

Production of Hydroxylethyl Cellulose from Cotton Fibre as a Thickener for Emulsion Paint

Manase Auta

Department of Chemical Engineering, Federal University of Technology, P.M.B. 65, Minna,
Nigeria

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Seri
Ampangan, Nibong Tebal, Pulau Penang, Malaysia

Tel.: +2348065440882

Abstract

Production of Hydroxylethyl cellulose from cotton fibre as a thickener for emulsion paint was carried out. The raw materials used for its production were alkaline cellulose, which is composed of cotton linter pulp, 25% sodium hydroxide solution, 90% acetone solution and liquefied ethylene oxide. The materials were used in their specified proportions thus: 23 mL of cotton linter pulp, 31 mL of acetone, 34 mL of NaOH, and 50 mL of ethylene oxide. The raw samples were splitted into six according to pH 6-8.5 variations and their viscosity, specific gravity, refractive index, and flash point in the course of the experiments. The best sample's properties were found to be within standard limit with minimal errors observed. The study showed that the possibility of producing hydroxyethyle cellulose is very high with little adjustments on the process variables and better selection of equipment.

Keywords: Hydroxylethyl cellulose, Emulsion paint, Cotton fibre, Thickener

1.0 INTRODUCTION

Hydroxylethyl Cellulose (HEC), is a white odourless solid which dissolves in water to increase its viscosity in order to achieve its function as a thickener agent. It readily dissolves in water (faster with temperature rising) but is usually insoluble in most organic solvents. It has been widely used in various industrial fields for example as a stabilizer for emulsion polymerization, as a dispersant for pigment in coating compositions, as a binder, a sizing agent, and a surface coating agent in paper industries, as a thickening agent in cosmetics, and as a water retention agent for cement. Furthermore, hydroxylethyl cellulose has attracted attention in oil and gas explorations, as a viscosifier for drilling mud, well stimulating fluid, cementing fluid, completion fluid, work-over fluid, or as a mobility control agent for polymer flooding or as a mobility buffer for polymer flooding in enhanced oil recovery EOR [1-6].

Although a cellulose derivative, it differs from plain regular cellulose in that some or all of the hydroxyl groups of the glucose repeat unit have been replaced with hydroxyethyl ether groups.

These hydroxyethyl groups get in the way when the polymer tries to crystallize. But because it can crystallize, hydroxyethyl cellulose is soluble in water. In addition to being a great laxative, it is also used to thicken shampoos. It makes the soap in the shampoo less foamy, and it helps the shampoo clean better by forming colloids around dirt particles normally, dirt particles are insoluble in water. But a chain of hydroxyethyl cellulose can wrap itself around a dirt particle. This mass can be thought of as a snack cake, with the polymer chain as the cake and the dirt as the creamy filling. This snack cake is soluble in water, so by wrapping around the dirt, the hydroxyethyl cellulose tricks the water into accepting the dirt. In this way, the dirt gets washed away instead of being deposited back onto the hair.

Cellulose is the earth's major biopolymer and is of tremendous economic importance globally. It is the major constituent of cotton (over 94%) and wood (over 50%). Together cotton and wood are the major resources for all cellulose products such as paper, textiles, and construction materials, cardboard, as well as such cellulose derivatives as cellophane, rayon and cellulose acetate [7,8].

Traditionally, cellulose is harvested from plant resources. Bolls from cotton plants collected, and the cotton fibres are detached from the seeds and processed into bales. These are in turn used as the prepared raw materials for the production of all possible products that can be obtained from cotton. These include hydroxyethyl cellulose and sodium carboxymethyl cellulose and, to a lesser extent, certain polyacrylates amongst many others, and have dominated the emulsion paint market [9].

The main raw materials for the production of hydroxyethyl cellulose are alkali cellulose and ethylene oxide.

1.1 Alkali cellulose

This comprises of a mixture of cotton linter pulp, an alcohol or acetone in this case, and a 25% sodium hydroxide solution. This mixture is in standard proportions such that maximum accuracy can be obtained at the end of the production process [10]. The cotton linter pulp can be prepared by mixing a certain amount fiber with water and blending in a blender.

1.2 Ethylene Oxide

Ethylene oxide also called oxirane, is the organic compound with the formula C_2H_4O . This colourless flammable gas with a faintly sweet odour is the simplest epoxide, a three member ring consisting of two carbons and one oxygen atom. It is commonly handled and shipped as a refrigerated liquid. It is the chief precursor to ethylene glycol and other higher volume chemicals but it is also used for medical sterilization. It is produced by oxidation of ethylene with oxygen at about 250 °C over a catalyst comprising metallic silver on alumina. Typically, promoters such as chloride are also included. Pressures are between 1-2 MPa [11]. It reacts with alkali cellulose to produce alkali hydroxyethyl cellulose that is being neutralized with hydrochloric acid by replacing some or all of the hydroxyl groups with hydroxyethyl ether groups. Others names include: epoxy ethane, dimethylene oxide and oxacyclopropene.

Viscosity is one of the major factors considered during formulation of paints as it speaks volumes of the product quality. Optimum viscosity of paints is required since higher viscosity is

characterized by poor leveling and pinholes appearance in the film caused by micro bubbles while too low viscosity paints drips and splatters on application [12].

The indispensable use of good thickener in paint production prompted the quest to investigate or explore other renewable means of sourcing for viscosity enhancing substances. Therefore, this research is aimed at producing hydroxyl ethyl cellulose from cotton fiber as a thickener for emulsion paint production. It will also involve testing the drying, pH, viscosity, specific gravity, refractive index, ash content and flash point of the product.

2.0 MATERIALS AND METHOD

Analytical reagents such as sodium hydroxide (NaOH), hydrochloric acid (HCl), sulfuric acid (H₂SO₄), ethylene oxide, epoxy ethane, 90% acetone (Merck and Sigma-Aldrich products) were purchased from Port-Harcourt, Nigeria and used without further purification. Equipment such as pH meter, viscometer, refractometer, muffle furnace, oven dryer, dessicator, hot plate with magnetic stirrer, flash point tester and blender were used.

Pure fiber of cotton was trimmed into short lengths and 3 g of it was weighed into a 500 mL beaker containing 200 mL of distilled water and then stirred. The stirred mixture was transferred to blender where it was blended for 20 min. About 23 mL of the resulting solution (cotton linter pulp) was mixed with 31 mL of acetone and 34 mL of 25% NaOH solution on a magnetic stirrer set at 50 °C for 1 hr to achieve desired alkali cellulose homogeneous solution. 50 mL of liquefied ethylene oxide was poured into the alkali cellulose solution mixed and then put back on the magnetic stirrer with similar conditions as above for 2 hr to finish the production process.

The final product was then allowed to cool to room temperature and then shared into six samples of 30 mL each. The six samples denoted as A, B, C, D, E and F were neutralized with 5 M HCl and their pH were adjusted from pH 13.46 to pH 8.5, 8.0, 7.5, 7.0, 6.5 and 6.0, respectively.

2.1 Drying of Sample

About 50g of each sample (A, B, C, D, E and F) were weighed and then dried in an oven for 2 hr, placed in desiccators to cool before re-weighing. This process was repeated five times until a stable weight of the sample was established.

2.2 Viscosity

About 15 mL of sample A was poured into a U-shaped glass apparatus and the content was sucked up passed the constriction. The liquid was allowed to drop through the constriction as the time was noted. The procedure was repeated with the other samples and their viscosity was calculated.

2.3 Specific gravity

A 25 mL clean dried density bottle was weighed, it filled with sample (A) and reweighed and finally, it was emptied washed and dried before filling with water and reweighed. The specific gravity of the sample was then determined. The procedure was repeated with the other samples.

2.4 Refractive index

Few drops of each sample were put on the glass slide of the refractometer. Through the eye piece of the refractometer, the dark portion was adjusted to be in line with the intersection of the cross. The refractive index of each sample was read and recorded.

2.5 Ash content

3g of the dried sample was weighed and put into a previously ignited porcelain dish of 75ml capacity. It was then ignited over a low Bunsen flame and allowed to burn, with an occasional application of heat until most of the carbonaceous material had burnt off. The residue was then cooled in desiccators and moistened with a 1:1 sulphuric acid. The excess acid was evaporated over a low Bunsen flame slowly so as to avoid spattering. The ignition was completed by placing the sample in a muffle at 550°C for 30 minutes. It was later cooled, desiccated and weighed. The percentage ash content was calculated by multiplying the weight of residue by 100.

2.6 Flash point

Sample A was carefully filled into a cup attached to the flash point tester to the 0 °C mark. A thermometer was inserted into the cup and the heating rate was set at 30 °C per minute. The flame test was initiated by starting the heating and covering the surface of the cup containing the sample at every 4 °C rise in temperature. The moment the first flash was observed, the temperature rise was noted as the flash point of the sample. This was repeated five times and the average was taken as the flash point of the sample. The procedure was repeated to determine the flash points of the remaining samples.

3.0 RESULTS AND DISCUSSION

3.1 Drying of sample

Drying helps to alleviate the moisture content of samples or keeping them from direct contact with atmospheric oxygen which adds error during actual measurement and in the overall, affects the result of the experiment. Drying as pretreatment process has been used by many researchers to ensure validity and reliability of their experimental results [13,14]. Drying process of the samples (A, B, C, D, E and F) was repeated five times to avoid experimental errors due to moisture presence. An illustration of result of sample D is shown in Table 1.

Table 1 Drying of Sample D

Weight of Petri dish + sample (g)	Time of drying (hrs)	Weight of Petri dish after drying (g)	Moisture loss (g)
93.52	2	78.55	14.97
78.55	4	65.53	13.02
65.53	6	54.22	11.31
54.22	8	48.10	6.12
48.10	10	46.94	1.16

The further test conducted to ascertain the dryness of the samples were moisture and ash content determination.

3.2 Moisture content

Good drying of the sample was reflected when its moisture content was determined. There was virtually insignificant difference between the third and fourth experiments for moisture content investigation with a total of 0.1 moisture loss (sample D), implying that the sample was well dried. The corresponding moisture content of 5% obtained is in concurrence with the standard value as shown in Table 3. The summary of the experimental moisture content determination of sample D is contained in Table 2.

Table 2 Moisture Content of Sample D from initial mass of 2 g

Weight of Petri dish + sample (g)	Time of drying (hrs)	Weight of Petri dish after drying (g)	Moisture loss (g)
43.52	1	43.47	0.05
43.47	2	43.44	0.03
43.44	3	43.42	0.02
43.42	4	43.42	0.00

3.3 Ash content

The ash content test conducted by heating 2 g of the sample in the muffle furnace for 15 min at 550 °C after 0.09 g was burnt off as determined from the final mass of 1.91 g of sample after heating; was found to be 4.5%. The ash burnt off was the inorganic/mineral matter contained in the sample. This ash content of sample D is within specification as shown in Table 3.

Table 3 Comparison of experimental results of sample D with standard values

Property	Experimental value	Standard value
pH	7.0	6-8.5
Viscosity (cP)	4247.98	1000-10000
Specific gravity	1.34	1.33
Refractive index	1.35	1.336
Flash point (°C)	105	>150
Moisture content (%)	5	5 maximum
Ash content (%)	4.5	5 maximum

3.4 Viscosity

The viscosities of the six samples decreased chronologically from sample A to F. This also shows that viscosity of hydroxyethyl cellulose decreases with an increased acidity. This is true because acetone and sodium hydroxide jointly increased the viscosity of the mixture, complemented by the presence of ethylene oxide. The viscosity values shown in Table 5 decreased from 4549.62 for sample A to 3946.35 for sample F. This trend in viscosity values also suggests that acidic hydroxyethyl cellulose may not be a good option as its viscosity may not be high enough to be used as a thickener. In a similar report, microgels sensitivity with respect to pH were observed in a study on novel thermo- and pH-responsive hydroxypropyl cellulose- and poly (l-glutamic acid)-based microgels for oral insulin controlled release [1].

3.5 Specific gravity

The specific gravity also decreased across the table with the greatest proximity observed in sample D with a value of 1.34 as opposed to the standard value of 1.33. This invariably suggests

that pH of HEC may be slightly above pH 7 of sample D used for comparison. It is also worthy to note that excessive increase in pH may lead to the degradation of cellulose product [15]. The result of specific gravity analysis for sample D and other samples are summarized in Table 5 and 4, respectively.

3.6 Refractive index

The refractive index was also observed to have decreased across the table indicating a clearer vision with every drop in pH value (decreased basicity or increased acidity). It was observed that the refractive index of sample D (1.35) was closest to the standard value (1.336) suggesting that the pH of the sample is close to the optimal value. Table 5 and 4 has summary of refractive index determined for the A, B, C, E, F and D, respectively.

3.7 Flash point

The flash point analysis for samples A, B, C, E, F and D are summarized in Table 5 and 4, respectively. It was also observed that the flash point of the samples increased from samples A to F chronologically. This could be attributed to the presence of acetone and ethylene oxide, both of which are highly flammable. The increase in the flash point across the samples as contained in Table 5 was due to neutralization effect of the slurry by the acid. The flash point of sample D of 152 °C was closest to the standard value of >150 °C for hydroxyethyl cellulose [16,17].

3.8 Volume of hydroxyethyl cellulose product

During the production process, volume of the mixture was decreasing with increase in degree of conversion. This was attributed to the high volatility of acetone which obviously formed about 60% of the total mixture and possibly the nature of the reactor promoted escape of solution to the surrounding consequently affecting the yield of the product (200 mL). However, despite the challenges stated above, the assertion that alkali cellulose is a good source of hydroxyethyl cellulose (HEC) when standard proportion of constituents is used [10], was observed from the total volume of the HEC slurry produced after repeated runs before neutralization with HCl as summarized in Table 4

Table 4 Hydroxyethyl Cellulose Slurry Product from its Individual Components

Item	Volume (mL)
Cotton linter pulp	46
90% acetone solution	622
25% NaOH solution	68
Ethylene oxide	100
Hydroxyethyl cellulose slurry (product)	200

Table 5 Liquid Sample Test Results for the Six Samples

Test conducted	Results for samples					
	A	B	C	D	E	F
Viscosity (cp)	4549.62	4474.21	4398.8	4247.98	4097.17	3946.35
Specific gravity	1.51	1.47	1.39	1.34	1.27	1.25
Refractive index	1.95	1.89	1.57	1.35	1.30	1.29
Flash point (°C)	104	120	133	152	155	162

CONCLUSION

Preparation of hydroxyethyl cellulose from cotton fiber was successfully carried out investigating the variation pH in six different ways. The results obtained showed that some parameters used with either in agreement or against literature on hydroxyethyl cellulose production. The errors discovered for specific gravity (0.01) and refractive index (0.014) for Sample D were insignificant compared with the standard values. Sample's D moisture content (5%) and ash content (4.5%) obtained were within the acceptable standard limit. Therefore, the results of parameters obtained in this research for sample D can be used as bases for carrying out hydroxyethyl cellulose production, and this research has further confirmed to us that HEC can be adequately prepared from cotton fiber.

REFERENCES

- [1] Yunyan, B., Zhe, Z., Aiping, Z., Li, C., Chaoliang, H., Xiuli, Z., Xuesi, C., Novel thermo- and pH-responsive hydroxypropyl cellulose- and poly (l-glutamic acid)-based microgels for oral insulin controlled release, *Carbohydrate Polymers* 89 (2012) 1207–1214
- [2] Baker, C. (1984): "Methyl cellulose and carboxymethyl cellulose: An evaluation for use in paper conservation through aging" International Institute of Conservation, Paris, pp55-59
- [3] Barnett, J.R. (2008), "Fire" Microsoft ® Encarta® 2009, Redmond, W.A. Microsoft Corporation
- [4] Brown, R.M. (1986), "A new resource for wood, paper, textiles, food and specialty products" Department of Botany, the University of Texas at Austin, Texas
- [5] Calven, R. (2001), "The taste of bread" Gaithersburg MD; Aspen Publishers
- [6] Yu, Y.C. and Shing, B.C., Rheological study of hydrophobically modified hydroxyethyl cellulose and phospholipid vesicles, *Journal of Colloid and Interface Science* 349 (2010) 236–245
- [7] Cao, Y., Wu, J. Zhang, J., Li, H.Q., Zhang, Y., He, J.S., Room temperature ionic liquids (RTILs): a new and versatile platform for cellulose processing and derivatization, *Chem. Eng. J.* 147 (2009) 13–21.
- [8] Klemm, D., Heublein, B., Fink, H.P., Bohn, A., Cellulose: fascinating biopolymer and sustainable raw material, *Angew. Chem. Int. Ed.* 44 (2005) 3358–3393.
- [9] David, G. B., Roy, L.W., (2008), "Cellulose" *AcessScience@McGraw Hill*
- [10] Kanda, E. (1983), "Method for stabilizing an acrylamide polymer in a petroleum recovery process" U.S.A.
- [11] Seigfried, R. and Dieter, M. (2005), "Ethylene oxide" *Ullmann's Encyclopaedia of Industrial Chemistry*, Wiley-VCH, Weinheim
- [12] Lauren, N.B., Christopher, M.F., Robert, G.G., Effect of surfactants used for binder synthesis on the properties of latex paints, *Progress in Organic Coatings* 53 (2005)112–118.
- [13] Erik, Y., Jenny, K., Britta, E., Comparison of toxicity and release rates of Cu and Zn from anti-fouling paints leached in natural and artificial brackish seawater, *Science of the Total Environment* 408 (2010) 2459–2466.

- [14] Huan-Yun, Y., Ru-Lang, S., Yan, L., Hefa C., Eddy Y.Z., Inputs of antifouling paint-derived dichlorodiphenyltrichloroethanes (DDTs) to a typical mariculture zone (South China): Potential impact on aqua-farming environment, *Environmental Pollution* 159 (2011) 3700-3705
- [15] Ellefsen, O, Mikami, T. (1963), Modified Polynosic Fibres, The Norwegian Pulp and Paper Research Institute, Oslo, Norway, Kokoku Rayon and Pulp Co. Ltd., Tokyo, Japan
- [16] Hercules incorporated available online on 23-06-2012 at: http://www.ashland.com/Ashland/Static/Documents/AAFI/PRO-250-1G_Natrosol11G.pdf
- [17] Cellulo size Hydroxyethyl Cellulose: [http://www.dow.com/PublishedLiterature/dh_004d/0901b8038004d22a.pdf? filepath=cello/pdfs/noreg/325-00001.pdf&fromPage=GetDoc](http://www.dow.com/PublishedLiterature/dh_004d/0901b8038004d22a.pdf?filepath=cello/pdfs/noreg/325-00001.pdf&fromPage=GetDoc)