THE PRODUCTION OF CARBOXYMETHYL CELLULOSE FROM RICE STRAW AND SUGARCANE BAGASSE

Elsebaie, E. M; Elsanat, S. Y. A.; Gouda, M. S. and Elnemr, K. M. *

- Food Technol. Dept., Fac. Agric., Kafr El-Sheikh Univ., Egypt

ABSTRACT

Cellulose is the main constituent of higher plants, including rice straw and sugarcane bagasse. The chemical analysis showed that the cellulose content was 34.6 % and 42.186 % in rice straw and sugarcane bagasse respectively. The optimum conditions to obtain cellulose from rice straw was 1.5 % NaOH concentration, 55°C, 1:15 and 150 minutes and in the same conditions silica content reduced from7.2% to 4.5% and cellulose content was increased from 34.6 % to 38.73 %. On the other hand, the optimum conditions to produce cellulose from sugarcane bagasse was 2.5 % NaOH concentration, 70°C, 1:15 and 150 minute and in the same conditions silica content reduced from 3% to 1.3% and cellulose content was increased from 42.186 % to 44.98 %. The results showed that the optimum temperature and time on the cellulose isolation was 110°C and 10 minutes which gave 38.52% and 43.73% cellulose in rice straw and sugarcane bagasse respectively. the most suitable solvent and time for carboxymethyl cellulose production were isopropyl alcohol and 360 minutes for cellulose produced from rice straw and sugarcane bagasse. On the other hand, the optimum temperature, NaOH concentration and amount of monochloroacetic acid were 30°C, 15% and 2.2gm for cellulose produced from rice straw and 90°C, 25% and 3 gm for cellulose produced from sugarcane bagasse, respectively.

Keywords: silica, CMC, cellulose isolation, bagasse and rice straw.

INTRODUCTION

So large quantities of lignocellulosic materials in the form of agro-industrial residues accumulate all over the world every year, causing environmental deterioration and loss of potentially valuable resources. In Egypt, rice straw is a cheap, widespread and quite abundant lignocellulosic material, especially in the Delta governorates where approximately 2.16 tons of straw is generated per each feddan of rice planted *(ASGA, 2007)*. However, the option for the deposition of straw are limited by the great bulk of material, slow degradation in the soil, harboring of rice stem diseases, and high mineral content, and therefore, field must be cleaned of straw to make way for the next crop. Unfortunately, soil incorporation and field burning have been the major practices for removing rice straw by farmers *(El-sanat, 2004)*. One of the main ways to address the pollution from straws is to use them as ruminant feed, there by contributing to enhanced meat and dairy supplies for people *(Gao et al., 2007)*. Rice straw burned directly in the field for the purpose of quick disposal of these wastes and land clearing. *(Mandal et al., 2004 and Barraclough et al., 2005)*. The smoke caused by open-field burning rice straw frequently results in serious air pollution and traffic trouble, hence new economical technologies for rice straw disposal and utilization must be developed *(Gong et al., 2008)*.

Sugarcane bagasse is a waste produced in large quantities by the sugar and alcohol industries, and is mainly used as a fuel to power the sugar mill. However, the remaining bagasse still continues to be a menace to the environment. The availability and the possibility of converting these cheap and inexpensive materials to generate products, in a practical and economical way, with relevant applications in the food and pharmaceutical industries, have called the attention of several researchers to utilization of the total biomass components *(Martinez et al., 2000)*.

The problem in using rice straw and sugarcane bagasse is the high content of silica. Silicic acid has been shown to inhibit invertase. The effect of sodium hydroxide is to dissolve lignin, silica, and hemicelluloses. Cellulose is not dissolved by alkali treatment. *Van Soest (2006)* found that Silica is not dissolved by sulfuric acid, ammonia and urea in contrast to the action of sodium hydroxide.

Cellulose is the main constituent of higher plants, including wood, cotton, flax, hemp, jute, sugarcane bagasse, ramie, cereal straws etc. This represents a waste potential feedstock for a number of industries. Cellulose is a linear polymer of anhydroglucose units linked at C_1 and C_4 by ß-glycosidic bonds. *(Karla and Gilbert, 2000)*. Carboxymethyl cellulose (CMC) is the most important water-soluble cellulose derivative, have many applications in the food industry and in cosmetics, pharmaceuticals, detergents etc. *(Olaru et al., 1998)*. The production of CMC is carried out by conversion of alkali cellulose swollen in aqueous NaOH and a surplus of an organic solvent with monochloroacetic acid or its sodium salt *(Heinze and Pfeiffer, 1999)*. The present work was conducted to study how to reduce silica content of rice straw and sugarcane bagasse, the optimum conditions for isolation pure cellulose of rice straw and sugarcane bagasse and the optimum conditions for converting it to carboxymethyl cellulose which had a lot of applications in food processing field.

MATERIALS AND METHODS

Rice straw samples were obtained from Rice Research Station, Agriculture Research Center, Sakha, Kafr El-Sheikh, Egypt, during the summer season of 2006. They were transferred to the Laboratory of Food Technology Department, Faculty of Agriculture at Kafr El-Sheikh, Kafr El-Sheikh University, Egypt. After sun drying for seven days, samples were cut to a practical size of 100-mm long and 1-mm thick fragments to be used for extraction of the cellulose fraction, according the method described by *(El-sanat, 2004)*.

Sugarcane bagasse was obtained from a local sugar Cane mill in Kafr El-Sheikh Governorate, Egypt. It was first soaked in water for three days and then it was dried in sunlight after that cut into small pieces (1-3 cm). The dried cut bagasse was ground to pass through an 1.0 mm size screen according the method described by *Sun et al.(2004)*.

Analytical methods:

Moisture was determined by drying in an air oven at 110 °C to a constant weight; crude protein, by using the Micro-Kjeldahl method to determine the total nitrogen and multiply its value by the factor of 6.25; ether extract, in a Soxhlet apparatus using the petroleum ether (40 - 60 °C) as a solvent and ash content by ashing in an electric muffle at 550 °C until constant weight, all were determined according to the methods described in the *A. O.A. C. (2000)*.

Cellulose in investigated samples was determined using the method mentioned by *Ahmed (1989)*. Lignin was also determined according to the method described by *Fahmi (1984)*. Hemicellulose was determined according to the method described in the *A. O.A. C. (2000)*.

Determination of silica:

The contents of silica were determined according to the method described by *Pan et al. (1999)* as follows: The sample was transferred to a crucible and carbonized gently in an electric muffle at 550 ± 10°C for 6 h. The ash obtained was treated with concentrated HCl. The acid-insoluble residue was filtered, washed with hot water until no chlorides were detectable, ignited, and finally weighed as silicon dioxide.

Alkaline pretreatment:

Sodium hydroxide was used to treat the investigated wastes in order to reduce silica percentage in these agriculture wastes. The waste sample was ground in laboratory mill 120(perten) and treated with a concentrated (0.5 , 1.00 , 1.5, 2.00 and 2.5) % NaOH at the temperature (25±2 , 55 , 70 , 100 and 120)°C and solid : liquid ratio was (1:5 , 1:10 , 1:15 and 1:20) for (30 , 60 , 90 , 120 and 150) min. The insoluble fraction was collected by filtration on cheese cloth, continuously washed with tap water to remove the residual of NaOH. The excess liquid was removed by squeezing the slurry through two layers of cheese cloths and dried in the oven at 70°C for 24 hrs, *(Han and Callihan, 1974).*

Cellulose extraction:

The method for isolation of cellulose with a mixture of acetic acid 80% and nitric acid 70% ratio (10:1, v/v) follows the chemistry described by *Brendel et al. (2000)* as follows: 5.0 g of the investigated materials was weighed into 200 ml Pyrex tubes. Subsequently, 100 ml aqueous acetic acid 80% (w/w) and 10 ml nitric acid 70% (w/w) were added. The tubes were sealed using screw-caps fitted with Teflon liners and placed into an autoclave at the required temperature at (100 – 120 – 130) °C for (10 - 20 – 30) min, respectively. When the tube was removed from the oil bath and cooled, 60 ml of distilled water was added, and the reagent was decanted off. The residue was then thoroughly washed with distilled water and ethanol 95% to remove the nitric acid and extraction breakdown products. The residue was then dried in an oven at 60 °C for 16 h and was labeled as cellulose.

Carboxymethyl cellulosc production:

The method for carboxymethylation of cellulose was described by *Toĝrul and Arslan, (2003)* was used as follows: Two grams of cellulose from all rice straw and sugar cane bagasse in optimized cellulose extraction condition. 100 ml of solvent (water, ethanol. isopropyl alcohol and isobutyl alcohol) and 20 ml of NaOH having concentrations of 5, 10, 15, 20. 25 and 30% were mechanically stirred for 90 min at 25 °C in a reaction vessel with the heat stabilization jacket. The mixture was filtered to a weight of about 6.5 g and shredded for 90 min in a shredder. Then suitable concentrations (1.0.

1.4, 1.8, 2.2, 2.6 and 3.0 g) of monochloroacetic acid (MCA) were added and shredding was continued at temperatures of 30, 45, 60, 75 and 90°C and times were 60, 90, 120, 180 and 360 min. Water from a constant temperature bath was circulated through the jacket of the reaction vessel to maintain the constant temperature during carboxymethylation. After the time of reaction was finished, the mixture was neutralized with acetic acid 90% and filtered. Cake was purified by washing with methanol 70% to remove undesired salts, filtered and dried at temperature 70 °C.

Determination of degree of substitution:

The degree of substitution of CMC was determined by the standard method *(ASTM, 1961)*. 108 ml of HNO_3 65% was made to one liter by methanol. Five grams of produced and commercial CMC was shaken with 200 ml of diluted HNO_3–methanol mixture, kept for 3 h then filtered and the surplus acid was washed with 70% methanol. Two grams of dried washed CMC was added to 200 ml of distilled water and 30 ml of 1N NaOH, After dissolving the mixture was titrated with 1N HCl. The DS of CMC was determined by the following equations reported by *ASTM (1961)* as modified by *Barai et al.(1997)*.

$$DS = 0.162A / (1 - 0.058A)$$

$$A = (BC - DE)/F$$

where A is the equivalent weight of alkali required per gram of sample; B, (ml) of NaOH solution; C, the normality of NaOH solution; D, (ml) of HCl solution; E, the normality of HCl solution and F, grams of sample(2gm).

RESULTS AND DISCUSSION

1. Proximate chemical composition of rice straw and bagasse:

Rice straw and sugarcane bagasse were chemically analyzed for these contents of moisture; protein; ether extract; ash, lignocellulosic components (lignin, cellulose and hemicellulose) and silica. The obtained data are presented in Table (1). It could be noticed from the results that the moisture content of studied wastes was 7.98 and 8.28% for rice straw and sugarcane bagasse, respectively. These results are in accordance with those reported by *Attia et al. (1988); Nasr (1994); Mohammady (1996); Khaled (1997); Khalafalla (1999) and Ali (2002).* They found that the moisture content of some lignocellulosic wastes was in the range from 7.7 to 14.0%.

Concerning the crude protein content, results disclose that the protein content of the rice straw and sugarcane bagasse, respectively was 3.46 and 2.18% (on dry weight basis). Such findings coincide with those reported by *Abd El-Rahem (1969); Michel et al. (1988); Mohammady (1996) and Ali (2002),* who reported that the crude protein content of different studied lignocellulosic wastes including rice straw and bagasse was ranged between 2.51 to 7.8% (on dry weight basis).

In respect to ether extract of the investigated waste materials it should be noted that rice straw contained 1.41 and sugarcane bagasse contained 0.74% (on dry weight basis). These results are in agreement with those obtained by *Attia et al. (1988); khalafalla (1999); Ali (2002) and El-sanat (2004),* who found that the ether extract of rice straw was between 1.0 and 2.5%.Also, *Beshay (2001) and Ali (2002),* reported that ether extract content of sugarcane bagasse about 0.88%.

Regarding the ash content of the wastes, results in Table (1) indicate that, ash content of rice straw and sugarcane bagasse was 13.40 and 3.30%, respectively. These results are in agreement with those obtained by *Nasr (1994); Beshay (2001) and Ali (2002)* who found that the ash content of rice straw was ranged between 5.0 and 17.75% .Also, *ALian et al. (1987); Hussain et al. (1997) and Beshay (2001)* stated that the bagasse contained ash ranged between 1.73 and 5.27 %.

Table (1): Proximate chemical composition of rice straw and sugar cane bagasse (on dry weight basis)

Component *	Rice straw %	Sugar can bagasse %
Moisture	7.98	8.28
Crude protein	3.46	2.18
Ether extract	1.41	0.74
Ash content	13.4	3.30
Lignin	16.87	18.09
Cellulose	34.6	42.19
Hemicellulose	30.26	33.50
Silica	7.20	3.00

The values were an average of three determinations

The results in the same Table also showed that lignin content of the rice straw and sugarcane bagasse was 16.87 and 18.09%, respectively (on dry weight basis). These values are within the range from 13.00 to 21.85% as mentioned by *Beshay (2001), Ali (2002); Lachke (2002) and Howard et al. (2003)* for different lignocellulosic wastes including rice straw and bagasse.

The data showed that the rice straw and bagasse content of cellulose was 34.60 and 42.19%, respectively (on dry weight basis). These findings are in accordance with those obtained by *Attia et al. (1988) and Howard et al. (2003)* who found that the cellulose content of rice straw was ranged between 32.1 and 35.0% (on dry weight basis).However, the bagasse content of cellulose was lower than that recorded by *Sun et al. (2004)* who found that bagasse content of cellulose was about 43.6%(on dry weight basis).

Regarding to the hemicellulose content of rice straw and bagasse, it was 30.26 and 33.5%, respectively (on dry weight basis). These values are within the range of 23.0 to 35.0 % as mentioned by *Beshay (2001); Ali (2002); Lachke (2002) and Howard et al., (2003)* for rice straw. Also, *Ali (2002)* reported that the hemicellulose content of bagasse was about 33.5 %.

In respect to the silica content of rice straw, it was 7.20 % this value is laying between the range of 6.80 to 9.8% as mentioned by *Vadiveloo and Phang (1996); Bae et al.(1997) and Agbagla-dohnani et al.(2001)* for rice straw. Also, the silica content of bagasse was 3.00%. this result is in almost agreement with *El-gamal (1991)* who found that the silica content of bagasse was 2.42%. From these results, it could be concluded that all wastes materials under investigation are a rich resource waste materials of cellulose.

2. Effect of alkaline pretreatment concentration on removing silica:

The effect of alkaline pretreatment by different concentrations on cellulose and silica content of rice straw and bagasse is given in Table (2). The Table shows that with increasing of sodium hydroxide concentration from zero to 2.5 % the concentration of silica was decreased On the other hand, cellulose content of rice straw was increased with increasing of sodium hydroxide concentration from zero to 1.5 %. The increasing in cellulose content could be attributed to the decreasing in lignin and hemicelluloses content according to *Sharma (1974)* who found similar results. On the other hand, cellulose content of rice straw was decreased with the increasing of sodium hydroxide concentration from 1.5 towards 2.5 % the decreasing in cellulose content due to the degrading effect of NaOH on cellulose. It could be noticed from the results that the most effective sodium hydroxide concentration was 1.5% which reduced silica content of rice straw from 7.2 to 5.2 % and the cellulose yield was increased to 37.8%. On the other hand, the Table(2) shows that with the increasing of sodium hydroxide concentration from zero to 2.5 % the concentration of silica in bagasse was decreased while, cellulose content of bagasse was increased with the increasing of sodium hydroxide concentration this increasing in cellulose content may return to decreasing in lignin and hemicelluloses content as reported by *Sharma (1974)*.

It could be noticed from the results that the most effective sodium hydroxide concentration was 2.5% which reduced silica content of bagasse from 3.00 to 1.8 % and the cellulose yield was increased to 43.7%.

3. Effect of alkaline pretreatment period on cellulose and silica contents:

This Table(2) also shows that the most effective period was 150 minute which increased the cellulose yield to 38.24 and 44.00% for rice straw and bagasse, respectively with reducing silica content to 4.9% and 1.6% for rice straw and bagasse respectively. The increasing of cellulose content may be attributed to the increasing of pretreatment time where the solubility of hemicellulose, lignin and silica was increasing.

4. Effect of alkaline pretreatment temperature on cellulose and silica contents:

The Effect of temperature of alkaline pretreatment on cellulose and silica contents of rice straw and sugar cane bagasse is given in Table (2). This table shows that the most effective temperature was 55°C which reduced silica content of rice straw to 4.9% and the cellulose yield was increased to 38.24%. but we can observe that when the temperature was over than 55°C cellulose content was decreased and silica content was increased this may be due to the effect of the temperature on the solubility of hemicellulose, lignin and cellulose. On the other hand, the most effective temperature was70°C which reduced silica content of sugarcane bagasse to 1.4% and the cellulose yield was increased to 44.61%. This difference between rice straw and bagasse may be return to that the bagasse is more rough than rice straw so that bagasse need a higher temperature in the alkali pretreatment than rice straw (*Sharma, 1974*).

Table (2): optimum conditions for alkaline pretreatment in rice straw and sugarcane bagasse for removing silica.

Raw material	NaOH concentration	Time minute	Temperature °C	Solid: liquid ratio	Cellulose (%)	Silica (%)	Removed silica (%)
Rice straw (1)	Un treated	zero	Zero	Zero	34.6	7.2	Zero
	0.5 %	120	55	1:10	36.00	6.2	13.89
	1 %	120	55	1:10	37.2	5.7	20.83
	1.5 %	120	55	1:10	37.8	5.2	27.78
	2.00%	120	55	1:10	37.61	5.2	27.78
	2.5 %	120	55	1:10	37.2	5.2	27.78
Bagasse (1)	Un treated	zero	Zero	Zero	42.186	3.00	Zero
	0.5 %	120	55	1:10	42.70	2.8	6.67
	1 %	120	55	1:10	42.9	2.7	10.00
	1.5 %	120	55	1:10	43.3	2.3	23.33
	2.00%	120	55	1:10	43.5	2.00	33.33
	2.5 %	120	55	1:10	43.7	1.8	40.00
Rice straw (2)	1.5%	30	55	1:10	35.3	6.7	6.94
	1.5%	60	55	1:10	36.58	6.1	15.28
	1.5%	90	55	1:10	37.1	5.9	18.06
	1.5%	120	55	1:10	37.8	5.2	27.78
	1.5%	150	55	1:10	38.24	4.9	31.94
Bagasse (2)	2.5%	30	55	1:10	42.58	2.8	6.67
	2.5%	60	55	1:10	43.09	2.5	16.67
	2.5%	90	55	1:10	43.38	2.1	30.00
	2.5%	120	55	1:10	43.7	1.8	40.00
	2.5%	150	55	1:10	44.00	1.6	46.67
Rice straw (3)	1.5%	150	Room temperature	1:10	37.33	5.6	22.22
	1.5%	150	55	1:10	38.24	4.9	31.94
	1.5%	150	70	1:10	37.62	5.4	25
	1.5%	150	100	1:10	36.93	5.7	20.83
	1.5%	150	120	1:10	35.01	6.1	15.28
Bagasse (3)	2.5%	150	Room temperature	1:10	43.19	2.00	33.33
	2.5%	150	55	1:10	44.00	1.6	46.67
	2.5%	150	70	1:10	44.61	1.4	46.67
	2.5%	150	100	1:10	44.47	1.4	53.33
	2.5%	150	120	1:10	43.05	1.8	40.00
Rice straw (4)	1.5%	150	55	1 : 10	38.24	4.9	31.94
	1.5%	150	55	1 : 15	38.73	4.5	37.5
	1.5%	150	55	1 : 20	37.00	5.3	26.39
Bagasse (4)	2.5%	150	70	1 : 10	44.61	1.4	53.33
	2.5%	150	70	1 : 15	44.98	1.3	56.67
	2.5%	150	70	1 : 20	43.75	1.5	50.00

(1) Effect of NaOH concentration (2) Effect of period
(3) Effect of temperature (4) Effect of solid: liquid ratio

5. Effect of alkaline pretreatment solid : liquid ratio on cellulose and silica contents:

The Effect of solid : liquid ratio of alkaline pretreatment on cellulose and silica contents of rice straw and sugarcane bagasse is given in Table (2). Data given in this table shows that the most effective solid : liquid ratio was 1:15 which increased the cellulose yield to 38.73% and 44.98% with reducing silica content to 4.5% and 1.3% for rice straw and bagasse, respectively. But we can observe that when solid/ Liquid ratio was 1:20 cellulose content was decreased and silica content was increased this may be due to that with the increasing of the solid : liquid ratio where the solubility of hemicellulose, lignin was increasing and cellulose will be damaged.

6. Effect of temperature and time of reaction on the yield of cellulose isolated from rice straw and bagasse:

Data given in Table (3) show that the most effective temperature was at 110°C for 10 minute at these conditions the cellulose yield was 38.52 % and 43.73 % in rice straw and sugarcane bagasse respectively. These results are in disagreement with those of *Brendel et al. (2000)*; they found that the optimum temperature and time for cellulose isolation from bagasse were 120°C for 20 minute. This difference may be due to the conditions of alkali pretreatment used which removed most of lignin and hemicellulose.

Table (3): Effect of temperature and time of reaction on the yield of cellulose from rice straw and bagasse.

Temperature °C	Time (minutes)	Cellulose %	
		Rice straw	Bagasse
110	10	38.52	43.73
	20	37.97	43.20
	30	36.94	42.5
120	10	37.85	43.1
	20	37.41	42.69
	30	35.63	41.8
130	10	36.02	41.77
	20	34.18	40.28
	30	32.43	39.55

7. Effect of various solvents on DS:

Fig. (1) shows the extent of carboxymethylation, expressed as degree of substitution when the reaction was carried out in five different solvent media. A maximum DS of 0.387 and 0.452 for rice straw and bagasse respectively were obtained with isopropyl alcohol as the solvent medium.

The role of the solvent in the carboxymethylation reaction is to provide miscibility and accessibility of the etherifying reagent to the reaction centers of the cellulose chain rather than glycolate formation *(Toğrul and Arslan, 2003)*. The differences in the extent of carboxymethylation can be explained by taking into consideration their solvent polarities and stereochemistry. The reaction efficiency increases as the polarity of the solvent decreases *(Baria et al., 1997)*. Isopropyl alcohol was the best choice, which is in agreement with other reports as well *(Khalil et al., 1990; Bhattacharyya et al., 1995)*.

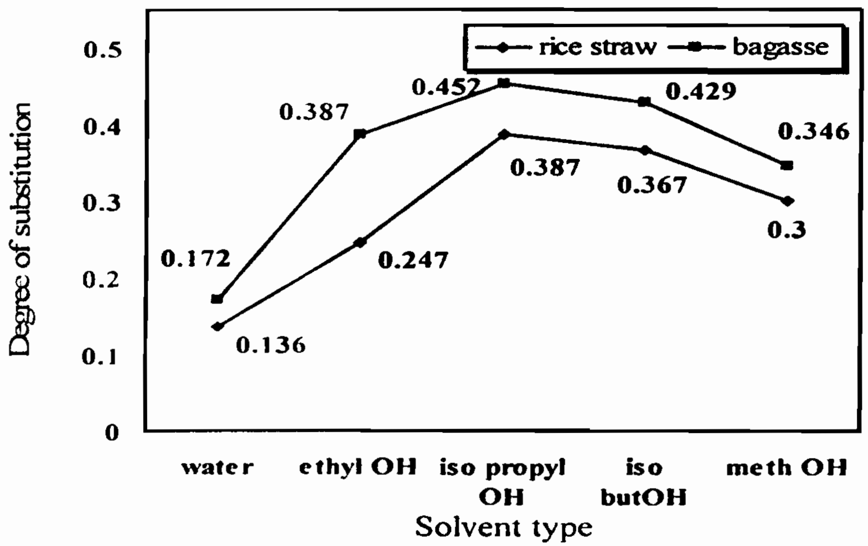

Fig. (1): Solvent effect on carboxymethylation of rice straw and bagasse cellulose.

8. Effect of various alkali concentration on DS:

As shown in Fig. (2), the effect of sodium hydroxide concentration was studied by varying the concentrations of the sodium hydroxide solutions. It was observed that by using isopropyl alcohol as the solvent medium, time 60 minutes, temperature 30°C and amount of monochloroacetic acid 3g per 2g sample, the DS values were increased with sodium hydroxide concentration and attained a maximum of DS 0.519 in rice straw and bagasse at an alkali concentration 15% and 25% (w/v) respectively. At particular alkali strength, the DS was maximum after which it started declining. This observation can be explained by considering the carboxymethylation process, where two competitive reactions take place simultaneously. The first involves a reaction between cellulose, and monochloroacetic acid in the presence of alkali to yield CMC as suggested by the following equation:

$$\text{Cell - OH} + ClCH_2COOH + NaOH \rightarrow \text{Cell - }OCH_2COONa + NaCl + H_2O$$

Cellulose Chloroaceticacid Sodium carboxymethylcellulose (1)

The second reaction involves the reaction of sodium hydroxide with monochloro acetic acid to form sodium glycolate:

$$\text{Cell - }OCH_2COONa + NaOH \rightarrow HOCH_2COONa + NaCl$$

Sodium carboxymethylcellulose Sodium glycolate (2)

Hence the first reaction seems to prevail above the second up to a sodium hydroxide concentration of 15 % and 25 % for rice straw and sugarcane bagasse, respectively. Above these concentrations, the second reaction predominates with the formation of larger amounts of glycolate, thereby lowering the DS. Similar findings have been reported in case of carboxymethylation of maize starch *(Khalil et al., 1990)*.

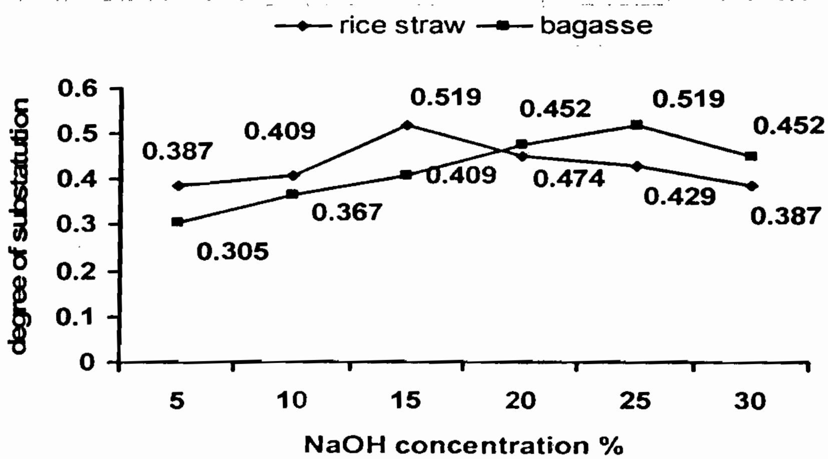

Fig. (2): **Alkali concentration for steeping. Effect on carboxymethylation of rice straw and bagasse cellulose.**

9. Effect of temperature and duration of reaction:

As shown in Table (4) in the case of rice straw, with isopropyl alcohol as the solvent medium, an alkali concentration of 15 % and duration of reaction 360 minute. A maximum DS of 0.797 was obtained with 45°C. While, in the case of bagasse with isopropyl alcohol as the solvent medium, an alkali concentration of 25 % and duration of reaction 360 minutes a maximum DS of 0.890 was obtained with 90°C. And the table also shows that with 360 minutes a maximum DS of 0.797 and 0.661 was obtained with rice straw and bagasse, respectively. The enhancement of DS with temperature and duration of reaction may be due to the fact that there is a better reaction environment created and a prolonged time available for carboxymethylation. This may lead to better reaction efficiency and higher DS of the final product. The favorable effect of temperature on carboxymethylation was reported previously *(Naterova and Polein, 1974).*

Table (4): Effect of temperature and time of reaction on degree of substitution (DS) of carboxy methyl cellulose (CMC).

Temperature	DS for CMC produced from rice straw	DS for CMC produced from bagasse
30	0.763	0.661
45	0.797	0.711
60	0.661	0.763
75	0.612	0.816
90	0.542	0.890
Time (min)	**DS for CMC produced from rice straw**	**DS for CMC produced from bagasse**
60	0.519	0.519
90	0.542	0.542
120	0.565	0.588
180	0.686	0.637
360	0.797	0.661

DS: degree of substitution.

9. Effect of various monochloroacetic acid concentration:

In the case of rice straw, by using isopropyl alcohol as the solvent medium, time 360 minutes, temperature 30°C and NaOH concentration 15%. As shown in Fig. (3) A maximum DS of 0.816 was obtained with 2.2 g of monochloroacetic acid per 2g of rice straw cellulose. There was an increase in the DS with amount of monochloroacetic acid up to 2.2 and thereafter it decreased. The increase probably is due to the greater availability of the acetate ions at higher concentrations in the proximity of cellulose molecules. At amount of monochloroacetic acid higher than 2.2 g per 2g of cellulose produced from rice straw, glycolate formation seems to be favored and the reaction efficiency decreases. This finding is supported by reports in the literature *(Khalil et al., 1990; Bhattacharyya et al., 1995).*

In the case of bagasse, with isopropyl alcohol as the solvent medium, alkali concentration 25%, time 360 minutes and temperature 90°C the degree of substitution of CMC was found to increase with an increase in the concentration of monochloroacetic acid. As shown in Fig. 3, a maximum DS of 0.890 was obtained with 3.00 g of monochloroacetate. There was an increase in the DS with amount of monochloroacetic acid up to 3.00 g. This may be due to the greater availability of the acid molecules at higher concentrations in the proximity of the cellulose molecules. This finding is supported by reports in the literature *(Khalil et al., 1990; Bhattacharyya et al., 1995).*

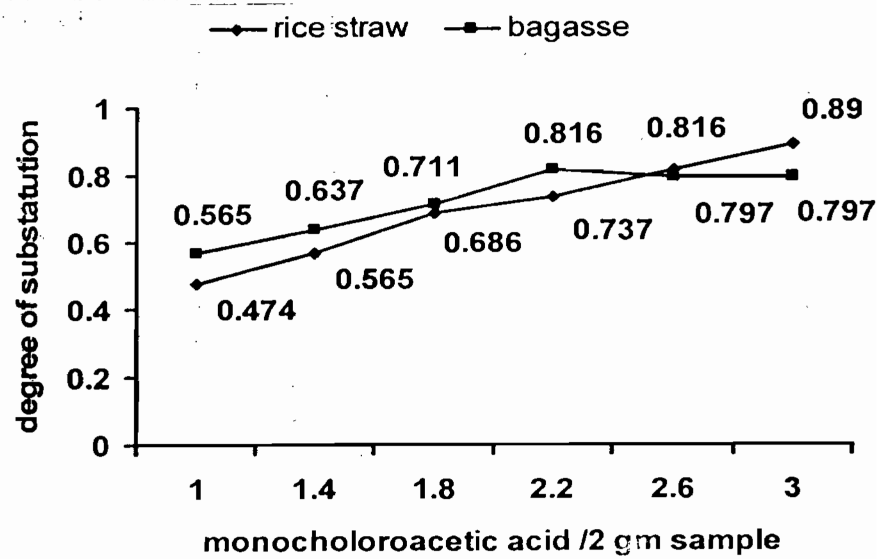

Fig.(3):Effect of various monochloroacetic acid concentrations on carboxymethylation of rice straw and bagasse cellulose.

CONCLUSIONS

The best set of conditions for carboxymethylation of cellulose obtained from rice straw was found to be cellulose:chloroacetic acid ratio of 1:1.1 (w/w), an alkali concentration was 15% with a steeping time of 30min, reaction temperature and time were 45°C and 6 h respectively with isopropyl alcohol as the solvent medium. On the other hand, The best set of conditions for carboxymethylation of cellulose obtained from bagasse was found to be cellulose:chloroacetic acid ratio was 1:1.5 (w/w), an alkali concentration of 25% with a steeping time was 30min, reaction temperature and time were 90°C and 6 h, respectively with isopropyl alcohol as the solvent medium.

REFERENCES

Abd-El-Rahem, E. A. (1969). Chemical studies on hemicelluloses isolated from farm by-products. M. Sc. Dept., Fac. of Agric. Cairo Univ.

Agbagla- dohnani, A.; Noziere, P.; Clement, G. and Doreau, M.(2001). In sacco degradability, chemical and morphological composition of 15 varieties of European rice straw. Anim. Feed Sci. Technol.94, 15-27.

ASGA "Agricultural Statistics General Administration" (2007). Ministry of Agricultural and Land Reclamation, Economic Center Administration, Egypt.

Ali, H. M. (2002). Utilization of some agricultural wastes in production of cellulose. Ph.D. Thesis Food Tech. Dep., Fac. of Agric. Cairo Univ.

Alian, A. M.; El.Masry, G. H. El-Magoli, S. B. and Mhamed, M. F. (1987). Producation of single cell protein from selected agro-industrial solid wastes. Egypt. J. Food Sci., Special Issue, 19-30

Association of Official Analytical Chemists (AOAC) (2000). Official methods of analysis.; 17 Th ed. Washington, DC., USA.

ASTM (1961). Tentative methods of testing sodium carboxymethyl cellulose. ASTM: D1439-61T, pp. 1164-1173.

Attia, R. M.; Mahrous, T. S.; Ghali, Y. and Nasr, A. A. (1988). Biochemical conversion of some agricultural wastes to produce some useful products (part II). J. Agric. Sci. Mansoura Univ. 13 (3), 1471-1480.

Bae, H. D.; Mcallister, T. A.; Kokko, E.G.; Leggett, F. L.; Yanke, L. J.; Jakober, K. D.; Ha, J. K.; Shin, H. T. and Cheng, K. G.

(1997). Effect of silica on colonization of rice straw by ruminal bacteria. Anim. Feed Sci. Technol.65, 165-181.

Barai, B. K.; Singhal, R. S.; and Kulkarni, P. R. (1997). Optimization of a process for preparing carboxymethyl cellulose from water hyacinth(Eichornai crassipes). Carbohydrate Polymers, 32, 229–231.

Barraclough, D.; Kearney, T. and Croxford, A. (2005) .Bound residues: environmental solution or future problems? Environ. Pollut, 133, 85.

Beshay, M. G. (2001). Chemical composition and nutritive values of various sugar cane by-products as affected by variety and drying methods. Egyptian J. of Appl. Sci., 16 (1): 83-98.

Bhattacharyya, D.; Singhal, R. S. and Kulkarni, P. R. (1995). A comparative account of conditions for synthesis of sodium carboxymethyl starch from corn and amaranth starch. Carbohydrate Polymers, 27, 247–253.

Brendel, O; Iannetta, P. P. M. and Stewart, D. (2000). A rapid and simple method to isolate pure alpha-cellulose. Phytochem Anal. 11, 7- 10.

El-gamal, I. M. (2004). Production of furfural from agricultural waste. M.Sc. Thesis, Chemical engineering. Dept., Fac. of Engineering. Cairo Univ.

El-sanat, S. Y. (2004). Utilization of rice straw as an environmental waste to produce xylitol. Ph.D. Thesis Food Tech. Dept., Fac. of Agric. Tanta Univ.

Gao, L.; Yang, H.; Wang, X.; Huang, Z.; Ishii, M.; Igarashi, Y. and Cui, z. (2007). Rice straw fermentation using lactic acid bacteria. Bioresource Technology. Article in press.

Gong, R.; Jin, Y.; Sun, J. and Zhong, K. (2008). Preparation and utilization of rice straw bearing carboxyl groups for removal of basic dyes from aqueous solution. Dyes and Pigments, 76, 519–524.

Han, Y. W. and Callihan, C.D. (1974).Cellulose fermentation : Effect of substrate pretreatment on microbial growth. Applied Microbiology, 27 (1): 159-165.

Howard, R. L.; Abotsi, E.; Jansen van Rensburg E. L. and Howard S. (2003). Lignocellulose biotechnology: Issues of bioconversion and enzyme production. African J. Biotechnol. 2 (12), 602-619.

Hussain, M. G.; Ali, M. M.; Chowdhury. M. F. K. N.; Jahan, M. S.; Rahman, M. L.; Khaleque,M. A. and Jalil, M. A. (1997). Preparation of sodium-carboxymethylcellulose from bagasse, a by-product of can sugar industry. Bangladesh-Journal-of-Scientific-and-industrial-research, 32 (2): 207-211.

Kadla, J,F, and Gilbert ,R,D. (2000). Cellulose structure: A review. Cellulose Chem Technol. 34:197.

Khalafalla, M. M. (1999). The effect of partial replacing concentrate mixture by sugar Beet by-products on the performance of ruminants. M. Sc. Thesis Fac. Of Agric. (Animal production) Tanta Univ.

Khaled, A. M. (1997). Studies on the production and valuation of Oyster mushroom. Ph. D. Thesis, Food Sci. Tech. Dept., Fac. Of Agric. Cairo Univ.

Khalil, M. I., Hashim, A. and Hebeish, A. (1990). Carboxymethylation of maize starch. Starch/Starke, 42, 60 - 63.

Lachke, A. (2002). Biofuel from D-xylose- the second most abundant sugar. Resonance, 5, 50-58.

Mandal, K. G.; Misra, A. K.; Hati. K. M.; Bandyopadhyay, K. K.; Ghosh, P. K. and Mohanty, M. (2004). Rice residue-management options and effects on soil properties and crop productivity, Food Agric. Environ. 2, 224.

Martínez, A. E; Silva, S. S. and Flipe, A. G. (2000). Effect of the oxygen transfer coefficient on xylitol production from sugar cane bagasse hydrolysate by continuous stirred-tank reactor fermentation. Appl. Biochem. Biotechnol., 84/86, 633 – 641y.

Michel, F.; Thiboult, J. F.; Barry, J. L. and Bayanast, R. (1988). Preparation and characterization of dietary fiber from sugar beet pulp. J. Sci. Food Agric., 42 (1): 77-85.

Mohammady, T. F. (1996). Utilization of organic wastes for cultivation and production of mushroom. Ph. D. Thesis, Horticulture Dept., Fac. Of Agric. Ain Shams Univ.

Nasr, A. A. M. (1994). Biochemical studies on utilization of rice straw as agricultural waste . Ph.D. Thesis Fac. of Agric. Cairo Univ.

Naterova, A. and Polein, J. (1974). Optimal conditions for carboxymethyl cellulose preparation. II. Effect of agent input, reaction time and temperature. Chemical Abstracts 81, 107621.

Olaru, N.; Olaru, L.; Stoleriu. A. and Timpu, D. (1998). Carboxymethylcellulose synthesis in organic media containing ethanol and/or acetone. Journal of Applied Polymer Science, 67, 481–486.

Pan. X. J.; Sano, Y. and Ito. T. (1999). Atmospheric acetic acid pulping of rice straw: behavior of ash and silica in rice straw during atmospheric acetic acid pulping and bleaching. Holzforschung, 53, 49-55.

Sharma, S. D.(1974) "A Study of Roughage Silica Solubility" M.Sc. thesis, G.B, Pant University, Pantnagar, India.

Sun. J. X.; Sun, X. F.; Zhao, H. and Sun, R. C. (2004). Isolation and characterization of cellulose from sugarcane bagasse. Polymer Degradation and Stability, 84, 331–339.

Toğrul, H. and Arslan, N. (2003). Flow properties of sugar beet pulp cellulose and intrinsic viscosity-molecular weight relationship. Carbohydrate Polymers, a in press.

Vadiveloo, J. and Phang, O. C. (1996). Differences in the nutritive value of two rice straw varieties as influenced by season and location. Anim. Feed Sci. Technol. 83, 57-65.

Van Soest, P. J. (2006). Rice straw, the role of silica and treatments to improve quality. Anim. Feed Sci. Technol. 130, 137–171.

الملخص العربي

إنتاج الكربوكسي ميثايل سليلوز من قش الأرز ومصاصة القصب.

عصام محمد السباعي – سمير يوسف السناط – محمود صابر جوده – كمال متولي النمر

قسم تكنولوجيا الأغذية – كلية الزراعة – جامعة كفر الشيخ – مصر

أجريت هذه الدراسة بغرض بحث إمكانية انتاج السليلوز من كل من مصاصة القصب و قش الأرز حيث أنه من المعروف أن السليلوز هو المكون الأساسي للنباتات و أمكانية تحويل السليلوز المنتج الي كربوكسي ميثايل سليلوز و قد أوضحت النتائج أن نسبة السليلوز في كل من قش الأرز ومصاصة القصب هي ٣٤,٦% و ٤٢,١٨٦ % علي الترتيب كما أظهرت النتائج أن أفضل الظروف المختبرة للتخلص من السليكا في قش الأرز هي صودا كاويه بتركيز ١,٥%و درجة حرارة ٥٥ °م ونسبة صلب : سائل هي ١٥:١ ولمدة ١٥٠ دقيقه وان استخدام مثل هذه الظروف أدي الي خفض نسبة السليكا الي ٤,٥% وكذلك الي ارتفاع نسبة السليلوز الي ٣٨,٧٣% وعلي الجانب الأخر أظهرت النتائج أن أفضل الظروف المختبرة للتخلص من السليكا في مصاصة القصب هي صودا كاويه بتركيز ٢,٥%و درجة حرارة ٧٠ °م ونسبة صلب : سائل هي ١٥:١ ولمدة ١٥٠ دقيقه وان استخدام مثل هذه الظروف أدي الي خفض نسبة السليكا إلي ١,٣% وكذلك الي ارتفاع نسبة السليلور الي ٤٤,٩٨%.

كما أوضحت النتائج أيضا أن أفضل الظروف المختبرة لعزل السليلوز من كل من قش الأرز ومصاصة القصب هي ١١٠ °م و ١٠ دقيقه

و التي تعطي كمية سليلوز ٣٨,٥٢% و ٤٣,٧٣ % لكل من كلا المخلفين علي الترتيب.

و بدراسة أنسب الظروف لإنتاج الكربوكسي ميثايل سليلوز من السليلوز الناتج من كل من المخلفين المذكورين كانت النتائج كالتالي:

أفضل مذيب هو كحول الأيزوبروبانول وأفضل مدة تفاعل هي ٣٦٠ دقيقه لكل من السليلوز الناتج من كل من المخلفين في حين كانت أنسب درجة حراره ، كمية صودا كاوية و كمية حامض مونوكلوروأسيتك هي ٣٠ °م ، ١٥ % و ٢,٢جم للسليلوز المنتج من القش في حين كانت هذه الظروف٩٠ °م ، ٢٥%و٣ جم للسليلوز المنتج من المصاصه.