Synthesis of Formic Acid from Carbon Dioxide Absorption

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering

By

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THESIS ACCEPTANCE CERTIFICATE

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All the praise and respect for the **Almighty Allah**, who is the ultimate source of all knowledge and wisdom gifted to mankind.

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-Muhammad Hanan Masood

Dedicated to my parents and siblings whose tremendous support and cooperation led me to this wonderful accomplishment.

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LIST OF ABBREVIATIONS

GHG	Greenhouse Gases
AFOLU	Agriculture, forestry and other land utilize
CCS	Carbon Capture and Storage
CCT	Carbon Capture Technology
IGCC	Integrated gasification combined cycle
PSA	Pressure Swing Adsorption
TSA	Temperature Swing Adsorption
X-RD	X-ray Diffraction
HPLC	High Performance Liquid Chromatography
N	Normality
Wt.	Weight
WMO	World Meteorological Organization

Abstract

High temperature and warming are growing environmental issues in Pakistan. The main reason for this is the releases of carbon dioxide from industrial, transportation and various anthropogenic activities. Carbon dioxide is mostly coming from the burning of fossil fuels. It is a greenhouse gas and is a major concern to the environment. Best and economical methods to recover and effectively reuse carbon dioxide is through absorption and adsorption. Absorption can be performed with different chemicals. In this study gas bubble method was used to absorb carbon dioxide in sodium hydroxide solution having variable concentrations (0.01, 0.1, 0.5, 1.0, 3.0 and 5.0N) and the impact of the solution pH on the product formation was developed. The products formed at a different pH of the absorbing solution were sodium carbonate at pH 10, Trona at pH 9 and sodium hydrogen carbonate at pH 8. All products formed were confirmed through XRD (X-ray diffraction) analysis. After optimization, a 3.0 N solution of sodium hydroxide at pH 8 was selected for the sodium formate production. For this sodium hydrogen carbonate at pH 8 was converted into sodium formate through the hydrogenation in the presence of nickel ferrite catalyst at 80^{o}C. Sodium formate was then used to synthesize the formic acid upon simple reaction with sulfuric acid, through vapors condensed which was later analyzed by HPLC (High-performance liquid chromatography). HPLC was used for the qualitative analysis of the synthesized produced. A reaction yield of 79±0.2 % is reported. Formic acid has multiple uses in the leather and textile industry as a hair removing and as a pH regulating agent. This research in this way has shown a way to convert a waste pollutant to a value-added marketable product.

Chapter 1

Introduction

1.1 Background of the study

Global warming is a growing environmental issue in the world including Pakistan. The main reason for this is the high release of carbon dioxide (CO_2) from industrial, and transportation sector besides anthropogenic activities. CO_2 in the atmosphere mostly comes from the burning of fossil fuels. It is a greenhouse gas and is a major concern to the environment as it can bring hurricanes more frequently resulting in humanitarian disasters.

With the increase in population and modernization in lifestyle, total energy demand is continually increasing all over the globe. To meet these energy demands many industrial processes are carried out on a daily basis (Bindlish, 2018; Chu *et al.*, 2016). The generation of electricity from coal, furnace oil, diesel, and gasoline burning at industries produces a substantial amount of carbon dioxide. The reported threshold concentration of carbon dioxide in the atmosphere is 350 ppm (Chan *et al.*, 2015), but due to increase in energy generation, this value has reached highs up to 406 ppm ("Daily CO_2 updates ", 2018). It is reported that between 1880 and 2012 the overall temperature of the globe has increased around 1˚C (Harris *et al.*, 2009; Kraaijenbrink *et al.*, 2017). Furthermore, carbon dioxide gas emissions are affecting human life on earth in the form of irregular weather pattern, polar ice caps depletion and by glaciers melting (Rintoul *et al.*, 2018). In order to reduce carbon dioxide emissions from the open atmosphere (coming from different sources such as fuel burning in the industrial sector, and through anthropogenic emissions), several separation techniques have been opted. However, the commercially utilized carbon dioxide separation techniques are adsorption on solid catalyst surfaces (Anas *et al*., 2017; Creamer *et al*., 2014) and absorption using chemical solvents (Feng *et al*., 2010; Wu *et al*., 2014).

The main advantage of practicing absorption technique over a large scale is that the utilized solvent chemical can be regenerated by simple heating at high temperatures and low pressures. Commonly absorption of carbon dioxide in industries is done by amine scrubbing, chemicals like alkanolamines. Various types of amines used as primary amine or Monoethanolamine (MEA), secondary amine or Diethanolamine (DEA), tertiary amine or N-Methyl diethanolamine (MDEA), cyclic amine piperazine (PZ), and sterically hindered amines 2-amino-2-methyl-1-propanol (AMP) (Mores *et al*., 2011; Uma Maheswari & Palanivelu, 2014; Wang *et al.*, 2017).

Alkali hydroxide solutions have also shown promising trades in the carbon dioxide absorption process. They have the advantage that they are cheap and easily available, other benefits of using alkali hydroxides is that of multi-reaction by-product formation (Kim *et al.*, 2016; Tavan & Hosseini, 2017), while no reaction products are formed in the case of absorption in amine solutions. Carbon dioxide is an excellent carbon source for organic compounds production on the absorption in hydroxide solutions (Tsuji & Fujihara, 2012). During the process of carbon dioxide gas absorption, phase transformation over a heterogeneous catalyst has been reported earlier to reduce its concentration in the exhausts. Christopher *et al*., (2010) have shown carbon dioxide transformation into organic compounds by intermolecular transfer of hydrogen from metallic hydrogen carbonate solutions using complex catalysts. Similarly, photocatalytic hydrogenation of the hydrated form of hydrogen carbonates has been studied earlier (Goren *et al*., 1990).

Hydrogenation of alkaline hydrogen carbonates is an endothermic process that requires high reaction temperatures, however, the presence of catalysts can reduce the reaction temperatures. Many catalysts are reported for use in the hydrogenation process like Palladium (Pd), Nickel (Ni) etc. The palladium catalyst is mostly used for the hydrogenation. Nickel has also gained importance for its reduction properties. Liu *et al*., (2018) studied the hydrogenation of anthracene over nickel nanoparticles supported on attapulgite powder. Chen *et al*., (2015) have reported the synthesis of organic acids by a reduction of sodium hydrogen carbonates, using a Ni powder catalyst supported with hydrazine monohydrate, $N_2H_4 \cdot H_2O$, as a reductant. González *et al*., (2018) produce sodium formate by the hydrogenation of sodium hydrogen carbonate using (Pd, Ru, Ni, Co, and Re) catalyst.

In the present study, sodium hydroxide was used to absorb carbon dioxide and the impact of solution concentration, pH and reaction time on various product formation was investigated. Nickel ferrite was used to enhance the conversion of sodium hydrogen carbonate, at pH 8, to formic acid. Sulfuric acid was used to turn the intermediate reaction product, sodium formate, into formic acid through the condensation.

This research would help in promotion of resource recovery, recycling, and reuse of waste gases in the industrial scenario, moreover this study can be applied in industries for absorption of carbon dioxide and converting it to different chemicals. It can also be applied for biogas cleaning for removing CO_2 and H_2S to increase methane concentration and energy content of the gas. Benefits of this research would be,

a. Import substitution of chemicals by absorption.
b. The release of high concentration of carbon dioxide emissions in atmosphere from different industries could be reduced to threshold level.

1.2 Problem statement

Carbon dioxide from different sources is increasing day by day due to which global warming is increasing. Absorption or removal of CO_2 from the atmosphere can help to reduce the concentration and also help to produce chemicals.

1.3 Objectives of study

1. To determine the sodium carbonate and sodium hydrogen carbonate (Bicarbonate) product formation from carbon dioxide absorption in sodium hydroxide solution by evaluating parameters.
    - Solution concentration
    - Solution pH
2. To synthesis formic acid with and without the presence of nickel ferrite catalyst.

1.4 Scope of study

1. In the first part of the study different concentration of sodium hydroxide were prepared and carbon dioxide (CO_2) was absorbed in it through the bubble method at constant pH. One concentration was selected and further absorption was performed at different pH.
2. Sodium Hydrogen carbonate was converted to a sodium formate with and without using Nickel ferrite catalyst.
3. Sodium formate was further converted to formic acid through a condensation process.

Chapter 2

Literature Review

2.1 Carbon dioxide impact on the earth

The percentage of CO_2 has the highest share in the GHGs. It is generated from different sources and causes global warming (Metz *et al.*, 2007). The atmosphere on earth has changed on unsurpassed scales with the increasing concentrations of CO_2 This increase concentration has increased frequency of hurricanes resulting in humanitarian disasters (Solomon *et al.*, 2007). Further, various human activities comprising deforestation, industrialization, and use of fossil fuels is the reason for the increase in concentration of carbon dioxide to 406 ppm (World Meteorological Organization 2015). Worldwide temperature rise, increase in ocean levels, warming oceans, glacial retreats, extraordinary occasions (hurricanes, intense rainfalls) ocean acidification, and decreases of snow cover are all proof of the quick environmental change that has been happening since the 1950s (Cambier, 2017).

2.2 Sources of carbon dioxide

There are two types of sources of carbon dioxide emissions

1. Anthropogenic Emissions
2. Natural Emissions

Anthropogenic CO_2 emissions are the real issue in regards to worldwide temperature alterations. In order to control the rise in temperature to 1°C by 2100 the threshold concentration value of CO_2 in atmosphere should be restricted to 450 ppm. This requires a 50 % cut of worldwide CO_2 discharges, from all activities. In 2010, the emissions of CO_2 from different anthropogenic activities was, 25% released from energy sector, 24% from AFOLU (agriculture, forestry, and other land utilize) and 21% by industry (concrete industry, iron and steel industry, and so forth), remaining 20% is from other sources which includes buildings, transport and other energy sources (Cambier, 2017). This is illustrated in figure 2.1. The substantial increment in the most recent decades of atmospheric CO_2 concentrations is because of the burning of fossil fuel, in order to meet the energy demand of 23 Gton-CO_2/year in industrial activities. Among industrial activities, the power plants are major springs of CO_2 emissions (Benson *et al.*, 2012). While Natural sources of carbon dioxide emissions include decomposition (weathering of carbonate rocks) ocean release and respiration. The natural sources are not the reason of increasing concentration of carbon dioxide in atmosphere. The only reason of increase in concentration are anthropogenic activities

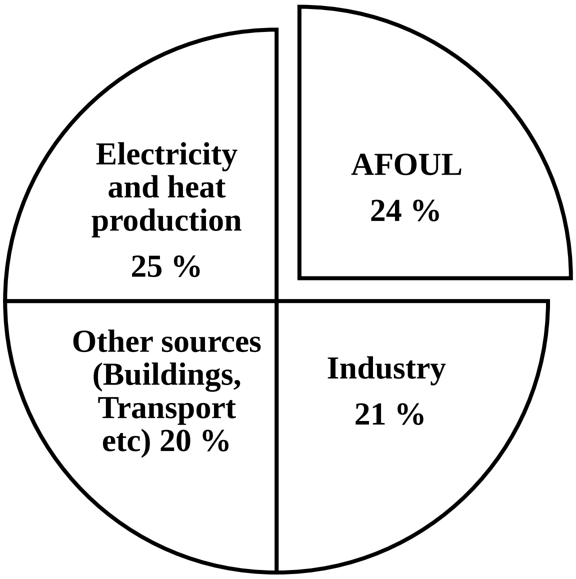


Figure 2.1: Carbon Dioxide emissions from different sources adopted from (Cambier, 2017)

2.3 Carbon capture technologies (CCT)

Carbon Capture Technology (CCT) is divided into three parts depending upon combustion i) Post Combustion ii) Pre-combustion iii) Oxy-fuel combustion as shown in figure 2.2. The capture of carbon dioxide relates to the significant cost of carbon capture and storage (CCS) and requires a more developing technique to apply economies at large. The decision of the capture will also rely upon the fuel composition (Olajire, 2010).

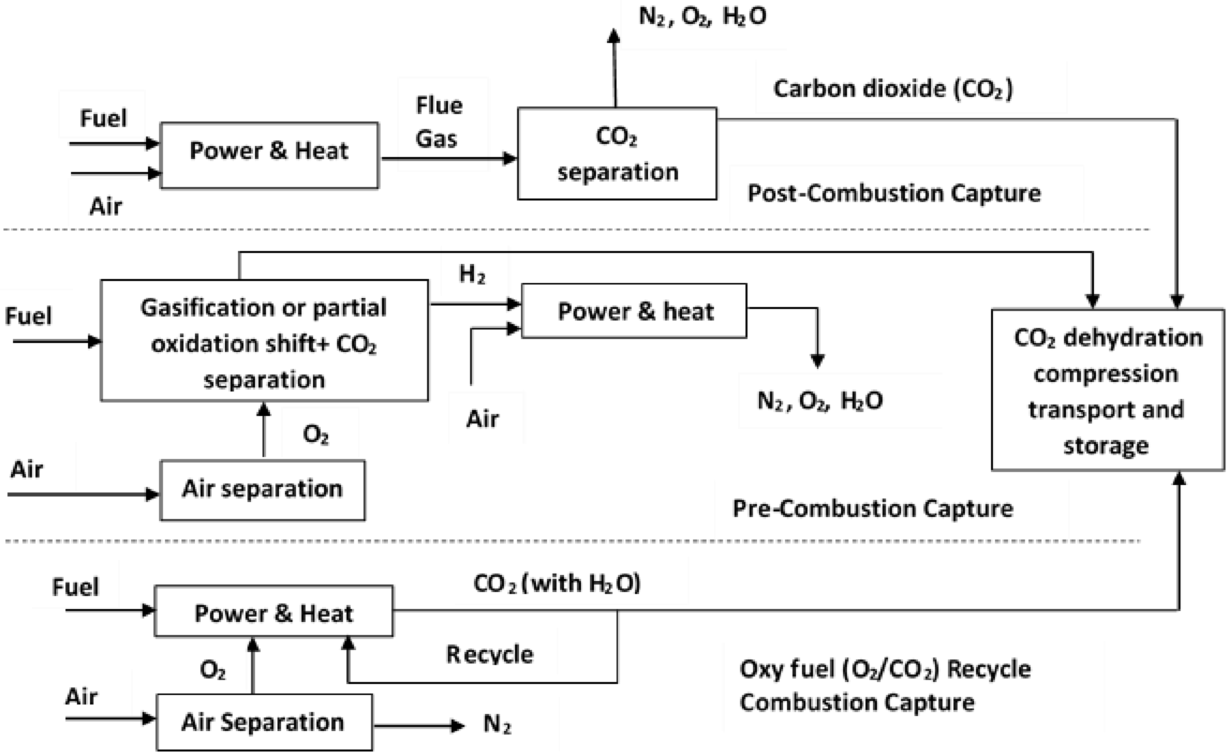


Figure 2.2: Schematic Diagram of Carbon Capture Adopted from (Cambier, 2017)

2.3.1 Post-Combustion CO_2 capture

This technology is the most popular technology in the world because of its ease, high economic efficiency, and product formation. In post-combustion CO_2 is captured from the exhaust gases after burning fossil fuel before releasing into the atmosphere. A large volume of CO_2 can be handled in this technology. Post-combustion capture is the most progressive technology since it is very well retrofitted to existing units (Awais, 2013). The post-combustion technology is membrane separators, cryogenic separation, adsorption, chemical absorption (Figueroa *et al*., 2008; Olajire, 2010).

2.3.2 Pre-Combustion of CO_2 capture

In pre-combustion carbon dioxide capture, CO_2 is isolated from the non-renewable energy source (coal or petroleum gas) before burning. In this procedure, the non-renewable energy source is changed over into combination gas, a blend of CO and H_2. This union gas is then sent to a water gas move reactor where it responds with steam to create a blend of CO_2 and H_2. CO_2 is then isolated from the (high weight) gas blend and H_2 is sent to the turbine, for hydrogen to be combusted. Adsorption and absorption both can be used for pre-combustion carbon dioxide removal (Aaron & Tsouris, 2005; Wook Lee *et al*., 2018). The primary advantage of pre-combustion CO_2 removal is of reducing the size of the capture unit. In reality, when hydrogen gas is used alone in turbine it releases less energy so a combined cycle system is required. Pre-combustion carbon dioxide capture is favorable for integrated gasification combined cycle (IGCC) operation that is mostly used in coal gasification systems or where natural gas is not available (Aaron & Tsouris, 2005; Cambier, 2017). The flow diagram of pre-combustion carbon dioxide capture is shown in figure 2.3.

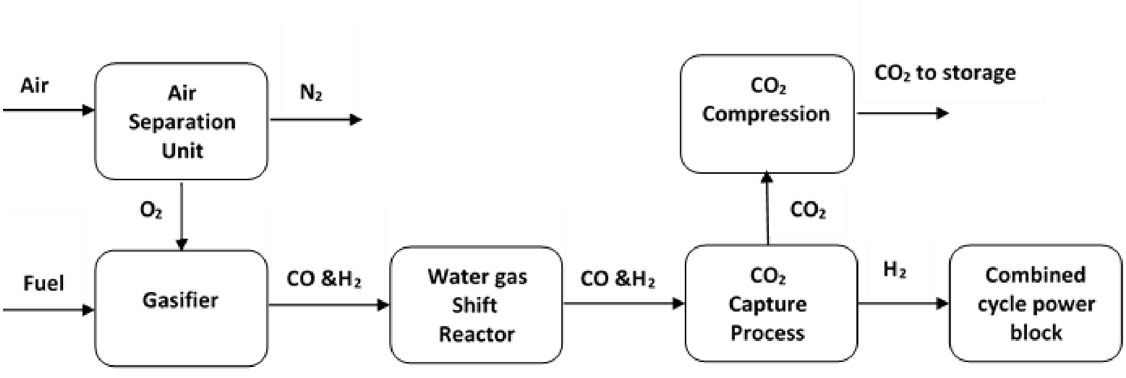


Figure 2.3: Process of Pre-Combustion Adopted from (Awais, 2013)

2.3.3 Oxy-Combustion

In Oxy combustion, fuel ignition is done in the presence of oxygen that is removed from the air. Oxygen detachment is the most costly, which is done by low temperature (cryogenic) air partitioning and/or using membranes. The oxy-combustion process, have the inconvenience of applying in existing units. Use of oxygen results in bringing a vent gas that mostly contains CO_2 and H_2O that is easily isolated by cooling. In this Oxy combustion, carbon dioxide capture technique water is made dense by cooling the gases, thus releasing carbon dioxide from the mixture. Water is dense, so it condenses out (Awais, 2013). The Oxy combustion process is shown in figure 2.4.

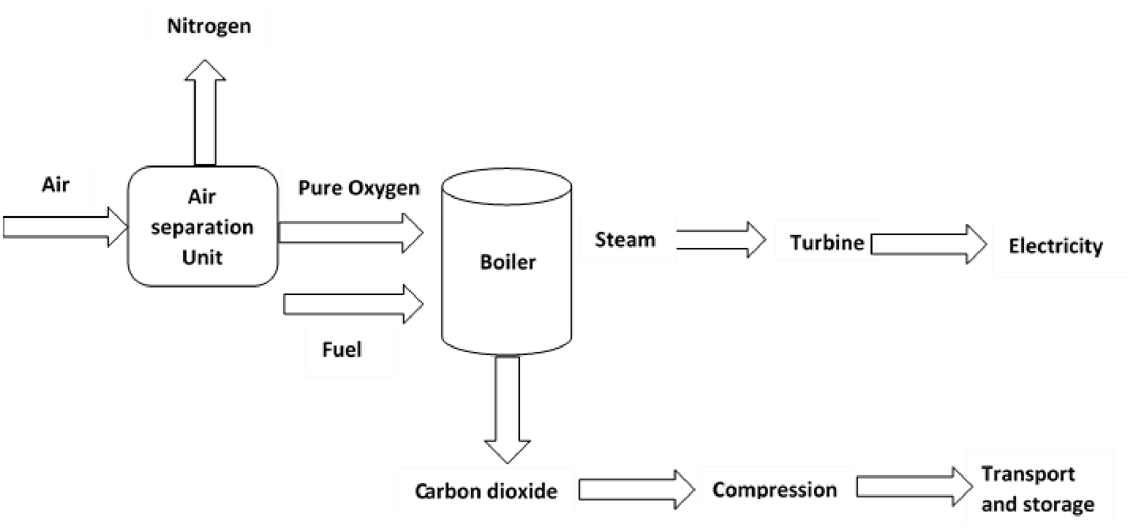


Figure 2.4: Oxy Combustion Process Adopted from (Awais, 2013)

Advantages and disadvantage of CCT technologies (Post combustion, Pre-combustion and oxy combustion) are shown in table 2.1.

Table 2.1: Advantages and Disadvantages of carbon capture technologies

Carbon dioxide capture technologies	**Advantages**	**Disadvantages**
Post-combustion	It is in application in industries for last 50 years Easily applied to all existing power plants	Energy intensive (solvent regeneration) Large amount of Solvent is required due to excess CO_2 emissions
Pre-combustion	90% - 95 % CO_2 is captured Applied to both natural gas and coal fire IGCC power plants	Capital cost is higher To capture CO_2 cooling of gas is required
Oxyfuel combustion	100 % CO_2 could be captured Easily applied to existing power plants	High energy is required to separate oxygen from air

2.4 Carbon removal techniques

Due to a high concentration of CO_2, there is a dire need to capture carbon dioxide. Many techniques are available for carbon dioxide removals such as membrane separation, cryogenic Separation, adsorption and chemical absorption (Aaron & Tsouris, 2005; Feron *et al*, 1992). In membrane separation technique size of the membrane are designed in such a way that only CO_2 molecules pass through that pores from flue gas (Drioli *et al*., 2011). In cryogenic Separation the mixture of gases containing CO_2 is liquefied and then CO_2 is removed through the distillation process. Adsorption is a technique for removing of carbon dioxide in which solid having pores are used. Many solids are used naturally like occurring are coal, man-made activated carbon, molecular sieves, and zeolites. pressure swing adsorption (PSA) and temperature swing adsorption (TSA) are two methods of adsorption. Besides adsorption, absorption also has its application in carbon dioxide removal. In absorption different chemicals like amines and alkali hydroxides are used for absorption of carbon dioxide depending upon their characteristics (Aaron & Tsouris, 2005). Carbon dioxide removal techniques is shown in table 2.2.

Table 2.2: Techniques of CO_2 removal

Different techniques of CO_2 removal	
Membrane	Flue gas is passed through the membrane having a pore size equal to CO_2 molecule size
Cryogenics separation	Flue gas is condensed up to freezing point of CO_2
Adsorption	Solids are used on which CO_2 is adsorbed
Absorption	Chemical is used for absorption of CO_2

2.4.1 Chemical absorption

The process of chemical absorption of removal of carbon dioxide is done by absorbing of carbon dioxide in amine chemicals like Monoethanolamine (MEA), Diethanolamine (DEA), N-Methyl diethanolamine (MDEA), piperazine (PZ), and 2-amino-2-methyl-1-propanol (AMP). It can also be removed using alkali chemicals like sodium hydroxide

(NaOH), calcium hydroxides(CaOH), magnesium hydroxide (Mg(OH)$_2$ etc (Bishnoi & Rochelle, 2002; I. Kim & Svendsen, 2007; Mores *et al*., 2011; Tontiwachwuthikul *et al*., 1992; Zhang *et al*., 2002). However, the amine solvents also have some drawbacks like limited CO_2 absorption at low concentrations up to 0.5 Mol of CO_2/Mol amine (Shariff *et al*., 2016). Favorably, alkaline hydroxides aqueous solutions have also shown promising characteristics in the CO_2 absorption process. Alkaline hydroxide solutions have the advantage that they show higher loading capacity than amines, (Yoo *et al*., 2013) they are cheaper and much easier to apply, other benefits of using alkaline hydroxides is that of multi-reaction by-product formation (Tavan & Hosseini, 2017), while no product is formed in the case of absorption in amine solutions (Vaidya & Kenig, 2007).

2.4.2 Absorption using sodium hydroxide (NaOH)

Using NaOH for absorption of carbon dioxide is economical and feasible to use. It is an easily available resource in Pakistan. The reaction of CO_2 with NaOH form sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$) which can be used as a raw material in many industries such as cement and ceramic industries etc and are also used in wastewater treatment (Cambier, 2017). The absorption of CO_2 depends upon the concentration of NaOH solution; more concentration means more of CO_2 will be absorbed (Tavan & Hosseini, 2017). Lin & Chu, (2015) have shown it decreases with increasing the CO_2 flow through the solution.

Different technologies are used for absorption of CO_2 in alkaline solutions such as packed columns, spray towers, rotating packed beds. The packed column is a column in which flue gas containing desired gas is entered from one side and absorbent flow is done in a countercurrent direction. While in the case of spray tower, the absorbent is sprayed on the flue gas entering from the other side of the tower. Similarly rotating packed bed absorbent follows the same countercurrent flow pattern (Cambier, 2017).

2.5 Hydrogenation

Hydrogenation is a process in which hydrogen (H_2) from a source is reacted with a compound to reduce its state. Hydrogenation is an endothermic process that requires high reaction temperatures, however, the presence of catalysts can reduce the reaction temperatures. Many catalysts are reported for hydrogenation process like Palladium (Pd), Nickel (Ni) etc. The palladium catalyst is mostly used for hydrogenation. Hydrogenation of NO &NO_2 (Barroo *et al.*, 2014) hydrogenation of alkenes (Johnstone *et al.*, 2003) and hydrogenation of alkyne has been done by using a Pd catalyst, (Teschner *et al.*, 2010).

2.5.1 Hydrogenation of sodium hydrogen carbonate ($NaHCO_3$)

Hydrogenation of $NaHCO_3$ is done in the presence of a catalyst to convert it into sodium formate ($NaHCO_2$). Hydrogen can be applied from any source in the presence of a catalyst. The hydrogenation of sodium hydrogen carbonate in aqueous stage ($NaHCO_3$) results in the formation of sodium formate, (González *et al.*, 2018) has reported this conversion in the presence of catalysts (Pd, Ru, Ni, Co, and Re).

2.6 Uses of formic acid

Uses of formic acid are very vast they are used in the leather industry, textile industry, the pharmaceutical industry, food additives, Gas desulphurization, Rubber coagulation and as a cleaning agent in industries. It is also used for the preservation of animal biomass. They are less corrosive to machinery in the industry than sulfuric acid. It is also a good source of hydrogen. Formic acid has a property of antimicrobial effects, in the poultry industry, it is used to prevent the growth of pathogens. In the textile industry, it is used as a pH regulating agent in dyeing wool nylon and synthetic fiber etc. It is also used for neutralizing alkaline solutions. In the leather industry, it is used for removing hair, wool etc. (leather depilation). It is also used for the removal of ash and as a softening agent. In the leather industry, it is used for dyeing and disinfection (Elvers, 2016).

Chapter 3

Material and Methods

3.1 Materials

In order to conduct experiment following chemicals were utilized in the present study, Sodium hydroxide (NaOH) with 99.0 % purity and iron nitrate Fe$(NO_3)_3$ with 98 % purity were purchased from Merck, a local supplier in Pakistan. Nickel nitrate Ni$(NO_3)_2$with 94.5-105.5 % purity was purchased from Sigma also a local supplier in Pakistan. Zinc (Zn) metal granular was purchased from Bio care scientific and Sulfuric acid with 99% purity was purchased from Sigma. Carbon dioxide (CO_2) cylinder with 99 % purity was purchased from Pakistan pure gas. All chemicals were of reagent grade and utilized as received without any further purification.

3.2 Methodology

The research study consists of three different phases or steps. In the first step absorption of carbon dioxide was done in sodium hydroxide solution for carbonates and sodium hydrogen carbonates product formation by considering the parameters (1). solution concentration and (2). solution pH. In the second phase conversion of Sodium hydrogen carbonate to sodium, formate was performed/done with and without using a catalyst. The last phase consists of Synthesis of formic acid by reaction of sodium formate crystals with sulfuric acid. Different phases are shown in figure 3.1.

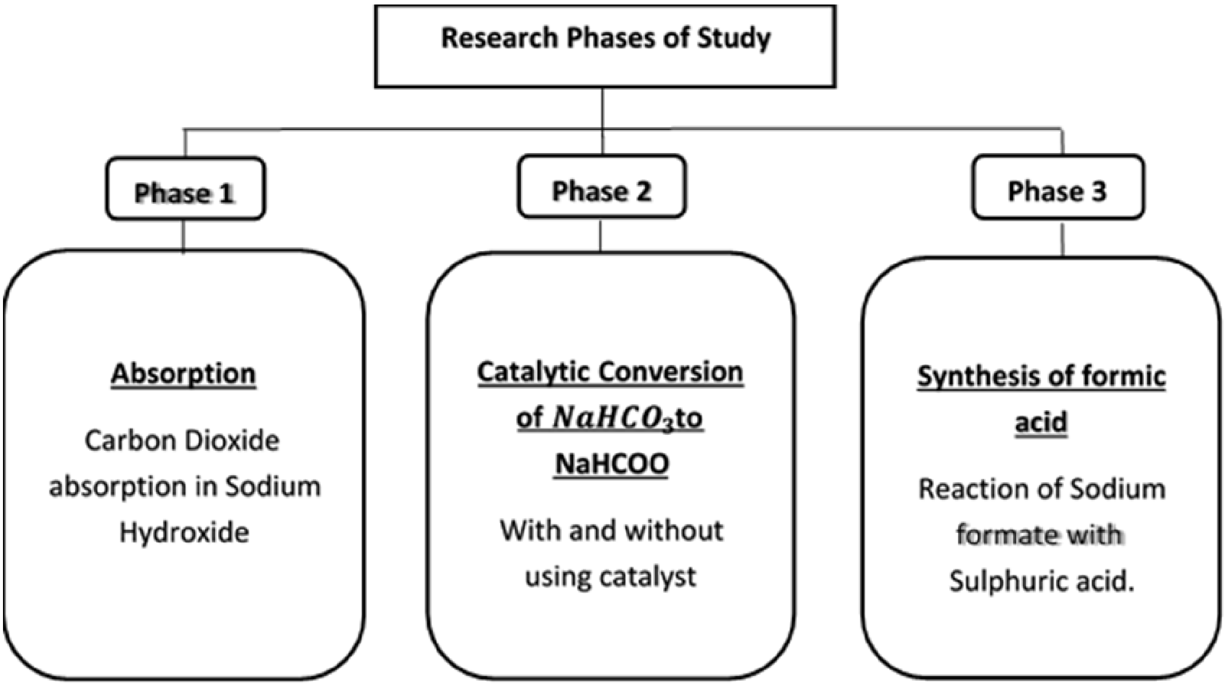


Figure 3.1: Different Phases of Research Study

3.3 Absorption

Absorption phase of research study consists of two parameters Solution concentration and solution pH. The flow diagram is shown in figure 3.2.

3.3.1 Solution concentration

In solution concentration, six concentrations of sodium hydroxide aqueous solution 0.01,0.1,0.5,1,3and 5N were prepared by dissolving NaOH pellets in 500 ml of distilled water. The experimental setup is shown in figure 3.3.

The temperature of the absorbing solution was maintained at room temperature (25˚C). CO_2 was bubbled at a flow rate of 0.4 L/min through the solution, the pH of the system was monitored for the whole period of time by keeping the electronic pH meter in the solution. CO_2 was absorbed in the solution till the initial solution pH drop to pH 09 and total time was noted. pH 09 was randomly selected. At pH 09 the flow of CO_2 was stopped. Reacted solution was then dried in an oven at 105˚C for 24 hours and the weight of the product obtained was noted. On the basis of the weight of the product obtained at 3N and 5N concentrations, these were selected for optimization.

The 3N solution was selected as the optimize concentration on the basis the fact that alkalinity suppresses after 1 N solution use and weight of the product obtained is maximum. X-ray diffraction (XRD, D8 Advance Germany) of the product (crystals) was then performed to analyze the type of the product formed. The XRD pattern obtained was then analyzed and compared using the Jade software. The XRD peaks were matched with the reference peaks.

3.3.2 Solution pH

CO_2 absorption was done again in the 3N optimize solution in order to get the pH drop up to 10.0 and 8.0, similarly time for pH adjustment was noted. The temperature of the absorbing solution was maintained at room temperature (25˚C). CO_2 was bubbled at a flow rate of 0.4 L/min through the solution, the pH of the system was monitored for the whole period of time by keeping the electronic pH meter in the solution.

X-ray diffraction (XRD, D8 Advance Germany) of the product crystals was then performed to analyze the type of the product formed at each pH. The XRD pattern obtained was then analyzed and compared using the Jade software. The XRD peaks were matched with the reference peaks.

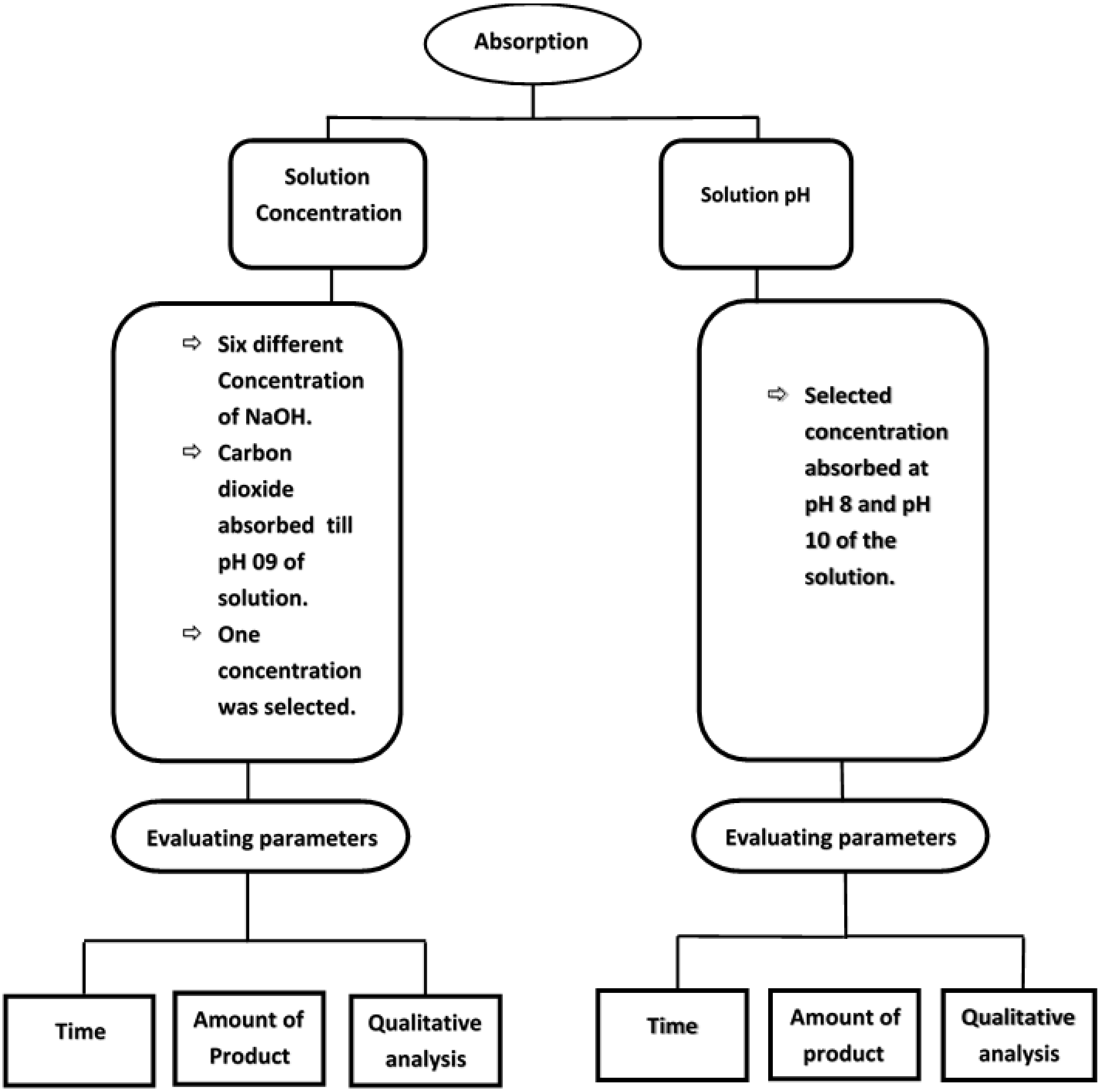


Figure 3.2: Methodology of absorption

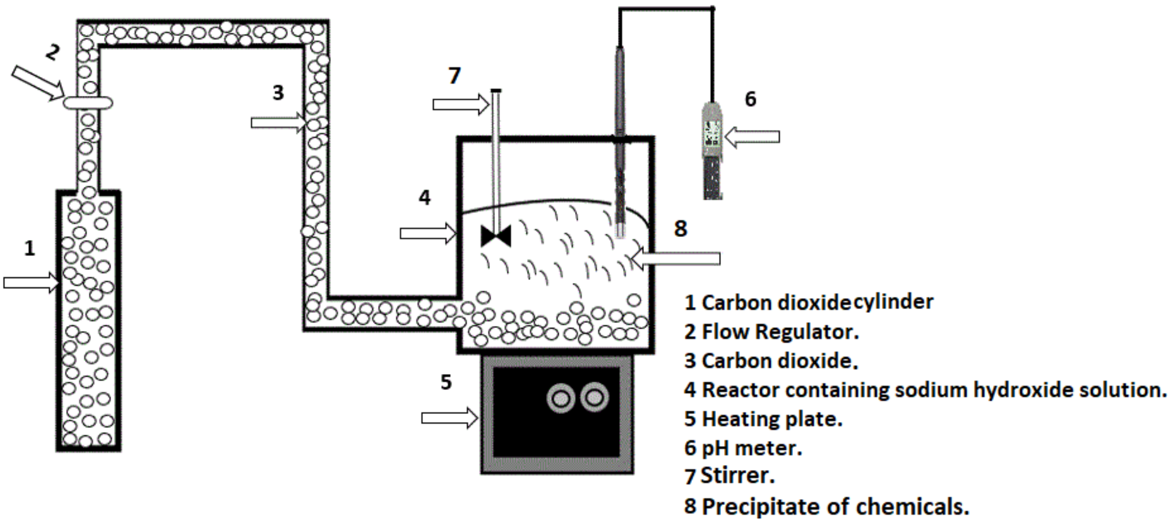


Figure 3.3: Experimental setup for CO_2 absorption.

3.4 Catalytic conversion of sodium hydrogen carbonate to sodium formate by hydrogenation

The methodology of conversion of sodium hydrogen carbonate to sodium formate is shown in figure 3.4. To produce the sodium formate ($NaHCO_2$) from sodium hydrogen carbonate ($NaHCO_3$) the reaction was carried out in a reactor attached with round bottom flask as shown in figure 3.5. Hydrogen gas was produced in the round bottom flask by the reaction of zinc metal rings with concentrated sulfuric acid. Sodium hydrogen carbonate (100 ml, 1 M) produced by the absorption of CO_2, was put in the reactor; hydrogen gas bubbled into the sodium hydrogen carbonate solution for 2 hours at a temperature of 80˚C. The solution was stirred at 100 rpm and after completion of reaction, the product was then kept in an oven at 105˚C for 24 hours to obtain sodium formate crystals.

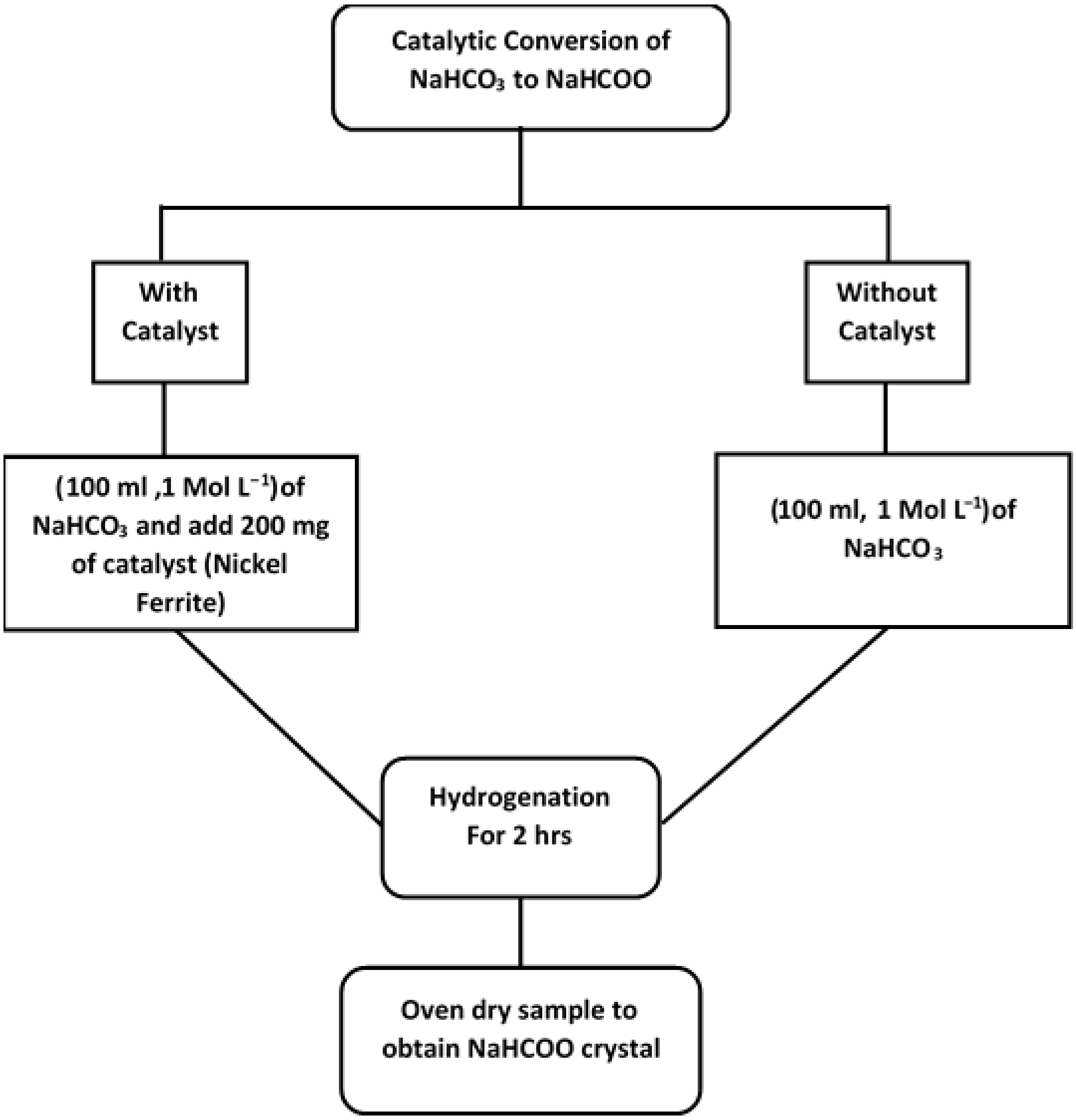


Figure 3.4: Methodology of Formation of Sodium Formate.

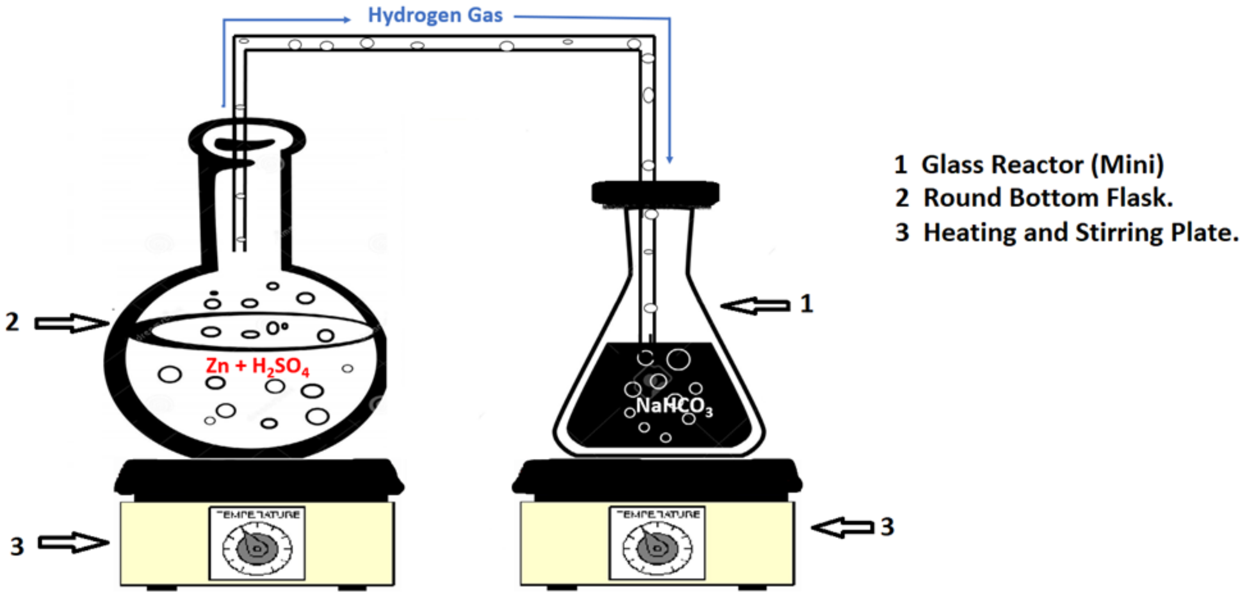


Figure 3.5: Conical flask attached with round bottom flask

3.4.1 Nickel ferrite catalyst

The nickel ferrite catalyst for the reaction was produced by mixing a solution of nickel nitrate (0.24 g /ml) and iron nitrate (0.12 g/ml). The two solutions were mixed thoroughly in a beaker at 100 rpm. The mixture pH was adjusted at pH 12 by adding 1 N sodium hydroxide solution drop by drop. Mixing proceeded at 80^0 C for 3 hours and the reaction mixture was then allowed to settle down overnight. Filtered nickel ferrite precipitates were finally washed with distilled water until pH 7 is achieved. Washed precipitates, were oven dried at the 110^o C for 24 hours. Dried crystals were then placed in a muffle furnace for 6 hours at 850^0 C. Produced nickel ferrite was then analyzed by XRD.

3.4.2 Conversion of sodium hydrogen carbonate to sodium formate in the presence of nickel ferrite catalyst.

A fresh solution of sodium hydrogen carbonate (100 ml, 1 Mol L^{-1}) was prepared and put into a conical flask, Nickel ferrite (200 mg) catalyst was then introduced into the conical flask. The same procedure was repeated as discussed above in 3.4 section. The sodium Formate formation was compared with and without using Nickel ferrite catalyst. For hydrogenation of sodium hydrogen carbonate to sodium formate, the high temperature is required, i.e. 300° -350° but in the presence of catalyst it can be achieved at low temperature i.e. below 100 °. The sodium formate quality and quantity produced was then compared with and without the presence of nickel ferrite catalyst in the reaction mixture.

$$NaHCO_3(aq) \underset{NiFe_2O_4}{\overset{H_2}{\rightarrow}} NaHCO_2(aq)$$

3.5 Synthesis of formic acid

For the synthesis of formic acid 5 grams (gm) of sodium formate was converted into formic acid by reacting it with concentrated sulfuric acid. Formic acid and sodium sulfate were obtained as reaction products, vapors of formic acid were condensed to get formic acid in the liquid phase. It was made sure that sulfuric acid dissolved all the crystals of sodium formate. Sodium sulfate and formic acid produced were then analyzed by XRD and High-Performance Liquid Chromatography (HPLC) (Agilent 1100 series) respectively.

HPLC test was performed by running first standard formic acid and its retention time was noted, this retention time was then compared with the time of analysis of formic acid produced; with and without the use of nickel ferrite in the reaction.

The procedure of synthesis of formic acid is shown in figure 3.6 and setup of distillation mechanism is shown in figure 3.7.

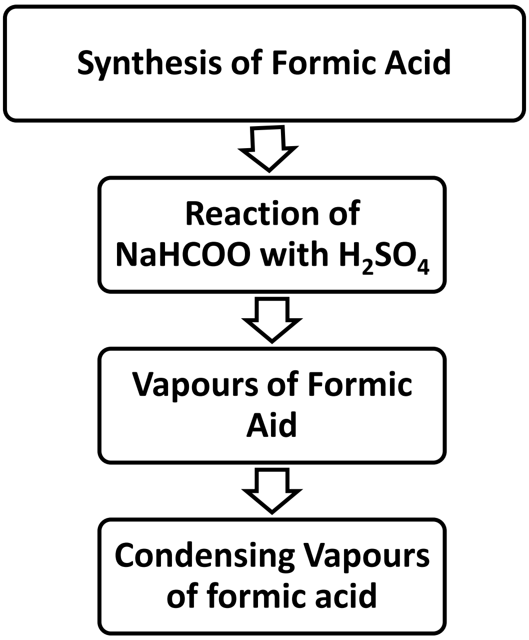


Figure 3.6: Procedure of synthesis of formic acid

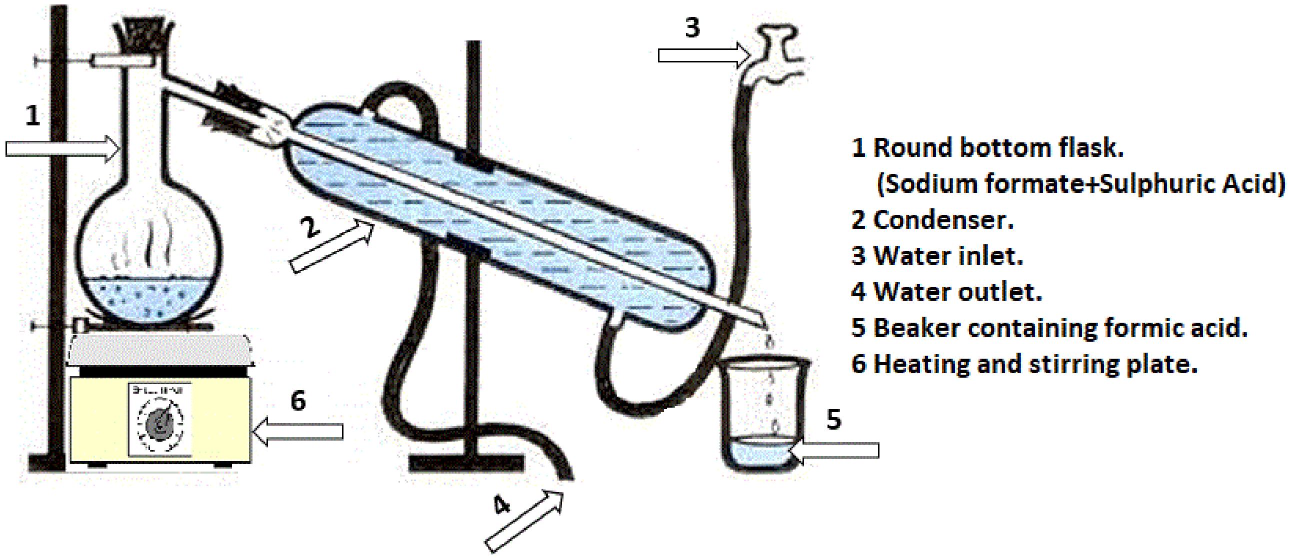


Figure 3.7: synthesis of formic acid by distillation Process.

3.6 Theory

Carbon dioxide absorption in sodium hydroxide solution is explained by the following mechanism (Krauβ & Rzehak, 2017; Yincheng *et al*., 2011; Yoo *et al*., 2013).

A solution of NaOH in pure water, Na+ ion and OH- ions are completely ionized in it. When CO2 is fed into the sodium hydroxide solution, it is physically absorbed in it as shown in equation 1

$CO_2(g) \rightarrow CO_2(aq)$ …………… (1)

Carbon dioxide that is fed into the sodium hydroxide solution reacts with OH ions to form HCO_3^- as shown in the equation below.

$CO_2(aq) + OH^-\ (aq) \rightleftharpoons HCO_3^-$ (aq) …………… (2)

HCO_3^- formed to further react with OH^- to CO_3^{-2} as shown in equation (3)

$HCO_3^-(aq) + OH^-(aq) \rightleftharpoons H_2O(I) + CO_3^{-2}\ (aq)$ …………… (3)

Eq (2) and (3) are reversible reaction with very high rates in high pH. HCO_3^{-1} , CO_3^{-2} formed immediately as shown in the equation.

Eq (3) is dominant than eq (2) due to which concentration of CO_3^{-2} is more than HCO_3^-. As Reaction proceeds the depletion in OH^- Occurs. These CO_3^{-2} react with Na^+ to formNa_2CO_3. The overall reaction is shown below.

2NaOH(aq) + CO_2(g) ⟶ $Na_2CO_3(aq) + H_2O\ (I)$ ...………… (4) pH=10.0

At pH > 10 the backward reaction in eq (3) is dominating, but as time passes and more carbon dioxide is fed into the solution the forward reaction becomes dominating at pH

< 10, So more Na_2CO_3 is formed which further reacts with CO_2 to form $NaHCO_3$ which is shown as follows.

$Na_2CO_3 + CO_2 + H_2O \rightarrow NaHCO_3$ ……………. (5) pH=8.0

3.7 Analytical methods

For characterization of crystals obtained by absorbing Carbon dioxide in NaOH solution for solution concentration parameter the XRD (X-ray Diffraction) test and Total Alkalinity test was performed. Similarly, for solution pH parameter also XRD test was performed for crystals. XRD test was performed for the confirmation of the formation of Nickel ferrite catalyst. Analysis of Sodium formed or formic acid was done by HPLC (High Performance Liquid Chromatography) test.

Chapter 4

Results and Discussion

4.1 Impact of sodium hydroxide solution concentration

Figure 4.1 interprets the results of CO_2 absorption in sodium hydroxide solution until the starting pH of the solution is dropped to pH 9.0. The minimum time to reach pH 9 was 3 minutes at the solution concentration of 0.01 N and the maximum was 17 hours and 68 hours at 3N and 5N respectively. This is due to the fact that by increasing the sodium hydroxide solution concentration, the concentration of Na+ and OH- ions increases and due to which the time for their neutralization increases. Moreover, at higher concentration higher CO_2 absorption takes place (Darmana *et al*., 2007; Lin & Chu, 2015; Yoo *et al*., 2013).

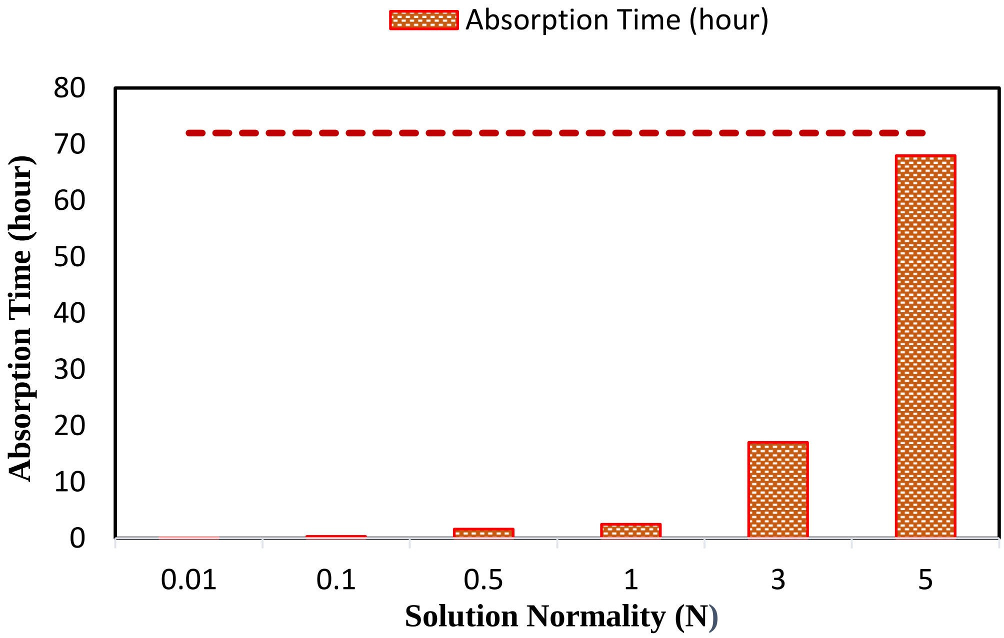


Figure 4.1: Impact of solution concentration on adsorption time

In figure 4.2, it was noted that minimum 381 mg of product were obtained at 0.01 N solution while 65 g and 121g were measured for 3N and 5N sodium hydroxide solution, respectively when the solution initial pH was dropped to pH 9.0 on carbon dioxide absorption. The amount of product obtained by absorption of carbon dioxide in the solution increases by increasing the solution concentration and so as the alkalinity increases. Minimum alkalinity was noted for 0.01 N solution, which was 24 mg/L equivalent of $CaCO_3$ and maximum, was 38000 and 67000 mg/L equivalent as $CaCO_3$ for 3N and 5N solution. This increase in alkalinity proves the fact that the absorption of CO_2 performs the reaction with the sodium hydroxide solution. Moreover, it can be said that the minimum Solution Normality required for the absorption should be above 1 N as after this normality, the alkalinity of the solution does not suppress the product formation.

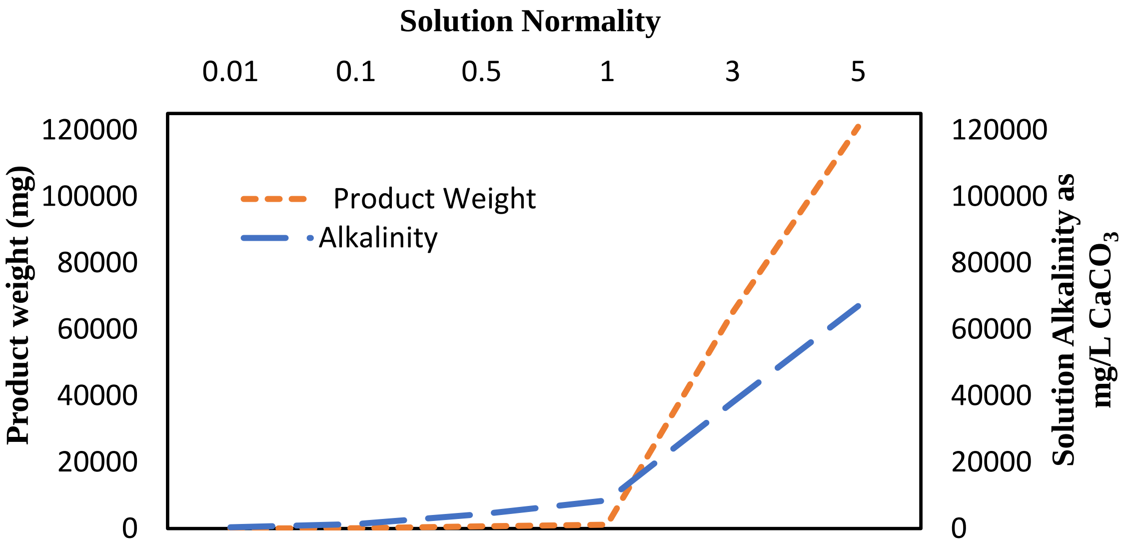


Figure 4.2: Impact of solution concentration on product formation

The data obtained after XRD were analyzed by jade software and peaks were matched with the reference peak. XRD test of the product obtained from 3N and 5N solution at pH 9 showed in both the cases, i.e 3N, 5N trona was formed at pH 09. Sharp long peaks were dominating at 18.3^{o},29.2^{o},33.9,40.1^{o},44.8^{o}. and lower peaks were present at, 27.5^{o},28.0^{o}, 33.9^{o} 34.8^{o},35.8^{o},36.4^{o}, 37.1^{o}, 40.1^{o}. This also illustrates that the solution normality has no impact on the type of product formation. The graph was also compared with the XRD card. All peaks showed the same product trona (Yoo, et al., 2013). XRD graph is shown in figure 4.3. **Trona** is a crystal having a formula $Na_2CO^3.NaHCO^3.2H_2O$.it is used in conditioning of water, used as food additive, for the removal of Sulphur from flue gases and as a source of soda ash.

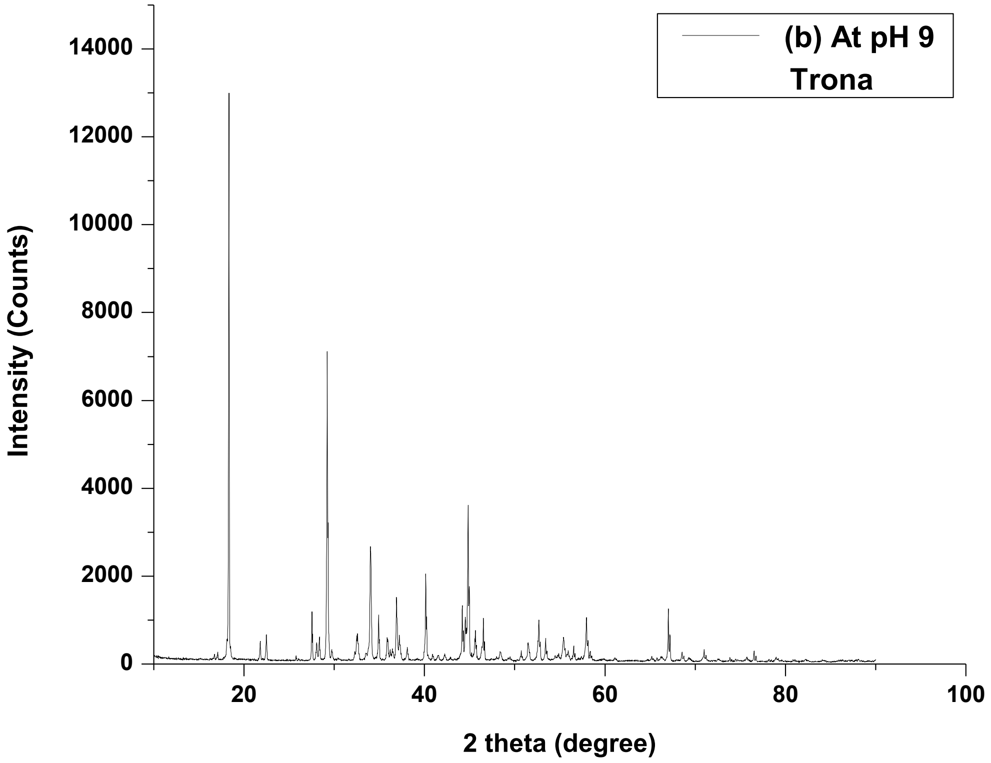
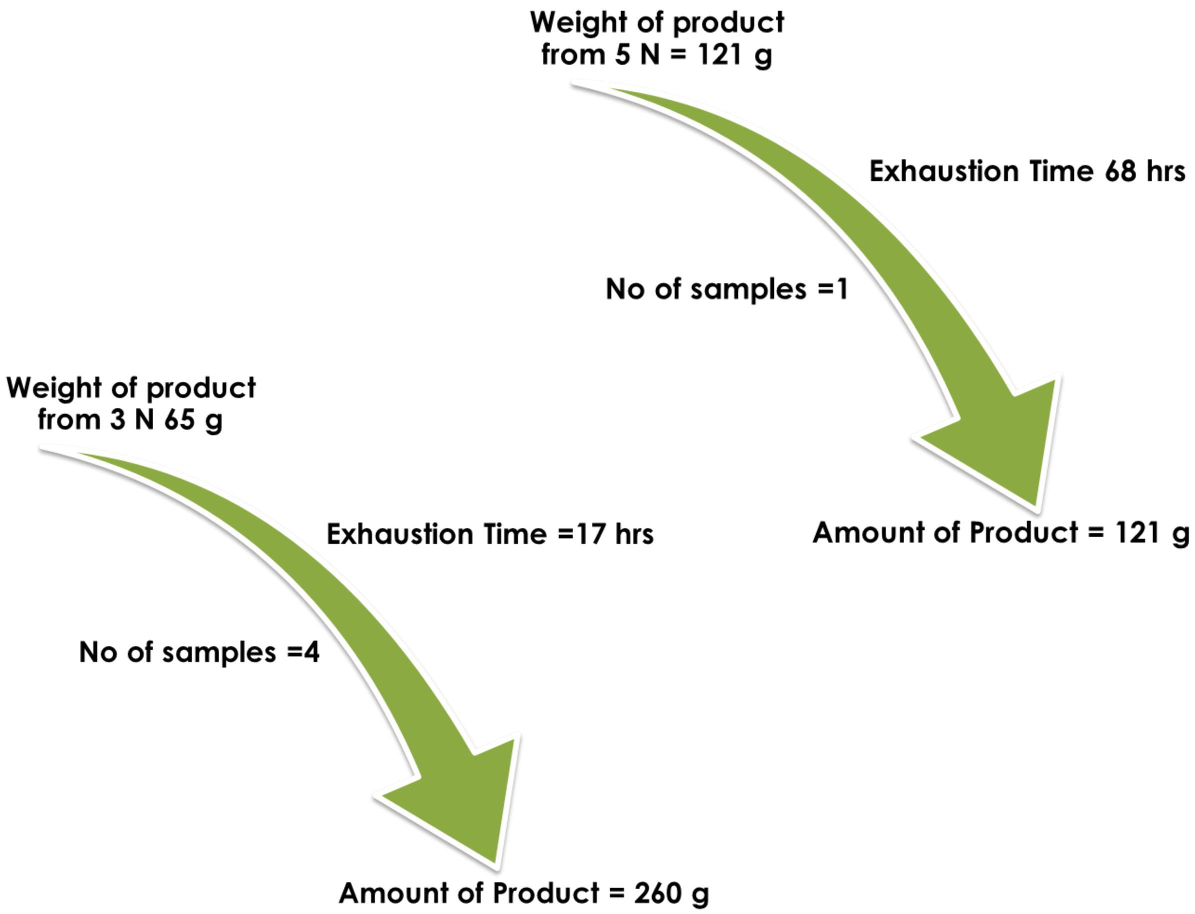


Figure 4.3 X-ray diffraction (XRD) test (Trona production)

Exhaustion time for a 3N solution is 17 hrs. and for 5N it is 68 hrs. So the number of absorption samples of 3N that can be applied for (Exhaustion time of 5N) 68 hrs are 4 and weight of total product obtained are 260 gm while only 121 gm of crystals obtained from 5 N during 68 hrs so 3N is selected as the optimized solution concentration for further study at different pH.



Further absorption of carbon dioxide was performed on 3N solution till pH 10 and 8 in order to have pH vs product relationship.

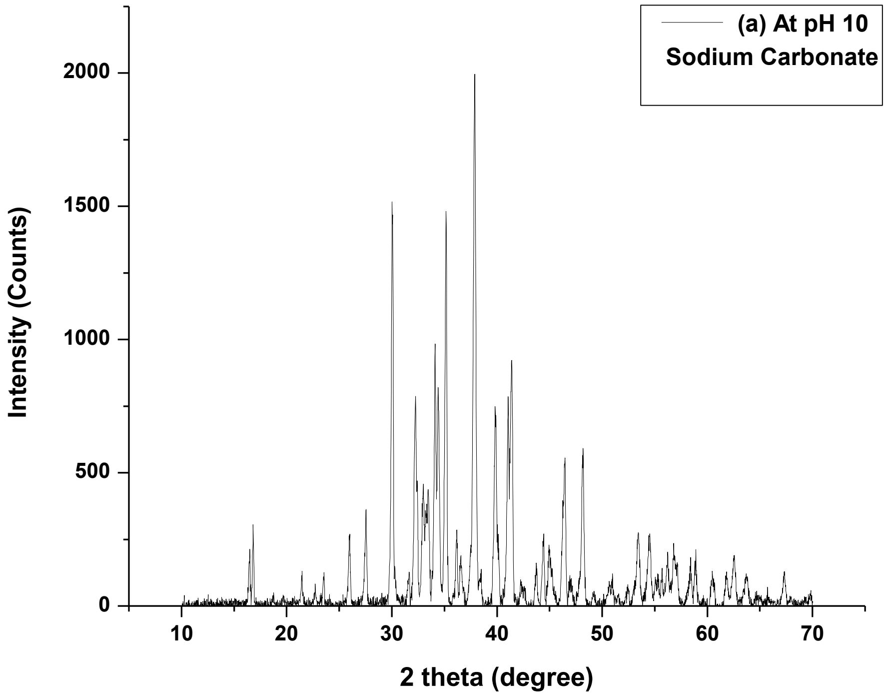
4.2 Impact of solution pH on product formation

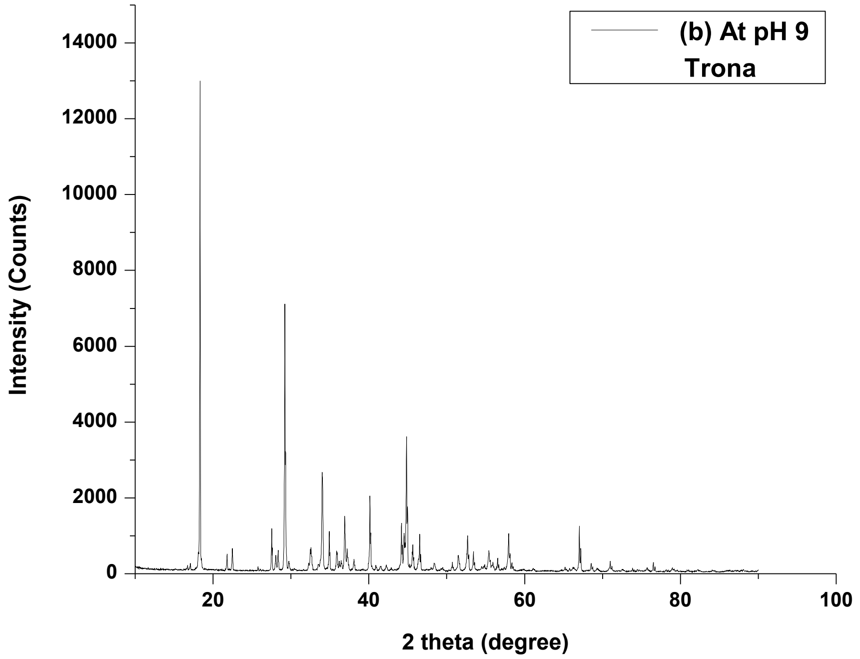
XRD of product formed at pH 8 and at pH 10 were analyzed by jade Software and peaks were matched with the reference peak. The peaks fitted match of sodium hydrogen carbonate and sodium carbonate reference XRD graph. The graph was also compared with the XRD card from literature or XRD card manual. XRD analysis of product formed at solution pH 8.0 showed the presence of pure sodium hydrogen carbonate figure 4.4. Major peaks were present at 29^{o} 30.2^{o}, 34.6^{o}, 38.1^{o} and at 44.6^{o} while lower peaks at 33.4^{o},34.6^{o},40.8^{o,} and 46.2^{o}.

Similarly, XRD of the product obtained at pH 10.0 revealed the presence of pure sodium carbonate crystals figure 4.4. Sharp peaks were prominent at 30.0^{o}, 34.1^{o}, 35.1^{o}, 37.8^{o},40.1^{o},41.3^{o} while the minor peak at 32.0^{o}, 33.4^{o},34.1^{o},43.7^{o},45^{o}.

Sodium carbonate is used in manufacturing of glass, paper soaps and detergents. Domestically it is used as water softener.

Sodium hydrogen carbonate is commonly used, in baking powder, as odor absorber, for pH balancing, paint removal and metal cleaning applications etc.


(a) At pH 10
Sodium Carbonate
Intensity (Counts)
2 theta (degree)
0
500
1000
1500
2000
10
20
30
40
50
60
70


(b) At pH 9
Trona
Intensity (Counts)
2 theta (degree)
0
2000
4000
6000
8000
10000
12000
14000
20
40
60
80
100

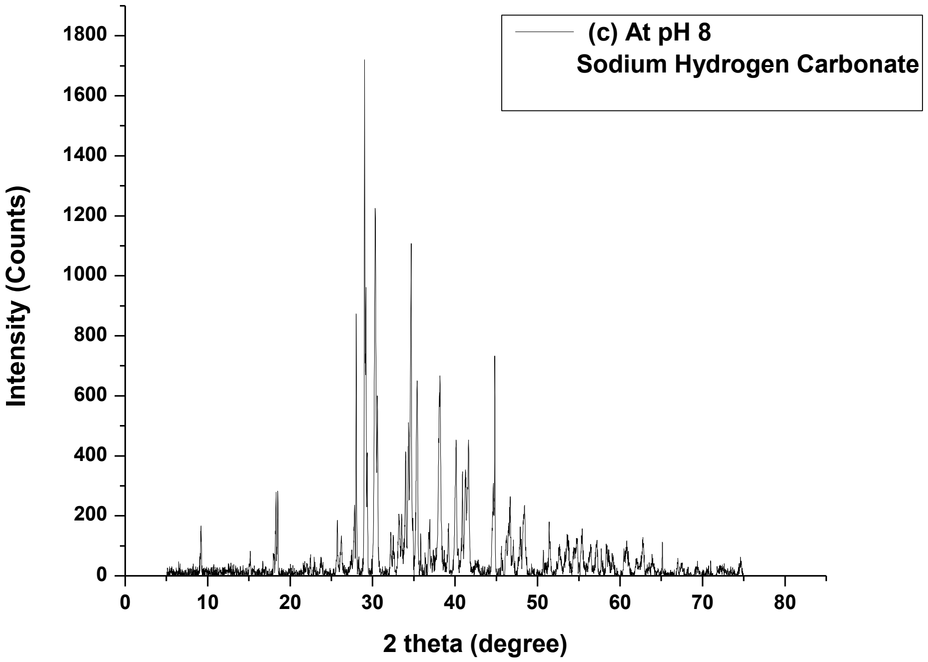


Figure 4.4: X-ray diffraction (XRD) of Sodium carbonate, Trona, and Sodium hydrogen carbonate

The weight of amount of sodium hydrogen carbonate is higher than that of sodium carbonate i.e. 76.6 g and 20.6 g, respectively, as shown in figure 4.5.

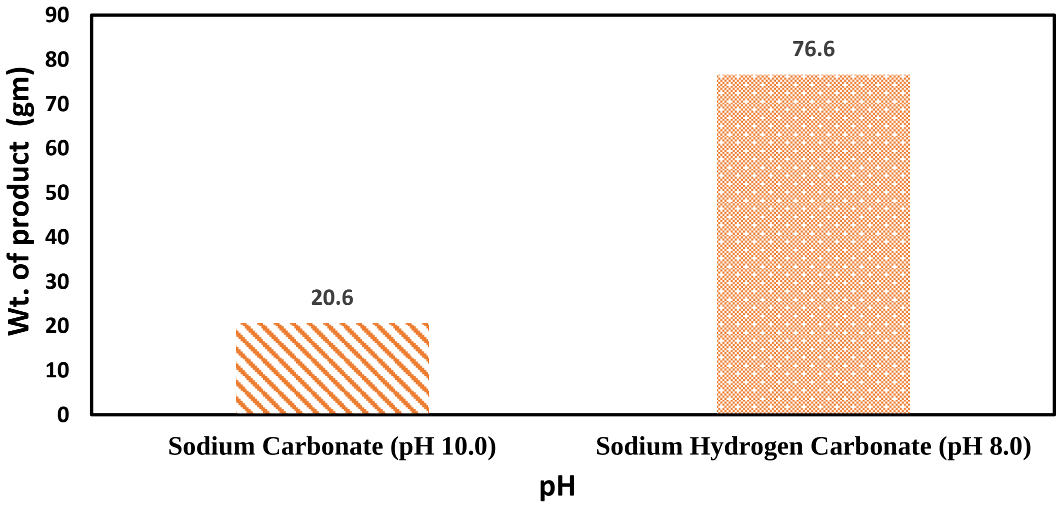


Figure 4.5: Solution pH VS product weight.

Eq (2) and (3) are a reversible reaction when pH is >10 the backward reaction dominates which leads to less amount of CO_3^{-2} (Darmana *et al.*, 2007; Krauβ & Rzehak, 2017; Yincheng *et al.*, 2011; Yoo *et al.*, 2013) when pH is < 10 the forward reaction dominates which leads to higher amount of CO_3^{-2} **.** As Carbon dioxide is continuously absorbed in the solution so sodium carbonate formed at pH < 10 react with Carbon dioxide in the presence of water and converted to Sodium hydrogen carbonate, that is why the amount of sodium hydrogen carbonate crystals is higher than sodium carbonate.

4.3 Solution exhaustion time

Figure 4.6 shows a sodium hydroxide solution exhaustion time when CO_2 absorbed in 3N solution. It represents the time taken by the solution to achieve different pH. The starting 3N solution pH on average was 13.75. The time to achieve pH 13 was 1 hr 15 min, similarly, time to achieve pH 10, 9 and 8 was 3 hrs, 17 hrs, and 22 hrs respectively.

The exhaustion time to reach a new solution pH was of the order pH 13 < 12 < 11 < 10 < 9 and so on up to pH 8. It is the total time taken from starting pH to the desired pH of sodium hydroxide solution. At the start of absorption of CO_2 in sodium hydroxide solution the concentration of Na+ and OH- was higher so more time was required to drop the pH to 13.00, but when it reaches pH 13 depletion in OH- occurs.

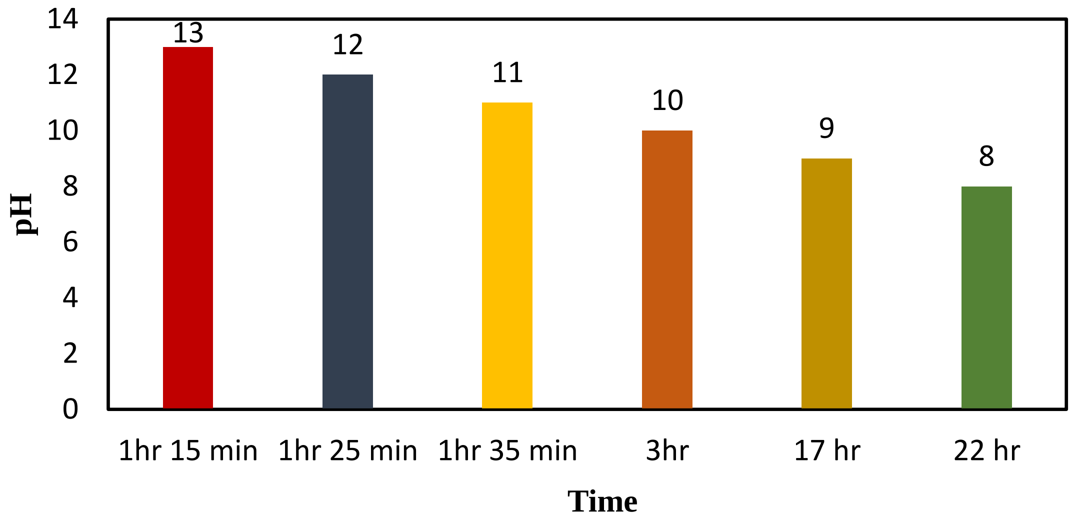


Figure 4.6: 3N solution exhaustion time to different pH

The rate of reaction (absorption reaction) is higher at higher pH, but it becomes slow at lower pH. The same trend was observed earlier (Fleischer *et al.*, 1996; Krauβ & Rzehak, 2017; Yoo *et al.*, 2013).

4.4 Production of sodium formate

The sodium hydrogen carbonate formed during CO_2 absorption at pH 8.00 was then converted to sodium formate through the hydrogenation reaction in the presence of nickel ferrite catalyst as discussed in the methodology section.

4.4.1 Nickel ferrite analysis

Formation of nickel catalyst used in the sodium hydrogen carbonate step is already discussed in the methodology section. The sharp peak in XRD graph shown in figure.4.7 are the crystalline structure and confirmation of nickel ferrite due to its sharp peaks as reported by (Maaz *et al.*, 2009; Sun *et al.*, 2017). An XRD graph of nickel ferrite is as shown in figure No 4.7.

The graph shows that major peaks are at 30°,35.7°,37.3°,43°,53.8°,57.3° and 62.9° having attribute (220), (311), (222), (400), (422), (511) and (440).

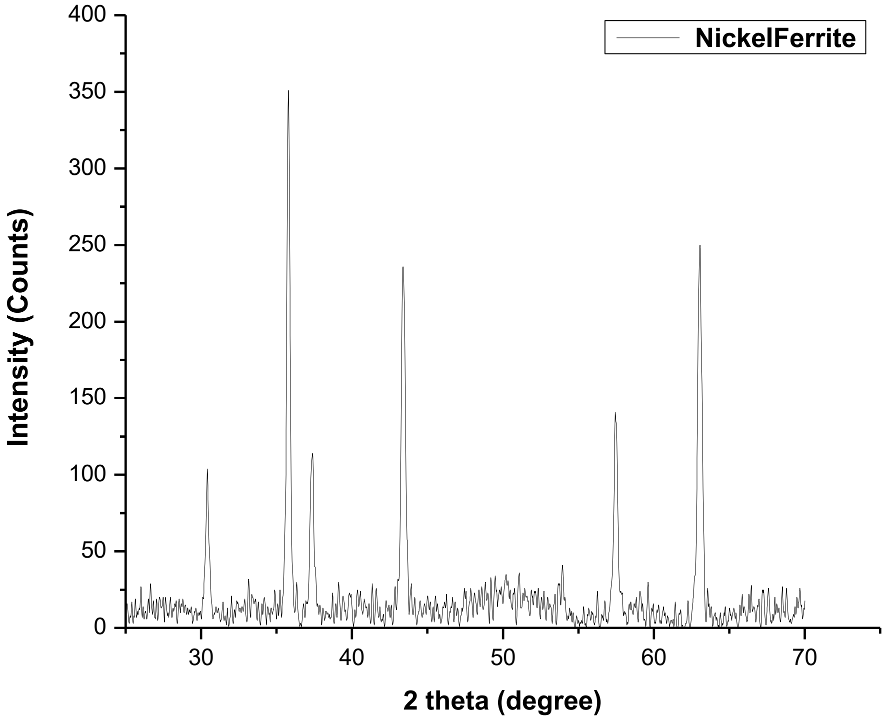


Figure 4.7 X-ray diffraction (XRD) graph of Nickel ferrite

The SEM analysis of nickel ferrite revealed that average particle size of nickel ferrite was 49.7 nm, which is within the range nickel ferrite particles. The same size range reported earlier (Sun, *et al*., 2017). SEM result of nickel ferrite shown in figure 4.8.

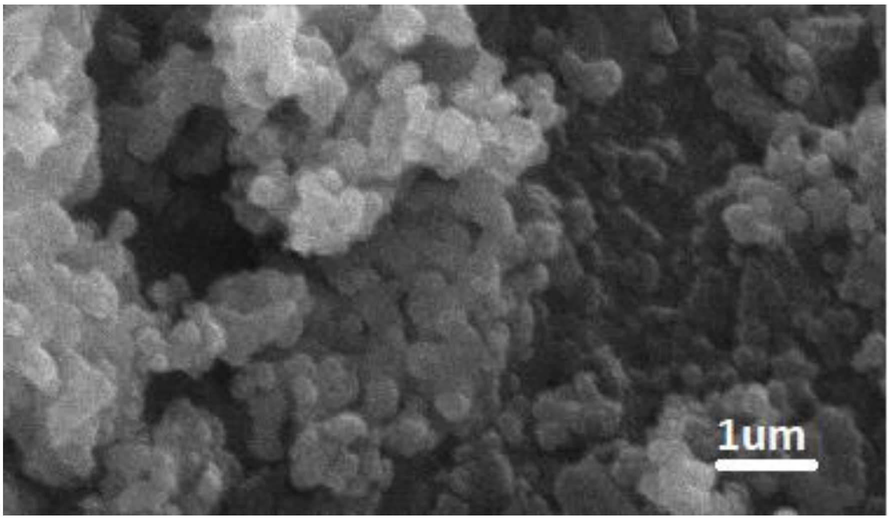


Figure 4.8 SEM results of Nickel ferrite

A reaction conversion yield of 79±0.2 % sodium formate from hydrogenation of sodium hydrogen carbonate resulted in the presence of nickel ferrite catalyst. However, this yield was less than 1% in the absence of the catalyst This is due to the fact that nickel ferrite has the surface property of decomposing CO_2 i.e. double bond of carbon with oxygen into a single bond between carbon and oxygen (Shin *et al*., 2001). Thus, during hydrogenation of Sodium Hydrogen Carbonate $NaHCO_3$, CO_3^- is decomposed into CO_2 and finally to sodium formate $NaHCO_2$.

4.4.2 Synthesis and analysis of formic acid

The synthesized formic acid was then analyzed by HPLC (Agilent 1100 series, Column C18, Mobile phase was buffer plus methanol). At first standard formic acid was run the retention time for the standard formic acid was noted 3.092 min figure 4.9 and after that sample of formic acid without crystal was run and its retention time was 3.12 min with a shoulder curve figure 4.10, which shows its impurity. The sample of formic acid prepared in the presence Nickel ferrite catalyst was then analyzed. Standard formic acid was run first and its retention time was noted 3.08 min figure 4.11 and retention time of formic acid produced in the presence of the catalyst was 3.11 min figure 4.12. This was without any shoulder peak as analyzed which also shows the purity of the formic acid produced when nickel ferrite was used as a reaction catalyst. Further in the previous case reaction yield was less than 1% and in the latter case, it was 79±0.2%.

Formic acid without catalyst

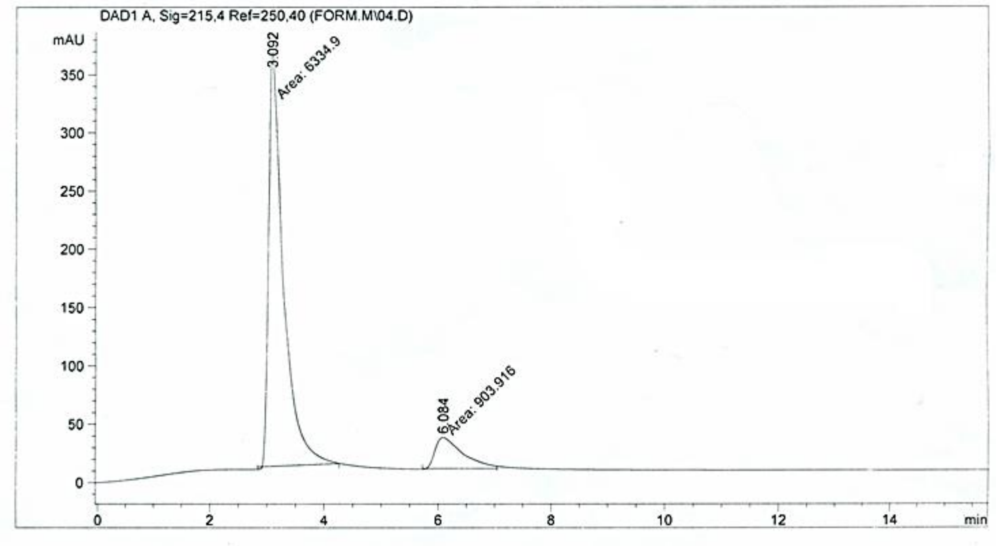


Figure 4.9 HPLC analysis of standard formic Acid

Retention Time 3.092 min

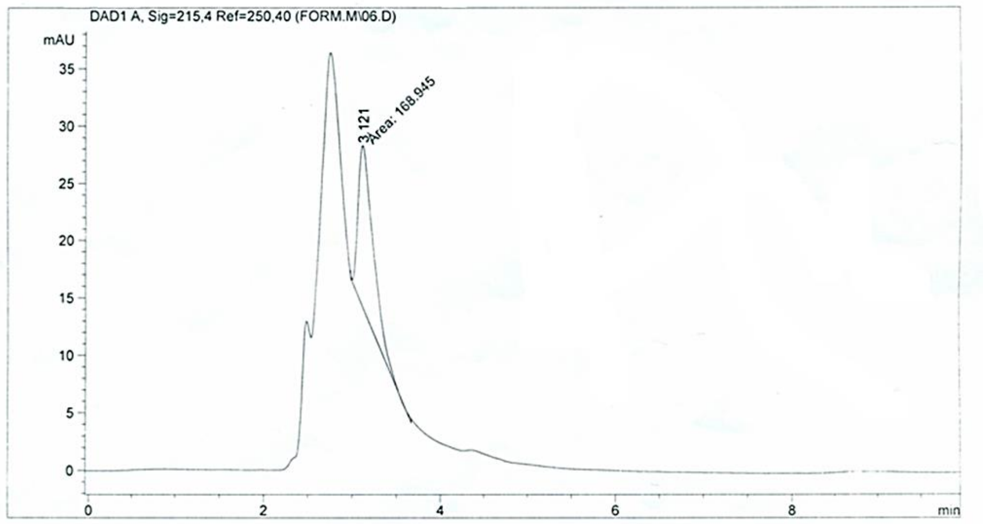


Figure 4.10 HPLC analysis of formic acid produced in the absence of nickel ferrite catalyst

Retention Time = 3.121 min

Formic acid with catalyst

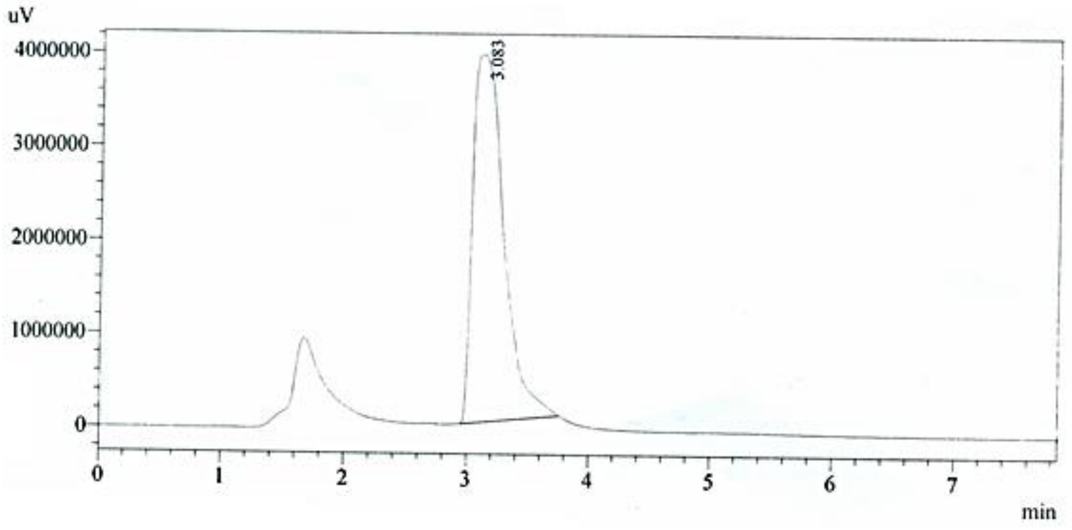


Figure 4.11 HPLC analysis of standard Formic Acid

Retention Time = 3.08 min

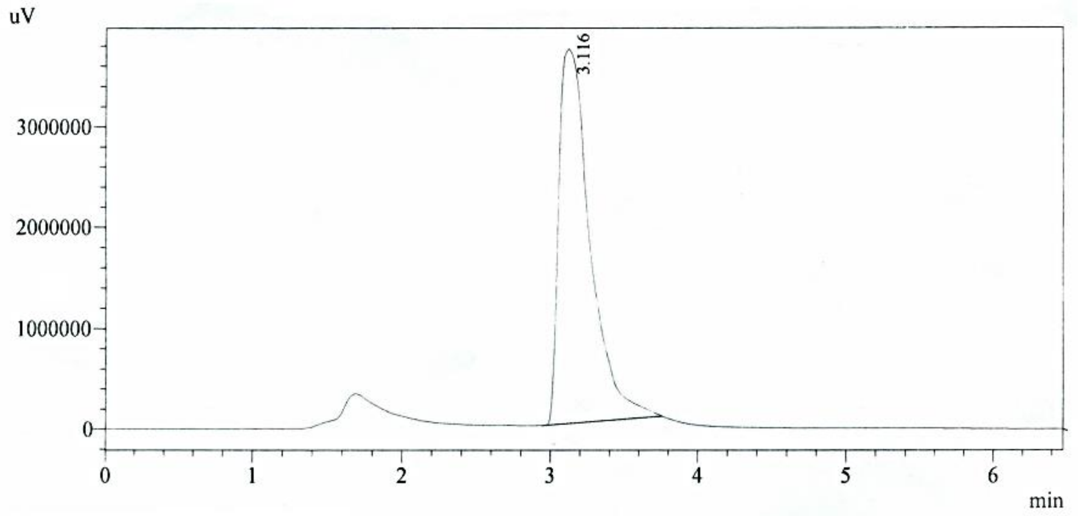


Figure 4.12 HPLC analysis of formic Acid produced in the presence of nickel ferrite catalyst

Retention Time = 3.11 min

The reaction by-product sodium sulfate was also formed by the reaction between sulfuric acid and sodium formate. XRD analysis of sodium sulfate formed during the reaction as a by-product is shown in figure 4.13 with major peaks at 19.0°,28.0°,29°, 32.0°,33.8°,48.7° and minor peaks at 23.1°, 38.5°,55.1°,54.5° Sharp peaks confirm the purity and crystal structure of sodium sulfate produced.

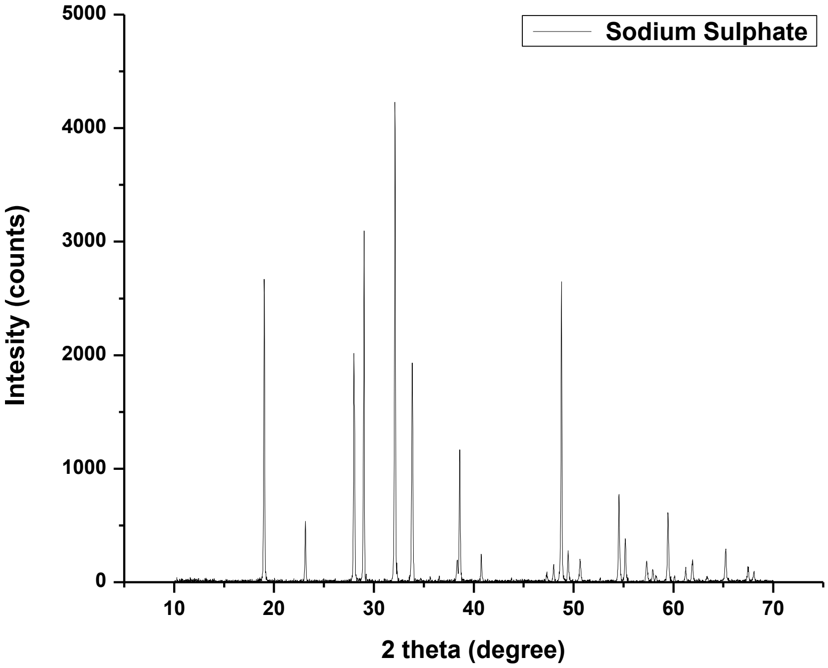


Figure 4.13 XRD of sodium sulfate

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

The following conclusions were drawn from the study

1. Absorption of CO_2 increases by increasing sodium hydroxide solution concentration. Absorption products formed are pH dependent,
    - I. At pH 10 sodium carbonate is formed.
    - II. At pH 8 sodium hydrogen carbonate is formed.
    - III. However, pH 9 gives trona.
2. Hydrogenation of sodium hydrogen carbonate provides sodium formate that is a precursor for formic acid synthesis. The hydrogen process is endothermic and the reported reaction temperature is up to 300° C. Addition of Nickel ferrite catalyst lowered the hydrogenation temperature up to 80° C. The synthesized formic acid percent reaction yield was (79±0.2) in the presence of nickel ferrite catalyst. However, it was less than 1% in its absence. Formic acid qualitative analysis by HPLC proved its presence in the reaction. Further, XRD analysis confirmed the reaction by-product sodium sulfate formation.

5.2 Recommendations

1. The absorption of carbon dioxide was performed using sodium hydroxide (NaOH) solution, it could also be done using other metal hydroxides like Calcium hydroxide, Magnesium hydroxides etc. and pH vs product relationship could be determined.

2. Temperature effect on absorption at different temperature could be studied.
3. The lab scale setup should be upgraded to pilot scale.
4. Absorption of a gas mixture of various industries could be studied.
5. Sodium formate preparation in the presence of other catalysts is also recommended.
6. This setup could be applied for biogas cleaning and also for removing CO_2 and H_2S to increase methane concentration and energy content of the gas.

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