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# Catalytic Pyrolysis of Poly Vinyl Chloride as a Viable Way of Waste Management

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CATALYTIC PYROLYSIS OF POLY VINYL CHLORIDE AS A VIABLE

WAY OF WASTE MANAGEMENT


By


Randy Santos Fermin


A creative project submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

PLAN B

in

Biological Engineering


Approved:


_____        _____
Foster A. Agblevor                     Ronald Sims
Major Professor                        Committee Member


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Issa Hamud
Committee Member


UTAH STATE UNIVERSITY
Logan, Utah

2016

# ABSTRACT

Catalytic Pyrolysis of Poly Vinyl Chloride as a Viable Way of Waste Management

by

Randy Santos, Master of Science

Utah State University, 2016

Major Professor: Dr. Foster A. Agblevor
Department: Biological Engineering

The main purpose of this investigation is to achieve the dechlorination and cracking of PVC producing a low chlorinated oil using a single step process; finding and using a suitable adsorbent that captures the chlorine released in the decomposition of the Poly Vinyl Chloride in the solid phase; then use the adsorbent to enhance red mud chlorine absorption activity. Find an alternative viable use for the waste PVC and red mud that will reduce landfilling. Calcium Hydroxide was selected as the main chlorine adsorbent since it captured 75% chlorine in the solid phase. The calcium hydroxide was mixed with red mud (50/50 wt/wt), and pyrolyzed at 400 °C in a $N_2$ environment for 60 min in a fixed bed reactor using PVC to catalyst ratio of 1:1. The oil had less than 10 ppm chlorinated products and had a higher heating value of 40.78 MJ/kg.

(44 pages)

# PUBLIC ABSTRACT

Catalytic Pyrolysis of Poly Vinyl Chloride as a Viable Way of Waste Management

Randy Santos Fermin

The main purpose of this investigation is to achieve the dechlorination and cracking of PVC producing a low chlorinated oil using a single step process. Using a suitable solid mineral that adsorbs the chlorine released in the decomposition of the PVC resin, then use the proposed adsorbent to enhance red mud (an Aluminum mining waste) adsorption activity to produce a non-toxic oil which can be used as a fuel. Thus, find alternative uses for the waste PVC and red mud, to avoid the landfill of these products.

Various potential solids were evaluated, with slaked lime selected as the chlorine adsorbent. The decomposition was done in the absence of oxygen to avoid burning of the material, the oil was extracted from the solids, then concentrated, and finally analyzed for its chlorine content. The oil contained less than 10 parts per millions of chlorinated compounds.

# ACKNOWLEDGMENTS

Sincerely,

*Randy Santos Fermin*

# CONTENTS

## Table of Contents

# LIST OF TABLES

# LIST OF FIGURES

# LEGEND AND CHEMICAL FORMULAS

- PVC: Polyvinyl Chloride

- VCM: Vinyl Chloride Monomer

- RM: Red Mud

- PE: Polyethylene

- PP: Polypropylene

- PS: Polystyrene

- XRD: X-ray Diffraction

- TGA: Thermogravimetric Analysis

- DGT: Differential Thermogravimetric Analysis

- AZCC: Aluminum Zinc Carbon Composite

- CSTR: Continuous Stirred Tank Reactor

- GC-MS: Gas Chromatography Mass Analyzer

- EPA: Environmental Protection Agency

- $Ca(OH)_2$: Calcium Hydroxide

- NaOH: Sodium Hydroxide

- HCl: Hydrochloric Acid

- KOH: Potassium Hydroxide

- $Fe_2O_3$: Iron Oxide (III)

- CaO: Calcium Oxide

- $CaCO_3$: Calcium Carbonate

- $MgSO_4$: Magnesium Sulfate

- $K_2CO_3$: Potassium Carbonate

- FeO: Iron Oxide (II)

- Fe: Iron

- X: conversion

- dx/dt: rate of conversion

- $m_0$: initial mass

- $m_t$: mass at time t

- $m_\infty$: residual mass

# CHAPTER 1: INTRODUCTION

Polyvinyl chloride (PVC) is a polymer widely used in the construction, automotive, packaging, electronics, medical, cards, leisure, office, and clothing industry (Barnes, et al. 2009). On global basis, is the third most produced synthetic polymer. Globally every year approximately 39.3 million of tons of PVC are consumed with a growing demand of 3.2% per year (Kanters, et al. 1996). Per the United Nations Environmental Program, between 22% and 43% of the plastic used worldwide is wasted.

PVC waste management is a major challenge because it takes more than 100 years to biodegrade, and most of the recycling techniques are not viable or involves the production of toxic chlorine compounds.
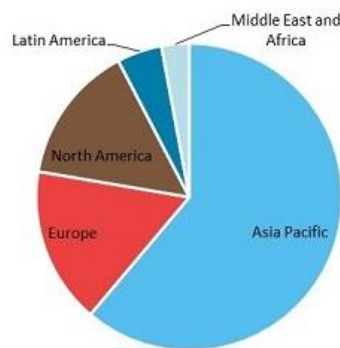


*Figure 1. Distribution of Global PVC Production (2016). Adapted from PVC:2016 World Market Outlook and Forecast up to 2020, Merchant and Consulting ltd.*

The waste management and recycling of PVC includes: re-extrusion, mechanical, chemical, and burning (Yue, et al. 2016). Re-extrusion/ mechanical involves destroying the plastic products, then re-shaping into new products. The problem with these treatments is that PVC is a thermos-plastic, which means it decomposes during heating, so using mechanical methods has limited applications. Burning the PVC releases HCl and can potentially produce dioxins and phthalates which are toxic and known carcinogens (Thornton 2002).

Chemical treatment includes: gasification, pyrolysis, and chemical depolymerization (Yue, et al. 2016), but still a dechlorination step is needed to produce an oil which can be used as an energy source, most of the PVC pyrolysis process includes a dechlorination step follow by the cracking of the polymer or vice versa, but this two-step process is not viable.

The purpose of this study was to evaluate different catalysts that exhibit chlorine capture properties using thermogravimetric analysis to determine which catalyst captures the most chlorine in the solid phase. Then mix the chlorine captor with Red mud to use this catalyst mixture to produce a low chlorine oil. The goal of this research is to achieve the dechlorination and cracking of PVC producing a low chlorinated oil using a single step process.

## 1.1 Background Information

### 1.1.1 Polyvinyl Chloride (PVC)

PVC with general chemical formula: $-(CH_2CHCl)_n-$ is a thermoplastic polymer made from the polymerization of vinyl chloride monomer (VCM), the monomer of the polymer molecule; PVC is obtained by reacting ethylene gas with chlorine gas to form ethylene dichloride (1,2-dichloroethane) "EDC" (equation 1).

$$H_2C=CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl \qquad (1)\ EDC\ production$$

$$ClCH_2CH_2Cl \rightarrow CH_2=CHCl + HCl \qquad (2)\ VCM\ production$$
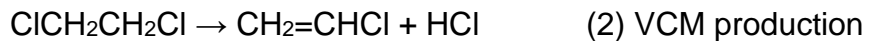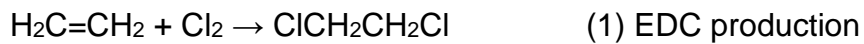
The EDC is converted to VCM through thermal decomposition at 500 °C and 15-30 atm of pressure (equation 2). The VCM is then purified and polymerized to obtain the PVC in powder form. Various polymerization methods are used, including suspension polymerization, emulsion polymerization, or bulk polymerization. Suspension polymerization is the most commonly used method, which consist of suspending the VCM in water at an average temperature of 50°C with Iron (III) Chloride which catalyze the reaction (The European Council of Vinyl Manufacturers 2008).
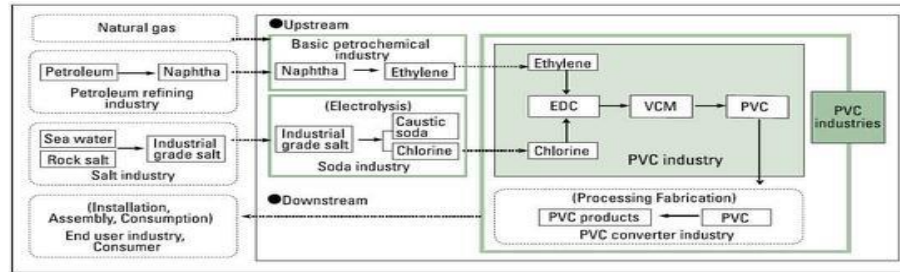
*Figure 2. PVC production process. Adapted from (The European Council of Vinyl Manufacturers 2008)*

PVC is mixed with plasticizers (phthalates, citrates) (Marcilla, et al. 2004), stabilizers (metals compounds: lead, calcium, cadmium) (Folarin and Sadiku 2011), lubricants (paraffin waxes, ester waxes, glycerol) (Fahey 1982), and others additives to impart the properties necessary for the required application of the polymer. PVC is the third most use polymer with broad products and applications, what makes it so useful is its compatibility with a wide range of materials (The European Council of Vinyl Manufacturers 2008).

For this current study, pure PVC (low molecular weight) resin without additives was obtained from Sigma Aldrich (Sigma Aldrich, St Louis, MO).

## 1.1.2 Red Mud

Red mud (RM) is a byproduct of the Bayer process for the extraction of alumina ($Al_2O_3$) from bauxite ($Al(OH)_3$). It is the insoluble product of the digestion of the bauxite with sodium hydroxide. Red mud is disposed as a slurry and it is highly caustic (pH ~13) with high ionic strength (Red Mud Organization 2015).

In the Bayer process, red mud is produced as much as two times the amount of alumina produced. This material is disposed in storage ponds to remove the water but the solids settled stay in the pond (Ritter 2014).

Red mud has applications in metallurgy (Erçag and Apak 1997), building materials (Singh et al. 1996), catalysis (Eamsiri, et al. 1992), ceramics (Yang, et al. 2008), and others; but it requires pre-treatment before it can be used for those purposes (Red Mud Organization 2015).

The application of interest is catalysis: RM has proven applications in hydrogenation (Llano, et al. 1994), hydrodechlorination (Yanik, et al. 2001), and oxidation in wastewater (Huang, et al. 2008).
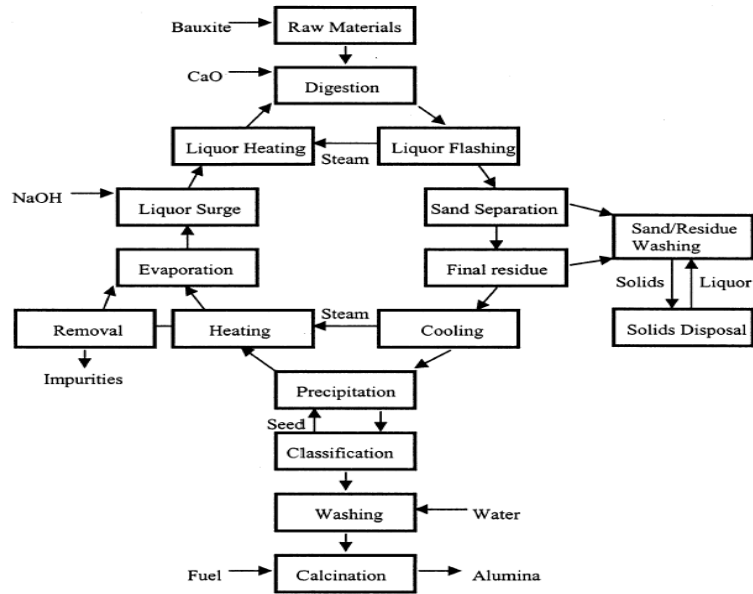
*Figure 3. Bayer Process. Adapted from* *(Hind, Bhargava and & Grocott 1999)*

For this study, the interest is in the hydrodechlorination properties of the RM as a catalyst and a stabilizer of PVC pyrolysis, to find an alternative use for red mud and avoid its landfilling turning this waste by-product into a potential commodity.

### 1.1.3 Pyrolysis

Pyro (heat) lysis (separation), is the chemical decomposition of organic materials in the absence of oxidizing agents. The material is transformed into gas, oil (bio-oil), and char (bio-char) (United States Department of Agriculture 2010).

During pyrolysis, the high temperature accelerates the vibration of the molecules reaching a point that the chemicals bonds start to cleave producing smaller molecules (Liu, et al. 2015). Pyrolysis offers new opportunities in reducing landfills plastic, biomass, and other natural and synthetic organic materials (Al-Salem et al. 2009) in the form of:

- Recycling
- Energy recovery from waste
- Pollution control and Solid waste management
- New and renewable energy
- Environment protection and carbon footprint reduction

## 1.2 Research Question and Proposed Solution

The question that this investigation was focused on is *"How to achieve dechlorination and cracking to produce a low chlorine bio-oil in a single step process of catalytic pyrolysis?"*. By:

1. Evaluating different adsorbents and combining the most promising one with RM. Then use catalyst mixture for the catalytic pyrolysis of pure PVC in a nitrogen atmosphere.

2. Evaluating the chlorine distribution in the pyrolysis products (oil, char, and gas). Using the catalyst/adsorbent mixture should produce a shift in the chlorine content from the gas to the solid.

3. Evaluating the decomposition kinetics and compare it to previous proposed models to find out if there is a synergistic or opposing catalytic effect between the catalyst and red mud.

# CHAPTER 2: LITERATURE REVIEW

## 2.1 Preface

In the past years, researchers tried to find alternatives ways for plastic waste management and PVC dechlorination. However, no viable way for achieving both the waste management and dechlorination has been reported (Yue, et al. 2016). Investigations have found good results using batch systems with two steps:

1. Dechlorination then thermal degradation. (Karayildirim, et al. 2001)

2. Thermal degradation followed by HCl scrubbing (Lingaiah, et al. 2001)

The two-step process is not viable to scale up because of the cost associated with the two steps besides the chlorine levels are still higher than 4 ppm (40 CFR 79.55 - Base fuel specifications.).

## 2.2 PVC Pyrolysis; Two Steps Process: Cracking and Dechlorination

Horikawa et al. (1999) used magnesium oxide, barium oxide, calcium oxide, titanium dioxide, chromium oxide, iron oxide, cobalt oxide, copper oxide, and zinc oxide as chlorine adsorbents in the pyrolysis of PVC at 300 °C for the recovery of the chlorine.

The process consisted of two reactors one for HCl production by heating the PVC at 300 °C and the other for HCl capture in the solid phase, then the solid with captured chlorine was heated to 400 °C with oxygen to release the pure chlorine gas. The solid that showed the best HCl capture and Chlorine release properties was Cobalt Oxide. Metal Oxides have the characteristic to react with chlorine and hydrochloric acid to form metal chloride, based on this different metals oxide were selected to evaluate which one captures chlorine in a single step reaction.

$$Me + 2\,HCl \longrightarrow MeCl_2 + H_2$$
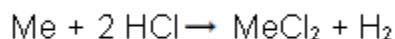
*Equation 3. Reaction of metals with hydrochloric acid.*

Lingaiah et al. (2001) used iron oxide and iron oxide carbon composite as catalyst in the dechlorination of PVC mixed plastics to produce pyrolysis oil with 1,894 ppm of organochloride. The oil was produced using a mixture of 33% polyethylene, polypropylene, and polystyrene with 1% PVC at 410 °C. The focus of this paper was to characterize the mechanism of chlorine capture and the stability of the catalyst, XRD was used to analyze the change in structure of the catalyst. The dechlorination had two main mechanisms: physical adsorption of the HCl and the reaction that produced iron chloride. Using this process, it is possible to get oil of around 100 ppm, the main problem is that it requires two step to be able to achieve the results.

Yanik et al. (2001) studied the catalytic properties of RM in the decomposition and dechlorination of PVC mixed plastic with PE, PP, PS, and compared to Iron Oxide (TR-99701) and Silica-Alumina (SA-1). For the study, they did three main experiments: stepwise pyrolysis, dechlorination then decomposition, and dechlorination and decomposition.

The process that yielded the least chlorine was at 430 °C with RM for the PS/PVC mixture that produced an oil with 543 ppm chlorine.
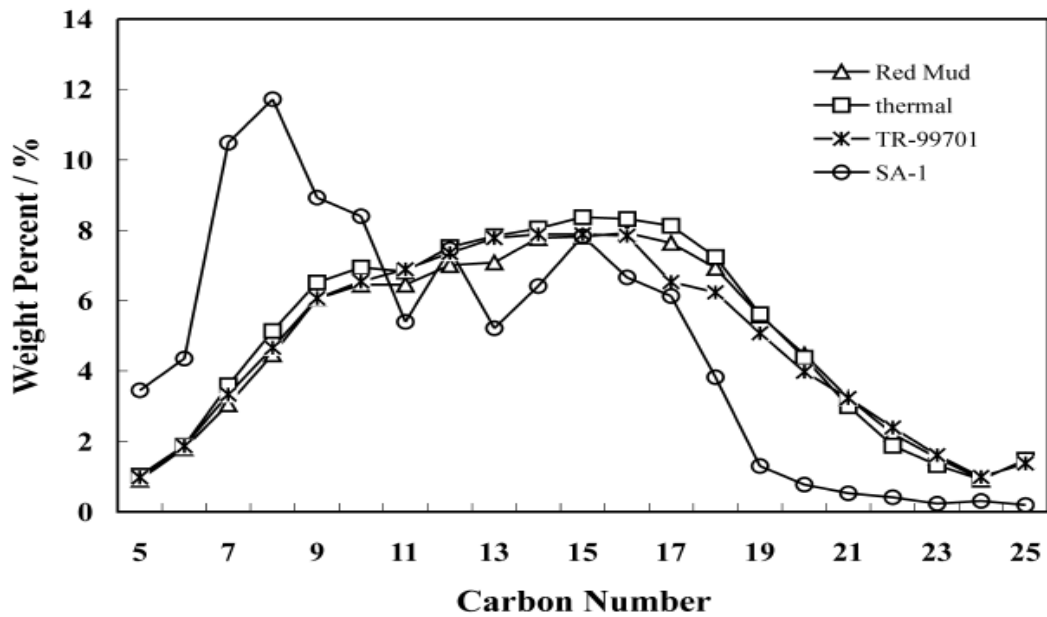


*Figure 4. Carbon Number Probability graph (C-NP gram) from thermal and catalytic degradation of PE/PVC at 430 °C. Adapted from (Yanik, et al. 2001).*

They reported that RM had chlorine capture properties but little to no effect on the decomposition of the PVC (see figure 4). Another conclusion was that the formation of some organochlorides compounds may be promoted by the interaction of HCl and the catalyst because the oil from the thermal degradation contained less chlorinated compounds.

Tang, et al. (2003) used Aluminum-Zinc carbon composite (AZCC) as catalyst for the decomposition and dechlorination of PP, PE, and PS mixed with PVC with an 8:2 ratio of plastics to PVC. The oil derived from the process had a chlorine content of 2,100 ppm. This paper focused on analyzing the boiling point distribution of the produced oil. The process was heating the mixtures of the PP/PVC at 380 °C, PE/PVC at 420 °C, and PS/PVC at 360 °C, and it contained 3 stages: liquid phase contact, vapor phase contact, and a sodium hydroxide (NaOH) gas trap.

They demonstrated that using the AZCC catalyst reduces the boiling point distribution of the oil, and the chlorine content of the oil by 70%, but still the amount of chlorine in the oil was high for energy recovery purposes.

Zhou, et al. (2004) used Aluminum-Magnesium composite oxide for the catalytic pyrolysis of PVC containing mixture with polypropylene, low density polyethylene, and polystyrene. They found that this catalyst accelerated the degradation of the polymers yielding lower hydrocarbon distribution in the liquid product, and showed chlorine capture properties. They used a vapor phase contact for the catalyst, an 8/2 ratio for the mixed polymers/PVC with the same amount of catalyst as PVC, yielding an average of 1,900 ppm of chlorine between the mixtures.

## 2.3 PVC pyrolysis, Single Step Process

Later the focus was using single steps, and continuous systems and try to achieve both the decomposition and dechlorination, but still the chlorine levels were high. The main issue with the catalysts is that they either exhibit good cracking properties or good chlorine capture properties, thus, this investigation is working in finding a mixture of catalyst with an adsorbent that could produce an oil with good heating value for production of energy while at the same time having a low chlorine content.

Masuda, et al. (2006) studied the chlorine capture properties of different metal oxides (zinc, calcium, iron, lead, lanthanum, cerium, aluminum, and neodymium). The pyrolysis was done at 400 °C for 30 minutes and 800 °C for 10 minutes in a batch operation setup with a glass tube furnace under a Helium atmosphere, with two acetone traps and a water trap. Each oxide exhibited a unique interaction with the PVC, lanthanum oxide reacted to form oxychloride capturing 95% of the chlorine at 800 °C and 75% at 400 °C. Iron oxide promoted the formation of carbon monoxide and carbon dioxide, while calcium oxide promoted the formation of polycyclic aromatics (Masuda, et al. 2006).

Keane (2007) used a mixture of Palladium/Aluminum oxide in a CSTR for the catalytic pyrolysis of PVC at 350 °C and 440 °C in an argon and/or hydrogen atmosphere in batch operation. The process consisted of a CSTR with a hot trap at 200 °C, a cold trap at 0 °C, and 1M NaOH trap.

With a liquid chlorine content of 182 ppm, the process appeared promising but using a precious metal as a catalyst can make the process expensive and not economically viable.

Lopez, et al. (2011) used ZSM-5 and RM in the pyrolysis of plastic waste with 3% PVC, then analyzed the main components with GC-MS. The pyrolysis oil with the less chlorine content was obtained using Red Mud at 440 °C and had 5 000 ppm chlorine. They analyzed and characterized both catalysts, ZSM-5 showed stronger acid sites which improved the degradation of the polymer but lacked chlorine capture characteristic, RM contained weaker acid sites that translated into requiring more temperature for achieving the same level of decomposition as the zeolite. The red mud exhibited chlorine captures properties. In the GC-MS results of the pyrolysis, most of the compounds were aromatics (68%-98%) and the rest were aliphatic hydrocarbons.

## 2.4 Current Interest

In recent years, the focus shifted from the pyrolysis of plastic polymers to the co-pyrolysis of plastic and biomass. This trend could be explained by the catalytic effect of the HCl over the cracking of the biomass lignin and cellulose producing higher quality bio-oils (Matsuzawa et al. 2001).

Sharypov, et al. (2006) published a four-part study of the co-pyrolysis of plastic and biomass; evaluating products distribution and composition, process optimization, synergy effect between the polymers and biomass.

Han, et al. (2014) evaluated the behavior of co-pyrolysis of biomass and plastic polymers blends using a Thermogravimetric Analyzer. Kinetics studied were performed to assess the effect of the materials on each other.

## 2.5 PVC Decomposition Kinetics

Bockhorn et al. (1999) applied isothermal and dynamic methods to measure the kinetics parameters of PE and PVC decomposition. Using a Thermogravimetric Mass Analyzer for the dynamic method and a Differential Scanning Calorimeter for the isothermal method. PVC decomposed in two stages: dehydrochlorination between 220 °C and 350 °C accompanied by benzene formation, and thermal cracking of the polymer backbone between 400 °C and 550 °C. They reported that the formation of HCl followed an apparent reaction order of 1.54.

$$-(CH_2CHCl)_n - \xrightarrow{\Delta} -(CH=CH)_n - + nHCl$$
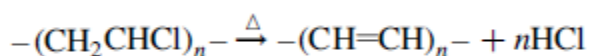
*Equation 4. Dehydrochlorination of PVC.*

Starnes Jr. (2002) studied the structural and the mechanistic aspects of the PVC thermal degradation. The thermal degradation of PVC began in polymerization defects, as allylic chloride and tertiary chloride, and other chlorinated branches.

The initial cleavage and the consequent polyene formation occurred via carbenium chloride ion pairs or four center quasi ionic route. Marongiu, et al. (2003) used a semi detailed and lumped kinetic model to describe the decomposition of PVC. 40 species and pseudocomponents were involved in about 250 reactions, then a method validation was done using dynamic and isothermal thermogravimetric analysis comparison allowing the product prediction.

## 2.6 Conclusions and Summary

The PVC decomposition kinetics occurs in two steps: a dehydrochlorination at around 300 °C (illustrated in equation 3), then a polymer backbone cracking at around 475 °C. Many catalysts have been evaluated for dechlorination of the PVC pyrolysis, and it served as a guide for selecting the chlorine adsorbent to be mixed with Red mud. Lanthanum Oxide was the most promising in the literature, but it presents the challenge that it's a rare-earth mineral and it could increase the cost of the process. Red mud is used because of the proven catalytic properties in pyrolysis, as an alternative use for it and avoid landfilling on this material. However, it was proven by Lopez, et al. (2011) that it lacks the ability to catalyze the cracking of PVC, kinetics studies are done to compare if the mixture of RM + $Ca(OH)_2$ has some catalytic properties in the pyrolysis of PVC.

# CHAPTER 3: METHODS AND PROCEDURES

## 3.1 Introduction

To provide the answer for the research question, the experiments are divided into two segments:

1. The chlorine adsorbent evaluation of different metals, metal oxides, and metal hydroxides by Thermogravimetric Analysis

2. The pyrolysis of PVC using the Red Mud/Calcium Hydroxide mixture.

The chlorine was analyzed using the EPA Method 5050 with Mohr Chlorine Titration with silver nitrate.

## 3.2 Methodology

### 3.2.1 Chlorine Adsorbent Evaluation

For the adsorbent evaluation, a TGA Q-500 (TA Instruments, New Castle, DE) was used. The sample was loaded with the adsorbent on top of it in a ceramic pan, a 20 °C/min ramp to 400 °C then the temperature was held for 30 min. Approximately 50 mg of sample and 50 mg of adsorbent were used for the experiment.

Since Calcium Hydroxide was selected as the chlorine adsorbent, it was physically mixed with Red Mud in a 25/75, 50/50, and 75/25 ratio, 50/50 was selected because there was no significance difference in the chlorine captured above 50% of each. Then three temperatures (350 °C, 400°C, and 450 °C) were evaluated with the mixture to determine the optimum chlorine adsorption temperature, which was 400 °C.

### 3.2.2 PVC catalytic pyrolysis

The reaction was done in a 25 mL stainless steel tube reactor in batch operation with 25 cm of length and a 5 cm diameter. 4 grams of PVC was loaded into the reactor then 4 grams of the mixture of 50/50 Red Mud/Calcium Hydroxide was added, then the air was purged with nitrogen. The temperature was raised to 400 °C at a rate of 7 °C/min, then the temperature was held for 60 min. After the reactor was cooled down, the gas was passed through a gas trap of 1M Sodium Hydroxide to capture the chlorine. Since the oil was adsorbed on the solid residue, the oil was extracted with toluene in a Soxhlet extraction apparatus.
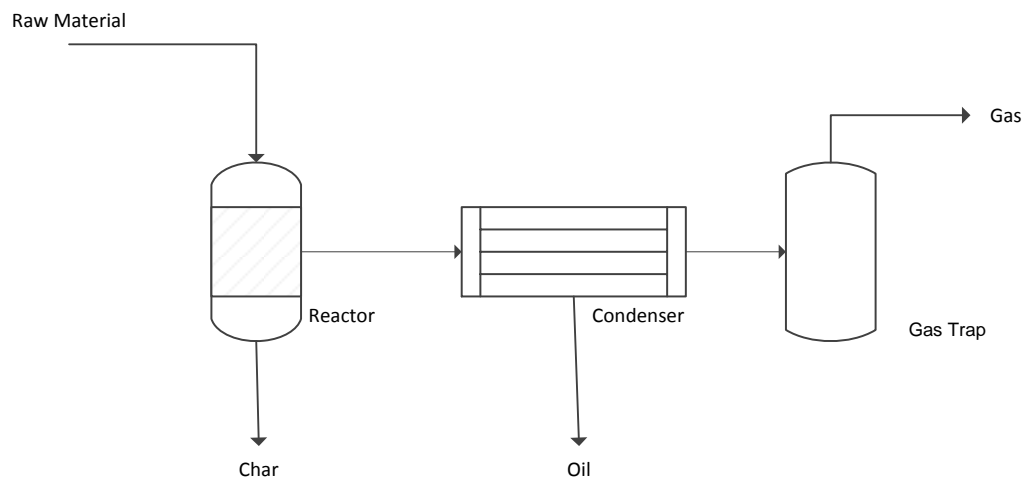
*Figure 5. Pyrolysis Schematic.*

## 3.2.3 Chlorine Analysis

The analysis was based on the EPA method 5050 "Bomb Preparation Method for Chlorine Analysis" and the Mohr Chlorine Titration. The oil/char sample was combusted using a bomb calorimeter IKA C200 (IKA Instruments, Germany), then the bomb was rinsed with deionized water, finally the rinse solution was titrated with silver nitrate solution 0.025 N. Before each set of titrations, a blank and a chlorine (1000 mg/L) standard in duplicate were analyzed to perform quality checks for the titrations.

# CHAPTER 4: RESULTS AND DISCUSSION

## 4.1 Chlorine Adsorbent Determination

The chlorine adsorbed by the catalyst was measured after simulating the pyrolysis of the sample with the TGA by raising the temperature to 400 °C in a nitrogen atmosphere, approximately 50 mg of PVC and 50 mg of RM + Ca(OH)$_2$. The thermogram of the reaction is shown in figure 5.
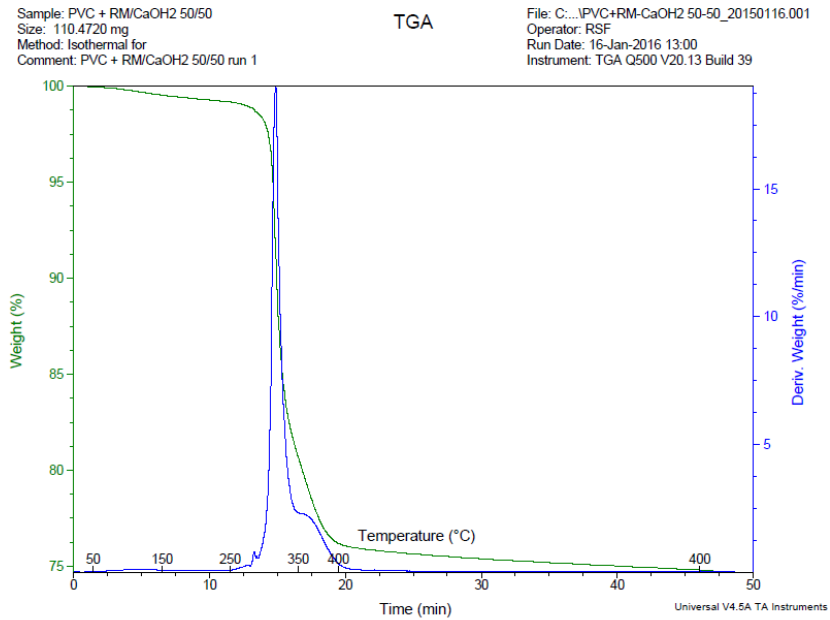


*Figure 6. Thermogram of PVC + RM/Ca(OH)$_2$ (50/50).*

The results of the TGA evaluation for the different potential chlorine adsorbents are presented in figure 7:
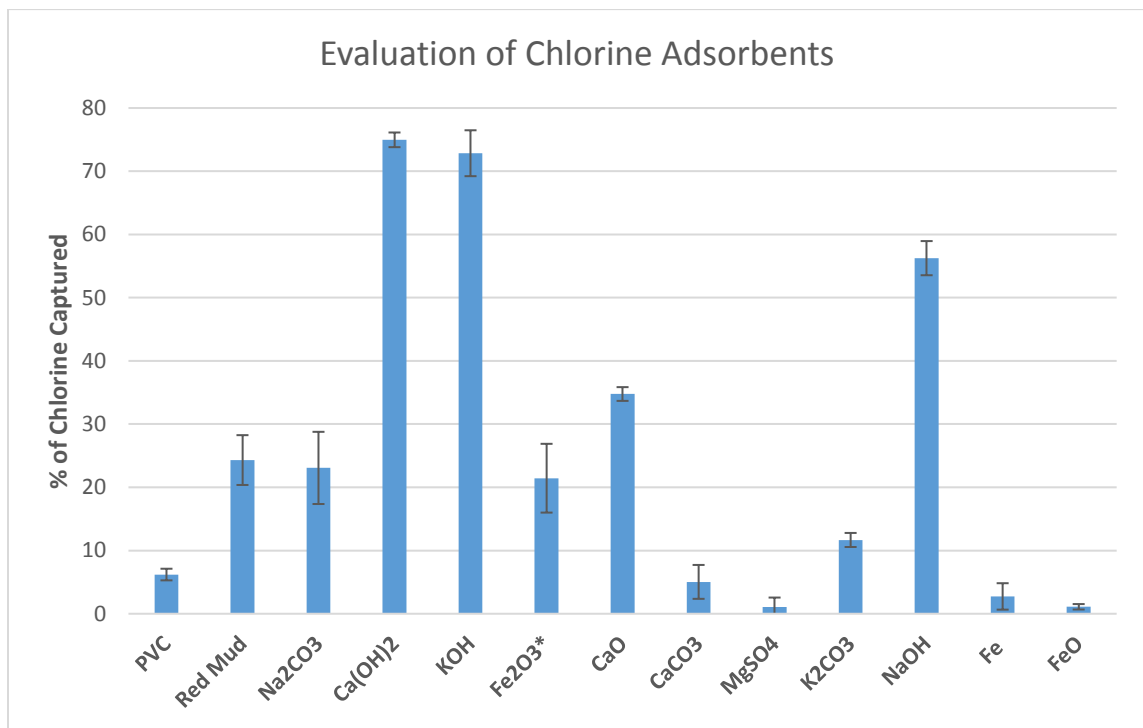


**Figure 7. Evaluation of Different Chlorine Adsorbents. *Iron Oxide was evaluated at 290 °C because the chlorine reacts with the Iron Oxide and produces FeCl$_3$ which decomposes at 316° C. The error bars are the standard deviation.**

Each run was done in duplicate. 5% of the chlorine from the PVC stayed in the char, possibly by physical adsorption from the char. The compounds with the most chlorine captured in the solid phase were the hydroxides. Given that sodium and potassium hydroxides are highly corrosive, that goes against the purpose of waste management. Calcium hydroxide is used to remediate acidic soils (Wallace and Terry 1998) thus, it was selected as the chlorine adsorbent.

Then an evaluation of the optimum temperature was done, which was 400 °C.
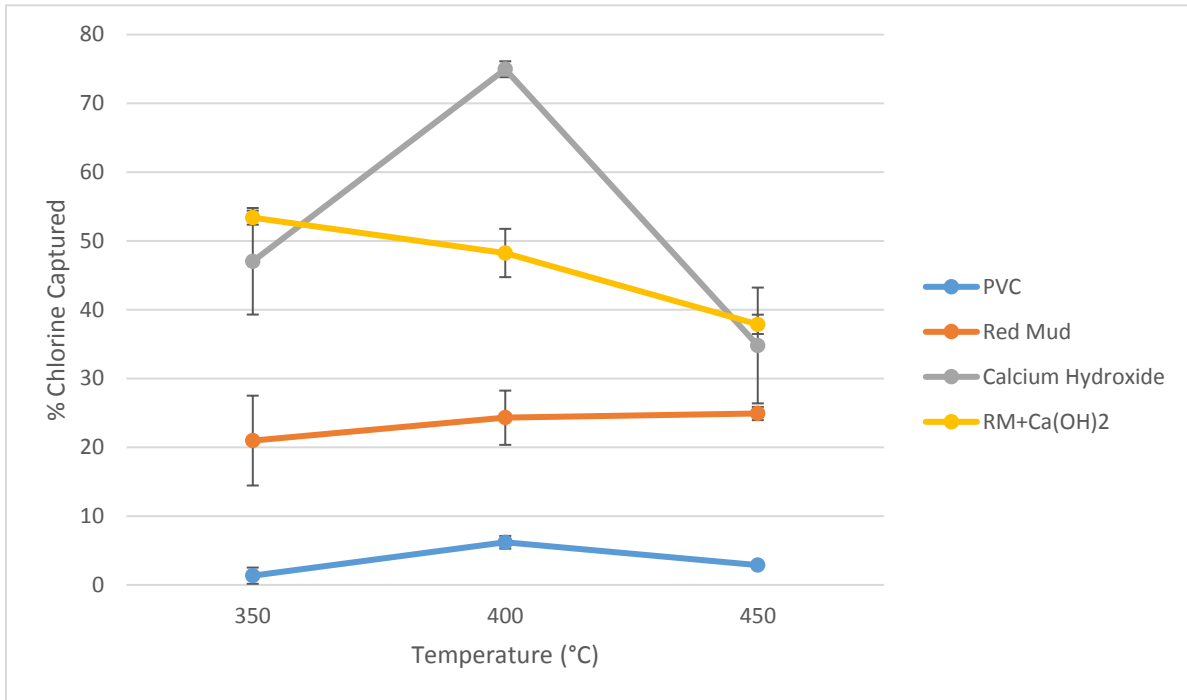


*Figure 8. Temperature Dependence on Chlorine Adsorption. The error bars are the standard deviation.*

400 °C was selected as the pyrolysis temperature since there was a decrease in the absorbed chlorine at higher temperatures. A possible explanation for this is that the neutralization of HCl with NaOH is an exothermic reaction, increasing the temperature decrease the extent of the reaction leading to less adsorption of chlorine with higher temperatures. (Chang 2001)

Using only calcium hydroxide captures 75% of the chlorine in the solid phase but it lacks cracking properties, only acidic compounds cracks the PVC (Yanik, et al. 2001). Metal compounds in the red mud imparts stability to the chlorine adsorption, the amount of chlorine adsorbed was not significantly different with the changes of temperature.

The last step was to determine the ratio of mixture between the Calcium Hydroxide and Red Mud, three ratios were evaluated 25/75, 50/50 and 75/25.
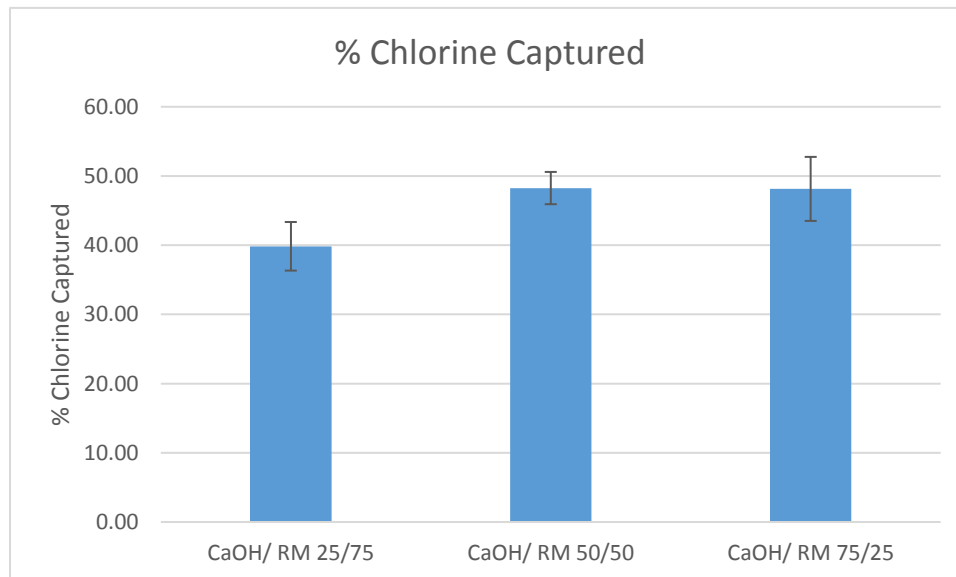


*Figure 9. Mixing of Red Mud and Calcium Hydroxide Ratios. The error bars are the standard deviation.*

50:50 was selected as the ratio for the pyrolysis, because an increase in hydroxide do not provide an increase in chlorine capture properties.

## 4.2 Pyrolysis of PVC

The results of the pyrolysis of PVC using the catalyst Red Mud/Calcium Hydroxide 50:50 are presented in the following tables.

*Table 1. Slow Pyrolysis of PVC.*

|  | Sample | Chlorine (mg/L) | Chlorine (mg) | Chlorine Distribution (%) |
|---|---|---|---|---|
|  | Oil* | n/a | n/a | n/a |
| PVC | Char | 77.9 | 7.8 | 0.34 |
|  | Gas | 9036.96 | 1807.39 | 78.80 |
| Maximum Pressure: 58 bar | | | Total | **79.14** |

*The oil produced was so low that it was not possible to analyze it for chlorine.

*Table 2. PVC+RM/Ca(OH)$_2$ pyrolysis results.*

|  | Sample | Chlorine (mg/L) | Chlorine (mg) | Chlorine Distribution (%) |
|---|---|---|---|---|
|  | Oil* | 1.69 | 0.17 | 0.01 |
| PVC + RM/Ca(OH)$_2$ | Char | 17450.68 | 1745.07 | 77.86 |
|  | Gas | 389.53 | 62.32 | 3.47 |
|  | Cleaning° | 29.00 | 29.00 | 1.29 |
| Maximum Pressure: 32 bar | | | Total | **82.63** |

*The titration volume was within the tolerance of the burette with the blank, with this method there is no way to distinguish between the oil and the blank. °The cleaning was a rinse with toluene and methanol (50/50 volume) of the reactor.

Using the catalyst, there was a shift in the chlorine content from the gas to the char.

Slow pyrolysis for the PVC yields very low oil, which defeat the purpose using this process as a waste management option. Still the chlorine capture properties in the solid phase demonstrate that it has potential. This was working with pure PVC. Working with a plastic mixture could yield even better results because the amount of total chlorine will decrease.

For a run with approximately 4 grams of PVC and 4 g of the red mud/calcium hydroxide mixture the product yields are shown in Table 3:

*Table 3. Product Distribution*

| Sample | Mass Collected (g) | Product Distribution (%) |
|--------|--------------------|--------------------------|
| Gas* | 2.52 | 30 |
| Oil | 1.19 | 14 |
| Char | 4.66 | 56 |
| **Total** | **8.36** | |

*The gas was calculated by difference.

The oil yields were extremely low, which is detriment to the purpose of using pyrolysis with Red Mud/Calcium Hydroxide for Waste Management of the PVC. In the literature, the best results for cracking and getting higher yields of oil were using zeolites, they possess stronger acid sites available (Yanik, et al. 2001).

Acid catalyst promotes an asymmetric breakage of bonds yielding pairs of ions of opposite charges (a carbocation and the very unstable hydride anion). These ions radicals are highly unstable and undergo scission in beta position of C-C bonds (Sadrameli 2016).

## 4.3 Kinetics Study of PVC Catalytic Decomposition

Using the data from the TGA the kinetic parameters for both the dehydrochlorination and the decomposition of the PVC were evaluated. The conversion (X) was calculated using equation 5. The conversion rate (dX/dt) is calculated using tangent equation for each point.

$$x = \frac{m_0 - m_t}{m_0 - m_\infty} \qquad \text{(Eq. 5)}$$

The next step is plotting the Differential Thermogravimetric (DGT) curve:
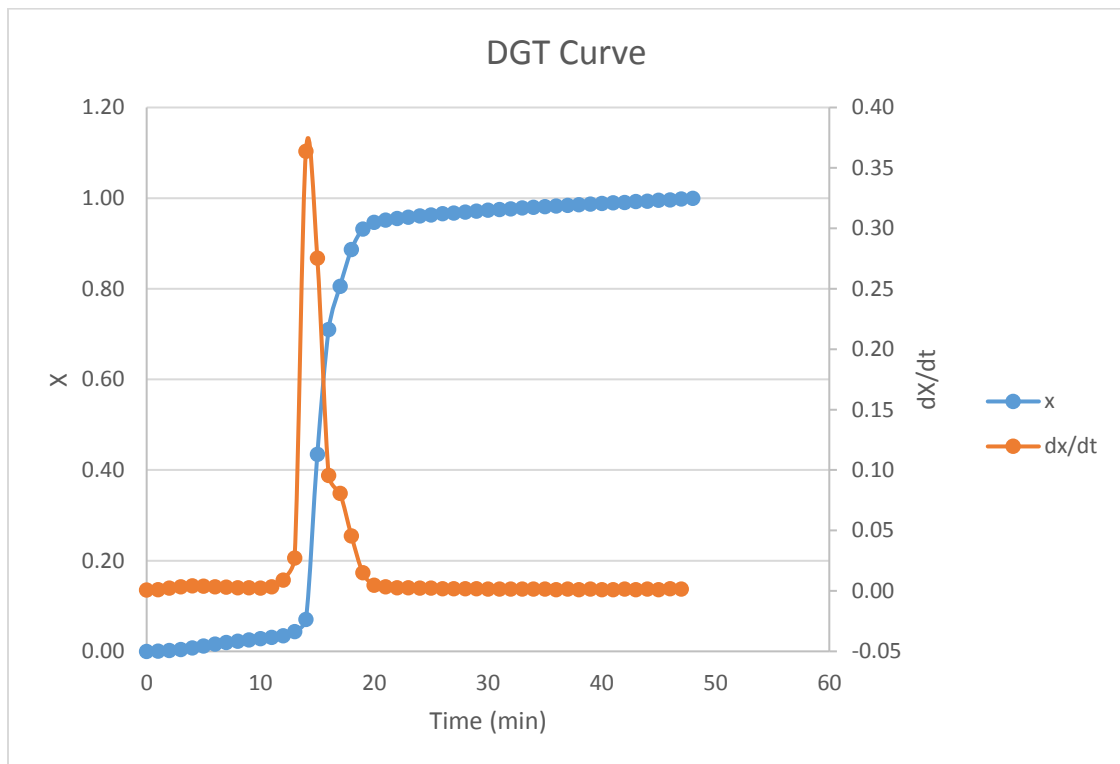


*Figure 10. Differential Thermogravimetric curve.*

The mechanism of thermal decomposition of plastic have been shown to follow a reaction rate that involves the conversion and the rate of conversion (Bockhorn, et al. 1999) shown in equation 6.

$$\frac{dx}{dt} = k(T) \cdot (1-x)^n$$

Linearizing equation 6 to solve for the reaction constant and the order of reaction for the dehydrochlorination and decomposition:



**Dehydrochlorination of PVC**

y = 1.1795x - 0.7605
$R^2$ = 0.9678
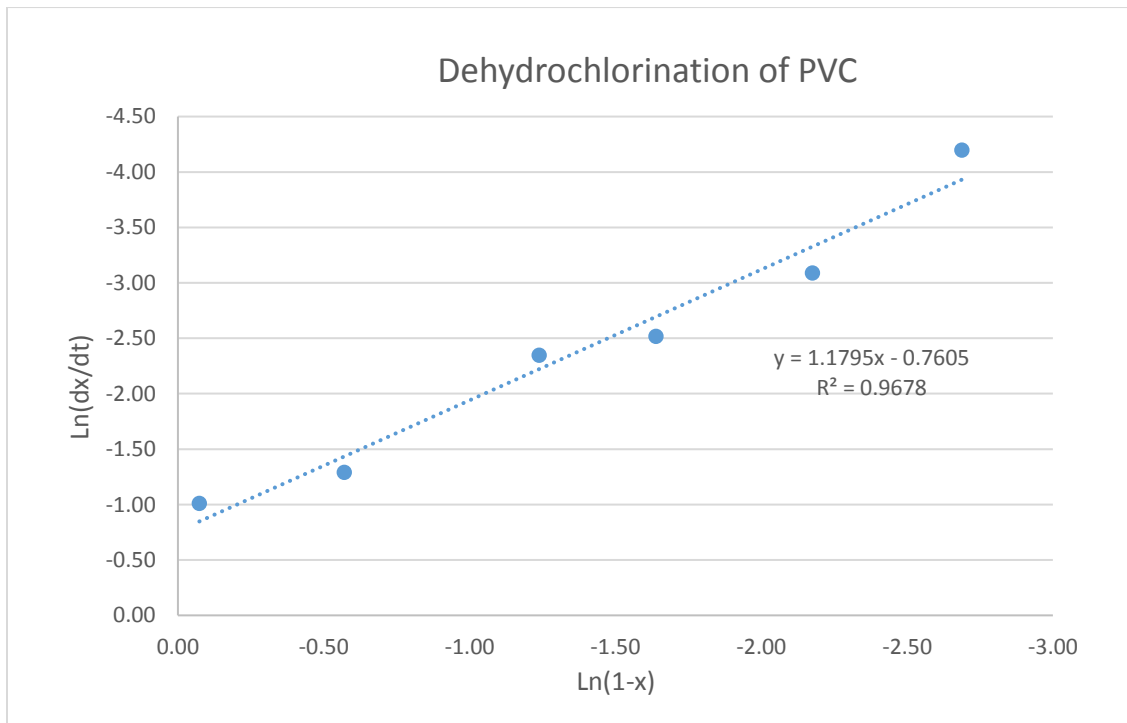
*Figure 11. Dehydrochlorination of PVC, Kinetic Study*

27

Results in a reaction order (n) of 1.18 and a reaction constant (k) of 0.47 min$^{-1}$ for the dehydrochlorination segment of the reaction. In the literature, it is mentioned that during this stage of the reaction benzene is produced parallel to the dehydrochlorination (Marongiu, et al. 2003). For this kinetics evaluation, it was assumed that only dehydrochlorination occurred.
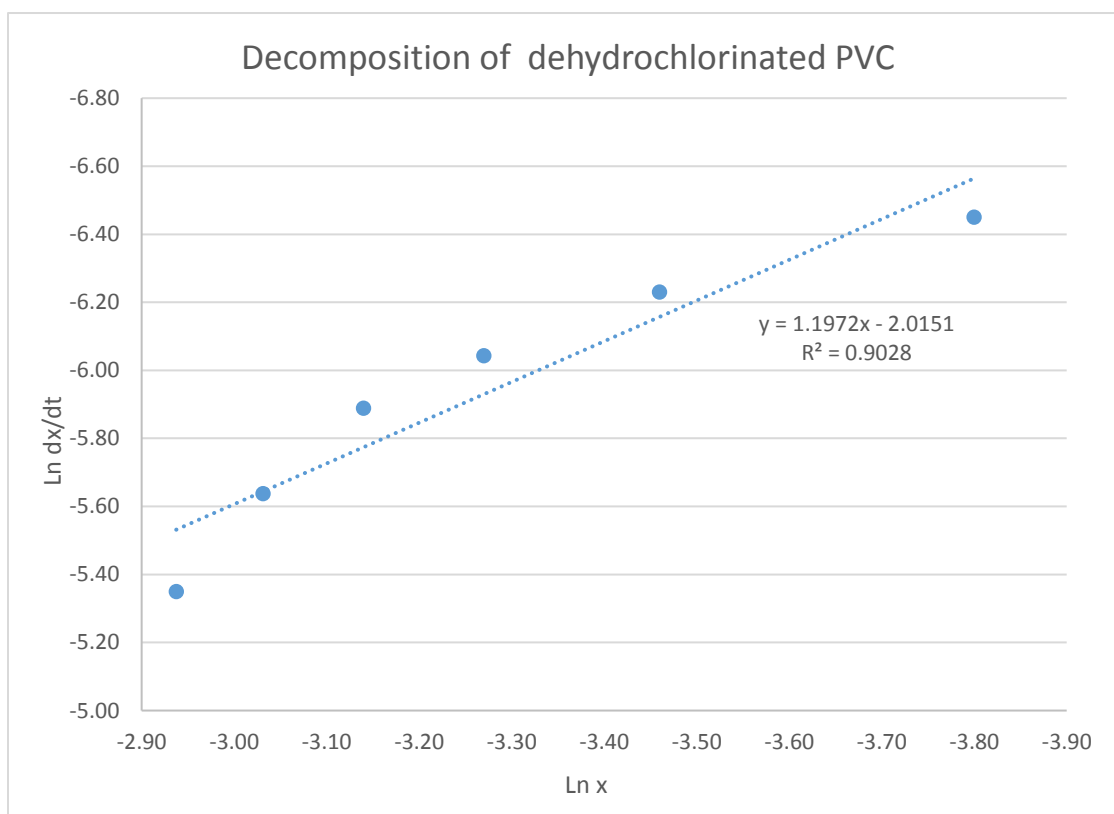


*Figure 12. Decomposition of Dehydrochlorinated PVC, Kinetic Studies.*

For the decomposition kinetics, a reaction order (n) of 1.2 and a reaction constant (k) of 0.13 min$^{-1}$.

These kinetics results explain the complexity of these reactions, yielding fractional numbers of order of reaction, which indicates a group of elemental reactions occurring at the same time (Steinfeld, et al. 1998). Both are fast reactions, but speaking in terms of the reaction constants, the dehydrochlorination occurs faster.

## 4.4 Catalyst Discussion

Red mud was selected as the catalyst because it has dehydrochlorination properties (Yanik, et al. 2001). The reasoning is finding an alternative use for RM to this byproduct, to avoid its landfilling.

Chlorine has two main ways of staying in the solid phase:

1. Chemical Reaction: the chlorine released from the PVC reacts with the compounds in the adsorbent forming metal chlorides.

2. Physical Adsorption: the chlorine attach to the molecules of the adsorbent.

To determine the mechanism of the adsorption X-ray Powder Diffraction is needed. With this the lifetime and regeneration could be explained. If it's a chemical reaction, the adsorbent will react with the chlorine until it reaches the extent of the reaction, and there is no viable regeneration method. If it's a physical adsorption, the chlorine will adsorb to the adsorbent until all adsorption sites are occupied, and regeneration is possible.

# CHAPTER 5: CONCLUSIONS AND FUTURE WORK

## 5.1 Conclusions

The slow pyrolysis of PVC in the presence of Red Mud + $Ca(OH)_2$ proved to be quite effective in the capture of the chlorine in the solid phase. The HCl shifted from the gas to the adsorbent almost entirely when using the RM + $Ca(OH)_2$. But the bio-oil yield was too low and there was no proof of any catalytic effect from the mixture, which agrees with previous findings. Still the production of a bio-oil with a chlorine content of < 10 ppm.

The kinetic of the PVC pyrolysis is very complex, fully understanding the pathways and mechanisms is quite a task. From the parameters found both the dehydrochlorination and the decomposition are fast reactions; the dehydrochlorination starts at around 270 °C, while the decomposition starts around 400 °C.

## 5.2 Future Work

With process optimization and instead of Red Mud, using another catalyst that has proven degradation properties in plastic, such as zeolites. However, zeolites are synthetic compounds and would increase the cost of the process. Investigations of other acidic catalyst with this process to substitute red mud, like alumina, sulfated zirconia, could be more effective.

Evaluate the mechanics of adsorption of chlorine in the adsorbent, to determine the lifetime and regeneration of the adsorbent.

The design of a process that uses fast pyrolysis to increase the yield of the bio-oil with the combination of a proper catalyst + $Ca(OH)_2$, while doing in line condensation of the bio-oil could explain better the viability of this process.

An evaluation of a landfill sample or a representative mixture of polymers to translate the results and feasibility of this process. Using plastic mixture dilutes the total amount of initial chlorine, yielding low chlorine levels in the products.

Finally, evaluate the scale-up of the process and the details for achieving this.

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