ASH CARBONATION USING CARBON DIOXIDE CAPTURED BY CARBONATES

AIZAT BIN MOHD AMINUDDIN

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ASH CARBONATION USING CARBON DIOXIDE CAPTURED BY CARBONATES

by

AIZAT BIN MOHD AMINUDDIN

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LIST OF SYMBOLS

	Symbol	**Unit**
A	Arrhenius factor	-
Ea	Arrhenius activation energy	J/mol
K	Rate costant	-
M_{CO2}	Mass of carbon dioxide	g
M_{POFA}	Mass of palm oil fuel ash	g
R	Ideal gas constant	J/mol K
T	Absolute temperature	K
T_B	Bulk temperature	K
T_i	Instantaneous temperature	K

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy
CCS	Carbon dioxide capture and storage
CDIAC	Carbon Dioxide Information Analysis Centre
CFA	Coal fly ash
CO_2	Carbon dioxide
CPOA	Coarse palm oil fuel ash
EBT	Eriochrome Black T
EDTA	Ediaminetetraacetic acid
EFB	Empty fruit bunch
FA	Fly ash
FBC	Fluidized bed combustion
FGD	Flue gas desulphurization
FPOA	Fine palm oil fuel ash
FTIR	Fourier transform infrared
L/S	Liquid-to-solid
MEA	Monoethanolamine
MPOA	Medium palm oil fuel ash
MSWI	Municipal solid waste incinerator
OPA	Oil palm ash
PCC	Precipitated calcium carbonate
PCFA	Petroleum coke combustion fly ash
PI	Process intensification
POFA	Palm oil fuel ash

rpm	Rotation per minute
SEM	Scanning electron microscope

PENGKARBONAN ABU MENGGUNAKAN KARBON DIOKSIDA DISERAP OLEH KARBONAT

ABSTRAK

Peningkatan bahan cemar alam sekitar seperti karbon dioksida (CO_2) dan sisa kelapa sawit telah menjadi satu kebimbangan di Malaysia. Dalam usaha untuk mengurangkan bahan cemar terbabit, pengkarbonan abu minyak kelapa sawit (AMKS) menggunakan CO_2 dari kalium hidrogen karbonat ($KHCO_3$) telah diselidik pada situasi operasi dan setup yang berbeza. AMKS mentah telah dirawat terlebih dahulu melalui pengeringan, pengisaran dan pangkalsinan dan seterusnya dikarbonat oleh $KHCO_3$ dalam keadaan akueus menggunakan penangas air. Kesan pengkalsinan (500-800 °C selama 90 & 180 minit), masa tindak balas (2-30 minit), suhu tindak balas (30-75 °C) dan kadar pengadukan (100-250 rpm) juga dinilai. Pembolehubah terbaik yang diperoleh menggunakan pentitratan kompleksometri Ca^{2+} ialah pada 800 °C (180 minit) pengkalsinan, 75 °C (20 minit) tindak balas dan 250 rpm yang memberi penyerapan 0.0023, 0.0079 and 0.0043 g CO_2 /g AMKS masing-masing. Menggunakan keadaan yang sama (60 °C), tindak balas pengkarbonan telah diulang dan dibandingkan menggunakan penggoncang inkubator dan pensintesis gelombang mikro dengan pelesapan haba yang berbeza. Pensintesis gelombang mikro merupakan peralatan terbaik untuk pengkarbonan, dengan penyerapan CO_2 sebanyak 0.0067 g/g AMKS. Pada 75 °C, AMKS telah berjaya menyerap 0.0098 g CO_2/g AMKS. Masa tindakbalas kemudiannya dipelbagaikan menggunakan pensintesis gelombang mikro yang menunjukkan prestasi yang tetap mulai minit ke-10. AMKS juga telah dicirikan menggunakan mikroskop imbasan electron (SEM) yang memaparkan pengurangan karbon dan bendasing di dalam abu setelah proses pengkalsinan.

ASH CARBONATION USING CARBON DIOXIDE CAPTURED BY CARBONATES

ABSTRACT

Rise of environmental pollutants such as carbon dioxide (CO_2) and oil palm waste have been a grave concern in Malaysia. In an effort to reduce the pollutants, carbonation of palm oil fuel ash (POFA) using CO_2 locked in potassium hydrogen carbonates ($KHCO_3$) was investigated at different operating conditions and setup. Raw POFA was first prepared by drying, grinding and calcining. After preparation, the ash was subsequently carbonated with $KHCO_3$ in aqueous condition using water bath shaker. The effect of calcination (500-800 °C at 90 & 180 min), reaction time (2-30 min), reaction temperature (30-75 °C) and stirring rate (100-250 rpm) were also evaluated. The best conditions obtained using complexometric titration of Ca^{2+} were at 800 °C (180 min) calcination, 75 °C (20 min) reaction as well as 250 rpm which have resulted in 0.0023, 0.0079 and 0.0043 g CO_2 captured/g POFA used respectively. Using similar operating conditions (60 °C), the carbonation reaction was repeated and compared using incubator shaker and microwave synthesizer with different heat dissipation. Microwave synthesizer demonstrates the best equipment to be used for carbonation, with CO_2 capture of 0.0067 g/g POFA. At 75 °C, POFA was able to capture 0.0098 g CO_2/g POFA. The reaction time was then varied for the microwave synthesizer which shows the constant performance starting from the 10th min. The POFA were characterized using scanning electron microscope (SEM) that shows a reduced carbon and impurities present in the ash after calcination.

CHAPTER ONE

INTRODUCTION

1.1 Carbon Dioxide Capture via Ash Carbonation

The world's population is expected to increase by 0.9 % from year to year. To meet the rising demands of energy consumption due to this population growth, the power plants are increasing their energy production through more combustion of fossil-fuel. As of the year 2001, 13.5 TW energy were consumed with 86 % of such energy coming from fossil fuel (Lewis and Nocera, 2006).

However, with the combustion of fossil fuel, carbon dioxide (CO_2) is expected to be released as a product. CO_2 which is a greenhouse gas have the ability to absorb reflected solar radiation; trapping and emitting them back to the earth's surface. As a result, heat is unable to escape the outer space causing rise in the planet's temperature (Raval and Ramanathan, 1989). This phenomenon is known as global warming. As a result, CO_2 emission rate is also expected to double from year 2001 to 2050 (Lewis and Nocera, 2006). Carbon Dioxide Information Analysis Centre (CDIAC) reported that the amount of atmospheric CO_2 to have reached 400 ppm in 2015 (Dlugokencky and Tans). CO_2 which is believed to be associated to global warming, can potentially cause adverse environmental, social and economic impacts. A greener solution has been long searched (Borhani et al., 2015).

CO_2 is the major greenhouse gas emitted at global scale due to human activities. It is relatively higher than other gases amounting to 76% of global greenhouse gas emission in 2010 (IPCC, 2014). As of 2015, the global CO_2 concentration reaches 400 ppm with an increase of approximately 1.8 ppm per year. Through prediction of climate modelling, it is estimated that 450 ppm is the top cap of

CO_2 concentration with 2034 being the expected end time (OECD, 2012). However, many leading scientists predicted that the safe CO_2 concentration level is only 350 ppm (Hansen et al., 2013). At the 15th Conference of Parties, Malaysia's current Prime Minister, Datuk Seri Najib Tun Razak announced that Malaysia will take steps for a voluntary reduction of up to 40% in terms of emissions intensity of GDP by the year 2020 compared to 2005 levels (COP15, 2009). In order to achieve such target, intensive carbon emission controls have to be implemented by the Malaysian society.

Although CO_2 is one of the major greenhouse gases, it is still useful in several industrial applications such as in urea production, methanol synthesis and as natural refrigerants (Borhani et al., 2015). Hence, a proper CO_2 capture and storage (CCS) technology that is not only cost-effective but also environmentally friendly must be employed. The modern CCS consists of three basic stages of CO_2 separation, transportation and storage. The CO_2 separation can be further classified into pre-combustion, oxy-fuel combustion and post-combustion capture (Wang et al., 2015). These capture methods including absorption, adsorption and membranes have been implemented to reduce the carbon emission (Zhang and Lu, 2015).

Absorption using amine has been established more than 60 years in oil and chemical industries. Although use of chemical absorbent such as monoethanolamine (MEA) is considered a benchmark of the field, it raises serious drawbacks including strong equipment corrosion rate and high energy requirement during regeneration (Borhani et al., 2015; Wang et al., 2015; Zhang and Lu, 2015; Saeed and Deng, 2016). Therefore, carbonate absorption method is introduced and offers an alternative to a reduced energy in CO_2 capture.

Carbonate absorption uses the alkaline components (absorbent) such as Ca, Mg, Na and K, where the CO_2 absorbed is incorporated into its chemical compounds. It provides easier regeneration, lower solvent cost as well as lower toxicity (Borhani et al., 2015). There are two routes for carbonation namely direct and indirect route (He et al., 2013). The former route directly injects the raw source materials into the carbonation process whereas needed alkaline components are extracted from source materials prior to carbonation for the latter route (Han et al., 2015). Additionally, carbonation can be divided into dry and wet processes.

Different materials are suitable for carbonation, for example silicate rocks, serpentine, olivine minerals, slag and ash (Mazzotti et al., 2005). In this case, ash is used due to its cheap and easy availability, thus able to meet requirements for large quantity treatment (Guo et al., 2015). Several CO_2 carbonation based on solid residue has been studied which includes municipal solid waste incinerator (MSWI) bottom ash, fluidized bed combustion (FBC) ash, flue gas desulphurization (FGD) spray dryer ash and fly ash (FA) (Huijgen and Comans, 2005).

1.2 Problem Statement

Ash carbonation can be performed by direct dry as well as direct and indirect aqueous route. From previous studies, direct dry routes are generally used due to its simplicity in reaction and heat generation. However, its slow reaction rate and low carbonation ratio makes it less favourable (Han et al., 2015). Indirect carbonation route enables production of purer precipitated calcium carbonate (PCC) that has an added market value (Eloneva, 2010). Unfortunately, it is considered to be energy and chemical intensive (Bobicki et al., 2012). On the other hand, direct aqueous carbonation have recorded high carbonate conversions and acceptable reaction rates in majority of its studies. Even though it is deemed as energy intensive due to the pre-treatment processes, many researchers thought this route to be the most promising technique for CO_2 mineralization (Bobicki et al., 2012). Wood ash such as palm oil fuel ash (POFA) is also favoured as it is recognized as an environmental pollutant hence solving two pollution problems simultaneously (Guo et al., 2015). Various studies have been done in order to evaluate the performance of ash carbonation on CO_2 capture. Majority of the study done is to investigate the effects of different parameters change such as solid-to-liquid ratio, reaction time as well as extraction agent type and concentration on the carbonation efficiency (He et al., 2013; Han et al., 2015; Guo et al., 2015; Rendek et al., 2016). Studies in other important parameters such as effect of ash calcination temperature, carbonation reaction temperature and stirring rate are lacking.

Conventionally, the carbonation process is done using either a water bath or simple reactor system to supply the required heat and mixing to the reaction (He et al., 2013; Guo et al., 2015; Han et al., 2015). All of this methods apply a conventional heating process with an external heat source. This method is slow and inefficient method of transferring energy compared to microwave–accelerated heating which uses microwave irradiation (Hayes, 2004).

1.3 Research Objective

The main objectives of this research are:

i. To study the CO_2 storage capacity of direct aqueous carbonation route of POFA at different operating parameters.

ii. To compare the ash carbonation performances using different experimental setups namely water bath shaker, incubator shaker as well as microwave synthesizer.

1.4 Scope of Study

In this work, the POFA was used to capture CO_2 from carbonates. The POFA was prepared physically via drying, grinding and sieving to allow better contact and reaction between the ash and carbonates. The POFA was calcined (500-800 °C), mixed with carbonates and allow to react at different time. At the optimum time achieved for carbonation of POFA, the experiment was proceeded at varying temperature (30-75 °C) and stirring rate (100-250 rpm) using a water bath shaker. The best operating parameters were then used for subsequent experiments. Using similar parameters from previous part, the carbonation efficiency of POFA with carbonates was then determined using incubator shaker and microwave synthesizer. The time of reaction was varied once again using the best mode of carbonation to determine its optimum value.

CHAPTER TWO

LITERATURE REVIEW

2.1 Mineral Carbonation

Mineral carbonation is a reaction whereby CO_2 is fixed to metal oxide-bearing minerals (Ca, Mg and etc.) to form a stable carbonate as the end product. CO_2 mineral carbonation or sequestration is a technique first mentioned in 1990 by Seifritz (1990). He suggested that we should copy a natural phenomenon which involves the reaction between atmospheric CO_2 and water to form soluble carbonic acid that forms insoluble carbonates with alkaline rocks subsequently. Following that, the first major research on mineral carbonation was later developed by Lackner et al (1995).

Calcium carbonate is the thermodynamically stable product of mineral carbonation (Newall et al., 200). Thus, CO_2 can be stored for a very long time without the necessary of CO_2 monitoring (Lackner, 2003). However, mineral carbonation is exothermic in overall, requiring a large amount of additives or energy to speed up the reaction (Eloneva, 2010). Due to recent alarming development in global warming, many studies have been conducted to curb the problem particularly by carbon capture. One of the technologies that received much attention is mineral carbonation using solid residue such as ash.

2.2 Ash Carbonation

In general, calcium and magnesium oxides or hydroxides are the most suitable raw materials for storing CO_2 through mineral carbonation. Unfortunately, these resources are too rare in nature for any large-scale CO_2 sequestration (Eloneva, 2010). Therefore, other readily available source of raw materials had been widely researched for mineral carbonation process. Currently, industrial waste materials, such as steelmaking slags, de-inking ash from paper recycling, ashes from various power plants and MSWI had been considered (Eloneva, 2010). Industrial wastes are also favourable as they tend to be more reactive than natural minerals (Teir et al., 2007).

Several studies have proven that usage of FA can successfully capture CO_2 during the carbonation reaction (Soong et al., 2006; Ukwattage et al., 2013; González et al., 2014; Dananjayan et al., 2016). Valuable carbonate products have also been successfully produced due to the presence of alkaline components present inside the ash. Similarly, bottom ash (Rendek et al., 2006) and biomass ash (Guo et al., 2015) also showed positive CO_2 captured by these ash. Bottom ash from MSWI was able to capture CO_2 generated from aerobic respiration of microorganisms inside the wastewater potentially eliminating the need of disinfection in wastewater treatment plant. Table 2.1 shows various ash used for the carbonation reaction.

2.3 Ash Properties and Compositions

The characterisation of ash is important to determine the success of carbonation. The ash availability, properties, compositions, solubility and reactivity must be taken into detailed consideration. The physical size of the ash plays an important role in its pozzolanic properties. Coarser particle size ash leads to a weak pozzolanic material that will not affect much on its application as a cement additive (Al-mulali et al., 2015).

FA is a fine, powdery particles that is spherical in shape. It is mostly amorphous in nature; and can be either solid or hollow. The particle size distribution of a CFA is usually less than 75 micron. FA surface area may vary from 170 to 1000 m^2/kg and

2.1 to 3.0 in specific gravity (Ahmaruzzaman, 2010). Amount of unburned carbon in the ash result in variation from tan to black colour of the ash. On the other hand, POFA or oil palm ash (OPA) is produced due to the incineration of palm oil biomass. Similar to FA, amount of carbon present affects the visual of the ash. Lower burning temperatures leads to a black to dark grey colour due to the high amount of unburned carbon. Increasing the burning temperature causes a lighter coloured ash production. POFA is a large particle sized substance with a porous texture. Due to its large size, grinding process is needed to produce a smaller size. This will increases both the finesse and specific gravity of the ash (Al-mulali et al., 2015).

Table 2.1 Ash carbonation researches reported in literature

Type of Ash	Remarks	Reference
FA	Two years old coal fly ash (CFA) from a power plant	Dananjayan et al., 2016
	Petroleum coked fly ash from power plant in Chile	González et al., 2014
	Combustion of Victorian brown coal	Ukwattage et al., 2013
	Victorian brown CFA from an electrostatic precipitator	Sun et al., 2012
	Co-utilizes brine and FA from coal burning power plant	Grace et al., 2012
	Class C FA and FGD FA	Soong et al., 2006
Bottom ash	From a mass burn MSWI in France	Rendek et al., 2006
Wood ash	Various preparation methods deriving from broad-leaved tree, rice stalks, wheat and sunflower	Guo et al., 2015

Ash can be categorized differently based on the techniques used for its handling and storage. Generally, its properties depend on the heating value, chemical composition, ash content and geological origin. Commonly, the major components of FA consists of silica (SiO_2), aluminium (Al_2O_3), iron (Fe_2O_3) and calcium (CaO). (Ahmaruzzaman, 2010). In contrast, biomass ash varies depending on type of biomass, type of soil and harvesting. Different sources produce ashes with different characteristics. In general, calcium (Ca), potassium (K), sodium (Na), silicon (Si), and phosphorus (P) are abundant. Certain ash such as rice husk are rich in silicon whereas wood ash has high alkali metal content. Similarly, POFA differs in properties based on its production process. In order to obtain its optimal condition, prior processing is required to remove any impurities present. Firstly, POFA needs to be sieved in order to obtain ash particles without any unburned fibres and to increase its pozzolanic reactivity. Unburned carbon can also be removed via heating in an electrical furnace (Al-mulali et al., 2015).

In 2006, Soong et al. (2006) studied the CO_2 sequestration using FA and brine solution. In this study, FA taken from Lignite, Freeman, Columbia, Waukegan, Muskogee and Montose in United States were used. Detailed analysis done using ICP-AES shows diverse compositions, but with generally higher amount of SiO_2 and CaO in all ashes. Due to the presence of CaO, $Ca(OH)_2$ is formed when exposed to brine. As it is readily oxidize, OH^- is released and produced $CaCO_3$ in presence of CO_3^{2-}. A study by Rukzon and Chindaprasirt (2009) was done for POFA from a power plant in south of Thailand. XRD analysis for three different sample of coarse (CPOA), medium (MPOA) and fine POFA (FPOA). The analysis shows major composition of SiO_2 (64.5, 62.8 and 63.6 %) followed by CaO (7.8, 7.7 and 7.6 %). As the CaO content increases, more CaO can be used as the cement additives. Thus, strength of the cement can be improved. Another study on interaction between CO_2 and MSWI bottom ash is done by Rendek et al. (2006). Major elements of the MSWI from Lyon, France analysed is SiO_2 (49.3 wt. %) and CaO (16.3 wt. %) using both ICP-AES and ICP-MS. As CO_2 is released from respiration of microorganisms in wastewater, CaO from the bottom ash are able to be self-carbonated to form $CaCO_3$. Hence, two major environmental problems were suggested to be solved. In 2012, Sun et al. (2012) tested a dry sample CFA collected directly from an electrostatic precipitator in Victoria, Australia. The sample contains mainly 29.7 wt. % CaO and 25.5 wt. % MgO. High amount of CaO compared to MgO aid in the formation of $CaCO_3$ compared to magnesium carbonate. From this study, it is stated that increasing the CO_2 concentration also lead to more calcium carbonation than magnesium.

CO_2 sequestration via indirect carbonation of CFA was conducted by He et al (2013). During this study, FA sample from China was used and analysed using XRF and XRD to give major compositions of 30.47 wt. % CaO and 20.64 wt. % SiO_2. The presence of SO_3 indicates that part of CaO occurs as sulphate. In 2014, CO_2 carbonation using petroleum coke combustion fly ash (PCFA) taken from Chile was evaluated by González et al. (2014). Using ICP-MS and ICP-AES, 34.1 % Ca was detected as the main element. Guo et al. (2015) has done a study on CO_2 capture and sorbent regeneration performances of wood ashes in 2015. In his study, five samples of wood ashes were obtained from dry stalks of rice, wheat, sunflower as well as branches and leaves of broad-leaved trees. All the samples were prepared by either sampled from biomass-fired power plants, collected from farmers or prepared manually. Composition analysis of wood ash using XRF shows similar elements present but with varying amount. Si content was noted to be higher in stalks of rice or wheat. On the other hand, broad-leaves tree and sunflower is highly enriched in Ca while content of K is higher in stalks of sunflower. Combustion temperature was also noted to have an effect in its composition. At high temperature, losses of silica and silicates is minimum leading to higher SiO_2 component compared to the rest. Different compositions can then lead to formation of various carbonate end products. A CFA-water solution system indirect mineral carbonation's performance was also recently done by Han et al. (2015). In this experiment, FA generated from South Korea was used as raw material with water as the solvent. The element composition calculated based on EDX recorded 42.28 mg Ca/g fly ash as its main composition. Based on its findings, not all CaO from the FA will be carbonated to $CaCO_3$. Other carbonate materials such as tetra calcium aluminium carbonate was also found during the product analysis. Table 2.2 below summarizes the analytical results of various studies done.

2.4 Methods of Carbonation

Currently, mineral carbonation research is mainly at the level of laboratory-scale research. Figure 2.1 illustrates the two basic mineral carbonation process concepts that is direct and indirect methods. Various pre-treatment methods, such as grinding, heat activation, magnetic separation, and surface activation, have been suggested in order to speed up the carbonation rate.

In direct methods, the mineral is carbonated in just a one step process. The raw source materials which contain alkaline components (Ca or Mg) can be directly reacted with CO_2. Direct gas-solid method is generally preferred as it is simple and cheap. Not only that, it is possible to upgrade the waste material to a more useful product. However, since the process is one step, it is unlikely for the product to be a pure carbonate and usually require a high pressure CO_2 (Eloneva, 2010). The direct method can be further classify into direct dry and direct aqueous routes.

Table 2.2 Composition of different ash type

Type of Ash	Analysis Method	Major composition	Reference
CFA	EDX	42.28 mg Ca/g fly ash	Han et al., 2015
Wood ash	XRF	Si, Ca and K	Guo et al., 2015
PCFA	ICP-MS and ICP-AES	Ca (34.1%)	González et al., 2014
CFA	XRF and XRD	CaO (30.47 wt. %) SiO_2 (20.64 wt. %)	He et al., 2013
Victorian brown CFA	-	CaO (29.7 wt. %) MgO (25.5 wt. %)	Sun, et al., 2012
POFA	XRD	SiO_2 (62.8-64.5 %) CaO (7.6-7.8 %)	Rukzon and Chindaprasirt, 2009
MSWI bottom ash	ICP-AES and ICP-MS	SiO_2 (49.3 wt. %) CaO (16.3 wt. %)	Rendek et al., 2006
FA	ICP-AES	SiO_2 and CaO	Soong et al., 2006

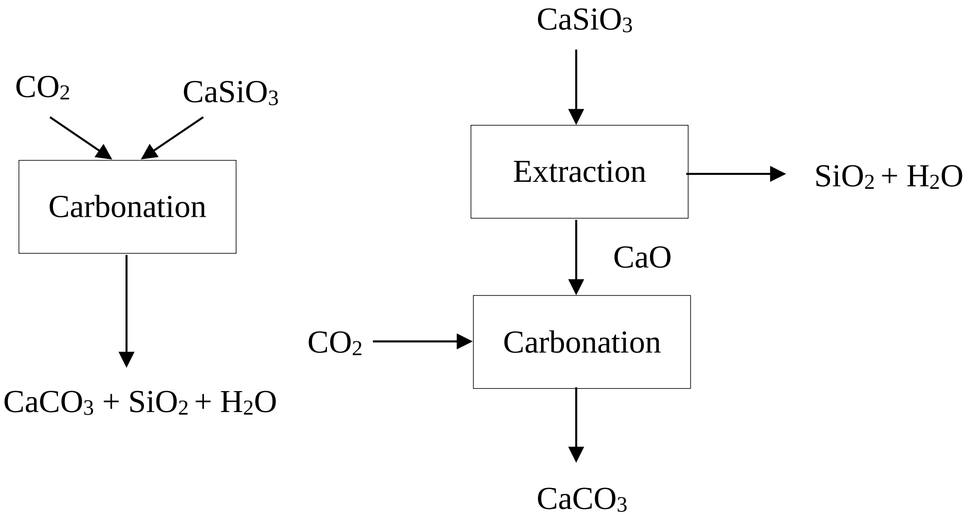

Figure 2.1 Basic principles of direct and indirect carbonation method ($CaSiO_3$ as example) (Eloneva, 2010)

In indirect methods, the reactive, alkaline element is first extracted from the ash prior to carbonation. Due to use of extraction agents, dry raw materials cannot be used in this route. It is a more favourable route since the end product of indirect mineral carbonation is usually a high purity PCC which is very valuable (He et al., 2013) due to its prior removal of the reactive element. However, additional chemicals for the extraction is needed in this route. Brief pros and cons of both carbonation routes are concluded in Table 2.3.

2.4.1 Direct Dry Carbonation

Ash and other additives are used as direct CCS materials in the dry process. The ash is used to support the catalytic sorbent for CO_2 capture and as a raw material of zeolite. Dry sorbents can be effectively used for CO_2 capture as the sorbents are generally regenerated. In this method, dry solid is directly bubbled with CO_2 gas at suitable operating conditions.

In 2010, Olivares-Marín et al. (2010) utilizes SiO_2 in FA to produce Li_4SiO_4 via solid state method. The Li_4SO_4 was then reacted with CO_2 at 950 °C as shown:

$$Li_4SO_4 + CO_2 \rightarrow Li_2SiO_3 + Li_2CO_3 \qquad (2.1)$$

The authors claimed that the sorbent regeneration improved but at the cost of capture performance. Addition of carbonates (K_2CO_3) also enhances the capture capacity up to 600 °C.

Table 2.3 Advantages and disadvantages of different carbonation methods (Eloneva, 2010)

Method	Route	Ash Used	Advantages	Disadvantages
Direct	Gas-solid	Silicate minerals MSWI ash	Upgrading of the waste material	Slow with natural minerals
	Aqueous	Silicate minerals Steel slag Oil shale ash	Simple process	End product not pure carbonate High pressure Require pure CO_2
Indirect	Gas-solid via $Mg(OH)_2$	Silicate minerals	High heat produced	Heat requirement of $Mg(OH)_2$ production
	Acid solvent	Silicate minerals	Reactive element extracted efficiently Pure end product	Requires addition of base
	Caustic alkali-metal hydroxide	Silicate minerals		Consumes chemicals
	Acid-base salt	Steel slag	Pure end product	
	Pressure change	Waste cement	Pure end product	Requires pure CO_2

A direct FA-flue gas carbonation reaction was performed by Reddy et al. (2011) in a pilot-scale plant. The results showed a CO_2 decrease from 13 % to 9.6 %. It is claimed that the CO_2 in the flue gas will react with Ca in the FA to generate $CaCO_3$ and various other carbonates. The study shows that 90% of the CO_2 emitted was captured, which compares to a CO_2 storage capacity of 0.207 g CO_2/g of FA. In 2015, Guo et al. (2015) uses wood ash to capture CO_2. At the end of carbonation process, the maximum capacity of 0.54 mmol CO_2/g was achieved. After that, the effects of reaction conditions such as temperature, H_2O concentration and gas flow rate were also studied. The results show that increasing the concentration and temperature will raise up the capacity whereas increasing the reaction temperature will cause the opposite effect.

Although the process is relatively simple, this direct gas-solid reaction is too slow even at optimized conditions (Bobicki et al., 2012). As mentioned earlier, the product of is not a pure carbonate making it a valueless product that can only be disposed in a landfill or sometimes used in construction sectors.

2.4.2 Direct Aqueous Carbonation

In contrast to the direct dry method, direct aqueous mineral carbonation reacted the CO_2 with aqueous alkaline material in a single stage. The CO_2 will react with water forming bicarbonate ion. This ion will then react with metal ion contained inside the mineral ash to produce carbonate precipitate. The operating conditions such as temperature and pressure plays an important role in this route (Bobicki et al., 2012). Optimizing these parameters can easily lead to a high carbonate conversion and reaction rate. Despite its many advantages, this route is considered too expensive to be utilized in large scale due to the required pre-treatment process which is very energy intensive. However, many studies have been done with reduced energy requirement but with similar advantages.

In 2008, Back et al. (2008) studied the mineral carbonation of alkaline lignite FA with CO_2 in aqueous state at varying conditions such as CO_2 concentration and temperature. From their findings, it is found that the carbonation occurs at three stages.

During the first stage, Ca and CO_2 begins to dissolve, initiating $CaCO_3$ formation. In the second stage, carbonation process was dominant while formation of bicarbonate occurs during third stage. The CO_2 dissolution in first stage is determined to be the rate controlling step. Reaction time and acidity was manipulated to enhance the CO_2 capture. From the mechanism, the CO_2 capture was calculated to be 90% of the acid neutralizing capacity value of FA. In addition, the carbonation $CaCO_3$ conversion efficiency was over 75%.

Montes-Hernadez et al. (2009) investigated the CO_2 storage capacity of coal combustion FA-water slurry conducted in an autoclave. The reaction was first done by dissolving CaO in the FA with water. This leads to a rapid carbonation to produce $CaCO_3$. The study claimed that carbonation efficiency is independent of initial CO_2 pressure. Reaction temperature and L/S ratio also does not affect the efficiency significantly. The best conversion was found to be 82 % with CO_2 storage capacity of 0.026. It is stated that CO_2 sequestered is smaller when compared to using steel slag. In similar year Uliasz-Bocheńczyk et al. (2009) researched on the mixed slurry of water and lignite FA. The results yield that the CO_2 storage capacity was very strongly dependent on the reaction time with highest storage capacity of 0.055 at 24 h. The authors stated that FA is a good material for CO_2 sequestration by means of mineral carbonation as well as solve problem of deposition of carbonation products.

By manipulating the L/S ratio, Ukwattage et al. (2013) researched on use of CFA on carbonation reaction. Temperature and time was kept constant at 40 °C and 12 h respectively. From the findings, zero moisture lead to an insignificant carbonation reaction at low duration. However, by increasing the moisture content, the carbonation reaction can proceed efficiently but then decreases gradually after a set point. It is also claimed that the ash can potentially reduce mass quantity of CO_2 emitted by power plant annually. González et al. (2014) conducted carbonation with aqueous PCFA. PCFA were first blended with deionized water before being contacted with CO_2. Resulting experiments show that the carbonation efficiency reaches 84 %. However, according to the study, specific optimizations have to be done prior to achieving this value.

2.4.3 Indirect Carbonation

For this aqueous technology, two or more stages are required for the mineral carbonation. Usually, alkaline components in FA are first leached out by using aqueous (acidic or other solvents) solution and then reacted with CO_2 in either gas or aqueous state during the carbonation reaction. Numerous technologies can be used as the extraction agent such as HCl extraction, molten salt process, bioleaching, ammonia extraction and caustic extraction (Bobicki et al., 2012).

For FA-brine carbonation by Soong et al. (2006), presence of CaO in both ash and brine allow formation of $CaCO_3$ when reacted with CO_2. The data presented a high purity of $CaCO_3$ product generated (>90 wt. %). However, no calculation was performed on its capacity to store CO_2. According to the study, both single and multi-stage process can be done to achieve formation of $CaCO_3$ from CO_2 sequestration. However, using extraction process (NaOH), more CO_2 can be sequester. The study implied that CaO in the FA contributes to the carbonation process.

A study by He et al. (2013) for indirect aqueous carbonation of CFA was done in 2013. During extraction, different agents that is NH_4Cl, NH_4NO_3 and CH_3COONH_4 were used with the latter being the most efficient. The effect of temperature and concentration lead to increased extraction efficiency. During carbonation, reaction with NH_4HCO_3 instead of CO_2 yields a higher product purity of 97-98 %. The NH_4HCO_3 used was formed in the ammonia−water CO_2 capture process. From the research, increasing temperature and agent concentration increases the extraction performance which in turn increases the carbonation efficiency. Similar effect can be seen when increasing the L/S ratio. Replacing the conventional method of bubbling CO_2 with aqueous hydrogen carbonate (HCO_3) also improves the carbonation efficiency and CO_2 capture. The authors note that applying this technology to an ammonia-water CO_2 capture facility can help in on-site application.

Han et al. (2015) stated in their research on CFA that both the extraction and carbonation reactions were carried out in ambient temperature and pressure. 15 and 33 mol % CO_2 were supplied for the carbonation process. It is found that both leaching and carbonation efficiency increases with increasing CO_2 concentration. The performance of the FA suspension solutions was found out to be higher than the filtrate as the mineral carbonation was carried out simultaneously with the leaching. They also declared that the process has great potential to be applied on-site such as in CFPP, cement and steel industries. Table 2.4 below demonstrates storage capacity of ash carbonation both direct and indirect aqueous carbonation.

Table 2.4 CO_2 storage capacity of direct and indirect wet-based application

Carbonated System	Liquid/Solid (L/S) Ratio (g/L)	Operating Condition	Storage Capacity (g CO_2 / g ash)	Reference
FA-brine solution [a]	-	20 °C, 1.36 MPa, 2 h	-	Soong et al., 2006
CFA-water slurry [b]	0-0.7	40 °C, 3-6 MPa, 12 h	0.00766	Ukwattage et al., 2013
FA-water slurry [b]	100	30-60 °C, 40 bar, 450 rpm, 2 h	0.026	Montes-Hernandez et al., 2009)
CFA-water slurry [a]	50	25 °C, 300 rpm, 2 h	0.0311	Han et al., 2015
Lignite FA-water slurry [b]	1.5 (w/w)	35 °C, 1 MPa, 24 h	0.055	Uliasz-Bocheńczyk et al., 2009
CFA [a]	20	25 °C, 1 atm, 500 rpm, 2 h	0.111	He et al., 2013
PCFA-deionized water [b]	12	90 °C, 600-1500 rpm, 10-90 min	0.21	González et al., 2014
Lignite FA-water slurry [b]	50	25-75 °C, 0.01-0.03 MPa, 600 rpm, 4.5 h	0.23	Back et al., 2008

a Indirect carbonation
b Direct carbonation

2.5 Precipitated Calcium Carbonate

Due to high calcium content of ash, the carbonate product would typically consist of $CaCO_3$. The produced $CaCO_3$ can potentially replace limestone used in industries and be sold at a high price if meeting its standard. Natural $CaCO_3$ is used for varying purposes such as manufacturing concrete, producing lime, glassmaking, water treatment or flue gas desulphurization. Synthetic or PCC can be used as a filler and coating pigment in plastics, rubbers, paints, and papers.

The advantage of PCC over limestone is that the properties of the produced calcium carbonate can be controlled. The $CaCO_3$ content of PCC is generally higher while the SiO_2 and MgO contents are lower in the limestone (Eloneva, 2010). The utilization of ash to replace limestone in PCC industry can save material resources, reduce CO_2 emissions, and solve problem of waste ash abundance all together.

Referring to Figure 2.2, there are three basic methods to produce PCC; namely the carbonation process, lime-soda process, and calcium chloride-sodium carbonate double salt decomposition process (Casey, 1983). All of these methods use milk of lime ($Ca(OH)_2$) produced from limestone ($CaCO_3$) by calcination and slaking.

At high temperature, limestone is decomposed into lime (CaO) and CO_2 gas. $Ca(OH)_2$ is then produced by slaking the CaO in water. The purity, activity, particle size, concentration, and temperature of the $Ca(OH)_2$ will affect the quality of the PCC (Eloneva, 2010). Since ash already contains significant amount of CaO, the calcination can be skipped altogether leading to a more effective PCC production.

In carbonation process, $Ca(OH)_2$ is bubbled with CO_2 producing $CaCO_3$. The lime soda process uses sodium carbonate (Na_2CO_3) to react with milk of lime to produce $CaCO_3$ and sodium hydroxide (NaOH). However, recovery of NaOH result in unsuitable practice. Milk of lime is first reacted with ammonium chloride (NH_4Cl) to produce calcium chloride (CaCl) during the double salt decomposition process. The CaCl is then reacted with soda ash solution producing $CaCO_3$ and sodium chloride (NaCl).

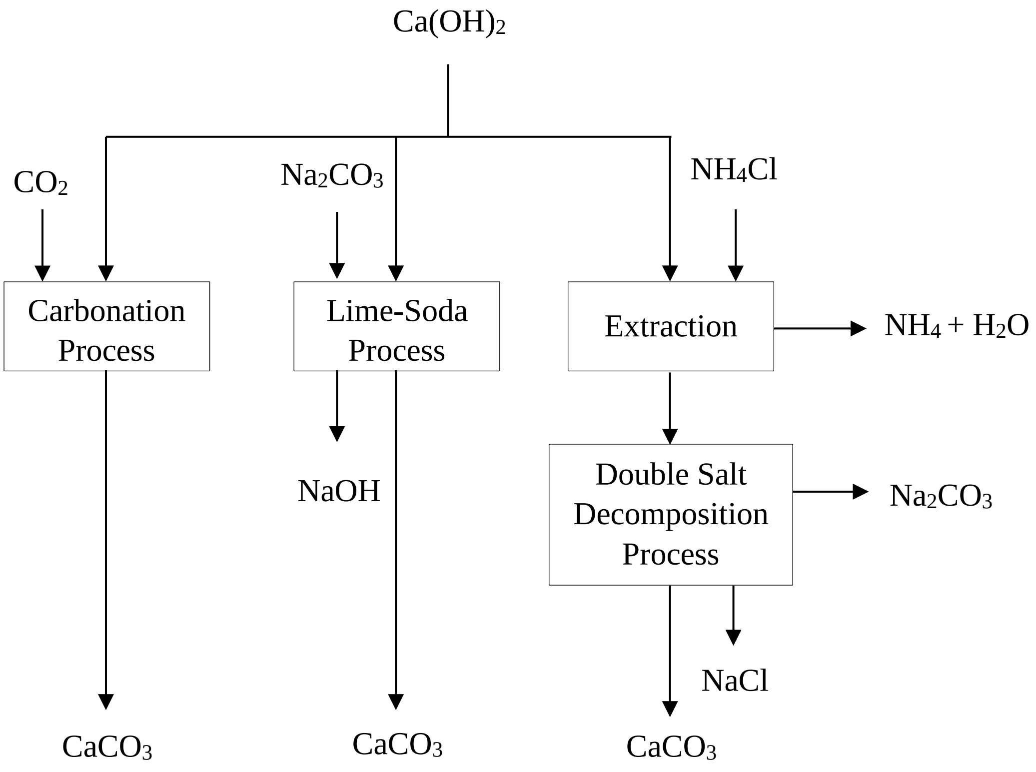

Figure 2.2 Basic principles of PCC production routes (Eloneva, 2010)

2.6 Utilization of Mineral Ash

Currently, FA is widely used as a cement additive. SiO_2 and Al_2O_3 in FA will react with slaked lime and water according to the Pozzolan reaction when FA is mixed with the Portland cement. As a result, calcium silicate and calcium aluminate hydrates are produced. These substances can considerably increase the resistance and strength of the cement (Wee, 2013). Besides cement additive, FA can also be used for the purpose of ceramic balls for water purification, zeolite synthesis, polish materials of steel plate, anti-flaming, building and fill materials. Nonetheless, these applications does not have much impact in terms of CO_2 emission reduction.

Conversely, POFA which originated from the incineration of palm oil empty fruit bunch (EFB) and fibres can be used as a soil fertilizer due to its high potassium content (Al-mulali et al., 2015). In addition, POFA is also used as low cost adsorbent for gaseous pollutants (Mohamed-Noor et al., 2004; Lee et al., 2005) as well as an absorbent for dispersed dyes in an aqueous solution (Chu and Hashim, 2002). Similar to FA, POFA can also be used as supplementary cementing material (Chindaprasirt and Rukzon, 2009). Table 2.5 shows the applications of the industrial waste ash.

Table 2.5 Application of different ash type

Ash Type	Application	Reference
FA	Cement additive	Wee, 2013
	Water purification, zeolite synthesis, polish materials, anti-flaming, building and fill materials	Wee, 2013
POFA	Solidification/stabilization of nickel hydroxide	Yin et al., 2008
	Removal of flue gas contaminants	Mohamed-Noor et al., 2004; Lee et al., 2005
	Removal of zinc ions	Chu and Hashim, 2002
	Cement additives	Chindaprasirt and Rukzon, 2009

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials and Chemicals

In this study, POFA was used as raw material for the ash carbonation reaction with potassium hydrogen carbonates ($KHCO_3$) used as the source of CO_2. Ediaminetetraacetic acid (EDTA), Eriochrome Black T (EBT) and potassium chloride (KCl) were used in complexometric titration of the carbonated solution for determination of Ca^{2+} content. Table 3.1 shows the list of chemicals used throughout the experiments.

Table 3.1 List of chemicals used in ash carbonation experiment

Chemicals	Purity	Supplier
POFA	-	Palm Oil Mill Boiler in Selangor, Malaysia
$KHCO_3$	> 99 %	R&M Chemicals
EDTA	98 %	Ajax Chemicals
EBT	65 %	Sigma Chemical Company
KCl	99.5 %	R&M Chemicals

3.2 Equipment

Oven, grinder and sieve shaker were used to prepare the POFA to the desired conditions while furnace was used to calcine the ash. Three equipment settings were used for carbonation reaction that is water bath shaker, incubator shaker and microwave synthesizer. Finally, scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the POFA. The list of equipment and its general use is tabulate in Table 3.2 below.

Table 3.2 List of equipment used in ash carbonation experiment

Equipment	Purpose
Oven	Drying of POFA
Grinder	Grind POFA to smaller size
Sieve shaker	Sieve only desired size of POFA to be used
Furnace	Calcination of POFA
Incubator shaker	Setting for carbonation reaction
Water bath shaker	Setting for carbonation reaction
Microwave synthesizer	Setting for carbonation reaction
SEM	Characterization of POFA
FTIR	Characterization of POFA

3.3 Project Management Plan

The overall experimental activities will be carried out as presented below.

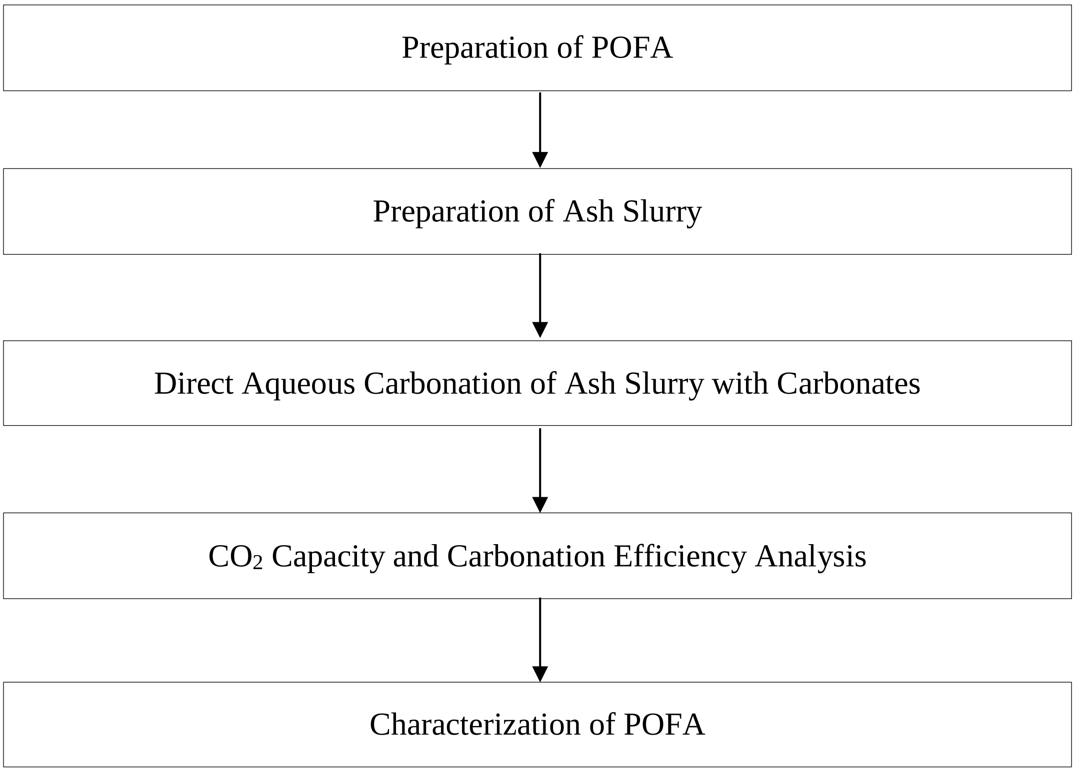

Figure 3.1 Schematic Flow Diagram of Experimental Activities