

A Study of the Heterogeneous Dilute Indigenous Carbonate Salt Hydrolysis of the Non-Woody Ligno-Cellulosic Plant Samples

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Abstract -The thermodynamic studies relating to the activated complex for the heterogeneous dilute indigenous carbonate salt hydrolysis of two non-woody ligno-cellulosic plant residues has been determined. The study was carried out on three indigenous basic salts; pH, percent concentration of CO_3^{2-} , and HCO_3^- and the degree of hydrolysis data are presented for three salt samples from Lake Magadi, Shores of Lake Victoria and the Hot Springs of the Kerio Valley Kenya. All treatments were done in triplicate in complete randomized block design. Fresh and dry weight were recorded at the end of the experiment and analyzed for anions; CO_3^{2-} , and HCO_3^- and pH values determined. Trace, anions, pH and structure of three different indigenous basic salts commonly available in Kenya namely 'Para', 'magadi', and 'Lebek', salts were quantitatively and qualitatively analyzed using FTIR and the wet methods; Gravimetry and titrimetry. The pH values ranged from 9.98 ± 0.01 to 11.26 ± 0.03 for magadi salt, 10.08 ± 0.03 to 10.88 ± 0.06 for Para salt and 10.09 ± 0.02 to 10.85 ± 0.06 for Lebek salt. Thus all the salts were alkaline. The bicarbonate concentration ranged from the highest of $25.3 \pm 0.3\%$ in magadi salt, to the lowest of $6.2 \pm 0.1\%$ in Lebek salt. Degree of hydrolysis for gallants soldier (GS) lignocellulosic sample ranged from the highest of $44.99 \pm 0.03\%$ with Magadi salt to the lowest of $29.98 \pm 0.05\%$ in Lebek salt. Hydrolysis with wheat straw (WS) lignocellulosic sample ranged from the highest of $30.75 \pm 0.05\%$ with Magadi salt to the lowest of $20.94 \pm 0.01\%$ Lebek salt. All salts had higher bicarbonate percent concentration values higher than carbonate percent concentration values. This clearly showed the role of the bicarbonate group in lignocellulosic hydrolysis. Lower the pH values, the lower the bicarbonate and the higher the degree of hydrolysis. FTIR analysis showed presence of bicarbonate group in all the salts.

Key words: Indigenous salts; pH; Characterisation; Bi-carboate; carbonate; Hydrolysis

INTRODUCTION

Microcrystalline cellulose in a lignocellulose is comprised glucose units connected by a 1-4 beta glycosidic bond. These linear cellulose chains are bundled together as microfibril spiralled together in the walls of plant cell.[6] Each microfibril exhibits a high degree of three-dimensional internal bonding resulting in a crystalline structure that is insoluble in water and inert to reagents. The "amorphous" region of cellulose is often assumed to be "freely" accessible to the hydrolysing medium. On the heterogeneous dilute acid hydrolysis of the cellulosic materials, Ananda and others [2], reported that the process is characterised by an initial fast rate of hydrolysis in the "amorphous" region of the material. The slow rate of hydrolysis in the crystalline portion has been attributed to restrictions to the conformational changes necessary for the hydrolytic reaction to occur. [6]

Hydrolysis of lignocellulosic biomass using an acid catalyst to produce sugars has been known for decades but the process can be costly and requires special equipment. The hydrolyzed sugars themselves are labile to the harsh hydrolysis conditions and may be degraded to unwanted or toxic byproducts. If exposed to acid for too long, the glucose derived from cellulose degrades into hydroxymethylfurfural, which can be further degraded into levulinic acid and formic acid. Xylose, a hemicellulose sugar, can be degraded into furfural and further to tars and other degradation products. [4]

Hydrolysis occurs in two stages to maximize sugar yields from the hemicellulose and cellulose fractions of biomass. The first stage is operated under milder conditions to hydrolyze hemicellulose, while the second stage is optimized to hydrolyze the more resistant cellulose fraction. Liquid hydrolyzates are recovered from each stage, neutralized, and fermented to ethanol.

Studies by Yan, and other workers [7] on spruce wood heated with aqueous sodium bicarbonate at 160°C showed only small amounts of lignin removal, together with larger amounts of the hemicellulose. The same study reported high percent hydrolysis yields when liquid ammonia with a solution ammonium chloride or sodium cyanide (52% lignin) than when only anhydrous liquid ammonia was used up to 100°C (25 to 30%). The solution of ammonium chloride or sodium cyanide in the liquid ammonia increased these percentages substantially and also the concomitant extraction of holocellulose [6, 7].

Ananda and others [2] found that 1- (1-propylsulfonic)-3-methylimidazolium chloride dissolve up to 20% w/w lignocellulosic biomass, and could be hydrolyzed into glucose at 70°C and atmospheric pressure in excellent yields.

Mahamadi and other workers [6], noted that for breaking of intermolecular H-bonds, penetration of the H_3O^+ ions into the crystallites is very slow. Addition of an inert electrolyte catalyses the penetration of the H_3O^+ ions into the

crystallites and the breaking of the glycosidic bond becomes limiting.

Present work aimed at investigating the behaviour of the heterogeneous dilute indigenous carbonate salt hydrolysis of the difficultly accessible portions of microcrystalline cellulose. The study was carried out on three indigenous basic salts; pH, percent concentration of CO_3^{2-} , and HCO_3^- and the degree of hydrolysis data are presented for three salt samples. hydrolysis of lignocellulosics under ambient conditions of temperature and pressure and both low and high carbonate concentrations. From the brief review above, it is also apparent that the indigenous salt hydrolysis of lingo-cellulosics has not been investigated fully.

The aim of the present work was to investigate the bicarbonate salt effect with respect to heterogeneous carbonate hydrolysis of lignocellulose due to different pH and bicarbonate values of the three indigenous salts; Magadi, Para and Lebek salts. Determine and interpret the concentrations of bicarbonate, carbonate, pH and percent degree of hydrolysis values on the non woody ligno-cellulosics materials.

Materials and Methods

Instrumentation and wet chemistry methods of Analysis

FTIR spectroscopy and potentiometry were used to identify the structure of each salt using carbonates and bicarbonates in them and measure pH respectively. The wet methods; pH meter, Gravimetry and titrimetry were used for the quantification of CO_3^{2-} and HCO_3^- and pH values.

Weighing plant samples;

Ligno-cellulosic plant sample portions of 20 to 30g were dried in the oven at 110°C for 2hrs then cooled for 30 minutes before weighing the exact mass needed and then was repeated several times until a constant weight was obtained.

A mass of 3.00g dried powder of each sample in 100.0mL beaker was weighed and carefully placed into a 500.0mL quick-fit round bottomed flask and a relevant salt solution added. The refluxing set up erected and the refluxing was done for varied times and conditions of temperature and salt to plant sample ratios.

Results and Discussion

Table 1.0: The pH of the salts (1% wt/v solution)

Salt sample	Sample treatment	
	Oven dried (OD)	Non-oven dried (NOD)
MS100	11.26 ± 0.03	9.98 ± 0.01
PS200	10.88 ± 0.06	10.08 ± 0.02
LS300	10.85 ± 0.06	10.09 ± 0.02

From table 1.0, the pH of MS100 oven dried recorded the

Refluxing was done for 3hrs at 100°C after which filtration was done. Weight of filter paper was noted. First washing was done using a dilute solution of the same hydrolyzing salt, followed by distilled water. The pulp obtained is oven dried at 110°C for 3hrs, cooled then weighed.

The loss-in-weight method of Meller for the determination of the hydrolysis rate was used in these experiments [6]

Sample Collection and Analysis

Magadi samples from Lake Magadi, (n=15), Para samples from Kendu-bay at the shores of Lake Victoria (n=30), Lebek samples from Kerio-valley (n=30) and market places (n=3) were collected, packaged dry in paper bags and taken to the laboratory. In the laboratory each sample were crushed and homogenized in a mortar. About 10.00-20.00 grams of each salt sample was oven dried in a 100.00mL beaker at a temperature of 110°C for 2.0 hours. Another portion of about 10 - 20 grams of each salt sample fresh (not oven dried) was taken. A triplicate mass of 2.000 grams of each of the salt sample was weighed and dissolved in 100.00mL beaker with 50.0 mL of de-ionized water. The solution was then filtered using Whatman filter paper No. 42 [9, 11]

The pH of each filtrate was measured after which the filtrate solution was used for hydrolysis.

For quantification of CO_3^{2-} and HCO_3^- a triplicate mass of 0.700 grams of each of the cooled dried salt sample was weighed and dissolved in 100.00mL beaker with 50.00mL of de-ionized water. The solution was then filtered using Whatman filter paper No. 42. The CO_3^{2-} and HCO_3^- were analyzed by titrimetry using 0.1M HCl solution.

The carbonate ($\text{CO}_3^{2-} + \text{HCO}_3^-$) concentrations were measured using the end point titration method according to the standard methods where the end point of pH = 4.5 was used. An aliquot of 5.00 ml of the magadi solutions (2.00 g/100.0 ml) was diluted to 50.0 ml and titrated automatically with 0.1 N HCl [10,12]

The samples were categorized as follows:

MS100 series, samples of mineral salts ('Magadi').

PS200 series, samples of mineral salts ('Para').

LS300 series, samples of mineral salts ('Lebek')

highest value, 11.20 ± 0.03.

PS200 and LS300 recorded pH values; 10.88 ± 0.06 and 10.85 ± 0.04 respectively in the oven dried category. The pH of MS100 non-oven dried recorded the least value 9.98 ± 0.01 . LS300 recorded the highest pH of 10.09 ± 0.02 , closely followed by PS200 with a pH value of 10.08 ± 0.02 . MS100 had the highest change in pH; with the raw salt recording the least pH. The other two salts recorded a slight variation in pH between the raw salt and the oven dried. Magadi salt recorded the least pH in its raw form because of the acidic hydrogen $[O_2CO-H]$ the bicarbonate. The large difference

between oven dried and non-oven dried clearly indicates the decomposition and loss of most of acidic hydrogen during the drying stage, increasing the pH proportionately with HCO_3^- . Magadi salt had the highest amounts of hydrogen carbonates as compared to both para and lebek salts. These findings correlate well with earlier studies done by Tatiana and Chunming and their co-workers [14, 16], which recorded similar observations of pH increase wherever HCO_3^- decomposed.

Functional group analysis of the salts using FTIR.

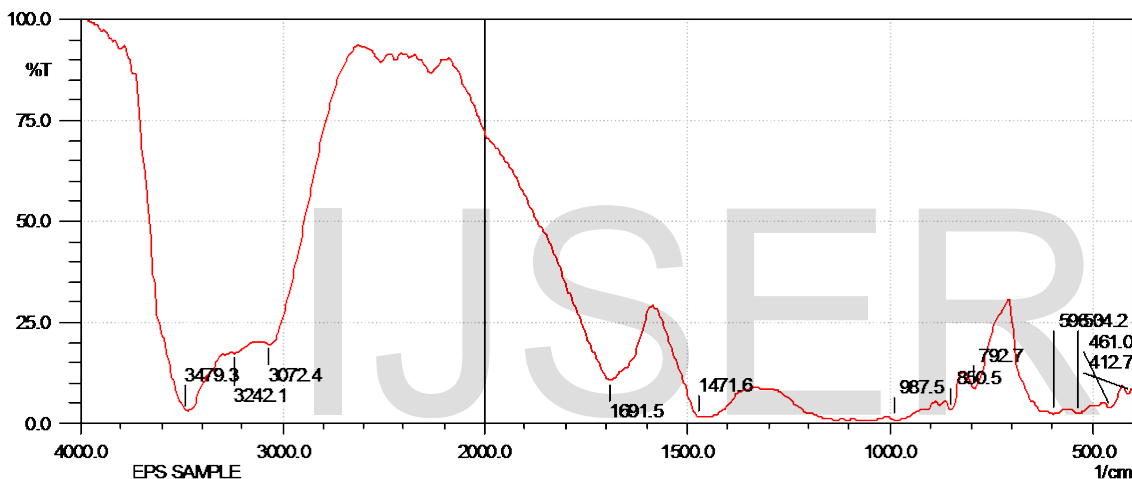


Figure 1: FTIR spectrum of PS200-salt

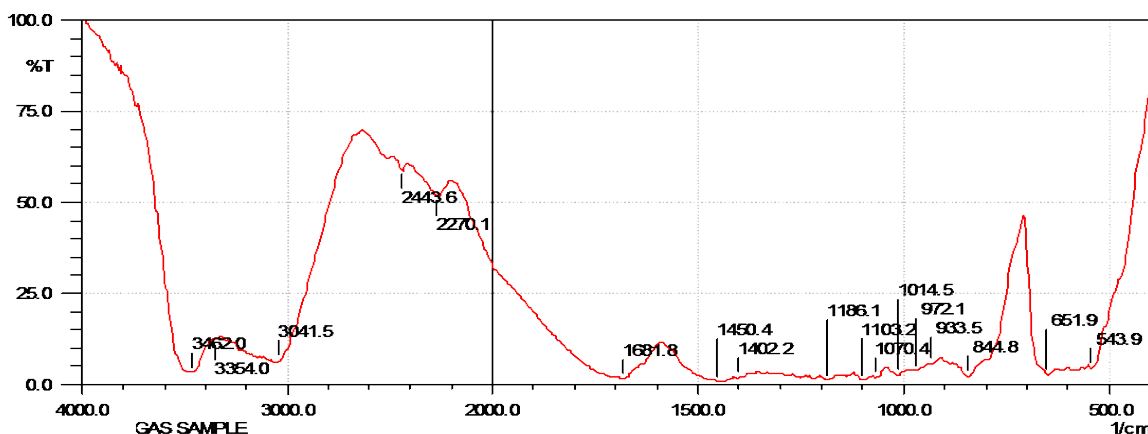


Figure 2: FTIR spectrum of MS100-salt

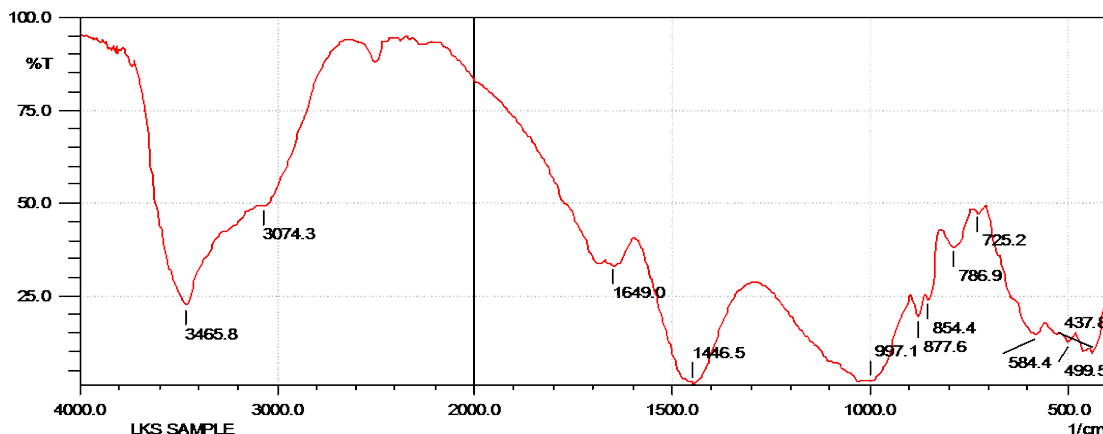


Figure 3: FTIR spectrum of LS300-salt

All the salts showed FTIR major peaks at 3479 – 3482 cm^{-1} range (charts 1-3) this is -O-H stretch. 1650-1690 cm^{-1} (Figures 1-3) which is the C=O stretch. In 950 - 1000 cm^{-1} (charts 1-3) which is C-O stretch. These charts show a carbonate and a bicarbonate structure. This correlates well with studies done by Huanc [13]. The salts contain the two anions. This is also true from the quantitative analyses of the two. This is in agreement with studies earlier done on metal carbonates and bi-carbonates[13]. The FTIR transmission spectra of metal salts bi-carbonate solids, bands for free HCO_3^-

ion in aqueous solution were assigned as follows: (stretching of C-OH) at 1010 cm^{-1} , (symmetric stretching of CO_2) at 1360 and 1310 cm^{-1} , (asymmetric stretching of CO_2) at 1668 cm^{-1} and 1605 cm^{-1} , and (out-of-plane bending of CO_3^{2-}) at 843 cm^{-1} . The rest of the fundamental vibration modes, (symmetric in-plane bending of CO_3^{2-}) and (asymmetric in-plane bending of CO_3^{2-}) should appear below 800 cm^{-1} , a spectral region which could not be observed. This is correlated well by studies done by Tatiana, Teleb and Chunming and co-workers [14, 15, 16], which showed similar peaks for carbonate salts.

3.0: Major anions content

Table 3.0: The table shows the percent (%) Anionic radical Content wt/wt in dry salt sample

Samples	Anionic radicals Content % wt/wt		
	Carbonate CO_3^{2-}	Hydrogen carbonate HCO_3^-	Total Carbonate $\text{CO}_3^{2-} + \text{HCO}_3^-$
MS100	21.9±0.5	25.3±0.3	47.2±0.2
PS200	6.5±0.4	7.3±0.2	13.9±0.3
LS300	5.5±0.1	6.2±0.1	11.8±0.4

The percentage concentration of CO_3^{2-} ranged from 5.5±0.1% to 21.9±0.5%. MS100-salt recorded the highest percentage of total carbonate with a mean percent concentration of 47.2±0.2%, with the mean percent CO_3^{2-} of 21.9±0.5% and hydrogen carbonate (HCO_3^-) 25.3±0.3%. PS200-salt recorded the second highest percentage of total carbonate (13.9±0.3%) of the salt samples analyzed; with the percent carbonate (CO_3^{2-}) being 6.5±0.4% and hydrogen carbonate (HCO_3^-) 7.3±0.2%. LS300-salt recorded the third

highest percentage of total carbonate (11.8±0.4%) of the salt samples analyzed; with the percent carbonate (CO_3^{2-}) being 5.5±0.1% and hydrogen carbonate (HCO_3^-) 6.2±0.1%. This conforms to the earlier studies by Guest and co-workers [8] which recorded similar results. This could be due to the fact that, the final major reaction that could influence the HCO_3^- contents in the deep aquifer is the addition in the system of CO_2 of deep origin, as reported in the studies by Makanjuola and Teleb and co-workers [9, 15].

Delignification and Hemicelluloses Removal

TABLE 4.0:Percent degree of delignification and hemicelluloses removal from a dry residue sample

Type of residue residue ratio(R:S)		Weight of residue in g with salts;			Weight of hydrolyzates /g			% Hydrolysis		
		MS100	PS200	KS300	MS100	PS200	KS300	MS100	PS200	KS300
GS residue	1:5	3.11 ± 0.02	3.21 ± 0.01	3.48 ± 0.01	1.40 ± 0.01	1.04 ± 0.01	1.04 ± 0.01	44.99 ± 0.01	32.28 ± 0.01	29.98 ± 0.02
Ws residue	1:5	3.06 ± 0.01	3.09 ± 0.01	3.07 ± 0.01	0.94 ± 0.02	0.65 ± 0.01	0.64 ± 0.01	30.75 ± 0.05	21.08 ± 0.02	20.94 ± 0.01

Gallant’s soldier-residue (GS)

MS100 salt with a delignification of 44.99±0.01%, exhibits the highest degree of hydrolyzing the lignin and hemicelluloses from a Gallant’s soldier-residue. PS200 salt and KS300 salt had a percent degree of delignification of 32.28±0.01% and 29.98±0.02% respectively. MS100 salt showed the highest degree of hydrolysis. This could be attributed to the high amounts of sodium chloride as reported by Mahamadi, and Yan, [6, 7]. The authors reported in their studies that, higher degrees of hydrolysis were recorded when an inert salt was added in the hydrolyzing regime than when it was absent. Osano, and co-workers [1] recorded high amounts of sodium in MS100 salt, followed by PS200 salt then KS300 salt, a trend witnessed in the degree of hydrolysis.

Wheat straw-residue (WS)

MS100 salt with a percent delignification of 30.75±0.05%) exhibited the highest degree of hydrolyzing the lignin and hemicelluloses from a Wheat straw-residue. PS200 salt and KS300 salt had degrees of delignification of 21.08±0.02%) and 20.94±0.01% which were close to each other. Also as for Gallant’s soldier-residue, MS100 salt recorded the highest percent hydrolysis with Wheat straw than both PS200 salt and KS300 salt. Studies have shown MS100 with higher concentration of neutral salts than PS200 and KS300 salts [1]. Gallants soldier recorded the highest degree of delignification with MS100 salt. This produced more hydrolysates than Wheat straw-residues. This could be attributed to lingo-cellulosic plant sample structure. This is in line studies by Fuess, and Ananda [2, 12] who reported that, high percent hydrolysis in Wheat rye (over 52%) were recorded than in Spruce wood (at 20% to 30%) using the same acid hydrolysis.

Conclusion

The three salts have the same carbonate and bi-carbonate structure which only differs in percent concentration levels (MS100 had 47.2%; PS200 had 13.9% and LS300 had 11.8% total carbonate). FTIR spectra showed that all the three salts had bicarbonate in their structure as was indicated by the peak at 1650 – 1690 cm⁻¹.

Magadi salt is basically a sodium carbonate-sodium bi-carbonate. The bicarbonate content is slightly higher than the carbonate. Para and Lebek salts have small amounts of carbonates and bi-carbonate and they are more of calcium and iron salts. All the three salts were found to be alkaline salts with pH ranges from 9.8 to 10.09.

The degree of hydrolysis of these salts depended on concentrations of hydrogen carbonate group.

Salts with high concentration of bicarbonates and lower pH recorded higher percent degree of lingo-cellulosic hydrolysis.

Percent degree of lingo-cellulosic salt hydrolysis depended on the type of lingo-cellulosic plant and the sample structure.

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