ABSTRACT

The Use of COD as an Indicator for Evaluation of Pretreatment of Nitrocellulose with Acid Hydrolysis

by
Han-Chung Lee

Nitrocellulose is a toxic waste by definition. It is widely used in military and commercial industries. Nitrocellulose fines escaped from the manufacture's process has created problems in receiving water. However, little information is available for the treatment of nitrocellulose. Nitrocellulose is difficult to treat by microorganisms without any pretreatment. Therefore, the main objective of this study is to use acid hydrolysis to break down this material before biological treatment, and find the optimal operation conditions in this process.

In this work, the results indicate that percentage of nitrocellulose decomposing in hydrolysis depends on types of acid, acid concentration, reaction temperature, and reaction time. For single stage hydrolysis system, the maximum decomposition occurred when acid was 18 N and 36 N H_2SO_4 at any reaction temperature or 38 % HCl at high temperature. In two stage hydrolysis system, it was found that the second stage reaction had significant effect on the yield of glucose. However, the rate and amount of nitrocellulose dissolved was smaller than that of the first stage system.

THE USE OF COD AS AN INDICATOR FOR EVALUATION OF PRETREATMENT OF NITROCELLULOSE WITH ACID HYDROLYSIS

by
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THE USE OF COD AS AN INDICATOR FOR EVALUATION OF PRETREATMENT OF NITROCELLULOSE WITH ACID HYDROLYSIS

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This thesis is dedicated to my parents.

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CHAPTER 1

INTRODUCTION

Wastes are unavoidable products of most industrial processes. In many cases, industrial wastes contain toxic and/or poorly degradable compounds. Therefore, industrial wastes are often considered much more difficult to treat than municipal wastes.

Physical, chemical, and biological treatment methods are grouped together to provide what is known as primary, secondary, and advanced treatment. In primary treatment, physical operations, such as screening and sedimentation, are used to remove floating and settled solids found in wastewater. In secondary treatment, biological and chemical processes are used to remove organic matter. In advanced treatment, additional combinations of unit operations and processes are used to remove other constituents such as nitrogen and phosphorus, which are not removed by secondary treatment [1].

Biological treatment of waste is accomplished by microorganisms that use wastes as sources for carbon and energy. Microorganisms utilize the waste that can pass through their cell walls for energy and cell synthesis, so the degree of degradation may influence the efficiency of treatment [2]. For biological treatment of poorly degradable compounds, pretreating the waste to alter its compositions through hydrolysis process can transform the substrate to facilitate microbial utilization. Acid hydrolysis is a common operation in the wood industry practice. It can decompose complex compounds to simpler compounds, such as monosaccharides, polysaccharides, and small molecular organic acids. Hydrolysis rate is dependent upon type of acids (alkaline), acid concentration, reaction time, and reaction temperature.

Nitrocellulose is a typical example of waste that is produced by industrial processes. Nitrocellulose, an organic ester of cellulose mixed with camphor, was the first-made plastic. It was developed originally as an explosive during the last century, but eventually found use in the manufacture of photographic film, ink, lacquers, and some coatings industry. Nitrocellulose is a toxic waste by definition and it is widely used in many industrial processes. This industrial waste has created problems in recent years because of the fine particles and difficulties encountered in the conventional treatment methods.

Significant amount of data can be found in the literature for the treatment of cellulose by acid hydrolysis. However, little and incomplete information is available for acid hydrolysis of nitrocellulose. Nitrocellulose resists biodegradation, and its molecule structure is similar to cellulose. Their molecular structures are shown in Figures 1 & 2, [4,5]. Therefore, the degradable efficiencies of nitrocellulose by acid hydrolysis and factors affecting acid hydrolysis are often estimated on the basis of the treatment of cellulose in acid hydrolysis system [7]. However, this may not be correct in reality. Therefore, the main objective of this study is to use acid hydrolysis as a pretreatment technology before the biodegradation of nitrocellulose and to experimentally determine the efficiency of acid hydrolysis under various control environmental conditions by using the COD test as an indicator.

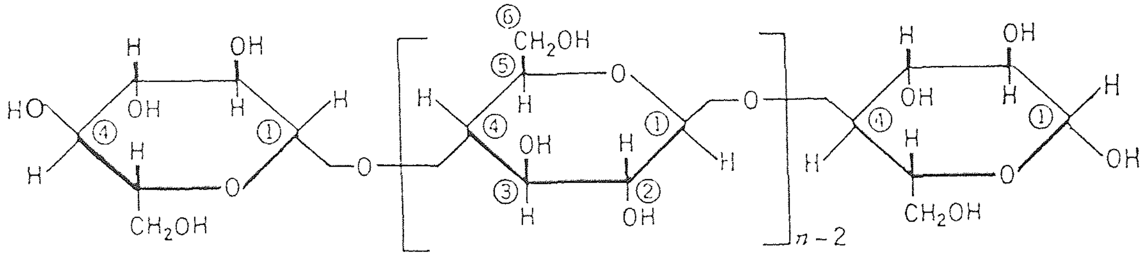

Figure 1 The Molecular Structure of Cellulose

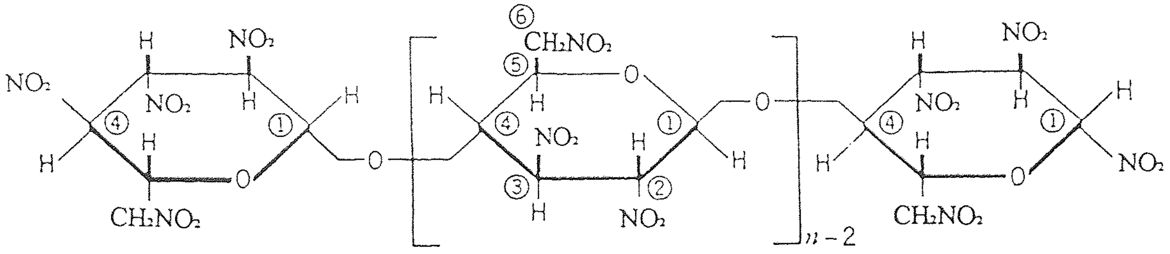

Figure 2 The Molecular Structure of Nitrocellulose

CHAPTER 2

LITERATURE SURVEY

The objective of biological waste treatment is to stabilize organic compounds in the wastes. Biological treatment processes are used to remove organic and nutrients from municipal, agricultural, and industrial wastes. Microorganisms utilize the waste for energy and cell synthesis [2]. Long chain macromolecule such as cellulose and nitrocellulose are converted to simpler compounds, by either hydrolysis or biochemical oxidation. Poorly degradable / undegradable waste can be converted to a usable form through some pretreatment processes, such as oxidation, acid hydrolysis, and alkaline digestion [3,9].

The waste studied in this research project was nitrocellulose. It was found that nitrocellulose is difficult to treat biologically and acid hydrolysis was used as a pretreatment technology for this compound. Since acid hydrolysis has been used for treating cellulose, a literature review on cellulosic material and acid hydrolysis of cellulosic material are provided in the following sections.

2.1 Cellulose and Nitrocellulose

It is not easy to give a chemical definition of the word "cellulose" which fits all the uses of the word. Cellulose is the chief constituent of plant cell units. It usually occurs in plants not in the pure form, but with what are called embedded substrates. Absorbent cotton, cotton textiles and linen, as well as high grades of filter paper consist, for the most part, of cellulose. Cellulose does not dissolve either in water, or in ether, or in alcohol, in ordinary conditions. It is quite stable to the Schweitizer's regent (a dilute solution of cupric hydroxide in concentrated ammonia), in a hydrochloric solution of zinc chloride, and in concentrated sulfuric acid [5].

In 1838 Payen suggested that cellulose is built solely from glucose units and is isomeric with starch [4]. Nageli (1858) used the word "mocelles" to name the crystalline particles which build the cellulose fiber and he described it as an strophic, submicroscopic crystal [5]. Nishikawa and Ono (1913) applied Van Laue's technique of X-ray diffraction to cellulose [5], which led to Freudenberg's (1930) proof that the cellulose is a beta linked polycondensate of glucose units [4,6]. The empirical formula is $C_6H_{10}O_5$ or $(C_6H_{12}O_6)_n$ - (n-1) H_2O. Its molecular structure is shown in Figure 1 .

The cellulose molecule, since it is bound together by acetal linkages, which possess excellent strength and good stability under certain conditions, will nevertheless undergo degradation by a variely of chemical and physical processes. Acetal linkages are extremely sensitive to acids. Acid hydrolysis, therefore, has been a distinct method in the development of theories concerning the structure of the cellulose mole as well as the fiber structure of the polymer.

Of the various inorganic esters of cellulose which could be made, the only one that has achieved large commercial production is nitrocellulose. Nitrocellulose is the oldest cellulose derivative. Braconnot in 1832 and Pelouze in 1838 had nitrated various materials including starch, wood fiber, cotton, and paper with concentrated nitric acid. However, in 1845, Schonbein nitrated cellulose with a mixture of nitric acid and sulfuric acid, and he is generally credited with the discovery of nitrocellulose. Nitrocellulose does not dissolve either in water, ether, or in alcohol. In ordinary conditions it can not react to the dilute acid and alkaline. The molecular structure of nitrocellulose as shown in Figure 2, are similar to cellulose, so in many cases, the reaction of cellulose can be applied to the nitrocellulose. But as nitrocellulose is not stable, it should be stored under ethanol in polystyrene bottle in the dark. The temperature should not exceed 60°C during drying [6].

A point of major importance in the chemistry of nitrocellulose is the fact that its usefulness in explosives or in ordinary article of commerce depends a great deal upon its stability, that is, upon its ability to resist decomposition after long period of time under various conditions. Thus, in guncotton, the decomposition of unstable nitrocellulose will cause explosion. In the first several years during the development of the manufacture of nitrocellulose, which were devoted almost exclusively to production of guncotton, a number of disastrous explosions occurred which were caused by the instability of the product. Nitrocellulose is a poorly degradable by microorganism and is a fine particle that is difficult to settle, so this military waste has drawn great attention in recent years. Not many technologies have been recommended for treating this waste. However, based upon the molecular structure, similar physical, and chemical characteristics between nitrocellulose and cellulose, pretreating method for cellulose can be applied to nitrocellulose. Acid hydrolysis is one such technology. In the decomposition of nitrocellulose at room temperature by dilute acid, some imformation have been obtained. According to Muraour (1931), there were no action at 15 °C to 20 °C on nitrocellulose even after 20 to 30 years. At 50 °C to 75 °C in a humid atmosphere, the deterioration of nitrocellulose is rapid [7].

2.2 Hydrolysis Theory

Hydrolysis is a common pretreatmental technology in the biological treatment. Several hydrolysis methods can be applied [10] :

(1) Dilute acid / alkaline hydrolysis at elevated temperature.
(2) Concentrated acid / alkaline hydrolysis at moderate temperature.
(3) Enzymatic hydrolysis.

In recent years there has been an interest in treating cellulose and recovering useful products from it as a way to relieve the pollution problems. Some attention has focused on the hydrolysis of cellulose to form glucose [8]. It has been known for over 150 years that cellulose can be converted to glucose by acid hydrolysis. However, it took almost 100 years before the first commercial plants began production in the Southern United States during World War I. In the USSR [10], the practice of acid hydrolysis in cellulose treatment has grown from a single plant in 1935 to tens of plants in operation today on wood and agricultural residues [11].

Cellulose, like starch, is hydrolyzed by acid solution to produce D-glucose:

$$(C_6H_{10}O_5) + H_2O \rightarrow C_6H_{12}O_6 \qquad (2.1)$$

The equation gives only the over-all result of hydrolysis. In reality, the hydrolysis of cellulose is a gradual process, which leads to the formation of simpler compound. Hydrolysis of cellulose leads to a decrease in chain length of the polymer, then to formation of oilgosaccharides and alternately to D-glucose.

Acid hydrolysis can be used as a pretreatment technology for cellulose waste, i.e., agricultural, wood, and paper industrial wastes. By virtue of their varying cellulose compounds all these wastes may be processed by acid hydrolysis with an end result of waste, useful material (glucose) and energy source (ethanol). The range of wastes that may be processed by acid hydrolysis are summarized in Table 1 [12].

Table 1 Types of Waste that May be Processed by Acid Hydrolysis

Waste	Types
Agricultural	cereal stalks, corn
Food	vegetables
Industrial	paper mill waste, guncotton
Wood	paper, board, timber
Municipal solid	textiles

There are many advantages of cellulosic material treated with acid hydrolysis, but one disadvantage is that, as a result of the nonspecificity of acid, the sugars formed will also be attacked and decomposed, if not removed from the acid [12]. The decomposition of glucose first produces 5-hydroxymethy-2-furfuraldehyde (HMF) and then to levulinic acid and formic acid. After a long reaction time, tars probably form from the polymerization of HMF [8]. The products of cellulose treated with acid hydrolysis are shown in Table 2 [12].

Table 2 The Products of Cellulose Treated by Acid Hydrolysis

Product	Formula	MW
Cellulose	$(C_6H_{10}O_5)_n$	$(162)_n$
Hexose	$C_6H_{12}O_6$	180
Pentose	$C_5H_{10}O_5$	150
Hydroxymethyl-Furfural	$C_6H_6O_3$	126
Levulinic Acid	$C_5H_8O_3$	116
Formic Acid	$HCOOH$	46
Furfural	$C_5H_4O_2$	96
Water	H_2O	18

Sulfuric acid and hydrochloric acid have been tested to study the effects of acid hydrolysis on cellulose. Being very strong acids, sulfuric acid and hydrochloric acid are widely used in the acid hydrolysis of cellulose to produce a variety of economically attractive degradation products, such as ethanol [9].

In the case of hydrolysis, there are several areas of uncertainty. Is the reaction random in process, or does it initiate at the ends of the chains and proceed by a systematic unzipping of the glucose units? A considerable amount of experiments have been performed on the kinetic of acid hydrolysis of pure cellulose substrates [8]. The reaction of acid hydrolysis of cellulose follows a series reaction proposed by Saeman [13], which is

$$\text{Crystalline cellulose} \rightarrow \text{Glucose} \rightarrow \text{Degradation products} \rightarrow \text{Tars}$$

The cellulose, since it is bound together by acetal linkages, is extremely sensitive to acid. Acid hydrolysis, therefore, has been studied extensively, and measurements of the rate of reaction have been a distinct method in the development of theories concerning the structure of cellulose molecule as well as the fiber structure of the polymer. Gibbons compared the rate of degradation of cellulose in sulfuric acid and hydrochloride acid, and find that the reaction appeared to follow first-order kinetics reasonably well in the range measured [4,6,15]. A homogenous first-order chemical reaction between reactant S and product P is normally represented by

$$S \xrightarrow{k} P \tag{2.2}$$

where k is the kinetic rate constant.

The rate or velocity of the first-order reaction is mathematically expressed as;

$$R = \frac{-d(S)}{d(t)} = \frac{d(P)}{d(t)} = k(P) \tag{2.3}$$

where the parenthesis indicates concentration and t time.

In order to estimate the value of k in this equation, concentration versus time data must be measured. One of the methods used to analyze experimental data is by integration of equation (2.3) from condition (P_0) at time zero to final condition (P) at time t :

$$\int_{P}^{P} \frac{d(P)}{P} = k \int_{0}^{t} dt \tag{2.4}$$

This yields :

$$\mathrm{P} = (\mathrm{P}_0) \times \exp(\mathrm{kt}) \tag{2.5}$$

data (P) versus t as shown in Figure 3 could now be used to find k by linearizing equation (2.5) into a form suitable for first-order analysis [20,26].

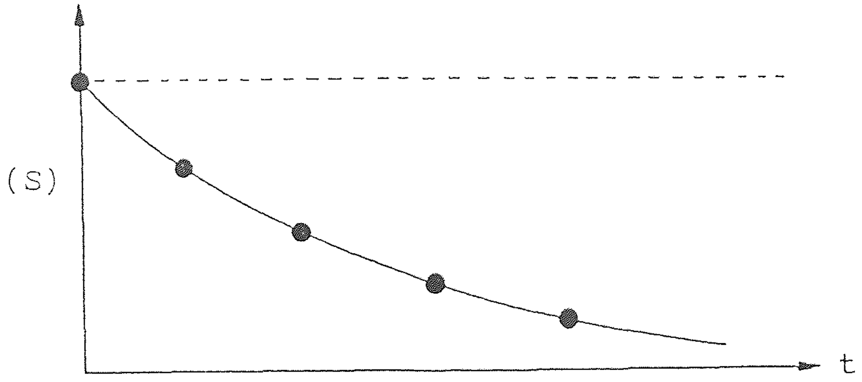

Figure 3 First-Order Kinetic Product Concentration versus Time Curve

Therefore from equation (2.5), the following equation is obtained:

$$\ln(P) = kt + \ln(P_0) \tag{2.6}$$

However, k would be different for each type of acid, its concentration, reaction time, and reaction temperature. Each hydrolysis condition would then be different. For cellulose and cellulose derivatives, there is a unique temperature at a fixed acid concentration and reaction time that gives optimal glucose yield.

2.3 Factors Affecting Acid Hydrolysis

The cellulose (nitrocellulose) is hydrolyzed to sugars through contact with acid solution, so the treatment of cellulose (nitrocellulose) by acid hydrolysis has the following several requirements [10] :

(1) Sufficient acid concentration to support the desired rate of hydrolysis.

(2) Adequate residence time at the desired reaction temperature or adequate reaction time at desired reaction time.

(3) Positive mixing and mechanical disruption of cellulose gels.

Therefore, the treatment of cellulosic material by acid hydrolysis is not only dependent upon the type of acid used and the concentration of acid, but also on the environmental condition of the hydrolysis process, including the shape, size of the substrates, the degree of mixing, reaction time, and reaction temperature.

2.3.1 Type of Acid

Acid hydrolysis is usually accomplished by treatment with mineral acid. At the University of Toronto a study has been conducted to establish the effectiveness of different acids on cellulose: sulfuric, sulfurous, nitric, hydrochloric and formic acid. The result was that a higher yield of total reducing sugars was achieved by using sulfurous, sulfuric, and hydrochloric acid. Other acids gave lower yields [12]. At Dartmouth College experiments with hydrochloric, phosphoric, sulfuric, and sulfurous acids showed glucose yield by hydrochloric and sulfurous acids was equal to that of sulfuric acid but that phosphoric acid gave low yields [12].

In the commercial processes, hydrochloric acid and sulfuric acid are used in acid hydrolysis of cellulosic material because of their lower cost, although other acids, such as formic, hydrofluoric, and sulfurous acid are also effective. Canertech has experimented with hydrogen fluoride which has been successful, but the removal of hydrofluoric acid leads to extensive sugar repolymerization. The treatment of cellulosic material by acid hydrolysis was based on either Scholler process or the Bergius process. The former used dilute sulfuric acid at 180 °C and the later, concentrated hydrochloric acid at ambient temperature [16]. Many experiments about hydrolysis with sulfuric acid and hydrochloric acid were performed in the past decades. Hydrochloride acid has been predominant since it is volatile and more readily recovered than sulfuric acid.

2.3.2 Acid Concentration

Acid hydrolysis of cellulosic material has evolved along two paths: concentrated acid hydrolysis at low temperatures and dilute acid hydrolysis at elevated temperatures. Both systems have been studied in the past :

Flechzing (1882) studied the effects of acid concentration on cellulosic material treatment by acid hydrolysis. The results indicated that cellulose can be degraded immediately in 41 % concentrated hydrochloric acid at room temperature, but it dissolves slowly in 38 % hydrochloric acid as the same temperature [7].

Saeman (1945) measured the glucose amount in dilute acid hydrolysis. The experiments were conducted using sulfuric acid concentrations of 0.5-2.0 %. His studies indicated that operating at a high temperature (175 °C) favors the hydrolysis reaction more than the degradation so that higher glucose can be obtained. But yield were still only approximately 50 % [11].

Wenzl (1970) found that concentrated sulfuric acid hydrolysis of cellulose is effective on any material without any other pretreatment. It can provide almost-quantitative yields of fermentable glucose, produce more highly concentrated solutions for fermentation, takes place within minutes, and afford a relatively reactive lignin residue with potential by-product value [10].

Goldstein (1983) conducted a research with 40.0 % concentrated hydrochloric acid in acid hydrolysis process. His studies pointed out that reaction kinetics have shown that over 90 % of cellulose is hydrolyzed in 10 minutes at 50 °C [11].

Porteous and Andersom (1987) reported a comparison of dilute and concentrated acids in acid hydrolysis system. The data indicate that for all types of acid hydrolysis reactors, an increase in acid concentration at a given temperature (within the limits) increases yields, although the maximum achievable yield is not altered very much by the increase. However, with higher acid concentrations the yield can be achieved at low temperatures [12].

2.3.3 Reaction Temperature and Time

Acid hydrolysis systems with various reaction temperature and time have been studied extensively, especially the reaction between temperature, time and sugar production in acid hydrolysis systems. Many investigators (Smuk, Dartmouth, Chen) have experimentally determined the temperature characteristics and efficiency of acid hydrolysis system. All the results so obtained indicated that higher temperature and longer reaction time provided high yield of sugar in the hydrolysis processes [17].

Dartmouth (1971) proposed a hydrolysis process for cellulose treatment with two stage hydrolysis system. Based on qualitative understanding of the kinetic model, that in order to maximize the glucose yield in cellulose, a two-stage hydrolysis would be desirable. That is, a low-temperature hydrolysis between 100 and 150 °C, which does not cause crystalline cellulose to hydrolyze but does remove the hemicellulose as soluble sugars followed by a high-temperature hydrolysis to convert the remaining cellulose [8].

Chen and Papadupoulos (1983) investigated the effect of temperature on sugar production. Their report also pointed out that higher temperature provided higher yield of sugar in the hydrolysis processes [22]. The results of test are shown in Table 3.

Table 3 Results of Acid Hydrolysis in Different Reaction Temperatures [22]

Acid concentration	Reaction time	Temperature	Glucose yield (%)
20 % HCl	120 mins	30 °C	65 %
		40 °C	80 %
		50 °C	95 %
30 % HCl	60 mins	30 °C	70 %
		40 °C	95 %
		50 °C	100%

In acid hydrolysis system, yield is a function of residence time, with increased glucose yield at longer residence times up to an optimum, after which yield rapidly decreases [12]. However, this could also result from the reaction temperature effects. Bergius (1970) reported that the efficiency of hydrolysis for the same reaction temperature is a function of the reaction time in acid hydrolysis processes and the results is shown in Table 4 [19].

Table 4 Effect of Reaction Time on Hydrolysis

Acid concentration	Reaction temperature	Time	Glucose yield (%)
30 % HCl	30 °C	20 mins	40 %
		40 mins	60 %
		120 mins	80 %

CHAPTER 3

EXPERIMENTAL APPARATUS AND METHOD

A schematic diagram of the basic experimental set-up is shown in Figure 4. The work was carried out in a covered, flat bottomed, cylindrical Plexiglas vessel whose volume is 1000 mL. (PYREX Resin Reaction Kettles : VWR). The vessel is equipped with a condenser and temperature meter. Temperature and mixing is controlled by a hot plate with stirring device.

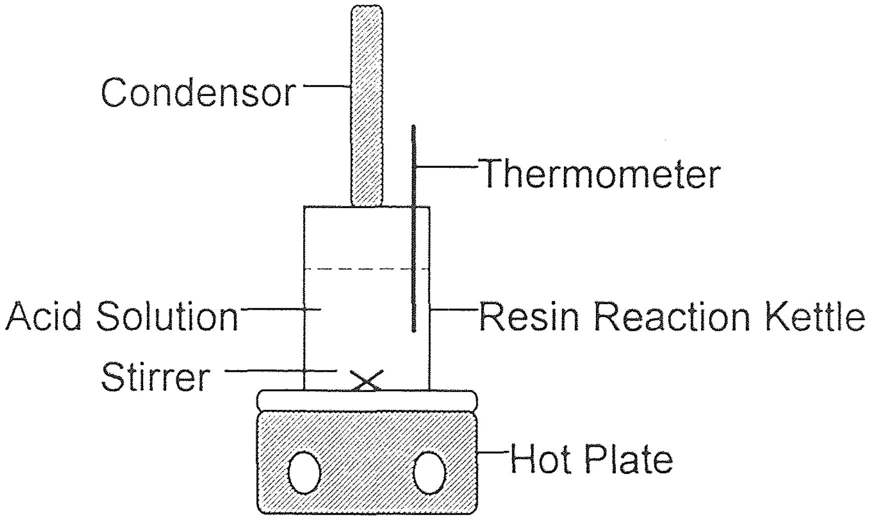

Figure 4 Schematic Diagram of Acid Hydrolysis Experiment.

Two types of controller were used in the hot plate: temperature tuner and mixing speed tuner. Temperature and mixing speed will affect the rate of hydrolysis, so a calibration of the controller of temperature and mixing speed was conducted before experiment. All experiments were performed at constant mixing speed. Temperatures were varied in each experiment and the control was based on the above calibration results.

Nitrocellulose used in this research project was obtained from US. Army Construction Engineering Research Laboratory at Champaign Illinois. Before the test, nitrocellulose was dried by vacuum oven at 60°C until it is completely dried. Since nitrocellulose is not stable, the temperature should not exceed 60°C during drying [6]. Hydrochloric acid with a concentration of 19-38%, and sulfuric acid with a concentration of 10 N, 18 N, and 36N were used in the study and the nitrocellulose concentration was maintained at 60,000 mg/L.

Experiments were carried out in completely mixed batch reactors for a designed reaction time. Degradation yields were measured in terms of COD and amount of glucose. Sampling was performed every 15 minutes in the first stage hydrolysis processes and every hour in the posthydrolysis processes. 10.0 mL of sample was withdrawn from the reactor with a pipet. COD measurement was conducted according to the Standard Methods [23]. Glucose was measured by the Colorimetric method.

Chloride reacts easily with Ag_2SO_4 (Sulfuric acid reagent) to produce precipitates that will interfere with the accuracy of COD test [20]. COD test can not be used when the sample contains more than 2,000 mg Cl/L, so after 10.0 mL of sample was withdrawn from the reactor, the sample was diluted by 500 times pure water for COD test.

The COD was determined by the Closed Reflux, Titrimetric Method. The Chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic material of a sample that is susceptible to oxidation by a strong chemical oxidant. A sample was refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ was titrated with ferrous ammonium sulfate (FAS) to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic material is calculated in terms of oxygen equivalent.

The procedure adopted to quantify the chemical oxygen demand (COD) content of the hydrolysis solution is outlined below:

1. Pipet a 5.0 mL of diluted sample into a test tube.
2. Add 7.0 mL of sulfuric acid regent and 3.0 mL of potassium dichromate.
3. Place tubes in Hack digester to 150 °C and reflux for 2.0 hours.

4. Allow the sample to cool to room temperature.
5. Add 0.05 to 0.10 mL (1 to 2 drops) ferroin indicator.
6. Stir rapidly with magnetic stirrer while titrating with 0.1 M FAS.
7. The end point is a sharp color change from blue-green to reddish brown.
8. Calculation

$$\text{COD as mg } O_2/L = [(A-B) \times 0.1 \times 8000 \times 500] / 5 \qquad (3.1)$$

where :

A : mL FAS used for blank.

B : mL FAS used for sample.

In the determination of glucose with the colorimetric method, samples were withdrawn from the reactor with a pipet. pH of sample was adjusted to 8.0 with Calcium hydroxide and measured with a standard pH meter. The concentration of glucose was then measured with a glucose strip and a glucose meter.

CHAPTER 4

EXPERIMENTAL PROCEDURE

Hydrolysis experiments were carried out in 1.0 L batch reactors (PYREX Resin Reaction Kettles : VWR). The reactors used were standard 1.0 L cylindrical plexglass beakers covered with heavy duty aluminum foil and connected with condenser to prevent evaporation losses. The reactors were filled with 6.0 gram nitrocellulose and 100.0 mL acid (60,000 ppm) in every experiment. The type and concentration of acid, hydrolysis reaction time, and reaction temperature tested were varied to determine their effects on hydrolysis.

A schematic diagram of the basic experiment set-up is shown as following :

1. Single stage hydrolysis :

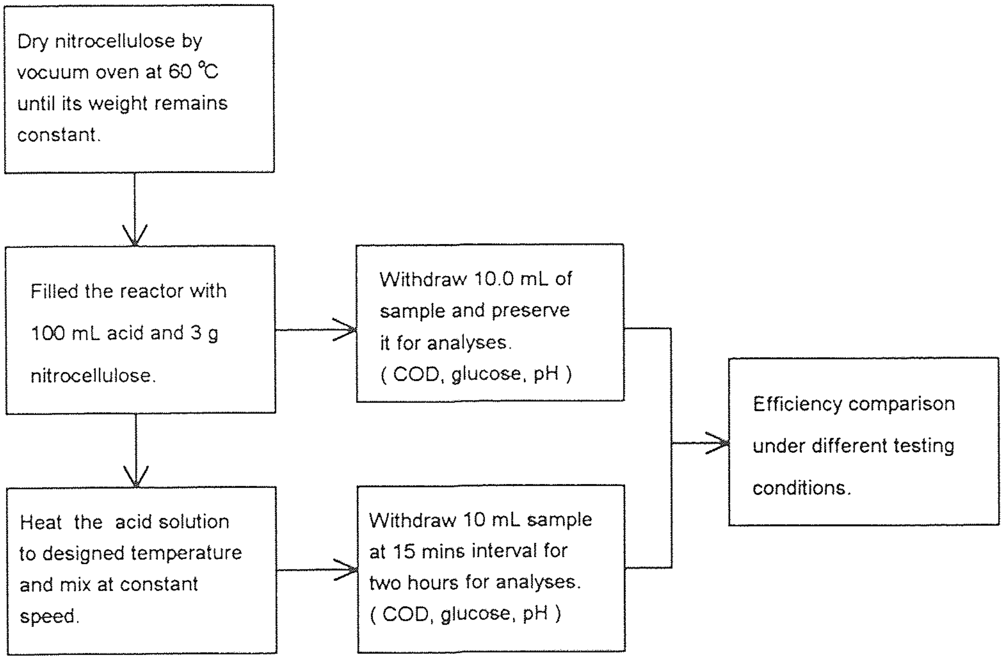

Figure 10 Single Stage Acid Hydrolysis for Nitrocellulose

2. Two stage hydrolysis :

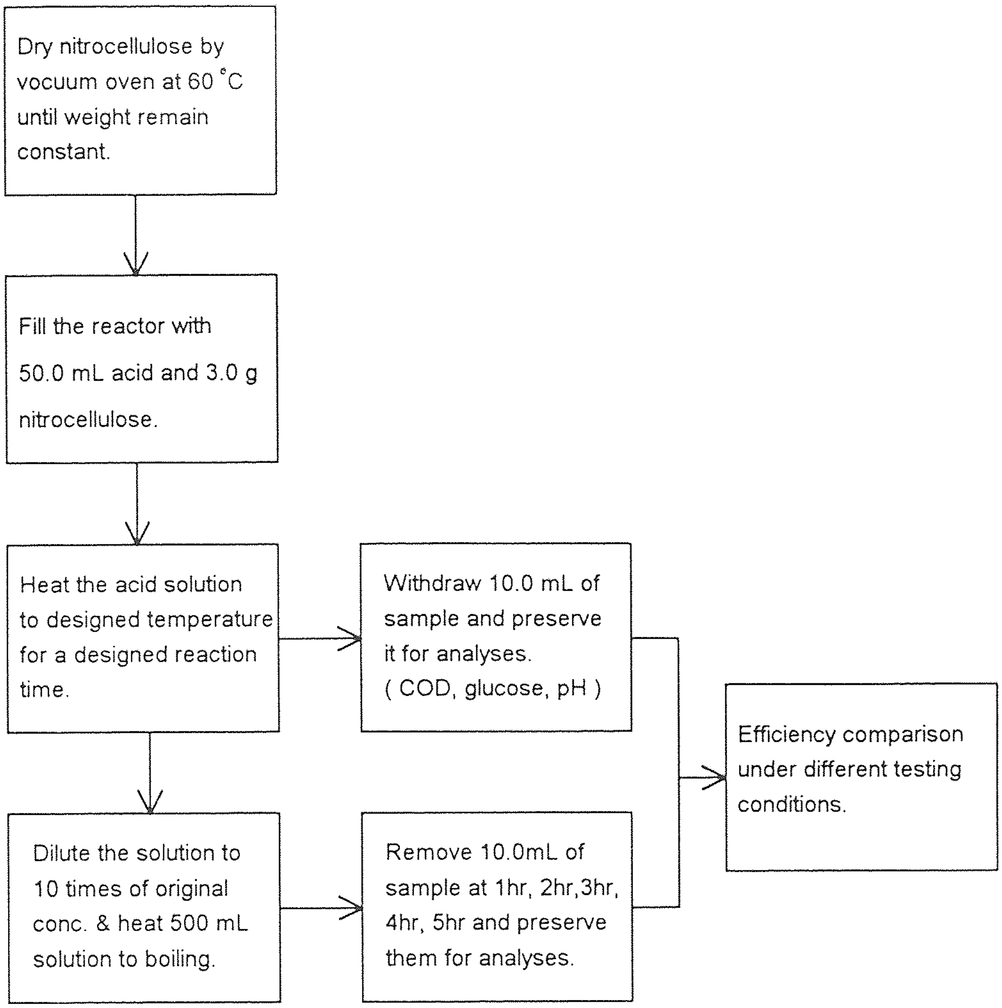

Figure 11 Two Stage Acid Hydrolysis for Nitrocellulose

In single stage hydrolysis, the nitrocellulose was dried by vacuum oven at 60°C before experiment, and then acid was added to a concentration of 60,000 ppm. Solution was then heated to a specified temperature and mixed. The type of acid, acid concentration, and reaction temperature used are shown in Table 5. Samples were taken from the reactors every 15 minutes for 2 hours. Samples were refrigerated at 4 °C before COD test and pH was adjusted to 8.0 for glucose test. The parameters tested are shown in Table 6.

Table 5 Type and Concentration of Reaction Acid Used in Single Stage Hydrolysis

Acid	Concentration	Reaction Temperature
HCl	38%	40°C, 70°C,100°C
	19%	40°C, 70°C,100°C
H_2SO_4	36N	40°C, 70°C,100°C
	18N	40°C, 70°C,100°C
	10N	40°C, 70°C,100°C

Table 6 Testing Parameters in Single Stage Hydrolysis

Measurement	Replicates	Sampling interval
COD (soluble)	3	every 15 mins for 2 hours
glucose	1	
pH	1	

In two stage hydrolysis, 3.0 grams of dried nitrocellulose was added in 50.0 mL acid and heated at a specified temperature for the designed reaction time. After the above procedure, 450.0 mL of pure water was added to reactors, and this solution was heated to the boiling point. The acid concentrations and reaction temperatures studied are shown in Table 7. Samples were taken from the reactors every hour for 5 hours. Samples were treated the same way for COD test and glucose test. The testing parameters are shown in Table 8.

Table 7 Type and Concentration of Reaction Acid Tested in Two Stage Hydrolysis

Acid	Concentration	Reaction Temperature
HCl	38% → 3.8%	(1) 40°C → 100°C (2) 70°C → 100°C (3) 100°C → 100°C
	19% → 1.9%	
H_2SO_4	36N → 3.6N	
	18N → 1.8N	
	10N → 1.0N	

Table 8 Testing Parameters in Two Stage Hydrolysis

Measurement	Replicates	Sampling interval
COD (soluble)	3	(1) 30 mins → 1hr,2hr,3hr,4hr,5hr (2) 45 mins → 1hr,2hr,3hr,4hr,5hr (3) 60 mins → 1hr,2hr,3hr,4hr,5hr
glucose	1	
pH	1	

The effectiveness of different acid hydrolysis conditions were compared by the dissolved efficiency ($S = COD_t /$ total COD) and amount of glucose produced.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Results for Single Stage Hydrolysis System

The purpose of this experiment was to determine the effect of acid concentration (C), reaction temperature (T), and reaction time (t) in single stage acid hydrolysis. In this experiment, two acids, i.e., hydrochloric acid and sulfuric acid, were used under the designed hydrolysis conditions. In single stage hydrolysis process, nitrocellulose (NC) concentration was kept constant, which was 60,000 mg/L.

In this test, the relationship between soluble COD (filtration) and total COD (without filtration) are shown in Figures 5 to 9. The results obtained for both experiments indicate that the difference between soluble COD and total COD is small, especially when the acid concentration was high. For 38 % HCl, 18 N H_2SO_4, and 36 N H_2SO_4, the values of soluble COD were almost the same as total COD during the whole hydrolysis processes. There were some differences between soluble COD and total COD when acid were 19 % HCl and 10 N H_2SO_4. However, the maximum difference was only 7.52 % for 10 N H_2SO_4 at 30 minutes reaction time. Therefore, the investigation of nitrocellulose hydrolysis in this study is expressed in terms of total COD for the evaluation of treatment efficiency.

5.1.1 Effect of Hydrochloric Acid Hydrolysis in Single Stage System

In this part of study, two types of hydrochloric acid concentration, i.e., 19 % and 38 % were used. The hydrolysis efficiency in the reactor is reported as percentage of NC decomposed (S), S is a ratio of COD_t/ COD_u where COD_t is COD at time t and COD_u is the ultimate COD for nitrocellulose, which has been predetermined to be 53,200 mg/L.

5.1.1.1 Effect of Hydrochloric Acid Concentration

The hydrolysis was conducted at a given temperature with concentrations range from 35 % to 38 % for reactor #1 and 17.5 % to 19 % for reactor #2. Tests were conducted at three temperatures, 40 °C, 70 °C, 100 °C, for each hydrochloric acid concentration. The results are shown in Figures 12 to 14 and the data for testing conditions are shown in Table 9.

For the case of low temperature (T = 40 °C) as shown in Figure 12, it was observed that the nitrocellulose dissolved slowly in low hydrochloric acid concentration. At 19 % HCl concentration, only 6.77 % of NC was dissolved for 60 minutes reaction time. However, when HCl concentration was increased from 19 % to 38 %, a moderate increase in efficiency was observed (from 6.77 to 40.75 %). The maximum amount of NC dissociated was 51.0 % when reaction time was 2 hours. This indicates that concentrated hydrochloric acid has better effect to break down large molecules. However, the hydrolysis efficiency is still not good enough either in 19 % or 38 % concentration at lower temperature.

For the case of moderate temperature (70 °C), various hydrochloric acid concentrations were tested. The results are plotted in Figure 13. The percentage of NC dissolved increased with higher acid concentration, i.e., from 19 % to 38 %. The amount of NC dissociated was also more at higher temperature. At 19 % HCl concentration, the percentage of conversion was increased slowly with increasing reaction time. When the reaction time was 60 minutes, the amount of NC dissolved was 15.85 %, and the value was only 32.00 % for two hours reaction time. However, when HCl concentration was increased from 19 % to 38 %, a large increase in the percentage of NC dissolved was observed (S from 32.00 % to 99.63 %) when reaction time was 2 hours. The change of the percentage NC dissolved shows that the hydrolysis was affected more at moderate temperature. That is, the efficiency for 38 % HCl was high at 70 °C, but the efficiency was not changed much for 19 % HCl at that temperature.

For the case of advanced temperature (100 °C) as shown in Figure 14, the influence of reaction temperature for 38 % HCl hydrolysis was not much different, because the amount of NC dissociated was still near 100 % (98.87 %). However, the percentage of NC dissociated for 19 % HCl, increased rapidly with increasing reaction time and reaction temperature. At 19 % HCl concentration, during the first 60 minutes, S increased sharply, from 0 % to 71.69 %, and then leveled off during the second 60 minutes.

Table 9 Effect of HCl Concentration on Single Stage System

Temperature	Percentage of NC Dissolved (S %)			
	38 % HCl		19 % HCl	
	t = 60 min.	t = 120 min.	t = 60 min.	t = 120 min.
40 °C	40.75	50.57	6.77	15.04
70 °C	82.71	99.63	15.85	32.00
100 °C	87.55	98.87	71.69	77.73

The results obtained for both reactors indicate that the effect of hydrochloric acid concentration on single stage hydrolysis was found to be significant, especially when the temperature was not very high. In this experiment, the data also indicates that the hydrolysis rate can be increased by higher acid concentration at a given temperature. Porteous and Anderson (1987) reported a comparison study of dilute and concentrated HCl in cellulose hydrolysis. Their data indicated that in all tests, an increase in HCl concentration at designed temperature increases decomposition. On the other hand, the yield can be achieved at lower temperature [12]. This conclusion is very similar to what observed in this study related to nitrocellulose.

5.1.1.2 Effect of Reaction Temperature

Effects of reaction temperature on single stage hydrolysis are shown in Figures 15 & 16. These results indicate that the efficiency of hydrolysis is strongly affected by the reaction temperature, and that effect is much more pronounced at lower acid concentration. Decomposition as a function of reaction temperature, for the case of 19 % HCl, at designed temperature, is shown in Figure 15. It can be seen from this figure that the amount of conversion is increased with reaction time, but at T = 40 °C, S increases very slowly for two hours reaction time (from 0 to 15.04 %). A moderate increase in S was observed when the reaction temperature increased to 70 °C, but the conversion was still low (S = 32.00 %). There was a appreciable change in decomposition when reactor was heated to 100 °C. The results show that the conversion raised from 0 to 71.69 % in the first hours. It can also seen from the slope of the curves that a slower rate of the conversion was observed at 40 °C and 70 °C, while fast rate was obtained at a temperature of 100 °C.

For the case of 38 % HCl as shown in Figure 16, a slowly increased rate at 40 °C, and a moderately increased rate occurred at reaction temperatures 70 °C and 100 °C. It is obvious that the reaction rate is also a function of the temperature. In this experiment, the results of test indicate that the effect of temperature was more evident when reactor was heated from 40 °C to 70 °C. At T = 40 °C, S increases slowly with increasing reaction time. Whereas the percentage of nitrocellulose dissolved increased sharply with time when the reactor was heated to 70 °C. At 70 °C , S reached to a maximum conversion (near 100 %) for two hours reaction time. However, this effect of temperature was not appreciable when temperature was increased from 70 °C to 100 °C.

Table 10 Effect of Reaction Temperature in Single Stage HCl Hydrolysis System (t = 120 minutes)

Concentration (HCl , %)	Percentage of NC Dissolved (S %)		
	40 °C	70 °C	100 °C
19 %	15.04	32.00	77.73
38 %	50.57	99.63	98.87

Effect of reaction temperature in HCl hydrolysis system obtained here are very close to other findings. From the literature available on cellulose hydrolysis process, it was reported that higher temperature provided higher efficiency of decomposition. To make the hydrolysis operate at higher efficiency in a single stage system at lower temperature, at least, a long reaction time is required (Smuk, 1960) [8]. However, the percentage of nitrocellulose dissolved also depends upon HCl concentration. On the other hand, even if reaction temperature was not very high (70 °C), maximum NC conversion (100 %) could still be achieved for 38 % HCl hydrolysis.

5.1.1.3 Effect of Reaction Time

In this experiment, the effect of reaction time on single stage hydrolysis system is shown in Figures 12 to 16 and Table 11. The efficiency of conversion increased with reaction time, but it is also a function of acid concentration and reaction temperature. At high HCl concentration (38 %) and/or at high reaction temperature (100 °C), by looking at Figures 15 & 16, the degree of conversion increases rapidly with reaction time levelling off, and then increasing slightly. The leveled off value depends on reaction time, concentration of hydrochloric acid, and reaction temperature.

For the case of 38 % HCl at 100 °C as shown in Figure 14, S increases fast during the first half hour of hydrolysis and then increases gradually. For the case of 19 % HCl at

100 °C, it shows a similar curve, that is S increases sharply during the first 60 minutes (from 0 % to 71.69 %), and then increases slightly to 77.73 %.

Table 11 Effect of Reaction Time in Single Stage HCl Hydrolysis System

Reaction Time (minutes)	Percentage of NC Dissolved (S %)					
	38 % HCl			19 % HCl		
	40 °C	70 °C	100 °C	40 °C	70 °C	100 °C
30	28.68	63.40	71.70	2.26	6.77	43.02
60	40.75	82.71	87.55	6.77	15.85	71.69
90	46.79	87.22	98.87	14.28	20.38	74.72
120	50.57	99.63	98.87	21.80	44.53	77.73

In comparison, the hydrolysis rate of cellulose by hydrochloric acid declines over reaction time and researchers ascribed it to the reaction reaching equilibrium (Bergius, 1970) [10]. This pattern was also found in this experiment, but it was not apparent in some cases, i.e., 19 % HCl hydrolysis at 40 °C and 70 °C (as shown in Figure 15). The reason could be that the amount of hydrogen ions generated in HCl hydrolysis were not enough to break down large molecules in a short time, and it was necessary to increase reaction time to complete the reaction. .

5.1.2 Effect of Sulfuric Acid on Single Stage System Hydrolysis

In the study, NC was treated with sulfuric acid and three types of sulfuric acid concentration, i.e., 36 N, 18 N, and 10 N were tested on single stage hydrolysis system. The hydrolysis efficiency in each reactor is also reported as a ratio of COD_t / COD_u. Three temperatures, i.e., 40 °C, 70 °C, and 100 °C, were studied and samples were taken every fifteen minutes during the test.

5.1.2.1 Effect of Sulfuric Acid Concentration

The effects of sulfuric acid concentration on NC hydrolysis for each fixed temperature are shown in Figures 17 to 19, and the data for NC decomposition are shown in Table 12.

For T = 40 °C, the decomposition of NC as a function of sulfuric acid concentration is shown in Figure 17. A lower percentage of NC dissolved was observed at 10 N sulfuric acid where S was only 25.66 % during the first ninety minutes reaction time. However, the efficiency of hydrolysis was more pronounced at 18 N and 36 N H_2SO_4. In both cases, a maximum conversion of NC (100 %) was observed in less than 30 minutes reaction time.

For the case of moderate temperature (70 °C) as shown in Figure 18, in 10 N H_2SO_4 hydrolysis, the conversion rate increased smoothly with the reaction time. The maximum amount dissociated was only 51.50 % at two hours reaction time. These results indicate that 10 N H_2SO_4 was not an ideal concentration in NC hydrolysis. Whereas for higher H_2SO_4 concentration (18 N and 36 N), a steep increase in NC dissolved percentage was observed.

For the case of advanced temperature (100 °C), the amount of NC dissociated at various sulfuric acid concentrations were tested. The results are illustrated in Figure 19. In general, conversion rate for 10 N H_2SO_4 increases slowly with reaction time, but in the advanced temperature, it increases fast in less than 30 minutes, and then increases moderately to 97.14 % for two hours reaction time. For higher concentration (18 N and 36 N), the conversion was completed in 15 minutes.

Table 12 Effect of H_2SO_4 Concentration in Single Stage System

Temperature	Percentage of NC Dissolved (S %)					
	36 N		18 N		10 N	
	t = 60	t = 120	t = 60	t = 120	t = 60	t = 120
40 °C	99.85	99.85	98.57	99.47	17.51	39.92
70 °C	99.85	99.25	99.40	99.85	43.61	51.50
100 °C	99.55	98.35	99.85	99.55	75.34	97.14

The results observed for these experiments indicate that the effect of sulfuric acid concentration on single stage hydrolysis was found to be significant. Wenzl (1970) studied the effect of concentrated sulfuric acid on hydrolysis of cellulose is effective at room temperature without any other pretreatment [10]. This conclusion is still true here where hydrolysis material was changed to nitrocellulose. Therefore, a conclusion can be made that if the H_2SO_4 concentration is strong enough ($C \geq 18$ N), then high conversion of NC can be achieved at low temperature and/or shorter reaction time. However, the amount of NC can be dissolved in 10 N H_2SO_4 hydrolysis would depend on the reaction temperature. In higher reaction temperature, it was noted that the hydrolysis rate of H_2SO_4 was high.

5.1.2.2 Effect of Reaction Temperature

Effects of reaction temperature on single stage hydrolysis with different sulfuric acid concentration are shown in Figures 20 to 22 and Table 13. These results indicate that the percentage of nitrocellulose dissolved in sulfuric acid was strongly affected by the reaction temperature when sulfuric acid concentration was less than 10 N.

At lower sulfuric acid concentration ($C = 10$ N), effect of reaction temperature is shown in Figure 20. It can be seen from this figure that nitrocellulose was dissolved slowly at 40 °C. The percentage of NC dissolved was only 20.23 % for 75 minutes reaction time, but it increased moderately when reaction time was 90 minutes or longer. Same pattern was found at 70 °C. However, the conversion rate was more smooth and its value was higher. Although the amount of NC dissolved increased at higher temperature, the maximum conversion was less than 55.0 %, at either 40 °C or 70 °C. Whereas at 100 °C, the maximum percentage of NC dissolved was closed to 100 %.

The effects of higher sulfuric acid concentration (18 N and 36 N) on single stage hydrolysis are shown in Figures 21 & 22. Larger decomposition was observed for higher reaction temperature and longer reaction time. In 18 N and 36 N H_2SO_4 hydrolysis, the maximum NC conversion was achieved in a short reaction time ($t \leq 15$ minutes) at all temperatures. In this case, a large conversion in short time implies that a higher hydrolysis rate occurred. It should be noted from Table 13 that a hydrolysis system is affected more by higher H_2SO_4 concentration than by reaction time or reaction temperature.

Table 13 Effect of Reaction Temperature in Single Stage Hydrolysis System with Sulfuric Acid (t = 120 minutes)

Concentration (H_2SO_4)	Percentage of NC Dissolved (S %)		
	40 °C	70 °C	100 °C
10 N	50.72	51.50	97.14
18 N	99.47	99.85	99.55
36 N	99.85	99.25	98.35

From the literature in cellulose hydrolysis, higher efficiency of solubilization was achieved at higher reaction temperature [12]. The effect of reaction temperature in NC hydrolysis for 10 N H_2SO_4 are very close to the above statement. However, in this experiment, reaction temperature has shown to have no significant effect in H_2SO_4 hydrolysis once higher concentration was used ($C \geq 18$ N).

5.1.2.3 Effect of Reaction Time

In this experiment, the effect of reaction time at given reaction temperature and acid concentration is shown in Table 14. These results indicate that the reaction time in hydrolysis system depends upon H_2SO_4 concentration and reaction temperature.

For the case of 10 N H_2SO_4 hydrolysis at 70 °C as shown in Figure 20, S increases fast during the first hour, and then shows down gradually. For the case of 10 N H_2SO_4 at 100 °C, it shows a similar curve with higher conversion (from 0 to 75.34 %) in the first hour, and then increases gradually to 97.14 %.

For the cases of 18 N and 36 N H_2SO_4, the results are shown in Figures 21 & 22. In these figures, it was observed that rapid solubilization occurred during the first 15 minutes and followed by a relatively slower rate of NC conversion during the next quarter hour period, then followed by an even slower rate.

Table 14 Effect of Reaction Time in Single Stage Hydrolysis System with H_2SO_4

Time (mins)	Percentage of NC Dissolved (S %)								
	36 N H_2SO_4			18 N H_2SO_4			10 N H_2SO_4		
	40 °C	70 °C	100°C	40 °C	70 °C	100°C	40 °C	70 °C	100°C
15	98.87	99.70	99.85	94.04	97.74	99.25	3.93	20.00	36.99
30	99.02	99.85	99.85	94.79	98.50	99.40	13.13	29.02	63.46
60	99.85	99.85	99.55	98.57	99.40	98.85	17.51	43.61	75.34
90	99.72	99.39	98.49	99.02	99.70	99.69	25.66	47.96	90.98
120	99.85	99.25	98.35	99.47	99.85	99.55	39.92	51.50	97.14

In comparison, the percentage of cellulose dissolved is increased with reaction time during the initial reaction period. As the reaction proceeds, the hydrolysis rate decreases and then reaches equilibrium (Bergius, 1970) [10]. This phenomenon was also found in nitrocellulose hydrolysis. For the case of 18 N and 36 N H_2SO_4 hydrolysis, the reaction consists of rapid solubilization of nitrocellulose during the first 15 minutes, and then is followed by a relatively slower rate of soubilization during the next 105 minutes period. However, this pattern was not apparent in 10 N H_2SO_4 hydrolysis at 40 °C. The reason could be that two hours reaction time was still not enough to hydrolyze nitrocellulose at low H_2SO_4 concentration.

5.1.3 Effect of Different Types of Acid on Single Stage Hydrolysis System

In this study, two acids, i.e., hydrochloric acid and sulfuric acid, were tested under designed hydrolysis conditions. The effect of acid were complicated, as shown in Figures 23 to 25. A significant difference of hydrolysis efficiency was found at different types of acid and different concentrations. The results also indicate that different types of acid and different concentrations would give different hydrolysis rate.

Several investigators have examined hydrolysis rate data on the basis of theoretical consideration given by Kuhn (1930) [6], and found that the acid hydrolysis of cellulostic material appeared to follow first-order kinetics reasonably well in the range measured. A homogenous first-order chemical reaction between reactant and product is normally represented by Equation 2.3. Apparent first-order rate constants for the solubilization of nitrocellulose were calculated using equation 5.1, which describes a first-order hydrolysis rate for a batch reaction as

$$d(\,COD_p\,) \,/\, dt = -\,K_h\,COD_p \qquad (\,5.1\,)$$

where

K_h = first-order hydrolysis rate constant (1/t)

COD_p = concentration of degradable particulate COD (mg/L)

t = time (t)

Integrating equation 5.1, the relationship can be written as

$$\ln\,(COD_t\,/COD) = -\,K_h\,t \qquad (\,5.2\,)$$

The value of K_h is given by the slope of the line drawn, plotting ln (COD_i/COD) to t. All rate constants for different types of acid and different concentrations of acid for various reaction temperatures were determined assuming a first-order batch reaction. The hydrolysis rate constants are shown in Table 15.

Table 15 Hydrolysis Rate Constant at Different Hydrolysis Condition

Acid Concentration	Hydrolysis Rate Constant (1/100 min.)		
	40 °C	70 °C	100 °C
19 % HCl	2.61	2.87	3.28
38 % HCl	2.97	3.34	3.36
10 N H_2SO_4	2.87	2.99	3.35
18 N H_2SO_4	9.75	9.77	9.78
36 N H_2SO_4	9.78	9.79	9.79

Figure 23 shows the effect of different acid at 40 °C in single stage hydrolysis system. It is apparent from this figure that 18 N and 36 N H_2SO_4 gave maximum NC conversion value (100 %) in a very short reaction time ($t \leq 15$ minutes). For 38 % HCl, S was larger than 10 N H_2SO_4 and 19 % HCl. However, the maximum decomposition was less than 55 %. The figure also illustrates that 18 N and 36 N H_2SO_4 had higher conversion rate for fifteen minutes reaction time. They also had better hydrolysis efficiency to treat the nitrocellulose. In comparison, 38 % HCl, the yield of S was only 51 % with two hours reaction time. For the case of 10 N H_2SO_4 and 19 % HCl, the amount of NC conversion was also low ($S \leq 40$ %). It can be concluded that 38 % HCl, 19 % HCl, and 10 N H_2SO_4 have poorly hydrolysis results at 40 °C.

Figure 24 shows the effects of different acids at 70 °C in single stage hydrolysis system. The effect of 18 N and 36 N H_2SO_4 observed in these experiments were similar to that found in 40° C hydrolysis system. For 38 % HCl, S increased very moderately during whole hydrolysis processes, and then reached the maximum value (100 %) for two hours reaction time. However, the percentage NC dissolved with 10 N H_2SO_4 and 19 % HCl, was low ($S \leq 50$ %). The results from this work indicate that 38 % HCl was an ideal acid solution to treat nitrocellulose in higher reaction temperature and longer reaction time.

Figure 25 shows the effects of different acids at 100 °C in single stage hydrolysis system. The results indicate that the effect of high temperature was pronounced where the acid concentration was low, i.e., 10 N H_2SO_4 and 19 % HCl. In general, percentage of NC dissolved increases with increasing reaction temperature. Therefore, higher decomposition was found at high temperature where the maximum conversion was more than 75 % for any reaction acid in this test.

From the results obtained and hydrolysis rate constant calculated in this study, it can be concluded that 36 N H_2SO_4 and 18 N H_2SO_4 were better acids to hydrolyze nitrocellulose at any reaction temperature and reaction time. The hydrolysis efficiency of 38 % HCl was weak at low temperature (40 °C), but it had better efficiency when temperature increased to 70 °C. In addition, the effect of reaction temperature was very important with 10 N H_2SO_4 and 19 % HCl, as stated previously in advanced temperature (100 °C).

5.2 Results for Two Stage Acid Hydrolysis System

The effect of reaction temperature and reaction time in two stage acid hydrolysis system is shown here in percentage of NC dissolved for different types of acid. In this study, three acids, i.e., 38 % HCl, 10 N H_2SO_4, and 18 N H_2SO_4, were tested under the designed hydrolysis conditions. In two stage hydrolysis system, NC concentration was kept constant at 60,000 mg/L during the first stage hydrolysis system. After the first hydrolysis stage, the reaction solution was diluted with ten times pure water, and then reheated it to 100 °C.

5.2.1 Effect of Hydrochloric Acid in Two Stage hydrolysis system

In this experiment, nitrocellulose was first reacted with a strong acid (38 % HCl) and then followed by a second stage hydrolysis in dilute acid (3.8 % HCl) at boiling point. Figure 26 shows that the production of glucose is a function of COD. A steep increase of glucose was observed in the range $30 \leq t \leq 45$ minutes. When $t = 45$ minutes, amount of glucose reached its maximum, and the percentage of NC converted was nearly 70 %. However, a rapid decrease in the yield of glucose was observed when reaction time was longer than 45 minutes. Figure 27 shows the relationship of total COD and glucose at 70 °C in two stage system. In this figure, the amount of glucose produced increased with both reaction time and total COD. These results indicate that more glucose was produced in the second stage, especially when the reaction time of first stage system was short (near 45 minutes).

The effects of reaction temperature in two stage hydrolysis system are shown in Figures 28 to 30. Figures show the percentage of NC conversion in both stages. The first 30 minutes in Figure 28 was the first stage hydrolysis and the rest was obtained in the second stage hydrolysis. Figures 29 and 30 were performed for 45 and 60 minutes of reaction time in the first stage, respectively. These results indicate that the efficiency of hydrolysis is affected by the reaction temperature. It can be seen from Figure 28 that small percentage of NC conversion was obtained in the second stage hydrolysis, 70 % verses 10 % for 100 °C and 62 % verses 15 % for 70 °C. In general, the percentage of nitrocellulose dissolved increased with increasing temperature. In first stage hydrolysis system as shown in Figure 16, the ability to break down large molecule for 38 % HCl was strongly affected by reaction temperature, and the effect was more pronounced at higher temperature. When $T = 40$ °C, percentage of NC conversion was small, but a large increase was observed when reaction temperatures were between 70 °C and 100 °C. However, these were not observed in two stage hydrolysis process as shown in Figures 28 to 30, where the percentage of decomposition are similar (10 to 15 %). In this test, the results obtained for three reactors under different reaction temperatures, i.e., 40 °C, 70 °C, and 100 °C, in the first stage hydrolysis process indicate that the reaction temperature in the first stage HCl hydrolysis system determines the major conversion of NC. Less than 15 % of the NC were decomposed in the second stage when reaction temperature increased from 40 °C to 100 °C.

The reaction time is related to acid hydrolysis in second stage, as shown in Figures 31 to 33. It can be seen from Figure 31 that the percentage of nitrocellulose converted increased with reaction time and reached equilibrium gradually in 38 % HCl hydrolysis. In first stage hydrolysis process as shown in Figure 16, S was strongly affected by the reaction time, especially at high temperature. 100 % conversion can be achieved for two hours reaction time at higher temperature (70 °C- 100 °C). However, it took longer time for two stage hydrolysis process to reach to a lesser degree of treatment as shown in Figures 31 to 33. Less then 50 % in 40 °C, and 90 % in 70 °C and 100 °C. These results were obtained for different first stage reaction time, i.e., t = 30, 45, and 60 minutes. It is obvious from these observations that longer reaction time is required for the second stage system, especially for lower HCl concentration. The rate of NC conversion was not affected by the reaction time from 30 to 60 minutes during the first stage hydrolysis process.

From the literature available in two stage systems, it seems that cellulose requires more stringent conditions, i.e., higher temperature or higher acid concentration because of the cellulose crystalline structure. Cellulose can be decomposed to glucose in high acid concentration and high temperature, but the reaction rate is very fast when glucose is decomposed to tars or various dehydration products in high concentration and/or high reaction temperature. To overcome this limitation, Dartmouth (1971) proposed a hydrolysis process for cellulose treatment with two stage hydrolysis system. In his work, maximum glucose yield was found in second hydrolysis stage [6]. This conclusion was also observed here for nitrocellulose as shown in Figure 27. It is also observed in two stage system that because of dilute acid used in the second stage. The amount of hydrogen ions available would be limited, which in turn would affect the decomposition rate and result in longer reaction time.

5.2.2 Effect of Sulfuric Acid on Two Stage Hydrolysis System

In this experiment, the reaction temperature and reaction time were designed at fixed hydrolysis conditions, i.e., T = 40, 70, 100 °C, and t = 30, 45, 60 minutes, for the first stage in 18 N H_2SO_4 and 10 N H_2SO_4 hydrolysis systems. After the first stage hydrolysis process, the reaction solution was diluted with 10 times of pure water, and reheated it to 100 °C.

For the case of 10 N H_2SO_4 as shown in Figures 34 to 36, the data indicate that the percentage of NC dissolved is affected by the first stage reaction temperature during two stage acid hydrolysis process. It can be seen from these figures that the temperature in second stage did not have much influence. This was very similar to what observed in 38 % HCl hydrolysis system. For the case of 18 N H_2SO_4 as shown in Figures 37 to 39, the results indicate that S was not affected by the temperature in most cases. At any reaction temperature, percentage of NC dissolved was nearly 100 %, and no significant effect of reaction time was noticed.

The effect of reaction time with H_2SO_4 in two stage hydrolysis system is not important, as shown in Figures 40 to 45. The most nitrocellulose conversion was accomplished in the first stage 10 N H_2SO_4 hydrolysis. In first stage 18 N and/or 36 N H_2SO_4 hydrolysis process (Figures 21 and 22), S was not affect by the reaction time. However, the conversion rate in 10 N H_2SO_4 hydrolysis as shown in Figure 20, was strongly affected by the reaction time, especially when the reaction temperature was high. However, this was not the same in two stage 10 N H_2SO_4 and 18 N H_2SO_4 hydrolysis process (Figures 40 to 45). The results obtained in two stage H_2SO_4 hydrolysis indicate that S increased very slowly with reaction time.

The reaction temperature and reaction time have shown previously to have no significant effect on two stage hydrolysis system. This is in agreement with Browning's report that the first stage hydrolysis plays an important role in two stage hydrolysis system [6]. For two stage H_2SO_4 hydrolysis system, a comparison of different first stage reaction time and different acid concentration at different temperature are shown in Figures 46 to 51. These figures show that the percentage of NC dissolved in 18 N H_2SO_4 were larger than that of 10 N H_2SO_4 at any conditions. On the other hand, higher acid concentration still produces better conversion.

CHAPTER 6

CONCLUSIONS

Based upon the experimental results, the major conclusions can be derived:

1. The relationship of soluble COD and total COD for NC was established. It was found that the difference between soluble COD and total COD was small, especially for high acid concentrations. Therefore, total COD can be used as an indicator for the study of nitrocellulose conversion in acid hydrolysis process.
2. In single stage hydrolysis system, the nitrocellulose decomposition was found to be strongly dependent on the type of acid, acid concentration, reaction temperature, and reaction time.
3. In both 36 N and 18 N H_2SO_4 hydrolysis system, the percentage of NC conversion was found to have maximum value ($S =\sim 100$ %) in a very short time ($t \leq 15$ minutes) at any reaction temperature.
4. In both 38 % HCl and 10 N H_2SO_4 hydrolysis systems, hydrolysis efficiency was found to be strongly dependent on the reaction temperature and reaction time. High conversion rate was observed at a higher reaction temperature ($T \geq 70$ °C) when reaction time was nearly two hours.
5. At low reaction temperature (40 °C) acid hydrolysis system, 10 N H_2SO_4 was found to have a less than 40 % of NC conversion.
6. In 19 % HCl hydrolysis system, hydrolysis efficiency was found to have smaller percentage of NC conversion (30 %) at lower reaction temperature ($T \leq 70$ °C) when reaction time was nearly two hours.
7. In this study, it was noted that second stage reaction produced more than 40 % of the total glucose yielded in the two stage hydrolysis system. However, little NC

conversion was observed in the second stage, especially for 10 N H_2SO_4 at low temperature ($T \leq 70$ °C).

APPENDIX A

FIGURES FOR SINGLE AND/OR TWO STAGE ACID HYDROLYSIS SYSTEMS

This appendix includes the figures showing the effects of filtration before COD test in 19 % HCl hydrolysis system, the effects of acid concentration, reaction temperature, and reaction time on the dissolved efficiency in single and two stage hydrolysis systems.

For comparison of filtration effect in COD test, figures are

HCl hydrolysis systems (Figure 5-Figure 6)
H_2SO_4 hydrolysis (Figure 7-Figure 9)

For single stage hydrolysis systems, these figures include:

Effect of concentration in HCl hydrolysis systems (Figure 12-Figure 14)
Effect of reaction temperature in HCl hydrolysis systems (Figure 15-Figure 16)
Effect of concentration in H_2SO_4 hydrolysis systems (Figure 17-Figure 19)
Effect of reaction temperature in H_2SO_4 hydrolysis systems (Figure 20-Figure 22)
Effect of type of acid in hydrolysis systems (Figure 23-Figure 25)

For relationship between COD and glucose in hydrolysis systems, figures are

Single stage hydrolysis system with 38 % HCl (Figure 26)
Two stage hydrolysis system with 38 % HCl (Figure 27)

For two stage hydrolysis systems, figures are

Effect of temperaturein HCl hydrolysis systems (Figure 28-Figure 30)
Effect of reaction time in HCl hydrolysis systems (Figure 31-Figure 33)
Effect of reaction temperature in H_2SO_4 hydrolysis systems (Figure 34-Figure 39)
Effect of reaction time in H_2SO_4 hydrolysis systems (Figure 40-Figure 45)

Effect of concentration in H_2SO_4 hydrolysis systems (Figure 46-Figure 48)

Effect of type of acid in hydrolysis systems (Figure 49-Figure 51)

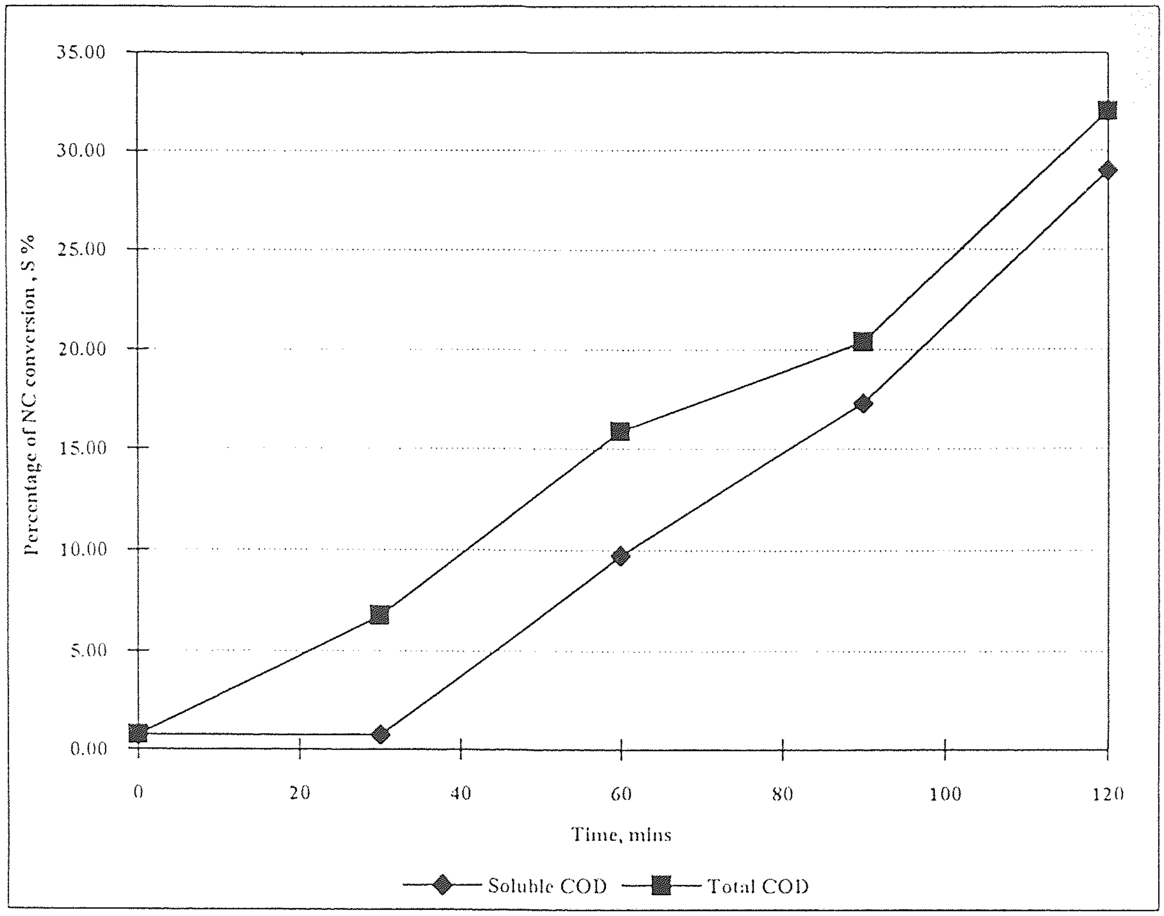

Figure 5 Relationship of Soluble COD and Total COD in 19 % HCl

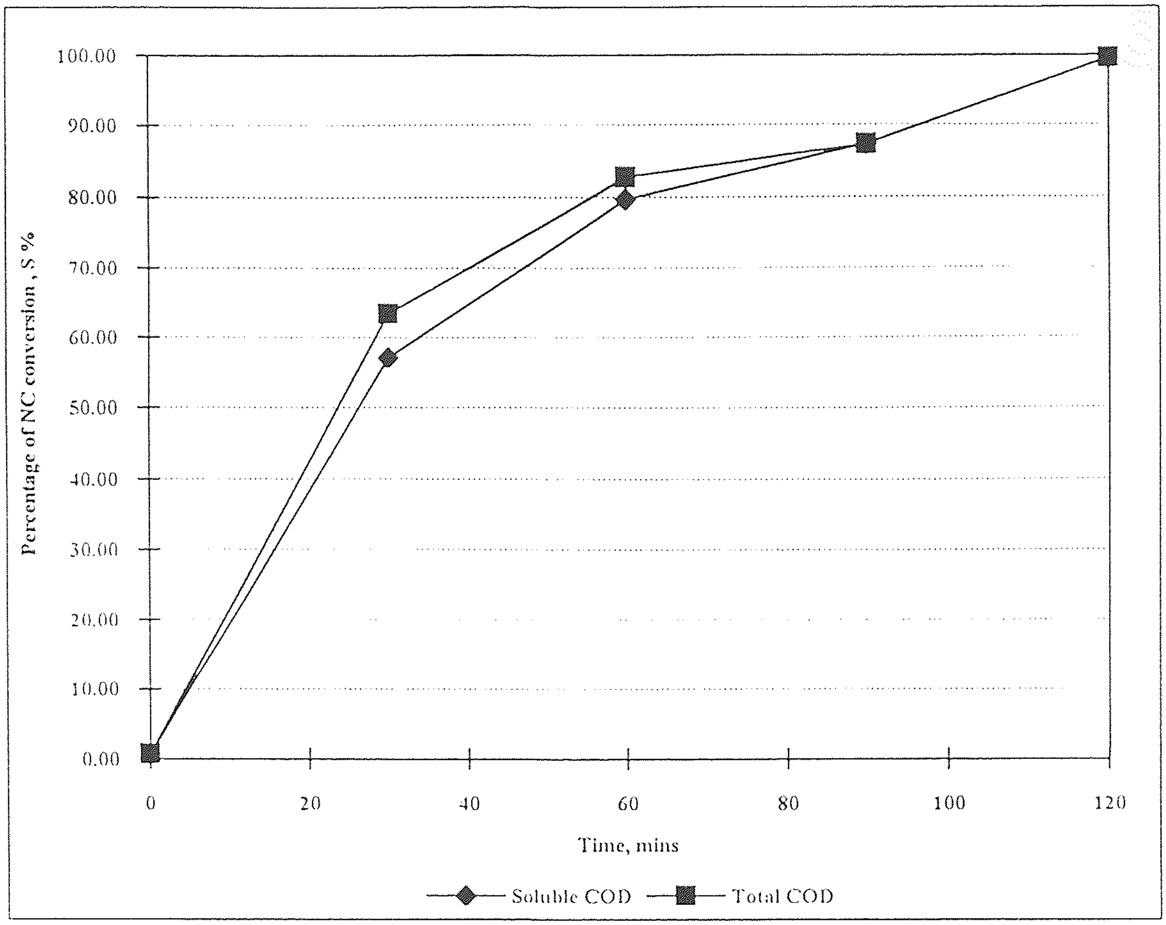

Figure 6 Relationship of Soluble COD and Total COD in 38 % HCl

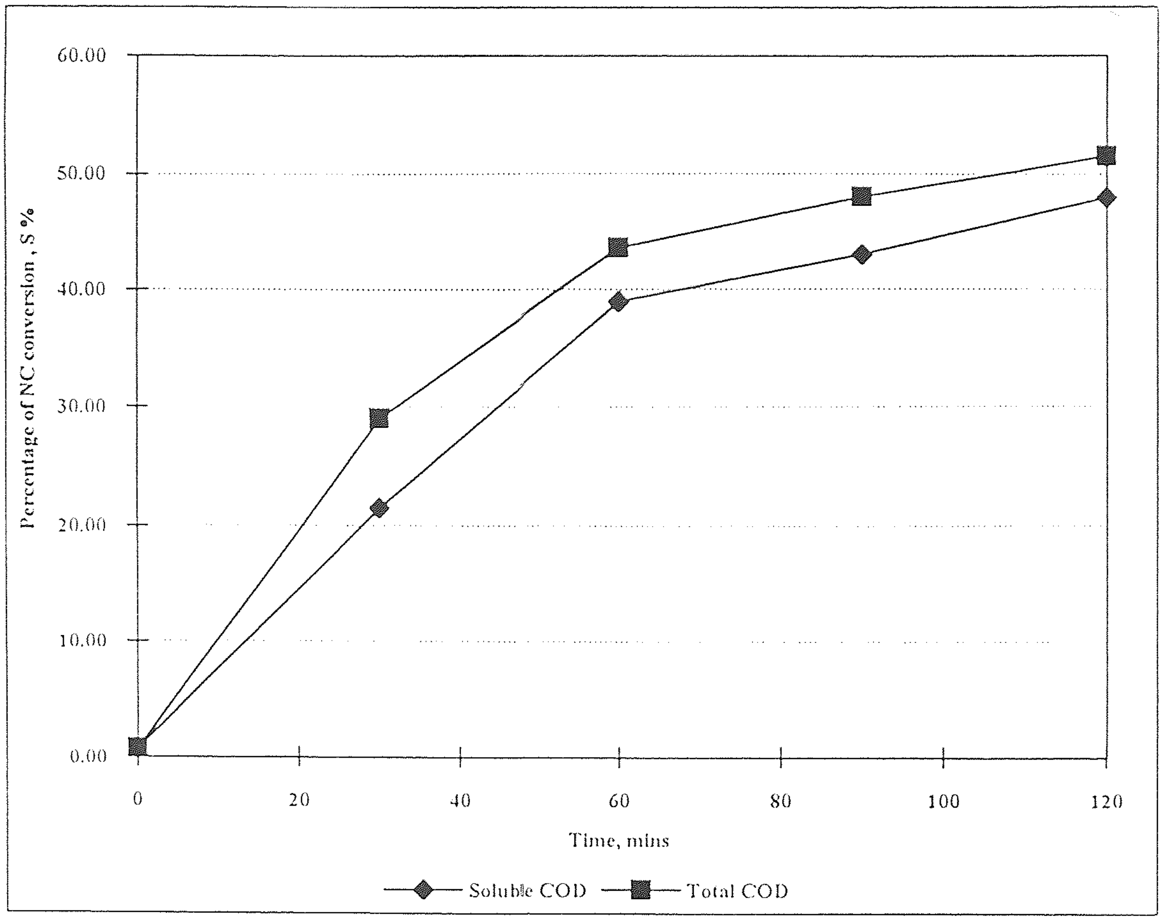

Figure 7 Relationship of Soluble COD and Total COD in 10 N H_2SO_4

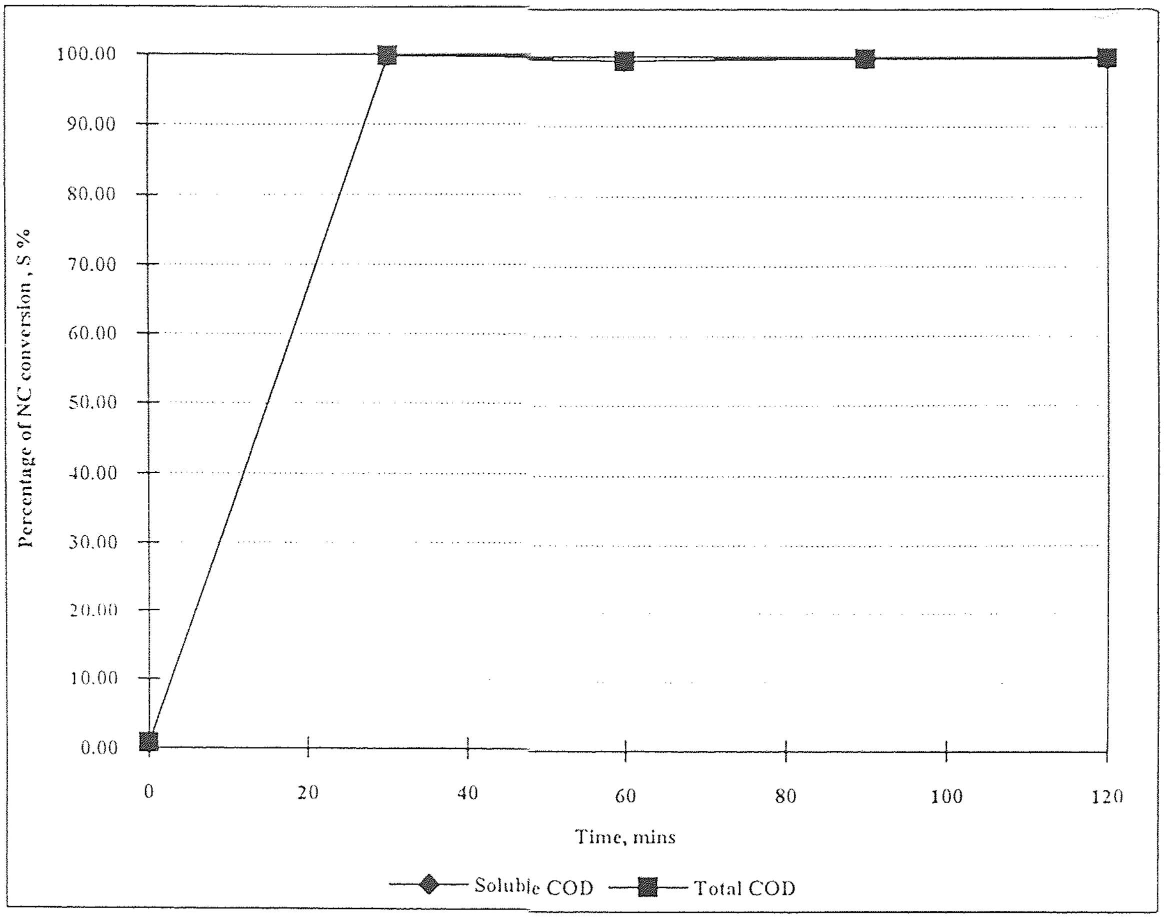

Figure 8 Relationship of Soluble COD and Total COD in 18 N H_2SO_4

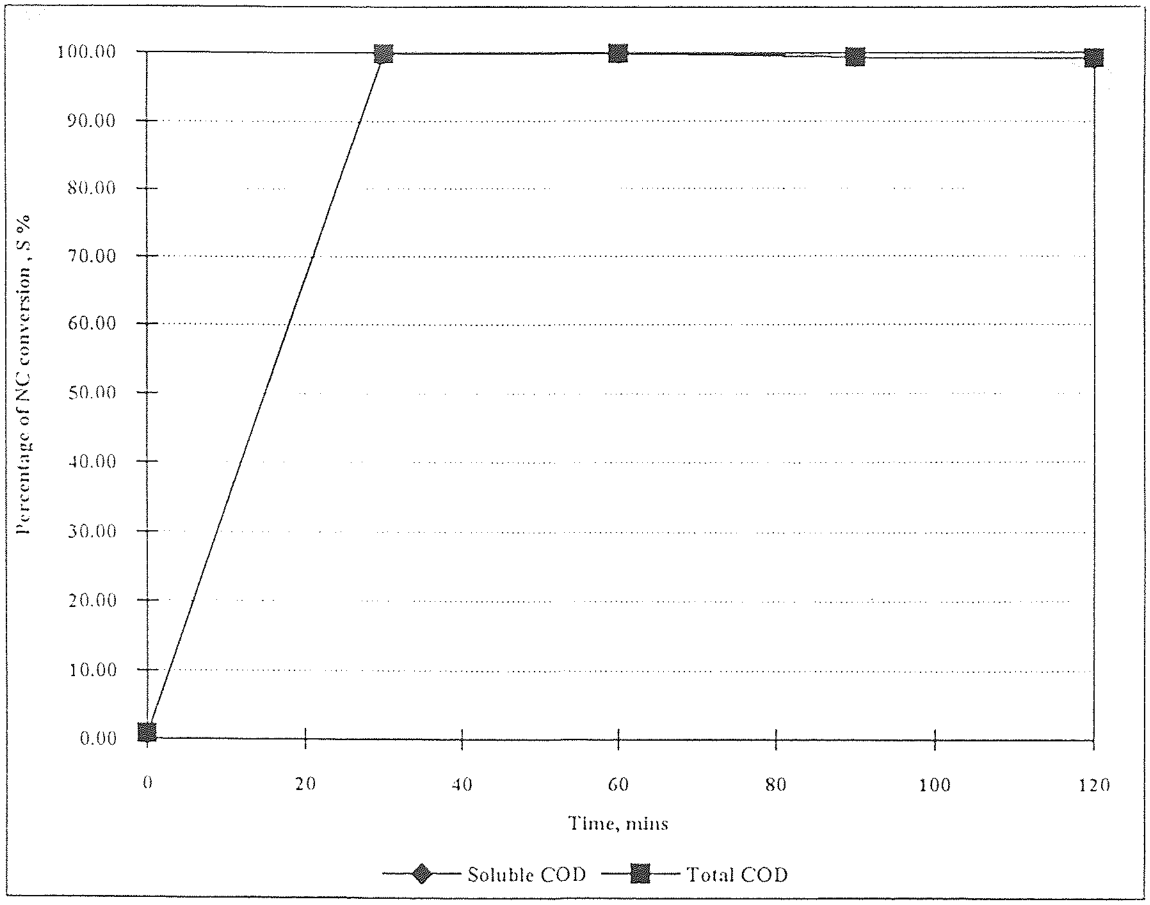

Figure 9 Relationship of Soluble COD and Total COD in 36 N H_2SO_4

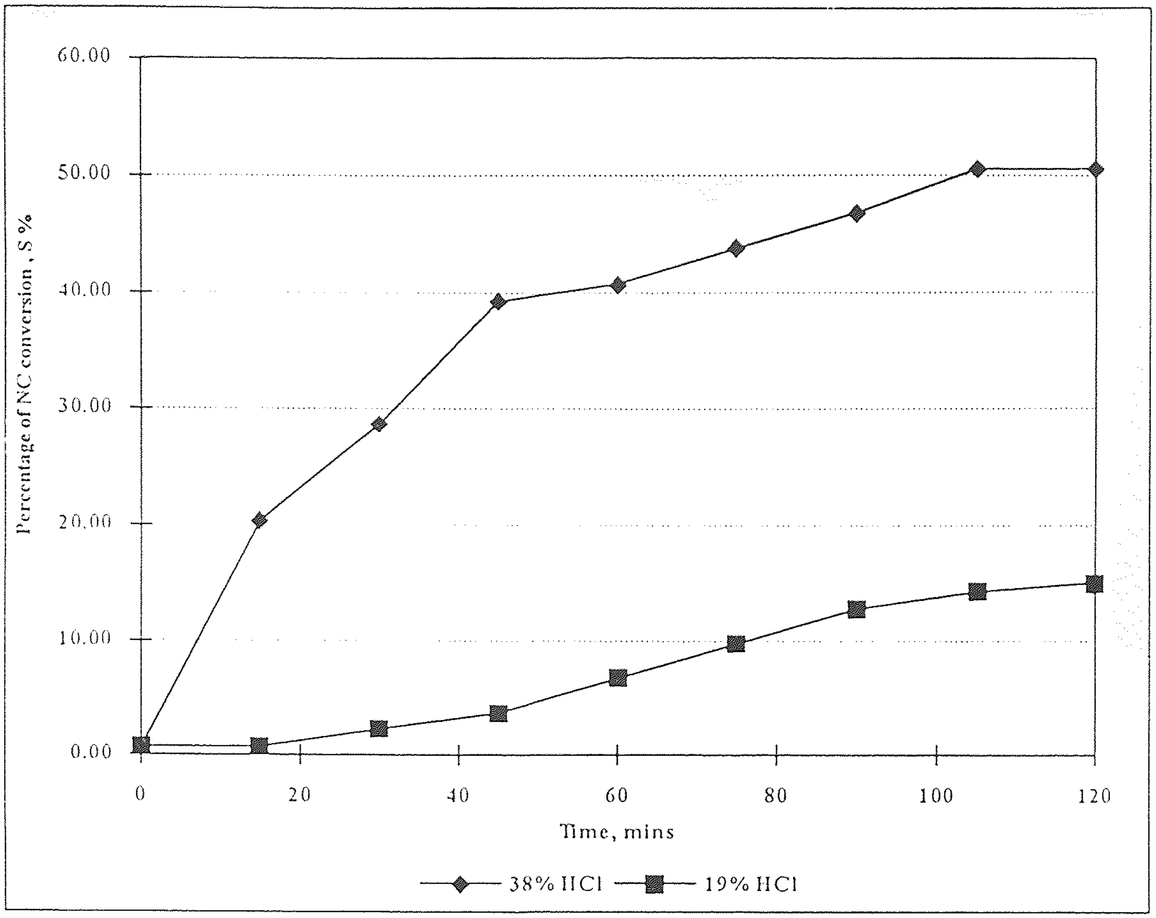

Figure 12 Effect of HCl Concentration on NC Hydrolysis at 40 °C in Single Stage System

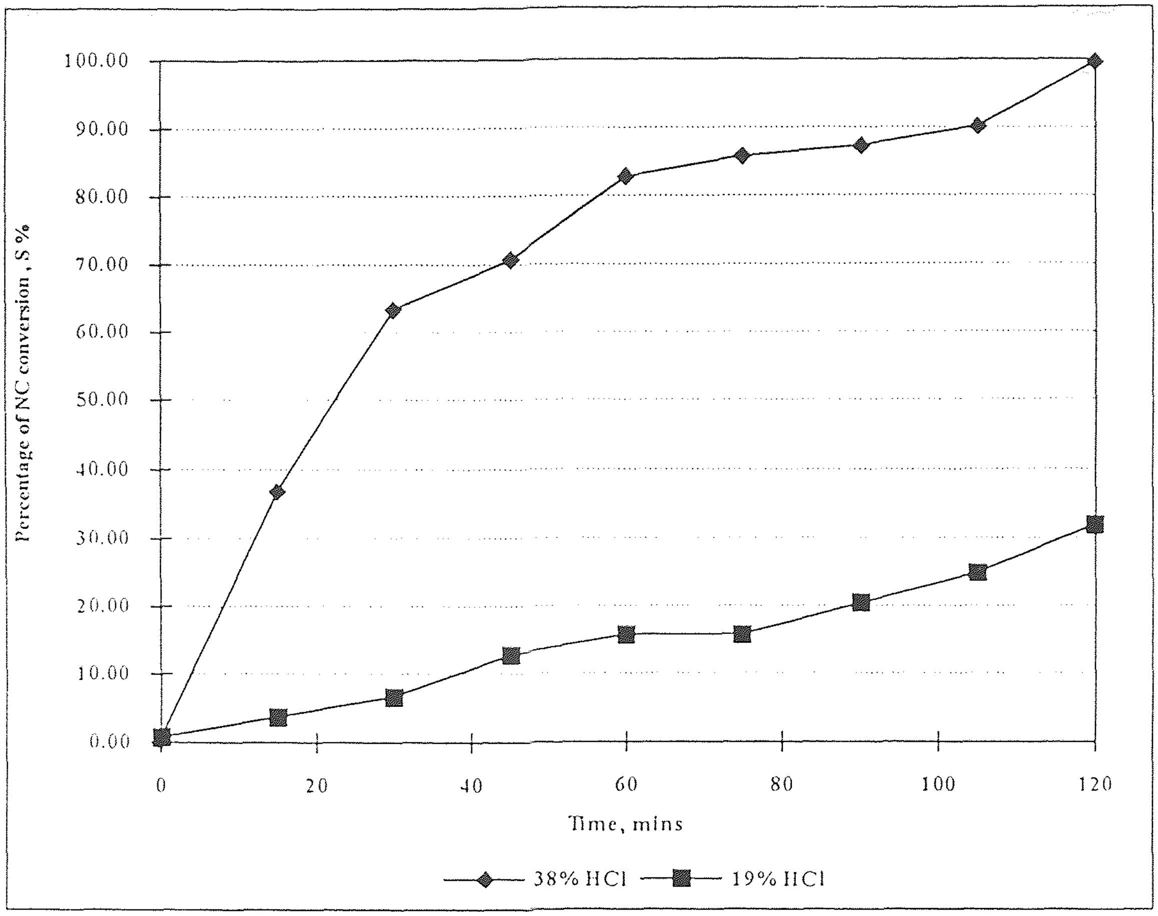

Figure 13 Effect of HCl Concentration on NC Hydrolysis at 70 °C in Single Stage System

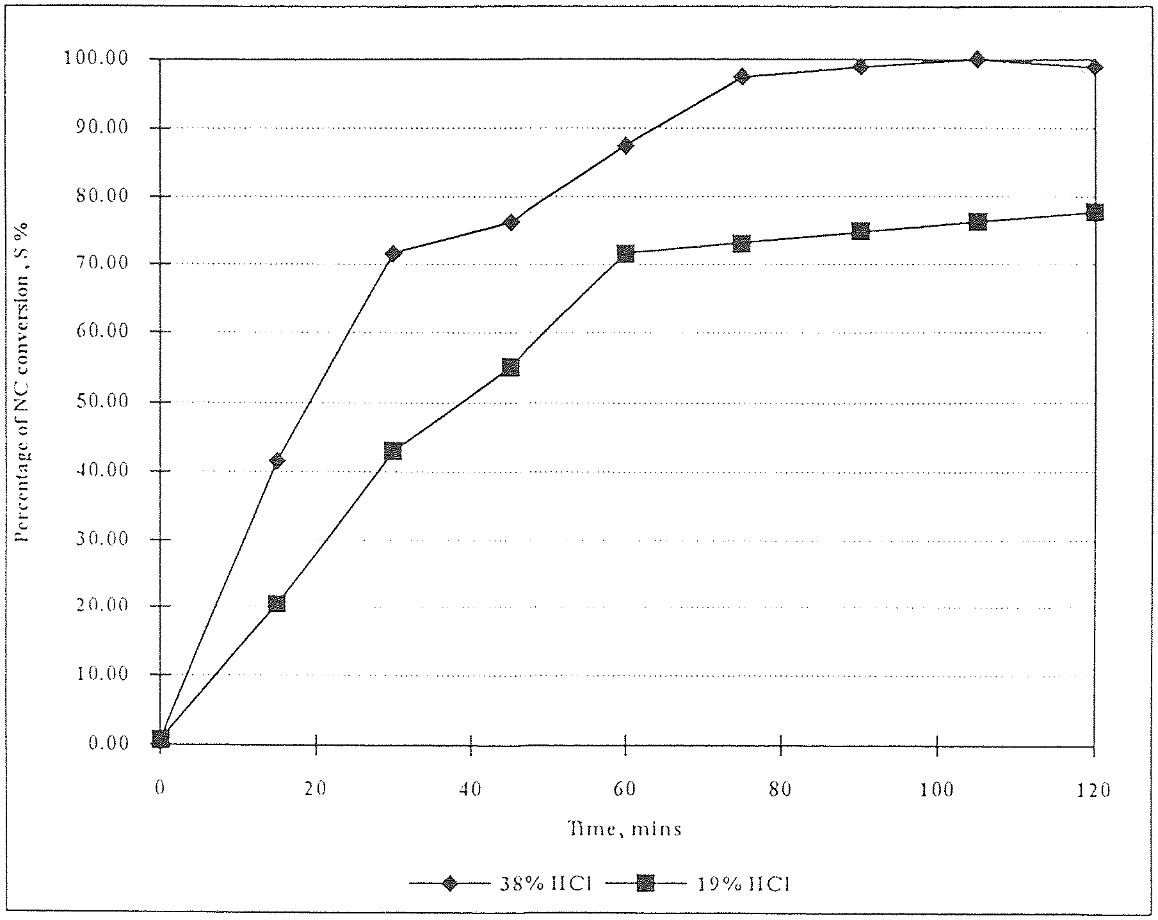

Figure 14 Effect of HCl Concentration on NC Hydrolysis at 100 °C in Single Stage System

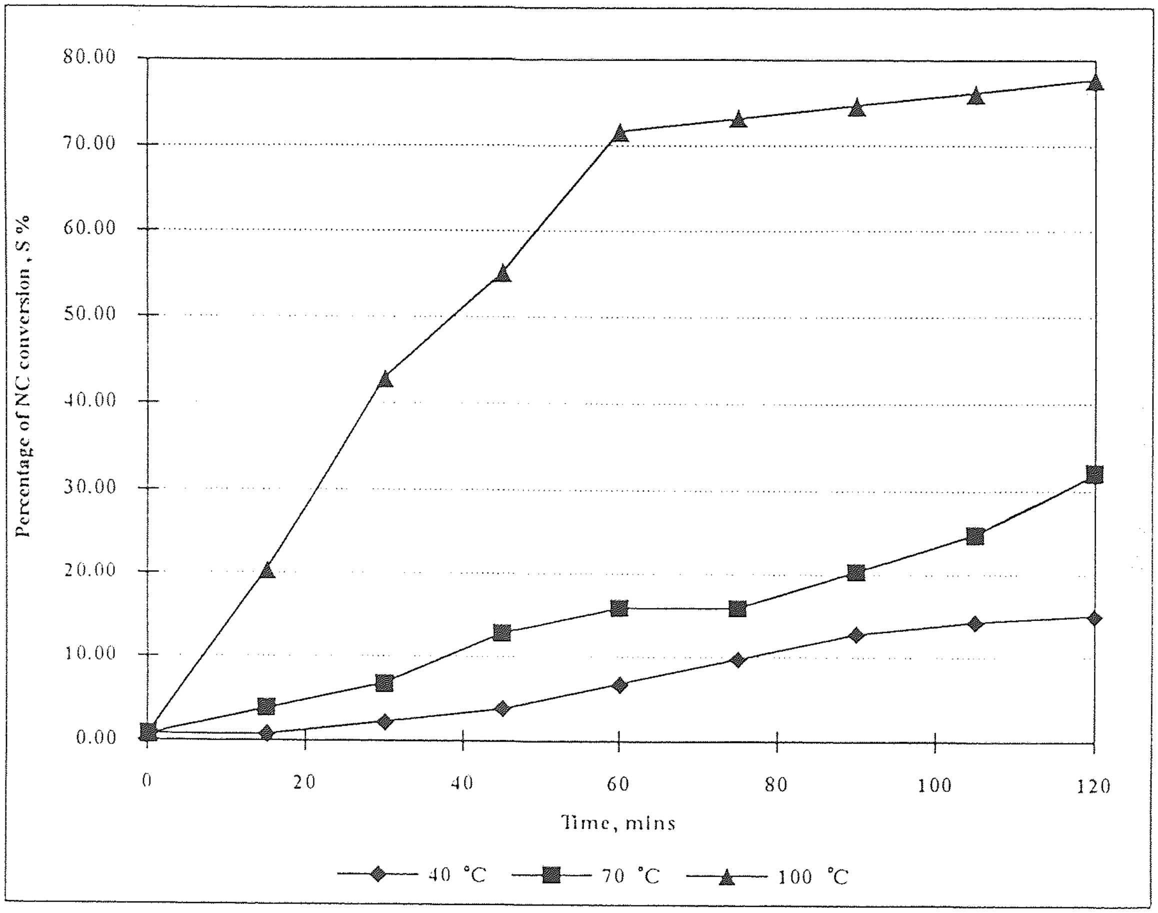

Figure 15 Effect of Temperature for 19% HCl in Single Stage Hydrolysis System

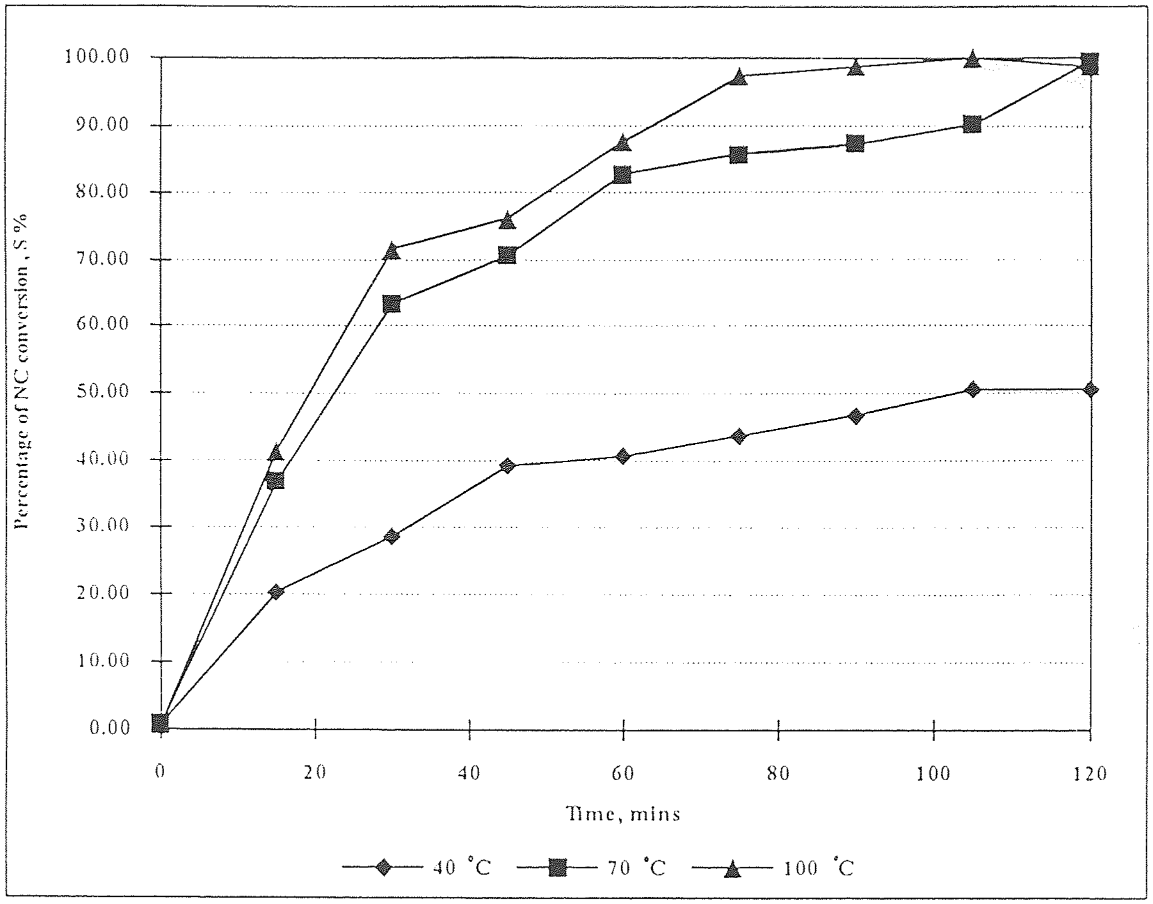

Figure 16 Effect of Temperature for 38% HCl in Single Stage Hydrolysis System

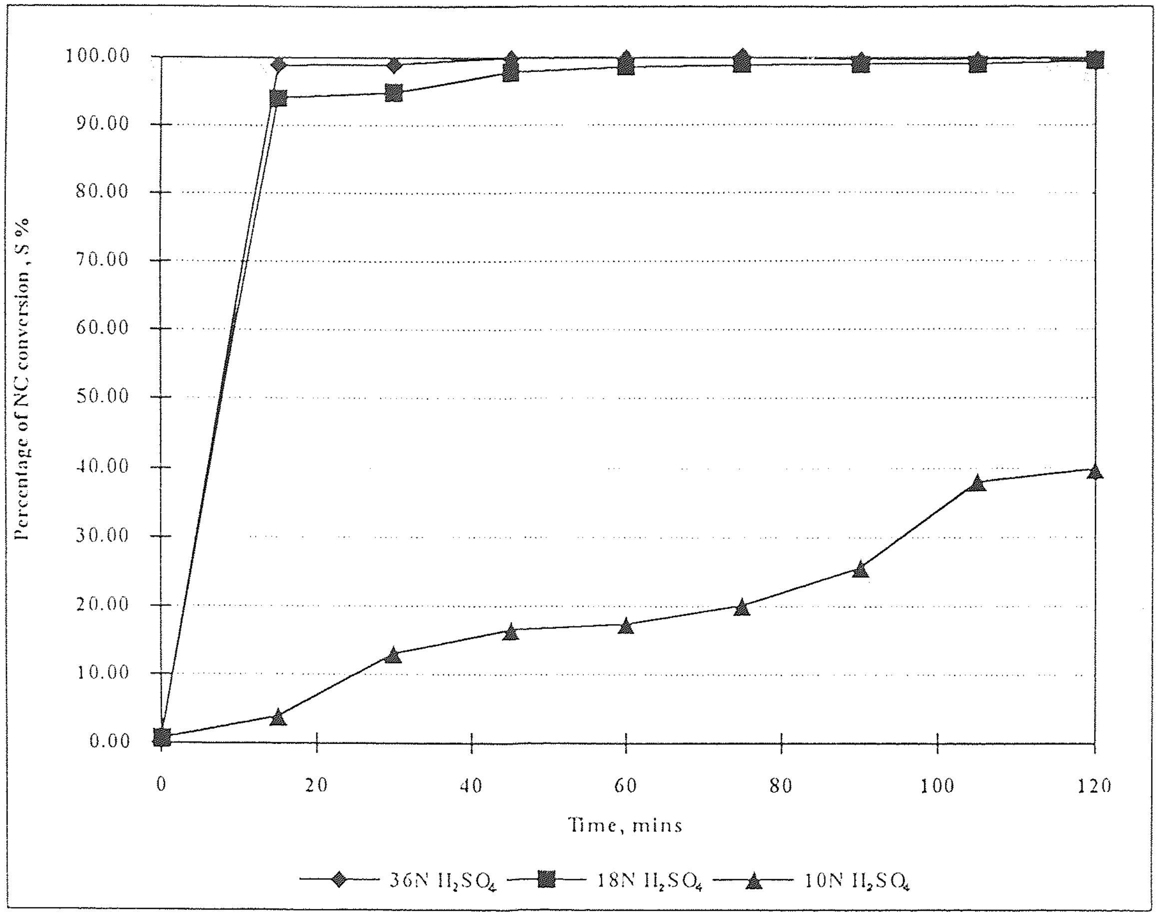

Figure 17 Effect of H_2SO_4 Concentration on NC Hydrolysis at 40 °C in Single Stage System

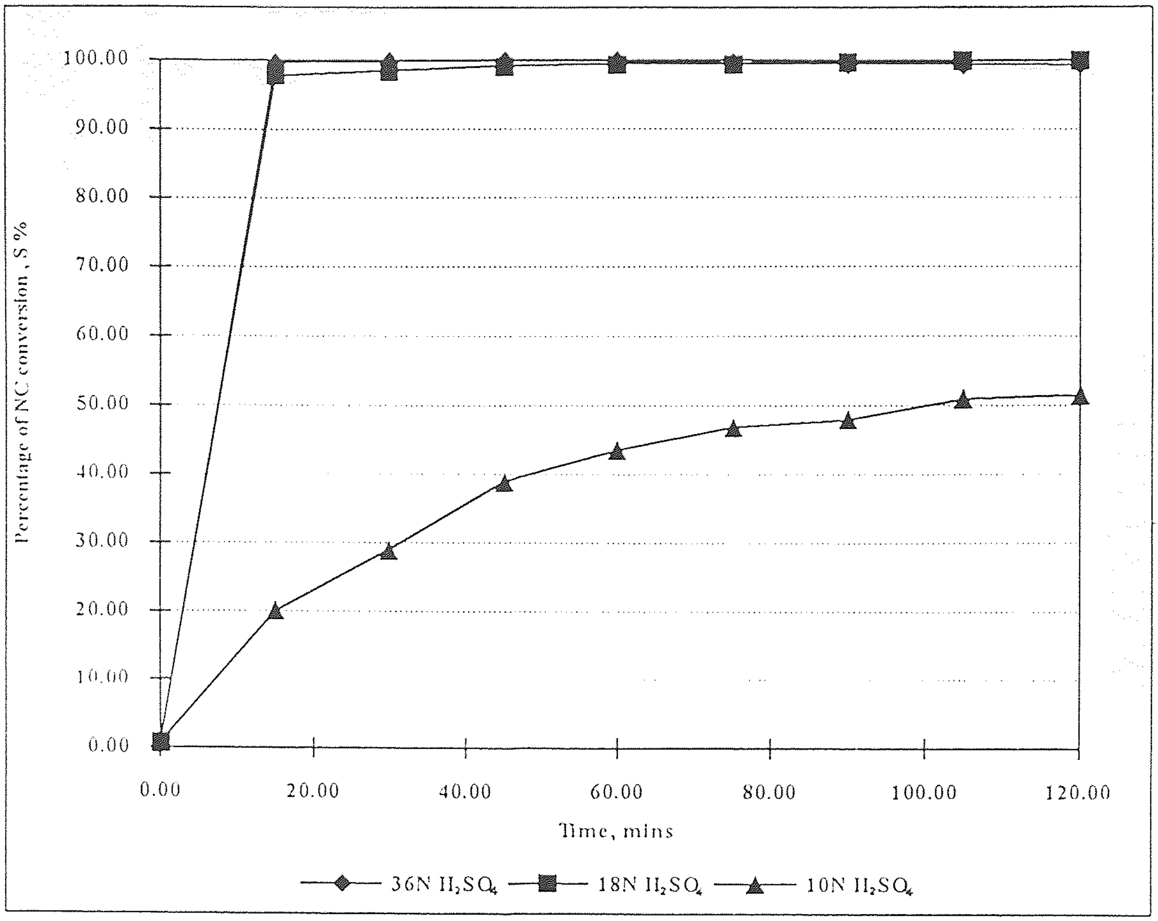

Figure 18 Effect of H_2SO_4 Concentration on NC Hydrolysis at 70 °C in Single Stage System

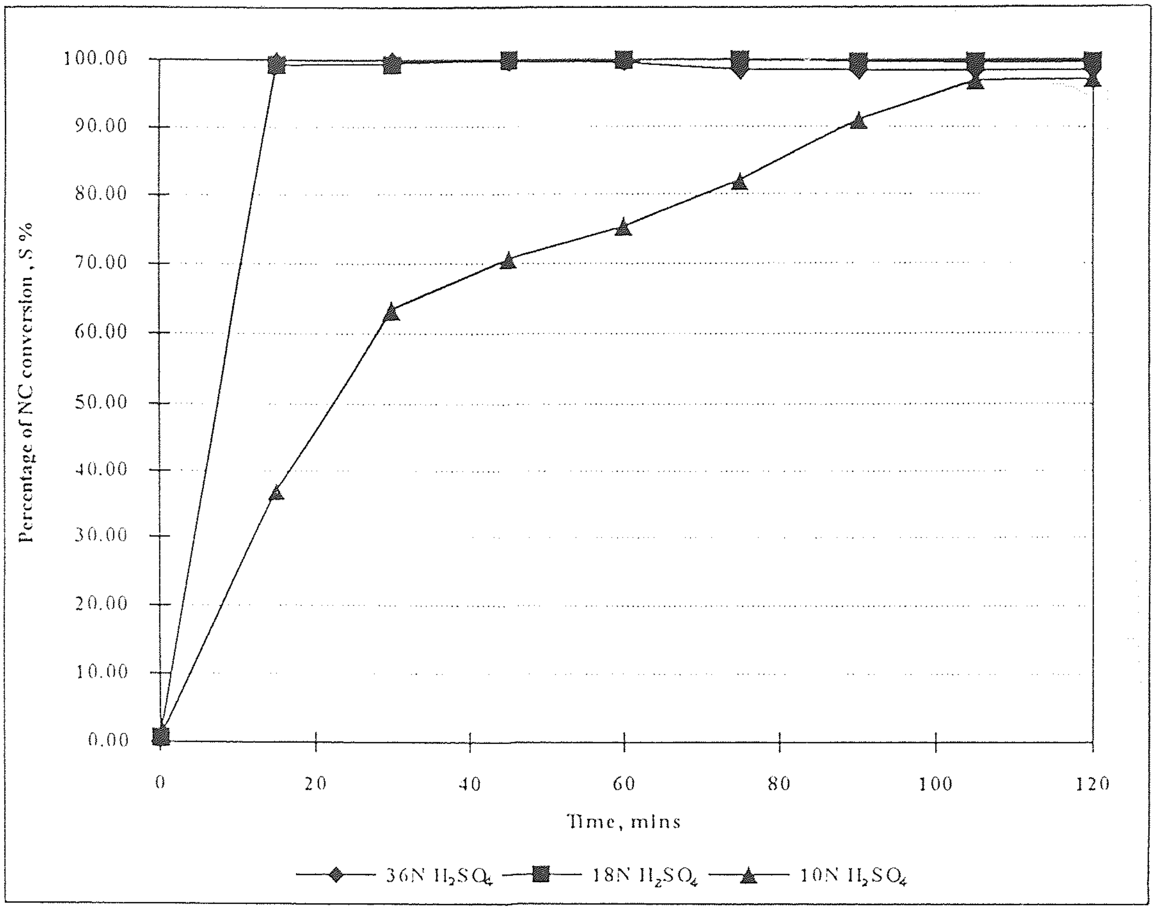

Figure 19 Effect of H_2SO_4 Concentration on NC Hydrolysis at 100 °C in Single Stage System

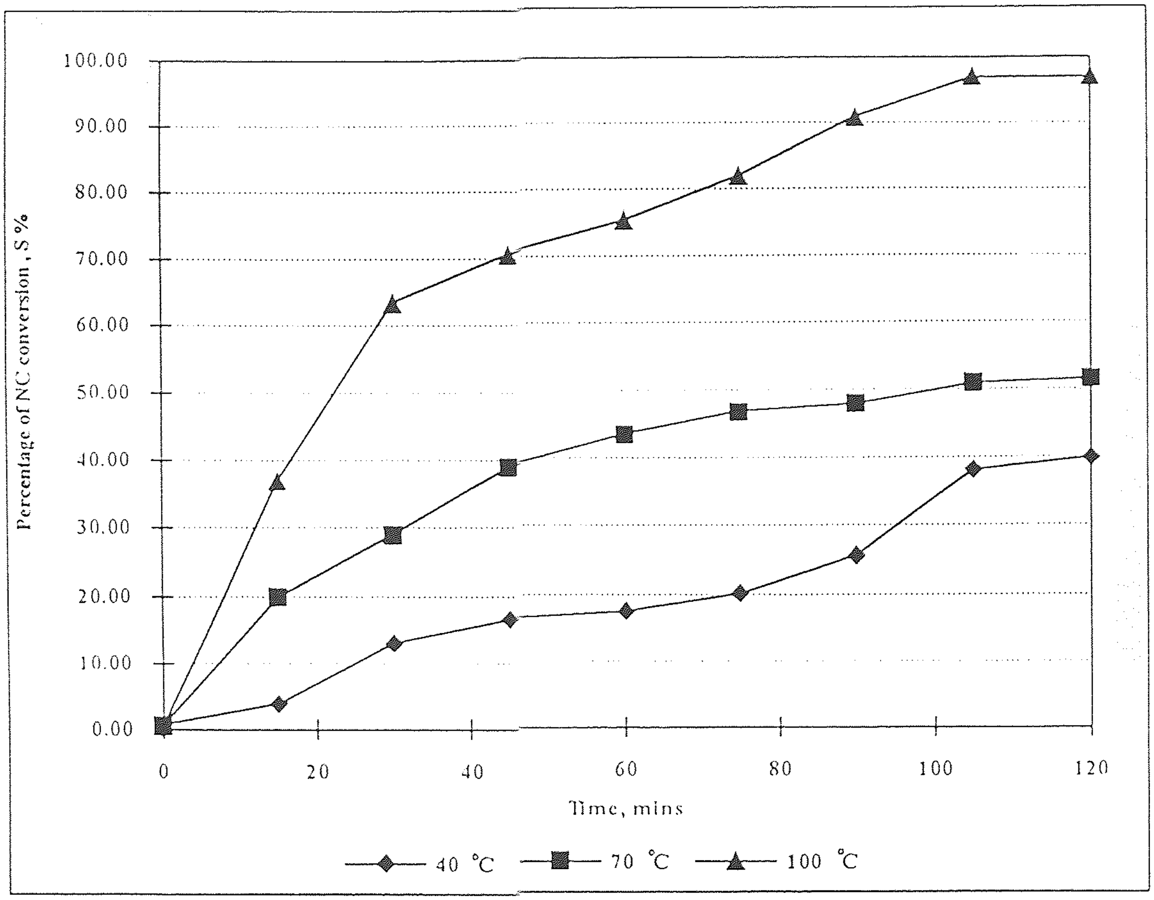

Figure 20 Effect of Reaction Temperature for 10N H_2SO_4 in Single Stage

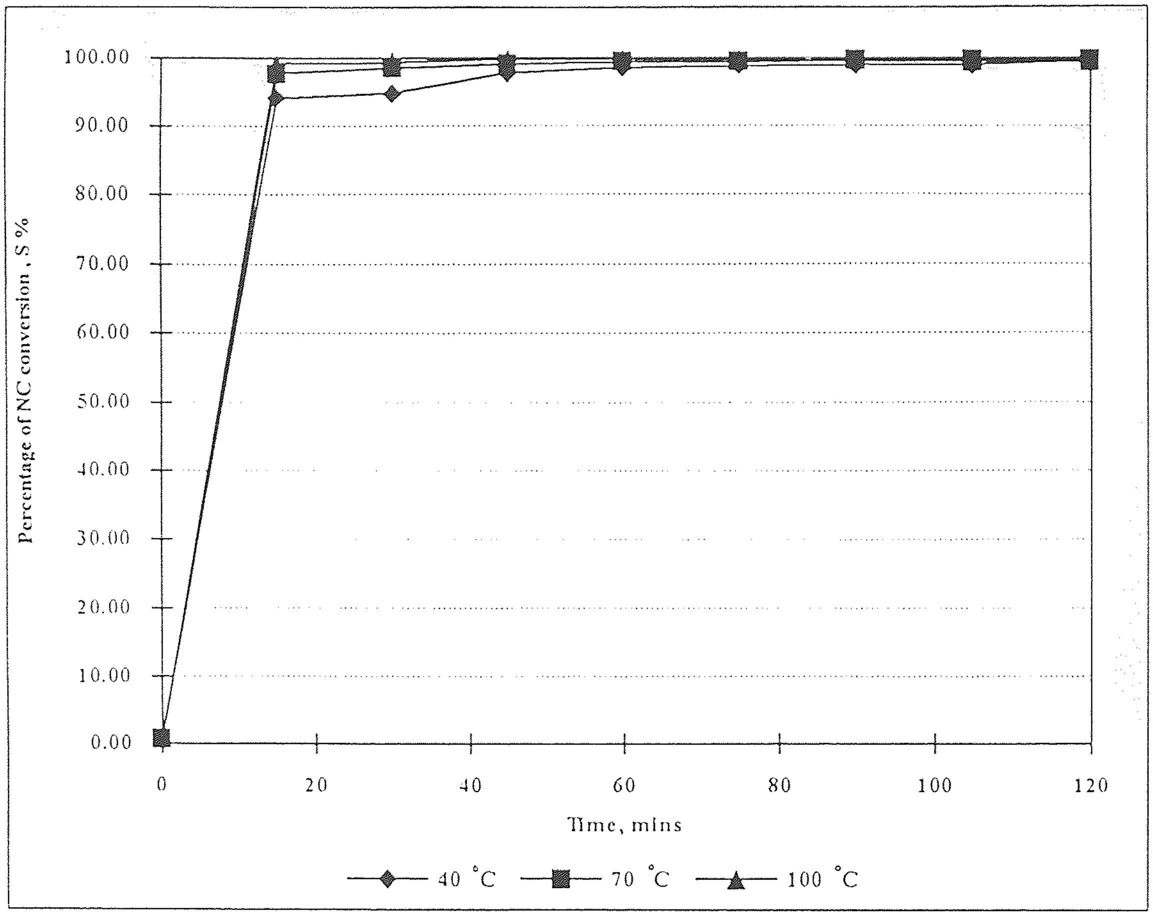

Figure 21 Effect of Reaction Temperature for 18N H_2SO_4 in Single Stage

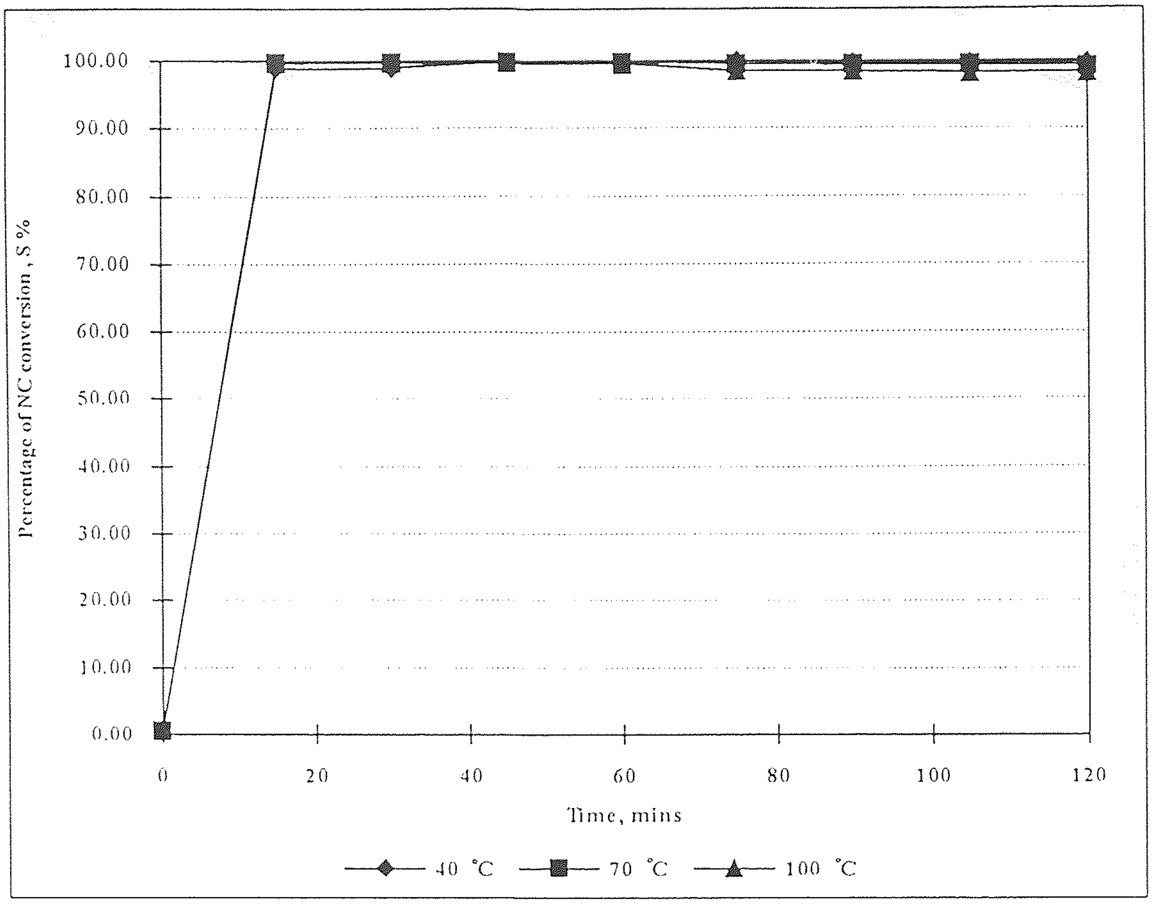

Figure 22 Effect of Reaction Temperature for 36N H_2SO_4 in Single Stage

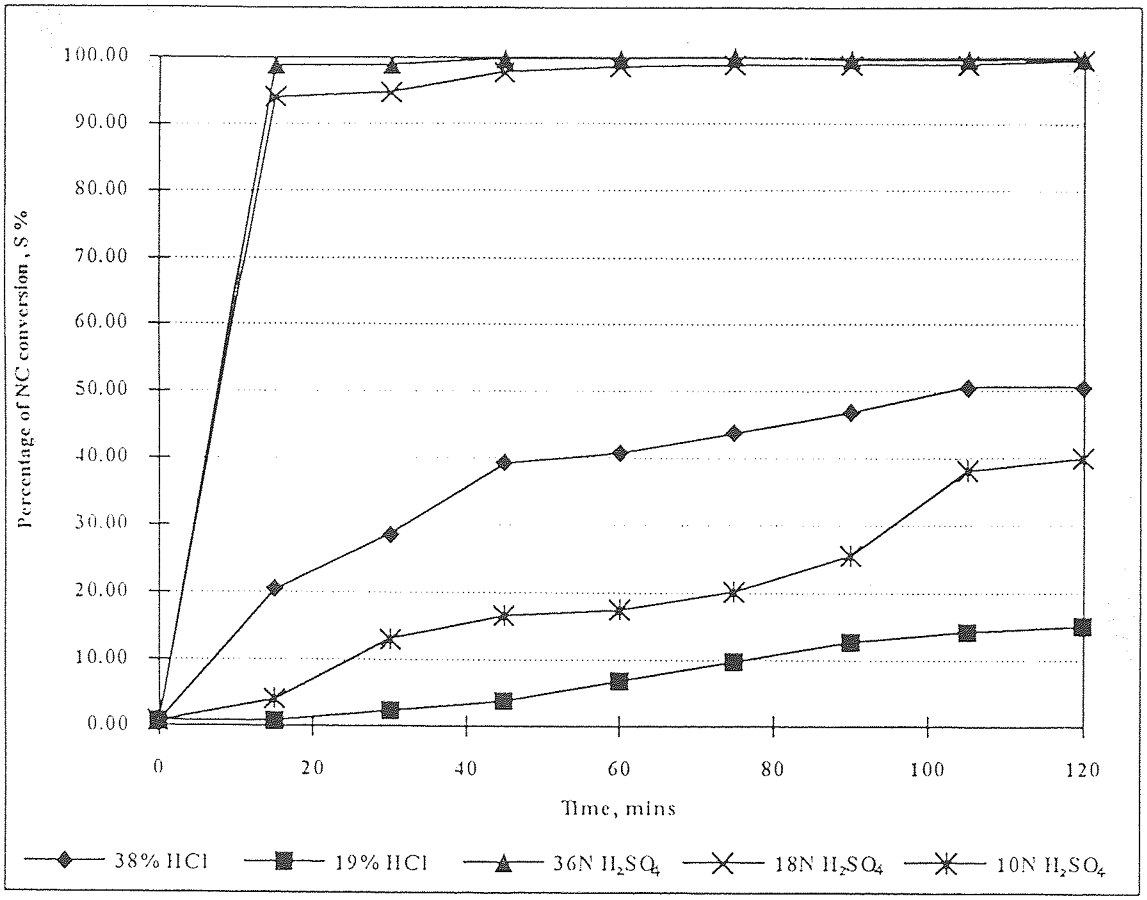

Figure 23 Effect of Different Acid at 40 °C in Single Stage System

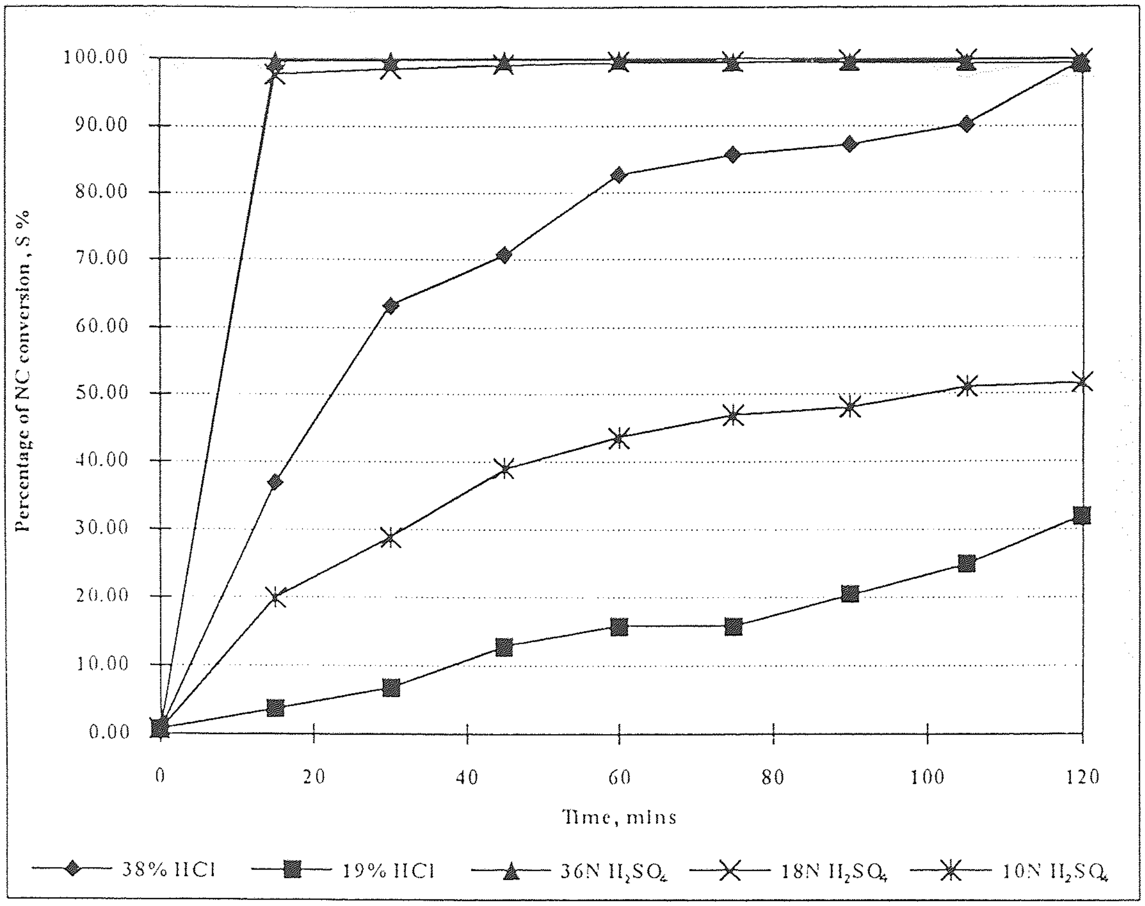

Figure 24 Effect of Different Acid at 70 °C in Single Stage System

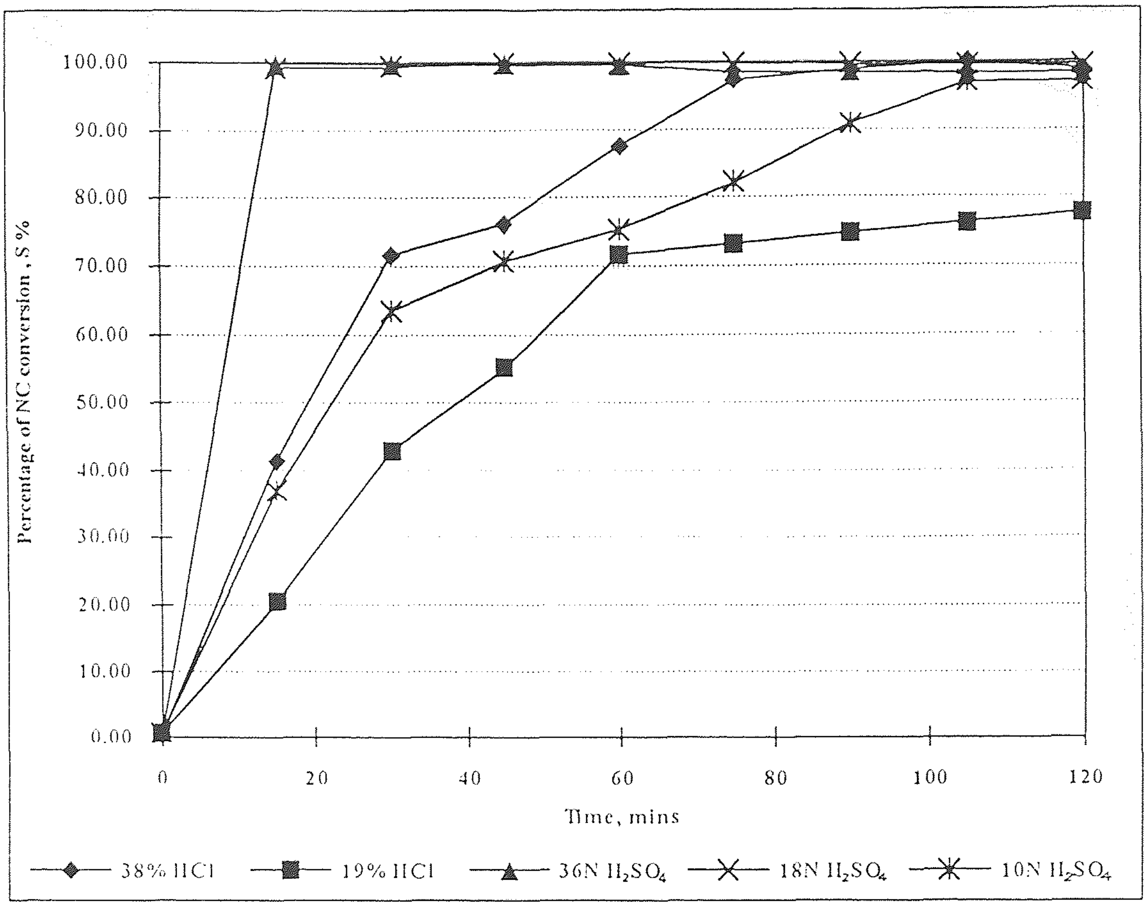

Figure 25 Effect of Different Acid at 100 °C in Single Stage System

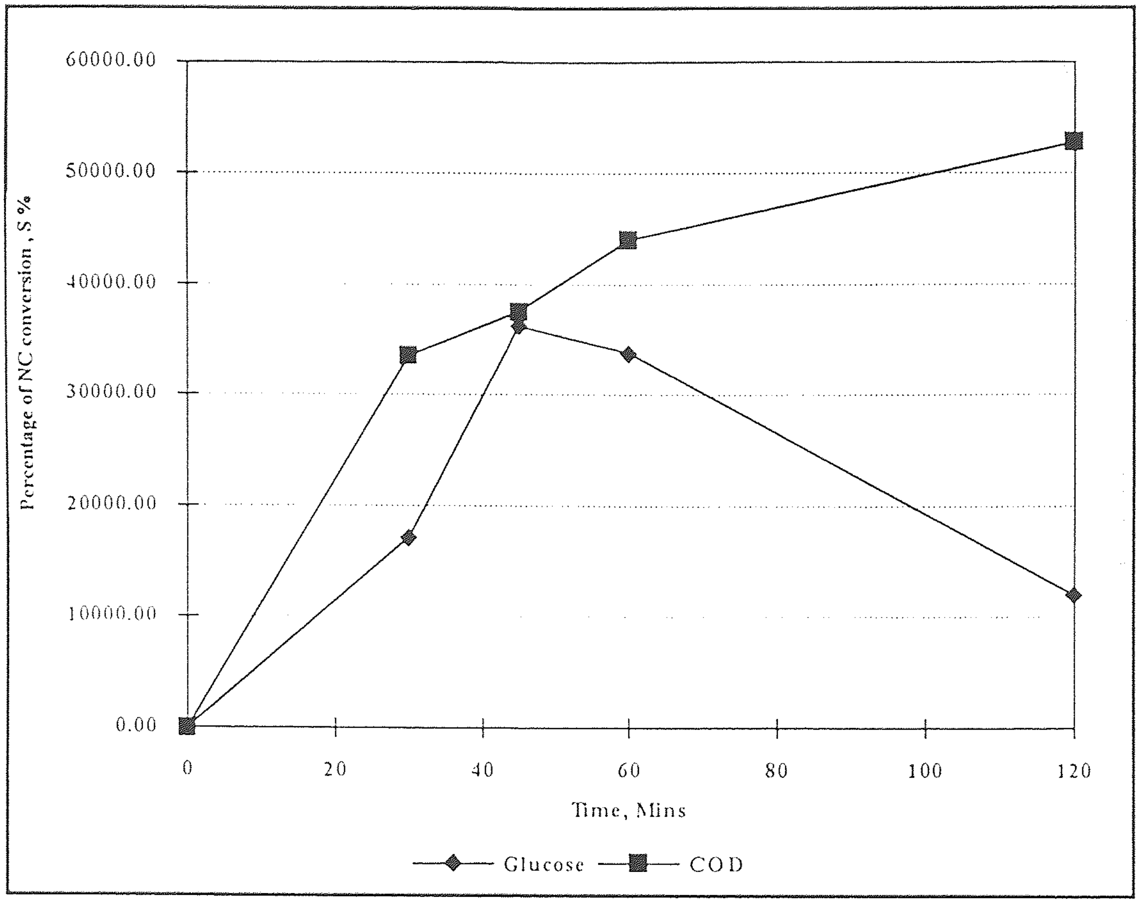

Figure 26 Relationship of Total COD & Glucose for 38 % HCl in Single Stage System

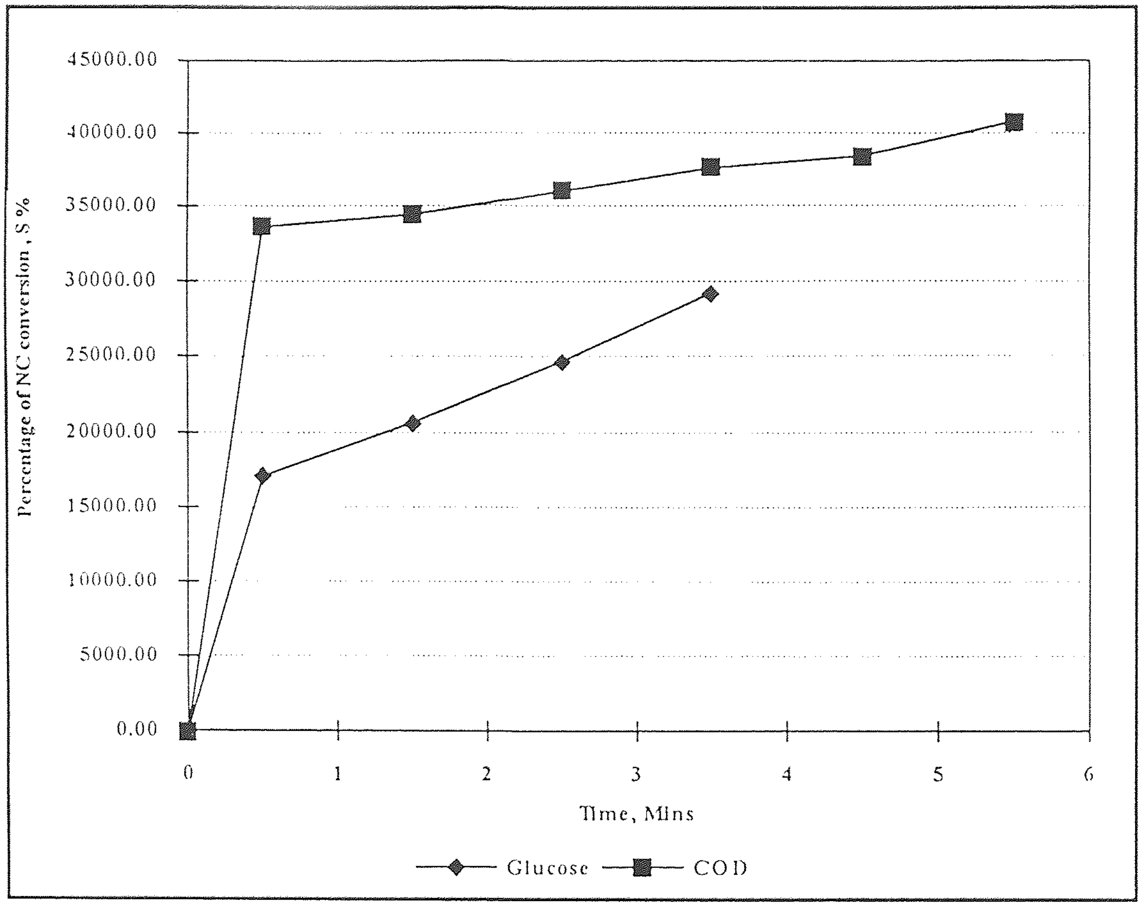

Figure 27 Relationship of Total COD & Glucose for 38 % HCl in Two Stage System

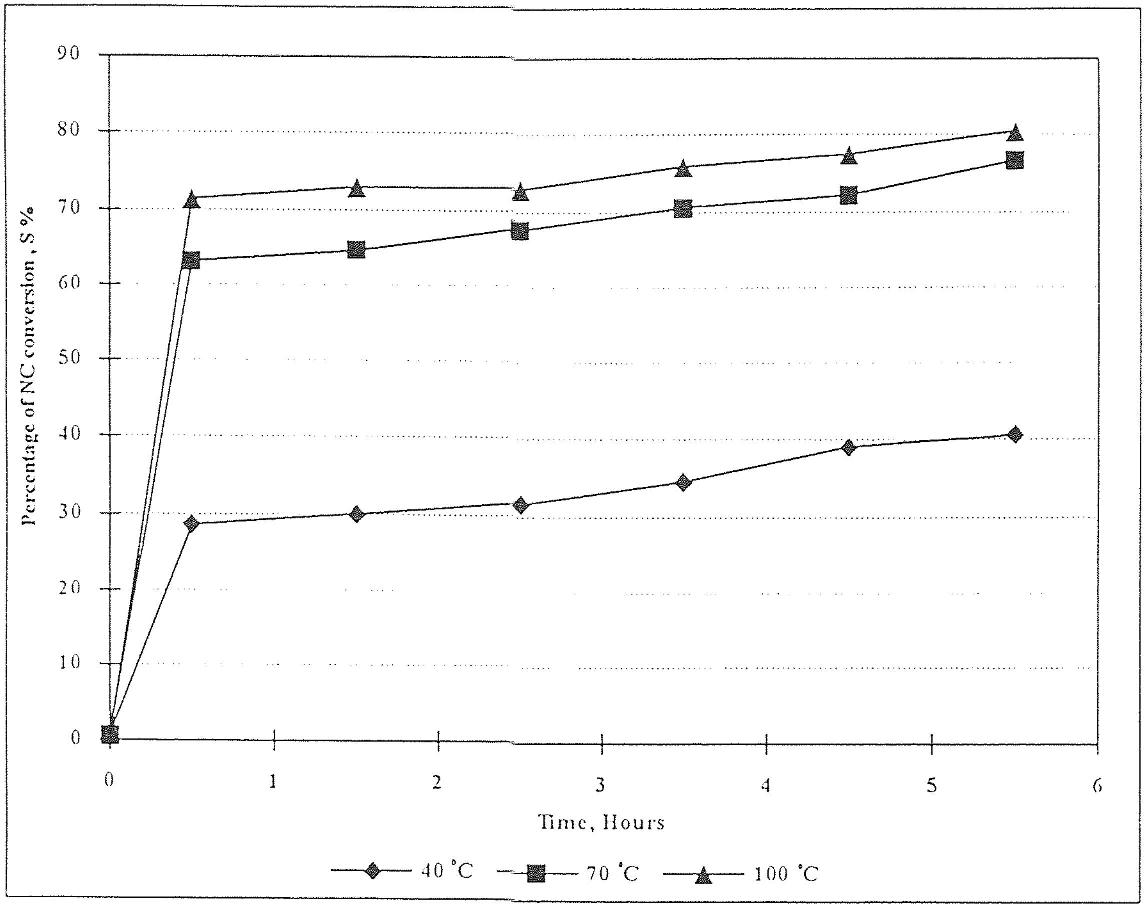

Figure 28 Effect of Temperature for 38% HCl in Two Stage System(1st Stage 30mins)

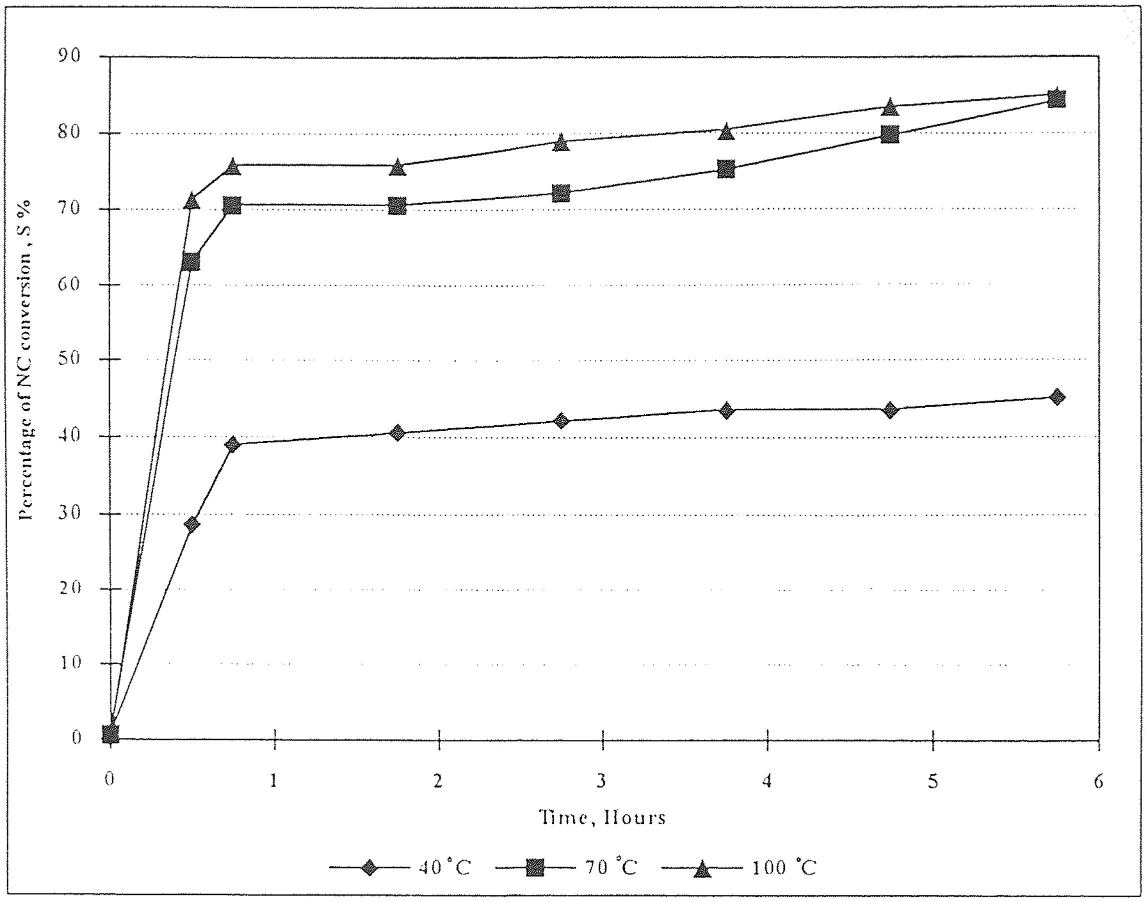

Figure 29 Effect of Temperature for 38% HCl in Two Stage System(1st Stage 45mins)

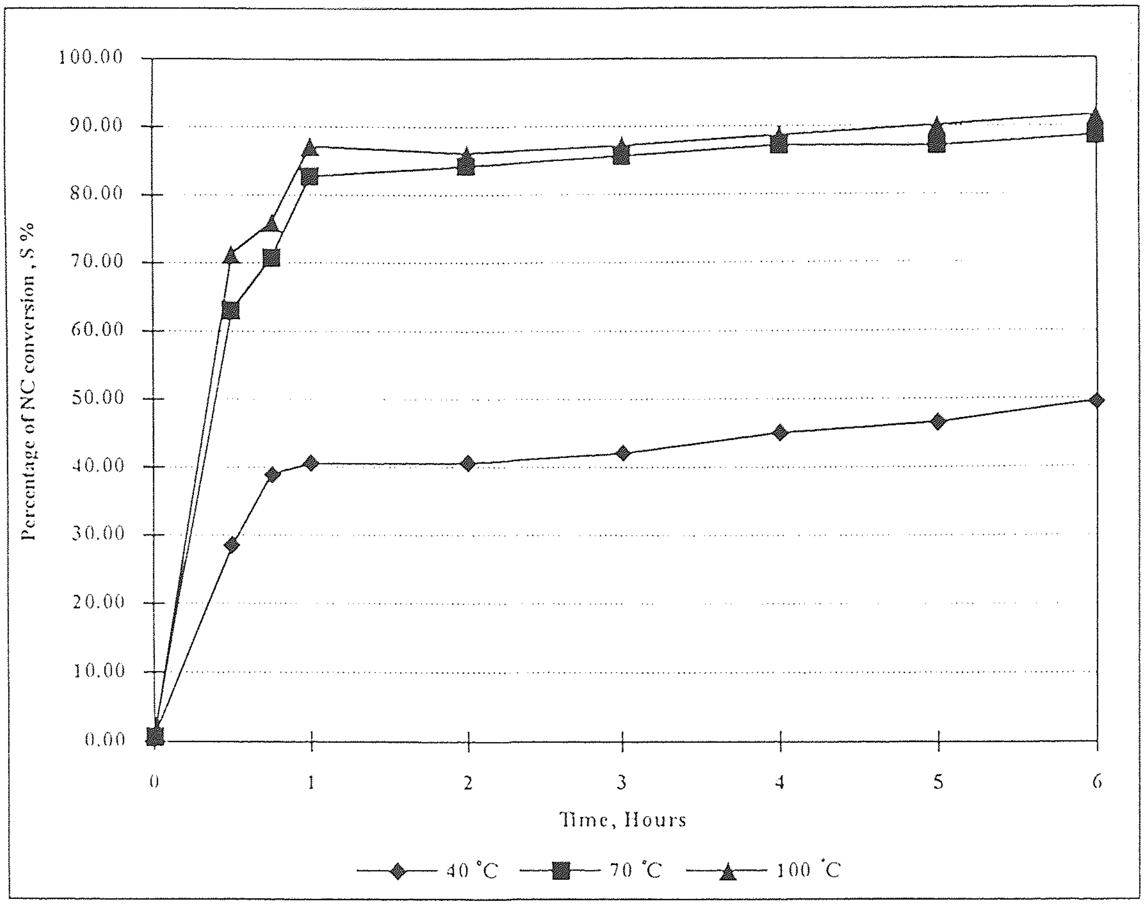

Figure 30 Effect of Temperature for 38% HCl in Two Stage System(1st Stage 60mins)

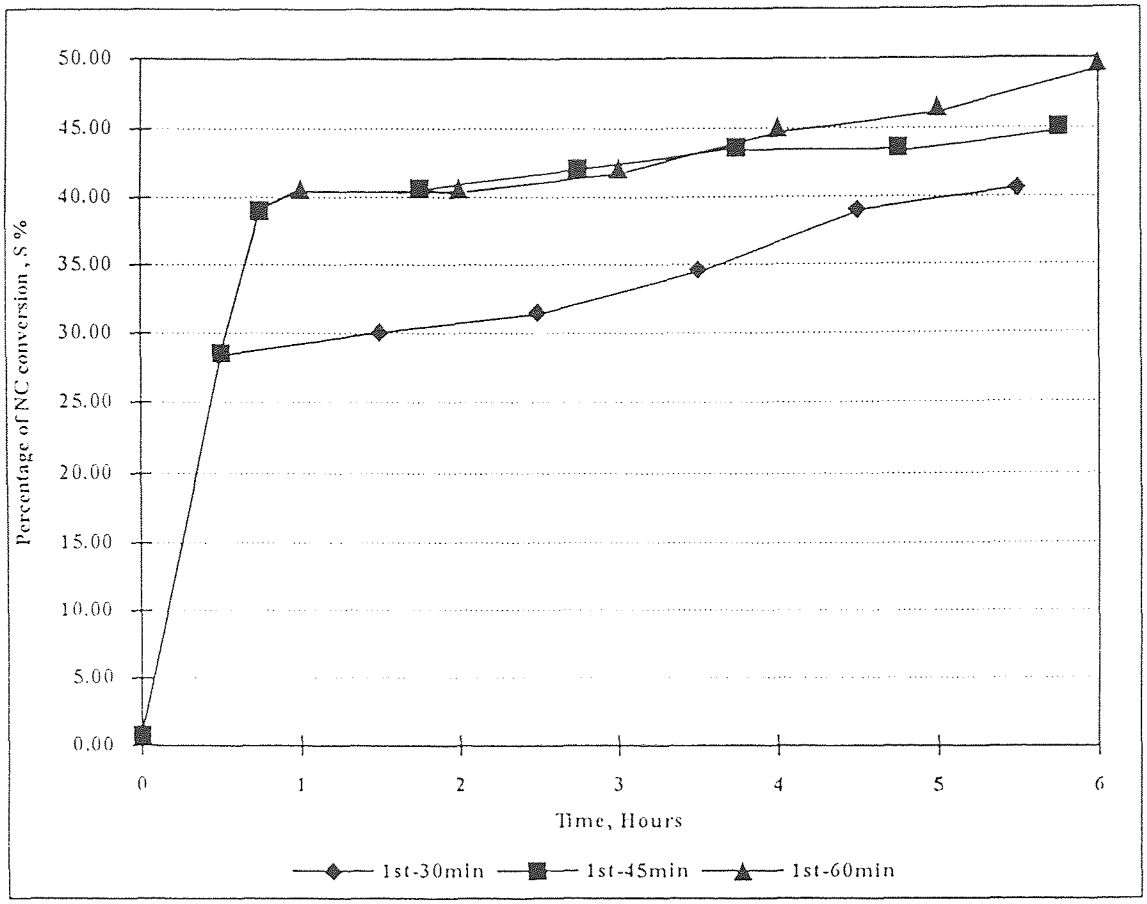

Figure 31 Effect of Reaction Time for 38% HCl, at 40 °C in Two Stage System

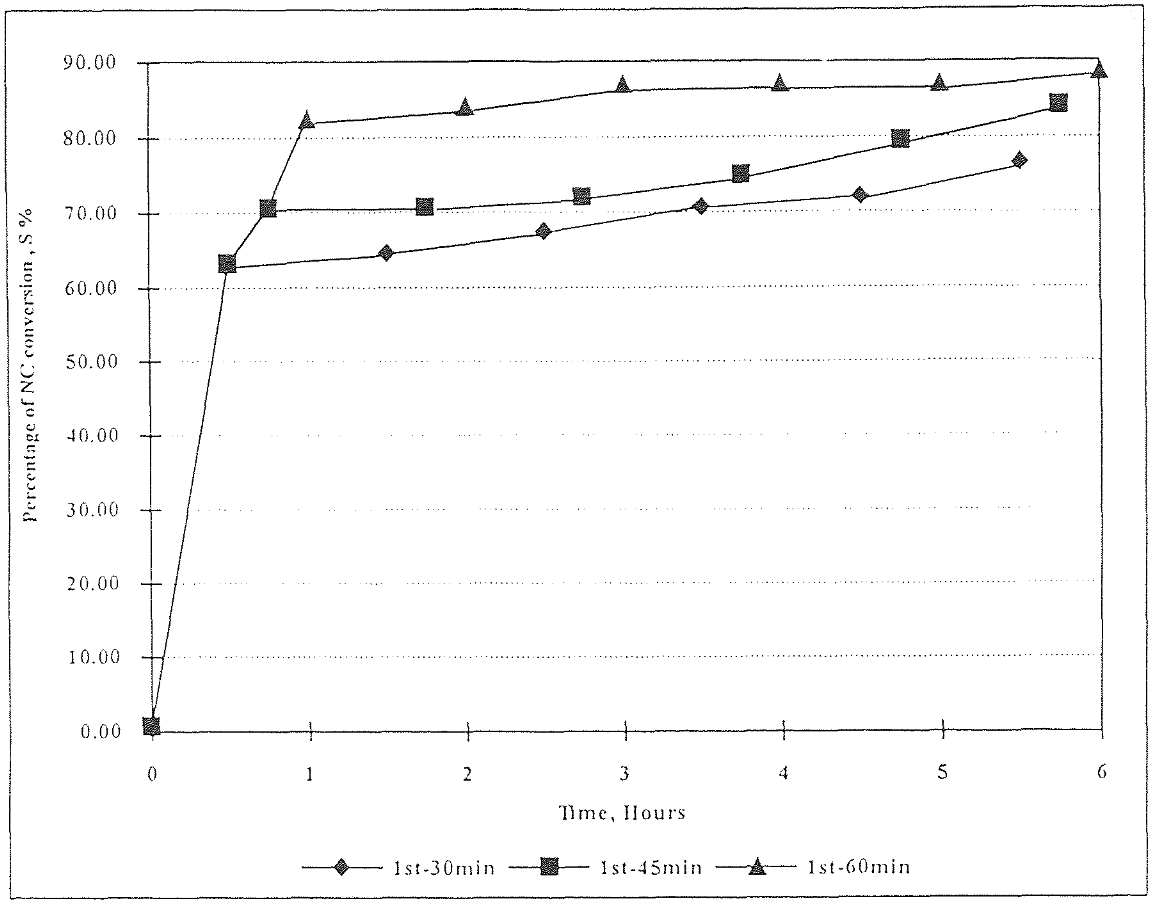

Figure 32 Effect of Reaction Time for 38% HCl, at 70 °C in Two Stage System

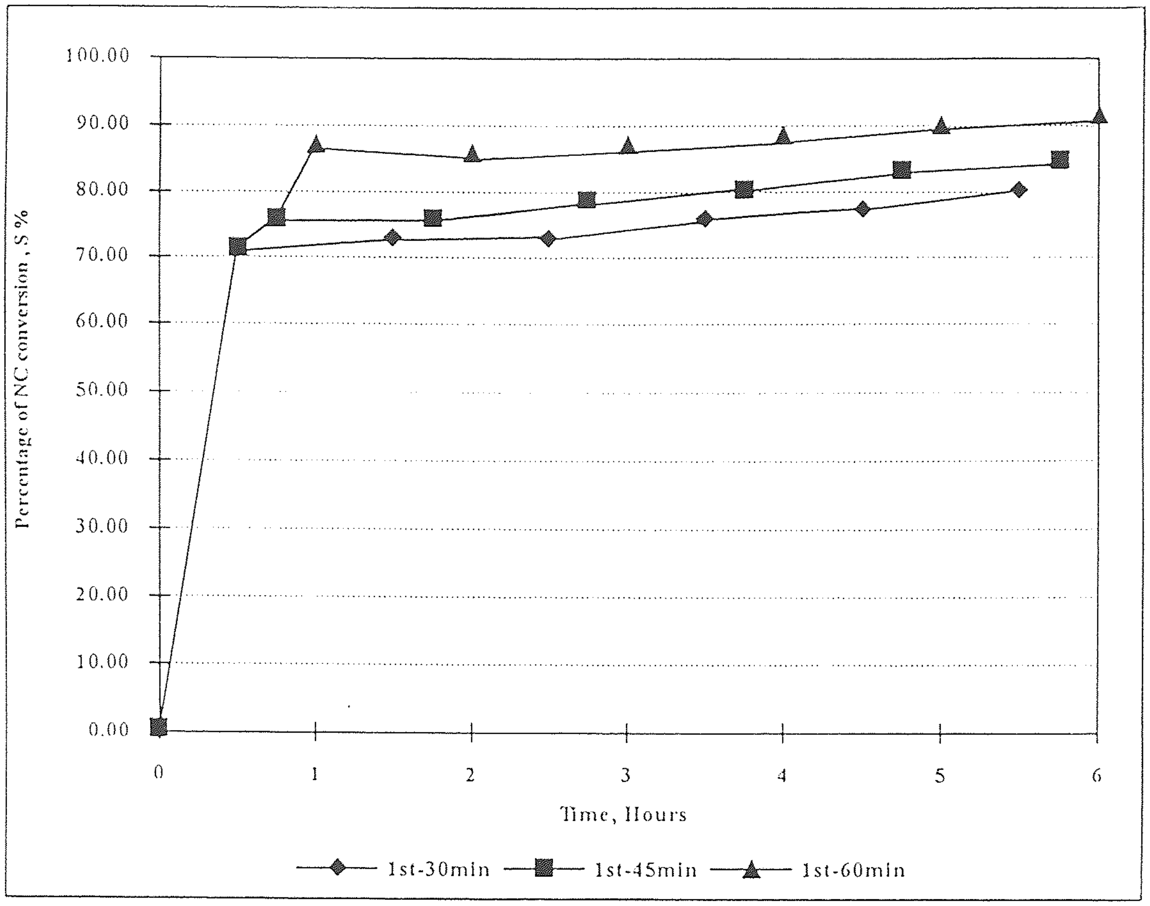

Figure 33 Effect of Reaction Time for 38% HCl, at 100 °C in Two Stage System

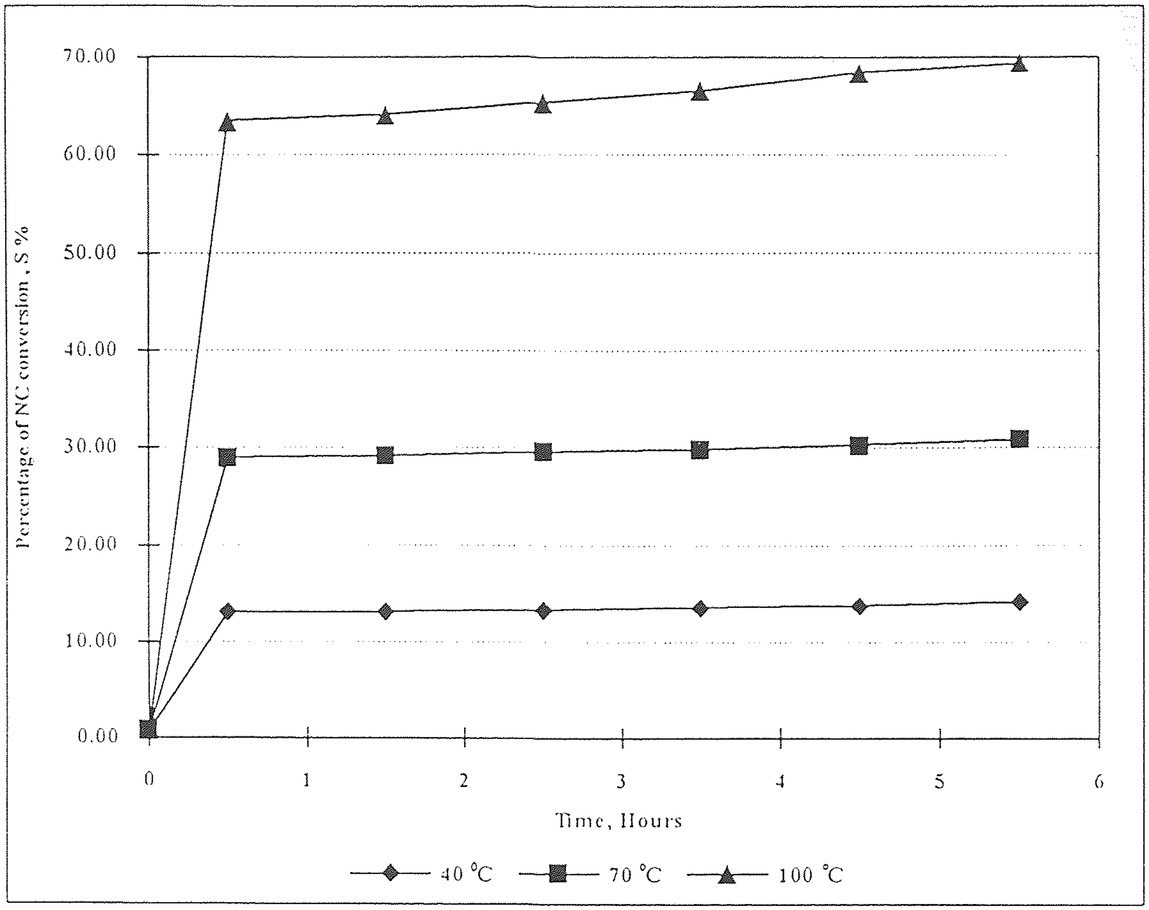

Figure 34 Effect of Temperature for 10N H_2SO_4 in Two Stage System (1st stage 30 mins)

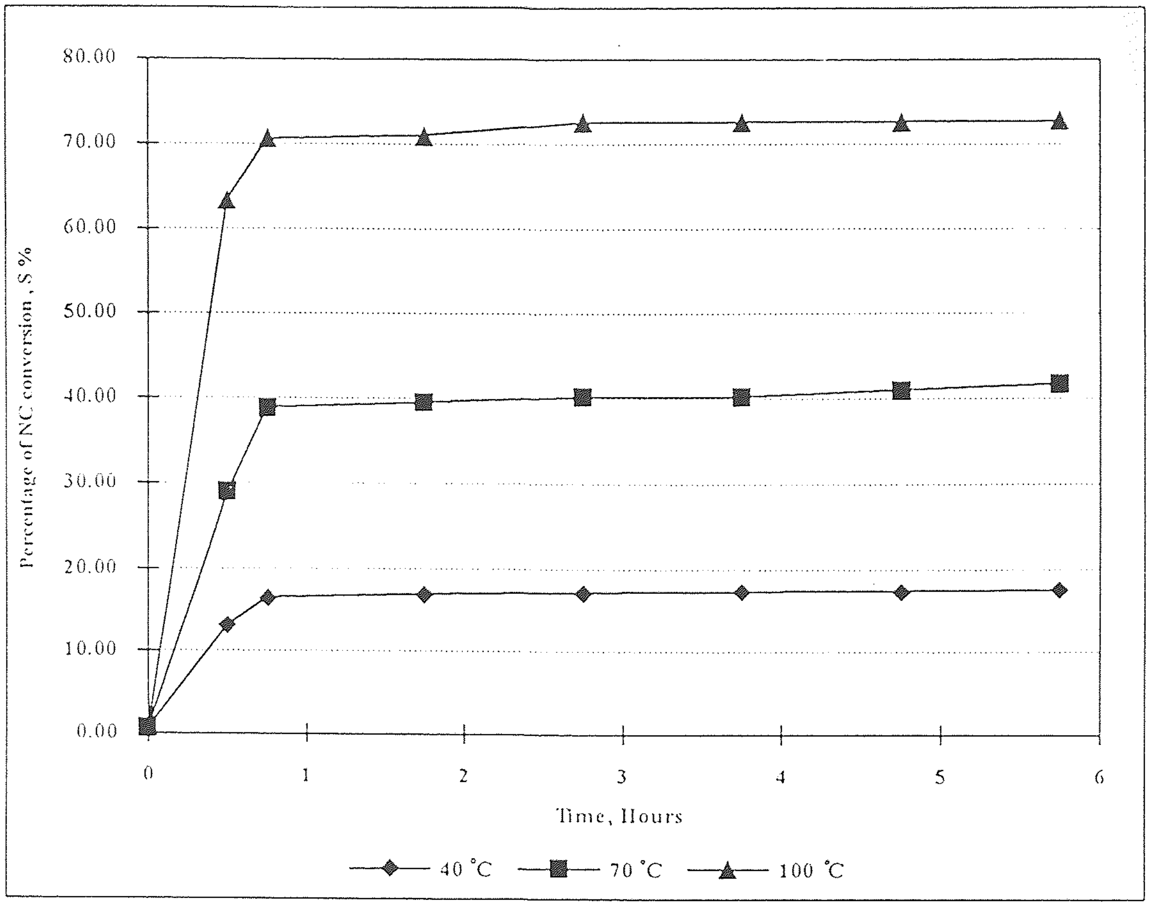

Figure 35 Effect of Temperature for 10N H_2SO_4 in Two Stage System (1st stage 45 mins)

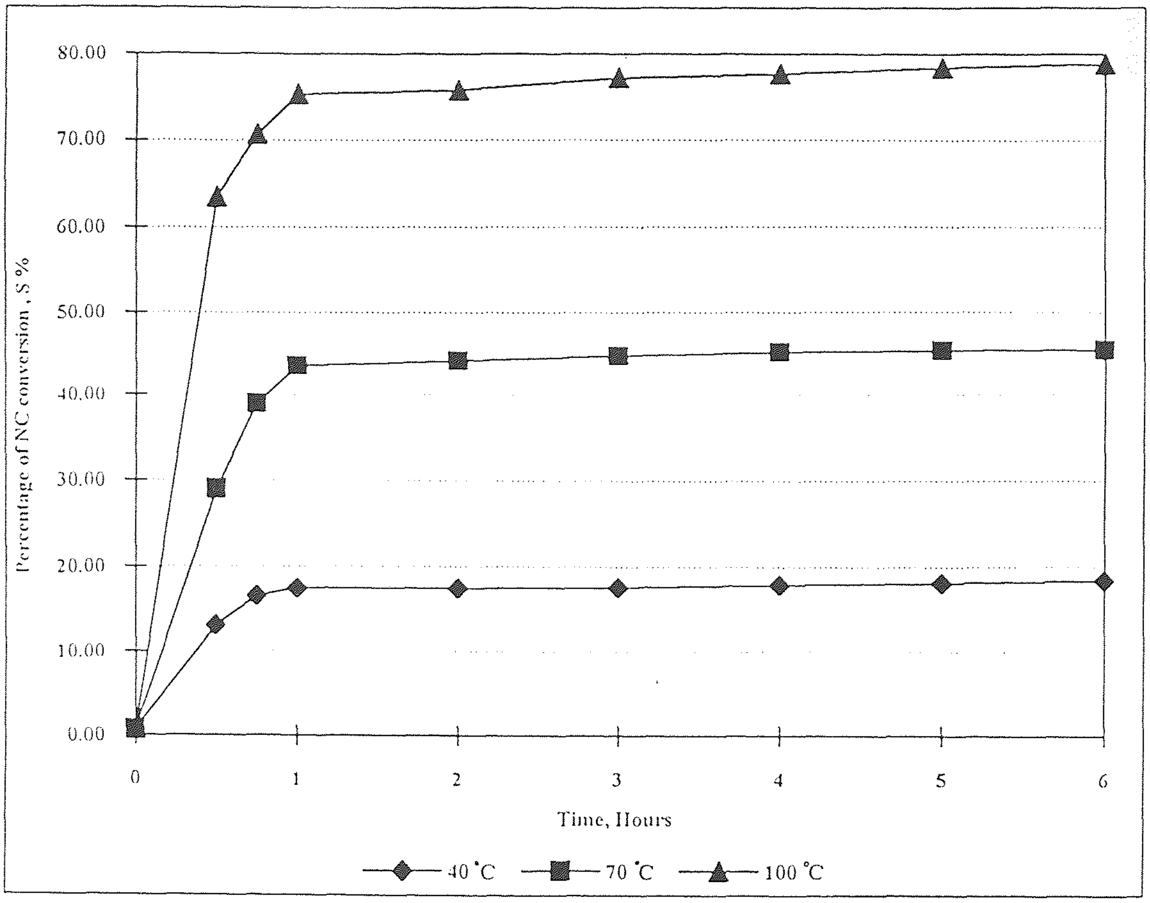

Figure 36 Effect of Temperature for 10N H_2SO_4 in Two Stage System (1st stage 60 mins)

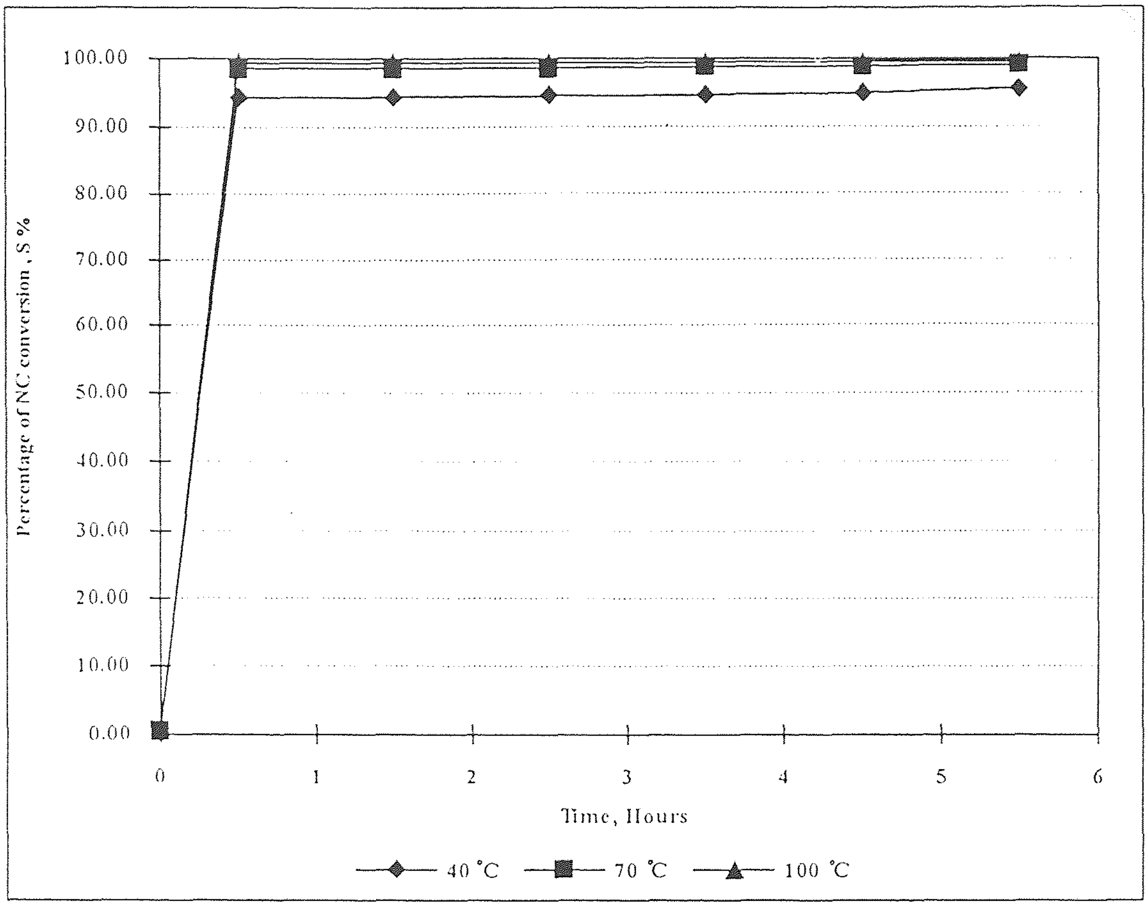

Figure 37 Effect of Temperature for 18N H_2SO_4 in Two Stage System (1st stage 30 mins)

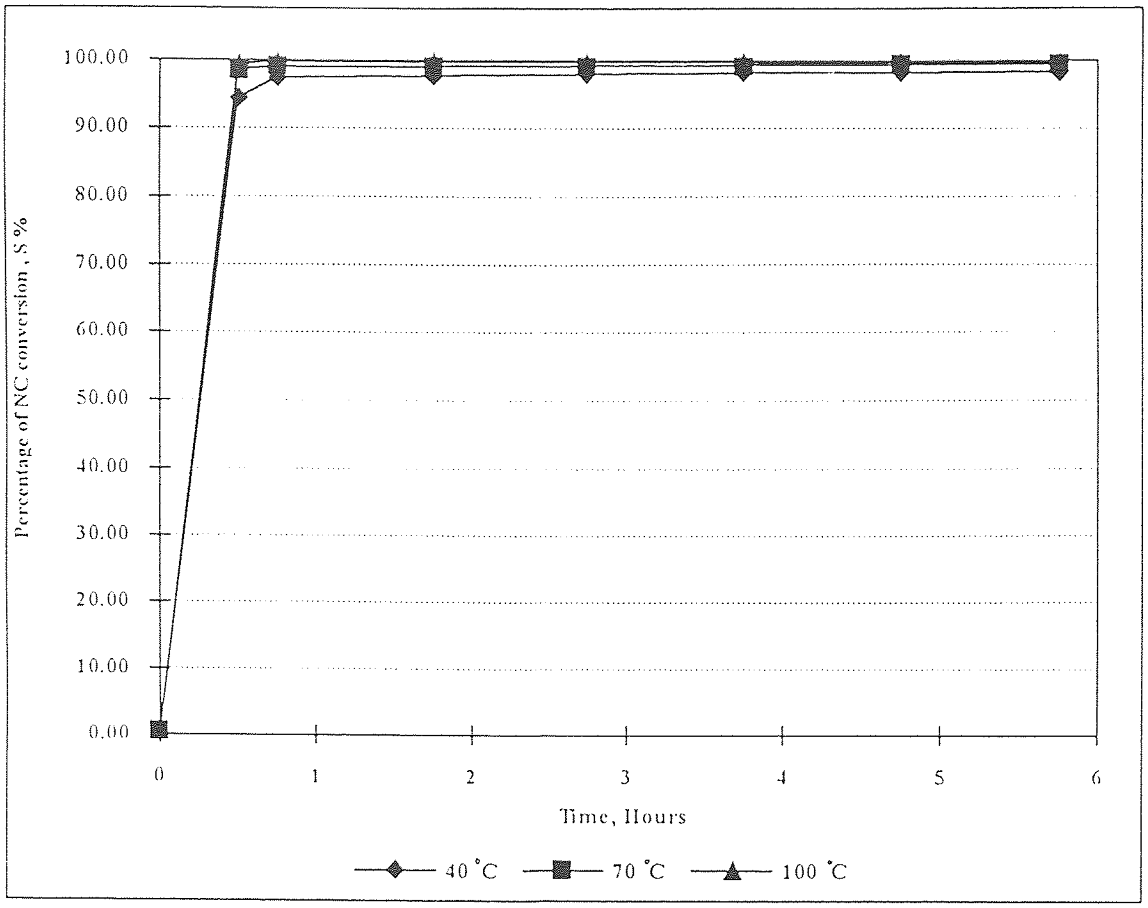

Figure 38 Effect of Temperature for 18N H_2SO_4 in Two Stage System (1st stage 45 mins)

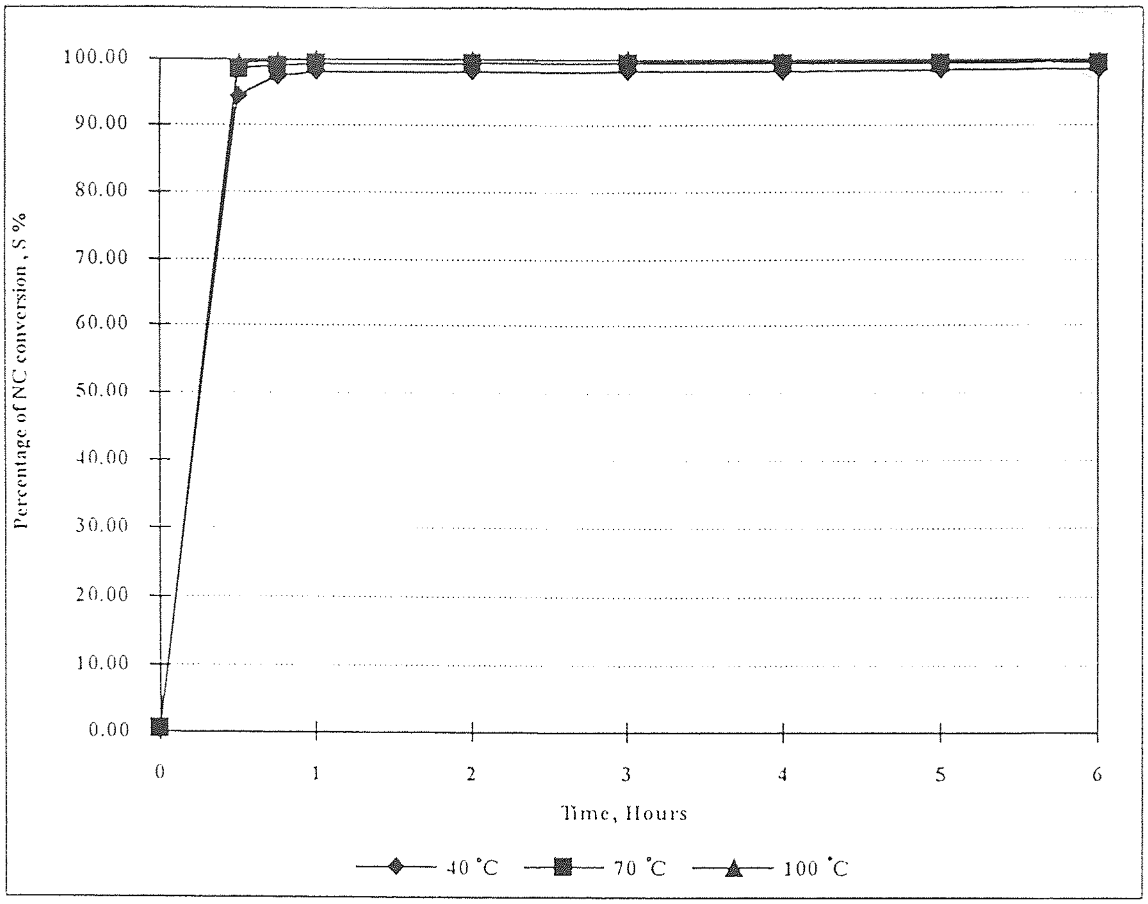

Figure 39 Effect of Temperature for 18N H_2SO_4 in Two Stage System (1st stage 60 mins)

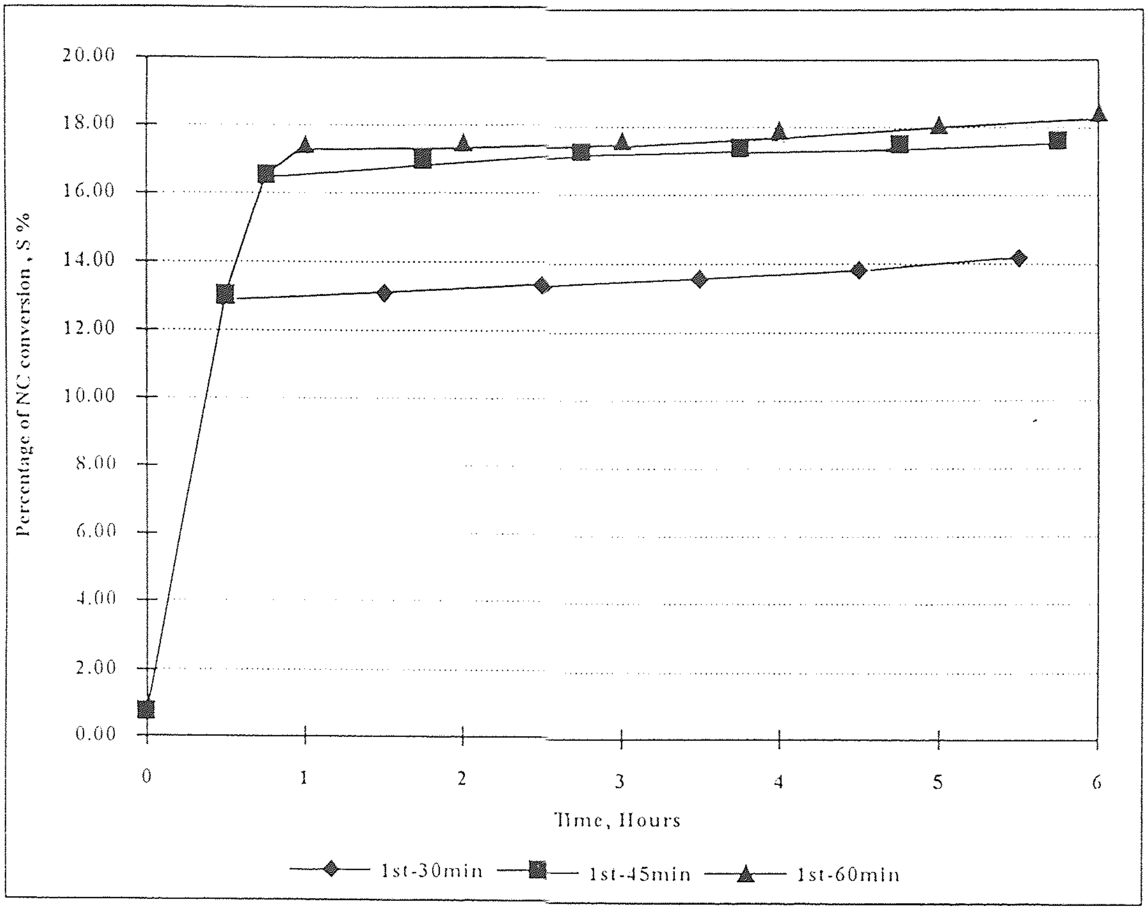

Figure 40 Effect of Reaction Time for 10N H_2SO_4 at 40 °C in Two Stage System

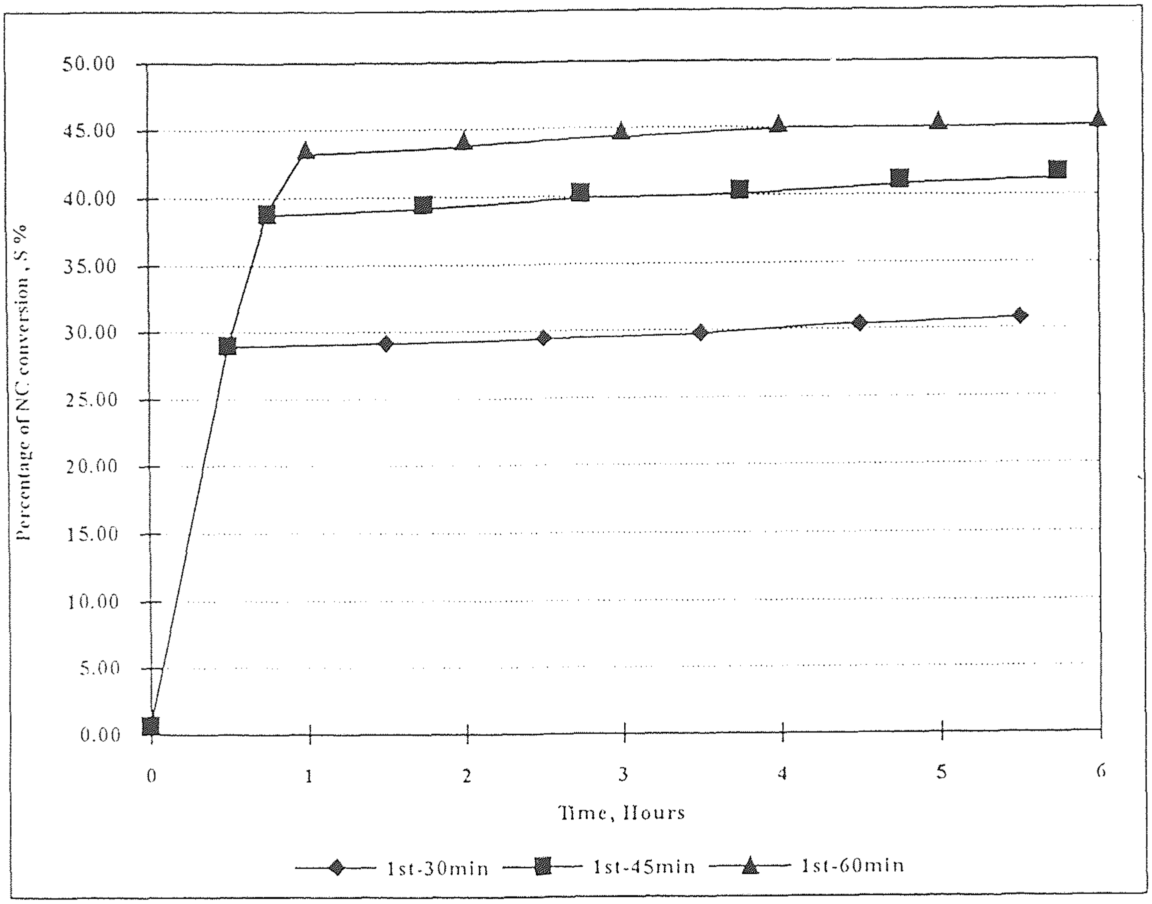

Figure 41 Effect of Reaction Time for 10N H_2SO_4 at 70 °C in Two Stage System

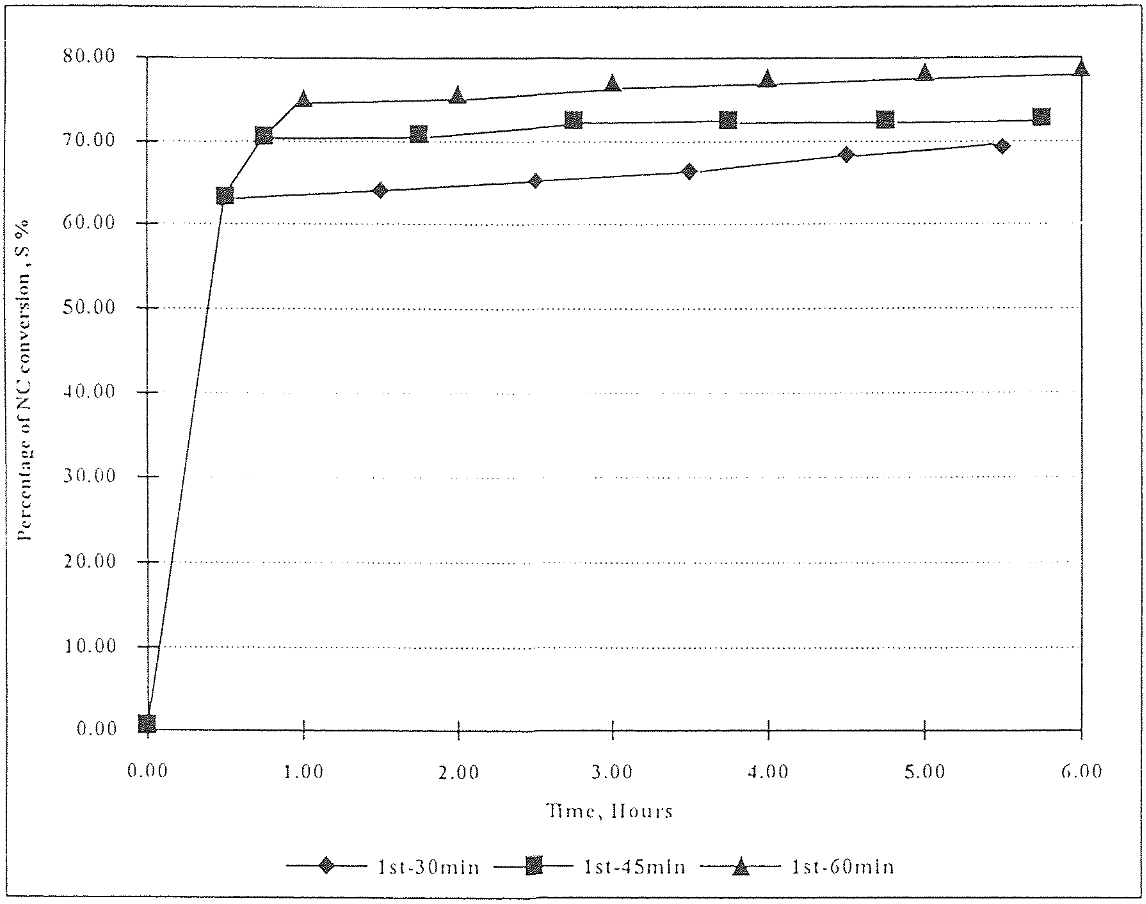

Figure 42 Effect of Reaction Time for 10N H_2SO_4 at 100 °C in Two Stage System

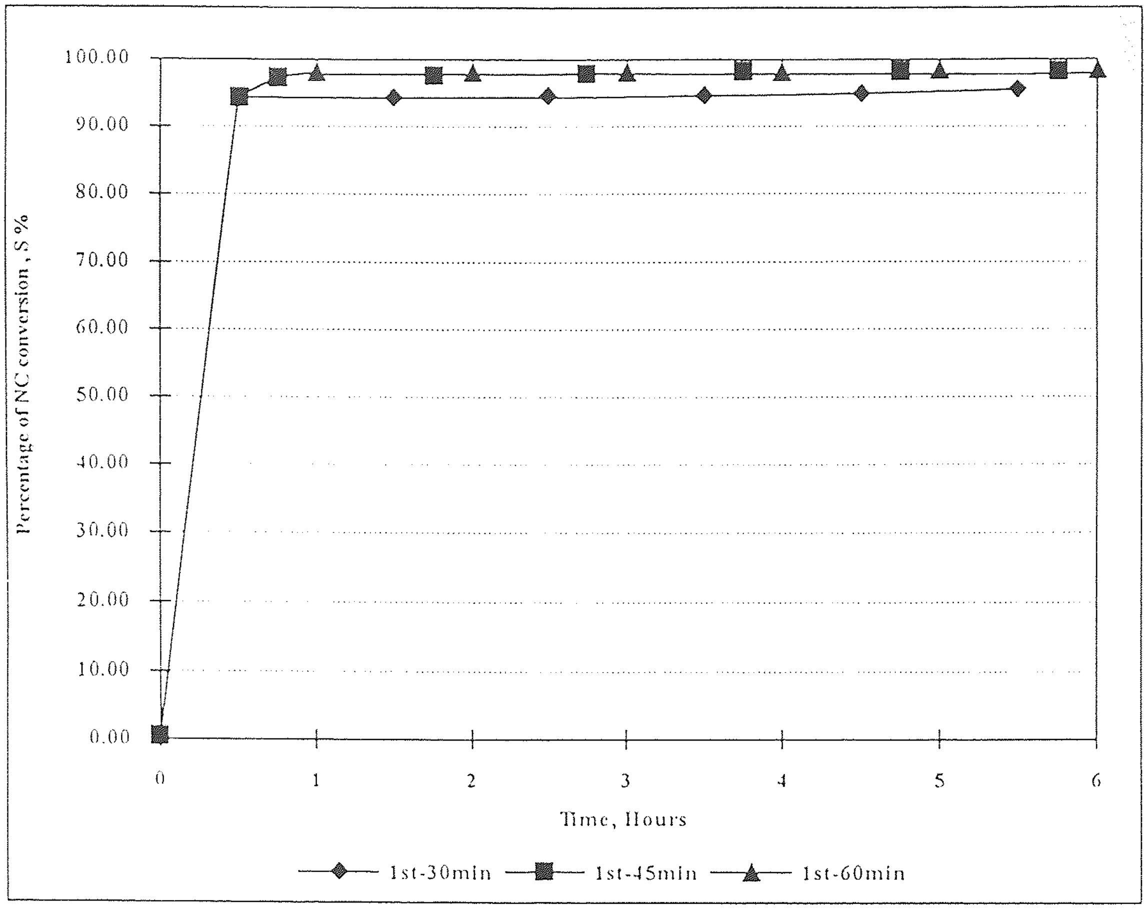

Figure 43 Effect of Reaction Time for 18 N H_2SO_4 at 40 °C in Two Stage System

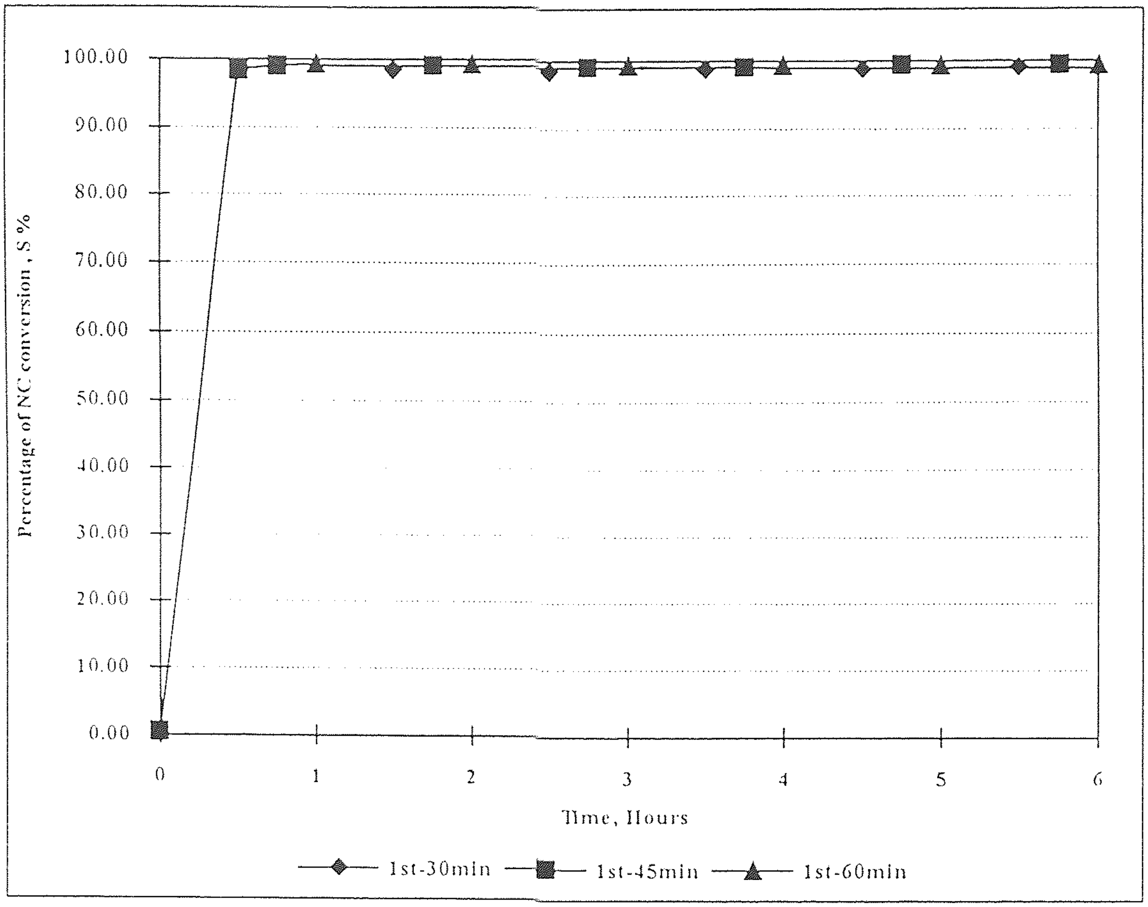

Figure 44 Effect of Reaction Time for 18N H_2SO_4 at 70 °C in Two Stage System

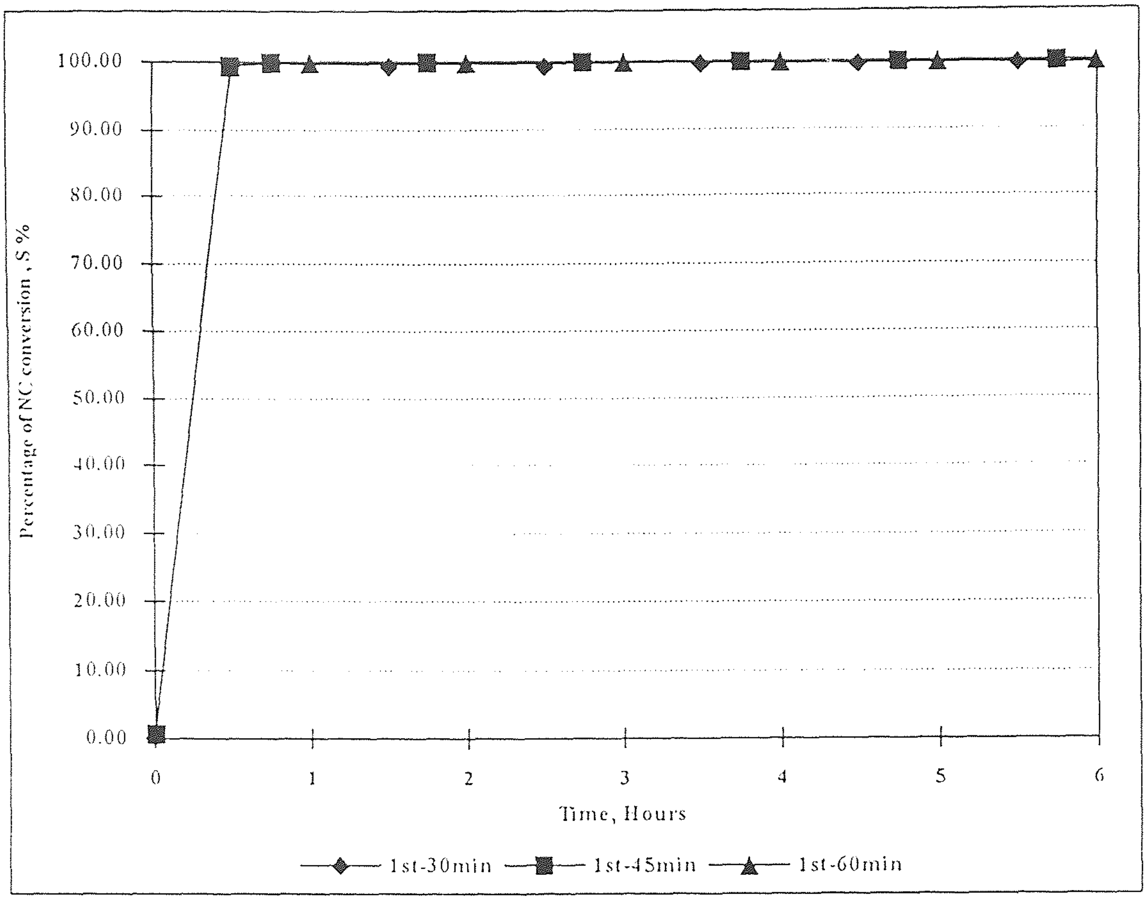

Figure 45 Effect of Reaction Time for 18N H_2SO_4 at 100 °C in Two Stage System

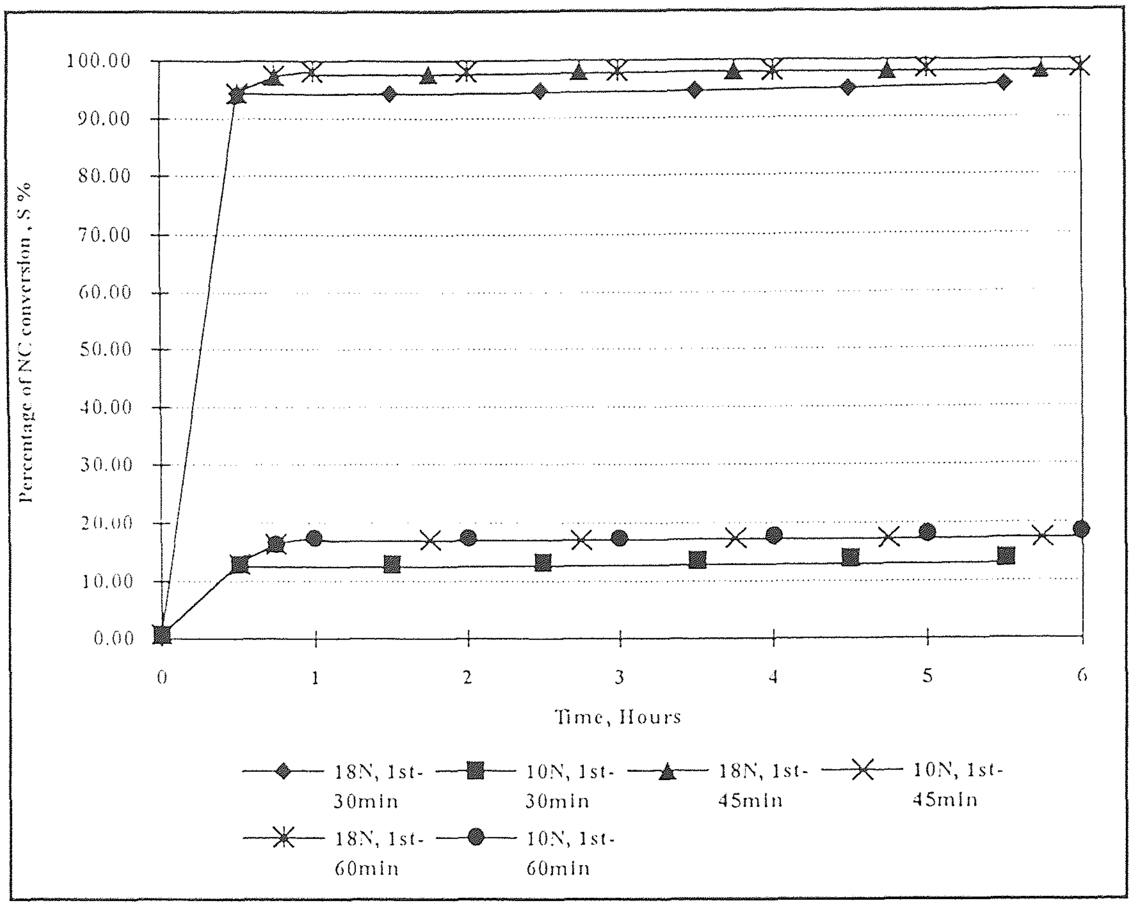

Figure 46 Effect of H_2SO_4 Concentration & Reaction Time at 40 °C in Two Stage System

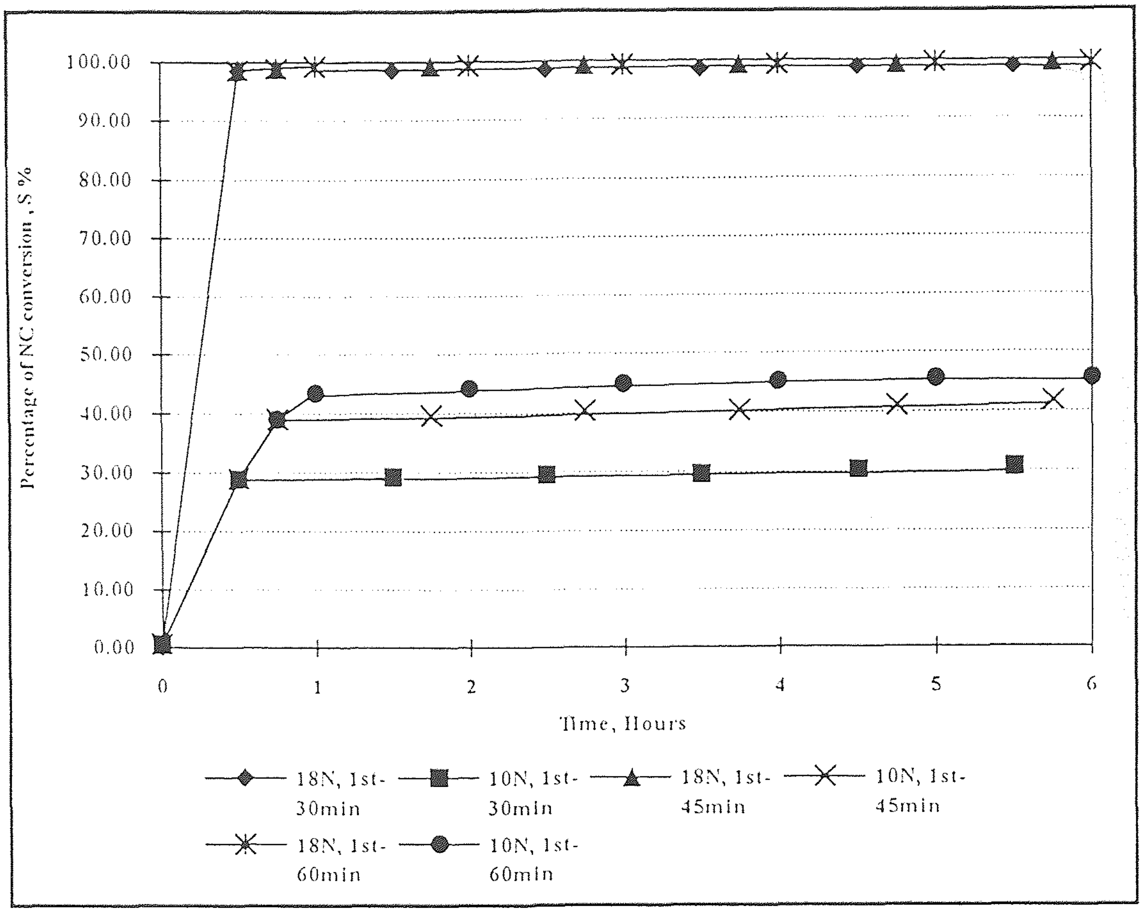

Figure 47 Effect of H_2SO_4 Concentration & Reaction Time at 70 °C in Two Stage System

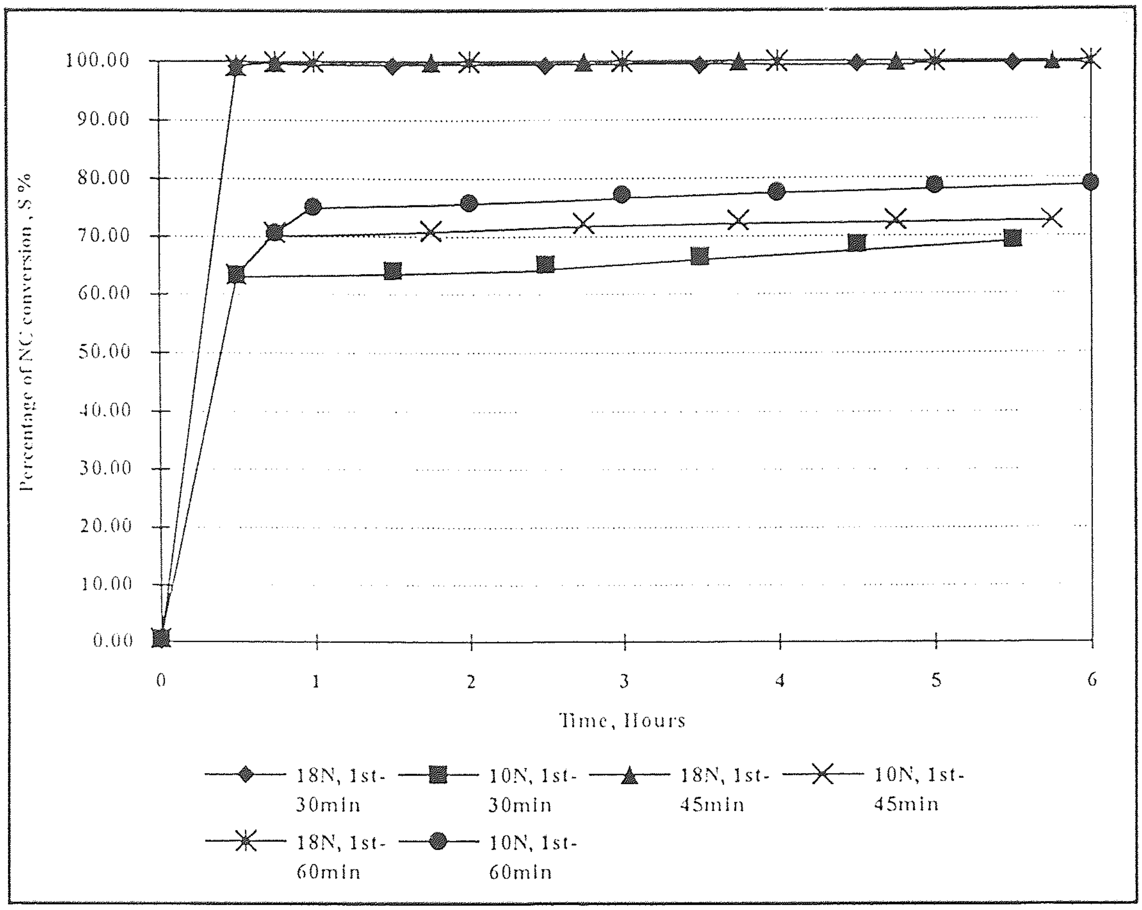

Figure 48 Effect of H_2SO_4 Concentration & Reaction Time at 100 °C in Two Stage System

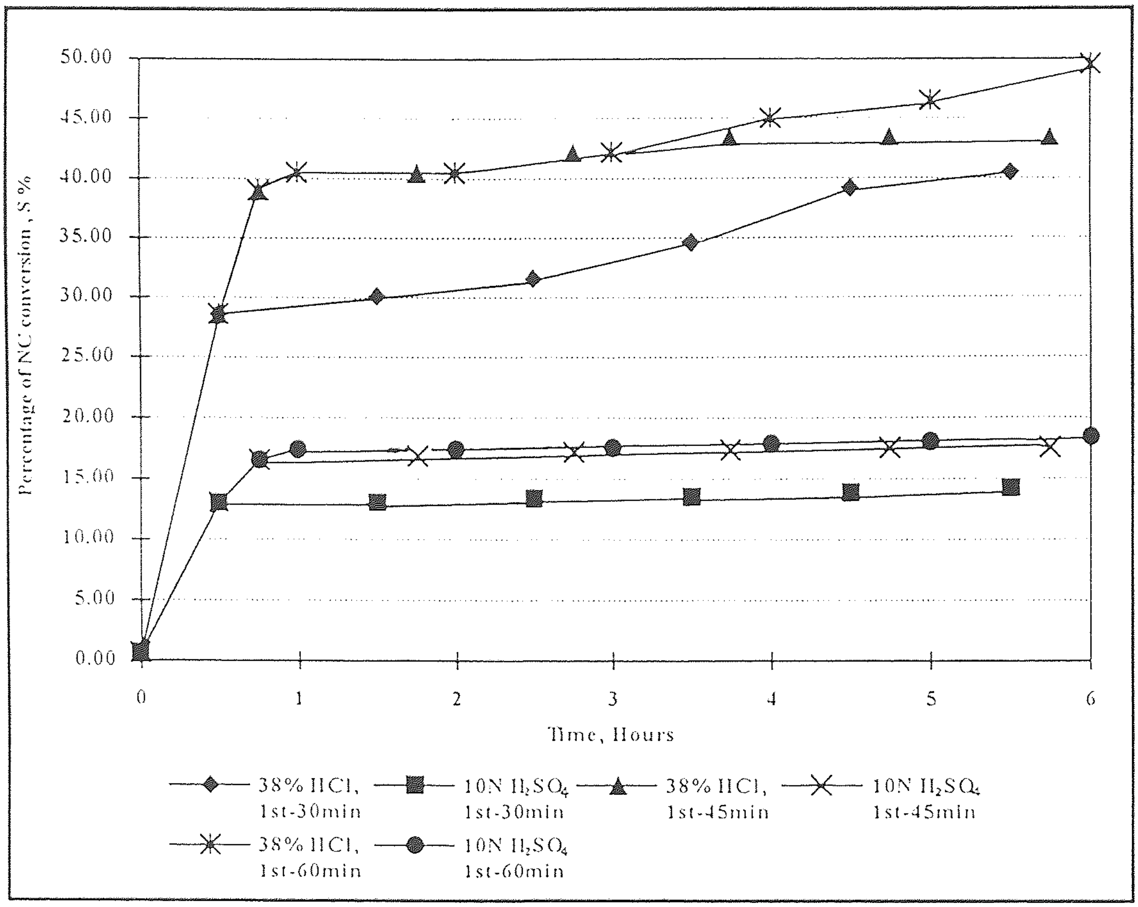

Figure 49 Effect of Different Acid & Reaction Time at 40 °C in Two Stage System

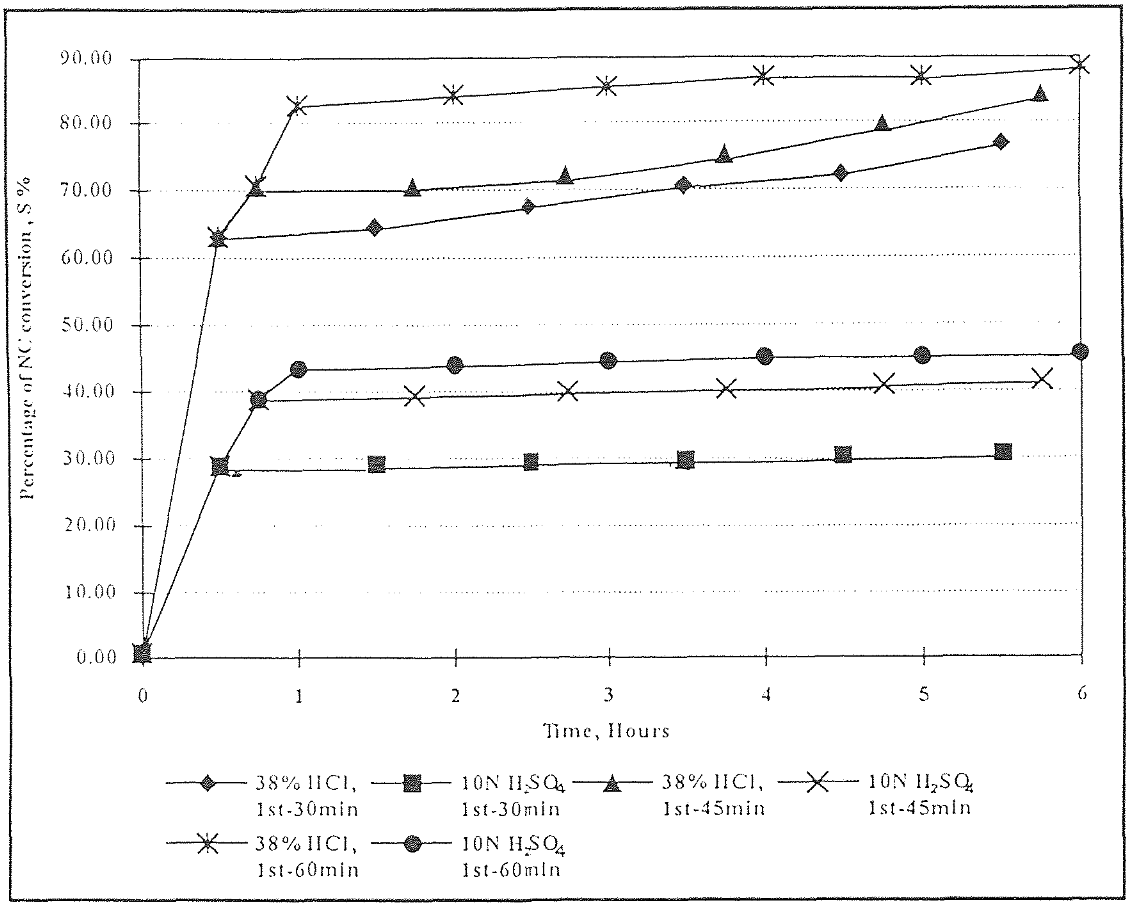

Figure 50 Effect of Different Acid & Reaction Time at 70 °C in Two Stage System

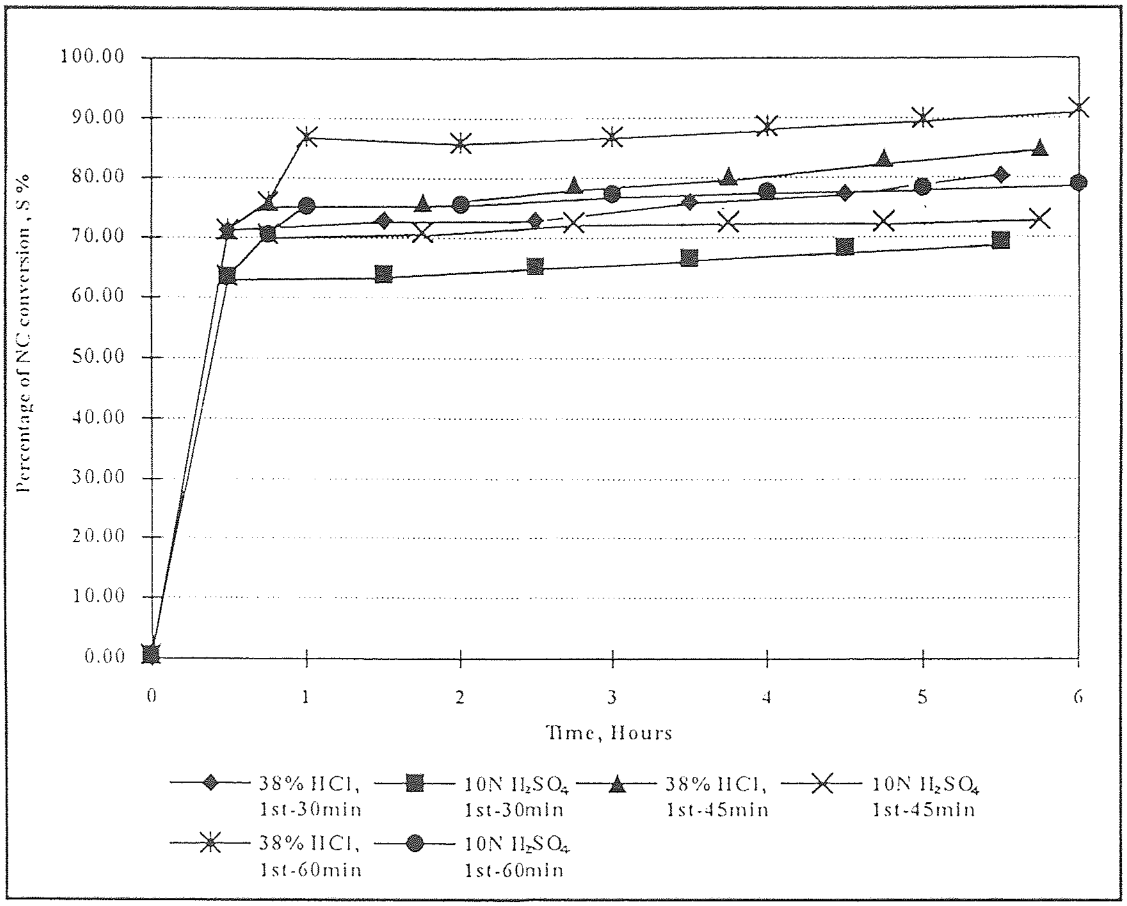

Figure 51 Effect of Different Acid & Reaction Time at 100 °C in Two Stage System

APPENDIX B

EXPERIMENTAL DATA FOR ACID HYDROLYSIS SYSTEMS

This appendix tabulates the experimental data for the results in both single and two-stage hydrolysis systems. For the single-stage hydrolysis systems, the effects of acid concentration, reaction temperature, and reaction time on dissolved COD of nitrocellulose are shown in Table 16 to Table 26. For the two-stage hydrolysis systems, these effects are shown in Table 27 to Table 35.

Table 16 Relationship of Soluble COD and Total COD in 19 % HCl Hydrolysis at 70 °C

Reaction Time (min)	Filtration		Non-filtration	
	COD (mg/L)	S %	COD (mg/L)	S %
30	400	0.75	3600	6.77
60	5200	9.77	8400	15.85
90	9200	17.30	10800	20.38
120	15424	28.99	17024	32.00

Table 17 Relationship of Soluble COD and Total COD in 38 % HCl Hydrolysis at 70 °C

Reaction Time (min)	Filtration		Non-filtration	
	COD (mg/L)	S %	COD (mg/L)	S %
30	30400	57.14	33600	63.40
60	42400	79.70	44000	82.71
90	46400	87.22	46400	87.22
120	52800	99.63	52800	99.63

Table 18 Relationship of Soluble COD and Total COD in10 N H_2SO_4Hydrolysis at 70 °C

Reaction Time (min)	Filtration		Non-filtration	
	COD (mg/L)	S %	COD (mg/L)	S %
30	11440	21.50	15440	29.02
60	20720	38.95	23200	43.61
90	22880	43.01	25520	47.96
120	25520	47.97	27400	51.50

Table 19 Relationship of Soluble COD and Total COD in18 N H_2SO_4 Hydrolysis at 70 °C

Reaction Time (min)	Filtration		Non-filtration	
	COD (mg/L)	S %	COD (mg/L)	S %
30	52480	98.50	52480	98.50
60	52880	99.40	52880	99.40
90	53120	99.70	53120	99.70
120	53200	99.85	53200	99.85

Table 20 Relationship of Soluble COD and Total COD in 38 N H_2SO_4 Hydrolysis at 70°C

Reaction Time (min)	Filtration		Non-filtration	
	COD (mg/L)	S %	COD (mg/L)	S %
30	53200	99.85	53200	99.85
60	53200	99.85	53200	99.85
90	52960	99.39	52960	99.39
120	52880	99.25	52880	99.25

Table 21 Effect of HCl Concentration at 40 °C in Single Stage System

Conc. /	38 % HCl		19 % HCl	
Time (min)	COD (mg/L)	S %	COD (mg/L)	S %
15	10800	20.38	400	0.75
30	15200	28.68	1200	2.26
45	20800	39.24	2000	3.76
60	21600	40.75	3600	6.77
75	23200	43.77	5200	9.77
90	24800	46.79	6800	12.78
105	26800	50.57	7600	14.28
120	26800	50.57	8000	15.04

Table 22 Effect of HCl Concentration at 70 °C in Single Stage System

Conc. /	38 % HCl		19 % HCl	
Time (min)	COD (mg/L)	S %	COD (mg/L)	S %
15	19600	36.84	2000	3.76
30	33600	63.40	3600	6.77
45	37600	70.67	6800	12.83
60	44000	82.71	8400	15.85
75	45600	85.71	8400	15.85
90	46400	87.22	10800	20.38
105	48000	90.23	13200	24.91
120	52800	99.63	17024	32.00

Table 23 Effect of HCl Concentration at 100 °C in Single Stage System

Conc. /	38 % HCl		19 % HCl	
Time (min)	COD (mg/L)	S %	COD (mg/L)	S %
15	22000	41.51	10800	20.38
30	38000	71.70	22800	43.02
45	40400	76.23	29200	55.10
60	46400	87.55	38000	71.69
75	51600	97.36	38800	73.21
90	52400	98.87	39600	74.72
105	53200	100.00	40400	76.23
120	52400	98.87	41200	77.73

Table 24 Effect of H_2SO_4 Concentration at 40 °C in Single Stage System

Conc. /	36 N H_2SO_4		18 N H_2SO_4		10 N H_2SO_4	
Time (min)	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
15	52400	98.87	49840	94.04	2080	3.93
30	52480	99.02	50240	94.79	6960	13.13
45	53200	99.85	51840	97.81	8800	16.60
60	53200	99.85	52240	98.57	9280	17.51
75	53280	100.00	52400	98.87	10720	20.23
90	53120	99.70	52480	99.02	13600	25.66
105	53120	99.70	52480	99.02	20240	38.05
120	53040	99.85	52720	99.47	51240	39.92

Table 25 Effect of H_2SO_4 Concentration at 70 °C in Single Stage System

Conc. /	36 N H_2SO_4		18 N H_2SO_4		10 N H_2SO_4	
Time (min)	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
15	53120	99.70	52080	97.74	10640	20.00
30	53200	99.85	52480	98.50	15440	29.02
45	53200	99.85	52720	99.10	20720	38.95
60	53200	99.85	52880	99.40	23200	43.61
75	53040	99.55	52880	99.40	24960	46.92
90	52960	99.40	53120	99.70	25520	47.96
105	52960	99.40	53200	99.85	27080	50.90
120	52880	99.25	53200	99.85	27400	51.50

Table 26 Effect of H_2SO_4 Concentration at 100 °C in Single Stage System

Conc. /	36 N H_2SO_4		18 N H_2SO_4		10 N H_2SO_4	
Time (min)	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
15	53200	99.85	52800	99.25	19680	36.99
30	53200	99.85	52880	99.40	33760	63.46
45	53040	99.69	53120	99.85	37600	70.68
60	52960	99.55	53200	99.85	40080	75.34
75	52400	98.49	53120	99.85	43640	87.03
90	52400	98.49	53040	99.69	48400	90.98
105	52320	98.35	52960	99.55	51600	96.99
120	52320	98.35	52960	99.55	51680	97.14

Table 27 Effect of Reaction Time at 40 °C in Two Stage System by 38 % HCl

first-time / Time (hr)	30 min		45 min		60 min	
	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
0	15200	28.57	20800	39.09	21600	40.60
1	16000	30.07	21600	4060	21600	40.60
2	16800	31.58	22400	42.11	22400	42.11
3	18400	34.59	23200	43.61	24000	45.11
4	20800	39.10	23200	43.61	24800	46.62
5	21600	40.60	24000	45.11	26400	49.62

Table 28 Effect of Reaction Time at 70 °C in Two Stage System by 38 % HCl

First-time Time (hr)	30 min		45 min		60 min	
	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
0	33600	63.16	37600	70.68	44000	82.71
1	34400	64.66	37600	70.68	44800	84.21
2	36000	67.67	38400	72.18	45600	85.71
3	37600	70.68	40000	75.19	46400	87.22
4	38400	72.18	42400	79.70	46400	87.22
5	40800	76.69	44800	84.21	47200	88.72

Table 29 Effect of Reaction Time at 100 °C in Two Stage System by 38 % HCl

First-time Time (hr)	30 min		45 min		60 min	
	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
0	38000	71.43	40400	75.94	46400	87.22
1	38800	72.93	40400	75.94	45800	86.10
2	38800	72.93	42000	78.95	46400	87.22
3	40400	75.94	42800	80.45	47200	88.72
4	41200	77.44	44400	83.46	48000	90.22
5	42800	80.45	45200	84.96	48800	91.73

Table 30 Effect of Reaction Time at 40 °C in Two Stage System by10 N H_2SO_4

first-time /	30 min		45 min		60 min	
Time (hr)	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
0	6960	13.08	8800	16.54	9280	17.44
1	6984	13.13	9040	16.99	9304	17.49
2	7104	13.35	9184	17.26	9368	17.61
3	7232	13.59	9248	17.38	9528	17.91
4	7360	13.83	9320	17.52	9624	18.10
5	7552	14.16	9384	17.64	9816	18.45

Table 31 Effect of Reaction Time at 70 °C in Two Stage System by 10 N H_2SO_4

First-time	30 min		45 min		60 min	
Time (hr)	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
0	15440	29.02	20720	38.95	23200	43.61
1	15536	29.20	21024	39.52	23520	44.21
2	15728	29.56	21384	40.42	23840	44.81
3	15880	29.84	21448	40.32	24080	45.26
4	16128	30.32	21872	41.11	24144	45.38
5	16368	30.77	22224	41.78	24240	45.56

Table 32 Effect of Reaction Time at 100 °C in Two Stage System by 10N H_2SO_4

First-time	30 min		45 min		60 min	
Time (hr)	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
0	33760	63.46	37600	70.68	40080	75.34
1	34080	64.06	37840	71.13	40320	75.79
2	34744	65.31	38624	72.60	41084	77.22
3	35384	66.51	38688	72.72	41344	77.71
4	36424	68.47	38712	72.77	41748	78.47
5	36904	69.37	38752	72.84	41960	78.87

Table 33 Effect of Reaction Time at 40 °C in Two Stage System by18 N H_2SO_4

first-time /	30 min		45 min		60 min	
Time (hr)	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
0	50240	94.44	51840	97.44	52240	98.19
1	50264	94.48	82032	97.81	52236	98.18
2	50328	94.60	52184	98.09	52248	98.21
3	50408	94.75	52248	98.21	52280	98.27
4	50544	95.00	52288	98.29	52416	98.53
5	50944	95.76	52336	98.39	52464	98.62

Table 34 Effect of Reaction Time at 70 °C in Two Stage System by 18 N H_2SO_4

First-time	30 min		45 min		60 min	
Time (hr)	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
0	52480	98.65	52720	99.09	52880	99.39
1	52480	98.65	52768	99.19	52896	99.43
2	52480	98.65	52832	99.31	52904	99.44
3	52560	98.80	52856	99.35	52928	99.49
4	52624	98.92	52904	99.45	52936	99.50
5	52704	99.07	52960	99.55	52984	99.59

Table 35 Effect of Reaction Time at 100 °C in Two Stage System by 18N H_2SO_4

First-time	30 min		45 min		60 min	
Time (hr)	COD (mg/L)	S %	COD (mg/L)	S %	COD (mg/L)	S %
0	52880	99.38	53120	99.85	53200	100.00
1	52888	99.40	53128	99.87	53200	100.00
2	52888	99.40	53128	99.87	53200	100.00
3	52928	99.48	53128	99.87	53168	99.94
4	52952	99.53	83136	99.88	53160	99.92
5	53016	99.65	53168	99.94	53136	99.88

REFERENCES

1. Metcalf & Eddy Inc., *Wastewater Engineering : Treatment, Disposal, Reuse.*, Second Edition, McGraw Hills, New York, NY, 1979.

2. Mitchell, P., *Introduction to Environmental Microbiology*, Third Edition, Happer & Row, Publishers, New York, NY, 1974.

3. Lee, Y. H. and L. T. Fan, " Kinetic Studies of Enzymatic Hydrolysis of Insoluble Cellulose : Analysis of the Initial Rates, " *Biotechnology & Bioengineering*, Vol. 24, No.2, pp 2383 - 2406, July 1983.

4. Ott, E., M. S. Harold and M. W. Grafflin, *Cellulose and Cellulose Derivatives*, First Edition, Interscience Publishers. Inc., New York, NY, 1954.

5. Khamis, A. A., " The Effect of Ultrasound on the Hydrolysis of Carbohydrates, " Ph.D. Thesis, New Jersey Institute of Technology, 1983.

6. Browning, B. L., *Methods of Wood Chemistry*, First Edition , John Willey & Sons Inc., New York, NY, 1967.

7. Gascoigene, J. A. and M. G. Margaret, *Biological Degradation of Cellulose*, Butterworth & Co., London, England, 1960.

8. Grethlein, H. E., " Comparison of the Economics of Acid and Enzymatic Hydrolysis of Mewsprint, " *Biothchnology & Bioengineering*, Vol. 20, pp 503 - 525, June 1978.

9. Sudhi, R. M., " Chemical Solubilization of Particulate Organics as a Pretreatment Approach, " MS. Thesis, Iowa State University, 1992.

10. Goldstein, I. S., " An Improved Process for Converting Cellulose to Ethanol, " *Tappi Journal*, Vol. 75, pp 135 - 142, August 1992.

11. Goldstein, I. S., " The Hydrolysis of Wood, " *Tappi Journa*l, Vol. 63, No. 9, pp 141 - 143, September 1980.

12. Mphil, A. J. and A. Porteous, " A Review of Developments in the Acid Hydrolysis of Cellulose Wastes, " *IMechE*, Vol. 201, No. C2, pp 117 - 123, March 1987.

13. Saeman, J. F., " Hydrolysis of Cellulose and Decomposition of Sugars in Dilute Acid at High Temperature, " *Industrial & Engineering Chemistry*, Vol. 37, No. 2, pp 43 - 52, May 1945.

REFERENCES
(Continued)

14. Leslie, C. P., " Biodegradation : Its Measurement and Microbiological Basis, " *Biotechnology and Bioengineering*, Vol. 27, pp 660 - 674, 1985.

15. McClelland, R. A. and K. Lam, " Kinetics and Mechanism of the Acid Hydrolysis, " *American Chemical Society*, Vol. 107, No. 18, pp 5182 - 5186, 1985.

16. Harris, E. E. and E. Beglinger, " Madison Wood Sugar Process, " *Industrial & Engineering Chemistry*, Vol. 38, No. 9, pp 890 - 895, September 1946.

17. Harris, E. E., E. Beglinger, G. J. Hajny, and E. C. Sherard, " Hydrolysis of Wood. Treatment with Sulphuric Acid in a Stationary Digester, " *Industrial & Engineering Chemistry*, Vol. 37, No. 1, pp 12 - 23, January 1945.

18. Fagan, R. D., H. E.,Grethlein, Converse, A. O., and A. Porteous, " Kinetics of Acid Hydrolysis of Cellulose Found in Paper Refuse, " *Environmental Science & Technology*, Vol. 5, No. 6, pp 545 - 547, June 1971.

19. Kennedy, J. F. and G. O. Phillips, *Cellulose and Cellulose Derivatives*, John Willey & Sons Inc., New York, NY, 1985.

20. Sawyer, M., *Chemistry for Environmental Engineering*, Springer-Verlag Inc., New York, NY, 1989.

21. Harris, J. F., Forest Products Laboratory, US Department of Agriculture. Medison, Wisconsin. 53705.

22. Timell, T. E., *Proceedings of the Eight Cellulose Conference I, Wood Chemicals - A Future Challenge*., John Willey & Sons Inc., New York, NY, 1975.

23. APHA, AWWA, and WPCF, *Stand Methods for the Examination of Water and Wastewater*, 17 th Edition, APHA, Washington D.C., 1989.

24. Arthur, J. C. and M. M. Gascoigne, *Cellulose Chemistry and Technology*, Second Edition, American Chemical Society, New York, NY, 1977.

25. Beall, G. and L. Jorgensen, " Hydrolysis of Cellulose in Dilute Sulfuric Acid, " *Textile Research Journal*, Vol. 21, No. 2, pp 203 - 209, May 1951.

REFERENCES
(Continued)

26. Zumdaahl, S. S., *Chemistry*, First Edition, Heath and Company, Washington D.C., 1986.

27. Sarko, *Proceedings of the Ninth Cellulose Conference, I. Wood Chemicals - A Furture Challenge*, John Willey & Sons Inc., New York, NY, 1983.