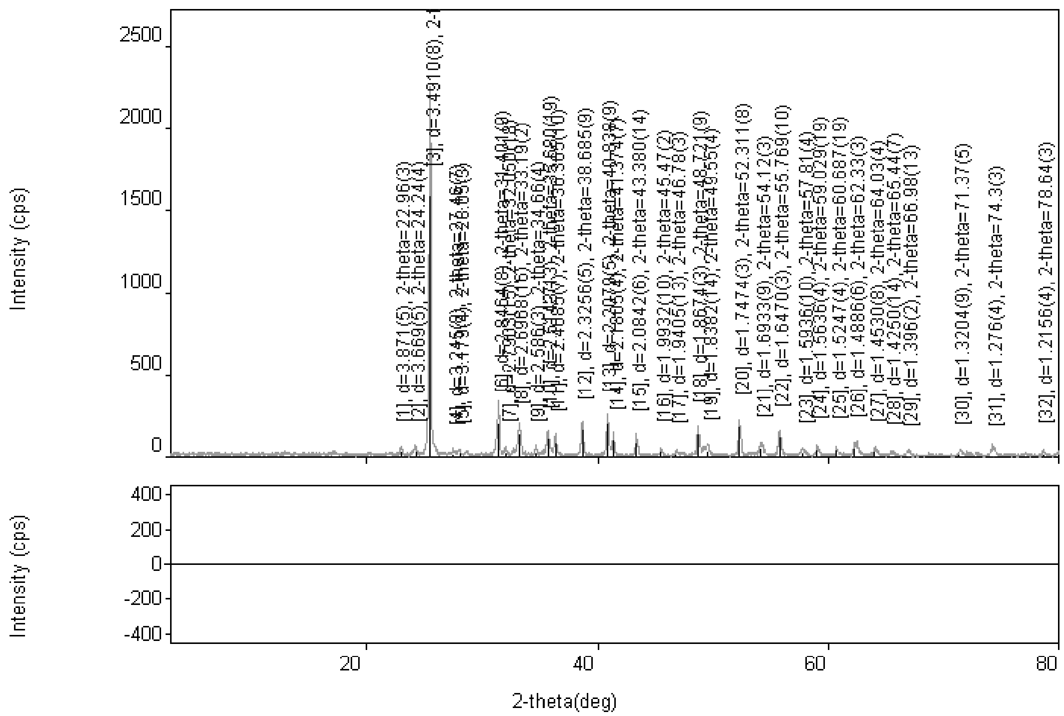
2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps¥deg)	FWHM(deg)	Size	Phase name
25.441(6)	3.4982(8)	975(31)	334(3)	0.229(5)	371(9)	Calcium Sulfate, (0,2,0)
31.254(13)	2.8595(12)	102(10)	38.1(15)	0.278(15)	310(17)	Calcium Sulfate, (0,1,2)
35.62(4)	2.518(3)	32(6)	10(2)	0.30(5)	291(46)	Calcium, (1,1,0)
36.27(5)	2.475(3)	37(6)	22(2)	0.54(7)	163(23)	Calcium Sulfate, (2,2,0)
38.70(2)	2.3250(13)	73(9)	24.0(12)	0.28(2)	312(26)	Calcium Sulfate, (0,2,2), hematite HP, iron(III) oxide, (1,1,0)
40.73(5)	2.213(2)	56(8)	45(3)	0.74(4)	120(7)	Calcium Sulfate, (2,1,2), Calcium Oxide, (2,0,0)
48.54(3)	1.8741(12)	55(7)	36.9(17)	0.58(3)	157(9)	Calcium Sulfate, (0,3,2)
52.29(3)	1.7480(8)	82(9)	30.7(11)	0.31(3)	299(25)	Calcium Sulfate, (0,4,0)
55.70(4)	1.6489(12)	44(7)	25.0(14)	0.45(4)	207(17)	Calcium Sulfate, (2,3,2)
74.21(6)	1.2768(9)	19(4)	14.3(10)	0.59(6)	176(17)	Calcium Sulfate, (0,5,2), Calcium Oxide, (2,2,2)

APPENDIX A.3 –XRD RESULT SAMPLE C

General Information

Analysis date	1/7/2013 3:03:13 PM		
Sample name	XRD Analysis	Measured time	1/4/2013 12:07:36 PM
File name	3.raw	Operator	administrator
Comment	FKKSA		

Measurement profile



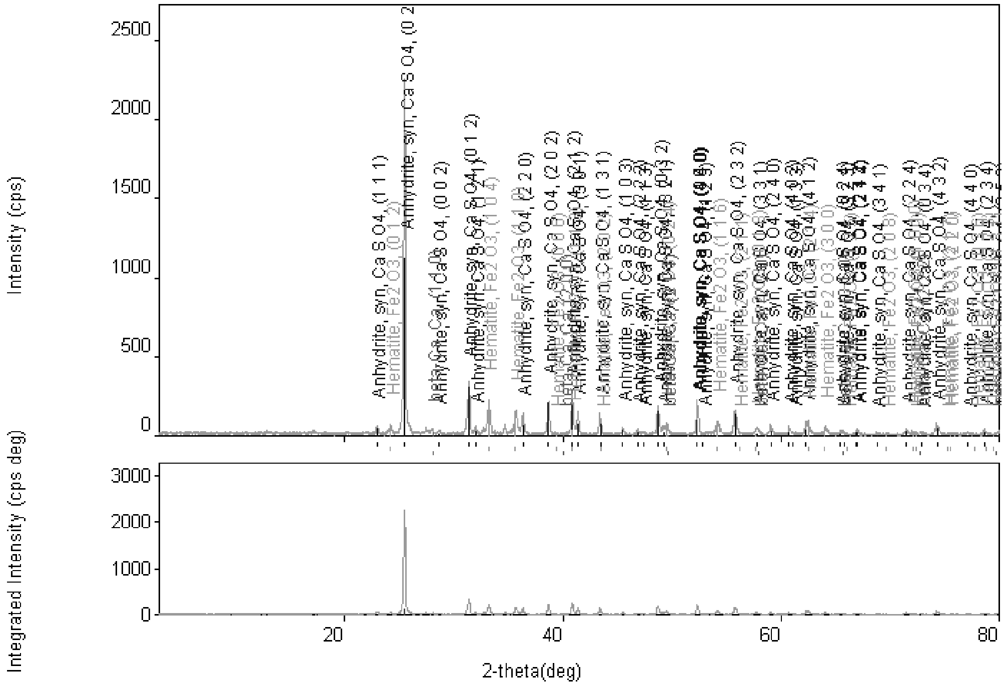
Measurement conditions

XG	Cu/30 kV/15 mA	Duration time / Scan speed	1 deg/min
Goniometer		Step / Sampling step	0.02 deg
Attachment	-	Measurement axis	2ƒÆ/ƒÆ
K-beta filter	-	Scan range	3-80 deg
Incident	-	Incident slit	-
Receiving	-	Vertical divergence slit	-
Counter	-	Receiving slit #1	-
		Receiving slit #2	-

Qualitative analysis results

Phase name	Formula	Figure of merit	ICDD
Anhydrite, syn	Ca S	0.421078975374841	371496 (ICDD)
Hematite	Fe2 O3	0.460843158744062	10720469
beta-Ca	Ca	1.208580068623328	10893684

Phase name	Formula	Space group	ICDD
Anhydrite, syn	Ca S O4	63 : Bmmb	371496 (ICDD)
Hematite	Fe2 O3	167 : R-	10720469
beta-Ca	Ca	229 : Im-3m	10893684



Peak list

2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps¥deg)	FWHM(deg)	Size	Phase name
22.96(3)	3.871(5)	33(6)	6.2(6)	0.16(2)	18(68)	Anhydrite, syn, (1,1,1)
24.24(4)	3.669(5)	34(6)	10.6(9)	0.27(4)	10(40)	Hematite, (0,1,2)
25.494(6)	3.4910(8)	1592(40)	319(4)	0.158(5)	37(17)	Anhydrite, syn, (0,2,0)
27.46(7)	3.245(8)	16(4)	7.2(16)	0.31(9)	77(80)	Unknown,
28.05(3)	3.179(4)	26(5)	6.1(13)	0.16(6)	49(197)	beta-Ca, (1,1,0)
31.401(9)	2.8464(8)	211(15)	56.3(12)	0.233(8)	69(12)	Anhydrite, syn, (0,1,2)
32.050(18)	2.7903(15)	29(5)	7.0(5)	0.21(2)	05(44)	Anhydrite, syn, (1,2,1)
33.19(2)	2.6968(16)	144(12)	47.3(13)	0.225(18)	85(31)	Hematite, (1,0,4)
34.66(4)	2.586(3)	31(6)	6.4(7)	0.18(3)	81(86)	Unknown,
35.680(19)	2.5143(13)	115(11)	34.8(11)	0.217(19)	03(35)	Hematite, (1,1,0)
36.365(10)	2.4685(7)	95(10)	23.1(11)	0.182(13)	80(35)	Anhydrite, syn, (2,2,0)
38.685(9)	2.3256(5)	170(13)	33.1(9)	0.167(8)	26(25)	Anhydrite, syn, (2,0,2)
40.838(9)	2.2079(5)	209(14)	47.3(11)	0.166(9)	35(30)	Anhydrite, syn, (2,1,2), Hematite, (1,1,3)
41.374(7)	2.1805(4)	108(10)	20.4(8)	0.139(11)	37(49)	Anhydrite, syn, (3,0,1)

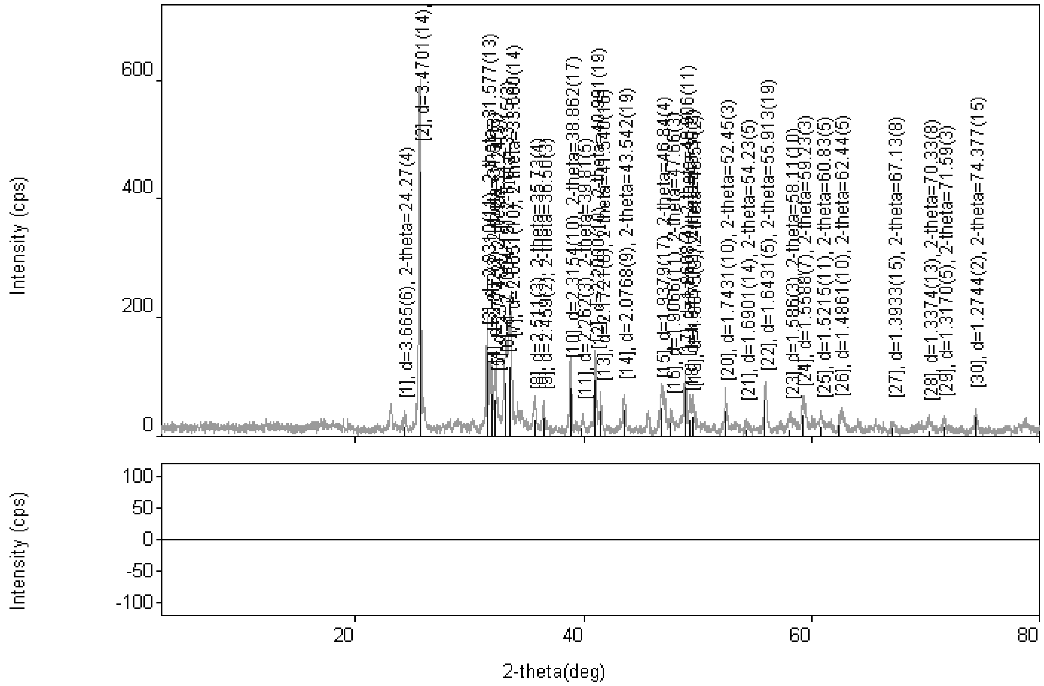
43.380(14)	2.0842(6)	92(10)	19.2(6)	0.183(11)	487(30)	Anhydrite, syn, (1,3,1), Hematite, (2,0,2)
45.47(2)	1.9932(10)	33(6)	6.8(5)	0.16(3)	548(89)	Anhydrite, syn, (1,0,3)
46.78(3)	1.9405(13)	19(4)	7.1(7)	0.25(7)	364(110)	Anhydrite, syn, (2,2,2)
48.721(9)	1.8674(3)	146(12)	25.6(18)	0.153(9)	594(36)	Anhydrite, syn, (0,3,2)
49.55(4)	1.8382(14)	37(6)	27.0(16)	0.63(7)	144(16)	Anhydrite, syn, (3,2,1), Hematite, (0,2,4), beta-Ca, (2,1,1)
52.311(8)	1.7474(3)	192(14)	35.2(11)	0.151(9)	611(35)	Anhydrite, syn, (4,0,0)
54.12(3)	1.6933(9)	56(7)	23.8(10)	0.33(3)	281(26)	Hematite, (1,1,6)
55.769(10)	1.6470(3)	123(11)	31.5(7)	0.210(11)	447(22)	Anhydrite, syn, (2,3,2)
57.81(4)	1.5936(10)	25(5)	9.4(7)	0.34(3)	279(27)	Anhydrite, syn, (3,3,1), Hematite, (0,1,8), beta-Ca, (2,2,0)
59.029(19)	1.5636(4)	47(7)	9.8(6)	0.188(19)	506(51)	Anhydrite, syn, (2,4,0)
60.687(19)	1.5247(4)	47(7)	9.1(6)	0.13(2)	724(119)	Anhydrite, syn, (4,0,2)
62.33(3)	1.4886(6)	56(8)	25.2(9)	0.37(2)	265(18)	Anhydrite, syn, (4,1,2), Hematite, (2,1,4)
64.03(4)	1.4530(8)	32(6)	10.0(7)	0.29(3)	334(32)	Hematite, (3,0,0)
65.44(7)	1.4250(14)	13(4)	4.6(7)	0.32(7)	304(63)	Anhydrite, syn, (0,2,4), beta-Ca, (3,1,0)
66.98(13)	1.396(2)	8(3)	5.1(8)	0.61(11)	162(29)	Anhydrite, syn, (2,4,2)
71.37(5)	1.3204(9)	18(4)	10.7(11)	0.40(7)	253(41)	Anhydrite, syn, (2,2,4)
74.3(3)	1.276(4)	8(3)	9.0(18)	0.9(2)	113(25)	Anhydrite, syn, (4,3,2)
78.64(3)	1.2156(4)	22(5)	5.2(6)	0.22(3)	489(64)	Anhydrite, syn, (2,3,4), Hematite, (2,2,3)

APPENDIX A.4 –XRD RESULT SAMPLE D

General Information

Analysis date	1/7/2013 3:06:22 PM		
Sample name	XRD Analysis	Measured time	1/4/2013 10:25:22 AM
File name	4.raw	Operator	administrator
Comment	FKKSA		

Measurement profile



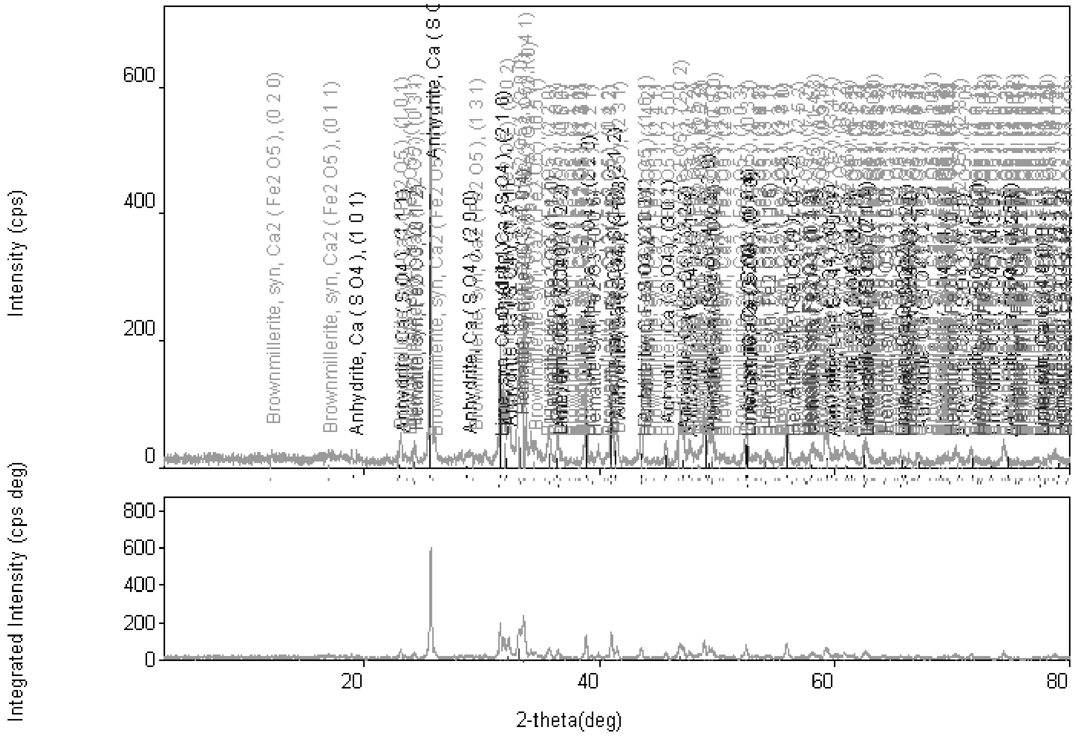
Measurement conditions

XG	Cu/30 kV/15 mA	Duration time / Scan speed	1 deg/min
Goniometer		Step / Sampling step	0.02 deg
Attachment	-	Measurement axis	2ƒÆ/ƒÆ
K-beta filter	-	Scan range	3-80 deg
Incident	-	Incident slit	-
Receiving	-	Vertical divergence slit	-
Counter	-	Receiving slit #1	-
		Receiving slit #2	-

Qualitative analysis results

Phase name	Formula	Figure of merit	ICDD
Anhydrite	Ca (S O4)	0.5798088197	10714906
Brownmillerite,	Ca2 (Fe2	1.1217665471	10768616
Hematite, syn	Fe2 O3	1.4835079704	10898103
Lime, syn	Ca O	2.7477856510	40777 (ICDD)

Phase name	Formula	Space group	ICDD
Anhydrite	Ca (S O4)	63 : Bbmm	10714906
Brownmillerite,	Ca2 (Fe2	62 : Pnma	10768616
Hematite, syn	Fe2 O3	167 : R-	10898103
Lime, syn	Ca O	225 : Fm-3m	40777 (ICDD)



Peak list

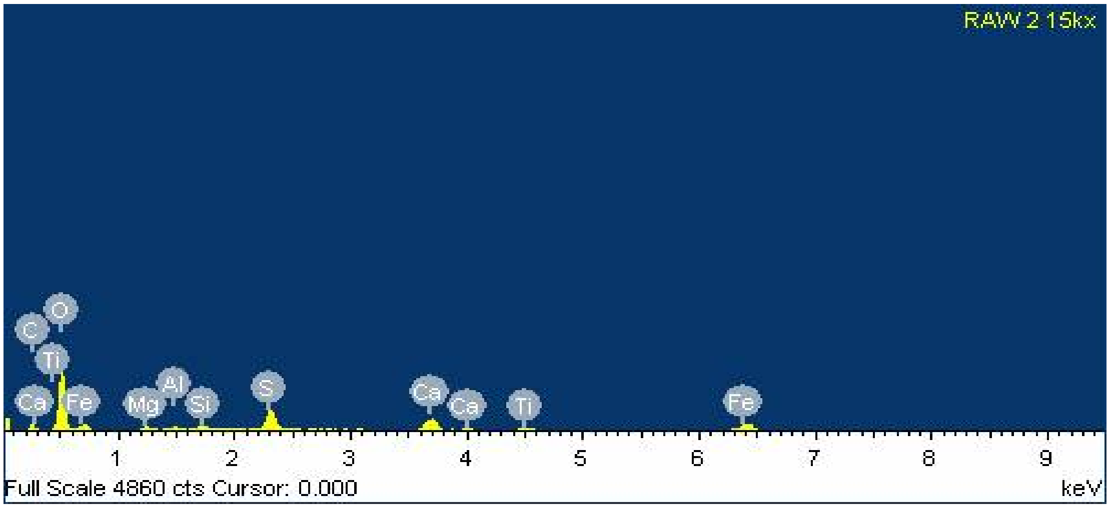
2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps¥deg)	FWHM(deg)	Size	Phase name
24.27(4)	3.665(6)	16(4)	4.3(5)	0.22(3)	383(56)	Brownmillerite, syn, (0,3,1), Hematite, syn, (0,1,2)
25.651(10)	3.4701(14)	448(21)	89.2(19)	0.152(8)	562(31)	Anhydrite, (0,2,0)
31.577(13)	2.8310(11)	139(12)	26.0(18)	0.160(13)	540(43)	Anhydrite, (2,1,0), Lime, syn, (1,1,1)
31.91(3)	2.802(2)	73(9)	16(2)	0.18(3)	470(82)	Brownmillerite, syn, (0,0,2)
32.24(3)	2.774(2)	62(8)	19.7(18)	0.25(4)	349(50)	Anhydrite, (1,2,1)
33.15(2)	2.7004(19)	92(10)	59(6)	0.49(8)	178(28)	Brownmillerite, syn, (2,0,0), Hematite, syn, (1,0,4)
33.600(14)	2.6651(10)	119(11)	26(5)	0.19(3)	461(66)	Brownmillerite, syn, (1,4,1)
35.73(4)	2.511(3)	29(5)	8.5(10)	0.28(3)	314(35)	Hematite, syn, (1,1,0)
36.50(3)	2.459(2)	31(6)	6.0(7)	0.16(4)	547(123)	Anhydrite, (0,2,2), Brownmillerite, syn, (0,6,0), Lime, syn, (2,0,0)
38.862(17)	2.3154(10)	83(9)	16.3(9)	0.172(17)	513(49)	Anhydrite, (2,2,0), Brownmillerite, syn, (2,2,1)
39.81(5)	2.262(3)	14(4)	3.6(7)	0.23(6)	392(102)	Unknown,
40.991(19)	2.2000(10)	97(10)	21.1(14)	0.166(19)	534(61)	Anhydrite, (2,1,2), Hematite, syn, (1,1,3)
41.540(16)	2.1721(8)	44(7)	10.5(12)	0.17(3)	511(82)	Anhydrite, (1,0,3), Brownmillerite, syn, (2,3,1)
43.542(19)	2.0768(9)	47(7)	10.6(5)	0.17(2)	511(66)	Anhydrite, (1,3,1), Brownmillerite, syn, (1,6,1), Hematite, syn, (2,0,2)
46.84(4)	1.9379(17)	49(7)	25.5(15)	0.41(5)	222(25)	Anhydrite, (2,2,2), Brownmillerite, syn, (2,0,2)
7.66(3)	1.9066(11)	23(5)	4.3(8)	0.13(4)	682(222)	Anhydrite, (3,1,1)

48.906(11)	1.8608(4)	85(9)	16.8(9)	0.127(17)	719(97)	Anhydrite, (2,3,0)
49.30(3)	1.8467(10)	28(5)	7(3)	0.16(7)	555(242)	Anhydrite, (1,2,3), Brownmillerite, syn, (1,7,1)
49.57(2)	1.8375(9)	34(6)	9(3)	0.17(7)	539(210)	Brownmillerite, syn, (0,8,0), Hematite, syn, (0,2,4)
52.45(3)	1.7431(10)	44(7)	11.7(10)	0.21(4)	431(83)	Anhydrite, (0,0,4), Brownmillerite, syn, (0,3,3)
54.23(5)	1.6901(14)	11(3)	2.6(6)	0.18(9)	527(254)	Hematite, syn, (1,1,6)
55.913(19)	1.6431(5)	62(8)	14.7(6)	0.216(14)	435(28)	Anhydrite, (2,3,2)
58.11(10)	1.586(3)	13(4)	5.2(9)	0.31(12)	310(117)	Anhydrite, (1,3,3), Brownmillerite, syn, (1,4,3)
59.23(3)	1.5588(7)	36(6)	10.4(8)	0.27(3)	353(36)	Anhydrite, (0,4,2), Brownmillerite, syn, (3,4,1)
60.83(5)	1.5215(11)	16(4)	4.6(7)	0.19(7)	502(184)	Brownmillerite, syn, (2,8,0)
62.44(5)	1.4861(10)	19(4)	7.4(9)	0.37(5)	264(35)	Anhydrite, (2,1,4), Brownmillerite, syn, (3,2,2), Hematite, syn, (2,1,4), Lime, syn, (3,1,1)
67.13(8)	1.3933(15)	15(4)	2.5(7)	0.15(9)	663(376)	Anhydrite, (2,4,2), Brownmillerite, syn, (0,7,3)
70.33(8)	1.3374(13)	10(3)	6.4(7)	0.44(8)	232(43)	Anhydrite, (1,5,1), Brownmillerite, syn, (2,8,2)
71.59(3)	1.3170(5)	17(4)	3.7(6)	0.18(3)	572(111)	Unknown,
74.377(15)	1.2744(2)	33(6)	7.3(6)	0.172(19)	604(65)	Brownmillerite, syn, (3,2,3)

APPENDIX B.1 EDX- RAW

Spectrum processing :
No peaks omitted
Processing option : Oxygen by stoichiometry (Normalised)
Number of iterations = 1
Standard :
C CaCO3 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM
Fe Fe 1-Jun-1999 12:00 AM

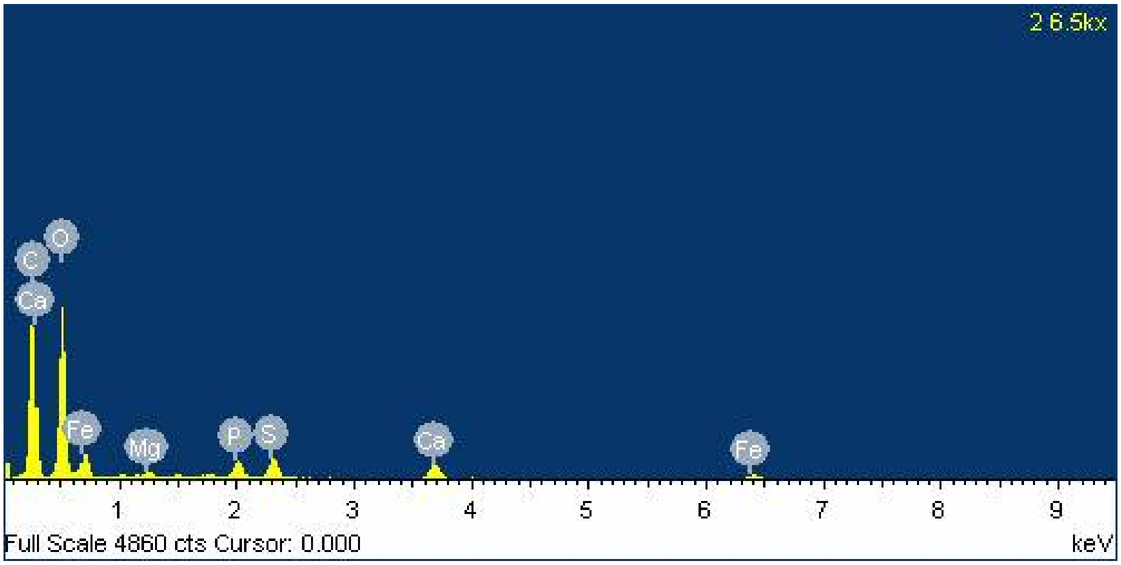
Element	Weight%	Atomic%	Compd%	Formula
C K	6.66	12.23	24.41	CO2
Mg K	0.90	0.82	1.50	MgO
Al K	0.74	0.60	1.39	Al2O3
Si K	1.13	0.89	2.42	SiO2
S K	8.39	5.77	20.94	SO3
Ca K	10.65	5.86	14.91	CaO
Ti K	4.47	2.06	7.46	TiO2
Fe L	20.96	8.27	26.97	FeO
O	46.09	63.50		
Totals	100.00			



APPENDIX B.2 EDX-SAMPLE B

Spectrum processing :
No peaks omitted
Processing option : Oxygen by stoichiometry (Normalised)
Number of iterations = 2
Standard :
C CaCO3 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Fe Fe 1-Jun-1999 12:00 AM

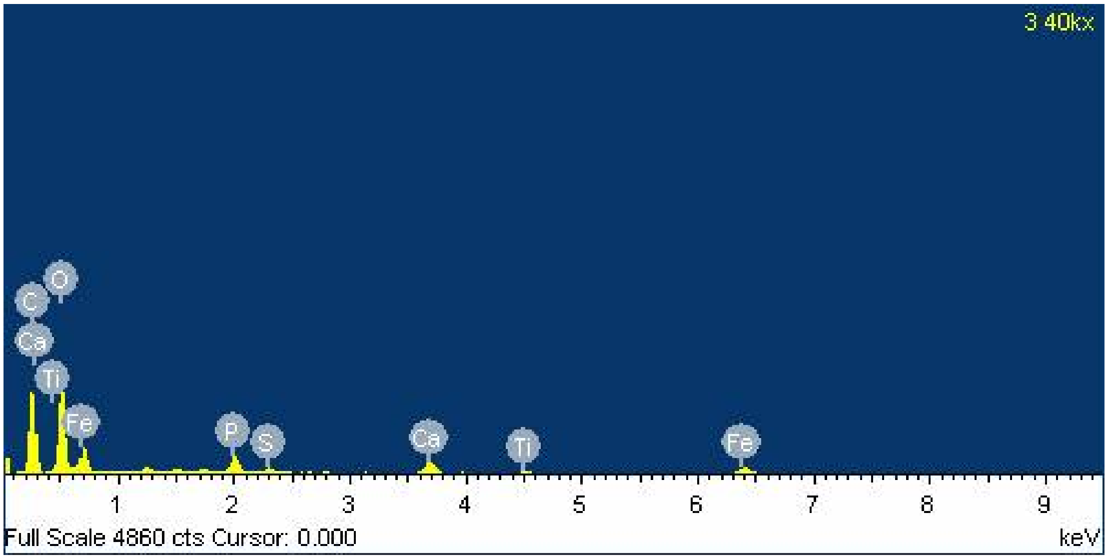
Element	Weight%	Atomic%	Compd%	Formula
C K	19.15	27.40	70.15	CO2
Mg K	0.23	0.16	0.38	MgO
P K	1.46	0.81	3.35	P2O5
S K	1.72	0.92	4.29	SO3
Ca K	2.69	1.15	3.76	CaO
Fe L	14.05	4.32	18.07	FeO
O	60.71	65.23		
Totals	100.00			



APPENDIX B.3 EDX-SAMPLE C

Spectrum processing :
Peak possibly omitted : 1.260 keV
Processing option : Oxygen by stoichiometry (Normalised)
Number of iterations = 2
Standard :
C CaCO3 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM
Fe Fe 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%	Compd%	Formula
C K	15.96	24.89	58.47	CO2
P K	2.21	1.34	5.06	P2O5
S K	0.62	0.36	1.55	SO3
Ca K	3.21	1.50	4.49	CaO
Ti K	1.09	0.42	1.81	TiO2
Fe L	22.24	7.46	28.62	FeO
O	54.67	64.02		
Totals	100.00			



APPENDIX B.4 EDX-SAMPLE D

Spectrum processing :
No peaks omitted
Processing option : Oxygen by stoichiometry (Normalised)
Number of iterations = 2
Standard :
C CaCO3 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM
Fe Fe 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%	Compd%	Formula
C K	5.75	11.15	21.08	CO2
Al K	0.76	0.66	1.44	Al2O3
Si K	2.34	1.94	5.00	SiO2
P K	1.91	1.43	4.37	P2O5
S K	0.55	0.40	1.37	SO3
Ca K	20.76	12.06	29.05	CaO
Ti K	10.45	5.08	17.43	TiO2
Fe K	15.76	6.57	20.27	FeO
O	41.73	60.72		
Totals	100.00